UNIVERSITAT JAUME I

Escuela Superior de Tecnología y Ciencias Experimentales

Departamento de Química Inorgánica y Orgánica

Tesis Doctoral

**Nuevos materiales basados en SILLPs (Supported
Ionic Liquid-like Phases) para aplicaciones
avanzadas en la Química y la Ingeniería Sostenible**

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La Dra. **María Isabel Burguete Azcarate**, Catedrática de Universidad en el Departamento de Química Inorgánica y Orgánica de la Universitat Jaume I de Castellón y el Dr. **Eduardo García-Verdugo Cepeda**, Profesor Titular de Universidad en el Departamento de Química Inorgánica y Orgánica de la Universitat Jaume I de Castellón,

CERTIFICAN: Que **Silvia Montolio Breva**, Licenciada en Química por la Universitat Jaume I de Castellón, ha realizado bajo su dirección la tesis doctoral titulada **“Nuevos materiales basados en SILLPs (Supported Ionic Liquid-like Phases) para aplicaciones avanzadas en la Química y la Ingeniería Sostenible”** dentro del programa de Doctorado en Química Sostenible coordinado por la Universitat Jaume I, y que el presente documento constituye su memoria de tesis doctoral para optar al grado de Doctora en Química Sostenible.

Y para que así conste y en cumplimiento con la legislación vigente, firman el presente certificado en Castellón de la Plana a 21 de octubre de 2016.

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A mi familia

A mis padres y hermana

A mi abuelo

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“Never consider the study as an obligation but as an opportunity to penetrate the beautiful and wonderful world of learning.”

Albert Einstein

Abreviaturas

ACVA	4,4'-Azobis(4-cyanovaleric acid)
AIBN	2,2'-Azobis(2-methylpropionitrile)
[APMIM][Br]	<i>N</i> -(3-aminopropyl)- <i>N'</i> -methyl imidazolium bromide
ATR-FT-IR	Attenuated total reflectance-Fourier transform infrared spectroscopy
ATRP	Atom transfer radical polymerization
AuNPs	Gold nanoparticles
Bn	Benzyl
Bu	Butyl
CD	Circular dichroism
CDCl ₃	Deuterated chloroform
CD ₃ OD	Deuterated methanol
CHCl ₃	Chloroform
CILs	Chiral ionic liquids
CMDTTC	Cyanomethyl dodecyl trithiocarbonate
CPA	4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid
CPILs	Chiral polymeric ionic liquids
CRP	Controlled radical polymerization
CTA	Chain transfer agent
DLS	Dynamic light scattering
DMAP	2-2-Dimethoxy-2-phenylacetophenone
DMF	<i>N,N</i> -dimethylformamide
DMSO	Dimethyl sulfoxide
D ₂ O	Deuterated water
DSC	Differential scanning calorimetry
DTT	1,4-Dithiothreitol
DVB	Divinylbenzene
Et ₃ N	Triethylamine
Et ₂ O	Diethyl ether
FAME	Fatty acid methyl esters
GPC	Gel permeation chromatography
IBN	2-Cyano-2-propyl benzodithioate
ILs	Ionic liquids
LCST	Lower critical solution temperature
LiNTf ₂	Lithium bis(trifluoromethane)sulfonimide

MeOD	Deuterated methanol
MeOH	Methanol
2-Me-THF	2-Methyltetrahydrofuran
NBP	4-(4-nitrobenzyl)pyridine
NMP	Nitroxide-mediated radical polymerization
NMR	Nuclear magnetic resonance
PAHT	Poly(acrylamide-homocysteine thiolactone)
<i>p</i> -AP	<i>p</i> -aminophenol
PClVB	Poly(vinylbenzyl chloride)
PDI	Polydispersity index
PdNPs	Palladium nanoparticles
Phe	Phenylalanine
PILs	Polymeric ionic liquids
PNIPAM	Poly(<i>N</i> -isopropylacrylamide)
<i>p</i> -NP	<i>p</i> -nitrophenol
Poly(VBC)	Poly(vinylbenzyl chloride)
Poly(VBCl-DVB)	Poly(vinylbenzyl chloride)-divinylbenzene
Poly(VBCl-VBN ₃)	Poly(vinylbenzyl chloride-4-azidomethylstyrene)
PS	Polystyrene
PVP	Poly(vinylpyrrolidone)
RAFT	Reversible addition-fragmentation chain transfer
SCF	Supercritical fluid
SEM	Scanning electron microscopy
SILPs	Supported ionic liquid phases
SILLPs	Supported ionic liquid-like phases
SPB	Surface plasmon band
T ₁	Longitudinal proton relaxation time
T ₂	Transverse proton relaxation time
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TCEP	<i>Tris</i> (2-carboxyethyl)phosphine
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UCST	Upper critical solution temperature
UV-Vis	Ultraviolet-visible
Val	Valine
WCA	Water contact angle

Símbolos

A_o	Initial absorbance
A_t	Absorbance at different time intervals
γ	Surface tension
$\Delta\delta$	Chemical shift variation
d_h	Hydrodynamic diameter
ε	Dielectric constant
k_{app}	Apparent rate constant
λ	Wavelength
M_w	Weight average molecular weight
μ	Viscosity
σ	Electric conductivity
t_o	Induction time
T_g	Glass transition temperature

Resumen de la tesis

La Tesis Doctoral se enmarca dentro del área de la química sostenible y más concretamente en el campo de los líquidos iónicos poliméricos. El principal objetivo es el diseño y desarrollo de nuevos materiales funcionalizados y estructurados basados en líquidos iónicos poliméricos que presenten propiedades y aplicaciones interesantes en la química y la ingeniería sostenible.

La memoria de la tesis se ha estructurado en 8 capítulos y se ha redactado siguiendo el formato de artículos científicos a partir del trabajo de investigación desarrollado. Los resultados obtenidos han permitido la publicación de 2 artículos en revistas de alto índice de impacto, cuyas referencias se citan posteriormente en el apartado de divulgación de este trabajo, y la preparación de otros 4 que serán publicados en breve. En cada capítulo se incluye, junto con el artículo y su información adicional, un resumen y unas conclusiones parciales de los resultados para facilitar la lectura de la tesis. Además, las abreviaciones y símbolos se recogen al principio de la tesis por orden alfabético.

En cuanto a la organización de los diferentes capítulos, el orden se ha establecido para un mejor seguimiento y una mayor comprensión de los resultados. De esta manera, en primer lugar, se incluye una introducción (capítulo 1) donde se recogen trabajos relacionados con el tema de la tesis en cuanto a la preparación y aplicación de materiales similares con la finalidad de poner en antecedentes al lector. Especialmente, se centra en la clasificación de los líquidos iónicos poliméricos (PILs) en función de su estructura y organización, en demostrar la influencia de la modificación química de los vectores moleculares en la eficiencia catalítica de dichos materiales y en describir las relaciones estructura-propiedad para entender las propiedades catalíticas derivadas tomando ejemplos de la literatura.

A continuación, se exponen los objetivos generales de la tesis (capítulo 2).

Posteriormente, en el capítulo 3 se describe la obtención de poli(clorovinilbenceno) (poly(VBC)) por la técnica de polimerización controlada RAFT utilizando tanto procesos en *batch* como en flujo continuo. Ambas metodologías sintéticas permiten la obtención del polímero lineal en condiciones controladas observándose diferencias en los pesos moleculares resultantes. Dichos polímeros se han utilizado como materiales de partida para sintetizar polímeros insolubles entrecruzados y funcionalizados con unidades de líquido iónico (IL) que han demostrado actuar como organocatalizadores en la condensación de Knoevenagel y como soportes para sintetizar y estabilizar nanopartículas metálicas.

En el siguiente capítulo (capítulo 4) correspondiente al artículo “*AuNP-Polymeric Ionic Liquid Composite Multicatalytic Nanoreactors for One-Pot Cascade Reactions*” se ha llevado a cabo la síntesis de diferentes nanocompuestos basados en AuNP-PILs partiendo de los polímeros obtenidos por polimerización en *batch* en el capítulo 1. Estos sistemas se comportan como catalizadores bifuncionales en los que las unidades de líquido iónico promueven la condensación de Knoevenagel mientras que el metal cataliza la reducción de los grupos funcionales del producto anterior en una reacción en cascada. La caracterización de estos materiales por diferentes técnicas permite explicar cómo la combinación controlada entre PILs y AuNPs empleando la metodología sintética adecuada genera compuestos altamente organizados con múltiples centros catalíticos y funcionalidad controlable, además de demostrar la influencia de la autoorganización del sistema en su eficiencia catalítica.

El artículo titulado “*LCST-type polymers based on chiral-polymeric ionic liquids*” correspondiente al capítulo 5 de la tesis describe la síntesis y caracterización de una nueva clase de líquidos iónicos poliméricos quirales (CPILs) en la que el adecuado autoensamblaje de las unidades de IL genera estructuras supramoleculares altamente ordenadas que exhiben un comportamiento termosensible que ha sido estudiado por UV-Vis, DC y RMN. Los diferentes elementos estructurales de los fragmentos de IL se pueden modificar con el fin de modular la transición LCST (*lower critical solution temperature*). Asimismo, la presencia de grupos adicionales en el polímero permite transferir dicha propiedad a estructuras 3D organizadas como los nanocompuestos basados en AuNPs-CPILs abriendo otros campos de aplicación.

Seguidamente, en el capítulo 6 se introduce el uso de la técnica de electrospinning para la preparación de membranas poliméricas nanoestructuradas a partir de mezclas de diferentes PILs y polivinilpirrolidona (PVP). La estructura química de ambos polímeros y las interacciones supramoleculares interpoliméricas definen tanto el autoensamblaje como la morfología y las propiedades de estos materiales. Por lo que, a través de la modificación de los vectores moleculares de los PILs somos capaces de cambiar la morfología y las propiedades hidrofóbicas/hidrofílicas de las membranas. Igualmente, estos sistemas han demostrado poseer aplicaciones en procesos de separación y como soportes nanoestructurados para estabilizar nanopartículas metálicas.

El último capítulo de resultados (capítulo 7) se centra en el desarrollo de nuevos materiales funcionalizados empleando como precursor macromolecular la poli(acrilamida homocisteína tiolactona) (PAHT) obtenida fácilmente por polimerización RAFT. Las diferentes estrategias de post-modificación se han basado en

la combinación de aminolisis con reacciones tiol-eno o formación de puentes disulfuro para la preparación de estos materiales avanzados con diferentes morfologías, desde polímeros solubles y materiales entrecruzados tipo gel hasta nanofibras, con propiedades controlables. El capítulo ilustra, en base a ejemplos de síntesis, la utilidad de esta aproximación para la preparación de materiales funcionalizados con ILs (PILs). Así, esta nueva metodología abre la posibilidad de diseñar PILs con propiedades controladas que pueden ser de gran interés para su aplicación en campos como la ciencia de los materiales, la separación o la catálisis.

Finalmente, la tesis termina con un capítulo (capítulo 8) donde se recopilan las conclusiones más relevantes de todo el trabajo expuesto en los artículos científicos presentados anteriormente.

Summary of the thesis

The present thesis is dealing with the preparation of advanced polymeric materials containing ionic liquid-like units. The thesis includes an initial chapter reviewing the previous efforts reported by our research group and others in the preparation and applications of similar materials. This chapter gives specially emphasis in how, by fine tuning of molecular structure of the polymeric ionic liquid, it can influence the catalytic properties, focusing on the structure-property relationship of polymeric ionic liquids (PILs) and how it affects the improvement of the catalytic efficiency. Noteworthy examples of the different approaches for synthesising PILs, their classification based on the structural variation and the derived catalytic properties are described and discussed.

After the introduction and the presentation of the general objectives, the thesis includes five different paper manuscripts (two published and three drafts to be submitted) summarising the experimental achievements obtained during the PhD studies.

The third chapter is dealing with the development of synthetic methodologies for the preparation of poly(*p*-chloromethylstyrene) by controlled radical polymerisation, in particular by RAFT polymerisation. Both batch and continuous flow processes are reported for the preparation of these types of polymers. The results show that the batch processes led to high molecular weight with low polydispersity, while for the flow process only polymers with low molecular weight can be obtained under controlled conditions. Both polymers with high and low molecular weights were assembled into insoluble crosslinked polymers with high loading of IL-like units. Only in the case of low molecular weight polymers, the phase separation was controlled and took place during the reaction between the soluble polymer and reactive units leading to the corresponding polymeric IL-like phase. The properties of these crosslinked PILs materials were evaluated as organocatalysts for the Knoevenagel condensation and in the formation and stabilisation of metal nanoparticles.

The following chapter (*ACS Catal.* **2016**, 6, 7230-7237) reports on the synthesis of different AuNP-PIL nanocomposites based on the polymers obtained by batch polymerisation in the chapter 1. These AuNP-PILs nanocomposites have been behaved as bifunctional catalysts in which the IL-like units promote the Knoevenagel condensation through a dual electrophilic/nucleophilic activation mechanism and metal nanoparticles catalyse the reduction of the functional groups of the Knoevenagel product in a one-pot tandem reaction. The characterisation of the composites by different techniques suggests that the self-assembly and self-organisation of the

constituent building blocks during the synthetic procedures define the precise shapes, sizes and catalytic performance of these advanced materials. The resulting catalytic efficiency reflects not only the presence of the corresponding individual catalytic motifs but also their hierarchical organisation.

Applying similar methodology, the fifth chapter (*Chem. Commun.* **2014**, 50, 10683-10686) reports the self-assembly of linear polymers containing chiral IL units to generate high-order supramacromolecular structures with a complex hierarchical architecture. The presence of IL-like units allows these materials to exhibit thermoresponsive behaviour (lower critical solution temperature: LCST). The different structural elements of the IL-like moieties can be used to fine tune this LCST. Potential applications of these systems for the synthesis and stabilisation of AuNPs-PILs composites are reported. The corresponding thermoresponsive composite showed a tunable LCST behaviour.

The sixth chapter introduces the use of electrospinning for the synthesis of polymeric membranes of blends of different PILs with poly(vinylpyrrolidone) (PVP). The interactions between PILs/PVP define the morphology and properties of the obtained membranes. Self-complementary interactions like hydrogen bonding, electrostatic interactions and hydrophobic interactions facilitate the electrospinning process. The differences observed for the solutions containing PILs and PVP (e.g. increase on viscosity, conductivity, etc), the final fibers morphologies and performance are related with the nature of these supramolecular interactions. They are dictated by the chemical information contained in the molecular structures of the two polymers defining self-complementary interactions and driving the self-organization and self-assembly of the polymers onto well-defined nanostructures assemblies under electrospinning conditions. Thus, the properties and the morphologies of the mats obtained can be tune by changing the molecular vectors of PILs. In this way, we were able to obtain materials with potential applications in different fields such as the oil-water separation or the synthesis and stabilisation of AuNPs.

The last chapter of the thesis covers the development of a new synthetic methodology for the preparation of new advanced polymeric materials based on the use of Poly(Acrylamide-Homocysteine Thiolactone) (PAHT). This polymer can be obtained by RAFT polymerisation and can be used as a starting material for the synthesis of a great variety of advanced materials with different morphologies and specific properties obtained by its post-modification. The chapter illustrates the utility of this approach for the preparation of functionalised polymers containing IL-like units (PILs). Different examples of how this methodology allows for the synthesis of a plethora of PILs are

given. This new methodology opens the possibility of design and obtaining PILs with a careful control of their properties according to the specific needs of the different fields such as materials science, separation or catalysis.

Divulgación de este trabajo

Algunos resultados de la presente Tesis Doctoral han sido publicados en revistas de carácter científico y otros se recogen en artículos aún pendientes de publicación.

1. Montolio, S.; González, L.; Altava, B.; Tenhu, H.; Burguete, M. I.; García-Verdugo, E.; Luis, S. V. **LCST-type polymers based on chiral-polymeric ionic liquids**. *Chem. Commun.* **2014**, *50*, 10683-10686.
2. Montolio, S.; Vicent, C.; Aseyev, V.; Alfonso, I.; Burguete, M. I.; Tenhu, H.; García-Verdugo, E.; Luis, S. V. **AuNP-Polymeric Ionic Liquid Composite Multicatalytic Nanoreactors for One-Pot Cascade Reactions**. *ACS Catal.* **2016**, *6*, 7230-7237.
3. Montolio, S.; Porcar, R.; Burguete, M. I.; García-Verdugo, E.; Luis, S. V. **Preparation and study of multifunctional crosslinked PILs based on RAFT-prepared linear polymers**. Manuscrito preparado para ser enviado a una revista científica.
4. Montolio, S.; Abarca, G.; Porcar, R.; Dupont, J.; Burguete, M. I.; García-Verdugo, E.; Luis, S. V. **Hierarchically structured Polymeric Ionic Liquids and Polyvinylpyrrolidone mat-fibers fabricated by electrospinning**. Manuscrito para enviar a *Journal of Materials Chemistry A*.
5. Montolio, S.; Zagorodko, O.; Porcar, R.; Burguete, M. I.; Luis, S. V.; Tenhu, H.; García-Verdugo, E. **Poly(acrylamide-homocysteine thiolactone) as suitable platform for the preparation of advanced materials by post ring-opening-orthogonal modifications**. Manuscrito para enviar a *Polymer Chemistry*.

Asimismo, parte de los resultados de la investigación también han sido presentados en diversos congresos científicos de carácter nacional e internacional.

1. Montolio, S.; Zagorodko, O.; Porcar, R.; Burguete, M. I.; Luis, S. V.; Tenhu, H.; García-Verdugo E. *Poly(acrylamide-homocysteine thiolactone) as suitable platform for the preparation of advanced materials* (Comunicación oral), Nordic Polymer Days 2016 Nordic Rheology Conference, Helsinki (Finlandia), **2016**.
2. Montolio, S.; Porcar, R.; Burguete, M. I.; García-Verdugo E.; Luis, S. V. *Diseño y estudio de materiales avanzados autoorganizados basados en líquidos iónicos poliméricos* (Comunicación oral), XII Simposio de Investigadores Jóvenes. RSEQ, Barcelona (España), **2015**.
3. Luis, S. V.; Burguete, M. I.; García-Verdugo E.; Porcar, R.; Peris, R.; Montolio, S.; Nuevo, D. *Polymer Supported Ionic Liquid-Like Phases (SILLPs) as efficient materials for the development of multicyclic processes* (Comunicación oral), 19th Annual Green Chemistry Conference, Washington (EE. UU.), **2015**.
4. Montolio, S.; Burguete, M. I.; García-Verdugo E.; Luis, S. V. *Síntesis y Caracterización de Membranas poliméricas obtenidas por electro estirado de poli-p-clorometilostireno y líquidos iónicos poliméricos* (Póster), XI Simposio de Investigadores Jóvenes. RSEQ/SIGMA-ALDRICH, Bilbao (España), **2014**.
5. García-Verdugo, E.; Burguete, M. I.; Porcar, R.; Restrepo, J.; Chen, X.; Bernal, J. M.; Lozano, P.; Luis, S. V. *Supported Ionic Liquid-Like Composites: Advanced Materials for Catalytic Processes* (Comunicación oral), 4th International Congress on Green Process Engineering, Sevilla (España), **2014**.
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“Science and everyday life cannot and should not be separated.

Science gives a partial explanation for life.

It is based on fact, experience and experiment.”

Rosalind Franklin

Chapter 1

Introduction

Chapter 1. Introduction

1.1. Towards greener catalytic processes using PILs and related IL-like polymeric Phases.

The main goal of the Green Chemistry is gradually to achieve the reduction and elimination of hazardous substances in the design, manufacture and application of chemical products and processes.[1] In this context, the use of solvents is one of the majors concerns to develop more environmentally benign processes.[2] Indeed, solvents often account for the vast majority of mass wasted in syntheses and processes.[3] Furthermore, many conventional solvents are toxic, flammable and/or corrosive. Their volatility and solubility have contributed to air, water and land pollution, have increased the risk of workers' exposure, and have led to serious accidents. Moreover, their recovery and reuse, when possible, is often associated with energy-intensive distillation and sometimes cross contamination.

Figure 1.1. Scheme of volatility and polarity characteristics of neoteric solvents.

Solvent elimination and/or substitution is not an easy task, as they are key elements in chemical processes. Indeed, solvent provides an environment where reactants meet. Solvent dilutes the reactants and/or the catalysts. Furthermore, by changing its nature (inert, polarizable, protogenic, protophilic, etc.) transition states and catalysts can be either stabilized or destabilized. Finally, the solvent should assist for the homogeneous distribution of the energy needed for the reaction activation.[4] Thus, new solvents systems should be design to deliver all these requirements and to be environmentally friendly.

In an effort to address all these issues, chemists started a search for safer new environmentally benign solvents or green solvents, which can easily be recovered/recycled and which can allow efficient application for the analytic processes. In this respect, ionic liquids (ILs), supercritical fluids (SCFs) and fluorous solvents are the non-aqueous alternative solvents, also named neoteric solvents, that are receiving most worldwide attention in recent years to reduce and replace traditional organic solvents (Figure 1.1.).[5]

ILs are a new class of polar liquid solvents and their use has led to a new green chemical revolution because of their unique array of physico-chemical properties, headed by its non-volatile character, which makes them suitable for numerous industrial applications.[6,7] In this way, during the last decades, the use of ILs has become one of the most useful techniques for the development of green chemistry tools.[8] The potential use of liquid salts based on delocalized organic cations (ammonium or phosphonium) as design green solvents represents one of the most significant contributions to modern chemistry. Their high structural modularity based on the proper selection of the cation and anion moieties has allowed developing an almost infinite number of compounds well suited for each specific application.[9] The lack of a measurable vapor pressure of ionic liquids (ILs) and their tailor-made physico-chemical properties are important reasons for their widespread use as green solvents and reaction media. [6] The low volatility of ILs makes them an attractive alternative to volatile organic solvents, as they are unlikely to act as air contaminants even though some ILs can be distilled at low pressure without decomposition.[10]

Despite their discovery about 100 years ago[11], this new class of materials did not draw much interest at the time. ILs, however, have attracted considerable attention in recent years because of their interesting and very particular physicochemical properties mentioned above including high ionic conductivity, excellent thermal/chemical stability, low vapor pressure, very reduced flammability, high density and viscosity, high polarity and strong solubilizing ability. Originally, ILs emerged as a new class of electrolytes to be used in batteries and as neoteric solvents, replacing volatile organic compounds in many organic reactions and in a wide variety of processes.[12 , 13]

Nevertheless, the application of ILs needs also to face some challenges and limitation, not foreseen when the boom of the ILs started, in order to become a real solution for practical applications.[14] These drawbacks might hamper the general use of ILs in scientific and technological applications. A first concern is the cost of ILs. It is

clearly much higher than for traditional solvents. Although some ILs are commercially available, they are still too expensive for high volume and low-price applications. It is also a raising worry about the toxicity and biodegradability of the ILs.[15] Although ILs have been described traditionally as environmentally friendly solvents because of the lack of any appreciable vapor pressure, some of the most usual ILs present some environmental concerns in particular in terms of their contact with aqueous media.[16] As a matter of fact and due to their significant solubility in water,[17] ILs may enter into the environment through industrial wastewater contaminating environmental recipients like soils, sediments, surface and groundwater. Indeed, some ILs can be classified as relatively stable in environment due to their resistant to photodegradation and small degree biodegradation.[18 , 19 , 20] Consequently, there are raising concerns about their potential impacts on the aquatic and terrestrial environments.[21 , 22]. Indeed, the toxicity data have been extensively reported and suggest the possible toxicity of ILs to the environment. [23]

Figure 1.2. PILs as new type of material combining the properties of molecular polymeric materials and ILs.

It should be remarked, however, that the structural flexibility of the ILs allows the development of a new generation of ILs using low toxic and well biodegradable structural elements able to provide the same proprieties than the first generation ones. Accordingly, the structural modification-based approaches allow the design and synthesis “greener” ILs being nontoxic and biodegradable.[24 , 25]

Alternatively, in the last few years, the use of supported ILs has emerged as a simple and straightforward solution to overcome many of above mentioned drawbacks. The immobilization of the ILs onto a solid support provides a substantial reduction of the amount of IL required for a given application.[26 , 27] It reduces accordingly the

associated cost and facilitates their handling and manipulation, and finally, greatly mitigates the potential environmental risks of an uncontrolled spill of the ILs to water.

In this context, intensive attention has been paid to polymeric ionic liquids (PILs) which are macromolecular structures formed by ionic liquid units connected through a polymeric backbone (Figure 1.2).[28 , 29] This new class of polyelectrolytes expands the properties and applications of ILs since they combine the unique characteristics of ILs with those of polymers.[30] The main advantages are the enhanced mechanical stability, improved processability, better flexibility and durability, as well as improved dimensional control over their structure.[31 , 32] The chemical structures of common types of cationic and anionic PILs are shown in Figure 1.3.

Building blocks of conventional PILs and related materials

Figure 1.3. Chemical structures of common types of (a) cationic and (b) anionic arms of branched polyelectrolytes. (c) Chemical structures of common ionic groups of branched poly- and oligo(ionic liquid)s and their counterions. (d) Commonly used polymeric backbones of linear poly(ionic liquid)s (taken from ref. 38)

It is well-known that the physico-chemical characteristics of ILs depend not only of the coulombic forces established between the cation and the anion, but also on the formation of extended networks of additional interactions (among others H-bonds, π - π or C-H... π interactions...) having strong implications on their three-dimensional (3D) organisation and therefore on the final properties of the ILs. Although in the liquid-phase this network of interactions is weaker than in the solid-phase, the local order in the liquid-phase resembles those found in solid phases. Indeed, ILs may be described as “*polymeric supramolecular fluids*” and, consequently, as systems that are highly structured in the liquid state.[33,34,35] These well-organized polymeric supramolecular networks of interactions can be reinforced by the introduction in the ILs of additional functional groups. Thus, for instance, the presence on the IL moieties of groups like alcohol, nitrile or urea has a big impact in the intermolecular interactions and therefore in the supramolecular organization of the IL.[36] Moreover, there is now much evidence indicating that some of the supramolecular organization can be maintained when they are mixed with other solvents.[37] These interactions, which define the ILs molecular structure and properties, are highly dependent on the substitution pattern of the salt (e.g. the length of the alkyl chain(s)) as well as on the nature of the counterion. In this way, it is expected that polymers functionalised with ionic liquid-like moieties can give rise the formation of specific supramolecular structures driving by similar forces for self-assembly include intra- and intermolecular interactions (covalent-bonding, electrostatic interactions, hydrogen bonding, hydrophobic interactions...).[38] Thus, the introduction of functional groups associated to ILs into polymers in combination with the corresponding molecular architectures and morphologies of the polymers can create a new family of materials with particular properties. Besides, these composites can be pre-designed, in principle, at the molecular level to self-assemble and form specific structures at the micro- or nanoscale. This is the main reason why nanostructured PILs have been increasingly receiving attention for the last decade.[39] Among the different potential applications we can highlight their use as catalysts,[40] responsive materials,[41] sensing,[42] CO₂ sorbents,[43, 44] separation,[45, 46] ion-transport materials or energy- and bio-related topics could be mentioned.[47] It is evident that both the pre-organization and self-assembly of the structures and the unique properties of PILs, together define their functionality and therefore their suitability for above mentioned applications.

Regarding catalytic applications, the preparation of well-defined hierarchically organized polymeric architectures is of great interest and a proper understanding of the structure-property relationships taking place is essential for a proper design and for the optimization of structures and applications.

Specifically, the final polymer architecture is very important for catalytic applications, since it must provide a suitable location and arrangement of the functional groups in order to achieve an efficient catalytic activity (fast and selective). In this way, we intend to focus here, specifically, on the structure-property relationships that can be found in PILs and how their knowledge and understanding can allow the improvement and optimization of their catalytic applications, through the analysis of some noteworthy examples.

In the context of this PhD-thesis, here we will examine and discuss some essential properties of polymeric ionic liquid (PILs) as well as the different approaches for synthesizing them. Their classification based on structural parameters and the derived properties will also be described and discussed in this context together with their application to develop new catalytic methodologies complying the Green Chemistry principles.

Our goal in this introduction is not to present a comprehensive summary of all examples reported for every category of catalytically applications but, instead, to present some significant cases. We will highlight how soluble and insoluble 3D polymeric frameworks, with different crosslinking degrees, containing IL-like units provide to these new polymeric materials the main features of the ILs at molecular level (stability, tunable polarity, etc.). Thus, they can be applied for catalytic processes in an analogous way to bulk ILs but simplifying product isolation and recycling of the catalyst-IL-phase. Thus, soluble and insoluble polymeric frameworks containing IL-like units can i) assist the activation of the catalyst, ii) generate novel catalytic species, iii) improve the catalyst stability, iv) optimize immobilization and recyclability, v) facilitate product isolation and vi) influence the selectivity of the reaction.

1.2. Synthesis and structures of PILs and related IL-like polymeric phases.

Polymeric Ionic Liquids (PILs) represent a direct and more common approach to the incorporation of IL-moieties in polymeric structures. However, ILs can also be immobilized on a large variety of materials such as porous surfaces, resins, monoliths or other polymeric matrices by impregnation, covalent bonding, adsorption, sol-gel routes, etc.

ILs have been supported either by coating the surface of an organic (polymeric) or inorganic support with a thin layer of the corresponding IL constitutes the initial

approach in the search of systems able to bring together the proprieties of advanced materials and ILs. Generally, materials prepared by absorption of ILs on a porous support are known as SILPs (Supported Ionic Liquid Phases).[48] These type of materials have proved their application in different fields, however they present an essential limitation: the leaching of the IL phase. This can be easily avoided by covalent attachment of structural fragments related to ILs to different functional groups present in the surface. ILs covalently supported on surfaces are designed as SILLPs (Supported Ionic Liquid-Like Phases).[49] In the last years, more attention has been paid to the study of this type of materials, where the IL-like unit is or even PILs chains are immobilized onto insoluble crosslinked porous materials using either “*grafting from*” or “*grafting to*” methodologies.[50]

However, most applications in this field have been associated to the development of soluble polymers containing structural moieties related to ILs: imidazolium, phosphonium or ammonium groups with the corresponding counter ion. In general, this type of materials can be classified as polyelectrolytes.[51]

Figure 1.4. Synthesis of supports ILs and related PILs obtained either by grafting or by polymerization techniques. (F.G.: functional group).

In principle, the more simple and versatile approach for the preparation of those materials is the use of already preformed common polymeric support having the appropriate morphological, chemical properties and functionality. The introduction of the IL-like units is obtained by grafting protocols. This is exemplified in Figure 1.4., in which linker (functional group, -NH₂, CH₂Cl, -CH₂SH, -CO₂H, etc.) attach to the support is used for the introduction of the IL-like units onto in the support backbone. The transformation of these functional groups into the corresponding IL-like phases

can be achieved by simple reaction precursor (i.e. imidazolium groups or with graftable PILs) with the functional groups at the surface of the support. A quantitative transformation of the functional groups can be obtained after a few hours of heating of the corresponding support with the desired precursor. The progress of the process can be easily monitored through different methods that have been developed through the years for analysing the transformation of solid support organic chemistry. The advantage of this approach is that the architecture and morphological characteristics of the support are well known and accordingly the expected properties of resulting modified support can be easily predicted and controlled.

An alternative strategy, usually exploited for organic polymeric supports, lays on the polymerization of the corresponding commercial standard precursor (tetraethyl orthosilicate (TEOS) for inorganic supports and monomers in the case of polymers) with modified precursor containing IL fragments. This is exemplified in Figure 1.4. for the case of matrix bearing imidazolium subunits as ILs-like fragments.

For instance, Polymeric Ionic Liquids (PILs) can be prepared by free radical polymerization of vinyl, (meth)acrylic, and styrenic monomers containing IL moieties. In PILs, the IL moieties are incorporated either in the polymer backbone or in the main polymeric side chains. Besides controlling the type of polymerization used either random or alternate copolymers can be obtained. In general, PILs are prepared as linear soluble polymers. However, when variable amounts of a crosslinking agent are added (i.e. divinylbenzene, diacrylate) the corresponding insoluble polymers can be also obtained.

Shaplov *et al.* have recently reviewed the synthesis and polymerization of different IL-like monomers to obtain PILs.[52] A majority of the reported PILs have been prepared by conventional free radical polymerization (FRP). However, since their appearance in the mid-1990s, the fast development of controlled/living radical polymerization (CRP) techniques has made a strong impact on polymer science.[53] The three most common types of CRP are: nitroxide mediated polymerization (NMP),[54] atom transfer radical polymerization (ATRP)[55] and reversible addition-fragmentation chain transfer (RAFT) polymerization.[56] The main difference between CPR and FRP is that in CRP the termination reactions are reduced considerably by addition of a control agent in the reaction to promote the reversible deactivation of propagating chains. For example, in NMP a nitroxide is added to the system to deactivate propagating radicals and minimize mutual termination. In ATRP, a transition metal catalyst is used while in RAFT a chain transfer agent is responsible for

The RAFT process was first reported by the group of Rizzardo, Moad and Thang,[59 , 60] and involves adding a small amount of a thiocarbonylthio compound that acts as a chain transfer agent (CTA) in addition to a traditional radical initiator. In the presence of the radical species generated, the CTA induces reversible addition-fragmentation transfer reactions to create a dynamic equilibrium between active species and dormant species. This equilibrium is responsible for the control of the polymerization (Figure 1.5.). When the polymerization is stopped, most chains retain a thiocarbonylthio end group,[61] which can be cleaved easily into thiol groups suitable for further modification and to act as precursors for novel materials.[62]

Thus, RAFT polymerization techniques allow the introduction of ionic liquid like units in a very versatile and controlled fashion leading to different polymeric architectures (i.e. synthesis of homo-, gradient, block copolymers and star polymers as well as more complex architectures including microgels and polymer brushes, Figure 1.6.). Furthermore, PILs are polyelectrolyte macromolecules with ionizable groups that can adopt any of the aforementioned structures and are able to self-assemble by noncovalent interactions to produce high ordered and complex hierarchical structures with different 3D final morphologies, organized at the nanolevel, such as micelles, vesicles, nanoparticles, films, etc.[38, 63] These second level of self-organization is going to define their final properties for a given application.

There are in the literature many publications reporting the controlled synthesis of PILs *via* RAFT processes. As illustrative examples to define the potential of the RAFT polymerization methodology, we can cited, for instance, the work developed by Mecerreyes, Taton and Gnanou and coworkers who succeeded in the synthesis of a series of PIL-based double hydrophilic block copolymers having ionic responsive properties by RAFT polymerizations (Figure 1.7.).[64]

Figure 1.6. Some possible PILs architectures obtained by RAFT polymerization (taken from ref. 61)

These novel composites combined the anionic sensitivity with self-assembly properties in water, which afforded them the capacity to act as sensors of anions. The solution properties of these polymers could be further manipulated, for instance, by chemical modification of the hydrophilic poly(methacrylic acid) block into a hydrophobic poly(methyl methacrylate acid) one. More interestingly, the anion sensitivity of these polymers, that is the change of solubility in water as a function of the counteranion associated with the ionic liquid block was found to occur reversibly. Thus, either soluble unimers with Br⁻-As-anion or micellar aggregates of varying size with NTf₂⁻ as counteranion were observed in water. Thus, by tuning a simple structural vector the physico-chemical properties and the polymer architecture can be tuned.

Figure 1.7. Chemical Manipulation of IL-Based Block Copolymers obtained by RAFT polymerization by anion Exchange Reactions and self-assemble into highly ordered 3D structures. (taken from ref. 64)

RAFT polymerization can also be used for the introduction on the main polymeric chain of additional functionality proving the PILs with unique characteristic. In this regards, thermoresponsiveness can be considered as a very important property derived from the self-assembly capacity of different polymers.[41] The phenomena of upper critical solution temperature (UCST)- and lower critical solution temperature (LCST)-type phase transition have been widely utilized to produce “smart” materials. Jain and coworkers reported the tunable LCST behaviour of a copolymer derived from the well-known poly(*N*-isopropylacrylamide), PNIPAM, containing different IL units.[65] Their results confirmed the great importance of the molecular structure in defining the interactions occurring and, accordingly, the final properties. The origin of the thermal responsiveness is inherent to the balance between polymer-polymer and polymer-solvent interactions. Thus, in this case, below the LCST, the polymer chains exist as individual coils due to the hydrogen bonding of the amide groups with water

but above this temperature, conformational equilibrium are activated and hydrophobic interactions from the backbone become dominant leading to the aggregation of hydrophobic moieties from different polymeric chains. Thus, structural factors that enhance polymer-water interactions result in an increase in the LCST. On the contrary, increasing the polymer-polymer interactions decreases the LCST. These stimuli-responsive polymers offer a wide range of applications in drug-delivery, sensors, separation, etc. [66] They can also be useful in catalysis as they allow catalyst separation just by changing the temperature of the solution. [67]

Lu *et al.* obtained by RAFT polymerization a “smart” material based on a PIL copolymer possessing thermoresponsive properties being able to facilitate the separation of natural products. In particular, they were used as extractants of tocopherols showing a good recyclability (Figure 1.8).[68] This is a good illustration of how the structure of the polymer can define a property that it can be exploited in a particular application.

Figure 1.8. Representative Cyclic Extractive Separation for Tocopherol Homologues Using Poly(VBIM-Ala₈-r-NIPAM₅) as Extractant (taken from ref. 68)

PILs can be also obtained by post-modification of a polymer obtained by RAFT polymerization of a functional monomer. For instance, Tang *et al.* have reported the preparation of a linear PIL homopolymer by post-polymerization modification of poly(*p*-chloromethylstyrene) (poly(VBCL)) using 1-butyylimidazole. After the RAFT polymerization of *p*-chloromethylstyrene, the quaternization of the chloromethyl units was carried out.[69] ILs are characterized by their ability for CO₂ capture and

separation. Nowadays, the efficient separation of CO₂ from other light gases such as N₂, CH₄ and H₂ is still an environmentally relevant and challenging task of significant importance from both the industry and basic science perspective. These functional materials not only retained the key macroscopic features of the original polymer but also possessed the main properties of ILs. Thus, this material is able to absorb CO₂ and it was proven that PILs exhibit higher CO₂ absorption capacity than the corresponding ILs. Some PILs exhibited an even higher CO₂ absorption capacity than the corresponding ILs.[70] Once again, the appropriate structural variations can serve to improve CO₂ permeability and selectivity as much as these properties were found to be dependent on the PIL polycation backbone. These results are important to highlight how the polymeric morphology can enhance the intrinsic properties of the ILs.

1.3. Physico-chemical characteristics of the polymeric ionic liquids and related polymeric IL-like phases.

In all these polymeric ILs derivatives, the proper transfer of essential properties of the ILs to the solid phase need to be guaranteed, and this is not a simple matter. However, it is reasonable to assume that if this goal of transferring IL properties to the polymer is achieved, the resulting materials would present the advantages associated to ILs at molecular level but would overcome some of the drawbacks currently limiting many technological applications of bulk ILs.

The physico-chemical characteristics of a given polymer are associated to their morphology and chemical properties of the material itself (porosity, surface area, mechanical resistance...), however many of their properties (polarity, thermal stability, conductivity, swelling, etc.) will be modified and tuned by the introduction of the ionic liquid-like fragments covalently attached to them. Thus, the introduction of IL-like units onto a polymeric structure will be able to transfer to this material the essential properties associated to the bulk ILs at molecular level. In this section, the analysis of a variety of the characteristic properties of ILs on the corresponding PILs and SILLPs will be briefly reviewed. This is an essential factor as much as some of the most important catalytic applications of ILs are dependent on their potential as “*designer solvents*” being able to provide the desired properties, almost in an unlimited way, through the proper modular modification of their structural parameters.

It is generally understood that ILs possess the capability to undergo a multitude of solvation interactions with the reactants and catalysts. This versatility in the interaction reactants/catalyst with ILs is one of the main drivers allowing the efficient use of ILs for different catalytic applications. For instance, the ILs possess a dual nature

in which they are able of undergoing interactions with both polar and nonpolar molecules. Indeed both cation and anion can undergo to specific interaction with the reactants and catalysts through ion exchange, hydrogen bond, $n-\pi$, $\pi-\pi$, dipolarity, hydrogen-bond acidity, hydrogen-bond basicity, π -stacking and hydrophobic (hydrophilic) interactions. The extent of these interactions can have a strong influence in the catalytic outcome of a given process.

Polarity: In this context, polarity of the ILs is an important property as a well-accepted concept used to characterize solvent behaviour. The polarity considers all the interactions (dispersion, dipole-type, hydrogen bond formation) that do not result in bond formation. The polarity of ILs can be significant tuned through changes in their structure, either by modification of the imidazolium substituents or by modification of the counteranion.[71]

The polarity assessment through the use of solvathocromic probes is one of the most simple and accessible techniques for a rapid and semiquantitative analysis.[72] Thus, in order to evaluate the modification of the polarity of a support upon modification with IL-like units the use of well-known solvathocromic probes such as pyrene[73] and the Reichardt's[74] probe constitute a simple and fast methodology.

For instance, commercial available polystyrene-divinylbenzene (PS-DVB) Merrifield resin can be simply modified by covalent attachment of alkyl-imidazole units (i.e. methylimidazole) and further counteranion exchange of Cl^- by BF_4^- , TfO^- and NTf_2^- to obtain a series of supported ILs (SILLPs, Figure 1.9.). The Reichardt's probe can be used to evaluate the polarity of these materials. From these $E_T(30)$ and $E_T(N)$ values, it can be deduced that there is a big change in polarity between the starting Merrifield resin, with a value of 0.292, and the supported polymers with values between 0.6 and 0.7.[75] The values obtained for $E_T(N)$ for these supported ILs are in good agreement with those reported for related bulk ILs (butyl imidazolium salts: BMIM).[76] The differences observed might be due to the fact that the cations are of a similar nature (both are imidazolium derivatives), but one of the substituents is different (benzylic in the case of *g*-SILLPs and butyl in the case of BMIM). This might explain the small deviations observed. These results reinforce the theory that the properties of the ionic liquids were transferred to the supported species.

Figure 1.9. Reichardt's dye for the determination of the polarity of the SILLPs.

The effect of the anion is more visible, however, when pyrene is used as the fluorescent probe. The ratio I_3/I_1 ratio is used to measure the polarity.[77] In this case the more coordinating anion (Cl⁻) is associated to a higher value of polarity (higher value of I_3/I_1), whereas the presence of the less coordinating NTf₂⁻ anion gives place to a lower value of I_3/I_1 . [78] The Figure 1.10. shows I_3/I_1 the values obtained for the same polymers modified with IL-like units. These values show a wide variation in polarity as a result of the metathesis of the anion. This observation is not in agreement with the values predicted employing the Reichardt's dye method. As pointed out above, the Reichardt's dye is not sensitive to the effect of the anion, and by this method it was proved that the anion plays an important role to determine the macroscopic properties of SILLPs. The pyrene method was also found to be more sensitive to polarity changes in the matrix. The general values obtained are again in good agreement with the values obtained in solution for related solvents and material and bulk ILs.[79]

Figure 1.10. Pyrene for the determination of the polarity of the SILLPs.

However, due to the high hygroscopicity of the *g*-SILLPs and the low polarity of the backbone polymeric matrix, the humidity contained by the polymer is expected to be located in the microenvironment of the SILLP. Therefore, a high affinity of the pyrene to the aromatic structure of the backbone polymer, together with a expected hydrophobic effect with the water associated to the imidazolium subunits would partially associate the pyrene to the backbone benzylic groups, leading to experimental values of I_1/I_3 (and thus of ϵ) lower than the expected in the highly polar environment of the ionic liquids. Hence, another measurement of the polarity of the ionic liquids was necessary. For this purpose ATR-FT-IR spectra from the *g*-SILLPs were recorded. The region corresponding to the water adsorbed to the anion was represented in all cases and the curves obtained were deconvoluted to identify the ν_1 and ν_3 bands. The displacements found in this study are in good agreement to those described by Cammarata and coworkers.[80] Köddermann and coworkers reported a method to determine the polarity of ionic liquids by studying the vibrational modes of the water associated with the ionic liquid.[81] This means that water is coordinated to the SILLPs in a similar way to the ILs in solution. Thus, the polarity in the microenvironment of the ionic species in the SILLPs is very similar to that of the bulk ILs. The Figure 1.11.

showed the discrepancies for the values found for the dielectric constant for these materials calculated either by pyrene or water coordinated to the IL-like units.

Significant differences in polarity were obtained as a function of the anion for both methods and the order of polarity decreased in the same order $\text{Cl}^- > \text{TfO}^- > \text{NTf}_2^- \approx \text{BF}_4^- \approx \text{SbF}_6^-$. A high affinity of the pyrene to the aromatic structure of the polymeric backbone, together with the expected hydrophobic effect induced by the water associated to the imidazolium subunits could favour the association of the pyrene to the backbone, leading to experimental values of I_1/I_3 (and thus of ϵ) lower than those expected for the highly polar environment of the ionic liquids. This fact may explain the differences found for the calculated polarity by Ludwig's methodology (Figure 1.11., blue squares) and those obtained using pyrene as probe (Figure 1.11., red dots), specially for the more polar anions.

Figure 1.11. Dielectric constants calculated for *g*-SILLPs as function of the anion by Ludwig's method (blue squares) and using pyrene as probe (red dots).

As clearly seen from the above data, as much as the former solvathochromic parameters are dependent on adsorption phenomena on a heterogeneous surface, the quantitative data obtained must be handled with caution. However, the results suggest the transference of the polarity of the ILs to the surface of these polymeric materials.

The solvation parameter model of different imidazolium, pyridinium, pyrrolidinium, and ammonium-based ILs was studied using these ILs as GC stationary phases. [82] The anion significantly influences the hydrogen bond basicity and

dipolarity of the ILs. An increasing hydrogen-bond basicity was observed for ILs containing the following anions: $[\text{PF}_6]^- < [\text{NTf}_2]^- < [\text{BF}_4]^- < [\text{TfO}]^- < [\text{Cl}]^-$. The higher the hydrogen bond basicity of an IL, the higher its retention of proton-donating analytes. On the other hand, the properties of the ILs can also be modified by tuning the anion. Thus, tris(pentafluoroethyl)-trifluorophosphate highly interacts with hydrogen-bond basic molecules exhibiting a significantly higher hydrogen-bond acidity and lower hydrogen-bond basicity than NTf_2^- (~ 2.5 fold at 50°C).[83].

The introduction of functional groups in the IL-phase can large influence the hydrogen-bond basicity as well as the dipolarity of the IL as well as the presence of an aromatic component into the cation of imidazolium-based ILs can increase the interactions with polycyclic aromatic hydrocarbons due to an enhanced π - π interaction. [84, 85].

Swelling: Other indication of the interaction of the supported ILs and PILs with the different solvents, especially for gel-type polymers containing low levels of crosslinking, is the swelling. The use of those polymers for applications requiring the accessibility of the functional sites on the polymeric backbone is always associated to the presence of a good solvent, compatible with the polymeric matrix, being able to expand the polymeric chains.[86] This will be of great importance in the polymeric phases based on modified support with PILs as well as with polymeric supported ILs-like phases. In this context, Muldoon and Gordon first reported on crosslinked poly(IL) beads formed from imidazolium cations with vinyl groups that were able to swell in organic solvents such as acetone, but did not quantify the degree of swelling.[87] Battrra and coworkers demonstrated that amphiphilic poly(IL) materials produced from the photopolymerization of 1-octyl acrylate-3-methylimidazolium chloride in the presence of 23 wt % water were capable of forming hydrogels that swell to nearly 200 times (w/w) in water, with approximately 50 times (w/w) swelling in EtOH, DMSO, MeOH, and DMF.[88] Although the inclusion of water was necessary to solubilize the monomer, which was a waxy solid at ambient temperature, it is not clear as to whether the water already present within the poly(IL) structure promoted uptake of these polar organic solvents. Less polar solvents such as 1-octanol, hexanes, EtOAc, and CHCl_3 had minimal or no swelling of the material.

On the other hand, gel type poly(styrene-divinylbenzene) (PS-DVB) modified with IL-like showed a significant changes depending of the nature of the imidazolium moieties. In general, PS-DVB polymers are considered hydrophobic materials, not being compatible with the use of polar solvents such as water or methanol. It can be expected that the introduction of imidazolium or others IL-like subunits will provide an important change in the polarity of the matrix, favouring the swelling of the polymer by polar solvents. In this regard, the swelling of a polymer with a polar solvent such as water can be considered an indirect measurement of polarity. Although the corresponding values cannot be used for a quantitative assessment of polarity, they represent a very interesting parameter for practical applications as much as water (and other polar solvents) are of great practical interest. Figure 1.13. shows some data obtained for SILLPs prepared from a gel-type Merrifield resin with a high loading of functional groups (4.3 mmol Cl/g). This figure allows observing the expected trends associated to the changes in the structure of the IL-like fragment.

Figure 1.13. Percentage of swelling calculated as relative size increase of Merrifield resin (4.3 meq/g) modified with methylimidazole. Influence of the anion ($X = \text{Cl}, \text{BF}_4$ and NTf_2).

DMF is a compatible solvent with all the resins employed. Especially noteworthy is the behaviour of the polymers in water and hexane. In water, the starting Merrifield shrank. However, after the reaction with 1-methylimidazole, the resin increased in size up to a 43% compared to its dry state. This implies a complete change in the properties

of the resin that became highly hydrophilic when the SILLP was formed. The different anions swelled in different degrees (Figure 1.13.). At the other extreme, NTf_2^- again shrank in water. This is consistent with the fact that this anion is a highly hydrophobic one, as evidenced by the high contact angle of water on a layer of gold covered by a supported ionic liquid with this anion.[58] In the case of hexane, the starting resin shrank due to the lack of compatibility between the solvent and the polymers. However, for BF_4^- and especially for NTf_2^- showed a higher swelling in this medium. Thus, a reaction carried out in hexane would in principle be favoured by a polymer with IL-like units containing this NTf_2^- relative to another with a different chemical composition. On the other hand, the substitution of the methyl substituent ($\text{R} = \text{CH}_3$) by a more lipophilic one ($\text{R} = \text{C}_{10}\text{H}_{21}$) produces an appreciable decrease on the swelling in water from 47 % to 15 % respectively.

Ono et al. reported on a crosslinked copolymer gel network containing with ammonium cations or octadecyl groups attached the polyacrylate backbone.[89] The material was observed to swell over 120 times (w/w) in CH_2Cl_2 and THF, 99 times in CHCl_3 , 70 times in chlorobenzene, and 11 times in hexane. Little or no swelling was observed for DMSO, DMF, MeOH, or CH_3CN . More recently, polyelectrolyte gels containing a ternary mixture of vinyl imidazolium monomers, crosslinkable vinyl gemini imidazolium salts, and tetradecyl acrylate were shown to swell in solvents with low dielectric constants (ϵ) such as CCl_4 , CHCl_3 , CH_2Cl_2 , THF, and toluene at levels of ~ 10 – 50 times (w/w), yet had no absorption of solvents with larger ϵ values such as CH_3CN , DMSO, and DMF.[90]

These examples where poly(IL) materials were swollen by molecular solvents employ relatively sophisticated, highly tailored monomers, and crosslinkers. Furthermore, the swelling behaviour is engineered based on a balance between long alkyl chains tethered to the imidazolium/ammonium cations as well as physical/chemical crosslinking. In this regards, a simple PILs not crosslinked materials are also prone to suffer significant swelling in neutral molecular solvents. Indeed, solvents having a dipole moments >2 D swells significantly being able to absorb nearly 400 times of its initial mass in propylene carbonate and more than 200 times in DMSO. The NMR studies, in particular ^1H -NMR, suggest a weakened of the cation–anion interactions and/or π –cation interactions between the benzene and imidazolium rings by interaction of the PILs with solvents with relatively large dipole moments leading to the PILs to swell. This study highlight the interaction into PILs-solvent or supported

ILs-solvent are of key importance to design functional or responsive materials for analytic application.[91]

Figure 1.14. Digital photographs of 10 mm diameter pristine poly(IL) sample punched from the bulk (left); and the poly(IL) material fully swollen to ~89 mm diameter in DMSO (right) (taken from ref 91).

A simple, fast, sustainable, and scalable strategy to prepare nanoporous materials based on PILs relies on the radical polymerization of crosslinker-type IL monomers in the presence of an analogous IL, which acts as a porogenic solvent.[92] This IL can be extracted easily after polymerization and recycled for further use. The properties of the resulting materials specific surface area, porosity, pore size and swelling depends on monomer/porogen ratios used. Noteworthy, the polymers showed very limited swelling in water, due to the hydrophobic nature of the anion, but presented a nonlinear increased of the swelling in acetone (correlated to the porogen quantity) reaching a maximum of 500 vol% for a ratio monomer:porogen 1:5.

Figure 1.15. Swelling test in water and acetone. PIL samples from left to right: PIL1:0, PIL1:0.5, PIL1:1, PIL1:2, PIL1:3, PIL1:5, and PIL1:10. a) Dry PIL samples. b) PIL samples in water. c) PIL samples in acetone. d) Percentage of swelling of PIL samples in acetone (taken from ref. 92).

Thermal stability: For many applications, the thermal stability of supported ionic ILs is a critical parameter that governs the suitability and long-term stability of supported ILs phases for application such as solid phase microextraction (SPME) and gas chromatography (GC), where appropriate working conditions should be used based on the maximum thermal stability of the supported ILs. [93] In general, the thermal stability of the bulk ILs depends on both the cationic and anionic. In general, imidazolium-based cations exhibited higher thermal stabilities than tetraalkyl ammonium counterparts.[94] The nature of the anion generally plays a more pronounced role in influencing the thermal stability of ILs [95]. ILs containing organic-based anions often have higher thermal stability compared to inorganic-based anions. [94]. It has been shown previously that imidazolium based ILs have thermal stabilities that increase in the order: $[\text{Cl}]^-$, $[\text{Br}]^-$, $[\text{I}]^- < [\text{BF}_4]^- < [\text{CF}_3\text{SO}_3]^- < [\text{NTf}_2]^- < [\text{PF}_6]^-$ [96]. The thermal stability of the PILs, SILPs and SILLPs, in general follow the same trends than the observed for related bulk ILs. [97] [98].

In this regard, Luis and coworkers have investigated the thermal stability of different modified crosslinked polymers with IL-like units by thermogravimetric analysis (TGA). Very interestingly, TGA data clearly show that the presence of imidazolium subunits provide an additional stabilisation of the supported IL-like phases when compared with the starting chloromethylated resin. Some results from TGA analyses are gathered on Figure 1.16. and demonstrate that those polymers follow the same trends observed for bulk ILs. Thus, the nature of the anion is the main parameter determining the thermal stability. This is higher for the less nucleophilic anions and lower for the most nucleophilic ones. The observed effects slightly increase with the loading of functional groups in the polymer. Thus the two extreme cases, in terms of the anion used, correspond, as we will see in all cases, to the chloride and the NTf_2^- anion. It is interesting to note that changes in the aliphatic chain of the imidazolium ring (i.e. changing from $\text{R}_2 = \text{CH}_3$ to $\text{R}_2 = \text{C}_4\text{H}_9$) have a much less pronounced effect on the thermal stability.

Figure 1.16. Effect of loading and nature of the anion on the thermal stability of Supported ILs measured by TGA. ΔT is defined as the difference in thermal stability between the starting Merrifield's resin and the polymer with the corresponding methyl-imidazolium subunits.

1.4. Application of the polymeric ionic liquid and related polymeric IL-like phases in catalytic processes.

ILs have been intensely exploited as the homogeneous phase for the immobilization of different types of reagents or catalysts.[99] The immobilization of a catalyst in an IL-phase can provide a series of advantages over the use of other supports, in particular solid supports: i) first of all, no modification of the homogeneous catalyst is required for the immobilization, a factor that often affects to the efficiency of solid-supported systems; ii) the presence of the counteranion can contribute to the activation of the catalyst; iii) the large variety of available ILs can be used to fine-tuning the overall efficiency of the catalytic system through straightforward modifications in the structure of the IL (anion and cation nature, aliphatic chains, presence of additional functional groups...); iv) finally, the IL phase can significantly contribute to the stabilization of the catalyst.[100] Although, under certain experimental conditions, the tunable miscibility of ILs with other solvents may facilitate the separation of both the catalyst and the reaction medium from the products by means of liquid-liquid extractions, the separation of the products and the recycling and re-use of the ILs/catalyst systems is not always a simple task.

A step forward for the simple implementation, the isolation and recycling IL-phase consists, as it has been mentioned above, in the absorption and/or the immobilization of the ILs on a support material (Supported IL Phase: SILP).[101] This strategy brings together the full potential of homogeneous biphasic IL-based systems with those provided by catalysts immobilised onto an insoluble support. Recently, PILs, SILPs and SILLPs have been the focus of much research in this field, demonstrating

their potential as catalysts, catalytic supports or precursors for catalytic species. A series of selected examples, taking into account the different morphologies of PILs, are summarized in the following section highlighting the strong relationships between the structure and the catalytic activity.

1.4.1. Soluble linear PILs .

The use of soluble polymer supported catalysts has gained significant attention as an alternative to traditional solid-phase synthesis as they combine some of the advantages of solution-phase chemistry with some of those for insoluble-polymer immobilized catalysts. The main application of soluble polymers in catalysis continues to be separation and recovery of catalysts and ligands. Membrane filtration or solvent precipitation were the original approaches for separating polymer-bound catalysts and low molecular weight products. These strategies are still used. More efficient separation strategies that minimize the use of extra solvent or that use a recyclable solvent have received more attention recently.[102] Such strategies can advantageously involve soluble polymers. In such cases, separations rely on the phase-selective solubility of the polymer support. One approach is to use a soluble polymer that is selectively soluble in one phase of a solvent mixture that is monophasic during the catalytic reaction but is biphasic during workup. Efficient separations can be achieved in such cases when the product is largely or completely insoluble in the phase in which the polymer-bound catalyst is soluble. Other separations have used soluble polymers that are soluble in a hot reaction solution but insoluble at lower temperature in solvents in which products remain dissolved. Such supports quantitatively precipitate on cooling and can then be physically separated from a solution of the product. These approaches have been used with both transition metal and organocatalysts.[102] A useful soluble polymeric support for a catalyst must be readily available or easy to prepare, demonstrate good mechanical and chemical stability, provide functional groups as well as exhibit appropriate solubility properties.[103] As it has been observed, PILs are characterized for owing most of these properties which make them appropriate for their application in catalysis.

Some ILs were demonstrated to behave as efficient catalysts (or precatalysts) in selected reactions. In particular, imidazolium-based ILs and PILs can generate N-heterocyclic carbenes (NHCs) for the purpose of organocatalysis.[11]

Several reports demonstrated that PILs could act as pre-catalysts for poly(N-heterocyclic carbene)s (poly(NHC)s). In the example studied by Powell *et al.*, [104] a

catalytically active self-supported poly(NHC) was synthesized via the cross-coupling copolymerization of the di-bromo imidazole with with a fluorenyl boronic acid diester to obtain a polymeric imidazole that by methylation leads to the imidazolium salt and the corresponding catalyst was generated *in situ* and used to catalyze the benzoin condensation (Figure 1.17.). The unique architectures developed through this approach increase the likelihood of achieving cooperative or synergistic effects between the catalytically active sites in each repeating unit along the polymer chain and this resulted in higher efficiencies and enhanced reactivities as compared to monomeric analogues. Moreover, the catalyst was successfully recovered and reused with minimal loss of performance over several cycles.

Figure 1.17. Poly(NHC) obtained from self-supported PILs (taken from ref. 104)

In the same area, Pinaud *et al.* also described a linear and soluble homopolymer used in an organocatalytic process based on poly(NHC)s.[105] Its synthesis is illustrated in Figure 1.18. and was achieved starting from the corresponding ionic liquid monomers in a three-step sequence, involving the free-radical polymerization of 1-vinyl-3-alkylimidazolium bromide monomers followed by an exchange with LiTFSI and a last step of deprotonation with a strong base. An additional step of carboxylation with CO₂ led to the poly(NHC-CO₂) adduct.

Figure 1.18. Proposed formation of NHCs and NHC- CO_2 adducts and their polymeric analogues. (taken from ref. 105)

Both poly(NHC)s and poly(NHC- CO_2)s adducts were used as (pre)catalysts, under homogeneous conditions, for transesterification and benzoin condensation reactions being possible their recycling and reuse. It is also worth mentioning that, unlike poly(NHC)s, poly(NHC- CO_2)s were air stable, less moisture sensitive and could be handled much more easily. The proper choice of the alkyl substituent (R) revealed to be crucial. Furthermore, poly([NHC(H)][HCO₃])s were also studied as an alternative of poly(NHC)s to overcome its poor stability when exposed to air and served as polymer-supported precatalysts for organocatalyzed molecular reactions.[106] Later the same authors, reported the synthesis of copoly(ionic liquid)s (coPILs) based on poly(styrene)-*co*-poly(4-vinylbenzylbutylimidazolium) salts, with chloride or hydrogen carbonate as counter-anions, PS-*co*-PVBnBuIm(Cl or HCO₃) by quaternization of a preformed statistical PS-*co*-PVBnCl copolymer.[107] This copolymer featuring a spacer group between the polymer backbone and the imidazolium moiety represent a versatile platform of reactive polymers due to the presence of imidazolium units, since they can be post-functionalized by a variety of organic and organometallic substrates (Figure 1.19.). Thus the corresponding poly(*N*-heterocyclic carbene)-silver transition metal complex referred to as poly(NHC-Ag) were obtained by a simple deprotonation/metallation sequence utilizing Ag₂O. Alternatively, the copolymers was found to quantitatively react with various electrophiles, including CS₂, isothiocyanate upon formal loss of H₂CO₃, affording the post-functionalized poly(NHC-CS₂), poly(NHC-isothiocyanate). The catalytic activity of both copolymers was also examined in cyclic carbonate formation by reaction between CO₂ and propylene oxide and in the benzoin condensation providing reasonable results.

Figure 1.19. Copoly(ionic liquid)s, PS-co-PVBnBuImCl **1** and PS-co-PVBnBuImHCO₃ **2** for various post-polymerization modifications (taken from ref. ¹⁰⁷).

The large potential structural diversity of IL-units plays an important role to define the final properties of the PILs. Among them, chirality can be considered one of the most interesting elements. Accordingly, a great deal of effort has been expended in the last few years to design and synthesize chiral ionic liquids (CILs).^[108] In this context, our group has reported a simple and robust modular synthetic strategy that leads to a large variety of configurationally and structurally diverse CILs.^[109] The in-depth study of these CILs has allowed us to analyse in detail the structure–properties relationships present in these compounds. These polymers can be obtained by the above explained methodologies including the chemical modification of pre-formed poly(VBCL) homopolymer or by CPR of the related monomers.^[110] In general, the CPILs obtained provided an adequate microenvironment for an efficient catalytic

activity for the aldol reaction in water. The polymeric system is able to catalyse the consecutive aldol-dehydration process behaving as a synthetic mimic of the aldolase-dehydrogenase enzymatic system. Indeed, under the right conditions of concentration and ratio acetone:water an enantioselective dehydration of the *R* aldol is preferentially obtained.

Figure 1.20. a) Relative kinetic constants for the aldol reaction between p-nitrobenzaldehyde and acetone 1 : 30 : 0.1 RCHO–acetone–catalyst molar ratio, 0.38 M solution, 24 mg polymer per mL, r.t., acetone- d_6 – H_2O 4 : 1. b) Optimised structure obtained from computational calculations for the polymer prepared from the enantiopure monomer c) CD spectra of PCIL obtained by ATRP (black dots), PCIL obtained by RAFT of the chiral monomer (red line) and PCIL obtained by chemical modification of poly(VBCL) (blue dashed line) in MeOH (0.032 mg mL $^{-1}$). (adapted from ref. 110).

A highly active and selective system for the aldol reaction can be obtained for reactions in both water or in the presence of water. Thus, for instance, in acetone in the presence of water (H_2O :acetone 1:4) the polymeric catalysts obtained can be up to ca. $6.6 \cdot 10^3$ folds more active than their corresponding monomeric counterpart, while in water the only active catalyst is the polymeric one. This enhancement on catalytic activity can be related with some degree of chirality transfer to the main polymeric chain, producing a more properly organised polymeric structure and, therefore, a more efficient catalyst. A better transfer of the chirality was obtained for the polymers prepared by RAFT polymerization. The catalysts prepared RAFT polymerization of the chiral monomer are more active and enantioselective than the analogous ones prepared by ATRP or grafting methods. This example highlight that the selection of synthetic

protocol has a deep impact in the way that the PILs are build up and self-assembled to generate a high-order macromolecular structure with a complex hierarchical architecture. Furthermore, the introduction of the CILs units on the polymer main chain has an important impact over the catalytic properties of the related CPILs.

1.4.2. Branched polyelectrolytes.

Hyperbranched cationic poly(ionic liquid)s are usually based on oligoesters, oligoethers, polyaminoamide and polyalkyleneimine as the cores and involve terminal imidazolium groups with interchangeable counteranions and tuneable alkyl chains (Figure 1.21).[38] This compositional versatility enables not only to possess functionality but also the ability to self-assemble into different molecular architectures favoring. Although different materials have been obtained and their self-assembly studied, only few examples dealing with catalysis have been reported. Here we highlight some of them.

Figure 1.21. Examples of hyperbranched polymer-based poly(ionic liquid)s with cationic and anionic end groups. (a) Pentaerythritol-based HBP PIL.(171) (b) Polyglycerol-based HB PIL.(169) (c) Structured semifluorinated PIL.(172) (d) Polyester-based protic anionic PIL.(174) (e) Branched PIL with imidazolium chloride main chain segments.(175)

The first one describes the positive effect of using branched PILs in hydroformylation reaction by a new generation of nanoPILs incorporating IL moieties in the periphery of hyperbranched polyether cores. This system was reported by Schwab and coworkers,[111] mimicking micelles and vesicles. They used a hyperbranched PILs as the catalyst support. Its post-functionalization using a

sulfonated phosphine for counteranion exchange provided access to well-defined polymer-attached ligands, affording polymers with a high number of phosphine functionalities that were able to form catalytically active complexes with transition metals such as rhodium. Moreover, these systems possessed a sufficient solubility in polar organic solvents. Hydroformylation of 1-hexene in methanol was used as a model reaction to test the catalytic activity and catalyst recovery and recycling of these supported catalysts. Higher selectivities were observed in comparison to the unbound complex, which was attributed to the high local phosphine concentration in the polymer periphery. It was also demonstrated that the catalytic activity was only little affected by the P:Rh ratio or the density/flexibility of the cationic groups.

Figure 1.22. Structure of hyperbranched polyether-based PILs (TPPMS = Ph₂P(C₆H₄-*p*-SO₃⁻) (taken from ref. 111).

Another noteworthy example is the water-soluble ionically tagged artificial enzyme designed by Ferreira *et al.* that promoted and enhanced the dephosphorylation reaction with nitroimidazole.[112]

Figure 1.23. ionically tagged water-soluble artificial enzyme that can efficiently cleave phosphate esters, with enhanced an ionic liquid effect (taken from ref 112).

It is known that imidazolium moieties can act as general acid-base pairs and nucleophilic catalysts. Thus, their presence may favor the so-called ionic liquid effect with an enhancement of both yields and selectivities as a consequence of ion pairing and the formation of supramolecular aggregates. The specific polymer architecture will be a key feature to provide this type of cooperative effects, in which imidazolium-based cations affording neighboring polar domains, being also able to generate favorable solubility effects. Thus, in this case, an important improvement was the possibility of carrying out the studied reaction in aqueous medium, which was not possible in the absence of branched PILs as nitroimidazole is a water-insoluble nucleophile. Besides, the branched PILs can behave as a catalytic nanoreactor with an enhanced ionic liquid effect through cooperative effects for the substrate activation and further nucleophilic reaction. In this regard, this branched PILs/MNI system catalyzed the cleavage of the triester 2,4-dinitrophenyl phosphate (DEDNPP) with rate enhancements of up to 2×10^6 -fold, comparing second-order constant k_N with that of the spontaneous reaction.

1.4.3. Poly(ionic liquid) complex (PILCs) with spontaneous micro-/mesoporosity by free templating synthesis.

Very recently, a template-free and easily scalable strategy to prepare porous ILs was developed by Zhao et al. through simple ionic complexation between the as-synthesized poly(ionic liquid)s (PILs) and polyacids triggered by deprotonation of the carboxylic acid groups. [113] Thus, poly(3-cyanomethyl-1-vinylimidazolium bis (trifluoromethylsulfonyl)imide) (PCMVImTf₂N) and poly(acrylic acid) (PAA) are first dissolved in a good solvent such as DMF to form a homogeneous, transparent solution.

The molecular-level mixing solution is then added drop wise into an excess of alkaline solution such as ethanol containing 0.5 wt% of NH_3 . Turbidity and insoluble aggregates form immediately via in situ deprotonation of the carboxylic acid (COOH) groups of PAA chains to form carboxylate groups (COO^-) and ionic complexation between $\text{PCMVImTf}_2\text{N}$ and deprotonated PAA. Micro-mesoporous IL nanoparticles with high surface areas ($330 \text{ m}^2 \text{ g}^{-1}$) and large pore volumes ($1.10 \text{ cm}^3 \text{ g}^{-1}$) are obtained after removing the placeholder solvents. It is expected that the strong ionic complexation and the high ionic crosslinking density of the system solidify and stabilize the polyelectrolyte network with minimized chain mobility. Several processing parameters, including the ratio of two charged species, the polymer concentration, and the types of complexation solvents, seem to affect the degree of ionic complexation and thus play a dominant role in controlling the porous structure.

Figure 1.24. Template-free synthesis of porous ILs in the state of (a) nanoparticles or (b) membranes via ionic complexation and their application for the synthesis of material Cu@PILC use in the aerobic oxidation reaction (taken from ref 114).

Initially PILCs were evaluated as a heterogeneous catalyst support for copper compounds for the aerobic selective oxidation of C–H bonds. The copper-based catalyst was obtained using PILC as a support (Cu@PILC) and by refluxing micro-/mesoporous PILC with CuCl₂ in ethanol overnight. Cu@PILC catalysts afforded an excellent dispersion in the reaction system due to their polar and small polymer nanostructures. Catalytic tests were performed for the oxidation of various hydrocarbons under mild conditions (50 °C), using Cu@PILC and *N*-hydroxyphthalimide (NHPI) as a combined oxygen-transfer system. Assisted by NHPI, Cu@PILC successfully catalyzed the oxidation of diphenylmethane with 91% conversion and 96% selectivity to diphenyl ketone in 10 h, while NHPI, PILC, or Cu@PILC alone was inefficient for the same reaction. The Cu@PILC can be easily recovered by centrifuge and reused for five cycles without losing its activity, which is a prerequisite for practical applications. SEM characterization confirms that morphologies of Cu@PILC were maintained after the catalysis and recycling. In general, by coupling with NHPI, the Cu@PILC is highly active and selective, and widely applicable to various C–H bond oxidations. Moreover, the PILCs are resistant to many organic solvents due to the strong internal electrostatic interactions, which is another merit of the specific catalyst system.

The same methodology was used for the preparation of PILCs from an imidazolium-based task specific poly(ionic liquid) homopolymer containing a ester group, which was prepared by free radical polymerization of the IL corresponding monomer as showed in the Figure 1.25. The removal of the ester group led to the corresponding homopolymers, after precipitation of the DMF or DMSO solution of PIL–COOH into ammonia-containing non-low polar solvents (Figure 1.25).[114] Although the precursor was a soluble polymer, NH₃-containing organic solvents triggered the in situ interpolyelectrolyte complexation that subsequently built up porous PIL complexes as explained above. The material obtained was essentially made up of mesopores (6–20 nm in size). The pore structure was robust in organic solvents, such as acetone, THF or acetonitrile, even after several cycles of wet–drying or refluxing, as its characteristics in gas sorption measurements changed little.

These materials were successfully used as catalysts for the cycloaddition of CO₂ to epoxides. The reactions were carried out at 1 MPa and the reactor was heated to 160 °C for 6–24 h. High values of productivity were observed (70.5 g_{sc}g_{cat}^{–1}). Moreover, the catalytic material was used in up to four cycles. The average conversion of these four runs was 94%, with slight deviation (4% in 2nd and 4th runs) within the experimental error. Meanwhile the catalytic selectivity remains constantly high (≥97%). The overall superior catalytic activity, high selectivity and excellent recyclability of mesoPILCs as a

heterogeneous catalyst could be attributed to their excellent structural stability and unique nanoscale morphology.

Figure 1.25. Synthesis of PILCs homopolymer and its use as catalyst for the formation of cyclic carbonates (taken from ref. ¹¹⁴).

1.4.4. Insoluble crosslinking IL-like phases materials.

In most cases, insoluble polymers are used as supports for catalysts and in solid-phase chemistry. This is due to the significant advantages provided by such systems over conventional solution-phase chemistry:[115]

- 1) Ease of separation from a reaction mixture.
- 2) Simple reuse of a catalyst after regeneration.
- 3) Adaptability to continuous flow processes and hence use in automated synthesis.[116]
- 4) Reduced toxicity and odor of supported species compared with low molecular weight species.
- 5) Chemical differences, such as prolonged activity or altered selectivity of a catalyst in supported form compared with its soluble analog [117 , 118].

Nevertheless, a brief list of obstacles associated with their use has also been evaluated:

- 1) Higher cost.
- 2) Lower reactivities caused by diffusional limitations.
- 3) Greater difficulty of structural analysis of the supported species.
- 4) The inability to separate solid-supported impurities.

Among the different insoluble polymers, the most widely used are polystyrene (PS) resins crosslinked with divinylbenzene (DVB).[119] Depending on their composition and the reaction conditions, they are classified as either microporous or macroporous.[⁸⁶] In general, the catalytic efficiency, in terms of activity and selectivity, of the immobilised catalyst polymer support is very sensitive to the method employed for its immobilisation. [120 , 121]

As it has been reviewed above, soluble PILs and related crosslinked materials exhibit the ability to swell in specific solvents originated from the electrostatic repulsion between ions fixed on the polymer chains and on the osmotic pressure induced by freely mobile counterions in the networked polyelectrolytes. The structure of the polymer and the nature of the IL-like moieties can be used to tune this property. In this context, Zhang and coworkers have reported a kind of crosslinked PILs with such a favorable swelling as to facilitate a quasi-homogeneous dispersion of the heterogeneous catalytic sites, achieving a significant enhancement in activity that became similar to the one for corresponding monomeric components, but with a clear simplification in separation processes. The reaction of ethylene carbonate with aniline was chosen as the model reaction (Figure 1.26.).[122]

Figure 1.26. Schematic illustration of the swelling of a crosslinked PIL and its application. (taken from ref 122).

These polymers were prepared by direct radical copolymerization of N-vinyl imidazolium and sodium acrylate using divinylbenzene as the crosslinker. As compared with porous or nanoporous materials, these crosslinked PILs having a good swelling in the reactants clearly favored the catalytic activity. In this way, a poor swelling ability made the polymer difficult to disperse and led to incomplete accessibility of the reactants to the catalytic sites. On the contrary, a good swelling ability prompted a high degree of exposure of the catalytic sites to the reactants and an enhanced catalytic

activity. Swelling was affected by the crosslinking density and the chain length of the substituents on imidazolium. An initial increase in the side chain length weakened the electrostatic attraction between the cation and anion on the polymer chains and made it easier for solvent molecules to replace the polymer-polymer interactions with polymer-solvent interactions. However, with the longer side chain lengths (C₆, C₈) a strong decrease in the swelling ratio in water associated to the presence of strongly hydrophobic domains. Thus, the *n*-butyl substituent provided the best swelling in polar solvents. This example highlights how the swelling crosslinked PILs may open an avenue for designing quasi-homogeneous catalysts to increase catalytic activity of heterogeneous catalysts.

It is known that ILs are very efficient in stabilizing transition metal nanoparticles. In their formation, the IL units are capable of forming a shell around the metal nanoparticle (MNP), being coordinated to its surface through the coordination with the anions present in their structure, and avoiding the further reaction and aggregation of the resulting MNPs.[123 ,124 , 125]

PILs containing a large number of IL-like functionalities enhance the adsorption of the metal precursors on their surface by different types of interactions and then can wrap around the surface of the resulting MNP providing a strong stabilization. Thus, PILs have been applied for the immobilisation and stabilisation of MeNPs.[126 , 127 , 128 , 129] Indeed, the combination of MeNPs with polymeric ILs as stabilisers usually exhibits an excellent synergistic effect, enhancing the activity and durability of the resulting composite.[130 , 131 , 132]

In this context, polymers bearing IL-like moieties were synthesized by grafting the corresponding imidazole onto commercial Merrifield-type resins to obtain the corresponding supported imidazolium units (SILLPs). The influence of the structure and morphology of the polymeric SILLPs on the catalytic activity of the immobilized AuNPs was studied in detail using a variety of systems. Variables considered were the functionalization degree of the support in imidazolium units (low *vs.* high), the resin morphology (gel type *vs.* macroporous), the nature of the alkyl substitution at the imidazolium moiety (methyl, butyl or decyl), the counteranion present (Cl⁻, NTf₂⁻,...) and the particle sizes.[133]

Thus, for instance, the type of resin (microgel *vs.* macro porous) and the alkyl-substitution of the imidazole can be used to tune the AuNPs sizes distribution. The

observed variations in NPs size between polymers with $R = \text{CH}_3$, $R' = \text{H}$ and $R = \text{C}_4\text{H}_9$, $R' = \text{H}$ are not significant, but a very important change, with a fivefold increase in size, is observed for polymers with $R = \text{C}_{10}\text{H}_{21}$, $R' = \text{CH}_3$. Interestingly, the TEM images for the polymers not only show an increase in the size of the gold particles, but also a change in their morphology and shape going from spherical particles to triangles or prismatic particles. In order to rationalize those observations, we must take into account the very significant effect observed in the swelling in water for corresponding SILLPs. Thus, the presence of the long aliphatic substituents on the imidazolium subunits decreases the swelling in water. As the reaction for AuNPs formation takes place in water, inside the polymeric beads, this involves the presence of a significantly higher effective concentration of the precursor for polymer with more hydrophobic nature. This factor can be further increased considering the potential association of the aliphatic tails inside the resin to form hydrophobic regions not available for the corresponding aqueous process. Both phenomena could cooperate favouring the aggregation of the initially formed AuNPs into larger NPs.

Figure 1.27. TEM pictures showing the effect of the imidazolium alkyl-substitution on the particle size for the AuNPs supported onto microgel SILLPs (1% crosslinking).

Nevertheless, the opposite trend was detected for the macroporous resins. In this case, the size of the NPs decreased when the size of the aliphatic residue was increased (Figure 1.28.). This is again particularly relevant when the $\text{C}_{10}\text{H}_{21}$ groups are present in the imidazolium subunit leading to smaller size particles. In macroporous resins the access to the IL-like sites is not regulated by swelling. Therefore, the NPs

formation is not affected by changes in the effective concentration of the supported gold precursor. Nevertheless, the association of the hydrophobic aliphatic chains on the surface of the polymer can contribute to regulate the diffusion processes in the microenvironment of the spaces generated by the crosslinked polymeric chains, and very particularly from/to the polar regions generated by the imidazolium groups.

Both the polymeric framework itself and the IL-like moieties contribute to the nucleation and stabilisation of gold nanoparticles. By the appropriate selection of the structural parameters of the polymeric SILLP such as resin morphology, loading and nature of IL-like groups, immobilised AuNPs with narrow size distributions in the range of 2–3 nm can be obtained. The simplicity of the methods for the synthesis of AuNPs makes possible their use for the large-scale production of MNPs. The stabilization of the AuNPs prepared is revealed by the long-term stability of the corresponding AuNPs–SILLPs, under atmospheric conditions, which allows their storage without any aggregation or decomposition for months.

Figure 1.28. TEM pictures showing the effect of the imidazolium alkyl-substitution on the particle size for the AuNPs supported onto microporous SILLPs (20% crosslinking).

The obtained AuNP-SILLPs composites were used as efficient catalysts for the oxidation of phenyl ethanol in water using H_2O_2 as the oxidant and under microwave irradiation.[134 , 135] The Figure 1.29. shows the effect of different variables on the mean reaction rate, by DoE analysis, for the oxidation of 1-phenyl ethanol. The alkyl chain length was the variable with a larger effect. An increase in the chain length on the imidazolium led to a bigger AuNP size distribution and to an enhancement of the reaction rate. Moreover, this parameter allows for a fine-tuning of the hydrophobicity/hydrophilicity balance. The use of long alkyl chains provides SILLPs with some degree of amphiphilic behaviour as well as favors the absorption of the

substrate from a polar solvent. The consequence is a higher local concentration of the substrate within the pores of the polymer, which enhances the observed catalytic activity of the AuNPs.

In general, a higher catalytic efficiency use to be associated with the smaller MNPs but in this case an unexpected activity *vs.* AuNPs size relationship was observed. A reasonable explanation was provided associated to the potential formation of “hot-spots” on the NPs through an efficient absorption of the microwave irradiation.

Besides, a better performance of the macroporous resins in comparison with gel-type was found, which was explained in terms of a facilitated diffusion of the reagents to the active sites improving the catalytic efficiency. It should be mentioned that, in the case of gel-type resins, an appropriate swelling in a compatible solvent or solvent mixture (having these polymers a low crosslinking degree) can decrease the diffusional limitations and this can also be tuned by changing the length of the alkyl chains of the imidazolium moieties.

On the other hand, the differences associated to the changes in the counteranion and the IL-like units loading did not seem to have a significant effect on the catalytic efficiency. Thus, this study demonstrated how the adequate choice and tuning of the SILLPs acting as the MNPs supports is essential for the design of an efficient catalyst.

Figure 1.29. Schematic illustration of the structural vectors of AuNP-SILLPs that influence on the mean reaction rate, by DoE analysis, for the oxidation of 1-phenyl ethanol: (a) 100 °C and (b) 150 °C. μw power = 50 W, $\text{H}_2\text{O}/\text{H}_2\text{O}_2 = 1.5/0.5$ mL. Bar: mean reaction rate constant (min^{-1}). Dots: AuNPs' mean size distribution (nm) (taken from ref 135).

Another interesting study carried out by Dani *et al.* should be mentioned.[136] They reported the synthesis, characterization and catalytic activities of PdNPs inside porous nonionic vinylimidazolium-based polymers and their related PILs in the selective hydrogenation of *p*-chloronitrobenzene to *p*-chloroaniline, which is an important intermediate in the manufacture of many agrochemicals and pharmaceuticals. It was found that in nonionic polymers, the nitrogen of the imidazole ring, acting as an electron donor, stabilizes both the precursor PdAc_2 and the resulting PdNPs. On the other hand, in the case of PILs, PdAc_2 was stabilized in its trimer form due to the absence of available nitrogen species and, once reduced, the resulting PdNPs were stabilized by the iodide anion.

In particular, the PILs/Pd catalysts with imidazolium groups bearing butyl chains showed an almost total selectivity toward *p*-chloroaniline at full *p*-chloronitrobenzene conversion. Since the average size of the PdNPs was the same in all the catalysts, these results suggested that this chemoselectivity depended on the polarity of the environment provided by the PIL scaffolds, which directly affects the electronic and surface properties of the hosted PdNPs.

Figure 1.30. Synthetic pathway to obtain the nonionic vinylimidazolium-based polymers and the corresponding PILs, followed by supporting of palladium nanoparticles (taken from 136).

Zhao *et al.* reported a facile approach for the *in situ* generation of PdNPs supported on imidazolium-based porous organic ionic polymers (OIPs) with the formation of well-dispersed PdNPs with small size and narrow distribution.[137] They displayed excellent catalytic performances in the hydrogenation of nitroarenes. The improvement in catalytic activity was ascribed to the higher specific surface area and to the smaller granular particles formed, which provided more opportunities for contact between substrates and the active sites in the polymer.

Additional examples on the synthesis and stabilization of MeNPs for catalytic applications can be found in a recent review by Giacalone and Gruttadauria,[⁴⁰] This review discuss in detail among different examples of the immobilization, stabilization and catalytic application, mainly to C-C bond formations, of metal nanoparticles and covalently supported ionic liquid (IL).

CO₂ capture and conversion, as a C₁ building block, to produce high-value products is of utmost importance in Green and Sustainable Chemistry. In this context, porous materials have attracted increasing attention due to their versatile and tunable structures, in particular, those based on ILs. Wang and coworkers reported the design of a monolithic meso-macroporous hierarchical crosslinked PIL that promoted the cycloaddition of CO₂ to epoxides to afford cyclic carbonates in the absence of any solvent or homogeneous co-catalyst.[138] The influence of the polymerizable monomers and the solvent were studied to further understand porous structure formation (Figure 1.31.). The use of the structurally rigid monomer [C₁DVIM]Br was shown to be a prerequisite for creating abundant porosity and the pore volume initially increased with the alkyl length in the IL. However, with [C₈MIM]Br the monolith suffered a great shrinkage during the drying process affording a nonporous structure with the collapse of the preformed meso-structure. Such a phenomenon suggested that the rigidity of the employed IL was also important for pore formation. Furthermore, a small amount of water favored porosity. This was explained through the formation of polar and nonpolar domains derived from imidazolium cations and alkyl chain aggregation to provide a nano-structured organization (Figure 1.31.B).

Figure 1.31. (A) Synthesis of mesoporous PILs (MPILs), (B) schematic illustration of the mechanism for the formation of the mesoporous structure (taken from ref 138).

The high catalytic activity observed was attributed to the large surface area and the specific hierarchical meso-macroporous structure that enabled a good dispersion of the active sites (Br⁻) and accelerated the mass transfer of the larger molecules (substrates and products). The good intrinsic CO₂-philicity, arising from the Br⁻-containing IL fragments on the internal surface, facilitated the local concentration of CO₂ at the catalytic centers inside the pores of the polymeric framework. It is the first example of a metal–solvent–additive free recyclable catalyst for the highly efficient heterogeneous cycloaddition of CO₂ at atmospheric pressure and low temperatures, and is even very active for the extremely inert long carbon-chain epoxides.

Additional examples on the synthesis and catalytic activity of hierarchical meso-macroporous PIL-based monoliths can be found in the literature.[139 , 140] In most

cases, catalytic improvements found are again attributed to similar effects, including amount of IL, large surface areas, accessibility of catalytic sites, acceleration of mass transfer, hydrophobic features and compatibility for substrates. All these examples demonstrate that the appropriate chemical composition of the monomeric mixture, the final morphology and hierarchical structure are key for catalytic applications.

On the other hand, the work of Wang *et al.* is also an interesting example.[141] In this case, a new type of imidazolium salt-modified porous hypercrosslinked polymer was synthesized through the Friedel-Crafts reaction of benzyl halides and subsequent functionalization with *N*-methylimidazole. These materials showed much higher activities for the conversion of CO₂ into various cyclic carbonates when compared to the corresponding homogeneous imidazolium catalyst. The CO₂ capture capacity was closely correlated with the micropore volumes and the imidazolium loading. In general, the introduction of functional groups decreased the porosity of the polymer as well as its capacity for CO₂ capture. The enhancement in the catalytic activity is attributed to the synergistic effect of the microporous structure and the catalytic centers, which are located in the pores. The polymers could capture and concentrate CO₂, which results in a higher CO₂ concentration near the catalytic centers and makes the catalytic reaction more efficient.

Figure 1.32. The synthesis of supported imidazolium salts and the typical structure of porous crosslinked PILs used as catalyst for catalytic activities for the conversion of CO₂ into various cyclic carbonates under metal-free conditions (taken from ref. ¹⁴¹).

Highly crosslinked polymeric nanoparticles (CLPNs) incorporating IL-like fragments have also been developed as potential supported ILs for catalytic applications. In general, the recovery and recycling of the polymeric ILs is done either by precipitation with antisolvent or by centrifugation. Thus, for instance, Xiong *et al.* have reported the preparation *via* a facile one-step synthesis CLPNs as spherical nanoparticles with the mean diameter range of 10–100 nm by radical copolymerization

of 4-vinylbenzyl-tributylphosphorous chloride and ethylene glycol dimethacrylate (EGDMA) in selective solvent, such as C₁~C₅ alcohols. The size of the CLPNs could be facilely tuned by the feed ratio of EGDMA to PIL.[142 , 143] These nanoparticles are effective catalysts for CO₂ cycloaddition with epoxides showing excellent yield (100%) and selectivity (100%) of cyclic carbonates under mild conditions (0.1 g CLPNs, 3.0 MPa CO₂, 140 °C and 3 h). The reaction can be performed without the addition of any solvents or co-catalysts. The CLPNs were dispersed in the products homogeneously, which resulted in the extremely high activity and selectivity. At the same time, the CLPNs can be easily separated by filtration after pouring the reaction mixture into toluene. CLPNs could be recycled six times with less than 1.5 % loss of catalytic activity.

Figure 1.33. Highly cross-linked polymeric nanoparticles (CLPNs) incorporating IL-like fragments as catalyst for CO₂ cycloaddition with epoxides (taken from ref 142).

Chen and coworkers have reported a class of poly(anionic liquid) microgels that undergo stimuli-responsive volume phase transitions. Such a microgel is synthesized by free radical precipitation polymerization of a tetrabutylphosphonium 4-styrenesulfonate monomer and a crosslinker *N,N'*-methylenebisacrylamide.[144] These microgels can not only undergo reversible volume phase transitions in response to changes in temperature in water, methanol, or water/methanol mixtures, but also undergo re-entrant swelling–shrinking–swelling transitions as the methanol content increases in water/methanol mixtures at a set temperature in our experimental temperature window of 25.0–64.0 °C. Such microgels can be post-functionalized, *e.g.*, *via* ion-exchange treatment with HSO₃CF₃ to partially transform sulfonate to the catalytic Brønsted acidic –SO₃H, whilst the yielded microgels can inherit the responsive properties. With both responsive and catalytic properties simultaneously harnessed on the same object, the functionalized microgels potentially can be used as a highly efficient catalyst for the esterification reaction of palmitic acid and the transesterification reaction of tripalmitin. The catalytic activity can be modulated to a

certain extent in a non-monotonous way, making it possible to boost the reactions at a relatively lower temperature (e.g., 42.0 °C) while retaining considerable catalytic activity.

Figure 1.34. Illustration of the synthesis of PTPSS microgels and CPIL microgels. (taken from ref 144).

In a different approach, Yang *et al.* designed a hybrid micelle-like hydrophobic/hydrophilic nanoreactor composed of a hydrophobic PIL core and a hydrophilic mesoporous silica shell stabilizing Pd nanoparticles in the polar domains and displaying a good dispersion in water. [145] This system provided a dramatic enhancement in the catalytic activity of the PdNPs and a good recyclability in the selective oxidation of aromatic alcohols to aromatic aldehydes.

Figure 1.35. Schematic illustration of the synthetic route to the PIL@SiO₂-Pd nanoreactor and the corresponding TEM images at each step. (A) Chemical structure of PIL (x denotes Br⁻ or dicyanamide anion), (B) PIL nanospheres, (C) after coating a layer of mesoporous silica via using micelles formed by CTAB as template, (D) the formation of PIL@SiO₂ nanostructure, and (E) the incorporation of Pd NPs in the PIL core (with CTAB residues inside the mesopores of silica shell). Inset in (B) is a cryo-TEM image. Scale bar in insets in (B) and (E) is 20 nm. (taken from ref. ¹⁴⁵).

This behaviour was assigned to the configuration of the nanostructure. The particles present a multilamellar centric vesicular morphology and experiment a self-

adaptive ability. Such a nanostructure is constructed at the core by alternating hydrophilic (charged polymer backbone) and hydrophobic (long alkyl side chains) nanodomains, similar to those in a multilayer liposome. This PIL polymer is intrinsically hydrophobic due to the long alkyl chain and insoluble in water. However, the resulting nanospheres are well-dispersed in water due to the preferential organization of the charged ionic backbone on the outer shell. The electrostatic repulsion present in this outer shell justifies the spherical organization. Upon silica coating, the contact of the outer surface with water is replaced by a silica-PIL interface. To fit the new environment, the PIL chains rearranged to rebalance their surface tension and afforded an important structural evolution.

The boosted catalytic activity was considered to be due to the synergistic effect of the adaptive hydrophobic core and the hydrophilic shell coupled in a hybrid nanoreactor. This PIL-SiO₂-Pd catalyst was highly dispersible in water through the assistance of the hydrophilic silica layer. The hydrophobic substrates could accumulate in the PIL core through Van der Waals interactions and this provides a local enrichment and close proximity of the substrates to the PdNPs enhancing catalytic performance.

Crosslinked PILs can be also used to the immobilization of organocatalyst. Thus, a recent example was described by Grobeheilmann *et al.*[146] In this case, they prepared a polymerized ionic liquid (PIL)-based hydrogel as a support for the immobilization of a quinine-based organocatalyst. This system was tested for an asymmetric nitroaldol (Henry) reaction, demonstrating an efficient catalytic activity and a high recyclability. The parameters defining the gelation time and gel consistency were studied. Results showed a direct relationship with the alkyl chain length of the cation and the size of the anion of the IL fragment. Increasing the alkyl chain length and the size of the anion, the gelation time increased. On the other hand, a greater amount of crosslinker increased the gel stiffness but simultaneously reduced the available space for the catalyst in the polymeric matrix.

Figure 1.36. Preparation of PIL-supported quinine-based organocatalysts.

1.4.4.1. Crosslinked IL-Phases and continuous flow towards green process.

A step forward for the simple implementation of continuous flow processes based on ILs consists in the absorption of the ILs on a porous support material (Supported IL Phase: SILP).[147] This strategy brings together the full potential of homogeneous biphasic IL-based systems with those provided by catalysts immobilised onto an insoluble support. The incorporation of the (bio)catalyst is then carried out by its adsorption on the surface modified with the IL-phase.[148] The resulting continuous flow catalytic processes can use either a gas-phase or a supercritical fluid phase as the mobile phase to deliver the reactants to the IL phase and to extract the products. The main limitation of this approach is the possible leaching of the IL-phase from the support. This phenomenon can be due to either certain solubility of the IL in the mobile phase or the products (which severely limits the use of liquid phases for delivery and extraction of reagents and products) or to physical abrasion during extended exposition to the mobile phase. The type and morphology of the support is also a key parameter to achieve an efficient system. This type of set-up has been evaluated for the development of different industrial relevant processes under continuous flow conditions.[149]

An alternative to the immobilization of the IL-phase by coating the surface of a support with a thin layer of the IL (SILPs) is to attach covalently structural

fragments related to ILs to the functional groups present in the surface of the support. The resulting materials have been termed as Supported Ionic Liquid-Like Phases (SILLPs). Both, inorganic (silica or other metal oxides) and organic (crosslinked polymers) supports have been used for the preparation of catalysts immobilized in SILLPs.[150] Solid materials with multilayer IL structures can also be obtained by the polymerization of polymerizable task specific ILs either directly or in combination with a support.[151 ,152] It is clear that in this case, when the IL-like fragment is covalently attached to the support, the problem of leaching is totally eliminated.

The incorporation of the catalyst to the SILLP is simply carried out by adsorption of the homogeneous catalyst as an adequate solution onto the modified surface of the support bearing IL-like units. The continuous catalytic reactions can be performed either in conventional solvents or alternatively, and moving towards greener methods, using different types of supercritical fluids or in solvent free processes.

The nature of the support provides an additional design vector, besides those related with the structure of the IL-like units, to tune the characteristics of the new materials, in particular in the case of polymeric supports. Thus, envisioning the different potential applications of SILLPs, a variety of polymeric supports can be obtained with different morphological, chemical and physical characteristics by a controlled variation of their synthetic protocol and the existing functionalities. This modular design facilitates both the immobilization and the stabilization of the catalytic moieties.

Based on the fact that the polymeric SILLPs present at the molecular level the same fundamental properties of the bulk ILs,[124] they can be used, for instance, for the simple preparation and stabilisation of metal nanoparticles (MNPs) from different metal precursors, reproducing the analogous behaviour observed for bulk ILs. The presence of IL-like moieties in the polymer help to stabilise the Pd(O), simultaneously reducing the leaching through a release and catch mechanism.[153] The morphological and chemical properties of the support and the IL-like fragments, including the loading, in the polymeric ionic-liquid-like phase has been shown to play an active role on the catalytic cycle.[154]

The combination in a single reactor of SILLPs with different functionalities can led to new catalytic systems (catalytic cocktails) with improved properties

towards their application for C-C coupling reactions. In this regard, it is important to understand that the chemical functionalities present in SILLPs can play different functions in the reaction medium. This can involve simultaneously (or consecutively) their actuation as supported reagents (i.e. supported bases or acids), precatalysts and scavengers of undesired reaction side-products.

The Heck reaction could also be conducted under continuous-flow conditions using a packed bed of a SILLPs polymeric cocktail containing basic functionalities and PdNPs and employing supercritical carbon dioxide (scCO₂) as the solvent (Figure 1.37.). This approach cannot be carried out with the use of soluble bases as this eventually leads to the clogging of the reactor. Finally, this kind of SILLPs cocktail enables the combination of different reaction and purification steps in a single reactor, which represents a significant improvement in terms of process intensification and green chemistry.[155]

Figure 1.37. Continuous flow Heck reaction using a SILLP cocktail in scCO₂. (taken from ref. 155).

Supported ionic liquid-like phases (SILLPs) have also been efficiently applied as organocatalysts for the cyanosilylation of carbonyl compounds using trimethylsilyl cyanide under solvent-free conditions. The effect of the morphology of the polymer (gel-type or macroporous bead resins or, alternatively, a monolithic polymer) was also studied, which allowed selecting the most suitable materials for the efficient continuous flow single pass synthesis of cyanohydrin trimethylsilyl ethers. The optimized system provided excellent productivities and high yields without observing any decrease in the activity of the catalyst with time. The results obtained showed a productivity of up to 45.1 g of cyanohydrin trimethylsilyl ether per g of SILLP used and hour.[156]

The exchange of the counter anion in the IL-fragments of SILLPs to introduce a basic anion such as OH^- or AcO^- led to developing a basic catalyst for the continuous flow solvent-free Henry nitroaldol reaction (Figure 1.38.). A total conversion of the substrate into the product was achieved with residence times as short as 1–3 min, using a monolithic mini-reactor with a free-volume of ca. 500–800 μL .

Indeed, if the TON for the related batch and continuous flow processes are compared, higher values are obtained for the flow systems. The base-supported systems present a high throughput and are advantageous for the upscale of the process.[157]

Figure 1.38. Continuous flow solvent-free Henry nitroaldol reaction catalysed by SILLPs. (taken from ref. ¹⁵⁵).

A partly related approach has been the immobilization of a biocatalytic lipase onto a covalently Supported Ionic Liquid-Like Phase (SILLP).[158] CALB supported on SILLPs was shown to be an efficient and very stable catalyst for the continuous flow synthesis of citronellyl propionate in scCO_2 . The presence of a high IL/enzyme ratio is reflected in a high stabilization of the CALB in those systems.[159 , 160] Thus, the process could be carried out at 80 °C with yields of 93 % for more than 10 h without any appreciable deactivation of the enzyme. The results substantially exceeded those obtained for packed-bed reactors with supported silica-CALB-Si-4 catalyst under the same experimental conditions, highlighting the key role played by the covalently attached IL-like units. The SILLPs not only provide an adequate microenvironment for the lipase action, but also improve the mass-transfer phenomena of hydrophobic substrates and products from the scCO_2 phase, leading to a highly selective and stable immobilised enzyme even at high temperatures and pressures.

Figure 1.39. Continuous flow enzymatic reactions in SILLPs/scCO₂. (taken from ref. ¹⁵⁵).

Similar PS-DVB-derived SILLPs can also be prepared starting from commercial Merrifield resins in the form of beads. Both, gel-type and macroporous resins containing covalently attached imidazolium subunits have shown to act efficiently for the immobilization of CALB, in particular for the polymers having a relatively high content in IL-like fragments. The macroporous resins are, however, more appropriate for being packed into tubular reactors and for the development of flow processes, according to their higher mechanical stability. In this way, CALB immobilised onto SILLPs bearing 1-decyl-2-methylimidazolium cations has been used as the biocatalyst for the continuous flow synthesis of biodiesel (methyl oleate) by the methanolysis of triolein in scCO₂ (18 MPa, 45 °C).^[161] The system showed very good stability (85 % mean yield of biodiesel after 45 cycles of 4-8 h) in scCO₂. Again, the nature of the SILLPs regarding both the substitution pattern at the IL-like units and the type of polymeric support used were key factors to obtain an efficient supported biocatalyst. These elements determine the efficiency of the mass-transfer processes at the interfaces, either of the substrates to the active site or the products from the enzyme. The selection of an IL that contains a large alkyl chain in the cation results in a clear improvement of the efficiency for the biotransformation in monophasic liquid systems and the same takes place when the

corresponding SILLPs are prepared. Thus, controlling the structure of the SILLPs, it is possible to develop efficient continuous processes for the transformation of vegetable oil into biodiesel .

The corresponding SILLPs-based fixed-bed biocatalytic mini reactors were assayed for the continuous KR of *sec*-alcohols, using scCO_2 at 50 °C and 10 MPa for feeding the substrates to the reactor. The results were excellent, as yields of 50 % in the expected enantiopure ester were obtained. A high level of stability was also observed for the mini bioreactor, as the activity and selectivity was maintained without any significant change after 6 days of use under the above-mentioned conditions. It is remarkable that, in this case, resins with imidazolium fragments containing chloride as the counter anion showed to be the more active, while the NTf_2^- anion had revealed to be the most appropriate for other enzymes supported either in SILPs or SILLPs.^[160]

As was mentioned above, development of an efficient DKR allows raising the yields of the desired ester to 100 % but requires the combination of the biocatalyst with an acidic or organometallic catalyst to produce the continuous racemization of the undesired enantiomer of the alcohol. Taking into account the former results discussed above, different zeolites (CP811C, CBV720 and CP811E) were studied as the acid catalysts for the racemization in combination with the CALB supported on SILLPs based on bead-type resins.

The complete isolation of the enzyme and the acid catalysts guarantees that no deactivation of the enzyme can be associated to the contact with the zeolite. The systems were maintained under continuous flow conditions using scCO_2 at 50°C and 10 MPa. A “one pot” single columnar minireactor was prepared using a mixture of the CALB-SILLP polymer with zeolite CP811E-150 (Figure 1.39.). Good results were obtained when the zeolite catalyst was coated with a small amount of an IL. This follows the same trend observed in the case of SILPs. Nevertheless, contrary to the observations obtained in that case with the use of commercial immobilized CALB (Novozym 435), no additional coating with an IL of the biocatalyst was required for the stabilization of the enzyme. This clearly highlights how SILLPs are able to efficiently stabilize CALB against deactivation by scCO_2 or the presence of acidic catalysts.

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Chapter 2

General objectives

Chapter 2. General objectives

2.1. Objectives

The aim of the thesis here presented is the design and the development of new functionalised and nanostructured materials based on polymeric ionic liquids with interesting properties and potential applications in different fields within the area of sustainable chemistry and engineering.

Considering the synthetic methodology of the different materials and their resulting structure, each chapter includes a type of these materials that are: multifunctional crosslinked PILs, AuNP-PIL composites, thermoresponsive CPILs, PIL nanofiber membranes and PIL-based materials derived from poly(acrylamide-homocysteine thiolactone).

According to the former classification, the general objectives for the current thesis were planned as follows:

1. Development of synthetic methodologies allowing the simple preparation of poly(*p*-vinylbenzylchloride) (poly(VBC)) obtained by controlled radical polymerisation (CRP), in particular by RAFT polymerisation, using either batch or continuous flow processes. These polymers will be used as starting materials for the synthesis of advanced materials to be developed later one.
 2. Development of new methodologies for the preparation of crosslinked polymers containing a high density of IL-units. The synthesis starts with a ready-made polymer, a soluble linear poly(VBC) obtained by CRP. The polymeric IL-like phase structure will be generated by controlled phase separation occurring during the reaction between the soluble polymer and reactive units leading to the corresponding insoluble material.
 3. Evaluation of the properties of the multifunctional crosslinked PILs materials as IL-like organocatalytic phase for the Knoevenagel condensation and for the synthesis and stabilisation of metal nanoparticles.
 4. Synthesis and characterisation of AuNP-PIL composites using different methodologies and description of how the controlled combination of PILs and AuNPs by using the adequate synthetic protocols leads to well-organised materials with multiple catalytic sites and tuneable functionality.
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5. Test the ability of these AuNP-PIL materials to act as bifunctional nanoreactors for the reduction of the functional groups of the Knoevenagel product in a one-pot tandem reaction and check the influence of their hierarchical organisation in the catalytic efficiency.
6. Synthesis and characterisation of a new class of CPILs by chemical modification of the poly(VBC) prepared by RAFT polymerisation using chiral imidazolium salt and study their thermoresponsive behaviour by UV-Vis, CD and NMR. Elucidate the origin of this phenomenon in order to control the LCST transition through the different structural vectors of the CILs. Check the structure-property relationship.
7. Preparation and characterisation of structured polymeric membranes based on PIL/PVP by electrospinning. Study and understand the effect of the chemical structure of PILs and the supramolecular interactions in the self-assembly and the properties of these systems in order to fine-tune not only the hydrophobic/hydrophilic properties but also the morphologies of the mats by changing the molecular vectors of PILs.
8. Test and demonstrate the potential applications of these materials in separation processes such as oil- water separation and as nanostructured supports for stabilisation of MNPs by sputtering deposition.
9. Preparation of new functionalised materials employing poly(acrylamide-homocysteine thiolactone) (PAHT) as macromolecular precursor and post-modification procedures. Carry out experiments combining aminolysis, thiol-ene reactions and disulfide bond formation to obtain these advanced materials with different morphologies and controllable properties. Explore their possible applications in material science.

Chapter 3

**Preparation and study of multifunctional
crosslinked PILs based on RAFT-prepared linear
polymers**

Chapter 3. Preparation and study of multifunctional crosslinked PILs based on RAFT-prepared linear polymers

3.1. Resumen del manuscrito

El empleo de líquidos iónicos (ILs) como disolventes medioambientalmente benignos para llevar a cabo distintas transformaciones orgánicas ha recibido una gran atención en los últimos años, debido a las propiedades fisicoquímicas únicas que poseen (presión de vapor baja, relativa estabilidad térmica, etc), si bien desde un punto de vista práctico presentan también algunas desventajas tales como su coste, su manejabilidad y su relativa toxicidad, lo que conlleva una limitación en su uso y aplicaciones. Por esta razón, la utilización de ILs soportados permite superar algunos de estos inconvenientes.

Entre las diferentes estrategias para su preparación, los materiales poliméricos constituyen una solución viable al combinar las propiedades de los ILs a nivel molecular y la mejor estabilidad, procesabilidad y durabilidad asociadas a la estructura polimérica. Así, el desarrollo y el estudio sobre esta nueva clase de polielectrolitos (líquidos iónicos poliméricos (PILs)) está ganando atención.

Los polímeros monolíticos se caracterizan por ser materiales con buena permeabilidad gracias a su continua estructura porosa por lo que representan una alternativa para la preparación de polímeros entrecruzados con unidades de IL. Existen principalmente dos estrategias sintéticas para su obtención. La primera consiste en la polimerización directa de los ILs monoméricos donde la formación del monolito ocurre durante la polimerización. Alternativamente, se pueden obtener por modificación química del soporte monolítico ya preformado donde la introducción de ILs se consigue por reacción de sustitución con el grupo funcional presente en el soporte. Así, se consiguen materiales con morfologías, propiedades químicas y funcionalidades interesantes para aplicaciones como el campo de la catálisis.

En este sentido, nuestro trabajo en este campo se ha centrado en la búsqueda de nuevos materiales entrecruzados y funcionalizados con ILs a partir de poli(clorovinilbenceno) (poly(VBCl)), un polímero lineal soluble obtenido por polimerización controlada RAFT. Asimismo, se ha evaluado tanto su comportamiento como organocatalizadores en la condensación de Knoevenagel como su viabilidad para sintetizar y estabilizar nanopartículas metálicas (MNPs).

Para ello se han empleado dos metodologías. En la primera de ellas, como el poly(VBCl) obtenido por RAFT puede actuar como un macroiniciador, en presencia de un monómero entrecruzante (divinilbenceno (DVB)), las cadenas lineales se entrecruzan únicamente por los extremos dejando los grupos cloro accesibles para reacciones con unidades de IL. La segunda estrategia para producirlos se basa en hacer reaccionar el grupo clorometilo con un bisimidazol de tal manera que la funcionalización y el entrecruzamiento ocurren al mismo tiempo.

En primer lugar, se ha estudiado la síntesis de poly(VBCl) por la técnica de polimerización controlada RAFT utilizando diferentes agentes de transferencia (CTAs) los cuales se muestran en la Figura 3.1. y dos iniciadores radicalarios (AIBN (*Azobisisobutyronitrile*) y ACVA (*4,4'-Azobis(4-cyanovaleric acid)*)) empleando tanto procesos en *batch* como en flujo continuo.

Figura 3.1. Síntesis de poly(VBCl) por polimerización RAFT.

Los resultados en *batch* han demostrado que es posible obtener poly(VBCl) con rendimientos, pesos moleculares y polidispersidades (PDIs) razonables. Sin embargo, el escalado de la reacción de 5 a 100 g provoca una polimerización descontrolada atribuida a una menor eficiencia en el control de las condiciones experimentales.

Así, con el propósito de mejorar la productividad de esta polimerización, se llevó a cabo la evaluación del proceso en flujo continuo según se ilustra en la Figura 3.2.

Entre los resultados obtenidos, se podría destacar que, para el mismo tiempo de reacción en ambos procesos se consiguen niveles de conversión y pesos moleculares similares aunque la polidispersidad es ligeramente menor en *batch* que en continuo. Cabe mencionar que los intentos para alcanzar niveles de conversión más elevados condujeron a un bloqueo del reactor dado el aumento de la viscosidad de la disolución durante la formación del polímero. A pesar de ello, es posible llevar a cabo la polimerización en continuo produciendo el polímero con PDIs aceptables aunque con

pesos moleculares bajos debido a los modestos niveles de conversión que se permiten alcanzar.

Figura 3.2. Montaje del sistema en flujo para la polimerización RAFT del *p*-clorovinilbeneno 1.

Por tanto, ambas metodologías sintéticas permiten la obtención del polímero lineal en condiciones controladas ($PDI < 1.5$) observándose diferencias en los pesos moleculares resultantes. Mientras que el proceso en *batch* conduce a polímeros de alto peso molecular (> 10 kg/mol), la polimerización en continuo proporciona polímeros de bajo peso molecular (< 2 kg/mol) aunque mejora la productividad bajo las mismas condiciones.

Seguidamente, dichos polímeros se han empleado como materiales de partida para la preparación de monolitos.

Por un lado, se han sintetizado materiales entrecruzados a partir de la copolimerización entre poly(VBCI) (elemento estructural y agente de transferencia macromolecular) y DVB en presencia de AIBN en tolueno. Estos monolitos no presentan hinchamiento (*swelling*) al sumergirlos en diferentes disolventes. Sin embargo, para conocer la accesibilidad de los grupos clorometilo, se han hecho reaccionar con diferentes *n*-alquilimidazoles tal y como muestra la Figura 3.3.

La caracterización de dichos materiales se realizó por espectroscopia infrarroja y complementariamente con el test de NBP (4-(4-nitrobencil)piridina) descrito en nuestro grupo de investigación para la detección de grupos clorometilo. Tanto la

desaparición de la banda a 1265 cm^{-1} como el resultado negativo del test colorimétrico confirmaron la modificación cuantitativa de estos materiales así como la buena accesibilidad de dichos grupos.

Figura 3.3. Síntesis de SILLPs a partir de la modificación química de los monolitos obtenidos por polimerización RAFT entre poly(VBCl) y DVB.

Por otro lado, se han preparado monolitos por reacción entre poly(VBCl) y bisimidazoles obteniéndose PILs al mismo tiempo que se produce el entrecruzamiento del polímero. La Figura 3.4. ilustra el proceso sintético así como el aspecto de los monolitos obtenidos en función del peso molecular del poly(VBCl) utilizado. Los resultados sugieren que es más adecuado el empleo de polímeros con pesos moleculares inferiores a 2 kg/mol para obtener un grado de entrecruzamiento menor que favorezca tanto el hinchamiento del monolito como la accesibilidad a los grupos funcionales. De esta manera, el poly(VBCl) obtenido en flujo continuo es más adecuado para la preparación de estos materiales.

Figura 3.4. Síntesis de los monolitos con bisimidazol empleando diferentes poly(VBCl).

Asimismo, también se ha evaluado la influencia de otros factores como: la concentración de los componentes de la mezcla, la naturaleza del espaciador del bisimidazol (4 y 6 metilenos) y la relación molar polímero/agente alquilante.

Según los resultados, la concentración de los reactivos en la mezcla no tiene un efecto significativo en el aspecto de los monolitos. El uso del bisimidazol con el espaciador más corto generó un material más denso y menos transparente y el empleo de exceso o defecto de agente alquilante mostró diferencias estructurales. Una menor cantidad de bisimidazol originó un monolito menos denso y mucho más gomoso. Como es de esperar, tanto el análisis por IR como el test de NBP confirmaron la presencia de grupos clorometilo.

Con el objetivo de caracterizar todavía más estos materiales, se llevó a cabo el análisis elemental para poder determinar la carga de imidazol y el grado de entrecruzamiento. En general, se obtuvieron cargas cercanas a los valores teóricos para materiales con bajo entrecruzamiento o entrecruzamiento no covalente. Estos resultados sugieren que la naturaleza no soluble de estos polímeros puede atribuirse a mecanismos de entrecruzamiento adicionales no covalentes. Así, las interacciones supramoleculares electrostáticas entre los fragmentos iónicos y las hidrofóbicas entre las cadenas alquílicas pueden definir del mismo modo la morfología de estos materiales.

Considerando el bajo grado de entrecruzamiento covalente de los monolitos preparados, es de esperar que presenten hinchamiento (*swelling*) en diferentes disolventes según su polaridad. Por tanto, se evaluó dicho comportamiento utilizando una serie de disolventes de diferente constante dieléctrica.

De manera general, el *swelling* es mayor para cargas mayores de IL. Sin embargo, si la carga de IL es alta, el grado de entrecruzamiento es mayor y el *swelling* debería ser menor debido a la mayor rigidez de la estructura. En realidad, existe un compromiso entre ambos factores.

Los resultados obtenidos muestran, por un lado, un gran hinchamiento en disolventes polares (agua y metanol) que indican que la estructura se mantiene gracias a las interacciones hidrofóbicas entre las cadenas alquílicas. En el caso del metanol en comparación con el agua, éste es capaz de competir con ambas interacciones iónicas e hidrofóbicas consiguiendo un *swelling* más elevado en algunos casos a pesar de ser menos polar.

El comportamiento en disolventes apolares se puede atribuir a la compatibilidad entre el disolvente y las regiones hidrofóbicas del material. Así, el grado de

hinchamiento en estos casos es menor observándose además en alguno de ellos un encogimiento. De este modo, se podría destacar la importancia del entrecruzamiento y la naturaleza del contraíón presente en la estructura para determinar las propiedades de *swelling*.

Adicionalmente, se ha evaluado su comportamiento como organocatalizadores en reacciones de formación de enlaces C-C como es la condensación de Knoevenagel. Concretamente, la reacción entre *p*-nitrobenzaldehído y cianoacetato de etilo en medio acuoso.

Los resultados han demostrado que los fragmentos de IL en la estructura monolítica son catalizados básicos eficientes en esta reacción. En general, mejoran el rendimiento de la misma en comparación con la reacción en ausencia de catalizador. En cuanto a las diferencias observadas, éstas radican principalmente en la carga de IL de los monolitos. Así, el monolito obtenido con un exceso de bisimidazol dio un 100 % de conversión. Además, el intercambio del anión Cl^- por NTF_2^- , menos básico y más hidrofóbico, redujo la actividad catalítica. Esto está de acuerdo con sus propiedades de *swelling*, pues en agua la estructura se encoge influyendo en su actividad catalítica ya que la accesibilidad de los sitios básicos está más restringida.

La metodología desarrollada para la síntesis de los SILLPs también permite la introducción de grupos básicos adicionales en la estructura monolítica pudiendo cooperar con las unidades de imidazol para mejorar la actividad catalítica de esta reacción.

En este sentido, la Figura 3.5. ilustra el esquema sintético utilizado para preparar los distintos materiales empleando bases orgánicas de distinta fortaleza. Todos los compuestos se analizaron por IR para confirmar las modificaciones correspondientes.

Del mismo modo, se estudió la actividad catalítica de estos materiales demostrándose que la introducción de un sitio básico adicional mejora la eficiencia catalítica con respecto a los SILLPs.

Resumiendo los resultados de la catálisis, se obtuvo el siguiente orden de reactividad: iminofosforano > pirrolidina > guanidina. La PPh_3 actúa como una superbase orgánica. A pesar de que la guanidina utilizada (triazabicyclodeceno) es más básica que la pirrolidina mostró una conversión ligeramente inferior que en el caso de la pirrolidina soportada. Una posible explicación es el mayor número de puntos de entrecruzamiento que tiene la guanidina lo que puede provocar una disminución de su basicidad.

Figura 3.5. Síntesis de los SILLPs funcionalizados con bases orgánicas.

Finalmente, para abrir el campo de aplicación de estos materiales, se ha evaluado la capacidad de los monolitos para ser utilizados como soportes en la síntesis y estabilización de nanopartículas metálicas (MNPs).

Así pues, se han obtenido tres sistemas diferentes conteniendo AuNPs, PdNPs y Au-Pd-NPs respectivamente. El tamaño de partícula para las AuNPs es menor que para las PdNPs, las cuales formaron agregados de tamaño significativamente mayor. Sin embargo, la combinación de ambos metales introduciendo en el polímero la sal de paladio seguida del precursor de oro y posterior reducción proporcionaron un sistema con nanopartículas de ambos metales con una distribución de tamaños muy pequeña.

Asimismo, se estudió su actividad como catalizadores bifuncionales en la reacción en cascada de la condensación de Knoevenagel seguida de la reducción *in situ* con NaBH_4 mostrando excelentes conversiones y selectividades. De esta manera, se abren nuevas posibilidades en el desarrollo de sistemas heterogéneos multicatalíticos.

Preparation and study of multifunctional crosslinked PILs based on RAFT-prepared linear polymers

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ABSTRACT: Poly(VBCI) of controlled properties has been prepared under batch and flow conditions using RAFT processes. This linear polymer has been used as the starting material for the preparation of insoluble crosslinked polymers containing IL-like fragments using several approaches. The crosslinking through the use of bis-imidazoles has been studied in more detail as it has allowed the preparation of a variety of multifunctional polymeric materials and composites containing MNPs. The presence and the amount of the different functionalities introduced (imidazolium, imidazole, amine, iminophosphorane, etc.) determine the overall properties of the final material both in terms of the morphological or swelling behavior and in terms of their potential applications. In this regard, many of these multifunctional crosslinked PILs have shown to be catalytically active for the Knoevenagel condensation and the specific activity can be adjusted through the tuning of the different functionalities present. In the same way the

crosslinked PILs-MNPs composites have shown to be able to act as multifunctional catalysts, with high activity and selectivity, for the one-pot tandem process that includes a Knoevenagel reaction followed in situ by the reduction of the initial product of condensation.

Introduction.

Ionic liquids (ILs) have received great attention in recent years as environmentally acceptable solvents for organic transformations.^{1,2} ILs present unique properties such as negligible vapor pressure, low flammability and reasonable thermal stability.³ However, from a practical point of view, they present some important limitations mainly associated to the high cost of many ILs and to the growing concerns about their toxicological and ecotoxicological properties.^{4,5} The use of supported ILs has emerged as a simple and straightforward solution to overcome some of these limitations. Thus, for instance, the immobilization of ILs onto a solid support provides a substantial reduction of the amount of IL required for a given application.^{6,7} This reduces accordingly the associated cost, facilitates their handling and manipulation and, finally, greatly mitigates the potential environmental risks of an uncontrolled spill of the ILs to water. Among the different strategies developed to prepare SIL-based systems, the use of polymeric materials containing in their structure monomeric units structurally similar to ILs represent a good option. These materials can combine the properties of the ILs at the molecular level with an improved mechanical stability, processability, durability and spatial controllability, over the bulk IL species, provided by the polymeric nature. In this regard, materials termed as Poly(ionic liquid)s (PILs) were originally developed as polyelectrolytes, although later on PILs have expanded their scope of potential applications to catalysis, as separation and adsorption materials, for thermoresponsive materials, porous polymers, source of nanostructured carbon materials, and many others.^{8,9}

The development of monolithic polymers, being porous bulk materials with a good permeability caused by their three-dimensionally continuous porous structures, represents a good alternative for the preparation of crosslinked polymeric matrices containing IL-like moieties in their architecture.^{10,11} Two main different strategies have been exploited for the synthesis of monolithic PILs. The first one consists in the direct polymerization of the corresponding IL-monomers, where monolith formation occurs simultaneously with polymerization.^{12,13,14,15,16,17} Alternatively, they can be prepared by chemical modification of an already preformed monolithic polymeric support with the appropriate functionality and morphological and chemical properties. Thus, the introduction of the IL-like is obtained by grafting protocols, where the transformation of these functional groups into the corresponding IL-like phases is often achieved through a simple substitution reaction with an adequate precursor (*i.e.* an imidazole for obtaining imidazolium groups) at the functional groups present on the surface of the polymeric support. For instance, crosslinked poly(*p*-vinylbenzyl chloride)-divinylbenzene (poly(VBCI-DVB)) monoliths have been successfully used for the preparation of polymeric materials containing ionic liquid-like units named as Supported Ionic Liquid-Like Phases (SILLPs).^{18,19,20} The physicochemical properties of these materials can be altered easily and at a large extent by changes on both the structural characteristics of polymer (degree of crosslinking and loading, etc) and the nature of the IL-like moieties (cation substitution and functionalization and counteranion exchange). The fine-tuning of these parameters has been demonstrated to allow improving the activity and stability of different catalytic species immobilized onto these crosslinked polymers.²¹

In the search of new monolithic architectures for the preparation of supported ILs, here we report a new approach for preparing sizable monolithic organic entities containing a high density of IL-units. The synthesis starts with a ready-made polymer, a soluble linear poly(*p*-

vinylbenzylchloride) (poly(VBCl)) obtained by controlled radical polymerization, with the monolithic structure being generated by controlled phase separation and covalent and/or supramolecular crosslinking occurring during the reaction between the soluble polymer and reactive units. The properties of these polymeric materials as IL-like phases have been evaluated as organocatalysts for the Knoevenagel condensation and in the formation and stabilization of metal nanoparticles.

Results and discussion.

The synthetic route envisioned for the preparation of the monolithic polymers bearing a high density of IL-units was based on the use of linear poly(*p*-vinylbenzylchloride) (poly(VBCl)) obtained by controlled radical polymerization (CRP). These polymers allow the simple introduction of the IL-like moieties by post-polymerization functionalization through the nucleophilic substitution of the pendant chloride groups using the free nitrogen atom of a N-substituted imidazole. The key issue to prepare suitable monolithic materials was the use of multifunctional reactive small molecules able to afford a nano-structured monolithic material by the controlled crosslinking and collapse of the polymeric chains in solution. In this regard, two different methodologies were explored to prepare these materials bearing IL-like units. The first one intended to take advantage of the fact that polymers prepared by RAFT polymerization are also macro-initiators, which can be used in further copolymerization processes. Thus, upon reaction of poly(VBCl), under RAFT polymerization conditions, with an additional crosslinking monomer (divinylbenzene, (DVB)) the linear chains can crosslink and collapse onto an organized monolithic material.²² This further crosslinking has to take place only at the ends of the polymeric chains, leaving, in principle, the chloromethyl groups accessible for being transformed into IL-like units through nucleophilic attack. The second strategy to produce monoliths from

these linear polymers was based on the reaction of the chloromethyl groups with a bifunctional reactive small molecule able to generate the corresponding IL-like units and simultaneously crosslink the soluble polymeric chains to provide the corresponding monoliths.

According to these two methodologies, the first objective was to establish a protocol to carry out the polymerization of the monomer **1** by CRP providing the corresponding poly(VBCl) in a reproducible way and with the desired properties. In this regard, it has been reported that the atom transfer radical polymerization (ATRP) of **1** can lead to hyperbranched structures *via* chain transfers to the dangling chlorine atom of the monomer.²³ Therefore, RAFT (Reversible Addition–Fragmentation Chain Transfer) polymerization was considered as an ideal alternative CRP process for the preparation of the homopolymer from **1**.²⁴ Table 1 summarizes the experimental conditions and results achieved for the RAFT polymerization of **1** in the presence of either 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPA, **2a**) and 2-cyano-2-propyl benzodithioate (IBN, **2b**) as RAFT agents (Scheme 1). Two different radical initiators (AIBN (2,2'-Azobis(2-methylpropionitrile)) and ACVA (4,4'-azobis(4-cyanovaleric acid)) were also assayed in the preparation of poly(VBCl) by CRP.

Scheme 1. Synthesis of poly(VBCl) by RAFT polymerization.

The first polymerizations were performed using toluene as solvent and **2a** as the transfer agent, while ACVA was used as radical initiator. Under these conditions, poly(VBCI) was obtained with a moderate conversion (27%, Table 1, Entry 1). The analysis of the isolated polymer revealed a molar molecular weight of 3.6 kg/mol and a low polydispersity (PDI = 1.1). Longer reaction times led to an improvement in conversion from 27% to 52% (Table 1, Entry 2). As expected, the polymer obtained also showed a larger molecular weight (M_n = 9.1 kg/mol) together with a moderate polydispersity (PDI = 1.28). An increase in the temperature from 90 °C to 100 °C provided a polymer with a slightly lower molecular weight (M_n = 8.4 kg/mol) due to the shorter reaction time applied (24 vs. 38 hours). However, similar levels of conversion (56%) and polydispersity (PDI = 1.28) were achieved under these conditions regardless the shorter polymerization time (Table 1, Entry 3). The use of DMF instead of toluene allowed carrying out the polymerization at higher temperature (120 °C). Under these conditions, a polymer with a reasonable molecular weight (M_n = 11.0 kg/mol) and a very low polydispersity (PDI = 1.1) was attained (Table 1, Entry 4).

Finally, the reaction was assayed under solvent-free conditions (Table 1, Entries 5-6). A good conversion (87%) was achieved after 21 hours. The corresponding polymer was isolated with a molecular weight of 9.2 kg/mol. However, under these conditions, a more reduced control of the polydispersity was reached according to its polydispersity (PDI = 1.46). A shorter reaction time (2.5 hours) provided a polymer with a lower molecular weight (4.4 kg/mol) and excellent polydispersity (PDI = 1.1), however, only a limited conversion was achieved (34%). As the solubility of CPA and ACVA was limited under these solvent-free conditions, they were replaced by IBN and AIBN for additional experiments. This modification yielded the corresponding

polymer with 38% of conversion, and presenting a molecular weight of 14.1 kg/mol and a good polydispersity (PDI = 1.29).

Table 1. Poly(VBCl) synthesis by RAFT polymerization of **1** under batch conditions.

Entry	[M]:[CTA]:[I]	Solvent	T (°C)	t (h)	Conv. (%) ^a	M _n (kg/mol) ^b	PDI
1	[1]:[2a]:[ACVA] 100:1:0.3	toluene	90	24	27	3.6	1.18
2	[1]:[2a]:[ACVA] 100:1:0.3	toluene	90	38	52	9.1	1.21
3	[1]:[2a]:[ACVA] 100:1:0.3	toluene	100	24	56	8.4	1.28
4	[1]:[2a]:[ACVA] 100:1:0.3	DMF	120	24	30	11.0	1.10
5	[1]:[2a]:[ACVA] 100:1:0.3	-	130	2.5	34	4.4	1.10
6	[1]:[2a]:[ACVA] 100:1:0.3	-	130	21	87	9.2	1.46
7	[1]:[2b]:[AIBN] 100:1:0.1	-	100	24	38	14.2	1.29

^aDetermined by ¹H-NMR of the reaction crude. ^bDetermined by GPC.

The results demonstrated that it was possible to obtain poly(VBCl) with reasonable levels of yield, M_n and polydispersity under batch conditions. In general, the polymerization reactions were performed in a scale able to produce between five and fifteen grams per batch. However, when the amount of the initial monomer (**1**) was increased to 100 g scale and the polymerization assayed under the previous optimized solvent-free conditions, using a 100:1:0.3 [**1**]:[**2a**]:[ACVA] ratio and 100 °C, the reaction failed to provide a controlled polymerization process. Thus, a polymer with a larger molecular weight of 10.8 kg/mol but far uncontrolled polydispersity (PDI = 5.4) was obtained. This uncontrolled polymerization in batch can be attributed a less efficient control of the homogeneity of the mixture when the scale increases from 5 to 100 g.

In the search of a methodology to enhance the productivity of the polymerization, the use of continuous flow processes was also explored. In the last few years, continuous flow

processing has demonstrated its potential as a disruptive technology to achieve different types of polymers by controlled radical polymerization.²⁵ In this regard, a tubular reactor presents a very practical and compact design for the continuous manufacture of CRP polymers in quantities that would otherwise be difficult to achieve in a batch system.

Figure 1 shows the reactor used for the continuous flow polymerization of **1**. The solution containing the monomer, the transference agent and the initiator was pumped with a HPLC pump through a tubular reactor confined in a thermostatic oven. RAFT polymerization is known to be extremely sensitive to any traces of oxygen, which can quench the radical reactions.²⁶ Therefore, the utmost care was taken to avoid the contact with air of the components before and during the polymerization. The starting materials solution was degassed carefully using three freeze-evacuate-thaw cycles and the systems kept under nitrogen during the polymerization procedure. The continuous flow reaction was conducted safely above atmospheric pressure by using a backpressure regulator (300 psi) allowing the work at temperatures higher than the boiling point of the solvent. In the initial attempts under flow conditions, a solution of **1** in toluene (20% by weight) was assayed for the polymerisation. Similar conditions than those reported above for the batch process were used. A 12 m long stainless-steel coil was employed for the tubular reactor ($d_{\text{external}} = 3.175$ mm and OD = 0.7112 mm, $d_{\text{internal}} = 1.753$ mm). The residence time could be adjusted by using two volumetric flow rates of 0.1 and 0.2 mL/min. Under these conditions and for the shorter residence time (2.4 hours), a pink-red viscous polymer solution was obtained at the exit of the reactor, from which conversion was determined by NMR. The polymer was precipitated in methanol, resulting in a pink polymer powder, indicative of the presence of the CTA at the end-chain of the polymer obtained.

Figure 1. Continuous flow set-up used in the RAFT polymerisation reaction of monomer **1**.

The initial conditions assayed (Table 2, Entry 1), only yielded a moderate conversion of **1** in the corresponding polymer (42 %), accompanied by a high polydispersity. Doubling the residence time by reducing to half the flow rate used (0.1 mL/min), led to an increase on the conversion (Table 2, Entry 2). However, the isolated polymer presented a similar molecular weight than before and a larger polydispersity, indicating the lack of control of the polymerization under these experimental conditions. Better results were obtained when the polymerization was performed under solvent free conditions at 100 °C and using the same RAFT agent and initiator and keeping a 100:1:0.3 ratio for the different polymerization mixture components ([**1**]:[**2a**]:[ACVA]) (Table 2, Entry 3). It should be mentioned that the residence time

was shortened to 90 min by using a four-meter reactor, instead of the six meter one, and maintaining the flow rate at 0.1 mL/min (Table 2, Entry 4). Under these conditions a polymer with a modest molecular weight 1827 g/mol and with acceptable polydispersity (PDI = 1.29) was obtained. An increase in the temperature rendered a slightly higher conversion (32%, Table 2, Entry 5), showing the polymer obtained after isolation a somewhat higher molecular weight (4.4 kg/mol) and polydispersity (PDI = 1.45). Noteworthy, at the same reaction time, the batch polymerization yielded a polymer with similar levels of conversion and molecular weight; although the polydispersity was slightly lower (Entry 5, Table 1 vs. Entry 4, Table 2). It is worth mentioning that, under these conditions, attempts to further increase the residence time in order to achieve higher level of conversion with acceptable polydispersity led to blockage of the reactor. Finally, when both the RAFT agent and the initiator were replaced by **2b** and AIBN, the results, again under the same experimental conditions, did not led to polymers with significantly larger molecular weight or lower polydispersity (Table 2, Entry 5). Thus, continuous flow processing under solventless conditions provided polymers with acceptable polydispersity, although due to the modest level of conversion attained only low molecular weight polymers could be obtained.

According to these results, both batch and continuous flow RAFT polymerization of **1** can lead to a polymer with reduced polydispersity (PDI < 1.5). The batch process tends to provide higher molecular weight (> 10 kg/mol), while the flow process is limited to the production of low molecular weight poly(VBCl) (< 2 kg/mol). However, the flow process can improve the productivity of this type of polymers. The productivities reached for the solvent free flow conditions were of *ca.* 1.4 g of poly(VBCl) hour and *ca.* 2 g of poly(VBCl) hour, in comparison with the *ca.* 0.7 g of poly(VBCl) hour achieved in batch for similar conditions (Table 1, Entry 4).

Table 2. Poly(VBC) obtained by RAFT polymerization under continuous flow conditions.

Entry	[M]:[CTA]:[I]	Solvent	T (°C)	P (psi)	Flow (mL/min)	Residence time (min)	Conv. (%) ^a	M _n (kg/mol) ^b	PDI
1	[1]:[2a]:[ACVA] 100:1:0.3	toluene	130	330	0.2	160 ^c	42	1.02	2.09
2	[1]:[2a]:[ACVA] 100:1:0.3	toluene	130	330	0.1	320 ^c	78	1.08	2.86
3	[1]:[2a]:[ACVA] 100:1:0.3	-	100	330	0.1	90 ^d	21	1.83	1.29
4	[1]:[2a]:[ACVA] 100:1:0.3	-	130	330	0.1	90 ^d	32	4.4	1.45
5	[1]:[2b]:[AIBN] 100:1:0.3	-	130	203	0.1	160 ^c	40	2.5	1.67

^a Determined by ¹H-NMR of the reaction crude. ^b Determined by GPC. ^c Reactor : 12 m. ^d Reactor : 4 m. ^e Reactor : 6 m.

Synthesis of polymeric IL-like phases.

Once the methodology for the synthesis of poly(VBCI) under controlled conditions was established, the synthesis of polymeric IL-like phases was studied using the aforementioned approaches. Recently, porous functional poly(styrene-co-divinylbenzene) monoliths have been obtained by RAFT polymerization of styrene and divinylbenzene (DVB) in the presence of 2-cyano-2-propyl dodecyl trithiocarbonate as the transfer agent. In a similar way, the preparation of a copolymer using poly(VBCI) as a macromolecular transfer agent and DVB was assayed in toluene in the presence of AIBN. In parallel, the same free radical polymerization was carried out using the monomer **1** instead of its polymeric analog. The poly(VBCI) polymer obtained by batch RAFT solvent-free polymerization of **1** with **2b** and AIBN (Table 1, Entry 7) was selected for this purpose. The homogenous polymerization solutions were prepared in toluene using either 25 % or 50 % weight of the reactive components (Table 3). In all the cases, AIBN (1% weight over the polymerization components) was used as the initiator.

Table 3. Synthesis of cross-linked materials by RAFT copolymerization of poly(VBCl) with DVB.

Entry	Monolith	Poly(VBCl) ^{a,b}	DVB ^b	1 ^b	Toluene ^c	Appearance ^e
1	M-3		50	50	50	White solid
2	M-4	50	50		50	Transparent solid
3	M-5		50	50	75	White solid
4	M-6	50	50		75	Transparent solid

^a Poly(VBCl) of $M_n = 14.2$ kg/mol and PDI = 1.29, prepared according to Table 1, entry 7. ^b percentages of the monomers are given in weight % of the monomeric mixture. ^c percentage of solvent in weight % of the final solution containing the monomers, AIBN (1 % in weight of total active components). ^d Calculated by weight. ^e Appearance at r.t. after heating at 70 °C for 24 h.

Figure 2. Polymerization mixtures, based on the compositions in Table 3, as they appeared after 24 hours of polymerization in test-tubes (**M-3**: 1:DVB 1:1, 50 % w toluene; **M-4**: poly(VBCl):DVB 1:1, 50 % w toluene, **M-5**: 1:DVB 1:1, 75 % w toluene; **M-6**: poly(VBCl):DVB 1:1, 75 % w toluene).

The solutions were poured into a mold, bubbled with N_2 and heated-up at 70 °C during 24 hours. Monoliths were obtained for all the conditions assayed. Nevertheless, the aspect of the monoliths was quite different (Figure 2). The polymerization mixtures prepared from

poly(VBCl) led to transparent rubber-like monolithic materials, while the monoliths obtained with the monomer **1** were white opaque monoliths. Monoliths were obtained for the two concentrations assayed. None of the monoliths obtained swelled appreciably when submerged in different solvents (MeOH, CH₂Cl₂, DMF).

In order to assess the accessibility of the chloromethyl groups for their conversion into the corresponding IL-like phases, the monolith **M-4** was reacted with three different n-alkyl-imidazoles: *N*-methyl and *N*-butyl-imidazole and 1,6-bis(1H-imidazole-1-yl)hexane (Scheme 2). The modification of **M-4** was carried out by introducing the monolith in a solution of the alkylating agent in DMF and heating for 90 °C during 24 hours and quantitatively monitored by ATR-FT-IR spectroscopy. The disappearance of the peak at 1265 cm⁻¹ (wagging bands of CH₂-Cl) indicates the substitution of these groups with the IL-like moieties.^{27,28} The modified materials were also tested with NBP test, which is a colorimetric assay to assess the presence of reactive CH₂-Cl on the polymers,²⁹ giving a negative result for this test after the reaction. Indeed, both the ATR-FT-IR and the NBP test data were in good accordance with a total substitution of the chloromethyl units (100% conversion). These results suggest that the chloromethyl units of the monoliths prepared by RAFT copolymerization with poly(VBCl) and DVB, present a good accessibility for substitution, being able to be further transformed into the corresponding polymer supported IL-like phases.

Scheme 2. Synthesis of the polymer supported IL-like phases **M-7**, **M-8** and **M-9** obtained by chemical modification of the monolith **M-4** obtained by RAFT polymerization of poly(VBCl) and DVB.

In the case of **M-9**, the use of a bis-imidazole as the alkylating agent can be accompanied by a significant increase in the crosslinking of the polymer matrix and the success in this reaction opened the way to the application of the second strategy envisaged. Thus, the preparation of well-structured insoluble crosslinked PILs was approached through the reaction of different soluble poly(VBCl) polymers with a bis-imidazole. Bis-imidazoles with different alkyl spacers can be easily prepared by reaction of imidazole with the corresponding di-bromoalkyl derivative.³⁰ For the initial studies, 1,6-bis(1H-imidazole-1-yl)hexane (**10**) was again selected (Figure 3). Several poly(VBCl) polymers with different molecular weight obtained either in batch processes (> 10 kg/mol) or alternatively by the flow process (< 2 kg/mol) were assayed in this regard. Three different reaction mixtures were prepared containing identical polymer to bis-imidazole molar ratios (4:6). The polymer concentration (weight %) was kept at 50% in DMF. The poly(VBCl) polymers selected were two polymers obtained in batch with a M_n value of 4.4 and 11.0 kg/mol (Table 1, Entry 5 and 4, respectively) and a third one obtained in flow with M_n = 1.83 kg/mol (Table 2, Entry 3). The three solutions were heated at 90 °C for 24 hours being transformed into the corresponding monolith. After demolding, it was observed that the polymers

with higher molecular weight led to less transparent, harder and more brittle materials, while the material derived from the low molecular weight precursor showed a clear transparent and more rubber like aspect. The difference in morphology can be related with the fast collapse of the structure when the higher molecular weight polymer was used, probably due to a larger crosslinking degree between the polymeric chains. These results suggest that the use of soluble polymers with molecular weight < 2 kg/mol can be more suitable when good mechanical properties are desirable. Thus, the polymers prepared by flow conditions were selected for further studies.

Figure 3. Synthesis of monoliths by reaction of poly(VBCl) polymers with bis-imidazole **10**. Pictures of the monoliths obtained after demolding.

The influence of other experimental factors was also evaluated for these poly(VBCl) polymers, namely: i) concentration of the components on the reaction mixture, ii) nature of the bis-imidazole (i.e. six vs. four carbon atoms in the spacer) and iii) polymer to alkylating agent molar ratio. Table 4 summarizes the conditions assayed. In all the cases, a homogeneous solution was obtained for the starting components in DMF, and this was poured in a mold and heated at

90 °C for 24 hours. During this period, the reaction mixture was transformed into a single monolithic material adopting the shape of the mold used for the reaction. The materials obtained showed, in some cases, different aspects after demolding (see pictures in Table 4). Regarding the different variables studied, the effect of the concentration of the reactive components (50 % and 70% w of DMF) was very minor, obtaining in both cases monoliths with similar rubber-like transparent character (Table 4, Entries 1 and 2). The NBP test and the ATR-FT-IR spectra of these materials confirmed the full substitution of the -CH₂Cl groups. The use of a bis-imidazole with a shorter spacer, four methylene groups instead of six, led to a denser, less transparent monolithic material. Again the NBP test and the ATR-FT-IR suggested the full substitution of the functional sites of poly(VBCl). Two additional materials were obtained using either a molar defect or an excess of alkylating agent (Table 4, Entries 4 and 5 respectively). Although both conditions led to monoliths, significant differences were found between them. The material obtained with a defect of alkylating agent (70:30, poly(VBCl):**10**) gave a positive NBP tests and its ATR-FT-IR spectrum confirmed the presence of unreacted -CH₂-Cl groups. Despite the uncomplete postsfunctionalization, its aspect was similar to that observed for the monoliths **M-11** and **M-15**. On the contrary, the material prepared with a large excess of bis-imidazole (poly(VBCl):**10**, 20:80, Table 4 Entry 5) showed a less dense structure with a more rubber-like nature. As expected, the used of an excess of **10** guaranteed the full substitution of the -CH₂Cl groups as confirmed by the negative NBP test and by IR spectroscopy.

It is important to bear in mind that the bis-imidazole can react with the chloromethyl units of poly(VBCl) to yield two different scenarios. In the first one, the reaction of the two imidazole units with two different chloromethyl groups of poly(VBCl) would afford a high level of

crosslinking through the formation of bis-imidazolium moieties covalently linking the polymeric chains.

Table 4. Synthesis of materials from the reaction of poly(VBCl) with a bis-imidazole at 90 °C.

Entry	Monolith	poly(VBCl) % wt	Bis(imidazole) % wt	DMF (% wt)	Poly(VBCl):10 (molar ratio)	NBP test	Image
1	M-11	50	50 (10)	50	40:60	-
2	M-15	50	50 (10)	70	40:60	-
3	M-16	50	50 (14)	50	40:60	-
4	M-17	75	25(10)	50	70:30	+
5	M-18	25	75(10)	50	20:80	-

The solution of the corresponding reagent mixture was reacted at 90 °C for 24 h in a test tube. The properties of the poly(VBCl) used are defined in Table 2, Entry 3.

Alternatively, the $-\text{CH}_2\text{Cl}$ units could preferentially react with soluble bis-imidazole molecules leading to the corresponding imazolium-imidazole functional moieties attached to the polymer chains if enough bis-imidazole is available. In this case, there will not be any covalent crosslinking, but the non-covalent interactions between the functional groups of the polymeric chain can lead to a structured material through supramolecular interactions. Indeed, the ionic imidazolium IL-like units can form complex coacervate clusters by columbic interaction that may act as supramolecular crosslinkers.^{31,32} Besides, the pendent nonionic hydrophobic alkyl-imidazole units can also form additional Van der Waals supramolecular interaction. Of course, both scenarios can coexist, but even in the absence of covalent crosslinking these supramolecular interactions could define the morphology of the materials obtained.³³

For the polymers **M-11-M-16** and **M-18** obtained with quantitative covalent crosslinking through bis-imidazolium moieties a loading of *ca.* 3.8 meq of imidazolium units per gram of polymer should be obtained (Scheme 3, possibility A).

Scheme 3. Possible structures obtained by reaction with bis(imidazole).

However, for a material for which all the methylchloride groups were substituted by an imidazolium-imidazole unit loading of *ca.* of 2.7 meq of imidazole groups per gram of polymer should be attained (Scheme 3, possibility B). Thus, a simple elemental analysis of the polymers obtained can shed light on the structure present on these materials. Table 5 shows the loading values obtained for the different polymers obtained. In general, the values found were in the 2.2-2.9 meq imidazolium units / g range. Only in the case of the monolith obtained with a defect of alkylating agent a different loading was observed (1.48 meq / g). Thus, in general, the loadings found were closer to the values expected for a material with a very low covalent crosslinking, having ditopic imidazolium-imidazole moieties as the major functionalities. In order to confirm the presence of imidazole units not transformed into imidazolium fragments, and indirectly the crosslinking degree, these polymers were reacted with 1,3-propane sultone, which will react with

the free imidazole units leading to the corresponding imidazolium propane sulfonic salt (Scheme 3). The loading of free and crosslinked imidazolium units can be estimated through the elemental analysis of these modified polymers. The nitrogen content provides the total loading of imidazole/imidazolium units and the sulfur content allows for the calculation of the unreacted imidazole present in the material.

The sulfur and nitrogen elemental analyses in these modified polymers confirmed previous data, confirming a very low covalent crosslinking or even the absence of covalent crosslinking. In this way, the monolith **M-11** prepared using the bis-imidazole with the longer alkyl spacer (**10**) showed a modest crosslinking degree (*ca.* 15 ± 3 %) while the absence of covalent crosslinking was suggested for the monolith **M-16** synthesized under identical conditions using the bis-imidazole **14** with the shorter spacer. For monolith **M-15**, similar to **M-11** but synthesized using a higher dilution of the reactive components of the mixture (70 % of DMF), elemental analyses suggested that this dilution was accompanied by a reduction in the covalent crosslinking from *ca.* 15 ± 3 % to *ca.* 5 ± 3 %. In the case of **M-17** prepared using a large excess of alkylating agent **10**, the data matched with the absence of any covalent crosslinking. The non-soluble nature of this polymer **M-17** must be attributed to the involvement of non-covalent crosslinking mechanisms. Polymer **M-18** obtained with a defect of alkylating agent **10** only showed, according to its elemental analyses, *ca.* 55 % substitution of the CH_2Cl groups and absence of covalent crosslinking.

It should be mentioned that the starting poly(VBCl) polymer presents in its structure a thio-ester functional group than in the presence of a base can be cleaved yielding the corresponding thiol.³⁴ These polymeric chains end-groups could react, under the experimental conditions described, with the $-\text{CH}_2\text{Cl}$ groups present, providing an additional crosslinking

mechanism. However, considering the molecular weight of the poly(VBCI) used, this mechanism could just provide very minor levels of crosslinking (1-2%).

Table 5. Loading and crosslinking for polymers **M-11-M18**.

Entry	Polymer ^a	Theoretical loading imidazolium meq/g ^b	Calculated loading imidazolium units meq/g ^c	Calculated loading of imidazole meq/g ^d	Crosslinking ^e
1	M-11	2.69	2.42	2.24	15
2	M-15	2.69	2.31	2.54	5
3	M-16	2.63	2.98	2.91	-
4	M-17	1.08	1.48	1.57	-
5	M-18	2.69	2.71	2.98	-

^a See Table 4, for the description of the different polymers. ^b Calculated for the quantitative substitution of all the chloromethyl groups by imidazole-imidazolium chloride units. ^c loading of imidazolium units calculated from N elemental analysis. ^d loading of imidazole units calculated from S elemental analysis. ^e Crosslinking degree = [(theoretical loading imidazolium for the full conversion of CH₂Cl units into imidazole-imidazolium chloride) – (loading of imidazole units calculated from S elemental analysis)] / (theoretical loading imidazolium for the full conversion of CH₂Cl units into imidazole-imidazolium chloride) x 100.

Swelling properties. According to their reduced covalent crosslinking degree, these polymeric materials (**M-11** to **M-18**) offer the possibility of developing interesting swelling properties in solvents. Thus, their swelling was investigated using a small disc of each material that was immersed in different solvents. A series of solvents with different dielectric constants (water ($\epsilon = 80.4$), methanol ($\epsilon = 33.1$), 2-Me-THF ($\epsilon = 6.3$), chloroform ($\epsilon = 4.81$) and hexane ($\epsilon = 2$)) were chosen for this purpose. The swelling/shrinking was calculated using the ratios for the measured volumes of the discs in the dry and in the wet states. Results obtained are presented graphically in Figure 4.

The swelling behavior should depend on both the compatibility of the polymer chains with the media and the ability of the solvents to disrupt the non-covalent supramolecular

interactions present including the ionic interactions between charged imidazolium groups and the hydrophobic interactions between apolar fragments. Highly polar solvents such as water ($\epsilon = 80.4$) and methanol ($\epsilon = 33.1$) are expected to be able to induce the dissociation of the ion pairs formed between the imidazolium cations and the chloride counteranions. Therefore, both the loading of imidazolium groups and the crosslinking must define the swelling properties. In general, a higher loading of IL-like units will enhance the swelling in polar solvents, but, at the same time this is associated to a higher covalent crosslinking in polymers **M-11** to **M-18** what makes more difficult an efficient swelling. Thus, the observed swelling will be a compromise between these two factors. This can explain that the polymer **M-11** having the highest covalent crosslinking degree (15 %) swelled in water better ($S = 107$ %) than **M-15** ($S = 82$ %) having a lower covalent crosslinking (5 %), although the most effective swelling in water was achieved for **M-16** ($S = 111$ %) essentially lacking the covalent crosslinking. In methanol the situation was reversed and **M-15** displayed a better swelling than **M-11**, most likely as this organic solvent is also able to better solvate the aliphatic chains of the spacer at the crosslinking sites.

Rather surprisingly, a modest swelling was observed for **M-11** and **M-15** (15 % and 20 % respectively) in hexane, being slightly larger for the polymer with a lower crosslinking degree. As this extremely non-polar organic solvent cannot be expected to favor the weakening of the ion-pairs, this effect must be associated to an efficient solvation of the hydrophobic regions of the polymer (polymer chains and alkyl spacers). The use of organic solvents of intermediate polarity like 2-Me-THF, not being able to facilitate ion-pairs dissociation and not being efficient for the solvation of the hydrophobic domains, led, in general, to a shrinking of the polymers. A further increase of the solvent polarity, for instance by using chloroform ($\epsilon = 4.81$), led to observe a shrinking ($S = -31\%$) for **M-11**, while **M-15** still showing a modest swelling ($S = 14\%$)

highlighting, once again, the importance of the crosslinking to determine the swelling. It must be noted that when the Cl^- anion of **M-11** was exchanged by NTf_2^- leading to the polymer **M-19**. The anion exchange reduces the strength of the ionic interactions and the overall polarity of the polymer,³⁵ an opposite behavior was observed, swelling in organic solvents (i.e. $S = 27\%$ for 2-Me-THF) and slightly shrinking in water.

Figure 4. Swelling studies of some monoliths in different solvents.

Catalytic assessment. The Knoevenagel condensation is one of the most powerful strategies for carbon–carbon bond formation in organic chemistry. This reaction is often used in the synthesis of important intermediates for the preparation of pharmaceutical drugs and fine chemicals.³⁶ The Knoevenagel condensation is generally carried out in organic solvents in the

presence of organic bases (alkylamine and ammonium salts)³⁷ or Lewis acid catalysts.³⁸ However the use of homogeneous conditions is associated with a difficult work-up of the reaction mixture and the generation of considerable amounts of liquid waste. The use of task specific ILs as environmentally benign solvents and/or co-catalysts has demonstrated an excellent performance in this process.³⁹ Materials modified with task specific IL-like units have also been tested as efficient immobilized catalysts for this reaction under solvent free conditions.⁴⁰ We have recently demonstrated that the self-organisation of composites formed by AuNP-PILs leads to active catalysts for the Knoevenagel reactions.⁴¹ Thus, in principle, the IL-like phases here prepared could be potential catalysts for this type of C-C bond formation reaction. In order to assess this possibility, and taking into account their swelling in water, the different monoliths prepared were tested as catalysts for the reaction of ethyl cyanoacetate and *p*-nitrobenzaldehyde in water.

The results obtained are summarised in Table 6. The reaction in the absence of any catalyst afforded the corresponding alkene in 38 % yield. In general, the presence of the polymers with IL-like fragments produced an enhancement of the yield obtained. Only in the case of **M-17** a low yield was observed (Table 6, Entry 5). The lower yield obtained for this case can be related with the fact that in this polymer only half of the methyl chloride groups were transformed into IL-like units and, accordingly, this material has a significant lower loading of basic sites. On the other hand, the monolith **M-9** obtained by the RAFT polymerisation of poly(VBCl) with DVB and further functionalised with the bis-imidazole **10** provided comparable or slightly better yields (88 %) than the one obtained by direct modification of the pol(VBCl) (Table 6, Entry 2 vs 3). The higher yield obtained for **M-15** (84 % yield) in comparison with **M-11** (70 % yield) can be related with their free imidazole loading, which are 2.54 and 2.24 meq/g respectively. Indeed, the monolith **M-18** obtained with a large excess of bis-imidazole and

providing the highest loading of basic imidazole (2.98 meq/g) led to 100 % yield for the alkene. Also **M-16**, obtained with a bis-imidazole with a shorter spacer, displays a high loading of free imidazole groups (2.91 meq/g) and consequently was a very efficient basic catalyst for the reaction (Table 6, Entry 7).

The exchange of the chloride anion by the less basic and hydrophobic NTf₂⁻ led to a significant reduction of the catalytic activity (Table 6, Entry 8). In this case, the exchange of the anion has a strong effect on the swelling of the material that shrinks in water (S = -17%), which can considerably reduce the accessibility of the basic catalytic.

The good catalytic efficiency of these systems can be explained considering the synergetic involvement of the IL-like units together with the basic catalytic sites provided by the free imidazole units present. On one hand, the IL-like moieties can interact (electrostatic and hydrogen bonding) with the aromatic aldehyde facilitating the attack by the nucleophile. On the other hand, the basic imidazole sites located in close proximity can enhance the nucleophilicity of the compound displaying an acidic methylene group improving its deprotonation. Besides, the IL-units control the swelling of the materials on water. In the presence of Cl⁻ as the counter ion an excellent swelling occurs, providing an easy accessibility to the catalytic sites and a non-permanent porous structure that can accommodate the reagents at the more hydrophobic domains in close proximity to the imidazole units. The resulting pseudo-concentration of the reactants near the active sites can also enhance the reaction rate and therefore the catalytic efficiency.

Table 6. Knoevenagel reaction between ethyl cyanoacetate and *p*-nitrobenzaldehyde in water catalysed by polymers containing IL-like fragments.^a

Entry	Monolithic IL-phase	Yield (%) ^b
1	-	38
2	M-11	70
3	M-9	88
4	M-15	84
5	M-17	10
6	M-18	100
7	M-16	100
8	M-19	48

^a 25 °C, 1 h, 1:1 cyanoacetate : *p*-nitrobenzaldehyde molar ratio, 30 mg cat. ^b determined by ¹H-NMR of the reaction crude.

The synthetic methodology developed for the synthesis of these IL-like phases also allows for the simple introduction of additional basic sites that in well-organised 3-D polymeric structure could cooperate with the imidazolium-imidazole units to enhance the catalytic activity. Thus, with this idea in mind, three different basic functional groups were introduced in the corresponding polymers. *N*-Alkyl amine groups could be easily introduced by the reaction of pyrrolidine with chloromethyl groups using a mixture of bis-imidazole **10** and pyrrolidine for the transformation of poly(VBCl) (the same material used for the polymers **M-11** to **M-18** was used, Scheme 4). The same strategy was used to introduce, along with the corresponding IL-phases, a guanidine group (1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD). In both cases, the corresponding base and **10** were mixed in a 1:4 ratio and heated at 90 °C with the poly(VBCl). The appearance

of the resulting polymers was similar to that obtained in the absence of the additional base. The ATR-FT-IR spectra of these polymers (Figure S4, ESI), confirm the introduction of the additional functionality. Thus, the spectrum for **M-20** displays peaks at 1060 cm^{-1} and 645 cm^{-1} assignable to the $-\text{CH}_2\text{NR}_2$ groups. The exchange of the Cl anions in **M-20** by NTf_2^- yielded the monolith **M-21**. The success of the exchange was assessed by ATR-FT-IR, with its spectrum presenting strong peaks assignable to NTf_2^- at 1321 , 1189 , 1125 and 1056 cm^{-1} .

Scheme 4. Synthesis of base functionalized monolithic IL-like phases.

Regarding the monolith modified with guanidine units, the introduction of the TBD fragment in **M-22** was confirmed by the appearance of a peak at 1607 cm^{-1} for the $\text{C}=\text{N}$ stretching together with a band corresponding to $\text{C}-\text{N}$ stretching at 1321 cm^{-1} (Figure S5, ESI).⁴²

Finally, a polymer bearing iminophosphorane superbase moieties, which are usually synthesized *via* a Staudinger reaction between a triarylphosphine and an azide,⁴³ was introduced using a two-steps approach. The reaction of the soluble poly(VBCl) (Table 2, Entry 3) with sodium azide in a 75:25 molar ratio afforded a modified soluble polymer bearing as functional sites -CH₂Cl and -CH₂N₃. This modification was easily monitored by ATR-FT-IR spectroscopy, which revealed the presence on the polymer of the two characteristics peaks at 2098 cm⁻¹ assignable to the N=N=N stretching and at 1265 cm⁻¹ for the C-Cl stretching (Figure S7, ESI). The quantification of these two functional groups was obtained through integration of the two different benzylic signals for -CH₂Cl and -CH₂N₃ in ¹H-NMR (Figure S6, ESI). The -CH₂Cl : -CH₂N₃ ratio experimentally obtained was 73:27, in good agreement with the values for the reagents mixture. A monolith (**M-23**) containing simultaneously IL-like fragments and azide groups was obtained by reaction of this modified soluble polymer with bis-imidazole **10** using the same protocol described above. The azide group in **M-23** was quantitatively reduced in the presence of NaBH₄ to yield the corresponding benzylamine group (**M-24**) (Figure S8, ESI). The synthesis of the iminophosphorane was initially attempted by the reaction of **M-23** with PPh₃ in toluene, as this phosphine is insoluble in water. However, this transformation did not take place as the monolith did not swell in this solvent. Thus, an alternative synthetic route based on the exchange Cl⁻ by NTf₂⁻ to improve the compatibility of the polymer with this solvent was assayed. Once the anion was exchanged, an almost complete conversion (95 %) of the azide group was achieved, giving place to polymer **M-25** (Figure S9, ESI). In the search of a more efficient protocol for the synthesis of a monolith modified with iminophosphorane, the soluble azide modified polymer (poly(VBCl)-(VBN₃)) was reacted simultaneously with a mixture of PPh₃ and

the bis-imidazole **10** in DMF. The ATR-FT-IR of the resulting polymer **M-26** showed a complete conversion of the azide groups into iminophosphorane groups (Figure S10, ESI).

Table 7. Knoevenagel reaction between ethyl cyanoacetate and *p*-nitrobenzaldehyde in water catalysed by multifunctional polymers containing IL-like fragments and additional basic sites.^a

Entry	Monolithic IL-phase	Basic functional group	Yield (%) ^b
1	M-11		70
2	M-20		93
3	M-21	/ NTf ₂ ⁻	58
4	M-22		83
5	M-26		100
6	M-25	/ NTf ₂ ⁻	89

^a 25 °C, 1 h, 1:1 cyanoacetate : *p*-nitrobenzaldehyde molar ratio, 30 mg cat. ^b determined by ¹H-NMR of the reaction crude.

The efficiency of this new series of polymers as catalysts for the Knoevenagel reaction between ethyl cyanoacetate and *p*-nitrobenzaldehyde in water was also assayed. Table 7 summarises the results obtained. As aforementioned, polymer **M-11** provided the alkene in a modest yield and was used as a reference for the new polymers taking into account the structural similarities (Table 7, Entry 1). The activity of the modified IL-phases followed the order iminophosphorane (**M-26**) > *N*-Alkyl amine (**M-20**) > guanidine (**M-22**) (100 %, 93 % and 83 % yields respectively). The lower activity obtained for the TBD functionalized material is likely to be related with the alkylation of this fragment leading to a reduced basic character. In the case of **M-19**, obtained by the exchange of Cl⁻ of **M-11** by NTf₂⁻ was accompanied by a drastic decrease

in the catalytic activity as mentioned above (Table 6, Entry 8). To evaluate the importance and generality of this effect, two additional monoliths **M-21** and **M-25** bearing pyrrolidine and iminophosphorane as additional functional groups and NTf₂⁻ as the imidazolium counteranion were prepared. Both polymers were active and yielded the corresponding alkene but presented a reduced catalytic activity when compared with the analogues displaying chloride as the counteranion (**M-20** and **M-26**). The polymer **M-21** bearing pyrrolidine groups showed a significant deactivation as previously observed for the monolith **M-19**. However, **M-25** still maintained a good activity (89 % yield).

Synthesis and application of polymeric composites containing metal nanoparticles and IL-like fragments.

Polymer-supported ILs and ionic liquid-like phases have demonstrated to act, as ILs themselves, as efficient media for the generation and stabilization of MNPs and our group has studied the application of different composites based on Au and Pd for a variety of application.^{18, 44, 45, 46, 47} In this regard, the potential use of the obtained crosslinked polymeric materials for the preparation of MNPs was also studied. Following the same approach that had been previously reported for the preparation of AuNPs supported on SILLPs,⁴⁴ polymer **M-11** was first treated with HAuCl₄ in water to produce the corresponding anion exchange affording polymer **M-27-AuCl₄⁻** (Figure 5). After the exchange was complete (ca. 6 h), reduction with NaBH₄ in water at r.t. for 2 h afforded Polymer **M-28-AuNPs** displaying a remarkable homogeneous and stable dispersion of small AuNPs with a high loading (ca. 10.1 % Au). As shown in the HRTEM images, the AuNPs displayed sizes below 4 nm, with a mean diameter of 2.85 ± 0.58 nm and the mode being at 2.3 nm. The DRX analysis of **M-28-AuNPs** also allowed confirming the presence of gold with the appearance of broad peaks at the positions expected for Au (Figure 6). Even

more interestingly, the DRX analysis of **M-11** revealed the presence of several broad bands that suggest the presence of well-defined organized domains in this polymer giving place to a modulated structure. Such level of organization is maintained in the **M-28-AuNPs** polymer.

Figure 5. Synthesis of composites **M-28-AuNPs**. TEM pictures of the AuNPs a) scale bar 20 nm. b) scale bar 5 nm.

Figure 6. DRX analysis for polymers **M-11** (black line) and **M-28-AuNPs** (blue line). Red lines correspond to the expected positions for gold.

Two additional composites related to **M-28-AuNPs** were prepared by substituting gold with palladium in the case of **M-30-PdNPs** and by a mixture of gold and palladium for **M-32-Pd-Au-NPs**. The same approach than before was used as summarized in Figure 7 for the preparation of the corresponding immobilized nanoparticles. In opposition to what was observed for **M-28-AuNPs**, in **M-30-PdNPs** the NPs tended to form agglomerates of 240 ± 70 nm made by PdNPs of 1-3 nm, as seen in the corresponding TEM images (Figure 7a). The combination of both metals in a composite was achieved by first introducing the palladium salt as PdCl_4^{2-} and then completing the anion exchange with HAuCl_4 . Reduction with NaBH_4 provided a system where both AuNPs and PdNPs could be found. The mean diameter size of the nanoparticles was very small 1.5 ± 0.3 nm, with most particles being below 2 nm and the mode located at 1.7 nm (Figure 7b and c). Preliminary data suggest that the nanoparticles are individual particles of each component.

Figure 7. Synthesis of composites **M-30-PdNPs** and **M-32-Pd-Au-NPs**. TEM pictures a) **M-30-PdNPs**. b) and c) **M-32-Pd-Au-NPs**.

As has been highlighted by previous results in our group, composites containing PILs and MNPs can be applied as bifunctional catalysts for the tandem one-pot Knoevenagel reaction followed by the *in-situ* reduction with NaBH_4 .⁴¹ In this regard, the three composite materials containing MNPs were assayed for this process. The results obtained are gathered in Table 8. As can be seen, the three polymers were able to catalyze this tandem process. Under The gold composite **M-28-AuNPs** was able to provide a 75 % of conversion with a high selectivity towards the fully reduced compound **38** in which the carbon-carbon double bond and the amino and ester groups had been reduced (70% with the remaining 30% being the ester **37**). A better

conversion was achieved with **M-30-PdNPs**, which afforded a quantitative conversion, under the same experimental conditions, maintaining the same selectivity. A further improvement was obtained with the polymer **M-32-Pd-Au-NPs** that allowed obtaining 80 % selectivity for the fully reduced compound **38**, while maintaining the quantitative conversion.

Table 8. Single-pot Knoevenagel reaction between *p*-nitrobenzaldehyde and ethyl cyanoacetate followed by the reduction with NaBH₄.^a

Entry	Cat.	Mean MNP diameter (nm)	Cycle	Conv. ^a (%) 35	(%) ^b 35/36/37/38
1	M-28-AuNPs	2.8 ± 0.6	1	75	0/0/30/70
2	M-30-PdNPs	240 ± 70	1	100	0/0/30/70
3	M-32-Pd-Au-NPs	1.5 ± 0.3	1	100	0/0/20/80

^a i) 25 °C, 3 h, 1:1 **33:34** molar ratio, 30 mg cat., H₂O; ii) r.t., 10 min., 5 eq. NaBH₄, 30 mg cat., H₂O; ^b determined by ¹H-NMR on the reaction crude.

Conclusions.

The results here presented demonstrate the utility of flow processes for the reproducible preparation via CRP processes, in particular RAFT approaches, of linear poly(VBCI) with a range of specific properties. The resulting linear polymer has shown to be a key starting material

for the preparation of crosslinked polymeric ionic liquids (PILs) using different strategies. The exact strategy selected determines significantly the properties of the resulting polymers. Of particular relevance are the results obtained for the crosslinking of poly(VBCI) using bis-imidazoles that provide insoluble materials with good swelling properties even when achieving relatively low covalent crosslinking degrees. An appreciable level of structural organization seems to be present in these materials. The fine tuning of the synthetic methodologies selected allow for the simple and efficient preparation of multifunctional polymeric materials, with the incorporation of IL-like moieties, imidazole subunits and additional groups like basic amine functions or iminophosphorane groups. Besides, composite polymeric structures including well-dispersed and stable MNPs (Au, Pd and Au + Pd) and with very high metal loadings (up to 10 % in weight) are easily developed. The multifunctional nature of these crosslinked polymers has been used with advantage for the use as catalysts. In the case of crosslinked PILs and crosslinked PILs containing additional basic functionalities, they act as efficient catalysts for the Knoevenagel reaction. In the case of composites of PILs and MNPs they have been assayed as very efficient multifunctional catalysts for the one-pot tandem process involving the Knoevenagel process followed by the reduction of the condensation product in the presence of NaBH_4 , with quantitative conversions being achieved as well as a very high selectivity for the fully reduced compound displaying the reduction of three different functional groups: carbon-carbon double bond, nitro group and ester group. Further studies are on the way in order to optimize and study in more detail some of these processes.

SUPPORTING INFORMATION

General synthetic procedures, structural characterization of polymeric materials and study of swelling properties are available in the Supporting Information.

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Preparation and study of multifunctional crosslinked PILs based on RAFT-prepared linear polymers

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General synthetic procedures

RAFT polymerization of *p*-vinylbenzyl chloride in batch. Poly(*p*-vinylbenzyl chloride) (**poly(VBCl)**) was prepared by bulk RAFT polymerization of *p*-chloromethylstyrene (**1**) with the corresponding chain transfer agent and initiator specified in Table 1. As an example, **poly(VBCl)** of entry 1, Table 1 was obtained as follows. A flask was charged with 0.062 g (0.223 mmol) of CPA, 3.285 g (21.52 mmol) of compound **1** and 0.018 g (0.066 mmol) of ACVA. Then, 3 mL of DMF was added as solvent. The flask was deoxygenated with five freeze-thaw-cycles and filled with nitrogen. The polymerization was allowed to proceed at 120 °C for 24 hours. The reaction was stopped by immersing the flask into liquid nitrogen. The product was diluted with acetone and isolated by precipitation with methanol. The product was further purified by two precipitations from acetone/methanol to yield **poly(VBCl)** with a 30 % polymerization degree, a molecular weight of 10.9 kg/mol and a polydispersity of 1.1 as determined by GPC.

RAFT polymerization of *p*-vinylbenzyl chloride in continuous flow. Scale-up RAFT polymerization experiments in continuous flow were performed using a 4, 6 or 12 m long stainless steel tube reactor (3.17 mm OD, 1.75 mm ID) rolled up and housed in a metal heating chamber. The reactor temperature can be controlled and the pressure is manually adjusted by an inline backpressure regulator situated at the the outlet of the reactor. The flow through the reactor was provided with a Gilson 305 piston pump. As an example, **poly(VBCl)** of entry 1, Table 2 was prepared as follows. A starting material solution of 51.98 g (0.34 mol) of monomer **1**, 0.95 g (3.4 mmol) of CPA and 0.29 g (1.0 mmol) of ACVA in 12 mL toluene was deoxygenated with five freeze-thaw-cycles and filled with nitrogen. After its connection to the system, polymerization was conducted at 130 °C, 330 psi and at a flow rate of 0.2 mL/min resulting in a reaction time of 2.4 h. The reaction at the end of the reactor was stopped by contact with air. The collected fraction was purified by two precipitations from acetone/methanol to yield **poly(VBCl)** with a 42 % polymerization degree, a molecular weight of 1022 g/mol and a polydispersity of 2.09 as determined by GPC.

Synthesis of polymers M-4 and M-9. Monolithic polymer **M-4** was synthesised by thermally induced radical solution polymerisation in a test tube charged with 1 g of **poly(VBCI)** and 1 g of divinylbenzene, using toluene as the porogen (porogen/monomers ratio 75:25) and 1 % of AIBN as the radical initiator. The polymerisation was performed at 70 °C for 24 h. The monolithic-supported ionic liquid like-phase was obtained by the post-alkylation of monolith **M-4** with 5 eq. of *N*-butylimidazole at 80 °C for 24 h. In the case of monolith **M-9**, 50 % w. of 1,1'-(1,6-hexanediyl)bis(imidazole) was added to monolith **M-4** in DMF, at 90 °C for 24 h.

Synthesis of polymers M-11-M-19. These polymeric materials were prepared using the quantities of **poly(VBCI)** tabulated in Table 4, which along with the corresponding bis(imidazole) were dissolved in DMF in a test tube. The reaction was allowed to proceed at 90 °C for 24 h. Metathesis with LiNTf₂ in the case of polymer **M-11** afforded **M-19**.

Synthesis of polymers M-20-M-22. This methodology intends the introduction of a functional group to obtain a polymeric material with a second level of functionalization. As an example, to the initial solution of **poly(VBCI)** (0.73 mmol) and 1,1'-(1,6-hexanediyl)bis(imidazole) **10** in DMF, pyrrolidine was added keeping the pyrrolidine/bis(imidazole) molar ratio at 1:4 (0.18 mmol/0.73 mmol). The reaction was allowed to proceed at 90 °C for 24 h. Metathesis with LiNTf₂ in the case of the polymer **M-20** afforded **M-21**. Instead of pyrrolidine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene was used to prepare the polymer **M-22**.

Synthesis of polymers M-23-M-26. The same procedure was used for the preparation of these compounds but starting from **poly(VBCI)** functionalised at 27 % with 0.25 eq. of NaN₃ in DMF at 60 °C for 24 h to afford poly(VBC-4-azidomethylstyrene) (**poly(VBCI-VBN₃)**). Metathesis of the polymer **M-23** with LiNTf₂ followed by the addition of 1.1 eq. of PPh₃ (0.16 mmol) in toluene afforded **M-25**. Polymer **M-26** was obtained by the direct reaction of **poly(VBCI)** with 1.1 eq. PPh₃ in DMF at 90 °C for 24 h. The polymer **M-24** was obtained after the reduction of **M-23** with an excess of NaBH₄.

Synthesis of composites with MNPs.

- Gold absorption: 28 mg of polymer **M-11** were added to a solution of 10 μL of HAuCl_4 in 2 mL of Mili-Q water (1.4 mg Au/mL). After 6 h the solution became colourless as all gold was absorbed in the polymer. The reduction with a solution of NaBH_4 (11.4 mg in 2 mL of Mili-Q water) afforded the composite **M-28-AuNPs** after 2 h, which was accompanied by a colour change to black due to the AuNPs generated.
- Palladium absorption: 16 mg of polymer **M-11** were added to an acidic solution of 5.5 mg of PdCl_2 in 5 mL of Mili-Q water (0.5 mg Pd/mL) and 100 μL of HCl. After 24 h, the polymer had absorbed the orange colour of the solution. Then, the reduction with NaBH_4 provided **M-30-PdNPs**.
- Palladium and gold absorption: 37 mg of polymer **M-11** were added to an acidic solution of 5.6 mg of $\text{Pd}(\text{OAc})_2$ in 4 mL of THF, 1 mL MeOH (0.5 mg Pd/mL) and 5 μL of HCl. After 24 h, the polymer had absorbed the orange colour of the solution. This polymer was added to a 20 μL of HAuCl_4 aqueous solution (1.4 mg Au/mL) until gold was absorbed. Finally, the reduction with NaBH_4 was carried out to form AuNPs and PdNPs in the composite **M-32-Pd-Au-NPs**.

Knoevenagel condensation. 45 mg (0.3 mmol) of 4-nitrobenzaldehyde (**33**), 31 μL (0.3 mmol) of ethyl cyanoacetate (**34**) and 30 mg of the corresponding catalyst were mixed in 1.445 mL of Mili-Q water. The mixture was stirred at room temperature for one hour. On completion, the reaction mixture was extracted with 3x2 mL CH_2Cl_2 , the organic phase was dried with anhydrous MgSO_4 and the solvent was evaporated. The reaction yield was calculated as previously explained (see supporting information).¹

Single-pot multicycatalytic reaction (Knoevenagel + reduction)

29 mg (0.2 mmol) of 4-nitrobenzaldehyde, 20 μL (0.2 mmol) of ethyl cyanoacetate and 23 mg of the corresponding catalyst were mixed in 941 μL of Mili-Q water. The mixture was stirred at room temperature for 3 hours. On completion, 20 mL of Mili-Q water and a solution of NaBH_4 (5 eq. in 10 mL of water) were added. The mixture was stirred for 10 minutes at room temperature. After that, the reaction mixture was extracted with 3x10 mL CH_2Cl_2 , the organic phase was dried with anhydrous MgSO_4 and the solvent was evaporated. The conversion was calculated as previously explained (see supporting information).¹

Structural characterization of polymeric materials

Figure S1. ^1H -NMR spectrum of the polymerization reaction crude (monomer **1** (green) and Poly(VBCI) (pink)) and the calculation of conversion with the equations given below.

$$Conv.(%) = \frac{I_{CH_2}(c)}{I_{CH_2}(c) + I_{Hb}} \cdot 100 \quad I_{CH_2}(c) = \frac{I_{CH_2}(c+f) - I_{CH_2}(f) \cdot 1H}{2H}$$

Figure S2. ATR-FT-IR spectra of **M-4** and **M-8** (black dots = new/characteristic peaks).

Figure S3. ATR-FT-IR spectra of **poly(VBCI)**, **M-16** and **14** (black dots = new/characteristic peaks, red squares = disappeared peaks).

Figure S4. ATR-FT-IR spectra of M-11, M-20 and M-21 (black dots = new/characteristic peaks).

Figure S5. ATR-FT-IR spectra of **M-11** and **M-22** (black dots = new/characteristic peaks).

Figure S6. ^1H -NMR: a) **poly(VBCl)** and b) **poly(VBCl-VBN₃)**, benzylic proton shifted upfield from 4.52 to 4.22 ppm.

Figure S7. ATR-FT-IR spectra of **poly(VBCI)** and **poly(VBCI-VBN₃)** (black dots = new/characteristic peaks).

Figure S8. ATR-FT-IR spectra of **M-23** and **M-24** (black dots = new/ characteristic peaks, red squares = disappeared peaks).

Figure S9. ATR-FT-IR spectra of **M-23** and **M-25** (black dots = new/ characteristic peaks, black circle = characteristic shoulder of P-Phenyl str. at 1114 cm^{-1} , red squares = disappeared peaks).

Figure S10. ATR-FT-IR spectra of **poly(VBCI-VBN₃)** and **M-26** (black dots = new/characteristic peaks, red squares = disappeared peaks).

Study of swelling properties

Figure S11. Swelling determination of **M-11** from DMF to water and vice versa.

Figure S12. Swelling of **M-13** in water. The high molecular weight of **poly(VBCI)** led to harder and more brittle monolith causing the breakup of the structure in this solvent.

¹ Montolio, S.; Vicent, C.; Aseyev, V.; Alfonso, I.; Burguete, M. I.; Tenhu, H.; García-Verdugo, E.; Luis, S. V. *ACS Catal.* **2016**, *6*, 7230-7237.

3.4. Conclusiones

- Se ha sintetizado poly(VBCL) por la técnica de polimerización radicalaria controlada RAFT en *batch* obteniéndose conversiones, pesos moleculares y polidispersidades razonables.
- Se ha llevado a cabo la obtención del polímero en flujo continuo permitiendo aumentar la productividad bajo las mismas condiciones. Los PDIs son aceptables aunque los pesos moleculares son bajos debido a los modestos niveles de conversión que se permiten alcanzar.
- Ambas metodologías sintéticas permiten la obtención del polímero lineal en condiciones controladas ($PDI < 1.5$). Mientras que el proceso en *batch* conduce a polímeros de alto peso molecular (> 10 kg/mol), la polimerización en continuo proporciona polímeros de bajo peso molecular (< 2 kg/mol).
- Se han preparado polímeros entrecruzados a partir de la copolimerización de dicho polímero con DVB y se han funcionalizado con diferentes imidazoles alquílicos para generar los correspondientes SILLPs. Por esta ruta sintética, el entrecruzamiento se origina en los extremos de las cadenas poliméricas ya que el poly(VBCL) actúa como elemento estructural y agente de transferencia macromolecular.
- Alternativamente, se han obtenido estos materiales por reacción entre poly(VBCL) y bisimidazoles obteniéndose PILs al mismo tiempo que se produce el entrecruzamiento del polímero. En este caso, la obtención controlada del monolito sólo es posible cuando el poly(VBC) utilizado es de bajo peso molecular (< 2 kg/mol). De esta manera, el poly(VBCL) obtenido en flujo continuo es más adecuado para la preparación de estos materiales.
- Se han evaluado la influencia de la concentración de los componentes de la mezcla, la naturaleza del espaciador del bisimidazol (4 y 6 metilenos) y la relación molar polímero/agente alquilante siendo ésta última la que más afecta a la estructura del material.
- La caracterización estructural se ha llevado a cabo a partir de la espectroscopia IR, del test de NBP y del análisis elemental. Así, se ha confirmado la obtención de estos compuestos además de explicar el bajo grado de entrecruzamiento covalente y la existencia de mecanismos de entrecruzamiento no covalentes

gracias a las interacciones supramoleculares electrostáticas entre los fragmentos iónicos y las interacciones hidrofóbicas entre las cadenas alquílicas que definen del mismo modo la morfología de estos materiales.

- El estudio de las propiedades de *swelling* de los PILs entrecruzados en diferentes disolventes ha mostrado que éstos presentan un gran hinchamiento en disolventes polares (H₂O y MeOH) mientras que en disolventes apolares (CHCl₃ y hexano) el hinchamiento es mucho menor observándose en algunos casos una reducción de su volumen. Un comportamiento opuesto se observa al intercambiar el contraión de Cl⁻ a NTF₂⁻.
- Se ha evaluado la aplicabilidad de estos materiales como organocatalizadores de la condensación de Knoevenagel observándose mejores conversiones cuando más alto es el contenido en IL ya que cataliza la reacción por presentar carácter básico. Una reducción de la actividad catalítica se observa con el intercambio de la naturaleza del anión de Cl⁻ a NTF₂⁻, la estructura se encoge en agua y se restringe la accesibilidad a los sitios básicos.
- La metodología desarrollada ha permitido introducir grupos básicos adicionales en la estructura monolítica que han mejorado significativamente la actividad catalítica de esta reacción obteniéndose el siguiente orden de reactividad: iminofosforano > pirrolidina > guanidina.
- Se ha conseguido emplearlos como soportes para la síntesis y estabilización de nanopartículas metálicas de oro, paladio y una mezcla de ambas y se ha demostrado su capacidad para actuar como catalizadores bifuncionales en la reacción en cascada de la condensación de Knoevenagel seguida de la reducción del producto. De esta manera, se abren nuevas posibilidades en el desarrollo de sistemas heterogéneos multicatalíticos.

Chapter 4

**AuNP-polymeric ionic liquid composite
multicatalytic nanoreactors for one-pot
cascade reactions**

Chapter 4. AuNP-polymeric ionic liquid composite multicatalyticnanoreactors for one-pot cascade reactions

4.1. Resumen del manuscrito

El desarrollo de sistemas multicatalíticos que permitan llevar a cabo reacciones catalíticas en cascada *one-potes* un desafío de gran interés. Aunque en los últimos años se han producido avances significativos dentro de este campo, para algunos sistemas la compatibilidad de los distintos centros catalíticos sin inactivación mutua sigue siendo un factor limitante. Una solución a este problema consiste en la compartimentación espacial que permite el aislamiento de reactivos o catalizadores incompatibles, protegiendo los centros catalíticos el uno del otro. Así pues, el desarrollo de sistemas que permitan la adecuada compartimentación de diferentes catalizadores que imiten a los sistemas biológicos es clave para conseguir sistemas capaces de llevar a cabo reacciones multicatalíticas en cascada.

En este contexto, este capítulo resume nuestros esfuerzos para desarrollar materiales avanzados mediante la combinación sinérgica de nanopartículas de oro y líquidos iónicopoliméricos (PILs). Estos materiales pueden actuar como nanoreactores multicatalíticos que poseen la habilidad de catalizar un proceso en cascada tal y como muestra la Figura 4.1.

Figura 4.1. Catálisis dual de los compuestos AuNP-PILs para la reacción en cascada de la condensación de Knoevenagel seguida de la reducción.

La segunda estrategia metodológica consiste en la obtención del PIL por modificación química del PCIVB seguida de la adición del precursor de oro y el reductor. En este caso, tanto el imidazol como el tiol generado participan en la estabilización de la nanopartícula adoptando una estructura donde las cadenas poliméricas se distribuyen aleatoriamente alrededor de la superficie metálica (AuNP-PIL-4).

La caracterización completa de estos compuestos se llevó a cabo utilizando diferentes técnicas (TEM, TGA, UV-Vis, DLS, DSC, NMR y FT-IR) que permitieron confirmar la distinta organización estructural que presentan los composites obtenidos por las dos metodologías anteriormente mencionadas.

De los resultados obtenidos, podemos señalar algunos más específicamente, como por ejemplo los relacionados con la banda superficial del plasmón del oro (SPB), (determinados por espectroscopia UV-Visible) y cuyo valor es característico del tipo de AuNPs. Así, las variaciones observadas (514 nm para AuNP-PIL-4 y 523 nm para AuNP-PIL-6) se asocian con el entorno químico presente alrededor de las AuNPs, lo que indica por tanto, la existencia para estos dos sistemas de una ordenación estructural diferente.

Por otro lado, el estudio de dinámicas de relajación por NMR evaluando los tiempos de relajación longitudinal (T_1) y transversal (T_2) de protón y su variación con la temperatura nos permitió mostrar los efectos que tiene la estructura del polímero sobre la movilidad de los fragmentos de IL ya que están relacionados con el movimiento molecular, el tamaño y la organización.

En nuestro caso, los valores de T_2 para los composites AuNP-PIL-6 fueron significativamente menores, lo que indica un movimiento mucho más restringido de las unidades de ILs. Esta menor movilidad está de acuerdo con una mayor organización del sistema, como consecuencia del autoensamblaje a nivel molecular inducido por la presencia de unidades de líquido iónico en las cadenas poliméricas que conforman el composite.

Dicha gran organización de los diferentes sistemas se confirmó igualmente a partir de los resultados obtenidos del análisis por FT-IR.

Una vez comprobado con las diferentes técnicas que la metodología empleada en la preparación de las AuNPs tiene una gran influencia en sus propiedades, organización y estructura, se ha evaluado el efecto de la diferente nanoestructura de las AuNPs en su

actividad catalítica. Para su estudio se ha escogido como reacción modelo la reducción del *p*-nitrofenol (*p*-NP) a *p*-aminofenol (*p*-AP).

A partir de los experimentos, se ha observado que todas las AuNPs son activas y accesibles estando su eficiencia catalítica controlada por la morfología adoptada por el componente polimérico.

Así, las AuNPs estabilizadas con citrato, en ausencia de PILs, catalizan la reacción más rápidamente ya que solo presentan una monocapa de citrato haciendo que el centro metálico sea altamente accesible. En cambio, para las AuNPs estabilizadas con el PIL se observó un tiempo de inducción inicial, el cual es mayor para AuNP-PIL-6. Lo que es indicativo de que se necesita más tiempo de difusión de los reactivos para que lleguen e interaccionen con la superficie catalítica que se encuentra más protegida por la disposición de las cadenas poliméricas.

La presencia de componentes estructurales diferentes dentro de la misma AuNP-PIL posibilita el desarrollo de sistemas multicyclic. Los sistemas AuNP-PIL presentan sitios con multifuncionales que puede actuar como catalizadores específicos para diferentes procesos. En este caso, las cadenas de PILs pueden actuar como catalizador básico en la condensación de Knoevenagel y lasnanopartículas de oro como catalizadores para la reducción de diferentes grupos funcionales. Aprovechando esta potencial sistema bicatalítico, se ha evaluado su acción como nanoreactoresmulticyclic en una reacción consecutiva en *one-pot* de la reacción de Knoevenagel entre el *p*-nitrobenzaldehído y el cianoacetato de etilo seguida de la reducción con NaBH₄ de los grupos funcionales del compuesto resultante de dicha reacción. De nuevo, la selectividad observada en la obtención de los diferentes productos muestra la influencia de la organización estructural del catalizador responsable del progreso de la reacción.

Así pues, se ha demostrado cómo la metodología sintética permite controlar el autoensamblaje y la autoorganización de estos sistemas así como también su actividad multicyclic en reacciones en cascada. La metodología sintética empleada en la preparación de los compositesno sólo proporciona un microambiente óptimo para cada reacción sino que además, define la morfologíafinal del compuesto, lo que determina la difusión de los intermedios de reacción permitiendo conseguir transformaciones sintéticas con el 100% de conversión y selectividad. El presente trabajo abre el camino hacia el estudio de sistemas más complejos que exploren reacciones en cascada en *one-pot* cuyas transformaciones catalíticas serían de otra manera incompatibles.

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Supporting Information

AuNP-Polymeric Ionic Liquid Composite Multicatalytic Nanoreactors for One-Pot Cascade Reactions

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Synthesis and structural characterization of AuNPs-PILs

Preparation of compound PCIVB-2. Poly(vinylbenzyl chloride) (**PCIVB-2**) was prepared by bulk RAFT polymerization of *p*-chloromethylstyrene (**1**) with IBN as chain transfer agent and AIBN as initiator. A flask was charged with 0.146 g (0.66 mmol) of IBN, 10.008 g (65.57 mmol) of compound **1** and 0.011 g (0.065 mmol) of AIBN. The flask was deoxygenated with five freeze-thaw-cycles and filled with nitrogen. The polymerization was allowed to proceed at 120 °C for 24 hours. The reaction was stopped by immersing the flask into liquid nitrogen. The product was diluted with acetone and isolated by precipitation with methanol. The product was further purified by two precipitations from acetone/methanol to yield **PCIVB-2** with a 56 % polymerization degree, a molecular weight of 18.9 kg/mol and a polydispersity of 1.5 as determined by GPC.

Preparation of compound PIL-3. The quantitative substitution of the chloride groups of **PCIVB-2** by 1-butylimidazole in 2-Me-THF yielded the corresponding polymeric ionic liquid (**PIL-3**). A flask was charged with 1.003 g (6.55 mmol) of **PCIVB-2** and 1.29 mL (9.825 mmol) of 1-butylimidazole. The mixture was dissolved in 4 mL of 2-Me-THF. The reaction was allowed to proceed at 40 °C for 24 hours. The product precipitates during the reaction. After that, it was dissolved in MeOH and was isolated by precipitation with Et₂O to yield **PIL-3** (56 %). The full conversion of the chloride groups can be monitored by NMR showing the appearance of the new bands corresponding to the ionic liquid-like moieties and the shift of the benzylic protons of the main polymeric chain from *ca.* 4.5 ppm to 5.5 ppm as well as the appearance of the peaks related with the imidazolium units (Figure S1). The formation of **PIL-3** was also confirmed by FTIR-ATR and Raman spectroscopy showing the disappearance of the C-Cl stretching at peak at 1265 cm⁻¹ and the one at 678 cm⁻¹ associated to the CH₂-Cl group as well as the appearance of new bands associated with the imidazolium units (Figure S2 and Figure S3).

Preparation of compound AuNP-PIL-4. A “grafting-to” strategy was used to prepare gold nanoparticles. To a vigorously stirred yellow solution of 69.2 μL (0.1 mmol) of HAuCl₄·xH₂O in 10 mL of Mili-Q water, 0.7339 g (0.02 mmol) of **PIL-3** in 10 mL of Mili-Q water (molar ratio **PIL-3**/HAuCl₄·xH₂O = 1/5) were added. The mixture was stirred for 20 min in an ice bath. Then, 1 mL of a 1M solution (1 mmol) of NaBH₄ in Mili-Q water was added dropwise to the vigorously stirred solution. The mixture turned immediately brown-purple with a little gas bubble evolution and was stirred in an ice bath for a further 4h. The resulting mixture was centrifuged at 8000 rpm and the supernatant was collected.

Preparation of compound AuNP-PIL-6. Initially, a similar procedure was carried out to obtain **AuNP-PCIVB-5** but using 0.223 g (0.02 mmol) of **PCIVB-2** instead of **PIL-3**, 2-Me-THF as the solvent and LiBEt₃H as reductant. Afterwards, the functionalization of the chloride groups followed the previous methodology for **PIL-3** preparation. Then, a flask was charged with 0.093 g (1.76 mmol) of the obtained **AuNP-PCIVB-5** and 400 μL (8.8 mmol) of 1-butylimidazole. The mixture was dissolved in 3 mL of 2-Me-THF. The reaction was allowed to proceed at 40 °C for 48 hours. The product precipitates during the reaction. After that, it was evaporated and washed several times with 2-Me-THF.

Figure S1. ^1H -NMR spectra (500 MHz) with peak assignments of **PCIVB-2** (CDCl_3 , *top*) and **PIL-3** (MeOD , *bottom*)

Figure S2. FTIR-ATR spectra of **PCIVB-2** (black) and **PIL-3** (red)

Figure S3. RAMAN spectra of **PCIVB-2** (black) and **PIL-3** (red)

Figure S4. ^1H -NMR spectra (500 MHz) of **AuNP-PIL-4** (MeOD)

Figure S5. ^1H -NMR spectra (500 MHz) of AuNP-PCIVB-5 (CDCl_3 , *top*) and AuNP-PIL-6 (MeOD, *bottom*)

Figure S6. FTIR-ATR spectra of AuNP-PIL-4 (*left*), AuNP-PCIVB-5 and AuNP-PIL-6 (*right*)

TGA and TEM studies

Figure S7. TGA profiles of a) AuNP-PCIVB-5 b) AuNP-PIL-4 and c) AuNP-PIL-6 obtained in a nitrogen atmosphere at 10 °C/min from 30 °C to 1100 °C (up to 1400 °C for AuNP-PIL-4)

Figure S8. TEM images of AuNP-PCIVB-5

Figure S9. TEM images of AuNP-PIL-4

Figure S10. TEM images of AuNP-PIL-6

UV-visible spectroscopy

Figure S11. UV-vis spectra of AuNP-PCIVB-5 in CHCl_3 (*left*), AuNP-PIL-4 and AuNP-PIL-6 in MeOH (*right*). Surface Plasmon Bands.

Dynamic Light Scattering (DLS) studies.

Figure S12. Normalized correlation functions of the intensity of scattered light, $|G_2(t)|$, measured at 20° C, 45° scattering angle and $\lambda_0=637$ nm. Blue circles ($\circ$) correspond to an **AuNP-PIL-6** solution of 1 mg/ml and green crosses ($\times$) correspond to an **AuNP-PIL-4** solution of 5 mg/mL, both in salt-free water. The lower inset shows corresponding correlation functions of electric field, $g_1(t)$, where solid lines are added as guide for eye and correspond to single exponential decays. The upper inset shows the corresponding distributions of hydrodynamic diameter.

NMR studies.

Figure S13. ¹H-NMR spectra (500 MHz) with peak assignments of **PIL-3** (D₂O)

Figure S14. ¹H-NMR spectra (500 MHz) of **AuNP-PIL-6** (*top*) and **AuNP-PIL-4** (*bottom*) (D₂O)

All ^1H NMR spectra were recorded on a Varian NMR System 500 MHz spectrometer, equipped with an inverse detected probe (BBI 5 mm with z gradients), at 303 K using D_2O as solvent. T_1 values were determined using a standard inversion-recovery pulse sequence INVREC provided in the Varian software library. The recovery delay (τ) between the inversion pulse and the read pulse was varied along 10 values. The number of scans was 8 and a recovery delay between scans of 15 s was set for all ^1H NMR experiments. T_2 values were determined using the standard Carr-Purcell-Meiboom-Gil pulse sequence CPMGT2 provided in the Varian software library using a variable delay list of 9 points. The number of scans was 4 and a recovery delay between scans of 15 s was set. The vnmrj2.2c software was used for spectral processing and to perform the exponential/linear fittings for T_1 , T_2 .

Figure S15. Temperature dependence of ^1H (D_2O) T_1 (left) and T_2 (right) for the protons H4, H6-H7, H9 and H10 (lines are guides for the eye) for **PIL-3** (top), **AuNP-PIL-4** (middle) and **AuNP-PIL-6** (bottom).

In general, the ^1H NMR spectra of **PIL-3**, **AuNP-PIL-4** and **AuNP-PIL-6** were very much alike (Figures S13 and S14), displaying broad resonances readily assigned to the imidazole protons (H2 and H3), benzyl (H4, H5 and H6) and butyl (H7, H8, H9 and H10) groups from the ionic liquid arms (see chemical structure in Figure S15 for the assumed atom numbering). Some of them appeared partially overlapped (H2, H3 and H5) and were not considered for T_1 and T_2 determination, but the rest of the signals were used as probes to evaluate the mobility of the pendant ionic liquid-like fragments. T_2 values at $T = 303$ K (and also covering the $T = 296$ to 358 K range, see Figure S15 and Table S2) for **PIL-3** revealed a continuous decrease on going from the periphery of the ionic liquid arm ($\text{H10} > \text{H9} > \text{H7}$ protons within the butyl group) to the core of the polymer (H4 and H6 protons). Since T_2 values are affected by the mobility of macromolecules, decreasing with the correlation time, it is evident that the experimentally observed decrease of the T_2 values on going from the periphery to the core is indicative of a reduced local mobility in the same direction. The same tendency was observed for **AuNP-PIL-4** and **AuNP-PIL-6** (Figure S15 and Tables S4 and S6). However, a comparison of the T_2 values for different samples provided rich insights on their specific morphologies. For example, the variation of T_2 values from **PIL-3** to **AuNP-PIL-4** was minor for all considered protons, thus indicating similar local mobility for both materials. In contrast, T_2 values were significantly smaller for **AuNP-PIL-6**, typically *ca.* 14-20 % for the peripheral protons from the butyl group and 24 % for the inner H4 and H6 protons. This experimental evidence supports slower dynamics for the composite **AuNP-PIL-6** and, accordingly, a more compact winding of the polymeric core.

T_1 values at $T = 296$ K for **PIL-3** (Figure S15, left top graph and Table S1) revealed a continuous decrease from H10 to H9 and H7 and an increase of the T_1 values for the nuclei located at the core of the polymer, namely H4 and H6. However, it is important to realize that a dynamical study based only on T_1 values recorded at one temperature can be misleading.

Opposed motional outcomes, in particular, the operation of slow or fast regimes for the considered nuclei, could be obtained depending on the relaxation data analysed. To further unravel the dynamic behaviour of **PIL-3**, **AuNP-PIL-4** and **AuNP-PIL-6** the determination of the temperature dependence of T_1 values, a parameter widely recognized as an accurate probe to analyse the relative dynamics within macromolecules was undertaken, covering the $T = 296$ to 358 K range (Figure S15 and Tables S1; S3 and S5).ⁱ

The minimum in T_1 with the temperature can be used to estimate the relative rates for the motions of the considered nuclei; the lower the temperature of the T_{1min} , the higher the rate. Graphs in Figure S15 show the temperature dependence of T_1 for all considered protons in **PIL-3**, **AuNP-PIL-4** and **AuNP-PIL-6**. We could distinguish two clear behavioural patterns, one for the protons from the periphery (H7-H10) and the other one for the protons from the inner part, namely H4 and H6. In the case of **PIL-3**, as the temperature increases from $T = 296$ to 358 K, the T_1 for nuclei at the periphery increases continuously, thus indicating that T_{1min} must be located below this temperature; however, for protons H4 and H6, T_1 values decrease down to a minimum around 343 K to slightly increase afterwards, in agreement with an increase in the rate of the motions from the core to the periphery.

The analysis of the temperature dependence of T_1 for nuclei from **AuNP-PIL-4** and **AuNP-PIL-6** displayed identical patterns, where peripheral butyl nuclei were in the fast motional regime in the temperature range investigated with T_{1min} below $T = 296$ K. Noticeably, it was observed that on going from **PIL-3** to **AuNP-PIL-4** and **AuNP-PIL-6**, T_{1min} for the inner nuclei shifted to a value higher than 343 K in agreement with a reduction of the mobility compatible with the dynamic interpretation based on the T_2 analysis.

Table S1. ^1H T1 values (s) vs $1000/T$ (K^{-1}) for **PIL-3**

$1000/T$ (K^{-1})		2.79	2.91	3.14	3.30	3.38
^1H T1 (s)	H1	-	0,89	1,21	1,33	1,23
	H23	1.92	1,67	1,92	1,86	1,75
	H4	1.22	1,11	1,40	1,53	1,48
	H5	0.94	0,89	1,17	1,39	1,37
	H6	0.78	0,59	0,94	1,15	1,16
	H7	1.18	1,09	0,90	0,91	0,90
	H8	0.98	0,76	0,86	0,92	0,94
	H9	1.40	0,99	1,06	1,01	0,96
	H10	1.85	1,34	1,43	1,29	1,19

Table S2. ^1H T2 values (s) vs $1000/T$ (K^{-1}) for **PIL-3**

$1000/T$ (K^{-1})		2.79	2.91	3.14	3.30	3.38
^1H T2 (s)	H1	-	0,36	0,16	0,12	0,09
	H23	0.92	0,62	0,27	0,18	0,12
	H4	0.16	0,27	0,10	0,08	0,06
	H5	0.31	0,11	0,05	0,03	0,02
	H6	0.15	0,11	0,06	0,05	0,04
	H7	0.77	0,40	0,14	0,09	0,07
	H8	0.46	0,31	0,12	0,08	0,06
	H9	0.84	0,62	0,20	0,12	0,10
	H10	1.14	0,77	0,30	0,17	0,12

Table S3. ^1H T1 values (s) vs $1000/T$ (K^{-1}) for **AuNP-PIL-4**

$1000/T$ (K^{-1})		2.79	2.91	3.14	3.30	3.38
^1H T1 (s)	H23	2.19	2,07	2,19	1,73	1,81
	H4	1.02	1,41	1,62	1,54	1,63
	H5	1.36	1,10	1,37	1,37	1,50
	H6	0.80	0,89	1,12	1,04	1,29
	H7	1.55	1,11	0,95	1,00	0,92
	H8	1.04	0,95	0,93	0,94	0,98
	H9	1.43	1,31	1,15	0,96	1,02
	H10	1.88	1,76	1,56	1,24	1,26

Table S4. ^1H T2 values (s) vs $1000/T$ (K^{-1}) for **AuNP-PIL-4**

$1000/T$ (K^{-1})		2.79	2.91	3.14	3.30	3.38
^1H T2 (s)	H23	1.01	0,69	0,36	0,18	0,11
	H4	0.13	0,26	0,12	0,08	0,07
	H5	0.29	0,13	0,04	0,02	-
	H6	0.15	0,12	0,07	0,05	0,02
	H7	0.82	0,39	0,12	0,10	0,13
	H8	0.43	0,32	0,15	0,08	0,07
	H9	0.81	0,64	0,22	0,14	0,09
	H10	1.07	0,64	0,34	0,18	0,13

Table S5. ^1H T1 values (s) vs $1000/T$ (K^{-1}) for **AuNP-PIL-6**

$1000/T$ (K^{-1})		2.79	2.91	3.14	3.30	3.38
^1H T1 (s)	H23	1.96	1,97	1,95	1,59	1,65
	H4	1.02	1,39	1,51	1,43	1,50
	H5	1.30	1,17	1,33	1,30	1,41
	H6	0.84	0,97	1,19	1,16	1,35
	H7	1.35	1,08	0,87	0,97	0,92
	H8	1.01	0,99	0,94	0,97	1,00
	H9	1.38	1,30	1,12	1,05	1,04
	H10	1.83	1,72	1,43	1,26	1,2

Table S6. ^1H T2 values (s) vs $1000/T$ (K^{-1}) for **AuNP-PIL-6**

$1000/T$ (K^{-1})		2.79	2.91	3.14	3.30	3.38
^1H T2 (s)	H23	0.62	0,55	0,27	0,15	0,10
	H4	0.11	0,20	0,09	0,05	0,05
	H5	0.22	0,09	0,04	0,02	0,02
	H6	0.12	0,09	0,06	0,04	-
	H7	0.64	0,32	0,11	0,08	0,13
	H8	0.21	0,25	0,13	0,06	0,06
	H9	0.46	0,48	0,17	0,11	0,07
	H10	0.61	0,56	0,27	0,13	0,10

DSC studies

Measurements of glass-transition temperatures were carried out on a Perkin Elmer differential scanning calorimeter (DSC), model DSC8. The instrument was calibrated for temperature and heat flow with zinc and indium reference samples provided by Mettler–Toledo. Samples were placed in a 40 mL hermetically sealed aluminum pan with a pinhole at the top of the pan. An empty aluminum pan was used as the reference.

The samples inside the differential scanning calorimeter furnace were exposed to a flowing N₂ atmosphere. Before the DSC test, each sample was dried at 90–100 °C and 10⁻²-10⁻³ mbar for 4 h, and was further dried *in situ* on the differential scanning calorimeter by holding the sample at 120 °C for 15 min. This is important because the presence of volatiles, especially water, can affect the glass-transition and melting temperatures. Melting transition temperatures were determined by multiple cycles of heating from 40°C to 180°C, followed by cooling from 180°C to 40°C both at a rate of 10°C min⁻¹. The T_g temperatures were determined as the onset of the transition.

Figure S16. DSC curves for the different compounds: 3rd heating cycle. Conditions: Heat flow 10°C/min., 1 cycle: 120°C 10 min.; 3 cycles 25°C-180°C

Reduction of *p*-nitrophenol.

Figure S17. Kinetics of the **7** reduction by UV-Vis absorption, a) AuNP-PIL-6, b) AuNP-PIL-4 (**7**/cat. (IL-like units) 1/5)

$$\text{Conv}(\%) = 100 - \frac{\text{Abs}(\mathbf{7})_t}{\text{Abs}(\mathbf{7})_{\text{ini}}} \cdot 100$$

To a volume of 1190 μL of a **7** 0.2 mM aqueous solution 320 μL of Mili-Q water and 1690 μL of NaBH_4 0.11 M aqueous solution ($V = 3200 \mu\text{L}$, initial concentration **7** = 0.074 mM) were added. Once the solution was homogeneous, the catalyst was added to initiate the reduction. The reaction is followed by UV-Vis.

The molar ratio **7**/ NaBH_4 /catalyst (IL-like units) is 1/787/5

$$\mathbf{7}: \frac{0.074 \text{ mmol}}{L} \cdot 3.205 \cdot 10^{-3} L = 2.37 \cdot 10^{-4} \text{ mmol} \rightarrow 1 \text{ eq.}$$

$$\text{NaBH}_4: \frac{0.11 \text{ mol}}{L} \cdot \frac{10^3 \text{ mmol}}{1 \text{ mol}} \cdot 1.695 \cdot 10^{-3} L = 0.18645 \text{ mmol} \rightarrow 787 \text{ eq.}$$

$$\text{AuNPs: } 2.37 \cdot 10^{-4} \text{ mmol } 4\text{-NP} \cdot \frac{1 \text{ mol } \mathbf{7}}{10^3 \text{ mmol } \mathbf{7}} \cdot \frac{5 \text{ mol IL-like units}}{1 \text{ mol } 4\text{-NP}} \cdot \frac{276.67 \text{ g(monomer)}}{1 \text{ mol}} \cdot \frac{10^3 \text{ mg}}{1 \text{ g}} = 0.328 \text{ mg}$$

PIL-3: 6.5 mg in 3 mL Mili-Q water. 320 μ L was added. 7/Cat. 1/10.7

AuNP-PIL-6: 3.4 mg in 1660 μ L Mili-Q water. 160 μ L + 160 μ L water were added. 7/Cat. 1/5

AuNP-PIL-4: 37 mg in 1 mL Mili-Q water. 8.82 μ L + 310 μ L water were added. 7/Cat. 1/5

Figure S18. a) Yield of **8** (%) vs. time profile. Red squares: **AuNP-PIL-6**. Blue circles: **AuNP-PIL-6** in 0.3 M NaCl. b) ^1H (D_2O) T_2 for the protons H1-H10 of **AuNP-PIL-6** without NaCl and in the presence of a 0.3 M NaCl.

Knoevenagel condensation

The reaction yield was calculated with the following equation. I_x refers to the integral at x ppm in the NMR spectrum. We have consider the methylenic signal of the product **11** and the aromatic signals belonging both to the aldehyde **10** and the product **11**. The subtraction corresponds to the double bond proton of **11**.

$$Yield(\%) = \frac{I_{4.43}/2}{\frac{I_{8-8.5} - I_{4.43}}{2}} \cdot 100$$

Figure S19. ^1H -NMR spectrum (500 MHz) of a crude from the Knoevenagel indicating the signals used to calculate the yield.

10 mg of the corresponding catalyst (0.25 eq.) were dissolved in 0.725 mL of Mili-Q water. After that, 0.023 g of 4-nitrobenzaldehyde (1 eq.) and 15.5 μL of ethyl cyanoacetate (1 eq) were added. The mixture was stirred at room temperature for one hour. On completion, the reaction mixture was extracted with 3x2 mL CH_2Cl_2 , the organic phase was dried with anhydrous MgSO_4 and the solvent was evaporated.

Figure S20. Knoevenagel condensation yields

Single-pot multicyclic reaction

10 mg of the corresponding catalyst (0.25 eq.) were dissolved in 0.725 mL of Mili-Q water. After that, 0.023 g of 4-nitrobenzaldehyde (1 eq.) and 15.5 μ L of ethyl cyanoacetate (1 eq) were added. The mixture was stirred at room temperature for one hour. On completion, 77 mL of Mili-Q water and a solution of NaBH_4 (5 eq. in 10 mL of water) were added. The mixture was stirred for 30 minutes at room temperature. After that, the reaction mixture was extracted with 3x30 mL CH_2Cl_2 , the organic phase was dried with anhydrous MgSO_4 and the solvent was evaporated.

Figure S21. Reaction crude ^1H -NMR spectrum (500 MHz) with peak assignments of the reduction products

S20

Figure S22. ATR-FT-IR spectra of the reagent (*top*) and product (*bottom*) of the reduction

The aromatic signals are shifted in the ^1H NMR spectrum (Figure S21) due to the reduction of the nitro to amino group. The IR spectrum confirms this reduction since we observe amino and alcohol bands. The double bond is also reduced because of the appearance of $\text{Csp}^3\text{-H}$ band. The intensity of the ester band is reduced because part of the compound is reduced to alcohol.

ⁱ Pinto, L. F.; Correa, J.; Martin-Pastor, M.; Riguera, R.; Fernandez-Megia, E. *J. Am. Chem. Soc.* **2013**, *135*, 1972-1977.

4.4. Conclusiones

- Se han sintetizado nanocompuestos basados en AuNPs-PILs utilizando dos estrategias metodológicas diferentes y se ha demostrado como en función de la metodología utilizada es posible controlar el autoensamblaje y la autoorganización de estos sistemas además de su actividad multicatalítica.
- Se ha llevado a cabo la caracterización completa de estos compuestos utilizando diferentes técnicas (TEM, TGA, UV-Vis, DLS, DSC, NMR y FT-IR) que han confirmado la distinta organización que presentan.
- Los análisis de TEM y los estudios de DLS demuestran el mayor tamaño de las AuNPs-PILs-6 en comparación con las AuNPs-PILs-4 originado por la asociación entre partículas a través de interacciones entre los grupos imidazolio disponibles.
- Las variaciones observadas para la SPB del oro pueden atribuirse a la constante dieléctrica diferente de la capa polimérica exterior ya que están asociadas al entorno químico de las AuNPs indicando la existencia de una ordenación estructural distinta.
- Las medidas de T_1 y T_2 obtenidas por RMN para los diferentes compuestos así como su variación con la temperatura han servido para relacionar la movilidad de los sistemas con su grado de organización. Así, T_2 (AuNPs-PILs-4) > T_2 (AuNPs-PILs-6) lo que indica una mayor restricción en el movimiento de las unidades de IL y, por tanto, una menor movilidad del compuesto que está asociado al mayor grado de organización del sistema debido al autoensamblaje.
- La alta organización de las nanopartículas se confirma igualmente por los resultados obtenidos a partir del análisis por FT-IR.
- El estudio por DSC de las T_g muestra la siguiente tendencia: T_g (PIL-3) < T_g (AuNPs-PILs-4) < T_g (AuNPs-PILs-6). El mayor valor para AuNPs-PILs-6 indica de nuevo que presenta una estructura altamente ordenada como consecuencia de las interacciones de los grupos imidazolio entre cadenas.
- Se ha evaluado el efecto de la nanoestructura de las AuNPs en su actividad catalítica a través de la reducción del *p*-nitrofenol (*p*-NP) a *p*-aminofenol (*p*-AP) y se ha comprobado como la morfología controla la eficiencia catalítica siendo el

sistema AuNPs-PILs-6 más lento debido a que presenta un tiempo de inducción mayor relacionado con la disposición de las cadenas poliméricas que protegen el centro metálico lo que afecta a la difusión de los reactivos. Además, en presencia de NaCl, este tiempo se incrementa ya que favorece la agregación de las AuNPs.

- Se ha estudiado la aplicabilidad de estos sistemas como nanoreactores multicasalíticos en una reacción consecutiva en *one-pot* de la reacción de Knoevenagel seguida de la reducción con NaBH₄ y se ha demostrado que la selectividad observada depende de la organización estructural del catalizador el cual es responsable del progreso de la reacción.

Chapter 5

**LCST-type polymers based on chiral-
polymeric ionic liquids**

Chapter 5. LCST-type polymers based on chiral-polymeric ionic liquids

5.1. Resumen del manuscrito

El desarrollo de nuevos materiales avanzados basados en líquidos iónicos poliméricos (PILs) constituye un área de investigación de gran interés. La presencia en estos polímeros de unidades estructurales equivalentes a las de los líquidos iónicos confiere a estos materiales excelentes propiedades físico-químicas. Entre las ventajas más importantes de estos compuestos podemos destacar su diversidad química y estructural que permite modular de manera sencilla las interacciones entre los aniones y cationes que los constituyen. En este capítulo se reporta cómo dicha modularidad a nivel molecular permite el diseño de nuevos materiales multifuncionales altamente estructurados. Así, la presencia de unidades de ILs quirales (CILs) en polímeros lineales solubles pueden inducir su auto-organización en estructuras supramoleculares auto-ensambladas que confieren a dichos sistemas propiedades únicas (i.e. comportamiento termosensible).

En primer lugar se llevó a cabo la síntesis de una nueva clase de Líquidos Iónicos Poliméricos Quirales (CPILs). Estos se obtuvieron por modificación química del poli(clorovinilbenceno) (poly(VBC)) obtenido por polimerización controlada (CRP) tipo RAFT del *p*-clorometilbenceno (Figura 5.1.).

Figura 5.1. Síntesis de los CPILs.

Estos nuevos CPILs presentaron una transición de fase tipo LCST (*lower critical solution temperature*) en CHCl_3 . Así, los CPILs son solubles por debajo de esta temperatura produciéndose su precipitación cuando la temperatura es superior a este valor, siendo el proceso completamente reversible en función de la temperatura. Aunque este comportamiento ya se conocía para otros tipos de PILs, nunca se había observado para el caso de CPILs.

El estudio del comportamiento termosensible de los CPILs se llevó a cabo empleando una solución de 1.0 mg/mL de los diferentes CPIL (Val, Bn Cl⁻) preparados en CHCl₃ empleando la espectroscopia de UV-Vis y dicroísmo circular (CD).

Este comportamiento termosensible de estos materiales puede explicarse en base a las interacciones inter e intramoleculares del polímero así como a efectos solvofóbicos. La utilización de disolventes no polares como el CHCl₃ favorecen interacciones fuertes entre el anión cloruro con el protón ácido del imidazol y el N-H de la amida en las unidades de imidazolio próximas entre sí, lo que conlleva que la cadena polimérica principal adquiera una estructura plegada donde los fragmentos iónicos quedan totalmente escondidos dentro de la cadena hidrofóbica principal del polímero. Con esta disposición, los fragmentos iónicos del polímero no quedan expuestos al medio hidrofóbico, mientras que los fragmentos apolares del mismo sí lo están, lo que hace que el polímero se solubilice en medios apolares como el CHCl₃. Al calentar la solución, se desfavorecen estas interacciones, quedando los fragmentos polares expuestos al medio, lo que provoca la precipitación.

Estudios mediante modelos computacionales realizados en el grupo de estos polímeros quirales han mostrado que su estructura adopta una conformación helicoidal y que la quiralidad de las unidades de IL se transfiere a toda la macromolécula.

A partir de medidas de CD se pudo confirmar esta estructura quiral ya que el espectro muestra un efecto Cotton negativo a 248 nm que disminuye y se desplaza a longitudes de onda mayores al aumentar la temperatura. Este hecho indica una pérdida parcial de la organización quiral al aumentar la temperatura lo que da lugar a una mayor exposición al medio de los grupos hidrofílicos que explicaría la precipitación del CPIL.

Adicionalmente, la técnica de ¹H-NMR se ha utilizado para determinar la presencia/ausencia de enlaces de hidrógeno y sus variaciones con la temperatura. Así se pudo observar el desplazamiento químico para las señales de los átomos de hidrógeno más ácidos (NH amida y C2-H imidazolio) así como para ciertas señales correspondientes a los grupos sustituyentes en la posición N de la amida se veía modificado con la temperatura. De esta manera, se confirma que este tipo de interacciones se ven afectadas por el cambio de la temperatura siendo las responsables del comportamiento termosensible observado.

Asimismo, para profundizar en el estudio de este fenómeno, se evaluó el efecto de la concentración y de la composición química en el valor de la temperatura de transición (LCST), pudiéndose observar una clara dependencia entre la concentración y

la temperatura. En nuestro caso, un aumento de la concentración de CPIL provoca una disminución de la LCST, llegando a ser insoluble a temperatura ambiente para concentraciones mayores a 5.0 mg/mL. Estos datos muestran la existencia de una competencia importante entre la formación de estructuras supramoleculares inter o intrapoliméricas, lo que es clave para explicar este comportamiento termosensible.

Por otro lado, se conoce que el valor de la LCST, para los sistemas basados en ILs, depende fuertemente del balance hidrofóbico/hidrofílico por lo que la modulabilidad estructural de los imidazoles puede utilizarse para modificar esta propiedad. Así, un cambio del sustituyente bencilo por un butilo en la amida da lugar a un aumento de la temperatura de transición. Sin embargo, un cambio de aminoácido (valina a fenilalanina) el valor decrece considerablemente. Una explicación razonable a este cambio puede justificarse considerando que los grupos aromáticos pueden interferir en la formación de una estructura helicoidal intrapolimérica adecuada a través de interacciones aromáticas.

Finalmente, se realizó un estudio sobre la naturaleza del contraión presente en los CPILs. El intercambio del anión Cl^- por NTf_2^- (no básico y menos coordinante) condujo a una disminución ligera de la LCST. Al ser este último de naturaleza menos coordinante, las interacciones anión-catión son más débiles y la estructura helicoidal está menos favorecida por lo que al calentar, la precipitación ocurre a temperaturas menores.

El estudio de las temperaturas de transición (T_g) de los CPILs obtenidas por calorimetría diferencial de barrido (DSC) proporcionó una información importante sobre la estructura supramolecular asociada principalmente a las interacciones por enlaces de hidrógeno y permitió establecer una relación adecuada entre la estructura y las propiedades físicas. Los resultados sugieren que las mismas variables estructurales son las responsables de ambos fenómenos (LCST y T_g) provocando cambios en la estructura y conformación del polímero así como en la ruptura y formación de enlaces de hidrógeno intrapoliméricos y otras interacciones inducidas por la variación de la temperatura.

Estos compuestos con propiedades termosensibles pueden presentar aplicaciones importantes en diferentes campos. En este capítulo, se ha evaluado su empleo para la estabilización de nanopartículas de oro (AuNPs) así como la transferencia del comportamiento termosensible a dichas nanopartículas mediante la generación de nanocomposites AuNPs-CPILs.

Así pues, todos estos resultados demuestran que es posible diseñar polímeros jerárquicamente estructurados a partir de CPILs basados en sales de imidazolio quirales cuyo apropiado autoensamblaje genera una estructura supramolecular altamente ordenada dotándola de comportamiento termosensible. Los diferentes vectores estructurales de los CILs (resto de aminoácido, sustitución de la amida y contraión) pueden ser fácilmente modificados para modular y controlar su LCST.

Además, la presencia de grupos adicionales en el polímero permiten la transferencia de estas propiedades a estructuras 3D organizadas como las AuNPs-CPILs abriendo una nueva vía para la preparación de AuNPs estabilizadas con CPILs para diferentes aplicaciones.

LCST-type polymers based on chiral-polymeric ionic liquids†

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The self-assembly of linear polymers containing chiral IL units generates a high-order supramacromolecular structure with a complex hierarchical architecture, which is able to exhibit thermoresponsive behavior (lower critical solution temperature: LCST) with different structural elements that can be used to fine tune this LCST.

Ionic liquids (ILs) encompass a variety of compounds and materials with great potential for applications ranging from new chemical technologies to use in industrial processes. Their physicochemical properties depend on the interactions established between the participating cations and anions that can determine variations in the self-assembled structure. Indeed, ILs have been described as “polymeric supramolecular fluids” and, consequently, as systems highly structured in the liquid state.¹ Interestingly, polymers having functionalities similar to those of ILs (polymeric ionic liquids: PILs) have been pursued for developing new advanced materials, which can provide all beneficial properties of ILs without their associated drawbacks.² Thus, the preparation of functional nanostructured materials or composites based on ILs represents an exciting and significant area of opportunity for developing multifunctional, hierarchically structured materials.³ As for ILs, one important advantage of PILs is their potential for displaying a large level of chemical and structural diversity and, hence, physico-chemical characteristics.⁴ Among them, chirality can be considered one of the most interesting characteristics,⁵ and we have reported a simple and robust modular synthetic strategy that leads to a large variety of configurationally and structurally diverse chiral ionic liquids (CILs).^{6,7} The in-depth study of these CILs has allowed us to analyse in detail the structure–property relationship for these compounds.⁶

Here, we report the synthesis and LCST-type phase transition based on a new class of chiral-polymeric ionic liquids (CPILs).

Scheme 1

These CPILs were prepared by chemical modification of the corresponding poly(vinylbenzyl chloride) (poly(VBC)) linear polymers (2) (Scheme 1) prepared by bulk RAFT polymerization of *p*-chloromethylstyrene (1), at 100 °C for 24 h (100:1:0.1 [M]:[CTA]:[I] molar ratio), with IBN as a chain transfer agent and AIBN as an initiator. The poly(VBC)-2 was obtained with a 56% polymerization yield, a molecular weight of 18.9 kg mol⁻¹ and a polydispersity of 1.5.⁸ The corresponding CPILs 4a–c were prepared by substitution of the chloride groups by different chiral imidazoles (CILs 3a–c) derived from several amino acids with variable N-amide substitution (Scheme 1 and ESI†).⁶

To our surprise, and as observed by the naked eye, the solution of CPIL-4a in chloroform became turbid when the temperature was increased, as shown in Fig. 1.⁹ This phenomenon is reversible when the stimulus is reversed and the poly-CPIL-4a re-dissolved upon cooling. This phenomenon is known as a lower critical solution temperature (LCST)-type phase transition. Although LCST-type behaviour has already been observed for poly-(*N*-isopropylacrylamide)-PIL copolymers and PIL homopolymers,¹⁰ such a behaviour had never been observed for CPILs. In view of this observation, a solution containing 1.0 mg mL⁻¹ of CPIL-4a in CHCl₃ was analysed at different temperatures by UV-Vis spectroscopy and circular dichroism (CD). The temperature was monitored using a thermocouple directly inserted into the solution. The transmittance of the solution fell exponentially with temperature in the vicinity of the LCST, which was determined to be 39.8 °C, and the turbid solution became transparent again upon cooling (Fig. 2). A small hysteresis is observed due to the fact that the rate of reversion is often slower as the polymer re-dissolves.¹¹

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Fig. 1 Temperature behaviour of 1.0 mg mL^{-1} of CPIL-**4a** in CHCl_3 (a): below LCST and (b): above LCST. The curves show the change in transmittance with temperature for this solution in the heating (blue) and cooling (green) processes.

Our previous studies, obtained for related bulk imidazolium salts, have shown that the acidic protons at the cationic component tend to form strong H-bonds with the anion and this can extend to form a polymeric structure. Hence, for the analogous polymeric derivatives, the solvophobic effect associated with the use of the non-polar solvent CHCl_3 can favor a strong interaction of the chloride anion with the amide N-H and the imidazolium C2 protons in proximal imidazolium subunits, leading to the main polymeric chain to acquire a tightly twisted helix in which the ionic moieties are completely buried within the hydrophobic polymer main chain. We have previously observed such effects for another closely related family of CPILs.⁸ Through this arrangement, the ionic part of the polymer, displaying a strong intrapolymeric supramolecular structure, would not be exposed to the hydrophobic media. Instead, the apolar fragments would be exposed, making the polymer soluble in a non-polar solvent such as CDCl_3 . The CD spectra confirm this chiral structure showing a negative Cotton effect at *ca.* 248 nm. It is noteworthy that the related poly(benzylbutylimidazolium-chloride) obtained by reaction of **2** with butylimidazole showed a very limited solubility in this solvent under the same conditions. This highlights the key role of the structural features of **4**, in particular, the chirality and the additional amide present in the CIL subunit. The H-bonding interactions between the amide NH fragments and the anions are likely to fix the orientation of the structural fragments giving place to the emergence of the observed Cotton effect ascribed to the exciton-coupling of the aromatic groups arranged in a mutual chiral orientation in a well-defined environment. Preliminary computational models suggest that the presence of $\text{C2-H} \cdots \text{Cl}^- \cdots \text{H-NCO}$ H-bonding between contiguous positions in the polymer favors a helical arrangement of the aromatic rings in the main chain (see ESI†). Indeed, the Cotton effect declines and the λ_{max} shifts to

Fig. 2 Temperature-dependent CD measurement of CPIL-**4a**, showing a shifted and reduced CD signal at higher temperatures.

higher wavelengths upon increasing temperature. This indicates a partial loss of the chiral organization with increasing temperatures leading to a larger exposure of the hydrophilic/ionic groups. Additionally, this will favor the eventual formation of interpolymeric hydrogen bonding interactions. Both factors could explain the observed precipitation of the CPIL.

VT $^1\text{H-NMR}$ experiments (see Fig. S3, ESI†) were carried out with CPIL-**4a** to determine the presence/absence of hydrogen bonding and its variation with the temperature. The chemical shifts observed for the more acidic hydrogen atoms (amide NH and imidazolium C2-H) reveal their strong involvement in H-bonding. A small highfield shift is observed for the NH signal upon heating, which should be in agreement with the weakening of the H-bonding pattern involving this proton. Significant changes are observed for the proton at the stereogenic center ($\Delta\delta = 0.13 \text{ ppm}$ from 30°C to 75°C) and additional variations are also observed for the signals corresponding to the CH of the isopropyl and the CH_2 of the *N*-benzyl substituent, suggesting that upon heating the conformational equilibria are modified and the *N*-substituents and the amino acid side chain experience different average environments.

The effect of concentration on the LCST-type phase transition was also evaluated. As shown in Fig. 3, a clear dependence was observed. It decreases with increasing CPIL concentration. According to measurements from 0.5 mg mL^{-1} to 2.5 mg mL^{-1} , the LCST value decreased from 48.5 to 19.4°C . Additionally, we found that the polymer was already insoluble at rt for concentrations $\leq 5.0 \text{ mg mL}^{-1}$. This indicates that the competence between the formation of intrapolymeric and interpolymeric supramolecular structures is key for the observed LCST behavior.

It has been already reported that the LCST of IL-based systems strongly depends on their hydrophobicity/hydrophilicity balance.¹² The intrinsic structural tunability of the chiral imidazoles could also be used to fine tune their LCST properties. Thus, we evaluated the role of the amino acid residue and the amide substitution through the synthesis of CPILs **4b** and **4c**. Their thermoresponsive behavior was also studied in chloroform at 0.5 mg mL^{-1} concentration.

Table 1 gathers the data obtained. The substitution of the benzyl *N*-substituent by an *N*-butyl fragment (CPIL **4b**) led to a shift of the LCST to higher temperature, from 48.5 to 58.8°C (Table 1, entries 1 and 3). In contrast, when the original amino acid used for the synthesis of the imidazole ring changed from (L)-valine (CPIL **4a**) to (L)-phenylalanine (CPIL **4c**) the transition

Fig. 3 Plot of the LCST vs. CPIL-**4a** concentration.

Table 1 LCST values in CHCl₃^a

Ent.	CPIL	R	R'	X ⁻	c	LCST ^b	T _g ^c
1	CPIL-4a	(L)-Val	Bn	Cl ⁻	0.5	48.5	156
2	CPIL-4a	(L)-Val	Bn	Cl ⁻	1	39.8	
3	CPIL-4b	(L)-Val	n-Bu	Cl ⁻	0.5	58.8	163
4	CPIL-4c	(L)-Phe	Bn	Cl ⁻	0.5	12.5	149
5	CPIL-5	(L)-Val	Bn	NTf ₂ ⁻	0.5	43.5	86.3
6	CPIL-5	(L)-Val	Bn	NTf ₂ ⁻	1	31.9	

^a The LCST value was taken as the temperature at which the transmittance of the mixture fell below 90% during heating. CHCl₃ stabilised with 2% ethanol. ^b LCST in °C. ^c 10 °C min⁻¹.

temperature considerably decreased from 48.5 to 12.5 °C (Table 1, entries 1 and 4). More likely, the observed changes can be due to the potential of aromatic groups to interfere with the formation of a suitable intrapolymeric supramolecular helical structure through their participation in aromatic interactions.

Finally, the nature of the counteranion in the CPIL was evaluated. Thus, CPIL-4a was converted into CPIL-5 with LiNTf₂ in MeOH at rt. The exchange of Cl⁻ by a non-basic, non-coordinating anion such as NTf₂⁻ is accompanied by a slight decrease in the LCST from 48.5 °C to 43.5 °C at 0.5 mg mL⁻¹ (Table 1, entries 1 and 5). The less coordinative nature of NTf₂⁻ will lead to weaker ion-cation interactions in CPIL-5 than in CPIL-4a. Accordingly, the signals of the C4 and C5 imidazolium protons shift from 7.86/7.60 ppm for Cl⁻ to 7.77/7.44 ppm for NTf₂⁻.¹³ In this way, the helical structure is less favored and the precipitation of the polymer under heating takes place earlier. When the concentration of CPIL-5 is doubled, the LCST shows the same trend observed for 4a, decreasing from 43.5 °C to 31.9 °C (Table 1, entries 5 and 6).

Additionally, we carried out differential scanning calorimetry (DSC) for the different CPILs. For bulk chiral ILs, the study of their phase transitions has provided important insights into their supramolecular structure, mainly associated with the presence of H-bonding interactions, and establishes the appropriate structure-physical property relationship.^{6,7} For CPILs 4 and 5, the DSC curves for the third heating cycle (see ESI† and Table 1) show, in general, the presence of a glass transition temperature (T_g), as confirmed by hot-plate optical microscopy experiments, following a similar trend to LCST values. CPIL-4b presents the highest T_g (163 °C) and LCST (58.8 °C) whereas CPIL-4c presents the lowest T_g (149 °C) and LCST (12.5 °C). The change in the counter anion from Cl⁻ (more coordinating) to NTf₂⁻ (less coordinating) is reflected in a decrease of both melting (from 156 °C to 86 °C) and LCST (from 48.5 °C to 43.5 °C) temperatures. The former data suggest that the same structural parameters are responsible for both phenomena (LCST and T_g) involving changes in the structure/conformation of the polymer chain and the breaking/reforming of intrapolymeric H-bonds and other interactions induced by the variation of the temperature.

Potential applications of these systems are important. A thermoresponsive polycation with tunable LCST can be applied, for example, for nanoparticle stabilization and manipulation. Taking this into consideration, stabilized AuNPs were prepared by direct synthesis from AuCl₄⁻ in the presence of polymer 2 prepared by RAFT polymerization.¹⁴ The thiocarbonylthio moiety of polymer 2 can

Fig. 4 Reversible LCST behaviour of AuNPs-CPIL-4a.

act as an anchoring group for the attachment to gold surfaces. The further quantitative modification of the chloromethyl groups allowed the introduction of chiral imidazolium units leading to the AuNPs-CPIL-4a nanocomposite. To our delight, this system also showed a LCST behavior (31.0 °C, 1 mg mL⁻¹ in CHCl₃). The system is reversible, not showing any signal of NP aggregation after nine consecutive cycles of heating and cooling (Fig. 4).

Our results demonstrate that CPILs based on chiral imidazolium salts can be used to build up polymers with a well-organized secondary structure. The right self-assembly of the IL-like units generates a high-order supramolecular structure with a complex hierarchical architecture, which can provide polymers with a thermoresponsive behavior. The different structural vectors of the CILs, namely the nature of the substitution at the chiral stereocenters and the amide substitution, can be easily modified to fine tune their LCST performance. These vectors are able to induce structural directionality ("entropic effect") on the polymer main chain mainly through well-defined networks of supramolecular synergetic interactions. Furthermore, the presence of additional groups in the polymer allowed us to transfer these properties to 3D-hierarchical structures such as AuNPs-CPILs composites, opening a new avenue for the preparation of chiral polymeric IL-stabilized AuNPs for different applications.

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Electronic Supplementary Information

LCST-type polymers based on Chiral-Polymeric Ionic Liquids

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CPILs Synthesis

Scheme S.I.1 Synthesis of CPIL polymers

Preparation of compound 2. Poly(vinylbenzyl chloride) (**2**) was prepared by bulk RAFT polymerization of p-chloromethylstyrene (**1**) with IBN as chain transfer agent and AIBN as initiator. A flask was charged with 0.1459 g (0.66 mmol) of IBN, 10.0079 g (65.57 mmol) of compound **1** and 0.0108 g (0.065 mmol) of AIBN. The flask was deoxygenated with five freeze-thaw-cycles and filled with nitrogen. The polymerization was allowed to proceed at 120 °C for 24 hours. The reaction was stopped by immersing the flask into liquid nitrogen. The product was diluted with acetone and isolated by precipitation with methanol. The product was further purified by two precipitations from acetone/methanol to yield Poly(VBC) **2** with a 56 % polymerization degree, a molecular weight of 18.9 kg/mol and a polydispersity of 1.5 as determined by GPC.

Preparation of compounds 4a-c. The different CPILs were prepared by substitution of the chloride groups in polymer **2** by several chiral imidazoles derived from amino acids (CILs **3a-c**). As an example, a flask was charged with 0.1513 g (0.588 mmol) of CIL-**3a** and 0.0603 g (0.395 mmol) of **2**. The mixture was dissolved in 3 mL of 2-Me-THF. The reaction was allowed to proceed at 40 °C for 4 days. The product precipitates during the reaction. After that, it was redissolved in MeOH and was isolated by precipitation with Et₂O to yield CPIL-**4a** (62 %).

Scheme S.I.2 Anion exchange

Preparation of compound 5. A flask was charged with 0.1746 g (0.426 mmol) of **CPIL-4a** and it was dissolved in 5 mL of MeOH. Then, 0.1478 g (0.515 mmol) of LiNTf₂ were added. The reaction was allowed to proceed at room temperature for 24 hours, after which the product **CPIL-5** was purified by dialysis against MeOH and isolated by evaporation.

¹H-NMR Spectra

¹H NMR (500 MHz, CD₃OD) δ 7.86 (s, 1H), 7.60 (s, 1H), 7.41 – 6.92 (m, 8H), 6.43 (s, 2H), 5.41 (s, 1H), 4.58 – 4.13 (m, 2H), 2.48 (s, 1H), 1.01 (s, 3H), 0.78 (s, 3H).

¹H NMR (300 MHz, cd_3od) δ 7.99 – 7.50 (m, 2H), 7.40 – 6.85 (m, 2H), 6.78 – 6.21 (m, 2H), 5.46 (s, 2H), 4.62 – 4.41 (m, 1H), 3.16 – 2.95 (m, 2H), 2.49 (s, 1H), 1.48 (s, 2H), 1.32 (s, 2H), 1.08 (s, 3H), 0.87 (s, 6H).

¹H NMR (300 MHz, CD_3OD) δ 7.72 (s, 2H), 7.42 – 6.77 (m, 12H), 6.75 – 6.19 (m, 2H), 5.65 – 5.12 (m, 2H), 4.65 – 4.07 (m, 3H), 3.50 (s, 2H), 2.00 – 1.20 (m, 3H).

IR Spectra

IR (ATR): 3385, 3217, 3056, 2969, 2931, 1675, 1551, 1452, 1360, 1226, 1154, 1120, 1024, 821, 749, 700 cm⁻¹

IR (ATR): 3274, 3216, 3051, 2960, 2930, 2872, 1675, 1557, 1512, 1456, 1421, 1394, 1372, 1153, 1092, 612 cm^{-1}

IR (ATR): 3360, 3203, 3029, 2927, 2853, 1681, 1555, 1512, 1496, 1453, 1424, 1360, 1295, 1267, 1228, 1153, 1027, 822, 741, 699, 639 cm^{-1}

IR (ATR): 3380, 3319, 3147, 3058, 3033, 2969, 1680, 1550, 1460, 1429, 1346, 1136, 1053, 821, 740, 698, 615 cm^{-1}

DSC Results

Fig. S.I.1 DSC curves for the different polymers prepared: 3rd heating cycle

Measurements of glass-transition temperatures were carried out on a Perkin Elmer differential scanning calorimeter (DSC), model DSC8. The instrument was calibrated for temperature and heat flow with zinc and indium reference samples provided by Mettler-Toledo. Samples were placed in a 40 mL hermetically sealed aluminum pan with a pinhole at the top of the pan. An empty aluminum pan was used as the reference. The samples inside the differential scanning calorimeter furnace were exposed to a flowing N₂ atmosphere. Before the DSC test, each sample was dried at 90–100 °C and 10⁻²–10⁻³ mbar for 4 h, and was further dried *in situ* on the differential scanning calorimeter by holding the sample at 120 °C for 15 min. This is important because the presence of volatiles, especially water, can affect the glass-transition and melting temperatures. Melting transition temperatures were determined by multiple cycles of heating from 40°C to 180°C, followed by cooling from 180°C to 40°C both at a rate of 10°C min⁻¹. The T_g temperatures were determined as the onset of the transition.

Fig. S.I.2 Turbidity curves of CPILs-4 at 0.5 mg/mL in CHCl_3 . Variation of transmittance with temperature at 600 nm

Fig. S.I.3 ^1H -NMR (500 MHz, CDCl_3) spectra of CPIL-**4a** at 1.0 mg/mL + 0.5% EtOH.
(a) 30 °C, (b) 40 °C, (c) 55 °C, (d) 75 °C

Fig. S.I.4 TEM images of AuNPs. a) AuNPs- Poly(VBC) **2**, b) AuNPs-CPII-**4a** after modification of AuNPs- Poly(VBC) **2**. Both of them have a 3 nm particle size and are unaggregated because of the stabilization by the polymer

Fig. S.I.5 Computational models for CPIL-4a based on the organization through the formation of C2-H $\cdots$ Cl $\cdots$ H-NCO interactions between vicinal groups in the side chain. A) CPK model showing the orientation of the vicinal aromatic rings on the main chain; the structure of the C2-H $\cdots$ Cl $\cdots$ H-NCO pattern is illustrated in the case shown inside the yellow rectangle. B) CPK representation of the aromatic rings on the main chain.

5.4. Conclusiones

- Se ha sintetizado una nueva clase de CPILs por modificación química del poly(VBC) lineal obtenido mediante polimerización controlada RAFT utilizando imidazoles quirales derivados de distintos aminoácidos.
 - Se ha observado que estos compuestos presentan un comportamiento termosensible en CHCl_3 . Las técnicas utilizadas tanto para conocer este comportamiento, así como para determinar la temperatura de transición de fase (LCST) fueron: espectroscopia UV-Vis, dicroísmo circular (CD), resonancia magnética nuclear (RMN) y calorimetría diferencial de barrido (DSC).
 - Este fenómeno es reversible y está asociado con las interacciones inter e intramoleculares que tienen lugar en el polímero, así como a los efectos solvofóbicos que afectan a la estructura supramolecular ordenada que adquieren los CPILs por medio del autoensamblaje.
 - Los resultados obtenidos a partir de las medidas de CD confirman la estructura helicoidal que adoptan estas macromoléculas inducida por la quiralidad y su dependencia con la temperatura lo que influye en su solubilidad en CHCl_3 .
 - Las variaciones en los desplazamientos químicos de las señales correspondientes a los H más ácidos observadas en ^1H -NMR confirman la gran implicación que presentan las interacciones de tipo enlace de Hidrógeno en el comportamiento termosensible.
 - Se ha estudiado el efecto de la concentración sobre el valor de la LCST observándose que la temperatura de transición disminuye al aumentar la concentración de CPIL. Ello indica que la competencia entre la formación de estructuras supramoleculares inter o intrapoliméricas es clave para observar dicho comportamiento.
 - Se ha demostrado la posibilidad de modular y controlar la LCST de este tipo de polímeros a través de los vectores estructurales de las unidades de CIL como son el resto de aminoácido, la sustitución de la amida y la naturaleza del contraión.
-

- El estudio de las temperaturas de transición (T_g) de los CPILs por DSC corrobora que las mismas variables estructurales son las responsables de ambos fenómenos (LCST y T_g).
- Se ha conseguido estabilizar AuNPs con los CPILs obteniendo sistemas AuNPs-CPIL con comportamiento termosensible reversible.

Chapter 6

**Hierarchically structured polymeric ionic
liquids and polyvinylpyrrolidone mat-fibers
fabricated by electrospinning**

Chapter 6. Hierarchically structured polymeric ionic liquids and polyvinylpyrrolidone mat-fibers fabricated by electrospinning

6.1. Resumen del manuscrito

El desarrollo de fibras poliméricas obtenidas por electroestirado (electrospinning), es de gran interés debido a sus posibles aplicaciones en diferentes campos incluyendo la catálisis, la liberación controlada de fármacos, el desarrollo de sensores, la preparación de membranas filtración selectiva, etc. Aunque existen diferentes técnicas para la obtención de microfibras la técnica de electroestirado es una de las más investigada actualmente, dado que se trata de un método sencillo, eficiente y versátil, para preparar membranas basadas en fibras micro- y nanométricas a partir de disoluciones poliméricas. La Figura 6.1. ilustra el esquema general del proceso.

Figura 6.1. Esquema ilustrativo de la formación de membranas poliméricas por electrospinning.

Los líquidos iónicos poliméricos (*Polymeric Ionic Liquids*, PILs) combinan las características y propiedades fisicoquímicas de los materiales moleculares con las de los líquidos iónicos (ILs). Esto les confiere propiedades únicas para el desarrollo de materiales avanzados. Una de las características más atractivas de los PILs es que sus propiedades pueden modularse fácilmente en función de la composición química. Así, en principio y atendiendo a su naturaleza, estos materiales presentan excelentes características para ser electroestirados formando membranas con morfologías y propiedades modulables, ya que cabe esperar que pequeñas modificaciones en la estructura del PILs permitan variaciones significativas de su morfología y características fisicoquímicas.

Así pues, en este capítulo se describe la síntesis, caracterización y estudios preliminares de aplicación de membranas poliméricas obtenidas a partir de distintas mezclas de PILs con poli-vinil-pirrolidona (PVP) utilizando la técnica de electroestirado.

Figura 6.2. Síntesis de los PILs. i) CPA, ACVA, 120 °C, 24h, DMF. ii) 2-Me-THF/MeOH, 40 °C, 2 días. iii) LiNTf₂, MeOH/Acetona, r.t., 24h. iv) CF₃(CF₂)₃SO₃K, MeOH/H₂O, r.t., 24 h.

La síntesis de los PILs, tal y como muestra la Figura 6.2., se llevó a cabo por modificación química del poli-clorometilestireno, obtenido por polimerización controlada, con diferentes imidazoles, seguida de una reacción de metátesis que permite intercambiar el anión Cl⁻ por aniones de carácter hidrofóbico (NTf₂⁻ y (CF₃)-(CF₂)₃-SO₃⁻).

Las membranas poliméricas se obtuvieron mediante el electroestirado de mezclas poliméricas formadas por los PILs con PVP, dado que en nuestros primeros intentos iniciales no fue posible obtener membranas por electroestirado a partir de soluciones conteniendo únicamente los PILs.

El PVP es un polímero sintético, biocompatible y lineal, capaz de aumentar la viscosidad de la solución polimérica y que puede ser fácilmente electroestirado, además de ser soluble en agua y en diferentes disolventes orgánicos. Por lo tanto, el PVP, se utiliza ampliamente en la fabricación de fibras por electroestirado donde actúa como un polímero guía que induce la formación de fibras. Así, la combinación PILs y PVP permitió obtener membranas obtenidas formadas por un entramado denso de fibras.

Estas membranas se estudiaron empleando diferentes técnicas para determinar su morfología y propiedades.

Así, su morfología se estudió mediante la microscopía electrónica de barrido (SEM). Este estudio permitió comprobar cómo la composición química de los PILs era determinante para la obtención de membranas con diferentes morfologías. De este modo, cuando las disoluciones poliméricas de partida contenían PILs hidrofóbicos se obtuvieron nanofibras cilíndricas. En cambio, para soluciones formadas con PILs de carácter hidrofílicos (anión Cl^- en su estructura) se observó la formación de membranas constituidas por cintas micrométricas.

Por otra parte, se evaluaron las propiedades hidrofóbicas/hidrofílicas de las membranas. Para ello se midieron los ángulos de contacto que forma superficie del agua al entrar en contacto con la superficie de las membranas preparadas (WCA). Este valor depende tanto de la composición química de la membrana como de su microestructura, por lo tanto proporciona información sobre la estructura molecular de las membranas. Los resultados han mostrado, a pesar de la presencia de un polímero hidrofílico como el PVP, que las membranas de PCIVB y las derivadas de PILs con NTf_2^- son de carácter hidrofóbico mientras que las aquellas basadas en PILs con Cl^- son de naturaleza hidrofílica y solubles en agua como cabe esperar. El WCA no sólo depende del anión sino también de la longitud de la cadena alquílica del imidazolio. Este hecho explica la diferencia observada en los valores obtenidos para las membranas hidrofóbicas en función de si la longitud de la cadena es metilo u octilo.

Además, el método de preparación de la membrana también es un factor que afecta al WCA. Así, la técnica de electrospinning produce fibras más hidrofóbicas y, por tanto, materiales más estructurados que cuando estos se preparan con la misma composición mediante un proceso de casting.

Asimismo, dada la posibilidad de controlar las características de la superficie, con objeto de conseguir membranas superhidrofóbicas, se preparó una membrana que contuviera un anión perfluorado en su estructura. En este caso, el WCA resultó ser mucho menor que el esperado. El análisis morfológico de dicha membrana por SEM, mostró que existe cierta segregación de los polímeros (PVP y PIL). Así, la presencia en la superficie de ensamblajes ricos en PVP podría explicar la disminución del WCA.

En el estudio de la naturaleza de las interacciones inter- e intrapoliméricas que conforman las membranas, el análisis por ATR-FT-IR y TGA proporciona información de gran interés puesto que el grupo carbonilo del PVP puede establecer enlaces de

hidrogeno con los grupos C-H ácidos del catión imidazolio así como con moléculas de agua e interacciones con el anión. Los resultados sugieren que los PILs y el PVP experimentan una serie de fuertes interacciones inter- y supramoleculares que definen las propiedades de las membranas.

Todos estos análisis indican la gran influencia que presentan los parámetros estructurales de los PILs en la capacidad de autoensamblaje para generar membranas con diferentes morfologías y propiedades físicoquímicas.

Finalmente, se llevaron a cabo estudios preliminares de aplicación de los materiales poliméricos preparados. En primer lugar, se evaluó su potencial aplicación en procesos de separación. Así, algunas de las membranas preparadas son capaces de separar una mezcla de agua y aceite simplemente bajo la acción de la gravedad permitiendo el paso selectivo del aceite a través de la membrana y repeliendo el agua permaneciendo sobre ella. Igualmente, estas membranas hidrofóbicas muestran posibilidades de aplicación en los procesos de síntesis del biodiesel donde la separación del glicerol (subproducto de la reacción) de los FAMES continúa siendo uno de los problemas principales. Los ensayos llevados a cabo, han mostrado que es posible realizar una separación eficiente de la fase aceite de una mezcla de glicerol/agua.

Alternativamente, se evaluó la posibilidad del empleo de las membranas obtenidas por electroestirado para depositar y estabilizar nanopartículas de oro (AuNPs) mediante la técnica de *sputtering*. Los estudios iniciales sugieren que la selección adecuada de los parámetros estructurales como la morfología de las fibras y la naturaleza de las unidades de líquido iónico presentes en la matriz polimérica, permite la preparación de AuNPs con tamaños de partícula modulables que se pueden obtener por la simple deposición del oro por la técnica de “*sputtering*”. Estos materiales nanoestructurados conteniendo en su estructura nanopartículas presentan un gran potencial de aplicación en catálisis, en el desarrollo de sensores, materiales luminiscentes, etc.

Resumiendo, es posible obtener membranas poliméricas altamente estructuradas basadas en PILs/PVP mediante electroestirado. La naturaleza de las interacciones inter- e intramoleculares desempeñan un papel muy importante durante el proceso de electroestirado. De este modo, pequeñas modificaciones en los vectores estructurales que definen a nivel moleculares dichas interacciones permiten modular la morfología y propiedades físicoquímicas de las membranas micro-fibrilares obtenidas. Estudios iniciales sugieren que estos sistemas pueden encontrar diferentes aplicaciones como materiales avanzados.

Hierarchically structured Polymeric Ionic Liquids and Polyvinylpyrrolidone mat-fibers fabricated by electrospinning

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Different polymeric ionic liquids/polyvinylpyrrolidone (PILs/PVP) fiber membranes were prepared by electrospinning from the corresponding polymeric blends. Supramolecular interpolymeric interactions between PILs and PVP define not only the solution properties but also the final morphology and performance of the mat-fibers. The fine tuning of the counter anion and the length of the alkyl chain allow modulating both their hydrophobic/hydrophilic properties and their morphology. The main differences observed are dictated by the chemical information contained in the molecular structures of the two polymers driving the self-organization and self-assembly of the polymers onto well-defined nanostructured assemblies under electrospinning conditions. In this way it was possible to obtain materials with potential applications in different fields as highlighted by the promising results obtained for oil-water separation or for the synthesis and stabilization of AuNPs.

Introduction.

Electrospun polymer fibers are of great current interest because they allow the preparation of nanostructures materials with potential applications in different fields such as filter media,¹ energy,² drug delivery,³ nanosensors,⁴ tissue engineering⁵ or catalysis.⁶ Ultrafine fibers can be produced by several techniques but the use of electrospinning is increasingly investigated.⁷ It is considered as one of the most simple, efficient and versatile methods for preparing mats of micro- and nanoscaled fibers from polymer solutions.⁸ The nanofiber morphology and microstructure obtained can be controlled and adjusted by the experimental electrospinning parameters and by the intrinsic physico-chemical properties of the polymer or polymer mixtures used in the preparation.⁸ Ionic liquids (ILs) are well-known materials with excellent tuneable physico-chemical properties.⁹ The application of ILs to material science has opened new scientific and technologic developments.¹⁰ ILs have been employed as functional advanced materials, advanced media for materials production or components for preparing highly functional materials.¹¹

Properly designed ILs can dissolve a wide spectrum of organic, organometallic and inorganic compounds and polymers. Their application in electrospinning has increased the families of materials from which fibers can be made, opening new avenues in the preparation of fibers by this technique. Thus, for instance, ILs provide a good solvent ability for biopolymers enabling the electrospinning of recalcitrant materials like cellulose.¹² The preparation of functional hybrid materials based on blends of ILs and conventional polymers can lead to advanced systems combining the properties of polymers (e.g. mechanical strength) and ILs (e.g. high ionic conductivity, high thermal stability, or catalytic activity).¹³ This can also be accomplished by the design of polymeric ionic liquids (PILs).¹⁴ The solution properties of this kind of polyelectrolytes make them electrospinnable polymers enabling the development PILs membrane systems with interesting morphologies.^{15,16} Besides, the properties of these membranes can be easily adjusted by fine tuning the PILs structure. The surface wetting behaviour,^{17,18} for instance, can be greatly affected by a simple exchange of PILs anions, with anions such as Cl⁻, Br⁻ and BF₄⁻ providing hydrophilicity, and those with PF₆⁻ and Tf₂N⁻ impairing hydrophobicity.¹⁹

Here, we report on the synthesis, characterization and application of polymeric membranes prepared by electrospinning of blends of different PILs with poly(vinylpyrrolidone) (PVP). The interactions PILs/PVP define the morphology and properties of the obtained membranes. The fine-tuning of the counter anion and the length of the alkyl chains on the IL-fragments allow modulating not only their hydrophobic/hydrophilic properties but also the morphology of the fibers obtained. The mats obtained can be used for oil-water separation and as nanostructured supports for

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the synthesis and stabilization of metal nanoparticles by sputtering deposition.

Fig. 1 Schematic diagram illustrating the formation of mats by electrospinning of a polymer blend solution of PVP ($M_w = 1300000$ g/mol) and PILs in either DMF or MeOH with a ca. 1/2.5 weight ratio.

Experimental

Materials

All the reagents and solvents used were commercially available. 4-vinylbenzyl chloride (*p*-chloromethylstyrene, 90%, Aldrich) was purified by passing over a column of basic aluminium oxide. 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPA, >97%, Aldrich), 4,4'-azobis(4-cyanovaleic acid) (ACVA, >98%, Aldrich), *N,N*-dimethylformamide (DMF, 99.5%, Scharlau), 1-methylimidazole (99%, Aldrich), 1-octylimidazole (98%, Aldrich), 2-methyl tetrahydrofuran (2-Me-THF, 99%, Acros), methanol (MeOH, 99.9%, Scharlau), bis(trifluoromethane) sulfonamide lithium salt (LiNTf_2 , 99%, Aldrich) and acetone HPLC (99.9%, Scharlau) were used as received. Polyvinylpyrrolidone (PVP) had $M_w = 1300000$ and was obtained from Aldrich.

Materials characterization. The surface morphology of the electrospun films was analyzed with a scanning electron microscope (SEM) (JEOL 7001F) after platinum coating. The diameter of the fibers was measured on the basis of SEM images. IR spectroscopy was used to check intra and inter-polymer interactions and the molecular structure of the membranes. FT-IR spectra were obtained using a spectrometer (JASCO FT/IR-6200) equipped with an ATR (MIRacle single-reflection ATR diamond/ZnSe) accessory at 4 cm^{-1} resolution (4000 - 600 cm^{-1} spectral range). Differential scanning calorimetry (DSC) (DSC8, Perkin Elmer) was performed in a nitrogen atmosphere at $10\text{ }^\circ\text{C/min}$ heating rate. Elemental analyses were obtained with a CHN Euro EA 3000 instrument. Wettability of the membranes was determined by a static contact angle goniometer in open air (Phoenix-150, Surface Electro Optics, Korea).

Synthesis of poly(vinylbenzyl chloride) 2. Compound **1** (50.0 g, 327 mmol), CPA (0.915 g, 3.27 mmol) and ACVA (0.275 g,

0.983 mmol) were dissolved in 46 mL of DMF. Then, the solution was deoxygenated with five freeze-thaw-cycles. The polymerization was allowed to proceed by heating the solution at $120\text{ }^\circ\text{C}$ for 24 hours. The polymerization was stopped by immersing the flask in liquid nitrogen. The mixture was diluted with acetone and the product isolated by precipitation with methanol, being further purified by two precipitations from acetone to methanol. Polymer **2** was isolated with 45 % yield and a molecular weight of 6.9 kg/mol (1.5 PDI, determined by GPC).

Synthesis of polymeric ionic liquids 4a-b.

Synthesis of 4a. 1-Methylimidazole (**3a**, 6.3 mL, 79.2 mmol) was added to a solution of polymer **2** (6.04 g, 39.6 mmol) in 2-Me-THF (24 mL). The reaction was allowed to proceed at $40\text{ }^\circ\text{C}$ for 2 days. The partially modified polymer precipitated during the reaction, so MeOH (40 mL) was added to keep the polymer in solution. The polymer **4a** was finally purified by dialysis with cellulose membrane against MeOH and isolated by evaporation to yield **4a** with 71 % yield.

Synthesis of 4b. PIL **4b** was obtained by the same methodology above described using octylimidazole (**3b**, 7.8 mL, 39.4 mmol) and **2** (3.00 g, 19.6 mmol) in 2-Me-THF (25 mL) at $40\text{ }^\circ\text{C}$ during 2 days. MeOH (35 mL) was added to the reaction mixture to avoid the precipitation of the partially modified polymer. The final polymer was obtained by dialysis against MeOH and isolated by evaporation to yield PIL **4b** (76 % yield).

Synthesis of polymeric ionic liquids 5a-b.

Synthesis of 5a. Polymer **5a** was obtained by anion exchange of the chloride ion in **4a** with LiNTf_2 . A solution of LiNTf_2 (3.40 g, 11.8 mmol) in acetone (20 mL) was added to a solution of **4a** (2.50 g, 10.6 mmol) in MeOH (35 mL). The mixture was stirred at room temperature for 24 hours. After evaporation, the residue was suspended in Mili-Q water (40 mL) and extracted with EtOAc (3 x 30 mL). The organic fractions were collected, dried over anhydrous MgSO_4 and vacuum evaporated affording polymer **5a** (80% yield).

Synthesis of 5b. Polymer **5b** was obtained by the same methodology than **5a**, using a solution of LiNTf_2 (1.90 g, 6.6 mmol) in acetone (20 mL) and a solution of **4b** (2.00 g, 6.0 mmol) in MeOH (30 mL), (82% yield).

Synthesis of polymeric ionic liquid 6a.

Synthesis of 6a. Polymer **6a** was obtained by mixing a solution of $\text{CF}_3(\text{CF}_2)_3\text{SO}_3\text{K}$ (3.70 g, 10.7 mmol) in Mili-Q® H_2O (60 mL) with a solution of polymer **4a** (2.54 g, 10.8 mmol) in MeOH (170 mL). The mixture was stirred at room temperature for 24 hours. After evaporation, the compound was suspended in Mili-Q® water (40 mL) and extracted with EtOAc (3 x 30 mL). The organic fractions were collected, dried over anhydrous MgSO_4 and vacuum evaporated affording polymer **6a** (99% yield).

Preparation and properties of electrospinning solutions.

Polymer solutions for electrospinning were prepared by mixing and sonicating for 40 min at room temperature the corresponding polymer **2**, **4a-b** or **5a-b**, (25 % by weight) with PVP (9 % by weight) in the appropriate solvent, alternatively DMF or MeOH.

Characterization of the electrospinning solutions. Three main parameters were determined for each solution assayed. Surface tension: It was obtained by the pendent drop method using a Phoenix-150 instrument (Surface Electro Optics, Korea). Viscosity: It was determined with a rotating viscometer (Brookfield R/S-CPS+ Rheometer, USA). Conductivity: It was measured by electrochemical impedance spectroscopy (broadband dielectric spectrometer NOVOCONTROL CONCEPT-80, BDS-80, Germany).

Electrospinning process.

The electrospinner used in this study was a Fluidnatek LE 100.V1 (BioInicia, Spain). The polymer solutions were loaded into a plastic syringe equipped with a stainless steel needle tip (0.9 mm inner diameter). The tip-collector working distance was fixed at 16 cm. The applied voltage was kept between +23, -13 kV and the flow rates ranged from 1 to 2 mL/h. The electrospun fibers were collected on aluminum foil that covered a rotating collector. All electrospinning experiments were carried out at room temperature and relative humidity of 36 %. The obtained membranes were vacuum dried overnight in the oven at 50 °C.

Sputtering process.

A film mat of the corresponding polymeric blend (40 mg) was placed into a Petri plate (3 cm in diameter) and degassed for 2 h at 298 K under vacuum prior to introduction into the sputter chamber. The vacuum chamber was placed under a sputtering working pressure of 3 mbar by adding Ar flow. The Au (99.999% purity) deposition was performed in a MED 020 (Bal-Tech, CMM-UFRGS), in the sputter mode, with discharge voltages of 345 V (40mA) for 120 s. After the deposition, the chamber was vented with N₂. The films were recovered and stored for their further characterization and application.

TEM

For the transmission electron microscopy (TEM) analyses, the samples were dispersed in ethanol at 25 °C and then submitted to ultrasonic agitation over 20 min. After this, two drops of the dispersion were placed on a carbon coated copper grid. Micrographs were obtained using a JEOL JEM1200 EXII operating at an acceleration voltage of 80 kV at 200 kV (CMM-UFRGS). The diameters of the particles in the micrographs were measured using the software ImageJ.

Ultraviolet–Visible Diffuse Reflectance Spectra.

UV-Vis spectroscopy measurements were performed in a Shimadzu UV2450 spectrophotometer (diffuse reflectance mode) using an integrated sphere accessory and a light wavelength range between 200 and 800 nm. The band gap was estimated from the intercept of the absorption edge with the energy axis in the plot $(k/s)^2$ vs. $h\nu$ as reported in the literature.²⁰

Results and discussion

Preparation of nano-structured PIL/PVP mats by electrospinning. PILs **4a-b** were prepared by chemical modification of polymer **2**, which was obtained by reversible addition-fragmentation chain-transfer (RAFT) polymerization. This modification was carried out using two different

imidazoles, bearing two different N-alkyl groups ($R = -CH_3$ (**3a**) and $R = -(CH_2)_7CH_3$ (**3b**), Scheme 1).²¹ Metathesis of the Cl⁻ counter anions by the more hydrophobic NTf₂⁻ and CF₃(CF₂)₃SO₃K led to the corresponding PILs **5a-b** and **6a** respectively (Scheme 1).

Initial electrospinning attempts of a solution composed solely by PIL **4a** failed to produce fibers. The obtained materials were mainly composed by beads. This can be due to the low molecular weight for the polymer precursor **2** (6.9 kg/mol). It is known that the molecular weight of the polymer is an important factor to define the resulting morphologies in this process.⁸

In order to overcome this problem, the blending of the PILs with an additional polymer of higher molecular weight and which could be easily electrospun was employed. Polyvinylpyrrolidone (PVP) was selected as the blending polymer. PVP is a linear biocompatible synthetic polymer able to increase the viscosity of the polymer solution and with good electrospinnability and, additionally, is soluble in water and different organic solvents.²² Furthermore, PVP presents specific benefits related to electrospinning like its extractability and ability to act as a non-ionogenic partner for the electrospinning of an ionogenic polymer.²³ Hence, PVP is widely used in the fabrication of fibers via electrospinning with various other materials that are unspinnable or hardly spinnable by acting as a polymer carrier, a partner, or a guide.

Scheme 1 Synthesis of PILs. i) CPA, ACVA, 120 °C, 24h DMF. ii) 2-Me-THF/MeOH, 40 °C, 2 days. iii) LiNTf₂, MeOH/Acetone, r.t., 24h. iv) CF₃(CF₂)₃SO₃K, MeOH/H₂O, r.t., 24 h.

Different polymer solutions were prepared by mixing polymers **2**, **4a-b** or **5a-b**, (25 % w) and PVP (9 % w) in the corresponding solvent. For polymer **2** and PILs **4a-b** DMF was used as the solvent. However, and due to the hydrophilic character of PILs **5a-b**, MeOH was used as the solvent instead of DMF. The use of PVP/PILs mixtures had a significant impact in the main properties of the polymeric solutions (surface tension, viscosity and electric conductivity, Table 1).

Table 1 Characterisation of polymeric blends solutions.

Entry	Pol. Mix. (Solv.)	PIL:PVP (% w/% w)	μ^a	γ^b	σ^c
1	2:PVP (DMF)	25:9	0.3120	32.6	$1.5 \cdot 10^{-4}$
2	PVP (DMF)	0:9	0.0596	-	-
3	PVP (MeOH)	0:9	0.0500	-	-
4	4a:PVP (MeOH)	25:9	0.5560	23.6	$4.2 \cdot 10^{-3}$
5	4b:PVP (MeOH)	25:9	0.5360	32.4	$1.3 \cdot 10^{-3}$
6	5a:PVP (DMF)	25:9	0.8430	32.1	$1.1 \cdot 10^{-3}$
7	5b:PVP (DMF)	25:9	0.6030	28.4	$2.7 \cdot 10^{-3}$

^a μ = viscosity (Pa.s). ^b γ = surface tension (mN/m). ^c σ = electric conductivity (S/cm)

These properties influence the electrospinnability of the corresponding polymer solutions to obtain fibers with the desired morphology. Furthermore, the N-alkyl substitution pattern of the imidazolium and the type of the counter ion in PILs also allows to fine tune the properties of the corresponding mixtures.¹⁹ Fiber formation is primarily governed by the viscosity of the polymer solution and by the applied electric field.²⁴ A significant increase on the viscosity was observed for the polymeric mixtures in comparison with solutions solely formed by PVP. The most viscous solution was found for the mixture 5a/PVP (Entry 6 Table 1) with a viscosity one order of magnitude greater than the one for PVP. This viscosity was more than 2.5 fold larger than the one obtained for the 2/PVP mixture corresponding to the unmodified polymer. This is consistent with the nature of the entanglements provided by the interactions between the two polymers used in the mixtures, being these interactions stronger for the polymers bearing IL-like units than for the unmodified poly(*p*-chloromethylstyrene). Interestingly, the behaviour of the viscosity as a function of the shear rate also differs for the different polymeric mixtures (Fig. S9, ESI).

On the other hand, as expected, the addition of the polymeric electrolyte increases one order of magnitude the electric conductivity of the polymeric mixtures in comparison with the non-charged solutions.²⁵

The solutions with one or two polymers were electrospun and collected as it is schematically described in Fig. 1. The electrospinning parameters were adjusted during the electrospinning by collecting samples *in-situ* and analysing the morphology of the materials obtained by optical microscope (see ESI). As the equipment is provided with two independent power supplies, negative voltages were applied to the collector in order to direct the electrospinning jet towards the collector.

Once stabilised the efficient electrospinning conditions, mats composed by a dense layer of entangled fibers were obtained and collected in aluminum foil as membranes of ca. 20x15 cm². The mats were dried under vacuum at 50 °C and their morphology analyzed by SEM.

Figure 2 and Figures S2-S8 at the ESI show some representative images of the morphologies observed for the electrospun mats prepared. Table 2 summarises the main data obtained.

In general, the formed mats did not show any indication of polymer phase separation at the compositions assayed. The

nature of the polymeric mixtures had a strong impact on the morphology of the mats obtained. Thus, the mixture 2/PVP led to continuous, cylindrical, bead-free fibers with an average diameter of 530 nm (Fig. S2, ESI). Nano-fibers with a similar morphology were also obtained for the mixtures of polymers having hydrophobic PILs, although, in these cases, the fibers were thinner (360 nm and 280 nm for the 5a/PVP and 5b/PVP blends, respectively). This can be associated with the increase in electric conductivity for the corresponding solutions in comparison with the mixture 2/PVP (entries 4 and 5 vs 1, Table 1). In an analogous way to that observed for ILs in solution, the enhancement in electric conductivity facilitates the formation of thin and more uniform fibers.⁹

Table 2 Electrospinning parameters used to fabricate the PILs:PVP fibers.^a

Entry	Pol. Mix.	Voltage (kV)	Fiber morphology	Size ^e
1	2:PVP	+14, -9 ^b	fibers	530 ± 120 nm
2	4a:PVP	+13, -8 ^c	ribbons, thickness 0.5 μm	13.9 ± 3.6 μm
3	4b:PVP	+14, -10 ^c	ribbons, thickness 1.14 μm	8.8 ± 2.5 μm
4	5a:PVP	+21, -10 ^d	fibers	360 ± 70 nm
5	5b:PVP	+21, -13 ^d	fibers	280 ± 110 nm

^a in all experiments the distance tip-collector was 16 cm. ^b flow rate 2 mL/min. ^c flow rate 1.5 mL/min. ^d flow rate 1 mL/min. ^e diameter and thickness determined by SEM analysis.

Surprisingly, polymeric mixtures containing PILs with the Cl⁻ anion formed micro-ribbons instead of cylindrical fibers (Figs. 2a and 2b). In addition, the size of these micro-ribbons was in the order of micrometers rather than nanometers ($13.9 \pm 3.6 \mu\text{m}$ and $8.8 \pm 2.5 \mu\text{m}$ for the blends 4a/PVP and 4b/PVP, respectively). A ribbon-like shape is usually attributed to the formation of a thin skin on the surface of a liquid jet in the early stage of the electrospinning due to the rapid evaporation of solvent. Thus, the change on the structure could be ascribed to the use of MeOH as the solvent instead of DMF for these mixtures.

However, it has been reported that PVP electrospun in MeOH leads to well-defined fibers.²³ Indeed, we were able to obtain well-defined PVP fibers in the absence of any PILs by electrospinning a PVP in MeOH solution (10 % w, Fig. S8, ESI). Hence, the ribbon-like shape observed for the blends 4a/PVP and 4b/PVP should be attributed to the presence of the PIL in the polymeric mixture. Koombhongse *et al.* proposed a mechanism for the formation of ribbon-shaped fibers whereby atmospheric pressure tended to collapse the skin as the solvent evaporated.²⁶ Solvent tends to evaporate more slowly with increase in viscosity, and a fraction of the solvent can also be trapped inside the fiber after the skin forms. Atmospheric pressure then collapses the resulting tube. The circular cross section becomes elliptical and then flat, forming ribbons. It is likely that the higher viscosity of the mixture induces such an effect leading to ribbons formation. Gudkova *et al.* have also found ribbons-like morphology when a SAN (styrene-acrylonitrile copolymer) solution in 1,2-dichloroethane was electrospun in presence of [BMIM][Cl].²⁷ In this sense, the increase in the interpolymeric interactions, as considered above,

Fig. 2 SEM images for the electrospun mats formed from polymer blends **4a**/PVP (a), **4b**/PVP (b), **5a**/PVP (c) and **5b**/PVP (d).

based on the strength of the hydrogen bonding, coulombic, the anion-cation and the hydrophobic (associated to N-substitution) interactions can favor the formation of such morphologies during the electrospinning process.

Another remarkable difference is that the mats derived from PILs **4a** and **5a** bearing IL-like units with an N-methyl substitution tend to give less dense entanglements than **4b** and **5b** displaying N-octyl substitution and thus providing increased hydrophobic interactions.

Wettability of PIL/PVP mats as a function of their composition. The surface wettability of the mats prepared was evaluated by performing water contact angle measurements (WCA, Table 3). The wettability of a solid surface is a very important property, which is governed by both the chemical composition and the geometrical microstructure of the solid surfaces.²⁸

The film formed by the **2**/PVP blend showed a slightly hydrophobic character. It presented a WCA of 79.1°, similar to the one obtained for a pure PS (polystyrene) membrane

obtained under analogous conditions (WCA = 78.8°, Table 3). This result is somehow surprising as the **2**/PVP mat is composed by *ca.* 9 % by weight of PVP, which is a hydrophilic polymer highly soluble in water. In contrast, when a water droplet (2 µL) was put in contact with the surface of the mats blended with PVP and polymers **4a-b** (PILs bearing Cl⁻ as anion) the water droplet immediately spread over the film giving a formal lecture of 0° contact angle. This indicates, as expected, that the mats are hydrophilic, both polymers being water soluble. However, the surface of the films derived from PILs having NTf₂⁻ as the counter ion showed a clear hydrophobic nature (105.3° and 82° for **5a**/PVP and **5b**/PVP, respectively). Noteworthy, these values are larger than those obtained for PS (78.8°) and for the blend **2**/PVP (79.1°). These results confirm that the anion exchange in the PILs can be used to modulate and enhance the hydrophilicity/hydrophobicity of the membrane surface. It should also be pointed out that the WCA values obtained for **5a**/PVP and **5b**/PVP are more

hydrophobic than other materials modified with N-alkyl IL-units having hydrophobic counter ions (see Fig. 3).^{29,30,31,32}

Table 3 Contact Angles (CA) measurements for water and glycerol.

Entry	Method	Pol. Mix.	WCA	glycerol
1	electrospinning	2:PVP	79.1	110
2	electrospinning	PS ^a	78.8	-
3	electrospinning	4a:PVP	0	0
4	electrospinning	4b:PVP	0	0
5	electrospinning	5a:PVP	105.3	102.6
6	casting	5a:PVP	39.8	-
7	electrospinning	5b:PVP	82	124.7
8	electrospinning	6a:PVP	65.4	108.1

^a PS polystyrene film prepared by electrospinning a solution 30% W of PS 35000 and 5% PS 280000 in DMF.

On the other hand, the previous results also put forward that surface wettability depends not only on the counter anion but also on the length of the alkyl chain. Lee *et al.* have shown that the wettability of Au surfaces coated with monolayers of thiol-functionalized ILs is largely dependent on the length of *N*-alkyl chains of the imidazolium salt.³¹ Two different trends were claimed. For the shorter *N*-alkyl-chains (C1-C4) the nature of the counter anion controlled the surface wettability (Fig. 3). On the contrary, for long *N*-alkyl-chains (C>4) little effect on the WCA was observed by exchanging the anion. For these cases, it is likely that anions are embedded in the long *N*-alkyl-chains and in close contact with the imidazolium cations. Thus, the wettability is mainly related with the length of the *N*-alkyl-chains (Fig. 3). Taking all this into account, it is noteworthy that the present films showed an opposite trend. The **5a**/PVP film, with PILs bearing an N-methyl substitution, presented a WCA of 105°, while the eletrospun **5b**/PVP composite film bearing an octyl residue showed a smaller contact angle (82°, 23° less than the **5a**/PVP film).

It is also remarkable that a significant difference on the WCA was also observed between films with identical composition (**5a**/PVP) but obtained either by casting or by electrospinning. The mats prepared by electrospinning led to hydrophobic surfaces with a WCA of 105.3°, while wettability of the film prepared by casting was larger showing a significantly smaller contact angle of 39.8°. The more structured material obtained by electrospinning is clearly improving the hydrophobic nature of the films.

It should be mentioned that in the case of self-assembled monolayers of long- chain fluorinated imidazolium ILs grafted via –Si–O– covalent bonds to Al surfaces, superhydrophobic materials (WCA above 160°) were obtained.³³ PIL **6a** bearing perfluorobutanesulfonate as the anion was prepared by simple anion exchange from **5a**. The presence of the fluorinated chain in the counter ion was expected to enhance the hydrophobic behaviour of the film formed by electrospinning the corresponding solution of **6a**/PVP. Surprisingly, the resulting film displayed a smaller WCA (65.4°) being even smaller than the obtained for **2**/PVP (79.1°).

Fig. 3 WCA values reported for different materials modified with IL-like units; data taken from references 29-32.

SEM images of the mats obtained from a **6a**/PVP mixture (Fig. 4) show a morphology displaying a combination of very thin fibers and larger ribbons. According to data obtained from pure PVP mats (Fig. S8, ESI) and from other PIL/PVP mixtures, this could correspond to the existence of some polymer segregation in which pure PVP or enriched PVP polymer assemblies are formed along with **6a** enriched assemblies. The presence of PVP rich entities on the surface would explain the decrease in the observed WCA.

Fig. 4 SEM imagines for the electrospun mats formed from polymer blends **6a**/PVP.

Overall, these analyses showed the influence of different structural parameters of the PILs on the self-assembly abilities leading to membranes with different morphologies and physico-chemical properties.

ATR-FT-IR studies. IR studies can be able to shed light on the nature of intra- and inter-polymeric interactions. It has been shown that the PVP carbonyl stretching frequency is very sensitive to hydrogen bonding with ILs.³⁴ In the present case, hydrogen bonds can be established between the oxygen of the PVP carbonyl and the acidic C-H groups of the imidazolium

cation, but also with water molecules giving place to the formation of hydrogen-bonded $\text{C}=\text{O}\cdots(\text{H}_2\text{O})_x$ -anion-cation arrays.³⁵ Fig. 5a shows the ATR-FT-IR regions of the C=O bands for the different mats. The spectrum for the mat prepared with pure PVP shows a complex band at 1680-1650 cm^{-1} . By increasing the adsorbed water the $\nu(\text{C}=\text{O})$ of PVP can shift from 1680 to 1652 cm^{-1} through hydrogen bond formation with water molecules.³⁶ Thus, the band for the PVP mat is composed by at least three components reflecting distinct water environments at 1678 cm^{-1} (not hydrated) 1663 cm^{-1} (polymer-water-polymer hydrogen bonds) and 1652 cm^{-1} (fully hydrated C=O band). The last two bands can be attributed to hydration of PVP during the electrospinning process at 36% humidity. The PVP C=O band experimented significant variations when the mats were prepared by blending with PILs. For the mat obtained with the most hydrophilic PIL, **4a**/PVP mixture, a broad red-shifted C=O signal is observed. The presence of **4a** is likely to favour the hydration of the carbonyl group during the electrospinning process along with the formation of strong $\text{C}=\text{O}\cdots\text{water}\cdots\text{Cl}^-\cdots\text{imidazolium}$ arrays. As expected a lower hydration for **4b** containing a larger hydrophobic N-substitution was observed by the smaller red-shift observed in the C=O bands.

In the case of the mats containing PILs bearing NTf_2^- , **5a**/PVP and **5b**/PVP, the spectra show a more symmetrical band with an increase in the contributions at higher frequencies. Thus, the relative weight of the fully hydrated C=O (1652 cm^{-1}) contribution is reduced while increasing the ones corresponding to polymer-water-polymer systems (1663 cm^{-1}) and non-hydrated groups (1678 cm^{-1}). It is expected that in the presence of these hydrophobic PILs the adsorption of water during the electrospinning process decreases.

The TGA analysis of the mats confirmed the presence of water in the different mats and the existence of clear differences between them in this regard (Fig. S10, ESI). The membrane formed by PVP alone showed the larger water content (ca. 16%), while films **4a**/PVP and **4b**/PVP hosted a lower water content (12.8 and 7.8 % respectively). As expected, the lowest water content was found for films formed with PILs bearing NTf_2^- (**5a**/PVP and **5b**/PVP, ca. 2.5%). The reduction of the water content is in good agreement with the structural changes provided by the imidazolium fragment, both in the N-substitution and in the anion.

An additional indication of the interactions between PVP and PILs (directly or through water molecules) can be found when the characteristics peaks of the PILs are compared with the ones obtained for the mats (Fig. 5b). The intense peak between 1000 and 1300 cm^{-1} in the spectra of PILs can be assigned to the skeletal symmetric stretching of the imidazolium ring along with components assigned to $\text{CH}_2(\text{N})$ stretching.³⁷ This band is found at 1161 cm^{-1} for **4a**/PVP and at 1157 cm^{-1} for **4b**/PVP while peaks at 1157 cm^{-1} and 1154 cm^{-1} are found for the corresponding original PILs. Finally, the bands at higher wavenumbers (3300 cm^{-1} to 2700 cm^{-1}) corresponding to the symmetric and asymmetric stretching vibrations of the C(4/5)H and C(2)H groups of the imidazolium, can provide further information.

Fig. 5 Selected regions for the ATR-FT-IR spectra of a) **4a**/PVP, **4b**/PVP, PVP, **5a**/PVP and **5b**/PVP. b) **5a** and **5a**/PVP

Fig. 5b depicts this region for PILs **5a** (blue/top) and the corresponding **5a**/PVP mat (red/bottom). The original PIL **5a** displays clearly visible bands at 3156 cm^{-1} (C(4)H) and 3124 cm^{-1} (C(5)H). Noteworthy, these bands appear at lower wavelengths (3149 cm^{-1} and 3112 cm^{-1}) in the fiber mat (**5a**/PVP). This is characteristic of the participation of C(2)H and C(4/5)H in extensive hydrogen bonding networks either directly or through $\text{C}=\text{O}\cdots\text{water}\cdots\text{H}\cdots\text{C}$ or polymer-water-polymer arrays.³⁸

The obtained mats were further investigated by differential scanning calorimetry (DSC). In a first cycle the mats were heated to 120 $^{\circ}\text{C}$ to eliminate water adsorbed and, after cooling, a second heating-cooling cycle was carried out from 25 to 200 $^{\circ}\text{C}$. A third cycle was again run from r.t. to 200 $^{\circ}\text{C}$. Data provided by the second DSC cycle (Fig. S11b, ESI), revealed the presence of two transitions, one associated to the PIL component and the second one associated to PVP (~ 172 $^{\circ}\text{C}$ for pure PVP). Interestingly, as the hydrophobic character of the PILs increases (**5b**>**5a**>**4b**>**4a**) the transition curves become

more diffuse and the $\Delta T_{g_{mat}}$ value ($T_{g_{PVP}} - T_{g_{PIL}}$) decreases relative to the one for the pure components.

The uniform character of the mat fibers and ribbons was analysed in the case of **5a** by washing the resulting mat with water at r.t. (3 days). Being PVP water-soluble and **5a** non water soluble, it could be expected that in the case of segregated or not uniform polymer mixtures selective washing out of PVP could take place. This would increase the rugosity of the surface but also modify other properties like the WCA (hydrophobic/hydrophilic balance) or the chemical composition, which could be detected through ATR-FT-IR spectroscopy. In this case, the ATR-FT-IR of the washed mat showed that more than 95 % of the PVP remained after washing. On the contrary, when a similar treatment was carried out for a **5a**/PVP polymeric film prepared by casting with the same composition, at least 20 % of the PVP was washed out. This confirms that an intimate blending is obtained through electrospinning in contrast with the situation obtained for the material prepared by casting.

Application of the fiber-mats to oil/water separation. In the search of possible applications for the materials here prepared, a series of proof-of-concept studies were carried out to test their oil/water separation capacities. Materials composed by electrospun fibers with selective oil/water absorption have found promising technical applications on separation.³⁹ These initial studies focused on the separation of a 1:1 (v/v) mixture of isopropyl palmitate and water. The separation procedure was performed as shown in ESI. The membrane was fixed between two glass tubes with flanged connections. The liquid mixture was poured into the upper tube and the filtrate was collected on a beaker, using gravity as the only flowing force. For this purpose, the mat **5a**/PVP displayed excellent isopropyl palmitate wettability (OCA = 0°) and a strong hydrophobicity (WCA = 105.3°). When a mixture (2 mL) of oil (isopropyl palmitate) and water (coloured with bromothymol blue) was used, no flow through the membrane was observed (being water the lower phase) until strong magnetic agitation was applied. Under agitation, an emulsion was formed (Fig. S12, ESI) allowing the contact of the formed oil droplets with the membrane. In this case, the oil selectively passed through the membrane and was collected at the container, while water was repelled and kept in the upper glass tube. Water flux of the membrane was obtained by calculating the permeation volume per unit time from the valid area. The membrane **5a**/PVP exhibited a water flux of 17 L h⁻¹ m⁻². These results demonstrate the potential of this kind of membranes for oil/water separations.

Application of the fiber-mats to enzymatic biodiesel production integrating synthesis and separation. Polymeric materials modified with IL-like units are suitable supports for the immobilization of enzymes (e.g. lipases).⁴⁰ These bioactive materials are excellent catalysts, for instance, for biodiesel synthesis. Thus, the use of the electrospun mats in a similar process can be foreseen. Two approaches can be considered, one combine a catalytic phase with the membrane as the separation unit and a second one involves supporting the biocatalyst in the same membrane, integrating in a single unit

and material transformation and separation processes. The separation of the glycerol side product from FAMES is the bottleneck in many processes for biodiesel synthesis. With this idea in mind, the contact angle for glycerol was evaluated for the different membranes (Table 3). The mat formed by **5b**/PVP showed the larger CA (124.7°), while the other hydrophobic mats presented a slightly smaller CA (110° for **2**/PVP, 102.6° for **5a**/PVP and 108.1° **6a**/PVP). As expected, the hydrophilic membranes were wetted by glycerol (**4a**/PVP and **4b**/PVP, CA = 0°). Thus, the membranes showed, in principle, the adequate features to facilitate the separation of biodiesel/water/glycerol mixtures (3/3/1 molar ratio). The mat **5a**/PVP was selected to assay this separation as it provided a good wettability by the oil while being incompatible with both water and glycerol. The oil phase (isopropyl palmitate) was easily separated from the mixture water/glycerol. The absence of glycerol in the oil phase and its presence in the water phase was confirmed by ¹H-MNR of the two separated phases with a recovery of oil and glycerol of > 99 %.

Application of the fiber-mats as supports of MNPs. Both bulk ILs and related polymeric materials have been used for the synthesis and stabilisation of metal nanoparticles MNPs.⁴¹ Among the different methods for the synthesis of MNPs in ILs,⁴² the sputtering-deposition techniques, where gold atoms, knocked out from a gold target cathode by the argon ions, are deposited on an ILs, has been revealed as an interesting alternative for the synthesis of soluble MNPs.

Generally, sputter deposition is a very clean synthesis method, because it does not introduce other chemical species. The nanoparticles prepared by this method were found to be very stable, even in the absence of stabilizing agents, with clean surfaces, being obtained under mild conditions with an easy control of their size and shape by appropriate tuning of the sputtering conditions.^{43,44}

In this vein, the nanostructured films based on PILs, here obtained by electrospinning, were evaluated for the preparation of mats of AuNPs-PILs. Sputter deposition of Au onto the mats was carried out for 120 s with a discharge voltage of 345 V (40mA) and a working pressure of 3 mbar generated by an Ar flow. After the deposition, the chamber was vented with N₂. After sputtering deposition, the films were recovered and further characterized. The change on their colour to purple was the initial indication of the deposition of the gold onto the films surface.

The morphology and composition of the films, after Au-sputtering, was studied by SEM and EDX analyses. Thus, the surface composition obtained by EDX analyses showed the presence of gold in all mats, confirming the successful modification. Regarding the morphology, the film without IL-like units, composed by the mixture **2**/PVP, showed similar continuous, cylindrical, bead-free fibers than the initial material. The mesh of this film had also a similar degree of porosity than the original one (Fig. S2 vs. Fig. S13). However, the average diameter size of fibers was slightly larger (740 vs. 530 nm).

A similar trend was also found for the gold modified mats (**5b**/PVP) obtained by the blend of PVP and a hydrophobic PIL

(5b). Accordingly, the fibers preserved, after modification, the original cylindrical morphology and porosity and again an increase on the fiber diameter size was detected (635 vs 380 nm, Fig. 6b vs. Fig. 2c). The larger increase observed in this case can be attributed to the more important interactions present between the AuNPs and the functionalized polymeric chains forming the mat as both IL-like and pyrrolidone side chain units can interact and stabilize AuNPs.

The mats obtained with PILs with Cl⁻ anion (4a/PVP and 4b/PVP) showed, after modification, an important change in their morphology. The SEM pictures revealed an almost complete loss of the porosity for these two fibers mats (Fig. 6a vs. Fig. 2a and Fig. S5 vs. Fig. S15). The original structure formed by entangled micro-ribbons before modification suffered, upon the gold sputtering, a collapse of the porosity, probably due to a strong increase in the interactions, as considered above between the functionalized polymer and the gold nanoparticles leading to a crosslinking of the fibers.

These results highlight again the close relationship between the nature of the PILs and the morphology of the material obtained opening the opportunity to fine tune morphology by changing the PILs nature.

The size-distribution of the formed AuNPs was obtained by TEM. Films were dispersed in ethanol at 25 °C and then submitted to ultrasonic agitation over 20 min. After this, two drops of the dispersion were placed on a carbon coated copper grid to be analyzed by TEM. Table 4 summarizes the sizes obtained using this methodology (micrographs in Figures S13-S16, ESI). Variations in NPs size between the different gold modified mats were observed. Thus, the smaller AuNPs average size distribution was obtained for the 2/PVP mat

composed by *ca.* 9 % by weight of PVP (4.11 ± 1.02). PVP is well known as polymeric nanoparticle stabiliser. For the films bearing a polymer functionalized with IL-units, the smaller AuNPs were obtained for 5a/PVP providing an average size of 6.96 ± 5.2 nm.

Table 4 Characterization of the polymeric mats after Au-sputtering.

Entry	Pol. Mix.	AuNPs (nm) ^a	Fiber morphology	Size ^b
1	2:PVP	4.11 ± 1.02	fibers	740 ± 109 nm
2	4a:PVP	7.55 ± 2.1	Collapsed ribbons	-
3	4b:PVP	9.40 ± 3.7	Collapsed ribbons	-
5	5a:PVP	6.96 ± 5.2	fibers	635 ± 120 nm

^a size determined by TEM analysis. ^b determined by SEM

The AuNPs obtained for the other PILs mats assayed varied slightly depending of the composition of the film. Thus, the change, in the N-substitution of the PIL, substituting the methyl group for a larger hydrophobic alkyl-chain led to an increase of the gold nanoparticles (9.40 ± 3.7 for 4b/PVP vs. 7.55 ± 2.1 for 4a/PVP). In the same way, for the mats containing PILs bearing Cl⁻ as counter larger particles were always detected. The surface composition of the ILs seemed to be the key factor to control the size of the AuNPs contributing both the polymeric framework itself and the IL-like moieties to the nucleation and stabilization of the gold nanoparticles. Indeed, similar behaviour was observed in neat ILs and hybrid IL/silica materials in which the nature of the anion and the strength of the ionic pair plays a major role on the size of the NPs produced by sputtering deposition.⁴⁵

Fig. 6 SEM images for the electrospun mats formed from polymer blends 4a/PVP after sputtering (a), 5a/PVP after sputtering (b).

The band gap of the AuNPs supported onto the nanostructured film 5a/PVP was estimated by diffuse UV-Vis spectra, using the ratio of absorption to scattering (k/s)² from

the diffuse reflection spectra and applying the Kubelka–Munk equations (Fig. S17).^{46,47} The determination of the band gap energy for the 5a/PVP film exhibited a value at 2.42 eV (513 nm).⁴⁸ This result is in agreement with the size of NPs

measured by TEM (6.96 ± 5.2 nm) and similar to those obtained for related polymeric composites obtained by reduction with an aqueous NaBH_4 .⁴⁹

This preliminary study suggests that by the appropriate selection of the structural parameters of the PILs mats such as fiber morphology and nature of IL-like groups (cation and anion), AuNPs-mats composites with tunable AuNPs size distributions can be obtained by simple gold sputtering deposition. This type of materials can have a wide range of potential applications as catalysts, luminescent probes in biological labeling or in chemical sensing.

Conclusions

Altogether, the experimental evidences obtained in this work suggest that PILs and PVP are able to undergo strong supramolecular interpolymeric interactions between the C=O groups of the PVP and the protons and counter ion of the IL-like units of the PILs that can be mediated by water molecules. Interactions like hydrogen bonding, electrostatic, and hydrophobic interactions can be involved providing homogeneous polymeric blends that facilitate their electrospinning in comparison with pure PILs.⁵⁰ Indeed, it has been reported that by enhancement these interactions low molecular weight polymers or even nonpolymeric species can be electrospun.^{51,52} The differences observed for the solution containing PILs and PVP (e.g. increase on viscosity, conductivity, etc) and for the morphology and performance of the final fibers are related with the nature of these supramolecular interactions. The main differences observed are dictated by the chemical information contained in the molecular structures of the two polymers defining self-complementary interactions and driving the self-organization and self-assembly of the polymers onto well-defined nanostructures assemblies under electrospinning conditions. Thus, the overall properties of the mats obtained can be easily tuned by changing the molecular vectors defining such interactions (also with the help of electrospinning parameters). Preliminary experiments presented here reveal that this approach allows the preparation of materials with a high potential for important applications in a broad range of currently relevant fields.

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Electronic Supplementary Information

Hierarchically structured Polymeric Ionic Liquids and Polyvinylpyrrolidone mat-fibers fabricated by electrospinning

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Electrospinning equipment

Figure S1. Image of the electrospinner Fluidnatek LE 100.V1, BioInicia.

Microscope and SEM images of films

Figure S2. Microscope and SEM images for film 2/PVP.

Figure S3. Microscope and SEM images for film **4a/PVP**.

Figure S4. Microscope and SEM images for film **5a/PVP**.

Figure S5. Microscope and SEM images for film **4b/PVP**.

Figure S6. Microscope and SEM images for film **5b/PVP**.

Figure S7. Microscope and SEM images for film **6a/PVP** (ribbons size 2.03 μm).

Figure S8. Microscope and SEM images for film **PVP** in MeOH (fine fibers size 0.2 μm and big fibers size 0.6 μm).

Viscosity results

Figure S9. Viscosity obtained for the different polymeric mixtures showed in Table 1.

The behavior of the viscosity as a function of shear rate differs for the different mixtures as observed in Figure S9. Thus, the mixture formed by **2/PVP** shows a quasi-newtonian behavior, displaying a minimum change with the shear rate. A partly related curve is observed for **5a/PVP** and **5b/PVP** containing NTf_2^- as the counteranion. In this case, the viscosity values are always significantly higher than those of **2/PVP** and only display a minor decrease with shear rate. A very different pattern is detected, however, for **4a/PVP** and **4b/PVP** containing Cl^- as the counteranion. In this case, the viscosity detected at low shear rates is higher than the one measured for **5a/PVP** and **5b/PVP**, but experiment a sharp decrease with the initial increments in shear rate. This is particularly relevant for **4b/PVP** containing Cl^- as the counteranion and octyl as the N-substitution in the imidazolium fragment, revealing that both coulombic/hydrogen bonding and hydrophobic interactions contribute to this behavior. This suggests the presence of very strong interactions in the mixture through the combination of these two structural elements.

TGA results

Figure S10. TGA obtained for the electrospun mats formed.

DSC results

Figure S11. DSC for the PILs (a) and the different electrospun mats formed (b) (second heating cycle).

Oil/water separation process

Figure S12. Separation of an oil / water emulsion.

SEM and TEM images of AuNPs-films

Figure S13. SEM picture of the film **2/PVP**. TEM images of the AuNPs obtained after dispersing the film **AuNPs-2/PVP** in ethanol at 25 °C and the corresponding histogram and surface composition obtained by EDX analyses over the fibers after sputtering deposition.

Figure S14. SEM picture of the film **4a/PVP**. TEM images of the AuNPs obtained after dispersing film **AuNPs-4a/PVP** in ethanol at 25 °C and the corresponding histogram and surface composition obtained by EDX analyses over the fibers after sputtering deposition.

Figure S15. SEM picture of the film **4b/PVP**. TEM images of the AuNPs obtained after dispersing film **AuNPs-4b/PVP** in ethanol at 25 °C and the corresponding histogram and surface composition obtained by EDX analyses over the fibers after sputtering deposition.

Figure S16. SEM picture of the film **5a/PVP**. TEM images of the AuNPs obtained after dispersing film **AuNPs-5a/PVP** in ethanol at 25 °C and the corresponding histogram and surface composition obtained by EDX analyses over the fibers after sputtering deposition.

Figure S17. Diffuse UV-Vis analysis for the band gap determination of AuNPs supported onto nanostructured films.

Structural characterization of PILs: ^1H -NMR and IR spectra

Figure S18. ^1H -NMR (500 MHz) with peak assignments for **PCIVB-2** (CDCl_3)

Figure S19. ^1H -NMR (500 MHz) with peak assignments for **PIL-4a** (MeOD)

Figure S20. ^1H -NMR (500 MHz) with peak assignments for **PIL-5a** ($\text{DMSO-}d_6$)

Figure S21. ^1H -NMR (500 MHz) with peak assignments for **PIL-4b** ($\text{DMSO-}d_6$)

Figure S22. ¹H-NMR (500 MHz) with peak assignments for **PIL-5b** (DMSO-*d*₆)

Figure S23. ¹H-NMR (500 MHz) with peak assignments for **PIL-6a** (MeOD)

Figure S24. ATR-FT-IR for **PCIVB-2**

Figure S25. ATR-FT-IR for **PIL-4a** (*blue*) and **PIL-5a** (*green*)

Figure S26. ATR-FT-IR for **PIL-4b** (*blue*) and **PIL-5b** (*green*)

Figure S27. ATR-FT-IR for **PIL-6a**

6.4. Conclusiones

- Se han sintetizado y caracterizado membranas poliméricas altamente estructuradas utilizando la técnica de electroestirado a partir de mezclas de diferentes PILs con PVP.
- Los PILs se han obtenido por modificación química de PCIVB sintetizado vía RAFT con diferentes imidazoles seguida de un simple intercambio iónico del anión.
- El estudio de las propiedades de las disoluciones poliméricas basadas en PILs/PVP han permitido determinar la influencia que tienen la viscosidad, la tensión superficial y la conductividad eléctrica durante el proceso de electrospinning así como explicar la morfología y tamaño de las fibras.
- Se ha determinado la morfología de las membranas por SEM y se ha comprobado cómo varía en función de la composición química de los PILs. Así, PILs con anión NTf_2^- en su estructura generan membranas basadas en nanofibras cilíndricas mientras que los PILs con anión Cl^- forman membranas de cintas de tamaño micrométrico.
- Las medidas del WCA han permitido evaluar las propiedades hidrofóbicas/hidrofílicas de las membranas que vienen determinadas por la composición química y su microestructura. Además, los resultados muestran la influencia del anión y la longitud de la cadena alquílica del imidazolio en el valor del WCA. La membrana 5a/PVP es la más hidrofóbica con un WCA de 105.3° .
- Se ha comprobado el efecto del método de preparación de la membrana sobre el WCA observándose que la técnica de electrospinning produce fibras más hidrofóbicas y estructuradas que el proceso de casting.
- Los resultados del estudio por ATR-FT-IR evidencian que los PILs y el PVP experimentan interacciones inter- e intramoleculares así como a nivel supramolecular que definen la autoorganización y las propiedades de las membranas. Las variaciones en la región de la banda C=O del PVP para las diferentes membranas ha proporcionado esta información.

- Los datos obtenidos por DSC confirman el diferente comportamiento de las membranas y el análisis de TGA muestra su contenido en agua que está de acuerdo con los cambios estructurales de los PILs.
- Se ha demostrado la aplicabilidad de las membranas hidrofóbicas en los procesos de separación evaluando la capacidad para separar una mezcla de aceite y agua. Asimismo, muestran posibilidades de aplicación en los procesos de síntesis del biodiesel al ser capaces de separar eficientemente el aceite de la mezcla de glicerol y agua.
- Se ha demostrado que las membranas fibrilares de PILs obtenidas por electroestirado permiten la obtención y estabilización de nano partículas de AuNPs por simple disposición empleando la técnica “*sputtering*”.
- El tamaño de las AuNPs se puede controlar en función de las variables estructurales del PILs.

Chapter 7

**Poly(acrylamide-homocysteine thiolactone)
as a synthetic platform for the preparation
of polymeric ionic liquids by post ring-
opening-orthogonal modifications**

Chapter 7. Poly(acrylamide-homocysteine thiolactone) as a synthetic platform for the preparation of polymeric ionic liquids by post ring-opening-orthogonal modifications

7.1. Resumen del manuscrito

Obtener materiales poliméricos avanzados y funcionalizados con unidades de IL que presenten diferentes morfologías y una gran variedad estructural así como con propiedades modulables es posible en función de las estrategias sintéticas utilizadas.

En los últimos años, la “química click” está adquiriendo una gran importancia en la preparación y modificación de materiales poliméricos debido a la gran flexibilidad que ofrece para unir de forma sencilla, rápida y fiable diferentes fragmentos estructurales. Entre las diferentes reacciones “click” desarrolladas, las reacciones tiol-eno presenta una gran versatilidad.

Así, recientemente en la literatura se han descrito distintas estrategias para la síntesis y modificación de polímeros basados en derivados de tiolactona. Las unidades de tiolactona presentes un polímero o un monómero proporciona la funcionalización adecuada para la introducción ortogonal de diferentes grupos funcionales mediante reacciones de aminólisis y reacciones “click” tiol/alqueno permitiendo el diseño de nuevas arquitecturas poliméricas.

Figura 7.1. Poli(acrilamida homocisteína tiolactona) (PAHT) como plataforma sintética para la obtención de materiales avanzados con diferentes funcionalidades y morfologías.

En este sentido, nuestros esfuerzos en este trabajo, han consistido en la utilización de poli(acrilamida homocisteína tiolactona) (PAHT) como un precursor macromolecular para la obtención de nuevos líquidos iónicos poliméricos (PILs) (Figura 7.1.). Ello ha permitido obtener polímeros tanto lineales como entrecruzados con diferentes morfologías y propiedades fisicoquímicas con posibles aplicaciones en el campo de la ciencia de los materiales tales como catálisis y procesos de separación.

En primer lugar, se llevó a cabo la síntesis del homopolímero PAHT (Figura 7.2.) por polimerización controlada RAFT a partir del monómero correspondiente, fácilmente preparado por reacción entre D,L-homocisteína tiolactona y cloruro de acrilóilo, utilizando CMDTTC (*cyanomethyl dodecyl trithiocarbonate*) como agente de transferencia y AIBN como iniciador. La reacción de polimerización funciona muy bien llegando a conseguir una conversión mayor del 95 % y un índice de polidispersidad (PDI) de 1.58.

Figura 7.2. Síntesis PAHT. i) NaHCO_3 (5 eq.), H_2O /dioxano 1/1, r.t., *overnight*. ii) CMDTTC, AIBN, DMF, 110 °C, 24 h.

Una vez obtenido y caracterizado el polímero, nos hemos centrado en probar diferentes metodologías para su post-funcionalización. La primera de ellas ha consistido en estudiar la apertura del anillo de tiolactona por aminólisis (Figura 7.3.) utilizando diferentes aminas primarias de manera que la liberación del tiol permita su funcionalización a través de reacciones tiol-eno.

Figura 7.3. Reacción de PAHT con diferentes aminas.

En este contexto, se han empleado varias aminas tales como la etanolamina, propilamina, octilamina, 3-dimetilaminopropilamina y aminas primarias conteniendo en su estructura un fragmento de IL basado en imidazolio con Br^- o NTf_2^- como

contraíón. Los cambios estructurales se observaron por FT-IR y también fue posible monitorizar la apertura del anillo por ^1H -RMN.

Los resultados demostraron que la velocidad de reacción es directamente proporcional a la concentración de la amina por lo que ésta es más rápida si se utiliza un exceso. Sin embargo, es posible utilizar cantidades estequiométricas si se adiciona una amina no reactiva como la Et_3N ya que proporciona el medio básico requerido para la apertura del anillo. Además, se ha comprobado que la basicidad de la amina define su reactividad ya que la derivada de IL con NTf_2^- no reacciona con la tiolactona debido a las propiedades estereo-electrónicas por contener un grupo electrón-atrayente por efecto inductivo reduce la nucleofilia y basicidad de la amina reduciendo su reactividad hacia la aminólisis de la tiolactona.

Como ya hemos señalado, la disponibilidad de un grupo tiol libre permite un segundo grado de funcionalización del polímero a través de una reacción tiol-eno. Para ello, después de la apertura del anillo, se adicionaron diferentes acrilatos permitiendo la introducción de funcionalidad adicional en el polímero con excelentes conversiones.

Por tanto, una combinación adecuada de aminas y acrilatos teniendo en cuenta el balance hidrofóbico/hidrofílico conduce a la obtención de polímeros post-modificados con diferentes solubilidades.

Basándose en esta metodología sintética, se pueden utilizar diferentes estrategias para la preparación de PILs. Una consiste en la utilización de aminas funcionalizadas con ILs seguida de la adición de acrilatos para la obtención de PILs solubles con diferente polaridad (Figura 7.4.).

Figura 7.4. Reacción de PAHT con diferentes aminas alquílicas y aminas funcionalizadas con ILs seguida de reacción tiol-eno con varios acrilatos.

La otra alternativa posible consiste en la post-modificación del homopolímero con aminas alquílicas seguida de la reacción del tior con ILs conteniendo en su estructura un fragmento vinílico (Figura 7.5.).

Aunque esta metodología se trata de una ruta sintética eficiente para introducir unidades de IL en la cadena polimérica, se requieren dos pasos de reacción para evitar la reacción de Michael entre la amina y el vinilo del IL.

Figura 7.5. Reacción de PAHT para la obtención de polímeros funcionalizados mediante post-modificación con ILs vinílicos o alílicos.

Para evitar este inconveniente, se decidió estudiar la introducción de las unidades de IL mediante reacción tior-eno fotoinducida entre el tior generado *in-situ* con una N-alkilamina y un IL funcionalizado alílico. Así, como la reacción necesita luz y un fotoiniciador, es posible mezclar ambos reactivos permitiendo una post-modificación en *one-pot*.

Así mismo, también se ha conseguido la preparación de materiales entrecruzados tipo gel (Figura 7.6.) aprovechando la capacidad del grupo tior para formar enlaces S-S. De esta manera, una vez llevada a cabo la apertura del anillo, en ausencia de un reactivo adicional, los grupos SH reaccionan entre sí formando puentes disulfuro intramoleculares lo que permite que las cadenas poliméricas se entrecrucen.

Figura 7.6. Formación de ionogeles a partir de PAHT.

Los resultados sugieren que la basicidad de la amina es clave para la formación del gel y el entrecruzamiento de los SH. Además, el uso de DMSO como disolvente favorece la oxidación para la formación de los puentes disulfuro. El estudio que se realizó consistió en preparar una disolución concentrada formada por el PAHT, una amina funcionalizada con IL y Et_3N en DMSO. En presencia de O_2 y a 70°C , la gelación ocurre en unas 4 horas observándose el aumento de la viscosidad durante el proceso. Esta metodología abre la posibilidad de obtener ionogeles.

Cabe señalar la influencia que ejerce el medio en la reacción, la cual se ve favorecida en disolventes polares apróticos. Esto se ha demostrado llevando a cabo la formación del gel en presencia de aminas con ILs Br^- donde la reacción funciona, mientras que en presencia de aminas con NTf_2^- el gel no se forma al tratarse de un IL apolar.

Por otro lado, una vez formado el gel, éste puede ser disuelto en agua al tratarlo con un agente reductor que permite destruir los puentes disulfuro, se trata de un enlace reversible. Esta nueva clase de materiales avanzados pueden presentar aplicaciones en el campo de la catálisis, como sensores, etc...

Finalmente, se ha conseguido la formación de fibras a partir del PAHT mediante la técnica de electrospinning (Figura 7.7.) siendo posible su post-modificación para la obtención de una variedad de materiales funcionales nanoestructurados. El estudio de su morfología por SEM determinó la presencia de fibras cilíndricas de 900 nm .

Figura 7.7. Esquema representativo del proceso de electrospinning para la preparación de fibras de PAHT.

Estas membranas se modificaron con diferentes aminas y diaminas (Figura 7.8.) observándose cambios en su morfología debido a la asociación y entrecruzamiento de las fibras también por puentes disulfuro además de amida lo que conlleva a una organización más compacta de las mismas y un aumento de su tamaño. Los cambios en la composición y su morfología se determinaron por FT-IR y SEM.

Figura 7.8. Post-modificación gota a gota de la membrana PAHT con diferentes aminas.

Esta estrategia sintética también permite introducir fragmentos de IL en la estructura de la membrana de la misma manera, empleando aminas con fragmentos de IL, lo que permite una doble funcionalización de este tipo de materiales. Por tanto, estas modificaciones conllevan cambios en la solubilidad de las membranas y posibilita el control de sus propiedades hidrofóbicas/hidrofílicas.

Finalmente, podemos concluir diciendo que todos estos resultados han demostrado la versatilidad que posee el PAHT para ser utilizado como plataforma sintética en la obtención de materiales avanzados funcionalizados con diferentes morfologías a partir de varias rutas sintéticas de post-modificación. Por esta razón, pensamos que esta aproximación abre un camino hacia la síntesis de gran variedad de PILs con propiedades controladas y con aplicaciones potenciales en diferentes campos de la ciencia de los materiales.

Poly(acrylamide-homocysteine thiolactone) as a synthetic platform for the preparation of polymeric ionic liquids by post ring-opening-orthogonal modifications

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Poly(Acrylamide-Homocysteine Thiolactone) (PAHT) obtained by RAFT polymerisation can be used as a starting material for the synthesis of a great variety of advanced materials with different morphologies and specific properties obtained by its post modification. The examples here presented illustrate the utility of this approach for the preparation of functionalised polymers containing IL-like units (Polymeric Ionic Liquids, PILs) and how this allows for the synthesis of a plethora of PILs that can be designed and obtained with a careful control of their properties control according to the needs for specific application different fields like materials science, separation or catalysis.

Introduction.

In the last few years, a useful and new synthetic strategy based on the application of so-called “click-chemistry” has emerged as a simple tool for the synthesis and modification of advanced and tailor-made materials.¹ In this context, the development of conjugated polymers associated to the application of the thiol-ene reaction is receiving an increasing attention. The high flexibility of this reaction allows obtaining a large variety of functional polymeric structures through the synthetic manipulation, in many cases, of a reduced number of common simple intermediates.²

The use of thiolactone derivatives has emerged as a suitable latent thiol platform for the development of multifunctional materials.³ The thiolactone ring can be opened by primary amine treatment liberating a thiol that can be utilized for further reactions such as the Michael addition to an electron deficient C-C double bond. Du Prez and others have extensively demonstrated the great potential of polymers bearing homocysteine-thiolactone derivatives for the design of new polymeric architectures.⁴ Two main different strategies have been used for the synthesis of polymers based on thiolactone derivatives. The first one exploits the reactivity of the thiolactone moiety to carry out controlled polycondensation. Thus, polymers are formed through a condensation reaction of the functionalised thioalactone in the presence of an amine, which *in-situ* generates a thiol group able to react further with an additional functionality of the thiolactone derivative.^{5,6,7,8,9} Alternatively, the radical (co)-

polymerisation of vinyl thiolactone derivatives has been exploited leading to polymers bearing thiolactone moieties as functional side-chains.¹⁰ Then, multifunctional substitution patterns can be introduced on demand by a double post-polymerisation modification of the thiolactone moieties. For this purpose, both styrene and *N*-isopropylacrylamide (NIPAAm) based copolymers with thiolactone derivatives have been obtained either by reversible-addition fragmentation chain transfer (RAFT) and nitroxide-mediated radical polymerisation (NMP).^{11,12}

Soluble multifunctional polymers

Gel self-crosslinked functionalised materials

Fibers Mats by electrospinning

Fig. 1. Poly(acrylamide-homocysteine thiolactone) as a polymeric platform for post-modification synthesis of advanced materials with tuneable functionalities and morphologies.

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However, under controlled polymerisation conditions, the homopolymerisation led to a lack of control and/or to low conversions as a result of solubility issues taking place during polymerisation. Therefore, only narrow-disperse copolymers with a limited content of thiolactone have been reported. Examples of homopolymerisation of either acrylic or styrenic thiolactone monomers under controlled radical polymerisation are scarce. Only recently, a thiolactone-functionalised maleimide homopolymer has been reported via free-radical polymerisation using AIBN and a photo-initiator.¹³ Polymeric ionic liquids (PILs) have received increasing attention in the last years as PILs combine the properties of both polymeric materials and ILs in a single system, providing the access to multiple applications in different fields.^{14,15} In order to broaden the scope of metal-free multi-step reactions for the flexible design and synthesis of PILs, here we report the preparation of homopolymers of the acrylamide-homocysteine thiolactone (PAHT, **4**) by reversible addition-fragmentation chain transfer (RAFT). This homopolymer can be used as a macromolecular precursor for the synthesis a variety of new PILs by post-modification procedures. The possibility to obtain these functionalised advanced materials with different morphologies enabling their potential applications in different fields has also been explored.

Results and Discussion.

Synthesis of PAHT by RAFT homopolymerisation. *N*-thiolactone acrylamide (**3**) was prepared in multigram scale by reacting acryloyl chloride (**2**) with *D,L*-homocysteine thiolactone (**1**) (Scheme 1).¹² Our initial attempts to homopolymerise **3** were based on the conditions reported by Du Prez. Accordingly, 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) was used as the chain transfer agent (CTA) and AIBN as the initiator in 1,4-dioxane ($[M]_0/[CTA]/[AIBN] = 150/1/0.095$). Besides, the polymerisation was also assayed using 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTBSPA) and cyanomethyl dodecyl trithiocarbonate (CMDTTC) as alternative CTAs. The reaction mixture was degassed through 3 freeze-thaw cycles and the polymerisation was carried out at 70 °C for 24 hours. At the end of this period, the presence of a precipitate was observed.

The solid obtained was isolated, washed with 1,4-dioxane and analysed. When DDMAT and CMDTTC were used as CTAs, the precipitate corresponded to the desired homopolymer and was isolated in modest yields (28% and 40%, respectively). The ATR-FT-IR spectra showed the disappearance of the band at 1620 cm⁻¹ that is characteristic for vinyl group and a broadening, overlapping and shifting of the bands at 1650-1720 cm⁻¹ associated with the thiolactone group (Fig. S16, ESI). However, when CTBSPA was used, the white precipitate isolated corresponded to the initial monomer. Thus, the low solubility of both the monomer and the homopolymer in 1,4-dioxane led to low yields and to a lack of reproducibility.⁴ Accordingly, the solubility of both systems was evaluated in different solvents and DMF, where homopolymer and

monomer were highly soluble, was selected. In this way, the polymerisation was performed using CMDTTC as CTA and AIBN ($[M]_0/[CTA]/[AIBN] = 100/0.67/0.06$ using DMF solvent. The use of DMF also allowed using a higher polymerisation temperature (110 °C vs 70 °C)(Scheme 1).

Scheme 1 Synthesis of the homo-polymer PAHT (**4**) from *D,L*-homocysteine thiolactone. i) NaHCO₃ (5 equiv.) H₂O/dioxane (1/1) r.t., overnight. ii) AIBN, DMF, 110 °C, 24 h

An appreciable increase on the viscosity of the reaction solution was observed during the polymerisation process as well as a complete absence of any precipitate. After 24 hours, the ¹H-NMR of the reaction crude confirmed that the polymerisation had taken place with a monomer conversion > 95%. The reaction solution was precipitated with cold methanol, purified by re-precipitation from DMF to methanol and finally washed with diethyl ether to afford a solid (85 % yield by weight). The polymer **4**, dissolved in DMF (8 mg/mL) containing 0.1% (w/w) of LiBr, was analyzed by size exclusion chromatography (SEC) showing a molecular weight of M_n of 20.7 kg/mol and a polydispersity (PDI) of 1.582.

Fig. 2 Comparison of the ¹H-NMR for the monomer **3** and the related homopolymer **4** obtained by RAFT polymerisation.

The ¹H-NMR spectrum of the polymer **4** obtained in this way is presented in Fig. 2. The characteristics bands of the amino-thiolactone can be observed as broad signals at 4.8-4.4, 3.4-3.3, 2.5 and 2.0 ppm. Besides, a new broad signal at 1.5 ppm from the aliphatic protons of main chain is also present. The homopolymer **4** was also characterised by TGA and DSC. Two mass losses are observable on the TGA curve (Fig. S19a, ESI). The first one (4.8 %) occurs from 50 to 120 °C and is attributed

to residual solvents loss. The second one takes place from 260 to 585 °C and corresponds to polymer decomposition. The curve has a S-shape without additional curvature suggesting the absence of intermediate decomposition steps, being the polymer thermally stable up to 260 °C. On the other hand, the DSC presents a single glass transition at 195 °C (Fig. S19b, ESI). Once obtained a simple and reliable methodology for the multigram preparation of the homopolymer **4**, the efforts were concentrated in the assay of different methodologies for its post-functionalisation.

Synthesis of multifunctional linear soluble polymers. The thiolactone ring can be opened by aminolysis with primary amines liberating a thiol group, which can undergo a further functionalisation through thiol-ene reactions. Thus, the aminolysis of the polymeric thiolactone **4** using several amines (see Scheme 2 for structures) including ethanolamine (**5a**), *n*-propylamine (**5b**), *n*-octylamine (**5c**) and 1,3-*N,N*-dimethyldiaminopropane (**5d**) was first investigated. Additionally, the reactions with the task specific ionic liquids (TSILs) *N*-(3-aminopropyl)-*N'*-methyl imidazolium bromide ([APMIM][Br], **5e**) and *N*-(3-aminopropyl)-*N'*-methyl imidazolium bis(trifluoromethylsulfonyl)imide ([APMIM][NTf₂], **5f**) containing a primary amine were also assayed.

Fig. 3 Reaction of the homopolymer **4** with different amines monitored by ATR-FT-IR.

The different *n*-alkyl-amines reacted with the homopolymer **4** at room temperature, as reported for similar polymers.⁴ The IR-spectra of the resulting polymers showed the disappearance of the shoulder at 1715 cm⁻¹ associated to the C=O stretching for the thiolactone group and a shift of the amide C=O stretching peak from 1659 cm⁻¹ to lower wavenumbers (1653 cm⁻¹ for **5a**, 1645 cm⁻¹ **5b** and 1651 cm⁻¹ for **5c** and **5d**, Fig. 3).⁹ The reaction could also be monitored by ¹H-NMR following the changes for the signal of the proton attached to the carbon alpha to the carbonyl of the thiolactone and to the NH of the amide in **4** (-CH-(d) in Fig. 2; 4.58 ppm). This signal shifts to higher fields (4.3 ppm) as the thiolactone evolves to the corresponding amide. Other significant changes were observed

for the signals of the NH protons with an additional broadening of the peak at 7.3-8.2 ppm and the appearance of a new amide proton at 8.5 ppm.

Fig. 4 illustrates the kinetic profile obtained for the reaction between **4** and *n*-octylamine (**5c**). When 10 equivalents of **5c** were used, the reaction took place very rapidly, reaching ca. 85 % conversion in less than 16 min, confirming that the reaction of *n*-alkyl-amines with the thiolactone ring of homopolymer **4** is very fast and efficient.

However, under similar conditions and to our disappointment [APMIM][NTf₂] (**5f**) did not react with the thiolactone group of **4**. Stereo-electronic properties of the primary amines are the basis for the relative rate differences observed in the ring opening reaction of thiolactones.⁹ The basicity of the amine defines its reactivity for this reaction and lower pK_a values (pK_a ≈ 8.5) seem not to be favourable.¹⁶ Thus, aliphatic non-functional amines react faster than amines containing an electron-withdrawing group. Thus, it is likely that the presence of the imidazolium moiety tethered the primary amine will reduce its basic/nucleophilic character and its reactivity for the aminolysis of the thiolactone.^{17,18}

Fig. 4 Kinetic profile for the reaction of the homopolymer **4** with *n*-octylamine monitored by ¹H-NMR (DMSO-*d*₆).

It has been reported that when a weaker base is used (e.g. ethanol amine, pK_a = 9) the aminolysis reaction rate can be enhanced by using an excess of amine as the rate is proportional to the concentration of the amine.^{9,16} The addition of a non-reactive amine such as Et₃N may provide the basic media required to facilitate the ring opening reaction with the stoichiometric amount of a less-reactive *n*-alkyl-amine. In order to evaluate this hypothesis, the aminolysis of polymer **4** was carried out with 1.2 equiv. of ethanolamine (**5a**) in the presence of 3 equiv. of Et₃N. In parallel, the same reaction was performed, under the same conditions, but in the absence of Et₃N and using 10 equiv. of **5a**. The progress of both reactions was monitored by ¹H-NMR in DMSO-*d*₆ (Fig. 5). Both conditions provided similar reaction rates with comparable conversions for a similar time scale, confirming the potential of Et₃N for enhancing this process. Accordingly,

the addition of 3 equiv. of Et₃N enabled the aminolysis of **4** with [APMIM][NTf₂] (**5f**) to afford the corresponding polymer **6f** in an excellent 89 % yield.

Fig. 5 Aminolysis profiles for the reaction between the homopolymer **4** and ethanolamine **5a** obtained by ¹H-NMR (DMSO-*d*₆). (I) **4** + 10 equiv. **5a** (squares). (II) **4** + 1.2 equiv. **5a** + 3 equiv. Et₃N (dots).

A second level of functionalisation on the polymer could be obtained by a nucleophilic thiol-ene reaction between the thiols generated through the ring opening of the thiolactone moieties and different acrylates or styrene derivatives (Scheme 2). The reaction was performed using the above-described conditions for thiolactone aminolysis using the homopolymer **4**, 1.1 equivalents of the corresponding amine (**5**) and 3 equivalents of Et₃N for one hour. After this period, 5 equivalents of the corresponding acrylate (**7a-c**) were added to the reaction mixture. The excess of acrylate was required to achieve a full conversion of the thiols and avoid disulfide bond formation that would lead to the crosslinking of the polymeric chains. The reactions were followed by ATR-FT-IR and by ¹H-NMR.

Scheme 2 Reaction of the homopolymer **4** with different amines (**5**) and amine functionalised ILs, followed by the thiol-ene reaction with several acrylates (**7**).

Table 1 summarises the combinations amine/acrylate assayed for the post-modification of **4**. The selecting combinations intended to explore the possibility of adjusting the hydrophobic/hydrophilic nature of the resulting polymers as

well as allowing the introduction of additional functional groups with specific properties (i.e. dimethylamine groups as CO₂-sensitive moieties). In general, excellent conversions were detected for each individual step (>95%) allowing the isolation of the corresponding polymers with moderate to good isolated yields.

The hydrophilicity/hydrophobicity balance of the combined amines and acrylates yielded provided significant changes on the solubility properties of the post-modified polymers **8**. Thus, for instance, when using *N,N*-dimethyl-1,3-diaminopropane (**5d**) and 2-hydroxyethyl methacrylate **7b** the resulting polymer (**8d**) was soluble in organic polar media like ethanol and slightly soluble in water (1 mg/mL), being its solubility thermal and CO₂ sensitive (Fig. S27, ESI) On the other hand, the combination of hydrophobic reagents like **5c** and **7c** can be used to produce polymers soluble in apolar solvents.

Table 1 Polymers (**8**) obtained by post-modification of **4**.^a

Entry	Amine 5	Acrylate 7	Pol. 8	Conv. (%) ^b (aminolysis)	Conv (%) ^b (thiol-ene) ^c	Yield ^c (isol.)
1	5a	7a	8a	99	98	85
2	5b	7b	8b	99	99	89
3	5c	7c	8c	99	98	82
4	5d	7b	8d	99	97	75
6	5e	7b	8e	99	99	55 ^d
7	5f	7b	8f	99	99	50 ^d

^a **4**/Et₃N/**5** (1/3/1.2 molar ratio) in DMF r.t. for 1 hour followed by the addition of 5 mol equivalents of **7**. ^b estimated by ATR-FT-IR and ¹H-NMR of the reaction crude. ^c isolated yield after purification by precipitation. ^d isolated yield after purification by precipitation and dialysis.

Once optimised the above synthetic methodology, different approaches can be envisioned for the preparation of PILs derived from PAHT. Thus, the use of the amine functionalised ILs [APMIM][Br] (**5e**) or [APMIM][NTf₂] (**5f**) followed by the addition of 2-hydroxyethyl methacrylate (**7b**) can provide access to PILs **8e** and **8f**.

Fig. 6 Comparison of the ¹H-NMR spectra for polymer **4** and modified polymer **8f** obtained by post-modification of **4** with **5e** and **7b**.

Once again, the evolution of the reaction could be monitored by ATR-FT-IR. For instance, both polymers showed a C=O band characteristic for aliphatic esters at 1728 and 1725 cm^{-1} for **8e** and **8f** respectively. Besides, when **5f** was used the presence of IL moieties was confirmed by the characteristic peaks of *N*-bistriflimide at 1179 and 1139 cm^{-1} . ^1H -NMR spectra also confirmed the successful modification to obtain the corresponding PILs (**8e** and **8f**). Fig 6 highlights the presence of peaks associated to the introduction of the new moieties in polymer **8e** (e.g. for the IL-like moiety the peaks at 9.17 and 9.6 ppm associated with the protons of the imidazolium ring, at 4.16 and 3.75 ppm for the CH_2 - or at 3.99 ppm for the CH_3 - of the propyl chain).

A possible alternative preparation for the PILs consists of the post-modification of the homopolymer **4** with an *n*-alkyl-amine followed by the reaction of the resulting thiol with an IL bearing a vinyl moiety (Scheme 3). Vinyl based monomeric ILs derivatives can be easily obtained by *N*-alkylation of the imidazole ring with *p*-chlorostyrene.^{19,20} Thus, following this strategy, the homopolymer **4** was reacted with *N*-propylamine (**5b**) in the presence of the Et_3N at r.t. After 1 hour the vinyl IL **9a**¹⁹ was added to the mixture together with AIBN.

Scheme 3 Reaction of the homopolymer **4** to obtain functionalised polymers with IL-like units by post-modification with allyl and vinyl-ILs.

The ^1H -NMR of the polymer **10a** obtained after precipitation in ether and dialysis against MeOH presented the characteristics bands of the IL units, especially the ones corresponding to the imidazolium ring (Figs. S32-S33, ESI). It should be noted that the spectrum for **10a** does not match with the one expected for the product obtained by the direct homopolymerisation of **9a** in the presence of AIBN.

Although this methodology enables an efficient synthetic pathway to introduce IL-like residues on the polymeric main chain, a two steps process is required in order to avoid the

Michael reaction between the amine (e.g. **5b**) and the vinyl moiety of the ILs (e.g. **9a**). Therefore, an alternative synthetic approach was evaluated to introduce the IL-like units by a photo-thiol-ene reaction between the thiol, generated *in-situ* by the aminolysis of **4** with the *N*-alkylamine, and the allylic functionalised ILs (e.g. **9b**) in DMF containing 2,2-dimethoxy-2-phenylacetophenone (DMPAP). The polymer **10b** (see Scheme 3) was isolated (45 % yield) after purification of the reaction mixture by precipitation in diethylether and dialysis against MeOH. The reaction did not proceed in the absence of light or without DMPAP. Thus, this approach allows a multiple post-modification of **4** in a single-pot process. The ^1H -NMR spectra of **10b** clearly showed the expected modification of **4** with the presence of the characteristics bands assignable to the protons of the imidazolium units and the *N*-alkyl residues (Figs. S34-S35, ESI). The same one-pot methodology was also applied to the synthesis of the polymer **10c** (40% isolated yield) by modification of **4** with **5d** and the hydrophilic IL **9c** obtained by reaction between imidazole and allyl bromide (Figs. S36-S37, ESI). Thus, this methodology is suitable for the synthesis of PILs, by the post-modification of **4**, using either hydrophilic or hydrophobic ILs.

Synthesis of self-crosslinked gel-type materials. Disulfide bond formation is a robust mechanism that Nature uses for protein stabilisation. Inspired by this natural phenomenon novel polymers have been developed as smart materials allowing a simple reversible crosslinking involving S-S bonds.²¹ The aminolysis of **4** in presence of an amine leads to a functionalised polymer with thiols as side-chain groups. In the absence of any other reagent, it can be expected that the polymers become crosslinked through the formation of intermolecular disulfide bridges, giving place to the formation of the corresponding gels. To evaluate this possibility, the reaction of **4** (17 % w/v in DMF) with 5 equiv. of different *n*-alkyl-amines was carried out. A strong gelation was observed at different times depending of the amine used. The gelation time was determined visually by inversion vial tests and defined as the time at which the polymer solution does not flow under its own weight when the vial was turn upside-down (Fig. S38, ESI).

Under the assayed conditions, the gelation time showed a strong dependence on the pK_a of the corresponding amine. Noteworthy, the gels were destroyed in the presence of reducing agents, such as di-thiothreitol (DTT) or *tris*(2-carboxyethyl)phosphine (TCEP), confirming the crosslinking via oxidative disulfide formation. After reduction, however, the atmospheric oxygen was able to re-induce the crosslinking.

It should be mentioned that for amines with $\text{pK}_a \leq 9.5$ such as *N,N*-dimethyl-1,3-diaminopropane ($\text{pK}_a = 9.33$) the gelation did not proceed under the same conditions. The gel was not formed even when the concentration of the polymer was increased. These results are in agreement with those reported by Du Prez for copolymers having a high 25-30% loading of thiolactone. In that case, a gel was not formed after reaction with 3-morpholino propylamine even when DMSO, considered as a mild oxidation agent favouring the oxidative disulfide formation, was used as the solvent.²² Thus, these results

suggest that the basicity of the amines is key to determine disulfide crosslinking and gel formation. In this regard, Et₃N could have a positive influence in the gelation as is the case for the aminolysis. To test this, a solution of the polymer **4** (22 % w/v), 1.2 equiv. of *N,N*-dimethyl-1,3-diaminopropane (**5d**) and 3 equiv. of Et₃N in DMSO was prepared. After 24 hours at 80 °C, some increase in the viscosity was observed but a clear gel was not formed. However, when a flow of O₂ was passed through the solution a fast gelation took place at r.t. (Fig. S39, ESI). Thus, this approach allows for the formation of polymeric gels by reaction of the homopolymer **4** with *n*-alkyl-amines, even for those amines displaying low pK_a values.

This polymer gel formation by sulfide bridge formation (S-S) opens the possibility to prepare ionogels using the corresponding amine tethered to an IL fragment. Ionogels represent a new class of advanced materials with a wide range of applications in different fields (e.g. catalysis, energy, sensing, etc.).^{23,24} As a proof of concept, a solution of **4** (15 % w/v in DMSO) was reacted with [APMIM][NTf₂] or [APMIM][Br] in the presence of Et₃N (3 equiv.) and O₂ at 70 °C. For the mixture with [APMIM][Br] an increase in the viscosity of the mixture was gradually observed and finally a gel was formed (Scheme 4).

Scheme 4 Ionogel formation from **4**.

When the more hydrophobic IL [APMIM][NTf₂] was used, an increase in the viscosity of the mixture was also observed, but the system did not evolve to form a gel. It is known that rates for the S-S formation are larger in polar aprotic solvents (DMSO, DMF) than in polar protic solvents (water, methanol). Thus, the use of reaction mixture formed by DMSO and [APMIM][Br] can favour the reaction in comparison with mixture formed by DMSO and apolar non-protic ILs ([APMIM][NTf₂]).

The ionogel **11a** once dried under vacuum led to a rubber type material. The reversible nature of the crosslinking disulfide network also imparts a reversible character to the gel formation. The reduction of the S-S bonds in the presence of a reducing agent such as DTT (Fig. S40, ESI) led to a non-crosslinked polymer soluble in water.

Synthesis of fiber-mats by electrospinning. Finally the development of electrospun polymer fibers was evaluated. These materials are of great interest because of their potential applications in different fields such as filter media,²⁵ energy,²⁶ drug delivery,²⁷ nanosensors,²⁸ tissue engineering²⁹ or

catalysis.³⁰ The possibility of electrospinning the homopolymer **4** provides a simple methodology for the preparation of nanofibers that can be modified by the post-polymerisation methodologies described above to afford a wide variety of nano-structured functional materials. The suitability of the homopolymer **4** for electrospinning was assayed using a solution of **4** in DMF (50% by weight). This concentration was selected because it was the same used for the homopolymerisation of **3**, which could allow considering the direct use of the polymerisation mixture for the electrospinning process without any further purification.

Electrospinning was performed using a horizontal polarised needle and collector (Fig. 7). Once the electrospinning conditions were optimized and stable, mats composed by a dense layer of entangled fibers were obtained and collected on aluminum foil as membranes of ca. 20-15 cm. The morphology of the fibers was analysed by scanning electron microscopy (SEM). The mats showed cylindrical fibers with diameter of ca. 900 nm (Fig. 7a and Fig. S41 ESI).

Fig. 7 Schematic representation of the electrospinning process (1) and post-modification methodology by drop-by-drop casting (2) to obtain mats **13** by modification of mat **4** with **12**. a) SEM picture of the mat obtained from **4** by electrospinning, scale bar 2 μ m.

Once demonstrated the suitability of **4** for the preparation of nanofiber mats, their post-modification was evaluated by adding dropwise a solution containing the corresponding amine onto the fiber mat entanglement and leaving the solvent to evaporate at 50 °C for 12 h (Fig. 7). Several diamines (hexamethylenediamine (**12a**), butylenediamine (**12b**) and ethylenediamine (**12c**)) and one monoamine (*n*-butylamine, **12d**) were assayed for this modification. The morphology of the modified mats (**13a-d**) was studied by SEM, revealing that

the post-modification of the membranes induced changes on their morphology.

In this way, when *n*-butylamine was used, the morphology was preserved but some merging of the fibers took place. Indeed, a larger average diameter (1.458 μm) was observed for **13d** relative to the one measured for fibers from **4** (900 nm) (Fig. S45, ESI). This increase can be associated with the crosslinking of the fibers via S-S bridges. This effect was even more pronounced for the fiber-mats modified with either hexamethylenediamine (**12a**) or butylenediamine (**12b**). The double crosslinking achievable through the formation of diamide and disulfide bridges led fibers to merge onto larger and more entangled arrangements displaying average diameters of 1.239, 2.12 and 1.488 μm for fibers modified with hexamethylenediamine (**12a**), butylenediamine (**12b**) and ethylenediamine (**12c**) respectively (Figs. S42-44, ESI). The fiber treated with butylenediamine (**12b**) also showed the presence of some granular agglomerates on the surface of the fibers (Fig. S43a, ESI). The cross-linking accompanied an entanglement of the fibers and an increase in their diameter seems to depend on the amount of the bisamine used. When 1.5 equivalents of **12b** were used instead of 0.5 equivalents, the modification of the mat led to fibers with a smaller diameter (938 nm), as less crosslinking took place between the fibers, (Fig S43b, ESI). Noteworthy the mats modified with diamines changed their solubility properties, becoming insoluble in DMF, while the mat modified with *n*-butyl amine was still soluble in this solvent.

Fig. 8 Schematic representation of the electrospinning process and post-modification methodology by drop-by-drop casting. SEM pictures of the mat **14** obtained after modification of the polymer mat obtained from **4** with **12b** and **7a**, scale bar 1 μm .

The methodology to produce the double post-functionalisation of the polymer mat obtained with **4** was also assayed. In a first approach the mat was modified with a solution of 1,4-butanediamine (**12b**) (1.5 eq) and methyl-methacrylate (**7a**, 2.5 eq) in MeOH/2-Me-THF (1:1) by drop-by-drop casting 50 $^{\circ}\text{C}$. The ATR-FT-IR spectra of the resulting mat showed a band at 1728 cm^{-1} associated to the C=O of the ester group, the disappearance of C=O stretching of carbonyl group of the thiolactone group and a shift of the amide peak from 1657 cm^{-1} to lower wavenumbers (1640 cm^{-1}). The modification also

affected the morphology of the fibers that showed a larger entanglement (1.35 μm average diameter) (Fig. 8 and Fig. S46, ESI).

Scheme 5 Modification mat **4** to obtain functionalised polymers with IL-like units by post-modification with **12b** and **5f**.

Finally, the synthesis of a PIL-mat (**15**) was assayed by reaction of the electrospun polymer **4** with the amine-functionalised IL **5f** (Scheme 5). Some butylenediamine (**12b**) was also added to provide some crosslinking degree and impart a higher stability to the fibers. The modified polymeric mat became insoluble in DMF and its ATR-FT-IR showed a shift of the amide peak from 1655 cm^{-1} to 1644 cm^{-1} together with the appearance of new peaks assignable to the IL-like moiety (e.g. N-bistriflimide at 1188 and 1146 cm^{-1}). This opens the way to the synthesis of new nanostructured materials from **4** bearing a wide variety of IL-like units.

Conclusions

In summary, the results here presented demonstrate that Poly(Acrylamide-Homocysteine Thiolactone) (PAHT) obtained by RAFT polymerisation is a suitable polymeric platform to develop new orthogonal functionalised materials by simple synthetic post-modification protocols. The synthetic protocols here developed allow not only the introduction of different new functionalities but also to obtain polymers with different morphologies ranging from soluble polymers, gel self-crosslinked materials to polymeric nanofiber mats. The initial examples here provided also demonstrate that they are suitable and simple platforms to synthesise (multi)functionalised polymers including the presence on them of IL-like units to afford new Polymeric Ionic Liquids, PILs. The experiments carried out reveal that this approach will allow the synthesis of a plethora of PILs, allowing a careful control of their properties, which can be of interest for applications in material science, separation, catalysis etc.

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Electronic Supplementary Information

Poly(acrylamide-homocysteine thiolactone) as a synthetic platform for the preparation of polymeric ionic liquids by post ring-opening-orthogonal modifications

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1.1. Chemicals

DL-homocysteine thiolactone hydrochloride, 2-chloropropylamine hydrochloride, 1-methylimidazole, lithium bis(trifluoromethane)sulfonimide, potassium hydroxide, 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTBSPA), cyanomethyl dodecyl trithiocarbonate (CMDTTC), triethylamine, ethanolamine, propylamine, 1-bromobutene, acrylic acid, methyl acrylate, hydroxyethyl methacrylate, chloromethylstyrene, 1,4-dioxane, DMF, DMSO, diethyl ether were purchased from Sigma Aldrich and used without further purification. Magnesium sulfate, sodium chloride, sodium hydrocarbonate were purchased from Riedel-de Haën (Seelze, Germany) and used without further purification. Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich and recrystallized from methanol before use.

1.2. Characterisation methods

Surface morphology of the electrospun films was observed under a scanning electron microscope (SEM) (JEOL 7001F) after platinum coating. The diameter of the fibers was measured on the basis of SEM images. IR spectroscopy was used to monitor the synthesis of the monomers and polymers. The FT-IR spectra were obtained at 4 cm⁻¹ resolution for the 4000 to 600 cm⁻¹ spectral range using a spectrometer (JASCO FT/IR-6200) equipped with an ATR (MIRacle single-reflection ATR diamond/ZnSe) or alternatively a Perkin Elmer Spectrum One P03011. Calorimetry was performed using a differential scanning calorimeter (DSC) (DSC8, Perkin Elmer or alternatively DSC Q2000 TA) in a nitrogen atmosphere at 10 °C/min heating rate. Elemental analyses were obtained with a CHN Euro EA 3000 instrument.

The polymeric mats were obtained using an electrospinner Fluidnatek LE 100.V1 (BioInicia, Spain).

1.3. Synthetic protocols

Synthesis of acryl homocysteine thiolactone (3).

Sodium hydrocarbonate (19.15 g, 227.9 mmol) were slowly added to an ice-cooled solution of DL-homocysteine thiolactone hydrochloride (**1**, 7.0 g, 45.6 mmol) in a 1:1 mixture of water/dioxane (100 mL). The resulting mixture was stirred for 30 min at 0 °C. After this, acryloyl chloride (**2**, 8.3 g, 91.2 mmol) was added to the mixture in several portions. The reaction mixture was allowed to reach room temperature overnight. Brine (100 mL) was added and the mixture was extracted with ethyl acetate

(3x200 mL). The organic fractions were dried with magnesium sulphate and the solvent vacuum concentrated. The crude residue was purified by column chromatography (silica gel, gradient elution 100 % CH₂Cl₂ followed by CH₂Cl₂:acetone 95:5). Yield – 80 %.

¹H NMR (500 MHz, DMSO-d₆, ppm) δ 8.45 (*d*, 1H), 6.23 (*dd*, 1H), 6.12 (*dd*, 1H), 5.65 (*dd*, 1H), 4.70 (*ddd*, 1H), 3.42 (*dt*, 1H), 3.30 (*ddd*, 1H), 2.44 (*m*, 1H), 2.09 (*m*, 1H).

¹³C NMR (125 MHz, DMSO-d₆, ppm) δ 205 (C=O), 131.0 (CH), 126.2 (CH₂), 58.2 (CH), 30.3 (CH₂), 26.8 (CH₂).

Synthesis of *N*-(3-aminopropyl)-*N'*-methyl imidazolium bromide ([APMIM][Br], 5e), 1-Methylimidazole (15 mL, 186 mmol) and 3-bromopropylamine hydrobromide (13.8 g, 61.8 mmol) were dissolved in toluene (23 mL). The mixture was refluxed for 4 hours under constant stirring. On completion, the solution was cooled down to room temperature and the toluene layer was decanted. The crude oil obtained was washed with diethyl ether (3x40 mL) and recrystallised in methanol and methyl *t*-butyl ether obtaining a white solid dried *in vacuo*. Yield 56 %. ¹H NMR (300 MHz, DMSO) δ 9.24 (*s*, 1H), 7.98 (*s*, 3H), 7.83 (*s*, 1H), 7.75 (*s*, 1H), 4.32 (*t*, *J* = 6.9 Hz, 2H), 3.86 (*s*, 3H), 2.88 – 2.76 (*m*, *J* = 7.3 Hz, 2H), 2.19 – 2.05 (*m*, 2H). ¹³C NMR (300 MHz, DMSO): (δ, ppm) 136.6, 123.6, 122.0, 45.8, 35.9, 35.5, 27.4. IR (ATR): (ν, cm⁻¹) 661, 737, 785, 844, 870, 1013, 1054, 1174, 1340, 1381, 1397, 1416, 1441, 1458, 1521, 1544, 1560, 1577, 2511, 2530, 2651, 2749, 2813, 2924, 3041, 3075, 3142, 3422.

Figure S1. ^1H -RMN of 5e.

Figure S2. ^{13}C -RMN of **5e**.

Figure S3. ATR-FT-IR of **5e**.

Synthesis of *N*-(3-aminopropyl)-*N'*-methyl imidazolium bis(trifluoromethylsulfonyl)imide ([APMIM][NTf₂], 5f)

N-(3-aminopropyl)-*N'*-methyl imidazolium bromide (5 g, 16.6 mmol) was dissolved in water (10 mL), the pH of the mixture was adjusted with potassium hydroxide to 8.0 and the mixture was left under stirring for 30 min. Lithium bistriflimide (5.8 g, 20 mmol) was added and the reaction allowed proceeding overnight at room temperature. The obtained crude oil was washed with diethyl ether (3x25 mL) and dried *in vacuo*. The final pure product was a light yellow viscous liquid. Yield – 82 %. ¹H NMR (500 MHz, DMSO) δ 9.09 (s, 1H), 7.75 (s, 1H), 7.69 (s, 1H), 4.23 (t, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 2.55 – 2.51 (m, *J* = 10.7, 4.1 Hz, 2H), 1.87 – 1.80 (m, 2H). ¹³C NMR (500 MHz, DMSO): (δ, ppm) 136.7, 123.7, 122.2, 46.1, 36.2, 35.8, 28.6. IR (ATR): (ν, cm⁻¹) 740, 762, 790, 838, 1051, 1132, 1178, 1328, 1347, 1463, 1574, 1601, 2886, 2962, 3120, 3159, 3305, 3370, 3601.

Figure S4. ¹H-RMN of 5f.

Figure S5. ^{13}C -RMN of **5f**.

Figure S6. ATR-FT-IR of **5f**.

Synthesis of 3-allyl-1-methylimidazolium bromide (9c). A mixture of 1-methylimidazole (14.0 mmol, 1.127 mL) and allyl bromide (14.0 mmol, 1.249 mL) in 10 mL of ethanol was stirred during 24 h at reflux. Then the reaction was cooled at room temperature and the solvent evaporated under reduced pressure. The resulting oil was washed with Et₂O (3×10 mL) affording 3.32 g of **9c** as a yellow oil (86 %). ¹H-NMR (CDCl₃, 500.13 MHz): δ 10.32 (s, 1H), 7.47 (s, 1H), 7.36 (s, 1H), 6.03 (ddt, J = 16.6, 10.1, 6.4 Hz, 1H), 5.52-5.41 (m, 2H), 4.12 (c, 3H) ppm. ¹³C-NMR (CDCl₃, 75.5 MHz): δ 137.1, 129.9, 123.9, 122.5, 122.0, 52.0, 36.8 ppm. IR (ATR): (ν, cm⁻¹) 3414, 3137, 3068, 2851, 1574, 1162, 757. Melting point: - 48.98°C. MS (ESI⁺, m/z): 83.4 [M-(C₃H₅)+H, 5%], 123.4 [(M⁺, 100%].

Figure S7. ¹H-RMN of **9c**.

Figure S8. ^{13}C -RMN of **9c**.

Figure S9. ATR-FT-IR spectra of **9c**.

Synthesis of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide. A mixture of 1-butylimidazole (9.9 mmol, 1.3 mL) and 4-bromo-1-butene (9.9 mmol, 1.0 mL) in 15 mL of ethanol was stirred during 24 h at reflux under nitrogen atmosphere. Then the reaction was cooled at room temperature and the solvent evaporated under reduced pressure. The resulting oil was washed with Et₂O (3×10 mL) affording 2.05 g of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide as a brown viscous liquid (79 %). ¹H-NMR (CDCl₃, 300.13 MHz): δ 10.51 (s, 1H), 7.42 (s, 1H), 7.35 (s, 1H), 5.88-5.75 (m, 1H), 5.11-5.02 (m, 2H), 4.49 (t, J = 6.8 Hz, 2H), 4.33 (t, J = 7.3 Hz, 2H), 2.68 (q, J = 6.8 Hz, 2H), 1.95-1.82 (m, 2H), 1.43-1.26 (m, 2H), 0.94 (td, J = 7.3, 4.9 Hz, 3H) ppm. ¹³C-NMR (CDCl₃, 75.5 MHz): δ 136.5, 132.3, 122.4, 122.0, 119.2, 49.5, 48.8, 34.3, 31.9, 19.1, 13.2 ppm. IR (ATR): (ν, cm⁻¹) 643, 754, 865, 920, 997, 1027, 1114, 1162, 1336, 1361, 1457, 1560, 1640, 2872, 2934, 2959, 3072, 3132, 3408.

Figure S10. ^1H -RMN of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide.

Figure S11. ^{13}C -RMN of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide.

Figure S12. ATR-FT-IR spectra of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide.

Synthesis of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bis((trifluoro methyl) sulfonyl)amide (9b). To a solution of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide (1.06 g, 3.8 mmol) in MeOH (3 mL) was added a mixture of lithium bis(trifluoromethane) sulfonimide (1.22 g, 4.2 mmol) in Milli-Q H₂O (1 mL), and the resulting solution was stirred for 24 h at room temperature. Then the MeOH was evaporated at reduced pressure and CHCl₃ (5 mL) was added to the mixture and the solution washed with Milli-Q H₂O (3×10 mL). The organic phase was dried over Na₂SO₄ and the solvent evaporated under reduced pressure affording 1.27 g of **9b** as a pale brown liquid (73 %).

¹H-NMR (CDCl₃, 300.13 MHz): δ 8.66 (s, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 5.30-5.20 (m, 1H), 4.58-4.49 (m, 2H), 3.76 (t, J = 6.8 Hz, 2H), 3.66 (t, J = 7.1 Hz, 2H), 2.10-2.04 (m, 2H), 1.31-1.22 (m, 2H), 0.78-0.69 (m, 2H), 0.40 (t, J = 7.3 Hz, 3H) ppm. ¹³C-NMR (CDCl₃, 75.5 MHz): δ 135.4, 132.1, 122.6, 122.4, 119.7, 49.9, 49.3, 34.3, 32.0, 19.3, 13.2 ppm. IR (ATR): (ν , cm⁻¹) 604, 616, 651, 739, 788, 850, 929, 997, 1052, 1134, 1181, 1226, 1330, 1348, 1463, 1563, 2878, 2938, 2965, 3091, 3115, 3149.

Figure S13. ¹H-NMR of **9b**.

Figure S14. ^{13}C -RMN of **9b**.

Figure S15. ATR-FT-IR spectra of **9b**.

Synthesis of Poly (acryloyl homocysteine thiolactone) (4). Acrylhomocysteine thiolactone **3** (171 mg, 1 mmol), CTA (6.6 μ mol) and AIBN (0.1 mg, 0.6 μ mol) were dissolved in 1,4-dioxane. The mixture was degassed through 3 freeze-thaw cycles. The reaction was allowed to proceed for 24 hours at 70 °C. The precipitate (if formed) was filtered, washed with 1,4-dioxane and dried *in vacuo*. If any precipitate is not formed, the product was purified by reprecipitation from 1,4-dioxane to methanol and washed with diethyl ether.

Modified procedure of poly(acryloyl homocysteine thiolactone) 4 synthesis. Acrylhomocysteine thiolactone **3** (171 mg, 1 mmol), CMDTTC (2.12 mg, 6.6 μ mol), AIBN (0.1 mg, 0.6 μ mol) were dissolved in DMF. The mixture was degassed through 3 freeze-thaw cycles. The reaction was allowed to proceed for 24 hours at 110 °C. The polymerisation was stopped by freezing the mixture in liquid nitrogen. The product was precipitated in methanol, purified by reprecipitation from DMF to methanol and washed with diethyl ether. Yield of crude product: 85-90 %.

¹H NMR (500 MHz, DMSO-d₆, ppm) δ 7.21-8.25 (*br. m*, 1H), 7.58 (*br. d?*, 1H), 3.40 (*br. d*, 2H), 2.47 (*br. s*, 1H), 2.11 (*br. s*, 2H), 1.52 (*br. d*, 2H).

¹³C NMR (500 MHz, DMSO-d₆, ppm) δ 206.4 (C), 174.3 (C), 58.9 (CH), 41.5 (CH), 36.0 (CH₂), 30.3 (CH₂), 27.2 (CH₂).

Synthesis of self-crosslinked gel 11b. Polymer **4** (103 mg), IL **5e** (210.7 mg, 1.2 equiv.) and Et₃N (340 μ L, 4.2 equiv.) were dissolved in DMSO (650 μ L). The reaction mixture was bubbled up with O₂ and allowed to proceed at 70 °C for 4 hours. During the reaction an increase on the viscosity was observed and finally a transparent gel was formed.

Procedure of cleavage of disulfide bonds in 11b. **11b** (25 mg) was stirred in distilled water (3 mL) together with DTT (14 mg, 0.09 mmol) for 24 h at room temperature until the insoluble network was completely dissolved.

1.4. Structural characterisation of polymeric materials: ^1H -NMR and IR spectra and SEM pictures

Figure S16. ATR-FT-IR spectra of monomer (a) and products of polymerisation with DDMAT (b) and CMDTTC (c) as a RAFT agent.

Figure S17. ^1H - ^{13}C HSQC spectra of PAHT.

In order to prove the assignment for **He** and to check if the doublet at 4.75 ppm belongs to a single proton, a phase-sensitive HSQC experiment was carried out. The broad peak of **Ha+Hb** at 1.2-1.6 ppm shows a weak correlation with **Ca** at 36.05 ppm because of the significant broadening on the ^{13}C NMR spectrum. Correlation for **Cb** and **Hb** was detected at 2.1 ppm and 41.57 ppm overlapped with one of the **He** signals. It is clear from PS-HSQC that peak at 4.75 ppm corresponds to one proton.

Muestra	Mn (Da)	Mw (Da)	Polydispersity (MW/Mn)	Volumen de retención (min)
SM_4P97	20669 Da	32709 Da	1,582	17,616

Figure S18. Size exclusion chromatography obtained for **4** in DMF (8 mg/mL) and 0.1% (w/w) of LiBr.

Figure S19. a: TGA obtained from 25 to 600 °C. for **4**. b: DSC obtained for **4** between 195 and 200 °C.

Figure S20. ATR-FT-IR spectrum for polymer **8a** obtained by post-modification of **4** with **5a** and **7a**.

Figure S21. Comparison of the ^1H -NMR for polymer **4** and modified polymer **8b** obtained by post-modification with **5b** and **7b**.

Figure S22. ATR-FT-IR spectrum for polymer **8b** obtained by post-modification of **4** with **5b** and **7b**.

Figure S23. Comparison of the ¹H-NMR for polymer **4** and modified polymer **8c** obtained by post-modification with **5c** and **7c**.

Figure S24. ATR-FT-IR spectrum for polymer **8c** obtained by post-modification of **4** with **5c** and **7c**.

Figure S25. Comparison of the ^1H -NMR for polymer **4** and modified polymer **8d** obtained by post-modification with **5d** and **7b**.

Figure S26. ATR-FT-IR spectrum for polymer **8d** obtained by post-modification of **4** with **5d** and **7b**.

Figure S27. Thermal and CO_2 sensitive behaviour in water of the polymer **8d** obtained by post-modification of **4** with **5d** and **7b**.

Figure S28. Comparison of the ^1H -NMR for polymer **4** and modified polymer **8e** obtained by post-modification with **5e** and **7b**.

Figure S29. ATR-FT-IR spectrum for polymer **8e** obtained by post-modification of **4** with **5e** and **7b**.

Figure S30. Comparison of the ¹H-NMR for polymer **4** and modified polymer **8f** obtained by post-modification with **5f** and **7b**.

Figure S31. ATR-FT-IR spectrum for polymer **8f** obtained by post-modification of **4** with **5f** and **7b**.

Figure S32. Comparison of the ^1H -NMR for polymer **10a** obtained by post-modification with **5b** and **9a** with polymer **4** and the homopolymer obtained by polymerisation of **9a**.

Figure S33. ATR-FT-IR spectrum for polymer **10a** obtained by post-modification of **4** with **5b** and **9a**.

Figure S34. Comparison of the ¹H-NMR for polymer **10b** obtained by post-modification of **4** with **5d** and **9b**.

Figure S35. ATR-FT-IR spectrum for polymer **10b** obtained by post-modification of **4** with **5d** and **9b**.

Figure S36. Comparison of the ¹H-NMR for polymer **10c** obtained by post-modification of **4** with **5d** and **9c**.

Figure S37. ATR-FT-IR spectrum for polymer **10c** obtained by post-modification of **4** with **5d** and **9c**.

Figure S38. Gel formation with different *n*-alkyl-amines and dependence of gelation time on pKa.

Figure S39. Gel formation procedure to prepare ionogels using amines functionalised with ILs.

Figure S40. Destruction of the gel through the reduction of the S-S bonds using DTT or TCEP.

Electrospinning process

The electrospinner used in this study was a Fluidnatek LE 100.V1 (Biolnacia, Spain). The polymer solutions were loaded into a plastic syringe equipped with a stainless steel needle tip (0.9 mm inner diameter). The tip-collector working distance was fixed at 16 cm. The applied voltage was kept between +12, -5 kV and the flow rate at 1.5 mL/h. The electrospun fibers were collected on aluminum foil that covered a rotating collector. All electrospinning experiments were carried out at room temperature and relative humidity of 36 %. The obtained membranes were vacuum dried overnight in the oven at 50 °C.

Figure S41. SEM pictures of the mat polymer fibers obtained by electrospinning of 50 % weight solution of **4** in DMF. **Electrospinning conditions:** J = 5 mL, d = 12 mm, A = 16 cm, c = 1.5 mL/h, V = +12, -5 kV Vol = 5 mL and Sweep = 200-230 mm. **Mean size diameter of the fibers:** 900nm.

Figure S42. SEM pictures of the mat polymer fibers **13a** obtained by post-modification of **4** with hexamethylenediamine (**12a**). **Mean size diameter of the fibers:** 1.239 μm .

Figure S43. SEM pictures of the mat polymer fibers **13b** obtained by post-modification of **4** with butylenediamine (**12b**). a) using 0.5 equiv. of **12b** **Mean size diameter of the fibers:** 2.12 µm b) using for 1.5 equiv. of **12b**. **Mean size diameter of the fibers:** 938 nm.

Figure S44. SEM pictures of the mat polymer fibers **13c** obtained by post-modification of **4** with ethylenediamine (**12c**). **Mean size diameter of the fibers:** 1.488 μm .

Figure S45. SEM pictures of the mat polymer fibers **13d** obtained by post-modification of **4** with n-butylamine, **12d**. a) using 0.5 equiv. of **12d** Mean size diameter of the fibers: 1.458 μm b) using for 1.5 eq of **12d**. Mean size diameter of the fibers: 990 nm.

Figure S46. SEM pictures of the mat **14** obtained after modification of the polymer mat **4** with **12b** and **7a**. Mean size diameter of the fibers: 1.35 μm .

Figure S47. ATR-FT-IR spectra for fiber mat **14** obtained by post-modification **7a** and **12b**.

7.4. Conclusiones

- Se ha sintetizado PAHT por polimerización controlada RAFT consiguiendo buenas conversiones y PDI. Este homopolímero ha demostrado ser un precursor macromolecular para la preparación de nuevos PILs a partir de su post-funcionalización.
- Se han obtenido polímeros lineales con diferentes solubilidades mediante la apertura del anillo de tiolactona por aminólisis empleando aminas funcionalizadas seguida de una reacción tiol-eno por la adición de un acrilato. La combinación adecuada de aminas y acrilatos teniendo en cuenta el balance hidrofóbico/hidrofílico permite controlar la polaridad de los PILs.
- La introducción de funcionalización en el polímero también se ha conseguido mediante reacción tiol-eno fotoinducida entre el tiol generado *in-situ* con una N-alquilamina y un IL funcionalizado alílico permitiendo una post-modificación en *one-pot*.
- Se han preparado materiales entrecruzados tipo gel (ionogeles) a partir de la formación de puentes disulfuro intramoleculares. Los resultados sugieren que la basicidad de la amina y el empleo de disolventes polares apróticos son clave para la formación del gel y el entrecruzamiento de los SH.
- El tratamiento del gel con un agente reductor conduce a su destrucción demostrando el carácter reversible del enlace S-S.
- Se ha conseguido la formación de fibras a partir del PAHT mediante la técnica de electrospinning siendo posible su post-modificación para la obtención de una gran variedad de materiales funcionales nanoestructurados. La morfología, determinada por SEM, se basa en fibras cilíndricas de 900 nm.
- La modificación de las membranas con diferentes aminas y diaminas provoca la asociación y el entrecruzamiento de las fibras por puentes disulfuro lo que conlleva a una organización más compacta y un aumento de su tamaño cambiando así su morfología.

- Se han funcionalizado las membranas empleando aminos con fragmentos de IL. Estas modificaciones conllevan cambios en su solubilidad y posibilitan el control de sus propiedades hidrofóbicas/hidrofílicas.
- Los resultados han demostrado la versatilidad que posee el PAHT para ser utilizado como plataforma sintética en la obtención de materiales avanzados funcionalizados con diferentes morfologías.

Chapter 8

Final conclusions

Chapter 8. Final conclusions

During the presentation of the results through the text of this thesis, the main conclusions for the different chapters have been presented. Therefore, in this section only the most relevant conclusions are highlighted.

- Both **batch and flow conditions** can be used to obtain **poly(*p*-vinylbenzylchloride)** (poly(VBC)) under controlled conditions. The batch processes led to **high molecular weight** polymers (> 10 kg/mol) with low polydispersity, while polymers with **low molecular weight** (< 2 kg/mol) can be obtained, under controlled polymerisation condition, using a **continuous flow set-up**.
- **Multifunctional crosslinked PILs** can be prepared by **RAFT copolymerisation between poly(VBC) and DVB**, where the soluble polymer acts as structural element and macromolecular transfer agent. These materials can be modified by reaction with *n*-alkyl imidazole to generate the corresponding polymeric IL-like phase. Alternatively, this type of materials can also be **obtained by reaction of poly(VBC) with bis-imidazole**. A controlled phase separation occurring during the reaction between the soluble polymer and reactive units led to the corresponding insoluble crosslinked material, this **only happened when polymers with low molecular weight** (< 2 kg/mol) were used. Thus, polymers poly(VBC) prepared by RAFT under flow conditions are suitable for the crosslinked PILs preparation.
- The multifunctional crosslinked PILs behaved as **organocatalyst for the Knoevenagel** condensation being also suitable for the synthesis and stabilisation of metal nanoparticles opening the possibility of the **development of multicatalytic heterogeneous systems**.
- The **different methodologies** employed in the synthesis of **AuNP-PIL composites** have demonstrated the ability to **control their self-assembly** and self-organisation as well as the **development** of controllable **multicatalytic nanoreactors**. The **characterisation** of these compounds suggests that the **appropriate self-organisation** of the building blocks during the synthesis can **provide optimal microenvironments for each catalytic reaction** since their architecture determines the diffusion. The **nanostructure effect** of AuNPs-PILs composites was **evaluated** in their

catalytic activities in the **p-nitrophenol reduction** and as multicycatalytic nanoreactor in a **cascade reaction** (Knoevenagel condensation + reduction). The **catalytic efficiency** found is not only due to the presence of different **catalytic motifs** but a result of their **hierarchical organisation**, which leads the reaction progress.

- A **new class of CPILs** has been synthesised by chemical modification of the poly(VBC) linear polymer prepared by RAFT polymerisation using chiral imidazolium salts. The **right self-assembly** of the IL-like units generates a high-order supramolecular structure which provide polymers with a **thermoresponsive behaviour** and has been studied by UV-Vis, CD and NMR. This **reversible phenomenon** is affected by the CPIL **concentration** and it is associated with **inter- and intramolecular interactions** of the polymeric structure. It has been demonstrated the ability to **control** the LCST through the different **structural vectors of the CILs** (nature of the amino acid, amide substitution and nature of the counteranion), they can be easily modified to fine **tune** their **LCST performance**. The presence of additional groups in the polymer has allowed to **transfer this property** to 3D-hierarchical structures such as **AuNPs-CPILs composites**.
- Highly **structured polymeric membranes** based on PIL/PVP have been synthesised by **electrospinning**. The **chemical structure** of both polymers and their **supramolecular intermolecular interactions** define the **self-assembly** and the **properties** of these nanostructured systems. The **morphologies** and hydrophobic/hydrophilic **properties** of the mats can be **tuned** by changing the **molecular vectors of PILs** defining such interactions. It has been demonstrated their potential **applications** in different fields such as **separation processes** and as nanostructured **supports** for stabilisation of **MNPs** by **sputtering deposition**.
- **Poly(acrylamide homocysteine thiolactone)** (PAHT) obtained by RAFT polymerisation is a **suitable platform** to develop new orthogonal **functionalised materials** by simple synthetic post-modification protocols. The different **post-functionalisation strategies** are based on the combination of aminolysis with thiol-ene reactions or disulfide bond formation. The results have demonstrated the **versatility** of PAHT to prepare polymers with different **morphologies** ranging from soluble polymers, gel self-

crosslinked materials to polymeric nanofiber mats. This approach will allow the **synthesis of plethora of PILs** with controllable properties and which can be of interest for **applications** in material science, separation, catalysis, etc...

“One never notices what has been done; one can only see what remains to be done.”

Marie Curie