2. Scope and objectives of the thesis

Although in recent years several reports have appeared about the copolymerization of styrene and carbon monoxide catalyzed by palladium(II) complexes, in comparison to the CO/ethene copolymerization or other catalytic processes, relatively few ligands have been discussed. In fact most of the reports deal with the optimization of reaction conditions or the mechanistic investigations of well-known catalytic systems. Therefore, the search for new ligands for this reaction, which would enlarge the scope of effective catalysts, seemed an attractive proposition.

The electronic and steric properties that ligands require for making active palladium catalysts for CO/styrene copolymerization have not been disclosed. In fact we found that there is a gap between the structure of the different ligands, which have been successfully reported, and the behavior of the palladium catalysts formed with those ligands. Therefore we decided to perform systematic studies on the effects of chelating ligands in the CO/styrene copolymerization reaction. Some of the ligands used in this work have been previously reported, while others have been designed and synthesized with this purpose. The modular design of the latter allowed systematic variations. The study of the coordination of these ligands to palladium, in solution and when possible in the solid state, enabled us to analyze how these modifications affect both the structure of the organometallic complexes and the activity of the copolymerization catalysts.

In *Chapter 3* sulfur donating ligands, bis-(thio)ethers, are used to synthesize new palladium(II) complexes. Bis-(alkylthio)ethers have been briefly reported previously for CO/styrene copolymerization. The ligands presented in this chapter were chosen from various sulfur ligands known for other catalytic processes and have different chelating ring sizes, and steric and electronic properties. The different behavior of the catalysts under copolymerization conditions as well as the influence of the sulfur ligand on the copolymer microstructure is analyzed.

In *Chapter 4* several nitrogen-donating bidentate ligands, containing the pyrazol fragment, are studied as chelating ligands for palladium(II) complexes. The effects of the various electronic and steric properties of the ligands are analyzed both in the coordination to palladium as well as in the activity of the catalysts in the copolymerization reaction. The stability of the complexes enabled their behavior to be studied over time.

Chapter 5 discusses the design and synthesis of a new group of bisnitrogen chiral ligands derived from imidazolines. The electronic properties of the series of synthesized ligands vary systematically. The structure of the palladium complexes that contain the various ligands is investigated in solution and, in some cases, in the solid state. The effect that the ligands have on the copolymerization reaction of *tert*-butylstyrene with CO is studied. The polyketones obtained with these catalysts are analyzed and their properties rationalized with the ligands used. The reactivity of the palladium catalysts with carbon monoxide is monitored by *in-situ* ^{1}H and ^{13}C NMR spectroscopy and the intermediates are determined.

Chapter 6 deals with the application of some of the new palladium catalysts, presented in the previous chapters, to the terpolymerization of *tert*-butylstyrene and ethene with carbon monoxide. A detailed investigation of the parameters that affect both productivity and the amount of the two olefins incorporated in the terpolymer chain is presented.