

Structure of poly(hexamethylene sebacate)

E. Armelin, M.T. Casas, J. Puiggali*

Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, Av. Diagonal 647, E-08028, Barcelona, Spain

Received 13 September 2000; received in revised form 9 November 2000; accepted 4 January 2001

Abstract

The crystalline structure of poly(hexamethylene sebacate) has been studied using transmission electron microscopy and X-ray diffraction. Molecular chains adopt a slightly distorted all-*trans* conformation and pack in a Monoclinic unit cell with space group $P12_1/n1$. The unit cell contains two chain segments, with a chain setting angle similar to that reported for polyethylene. Similar results were obtained from energy calculations that took into account both van der Waals and electrostatic interactions. Sectorized lamellar crystals were observed by decoration with polyethylene. Different folds involving methylene or ester groups exist at the lamellar surface depending of the growth sector. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyester; Structure; Molecular packing

1. Introduction

Interest in aliphatic polyesters derived from diols and diacids is nowadays increasing due to their expected degradable properties. Furthermore, the use of new catalysts and coupling reactions increased the molecular weights and improved the mechanical properties of polymers that were initially obtained following the polycondensation reaction reported by Carothers [1]. Thus, biodegradable polymers constituted by adipic acid and/or succinic acid, and ethylene glycol and/or 1,4-butanediol are commercialized under the trademark of BIONOLLE (Showa Highpolymer Co.) with molecular weights in the range 10^5 – 10^8 and good processability [2].

X-ray diffraction studies have demonstrated that the conformation of this kind of aliphatic polyesters depends on the methylene content of both diacid and diol units. A departure from the all-*trans* conformation towards a twisted conformation is characteristic of polymers with low methylene content such as those derived from ethylene glycol, 1,4-butanediol, succinic acid and adipic acid. In this way, gauche bonds have been deduced from X-ray analysis [3–5] and/or energy minimizations [6] for 2-4, 2-6, 2-8, 4-4, 4-6 and 6-6 polyesters. In the same sense, quantum mechanical calculations on small diesters [7] showed the tendency of the methylene units to adopt gauche conformations when a short aliphatic segment is placed between two carbonyl

groups. On the other hand, an almost extended conformation was found for the 6-10 polyester [8]. Although, unit cell parameters have been given for a large number of polyesters [9], a detailed structure refinement has only been reported in a few cases.

Nowadays, our research is focused to the study of poly(ester amide)s such as those derived from hexanediol, sebacic acid and different amino acids [10]. In this work, we undertook the packing analysis of the related 6-10 polyester for comparative purposes.

2. Experimental

6-10 polyester was synthesized from sebacic acid and an excess of 1,6-hexanediol (molar ratio 2.2/1) by thermal polycondensation in vacuum at 200°C and using titanium butoxyde as catalyst. An intrinsic viscosity of 1.0 dl/g was measured in dichloroacetic acid at 25°C. This value demonstrated a high molecular weight as suggested by the film- and fibre-forming characteristics of the polymer. Density of fibres was measured at 25°C by the flotation method in mixtures of ethanol and CCl_4 . Isothermal crystallization was carried out from dilute solutions (0.01% w/v) in 1-hexanol. The polymers were dissolved at 55°C and the solutions were transferred to constant temperature baths at 45°C for 12 h. These conditions were similar to that reported by Kanamoto and Tanaka [8]. The crystals were recovered from mother liqueur by centrifugation, repeatedly washed with *n*-butanol and deposited on

* Corresponding author. Fax: +34-934017150.

E-mail address: puiggali@eq.upc.es (J. Puiggali).

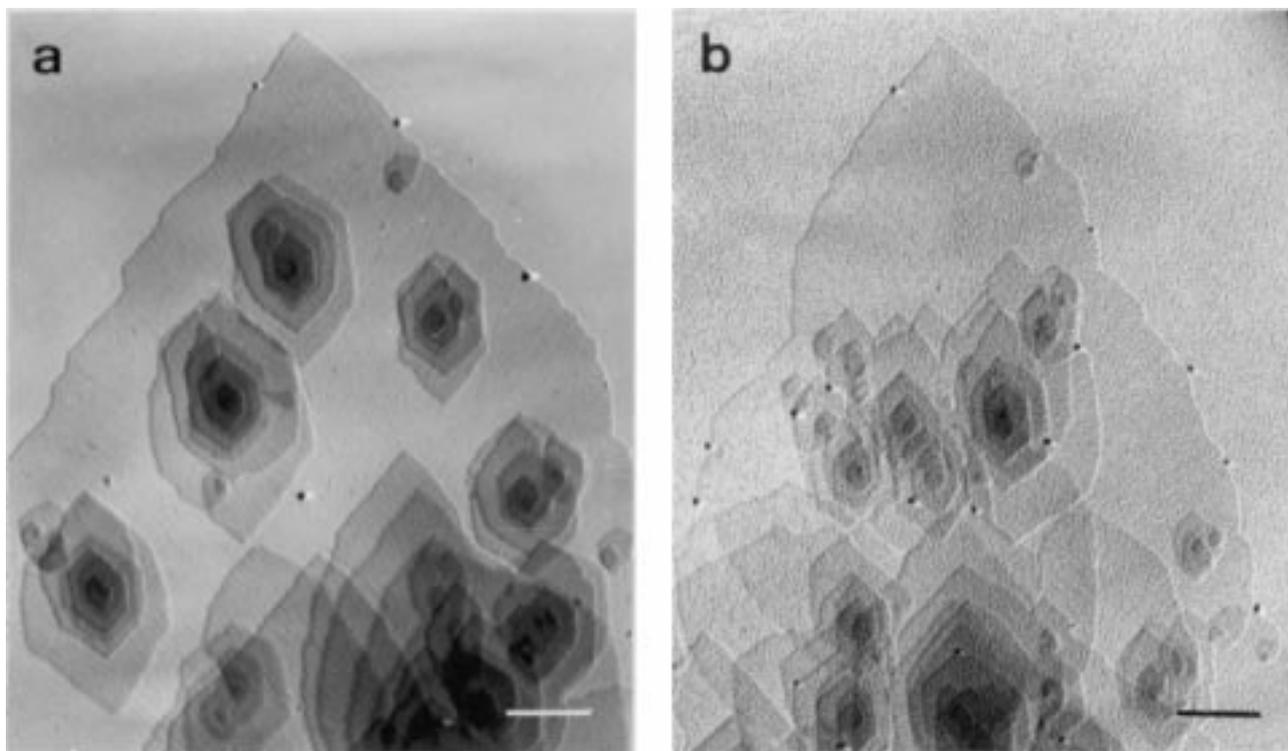


Fig. 1. Transmission electron micrographs of lamellar crystals of 6-10 polyester. (a) Single crystals shadowed with Pt/C show a regular thickness close to 8 nm and variable morphologies. (b) Decorated single crystals of 6-10 polyester. The orientation of the polyethylene rods demonstrated the sectorization of crystals. Scale bars 1 μm .

carbon-coated grids, which were shadowed with Pt–Carbon at an angle of 15° for bright field observations. Polymer decoration was achieved by evaporating polyethylene onto the surface of single crystals as described by Wittmann and

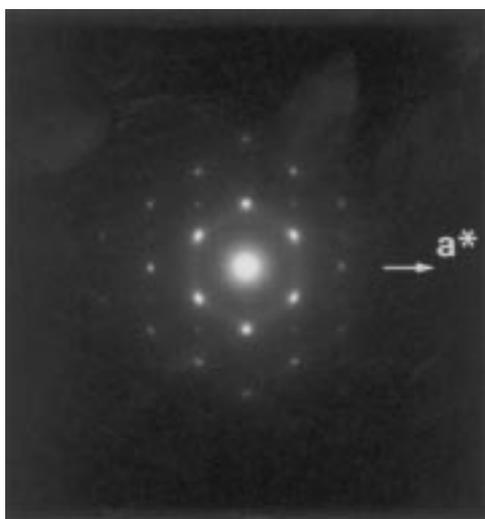


Fig. 2. Selected area electron diffraction pattern of a crystal of 6-10 polyester. The pattern was obtained with the electron beam perpendicular to the basal plane of the lamella. The c -axis is supposed to be parallel to the electron beam, as discussed in the text. a^* appears always oriented along the large dimension of the crystals.

Lotz [11]. A Philips EM-301 electron microscope was used and operated at 80 and 100 kV for bright field and electron diffraction modes, respectively. Selected area electron diffraction patterns were recorded on Kodak Tri-X films. The patterns were internally calibrated with gold ($d_{111} = 0.235 \text{ nm}$).

X-ray diagrams were recorded under vacuum at room temperature, with calcite as a calibration standard. A modified Statton camera (W. R. Warhus, Wilmington, DE, USA) with Ni–Copper radiation of wavelength 0.1542 nm was used. Fibres were prepared from the melt and annealed under stress at 55°C .

Structural modelling was carried out by using the software package CERIU² (Biosym/Molecular Simulations Inc.) [12] and the Prediction of Crystal Structure of Polymers [13] (PCSP) computer programs. Basically, the latter determines the relative stability of the different arrangements for a given packing when the azimuthal orientation of the molecules is varied. Energy contributions of both van der Waals and electrostatic interactions concerning closely-spaced non-bonded atoms were taken into account. The values for potential constants were taken from the Amber force-field library [14], whereas the partial charges were explicitly derived from a representative small compound by using a well established methodology [15]. All the calculations were run on a Silicon Graphics Indigo Workstation.

Table 1
Measured and calculated electron and X-ray diffraction spacings from single crystals and fibres of 6-10 polyester

Index	$d_{\text{cal}}^{\text{a}}$	$d_{\text{meas}}^{\text{b}}$	
		X-ray diffraction ^c	Electron diffraction ^d
002	1.010	1.015 s	
10 $\bar{1}$	0.537	0.535 w	
10 $\bar{3}$	0.509	0.506 m	
004	0.505	0.506 m	
110	0.412	0.411 vs	0.409 vs
10 $\bar{5}$	0.401	0.402 m	
020	0.365	0.365 vs	0.365 vs
120	0.295	0.295 m	0.293 vw
200	0.250	0.250 m	0.246 m
210	0.236	0.236 w	0.232 vw
11 $\bar{9}$	0.231	0.231 m	
130	0.219	0.219 m	0.220 m
019	0.215	0.214 m	
220	0.206	0.207 m	0.205 m
21 $\bar{9}$	0.206	0.207 m	
029	0.191	0.191 w	
040	0.183	0.184 vw	0.182 m
109	0.180	0.179 w	
230	0.174		0.178 vw
13 $\bar{9}$	0.172	0.173 vw	
310	0.162		0.161 vw

^a On the basis of a monoclinic unit cell with $a = 0.544$ nm, $b = 0.730$ nm, $c = 2.20$ nm and $\beta = 113.3^\circ$.

^b Abbreviations denote relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

^c Fibre diffraction pattern.

^d Single crystal diffraction pattern.

3. Results and discussion

Single crystals of 6-10 polyester (Fig. 1) were prepared in order to obtain electron diffraction data (Fig. 2 and Table 1) for packing refinement. Data from X-ray fibre diffraction patterns (Fig. 3) were also taken into account. We were able to obtain a pattern of a wholly monoclinic structure ($a = 0.544$ nm, $b = 0.730$ nm, c (chain axis) = 2.20 nm and $\beta = 113.3^\circ$), where the additional reflections normally observed and attributed to an orthorhombic modification [8,16] do not appear. The unit cell dimensions were in close agreement with the reported values [8], since a maximum deviation of 2% was found for each parameter. A density of 1.12 g/cc that compares well with the experimental value (1.17 g/ml) is calculated when two chain segments are considered in the unit cell. Large crystals (>20 μm) with a leaflike morphology were obtained, from isothermal crystallizations (45°C), together with smaller spiral growths that exhibit an elongated (along the a crystallographic axis) hexagonal morphology (Fig. 1). A loss of facetting is observed with increasing size of crystals. Correlation of the bright-field micrographs and the electron diffraction patterns indicated that the growth faces correspond to both (110) and (010) planes. In general, the experimental angle between the (110) growth faces reaches the

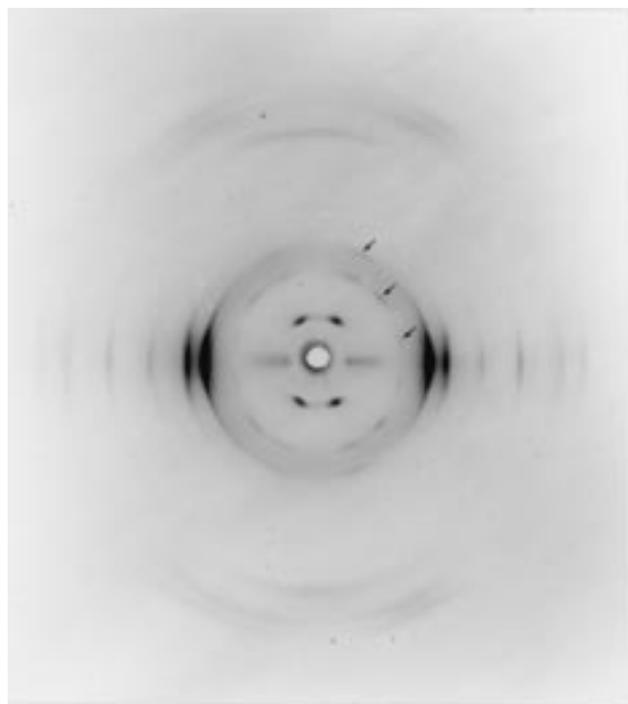


Fig. 3. X-ray fibre diffraction pattern of 6-10 polyester. Note the presence of reflections indexed as 10 $\bar{1}$, 10 $\bar{3}$ and 10 $\bar{5}$ (see arrows).

theoretical value of 110° that is deduced for the calculated unit cell parameters. Decoration with polyethylene highlighted the sectorization of the crystals (Fig. 1b). Note that the polyethylene decoration rods are disposed normal to the growth faces, which suggests that folds occur along both the (110) and (010) planes. These correspond to the planes where the neighbouring chains are closer (5.0 and 4.4 nm for (010) and (110) planes, respectively). Previous studies [8] on 6-10 polyester lamellae suggested a non-planarity of the single crystals and a disposition of molecular chains perpendicular to the basal plane that agree to the observed $hk0$ electron diffraction pattern. The absence of some expected hkl reflections, $l \neq 0$, for a monoclinic structure with $\beta \neq 90^\circ$ (c , chain axis) could also be explained by the model given for the 10-10 polyester [16]. In this case, the $00l$ planes and the molecular chains were supposed to be inclined and normal to the lamellar surface of flat crystals, respectively.

The molecular conformation is postulated to be all-*trans*, although a small perturbation from planarity exists reducing the experimental c parameter to 2.20 nm; slightly shorter than the calculated value (2.23 nm) for an extended conformation. Distorted planar structures were found to be energetically favoured with respect to the all-*trans* conformation for different aliphatic polyesters (2-4, 2-6, 2-8, 4-6 and 6-6) when the setting angle of molecular chains was similar to polyethylene [6].

The expected molecular symmetry for an extended conformation is $2/m$ with inversion centres in the middle of both diol and diacid units, and binary axes perpendicular

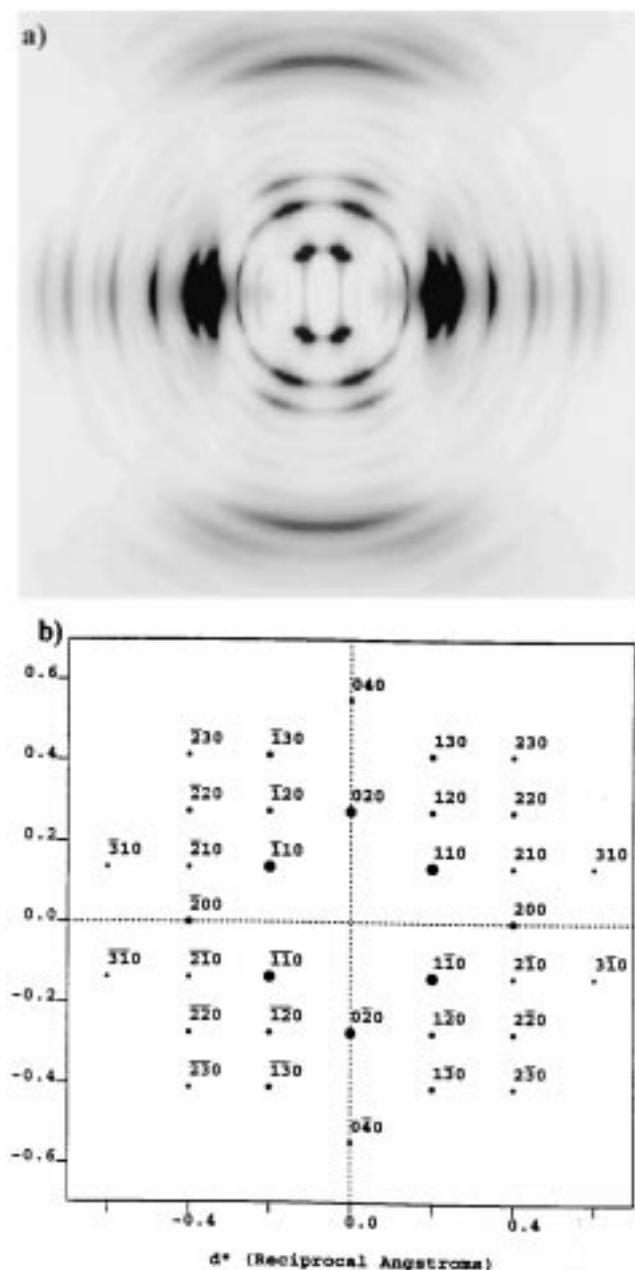


Fig. 4. Simulated X-ray fibre diffraction pattern (a) and $hk0$ electron diffraction pattern (b) of 6-10 polyester. A $P12_1/n1$ space group and a setting angle orientation of 45° were assumed.

to the chain axis direction passing through these points. Only the centres of symmetry could be preserved in the space group when the setting angle is different to 0 and 90° . In the same sense, we have to consider that the mirror plane symmetry will be lost for a distorted all-*trans* conformation. A binary screw axis parallel to the crystallographic *b*-axis is compatible with the monoclinic cell ($\beta \neq 90^\circ$) and relates the two molecular chains in the unit cell. Consequently, the space groups $P12_1/a1$, $P12_1/n1$ and $P12_11$ were considered in the packing analysis. The former was found in the 2-6 and 2-8 polyesters [4] and was extrapolated

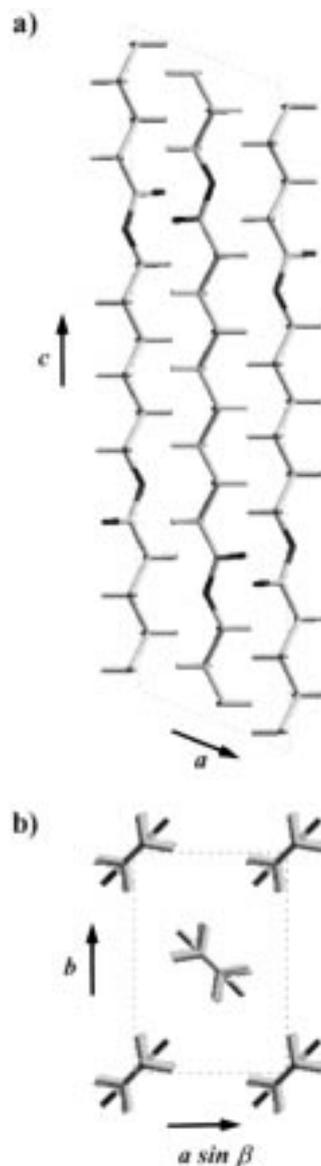


Fig. 5. Views of the proposed 6-10 polyester structure refined against electron and X-ray diffraction data and assuming an all-*trans* conformation: (a) View parallel to the *b*-axis direction, (b) View parallel to the *c*-axis direction. Colour code: hydrogen and carbon, grey; oxygen, black.

to the 6-10 polyester in a previous study [6] carried out taking only energy calculations into account. However, the $10\bar{1}$, $10\bar{3}$ and $10\bar{5}$ reflections observed in the X-ray fibre patterns (Fig. 3 and Table 1) are not compatible with this space group, since $h0l$ systematic absences, for *h* odd, are required. Structural refinement was undertaken assuming the less restrictive $P12_11$ space group. Both the relative *c*-axis shift between molecules and the setting angle were allowed to vary. The results show that molecules pack in a $P12_1/n1$ space group that accounts for the observed systematic absences for $h0l$, with $h + l = \text{odd}$. The best agreement was also found when the setting angle was in the $43\text{--}47^\circ$ range, which is similar to the value of 45°

reported for polyethylene [17]. Fig. 4 shows the simulated electron and X-ray diffraction patterns for the final structure. It should be pointed out that some minor discrepancies still exist, i.e. the low intensity of the $10\bar{3}$ reflection in the fibre pattern, and the high intensity of the 120 and 210 reflections in the $hk0$ electron diffraction pattern. It is worth to note that the refinement has been undertaken assuming a perfect all-*trans* conformation; distortions from this geometry will obviously affect the resulting diffraction patterns.

Projections of the refined structure are shown in Fig. 5. Neighbouring molecules in the (010) planes are shifted approximately 0.215 nm according to the β monoclinic angle, whereas a shift of $c/2$ has to be added to that caused by the monoclinic cell (0.108 nm) for neighbouring molecules in the (110) planes. This shift is the main difference with respect to previous models and with the reported structures of aliphatic polyesters. Some interesting features on the geometry of folds can also be deduced from the indicated c -axis shifts. Thus, folding in the (010) planes may take place through polymethylene segments (diol or diacid units), whereas the ester groups must be involved in the folds that occur along the (110) planes. Note in Fig. 5 that an hydroxyacid unit will appear if the folding along the (110) direction takes place through a polymethylene segment due to the reversal of the O–CO sequence. As a consequence, the lamellar surface must be different in the well-defined (010) and (110) sectors, since different groups (methylene or ester) are implied in the folding.

The results obtained from energy minimization were similar. Thus, packing was energetically favoured for the $P12_1/n1$ space group (1 kcal mol⁻¹ residue⁻¹ in relation to the $P12_1/a1$ space group) and a setting angle in the range 30–40°. In fact, the variation in energy was limited within this margin, since electrostatic interactions (favoured at low setting angles) balance the van der Waals interactions (optimum near 40°).

4. Conclusions

Poly(hexamethylene sebacate) adopts a quasi-planar chain conformation and packs in a monoclinic unit cell

with a setting angle similar to polyethylene. Thus, influence of ester groups are suppressed due to the long polymethylene segments. A monoclinic $P12_1/n1$ space group can also be deduced from the diffraction data and appears energetically favoured with regard to $P12_1/a1$; a space group that is more usual in polyesters. Lamellar crystals appear sectorized and present different fold orientations. In addition, folds constituted by methylene or ester groups must exist in the distinct growing sectors. These changes on the lamellar surface are consequence of the chain packing, which means different shifts between neighbouring molecules along the (110) and (010) folding planes.

Acknowledgements

This research has been supported by CICYT (MAT97-1013). The authors express their gratitude to Dr A. Rodríguez-Galán for polymer synthesis and L. Franco for fibre preparation.

References

- [1] Carothers WH. Chem Rev 1931;8:353.
- [2] Fujimaki T. Polym Degrad Stab 1997;30:7403.
- [3] Ueda AS, Chatani Y, Tadokoro H. Polym J 1971;2:387.
- [4] Turner-Jones A, Bunn CW. Acta Crystallogr 1962;15:105.
- [5] Chatani Y, Hasegawa R, Tadokoro H. Meeting of the Society of Polymer Science (Japan). 1971;420.
- [6] Liao WB, Boyd RH. Macromolecules 1990;23:1531.
- [7] Alemán C, Puiggalí J. J Org Chem 1997;62:3076.
- [8] Kanamoto T, Tanaka K. J Polym Sci, Part A-2 1971;9:2043.
- [9] Brandrup J, Immergut EH. Polymer handbook. New York: Wiley Interscience, 1989.
- [10] Paredes N, Rodríguez-Galán A, Puiggalí J. J Polym Sci, Polym Chem Ed 1998;36:1271.
- [11] Wittmann JC, Lotz B. J Polym Sci, Part B: Polym Phys 1985;23:205.
- [12] CERIU² 2.0, Biosym Molecular Simulations Inc., Burlington, MA.
- [13] León S, Navas JJ, Alemán C. Polymer 1999;40:7351.
- [14] Weiner SJ, Kodman PA, Nguyen DT, Cabe DA. J Comp Chem 1986;7:230.
- [15] Alemán C, Luque FJ, Orozco M. J Comput Aided Mol Des 1993;7:721.
- [16] Girolamo M, Keller A, Stejny J. Makromol Chem 1975;176:1489.
- [17] Swan PR. J Polym Sci 1962;56:403.