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Crystalline Orientation and Molecular Transport Properties in Nanoporous Syndiotactic Polystyrene Films

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Summary: The orientation of the crystalline δ nanoporous phase in syndiotactic polystyrene films, obtained by different procedures, have been characterized. For both solution cast and biaxially stretched films a high degree of uniplanar orientation, corresponding to the tendency of the *ac* crystallographic planes, to be parallel to the film plane has been observed and rationalized. According to molecular dynamics simulations of diffusion of small molecules into the δ nanoporous phase, this uniplanar orientation would minimize the molecular diffusivity through the nanoporous crystalline phase.

Introduction

Syndiotactic polystyrene (s-PS) is a high performance thermoplastic semicrystalline material, which has recently become commercially available. It presents good mechanical properties associated with a high melting temperature (close to 270°C).

This polymer presents a very complex polymorphic behavior [1,2]. By melt crystallization procedures both high melting α [3-5] and ß [6-8] forms, which are characterized by chains in the *trans* planar conformation, can be obtained.

By solution crystallization procedures, besides ß form, the thermally unstable γ and δ forms as well as clathrate forms, all including chains in the **s**(2/1)2 helical conformation,

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can be obtained. In all the described s-PS clathrate phases, s(2/1)2 helices (the host) form a crystal lattice containing spaces in which molecules of a second chemical species (the guest) are located. Semicrystalline samples including clathrate phases can be obtained by sorption of suitable compounds (e.g. methylene chloride, toluene, chloroform etc.) in amorphous s-PS samples as well as in semicrystalline s-PS samples in the α, γ or δ form. For these clathrate structures the intensities and the precise locations of the reflections in X-ray diffraction patterns only slightly change with the kind and the amount of the included guest molecules [1,9]. The crystal structures of clathrate phases including as guest molecules toluene [10], iodine [11] or 1,2 dichloroethane [12], which have been determined with good accuracy, are in fact all similar to each other.

The δ form, which can be obtained by suitable solvent extraction procedures on samples in all clathrate forms [13-15], presents the lowest density (0.977 g/cm3), lower than that one of the amorphous phase (1.05 g/cm3), due to its nanoporous crystal structure [2]. It is nanoporous since, in place of the guest molecules, it includes two identical cavities per unit cell [16], whose shape and volume have been characterized [17]. s-PS samples in the nanoporous δ form rapidly absorb molecules of suitable volatile organic compounds and transform into the corresponding clathrate forms also if they are present at very low activities [13-15]. Sorption studies from liquids and vapors have suggested that this thermoplastic material is promising for applications in chemical separations as well as in water purification [18-20].

Since physical properties of polymeric manufacts largely depend on molecular orientation produced by processing, the type and degree of orientation which are present in oriented s-PS films prepared by different procedures will be described. It is worth noting that in oriented films, beside the possible axial orientation (orientation of the chain axes with respect to the main drawing direction, which is typical of fibers) also a planar orientation (making some simplification, orientation of the chain axes with respect to the film plane) can be achieved [21].

The main objective of our studies is to find possible correlations between molecular orientation and molecular transport properties. In fact, it is well known that, in general, the transport of small molecules in semicrystalline polymers involves exclusively the amorphous phase and in the presence of molecular orientation (which involves mainly the crystalline phase) the diffusion coefficient can be strongly reduced.

On the other hand, for the specific case of the nanoporous form of syndiotactic polystyrene, the transport of small molecules, mainly for low concentrations, involves essentially only the crystalline phase [18-19]. It is hence expected that by suitable crystallite orientations it is possible to substantially alter and eventually maximize or minimize the sorption kinetics.

In particular, in this paper δ semicrystalline films, obtained by solution casting or by exposition to solvent vapors of melt extruded and biaxially stretched films are considered.

Experimental part

The s-PS used in this study was manufactured by Dow Chemical Company under the trademark Questra 101. The ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 135°C was found to be $M_w=31.7 \times 10^4$ with the polydispersity index, $M_w/M_n=3.9$.

Chloroform clathrate films, 25-40 μm thick, were obtained by casting procedure from 1% wt/wt solution in chloroform at room temperature. Amorphous films, ≈100 μm thick, were obtained by extrusion process conducted at 290°, the extruded films were biaxially simultaneously balanced stretched at 105°C and at a constant strain rate of 10% along two mutually perpendicular directions at draw ratios in the range 1.5 ÷ 2.5.

δ semicrystalline films were obtained by exposing chloroform clathrate film and balanced stretched films, to vapors of CS_2 and by subsequent drying at 50°C under vacuum.

Wide-angle X-ray diffraction patterns with nickel filtered Cu Kα radiation were obtained, in reflection, with an automatic Philips diffractometer as well as, in transmission, by using a cylindrical camera (radius=57.3 mm). In the latter case the patterns were recorded on a BAS-MS Imaging Plate (FUJIFILM). In particular, in order to recognize the kind of crystalline orientation present in the samples, photographic X-ray diffraction patterns were taken with X-ray beam both perpendicular and parallel to the film surface.

The degree of uniplanar orientation (parallelism of a crystallographic plane to the film plane) can be formalized on a quantitative numerical basis using the Hermans' orientation function, f_x, which describes the orientation of the crystallographic planes (0k0), for the uniplanar orientation, with respect to the film surface. The orientation function is defined as follow [22,23]:

$$f_x = (3\overline{\cos^2 x} - 1)/2 \qquad (1)$$

where $\overline{\cos^2 x}$ designates the squared average cosine value of the angle, between the normal to the film surface and the normal to the (0k0) crystallographic plane for the uniplanar orientation.

Since, in our cases, a θ_{hkl} incidence of X-ray beam is used, the quantity $\overline{\cos^2 x}$ can be easily experimentally evaluated with the following expressions:

$$\overline{\cos^2 x} = \overline{\cos^2 \chi_{0k0}} = \frac{\int_0^{\pi/2} I(\chi_{0k0}) \cos^2 \chi_{0k0} \sin \chi_{0k0} d\chi_{0k0}}{\int_0^{\pi/2} I(\chi_{0k0}) \sin \chi_{0k0} d\chi_{0k0}} \qquad (2)$$

where $I(\chi_{0k0})$ is the intensity distribution of a (0k0) diffraction on the Debye ring as collected by sending the X-ray beam parallel to the film surface, χ_{0k0} is the azimuthal angle measured from the equator, that is the line defined by the (0k0) reflections.

Once $\overline{\cos^2 x}$ has been determined experimentally the orientation function of the desired crystallographic planes can be calculated using equation (1).

In these assumptions, for the uniplanar orientation $f_x = f_{0k0}$ is equal to 1 if (0k0) planes of all crystallites are perfectly parallel to the plane of the film, whereas it is equal to -0.5 if the (0*k*0) planes are perpendicular to it.

The diffracted intensities $I(\chi_{0k0})$ of equation (2) were obtained, in transmission, by using an AFC7S Rigaku automatic diffractometer (with a monochromatic CuKα radiation), and were collected sending the X-ray beam parallel to the film surface and maintaining an equatorial geometry. Because the collection was performed at constant 2θ values and in the equatorial geometry, the Lorenz and polarization corrections were unnecessary.

Results and discussion

Typical X-ray diffraction patterns, obtained by an automatic powder diffractometer, of δ form unoriented semicrystalline s-PS samples and s-PS films, obtained by casting procedures followed by exposition to CS_2 vapors and by subsequent drying at 50°C under vacuum, are reported in Figure 1. The Miller indexes of the calculated most intense reflections are indicated near to the peaks.

The occurrence of strong molecular orientation is clearly pointed out by the substantial variation of the reflection intensities with respect to the unoriented samples of Figure 1.

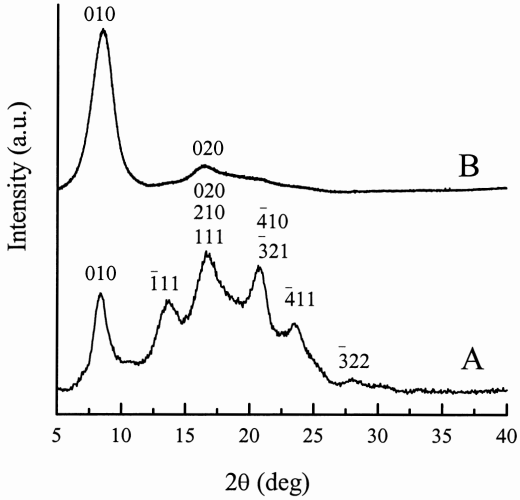

Figure 1. Typical X-ray diffraction patterns obtained by an automatic powder diffractometer, of unoriented semicrystalline s-PS samples in δ form (A) and s-PS films in δ form obtained by casting procedures followed by exposition to CS_2 vapors and by subsequent drying at 50°C under vacuum (B). The Miller indexes of the most intense reflections are indicated near to the peaks.

In particular, for δ form film obtained by casting procedures (Figure 1B) the (010) remains the only intense reflection, while the (020) which is not detectable in unoriented samples becomes second in intensity. This suggests an orientation of *ac* planes prevailingly parallel to the film plane.

A better understanding of the crystalline orientation present in these films obtained by casting procedures, can be achieved by X-ray patterns taken with beams perpendicular and parallel to the film plane on a photographic cylindrical camera (Figure 2).

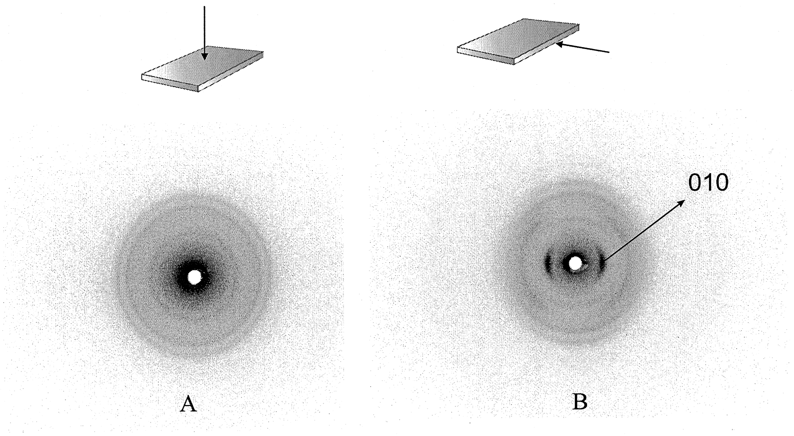

Figure 2. X-ray diffraction patterns obtained with beams perpendicular (A) and parallel (B) to the surface of a δ form s-PS cast film. The patterns were collected by using a photographic cylindrical camera and recorded on a imaging plate.

It is worth noting that the X-ray diffraction patterns collected with beams perpendicular to the film plane show only Debye Sherrer rings, indicating that there isn't any axial orientation in the film plane whereas, the X-ray patterns collected with beams parallel to the film plane, differently from the patterns obtained with beams perpendicular to the film plane, show arcs rather than Debye Sherrer rings.

In particular, X-ray diffraction patterns obtained with beam parallel to the film plane show a very intense reflection due to the (010) crystallographic planes (Figure 2B), which disappears in X-ray diffraction patterns obtained with beam perpendicular to the film plane (Figure 2A). This again indicates that the (010) planes (i.e. the *ac* planes) of the crystallites are characterized by an orientation distribution, whose maximum corresponds to parallelism to the film plane.

The tendency to parallelism of the (010) planes with respect to the film plane can be easily rationalized by looking at the packing of the s-PS helices in the δ form, which is shown, for instance, in Figure 3. In fact, this set of planes corresponds to rows of parallel helices with minimum interchain distance of 8.7Å and a maximum interplanar distance of $d_{010}= \lambda/2\mathrm{sen}\theta = 10.56$Å.

As expected for an hydrocarbon polymer for which the only interchain interactions are of van der Waals type, the crystalline plane which tend to be parallel to the film surface (primary slip plane) is that one containing the chain axis and having the highest density (that is, the minimum interchain distances and the maximum interplanar distances).

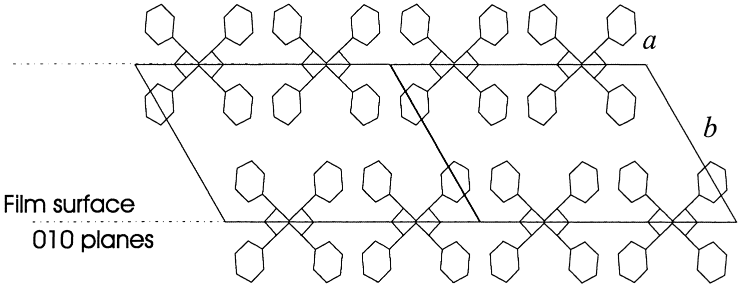

Figure 3. Along the chain projection of packing of δ form of s-PS showing (010) planes which correspond to rows of parallel helices with minimum interchain distances (8.7Å) and maximum interplanar distances (10.56Å). These planes tend to be parallel to the film surface for cast films.

As for the films in δ forms obtained by casting procedures and subsequent suitable treatments, the uniplanar orientation, evaluated by using the Hermans' orientation function, f_{010}, (see experimental part), and measuring the tendency of the rows of the closest helices to be parallel to film plane, is 0.76.

The same kind of uniplanar orientation of the crystalline phase has also been observed on δ form s-PS films obtained by simultaneous and balanced biaxial stretching of extruded samples (see experimental part).

The Hermans' orientation factors, f_{010}, for δ form films obtained by simultaneous biaxial stretching at different draw ratios is reported in Figure 4. For comparison the orientation factor of δ film obtained by casting is also reported.

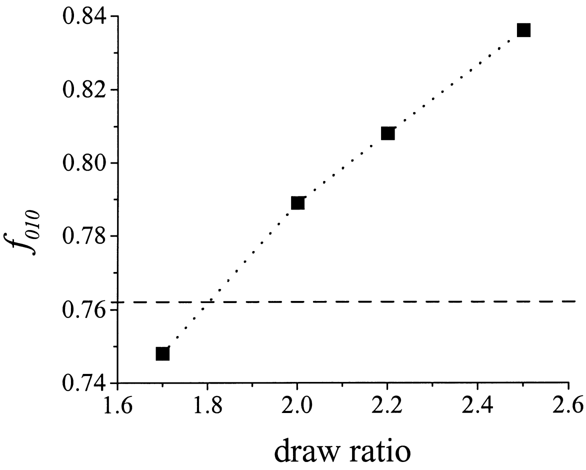

Figure 4. Orientation factors, f_{010}, of δ form films obtained by simultaneous and balanced stretching versus the draw ratio along each of the perpendicular drawing directions. The dashed line represents the level of uniplanar orientation which has been reached by our casting procedures.

For the considered range of draw ratio a nearly linear increase of the orientation factor has been observed. The orientation factor of δ form films obtained by casting is close to that one of the sample obtained by simultaneous biaxial stretching at a draw ratio ≈1.8×1.8.

Experimental procedures suitable to obtain films with different kinds of orientation of the δ crystalline phase have been recentely studied in our laboratories and will be presented in future reports.

Molecular dynamics simulations (MD) techniques have been used to understand the diffusive behaviour of helium in the crystalline δ phase of s-PS and particularly its anisotropy as a function of temperature. In particular, helium atom pathways obtained from simulations trajectories at 25 °C and 80 °C are shown in Figure 5 for *ab* and *ac* projections of the δ crystal structure. Diffusion proceeds by hopping between different crystalline cavities. For some period of time, the penetrant stays in a cavity region. During such a quasi-stationary period, it explores this region but does not move beyond the cavity confines. The quasi-stationary periods are interrupted by quick leaps from one cavity into a neighbouring one. Since for the nanoporous δ form of s-PS all cavities are of the same size and occupy well defined crystallographic positions, jumps between different cavities generally occur along well defined directions.

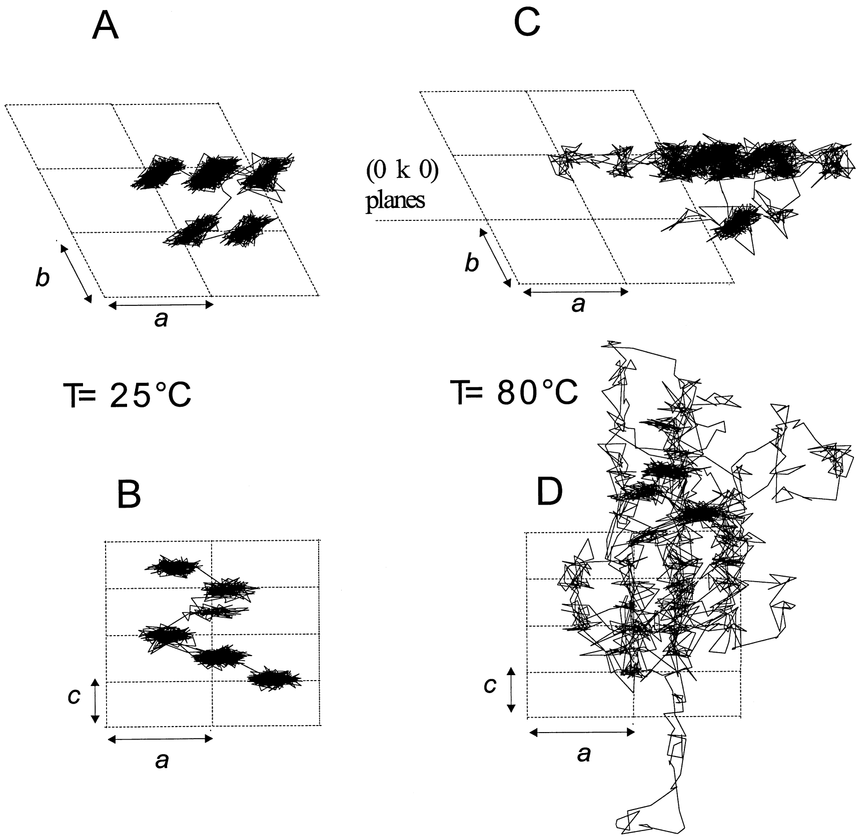

Figure 5. Trajectory (trace) of one helium atom in crystalline syndiotactic polystyrene in its nanoporous δ form during 2 ns of simulations at (A, B) 25 °C and (C, D) 80 °C. Different views (A, C) along *c* and (B, D) perpendicular to the *ac* plane are shown. At room temperature (A, B), a hopping motion mechanism between different crystalline cavities, prevailing along <101> directions, is apparent. Pathways at 80°C (C, D) could be interpreted as penetrants motion mainly along [001] and <101> directions.

For both temperatures, the hopping between cavities generally occurs along directions which are parallel to the crystalline *ac* planes (Figures 5A and 5C). This behavior can be easily rationalized by the presence in the planes of rows of parallel helices with minimum interchain distances (8.70 Å). In fact, most jumps occur along [101] and [10$\bar{1}$]

directions (that is along the family of directions <101>) or along the *c* axis (or [001] direction).

It is worth noting that the distance between two neighbor cavities is much larger along the <101> directions (1.9 nm) than along [001] direction (0.77 nm = *c*). Nevertheless, at room temperature, jumps along <101> directions are favored (Figure 5B).

At higher temperature, the penetrant's pathway appears quite different (Figures 5C and 5D). The cavities are still visible, but they are explored less thoroughly, as the stationary periods between leaps are shorter. Although many more leaps occur along <101> directions, that is the prevailing ones at room temperature, most leaps occur along the chain axes that is along the [001] direction (Figure 5D).

Diffusion coefficients of helium for different temperatures have been calculated. For both penetrants, the diffusion is anisotropic. The analysis of the results of our simulations has shown that for all temperatures the minimum diffusivity corresponds to the direction perpendicular to the *ac* plane [24]. Moreover, the maximum of diffusivity are expected to correspond to the *a* and *c* direction at low and high temperatures, respectively.

In qualitative agreement with the prediction of these calculations, preliminary permeability tests have shown that for δ form s-PS cast films presenting the uniplanar orientation the diffusivity is much lower that that observed for unoriented δ form s-PS samples.

Conclusions

The precise knowledge of the crystalline orientation is particularly relevant for δ form s-PS films for a possible control of the permeability to small molecules.

δ form films obtained by solution casting procedures as well as by balanced simultaneously stretching along two mutually perpendicular directions present high degree of uniplanar orientation, corresponding to the tendency of the *ac* crystallographic planes, to be parallel to the film plane. The driving force for this kind of orientation is the tendency of rows of parallel **s**(2/1)2 helices with minimum interchain and maximum interplanar distances to be parallel to the film plane.

Molecular dynamics studies of the transport of helium through crystalline syndiotactic polystyrene in its nanoporous δ crystal form have shown, for all considered temperatures, a low diffusivity through the *ac* plane. As a consequence, a strong diffusional anisotropy at low and high temperatures has been always obtained. For low temperatures, preferential diffusion pathways, between neighbor cavities along <101> directions, determine maximum diffusivities along the *a* direction. At higher temperatures, prevailing diffusion pathways as well as maximum diffusivity occur along *c* direction (parallel to the helices).

Experimental studies on the permeability for both oriented and unoriented δ form s-PS films are in progress.

[1] Guerra, G.; Vitagliano, V. M.; De Rosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *23*, 1539.
[2] Chatani, Y.; Shimane, Y.; Inoue, Y.; Inagaki, T.; Ishioka, T.; Ijitsu, T.; Yukinari, T. *Polymer* **1992**, *33*, 488.
[3] De Rosa, C.; Guerra, G.; Petraccone, V.; Corradini, P. *Polym. J.* **1991**, *23*, 1435.
[4] De Rosa, C. *Macromolecules* **1996**, *29*, 8460.
[5] Cartier, L.; Okihara, T.; Lotz, B. *Macromolecules* **1998**, *31*, 3303.
[6] De Rosa, C.; Rapacciuolo, M.; Guerra, G.; Petraccone, V.; Corradini, P. *Polymer* **1992**, *33*, 1423.
[7] De Rosa, C.; Guerra, G.; Corradini, P.; .*Rend. Fis. Acc. Lincei* **1991,** *2*, 227.
[8] Chatani, Y.; Shimane, Y.; Ijitsu, T.; Yukinari, T. *Polymer*, **1993**, *34*, 1625.
[9] Immirzi, A.; De Candia, F.; Iannelli, P.; Vittoria, V.; Zambelli, A. *Makromol.Chem.Rapid Commun.* **1988**, *9*, 761.
[10] Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikuma, H. *Polymer*, **1993**, *34*, 1620.
[11]Chatani, Y.; Inagaki, T.; Shimane, Y.; Shikuma, H. *Polymer*, **1993**, *34*, 4841.
[12]De Rosa, C; Rizzo, P; Ruiz de Ballesteros, O.; Petraccone,V.; Guerra, G. *Polymer*, **1999**, *40*, 2103.
[13]Guerra, G.; Manfredi, C.; Rapacciuolo, M.; Corradini, P.; Mensitieri, G.; Del Nobile M.A. *Ital. Pat. 1994 (C.N.R.).*
[14]Manfredi, C.; Del Nobile, M.A.; Mensitieri, G.; Guerra, G.; Rapacciuolo M. *J.Polym.Sci.,Polym.Phys.Ed.*, **1997**, *35*, 133.
[15] G.Guerra, G.; Reverchon, E.; Venditto, V.; *It. Pat. n. SA98A8*
[16] De Rosa, C; Guerra, G.; Petraccone, V.; Pirozzi, B. *Macromolecules* **1997**, *30*, 4147.
[17] Milano, G.; Venditto, V.; Guerra, G.; Cavallo, L.; Ciambelli, P.; Sannino, D. *Chem. Mat.,* **2001**, *13*, 1506.
[18] G.Guerra, C.Manfredi, P.Musto, S.Tavone, *Macromolecules*, **1998**, *31*, 1329.
[19] Musto, P.; Manzari, M; Guerra, G. *Macromolecules*, **2000**, *33*, 143.
[20] Guerra, G.; Milano, G.; Venditto, V.; Musto, P.; De Rosa, C.; Cavallo, L.; *Chem. Mat.* **2000**, *12*, 363.
[21] Rizzo, P.; Lamberti, M.; Albunia, A.; Ruiz de Ballesteros, O.; Guerra G. *Macromolecules* in press.
[22] Samuels, R.J. in *"Structured Polymer Properties"* Eds.John Wiley & Sons, New York, 1971, p. 28.
[23] Kakudo, M. , Kasai, N. "*X-Ray Diffraction by Polymers"*, Eds. Elsevier, Amsterdam,1972, p. 252.
[24] Milano,G; Guerra, G; Muller Plathe, F. *Chemistry of Materials* submitted.