On the crystal structure of the orthorhombic form of syndiotactic polystyrene

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The crystallization conditions for the preparation of different modifications of the orthorhombic form (β form) of syndiotactic polystyrene (s-PS) are described. Crystallizing from the melt produces the β' or α form depending on the cooling rate. Crystallization by casting a film from *o*-dichlorobenzene solutions produces clathrate structures (δ form) at low temperatures ($T < 130°C$) and ordered β'' modifications at higher temperatures. In particular, modification very close to the β'' limiting one are obtained in the temperature range 130–140°C. Recrystallization of the β form has been detected by differential scanning calorimetry and studied by X-ray diffraction analysis of the annealed samples. These studies indicate that the recrystallization of the β' form in the melting region does not involve a β' to β'' transition, but only morphological changes. Models for the chain packing of the limiting modifications of the β form are suggested, by quantitative comparisons of the X-ray diffraction intensities and calculated structure factors.

(Keywords: crystallization; crystal structure; syndiotactic polystyrene)

INTRODUCTION

The polymorphic behaviour of syndiotactic polystyrene (s-PS) is very complex and several papers have recently appeared in the literature relative to the interchange and characterization by X-ray diffraction[1–8], electron diffraction[9], *FT*i.r. spectroscopy[10–15], solid state n.m.r. studies[16,17] and conformational energy analyses[18,19] of three different crystalline structures as well as of clathrate structures of s-PS.

Following the nomenclature of ref. 6, the two crystalline forms α and β contain planar zig-zag chains, with an identity period of $c = 5.1$ Å, while the third the γ form, as well as the clathrate structure the δ form contain (2/1)2 helical chains, with an identity period of $c = 7.8$ Å.

The general pattern is further complicated by the fact that both the α form with a hexagonal unit cell with $a = 26.26$ Å[7,9] and the β form with an orthorhombic unit cell with $a = 8.81$ Å, $b = 28.82$ Å[1] can exist in different modifications characterized by differing degrees of structural order, so that two limiting disordered modifications (the α' and β') and two limiting ordered modifications (α'' and β'') have been described[6].

A possible structural disorder which could be present in the α' modification of the α form has been also suggested[6,7] and refers to the positioning of the polymer backbones, while the order in the positioning of the substituent phenyl rings remains substantially unaltered.

As far as the β form is concerned, structurally more ordered samples (β'' modification) can be obtained by casting from a suitable solvent[1,6] while structurally less ordered samples (β' modification) can be obtained by melt crystallizations under suitable conditions[4,6].

Unoriented samples in the β'' modification are characterized by X-ray diffraction patterns which present two additional reflections at $2\theta = 11.8°$ and $2\theta = 15.8°$ (CuKα) with respect to the pattern of samples in the β' modification[4,6].

D.s.c. studies of samples in the β' modification show two melting peaks, whose relative intensities change with the heating rate. This typically occurs in the case of recrystallization[6]. It has also been clarified, by X-ray diffraction measurement in the region of the melting temperature, that in these recrystallizations no β to α transition occurs[6].

In this contribution the crystallization conditions of the different modifications of the β form of s-PS have been studied in more detail. The possible existence of transitions in the melting region from less ordered to more ordered modifications of the β crystalline form of s-PS (as observed for instance, for the α-form of isotactic polypropylene[20–24]) has been also investigated, by d.s.c. and X-ray diffraction analysis of the annealed samples.

In the final section of the paper, models for the chain packing of the different modifications of the β-form are proposed, on the basis of quantitative comparisons between X-ray diffraction intensities of unoriented samples and calculated structure factors.

EXPERIMENTAL

The s-PS ($M_w = 6.6 \times 10^5$ as determined by g.p.c.) was supplied by Himont Italia. The fraction insoluble in methyl ethyl ketone (93% by wt) was used.

Melt-crystallization processes at different cooling rates were conducted in an Anton-Paar TTK-HC camera. Samples originally in β' form (obtained by melt-crystallization as described in ref. 6) were melted at 280°C and then crystallized on cooling at different cooling rates.

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Solution-crystallizations were carried out from 5% by wt solutions of s-PS in *o*-dichlorobenzene (*o*-DCB) at different temperatures.

Wide angle X-ray diffraction patterns were obtained with nickel-filtered CuKα radiation with an automatic Philips powder diffractometer. The percent content of the α and β forms in the samples with mixed crystals was evaluated according to the method described in ref. 6.

The observed structure factors (F_o) were obtained as the square root of the experimental intensities corrected by $LP = (1 + \cos^2 2\theta)/(\sin^2\theta\cos\theta)$, $F_o = (I/LP)^{1/2}$. The experimental intensities were evaluated measuring the area of the peaks in the X-ray powder diffraction patterns, after subtraction of the amorphous halo.

Calculated structure factors (F_c) were obtained from $F_c = (\sum_i |F_i|^2 M_i)^{1/2}$, where M_i is the multiplicity factor and the summation is taken over all the reflections included in the 2θ range of corresponding observed reflection peak. The thermal factor $B = 8$ Å^2 and atomic scattering factors used in ref. 25, were assumed.

The d.s.c. scans were carried out in a Mettler TA 3000 (DSC-30) calorimeter, in a flowing-nitrogen atmosphere. All the reported scans correspond to a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Crystallization conditions for the different modifications of the β form

Melt crystallizations. In a previous paper it has been shown that for the case of melt crystallizations of s-PS, if the crystalline form of the starting material is β (β' or β'') the crystalline form of the compression moulded samples depends essentially on the cooling rate[6]. In particular, β form samples are obtained for low cooling rates while α form samples can be obtained in quenching conditions[6]. The effect of different cooling conditions are considered in more detail.

The X-ray diffraction patterns of the s-PS samples, originally in the β' form, melted at $T = 280$°C and then crystallized on cooling at different cooling rates, are reported in *Figure 1*.

For low cooling rates up to 10°C min^{-1} the β' form samples are always present: the typical β' form peaks are present at $2\theta = 6.1°$, 10.4°, 12.3°, 13.6°, 18.6°, 20.2°, 21.3°, 23.9°, 24.9° and 35.0°, while two additional peaks at $2\theta = 11.8°$ and 15.8°, which characterize the β'' form[6], are not (*Figures 1A* and *1B*). Moreover, we have verified that very slow crystallizations (e.g. isothermally at 262°C) also produce β form samples in the β' modification.

For cooling rates higher than 10°C min^{-1} peaks typical of the β' and α forms are present (e.g. the peaks at $2\theta = 6.7°$, 11.8° and 18.0°), the amount of the α form in the samples increasing with the cooling rate. The percentages of the α form in the crystalline phase, evaluated for the samples of *Figures 1A* (and *1B*), *1C*, *1D* and *1E*, are 0%, 10%, 30% and 100%, respectively.

Solution crystallizations. X-ray diffraction patterns of samples obtained by casting from 5% by wt solutions in *o*-DCB at different temperatures, are shown in *Figure 2*. For casting temperatures lower than 100°C a clathrate structure (δ form) is obtained: the diffraction patterns present, in fact, reflections at $2\theta = 7.8°$, 10.1°, 14.6°, 16.8°, 18.8°, 19.3°, 19.7°, 22.3°, 23.3°, 24.6° and 28.3° (*Figure 2A*) which are analogous to those of other

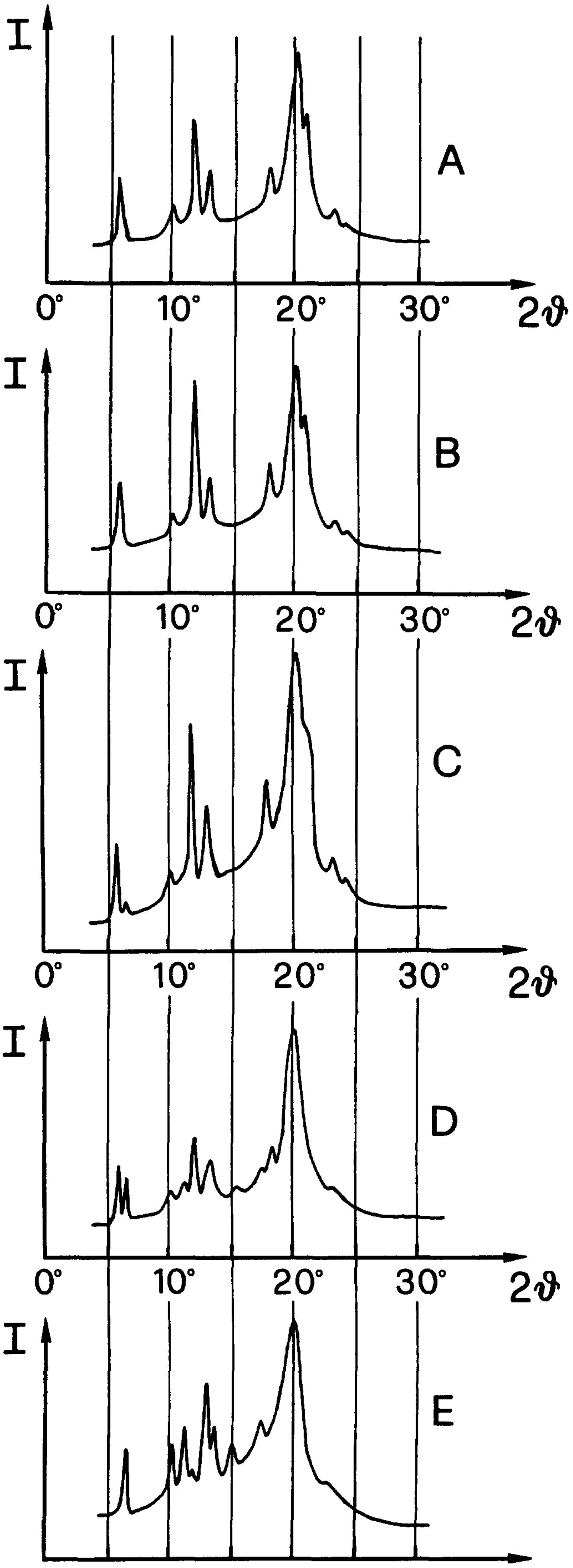

Figure 1 X-ray diffraction patterns (CuKα) of samples crystallized from the melt at different cooling rates: (A) 0.1°C min^{-1}; (B) 10°C min^{-1}; (C) 20°C min^{-1}; (D) 40°C min^{-1}; (E) quenched in H_2O at 0°C

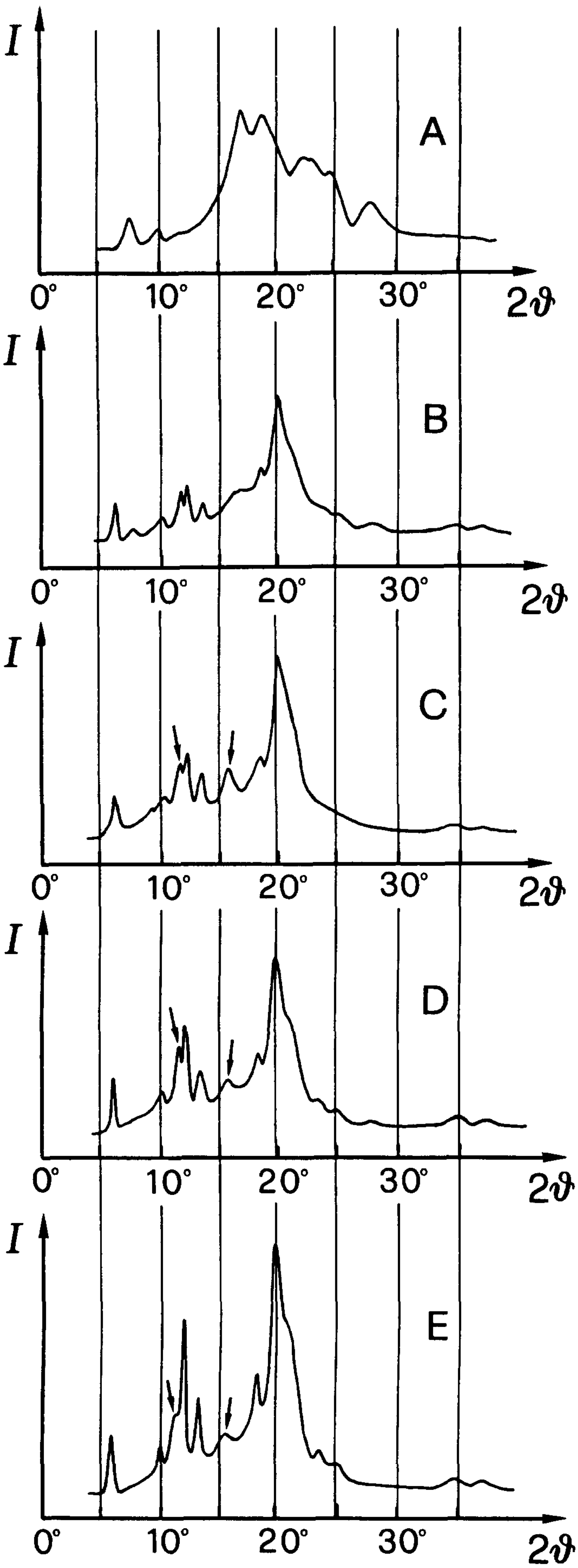

Figure 2 X-ray diffraction patterns (CuKα) of samples crystallized by casting from solutions in *o*-DCB at different temperatures: (A) 100°C (δ-form); (B) 130°C (δ-form + β''-form); (C) 130°C followed by annealing at 170°C (γ-form + β''-form); (D) 140°C (β''-form); (E) 170°C (β''-form). The arrows indicate the two additional peaks which characterize the β'' modification (with respect to the β' modification)

clathrate structures with different included solvents (e.g., see Table 1 of ref. 2)[*].

By casting at 130°C, together with minor quantities of δ form crystals, crystals are obtained (*Figure 2B*). As usual, the δ crystals are transformed into γ crystals by annealing (*Figure 2C*). The presence of the β'' modification is clearly shown by the diffraction peaks at $2\theta = 11.8°$ and 15.8° (*Figures 2B* and *C*).

For higher casting temperatures, diffraction peaks typical of the β modification only are obtained (*Figures 2D* and *2E*).

A reduction of the half widths with the increase of casting temperature is observed at least for the reflections with $(h + k)$ even[†]. This indicates an increase of the crystal size with the casting temperature, as expected.

On the other hand, a quantitative comparison of the relative heights of the peaks (e.g. compare the peaks at 11.8° and 12.3°, or the peaks at $2\theta = 13.6°$ and 15.8°, in *Figures 2C* and *2E*) seems to indicate that the modification closest to the ordered β'' limiting one is obtained by casting at the lower temperature (130°C). This phenomenon is possibly related to the dramatic increase of the evaporation rate of the solvent with the temperature in the range 130–170°C.

Recrystallizations of β-form samples

The d.s.c. scans at 10°C min^{-1} of two β form samples, the first one obtained by melt crystallization (β' modification), the second by casting at 140°C (closer to the limiting β'' modification) are shown in *Figures 3A* and *3B*, respectively. A double peak melting endotherm is observed for the first sample with the higher at 266°C (*Figure 3A*) while a single melting peak at 270°C is observed for the sample in the β'' modification (*Figure 3B*).

In ref. 6, on the basis of d.s.c. scans at different heating rates, it has been shown that the double peak shape of samples in the β' modification is due to recrystallization phenomena that occur during the d.s.c. measurements.

Analysis of X-ray diffraction patterns of a β-form sample at high temperatures, and in particular in the melting region, has allowed us to conclude that during the heating no β to α transition occurs but only recrystallization to the more perfect β form crystals[6]. However, these recrystallizations could involve transitions from the modification closer to the disordered limiting one (β') to modifications closer to the ordered limiting one (β'').

The d.s.c. scans of the β' form sample of *Figure 3A*, after annealing at 260°C, are reported in *Figure 3C*. It is

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[*] The X-ray diffraction patterns of the clathrates obtained by casting from *o*-DCB can appear very different from those of the clathrates obtained by precipitating from *o*-DCB solutions (e.g. Figure 4A of ref. 6). However, these differences are mainly due to the very low degree of crystallinity and the small size of the crystals in the precipitated powders, which produce diffraction patterns corresponding to the superposition of a strong amorphous halo with very broad diffraction peaks.

[†] The only well resolved reflections with $(h + k)$ odd, the (140) at $2\theta = 15.8°$ do not show this reduction. Analogously, a different behaviour for reflections with $(h + k)$ even or $(h + k)$ odd, which characterize modifications with different degrees of order, has been also observed for isotactic polypropylene and has received a possible interpretation by Ikosaka and Seto[20] and some of us[21]

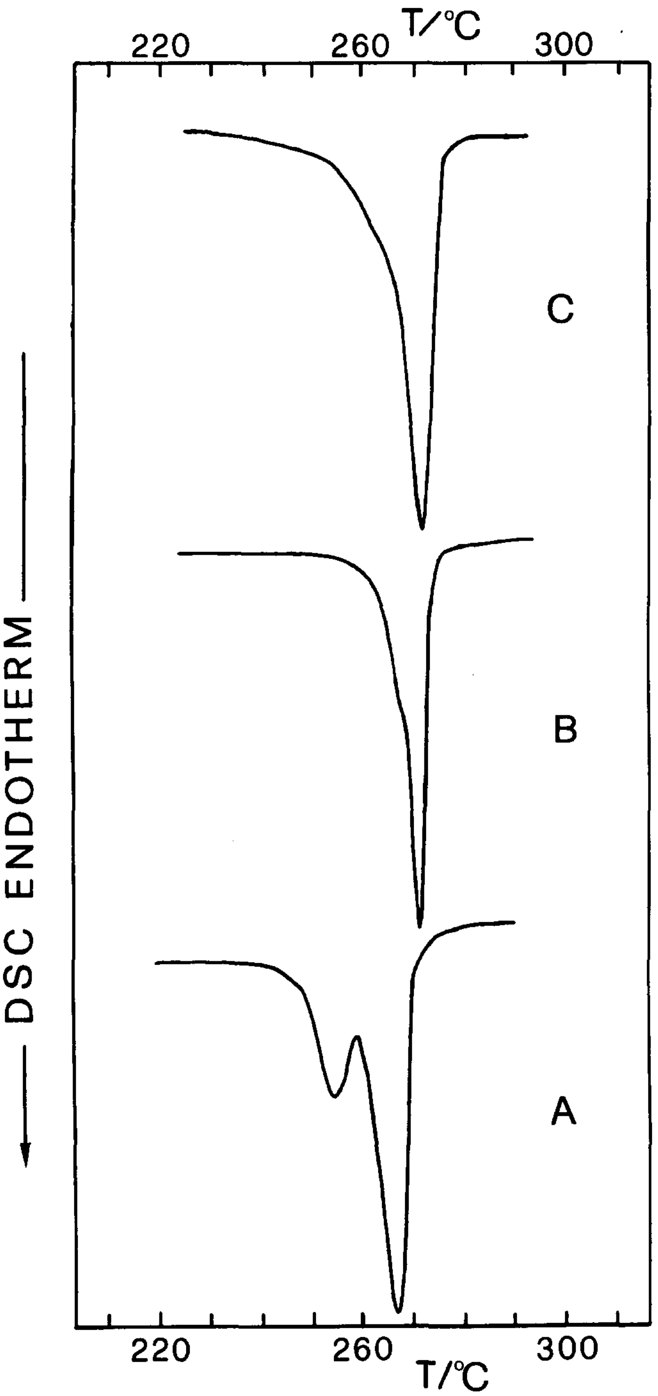

Figure 3 D.s.c. scans at 10°C min^{-1} of two β form samples obtained by: (A) melt crystallization (β' modification); (B) casting from *o*-DCB solutions at 140°C (β'' modification); (C) annealing at 260°C of the melt-crystallized sample A (β' modification)

apparent that this annealing procedure increases the melting temperature of the sample up to 270°C and substantially eliminates recrystallization phenomena during the d.s.c. scan and the related double peak shape. The X-ray diffraction pattern of the annealed sample, as well as those of samples annealed at higher temperatures, is very similar to that of the original sample (*Figure 1B*) and they do not present any evidence of reflections with $(h + k)$ odd. This indicates that the recrystallization of the β' sample in the melting region is not able to induce, in the samples considered, a transition to a modification sufficiently close to the β'' limiting one to produce the corresponding reflections in the X-ray diffraction patterns.

Morphological changes are possibly more relevant in determining the observed increase in the melting temperature due to the annealing.

Models for the different modifications of the β-form

In Table II of ref. 6 the Bragg distances observed in the powder patterns for samples, close to the β' and β'' limiting modifications, have been compared to the distances calculated according to the orthorhombic unit cell reported by Chatani *et al.*[1] ($a = 8.81$ Å, $b = 28.82$ Å). It was concluded that the absence from the pattern of the β' modification of the (hkl) reflection with $h + k = 2n + 1$ is consistent with a statistical pseudo-centring on the $a - b$ face of the unit cell[1,6].

Quantitative comparisons between the observed diffraction intensities (for the prepared samples which seem closest to the limiting β'' and β' modification) and the calculated intensities (for a fully ordered model and for a particular disordered model, respectively) are now presented.

The observed structure factors have been obtained from the X-ray diffraction patterns of *Figure 2D* and *Figure 1A* and are reported, as full rectangles in the plots of *Figures 4A* and *4B*, respectively.

The unit cell with s-PS chains in the *trans*-planar conformation packed according to the space group $P2_12_12_1$, proposed by Chatani *et al.*[1], is shown in *Figure 5*. A statistical disposition of the chains which produces a pseudocentring on the a–b face of the unit cell, corresponding to the space group *Cmcm* is shown in *Figure 6*. The calculated structure factors for the models of *Figures 5* and *6* are shown as empty rectangles in the plots of *Figures 4A* and *4B*, respectively.

Fairly good agreement between observed and calculated intensities is obtained with the fractional coordinates of

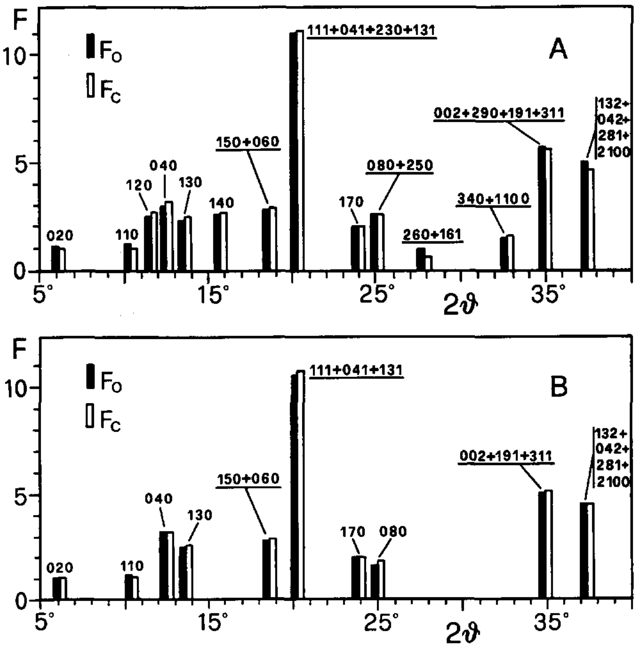

Figure 4 Observed structure factors, F_o, (full rectangles) obtained from the X-ray powder diffraction spectra of *Figure 2D* (A) and *Figure 1A* (B) corresponding to the prepared samples, closest to the β'' ordered (A) and β' disordered (B) limiting modifications, respectively. Calculated structure factors, F_c, (empty rectangles) for the models of *Figure 5* (A) and *Figure 6* (B). Only the values greater than the observable limit are reported

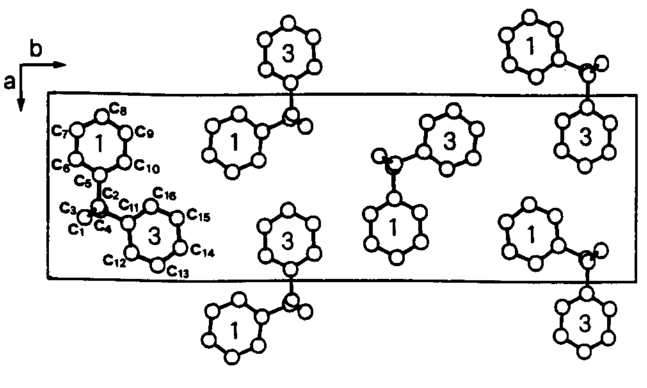

Figure 5 Model of packing proposed for the limiting ordered β'' modification (space group $P2_12_12_1$). Relative heights of the centres of the benzene rings are in units $c/4$

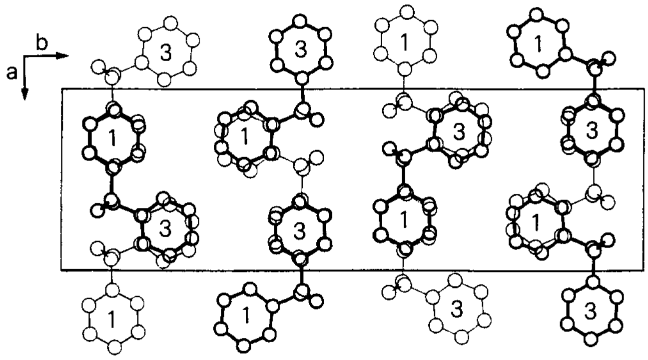

Figure 6 Statistical model of packing proposed for the limiting disordered β' modification (space group *Cmcm*). The disorder corresponds to the statistical disposition of the chains in the two alternative positions shown as thick and thin lines

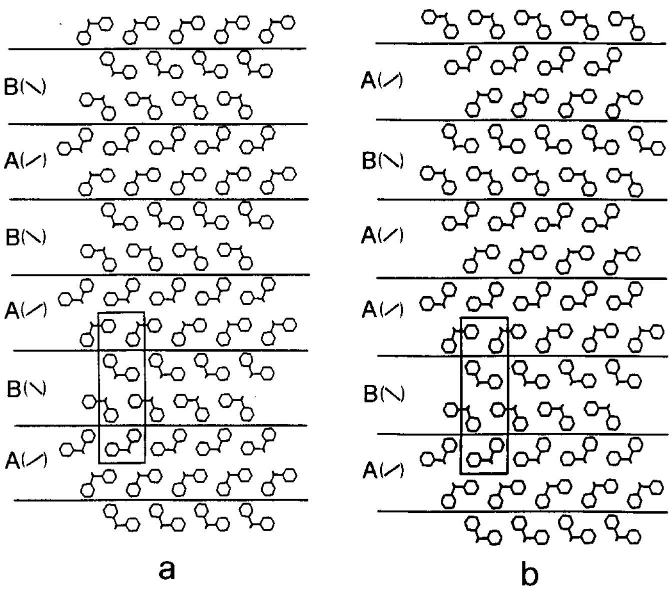

Figure 7 Possible stacking of macromolecular bilayers in the β form crystals. The regular succession of bilayers ABAB... gives rise to the ordered β'' modification (a); defects, corresponding to pairs of bilayers of the kind AA or BB, would characterize the disordered β' modification (b). The symbols (/) and (\) indicate the orientation of the lines connecting the adjacent phenyl rings of each chain inside the macromolecular bilayers A and B, respectively

Table 1 Fractional coordinates of the carbon atoms of the asymmetric unit in the model of *Figure 5*

	x/a	y/b	z/c
C_1	0.670	0.062	0.000
C_2	0.610	0.085	0.251
C_3	0.670	0.062	0.502
C_4	0.627	0.089	0.753
C_5	0.439	0.087	0.250
C_6	0.354	0.047	0.258
C_7	0.196	0.049	0.258
C_8	0.123	0.091	0.249
C_9	0.208	0.132	0.241
C_{10}	0.366	0.130	0.241
C_{11}	0.695	0.137	0.752
C_{12}	0.852	0.142	0.760
C_{13}	0.914	0.187	0.760
C_{14}	0.820	0.225	0.751
C_{15}	0.664	0.220	0.743
C_{16}	0.601	0.175	0.743

the asymmetric unit shown, for the case of the space group $P2_12_12_1$, in *Table 1*.

These results suggest that β form samples presenting X-ray diffraction patterns similar to those of *Figures 2D* and *1A* are in modifications close to the limiting ordered and disordered ones (β'' and β') and that these limiting modifications can be well represented by models shown in *Figures 5* and *6*, respectively.

Both ordered and disordered modifications of the β form can be described in terms of a stacking of the two kinds of a–c macromolecular bilayers, indicated as A and B in *Figure 7*. The two bilayers are characterized by different orientations of the lines connecting two adjacent phenyl rings inside each chain. (These different orientations are indicated by the symbols (/) and (\) close to the bilayers A and B, respectively).

In particular, the ordered structure corresponds to a regular alternation of bilayers of type A and B (*Figure 7a*), while the disordered structure would present some disorder in the stacking of these bilayers (*Figure 7b*). The statistical occurrence of these two different kinds of stacking of macromolecular bilayers gives rise to the statistical model of *Figure 6*.

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