eters to being orthorhombic as observed for the planar form. It is difficult to know whether these calculated values for the kink and planar forms are close enough to permit polymorphism. They apply to the energy difference at 0 K as opposed to the free energy difference at somewhere in the region of room temperature. The energy difference of 13.4 kJ/(mol repeat) corresponds to $\sim$1 kJ/(mol chain atom) and about 13% of the calculated lattice dissociation energy. In the case of 6-6 polyester, the calculations place the planar-2 form as 9 kJ/(mol repeat) more stable energetically than the kink structure, the latter representing the experimentally observed one. This amounts to $\sim$0.6 kJ/(mol chain atom) and about 8% of the lattice dissociation energy. This is probably near the level of reliability of the calculations.

In summary, it can be concluded that the kink containing structures are stable because, in the appropriate examples, the energy penalty for forming them compared to the planar counterparts is modest and they pack competitively or better than the planar forms. By the time aliphatic lengths of those in 6-10 polyester are reached the packing in planar form is less perturbed by the ester groups, the packing is favored in the latter, and the intramolecular penalty for kink formation is apparent.

Acknowledgment. We are indebted to the Polymers Program, Division of Materials Research, National Science Foundation, for financial support of this work. They are also grateful to the San Diego Supercomputer Center for a grant of computer time.

References and Notes

(1) *Collected Papers of W.H. Carothers on High Polymeric Substances*; Mark, H., Whitby, G. S., Eds.; Interscience: New York, 1940; Vol. I.
(2) Fuller, C. S. *Chem. Rev.* **1940**, *26*, 143.
(3) Turner-Jones, A.; Bunn, C. W. *Acta Crystallogr.* **1962**, *15*, 105.
(4) Ueda, A. S.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1971**, *2*, 387.
(5) Tripathy, S. K.; Hopfinger, A. J.; Taylor, P. L. *J. Phys. Chem.* **1981**, *85*, 1371.
(6) Sorensen, R. A.; Liau, W. B.; Boyd, R. H. *Macromolecules* **1988**, *21*, 194.
(7) Sorensen, R. A.; Liau, W. B.; Kesner, L.; Boyd, R. H. *Macromolecules* **1988**, *21*, 200.
(8) Boyd, R. H.; Kesner, L. *J. Chem. Phys.* **1980**, *72*, 2179.
(9) Boyd, R. H.; Kesner, L. *Macromolecules* **1987**, *20*, 1802.
(10) Colpa, J. H. P. *Physica* **1971**, *546*, 185, 205.
(11) Liau, W. B. Ph.D. Dissertation, University of Utah, 1989.
(12) Smith, G. D.; Boyd, R. H. *Macromolecules*, preceding paper in this issue.
(13) Fuller, C. S.; Erickson, C. L. *J. Am. Chem. Soc.* **1937**, *59*, 344.
(14) Minke, R.; Blackwell, J. *J. Macromol. Sci., Phys.* **1979**, *B16*, 407.
(15) Minke, R.; Blackwell, J. *J. Macromol. Sci., Phys.* **1980**, *B18*, 233.
(16) Aylwin, P. A.; Boyd, R. H. *Polymer* **1984**, *25*, 323.
(17) Kanamoto, T.; Tanaka, K. *J. Polym. Sci., Part A-2* **1974**, *9*, 2043.
(18) Swan, P. R. *J. Polym. Sci.* **1962**, *56*, 403.
(19) Tadokoro, H. *Structure of Crystalline Polymers*; Wiley-Interscience: New York, 1979.

Registry No. (Ethylene glycol)(butanedioic acid) (copolymer), 25569-53-3; (ethylene glycol)(butanedioic acid) (SRU), 25667-11-2; (ethylene glycol)(adipic acid) (copolymer), 24938-37-2; (ethylene glycol)(adipic acid) (SRU), 24937-05-1; (ethylene glycol)(octanedioic acid) (copolymer), 25776-26-5; (ethylene glycol)(octanedioic acid) (SRU), 26762-06-1; (adipic acid)(1,4-butylene glycol) (copolymer), 25103-87-1; (adipic acid)(1,4-butylene glycol) (SRU), 24936-97-8; (adipic acid)(1,6-dihydroxyhexane) (copolymer), 25212-06-0; (adipic acid)(1,6-dihydroxyhexane) (SRU), 24937-10-8; (1,6-dihydroxyhexane)(sebacic acid) (copolymer), 26745-88-0; (1,6-dihydroxyhexane)(sebacic acid) (SRU), 26762-10-7; polyethylene, 9002-88-4.

Polymorphism in Melt Crystallized Syndiotactic Polystyrene Samples

Gaetano Guerra, Vincenzo M. Vitagliano, Claudio De Rosa,
Vittorio Petraccone, and Paolo Corradini

Dipartimento di Chimica, Università di Napoli, via Mezzocannone 4, I-80134 Naples, Italy.
Received June 6, 1989; Revised Manuscript Received July 24, 1989

ABSTRACT: Both the crystalline forms containing zigzag planar conformations (pure or mixed) can be obtained by melt crystallization of syndiotactic polystyrene. Some of the factors that influence the polymorphic behavior in samples crystallized on cooling from the melt are described: the cooling rate from the melt, the crystalline form of the starting material, the maximum temperature of the melt, the time of residence in the melt at that temperature, and, in some cases, also the heating rate to reach melting. A possible interpretation of the observed polymorphic behavior in melt crystallizations for moderate cooling rates is that when a memory of α-form crystals remains in the melt, the acquisition of the α form is favored, otherwise the β form is obtained. The formation of the α form, also by quenching from the melt or by annealing from the amorphous phase, could be a kinetically controlled process.

Introduction

The polymorphic behavior of syndiotactic polystyrene (s-PS) is very complex. Two crystalline forms containing molecular chains in a zigzag planar conformation (with an identity period of 5.1 Å)[1] and two crystalline forms containing molecular chains with $s(2/1)2$ symmetry and an identity period close to 7.7 Å have been very recently described.[2,3] For the chains with $s(2/1)2$ symmetry a conformation TTGG was proposed on the basis of energy calculations.[3]

Although the preparation by melt crystallization is described in the literature for only one form, a careful

0024-9297/90/2223-1539$02.50/0

analysis of the crystallization from the melt shows that both the crystalline forms containing zigzag planar chain conformations (as pure forms or as mixtures of them) can be obtained.

In the present paper, some of the factors that influence the polymorphic behavior in samples crystallized on cooling from the melt are described and an interpretation of the experimental results is attempted.

Experimental Section

The s-PS ($M_w = 6.6 \times 10^5$ determined by GPC) was supplied by Istituto Guido Donegani of Montedison. The polymer fraction insoluble in methyl ethyl ketone is 93%.

The melt-crystallization processes were generally conducted in a moulding press. The polymer powders were introduced in the press already heated at the maximum temperature (T_{max}) and held at that temperature under pressure (~2 kg/cm^2) for a given time (t_{max}). The cooling to room temperature was in the press at a cooling rate close to 10 °C/min. The samples obtained were about 0.5 mm thick. To achieve more controlled conditions for T_{max} and for the cooling rates, melt-crystallization experiments were also conducted in a DSC apparatus.

Wide-angle X-ray diffraction patterns were obtained with nickel-filtered Cu Kα radiation. The compression-moulded samples were analyzed with an automatic Philips powder diffractometer while the much smaller samples prepared in the DSC apparatus were analyzed with a photographic flat camera.

From the patterns of the diffractometer, quantitative evaluations of the content of the two crystalline forms possibly present in the melt-crystallized samples were also obtained. The 2θ region 10°–15° is considered, and a base line between the two intensity minima located at $2\theta = 10.8°$ and $2\theta = 14.8°$ is drawn. The areas (A) of the two peaks located at $2\theta = 11.6°$ and $2\theta = 12.2°$ are measured, and the percent content of the α form in the crystalline fraction is evaluated by the approximate relation

$$P_\alpha = \frac{1.8A(11.6)/A(12.2)}{1 + 1.8A(11.6)/A(12.2)} \times 100$$

where 1.8 is the ratio between the intensities (measured in the same experimental conditions) of the peaks at 11.6° and 12.2° for samples of equal thickness and crystallinity in the pure α and β forms, respectively.

The DSC scans were carried out in a Mettler TA3000 (DSC 30) calorimeter, in a flowing-nitrogen atmosphere at a heating rate (if not otherwise specified) of 10 °C/min.

Results and Discussion

Powder Patterns of the Known Modifications of the Crystalline Forms of s-PS. The X-ray diffraction patterns of unoriented samples of the four crystalline forms of s-PS, prepared as described in the literature, are reported in Figure 1. Since it is not yet present in the literature, the nomenclature for the different forms used in a previous patent[4] will also be defined.

The α form (Figure 1A), which can be obtained by compression moulding,[1,2,5] and the β form (Figure 1B), which can be obtained by solvent casting at high temperatures,[1] are characterized by an identity period of 5.1 Å (as derived by diffraction patterns of oriented samples).

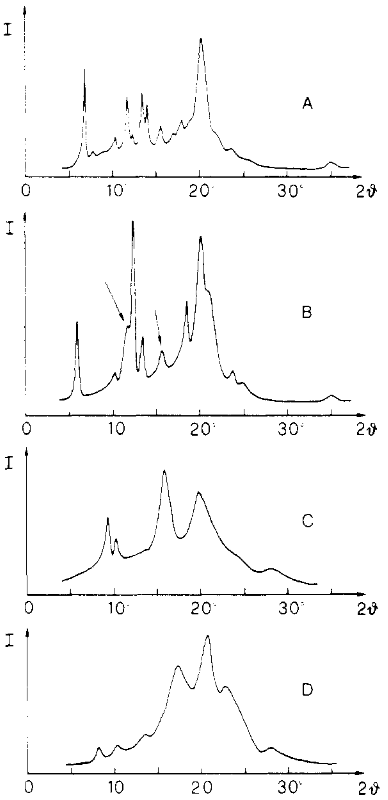

Figure 1. X-ray diffraction patterns of the four crystalline forms of s-PS associated with the proposed nomenclature and the preparation method described in the literature:[1-3] (A) α form, compression-moulded sample; (B) β form, cast from a o-dichlorobenzene solution at 170 °C; (C) γ form, α-form sample swelled by dichloromethane and then completely desiccated; (D) δ form, α-form sample swelled in dichloromethane (see text).

The two forms having an identity period of 7.7 Å can be obtained by swelling of samples of the α form in different solvents and by successive removal of the solvents.[2] For completely desiccated samples, patterns like that of Figure 1C are obtained, corresponding to a different crystalline form, which is thereafter called the γ form. For the swelled samples, the diffraction intensities of the different reflections as well as the precise location of the reflections are changing with the solvent; this clearly indicates the inclusion of molecules of the solvents in the crystalline structure. This variable crystalline structure of s-PS, which includes molecules of solvent, will thereafter be called the δ form. Just as an example of the various possible patterns of the δ form, the X-ray diffraction pattern of a sample swelled in dichloromethane and held at 60 °C for 14 h under vacuum (residual solvent content close to 13% by weight) is reported in Figure 1D.

Powders in the γ and δ forms can be also obtained by precipitation from polymer solutions followed by desiccation in drastic or mild conditions, respectively. The X-ray diffraction patterns of the δ form samples depend again on the kind of solvent and on its residual content.

Melt Crystallization of s-PS. In our analysis of the crystalline forms of samples crystallized on cooling from the melt, conditions of moderate cooling rates and rapid quenching from the melt are treated separately.

Moderate Cooling Rates. The polymorphic behavior of s-PS for moderate cooling rates is substantially independent of the cooling rate, at least for the range 1–40 °C/min. In this case the crystalline form of the melt-crystallized samples is mainly related to the thermal history of the melt; the maximum temperature at which the melt is heated up (T_{max}) and the time of permanence of the melt at that temperature (t_{max}) are particularly relevant.

The X-ray diffraction patterns of some samples obtained by compression moulding of powders in the γ form with different T_{max} values and t_{max} = 3 min are, for instance, reported in Figure 2.

For sufficiently high values of T_{max} and t_{max} (e.g., T_{max} = 340 °C and t_{max} = 1 min or T_{max} = 300 °C and t_{max} = 60 min), melt-crystallized samples always present diffraction patterns like one reported in Figure 2A, inde-

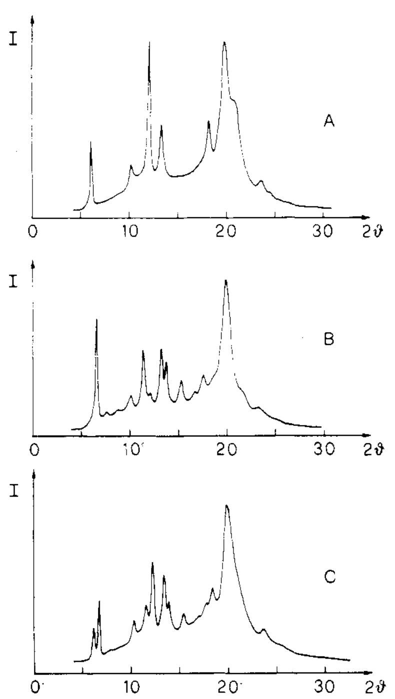

Figure 2. X-ray diffraction patterns of compression-moulded samples, from γ-form powders, obtained for t_{max} = 3 min and for (A) T_{max} = 340 °C, (B) T_{max} = 280 °C, and (C) T_{max} = 310 °C.

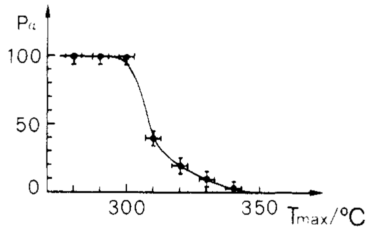

Figure 3. Percent content of the α form in the crystalline phase (P_α) for compression-moulded samples from γ-form powders versus the maximum temperature of heating of the melt (T_{max}). The time of permanence of the melt at T_{max} is 3 min.

pendent of the crystalline form of the starting material. This pattern is quite similar to that of the β form (Figure 1B); however, the peak at 2θ = 15.7° and the shoulder at 2θ = 11.5° (indicated by arrows in Figure 1B) are not present here. The peak at 2θ = 15.7° is slightly broader than the other peaks. This ensemble of data seems to indicate the presence of different crystalline modifications for the β form. The modifications presenting the patterns of Figure 2A (sample obtained by melt-crystallization) and Figure 1B (sample obtained by high-temperature casting) will be named thereafter β' and β'', respectively.

The crystalline form which is obtained for lower values of T_{max} and t_{max} is dependent on the crystalline form of the starting material. In particular, if the starting material is in the β (β' or β'') form, again the β' form is obtained, while if the starting material is in one of the other three forms, the melt-crystallized samples can contain pure α-form crystals (Figure 2B) or mixtures of crystals in the α and β' forms (Figure 2C).

The percent content of the two forms in the crystalline phase, for compression-moulded samples from γ-form powders, is reported versus T_{max} (for t_{max} = 3 min) in Figure 3. The overall crystallinity of these samples, as evaluated on the basis of the X-ray diffraction patterns, is instead scarcely dependent on T_{max}.

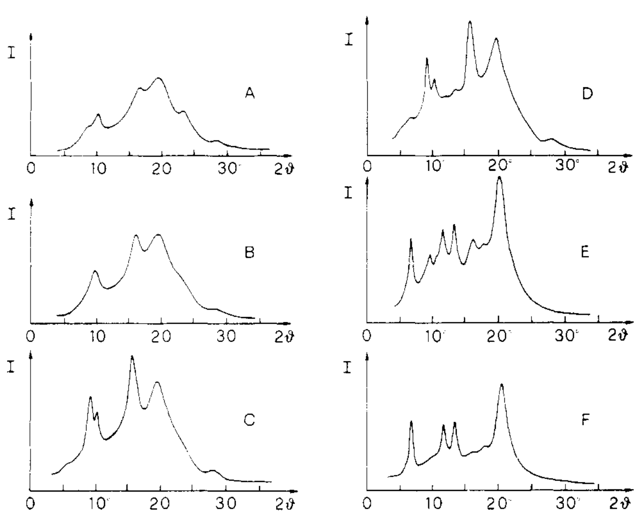

Figure 4. X-ray diffraction patterns of a sample precipitated from o-dichlorobenzene (and desiccated under vacuum at 60 °C) at different temperatures: (A) 60, (B) 100, (C) 140, (D) 160, (E) 180, (F) 200 °C.

Substantially the same behavior is observed for the melt crystallization from samples in the α form. For melt crystallization from samples originally in the δ form, the polymorphic behavior is strongly dependent also on the thermal history during the heating up to the melting temperature. For very low heating rates (e.g., 1 °C/min) the behavior is very similar to that of the γ form. For intermediate heating rates the minimum values of T_{max} and t_{max}, which give rise to the formation of the pure β' form, are lowered. In fact, for instance, powders in the δ form, heated up in a DSC apparatus at a heating rate of 40 °C/min, produce, for t_{max} = 1 min, pure β' form samples already for T_{max} = 300 °C and mixed α and β' forms for T_{max} = 280 °C. For very high heating rates (as, for instance, for powders suddenly heated between hot plates of a moulding press) always the β' form is obtained.

The similar crystallization behavior of samples originally in the α, γ, and δ form can be easily understood, since, by thermal treatments for low heating rates, δ-form crystals are firstly transformed into γ-form crystals and subsequently into α-form crystals.[2] This is shown, for instance, by the X-ray diffraction patterns of a sample originally in the δ form (precipitated from o-dichlorobenzene solution and desiccated under vacuum at 60 °C) subjected to successive increases of the temperature of 20 °C in the range 60–200 °C (Figure 4). It is apparent that in these conditions the pure γ form is present above 140 °C and the pure α form above 200 °C. In particular, the pattern of Figure 4F corresponds to a disordered modification of the α form (described in detail in the next section).

Similar information can be obtained by the analysis of the DSC scans at 10 °C/min of the samples in the three forms, reported in Figure 5. The scan of the α form (Figure 5A) presents only one melting endotherm close to 270 °C. The scan of the γ form (Figure 5B) presents a very similar melting peak together with a smaller endothermic peak centered close to 180 °C; the smaller peak is associated with the $\gamma \rightarrow \alpha$ transition, the larger peak, with the melting of the α form. The scan of the δ form (Figure 5C) presents besides the usual melting peak a very complex endothermic behavior in the range 100–220 °C; this corresponds to the gradual transformation from the δ to the γ form and from the γ to the α form combined with the removal of the solvent while the high-

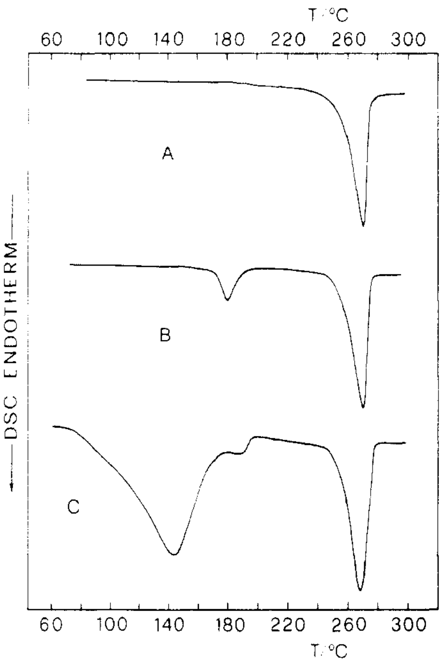

Figure 5. DSC scans of the samples in α form (A), γ form (B), and δ form (C), which present the X-ray diffraction patterns of parts F, C, and A of Figure 4, respectively.

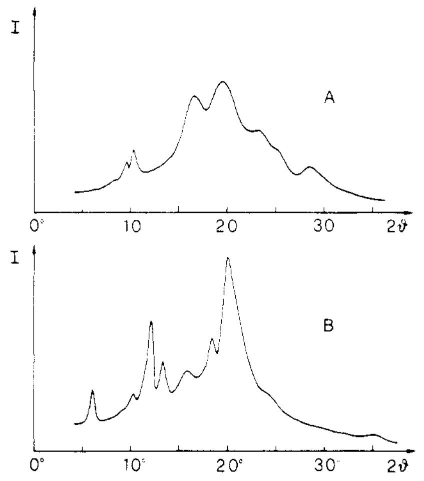

Figure 6. X-ray diffraction patterns of a sample originally in the δ form and suddenly heated up to 150 °C (A) or up to 160 °C (B).

temperature endothermic peak corresponds again to the melting of the α form.

The peculiar behavior of powders in the δ form, when suddenly heated up to the melting temperature, can also be understood on the basis of the following annealing experiments. In fact the annealing of δ-form powders at high temperatures (above 150 °C), when the annealing temperature is suddenly reached, seems to produce a direct transformation into the β form rather than into the γ (and subsequently α) form. The X-ray diffraction patterns of a sample originally in the δ form (the same sample as Figure 4A) suddenly heated up to 150 and 160 °C (between hot plates of a moulding press) are shown, for instance, in parts A and B of Figure 6, respectively. A direct transition from the δ to the β'' form is apparent.

The DSC melting behavior of pure α- and β'-form samples, for different heating rates, is compared in Figure 7. The increase of the melting temperatures by reduction of the heating rate suggests the occurrence of reorganization phenomena for both the crystalline forms. For the β form two melting peaks, whose relative intensities change with the heating rate, are observed, as typically occurs for the case of recrystallization phenomena.[6] The very close location of the higher peak of the β form and the single peak of the α form could suggest a possible recrystallization of the β-form samples into the α form. However, X-ray diffraction analyses at high temperatures allow us to discard this hypothesis. A typical X-ray diffraction pattern of a sample in the β form in the melting region is shown, for instance, in Figure 8. It is apparent that also in this predominantly melted sample the residual crystalline phase is still in the β form. It is possible to conclude that during the heating no $\beta \rightarrow \alpha$ transition but only a recrystallization to more perfect β form crystals occurs.

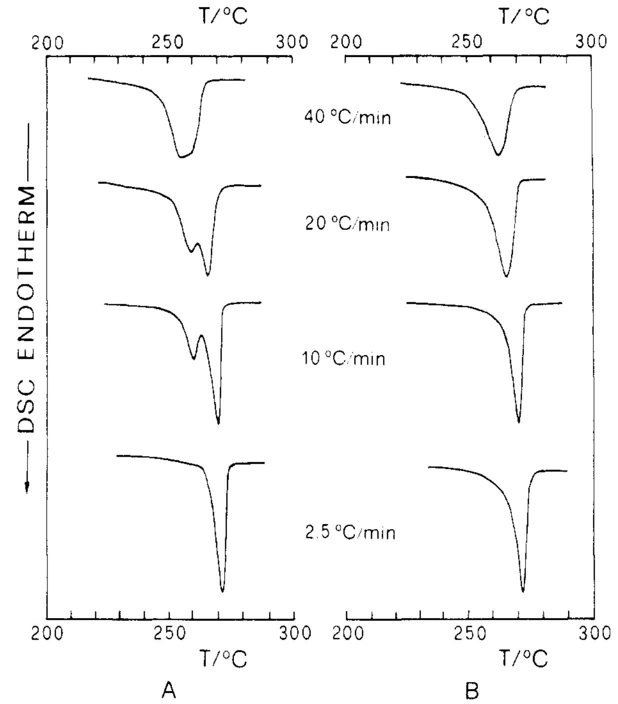

Figure 7. DSC melting behavior of pure β'-form (A) and α-form (B) samples at different heating rates.

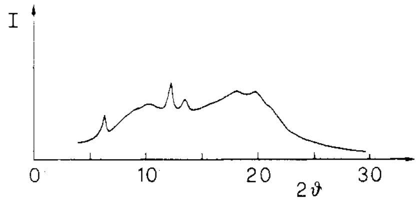

Figure 8. X-ray diffraction pattern of a β-form sample in the melting region.

On the basis of these observations, our interpretation of the polymorphic behavior in melt-crystallized samples is that when a memory of the α-form crystals is still present in the melt the attainment of the α form is favored, otherwise the β form is obtained. This happens under mild melting conditions, whenever we start from a sample in the α form or from samples originally in the γ form (or slowly heated δ form), which are transformed into the α form prior to melting (as indicated before). According to our interpretation, a memory of the α-form crystals would hence be maintained, at least for short times, also in a wide temperature range above its melting temperature. The presence of a memory of the crystalline structure in macromolecular melts is well-known and related with the largely studied phenomenon of self-

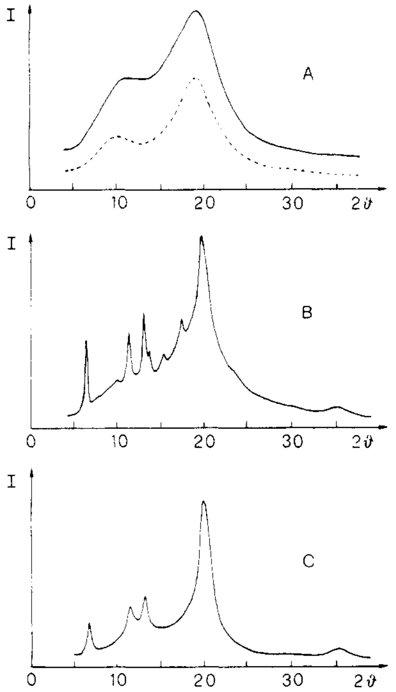

Figure 9. X-ray diffraction patterns of (A) a quenched film of s-PS (continuous curve) and an atactic polystyrene film (dashed curve), (B) a quenched thick sample (0.7 mm), and (C) a sample crystallized from the amorphous phase upon heating up to 250 °C.

Table I
Intensities and Bragg Distances Observed in the Powder Spectra for Two α Modifications (α' and α'', See Text) of s-PS Compared with the Bragg Distances Calculated According to the Unit Cell Proposed by Greis et al.[9,10]

		α'		α''	
hkl	d_{calc}	d_{obs}	I_{obs}	d_{obs}	I_{obs}
110	13.13	13.07	ms	13.11	s
200	11.37			11.37	w
210	8.595			8.56	mw
300	7.580	7.51	m	7.58	ms
220	6.565	6.53	m	6.56	ms
310	6.307			6.31	ms
400	5.685			5.67	m
320	5.217			5.18	vw
410	4.962	4.94	w	4.94	mw
211	4.351	4.34	vs	4.37	vs
510	4.084			4.01	vw
600	3.787	3.77	w	3.74	w
002	2.523	2.55	mw	2.54	mw

Table II
Intensities and Bragg Distances Observed in the Powder Spectra for Two β Modifications (β' and β'', See Text) of s-PS Compared with the Bragg Distances Calculated According to the Unit Cell Proposed by Chatani et al.[1]

		β'		β''	
hkl	d_{calc}	d_{obs}	I_{obs}	d_{obs}	I_{obs}
020	14.40	14.37	ms	14.34	ms
110	8.425	8.46	w	8.48	w
120	7.516			7.48	m
040	7.205	7.18	vs	7.17	vs
130	6.493	6.52	m	6.49	m
140	5.577			5.56	mw
060	4.803	4.78	m	4.78	m
111	4.338	4.39	vs	4.38	vs
041	4.141	4.18	ms	4.20	ms
170	3.730	3.72	w	3.72	w
080	3.603	3.58	vw	3.56	vw
002	2.530	2.56	m	2.55	mw

nucleation in the melt crystallization.[7,8] Starting with samples in the β or in δ forms suddenly heated up, since the α form during heating is not formed, no memory of it can be present in the melt and consequently the β' form is always obtained.

Quenching Conditions. An efficient quenching of melted samples in liquid nitrogen, as for instance for thicknesses lower than 0.5 mm, produces amorphous samples. The X-ray diffraction pattern of an amorphous film of s-PS is reported in Figure 9A, where it is compared with the pattern of atactic polystyrene.

Less efficient liquid-nitrogen quenching procedures, which do not lead to amorphous samples (e.g., quenching of thicker samples), lead to the formation of α-form crystals, independently of the melting conditions; the diffraction pattern of a 0.7-mm-thick sample maintained at 320 °C for 5 min and then quenched is shown in Figure 9B. An increased width of all the reflections as well as a depression of some of them (e.g., those at $2\theta = 14°$ and $2\theta = 15.6°$) with respect to the pattern of Figure 1A indicates that, due to the quenching procedure, lower degrees of crystal perfection are obtained.

Annealing of the amorphous samples above 140 °C allows crystallization; by crystallization from the amorphous phase, samples in the α form are again obtained. Depending on the annealing conditions they present different (but generally very low) degrees of crystal perfection. A representative diffraction pattern of a sample crystallized from the amorphous phase (in particular, upon heating up to 250 °C with a heating rate of 4 °C/min) is reported in Figure 9C. In this pattern the reflections, which in Figure 1B are only depressed, have now nearly completely disappeared.

Hence, by quenching or crystallization from the amorphous phase crystallites are obtained that are different not only in morphology (smaller and less perfect) but also in the fine structure, as compared to those obtained by compression moulding. The sample with the pattern of Figure 9C is possibly close to a limiting disordered modification (α') of the α form while the sample with the pattern of Figure 1A is possibly close to a limiting ordered modification (α'') of the α form. A "continuum" of different modifications may exist between the two limiting ones.

On the basis of the conclusions of the previous section, the formation of the α form also by rapid quenching and by annealing from the amorphous phase could be a kinetically controlled process.

Structural Considerations. The results of the X-ray diffraction experiments on the α (α' and α'') and β (β' and β'') modifications of s-PS can be correlated with structural data already known[1,9,10] or in formulation in our laboratories.

The intensities and Bragg distances observed in the powder patterns for the α and β modifications are compared in Tables I and II to the distances calculated according to the unit cell reported by Greis et al.[9,10] and Chatani et al.,[1] respectively.

As for the disordered β' modification, the absence of the (*hkl*) reflections with $h + k = 2n + 1$ is consistent with a statistical pseudocentering on the $\bar{a}$–$\bar{b}$ face of the unit cell.[1]

As for the α modifications, we stress that the observed diffractions are all accounted for by a unit cell having hexagonal axes $a = 26.26$ Å and $c = 5.04$ Å as reported by Greis.[10] However, the absence in the α' modification of the reflections with $-h + k + l \neq 3n$ (and their weakness in the α'' modification) is indicative of a quasi-rhombohedric symmetry, presenting a packing of the phe-

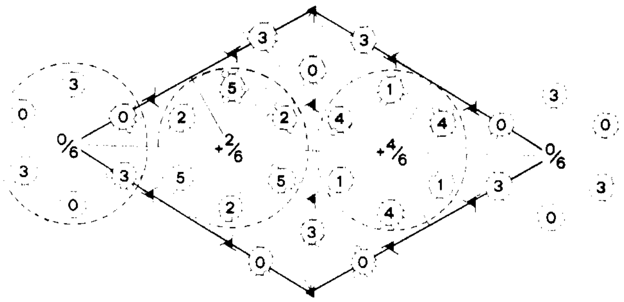

Figure 10. Possible mode of packing of benzene rings in a rhombohedral lattice as it occurs in the α modifications of s-PS. Relative heights of the centers of the benzene rings are in the units $c/6$. The three groups of six benzene rings around 3-fold axes, which present different heights, are enclosed in dashed circles; the relative displacements of sextets are 0, $2c/6$, and $4c/6$.

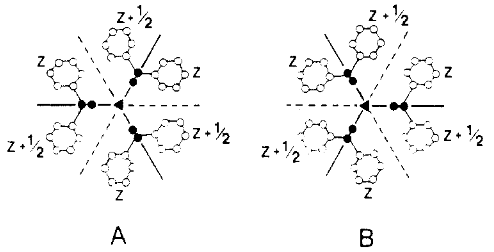

Figure 11. Two different and isosteric orientations of triplets of s-PS chains corresponding to the groups of six benzene rings defined in Figure 10. Dark circles indicate the main-chain carbon atoms. The presence of a statistical disorder in these orientations characterizes the α' modification.

nyl groups as shown in Figure 10. Groups of six benzene rings are shifted along z of $2c/6$. This mode of packing is curiously reminiscent of that present in isotactic polystyrene (compare Figure 10 of this paper with Figure 4 of ref 11), giving rise in both cases to a very strong (211) reflection. In the α' modification there is a statistical disorder with respect to two different and isosteric orientations of triplets of chains around 3-fold axes, as shown in parts A and B of Figure 11. Notice that in the two models of parts A and B of Figure 11, while the six benzene rings have essentially the same positions (as that in Figure 10), the main chain atoms (dark circles in figure) are rotated by 60°. The presence of a statistical disorder in these orientations characterizes the α' modification; an ordering of the orientations of the triplets occurs in the α'' form. These models are supported by diffraction intensity calculations, which will be reported in a forthcoming paper.

Acknowledgment. We thank Prof. U. Giannini, Dr. E. Albizzati, and Dr. G. Giunchi of the Istituto Guido Donegani and Prof. A. Immirzi of the University of Salerno for useful discussion. This work was supported by the Ministry of Public Education and by Istituto Guido Donegani (Montedison).

References and Notes

(1) Chatani, Y.; Fujii, Y.; Shimane, Y.; Ijitsu, T. *Polym. Prepr. Jpn. (Engl. Ed.)* **1988**, *37*, E428.
(2) Immirzi, A.; De Candia, F.; Iannelli, P.; Vittoria, V.; Zambelli, A. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 761.
(3) Corradini, P.; Napolitano, R.; Pirozzi, B. *Eur. Polym. J.* **1990**, *26*, 157.
(4) Guerra, G.; Vitagliano, V. M.; Corradini, P.; Albizzati, E. Ital. Pat., 1989 (Himont Inc.).
(5) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2465.
(6) Wunderlich, B. In *Macromolecular Physics: Crystal Melting*; Academic Press: New York, 1980; Vol. 3, Chapter IX.
(7) Vidotto, G.; Levy, D.; Kovacs, A. J. *Kolloid Z. Z. Polym.* **1969**, *230*, 289.
(8) Wunderlich, B. In *Macromolecular Physics: Crystal Nucleation, Growth, Annealing*; Academic Press: New York, 1976; Vol. 2, Chapter V.
(9) Greis, O.; Asano, T.; Xu, Y.; Peterman, J. *Z. Kristallogr.* **1988**, *182*, 58.
(10) Greis, O.; Xu, Y.; Asano, T.; Peterman, J. *Polymer* **1989**, *30*, 590.
(11) Natta, G.; Corradini, P. *Makromol. Chem.* **1955**, *16*, 77.