Noncrystalline Order in Swollen Syndiotactic Polystyrene

F. de Candia,*,[†] **M. Carotenuto,**[‡] **L. Guadagno,**[§] **and V. Vittoria**[§]

Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, Salerno, Italy, Dipartimento di Fisica, Università di Salerno, Salerno, Italy, and Istituto di Ricerche su Tecnologia dei Polimeri, CNR Arco Felice, Napoli, Italy

Received March 9, 1992; Revised Manuscript Received July 20, 1992

ABSTRACT: The syndiotactic polystyrene shows a complex polymorphism, and the structural organization depends on thermal or solvent treatments. The effect of different solvents on oriented samples crystallized in a zigzag conformation has been investigated, and in some cases a transition to the helix conformation is observed. The obtained results show that the transition occurs through an intermediate amorphous state in which the molecular orientation is maintained. This evidence points to the conclusion that some kind of noncrystalline order is present in the intermediate swollen state.

Introduction

The syndiotactic polystyrene (sPS) shows a complex polymorphism, and different crystalline forms can be obtained, depending on thermal and/or solvent treatments. Two forms characterized by a zigzag conformation can be obtained by thermal crystallization; one of these, first observed by Ishihara et al.[1] and previously indicated as form I,[2] is indicated in the more recent literature as the α form.[3] Its structure has been analyzed by electron diffraction,[4] and a hexagonal unit cell was suggested. The second form characterized by chains in a zigzag conformation, first indicated as form II,[2] is now definitely indicated as the β form.[3] The unit cell is orthorhombic,[5] and as for the α form the period along the chain axis is 0.51 nm. Two more forms characterized by a helix conformation can be obtained by solvent-induced crystallization.[2,6,7] The period along the chain axis is 0.75 nm. These forms, first observed by Immirzi et al.,[6] are now indicated as the δ and γ forms. They can be obtained by starting from amorphous glassy films[7,8] or by dissolving the α form in appropriate solvents.[2,6] At variance with the α form, the β form is stable to the solvent treatments.[9] Zigzag and helix conformations have also been observed in mesomorphic structures in which the organization is restricted to the conformational and short-range order.[10,11] From this very short picture the complex network of relationships between structure and thermal and solvent treatments is clearly evident. In the present paper we report further evidence of the great tendency of sPS to arrange different levels of structural organization. In fact the analysis of the swelling behavior of oriented samples points to the conclusion that some kind of noncrystalline order is present in the swollen state.

Materials and Experimental Section

The syndiotactic polystyrene was kindly supplied by Istituto Donegani of Himont-Italia (Novara, Italy). Glassy films were obtained according to a previously described procedure, quenching to −80 °C the molten sample.[7] The glassy film was drawn at two different temperatures using an extensometer cell and controlling the drawing degree with reference ink marks. A first sample, indicated as sample A, was obtained by drawing at 110 °C up to $\lambda = 4$; a second sample, indicated as sample B, was obtained by drawing at 160 °C up to $\lambda = 3$ (λ is the ratio between the final and initial length); a third sample, indicated as sample C, was obtained by annealing sample B 1 h at 180 °C. The thickness of the samples after drawing was about 0.02 cm. The structural rearrangements induced by different solvents were analyzed by wide-angle X-ray scattering (WAXS). The solvents used were chloroform, toluene, and tetralin. WAXS was analyzed using a Seifert Debyeflex diffractometer; the radiation was Cu Kα. The sample and swelling solvents (in large excess) were sealed in a glassy capillary tube and collimated with the X-ray beam. The diffraction patterns were detected using a flat-camera (6-cm distance from the sample). The sample birefringence was evaluated at a qualitative level using an optical microscope.

Results

(a) Dry Sample Structure. The structural organization of samples A–C, before any solvent treatment, was analyzed by detecting the X-ray diffraction patterns. Samples A shows a diffraction pattern indicative of low structural order; however, a reflection of the first layer is observable, and a period of 0.51 nm along the chain axis can be calculated. In a previous paper, for samples obtained at the same drawing temperature, the experimental data suggest the presence of mesomorphic order induced by drawing.[12] The organization is restricted mainly to the conformational order which is zigzag planar, and a periodicity of 0.51 nm can be detected by the WAXD data. The same period is observed in the two crystalline α and β forms.[1–5,13] Sample B shows the diffraction pattern of an oriented crystalline system, and the observed reflections are indicative of the α form. In sample C the oriented α form is still present, but the diffraction spots are sharper, indicating better formed and larger crystals.

(b) Solvent Treatments. The swelling with the three solvents gives rise to different effects depending both on the solvent and on the structural organization of the sample.

When chloroform is used, any discrete diffraction disappears in less than 1 h, and the sample appears amorphous. The optical microscope, however, indicates the persistence of an appreciable birefringence. This situation remains unchanged until the sample is immersed in the solvent, also for days. After solvent removal, diffraction of an oriented crystalline system is observed; the reflections are those previously reported for the δ form,[3,6] characterized by a helix conformation with a period along the chain axis of 0.75 nm. The diffraction pattern of sample B after solvent removal is shuown in Figure 1.

When tetralin is used as the swelling solvent, the diffraction pattern remains unchanged, and only at very long swelling times, and for sample A only, some weak evidence of destructuration is observable. It is interesting to note that tetralin induces crystallization in the δ form

---

[†] Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno.

[‡] Dipartimento di Fisica, Università di Salerno.

[§] CNR Arco Felice.

0024-9297/92/2225-6361$03.00/0

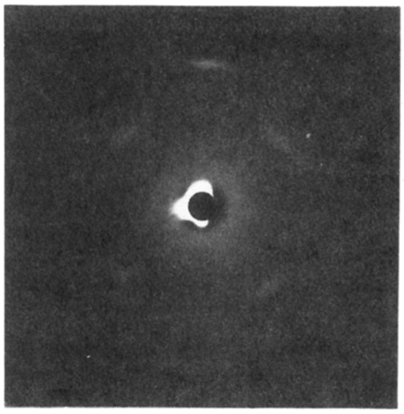

Figure 1. X-ray diffraction pattern of sample B, immersed in chloroform and then dried.

Table I
Diffraction Data for Sample B Swollen in Toluene

time in toluene (h)	period along chain axis (nm)	2θ		distance (nm)
0	0.51	*hk*0	6.8	1.30
			11.7	0.76
			13.5	0.65
		*hk*1	20.5	0.43
2	0.51	*hk*0	12.2	0.72
		*hk*1	20.5	0.43
12		diffused scattering		
27	0.75	*hk*0	7.9	1.12
			10.2	0.87
		*hk*1	17.3	0.51
52	0.73	*hk*0	7.8	1.13
			10.2	0.87
		*hk*1	16.8	0.53
			20.0	0.44
			23.1	0.38
		*hk*2	25.0	0.35

when the swelling is carried out on isotropic amorphous films.[14]

Much more interesting is the behavior observed when toluene is used; in this case it is possible to observe the disappearance of the oriented α form, the persistence of the amorphous birefringent state, and the appearance, still in the presence of the swelling solvent, of the oriented δ form. This sequence of structural transitions occurs on a time scale which increases from sample A to C, i.e., as the structural order of the dry sample increases. In Table I, the more intense diffractions and the corresponding Bragg distances are reported for sample B, at different times of immersion in toluene.

As is evident in Table I, after 2 h of immersion the zigzag conformation, characterized by a period of 0.51 nm, is still present and the equatorial reflection at 6.8 nm is absent, while a new equatorial reflection at 12.2 nm (intermediate between 11.7 and 13.5 nm) is observable; the system transforms into an intermediate amorphous form (amorphous on the basis of WAXS data), and after about 2 days the period of 0.75 nm, which characterizes the helix conformation, appears. The number of detectable diffractions increases with time, indicating an increasing crystalline order. The diffraction pattern, also at very long immersion time, clearly indicates that the orientation is maintained during the entire process, as is also confirmed by optical observations.

This sequence is shown in Figure 2, where some more significant diffraction patterns are observable. In Figure 2a the diffraction of sample B before any solvent treatment is shown; in Figure 2b after 2 h of immersion in toluene the zigzag form is still observable; Figure 2c shows the diffused halo of the amorphous intermediate; Figure 2d shows the diffraction pattern of the helix form observable in the swollen state after 27 h of immersion, while Figure 2e shows the diffraction pattern after drying. The time scale of this sequence is not perfectly reproducible for different specimens of sample B, obtained with the same procedure but in different preparations. However, with some fluctuations, the disappearance of the α form occurs within 6 h and the sample remains amorphous within about 15 h, while at longer times the helix form appears. The observed fluctuations, even if well appreciable, are negligible when comparing sample B with samples A and C. In fact in sample A the presence of the helix form is observable in less than 1 h after immersion, with the consequence that it is very difficult to observe the intermediate amorphous state. On the other hand, in sample C the time required to observe the disappearance of the initial α form is on the order of 15 h.

Discussion

The obtained results show that the transition to the helix conformation induced by the solvent treatment depends both on the initial sample structure and on the solvent. One can start from the trend observed using toluene; the mechanism must involve three different stages: (i) permeation into the crystalline phase; (ii) solvent-induced "melting"; and (iii) crystallization in the new crystalline form.

It seems clear that the first stage is affected by the degree of order of the existing structural organization, the entry of the solvent in more ordered structures being more difficult. In sample A, for which the presence of mesomorphic order was suggested,[12] the solvent rapidly dissolves the preexisting structure, and the new organization appears in less than 1 h. The process is slower in sample B, and the initial induction time is even longer in the annealed sample C. Probably a role is also played by the dimensions of the ordered domains, because a larger size means a smaller specific surface available for the solvent entry.

However, particularly interesting is the evidence that some kind of structural organization must be present in the amorphous intermediate state. In fact the orientation is maintained, as is confirmed by the optical observations and more clearly by the diffraction of the helix form, when it grows, which is typical of an oriented structure. This evidence suggests that the interchain aggregation, even in the swollen state, must be strong enough to prevent the relaxation of the chain orientation, in spite of the complex conformational reorganizations, required to crystallize in the new form. Some kind of solvated noncrystalline structure can be suggested, as was previously reported for the swollen forms obtained with toluene, starting from an isotropic amorphous film.[15] In that case the helix crystalline δ form does not appear in the swollen state but after solvent removal, indicating that in the present case the preexisting structure promotes the structural transition. The presence of noncrystalline order in the swollen state has been suggested by other authors. Nematic-like structures in gels of isotactic polystyrene have been suggested by Guenet et al.,[16] and similarly noncrystalline order was suggested by Tadokoro et al. to explain, as in the present case, the persistence of molecular orientation in gels of syndiotactic poly(methyl methacrylate).[17]

In the third stage the helix structure appears; the diffraction angles are slightly different from those first reported for the δ form,[6] indicating that the chain packing is affected by the nature of the solvent, which in some cases can be included in the crystalline structure.

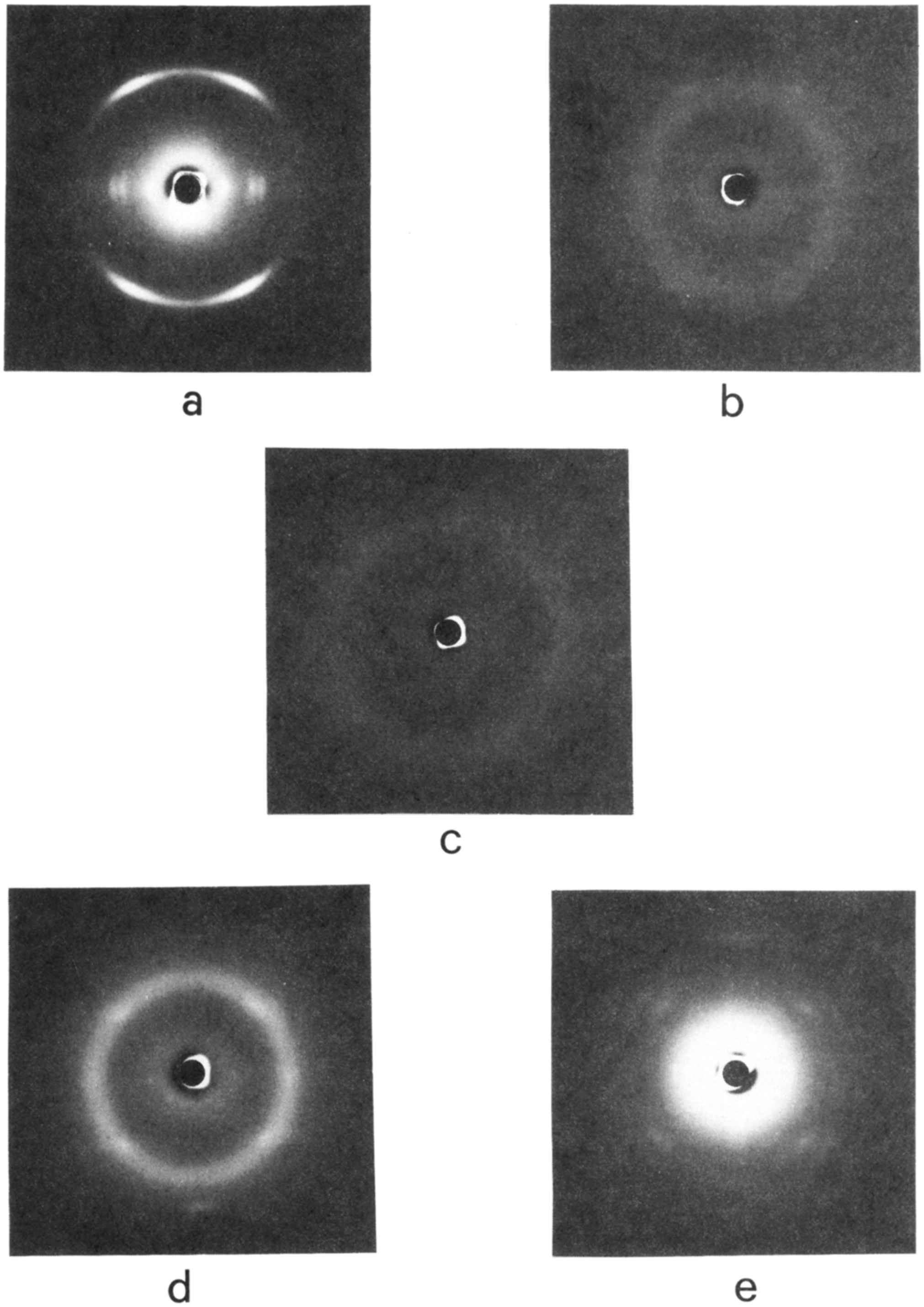

Figure 2. X-ray diffraction patterns of sample B: (a) dry sample before any solvent treatment; (b–d) detected in the swollen state after 2, 27, and 45 h; (e) dried.

When chloroform is used, the destructuration process is rapid, but the onset of the new crystalline order is observable only after solvent removal; this effect is probably related to the degree of swelling observable in chloroform, which is larger than that in toluene, with the consequence of increasing the chain segmental mobility at levels that are high for any crystallization process.

However, also in this case the chain orientation is maintained, and therefore a solvated noncrystalline order can be suggested in analogy with the previous considerations.

When the behavior of tetralin is considered, one can suggest that the size of the tetralin molecules is too high for permeation in the preexisting ordered domains, and therefore the initial structure remains substantially stable to the solvent action, at least on the time scale of our observations. The influence of the molecular size on solvation phenomena is expected and has been discussed by Klein and Guenet.[18] However, as herein noted, tetralin induces crystallization in isotropic amorphous films;[14] the helix form is observable after solvent removal, but in that case the first stage, required when a preexisting order is present, is of course absent.

The conclusive picture that can be drawn assumes a three-stage model for the transition process. The first stage is affected by the degree of order of the preexisting structure and by the specific tendency of the solvent to induce phase transitions. This statement implies that different levels of organization are possible in the zigzag form, as is indeed suggested.[3,13] The second stage, when activated (with toluene and chloroform), is characterized by the formation of a solvated noncrystalline structure, in which the chain–chain interactions are strong enough to prevent the relaxation of the chain orientation. The third stage can be activated in the swollen state, or after solvent removal, on the basis of conditions probably related to the degree of swelling and therefore to the molecular mobility in the noncrystalline structure.

Work is in progress, with different techniques, to analyze the organization of the intermediate state.

Acknowledgment. The present work was supported by Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate" of CNR.

References and Notes

(1) Ishihara, N.; Seimiya, T.; Kuramoto, N.; Uoi, M. *Macromolecules* **1986**, *19*, 2464.
(2) Vittoria, V.; Russo, R.; de Candia, F. *J. Macromol. Sci., Phys.* **1988**, *B28*, 419.
(3) Guerra, G.; Vitagliano, V.; De Rosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *23*, 1539.
(4) Greiss, O.; Xu, Y.; Asano, T.; Peterman, J. *Polymer* **1989**, *30*, 590.
(5) Chatani, Y.; Fujii, Y.; Shimane, Y.; Ijitsu, T. *Polymer Prepr. Jpn. (Engl. Ed.)* **1988**, *37*, E428.
(6) Immirzi, A.; de Candia, F.; Iannelli, P.; Vittoria, V.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 761.
(7) Vittoria, V.; de Candia, F.; Iannelli, P.; Immirzi, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 765.
(8) Vittoria, V.; Russo, R.; de Candia, F. *Polymer* **1991**, *32*, 3371.
(9) Vittoria, V.; Ruvolo, A.; de Candia, F. *J. Macromol. Sci., Phys.* **1992**, *B31*, 133.
(10) de Candia, F.; Ruvolo, A.; Vittoria, V. *Colloid Polym. Sci.* **1991**, *269*, 650.
(11) Vittoria, V.; Ruvolo, A.; de Candia, F. *Polym. Bull.* **1991**, *26*, 445.
(12) de Candia, F.; Ruvolo, A.; Vittoria, V. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 295.
(13) Vittoria, V.; Ruvolo, A.; de Candia, F. *J. Macromol. Sci., Phys.* **1991**, *B30*, 155.
(14) Unpublished results.
(15) Vittoria, V.; Russo, R.; de Candia, F. *Makromol. Chem., Macromol. Symp.* **1990**, *39*, 317.
(16) Guenet, J. M.; Lotz, B.; Wittman, J. C. *Macromolecules* **1986**, *19*, 1960.
(17) Kusuyama, H.; Takase, M.; Higashihata, Y.; Tseng, H.; Chatani, Y.; Tadokoro, H. *Polym. Commun.* **1982**, *23*, 1256.
(18) Klein, M.; Guenet, J. M. *Macromolecules* **1989**, *22*, 3716.

Registry No. PS (syndiotactic), 28325-75-9; $CHCl_3$, 67-66-3; toluene, 108-88-3; tetralin, 91-17-8.