Crystalline structure of α-form syndiotactic polystyrene

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X-ray diffraction analysis has been used to study the crystalline structure of syndiotactic polystyrene. A highly oriented specimen was obtained by stretching a tensile bar in the solid state for 500% at 200°C. A total of 23 Bragg reflections were identified. The appearance of many Bragg reflections on higher layer lines indicates that three-dimensional regularity of the crystal structure is significantly improved after annealing under tension. All Bragg reflections could be indexed with a hexagonal unit cell $a = 26.3$, $c = 5.1$ Å, which supports a previous observation by Greis *et al.* using electron diffraction analysis.

(Keywords: crystalline structure; syndiotactic polystyrene; X-ray diffraction)

Introduction

Since the successful synthesis of syndiotactic polystyrene (sPS) using stereospecific polymerization, there has been a considerable interest in characterizing the material[1–6]. Enhanced mechanical properties are expected for sPS, especially at elevated temperatures, due to its crystalline structure. Furthermore, a rapid crystallization rate relative to that of isotactic polystyrene, and possible high tensile modulus due to its inherent α-form planar zig-zag conformation, lead to a potentially commercial application of sPS as a low cost engineering plastic.

Unit cell dimensions of crystalline materials are critical for understanding molecular interactions on a microscopic level, which is of great concern to the related mechanical properties such as modulus and strength. Polymorphism has been well documented for sPS but the α-form is frequently encountered and is reported to be more stable than the helical form[7]. There are only limited crystallographic data available for α-form sPS; among them the most comprehensive information is provided by Greis *et al.*[1] using high energy electron diffraction indicating a hexagonal unit cell. However, most reflections were on the equator and only a few were observed on higher layer lines. Chatani *et al.*[3] reported two modifications for α form sPS using different preparation methods: a monoclinic structure from melt-crystallization, and an orthorhombic structure when cast from solution. Both of them have planar zig-zag conformations. Nevertheless, no observed X-ray diffraction data were detailed. Using X-ray powder diffraction, Guerra *et al.*[4] observed four crystalline modifications all with *trans–trans* conformations. However, indexing becomes difficult since overlapping occurs among many reflections with close *d*-spacings. In this paper, relying on a highly oriented crystalline specimen, X-ray diffraction analysis has been applied successfully to determine the unit cell dimensions of the α-form of sPS.

Experimental

Specimen preparation. sPS pellets were kindly provided by Dow Chemical Co. Injection moulded tensile bars were made by Dr D. Lewis (Michigan Molecular Institute) using a Boy injection machine. The tensile bar was then stretched to 500% of its original length in a heated oven at 200°C using an Instron tensile machine and was annealed at 250°C for 30 min at constant length.

X-ray diffraction. X-ray diffraction patterns of annealed sPS were recorded on Kodak DEF-5 diagnosis film using a Statton camera with pinhole collimation and with CuKα X-ray radiation. The *d*-spacings of the Bragg reflections were calibrated by dusting the specimen with NaCl powder.

Results and discussion

Figures 1a and *b* show the X-ray diffraction pattern of the sample of sPS and its corresponding schematic diagram as a reference. Orientation apparently has been developed after stretching and retained while annealing the specimen under an applied tension. A total of 23 Bragg reflections can be identified, 13 of which lie on the equator. Observed *d*-spacings and relative intensities are listed in *Table 1*. The existence of Bragg reflections on high layer lines and the lower intensity of the amorphous halo at a *d*-spacing around 4.5 Å are clear indications that the three-dimensional regularity of the crystal structure has been greatly improved after annealing. From the X-ray diffraction pattern (*Figure 1a*), it is not immediately evident whether reflections 14 ($d = 4.93$ Å), 20 ($d = 2.51$ Å) and 21 ($d = 2.39$ Å) are on the meridian or are just the extended streaks of off-meridional reflections owing to a slight disorientation of the crystallites. In order to clarify the ambiguity, we have tilted the specimen at two different angles corresponding to the positions where those reflections occur. *Figure 2a* shows the X-ray pattern with the sample tilted about 9° with respect to the direction of the incident beam. The tilted X-ray pattern clearly shows the splitting of reflection 14 ($d = 4.93$ Å) and rules out the possibility of it being a meridional reflection. *Figure 2b* shows the X-ray diffraction pattern tilted at 18° and the splitting of

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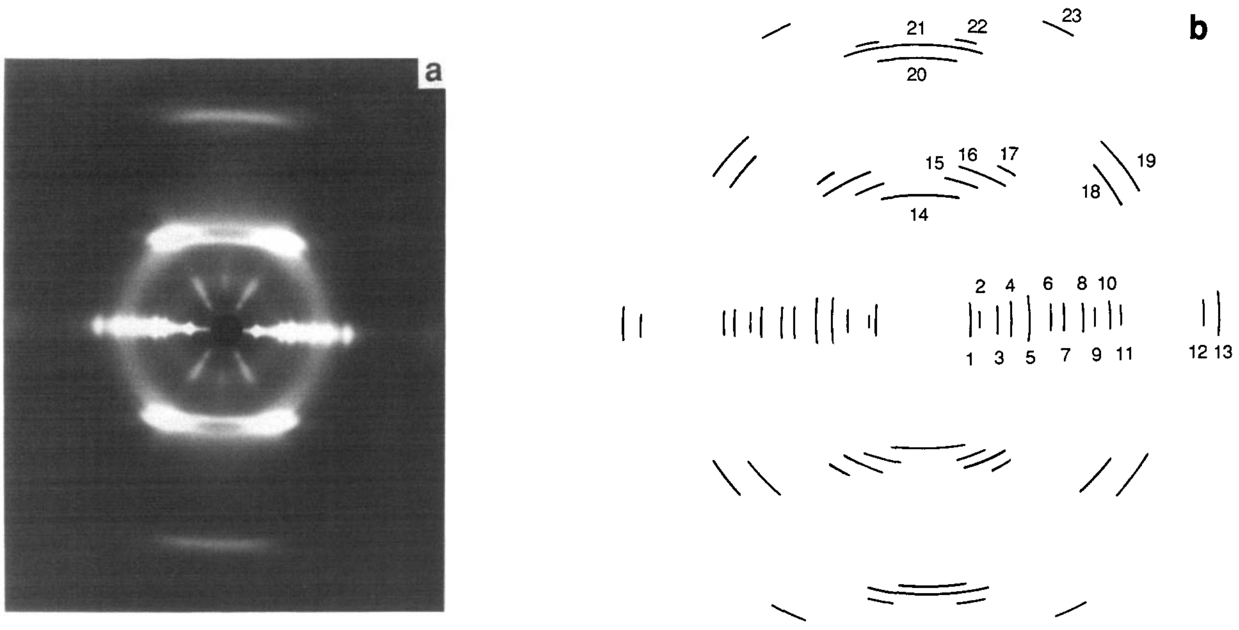

Figure 1 (a) X-ray diffraction pattern of α-form syndiotactic polystyrene; (b) schematic diagram of X-ray diffraction pattern

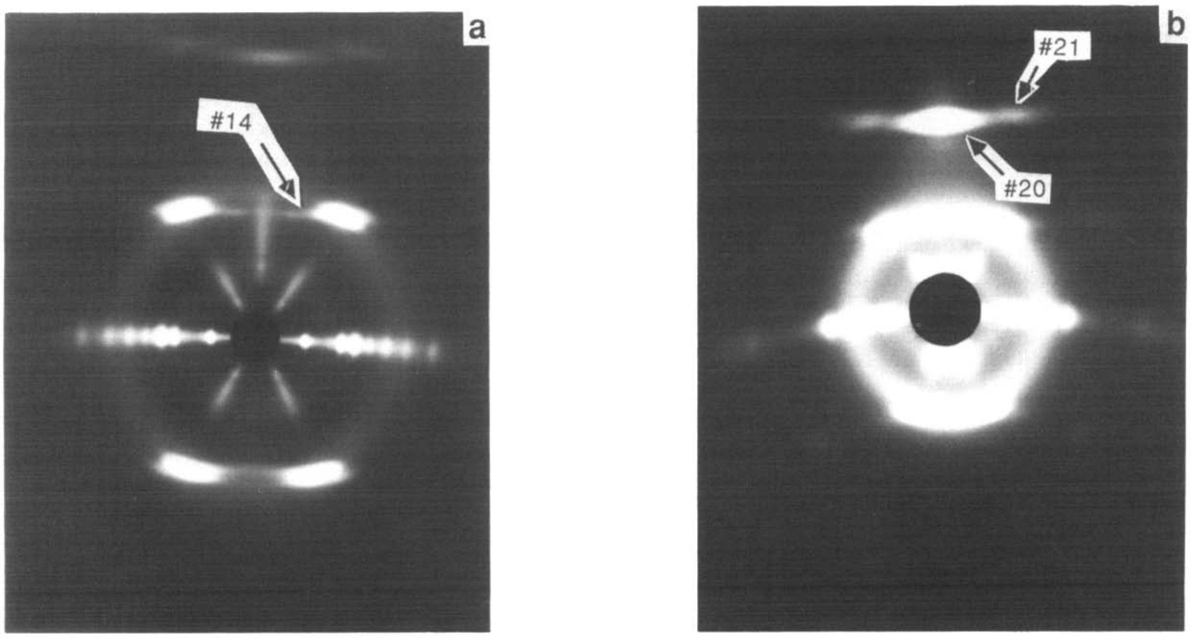

Figure 2 (a) X-ray diffraction pattern of α-form syndiotactic polystyrene, tilted about 9°; (b) X-ray diffraction pattern of α-form syndiotactic polystyrene, tilted about 18°

reflection 21 ($d=2.93$ Å) is obvious. The intensified reflection 20 indicates that it belongs on the meridian. The c axis of the unit cell thus derived is 5.02 Å, corresponding well to the chemical repeat 5.06 Å for a fully extended α-form sPS. The larger observed d-spacings at 13.2 Å on the equator and 4.93 Å on the first layer line imply a sizable unit cell, which would be anticipated since benzene groups need more space to be accommodated. Evaluation of all of the diffraction data gave a hexagonal unit cell with dimensions $a=26.3$ Å, $c=5.1$ Å containing 18 molecular chains with theoretical density 1.03 g cm^{-3}. Calculated d-spacings and Miller indices for each reflection are summarized in *Table 1*.

A planar zig-zag conformation for α-form sPS has already been recognized. However, lateral packing of these molecules in the ab dimension is still somewhat controversial. Using high energy electron diffraction, Greis *et al.*[1] obtained a hexagonal unit cell with dimensions $a=26.26$ Å, $c=5.1$ Å, which is identical to the result we obtained from X-ray diffraction. Compared with the electron diffraction data reported by Greis *et al.*[1], more reflections were observed on higher layer lines in our X-ray diffraction study. The seven extra reflections not seen in the electron diffraction pattern, namely reflections 16–19 on the first layer line and 21–23 on the second layer, can be indexed quite well with the hexagonal unit cell. Some equatorial reflections, within the region $d\approx 3.5$–3.7 Å, observed in the electron diffraction pattern, are not explicitly identified in our X-ray diffraction pattern, although a series of weak and diffuse arcs occur in this region. It is less reliable to measure the d-spacings of those reflections, so they were excluded from the

Table 1 Crystallographic data of α-form syndiotactic polystyrene obtained from X-ray diffraction analysis

No.	d_{obs} (Å)	d_{calc} (Å)	I^a	h	k	l
1	13.2	13.2	s	1	1	0
2	11.3	11.4	vw	2	0	0
3	8.61	8.61	m	2	1	0
4	7.55	7.59	s	3	0	0
5	6.52	6.57	s	2	2	0
6	5.68	5.69	m	4	0	0
7	4.98	4.97	m	4	1	0
8	4.34	4.38	m	3	3	0
		4.30		4	2	0
9	4.12	4.09	w	5	1	0
10	3.74	3.74	m	4	3	0
11	3.47	3.47	w	6	1	0
12	2.64	2.66	vw	8	1	0
		2.63		5	5	0
		2.61		6	4	0
13	2.45	2.48	w	8	2	0
14	4.93	4.97	m	1	0	1
15	4.35	4.38	vs	2	1	1
16	3.98	3.97	m	3	1	1
17	3.57	3.56	w	4	1	1
18	2.73	2.74	vw	7	0	1
		2.74		5	3	1
19	2.59	2.60	w	7	1	1
20	2.51	2.55	m	0	0	2
21	2.39	2.41	m	3	0	2
		2.38		2	2	2
		2.36		3	1	2
22	2.29	2.32	w	4	0	2
		2.29		3	2	2
		2.27		4	1	2
23	2.09	2.11	vw	6	0	2
		2.11		4	3	2
		2.09		5	2	2

[a] Relative intensity: vs, very strong; s, strong; m, medium; w, weak; vw, very weak

diffraction data. Chatani *et al.*[3] reported two α-forms for sPS; monoclinic ($a=19.8$, $b=12.9$, $c=5.06$ Å and $\gamma=95°$) and orthorhombic ($a=8.81$, $b=28.82$, $c=5.06$ Å) structures depending on the sample preparation. However no observed X-ray diffraction data was published and a detailed comparison is not possible. Neither of these unit cells fit the data in *Table 1* adequately. The orthorhombic option was later indicated by Guerra *et al.*[4] as β modification for α-form sPS. The monoclinic option can physically fit all our observed d-spacings except the one at $d=8.61$ Å. If we force a match to the d-spacing for the reflection at $d=8.61$ Å, the agreement of the d-spacings for the other reflections deteriorates and also leads to unit cell dimensions and calculated density incompatible with experimental values. Thus we conclude that the hexagonal packing is preferred for the α-form sPS. Determination of a space group from the X-ray diffraction pattern is difficult, since systematic absence cannot be confirmed due to degeneracy of d-spacings attributed to hexagonal packing. Greis *et al.*[1] proposed a structure for sPS with space group $P\bar{6}2c$ and postulated a model in which three macromolecules form clusters through van der Waals' contact. Later Guerra *et al.*[4] claimed that absence of the reflections with $-h+k+l\neq 3n$ was indicative of a quasirhombohedric symmetry. From an examination of the *hkl* reflections on the higher layer lines in our X-ray data, we find insufficient evidence to support the selection rule for rhombohedral symmetry. We plan to use molecular modelling to construct packing patterns with different space groups, and investigate the associated potential energy systematically to find out spatial correlations between molecular chains.

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