Structural study on syndiotactic polystyrene: 2. Crystal structure of molecular compound with toluene

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The crystal structure of the syndiotactic polystyrene–toluene molecular compound was studied by X-ray diffraction. The crystal data are as follows: monoclinic system, space group $P2_1/a$ (no. 14), $a = 17.58$, $b = 13.26$, c(chain axis) $= 7.71$ Å, $\gamma = 121.2°$, eight monomer units (two chains) and two toluene molecules per unit cell, the molar ratio of monomer: toluene being 4:1. The polymer chains take a twofold helical structure of $(-TTGG-)_2$ conformation, and the packing of the polymer chains enables each toluene molecule to occupy an isolated hole between the benzene rings of adjacent polymer chains. The molecular compounds with benzene, chlorobenzene, p-xylene, 1,2,4-trichlorobenzene and so on are isomorphous to the toluene molecular compound. These molecular compounds are commonly transformed on heating between 120 and 150°C to another crystalline phase free from the guests, in which the polymer chains retain the helical structure.

INTRODUCTION

In a previous paper[1], the relationship between sample preparation and polymorphism for syndiotactic polystyrene (sPS) was reported. Four distinct crystalline phases could be detected by X-rays: they were named molecular compound, helical form, planar form I and planar form II. The polymer chains in these crystalline phases take either a planar zigzag structure or a twofold helical structure of $(-TTGG-)_2$ conformation as in the case of syndiotactic polypropylene[2–4], although in the latter polymer the planar zigzag form is less stable than the helical form in contrast to sPS. Of the four crystalline phases, the most interesting is the molecular compound[1,5,6] with a variety of organic solvents. This paper presents the cyrstal structure of the sPS–toluene molecular compound.

EXPERIMENTAL

Syndiotactic polystyrene with a weight-average molecular weight of 1.3×10^6 ($M_w/M_n = 2.8$) and a triad syndiotacticity greater than 99% was used[7]. As-cast sPS samples from solutions with a variety of solvents are the molecular compounds of sPS with those solvents used[1]. However, in spite of attempts to prepare their uniaxially oriented specimens by drawing in hot water, the X-ray patterns for these specimens exhibited an abnormal orientation of the poorly crystalline molecular compounds involving the growth of uniaxially oriented planar form I, as already reported in a previous paper[1]. Therefore the uniaxially oriented samples which were indispensable to X-ray crystal structure analysis were obtained by exposing drawn amorphous sPS samples, which were previously prepared by quenching the melt in ice–water followed by drawing to about four times the original length in hot water, to toluene vapour at room temperature for 12 h or, if needed, more.

X-ray measurements were performed with nickel-filtered $CuK\alpha$ radiation. A cylindrical camera of diameter 100 mm was employed to record the diffraction. *Figure 1* shows the X-ray fibre photograph for the sPS–toluene molecular compound. The d-spacings of the reflections were calibrated using NaCl powder. The reflection intensities were observed by the multiple-film method and measured visually with an intensity scale. To observe the meridional reflections, the Norman method was employed with a Weissenberg camera.

The procedures of thermogravimetric and density measurements have already been reported in a previous paper[1].

STRUCTURE ANALYSIS

All the observed reflections in the fibre photograph were indexed in terms of a monoclinic cell with cell constants $a = 17.58$, $b = 13.26$, c(chain axis) $= 7.71$ Å and $\gamma = 121.2°$. In addition to these reflections, the 0 0 2 (very strong) and 0 0 4 (very weak) meridional reflections observed in
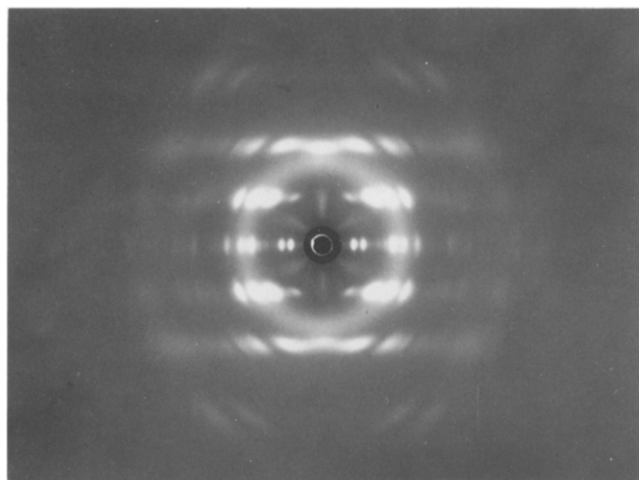
Figure 1 X-ray fibre photograph 1 for sPS–toluene molecular compound

the Weissenberg photograph satisfied the following systematic appearance conditions: $hk0$ when h is even and $00l$ when l is even. The space group was therefore unequivocally determined to be $P2_1/a$ (no. 14). Based on the space group together with the weight loss on heating thermogravimetric measurement (14.1%), the molar ratio of monomer:toluene was assumed to be 4:1. This idea was again supported by density measurements: the observed density of $1.05\,\mathrm{g\,cm^{-3}}$ was comparable to the calculated density of $1.11\,\mathrm{g\,cm^{-3}}$ for the unit cell containing eight monomer units and two toluene molecules. The observed chain repeat of 7.71 Å suggested that the polymer chains take a (-TTGG-)$_2$ twofold helical conformation. The space group $P2_1/a$ enables the axis of the twofold helical polymer chain, the asymmetric unit of which comprises two successive monomer units, to coincide with the twofold screw axis parallel to the c-axis at $x=1/4$ and $y=1/2$, and the toluene molecule can be disposed so that the centre of the benzene ring coincides with the centre of symmetry at $x=y=z=0$ (the molecular compounds with benzene, toluene and p-xylene gave essentially the same X-ray diffraction patterns, and so the methyl group of toluene was assumed to be disposed statistically at p-positions).

The crystal structure model was refined by changing the orientation of the polymer chain about the twofold screw axis and the torsional angles of the phenyl groups, assuming that the bond lengths and bond angles were normal. The final discrepancy factor was 17% for all the observed reflections, where all the hydrogen atoms except for the methyl hydrogen atoms of toluene were included in the structure factor calculation. Since some reflections on the layer lines are very diffuse because of overlap of many reflections, their intensities could not be observed quantitatively. However, the calculated structure factors for these reflections explained qualitatively the observed intensities. The atomic coordinates are listed in *Table 1*, where the thermal parameters for all the atoms are commonly assumed to be 6.5 Å^2. The observed and calculated structure factors are compared in *Table 2*. The crystal structure viewed along the chain axis is shown in *Figure 2*.

RESULTS AND DISCUSSION

The crystalline molecular compound of sPS with toluene consists of sPS chains taking a (-TTGG-)$_2$ twofold helical

conformation and toluene molecules with a stoichiometric molar ratio (monomer:toluene) of 4:1.

The crystal structure is characterized as follows.

(a) Along the a-axis, right-handed (-TTGG-)$_2$ and left-handed (-TT$\bar{\mathrm{G}}\bar{\mathrm{G}}$-)$_2$ polymer chains (R and L, respectively, in *Figure 2*) align alternately, coming into contact at the van der Waals distances (the shortest intermolecular distances are 3.94 Å for C---C and 2.46 Å for H---H). Therefore there is no open space sufficient to accommodate a toluene molecule between the adjacent polymer chains.

(b) Along the b-axis, toluene molecules occupy isolated holes between the polymer chains: each toluene molecule is surrounded by 10 polymer benzene rings as shown schematically in *Figure 3* (the shortest polymer carbon---toluene carbon distance is 3.47 Å and the shortest polymer hydrogen---toluene hydrogen distance is 2.38 Å). The molecular compounds with benzene, toluene, p-xylene, chlorobenzene and so on have the same unit cell constants within experimental accuracy, and the reflection intensities for these compounds were changed depending on the X-ray scattering power of the guest. Accordingly these molecular compounds must be isomorphous to the toluene molecular compound. The molecular compounds with o-dichlorobenzene, o-xylene, chloroform and so on have another crystal symmetry. Based on their X-ray diffraction patterns, however, their crystal structures are fairly similar to that of the toluene compound.

(c) As already reported in a previous paper[1], the as-cast specimens of the sPS–toluene molecular compound exhibits an abnormal orientation by hot drawing. *Figure 4* shows the X-ray pattern for the drawn as-cast specimen of the toluene molecular compound and its schematic diagram.

After completion of crystal structure analysis, the abnormal orientation of the crystallites of the molecular compound in the drawn as-cast specimen could be assigned to the a-axis orientation along the direction of stretch. In the schematic diagram in *Figure 4b*, the hkl indexes are shown by assuming the a-axis orientation.

Table 1 Fractional atomic coordinates[a]

Atom	x	y	z
C (H$_2$)	0.250	0.500	0.000
C (H)	0.232	0.576	0.126
C (H$_2$)	0.157	0.496	0.252
C (H)	0.325	0.580	−0.126
C	0.409	0.660	−0.024
C	0.449	0.612	0.085
C	0.526	0.684	0.180
C	0.565	0.806	0.167
C	0.527	0.857	0.061
C	0.450	0.783	−0.033
C	0.206	0.651	0.024
C	0.128	0.595	−0.085
C	0.103	0.665	−0.180
C	0.156	0.788	−0.167
C	0.230	0.840	−0.061
C	0.257	0.774	0.033
C	0.451	1.050	0.472
C	0.408	0.931	0.472
C	0.459	0.874	0.499
C(H$_3$)(weight: 0.5)	0.313	0.846	0.465

[a] All the hydrogen atoms except for the methyl hydrogen atoms of toluene were included in the structure factor calculation, but they are omitted in this table for simplicity
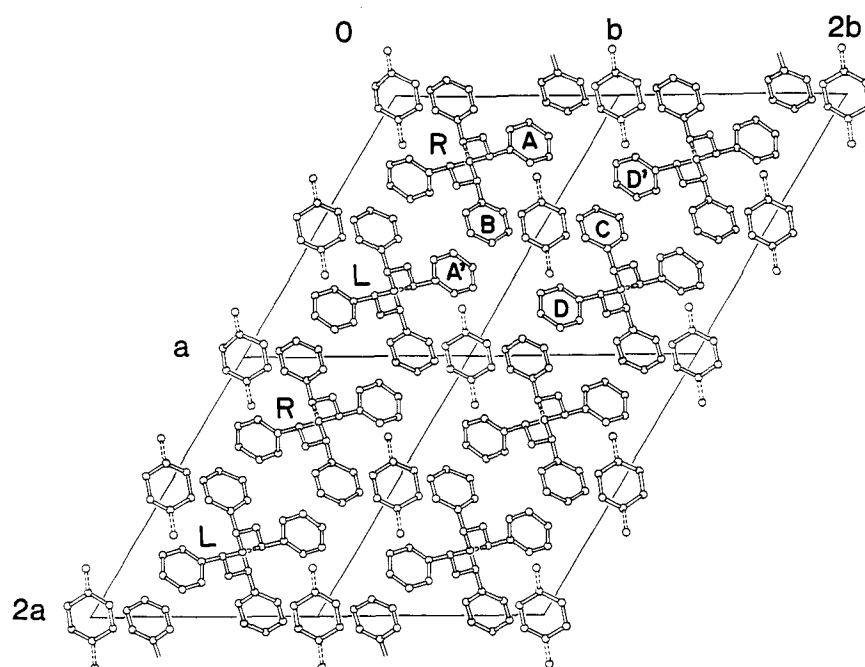
Figure 2 Crystal structure of sPS–toluene molecular compound viewed along the polymer chain axis. The methyl group of toluene molecules is statistically disposed at *p*-positions

Table 2 Observed (F_o) and calculated (F_c) structure factors

hkl	F_o	F_c	hkl	F_o	F_c
0 1 0	77	73	−6 2 1, −6 3 1	28	25
−2 1 0	72	58	−6 4 1, −3 5 1, −4 5 1	32	35
2 0 0	16	5	−5 5 1, 1 4 1, −2 5 1, 5 1 1, 4 2 1	33	37
−2 2 0	25	28	3 4 1, −7 6 1, −8 1 1, −1 6 1	45	58
0 2 0	31	10	6 2 1, −9 4 1, −9 3 1, 7 1 1	26	30
2 1 0	78	97	6 2 1, −9 4 1, −9 3 1, 7 1 1	26	30
−2 3 0, −4 2 0, −4 1 0	73	88	−9 6 1, −9 1 1, −2 7 1	29	32
0 3 0, 4 0 0, 2 2 0	54	59	−9 7 1, 5 4 1, −10 6 1, 9 0 1, −5 8 1, −6 8 1	31	26
−2 4 0, −4 4 0	22	30	−2 1 2, 2 0 2	88	88
2 3 0, 0 4 0	42	47	−3 2 2, 2 1 2, 3 0 2	77	70
−6 4 0	24	40	−4 2 2, −4 1 2, −3 3 2, −1 3 2	59	67
6 0 0	31	43	−4 3 2, 0 3 2, 4 0 2	49	74
2 4 0, 0 5 0	22	35	−5 1 2, −5 3 2	52	49
−8 5 0	28	32	−4 4 2, 4 1 2, −1 4 2	57	48
0 6 0, −4 7 0, 8 0 0, −6 7 0	34	25	5 2 2, 6 1 2, −4 6 2, −8 3 2, −5 6 2, −3 6 2, −8 4 2	61	60
−10 4 0, −8 7 0	25	20	−3 1 3, −3 2 3, 2 1 3, 3 0 3	25	19
−10 2 0, −10 6 0, −6 8 0	31	28	1 2 3, −2 3 3, −4 2 3, −4 1 3, −3 3 3, −1 3 3	60	56
10 0 0, −10 8 0	36	37	2 2 3, −5 2 3, −5 1 3, −5 3 3, −3 4 3, 1 3 3, −2 4 3	82	88
10 1 0, −12 2 0, −10 9 0	28	25	−5 4 3, −6 2 3, −6 3 3	42	29
−12 9 0, −10 10 0, 2 8 0, 4 7 0, 8 4 0	31	31	6 0 3, −7 2 3, 3 3 3, −1 5 3, −7 4 3, −6 5 3, −7 1 3	54	32
−1 1 1	39	44	6 1 3, −4 6 3, −8 3 3, −5 6 3, −3 6,3, −8 4 3, 4 3 3	40	42
2 0 1, 1 1 1, −1 2 1, −2 2 1	175	166	0 0 2	vs	114
−3 1 1, 0 2 1, 2 1 1, −3 2 1, 3 0 1	167	129	0 0 4	w	28
−2 3 1, −4 2 1, −4 1 1, −3 3 1	153	140			
−5 3 1, −5 1 1, −3 4 1	23	27			

vs, very strong; w, weak

[a] There are many non-observed reflections, which are omitted from this table for simplicity

The question of the generation of the abnormal *a*-axis orientation might be solved when the molecular compound has the following structural features at the molecular and morphological level: (1) the lamellar crystals are extremely large in the *a*-direction, and (2) the chain-foldings in the lamellar crystallites are performed along the *a*-direction. (3) These features seem favourable for the *a*-axis orientation on hot drawing, being accompanied by crystallization of the amorphous region and breaking up of the crystallites of the molecular compound parallel to the 0 1 0 plane, which will, as observed, promote the growth of the *c*-axis oriented planar form II.

(d) When the toluene molecular compound was annealed at 120°C, it was transformed to helical form involving removal of the toluene molecules (cf. on annealing of the molecular compound above 190°C, planar form I was directly obtained). Such a transition
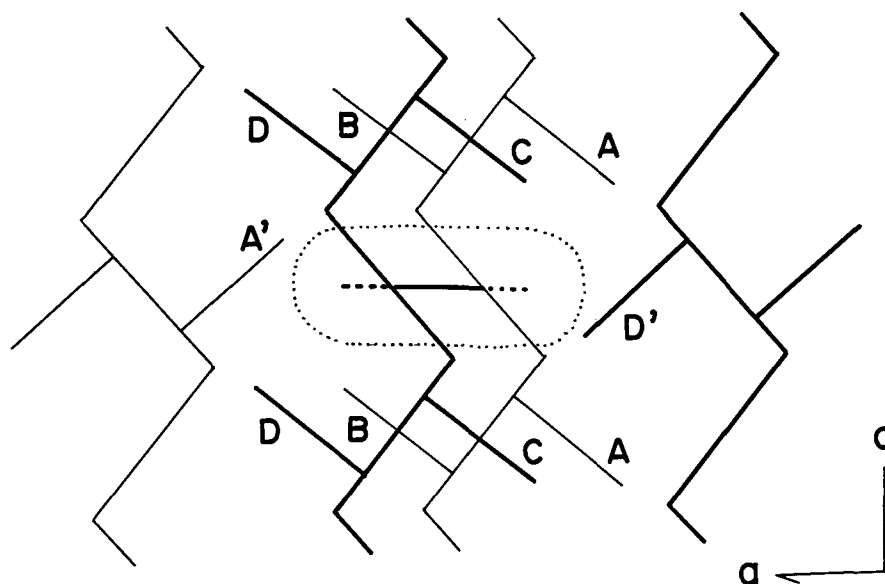
Figure 3 Environment for a toluene molecule in the sPS–toluene molecular compound viewed along the normal of 0 1 0 plane. Letters A, B etc. are polymer benzene rings shown in *Figure 2*
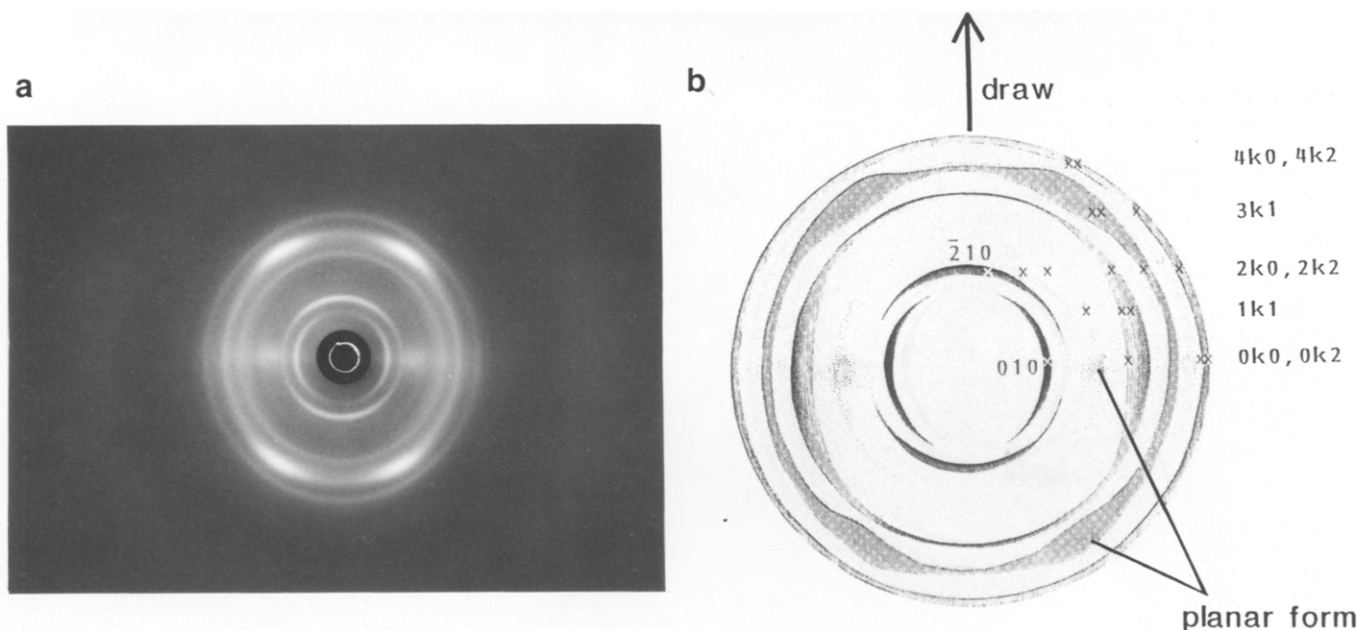

Figure 4 (a) X-ray photograph and (b) schematic diagram of drawn sample cast from toluene

commonly takes place in other molecular compounds; the endothermic peak due to the phase transition in the d.s.c. trace shifts slightly depending on the guest.

The crystal structure analysis of the helical form is now in progress. The chain repeat remains almost the same as that of the molecular compound, 7.71 Å, and the unit cell is again monoclinic. However, the b-dimension of the helical form is shortened by about 2 Å, while the a-dimension is retained. This feature undoubtedly indicates that the crystal lattice is reformed so as to perform direct contacts between the polymer chains along the b-axis as well as along the a-axis.

(e) Several polymer–low-molecular-weight compound systems are known to form crystalline molecular compounds. Polyethylenimine forms complexes with water[8,9], hydrochloric acid[10], acetic acid[11] and so on. In

these systems N–H---O, N---H–O or N–H---Cl hydrogen bondings between the polymer and the guest play the most important role in the construction of these crystal lattices: these crystal structures realize as many potential hydrogen bonds as possible. Polyethylene oxide forms crystalline complexes with alkaline metal salts[12,13] by coordination bondings between the metal ion and the polymer oxygen. Hydrogen bondings and coordination bondings are rather directional. When polymer and guest interact mainly due to non-directional van der Waals forces, several types of structures can be expected: the intercalate compound of polyethylene oxide with p-dibromobenzene[14] and the channel-type inclusion compound of syndiotactic polymethyl methacrylate as a host and many kinds of organic compounds as the guest[15] are examples. In the sPS molecular compounds, the

interaction between the polymer and the guest is again due to van der Waals forces. However, the open spaces supplied by the polymer are not channel-type but isolated holes, therefore the sPS molecular compounds are basically stoichiometric, whenever a defect due to escape of a small amount of the guest molecules is realized.

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