

Structural study on syndiotactic polystyrene: 4. Formation and crystal structure of molecular compound with iodine

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Syndiotactic polystyrene was found to form a molecular compound with iodine as well as with a variety of organic compounds. The iodine molecular compound with uniaxial orientation was obtained by immersing amorphous polystyrene (obtained by quenching the melt into ice-water followed by stretching) into molten iodine at 120–130°C. The crystal structure of the iodine molecular compound is isomorphous to that of the molecular compound with toluene. The crystal data are as follows: monoclinic, space group $P2_1/a$, $a = 17.29$, $b = 12.85$, c (chain axis) = 7.79 Å, $\gamma = 120.3^\circ$ (c -unique), and there are eight monomer units (two chains) in the unit cell. The polymer chains take a $(-TTGG-)_2$ twofold helical structure and it is expected, from the viewpoint of the crystal symmetry and the size of the hole, that two iodine molecules occupy one isolated hole formed between the polymer chains. However, in spite of several attempts to prepare the molecular compound, not all the holes contained iodine. The sample used for X-ray structure analysis was estimated to contain about 70% of the expected iodine content. On annealing in the range 130–150°C, the X-ray reflection intensities changed, indicating escape of iodine to some extent. However, the pure helical form free from the guest molecule was not obtained, in contrast to the case of molecular compounds with organic compounds; on annealing at temperatures higher than 160°C the iodine molecular compound was directly transformed to the planar form I.

(Keywords: syndiotactic polystyrene; iodine; crystal structure)

INTRODUCTION

Syndiotactic polystyrene (sPS) exhibits interesting polymorphism^{1–9}. The relation between the conditions of sample preparation and crystalline forms has been reported in detail⁷. sPS has four distinct crystalline phases i.e. molecular compound, helical form, and planar forms I and II, of which molecular compounds with a variety of organic compounds are of particular interest. These molecular compounds have isomorphous structures except for slight differences in cell dimensions, or may have quite similar structures with different space groups depending on the size and shape of the guest; each guest molecule is disposed in an isolated cavity formed between polymer chains having a $(-TTGG-)_2$ twofold helical conformation. The crystal structure of the sPS–toluene molecular compound, as an example, has been reported⁸. Besides the molecular compounds with organic compounds, it is interesting to examine the possibility of molecular compound formation with inorganic compounds, and a molecular compound of sPS with iodine has been obtained. This paper is concerned with the formation,

crystal structure and phase transition of the sPS–iodine molecular compound.

EXPERIMENTAL

sPS with a weight-average molecular weight of 1.31×10^6 ($M_w/M_n = 2.8$) and a triad syndiotacticity greater than 99% was used. X-ray, thermogravimetric and density measurements were performed as in previous studies for the toluene molecular compound⁸ and the planar form I⁹ obtained from the molecular compound on heating. First, amorphous sPS specimens were prepared by quenching molten sPS into ice-water followed by stretching to about three times the original length in hot water. These uniaxially oriented amorphous sPS samples were immersed in hot iodine KOH aq. or methanol solution. However, the X-ray diffraction patterns for these samples did not change from that of the original amorphous sample. Alternatively, the uniaxially oriented amorphous samples were immersed directly into molten iodine above the melting point of iodine (114°C) for various times ranging between one and several hours. The samples thus obtained were black and displayed a chain repeat of 7.79 Å in the X-ray fibre pattern, indicating that the formation of a molecular compound with iodine

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was effected. (The iodine molecular compound in the unoriented state was obtained from unoriented amorphous sPS samples.) Again, the observed chain repeat of 7.79 Å indicated that the polymer chains take the $(-TTGG-)_2$ twofold helical conformation as in the molecular compounds with organic compounds. However, the X-ray reflection intensities varied slightly from sample to sample; the d-spacings were not changed. Since the X-ray scattering amplitude of iodine is about 10 times larger than that of carbon, the variation in the reflection intensities was thought to depend on a slight change in iodine content. In practice, the molecular compound samples were prepared at quite high temperatures, ranging from 120 to 135°C, at which most molecular compounds with organic compounds are transformed to the helical form, which has the same twofold helical chains but is free from the guest¹. Under such severe preparation conditions, formation and decomposition (escape of iodine) of the molecular compound probably competed with each other. In practice, three samples thus obtained exhibited weight losses of 37, 43 and 44.3% in thermogravimetric measurements; Figure 1 shows the thermogravimetric traces for the last sample.

To prepare the molecular compound with iodine by another method, the amorphous sPS sample was immersed in an iodine solution in *p*-xylene or toluene; *p*-xylene itself forms a molecular compound with sPS, which is isomorphous to the toluene molecular compound. The X-ray patterns for these samples were basically the same as that of the iodine molecular compound. However, they exhibited an intensity distribution that might be interpreted in terms of the coexistence of both iodine and a slight amount of *p*-xylene or toluene as the guest. Moreover, they gave rather broad reflections as compared with the samples obtained by the direct immersion method. Again, the iodine molecular compound was prepared by exposing the toluene molecular compound to iodine vapour above the melting point of iodine. (Such replacement of the guest has been found to be possible between two organic compounds.) In this case again, the X-ray pattern was rather similar to those of the samples prepared by the direct immersion method, but still indicated the coexistence of a slight amount of toluene. The X-ray patterns for samples prepared by the different methods, or under different conditions, varied to some extent. Therefore, X-ray reflection intensities were measured for the sample that exhibited the greatest weight loss by thermogravimetric

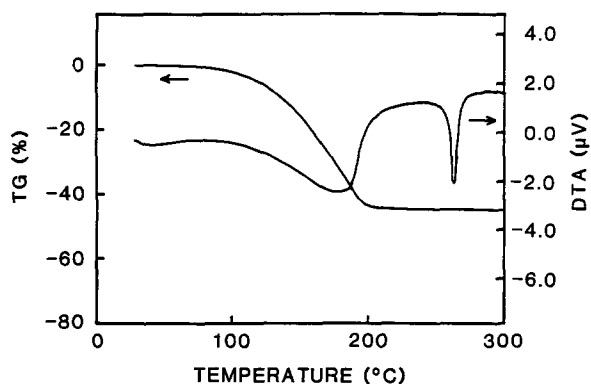


Figure 1 D.t.a. and t.g. traces in thermogravimetric measurement for a specimen of sPS-iodine molecular compound

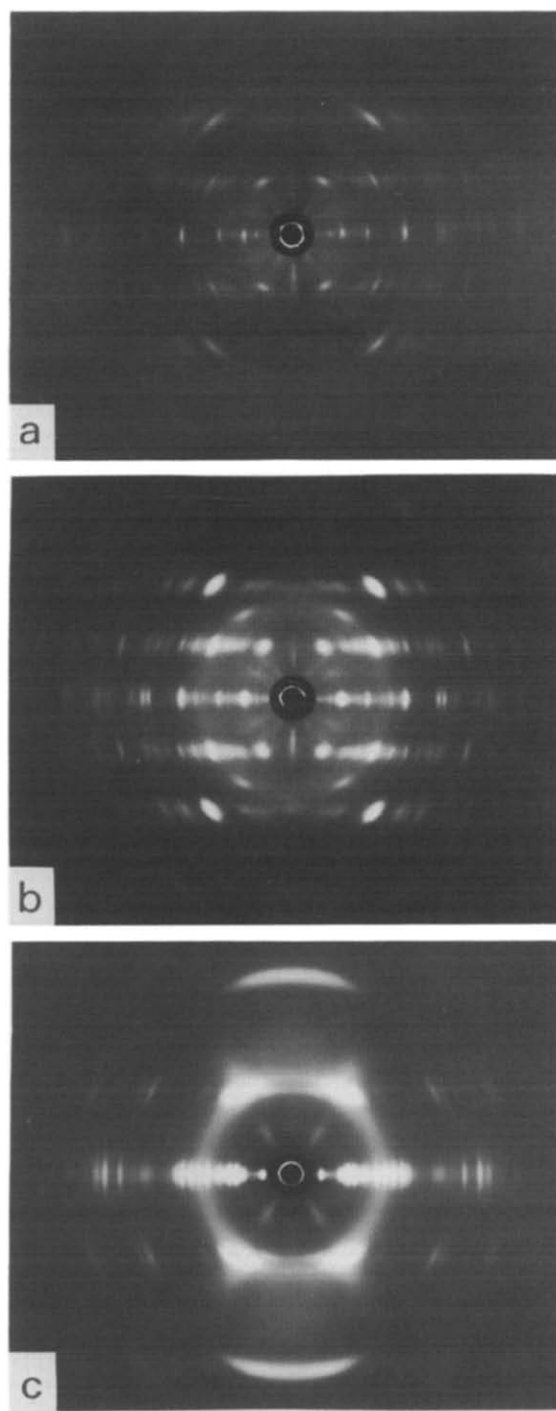


Figure 2 (a) X-ray fibre photograph of sPS-iodine molecular compound; (b) after annealing at 130°C for 7 h; (c) after annealing at 190°C

measurement, which was prepared by the direct immersion method. Figure 2a shows the X-ray fibre pattern for this sample.

STRUCTURE ANALYSIS

All the observed reflections in Figure 2a were explained in terms of a monoclinic cell with dimensions: $a = 17.29$, $b = 12.85$, c (chain axis) = 7.79 Å, and $\gamma = 120.3^\circ$ (c -unique). These dimensions are comparable to those for the toluene molecular compound: $a = 17.58$, $b = 13.26$, c (chain axis) = 7.71 Å, and $\gamma = 122.0^\circ$. The systematic absence of reflections ($hk0$ when h is odd, $h00$ when h is odd, and

00 l when l is odd) are also identical to the case of the toluene molecular compound, the space group being $P2_1/a$. The number of monomeric units in the unit cell was then reasonably assumed to be eight (two chains), as in the toluene molecular compound. Based on the space group, together with the size of the holes formed between the polymer chains, the number of iodine atoms was expected to be eight, the calculated density being 2.05 g cm^{-3} . However, the observed densities of the samples varied between 1.60 and 1.70 g cm^{-3} . As noted in the Experimental section, it is difficult to estimate the degree of performance of the crystalline molecular compound formation. The iodine content in amorphous regions is probably less than that in the crystalline regions, because in the sample prepared at a fairly high temperature, the amorphous regions hardly capture iodine. Also, escape of iodine from the crystal lattices, i.e. the existence of defects as mentioned in the Experimental section, may occur.

The crystal structure model was then assumed to be isomorphous to that of the toluene molecular compound. The arrangement of the twofold helical polymer chains was reasonably assumed to be the same as in the toluene molecular compound. As for the iodine, it was concluded by trial-and-error procedures that iodine exists in the form of I_2 molecules; the possible existence of one I_3 ion in the hole was disproved by examination of the calculated structure factors. (Iodine dissolves in toluene or p -xylene in the form of I_2 molecules.) However, the iodine content, i.e. the degree of perfection, of the molecular compound in the sample examined was not always certain. The structure was then refined by changing the iodine content together with the atomic positions. The final discrepancy factor, R , was 16% for all the observed reflections, where the weight (degree of occupancy) of iodine was assumed to be 0.7 (this model gives a calculated crystal density of 1.71 g cm^{-3}). The atomic coordinates are listed in Table 1. The observed and calculated structure factors are compared in Table 2, where the thermal parameters of whole atoms are assumed to be 7 \AA^2 . The crystal structure viewed along the polymer chain axis and along the normal of the 010 plane are shown in Figures 3 and 4, respectively.

Table 1 Fractional atomic coordinates

Atom	x	y	z
C (H_2)	0.250	0.500	0.000
C (HR)	0.229	0.576	0.125
C (HR)	0.325	0.583	-0.125
C (H_2)	0.154	0.429	0.250
C	0.409	0.667	-0.024
C	0.451	0.620	0.084
C	0.528	0.695	0.178
C	0.564	0.820	0.166
C	0.524	0.870	0.060
C	0.446	0.792	-0.033
C	0.200	0.650	0.024
C	0.122	0.593	-0.084
C	0.093	0.661	-0.178
C	0.143	0.786	-0.166
C	0.221	0.846	-0.060
C	0.248	0.777	0.033
I ^a	0.303	0.845	0.610
I ^a	0.429	0.829	0.440

^aThe degree of occupancy of iodine atoms was assumed to be 0.70

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

$h k l$	F_o	F_c
0 1 0	90	20
-2 1 0	153	152
-2 2 0	72	78
0 2 0	181	150
-2 3 0, -4 1 0, -4 2 0	94	85
4 0 0, -4 3 0, 0 3 0, 2 2 0	276	324
-2 4 0	90	107
-6 2 0, -6 3 0	150	167
2 3 0, 0 4 0, -6 1 0	176	165
-6 4 0	108	112
-2 5 0, 6 0 0	122	106
-6 5 0	120	131
2 4 0, 0 5 0, 6 1 0	139	154
-8 3 0, 4 3 0, -4 6 0	145	145
-8 4 0, -6 6 0, -8 2 0	137	129
-2 6 0, -8 1 0, -8 5 0	128	113
8 0 0, -8 6 0, 0 6 0, 2 5 0, -4 7 0	184	198
1 0 1, -1 1 1	119	120
-2 1 1	76	109
-1 2 1, -2 2 1	118	176
-3 1 1, 0 2 1	78	34
-3 2 1, 2 1 1, 3 0 1	179	207
1 2 1	102	190
-3 3 1, -1 3 1	110	121
3 1 1	82	83
4 0 1, -4 3 1, 0 3 1, 2 2 1	140	156
-5 3 1, -5 1 1	104	76
1 3 1, -3 4 1, -2 4 1	113	115
4 1 1, -4 4 1, 3 2 1, -1 4 1	127	130
-5 4 1, -6 2 1	112	120
-6 4 1, 5 1 1, -3 5 1	76	52
-7 3 1, -7 2 1, 3 3 1, -5 5 0, 6 0 1	191	190
2 4 1, 0 5 1, 5 2 1	88	65
-7 5 1, -8 3 1, 4 3 1, -4 6 1, 7 0 1	176	147
-2 6 1, 1 5 1, 3 4 1	122	127
-7 6 1, -1 6 1, 6 2 1, 7 1 1, -9 3 1, -9 4 1	190	175
5 3 1, 2 5 1, -9 2 1, -8 6 1, -9 5 1	147	120
0 1 2, -1 1 2	73	51
-2 1 2	80	128
-3 1 2, 0 2 2	78	62
2 1 2, -3 2 2, 3 0 2	255	269
-1 3 2, -3 3 2, 3 1 2	155	168
4 0 2, -4 3 2, 0 3 2, 2 2 2	110	129
-5 2 2, -5 1 2	165	180
4 1 2, -4 4 1, 3 2 2, -1 4 2	110	112
-5 4 2, -6 2 2, -6 3 2, 2 3 2, 0 4 2	111	122
-3 5 2, 4 2 2, -4 5 2, 5 1 2, 1 4 2, -2 5 2, 6 0 2,		
-5 5 2, -7 3 2, -7 2 2	161	180
2 4 2, 0 5 2, -7 1 2, 5 2 2	119	139
4 3 2, -4 6 2, 7 0 2, -5 6 2, -8 2 2, -8 4 2,		
-3 6 2, -6 6 2, -2 6 2, 1 5 2, 3 4 2	165	140
4 0 3 -4 3 3, 0 3 3, 2 2 3	161	193
-2 4 3, 4 1 3, -4 4 3, 3 2 3	133	137
-6 4 3, 5 1 3, 4 2 3, 1 4 3, -3 5 3, -4 5 3	110	90

^aThere are many unobserved reflections, which are omitted

RESULTS AND DISCUSSION

sPS was found to form a crystalline molecular compound with iodine as well as with a variety of organic compounds. The molecular compound with iodine consists of sPS chains having a twofold helical conformation of type $(-TTGG-)_2$ and I_2 molecules, the crystal structure being isomorphous to that of the toluene molecular compound. In the toluene molecular compound, one toluene molecule is included in the hole formed between neighbouring polymer chains along the b -direction; the benzene, p -xylene, chlorobenzene and p -dichlorobenzene molecular compounds are

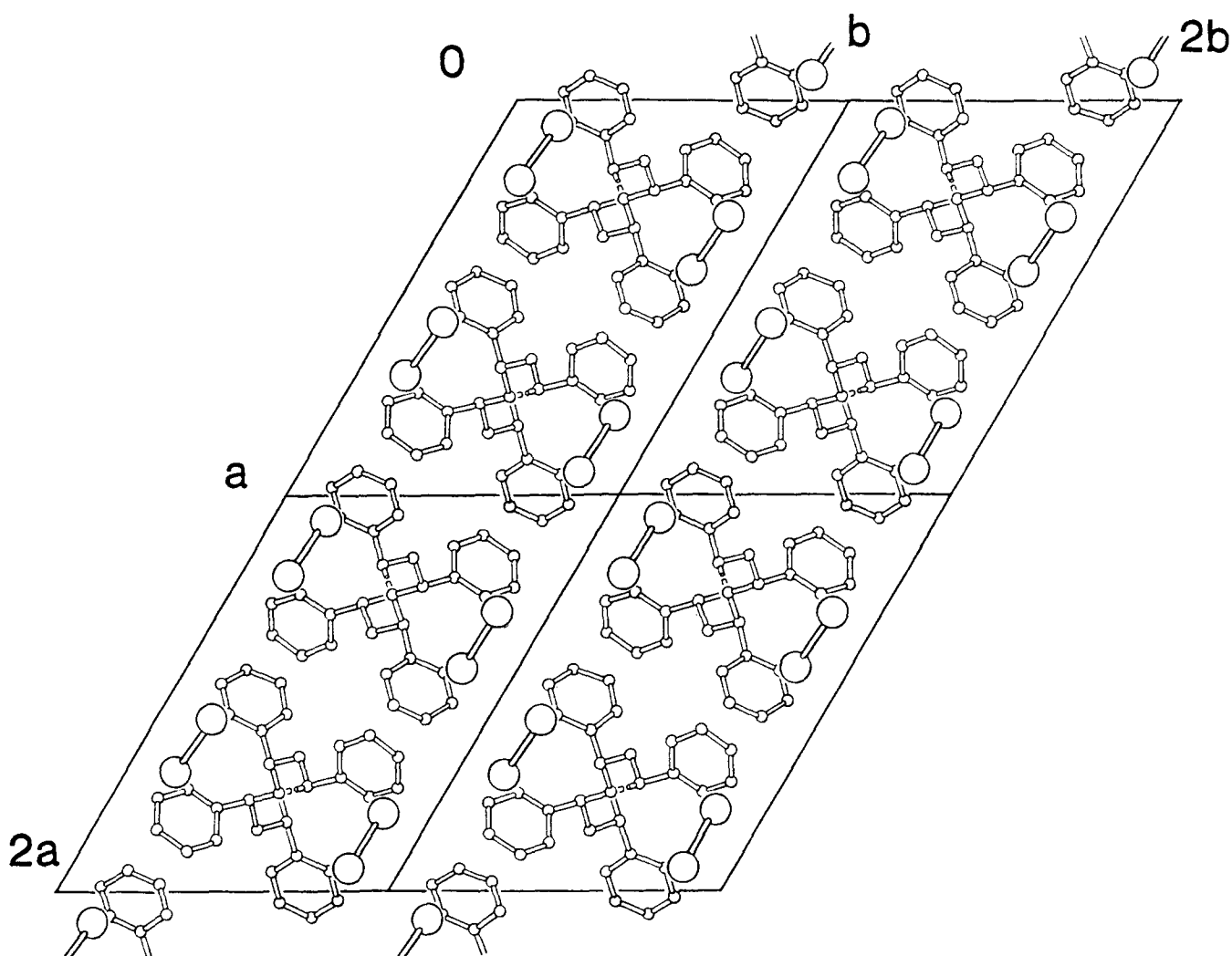


Figure 3 Crystal structure of sPS-iodine molecular compound viewed along the polymer chain axis, assuming that two iodine molecules are included without defect in each hole. Large and small circles represent iodine and carbon atoms, respectively

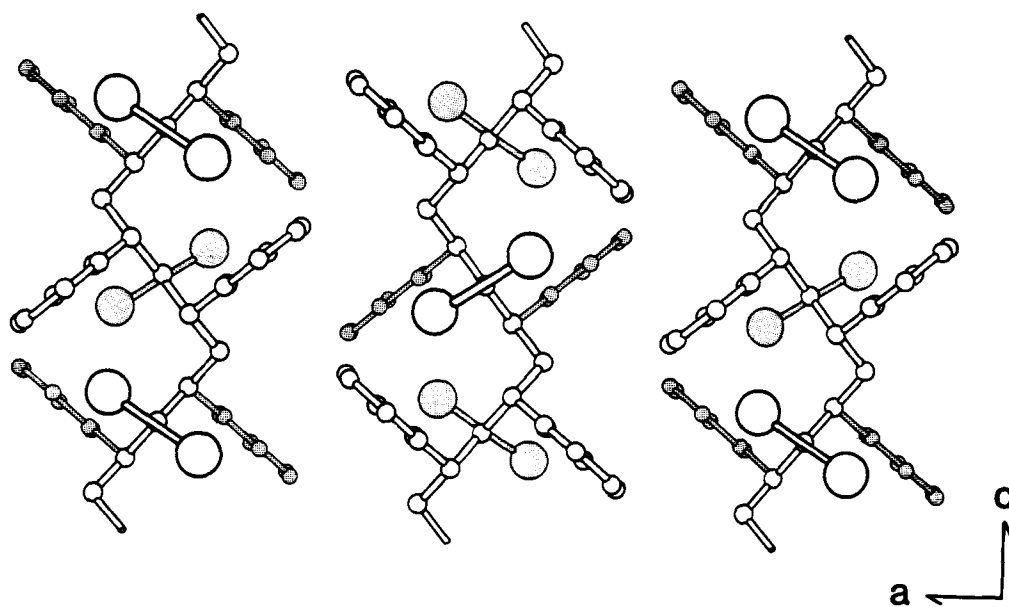


Figure 4 Crystal structure of sPS-iodine molecular compound viewed along the normal of the 010 plane

isomorphous to the toluene molecular compound (the stoichiometric molar ratio of monomer:guest is 4:1). Therefore the hole has a sufficient size to accommodate two I₂ molecules (the molar ratio of monomer:I₂ is 2:1). In the ideal structure, two I₂ molecules must occupy one isolated hole that is formed between sPS chains, as shown in Figures 3 and 4. However, the sample used for the crystal structure analysis was estimated to include only 70% of the expected iodine content, indicating the existence of some vacancies. In a hole containing only one iodine molecule, the iodine molecule must be disposed in a different way from the ideal structure, though such a situation was ignored in the structure factor calculation. Therefore, it is not possible to discuss the molecular dimension of iodine in detail, although the obtained I-I bond length of 2.64 Å (cf. values of 2.66 Å in gas and 2.68 Å in solid) and the shortest intermolecular I...I distance of 3.92 Å are not unreasonable.

As already reported¹, the molecular compounds of sPS with organic compounds were confirmed to be fully transformed, involving the loss of the guest to the helical form by annealing at about 130°C (the temperature depends slightly on the guest), followed by the transition to the planar form I on increasing temperature to about 190°C. When the iodine molecular compound was heated at 130°C in the atmosphere, the X-ray pattern changed slightly, indicating the escape of some iodine from the crystal lattice (Figure 2b). A sample annealed at 145°C displayed a few extra, very weak reflections, which might be due to a trace of the helical form free from the guest. However, this sample retained the structure of the iodine molecular compound. In other words, the X-ray pattern of the genuine helical form, which is readily distinguishable by X-ray diffraction, was not obtained on further heating. On annealing at 160°C for 1 h, the iodine molecular compound was completely transformed to the planar form I, as shown in Figure 2c. Again, as shown in Figure 1, the heating thermogravimetric traces exhibited a very broad endothermic peak at 182°C, which occasionally appeared as two close peaks in other samples. [In the toluene molecular compound (Figure 1a in ref. 7), an endothermic peak at 140°C, corresponding

to the phase transition from the molecular compound to the helical form, and a small endothermic peak at 190°C followed by an exothermic peak at 200°C (from the helical form to the planar form I) were observed.] In the iodine molecular compound, two iodine molecules are contained in one hole. Therefore, it is likely that the structure of the iodine molecular compound is rather stable, even if one of the two iodine molecules escapes from some holes; this differs from the case of molecular compounds with organic compounds.

CONCLUSION

It was found that sPS forms a crystalline molecular compound with iodine as well as with a variety of organic compounds, and the scheme of inclusion of the guest, i.e. the polymer chain conformation and the formation of holes for the guest, is essentially the same as in the case of organic compounds. However, in the present study we concluded that the samples prepared by several methods contained defects to some extent: not all the holes between the polymer chains were fully occupied by iodine molecules. It is desirable to develop more effective methods by which more perfect molecular compound samples may be prepared.

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