Structural study of syndiotactic polystyrene: 1. Polymorphism

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The features of the crystallization of syndiotactic polystyrene were investigated by X-ray diffraction, differential thermal analysis, thermogravimetry and density measurements. This polymer exhibits polymorphism: there are principally four distinct crystalline phases. Melt-crystallization yields a planar zigzag form. As-cast samples from solutions with a variety of solvents are molecular compounds with the solvents used, in which the polymer chains assume a twofold helical conformation of type $(TTGG)_2$. On annealing the molecular compounds at moderate temperatures below ~130°C, they are transformed in common, by removal of the solvent molecules, to a $(TTGG)_2$ twofold helical form free from solvents. On annealing at higher temperatures, the helical form is transformed to a planar zigzag form, which is distinguished from the melt-crystallized planar zigzag form in terms of the mode of molecular arrangement.

(Keywords: syndiotactic polystyrene; polymorphism; molecular compound; X-ray diffraction; thermal analysis)

INTRODUCTION

Structural studies on syndiotactic polystyrene (sPS) by several workers[1–9] have revealed that there are two types of chain conformation in the crystalline phases: a planar zigzag form T_4 and a twofold helical form of type $(TTGG)_2$. This situation is similar to the case of syndiotactic polypropylene[10,11]. Especially molecular compounds of sPS with several organic compounds were reported independently by us[2] and Immirzi and coworkers[3]. Quite recently, Corradini and coworkers[9] examined the polymorphism of sPS in more detail. However, the behaviour of sPS during crystallization is not yet fully understood. We found that there are principally four distinct crystalline phases by X-ray diffraction, differential thermal analysis, thermogravimetry and density measurements. In this paper, the polymorphism and phase transitions of sPS will be reported. The crystal structure of each phase will be reported in succeeding papers.

EXPERIMENTAL

sPS with a weight-average molecular weight of 1.3×10^6 ($M_w/M_n = 2.8$) and a triad syndiotacticity greater than 99%[12] was used. The glass transition and melting temperatures of this polymer are 105 and 260°C, respectively. The scheme of sample preparation is shown in *Figure 1*. Melt-crystallized samples were prepared by quenching the melt in ice–water followed by drawing and annealing above 200°C. Film samples were prepared by casting from solutions with several kinds of solvents, such as toluene and 1,2,4-trichlorobenzene, where evaporation of solvents was performed below 100°C (they will be called as-cast samples in this study). Uniaxially oriented as-cast samples were prepared by another method, as shown later. Single crystal mats of sPS were also prepared from dilute solutions using the same solvents. X-ray measurements were done with nickel-filtered Cu Kα radiation and a cylindrical camera of 100 mm diameter. Differential thermal analysis (d.t.a) and thermogravimetric analysis (t.g.) were performed using a TG-DTA 2010 of MAC Science Co. Ltd at a heating rate of 10°C min^{-1}. Density measurements were done by flotation using the densities of liquid media measured with a pycnometer. The details of the experiment will be described in the following sections.

RESULTS AND DISCUSSION

As-cast samples

Undrawn as-cast samples of sPS using several kinds of solvents gave similar but significantly different X-ray patterns from one another. The cast samples from benzene and toluene solutions gave almost identical X-ray patterns, but the samples from heavy halogen-atom-containing solvents, such as bromobenzene and 1,2,4-trichlorobenzene, gave remarkably different X-ray patterns, indicating that these solvents participate coherently in the X-ray scatterings with sPS.

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Abnormal orientation in drawn as-cast samples

The as-cast samples again gave unusual X-ray fibre patterns in orientation when they were drawn below 100°C. (As shown later, annealing at higher temperatures above 100°C brought about the appearance of other crystalline phases.) The abnormal orientation in the drawn as-cast sample was confirmed by comparing the X-ray pattern with that of the single crystal mat obtained using the same solvent. *Figure 2* shows the X-ray patterns for two such kinds of samples. The single crystal mat exhibits layer lines explained in terms of a chain repeat of 7.7 Å along the normal of the lamellar crystal surfaces, while the drawn as-cast sample does not exhibit such periodic layer lines, and again the innermost equatorial reflection for the single crystal mat appears on the meridian for the drawn as-cast sample. (This abnormal orientation could be explained in terms of the morphology and crystal structure as will be reported in a succeeding paper).

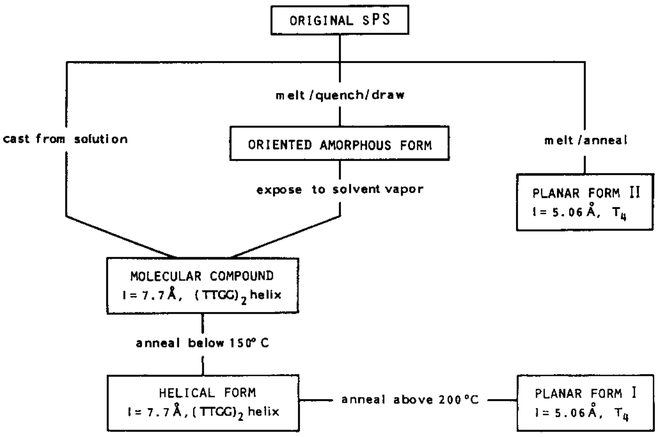

Figure 1 Scheme of sample preparation and polymorphism of sPS

Uniaxially oriented as-cast samples

In order to obtain uniaxially oriented X-ray fibre patterns for the as-cast samples, which are indispensable for crystal structure analysis, an alternative method was applied. First, oriented amorphous sPS samples were prepared by quenching the melt in ice–water followed by drawing below 100°C. These samples gave a broad X-ray pattern involving a small amount of a premature planar zigzag form having a chain repeat of 5 Å (*Figure 3a*). These samples were then exposed to many kinds of organic solvent vapour at room temperature or, if needed, higher temperatures for one day or more. The samples thus obtained gave fairly well oriented X-ray fibre patterns for the cases of benzene, toluene, acetone, *o*-xylene, *p*-xylene, bromobenzene, chlorobenzene, *o*-dichlorobenzene, *m*-dichlorobenzene, *p*-dichlorobenzene, chloroform, 1,2,4-trichlorobenzene and so on. (1,2-Dichloroethane as reported by Immirzi and coworkers[3] gave a fibre pattern, but methanol and ethanol did not change the original X-ray pattern.) Examples of the X-ray fibre patterns are shown in *Figures 3b* and *4a–c*. These X-ray patterns are identical to those of the corresponding as-cast samples except for the difference in orientation. They give commonly the same chain repeat of ~7.7 Å of $(TTGG)_2$ helical conformation, but the intensity distributions differ from sample to sample, indicating that these samples are undoubtedly molecular compounds of sPS with the solvents used. This idea was further confirmed by d.t.a. and t.g. (and finally crystal structure analysis together with density measurements, as will be reported in a succeeding paper).

D.t.a. and t.g. for as-cast samples

D.t.a. and t.g. traces for the sample exposed to toluene vapour are shown in *Figure 5a*. An endothermic peak involving the onset of weight loss appears at about 130°C.

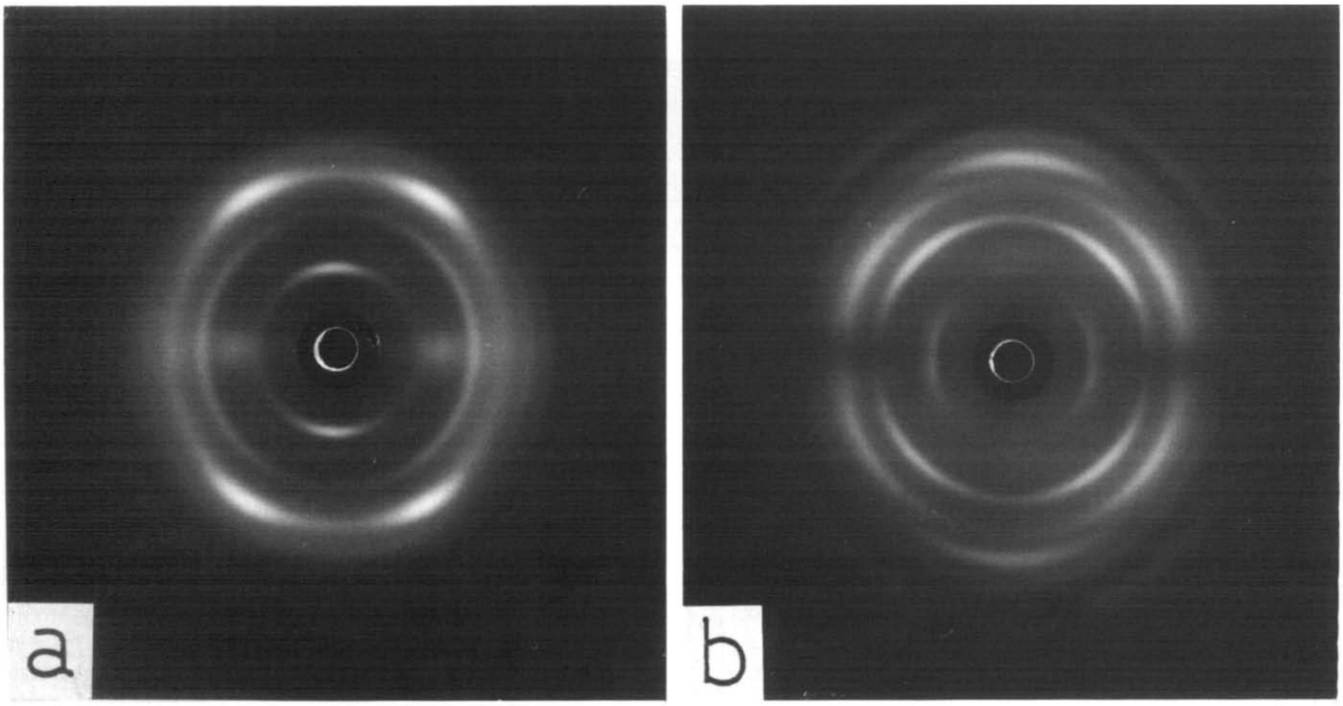

Figure 2 X-ray photographs for sPS. (a) Drawn sample cast from 1,2,4-trichlorobenzene solution. The draw direction is vertical. (b) Single crystal mat from 1,2,4-trichlorobenzene solution. The normal of the lamellar surfaces is vertical. Both samples were annealed at 130°C, and then transformed to helical form (see *Figure 1*)

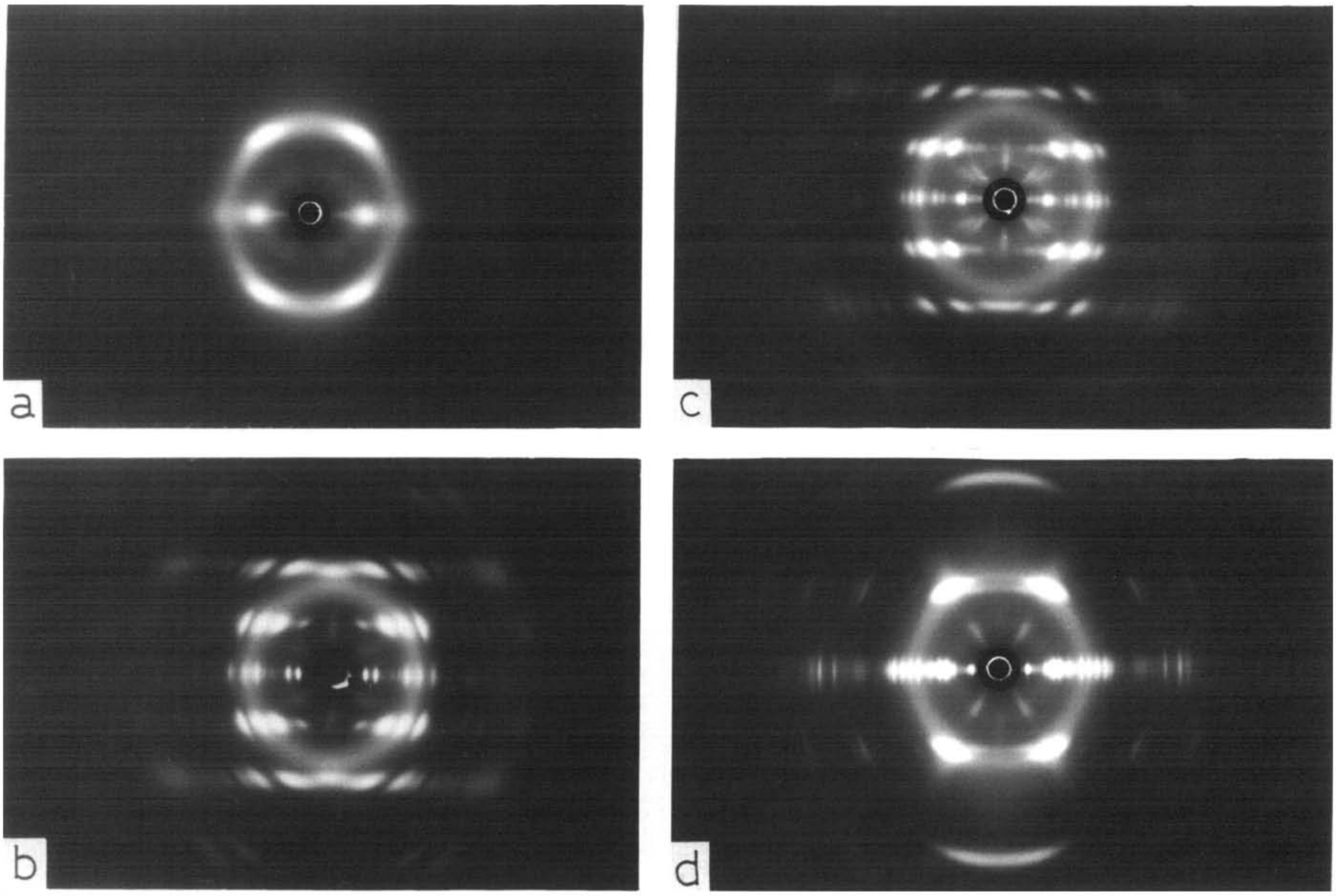

Figure 3 X-ray fibre photographs for sPS. (a) Oriented amorphous sample. (b) After exposure to toluene vapour. (c) After annealing at 130°C. (d) After annealing at 200°C

Around 190°C, there appears a small endothermic peak immediately followed by a small exothermic peak. Finally a large endothermic peak of melting appears at 260°C. The total weight loss for the sPS–toluene system was 14.1%. (The crystal structure analysis of this system gave a stoichiometric molar ratio (monomer/toluene) of 4/1 corresponding to a weight loss of 18.1%. The difference between the observed and theoretical weight losses might be ascribed to heterogeneity in the fine structure of the sample: for example, toluene molecules are not incorporated into the remaining premature crystallites of the planar zigzag form.)

The samples exposed to other kinds of solvent vapour exhibited a similar behaviour except for slight shifts of thermal peaks and differences in amount of weight loss. *Figure 5b* shows the traces for the sPS–1,2,4-trichlorobenzene system.

Annealing of as-cast samples

When the as-cast samples, which are now asserted to be molecular compounds, were annealed at moderate temperature, practically around 130°C, they gave identical X-ray fibre patterns irrespective of the starting systems. The chain repeat is, however, still retained to be ~7.7 Å as shown in *Figure 3c*. This experimental fact indicates that the molecular compounds are transformed to a new crystalline phase consisting of the $(TTGG)_2$ helical chains free from solvents. Therefore the first endothermic peak in *Figure 5* for the molecular compound must correspond to the decomposition of the molecular compounds.

On annealing at higher temperatures, practically 200°C, the X-ray fibre pattern changed drastically as shown in *Figure 3d*. The chain repeat in this phase is 5.06 Å, indicating that the helical form is transformed to a planar zigzag form. The planar zigzag form thus obtained, however, gives a different X-ray pattern from that of the melt-crystallized planar zigzag form (*Figure 6*). Both the planar zigzag forms are therefore distinguished in terms of the mode of molecular arrangement. The endothermic and exothermic peaks around 190°C must be related to the transition from the helical form to the planar zigzag form.

Variations of structures

When the sPS–toluene molecular compound was exposed to other kinds of solvent vapour, for example, 1,2,4-trichlorobenzene, the X-ray fibre pattern was changed depending on the solvent vapour, indicating that the toluene molecules in the crystal lattices were replaced by other molecules. Such replacements are feasible for many kinds of pairs of solvent. Therefore, replacement or removal of guest molecules to some extent yields a variety of X-ray diffraction patterns for the molecular compounds: if the transition from the molecular compound to the helical form is not accomplished, the X-ray patterns for both phases are superimposed.

As reported by Peterman and coworkers[5], the planar

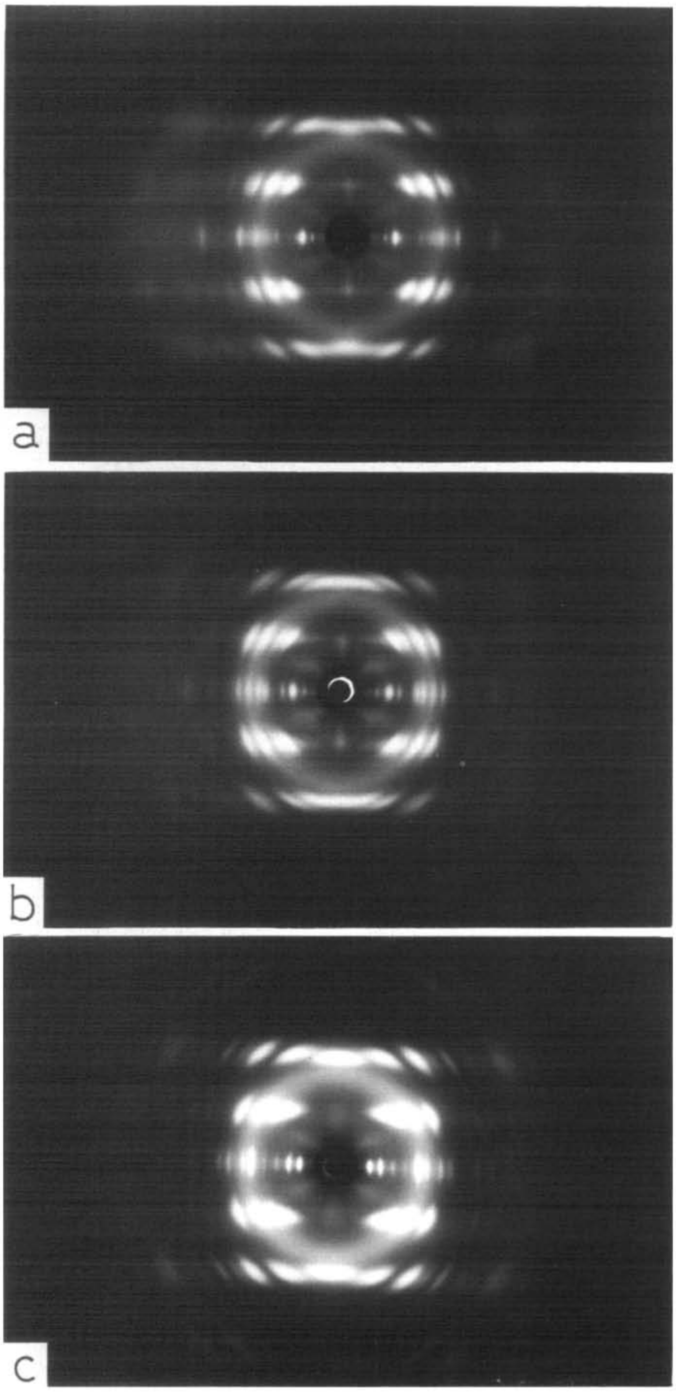

Figure 4 X-ray photographs for amorphous samples exposed to (a) bromobenzene, (b) chloroform and (c) *o*-xylene vapour

zigzag form from the melt also exhibits some changes in the electron diffraction pattern, indicating variations of order in the molecular arrangement depending on the history of the sample. As shown in a succeeding paper, the planar zigzag form from the cast samples again gives slightly different X-ray patterns from sample to sample, mainly owing to the remaining (premature) planar zigzag form, which is not the planar zigzag form produced via the molecular compound but from the melt. These variations indeed complicate the polymorphism of sPS. In conclusion, however, there are principally four distinct crystalline phases as shown in *Figure 1*, which will be called in succeeding papers the molecular compound, helical form, planar form I and planar form II, respectively.

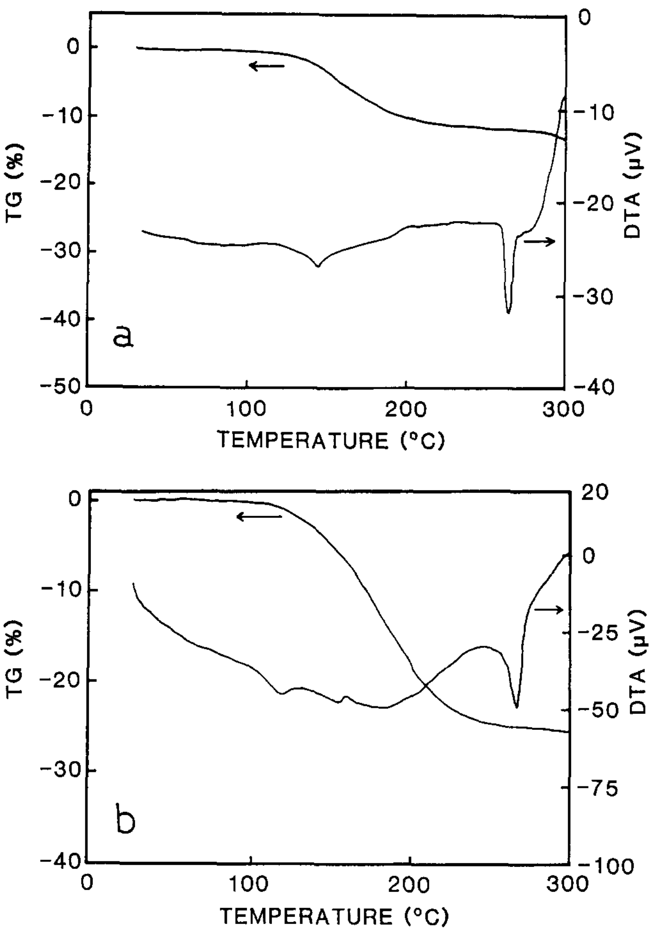

Figure 5 D.t.a. and t.g. traces for (a) sPS–toluene system and (b) sPS–1,2,4-trichlorobenzene system

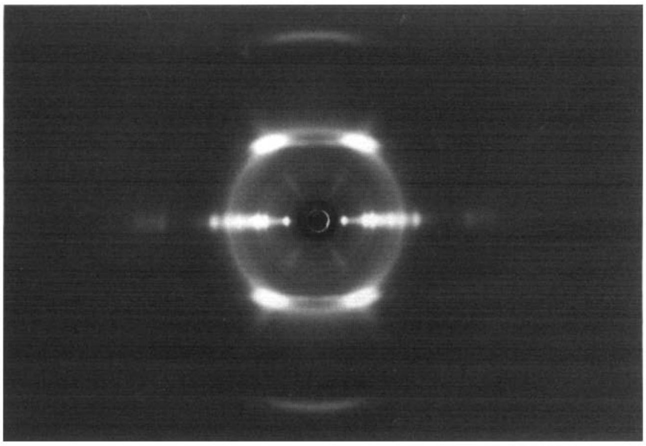

Figure 6 X-ray fibre photograph for melt-crystallized sPS

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