



# Decisive properties of solvent able to form gels with syndiotactic polystyrene



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## ABSTRACT

The thermoreversible gel formation of syndiotactic polystyrene (SPS) was studied in detail. Even if SPS solutions with high concentrations did not form gels, there were the cases where SPS formed gels at lower concentrations of SPS, which favor the formation of a polymer-solvent molecular compound. Sixty-two solvent compounds were examined in regard to whether they could form SPS gels. All the compounds whose molecular volume is between 69 and 153 Å<sup>3</sup> and whose Fedors' solubility parameter value is between 8.8 and 12.3 (cal/cm<sup>3</sup>)<sup>1/2</sup> were found to produce SPS gels as solvent. Since a solvent molecule that can form SPS gel can be a guest of SPS  $\delta$  co-crystalline phase, it has become convenient to find functional molecules able to co-crystallize with SPS by taking into account these conditions of gelation solvent molecules.

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## 1. Introduction

Syndiotactic polystyrene (SPS), which was first synthesized in 1986 by using metallocene catalyst [1], is known to have a complex polymorphic behavior [2–5]. Nonsolvated crystalline phases,  $\alpha$  and  $\beta$ , consist of all trans zigzag (TTTT) conformation [6], while the other crystalline phases  $\gamma$ ,  $\delta$  and  $\epsilon$  consist of 2<sub>1</sub>-helix (TTGG) conformation [7]. The  $\delta$  and  $\epsilon$  phases have cavities inside able to fix some guest molecules: for example, a  $\delta$  empty phase [8] is monoclinic (space group P2<sub>1</sub>/a; a = 1.74 nm; b = 1.18 nm; c = 0.78 nm;  $\gamma$  = 117°) and exhibits per unit cell two identical cavities centered on the center of symmetry and bounded by ten phenyl rings [8,9]. Recently SPS/guest clathrate co-crystalline phases were reported to have two crystal systems of monoclinic and triclinic unit cells according to volume sizes of guest molecules [10,11].

The definition of physical gels is usually after Guenet [4]: (i) a gel is a network, and (ii) gel formation and gel melting should proceed via a first-order transition. On the basis of the definition, thermoreversible gels of SPS have been extensively studied so far since Kobayashi et al. [12]. Finally the gel morphology of SPS is

established to be a three-dimensional network of fibril structures that consist of SPS chains with the 2<sub>1</sub>-helix conformation [13,14] and solvent molecules that are staying between these SPS helix chains as polymer-solvent molecular compounds [15,16]. The structure of these SPS fibrils was demonstrated to be a  $\delta$  crystalline clathrate phase [17,18]. Moreover, the neutron diffraction peaks of SPS/benzene gel reported by Daniel et al., in 1996 [19] was later assigned to those of  $\delta$  intercalate form [19,20]. Thus, the crystalline phase of SPS fibrils forming gel networks are concluded to be of  $\delta$  clathrate phase or  $\delta$  intercalate phase. If all the solvent molecules are evacuated from SPS gels, the x-ray diffraction peaks of the SPS samples are assumed to be identical with those of SPS  $\delta$  empty crystalline form.

We employed serial n-alkylbenzenes (NB: C<sub>6</sub>H<sub>5</sub>–C<sub>N</sub>H<sub>2N+1</sub> (N = 1–10)) [21] and several typical fragrant molecules [22] as solvents of SPS in order to clarify what conditions of solvent can produce SPS gel when SPS concentration is 10 wt/wt%. After dissolving SPS at high temperatures, we checked what morphologies they showed after cooling. Their morphologies can be divided into three: a gel with three-dimensional network consisting of fibril structure of SPS  $\delta$  phase, a paste-like state consisting of non-lamellar spherulitic structure with SPS  $\gamma$  phase, and a sherbet-like state consisting of lamellar structure with SPS  $\beta$  phase. Finally the necessary conditions of a solvent able to form an SPS gel have turned out to be its molecular size being less than ~160 Å<sup>3</sup>, which is the maximum cavity size of SPS  $\delta$  empty crystalline phase.

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However, we also found that some solvent molecules did not produce SPS gels though the molecular sizes were smaller than  $\sim 160 \text{ \AA}^3$ . It suggests that the interaction between SPS and a solvent is another important factor for the gelation. Then we estimated the interaction by means of Fedors' solubility parameters (SP) [23,24] and obtained rough range of SP values for solvent able to produce gels with SPS [22], though the number of solvent molecules was not enough to determine it.

In the present paper, we have tried to determine a universal condition of solvent able to produce SPS gels by observing whether 62 solvent molecules could form gels or not. In particular, we are interested in whether SPS can form gels with solvent molecules whose SP values are far from the SP value of SPS.

## 2. Experimental section

### 2.1. Materials

Syndiotactic Polystyrene (SPS) used for the measurements was kindly supplied from Idemitsu Kosan Co., Ltd. It is 98% syndiotactic with an Mw of 152,000 and an Mw/Mn of 1.9. All the solvents were purchased from Wako Chemicals and Aldrich Co. and used without any further purification, whose structures are summarized in Table 1. Each code such as 1B or M1 is given to each solvent in Table 1 and used in the text and captions of figures.

SPS was dissolved with a solvent in a screw tube by heating the mixture at high temperature after influx of dry nitrogen gas for 1 min. Heating temperature of a sample was sometimes higher than the boiling temperature of solvent by 10–20 °C. After SPS was perfectly dissolved, the solutions were well stirred by using a vortex mixer, heated again for 2 min, and finally cooled at room temperature (around 25 °C) for more than 2 days.

All the SPS films were first prepared by melting polymer pellets at 300 °C for 4 min, compressing them at 15 MPa for 4 min, and then quenching them quickly in ice water. Amorphous SPS films obtained were dried for more than 24 h under vacuum at 40 °C. The films of SPS/thiophene (S2)  $\delta$  clathrate co-crystalline phase were prepared by immersing the amorphous SPS films in thiophene for 1 h at 60 °C. The films of SPS/1,4-dimethylnaphthalene (NP3)  $\delta$  intercalate co-crystalline phase were prepared by immersing the amorphous SPS films in 1,4-dimethylnaphthalene for 3 h at 95 °C.

### 2.2. Measurements

Scanning electron microscopy, SEM, pictures were obtained using a JEOL JSM-6300 after drying an SPS gel on a glass plate under vacuum for more than 3 days. Dried SPS samples were stuck on a double-sided tape of carbon and coated with platinum or gold. Wide-angle X-ray diffraction, WAXD, patterns were measured at room temperature using a Rigaku MicroMax7HFM with a beam of CuK $\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) that was finely focused by a confocal mirror and a collimator. The diffraction patterns were detected by a Rigaku R-axisIV++ and recorded on an imaging plate. The data were analyzed by using FIT2D program. Diffraction intensities at constant  $2\theta$  shown in a diffraction pattern were obtained by the integration of all the diffraction intensities around the beam. Infrared absorption, IR, spectra were measured on a Perkin Elmer SPECTRUM1000 FT-IR spectrophotometer with resolution of  $1 \text{ cm}^{-1}$ . The samples of SPS gels for the measurements of WAXD and FT-IR were dried at 40 °C under vacuum in order to remove solvent molecules more or less. The reason why we chose 40 °C is to avoid the transition from SPS  $\delta$  crystalline phase to  $\gamma$  phase that was reported to take place at 90 °C by Tashiro et al. [25]. Dried gel samples were reduced in fine powder. A capillary made of soda lime glass with a diameter of 1.0 mm (Hilgenberg GmbH) filled with dried gel

was set for the measurements of WAXD. For the measurements of FT-IR, gel powders were mixed with KBr and pressed to a disk form.

## 3. Results and discussion

### 3.1. Determination of gel morphology of SPS/solvent systems

Sixty-two solvent molecules with different volume sizes and solubility parameters were examined in regard to whether they could form thermoreversible gels of syndiotactic polystyrene (SPS) or not. SPS was dissolved at high temperatures in 54 compounds among 62 compounds used in the present study. After cooling, the appearances of the SPS/solvent systems were divided into three categories: (1) gel, (2) paste, and (3) sherbet states. These results perfectly corresponded to the case where SPS was dissolved in NB [21] and fragrant molecules [22]. The solutions categorized to be a gel state were transparent and elastic, and did not change their shapes by tilting them for months. The solutions of SPS assigned to a paste state apparently looked to be of gel form, but the shapes finally changed by tilting them for a long time. When they were pushed by a spatula, they did not show any elasticity rather behaved like paste, namely being soft. In the case of the solutions assigned to a sherbet state, they changed the shapes by tilting for a while, followed by the separation of liquid solvent.

We can define SPS gel on the basis of the following characteristics, which was explained in Introduction: (i) three-dimensional networks of fibril structures observed by SEM, (ii) an IR absorption peak around  $571 \text{ cm}^{-1}$  assigned to the  $2_1$ -helix (TTGG) conformation of the SPS chain, and (iii) WAXD peaks assigned to either those of the SPS  $\delta$  empty crystalline phase when solvent molecules were almost removed, or those of the SPS/solvent  $\delta$  clathrate co-crystalline phase or SPS/solvent  $\delta$  intercalate co-crystalline phase when solvent molecules remained in the crystals. Therefore, we measured SEM, IR, and WAXD of all the solution samples. Needless to say, the majority of these gel characterization was carried out for dried gels after perfectly or partially removal of solvent. However, we have already shown that the pristine SPS/NB solutions assigned to a gel state consist of polymer-solvent molecular compounds by means of DSC, and their dried gels exhibited the spectroscopic evidence (i) to (iii) shown above [21].

Fig. 1 shows typical three-dimensional fibril networks of dried SPS/solvent systems observed using SEM: all were defined to be of the gel form. The morphologies of SPS dried from paste and sherbet states were of non-lamellar spherulitic structure (e.g., 6B and cis-jasmone (F7)) and lamellar structure (e.g., 1H-1,3,5-triazine (N3), pyrazole (Z1)), respectively. The appearance of SEM pictures was found to coincide with macroscopic characters such as gel, paste, and sherbet states.

As described in Introduction, the fibril structure consists of polymer-solvent molecular compounds where the conformation of SPS chains is of  $2_1$ -helix structure. Fig. 2 demonstrates the IR absorption spectra of some SPS gels. Kobayashi et al. first clarified that IR absorption peaks at  $1223$  and  $571 \text{ cm}^{-1}$  of SPS gels corresponded to TT and TTGG, respectively [12]. Recently Torres et al. made use of two IR absorption peaks at  $1223$  and  $571 \text{ cm}^{-1}$  of SPS solids corresponding to the trans planar [26] and  $2_1$ -helix [27] structure, respectively. Fig. 2 shows some examples of IR spectra for SPS gels exhibiting bands assigned to the  $2_1$ -helix conformation. It should be emphasized that the SPS/solvent systems showing the IR band around  $571 \text{ cm}^{-1}$  in Fig. 2 did not have the IR band around  $1223 \text{ cm}^{-1}$  assigned to the trans zigzag conformation.

Fig. 3A–F shows the X-ray diffraction patterns of SPS/solvent systems that formed gels. All the WAXD patterns (A)–(F) shown in Fig. 3 were assigned to those of the SPS  $\delta$  crystalline phase, but they were classified into two different phases, i.e., the  $\delta$  clathrate (A–D),

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