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# Gelation Crystallization of Isotactic Polystyrene in Solvents of Varying Molecular Size

**Gi Xue,* Jun Zhang, Jinglu Chen, Yuqin Li, Jianbiao Ma, Guochang Wang, and Pingchuan Sun**

*The State Key Laboratory of Functional Polymer Materials for Adsorption and Separation at Nankai, Department of Polymer Science and Engineering, Nanjing University, Nanjing 210093, P. R. China*

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**Introduction.** Isotactic polystyrene (iPS) is a semicrystalline polymer characterized by slow crystallization rates and low crystallinity (about 30%).[1] Several papers dealt with the crystalline growth rate of iPS as a function of temperature in solution.[2−5] Blais and Manley[2] found that solutions in toluene do not yield detectable iPS crystals even after the solutions were allowed to stand at room temperature for more than a year. They reported, however, that small crystals were precipitated from mesitylene (1,3,5-trimethylbenzene) after 1000 h. It is known that polymers can often be crystallized with greater ease from poor than good solvents.[6] As relatively poor solvents, dimethyl phthalate or a mixture containing two parts by volume of *n*-tetradecane and one part Decalin were used, but 2−3 days were still needed to grow crystals from these solutions.[3]

The effect of solvent quality on the static-equilibrium conformational behavior is well-established.[7,8] While some experimental work has been done on the effect of solvent quality on the mechanical, optical, and rheological response of polymer solutions,[9−13] very little, if any, work has been done on the modeling and theoretical investigation of the effect of solvent size on the conformational transition of polymer chains. In this paper, we describe our experimental results about the formation of $3_1$ helices of iPS and the rapid crystallization in large molecule solvents.

**Experimental Section.** The iPS used in this study was kindly supplied by Prof. Lin Shang-An's research group at the Institute of Polymer Science, Zhong Shan University, P. R. China, which contained more than 99% isotactic triads. The number-average molecular weight of this highly stereoregular iPS was about $18 \times 10^4$. A desired amount of iPS and an alkyl benzoate solvent were added into a 10 mL Erlenmeyer flask. The mixture was initially heated to 220 °C while being stirred in a silicon oil bath and then held at this temperature for 10 min to ensure that all of the iPS fully dissolved, and a homogeneous solution was obtained. The solution was then cooled to room temperature in the oil bath at a rate of 10 °C/min without further agitation. For iPS in octadecyl benzoate solution crystals could be visually observed to be precipitating at about 140 °C, and mechanically weak and touch-broken gels formed on further cooling. For solutions of iPS in ethyl phthalate and in butyl phthalate, no crystals were observed on cooling to room temperature. An excess of ethanol was added to the solution to precipitate the iPS.

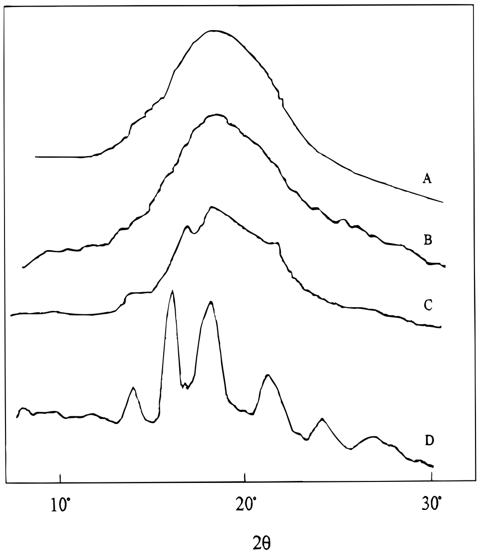

**Figure 1.** Wide-angle X-ray diffraction curves of iPS recovered from (A) ethyl benzoate, (B) butyl benzoate, (C) octyl benzoate, and (D) octadecyl benzoate.

Infrared spectra were taken using an IFS66V FT-IR spectrometer. The iPS/octadecyl benzoate gel with concentration of 20 wt % was put into a cell which was formed by two NaCl windows sealed by a Teflon gasket. The cell, filled with the gel, was mounted on the sample holder of the heating device. Wide-angle X-ray diffraction patterns for the dried gel were obtained with nickel-filtered Cu Kα radiation on an automatic Philips powder diffractometer, Rigaku D/Max-Ra. The melting temperature ($T_m$) of polymer gel was measured by thermogravimetry analysis using Thermal Analyst 2100, TA Instruments.

**Results and Discussion.** Figure 1A−D shows the wide-angle X-ray scattering patterns recorded from an iPS sample which had been recovered from iPS/ethyl benzoate, iPS/butyl benzoate, iPS/octyl benzoate, and iPS/octadecyl benzoate, respectively. Figure 1D shows several finely resolved crystalline peaks in the range of $2\theta = 5-30°$, which could be indexed according to ref 14.

| $2\theta$ | 14.3° | 16.5° | 18.4° | 21.7° | 24.5° | 27.3° |
|---|---|---|---|---|---|---|
| *hkl* | 300 | 220 | 211 | 410<br>311 | 330<br>321 | 222<br>421 |

Crystallinities are obtained by dividing the crystalline intensity by the total diffracted intensity.[8,9] A BASIC computer program was edited to resolve the band and to calculate the crystallinity content. After the computer calculation, the extent of the crystallinity of iPS recovered from iPS/1-chlorotetradecane was near 0.68 measured by wide-angle X-ray scattering. Figure 1C indicates that the crystallinity of iPS recovered from octyl benzoate is low. In parts A and B of Figure 1, only broad reflections can be observed, indicating that the iPS samples obtained from ethyl benzoate and from butyl benzoate solutions were mainly in the amorphous phase.

Sundararajan et al.[15] considered that a crystallinity of ∼0.3 was typical for annealed iPS films, and Overbergh et al.[16] arrived at a maximum crystallinity of 0.33 for iPS samples annealed for several hours following solvent-induced crystallization. It is clear that iPS

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* Correspondence author. E-mail: xuegi@nju.edu.cn.

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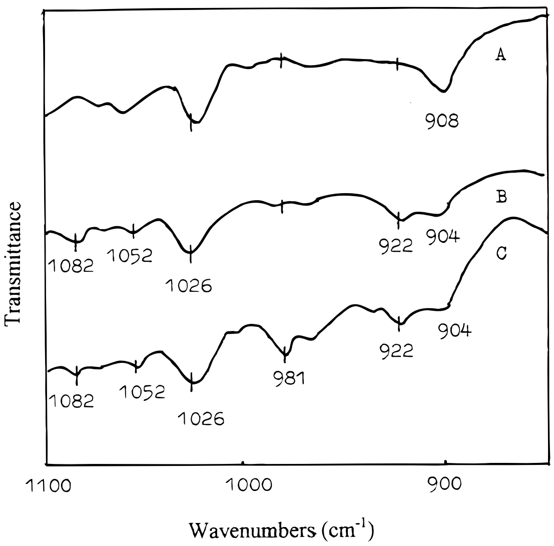

**Figure 2.** IR spectra recorded from (A) iPS in butyl benzoate solution at 80 °C, (B) iPS in octadecyl benzoate at 220 °C, and (C) wet gel in octadecyl benzoate at 60 °C. The contribution of the solvents in the spectra was removed using spectral subtraction routine.

recovered from octadecyl benzoate gel is more highly crystalline than samples prepared by normal physical techniques, such as solution crystallization in small molecule solvents, annealing, solvent-induced crystallization, and their combination.

Since the iPS chain in the crystalline phase is a $3_1$ helix,[17] the helical conformation of the iPS molecule is an important factor during crystallization. Keith et al.[3] assumed conformational differences to be responsible for their observed difference in the growth rate. The IR vibrational characteristics were used in this study to show the conformational changes of the sample. Figure 2 illustrates the in situ IR spectrum (A) for iPS in butyl benzoate recorded at 80 °C, the in situ IR spectrum (B) for iPS in octadecyl benzoate recorded at 220 °C, and the spectrum (C) for a wet gel in octadecyl benzoate recorded at 60 °C. The contribution of the solvents in the spectra was removed using the spectral subtraction routine.[18] Both difference spectra (Figure 2B) for iPS in the solution and in the wet gel (Figure 2C) exhibit $3_1$ helix doublet bands at 1082−1052 and 922−904 cm$^{-1}$. But a marked difference was observed for the crystallization-sensitive band at 981 cm$^{-1}$ between the two difference spectra. The 981 cm$^{-1}$ band was strong for the wet gel, but very weak for the solution. This indicated the formation of the $3_1$ helix conformation in octadecyl benzoate solution at 220 °C and its packing into the crystalline phase in the wet gel at 60 °C. We concluded that the iPS chains in the original octadecyl benzoate solution contained a considerable amount of helical segments. It is possible for some of them to encounter each other and line up by van der Waals force interaction and become a node in the solution. As the solution was cooled, the nodes formed nuclei. Then the polymer crystallized quickly and the obtained crystallinity was very high. However, in Figure 2A, neither the crystalline band at 981 cm$^{-1}$ nor the $3_1$ helix band at 922 cm$^{-1}$ are intensified, indicating that there were neither crystals nor helices in the butyl benzoate solution of iPS.

The conformation of iPS in various solvents has been investigated by different authors. Kobayashi et al.[19] showed that, in CS$_2$, the iPS chains would take the highly ordered $3_1$ helical conformation only when the temperature was cooled to −60 °C and the concentration was very low.[1,3,19,20] We reported previously[21−23] that, in a very dilute solution of benzene ($C < 0.04$ g/dL), iPS chains contain many helical segments with few chain entanglements. As the concentration increased, chains are highly interpenetrated and fewer helical segments exist. It seems that the results obtained for iPS chains in octadecyl benzoate solution disagree with general conclusions. The rapid crystallization rate, the invariance of the crystallinity with concentration, and the highly ordered conformation of molecules in the concentrated solutions of iPS/octadecyl benzoate system are very interesting observations. We ascribe these special results to the large molecular size of the solvent. Table 1 illustrates the crystallinity of iPS recovered from solvents with various molar volumes. It is clear that iPS recovered from large molecule solvents, such as octadecyl benzoate, were highly crystalline, while the samples recovered from small molecule solvents were mostly amorphous. It is considered easier for iPS chains to assume the helical conformation and to pack into crystals in a solvent with a large molecular size. This interpretation is mostly speculative.

**Table 1. Crystallinities of IPS Condensed from Various Solvents**

| solvent | molar vol ($V_m$, cm$^3$/mol) | $T_m$ for 20 wt % gels (°C) | crystallinity of recovered iPS (%) |
|---|---|---|---|
| 1,2-dichloromethane | 64 | <0 | <5 |
| decalin | 154 | 28 | <5 |
| ethyl benzoate | 142 | <0 | <5 |
| butyl benzoate | 176 | 20 | <5 |
| octyl benzoate | 218 | 90 | 25 |
| octadecyl benzoate | 360 | 180 | 68 |
| 1-chlorohexadecane | 302 | 170 | 67 |
| dioctyl phthalate | 397 | 165 | 66 |

In iPS solution, the rate of helix formation can be given by[24]

$$\frac{dC_H}{dt} = k_i C_c \left(1 - \frac{k_b}{k_f}\right) \qquad (1)$$

where $C_H$ and $C_C$ are the concentrations of units that are helical and coiled, respectively and $k_i$ is the rate constant for initiation. The ratio $k_b/k_f$ equals $K^{-1}$, where $K$ is the equilibrium constant for a helix-to-random coil transition. In the vicinity of the melting or transition temperature for this process

$$\frac{dC_H}{dt} = k_i C_c \frac{\Delta H_u}{RT^2}(\Delta T) \qquad (2)$$

Here, $\Delta H_u$ is the enthalpy change per unit in going from helix to coil; $T_m$ is the melting point of polymer in solution, and $\Delta T = T_m - T$ is the supercooling.

According to eq 2, the rate of helix formation depends on the temperature $T$ and supercooling $\Delta T$. At constant supercooling, the rate should pass through a maximum as the temperature is lowered, since $k_i$ will decrease with a decrease in temperature. However, at a given temperature being equal, the rate should increase with increasing $\Delta T$ or $T_m$. In Table 1, $T_m$ for iPS in 20 wt % solution increases with increasing solvent molar volume. Actually, a smaller depression of the melting temperature, and correspondingly a larger supercooling, would

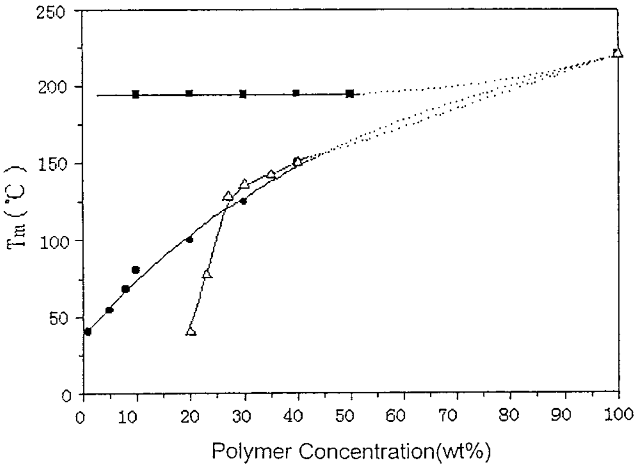

**Figure 3.** Plot of melting temperature–composition relations for iPS for different diluents: solid squares, octadecyl benzoate; solid circles, Decalin; open triangles, ehtyl benzoate. Dotted lines represent the supposed continuation of the diagram.

be observed for diluents of larger molar volume, as well as for a poor solvent (larger values of $\chi_1$). When solvent molecules are too large, they are unable to fully solvate a randomly coiling iPS chain, thus forming the low intramolecular energy $3_1$-helical conformation, because of a limited solvation energy and entropy. Thus, in a larger size solvent, it would be easier for iPS chains to take the helical conformation in solution, and that would result in the increase in crystallinity in the condensed state.

In Figure 3 the melting temperature–composition relations of iPS with different dilutions are illustrated. The two lower curves represent the results for ethyl benzoate and Decalin as diluents. A continuous decrease of the melting temperature is observed as increasing amounts of diluent were added. Such behavior is expected for these relatively good solvents. The upper curve, which represents iPS and octadecyl benzoate as the diluent, is quite different. The melting temperature remains invariant for the solutions from 5 to 50 wt %. The contrasting behavior of the three systems results from the fact that molten iPS is miscible with ethyl benzoate and with Decalin but is immiscible with octadecyl benzoate. It seems that phase-separation and gelation–crystallization appeared when the iPS/octadecyl benzoate system was cooled to $T_m$. The observed invariance of the melting temperature in solvents of large molecular volume may give an explanation for the invariance of the crystallinity on the polymer concentration.

These data shown in Table 1 are for specimens cooled at 10°/min, a relatively rapid cooling. When the samples were cooled at 0.5°/min, no significant differences were observed, since 2–3 days are needed to grow crystals from solvents of small molar volumes.[3] It is interesting to find that the crystallinity increases rapidly when the solvent molar volume changed from 140 to 300 $cm^3$/mol, and the crystallinity reaches a nearly constant value when the solvent is larger than 300 $cm^3$/mol, as shown in Table 1. Further research work on the gelation–crystallization of iPS in solvents of large molar volume is necessary to find the detailed mechanism.

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## References and Notes

(1) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1995.
(2) Blais, P.; Manley, R. St. J. *J. Polym. Sci., A-2* **1966**, *4*, 1022.
(3) Keith, H. D.; Vadimsky, R. G.; Padden, F. J. *J. Polym. Sci., A-2* **1970**, *8*, 1687.
(4) Tanzawa, Y. *Polymer* **1992**, *33*, 2659.
(5) Miyamotor, Y.; Tanzawa, Y.; Miyaji, H.; Kiho, H. *Polymer* **1992**, *33*, 2497.
(6) Geil, P. H. *Polymer Single Crystals*; Interscience: New York, 1963.
(7) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon: Oxford, U.K., 1986.
(8) Gujrati, P. D. *Phys. Rev. E* **1996**, *54*, 2723.
(9) Andrews, N. C.; Doufas, A. K.; McHugh, A. J. *Macromolecules* **1998**, *31*, 3104.
(10) Narh, K. A.; Odel, J. A.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 335.
(11) (a) Nguyen, T. Q.; Yu, G.; Kausch, H. H. *Macromolecules* **1995**, *28*, 4851. (b) Douglas E. S.; Chu, S. *Science* **1998**, *281*, 1335.
(12) de Gennes, P.-G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 842.
(13) Qian, R. Excimer studies of polymer solutions over the entire concentation range. In *New trends in physics and physical chemistry of polymers*; Lee, L.-H., Ed.; Plenum Publishing Co.: New York, 1989.
(14) Lemstra, P. J.; Postma, J.; Challa, G. *Polymer* **1974**, *15*, 757.
(15) Tyrer, N. J.; Bluhm, T. L.; Sundararajan, P. R. *Macromolecules* **1984**, *17*, 2296.
(16) Overbergh, N.; Bergmans, H.; Smets, G. *Polymer* **1975**, *16*, 703.
(17) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento Suppl.* **1960**, *15*, 69.
(18) Coleman, M. N.; Painter, P. C. *J. Macromol. Sci.—Rev. Macromol. Chem.* **1978**, *16*, 197.
(19) Nakaoki, T.; Kobayashi, M. *J. Mol. Struct.* **1991**, *242*, 315.
(20) Itagaki, H.; Takahashi, I. *Macromolecules* **1995**, *28*, 5477.
(21) Xue, G.; Wang, Y.; Liu, S.; Liao, Y.-T. *Macromolecules* **1995**, *28*, 4344.
(22) Ji. G.; Ni, H.; Wang, C.; Xue, G. *Macromolecules* **1996**, *29*, 2691.
(23) Xue, G.; Wang, Y.; Liu, S. *Macromolecules* **1995**, *28*, 3476.
(24) Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill Book Co.: New York, 1964.

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