3984 *Macromolecules* **1999,** *32,* 3984−3988

Rapid Crystallization of Isotactic Polystyrene from Large Molecule Solvent Octadecyl Benzoate

Yuqin Li and Gi Xue*

Department of Polymer Science and Engineering, Nanjing University, Nanjing 210093, P.R.China

Received February 2, 1998; Revised Manuscript Received March 15, 1999

ABSTRACT: Isotactic polystyrene (iPS) was rapidly crystallized by cooling a solution in the large molecule solvent octadecyl benzoate at a rate of 10 °C/min. The crystallinity is near 0.7 measured by the wide-angle X-ray diffraction method, which is much higher than that for iPS samples crystallized by solution crystallization in a small molecule solvent, solvent-induced crystallization, high temperature annealing, and their combinations. Fourier Transform infrared spectroscopic shows that the iPS chains in the concentrated solution in octadecyl benzoate had a highly ordered 3_1 helical conformation. It is presumed that the molar size of solvent exerted a large influence on the formation of helical conformation and, thereby, on the crystallization rate of iPS in the solution.

Introduction

Isotactic polystyrene (iPS) has been considered to be a slowly crystallizing polymer.[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 standing 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 empirically that polymers can often be crystallized with greater ease from poor rather 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, 2−3 days are still needed to grow crystals from these solutions.[3] The half-times for crystallization of iPS from solution were a few hundred to 10000 min depending upon the solvent used and the crystallization temperature.[1]

In this paper, we will describe our experimental results about the rapid crystallization of iPS in octadecyl benzoate.

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. ^{13}C NMR spectra showed that the iPS sample contained more than 99% isotactic triads. The number-average molecular weight of this highly stereoregular iPS was about 18×10^4. The iPS sample was in particular brought to the vitreous state by rapid quenching after complete melting at $T = 260$ °C. This thermal treatment ensures that the polymer is rid of the effect of its thermal history. The solvent octadecyl benzoate was prepared in this laboratory.

A desired amount of iPS and octadecyl benzoate was 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 30 min to ensure that all of the iPS had fully dissolved in the octadecyl benzoate 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. Crystals could be visually observed precipitating at about 140 °C; mechanically weak and touch-broken gels formed at 100 °C on further cooling. Upon cooling to room temperature, the nascent wet gels were repeatedly extracted with cold ethanol followed by drying in a vacuum.

On the other hand, the iPS/octadecyl benzoate solutions (at 220 °C) were injected directly into large amount of liquid nitrogen so that they were frozen in a fraction of a second. The frozen solution was then repeatedly extracted with cold ethanol followed by drying in a vacuum. The recovered powder was termed as freeze-extracted iPS.

Infrared spectra were taken using an IFS66V FT-IR spectrometer. The iPS/octabecyl 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 gel, was mounted on the sample holder of the heating device. Wide-angle X-ray diffraction patterns for the dried gel were obtained with nickle-filtered Cu Kα radiation of an automatic Philips powder diffractometer, Rigaku D/Max-Ra.

Results and Discussion

Figure 1A shows the wide-angle X-ray scattering pattern recorded from an iPS sample which had been recovered from a iPS/octadecyl benzoate gel with a concentration of 20 wt %. For comparison, two iPS samples crystallized by conventional methods are also studied. The diffractogram of Figure 1B is recorded from an iPS sample which had been cooled at 0.5 °C/min from its melt to room temperature. The sample for Figure 1C is recovered from an iPS/decalin gel with concentration of 20 wt % which was formed by cooling the solution at 10 °C/min to room temperature. Figure 1A shows several fine resolved crystalline peaks in the range $2\theta = 5{-}30°$, which could be indexed according to ref **7**.

2θ, deg	14.3	16.5	18.4	21.7	24.5	27.3
hkl	300	220	211	410 311	330 321	222 421

Crystallinities are obtained by dividing the crystalline intensity by total diffracted intensity.[8,9] The crystallinity of iPS recovered from iPS/octadecyl benzoate was near 0.7 measured by wide-angle X-ray scattering. The X-ray crystallinity corresponding to Figure 1B was 0.23, which was in agreement with what has been reported previously.[10] Sundararajan et al.[11] considered that a crystallinity of ∼0.3 was typical for annealed iPS films, and

---

*Correspondence author. E-mail: xuegi@nju.edu.cn. Fax: 86-25-3317761.

10.1021/ma980144m CCC: $18.00

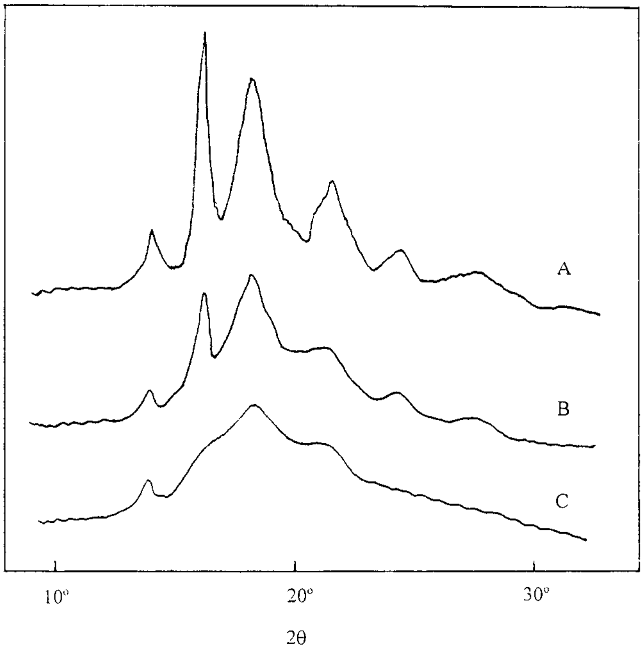

Figure 1. Wide-angle X-ray diffraction curves recorded from (A) iPS recovered from octadecyl benzoate, (B) a normal iPS cooled at 0.5 °C/min from its melt to room temperature, and (C) iPS recovered from decalin.

Overbergh et al.[12] arrived at a maximum crystallinity of 0.33 for iPS samples annealed for several hours following solvent-induced crystallization. In Figure 1C, only three reflections can be observed which are rather broad and weak. They are not typical of crystalline order but rather of liquid crystalline systems.[13] This sample may have a kind of smecticlike arrangement. This type of situation is also encountered with liquid crystalline polymers containing mesogenic segments.[14] It is clear that iPS recovered from octadecyl benzoate gel is more highly crystalline than samples prepared by normal physical techniques, such as solution crystallization in small molecule solvent, annealing, solvent-induced crystallization, and their combination.

The high crystallinity of iPS crystallized from octadecyl benzoate solution can be confirmed by vibrational spectroscopy. Figure 2 illustrates IR spectra A, B, and C which were recorded from an iPS recovered from iPS/octadecyl benzoate gel, an iPS cooled from the melt, and an iPS recovered from the iPS/decalin gel, respectively. It is well-known that the band at 983 cm^{-1} is a typical crystallization-sensitive band, and its intensity can be used as a measure of the crystallinity.[15] This band is much stronger in Figure 2A than that in Figure 2B and Figure 2C, indicating a highly crystalline phase in the iPS sample recovered from iPS/octadecyl benzoate gel.

Of particular interest here is the observation in Figure 3, which shows a plot of the relative intensity, $I_{983\ \mathrm{cm}^{-1}}/I_{1026\ \mathrm{cm}^{-1}}$, vs concentration. The 1026 cm^{-1} band in the IR spectra of iPS is less sensitive to crystallinity, which can be used as an internal standard for quantitative measurement for crystallinity.[16] The plot in Figure 3 indicates that the changes in iPS concentration in octadecyl benzoate solutions have little influence on the crystallinity level for the recovered iPS. A highly crystalline iPS phase could be obtained either from a dilute solution (5 wt %) by simple precipitation upon cooling or from a very concentrated system (35 wt %) through gelation.

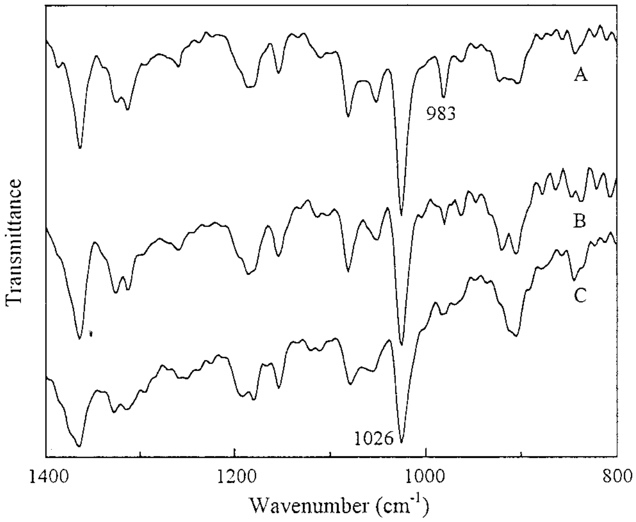

Figure 2. IR spectra recorded from (A) iPS recovered from octadecyl benzoate, (B) a normal iPS cooled at 0.5 °C/min from its melt to room temperature, and (C) iPS recovered from decalin.

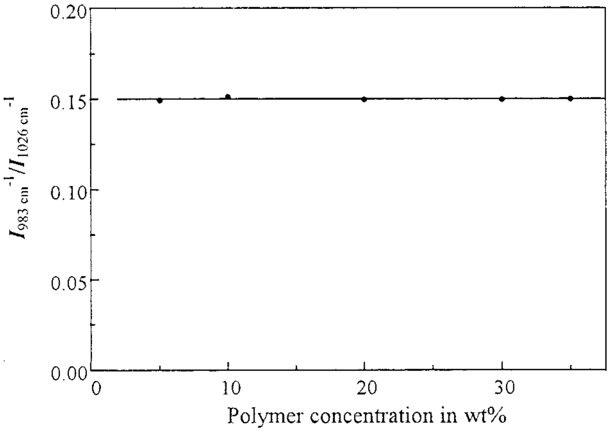

Figure 3. Concentration dependence of crystallinities of iPS recovered from octadecyl benzoate.

How did these polymer solutions form gels? Why can the iPS crystallize quickly from octadecyl benzoate solution? And is there any relation between the rapid crystallization and gelation? It is necessary to establish the phase diagram to resolve these problems. Gel formation of all polystyrene that have been studied occurs in the vicinity of the liquid–liquid-phase separation.[17] Hence, in the analysis of a given polymer–solvent system, it is important to establish the binodial. Due to the rapid crystallization rates, liquid–liquid phase separation was not directly observed for iPS in octadecyl benzoate. However, on the basis of other studies of iPS, epimerized PS, and conventional aPS, the location of the binodial curve does not change by more than 5 °C with variations in the tacticity.[18] Therefore, we have estimated the binodial for iPS in octadecyl benzoate to be that directly observed for aPS in this solvent. This binodial together with some thermodynamic information is shown in Figure 4 which is termed a pseudo-phase diagram. In addition to the estimated binodal, the gelation temperature as the temperature for the formation of precipitates are plotted against the concentration of the solution. The occurrence of gelation apparently does not require a liquid–liquid-phase separation since gels were formed 30 °C above the estimated binodal. Furthermore, the precipitate formation (crystallization),

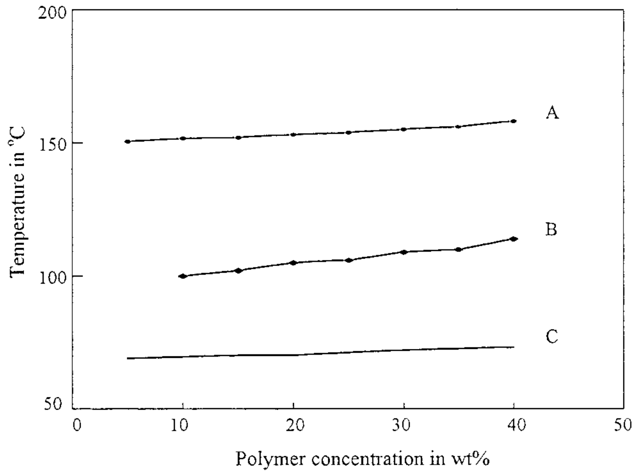

Figure 4. Pseudo phase diagram of iPS in octadecyl benzoate: (A) temperature for the formation of precipitates; (B) gelation temperature; (C) the estimated binodial curve.

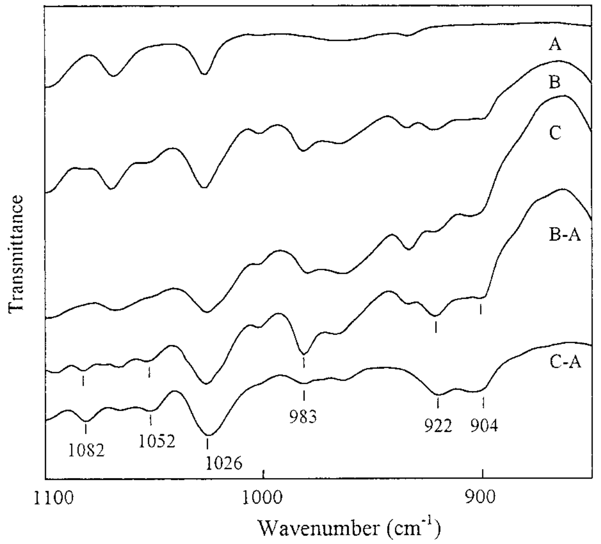

Figure 5. IR spectrum in the region 1100-850 cm^{-1} for (A) octadecyl benzoate, (B) iPS/octadecyl benzoate gel at 60 °C, (C) iPS/octadecyl benzoate solution at 220 °C, (B − A) subtraction of B − A, and (C − A) subtraction of C − A.

i.e., the solid–liquid-phase separation occurs about 70 °C above the liquid–liquid-phase separation. Obviously, crystallization is the primary cause of gelation, with crystals acting as junction points in the network. In other words, the gelation phenomenon or the liquid–liquid-phase separation is not the cause for rapid crystallization of iPS in octadecyl benzoate solution.

Since the iPS chain in the crystalline phase is a 3_1 helix,[19] the helical conformation of the iPS molecule is an important factor during crystallization. Keith et al.[3] assumed the conformational differences to be responsible for their observed difference in the growth rate. The IR characteristic were used in this study to show the conformational changes of the sample. Figure 5 illustrates the spectrum (A) for the pure solvent, the in situ IR spectrum (C) for the solution recorded at 220 °C, and the spectrum (B) for a wet gel recorded at 60 °C. The contribution of the solvent in the spectra was removed using the spectral subtraction routine,[20] and the difference spectra are also shown in Figure 5. Both difference spectra for iPS in the solution (C − A) and in the wet gel (B − A) exhibit 3_1 helix doublet bands at 1082–1052 and 922–904 cm^{-1}. However, a marked difference was observed for the crystallization-sensitive band at 983 cm^{-1} between the two difference spectra. The 983 cm^{-1} was strong for the wet gel, but very weak for the solution. In the region 650–500 cm^{-1}, the solvent octadecyl benzoate has no distinct absorption peaks, leaving a spectral window as shown in Figure 6A. We can take advantage of this to compare the IR spectra of the solution with the wet gel directly. The 562 cm^{-1} band appeared in the spectrum of the solution (Figure 6C), which was related to the 3_1 helical conformational structure before packing into crystallites. It shifted to 566 cm^{-1} in the wet gel (Figure 6B), indicating that crystallization occurred during cooling. These spectral evidence indicated the formation of the 3_1 helix conformation in octadecyl benzoate solution at 220 °C and its packing into crystalline phase in the wet gel at 60 °C.

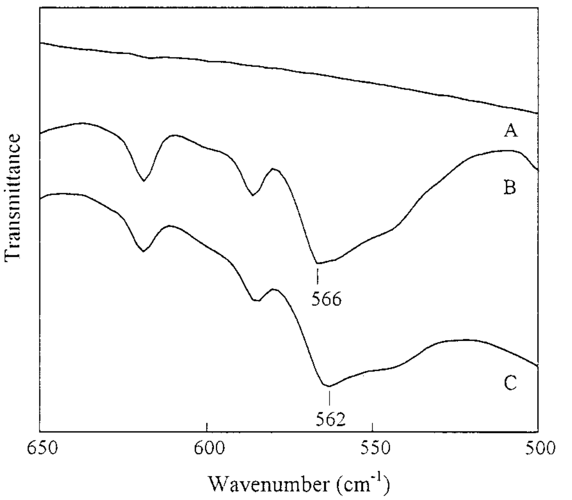

Figure 6. IR spectrum (650-500 cm^{-1}) of (A) octadecyl benzoate, (B) iPS/octadecyl benzoate gel at 60 °C, and (C) iPS/octadecyl benzoate solution at 220 °C.

Some recent measurements have focused on the consequences of rapidly taking a polymer from solution to the solid state.[21] It is presumed that during the rapid freezing, the chains' status that had existed in solution would be partially preserved. Rapid crystallization for isotactic polystyrene, poly(ethylene terephthalate), and poly(vinylidene fluoride) arose from freeze-drying or freeze-extracting dilute solutions.[22–25] Parts A and B of Figure 7 show the IR spectra recorded from a freeze-extracted iPS from a concentrated solution in octadecyl benzoate (20 wt %) and from a highly crystallized iPS, respectively. The helix-sensitive bands[15,16] at 1365, 1314, 1297, 1261, 1189, 1082, 1052, and 922 cm^{-1} could be found in both spectra. However, in the spectrum of freeze-extracted iPS the crystallinity sensitive[15,16] band at 983 cm^{-1} was not intensified, unlike the crystal; instead, there is an additional band at 562 cm^{-1}. We concluded that the iPS chains in the original octadecyl benzoate solution as well as in the freeze-extracted iPS contained a considerable amount of helical segments. The result obtained from the spectral subtraction is in accordance with that from the freeze-extracted method. 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 presented as nuclei. Then the polymer crystallized quickly, and the obtained crystallinity was very high.

The conformation of iPS in various solvents has been investigated by different authors. The general conclusion has been that iPS molecules would contain helical segments. However, Kobayashi et al.[27] 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 dilute.[1,3,27,28] We reported[22−25] previously 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 become highly interpenetrated and fewer helical segments exist. It seems that the results about iPS chains in octadecyl benzoate solution disagree with the 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. Very recently we shown that poly(ethylene terephthalate) could crystallize rapidly through thermorevisible gelation in a liquid ethylene glycol oligomer or in epoxy resin.[29,30] A series of solvents for iPS with different molecular size have been investigated. The experimental results is in accordance with our presumption. In solvents of smaller molecular size, such as ethyl benzoate and butyl benzoate, the recovered iPS samples were mostly in the amorphous state. It is considered that it would be easier for iPS chains to take helical conformation and to packing into crystals in a solvent with large molecular size. The answer is mostly speculative.

In iPS solution, the rate of helix formation can be given by[31]

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

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

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

Here, ΔH_u is the enthalpy change per unit in going from helix to coil, ΔT is the supercooling, which equals T_m − T, and T_m is the melting point of polymer in solution.

According to equation **2**, the rate of helix formation depends on temperature T and supercooling ΔT. With the supercooling being equal, the rate should pass through a maximum as the temperature is lowered, since k_i will decrease with a decrease in temperature. However, with the temperature being equal, the rate should increase with an increase in ΔT or T_m.

T_m is the melting temperature of polymer, which will decrease according to equation **3** as diluent is added.[31]

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{RV_u}{\Delta H_u V_1}(\phi - \chi_1 \phi^2) \tag{3}$$

Here ϕ is the volume fraction of diluent in the mixture, χ_1 is the polymer-diluent interaction parameter, and $\mathbf{V}_u$ and $\mathbf{V}_1$ are the molar volumes of the repeating unit and diluent, respectively. The two quantities ϕ and χ_1, which have an influence upon the melting temperature, have gained much attention in the previous study of polymer behavior in solution.[1,3,26] However, the size of diluent molecule, which exerts a greater influence on melting temperature, and hence the solution behavior, is usually ignored. Actually, a smaller depression of the melting temperature, and correspondingly a larger supercooling, would be observed for diluents of larger molar volume, as well as what would be observed for a poor solvent (larger values of χ_1). So in a larger size solvent, it would be easier for iPS chains to take the helical conformation, and that would result in the increase in crystallization rate and the level of crystallinity of the polymer.

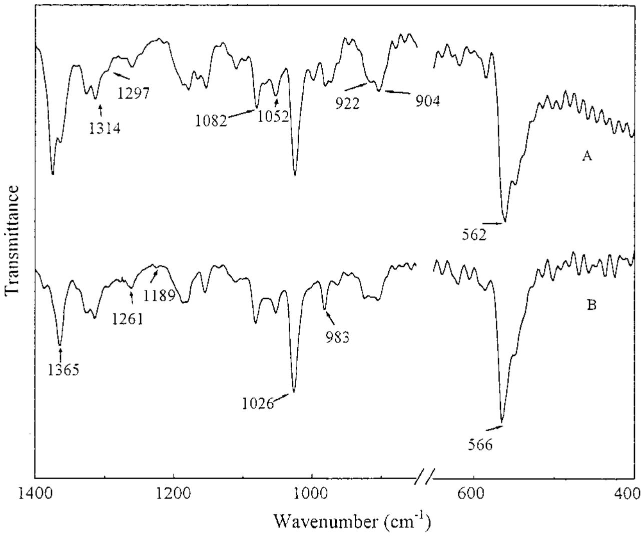

Figure 7. IR spectra recorded from (A) iPS freeze-extracted from octadecyl benzoate solution and (B) a highly crystallized iPS.

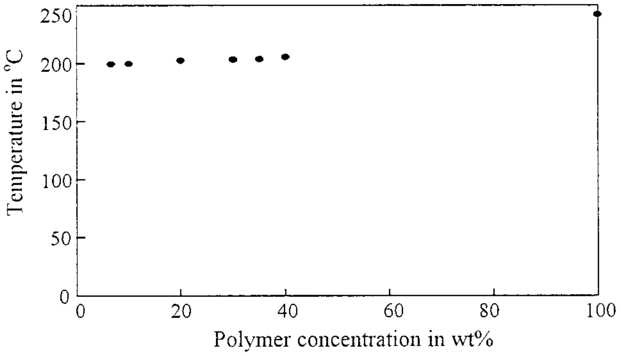

Figure 8. Plot of melting temperature−composition relation for iPS in octadecyl benzoate solution.

For the iPS/octadecyl benzoate system, with the initial addition of diluent, a small depression of the melting point is observed. However, the melting temperature remains invariant with further dilution (as shown in Figure 8). The observed invariance of the melting temperature in octadecyl benzoate may give an explanation for the invariance of the crystallinity on the polymer concentration.

Acknowledgment. We are grateful to Dr. A. Keller for an enlightening discussion. This work was supported by the National Natural Science Foundation of China and by the Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Science.

References and Notes

(1) Lemstra, P. J.; Challa, G. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1809.
(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) Lemstra, P. J.; Postma, J.; Challa, G. *Polymer* **1974**, *15*, 757.
(8) Rabiej, S.; Andrzej, W. *Angew. Makromol. Chem.* **1990**, *175*, 81.
(9) Jog, J. P. *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.* **1995**, *C35* (3), 531.
(10) Challa, G.; Hermans, P. H.; Weidinger, A. *Makromol. Chem.* **1962**, *56*, 169.
(11) Tyrer, N. J.; Bluhm, T. L.; Sundararajan, P. R. *Macromolecules* **1984**, *17*, 2296.
(12) Overbergh, N.; Bergmans, H.; Smets, G. *Polymer* **1975**, *16*, 703.
(13) Klein, M.; Mathis, A.; Menelle, A.; Guenet, J.-M. *Macromolecules* **1990**, *23*, 4591.
(14) Jonsson, H.; Werner, P. E.; Gedde, U. W.; Hult, A. *Macromolecules* **1989**, *22*, 1683.
(15) Kobayashi, M.; Nakaoki, T. *Macromolecules* **1990**, *23*, 78 .
(16) Painter, P. C.; Koenig, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1885.
(17) Prasad, A.; Marand, H.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1993**, *32*, 1819.
(18) Wunderlich, B. *Macromolecular Physics: Crystal Melting*; New York, 1980; Vol. 3.
(19) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento Suppl.* **1960**, 15, 69.
(20) Coleman, M. N.; Painter, P. C. *J. Macromol. Sci.—Rev. Macromol. Chem.* **1978**, *16*, 197.
(21) Morawetz, H. *Science* **1988**, *240*, 172.
(22) Xue, G.; Wang, Y.; Liu, S.; Liao, Y.-T. *Macromolecules* **1995**, *28*, 4344.
(23) Ji. G.; Ni, H.; Wang, C.; Xue, G. *Macromolecules* **1996**, *29*, 2691.
(24) Xue, G.; Wang, Y.; Liu, S.*Macromolecules*, **1995**, *28*, 3476.
(25) Xue, G.; Wang, Y.; Lu, Y. *Macromolecules*, **1994**, *27*, 4016.
(26) Xie, X.-M.; Tanioka, A.; Miyasaka, K. *Polymer* **1993**, *34*, 1388.
(27) Nakaoki, T.; Kobayashi, M. *J. Mol. Struct.* **1991**, *242*, 315.
(28) Itagaki, H.; Takahashi, I. *Macromolecules* **1995**, *28*, 5477.
(29) Xue, G.; Ji, G.; Li, Y. *J. Polym. Sci. B: Polym. Phys.* **1998**, *36*, 1219.
(30) Xue, G.; Ji, G.; Yan, H.; Guo, M. *Macromolecules*, **1998**, *31*, 7706.
(31) Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill Book Company: New York, 1964.

MA980144M