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Metastable Isotactic Polystyrene Prepared by Freeze-Extracting Concentrated Solutions in Solvents of Middle Molecular Size

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ABSTRACT: The morphology and crystallization behavior of freeze-extracted isotactic polystyrene (*i*PS) derived from concentrated solutions in solvents of middle molecular size were characterized by the wide-angle X-ray diffraction, infrared spectroscopy, and differential scanning calorimetry. It was found that the freeze-extracted *i*PS sample is poorly crystallized, but the chains are in an ordered 3_1 helix conformation, which can be easily transferred to a highly crystalline state upon heating. It can easily crystallize even cooled from the melt. The ordered 3_1 helix structure could be maintained even after melting at 520 K, which is 30 K higher than the melting point, but diminished at 530 K. The metastable property of the freeze-extracted sample from concentrated solutions in solvent of middle size can be attributed to fewer interchain entanglements, like the behavior of collective particles from very dilute solution in benzene.

Introduction

Some recent measurements have focused on the consequences of rapidly taking polymers from the dilute solution regime to a concentrated state.[1−4] This was interpreted as an indication that during rapid freezing the extent of chain interpenetration which had existed in the solution would be preserved. Recently, freeze-dried isotactic polystyrene (*i*PS) powders from very dilute solutions in benzene were characterized by wide-angle X-ray diffraction (WAXD), infrared spectroscopy (IR), and differential scanning calorimetry (DSC).[4,5] It was found that the thermal behavior of a freeze-dried *i*PS sample depends strongly on the concentration of the original solution.[4] There is a concentration boundary (about 0.04 wt %) for the original solution: below the boundary, because of much fewer interchain entanglements within and between particles, the freeze-dried *i*PS samples could crystallize quickly upon heating; above the concentration boundary, the freeze-dried *i*PS is in a completely disordered amorphous conformation.[4,5]

In this article, we report that *i*PS particles prepared by freeze-extracting concentrated solutions (15 wt %) of *i*PS in solvents of middle molecular sizes are in a highly ordered 3_1 helix state and can crystallize much faster than bulk polymer. The freeze-drying of *i*PS solution in 1-chlorotetradecane or in octadecyl benzoate differs in a number of respects from earlier reports from solutions in benzene. First, 1-chlorotetradecane and octadecyl benzoate are fairly large molecules with molar volumes of 278 and 360 cm^3/mol, respectively. These molecules are about 3 times as big as a repeating segment in *i*PS but are smaller than the average size of a polymer and are named as “middle-size solvents”. Second, the concentrations of the solutions used for freeze-drying study were in the concentrated regime (10−20 wt %), which is much more concentrated than that in a previous report (0.01−0.1 wt %) in small solvents.

Experimental Section

The *i*PS was kindly supplied by Professor Lin Shang-An’s research group at the Institute of Polymer Science, Zhong Shan University, China. ^{13}C NMR spectra showed that the *i*PS sample contained more than 99% isotactic triads. The number-average molecular weight of this highly stereoregular *i*PS was about 18.0×10^4. Two solvents of large molar size, 1-chlorotetradecane and octadecyl benzoate, were obtained from Aldrich. A desired amount of *i*PS and 1-chlorotetradecane or 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 10 min to ensure that all of the *i*PS had fully dissolved in the 1-chlorotetradecane and to make a homogeneous solution with concentrations of 15 wt %. The hot solution was then added directly into large amount of liquid nitrogen so that it was frozen in a fraction of a second. The frozen solution was then repeatedly extracted with cold ethanol followed by drying in a vacuum until the constant weight. The collective powders from concentrated solutions in solvents of large molecular size were designated as sample freeze-extracted *i*PS. They were examined by wide-angle X-ray diffraction (Rigaku D/Max-Ra diffractometer), DSC (Perkin-Elmer model DSC-2C system with a data station), and IR (IFS 66V vacuum-type FT-IR spectrophotometer).

Results and Discussion

In parts A and B of Figure 1 are shown the WAXD patterns recorded at room temperature from the freshly freeze-extracted *i*PS (curve A) and the polymer after it had been heated to 460 K at 5 K min^{-1} (curve B), respectively. For comparison, WAXD patterns recorded from a bulk *i*PS and a sample prepared from 1,2-dichloroethane after heating under the same conditions are shown in parts C and D of Figure 1, respectively. Figure 1A exhibits a broad and intense band, with the center at $2\theta = 18.4°$. It is obvious that the sample *i*PS freeze-extracted from concentrated solution in 1-chlorotetradecane is mainly in the amorphous phase. Figure 1B shows several finely resolved crystalline peaks in the range of $2\theta = 5°−30°$, which could be indexed according to ref 8b. Crystallinities are obtained by dividing the crystalline intensity by the total diffracted intensity. A BASIC computer program was edited to resolve the

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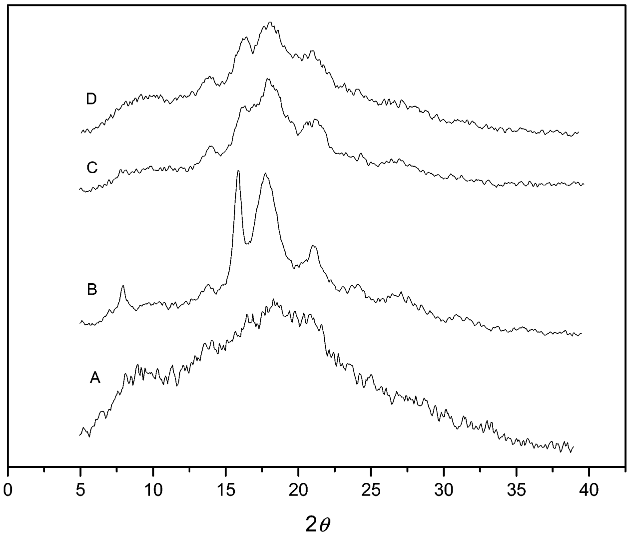

Figure 1. Wide-angle X-ray diffraction curves recorded from (A) *i*PS prepared by freeze-extracting the solution in 1-chlorotetradecane, (B) the sample in (A) that had been heated to 460 K at 5 K min^{-1}, (C) a bulk *i*PS that had been heated to 460 K at 5 K min^{-1}, and (D) the heated *i*PS recovered from the solution in 1,2-dichloroethane.

band and to calculate the crystallinity content. After the computer calculation, the extents of the crystallinity of *i*PS freeze-extracted from 1-chlorotetradecane before and after heating treatment were 0.08 and 0.6, respectively, measured by wide-angle X-ray scattering. Figure 1C,D indicates that the crystallinities of bulk *i*PS and the sample recovered from 1,2-chloroethane were very low.

Isotactic polystyrene was considered as a semicrystalline polymer characterized by slow crystallization rates and low crystallinity.[6-9] Sundararajan et al.[6] considered that a crystallinity of ~0.3 was typical for annealed *i*PS films, and Overbergh et al.[7] arrived at a maximum crystallinity of 0.33 for *i*PS samples annealed for several hours following solvent-induced crystallization. It is clear that *i*PS recovered by freeze-extracting concentrated solution in 1-chlorotetradecane was in the amorphous state, but it became a phase of 0.6 crystallinity after heating. The freeze-extracted *i*PS from a solvent of large molecular size could crystallize much faster than bulk polymers prepared by normal physical techniques, such as solution crystallization in small molecule solvents, annealing, and their combination.

Since the *i*PS chain in the crystalline phase is a 3_1 helix,[10] the helical conformation of the *i*PS molecule is an important factor during crystallization. The IR vibrational characteristics were used in this study to show the conformational changes of the sample. Figure 2 illustrates the IR spectra recorded for a solid *i*PS freeze-extracted from 1-chlorotetradecane before and after it had been heated to 460 K at 5 K min^{-1}. Both spectra 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 spectra. The 981 cm^{-1} band was strong for the heated sample, but very weak for the freshly freeze-extracted *i*PS. This indicated the formation of the 3_1 helix conformation in the freeze-extracted *i*PS and its packing into the crystalline phase after heating. We propose that the *i*PS chains freeze-extracted from concentrated solutions in 1-chlorotetradecane are in a highly metastable conformation. In our previous study,

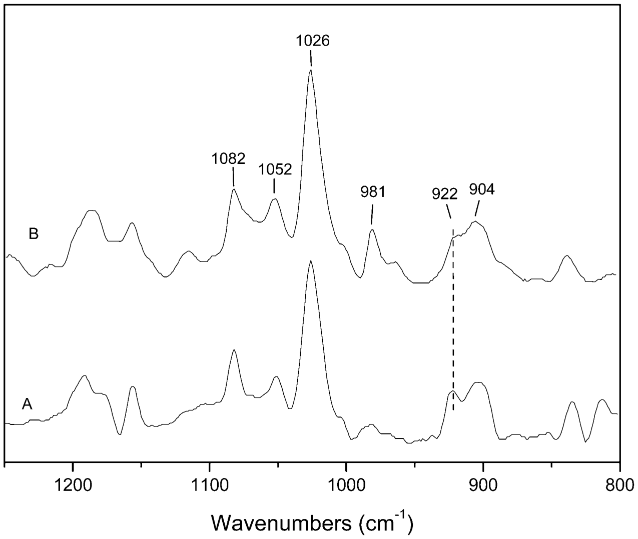

Figure 2. (A) FT-IR spectrum for a nascent *i*PS prepared by freeze-extracting 1-chlorotetradecane solution. (B) FT-IR spectrum of the sample in (A) after heating to 460 K at 5 K/min.

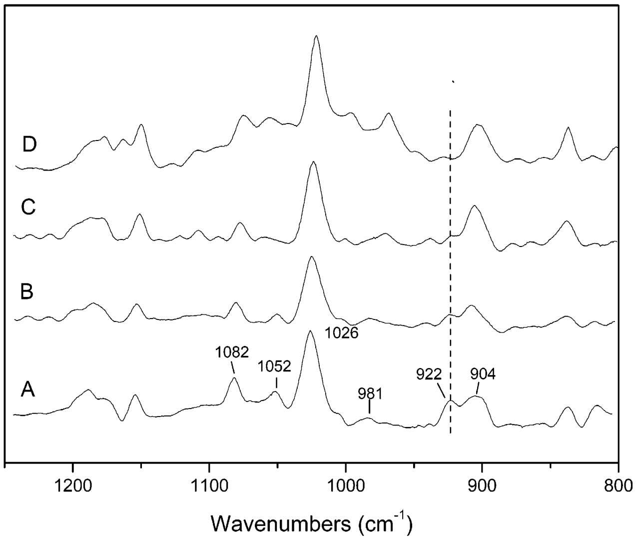

Figure 3. IR spectra recorded from *i*PS prepared by freeze-drying benzene solutions of various concentration: (A) 0.03 wt %; (B) 0.08 wt %; (C) 0.5 wt %; (D) 6 wt %.

iPS freeze-dried from very dilute solutions in benzene could easily crystallize upon heating.[4] Curves A−D in Figure 3 illustrate IR absorption spectra recorded from freeze-dried *i*PS from 0.03, 0.08, 0.5, and 6 wt % solutions in benzene, respectively. The spectrum of (curve A) *i*PS freeze-dried from 0.03 wt % solution shows 1082−1052 cm^{-1} doublets and the 922 cm^{-1} band, indicating the formation of the 3_1 helix conformation in the benzene solution at extremely dilute concentration. However, in curves C and D of Figure 3, both the crystalline band at 981 cm^{-1} and the 3_1 helix band at 922 cm^{-1} are missing, indicating that there are neither crystals nor helices in the benzene solution of *i*PS at a semidilute concentration. Of particular interest is that both IR spectra for *i*PS recovered from concentrated (15 wt %) solution in middle-sized solvent (1-chlorotetradecane) and that recovered from very dilute solution (0.03 wt %) in benzene show typical helices bands, as shown in Figure 2A and Figure 3A.

Figure 4 shows the DSC thermograms of freeze-extracted *i*PS samples from 15 wt % solution in octa-

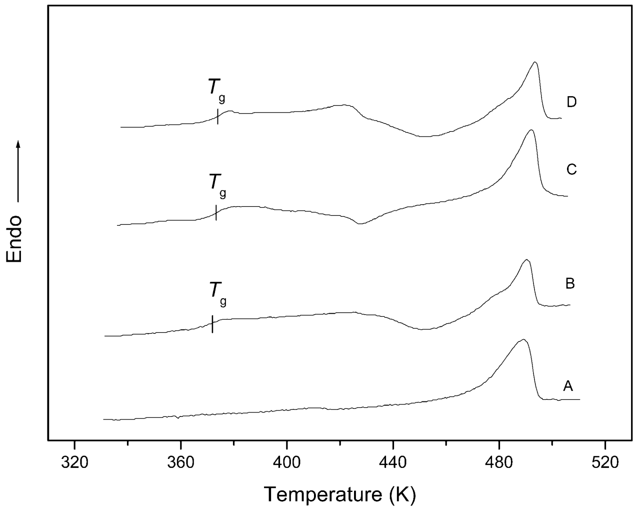

Figure 4. DSC curves with a heating rate of 5 K min^{-1}: (A) the first scan for the freeze-extracted *i*PS; (B) the third scan of the sample in (A); (C) the first scan of a bulk *i*PS; (D) the third scan of the bulk sample.

decyl benzoate and for a bulk *i*PS. They were first scanned from 310 to 510 K (curves A and C), followed by rapid quenching to 310 K in a DSC cell. A second scan from 310 to 510 K was then carried out followed by quenching to 310 K. Then the third scan from 310 to 510 K was taken (curves B and D). All of the heating rates were 5 K min^{-1}. The DSC curves for *i*PS freeze-dried from concentrated solution in 1-chlorotetradecane, which were similar to Figure 4A,B, are omitted. The DSC heating curve for ordinary semicrystalline *i*PS usually shows a glass transition in the region of 363–373 K, as shown in Figure 4C,D. It is generally considered that the change of heat capacity at the glass transition temperature (T_g) reveals the content of the amorphous part of the sample. For the sample *i*PS from octadecyl benzoate solution, its first-run scans show no measurable or very little glass transition (Figure 4A). Their change in heat capacity (ΔC_p) in the region of T_g for normal PS is near zero. It can be estimated from ΔC_p that the amorphous fraction in this sample is little. This conclusion is inconsistent with the WAXD pattern, which indicated that *i*PS prepared by freeze-extracting a concentrated solution in solvent of middle molar size is mainly in the amorphous state as shown in Figure 1A. Generally, what we get from the X-ray diffraction pattern is the situation about the three-dimensional order of samples. Most of that three-dimensional disordered part of the *i*PS sample freeze-dried from 1-chlorotetradecane or from octadecyl benzoate reflected by the X-ray diffraction does not show the change of heat capacity around T_g. IR spectra in Figure 2 confirmed that the three-dimensional disordered fraction of the freshly prepared freeze-extracted *i*PS has highly ordered 3_1 helix chains although they are not in the crystalline state.

It is presumed that it is these highly ordered chains that show no glass transition. For a normal amorphous sample, only the smaller units such as pendant groups and branched groups can move, but the conformation cannot be changed below T_g. Upon heating to T_g, the movement of chain segments is activated, and conformational transitions can be realized. The change of heat capacity at the glass transition temperature reflects the difference in mobility of the chains. If the *i*PS chains are highly ordered with a 3_1 helix conformation, the local motion is then restricted by the helix structure and the chains cannot move just above T_g. A contradiction resulted from the wrong attribution of this special amorphous phase. Since it has no glass transition, it was considered as the crystalline part in the DSC thermograms, and since it does not show crystal diffraction, it was considered as the amorphous part in the WAXD pattern. It is actually an intermediate state between the crystalline and the usual amorphous phase. This intermediate state is highly ordered in the chain, but it is three-dimensional disordered. This third phase was called the rigid amorphous fraction or the metastable state in several polymers such as polypropylene[11] and poly(oxymethylene)[12] and in polymers with less flexible structures such as poly(phenylene sulfide).[13] Recently, Cheng and Keller pointed out the role of metastable states in polymer phase transitions.[14] To our knowledge, no papers have ever dealt with the rigid amorphous fraction of *i*PS. The WAXD pattern in Figure 1B, which was described as a highly crystalline *i*PS, was recorded from the freeze-extracted iPS after it had been heated to 460 K (before the onset of melting). Its crystallinity calculated from its WAXD pattern is 0.6. During heating from 310 to 460 K at a rate of 5 K min^{-1}, the crystallinity (obtained from the WAXD pattern) of the sample increases drastically (from 0.08 to 0.6). But the crystalline exothermic value in this DSC curve as shown in Figure 4A is very small (−0.6 cal g^{-1}) compared with the melting endothermic peak (6.0 cal g^{-1}), indicating that little heat is required to induce crystallization of the metastable *i*PS. This confirms that the state of the chains in this special amorphous phase is close to the crystalline state. This result is in accordance with the conclusion that most of the chains are in the highly ordered helix state with lower energy.[14] The third scan shown in Figure 4B is the same as the DSC curve of a normal amorphous *i*PS: the glass transition is prominent, and the heat capacity of the crystalline exothermic peak becomes large. The complete difference between the first scan (Figure 4A) and the third scan (Figure 4B) illustrates the difference between the amorphous phase in the original freeze-extracted *i*PS and ordinary amorphous *i*PS (frozen from the melt). Moreover, the original freeze-extracted *i*PS turned back into the ordinary state after being repeatedly heated and quenched.

Figures 5 and 6 show the in situ wide-angle X-ray scattering patterns for *i*PS samples recovered from 1-chlorotetradecane and from 1,2-dichloroethane, respectively. Both X-ray diffractometer tracers in Figures 5 and 6 show crystalline peaks in the heating runs and show amorphous curves in the melt. However, the patterns in the cooling runs from the melt show big differences for the two samples. WAXD patterns for *i*PS recovered from 1-chlorotetradecane show obvious crystalline peaks during cooling from the melt, while those for the polymer recovered from 1,2-dichloroetane show mainly amorphous curves. The crystallization behavior from the melt was also followed by DSC measurements. The *i*PS samples were first heated to 520 K, which is 30 K higher than the melting temperature for 3 min, and then cooled at 5 and 10 K, resulting in different DSC traces as shown in Figures 7 and 8, respectively. From the WAXD patterns in Figures 5 and 6 and the DSC traces in Figures 7 and 8, one clearly see that *i*PS recovered from 1-chlorotetradecane shows much higher crystallizing ability that that prepared from 1,2-dichlo-

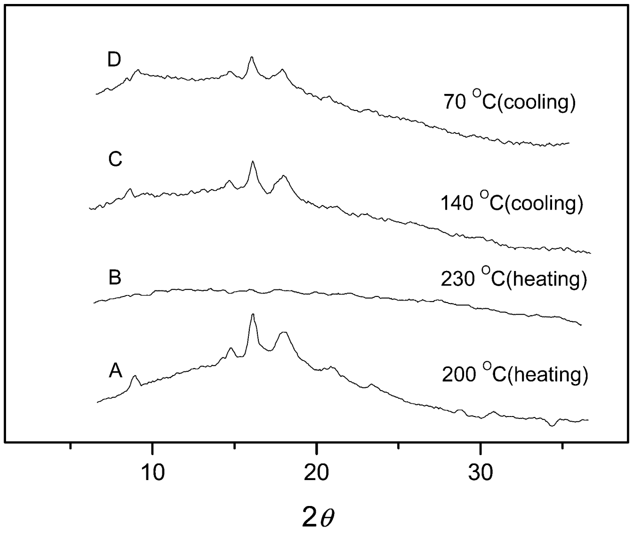

Figure 5. X-ray diffractometer tracers recorded at indicated temperatures from *i*PS sample which was recovered from 1-chlorotetradecane solution.

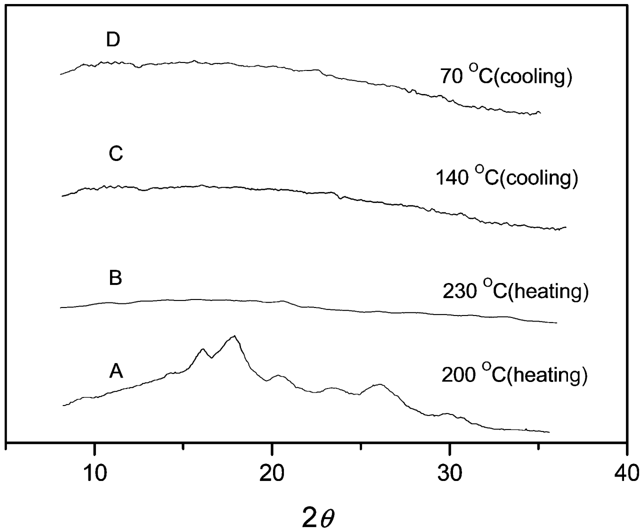

Figure 6. X-ray diffractometer tracers recorded at indicated temperatures from *i*PS sample which was recovered from the *i*PS/1,2-dichloroethane system.

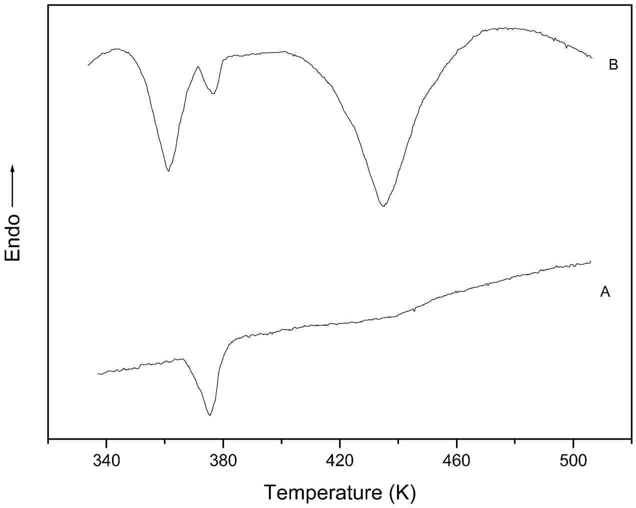

Figure 7. DSC thermograms of nonisothermal melt crystallization of *i*PS with a cooling rate 10 K/min from 520 K: (A) *i*PS recovered from 1,2-dichloroethane; (B) *i*PS recovered from 1-chlorotetradecane.

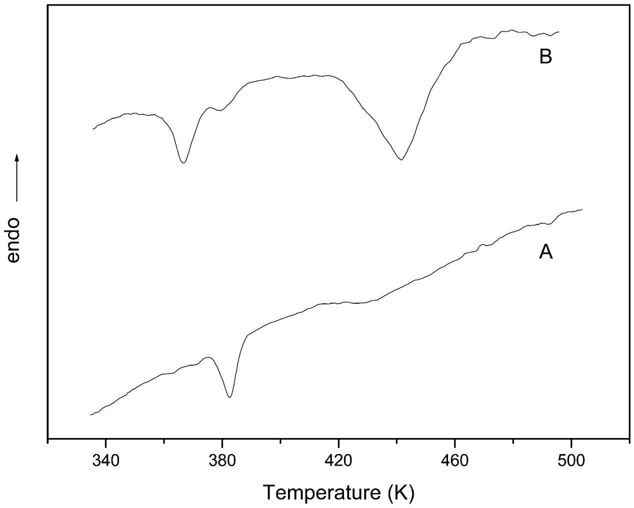

Figure 8. DSC thermograms of nonisothermal melt crystallization of *i*PS with a cooling rate 5 K/min from 520 K: (A) *i*PS recovered from 1,2-dichloroethane; (B) iPS recovered from 1-chlorotetradecane.

roethane. We propose that the freeze-extracted samples consist of certain amount of helices even at temperatures 30 K higher than the melting point. However, the helices gradually diminished upon further heating. Figure 9 shows the DSC cooling curves for the freeze-extracted samples from 520, 525, and 530 K. One can find that the exothermal heat became weak for the nonisothermal melt crystallization from 530 K, indicating diminishing of ordered 3_1 helices at higher temperature.

Figure 10 illustrates the cooling rate on the heating–crystallization of *i*PS recovered from 1-chlorotetradecane. One can see that the quenched sample shows a higher melting temperature, a similar temperature shift as observed in poly(vinylidene flouride).[16]

IPS is a semicrystalline polymer characterized by slow crystallization rates and low crystallinity (about 30%).[6−9,15] Several papers dealt with the crystalline growth rate of *i*PS as a function of chain entanglements.[4,5] Single- and pauci-chain collective particles were prepared by a freeze-drying method from dilute solutions of *i*PS in benzene. Thermal analysis revealed that the collective particles crystallize much faster than bulk polymer, which can be attributed to much fewer interchain entanglements within and between particles.[4,5] The Flory–Krigbaum theory of the thermodynamic properties of dilute solutions of flexible-chain polymers predicts that the interpenetration of the molecular coils is strongly resisted in good solvent media. As the solution concentration is increased, a point is eventually reached where the total space can no longer accommodate the swollen molecular coils without some chain entanglement. Beyond this “critical concentration”, conventionally denoted by C^*, the dependence of thermodynamic and hydrodynamic properties of the system on polymer chain length and concentration changes because of the interpenetration of the molecular coils. Xue et al.[4] have found that the coils of the freeze-dried *i*PS from very dilute solution (less than 0.04 wt %) were in the expanded state with fewer entanglements which could crystallize upon annealing at a much higher rate. Recently, Strobl et al.[17] studied the mechanisms of recrystallization after melting in isotactic polystyrene using small-angle X-ray scattering.

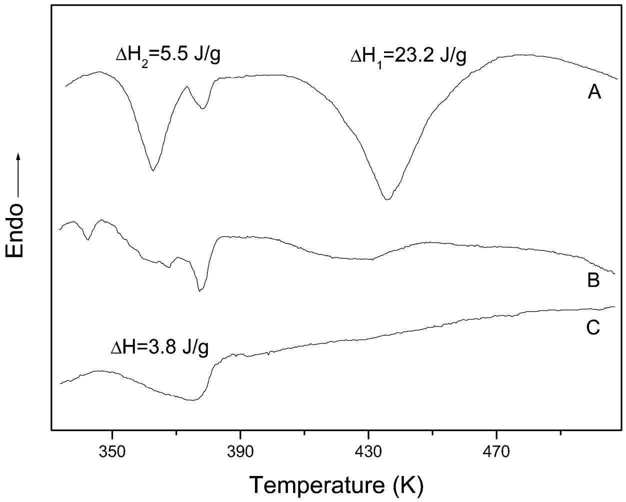

Figure 9. DSC thermograms of nonisothermal melt crystallization from different temperatures for freeze-extracted *i*PS: (A) 520 K, (B) 525 K, and (C) 530 K, with a cooling rate 10 K/min.

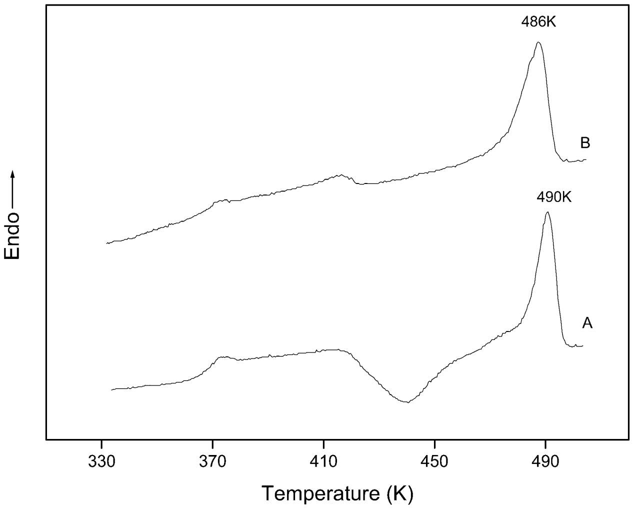

Figure 10. Effect of both cooling rate and heating rate on the cycled samples: (A) a quenched *i*PS sample heated at 5 K/min; (B) a slow cooled sample (5 K/min), subsequently heated at 5 K/min.

He found that growth from the locally disentangled melt followed a one-step process while the growth from the entangled melt followed a multistage route. And he also found a one-step process was much faster than a multistage route. In our study, we demonstrated that *i*PS prepared by freeze-extracting from concentrated solutions (10−20 wt %) in solvents of middle molecular size could crystallize much faster than the bulk *i*PS. This suggests that freeze-extracting concentrated solution in solvents of middle molecular size produced *i*PS powders with the same level of chain disentanglement as that derived from a very dilute solution in small size solvent benzene. The finding for faster recrystallization of the partially disentangled *i*PS prepared from middle-sized solvent than the bulk sample is in good agreement with Strobl's conclusion.[17] Additionally, we reported recently that PET and PVC could be also easily crystallized in some middle-sized solvent such as PEG oligomer or DOP.[18] The complexity of the solvent effect, including its molar volume and solvophobical effect, on the conformation of nonbiological polymers in solution is currently under further investigation in this lab.

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References and Notes

(1) Morawetz, H. *Science* **1988**, *240*, 172.
(2) Liu, C. Y.; Morawetz, H. *Macromolecules* **1988**, *21*, 515.
(3) Chang, L. P.; Morawetz, H. *Macromolecules* **1987**, *20*, 428.
(4) (a) Xue, G.; Wang, Y.; Liu, S.; Liao, Y. T. *Macromolecules* **1995**, *28*, 4344. (b) Ji. G.; Ni, H.; Wang, C.; Xue, G. *Macromolecules* **1996**, *29*, 2691. (c) Xue, G.; Wang, Y.; Liu, S. *Macromolecules* **1995**, *28*, 3476. (d) Xue, G.; Wang, Y.; Lu, Y. *Macromolecules* **1994**, *27*, 4016.
(5) Bu, H.; Gu, F.; Bao, L.; Chen, M. *Macromolecules* **1998**, *31*, 7108.
(6) Tyrer, N. J.; Bluhm, T. L.; Sundararajan, P. R. *Macromolecules* **1984**, *17*, 2296.
(7) Overbergh, N.; Bergmans, H.; Smets, G. *Polymer* **1975**, *16*, 703.
(8) (a) Keith, H. D.; Vadimsky, R. G.; Padden, F. J. *J. Polym. Sci., Part A-2* **1970**, *8*, 1687. (b) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento Suppl.* **1960**, *15*, 69. (c) Sundarajan, P. R.; Tyrer, N. J. *Macromolecules* **1982**, *15*, 1004. (d) Nancy, J. T.; Terry, L. B.; Sundarajan, P. R. *Macromolecules* **1984**, *17*, 2296.
(9) (a) Atkins, E. D. T.; Isaac, D. H.; Killer, A.; Miyasaka, K. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 211. (b) Sundarajan, P. R.; Tyrer, N. J.; Bluhm, T. L. *Macromolecules* **1982**, *15*, 286.
(10) (a) Kobayashi, M.; Nakaoki, T. *Macromeolecules* **1990**, *23*, 78. (b) Lemstra, P. J.; Postma, J.; Challa, G. *Polymer* **1974**, *15*, 757.
(11) Grebowicz, J.; Law, S. F.; Wunderlich, B. *J. Polym. Sci., Polym Symp* **1984**, *71*, 19.
(12) Suzuki, H.; Grebowicz, J.; Wunderlich, B. *Makromol. Chem.* **1985**, *186*, 1109.
(13) Cheng, S. Z. D.; Wu, Z.; Wunderlich, B. *Macromolecules* **1987**, *20*, 2802.
(14) Cheng, S. Z. D.; Keller, A. *Annu. Rev. Mater. Sci.* **1998,** *28*, 533.
(15) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1995.
(16) Weinhold, S. Some aspects of crystal nucleation, growth and reorganization in poly(vinylidene fluoride) (polyvinylidene). PhD Thesis, Case Western Reserve University, 1982.
(17) (a) Al-Hussein, M.; Strobl, G. *Eur. Phys. J. E* **2001**, *6*, 305. (b) Grasruck, M.; Strobl, G. *Macromolecules* **2003**, *36*, 86.
(18) (a) Chen, J.; Xue, G.; Li, Y. *Macromolecules* **2001** *34*, 1297. (b) Sun, Q.; Zhou, D.; Wang, X.; Xue, G. *Macromolecules* **2002**, *35*, 7089.

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