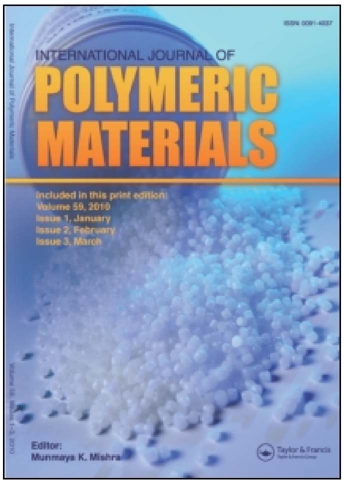

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Crystallization behavior of syndiotactic polypropylene: Effect of solvent of varying molecular size

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CRYSTALLIZATION BEHAVIOR OF SYNDIOTACTIC POLYPROPYLENE: EFFECT OF SOLVENT OF VARYING MOLECULAR SIZE

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Syndiotactic polypropylenes (s-PPs) were freeze-extracted from alkyl solvents of varying molar volume. Higher degree of crystallinity was found for s-PP recovered from hexadecane than that from octane by wide-angle X-ray diffraction. DSC analysis indicated that s-PP freeze-extracted from alkyl solvents of larger molar volume crystallized at a faster rate. FT-Raman spectra were used to characterize s-PP gels in octane and in hexadecane. It is found that interaction existed between the segments of s-PP chains and octane, while no interaction was found between s-PP and hexadecane, which may account for the faster crystallization rate and high degree of crystallinity.

Keywords: syndiotactic polypropylene, solvent of large molar size, crystallization behavior

INTRODUCTION

As is well known, there are a number of factors affecting the crystallization of polymers, including stereoregularity, molecular weight,

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molecular weight distribution, etc. Besides, high crystallinity polymer can be prepared by some physical techniques [1–2], such as solution crystallization in small molecule solvent, hot-drawing film or fibers, annealing samples at elevated temperatures, etc. All of these physical techniques increase the activity of polymer molecules by means of dilution, force, heat, etc., which improve crystallization of polymers. Solution crystallization is widely used both in science and in technology. The solvents used in polymer solution are usually organic compounds with small molar volume, such as ethanol, acetone, benzene, etc. Recently, however, works in our laboratory [3] have demonstrated that isotactic polystyrene (i-PS) can crystallize quickly in solvents of larger molar volume than in usual organic solvents.

The effect of solvent quality on the static-equilibrium conformational behavior is well established [4–5]. Some experimental work has been done on the effect of solvent quality on the mechanical, optical, and rheological response of polymer solution [6–10]. However, very little work has been done on the investigation of the effect of solvent size on the crystallization behavior of polymer. In this paper, we freeze-extracted s-PP from a series of alkyl solvents with varying numbers of carbon atoms. The purpose of our study is to investigate the effect of solvent size on the crystallization behavior of polymer and to propose an explanation for the experimental results in terms of chain entanglement.

EXPERIMENTAL SECTION

The metallocene-catalyzed syndiotactic polypropylene (s-PP) used in this study was kindly supplied by Prof. Chen Wei of Research Institute of Petroleum Processing SINOPEC, which contained more than 90% syndiotactic dyads and has a molecular weight of about 260,000. Octane, decane, dodecane and hexadecane were commercially available. The molar volume of the solvent is listed in Table 1.

The s-PP was fully dissolved under nitrogen atmosphere in octane, decane, dodecane and hexadecane, respectively, at concentration of 10%, containing 0.5% antioxidant with respect to the sample weight. Freeze-extracting method was used to get the prepared s-PPs. After it

TABLE I Molar Volume of Solvents

Solvent	Octane	Decane	Dodecane	Hexadecane
Molecular formula	C_8H_{18}	$C_{10}H_{22}$	$C_{12}H_{26}$	$C_{16}H_{34}$
Molar volume (V_m, cm^3/mol)	163	195	227	293

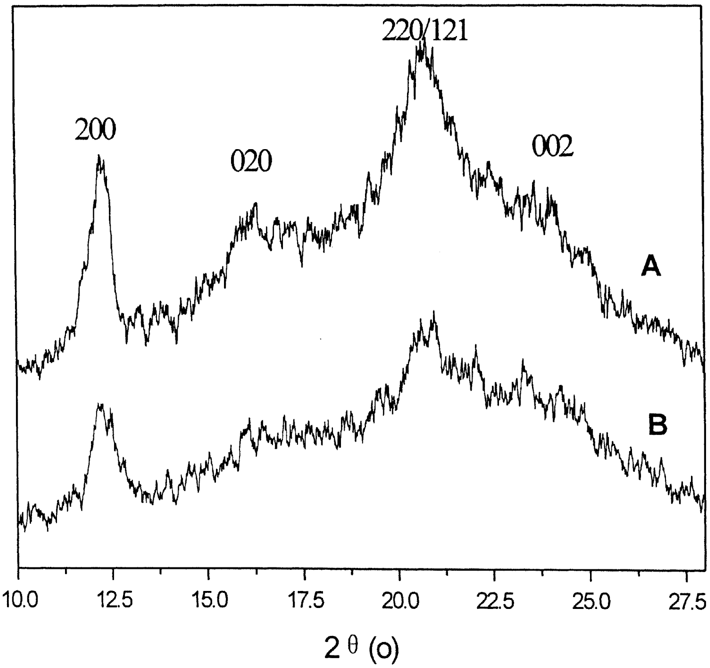


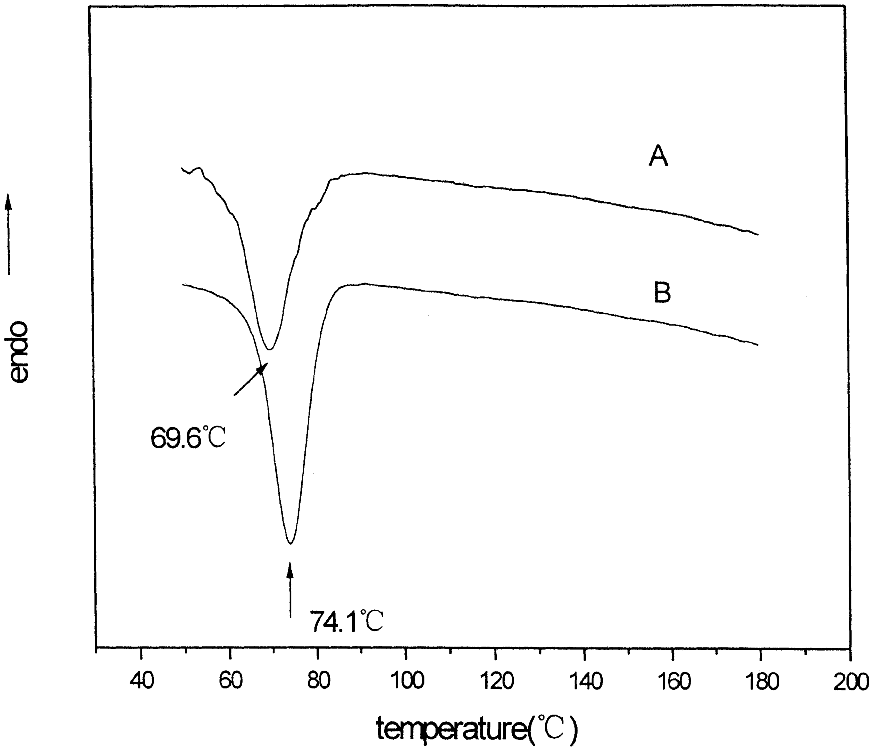
FIGURE 1 Wide-angle X-ray spectra of s-PPC8 and s-PPC16. A: s-PPC16; B: s-PPC8.

dissolved completely, the solution was injected 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 acetone followed by drying in a vacuum. FTIR spectra were used to ensure no disintegration happened and no solvent remained in the dried powder. The collected particles were then named s-PPC8, s-PPC10, s-PPC12 and s-PPC16, respectively.

On the other hand, the s-PP gels were obtained by cooling the s-PP solution to room temperature in the oil bath at a rate of about 10°C/min.

A Perkin-Elmer series 7 Differential Scanning Calorimeter (DSC-7) was used to follow the isothermal crystallization behavior of samples in this study. Temperature calibration was performed using indium as a standard. All of the samples were heated to 180°C and were held there for 3 min before quenching at a cooling rate of 200°C/min to a desired isothermal crystallization temperature, T_c.

The WAXD technique was employed to determine the crystal modification and the apparent degree of crystallinity in the samples



FIGUE 2 DSC cooling traces of s-PP recovered from alkyl solvent of varying molar size, (A): s-PPC8; (B): s-PPC16, at a cooling rate of 20°C/min.

prepared. The WAXD intensity patterns were collected on a Rigaku D/Max-Ra diffractometer (CuK radiation, $\lambda = 0.154$ nm) equipped with a computerized data collection and analytical system. The operating condition of the X-ray source was set at a voltage of 35 kV and a current of 15 mA.

FT-Raman spectra were recorded with 1.064 nm excitation using a Bruker RFS-100 FT-Raman spectrometer.

RESULTS AND DISCUSSION

The wide-angle X-ray powder diffraction patterns of the recovered s-PP samples are shown in Figure 1. The characteristic X-ray peaks are observed at $2\theta = 12.2°$, 15.8°, 20.8° and 24.5°, corresponding to reflection planes at (200), (020), (220/121) and (002). This indicates that s-PP freeze-extracted from octane and hexadecane both crystal-

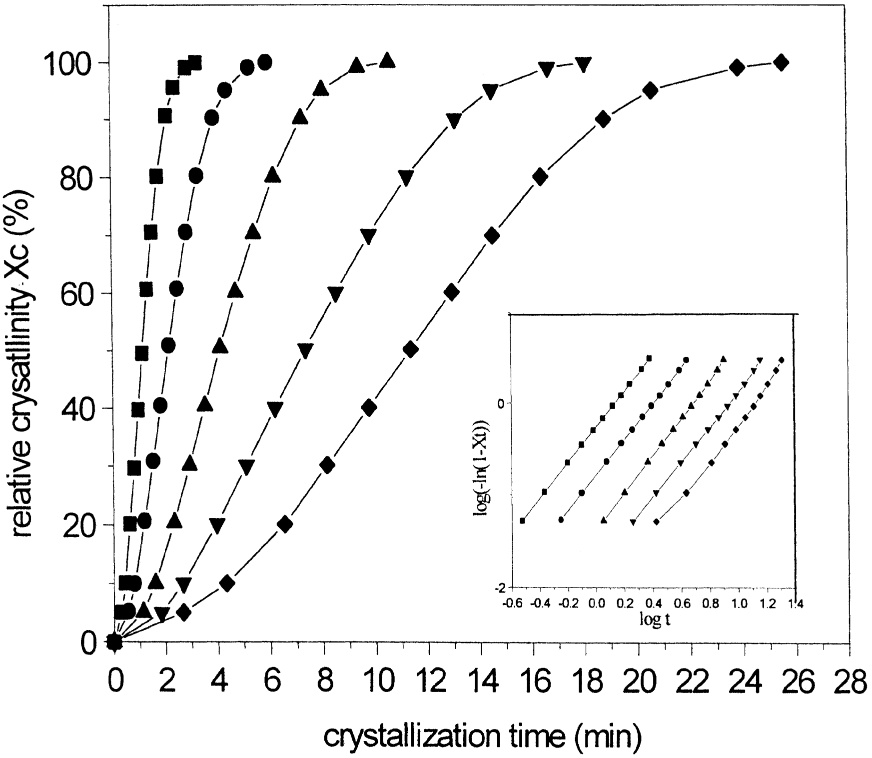


FIGURE 3 Relative crystallinity as a function of time, inset: Typical Avrami plots, for sample sPPC16. Isothermal crystallization temperature: (■) 90°C; (•) 95°C; (▲) 100°C; (▼) 105°C; (◆) 110°C.

lize in the stable helical conformation [11–13]. However, it is clear that the crystallinity of s-PPC16 is much higher than that of s-PPC8.

Figure 2 shows the DSC traces of s-PPC8 and s-PPC16 at a cooling rate of 20°C/min from the melt. The samples were molten at 200°C for 5 min before the measurements. It is interesting that a narrow crystallization peak at a higher temperature of about 74°C was found for s-PPC16 compared with a broad, lower peak of about 70°C for s-PPC8. This indicates that s-PP freeze-extracted from hexadecane solution crystallized faster than that from octane solution, even after heating at 200°C for 5 min.

Isothermal crystallization is an effective method to investigate the crystallization rate of polymer. We analyzed isothermal crystallization behavior of s-PPC8, s-PPC10, s-PPC12 and s-PPC16 by means of the Avrami equation [14]. Figure 3 and Figure 4 depict for samples s-PPC8

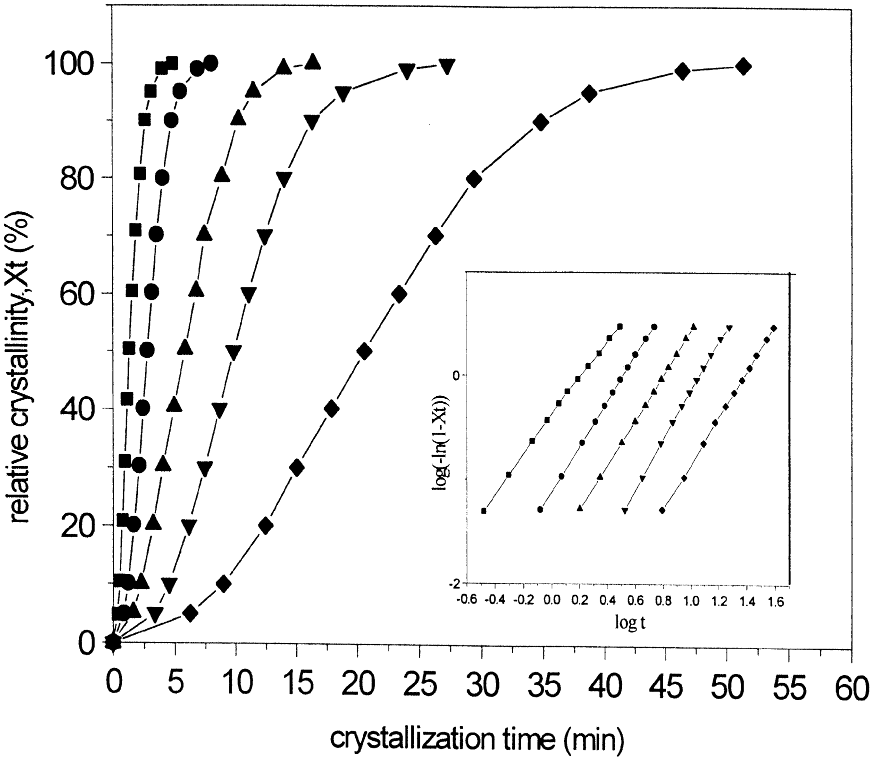
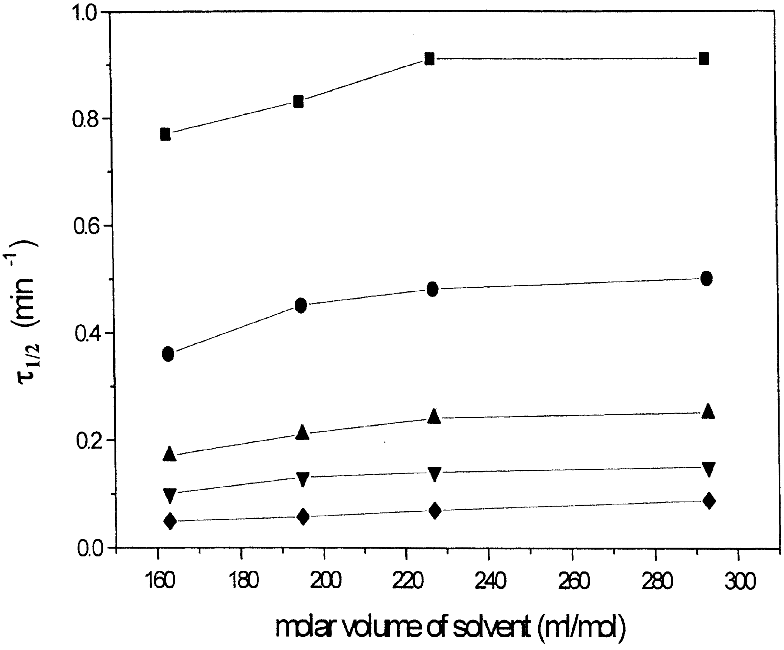


FIGURE 4 Relative crystallinity as a function of time, inset: Typical Avrami plots, for sample sPPC8. Isothermal crystallization temperature: (■) 90°C; (•) 95°C; (▲) 100°C; (▼) 105°C; (◆) 110°C.

and s-PPC16 the typical isotherms of the relative amount of crystallinity at the indicated isothermal crystallization temperature. The plots of log [-ln(1-X_t)] versus log t are shown as the inset figures in Figure 3 and Figure 4. The curves for s-PPC10 and s-PPC12, which were similar to those of s-PPC8 and s-PPC16, are omitted.

It is evident, according to Figure 3 and Figure 4, that it takes a much longer time for s-PPTC8 than for s-PPC16 to reach complete crystallization. The plots of $\tau_{1/2}$ (reciprocal of half crystallization time, which represents the crystallization rate of the recovered s-PP) against the molar size of the solvent from which the s-PP was freeze-extracted are shown in Figure 5. Surprisingly, experiments yielded accurate results for the relation of the crystallization rate with the molar size of the solvents. The crystallization rate of freeze-extracted s-PP increases with increased number of carbon atoms in



FIGUE 5 Plots of $\tau_{1/2}$ versus molar volume of solvents for sPP recovered from alkyl solvents of different molar volume. Isothermal crystallization temperature: (■) 90°C; (•) 95°C; (▲) 100°C; (▼) 105°C; (◆) 110°C.

the molecular chain of the solvent, at least in the range investigated. In classical solution theory, little attention has been focused on the effect of solvent size on the crystallization of polymer. The result completely changes our views about the solution crystallization behavior of polymers.

We [15] have studied the crystallization rate of s-PP freeze-dried from toluene and found that s-PP freeze-dried from toluene at a concentration of 0.1%-wt crystallize faster than that at a concentration of 10% wt. We suggested that disentanglement of the polymer chain accounts for the high crystalline and rapid crystallization rate of the freeze-dried s-PP from very diluent solution.

However, in this study, does the molar size of the solvent affect the disentanglement of the polymer chain in solution and does it furthermore account for the increasing degree of crystallinity and the crystallization rate? We selected two samples, s-PPC8 and s-PPC16, as the typical samples to be studied. Figure 6 and Figure 7 show the FT-Raman spectra of s-PP gels from hexadecane and octane, respectively. Figure 6A, B and D are the Raman spectra of 10% s-PP/

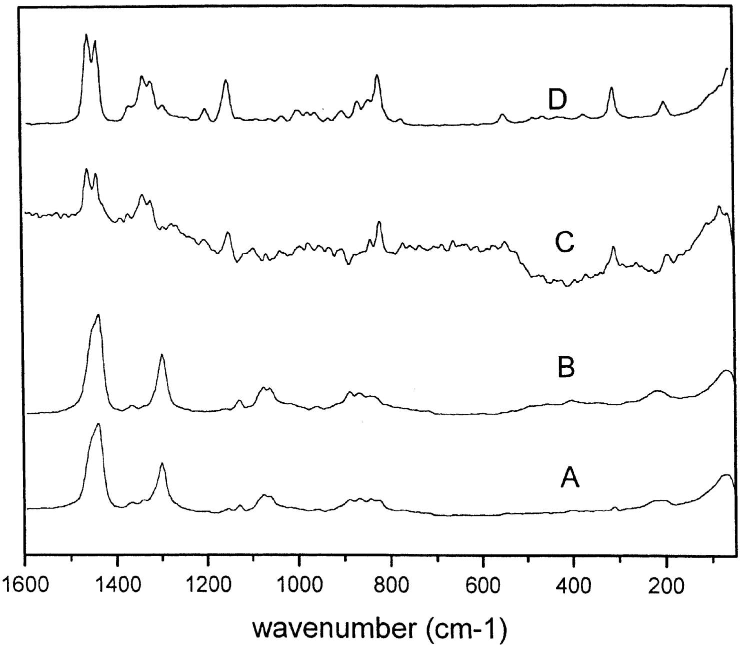


FIGURE 6 FT-Raman spectra recorded from (A) s-PP/hexadecane gel, (B) hexadecane, (C) subtraction of A-B, and (D) s-PP control.

hexadecane gel, pure hexadecane solvent and control s-PP, respectively. Figure 6C is the subtraction spectrum (Figure 6A–B), which is similar to the spectrum of the control s-PP (Figure 6D). Figure 7A, B and D are the Raman spectra of 10% s-PP/octane gel, pure octane solvent and control s-PP, respectively. Figure 7C is the subtraction spectrum (Figure 6A–B). The difference spectrum of Figure 7C is quite different from that of control s-PP (Figure 6D), indicating [16] the existence of strong interaction between s-PP and octane, which causes the Raman line of s-PP to shift from its original position, while in the s-PP/hexadecane gel, no solvent-solute interaction existed.

The chain movement of s-PP in the environment of solvent molecules may be represented by the reptation model proposed by de Gennes [17–19]. In s-PP/octane gel, the interactions with the solvent are strong and the molecule diffuses slowly. In s-PP/hexadecane gel, however, no solvent constraints existed. The molecular motion of segments with the s-PPC16 is relatively easy. This resulted in less entanglements of s-PP chain freeze-extracted from hexadecane solvent than from octane solvent.

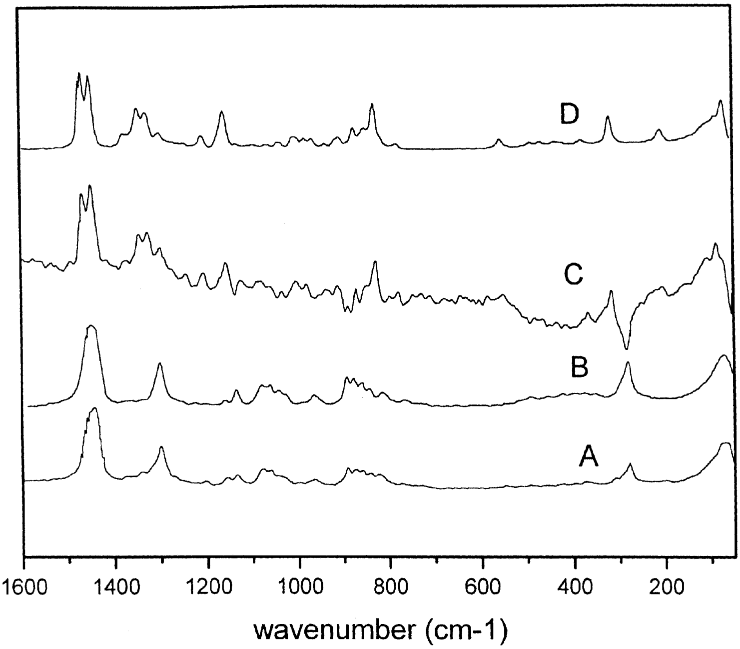


FIGURE 7 FT-Raman spectra recorded from (A) s-PP/octane gel, (B) octane, (C) subtraction of A-B, and (D) s-PP control.

Based on the straight experimental results, we suggest that s-PP freeze-extracted from hexadecane is partly disentangled. The fewer interchain entanglements lead to an increase in crystallization rate and degree of crystallinity. The larger the molar sizes of the solvents, the higher the degree of crystallinity, and the faster the rate of crystallization of the polymer, at least in this family of solvents.

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