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Short communication

Isothermal crystallization of low ethylene content polypropylene random copolymer recovered from decalin and *n*-hexadecane

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Abstract

The kinetics of isothermal crystallization from the melt of low ethylene content polypropylene random (PPR) copolymer with isotactic propylene sequence recovered from physical gel formed in solvents of varying molecular size was studied by differential scanning calorimetry (DSC). The kinetics analysis for these samples indicates that the PPR recovered from *n*-hexadecane is easier to crystallize and exhibits higher crystallization rate than the sample recovered from decalin. The influence of melt annealing time on isothermal crystallization was also investigated.

Keywords: Polypropylene random copolymer; Differential scanning calorimetry; Crystallization rate

1. Introduction

Random or block ethylene–propylene copolymer with low content ethylene is commercially important since the ethylene improves the impact properties of polypropylene without seriously detracting from other desirable properties. The crystallization behavior of these copolymers is changed because the ethylene sequence decreases the structural regularity. The crystallization characteristics of polypropylene (PP) and low ethylene content polypropylene random (PPR) copolymer have been studied, mainly in regard to the influence of nucleating agents on the crystallization rate [1]. The overall crystallization rate of the copolymer is usually depressed compared with the homopolymer, which may affect the mechanical properties of the copolymer.

Solvent can have a dramatic effect on the conformational state of macromolecular chains, and the effect of solvent on the static-equilibrium conformational behavior has been well established. Recently, the effect of solvent and temperature on the transient rheological and rheooptical dynamics has been studied [2]. However, the effect of the molar volume of solvent was not incorporated in those studies [3]. Previously, we found the molar volume of solvent affects the conformation transition of isotactic polystyrene (iPS) both in the solution and in the solid state [4].

Very recently, thermal properties of PPR solid sample recovered from physical gel formed in solvents of varying molecular size have been investigated in this lab. The effect of solvent molecular size on the overall crystallization rate from the melt of PPR is reported in this paper.

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2. Experimental

Low ethylene content (about 8 mol%) PPR copolymer with isotactic propylene sequence was kindly supplied by Yangzi Petroleum Company of China. The melting temperature (T_m) of PPR is about 145 °C (ranging from about 125 to 155 °C, determined by differential scanning calorimetry (DSC) at 10 °C min^{-1}).

Decalin and *n*-hexadecane were purchased from Aldrich and used without further purification. Solvent and 5 wt.% PPR were added into a 10 ml Erlenmeyer flask and heated in a silicon oil bath to 140 °C while being stirred under nitrogen atmosphere, then held at this temperature for 10 min to ensure that all of the PPR fully dissolved. A homogeneous solution was obtained. The solution was then cooled to room temperature in the oil bath without further agitation. A thermoreversible physical gel formed. The gels were repeatedly extracted with ethanol or acetone followed by drying in a vacuum for 48 h at room temperature. For the PPR powder obtained, no weight loss was observed with thermogravimetric analysis (Thermal analyst 2100, TA Instrument) at about 150 °C, and no solvent absorption band appeared in the IR spectra. FT-IR spectra were recorded using a Bruker VECTOR 22 FT-IR spectra photometer. All spectra were taken from KBr pellets and with 4 cm^{-1} resolution. These results indicated that no detectable solvent remained in the PPR powder.

The PPR solid samples recovered from the physical gel formed in decalin and in *n*-hexadecane (or recovered from decalin and *n*-hexadecane in this context for short) are denoted by the letters of A, B, respectively. Wide-angle X-ray diffraction (WAXD) was done with a Rigaku D/Max-Ra diffractometer using Ni-filter Cu Kα radiation ($\lambda = 0.154$ nm).

Isothermal crystallization was carried out with a Perkin-Elmer Pyris-1 differential scanning calorimeter equipped with data processing system. Temperature calibration was performed with indium as a standard. DSC runs were made on samples of about 5 mg, in a stream of nitrogen (20 ml min^{-1}). Before each thermal measurement, the samples were heated rapidly (50 °C min^{-1}) to 180 °C (about 25 °C above the melting temperature) and maintained at this temperature for 5 min to destroy the thermal history. Then, the melted samples were cooled down quickly (−100 °C min^{-1}) to the required crystallization temperature (T_c) in the range of 109–117 °C and held for 30 min. The half-time of isothermal crystallization ($t_{1/2}$) defined as the time taken for 50% crystallization.

3. Results and discussions

Crystallinity of PPR. Fig. 1 illustrates the FT-IR spectra for PPR solid samples recovered from gel formed in decalin (Fig. 1A) and *n*-hexadecane (Fig. 1B).

The absorption band at 723 cm^{-1} is characteristic of the rocking vibration of methylene sequences, $(CH_2)_n$ for $n > 3$ [5]. As shown in Fig. 1, however, the PE segments in PPR could not crystallize as indicated by the absence of doublet at 720–740 cm^{-1}. The absorption bands at 998 and 841 cm^{-1} indicate that there are long iPP segments that can crystallize [6].

Fig. 2 illustrates the WAXD patterns for the samples. The propylene-rich random copolymer with isotactic propylene sequence shows the monoclinic form of isotactic propylene. The crystalline peaks show the following significant X-ray reflections (2θ Cu): 14° (1 1 0), 17° (0 4 0), 18.5° (1 3 0), and 22° ($\bar{1}$ 3 1), (0 4 1) [7]. The curve for PPR recovered from decalin (Fig. 2A) exhibits an intensive amorphous halos, while the curve for PPR recovered from *n*-hexadecane (Fig. 2B) shows sharper crystalline peaks and reduced amorphous halos consistent with an overall increase in crystallinity.

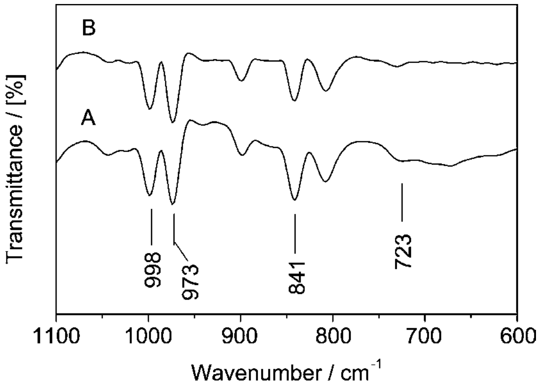


Fig. 1. FT-IR spectra recorded from PPR recovered from (A) decalin and (B) *n*-hexadecane.

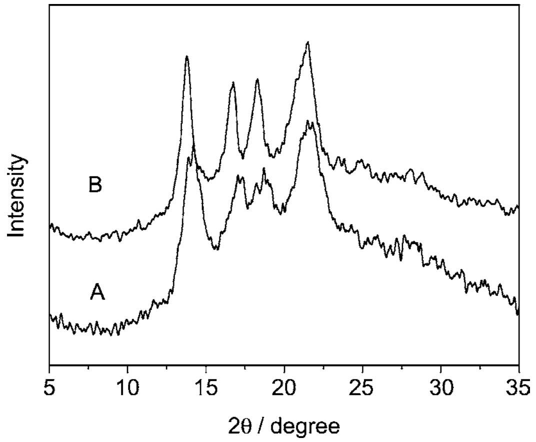


Fig. 2. WAXD patterns of PPR recovered from (A) decalin and (B) *n*-hexadecane.

The volume fraction crystallinity, X_c, can be measured with WAXD from the ratio of areas under the crystalline and amorphous reflection, A_c and A_a [8]

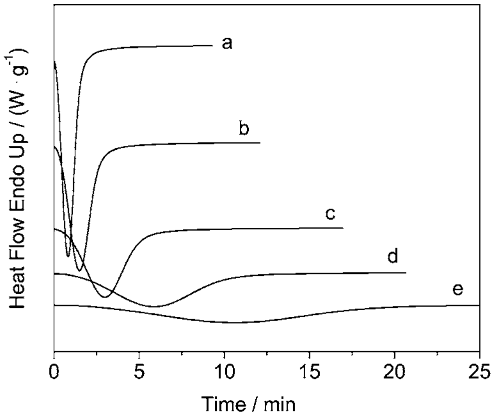
$$X_c = \left[1 + \left(\frac{K_a A_a}{K_c A_c}\right)\right]^{-1} \tag{1}$$

where K_a and K_c are the constants normally assumed to be equal. PPR recovered from *n*-hexadecane has a crystallinity of 32%, while the sample recovered from decalin only has a crystallinity of 23%. The higher crystallinity of PPR recovered from *n*-hexadecane indicates a relatively more ordered structure than in PPR recovered from decalin. And the melting temperatures of the two dried samples, 145.8 °C for PPR recovered from *n*-hexadecane and 144.4 °C for PPR recovered from decalin are also different (heated at 20 °C min^{-1}).

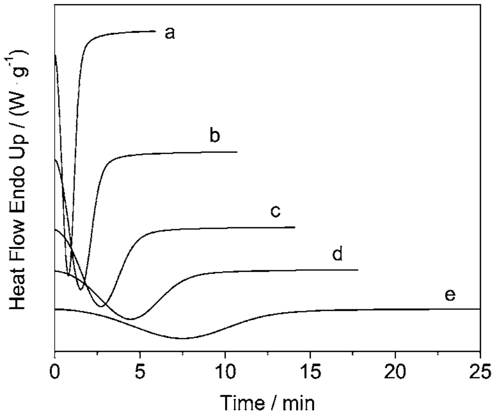
Isothermal crystallization kinetics of PPR. Isothermal crystallization curves of PPR recovered from decalin and *n*-hexadecane at various temperatures are shown in Fig. 3A and B, respectively. As the crystallization temperature increases, the curves shift to longer times and the peak broadens.

Fig. 4 shows the half-time $t_{1/2}$ of isothermal crystallization for the two dried samples as a function of temperature. Clearly, $t_{1/2}$ of PPR from *n*-hexadecane is less than that of PPR from decalin at the same isothermal crystallization temperature, thus showing faster overall crystallization rate.

To obtain further information on the crystallization process, the isothermal crystallization data were analyzed with the Avrami equation [9]



(A) (a) 109°C; (b) 111°C; (c) 113°C; (d) 115°C; (e) 117°C



(B) (a) 111°C; (b) 113°C; (c) 115°C; (d) 117°C; (e) 119°C

Fig. 3. Isothermal crystallization curves of PPR recovered from (A) decalin and (B) *n*-hexadecane at various crystallization temperatures.

$$\theta(t) = 1 - \exp(-kt^n) \tag{2}$$

$$\log[-\ln(1-\theta(t))] = n \log t + \log k \tag{3}$$

where θ is the relative crystallinity at time t, n the Avrami exponent that provides a qualitative indication of the mechanisms of the nucleation processes and crystal growth, and k is the isothermal crystallization rate constant. A plot of $\log[-\ln(1-\theta(t))]$ versus $\log(t)$ should yield a straight line with slope n and intercept $\log(k)$.

The typical Avrami analysis for PPR recovered from *n*-hexadecane is shown in Fig. 5. Each curve has a

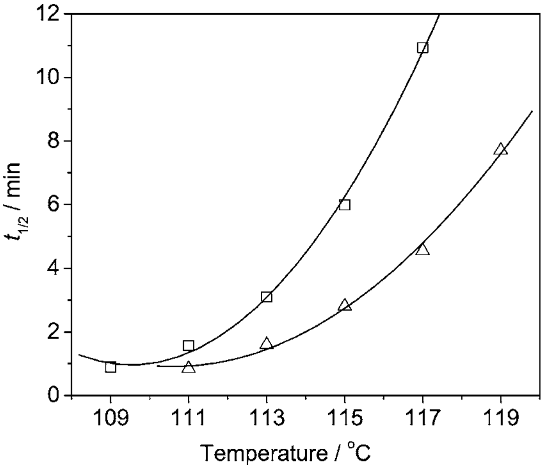
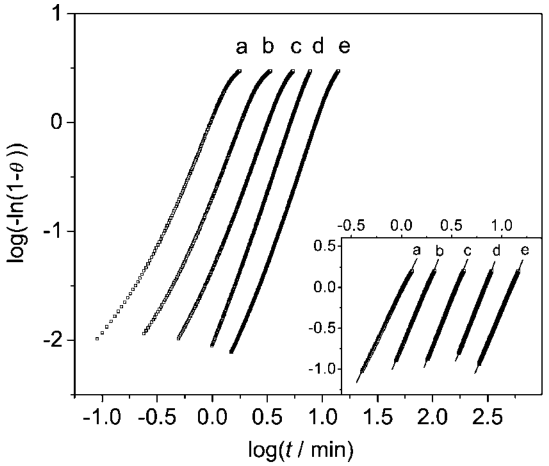


Fig. 4. Half-time $t_{1/2}$ of isothermal crystallization of PPR recovered from decalin (□) and *n*-hexadecane (△) as a function of crystallization temperature.

linear portion followed by a gentle roll-off at longer times. The plot exhibit a deviation from linearity at the later stages of crystallization. This deviation has been attributed to the occurrence of second crystallization [10]. So relative crystallinity between 5 and 80% may be fitted (see Fig. 5 inset) to obtain the Avrami kinetic parameters *n* and *k*, which are listed in Table 1. The high values of the correlation coefficient indicate a good fit of the isothermal crystallization data to Avrami equation. The Avrami exponent of PPR sample recovered from *n*-hexadecane ranging from 2.45 to 3.03 with a mean values of 2.79 is smaller than that of PPR samples recovered from decalin ranging from 2.51 to 3.10 with a mean values of 2.90. So the Avrami exponent of PPR samples recovered are primary dependent on the solvent. Many researchers [11] suggest that the faster overall crystallization rate resulted in the smaller Avrami exponent. This is consistent with the studies in this paper.



(a) 111°C; (b) 113°C; (c) 115°C; (d) 117°C; (e) 119°C

Fig. 5. Avrami analysis for PPR recovered from *n*-hexadecane undergoing crystallization at different crystallization temperatures. Inset: fitted plot for relative crystallinity between 5 and 80%.

The rate constant *k* in Table 1 can be approximately described by the Arrhenius equation to determine an activation energy for isothermal crystallization [12,13]

$$k^{1/n} = k_0 \exp\left(-\frac{\Delta E}{RT_c}\right) \tag{4}$$

Table 1
Tabulation of Avrami kinetic parameters *n* and *k* of isothermal crystallization at different crystallization temperature for recovered samples

T_c (°C)	Correlation coefficient (*R*)	*n*	Intercept [log(*k*)]	*k* (min^{-n})	$k^{1/n}$ (min^{-1})
PPR recovered from decalin					
109	0.9998	2.51 ± 0.01	−0.0363 ± 0.0009	0.9198	0.9673
111	0.9998	2.91 ± 0.01	−0.7304 ± 0.0009	0.1860	0.5611
113	0.9998	3.06 ± 0.01	−1.6699 ± 0.0020	0.0214	0.2846
115	0.9999	3.10 ± 0.00	−2.5684 ± 0.0008	0.0027	0.1484
117	0.9999	2.90 ± 0.00	−3.1751 ± 0.0007	0.0007	0.0804
PPR recovered from *n*-hexadecane					
111	0.9997	2.45 ± 0.01	0.0374 ± 0.0012	1.0899	1.0358
113	0.9999	2.64 ± 0.00	−0.6875 ± 0.0006	0.2054	0.5490
115	0.9999	2.79 ± 0.00	−1.4119 ± 0.0008	0.0387	0.3119
117	0.9999	3.03 ± 0.00	−2.1512 ± 0.0007	0.0071	0.1950
119	0.9999	3.02 ± 0.00	−2.8398 ± 0.0014	0.0015	0.1147

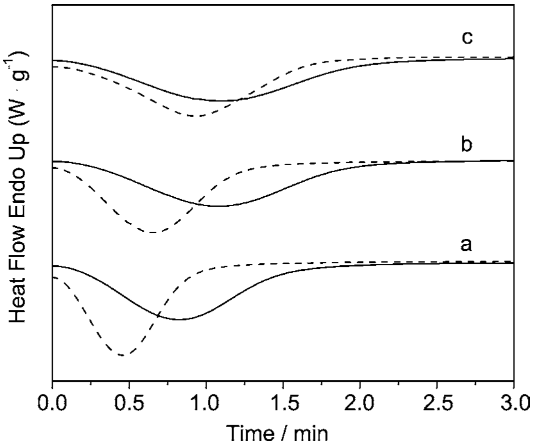


Fig. 6. Isothermal crystallization at 113 °C of PPR recovered from decalin (solid line) and *n*-hexadecane (dash line) after different melt annealing times: (a) 5 min, (b) 10 min, and (c) 15 min at 180 °C.

The slope of the Arrhenius plot of $(1/n)\ln(k)$ versus $1/T_c$ determines $\Delta E/R$. The value of the activation energy, ΔE, is found to be 340.3 ± 9.7 and $390.5 \pm 8.0\,\mathrm{kJ\,mol^{-1}}$ for melt crystallization of PPR recovered from *n*-hexadecane and decalin, respectively. The results clearly show that crystallization from melt is more favorable for PPR recovered from *n*-hexadecane than from decalin.

Influence of melt annealing on isothermal crystallization. To study the influence of melt annealing on isothermal crystallization behavior, melts were held at 180 °C for various time intervals before crystallization at 113 °C. The exotherms recorded during crystallization after annealing are shown in Fig. 6. As the melt annealing time increases, the crystallization curves of both samples shift to longer times, and after melt annealing for 15 min, a unification of the curves for PPR samples recovered from the two solvents is apparent. The same influence of melt annealing on isothermal crystallization was observed in a crystallization study of lowered chain entanglement PE [14].

It is well known that the thermal history in the melt or solution affects the crystallization behaviors of many polymers [15]. The effects of thermal history on crystallization have been attributed to the persistence of small crystalline regions [16]. Morgan [17] proposed that residual minute crystalline regions persist above the nominal melting temperature of a polymer. The destruction of these crystals took place at a temperature higher than T_m, but some nuclei were able to survive in the melting process. If the melting temperature is not sufficiently high, remnants of relatively more ordered structure in the melt will act as nuclei for crystallization on subsequent isothermal crystallization. Accordingly, the presence of such primary nuclei decreases the crystallization free energy barrier ΔE and thus increases the crystallization rate. This phenomenon is also defined as self-nucleation [15].

In our experiments, the PPR recovered from different solvents were melted and annealed at 180 °C, which is about 25 °C above the melting temperature. Some nuclei may remain undestroyed during melting for the highly ordered samples leading to different kinetics and rate for the subsequent crystallization. It is therefore conceivable that the relatively ordered state of the polymer should be maintained within a time scale that could have an important effect on the subsequent crystallization behaviors as reflected by the results of our experiments. PPR recovered from *n*-hexadecane indicates a relatively more ordered structure than the sample recovered from decalin. However, an equilibrium state of isothermal crystallization is approached asymptotically with the increasing melt time or melt annealing temperature. In this study, 15 min of melt annealing unified the isothermal crystallization behavior.

Acknowledgements

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