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# DSC studies on the melting crystallization of polyethylenes prepared from alkanes of varying molecular size

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## Abstract

The melting crystallization behavior of narrow-disperse polyethylene sample prepared from alkane solutions was studied by using differential scanning calorimetry. Avrami analysis of isothermal crystallization of these samples indicates that the PE sample prepared from *n*-octadecane has significantly higher crystallization rate than that from *n*-octane. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Differential scanning calorimetry; Melting crystallization; Polyethylene

## 1. Introduction

The macromolecular chain conformation in solution changes with the solvent and temperature, which will affect the formation of crystalline structure in the subsequent crystallization process. Polyethylene (PE) is one of the basically important polymers from both the industrial and scientific point of view. It has been studied extensively and could be considered as the paradigm for polymer crystallization studies. Many studies of crystallization of polyethylene from solution have been carried out since the discovery of folded chain single crystal growth from solution [1]. Investigations of crystallization mechanism viewed from the crystalline lamellar scale have been reported for many polymer materials [2]. The structural change during the isothermal crystallization of PE has also been investigated extensively from the view points of lamellae and spherulite [3]. PE crystallizes too fast and makes it difficult to trace the structural change in the crystallization process step by step. Recently, the detailed discussion on the PE crystallization has begun to be reported on the basis of the time-resolved small-angle X-ray scattering data measured by using the synchrotron radiation source and/or highly sensitive detector [3].

Most of the previous studies concentrated on the dilute solution crystallization behavior of polyethylene, the

solution concentration and crystallization temperature are often considered [4,5]. Polyethylene solutions show the phenomenon of gelation crystallization, and such gels drew renewed interest after Smith and co-workers developed ultra-high modulus PE fibers by gel spinning [6,7]. There are also some reports on the gelation crystallization behavior and gel morphology of PE [7–9]. However, little study has focused on the effect of solvent molecular size on the crystallization behavior of PE. In the present work, the melting crystallization of PE samples prepared from alkane solvents of varying solvent size will be reported.

## 2. Experimental section

The narrow-disperse polyethylene had a weight average molecular weight  $M_w$  53 200 and molecular weight distribution  $M_w/M_n$  of 1.22 was obtained from Petroleum Company at Bartlesville, Oklahoma. Reagent grade *n*-octane ( $C_8H_{18}$ ) and *n*-octadecane ( $C_{18}H_{38}$ ) were used as received without purification.

Polymer solutions with concentration of 10 wt% were prepared by heating and stirring the well-blended polymer–solvent mixture containing 0.1 wt% of antioxidant, di-*t*-butyl-*p*-cresol, in a silicon oil bath under nitrogen atmosphere. After the polymer sample was dissolved completely, the solution was then cooled at 3 °C/min to room temperature and a thermoreversible gel formed. Powdered PE sample was recovered by washing the gel

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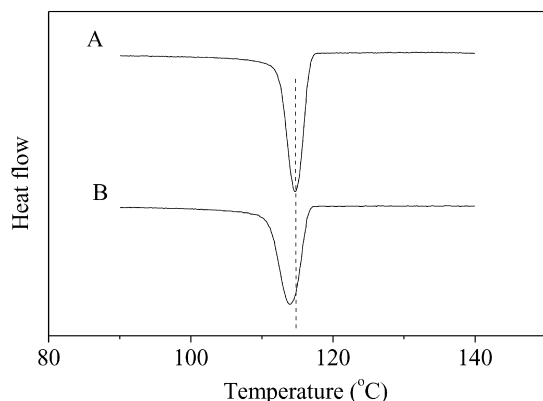


Fig. 1. Nonisothermal crystallization DSC thermograms of PE gelation-crystallized from 10% *n*-octadecane (A) and *n*-octane solution (B).

with acetone for several times to remove the solvent, and then dried under vacuum.

Differential scanning calorimetry measurement was carried out using a Perkin–Elmer model DSC-7 system calibrated with indium and zinc standards. Sample weights were between 5 and 9 mg. Isothermal melt crystallization kinetics were performed in situ as follows: the sample was quickly heated (at 80 °C/min) up to 160 °C, held there for 10 min to eliminate residue crystals, then the melt sample was cooled (at –200 °C/min) to the designated crystal-

lization temperatures ( $T_c$ ). The exothermal curve of heat flow as a function of time was recorded and investigated.

### 3. Results and discussion

Thermoreversible gels can be formed by cooling solutions of polyethylene from a temperature above the dissolution temperature of PE to room temperature. A measure of the efficiency of gelation is the critical gelation concentration. This is the minimum polymer concentration under given conditions that will form a gel. The lower the critical gel concentration, the more developed and stronger the gel is when formed at higher concentrations [8]. Electron microscopy experiments on dried polyethylene gels showed agglomeration of interconnected single crystals [7], and a network formed from bridges of isolated lamella locally linked by adhesion of the crystal surfaces was observed on ‘solvent’-containing gels [9]. In the present study, we find that the gel formed from *n*-octadecane is obviously stronger than that from *n*-octane with same polymer concentration. The melting crystallization behaviors of these gelation recovered PE samples were studied, and the results were explained in view of solvent molecular size effect, instead of solvent quality (solvent–polymer interaction parameter  $\chi$ ) which is a parameter usually considered in the study of polymer solution.

The crystallinity degree of gelation-prepared PE is measured from wide angle X-ray diffraction by resolving the total intensity curve into three curves representing diffracted X-ray intensities from amorphous material and (110) and (200) crystalline planes, then calculated according to the following equation [10,11]:

$$X_c = (I_{110} + 1.46I_{200}) / (I_A + I_{110} + 1.46I_{200}) \quad (1)$$

In this experiment PE prepared from *n*-octadecane shows crystallinity of 69.3%, while the sample prepared from *n*-octane has only crystallinity of 55.2%.

The melting crystallization behavior for these dried gels were studied by DSC. Fig. 1 shows an example of the DSC thermograms of nonisothermal crystallization of PE prepared from 10% *n*-octadecane (A) and *n*-octane (B), respectively. The sample prepared from *n*-octadecane shows higher crystallization temperature and sharper exothermic peak than that prepared from *n*-octane. This indicates that the dried gel from *n*-octadecane exhibits better crystallization ability even after melting. The isothermal crystallization behavior of these gelation-crystallized samples will be reported in detail in the following.

Isothermal melt crystallization was studied by cooling the melt rapidly to a designated crystallization temperatures ( $T_c$ ). Heat flow curves were recorded as a function of time. Two sets of isothermal crystallization curves are shown in Fig. 2. As the  $T_c$  increased, the crystallization exotherms shifted to higher temperatures and became broad. From Fig. 2, it can be seen obviously that the time of exothermic peak

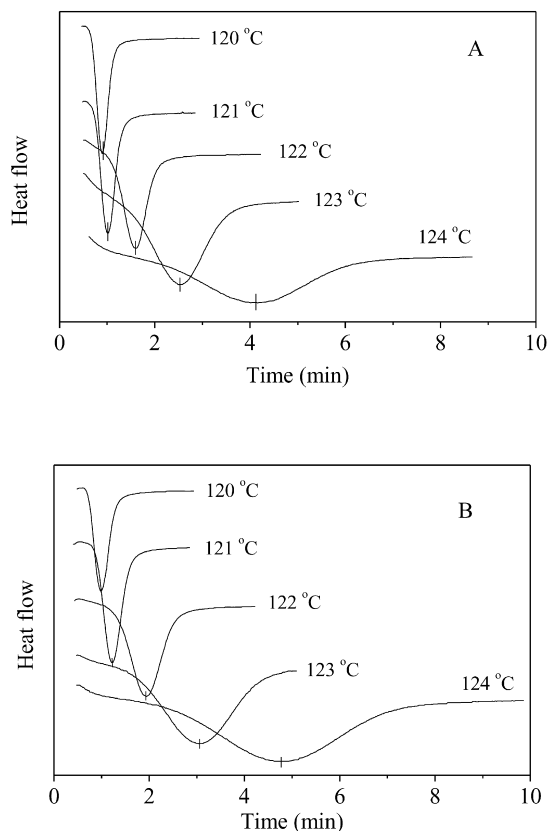


Fig. 2. DSC curves of heat flow vs. time during isothermal crystallization of PE gelation-crystallized from 10% *n*-octadecane (A) and *n*-octane solution (B) at the indicated temperatures.

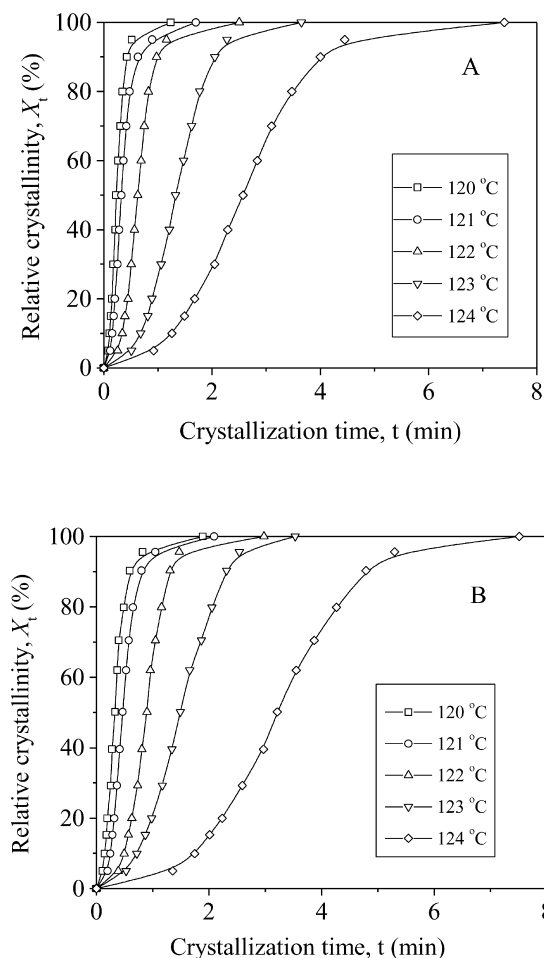


Fig. 3. Development of relative crystallization with time for isothermal crystallization of PE gelation-crystallized from 10% *n*-octadecane (A) and *n*-octane solution (B) at the indicated temperatures.

position is always shorter for sample gelation-crystallized from *n*-octadecane (A) than that from *n*-octane (B). The Avrami equation, which assumes that the relative degree of crystallinity develops with time *t*, was used to analyze the isothermal crystallization process of PE [12,13]. The

Table 1  
Parameters *n*, *k*, *t*<sub>max</sub>, *t*<sub>1/2</sub> from Avrami analysis of isothermal melt crystallization for PE

<i>T</i> <sub>c</sub> (°C)	<i>n</i>	<i>k</i> (min <sup>-<i>n</i>)</sup>	<i>t</i> <sub>max</sub> (min)	<i>t</i> <sub>1/2</sub> (min)
<i>Gelation-crystallized from n-octadecane</i>				
120	2.5	22.54	0.234	0.248
121	2.5	11.69	0.305	0.323
122	3.0	2.86	0.615	0.623
123	2.8	0.319	1.28	1.32
124	2.6	0.059	2.46	2.58
<i>Gelation-crystallized from n-octane</i>				
120	2.4	10.17	0.304	0.327
121	2.9	6.20	0.461	0.470
122	3.2	0.989	0.893	0.895
123	2.6	0.249	1.42	1.48
124	3.0	0.020	3.22	3.26

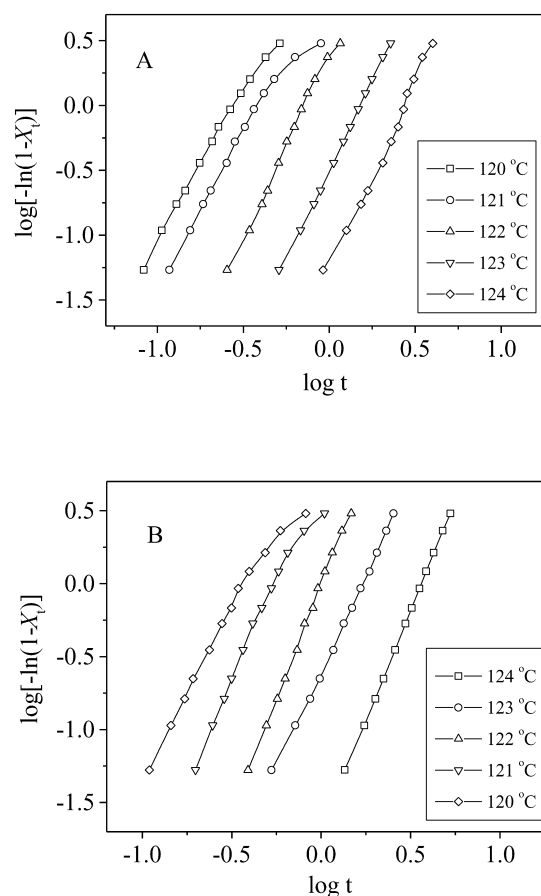


Fig. 4. Plots of  $\log[-\ln(1 - X_t)]$  vs.  $\log(t)$  for isothermal crystallization of PE gelation-crystallized from 10% *n*-octadecane (A) and *n*-octane solution (B) at the indicated temperatures.

development of relative crystallization with time for isothermal crystallization from melt was shown in Fig. 3. The relative amount of crystallinity that developed at a definite time *t* decreases with increasing the crystallization temperatures *T*<sub>c</sub>. At the same *T*<sub>c</sub> and relative amount of crystallinity, the crystallization time for sample prepared from *n*-octadecane is shorter than that from *n*-octane. This implies that samples prepared from *n*-octadecane have significant higher crystallization rate than that from *n*-octane.

The well-known double logarithmic plots of  $\log[-\ln(1 - X_t)]$  vs.  $\log(t)$  are shown in Fig. 4. Each curve shows an initial linear portion, subsequently tending to level off. This deviation was considered to be due to the secondary crystallization which was caused by the spherulite impingement in the later stage [14,15]. The Avrami parameters *n* and *k* for PE crystallized from *n*-octadecane and *n*-octane, determined from the initial linear portion in Fig. 4, are listed in Table 1. The obtained Avrami exponent *n* was 2–3 in all cases. The crystallization rate parameter *k* was larger for samples prepared from *n*-octadecane than that from *n*-octane.

The crystallization half-time *t*<sub>1/2</sub> is defined as the time at which the extent of crystallization is 50% complete and is

determined from the measured kinetic parameters, that is,

$$t_{1/2} = (\ln 2/k)^{1/n} \quad (2)$$

Since the peak time for maximum crystallization to occur,  $t_{\max}$ , corresponds to the point where  $dQ/dt = 0$ ,  $Q(t) = dHc/dt$  being the heat flow rate, we can use the Avrami equation to write  $t_{\max}$  in terms of  $n$  and  $k$ , obtaining

$$t_{\max} = [(n-1)/nk]^{1/n} \quad (3)$$

The calculated values of  $t_{1/2}$  and  $t_{\max}$  for PE are also presented in Table 1. Both parameters obtained from Avrami analysis implied that the crystallization rate for samples prepared from *n*-octadecane is higher than that from *n*-octane.

As the crystallization process is assumed to be thermally activated, the crystallization rate parameter  $k$  can be approximately described by an Arrhenius form [15]

$$k^{1/n} = k_0 \exp(-\Delta E/RT) \quad (4)$$

where  $k_0$  is the temperature-independent pre-exponential factor,  $\Delta E$  is the total activation energy which consists of the transport activation energy  $\Delta E^*$  and the nucleation activation energy  $\Delta F\Delta E^*$  refers to the activation energy required to transport molecular segments across the phase boundary to the crystallization surface.  $\Delta F$  is the free energy of formation of the critical size crystal nuclei at crystallization temperature  $T_c$ .  $R$  is the universal gas constant and  $T$  is the absolute temperature. The slope of the Arrhenius plot of  $1/n \ln(k)$  vs  $1/T$  determines  $\Delta E/R$ . The value of the activation energy was found to be  $-800$  and  $-880$  J/mol for melt crystallization of PE prepared from *n*-octadecane and *n*-octane, respectively. Since released energy is needed while crystallizing from the molten fluid to the ordered crystalline state, the value of activation energy for the melt crystallization is negative in the light of the concept of physical chemistry. On the other hand, while crystallizing from the 'frozen' amorphous glassy state to the ordered crystalline region, as it needs to absorb energy, the value of activation energy for cold crystallization is positive. Our DSC results show clearly that the crystallization from melt is easier for sample prepared from *n*-octadecane than that from *n*-octane.

The motion of chains in quiescent polymer melts is confined to a reptative diffusion along the contour length, as proposed by de Gennes [16,17]. In the constitutive equations based on the concept of chain reptation, it is assumed that the longest relaxation times in polymer melts correspond to the reptative motion of complete chains [18]. In the case of ultra-high molecular weight polyethylene, possessing a weight average molar mass  $M_w$  over  $10^6$  g/mol, the experimentally determined longest relaxation times exceed  $10^4$  s derived from the stress relaxation modulus as a function of time at  $180$  °C [19]. In this study, the relatively ordered structure of gelation-crystallized PE from *n*-octadecane was kept after melting it at  $160$  °C for 10 min,

and so in the subsequent isothermal crystallization process, higher crystallization rate was found in thus prepared sample than that prepared from *n*-octane. *n*-Octadecane and *n*-octane have similar chemical structure as the repeated units in polyethylene. One of the major differences between the two alkanes is the molar volume, which is  $327$  cm<sup>3</sup>/mol for *n*-octadecane, while it is  $164$  cm<sup>3</sup>/mol for *n*-octane.

The effect of solvent molecular size on the polymer behavior in solution can be elucidated qualitatively from statistic thermodynamics discussion of polymer–solvent mixture [20]. The effect of a heat of mixing of polymer and solvent may be introduced through use of an expression of the van Laar form

$$\Delta H = Bn_1V_1v_2 \quad (5)$$

where  $B$  is the cohesive energy density constant characteristic of a given solvent–polymer pair;  $V_1$ , the molar volume of solvent;  $n_1$ , is the molecule number of solvent;  $v_2$  is the volume fraction of polymer. Employing the conventional procedure

$$\Delta H/kT = \chi n_1v_2 \quad (6)$$

where  $\chi$  (Flory–Huggins parameter) is defined as

$$\chi = BV_1/kT \quad (7)$$

We can find that solvent–polymer interaction parameter  $\chi$  increases with increasing solvent molar volume  $V_1$ , i.e. the polymer chains become less soluble and more compact in solvents with large molar volume.

From statistic thermodynamics deduction of lattice model, Flory deduced the relationship between expansion factor  $\alpha$  and Huggins parameter  $\chi$ , while the free energy of dilution system is lowest [20]

$$C(1/x_s - 2\chi)N^{1/2} = \alpha^5 - \alpha^3 \quad (8)$$

where  $x_s$  is the number of lattice cells occupied by a molecule of solvent and  $N$  is the polymerization degree of polymer. As the size of solvent molecule increases,  $\chi$  increases,  $1/x_s$  decreases, so the term on the left-hand side of Eq. (8) decreases and the expansion factor  $\alpha$  decreases. This means that the polymer chain contracts with the increasing solvent molecular size so that it collapsed to a more ordered state which can act as a crystallization nucleus [21]. The rapid crystallization of isotactic polystyrene was observed in large solvent molecules [22]. The relatively ordered structure of gelation-crystallized PE from *n*-octadecane was kept after melting it at  $160$  °C for 10 min, and so in the subsequent isothermal crystallization process, higher crystallization rate was observed in thus prepared sample than that prepared from *n*-octane.

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