Effect of Self-Nucleation on Crystallization and Melting Behavior of Polypropylene and Its Copolymers

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ABSTRACT: The effect of self-nucleation on the crystallization and melting behavior of isotactic polypropylene (i-PP) and low ethylene content propylene–ethylene copolymers were investigated. Isothermal crystallization kinetics were studied using the Avrami equation and Lauritzen-Hoffman nucleation theory. It was found that self-nucleation can enhance the crystallization. The surface free energy σ_e decreased for the self-nucleated sample. The melting behavior was affected by the preselected temperature, T_s , at which the polymer was partially melted. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1559–1564, 1999

Key words: self-nucleation; crystallization; melting behavior; isotactic polypropylene; low ethylene content propylene–ethylene copolymer

INTRODUCTION

The overall crystallization in polymers is a combination of the nucleation and growth. Nucleation increases the number of crystal growth sites in a polymer. There are three kinds of nucleation¹: homogeneous nucleation, heterogeneous nucleation, and self-nucleation. Homogeneous nucleation is the process of the birth of small regions of the crystalline phase in the supercooled melt. The process occurs in the absence of surfaces and as the result of random fluctuations of order in the melt. Heterogeneous nucleation is the process of the birth of small crystalline regions on or near surfaces. It arises from a foreign agent that provides nucleating sites. The foreign substance provides a surface that reduces the free-energy barrier to primary nucleation. The term self-nucleation or self-seeding has been introduced by Blundell, Keller, and Kovacs to describe the nucleation of folded-chain crystals grown from solution on high molecular weight remnants of its

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Journal of Applied Polymer Science, Vol. 72, 1559–1564 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/121559-06 own crystals that remained through the dissolution step.² Self-nucleation is now used as the general term describing nucleation of a macromolecular melt or solution by its own crystals grown previously.

The potentiality of the self-nucleation technique for growing crystals of macromolecules from solution has been established by Blundell and coworkers.² The technique is of importance for crystallization from the melt as well, because polymers offer a wide temperature range wherein neither the crystals melt nor the nucleated melts crystallize. Wunderlich's review gives a detailed account of the types of self-nucleation procedures that could be used in crystallization of a polymer.¹

Macromolecules are particularly well suited for self-nucleation because of a large temperature range where crystals do not melt, but even nucleated melt does not crystallize. Self-nucleation has much influence on polymer morphology, crystal form, and polymer properties,³ so that it is of importance to study the self-nucleation process.

The present investigation deals with the effect of self-nucleation on the crystallization and melting behavior of isotactic polypropylene (i-PP) and low ethylene content propylene–ethylene copolymers. The Avrami equation and the Lauritzen and Hoffman's nucleation theory are used to analyze the isothermal crystallization experimental results.

EXPERIMENTAL

Materials

All of the samples were provided by SOLVAY; the grade numbers of block and random propylene–ethylene are RV210 and KV202, and the ethylene contents are about 8 and 5%, respectively. The grade number of i-PP is HV202. There are no any additves in these samples.

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer differential scanning calorimeter, DSC-2, interfaced to a BBC-Master computer via an analog-to-digital converter, was used to characterize the samples. The temperature scale of the DSC instrument was calibrated using the melting point of zone-refined stearic acid (m.p.: 343.50 K) and those of highly purified metals such as indium (m.p.: 429.78 K), tin (m.p.: 505.06 K), lead (m.p.: 600.50 K), and zinc (m.p.: 692.65 K). The thermal response of the calorimeter was calibrated using the heat of fusion of ultrapure indium, 28.4 J g⁻¹. Samples were encased in aluminum pans, and a vacant aluminum pan was used as a reference.

The Self-Nucleation Procedure as Applied to the DSC Technique

Four thermal steps are required in the self-nucleation procedure, corresponding to (a) erasure of the previous thermal history, (b) creation of a crystalline state in the sample at a temperature, (c) partial melting of the sample at a temperature, T_s , and (d) crystallization at a temperature, T_c



Figure 1 Thermal history for self-nucleation.



Figure 2 The crystallization exotherms of iPP after partial melting at various T_s s, as indicated.

(steps A, B, C, and D in Fig. 1). (A) To erase the former thermal history, samples were heated well above the melting temperature, T_m (step A in Fig. 1). Samples were heated to 470 K and were held at that temperature for 5 min. (B) The crystalline state was obtained by cooling the "erased" melt to 320 K at a cooling rate of 160 K min⁻¹ and holding at this temperature for 10 min. (C) The essential step in self-nucleation (step C in Fig. 1) is achieved by heating the polymer to a preselected temperature, T_s , for a fixed period of time. In this experiment, the heating rate was 10 K min⁻¹, and the sample was maintained at T_s for 5 min. T_s was selected in the temperature range between the maximum value of the melting endotherm and the end of the melting endotherm of the sample. (D) Further crystallization (step D in Fig. 1) was carried out by cooling the sample rapidly to T_c (isothermal crystallization) or by cooling at 10 $K \min^{-1}$.

RESULTS AND DISCUSSION

Crystallization Behavior

Figures 2 and 3 show the crystallization exotherms of the polypropylene homopolymer and the block propylene-ethylene copolymer after partial melting at various T_s s. For both, the crystallization temperature was significantly shifted to a lower temperature as T_s increased. This result indicates that self-nucleation can enhance the crystallization.



Figure 3 Crystallisation exotherms of block PP after partial melting at various T_s s, as indicated.

Table I lists the enthalpy of crystallization for samples at various T_s . The nucleation for $T_s = 470$ K is supposed to be homogeneous, because the samples are in a molten state when the temperature is above 450 K, and there is no any additives in the samples. It can be seen that the enthalpy of crystallization decreases with decreasing the T_s . At lower T_s , more seeds exist; there are fewer crystallizing molecules than those at a higher T_s , so that the enthalpy of crystallization is lower.

DSC can be used to measure the rate of heat evolution from a crystallizing sample under strictly isothermal conditions. Assuming that the fractional crystallinity, X(t), can be evaluated by integrating the heat evolution vs. the time curve from the beginning of the scan until time t, i.e.,

Table I Dynamic Crystallization Enthalpy of Samples at Different T_s

Sample	T_s (K)	$\Delta H_c ~(\mathrm{J}~\mathrm{g}^{-1})$
Block copolymer	470	101.32
	441	90.20
	440	82.41
	439	80.76
i-PP	470	103.75
	441	90.47
	439	84.84
	438	78.98
	437	54.67
	436	51.28

Cooling rate: 10 K min⁻¹.



Figure 4 Variation of the half-time of crystallization with the isothermal crystallization temperature for self-nucleated block PP treated at various T_s .

$$X(t) = \int_{0}^{t} \frac{dH}{dt} dt / \int_{0}^{\infty} \frac{dH}{dt} dt \qquad (1)$$

The fractional extent of crystallinity as a function of time can be analyzed using the Avrami equation⁴:

$$-\ln[1 - X(t)] = Kt^n \tag{2}$$

The exponent, n, depends on the type of nucleation and the crystal growth geometry. The parameter K is also a function of nucleation and growth. The Avrami parameters, n and K, can be determined by taking the logarithm of eq. (2) to yield a plot of $\ln\{-\ln[1 - X(t)]\}$ vs. $\ln t$. K can also be obtained from the expression:

$$K = \frac{\ln 2}{t_{1/2}^n}$$
(3)

where the half-time, $t_{1/2}$, is the time required for 50% of the total crystallization to occur.

Figures 4 and 5 show the relationships between log $t_{1/2}$ and the isothermal crystallization temperature, T_c , for block propylene–ethylene copolymer and i-PP. It can be seen that the crystallization temperature and the crystallization rate increased as T_s decreased. Table II shows that the Avrami exponent, n, tends to decrease for selfnucleated samples.

The crystallization kinetic data were analyzed using the Lauritzen-Hoffman equation⁵:



Figure 5 Variation of the half-time of crystallisation with the isothermal crystallization temperature for self-nucleated i-PP treated at various T_s .

$$g = g_0 \exp\left[-\frac{\Delta E}{R(T_c - T_{\infty})}\right] \exp\left[-\frac{K_g}{T_c \Delta T f}\right] \quad (4)$$

where $g = 1/t_{1/2}$, g_0 is a preexponential factor, $\Delta T = T_m^0 - T_c$ is undercooling, ΔE is activation energy for transport of polymer segments to the site of crystallization, R is the gas constant, T_{∞} $= T_g - 30$ K, K_g is a nucleation constant, and f $= 2T_c/(T_c + T_m^0)$. The equilibrium melting temperature, T_m^0 , can be obtained by a plotting of the melting temperature, T_m , against the crystallization temperature, T_c , according to Hoffman and Weeks.⁶ The intersection with the line $T_m = T_c$ will occur at T_m^0 . This treatment assumes that nucleation and growth rates can be averaged.

From eq. (4):

$$\ln g + \frac{\Delta E}{R(T_c - T_{\infty})} = \ln g_0 - \frac{K_g}{T_c \Delta T f} \qquad (5)$$

Figures 6 and 7 show the plots of $[\ln g + \Delta E / R(T_c - T_{\infty})]$ as a function of $1/T_c \Delta T f$ for the

Table IIEffect of Self-Nucleation on theAvrami Exponent, n, for i-PP

T_s (K)	$n~(\pm 0.1)$
470	2.8
441	2.5
440	2.2
439	2.2
438	2.0



Figure 6 Lauritzen-Hoffman plot for the self-nucleated block propylene–ethylene copolymer.

self-nucleated block propylene–ethylene copolymer and i-PP, obtained from the experimentally determined values of g, T_c , and T_m^0 , and using standard values of $\Delta E = 6280$ J mol⁻¹ and $T_{\infty} = T_g - 30$ K = 239.6 K.⁷

Values for K_g and g_0 can be obtained directly from the graph, where the slope is $-K_g$ and the intercept is equal to $\ln(g_0)$. Once K_g is known, parameters characteristic of crystal growth can be determined.

Nucleation constant, K_{g} , can be expressed as:

$$K_g = \frac{n b_0 \sigma \sigma_e T_m^0}{\Delta h_f K}$$

where σ and σ_e are the fold and side surface free energies, respectively, of the growing crystal, b_0 is



Figure 7 Lauritzen-Hoffman plot for the self-nucleated i-PP.

Table III	Values of t	the Crystallographic U	Jnit
Cell Dime	nsions for l	Polypropylene ⁷	

(110) growth plane	
a_0 (m):	$5.49 imes10^{-10}$
b_0 (m):	$6.26 imes10^{-10}$
$(a_0 b_0)$ (m ²):	$3.43 imes10^{-19}$

the molecular thickness, and K is the Boltzmann constant. The value of n depends on the regime of crystallization. At high temperatures (low undercooling) each surface nucleation occurrence leads to rapid completion of the growth strip prior to the next nucleation event. This is referred to as regime I, and n = 4. At lower temperature, in regime II, multiple surface nuclei form on the substrate, and n = 2. When crystallization occurs at a still lower temperature, the separation between the multiple nuclei characteristic of regime II reaches its minimum value. This is regime III, and n = 4.

Compared with ref. 8, it is assumed that all of the crystallizations in this work were carried out in Regime III, so that:

$$K_g = \frac{4b_0 \sigma \sigma_e T_m^0}{\Delta H_f k} \tag{6}$$

where ΔH_f is the heat of fusion. In determining σ_e , σ is estimated using:

$$\sigma = \sigma (a_0 b_0)^{1/2} \Delta H_f \tag{7}$$

where a_0 and b_0 are crystallographic unit cell dimensions, and σ can be derived empirically to be 0.1 by the Thomas-Stavely relationship.⁹ The material constants for i-PP used in the analysis are listed in Table III. The fold-surface free energy, σ_e , for self-nucleated block propylene-eth-

Table IVKinetic Parameters for Self-
Nucleated Samples

Samples	$\begin{array}{c} T_s \\ (\mathrm{K}) \end{array}$	K_g (×10 ⁻⁵)/K ²	$\sigma_e/{ m J}~{ m m}^{-2}$
Block copolymer	470	1.9478	0.0398
1 0	441	1.2617	0.0258
	440	1.1302	0.0231
i-PP	470	3.2203	0.0658
	441	2.2687	0.0464
	439	1.8423	0.0376



Figure 8 DSC melting curves for self-nucleated block propylene–ethylene copolymer.

ylene copolymer and i-PP are listed in Table IV. The results show that the chain-folding surface free energy decreased for the self-nucleated block propylene–ethylene copolymer and i-PP, suggesting that the self-nucleation can enhance the crystallization of the polymer.

Melting Behavior

Figures 8 and 9 show the DSC melting curves for self-nucleated block and random propylene-ethylene copolymers. A high-temperature melting peak appears as T_s decreases; it becomes greater in magnitude as T_s decreases. The temperature of the high-temperature melting peak decreased as T_s decreased. The high-temperature peak is attributed to the unmelted portions of the polymer,



Figure 9 DSC melting curves for the self-nucleated random propylene-ethylene copolymer.



Figure 10 Melting curves for the self-nucleated i-PP isothermally crystallized at various indicated temperatures.

which act as nuclei. As T_s decreases, the content of unmelted polymer increases, but the peak melting temperature of the unmelted polymer decreases. On cooling, crystallization of the melted polymer occurs immediately, so that it does not have sufficient time to make the chain structure more ordered. In such a case, the polymer has lower melting temperature.

For isothermal crystallization having the same T_s (Fig. 10), with increasing of the T_c , the hightemperature peak remains almost the same magnitude, but the peak melt temperature of both peaks increases. This is because the melted portion can crystallize more perfectly at high crystallization temperatures, producing an ordered crystal structure having a higher melting temperature. Meanwhile, the seed polymer can achieve a more ordered structure (annealing) at a higher temperature, so the melting temperature of the seed polymer is also shifted to a higher temperature.

CONCLUSION

The effect of self-nucleation on the crystallization and melting behavior of isotactic polypropylene and low ethylene content propylene-ethylene copolymers were investigated. It was found that the crystallization temperature was shifted, depending on the preselected temperature, T_s , at which the polymer was partially melted, suggesting that self-nucleation can enhance the crystallization. The crystallization kinetics were studied using the Avrami equation. The crystallization temperature and crystallization rate increased as T_s decreased, and the Avrami exponent, n, decrease. The chain-fold surface free energy, σ_e , was calculated from the Lauritzen-Hoffman nucleation theory, and it decreased for the self-nucleated samples. A high-temperature melting peak appears for the self-nucleated sample. It increases in magnitude as T_s decreases, and is shifted to a higher temperature with increasing crystallization temperature, T_c .

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