Kinetics of crystal growth in mixtures of isotactic polypropylene and liquid paraffin

Tetsuo Okada, Hiromu Saito and Takashi Inoue*
Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan
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We investigated the spherulite growth rate (G) in a 40/60 isotactic polypropylene (PP)/liquid paraffin (LP) mixture under a polarized microscope with a TV video recording system. The molecular weight of LP (M) was changed. Subtracting the supercooling contribution from the overall G, we obtained the chain mobility (β_g) factor, as a function of M and crystallization temperature (T_c). As T_c increased, a transition from regime III to II was found to occur. An Arrhenius plot of the β_g term showed that the activation energy in regime II is much larger than that in regime III, suggesting different diffusion modes. The β_g term in regime III was found to depend strongly on M ($\beta_g \propto M^{-1}$), indicating a mutual-diffusion mode. In contrast, the β_g term in regime II weakly depends on M, indicating a self-diffusion mode ($\beta_g \propto M^{-1/2}$).

(Keywords: polypropylene; liquid paraffin; crystal growth rate)

INTRODUCTION

The crystallization kinetics of polymer mixtures is described by the Hoffman–Lauritzen theory[1,2] and is formulated by a combination of the chain mobility (β_g) term and the secondary nucleation (or supercooling, ΔT) term[3]. Empirical studies have mainly been devoted to the ΔT term but some have considered the β_g term. In this paper, on the basis of kinetic studies on isothermal crystallization in isotactic polypropylene (PP)/liquid paraffin (LP) mixtures, we deal with the β_g term to discuss the chain diffusion mechanism near the growth front.

THEORETICAL BACKGROUND

The crystal growth process in a polymer has been described as consisting of two elementary processes; the deposition of the first stem on the growth front ('secondary nucleation process') and the attachment of subsequent stems in the chain on the crystal surface ('surface spreading process'). According to the Hoffman–Lauritzen theory, the spherulite growth rate (G) is mostly governed by the rate of secondary nucleation (i) in regime III, but by both i and the rate of surface spreading (g) in regime II[1–5]:

$$G \propto (ig)^{1/2} \qquad \text{(regime II)} \qquad (1)$$

$$G \propto i \qquad \text{(regime III)} \qquad (2)$$

where i consists of the mobility term $\beta_g(i)$ and the supercooling term [the exponential term in equation (3)] and g consists of the mobility term $\beta_g(g)$ and the chain fold term [exponential term in equation (4)]. We denote the diffusion coefficients in the surface nucleation process and the surface spreading process by D_M and D_S, respectively, and assume that $\beta_g(i)$ and $\beta_g(g)$ are proportional to D_M and D_S, respectively. Then, i and g may be given by:

$$i \propto D_M \exp\left(-\frac{KT_m^\circ}{T_c \Delta T f}\right) \qquad (3)$$

and

$$g \propto D_S \exp\left(-\frac{q}{kT_c}\right) \qquad (4)$$

$$q = (a_0 k \Delta h_f K)/2\sigma \qquad (5)$$

where K is the nucleation parameter, T_m° is the equilibrium melting temperature, T_c is the crystallization temperature, $\Delta T\ (=T_m^\circ - T_c)$ is the supercooling, f is the correction factor given by $2T_c/(T_m^\circ + T_c)$, q is the work of folding, k is the Boltzmann constant, a_0 is the width of the crystal stem, Δh_f is the heat of fusion and σ is the surface free energy of the lateral surface of lamella. From equations (1)–(4), the mobility term β_g of G is given for regime II by:

$$\beta_g \propto (D_M D_S)^{1/2} \propto G \exp\left(\frac{KT_m^\circ}{2T_c \Delta T f}\right) \exp\left(\frac{q}{2kT_c}\right) \qquad (6)$$

and for regime III by:

$$\beta_g \propto D_M \propto G \exp\left(\frac{KT_m^\circ}{T_c \Delta T f}\right) \qquad (7)$$

In the neat crystalline polymer system, it has been assumed[1,2] that there is no distinction between D_M and D_S. However, in a mixture of crystalline polymer and diluent, the situation should be different. This may be due to the exclusion of diluent polymer from the crystal growth front. The diffusion in the secondary nucleation should be controlled by two competing rate processes: the attachment of crystalline polymer onto the crystal

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*To whom correspondence should be addressed

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surface and the exclusion of diluent from the surface. This competitive situation could be characterized by mutual diffusion. However, surface spreading may be controlled by the rate of the 'pull-out' of residual segments in the crystalline chain from the melt near the growth front. This could be characterized by self diffusion, as in the neat system.

The mutual-diffusion coefficient in the mixture of polymer 1 and diluent 2 is given by[6]:

$$D_M \propto \left(\frac{\phi_1}{D_1^\circ/n_1}+\frac{\phi_2}{D_2^\circ}\right)^{-1}\left(\frac{1}{\phi_1 n_1}+\frac{1}{\phi_2 n_2}\right) \tag{8}$$

where ϕ is the volume fraction, D° is the diffusion coefficient of the monomer unit and n is the degree of polymerization. When n_1 is much larger than n_2 and constant, equation (8) can be rewritten as:

$$D_M \propto n_2^{-1} \tag{9}$$

The self-diffusion coefficient in the surface spreading process is given by[7]:

$$D_S \propto n_1^{-1} \tag{10}$$

From equations (6), (9) and (10), β_g in regime II is described by:

$$\beta_g \propto n_2^{-1/2} \tag{11}$$

From equations (7) and (9), β_g in regime III is given by:

$$\beta_g \propto n_2^{-1} \tag{12}$$

Note, there is a stronger n_2 dependence of β_g than in regime II.

In a neat polymer system the temperature dependence of β_g is empirically described by[1,2]:

$$\beta_g \propto \exp\left[-\frac{U}{R_g(T_c-T_\infty)}\right] \tag{13}$$

where R_g is the gas constant, U is 6285 J mol^{-1} and T_∞ is T_g-30 (where T_g is the glass transition temperature).

EXPERIMENTAL

PP was supplied by Mitsui Toatsu Chem., Inc. (J3HG: $M_w=3.5\times10^5$, $M_n=5.0\times10^4$). Liquid paraffins with various molecular weights were supplied by Chuo Kasei Co. Ltd (LP1: $M_w=338$, $M_n=333$; LP2: $M_w=358$, $M_n=351$; LP3: $M_w=382$, $M_n=375$; LP4: $M_w=435$, $M_n=427$).

PP was dissolved in LP at 200°C to prepare a 40/60 (w/w) PP/LP mixture. The mixture had low viscosity at 200°C and a thin layer specimen (~40 μm thick) was easily prepared by holding the mixture between two cover glasses.

The specimen was maintained at 200°C for 1 min, and then the melt underwent a rapid quench to a crystallization temperature by inserting a hot-stage (Linkam TH600 heating–cooling stage, Linkam Scientific Instruments Ltd) on an optical microscope stage. The time variation of the radius of the spherulite during isothermal crystallization was observed by a polarized optical microscope (Olympus BH-2) equipped with a TV video recording system.

To measure the melting point, the mixture was placed in an aluminium pan (for d.s.c.) and was isothermally crystallized for > 15 h at various crystallization temperatures. The melting point was measured by d.s.c. (910 DSC, Du Pont) at a heating rate of 20°C min^{-1}. The equilibrium melting temperature was estimated using the Hoffman–Weeks plot.

RESULTS AND DISCUSSION

The equilibrium melting temperatures of neat PP and its blends with LPs are shown in *Table 1*.

Figure 1 shows typical examples of the variation with time of the spherulite radius (R). R initially increases linearly with time and later the growth rate decreases. This non-linear growth was observed in all the mixtures studied. The spherulite growth rate (G) was obtained from the initial slope of the plot.

Figure 2 shows the temperature dependence of G in neat PP. The analysis is based on equations (6), (7) and (13). The plot consists of two straight lines. The slope

Table 1 Equilibrium melting temperature (°C) for neat PP and its blends with LPs

PP	203.5
40/60 PP/LP1	187.5
40/60 PP/LP2	188.3
40/60 PP/LP3	189.3
40/60 PP/LP4	191.7

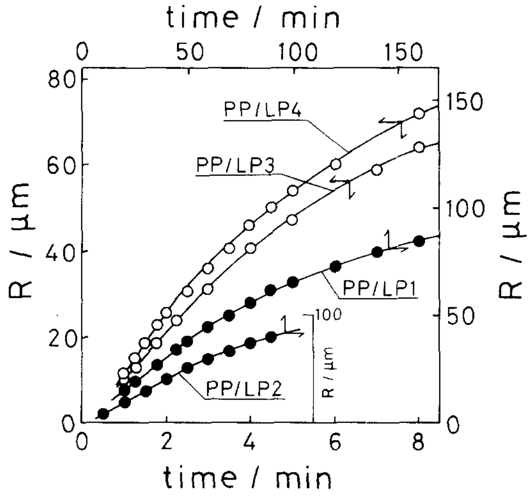

Figure 1 Typical examples of the variation with time of spherulite radius R in 40/60 PP/LP mixtures: (○) 110°C; (●) 120°C

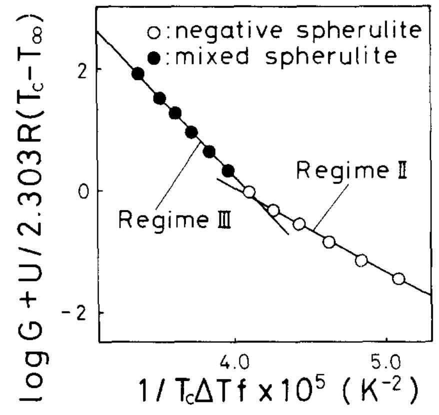

Figure 2 Log $G+U/2.303R_g(T_c-T_\infty)$ *versus* $(T_c\Delta Tf)^{-1}$ plot for neat PP ($U=6285$ J mol^{-1}; $T_\infty=T_g-30$)

increases by a factor of 2 with decreasing $(T_c\Delta Tf)^{-1}$. This suggests a regime transition as T_c decreases. The spherulites also exhibit a transition, from negative to mixed[8] birefringence. The transition is assigned to be from regime II to regime III[5,9]. From the slopes of the two straight lines (SIII and SII, SIII = SII) in *Figure 2* and equation (5), the parameters K and q can be calculated[5]: $K=2.303\mathrm{SIII}/T_m^\circ=1290\,\mathrm{K}$ and $q=50\,\mathrm{kJ\,mol^{-1}}$. Putting these values into equations (6) and (7), one obtains the mobility term β_g.

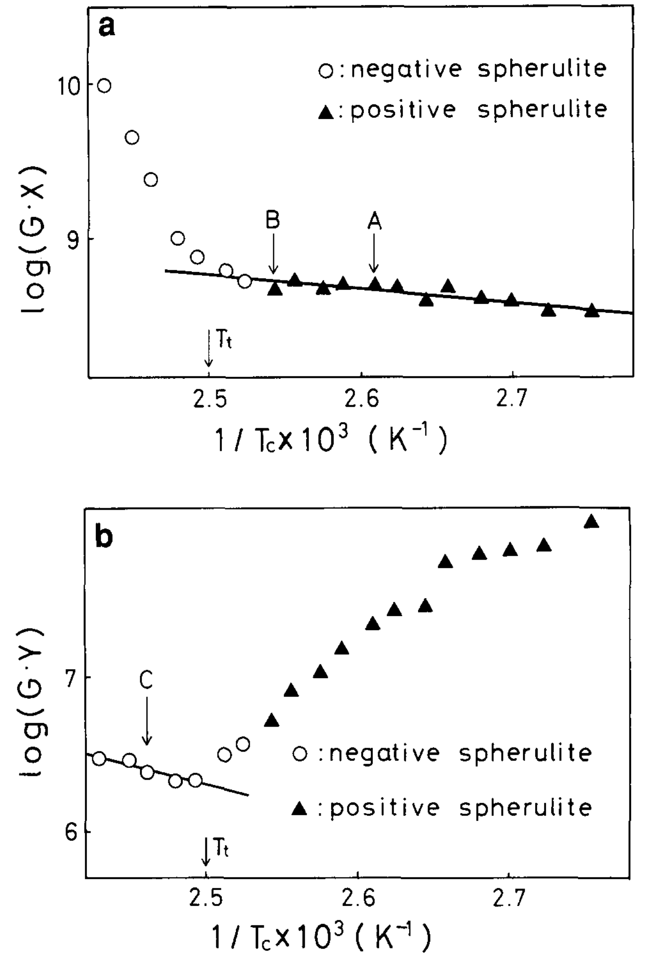

Figure 3 Arrhenius plot of the mobility factor for a 40/60 PP/LP1 mixture: (a) regime III, $X=\exp(KT_m^\circ/T_c\Delta Tf)$; (b) regime II, $Y=\exp(KT_m^\circ/2T_c\Delta Tf)\exp(q/2kT_c)$

Since the Williams–Landel–Ferry type formulation in equation (13) can be approximately given by an Arrhenius type at the T_c which is much higher than T_g, the temperature dependence of β_g in *Figure 3* is given as a function of T^{-1}. Plots for a 40/60 PP/LP1 mixture in regime III are shown in *Figure 3a*, while those in regime II are given in *Figure 3b*. In both regimes, the temperature dependence of β_g changes around a particular temperature $T_c^{-1}=T_t^{-1}=2.5\times10^{-3}\,\mathrm{K^{-1}}$. As shown in our previous paper[9], this is the regime transition temperature, i.e. regime II at $T_c>T_t$ and regime III at $T_c<T_t$. The activation energies given by the slopes of the straight lines in *Figures 3a* and *b* are 17.6 and 49.0 kJ mol^{-1}, respectively. The activation energy in regime II is much larger than that in regime III. This clearly suggests that the rate-determining diffusion mode in regime II differs from that in regime III. In other words, a two-step diffusion mechanism, which is characteristic of the crystallization of binary polymer systems, is suggested.

Figure 4a shows the LP molecular weight (M) dependence of β_g at two representative points in regime III (points A and B in *Figure 3a*; $T_c=110°\mathrm{C}$ and 120°C). The β_g term strongly depends on M. That is, the M^{-1} dependence in equation (9) is observed in regime III. This implies that β_g in regime III is controlled by the mutual-diffusion mode. In contrast, in *Figure 4b* one sees a weak M dependence of β_g at a representative point in regime II (point C in *Figure 3b*; $T_c=133°\mathrm{C}$). This suggests that the diffusion in regime II is mostly governed by the self-diffusion mode, as discussed in equation (11). These results should be taken as additional evidence for the above scenario of a two-step diffusion mode.

In an earlier paper[10], we pointed out a two-step diffusion mechanism in poly(vinylidene fluoride)/poly(methyl methacrylate) blends. This was a polymer/polymer system. In the present paper we have found a similar mechanism for a polymer/low molecular weight moiety system. Thus, the two-step diffusion mechanism seems to be rather general for crystallization in polymer/diluent systems.

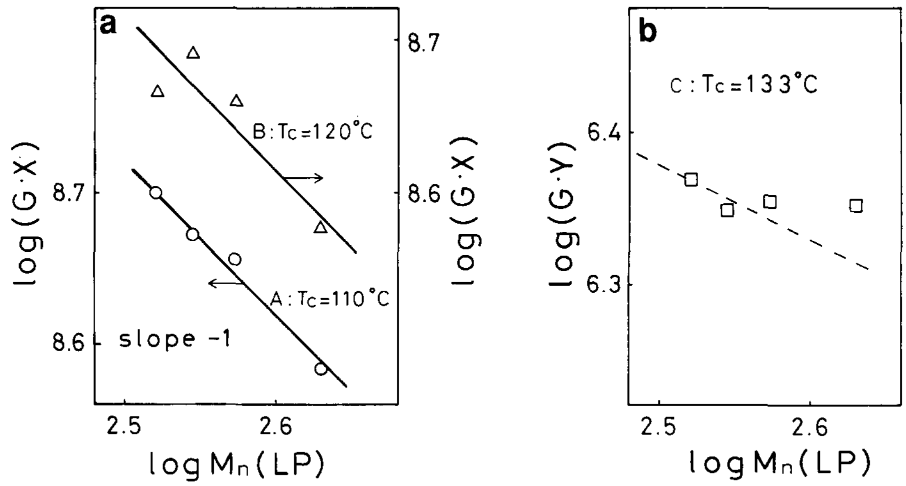

Figure 4 Mobility factor for 40/60 PP/LP mixtures as a function of molecular weigut of LP: (a) regime III, $X=\exp(KT_m^\circ/T_c\Delta Tf)$; (b) regime II, $Y=\exp(KT_m^\circ/2T_c\Delta Tf)\exp(q/2kT_c)$. The broken line is based on equation (10)

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