Nonlinear Crystal Growth in the Mixture of Isotactic Polypropylene and Liquid Paraffin

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ABSTRACT: We investigated the spherulite growth behavior in a mixture of isotactic polypropylene and liquid paraffin. For an isolated spherulite, the time variation of its radius R was found to depend on time of crystallization; $R \propto t$ at early stages and $R \propto t^{1/2}$ at late stages. The temperature dependence of growth rate in the early stage was well described by the Hoffman–Lauritzen theory, and a regime transition from II to III was found to take place as the temperature decreased, implying that the growth in the early stage is basically controlled by the secondary nucleation process as in the case of bulk crystallization ($R \propto t$). The late stage was successfully interpreted by the Cahn theory, which describes the crystal growth under a concentration gradient formed near the growth front due to the continuous segregation of the diluent.

Introduction

The crystallization kinetics in semicrystalline polymers has been successfully described by Hoffman and Lauritzen.[1,2] It implies that the growth kinetics is basically governed by the chain mobility and the quench depth. For the polymer/diluent system, if one takes into account the melting point depression and the change in mobility with dilution, the growth rate can be similarly formulated. However, from a microscopic point of view, the crystallization behavior in the polymer mixture essentially differs from that in a neat polymer system. In the mixture, the exclusion process of noncrystallizing component may contribute to the crystal growth. This contribution has not been involved in the present kinetic theory.

The crystallization kinetics in polymer/diluent systems is known to be nonlinear; i.e., the spherulite growth rate is constant at early stages, but it decreases at late stages. Keith and Padden[3,4] have suggested that the origin of the nonlinear growth is a large mobility of the diluent; i.e., when the diluent can rapidly diffuse away from a growing spherulite, the concentration gradient at the growth front is established by the exclusion[5] and the spherulite growth is governed by a diffusion process.[3,6,7] However, the late-stage kinetics in polymer/diluent system has not been investigated quantitatively.

In this paper, time variation of the radius of spherulites in the isotactic polypropylene (PP)/liquid paraffin (LP) mixture is investigated. We pay attention to the growth rate of isolated spherulites, especially to discuss the nonlinear behavior. The whole time variation of the growth rate of the isolated spherulite is quantitatively discussed in terms of the Cahn's equation involving the exclusion effect.

Experimental Section

Isotactic polypropylene (PP) was supplied by Mitsui Toatsu Chemicals, Inc. (J3HG; $M_w = 3.5 \times 10^5$, $M_n = 5.0 \times 10^4$). Liquid paraffin (LP) was supplied by Chuo Kasei Co., Ltd. (70S; $M_w = 338$, $M_n = 333$).

PP pellets were pressed at 210 °C to obtain a film specimen of neat PP (ca. 40 μm thick).

PP was dissolved in LP at 200 °C to prepare a 40/60 PP/LP mixture. The mixture had low viscosity at 200 °C, and the thin-layer specimen (ca. 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 putting in a hot-stage (Linkam TH600 heating–cooling stage, Linkam Scientific Instruments, Ltd.) set on an optical microscope stage. The time variation of the radius of PP spherulites during isothermal crystallization was observed with a polarizing optical microscope (Olympus BH-2) equipped with a TV video recording system.

For the melting point measurement, the mixture was placed in an aluminum pan (for DSC) and it was isothermally crystallized for more than 15 h at various crystallization temperatures (to carry out the "Hoffman–Weeks plot"). The melting point was measured by DSC (910 DSC, Du Pont) at a heating rate of 20 °C/min.

Results and Discussion

Nonlinear Crystal Growth. Figure 1 shows a typical micrograph of the PP/LP mixture during crystallization. Six spherulites are seen. We watched the growth rate of individual spherulites and found that the rate depended on the distribution; i.e., the rate was a function of geometrical parameters: the number of adjacent spherulites, N, and number average distance, d (in micrometers), between a spherulite and the adjacent ones, as shown in Figure 1. When a single spherulite is seen in microscopic view, we call it an "isolated spherulite" ($N = 0$ and $d = \infty$). When many spherulites are seen as shown in Figure 1 ($N = 5$ and $d = 318$), we call them "crowded spherulites".

A few examples of the d and N dependence of growth rate are shown in Figure 2. The spherulite radius, R, initially increases linearly with time, and later the growth rate decreases. This tendency is more pronounced for the shorter d and/or the larger N.

We now plot log R versus log t in Figure 3. For the isolated spherulite, R is initially proportional to time, $R \propto t^1$ (stage I), and later it changes to be proportional to the square root of time, $R \propto t^{1/2}$ (stage II). In other words, the spherulite growth rate G (dR/dt) changes from $G \propto t^0$ (constant G) to $G \propto t^{-1/2}$. On the other hand, in the case of the crowded spherulites, the initial time variation is the same as the isolated case ($G \propto t^0$), but the later stage cannot be described by a single power law.[8] This may be caused by an interference between neighboring spherulites, i.e., by a concentration gradient formed by continuous segregation of LP from a spherulite and also from adjacent spherulites. We believe that the essentials in the spher-

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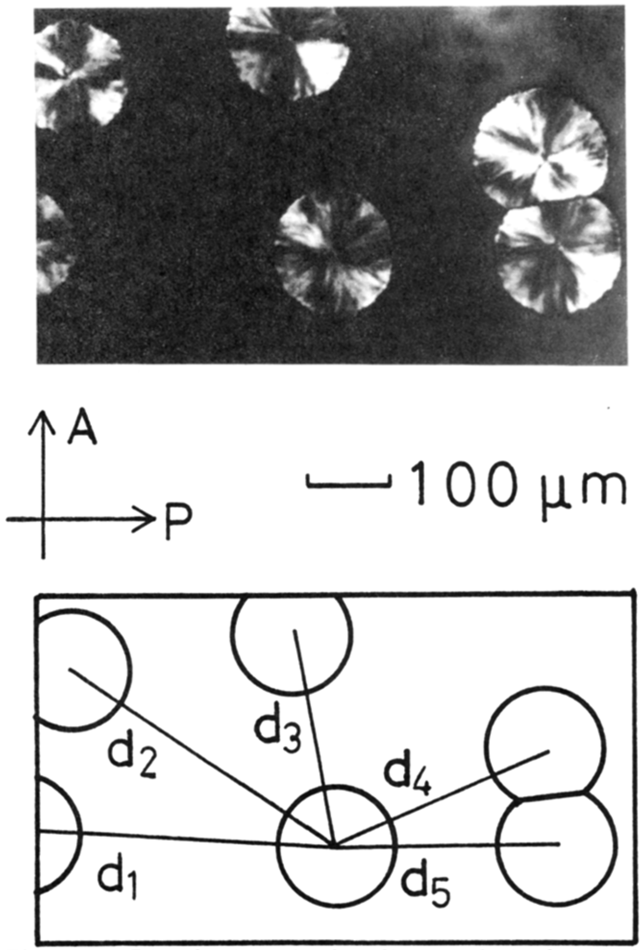

Figure 1. Distribution of spherulites: polarized optical micrograph of a 40/60 PP/LP mixture crystallized at 110 °C for 8 min (above) and the sketch (below), defining interspherulite distance d_i.

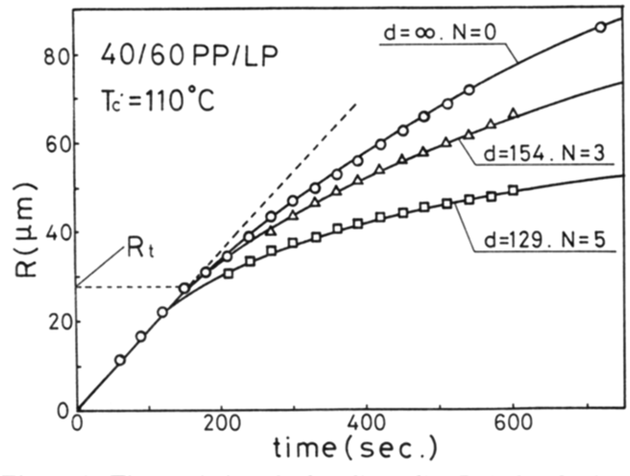

Figure 2. Time variation of spherulite radius R: isolated spherulite (○) and crowded spherulites (△,□).

ulite growth in polymer/diluent mixtures will be elucidated by watching the growth behavior of the isolated spherulite. Hence, in this paper, we consider the isolated spherulite and its growth behavior.

Early Stage (Stage I). As discussed above, the initial growth rate (G_I) does not depend on N and d but is constant. The linear growth at early stages seems to be controlled by the usual secondary nucleation process. It may be confirmed by an analysis based on the Hoffman–Lauritzen theory[1,2,9]

$$G_I \propto \exp(-Q/R_gT_c)\exp(-K/T_c\Delta Tf) \qquad (1)$$

where R_g is the gas constant, ΔT ($=T_m° - T_c$) is the supercooling, $T_m°$ is the equilibrium melting temperature, T_c is the crystallization temperature, Q is the activation energy for segmental jump, f is the correction factor given by $2T_c/(T_m° + T_c)$, and K is the parameter that depends on the crystallization regime, such as regime I (single nucleation) and regimes II and III (multiple nucleation).[10,11]

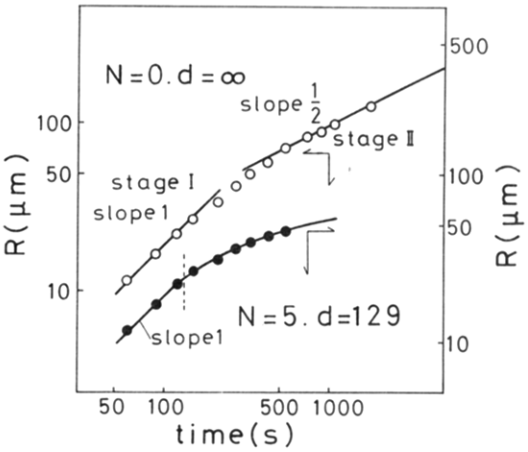

Figure 3. log R versus log t plot of the data in Figure 2: (○) isolated spherulite (N = 0, d = ∞) and (●) crowded spherulite (N = 5, d = 129).

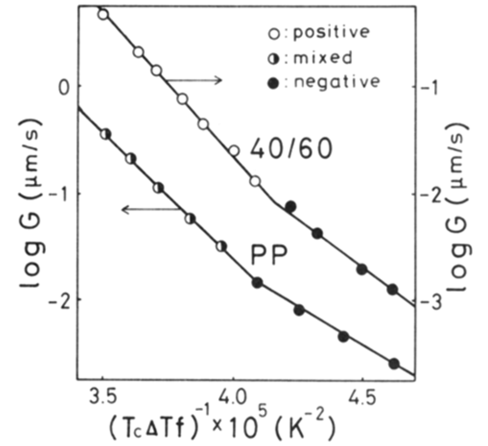

Figure 4. log G versus $(T_c\Delta Tf)^{-1}$ plot for the 40/60 PP/LP mixture and neat PP.

The results of kinetic analysis are shown in Figure 4. The equilibrium melting temperatures used are 187.5 °C in a 40/60 PP/LP mixture and 203.5 °C in neat PP, being estimated by the Hoffman–Weeks plot in Figure 5.[12] The log G versus $(T_c\Delta Tf)^{-1}$ plot for the PP/LP mixture consists of two straight lines, suggesting a regime transition as the crystallization temperature decreases. The spherulites also exhibit a transition, from negative to positive birefringence.[13] Similar results are seen in neat PP. Thus, the transition in the mixture seems to be from regime II to regime III, as has been discussed for neat PP by Clark et al.[14] Anyway, these results suggest that initial spherulite growth in the mixture is controlled by the secondary nucleation process.

Late Stage (Stage II). As shown in Figures 2 and 3, as the crystallization proceeds, the growth rate starts to slow down, from $G \propto t^0$ to $G \propto t^{-1/2}$. The transition from $G \propto t^0$ to $G \propto t^{-1/2}$ has been suggested by Cahn.[15,16] He formulated the growth kinetics governed by a diffusion process under a concentration gradient formed near the

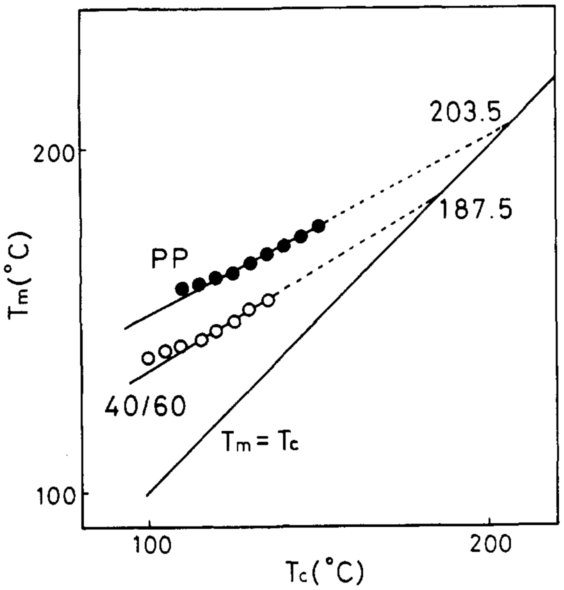

Figure 5. Hoffman-Weeks plot in a 40/60 mixture and neat PP.

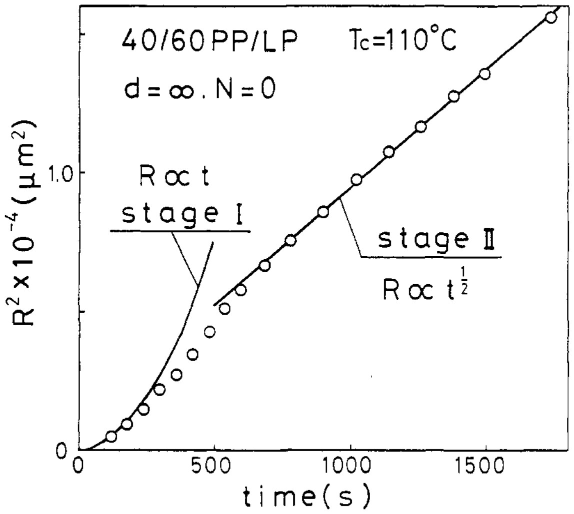

Figure 6. R^2 versus t plot to analyze the kinetics in stage II.

growth front due to the continuous segregation of diluent

$$dR/dt = [(\phi_\infty - \phi_e)D/\Phi]/(R_t + R) \tag{2}$$

$$R_t = D\phi_e/(\beta\Phi) \tag{3}$$

where ϕ_∞ is the volume fraction of the crystal component at a point far from the growth front, ϕ_e is the equilibrium volume fraction at the growth front, Φ is the volume fraction of the crystal component in the solid ($\Phi \gg \phi_e$), D is the diffusion coefficient, β is the surface kinetic coefficient, and R_t is the crossover radius at which the time variation of R begins to change from $R \propto t$ to $R \propto t^{1/2}$. Note that, for large R, eq 2 gives

$$R^2 = [2(\phi_\infty - \phi_e)D/\Phi]t \tag{4}$$

and it corresponds to the powder law of $R \propto t^{1/2}$.

The proportional factor, U [$\equiv 2(\phi_\infty - \phi_e)D/\Phi$], in eq 4 is empirically estimated by the slope of the straight line in R^2–t plots as typically shown in Figure 6. In Figure 7 is shown the estimated U as a function of crystallization temperature (open circles).

For small R, eq 2 yields

$$(dR/dt) = \beta(\phi_\infty - \phi_e)/\phi_e \tag{5}$$

It implies that the initial growth rate $dR/dt = G_I$ is equal to $\beta(\phi_\infty - \phi_e)/\phi_e$. Then the proportional factor, U, can be rewritten by

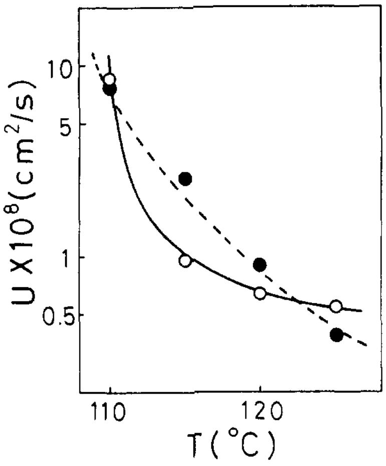

Figure 7. Temperature dependence of the U values estimated by the R^2 versus t plot (open circles) and by G_I and R_t (closed circles).

$$U = 2R_tG_I \tag{6}$$

Taking account of the crude approximation in eqs 4 and 5 and the some arbitrariness in determining R_t, the agreement between the two U values, i.e., from the late stages (open circles by the R^2 vs t plot) and from the early stages (closed circles by G_I and R_t), seems to be fairly good. One should be satisfied with the similar temperature dependences in a wide range of U. The results in Figure 7 may imply that the Cahn's theory is applicable for the crystallization kinetics of the polymer/diluent system not only in the late stages but also in the early stages. In this aspect, an interesting future subject would be to understand the phenomenological parameter β in terms of Hoffman–Lauritzen theory, on the basis of eq 5.

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References and Notes

(1) Lauritzen, J. I., Jr.; Hoffman, J. D. *J. Appl. Phys.* **1973**, *44*, 4340.
(2) Hoffman, J. D.; Frolen, L. J.; Ross, G. S.; Lauritzen, J. I., Jr. *J. Res. Natl. Bur. Stand., Sect. A* **1975**, *79*, 671.
(3) Keith, H. D.; Padden, F. J., Jr. *J. Appl. Phys.* **1964**, *35*, 1270.
(4) Keith, H. D.; Padden, F. J., Jr. *J. Appl. Phys.* **1963**, *34*, 2409.
(5) Tanaka, H.; Nishi, T. *Phys. Rev. Lett.* **1985**, *55*, 1102.
(6) Frank, F. C. *Proc. R. Soc.* **1950**, *A201*, 586.
(7) Goldenfeld, N. *J. Cryst. Growth* **1987**, *84*, 601.
(8) Keith and Padden found the (−1/2) power law for a mixture of atactic PP and isotactic PP.[3] They paid no attention to whether the spherulites were crowded or isolated. When we refer to the results in Figure 3, it is speculated that their spherulites were not so crowded.
(9) Hoffman, J. D.; Davis, G. T.; Lauritzen, J. I., Jr. *Treaties on Solid State Chemistry*; Hanny, N. B., Ed.; Plenum: New York, 1976; Vol. 3, Chapter 7.
(10) Hoffman, J. D. *Polymer* **1983**, *24*, 3.
(11) Lovinger, A. J.; Davis, D. D.; Padden, F. J., Jr. *Polymer* **1985**, *26*, 1595.
(12) The PP crystallized at a temperature range of 135–150 °C shows two endotherm peaks in a DSC thermogram. The Hoffman–Weeks plot of the low-temperature peak is reported to be to $T_m°$ = 185 °C and the high-temperature peak to $T_m°$ = 220 °C: Cox, W. W.; Duswalt, A. A. *Polym. Eng. Sci.* **1967**, *7*, 1. When the crystallization temperature is higher than 150 °C, $T_m°$ is reported to be 220 °C: Samuels, R. J. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1417. The low-temperature endotherm peak may be assigned to the melting point of cross-hatched lamella. In this article, we employ the high-temperature peak to estimate $T_m°$.
(13) The terms "positive", "negative", and "mixed" refer to the sign of birefringence of the spherulite: Padden, F. J., Jr.; Keith, H.

D. *J. Appl. Phys.* **1959**, *30*, 1479. Norton, D. R.; Keller, A. *Polymer* **1985**, *26*, 704.
(14) Clark, E. J.; Hoffman, J. D. *Macromolecules* **1984**, *17*, 878.
(15) Parker, R. L. *Solid State Phys.* **1970**, *25*, 152.
(16) Cahn, J. W. *Crystal Growth*; Peiser, H. S., Ed.; Pergamon: New York, 1967; p 681.

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Communications to the Editor

Comment on a Paper by Hurung-Rern Lee, Tsai-An Yu, and Yu-Der Lee

The recently published paper "Characterization and Dissolution Studies of a Benzophenone-Containing Organic-Soluble Polyimide", by H. R. Lee et al. (*Macromolecules* **1990**, *23* (2), 502), contains numerous paragraphs and a mathematical model previously published in our contribution (Parsonage et al. "Properties of positive resists. II. Dissolution characteristics of irradiated poly(methyl methacrylate) and poly(methyl methacrylate-*co*-maleic anhydride)", *J. Vac. Sci. Technol.* **1987**, *B5*, 538). Their mathematical model uses virtually the same definitions, the same words, the same equations, and the same parameter evaluation as our previous work—albeit with an error in one of the boundary conditions—without any statement acknowledging that their model is in fact our 1987 model.

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Liquid-Crystalline Polymer Gels. 2. Anisotropic Swelling of Poly(γ-benzyl L-glutamate) Gel Cross-Linked under a Magnetic Field

Polymer gels are usually isotropic and swell and shrink equally in all directions.[1-6] If gels of anisotropic molecular structure were prepared, anisotropic mechanical behavior will be expected.

Liquid crystals are typical anisotropic materials in which molecules are arranged along a specific direction. Polymer gels with liquid-crystalline order have been prepared by cross-linking lyotropic cholesteric liquid crystals (CLC) of poly(γ-benzyl L-glutamate) (PBLG) with several diamino compounds as cross-linkers.[7] The gel retained original CLC order when the PBLG molecules take helix conformation, but it became isotropic when it was immersed in a random-coil solvent. The CLC–isotropic change was reversible and could be repeated many times.[7]

However, since the PBLG CLC gels had a multidomain structure (texture), the CLC–isotropic change induced a volume change with a very small anisotropy. In this study, a concentrated solution of PBLG in dioxane (DOX) was cross-linked under a magnetic field to prepare polymer gels with a nematic liquid-crystalline (NLC) order. In the NLC state the polypeptide helices are known to be oriented along the magnetic field.[8-10] The NLC gel showed an anisotropic volume change when the solvent was changed from a helix-supporting one to a random-coil one. Preparation of PBLG films oriented under a magnetic field has been reported.[10] The non-cross-linked *film* showed an anisotropic swelling in benzene. The anisotropic change of cross-linked PBLG *gels* that are oriented under a magnetic field is first reported in this paper.

PBLG (a gift from Ajinomoto Co., Ltd., $M_w = 170\,000$) was dissolved in DOX (17–25 wt %) containing triethylenetetramine (TETA) or diethylene glycol bis(3-aminopropyl) ether (DGBA) as a cross-linker. The concentration of the cross-linker was 10 mol % with respect to the monomer unit of PBLG. The solution was placed in a glass tube of 2–5-mm diameter. The tube was allowed to stand under a magnetic field (21 kG) at 25 °C. The magnetic field was applied perpendicular to the glass tube. After the orientation of PBLG was equilibrated (24 h), the mixture was heated to 55–70 °C and maintained at this temperature for 7–10 days under the magnetic field. Under this condition, the helix axis of the polypeptide chain has been reported to orient along the magnetic field.[8-10] The cylindrical gels prepared were sliced into disks in which PBLG helices are aligned along the disk surface and oriented to the direction of the magnetic field. Macroscopic dimensions of the gel were measured for the disk-like gel (2–5-mm diameter).

The texture of the gel was observed for a sample prepared in a flat cell with a thickness of 0.2 mm under the magnetic field applied perpendicular to the cell. An optical microscope equipped with a cross-polarizer was used for the observation of the texture.

Microscopic pictures of the LC gels prepared from a mixture of PBLG (20 wt %) in DOX containing TETA were taken under crossed polarizer. The gel prepared

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