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## Simulations of polymer crystallization under high pressure

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**Abstract** High pressure crystallization of polypropylene was studied by means of PVT measurements and computer simulations. The isothermal crystallization behaviors were described by using a model which takes into account the effect of pressure on the temperature dependence of nucleation rate and linear growth rate. The agreement between the simulation and the experiments was seen in the tendency

that the crystallization was accelerated by the high pressure. The non-isothermal crystallization behavior was also simulated by applying a generalized Avrami equation. The simulation curves well reproduced the experimental values below relative crystallinity 0.5 and below 100 MPa.

**Key words** Simulation – crystallization – high pressure – linear growth rate – nucleation

### Introduction

Most studies of the effects of pressure on the polymer crystallization have been carried out for the understanding of the morphology, structure, and phase diagram rather than the crystallization kinetics. For example, it has been reported that the crystals of polyethylene are extended-chain crystals (ECC) under high pressure [1, 2], while the ECC is not observed for poly(ethylene terephthalate) up to 200 MPa [3]. On the other hand, there have been only a few reports on crystallization kinetics under high pressure [4, 5, 6] despite the importance of the kinetics in predicting crystallization during polymer processings. The isothermal crystallization kinetics of some polymers under high pressure has been studied, and the kinetics under pressure is generally expressed by Avrami equation [4, 5]. The border of growth regime under high pressure was determined by calculating energy parameters of linear growth by using crystallization kinetic data [6]. Application of the crystallization kinetics for simulation under high pressure

should be useful for the prediction of crystallization in polymer processings.

In the present paper, isothermal crystallization behaviors of iso-polypropylene are studied under several high pressure conditions. The data are analyzed by using the Avrami equation. The pressure effect is introduced to the melting point and the glass transition temperature of nucleation rate and linear growth rate. The non-isothermal crystallization behaviors are also analyzed by applying a generalized Avrami equation.

### Experimental

Iso-polypropylene (iPP) pellet was purchased from Chisso Petrochemical Co., Ltd. The intrinsic viscosity  $[\eta]$  of the sample was 3.0 dl/g, which was determined in decalin at 135 °C. The PVT measurements were carried out under a constant pressure for two cases, isothermal crystallization and non-isothermal crystallization, by using a PVT system (Toyo Seiki Seisakusho, Ltd.).

Here we define the relative crystallinity ( $X_c$ ) as the following equation:

$$X_c = \frac{v_0 - v}{v_0 - v_\infty} \quad (1)$$

Here  $v$ ,  $v_0$ , and  $v_\infty$  are the specific volumes at a given time, at initial state, and at the termination of the crystallization, respectively. The isothermal measurements were carried out at 140, 145, and 150 °C under 50 MPa and at 155, 160, and 165 °C under 100 MPa. For non-isothermal crystallization, the temperature was changed from 190 °C to 90 °C with a cooling rate of 2 °C/min under constant pressures of 3, 50, 100, and 150 MPa. The  $X_c$  values were also calculated with Eq. (1), using the  $v_0$  and  $v_\infty$  values corrected for the effect of thermal expansion.

## Results and discussion

### Isothermal crystallization

The specific volume abruptly decreased at 60, 300, and 600 sec at 140, 145, and 150 °C, respectively, under 50 MPa for the isothermal measurements. The volume decrease indicates the initiation of crystallization. Similar behavior was observed in the crystallization under 100 MPa. The relative crystallinities calculated from the experimental data for 50 MPa and for 100 MPa are plotted in Figs. 1 and 2, respectively. It is found that the crystallization occurs rapidly under the high pressures even at high temperature.

Fig. 1 Experimental and calculated crystallinities versus time under 0.1 and 50 MPa. Symbols represent experimental data, and the solid and broken curves represent calculated values. The experimental data for 0.1 MPa were taken from Ref. 18.

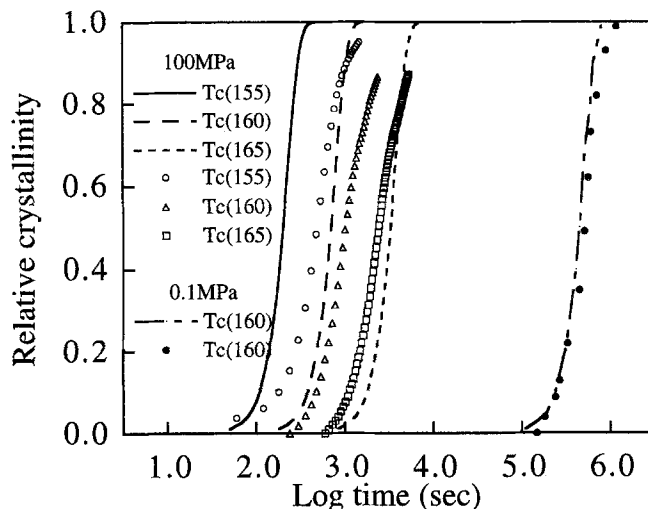
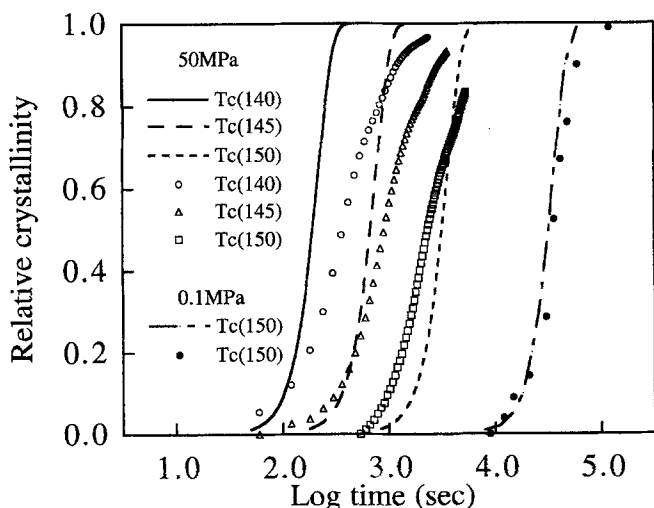


Fig. 2 Experimental and calculated crystallinities versus time under 0.1 and 100 MPa. Symbols represent experimental data, and the solid and broken curves represent calculated values. The experimental data for 0.1 MPa were taken from Ref. 18.

The high-pressure crystallization can be explained with the theories of phase transformation proposed by Avrami [7, 8]. The crystallization process of polymer melts is divided into nucleation and linear growth processes. For the isothermal crystallization of iPP, several researchers reported that the crystal is spherulite and Avrami exponent  $n = 3$ , suggesting the heterogeneous nucleation with three-dimensional growth [9–12]. Though Avrami exponent  $n$  changes under very high pressure conditions [4, 5], the exponent can be regarded as a constant below about 200 MPa, which is high enough for usual condition of polymer processings. Thus, we have carried out the all calculations assuming  $n = 3$ . According to the Avrami theory, the degree of transformation at time  $t$  for three-dimensional heterogeneous nucleation is represented by the following equation:

$$-\ln\left(1 - \frac{X_c}{X_\infty}\right) = \frac{1}{X_\infty} \frac{\rho_c}{\rho_l} K_f \bar{G}^3 \bar{N} t^n \quad (2)$$

Here  $X_\infty$  is the crystallinity at the termination of the crystallization process, which is assumed to be 1.0 for simplification.  $\bar{G}$  is the rate of linear growth,  $\bar{N}$  the number of nuclei,  $k_f$  the shape factor and  $n$  the Avrami exponent.  $\rho_c$  and  $\rho_l$  are the density of the crystalline and liquid phases, respectively. These density values changed in the range of about  $\pm 5\%$  under the conditions from 0.1 MPa to 150 MPa and 190 °C to 90 °C. However, the change of the ratio  $\rho_c/\rho_l$  is negligibly small because both  $\rho_c$  and  $\rho_l$  increase with the pressure increase and/or temperature decrease. Therefore, we assume  $\rho_c/\rho_l = 1.09$  without considering the effects of temperature and the pressure on

the  $\rho_c/\rho_1$ . The shape factor  $k_f = 4\pi/3$  is adopted in isothermal crystallization calculations. The Hoffman–Lauritzen equation is used as a general expression in the analysis of linear growth rates [13].

$$\log \dot{G} = \log \dot{G}_0 - \frac{U^*}{R(T - T_\infty)} - \frac{4T_m \sigma \sigma_e b}{kT \Delta T \Delta H_f f} \quad (3)$$

$U^*$  is the activation energy of a WLF type expression,  $T_\infty$  the WLF reference temperature, and  $\Delta T$  the difference between the crystallization temperature  $T$  and the equilibrium melting point ( $T_m$ ) of the polymer.  $b$  is the thickness of the depositing growth layer,  $\sigma$  and  $\sigma_e$  the lateral and fold surface free energies, respectively,  $\Delta H_f$  the heat of fusion per unit volume, and  $f$  a factor to correct the change in  $\Delta H_f$  with temperature (put equal to  $2T/(T_m + T)$ ). This equation consists of free energies, which cannot be directly measured, and various factors of melt polymers. For example, the values of  $\sigma$  and  $\sigma_e$  under 200 MPa were estimated from spherulite size [3]. The increase of fold surface energy  $\sigma_e$  with increasing pressure was reported. The free energy is influenced by pressure. However, it is difficult to measure these values directly under high pressure.  $\Delta H_f$  is determined with the cohesive energy of molecule, and it is influenced by an intermolecular force and injection density of molecules. According to Gibbs theory of thermodynamics, the melting point is expressed as the ratio of  $\Delta H_f$  to the entropy change  $\Delta S$ . The melting point shifts toward high temperature with increasing pressure. For semi-crystalline polymer such as iPP, the elastic property of the polymer is due to the entropy elasticity above the glass transition temperature. Therefore, the pressure mainly influences the entropy of melt polymer. On the other hand, according to free volume theory of Flory–Fox, the glass transition temperature is governed by the free volume of activation in long polymer segment. The degree of free volume below glass transition temperature is expressed by WLF equation in some polymers. The second term on the right-hand side of Eq. (3) is related to the glass transition temperature, and it is a part of the activation energy of crystallization. The glass transition temperature shifts toward high temperature with increasing pressure. The free volume of activation is influenced by pressure. However, the effects of pressure on the activation energy have not been clarified theoretically or experimentally.

Though the experimental data of growth rate well agrees to the values calculated with Hoffman–Lauritzen equation, this equation is not convenient for simulations because of its complexity. Takayanagi and Kusumoto proposed simple equations of linear growth rate and nucleation rate [14]. The equations well reproduced the experimental data for poly(ethylene succinate), natural

rubber and nylon-6. We adopt these equations to the temperature dependence of growth rate  $\dot{G}$  and of nucleus number  $\bar{N}$  as Eqs. (4) and (5), respectively [14, 15].

$$\log \dot{G} = \log \dot{G}_0 = \frac{\rho C_1 T}{(T - (T_g - 51.6))^2} - \frac{C_2 T_m}{T \Delta T} \quad (4)$$

$$\log \bar{N} = \log \bar{N}_0 - \frac{C_3 T_m}{T \Delta T} \quad (5)$$

Here  $C_1 = 900$  is the universal constant, and  $\rho = 0.125$  is the fitting parameter. The material parameters of  $\log \dot{G}_0$ ,  $\log \bar{N}_0$ ,  $C_2$ , and  $C_3$  are hardly dependent on temperature, and thus  $\log \dot{G}_0 = 7.14$ ,  $\log \bar{N}_0 = -1.74$ ,  $C_2 = 320$ , and  $C_3 = 222$  are adopted for iso-polypropylene [15].  $\Delta T$  is the difference between the crystallization temperature  $T$  and the equilibrium melting point ( $T_m$ ) of the polymer.  $T_m$  and  $T_g$  are typically 184 °C and 0 °C for iso-polypropylene [16, 17]. The second term on the right-hand side of Eq. (4) is the activation energy term of a WLF type expression, and the third term on the right-hand side of Eq. (4) is the free energy term.  $C_1$  of Eq. (4) contains a part of activation energy.  $C_2$  of Eq. (4) and  $C_3$  of Eq. (5) include the values of both the heat of fusion per unit volume and the free energies of lateral and fold surface.

These pressure effects are approximated by introducing the pressure dependence of  $T_g$  and  $T_m$  as the following equations:

$$T_m^P = \alpha_m \times P + T_m \quad (6)$$

$$T_g^P = \alpha_g \times P + T_g \quad (7)$$

Here  $P$  is a given pressure value (MPa), and  $T_m^P$  and  $T_g^P$  are the melting point and the glass transition temperature, respectively, under the pressure  $P$ .  $\alpha_m$  is the pressure shift factor, which was found to be about 0.3 °C/MPa from the experimental values of  $T_m$ . The pressure dependence of  $T_g$  is assumed to be the same as that of  $T_m$  ( $\alpha_g = \alpha_m$ ). The simulated crystallinities are shown as solid and broken curves in Figs. 1 and 2.

Figure 1 represents the simulation curves and the experimental behaviors at 140, 145 and 150 °C under 50 MPa, and at 150 °C under 0.1 MPa. The experimental points for 0.1 MPa [18] are shown in order to compare the simulation with experimental data under both atmospheric pressure and under high pressure. The simulation curve under atmospheric pressure well agreed to the experimental points, and showed that the induction time becomes longer at higher crystallization temperature. The simulation under high pressures also exhibited a tendency similar to the experimental behaviors. Figure 2 shows the simulation curves and the experimental behaviors at 155, 160 and 165 °C under 100 MPa, and at 160 °C under 0.1 MPa [18]. The simulation curves well

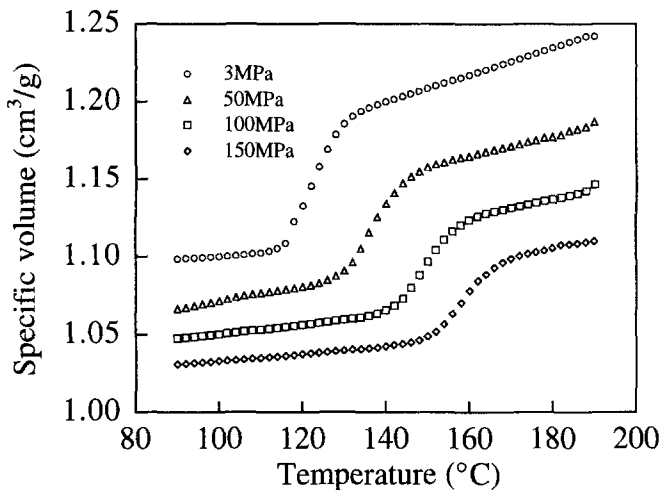


Fig. 3 Specific volume calculated from experimental data versus temperature under 3, 50, 100, and 150 MPa

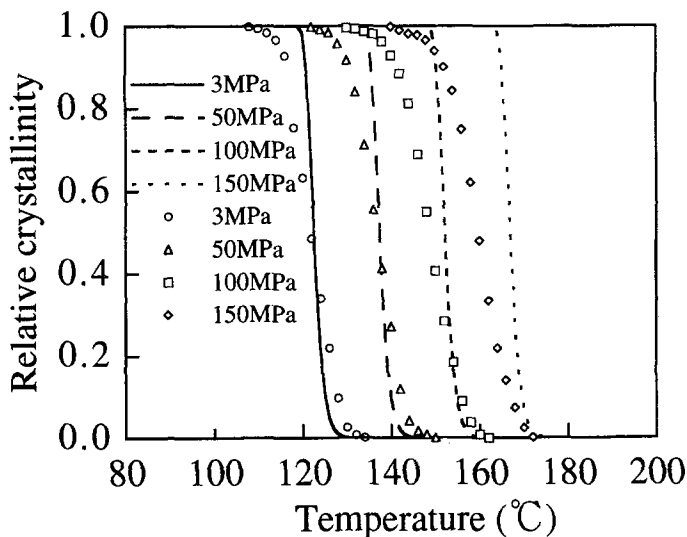


Fig. 4 Crystallinity as a function of temperature under four different pressures. Symbols represent experimental data, and the solid and broken curves represent calculated values

reproduced the experimental behavior at 0.1 MPa. The crystallization half-times under 100 MPa at 160 °C was three orders shorter than that under 0.1 MPa at the same temperature. The agreement between the simulation and the experiments is seen in the tendency that the crystallization is facilitated by the high pressure. In particular the initiation of the crystallization is precisely reproduced by the simulation.

### Non-isothermal crystallization

The non-isothermal crystallization with linear growth rate and nucleus number is theoretically explained as follows. The degree of transformation at time  $t$  for heterogeneous nucleation is represented by the following equation [15]:

$$-\ln\left(1 - \frac{X_c}{X_\infty}\right) = \frac{1}{X_\infty} \frac{\rho_c}{\rho_l} \left\{ \int_0^t \frac{d\bar{N}(\tau)}{d\tau} v(t, \tau) d\tau + \bar{N}(0) v(t, 0) \right\}, \quad (9)$$

where

$$v(t, \tau) = k_f \left[ \int_\tau^t G(u) du \right].$$

Here  $\dot{G}(u)$  is the rate of linear growth at time  $u$ ,  $\bar{N}(\tau)$  the number of nuclei at time  $\tau$ .  $\bar{N}(\tau)$  and  $\dot{G}(u)$  are functions of temperature and pressure. The effects of temperature and pressure on  $\rho_c/\rho_l$  are ignored and the Avrami exponent  $n = 3$  and shape factor  $k_f = 4\pi/3$  are adopted.

Figure 3 shows plots of the specific volume calculated from experimental data against temperature for non-isothermal crystallization on cooling from melt. The abrupt decrease in specific volume corresponds to the initiation of crystallization. The crystallization temperature, which is defined as the temperature where this rapid change of specific volume is initiated, was elevated with the pressure increase.

The crystallization curves were simulated by using a modified isothermal kinetics. Figure 4 shows relative crystallinity against temperature for the non-isothermal crystallization. The simulation curves well reproduce the experimental values below relative crystallinity 0.5 and below 100 MPa. Since the change of the temperature with time was taken into account, the non-isothermal crystallization could be described by the isothermal kinetics. The slight deviation of the curves from the experimental points at higher crystallinity is presumably due to the impingement of crystals which decreases the overall crystallization rate. The simulation curve disagreed to the experimental one for 150 MPa. There are two possible reasons for this deviation; (i) experimental error due to the difficulty in controlling a high pressure because of the limit of pressure tank in the PVT system, and (ii) overestimation of the temperature for  $T_m$  and  $T_g$  values in the high pressure region, where the pressure dependence of the  $T_m$  and  $T_g$  may deviate from the linearity.

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