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Crystallization kinetics of polypropylene under high pressure and steady shear flow

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Abstract

We investigate the simultaneous effect of pressure P and shear flow on the crystallization process of polypropylene using a modified pressure–volume–temperature measurement system that has been developed in our laboratory. We focus on the inverse of half-conversion time $1/t_{1/2}$ that is defined by the inverse of the time when the relative crystallinity of system reaches to one half. It is found that the pressure dependence of the quantity $1/t_{1/2}$ can be expressed by a shifted degree of super-cooling $\Delta T(P)$ by pressure. We also find that $1/t_{1/2}(T, P, \dot{\gamma})$ under both pressure and shear flow can be described by a sum of $1/t_{1/2}(T, P, \dot{\gamma} = 0)$ under no shear and a linearly increasing term with shear rate $\dot{\gamma}$.

Keywords: Shear flow PVT measurement system; Polypropylene; Crystallization kinetics

1. Introduction

In the 1970s it has been investigated that the crystallization of polymer is induced and accelerated by an imposed flow [1–3] and pressure [4–12]. The study of flow-induced crystallization has been practically applied to the melt spinning of fiber, film moldings and so forth [13,14]. In recent years, analyses [4,5] using a computer aided engineering (CAE) which can deal with flow induced crystallizations and experimental investigations for polymer crystallizations during injection molding processes [15,16] have been carried out in our laboratory. For these experimental studies, we have already developed two apparatuses. The first one is a shear flow thermal rheometer (SFTR) having a differential thermal analysis, which has been successfully developed using a rotational shear rheometer to perform the direct measurement of crystallization fraction under shear flow [15,16]. The second one is the shear flow direct observation system (SF-DOS) to observe crystallization processes under shear flows directly [17]. Using the SF-DOS we have been investigated the nucleation and growth rates under shear flow [17].

So far most studies of pressure effects on the polymer crystallization have been carried out to understand the pressure dependency of morphology, internal structure and phase diagram [6,7] rather than that of the crystallization kinetics. There have been some reports on crystallization kinetics under high pressures, and they are generally described by Avrami equation [5,8–10]. Only a few studies [11,12] have been reported on the crystallization kinetics under both high pressure and shear flow. Since various shear flows and high pressures are simultaneously applied to the melted polymers in industrial polymer processes, it is practically very important to study the simultaneous effect of an applied shear and pressure. Cogswell [11] revealed the influence of shear and high pressure on the viscosity by using a rotating cylinder type viscometer, but he did not discuss the crystallization kinetics. Koran et al. [12] developed a high pressure sliding plate rheometer to investigate the effect of pressure and shear on the rheological behavior of melt polymers. The design of the rheometer eliminates the spatial inhomogeneity in pressure and shear flow that occur in their developed high-pressure

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sliding plate rheometers. However, this device seems not to be suitable for experiments, which require a long steady shearing time due to its structure. They evaluated the effect of shear and high pressure on crystallization but they mainly focused on the induction time of crystallization process. In this paper, we focus on the crystallization rate to investigate the influence of both imposed shear flow and pressure on the crystallization kinetics of polypropylene. For this purpose, we develop a modified pressure–volume–temperature (PVT) measurement system that enables us to apply a high pressure and shear flow simultaneously to a sample, and we call this 'shear flow PVT measurement system (SF-PVT)'. The SF-PVT allows us to impose a shear flow on the system during a longer shearing time, but shear rates and pressure are lower than those in the literature [12]. Using the SF-PVT, we study the kinetics of isothermal crystallization process of isotactic-polypropylene under imposing several pressures and steady shear flows simultaneously. From the obtained experimental data, we derive an empirical equation for the inverse of half-conversion time $1/t_{1/2}(T, P, \dot{\gamma})$, which is defined by the inverse of the time when the relative crystallinity of system reaches to one half.

This paper is organized as follows. In Section 2, we describe the experimental equipment in detail. In Section 3, we give results and discuss the obtained experimental data, and in Section 4, we give conclusions of this study.

2. Experimental

2.1. Development of shear flow PVT measurement system

Fig. 1 shows (a) photographs and (b) schematic diagram of our newly developed PVT measurement system to apply a high pressure using a compressor and shear flow simultaneously to a sample (SF-PVT). We have modified a PVT measurement system (Toyo Seiki Seisaku-sho, Ltd.) so that the lower buffer rod can be rotated by a motor (Oriental Motor Co., Ltd.) to apply a shear flow to the sample in a furnace. The upper piston and the lower buffer rod are made of stainless steel. The bearing (NTN Co., Ltd.) is equipped in the stopper in order to rotate the buffer rod. The motor is connected to a speed controller and the shear rates can be controlled up to $1.0\ \mathrm{s}^{-1}$. Four heaters and a thermocouple are installed into the furnace. They are connected to a thermal control system (Toshiba Co., Ltd.) in order to keep the system temperature a target value with a fluctuation within ±1.0 °C. Since the change of temperature of PVT measurement system just after imposing a shear could not be observed, it is considered that there is no effect of heating by shear on the crystallization kinetics.

We have performed preliminary experiments in order to examine whether there is a leak of sample or not. Fig. 2(a) shows a photograph of a typical sample after a measurement by the SF-PVT. It is clear that we can see the burr, which indicates the leak of sample. However, the burr was stopped at a constant place, namely, at the Teflon stopper between the piston and the buffer rod. In Fig. 2(b) we show the time evolution of specific volume at 200 °C under 20 MPa and $0.5\ \mathrm{s}^{-1}$. During this experiment, the system was always at a melt state and there was no crystallization. Both the imposed pressure and shear rate in this preliminary experiment are maximum values in all the experiments of this study. If there is no leak of sample, the specific volume should be constant. As seen from Fig. 2(b), the specific volume decreased only by 1% of that at the initial time until $t = 6000$ s. Therefore, it is considered that the small mount of leak of the sample during the experiment does not influence the kinetics of crystallization. Since it is found from these preliminary experiments that the Teflon stoppers are broken and the sample starts to leak at the pressure of 25 MPa, all the experiments in this study are performed at a lower pressure and shear rate than 25 MPa and $1.0\ \mathrm{s}^{-1}$, respectively.

2.2. Sample

Isotactic-polypropylene (PP, K1014) was kindly supplied by the Chisso Petrochemical Corp., Ltd. In this sample, the weight-averaged molecular weight M_w is 225,000 and the molecular weight distribution index ($M_\mathrm{w}/M_\mathrm{n}$) is 4.48. In all the experiments in this paper, the iso-PP was used. Disk like samples (sample weight is 0.165 g) with 11 mm diameter and 2 mm thickness were made from pellets using a hot press machine and were used for the measurement using the SF-PVT.

2.3. Measurement by the SF-PVT system

In order to eliminate a thermal history, the samples were kept at 200 °C for 10 min, and then cooled to measurement temperatures around 140–150 °C. The cooling rate was about −4 °C/min. Then the samples were kept at the measurement temperatures for 5 min to stabilize the temperature. Throughout these preparation processes, a relatively low pressure (1.5 MPa) was applied to the samples (Fig. 3). Then a high pressure and shear flow were simultaneously applied to the samples, and the isothermal crystallization was monitored by the change of the specific volume $V(t)$ at a time t ($t = 0$ corresponds to the moment of the application of the high pressure and flow). The relative crystallinity $X(t)$ was calculated by

$$X(t) = (V_0 - V(t))/(V_0 - V_\infty), \qquad (1)$$

where V_0 and V_∞ are the specific volumes at $t = 0$ and at the termination time when the specific volume does not change any longer, respectively. The shears were stopped when the crystallinity reached to approximately 80% of that in the static condition in order not to

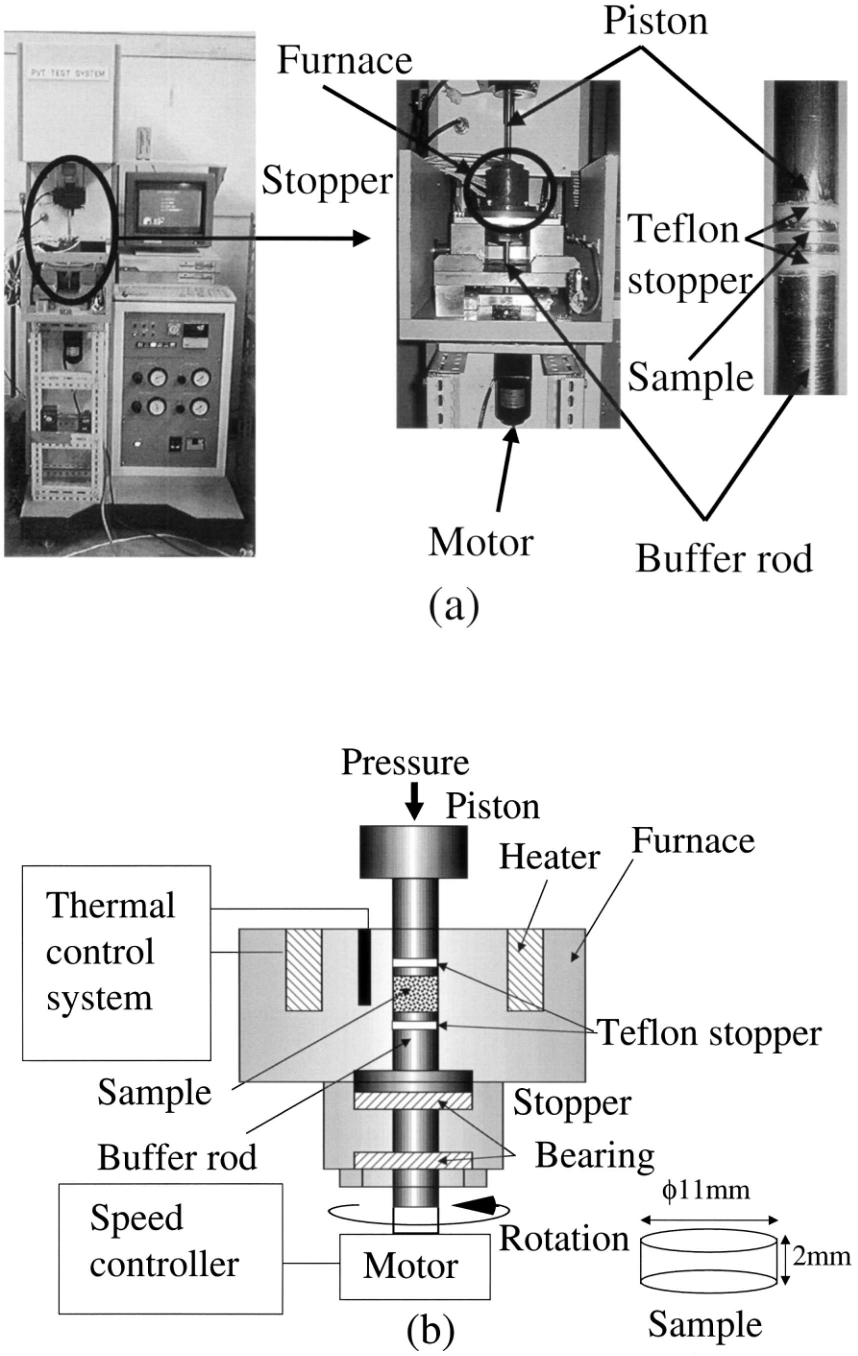

Fig. 1. (a) Photographs of the developed SF-PVT apparatus. (b) Its schematic diagram.

destroy the sample and machine. Although there is a possibility that a slip between the sample and the rod might happen at a crystallinity of around 80%, we could not confirm whether a slip took place or not in our used equipment. The shear rates used in the experiments were 0, 0.1, 0.2 and 0.5 s^{-1}, and the pressures were 5, 10, 15 and 20 MPa. Using the combination of these values, the SF-PVT measurements are carried out under constant pressures and shear rates for isothermal crystallizations.

3. Results and discussion

3.1. Time evolution of relative crystallinity

The Avrami equation [18–20] has been used to analyze the crystallization kinetics of polymers, both at atmospheric and higher pressures,

$$X(t) = 1 - \exp(-kt^n), \qquad (2)$$

where k is a crystallization rate constant and n the Avrami

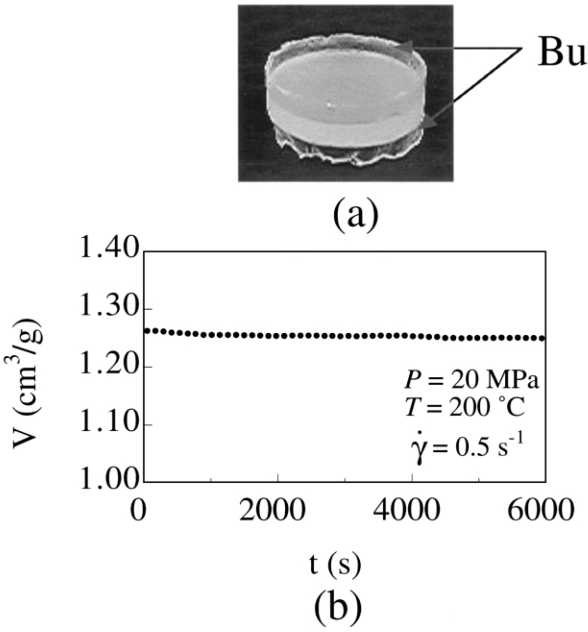

Fig. 2. (a) Sample after SF-PVT measurement. (b) Time development of specific volume at 200 °C under 20 MPa and $0.5\ \mathrm{s}^{-1}$.

exponent. In order to take into account induction time t_0 of crystallization process under shear, Masubuchi et al. [16] used the following Avrami type equation:

$$X(t) = 1 - \exp\{-k(t - t_0)^n\}. \tag{3}$$

In our present study, we also used the above Eq. (3). Graphs in Fig. 4 show time evolutions of relative crystallinity $X(t)$ for (a) various pressures in static condition, (b) various pressures under the shear rate of $0.2\ \mathrm{s}^{-1}$, and (c) various shear rates under a pressure (10 MPa) at 140 °C. In these figures, symbols denote experimental data and the lines are the best fits of Eq. (3) with $n = 3$ to the experimental data. Although we tried other integer values for n to obtain the best fit with experimental data, the case of $n = 3$ was the best among those of $n = 1$, 2, 3 and 4. Moreover, we tried another fitting procedure where the exponent n is used as a fitting parameter as well as k and t_0.

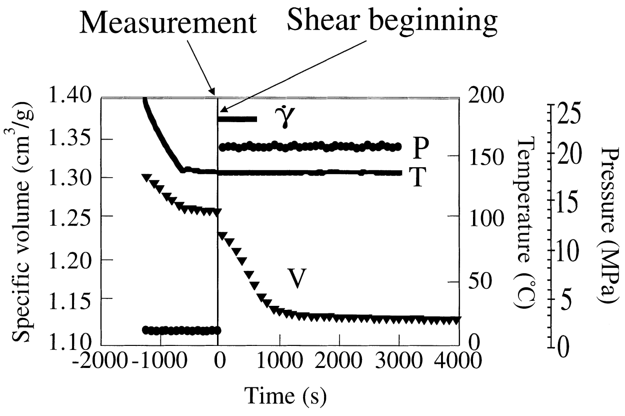

Fig. 3. Experimental procedure for crystallization under shear and pressure ($T = 140$ °C, $P = 20$ MPa, $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$).

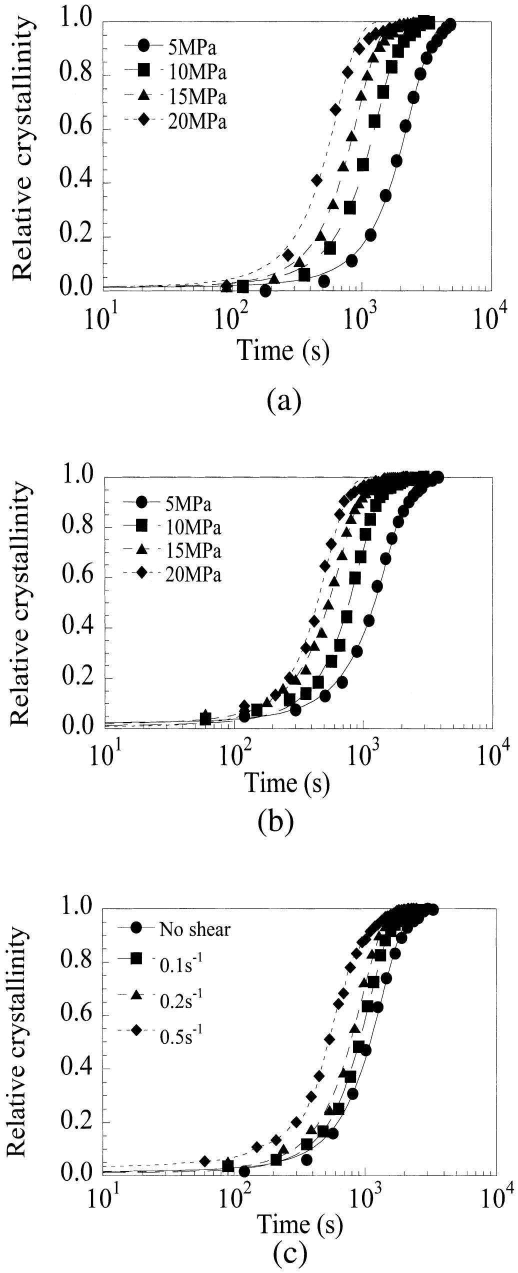

Fig. 4. Time evolutions of relative crystallinity at 140 °C (a) under various pressures, (b) under various pressures ($\dot{\gamma} = 0.2\ \mathrm{s}^{-1}$), and (c) under various shear rates ($P = 10$ MPa). The symbols represent experimental data. Solid, dashed and dotted lines denote the best fits of Eq. (3) with $n = 3$ to the experimental data.

In the analysis, the obtained exponents were distributed around $n = 3$. Although we got a more better fitting function than that of $n = 3$, the physical meaning of such a non-integer exponent n is not clear. In addition to this, if the non-integer exponent n around three is used, the other parameters k and t_0 was not so sensitive to the exponent n. Previous researchers [4,10] also reported that polypropylene crystal is spherulite and Avrami exponent $n = 3$ under pressure (below about 200 MPa), suggesting the three-dimensional growth. Therefore, in all the analysis of this paper we have used $n = 3$. Parameters in the equation were optimized by Levenberg–Marquardt non-linear fitting method [21]. It can be seen from these results that the crystallization rates were accelerated both by the pressure and the shear flow. Our results are qualitatively in good agreement with previous studies [4,16]. Ito et al. [4] measured the time evolutions of relative crystallinity of polypropylene (sample weight is 2 g) under higher pressures (50 and 100 MPa) than our study in static condition. Masubuchi et al. [16] measured the relative crystallinity of polypropylene (sample weight is about 2 g) under various shear flows (0.05–1.0 s^{-1}) and no pressure. Crystallization rates in their results are slower than those in our study (Fig. 4(b) and (c)) due to the acceleration effect of pressure on the kinetics. Koran et al. [12] studied the induction time of linear low density polyethylene under pressure and shear simultaneously. The induction times are decreased as the pressures and shear rates are increased [4,12,16]. The induction times under pressures and shear flows in our experiments are much smaller than those in the results [4,12, 16].

Under both quiescent condition and shear flow, the Avrami type Eq. (3) shown as solid, dashed and dotted lines in Fig. 4 are in good agreement with the experimental results. However, the induction times t_0 obtained by the best fits of the Avrami type Eq. (3) were very short as compared with the half-conversion time $t_{1/2}$, and sometimes became small negative values. The obtained data for the induction time were too short to discuss the pressure dependence of the induction times t_0. Therefore in the following analysis, the induction time t_0 is set to be zero. The half-conversion time $t_{1/2}$ is defined as the time period from $t = 0$ to the time when the relative crystallinity of system reaches to one half. The crystallization rate constant k in Eq. (3) can be determined from this half-conversion time $t_{1/2}$. We analyzed the inverse of half-conversion time $1/t_{1/2} \equiv (\ln 2/k)^n$ in our following investigation of crystallization kinetics, since this quantity is very convenient to characterize the speed of crystallization process.

3.2. Crystallization rate

For polypropylene, the melting temperature T_m increases slightly with pressure. The pressure dependence of the melting temperature T_m is shown in Fig. 5. The increasing rate of the melting temperature T_m due to the increase of pressure is about 0.3 °C/MPa. The equilibrium melting temperature $T^0_\mathrm{m}(P_0)$ under the pressure of the atmosphere P_0 is typically 184 °C for iso-polypropylene [22]. It should be noted that the definition of T_m and T^0_m is different. The former is the actual melting temperature and the latter is the ideal melting temperature of polypropylene solid that the crystallinity is 100%. As far as we know, there is no theoretical work to predict the pressure dependence of the equilibrium melting temperature $T^0_\mathrm{m}(P)$ by using that of actual melting temperature $T_\mathrm{m}(P)$. According to the previous work done by Ito et al. [4], we also simply assumed that the pressure dependence of the equilibrium melting temperature $T^0_\mathrm{m}(P)$ is the same with that of actual melting temperature $T_\mathrm{m}(P)$. Using this assumption, the pressure dependence of the equilibrium melting point $T^0_\mathrm{m}(P)$ can be written by the following equations,

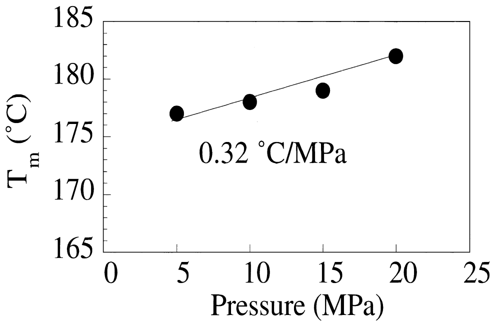

Fig. 5. Melting point T_m as a function of pressure. Heating and cooling rates were about 4 °C/min.

$$T^0_\mathrm{m}(P) = \alpha_\mathrm{m}(P - P_0) + T^0_\mathrm{m}(P_0) \cong \alpha_\mathrm{m}P + T^0_\mathrm{m}(P_0) \tag{4}$$

for $P \gg P_0$

where P is an imposed pressure (MPa), and α_m is a constant which was found to be about 0.3 °C/MPa from the experimental data of T_m (see Fig. 5). Hence the degree of super-cooling under a pressure is described by $\Delta T(P) = T^0_\mathrm{m}(P) - T$, which increases with pressure, where T is a measurement temperature.

3.3. Crystallization under pressure and no shear flow

The inverse of half-conversion time $1/t_{1/2}(T, P, 0)$ under no shear flow is plotted as a function of degree of

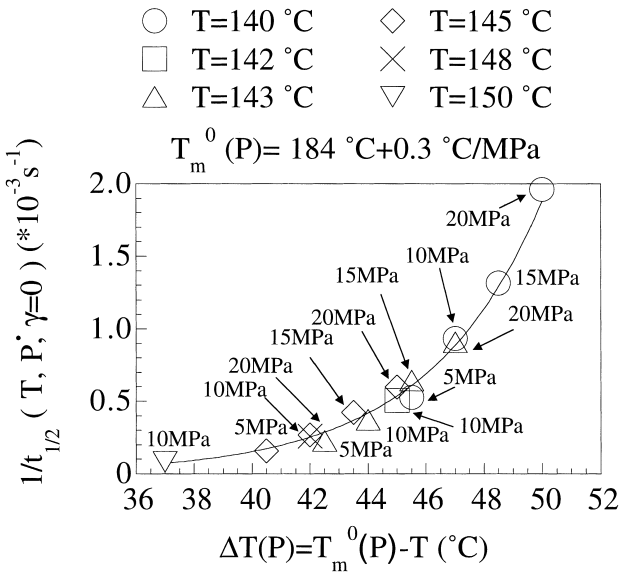

Fig. 6. Inverse of half-conversion time $1/t_{1/2}(T, P, 0)$ under no shear flow as a function of super-cooling $\Delta T(P) = T_\mathrm{m}(P) - T$, T being a measurement temperature.

super-cooling $\Delta T(P)$ in Fig. 6. As the degree of super-cooling $\Delta T(P)$ increases, $1/t_{1/2}(T,P,0)$ monotonously increases. In spite of being different pressures and temperatures, the quantity $1/t_{1/2}(T,P,0)$ can be fitted by the same master curve. This is a remarkable result. This means that the influence of pressure on the kinetics of crystallization is merely a shift of the degree of super-cooling and therefore $1/t_{1/2}(T,P,0)$ is not a function of two independent variables T and P, but a function of the degree of super-cooling $\Delta T(P)$.

3.4. Crystallization rate under pressure and shear flow

Fig. 7 shows the inverse of half-conversion time $1/t_{1/2}(T,P,\dot{\gamma})$ as a function of shear rate at various pressures and measurement temperatures. From this figure, we can see $1/t_{1/2}(T,P,\dot{\gamma})$ has a linear dependence on the shear rate, in addition, their slopes for various temperatures and pressures are almost the same. The constant slope β is 1.91×10^{-3}. This means the slope β is independent of the degree of super-cooling $\Delta T(P)$. The effect of pressure P and that of shear rate $\dot{\gamma}$ can be separated, and the inverse of half-conversion time $1/t_{1/2}(T,P,\dot{\gamma})$ is expressed by the sum of that under the static condition $1/t^0_{1/2}(\Delta T(P))$ and a linear function of shear rate,

$$1/t_{1/2}(T,P,\dot{\gamma}) \cong 1/t^0_{1/2}(\Delta T(P)) + \dot{\gamma}/\gamma_f \tag{5}$$

where $\gamma_f = 1/\beta$ and its value is about 500. We call this value γ_f the flow-induced strain, which is independent of the measurement temperature T and pressure P.

4. Conclusions

The effect of pressure and shear flow on the speed of crystallization of the isotactic polypropylene was investigated. The crystallization was enhanced by imposing a pressure and shear flow. We focused on the inverse of half-conversion time $1/t_{1/2}(T,P,\dot{\gamma})$ in order to investigate the kinetics of crystallization under high pressures and shear flows. In the case of no shear flow, the quantity $1/t_{1/2}(T,P,0)$ has an exponential dependence on the degree of super-cooling $\Delta T(P)$, and can be fitted by a master curve despite applied pressures and observed temperatures are different. This means that the influence of pressure on the kinetics of crystallization is merely a shift of the degree of super-cooling and the half-conversion time $1/t_{1/2}(T,P,0)$ is a function of $\Delta T(P)$, namely $1/t_{1/2}(T,P,0) = 1/t^0_{1/2}(\Delta T(P))$. In the systems under both high pressures and shear flows, it was found that the influence of pressure P and shear rate $\dot{\gamma}$ on the inverse of half-conversion time $1/t_{1/2}(T,P,\dot{\gamma})$ can be separated. The quantity $1/t_{1/2}(T,P,\dot{\gamma})$ under pressure and shear flow can be expressed by the sum of that under no shear, $1/t^0_{1/2}(\Delta T(P))$ and the linear function of shear rate as:

$$1/t_{1/2}(T,P,\dot{\gamma}) \cong 1/t^0_{1/2}(\Delta T(P)) + \dot{\gamma}/\gamma_f$$

in the following experimental range, $140\,^\circ\mathrm{C} \le T \le 150\,^\circ\mathrm{C}$, $0\ \mathrm{s}^{-1} \le \dot{\gamma} \le 0.5\ \mathrm{s}^{-1}$ and $5\ \mathrm{MPa} \le P \le 20\ \mathrm{MPa}$. The flow-induced strain γ_f obtained from our measurements is approximately 500 for our polypropylene sample, and is independent of the measurement temperature and pressure.

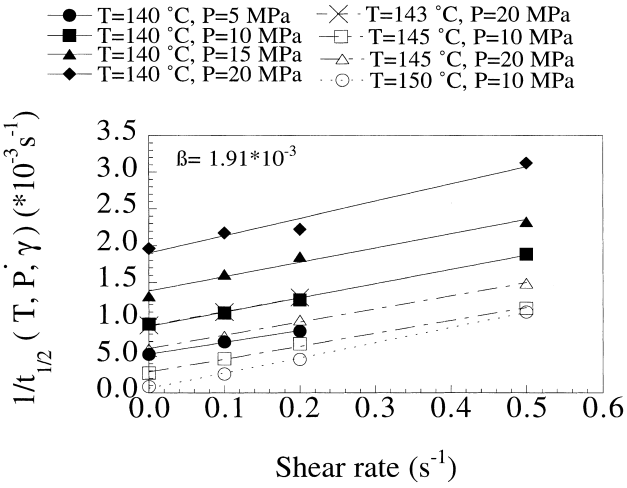

Fig. 7. Inverse of half-conversion time $1/t_{1/2}(T,P,\dot{\gamma})$ as a function of shear rate under various pressures and temperatures.

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References

[1] Krueger D, Yeh GSY. J Appl Phys 1972;43:4339.
[2] Fritzsche AK, Price FP. Polym Engng Sci 1974;14(6):401.
[3] Haas TW, Maxwell B. Polym Engng Sci 1969;9(4):225.
[4] Ito H, Tsutsumi Y, Minagawa K, Takimoto J, Koyama K. Colloid Polym Sci 1995;273(8):811.
[5] Ito H, Takimoto J, Tada K, Koyama K. Kobunshi Ronbunshu 1996;53(6):333.
[6] Hikosaka M, Kawabata H, Keller A, Rastogi S. J Macromol Sci (Phys) 1992;B31(1):87.
[7] Rastogi S, Hikosaka M, Kawabata H, Keller A. Makromol Chem Macromol Symp 1991;48/49:103.
[8] Hatakeyama T, Hashimoto T, Kanetsuna H. Colloid Polym Sci 1974;252:15.
[9] Kyotani M, Kanetsuna H. J Polym Sci Polym Phys Ed 1974;12:2331.
[10] He J, Zoller P. J Polym Sci Polym Phys 1994;32:1049.
[11] Cogswell FN. Plast Polym 1973;39.
[12] Koran F, Dealy JM. J Rheol 1999;43:1279.
[13] Ishizuka O, Koyama K. Polymer 1977;18:913.
[14] Alfonso GC, Verdona MP, Wasiak A. Polymer 1978;19:711.
[15] Nagatake W, Takahashi T, Masubuchi Y, Takimoto J, Koyama K. Polymer 2000;41:523.

[16] Masubuchi Y, Watanabe K, Nagatake W, Takimoto J, Koyama K. Polymer 2001;42:5023.
[17] Watanabe K, Nagatake W, Takahashi T, Masubuchi Y, Takimoto J, Koyama K. Polym Test 2003;22:101.
[18] Avrami M. J Chem Phys 1939;7:1103.
[19] Avrami M. J Chem Phys 1940;8:212.
[20] Avrami M. J Chem Phys 1941;9:107.
[21] Marquardt DW. J Soc Ind Appl Math 1963;11:431.
[22] Danusso F, Giannotti G. Eur Polym J 1968;4:15.