A New Crystallization Kinetics Study of Polycarbonate Under High-Pressure Carbon Dioxide and Various Crystallinization Temperatures by Using Magnetic Suspension Balance

G. Li, C.B. Park

Microcellular Plastics Manufacturing Laboratory, Department of Mechanical and Industrial Engineering, University of Toronto, Canada

ABSTRACT: A new approach for researching the effects of induced crystallization of polycarbonate (PC) by pressurized supercritical CO_2 using a magnetic suspension balance is described herein. Our study systematically investigated the effects of saturation temperature and pressure on crystallization kinetics and thermal behavior of crystallized PC. It was observed that either increasing the saturation pressure of CO_2 or the crystallization temperature was effective in promoting the mobility of PC's molecular chains. Thermal behavior and crystallization rate were affected in the following manner: a higher PC molecular chain mobility increased the degree of crystallinity, the melting temperature, and the crystal growth rate. However, the crystal growth dimension changed from a three-dimensional to a one-dimensional configuration as the isothermal crystallization temperature was raised incrementally from 140°C to 160°C to 180°C, resulting in an overall decrease in the crystallization rate. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2898–2903, 2010

Key words: magnetic suspension balance; polycarbonate; crystallization; carbon dioxide

INTRODUCTION

Beckman et al.[1] were the first to report on high-pressure CO_2-induced crystallization of amorphous polycarbonate (PC). Other researchers, such as Gross et al.[2] and Liao et al.,[3] have similarly investigated the nature of this phenomenon. It was believed that the motion of PC's frozen molecules in the amorphous state could be activated by incorporating high-pressure gas molecules, which act as a plasticizer/lubricant, into the polymer matrix. In this model, the mobility of the molecular chains was increased and crystallization was promoted by a large degree of undercooling.[1]

Kinetics studies are important to the investigation of crystallization process. Takada et al. have examined the crystallization kinetics of PP, PET, and PLA exposed to pressurized CO_2 using a high-pressure differential scanning calorimeter (DSC).[4–6] However, no studies have yet examined the crystallization rate of PC under high-pressure CO_2. Because of the extremely low crystallization rate of PC, it has been impossible to derive crystallization kinetics data for PC using conventional experimental equipment, specifically a high-pressure DSC. Moreover, the maximum allowable pressure of any commercial high-pressure DSC is limited to the order of 10 MPa.[7,8] In this work, a gravimetrical technique, based on a magnetic suspension balance (MSB), was used to investigate the crystallization kinetics in PC; crystallization was induced using high-pressure CO_2 at isothermal conditions. A supercritical CO_2 pressure range of up to 27 MPa and temperatures of up to 180°C were applied during the isothermal crystallization process. This work is mainly focused on a new approach to show the effects of induced crystallinization of PC by pressurized CO_2 and applied crystallization temperature using a MSB method.

EXPERIMENTAL

Materials

The PC was provided by Bayer Polymers (Makrolon™ 3158, $M_n = 3.1 \times 10^4$) and the carbon dioxide (CO_2) was supplied by BOC Canada (Coleman grade, 99.99% purity). All other materials were used as received.

Apparatus for the sorption of high-pressure CO_2 in PC

The sorption isotherms of CO_2 in PC were determined gravimetrically using an MSB[9] from Rubotherm GmbH. A detailed description of the apparatus and its applications can be found in the corresponding literature.[9–13] The MSB is a unique contactless weight-measurement instrument that provides precise mass change measurements of samples under controlled environments (i.e., under regulated pressure and temperature). These measurements enable quick and accurate determination of transport and state quantities. The MSB is widely used for studies of sorption, diffusion, surface tension, thermogravimetry, and density measurements under monitored conditions. It is a gravimetric measurement device that consists of two parts: the absorption chamber and the microbalance. The gravimetric sorption measurements of supercritical CO_2 in the PC samples were carried out in a closed absorption chamber that was completely thermostated and at pressures that ranged up to 28 MPa. The microbalance was always isolated from the absorption chamber under ambient conditions. The microbalance was able to detect mass to an accuracy of 0.01 mg. The weight change of the PC sample caused by the dissolution of high-pressure gas was monitored with the microbalance.

Before commencing the sorption experiment, a PC sample of ~ 0.5 g, in the form of a 3 mm thick and 13 mm diameter disk, was placed in the sample container inside the absorption chamber. The absorption chamber was then sealed, evacuated, and preheated to a designated temperature. During the experiment, the temperature of the chamber was kept constant using a Julabo TD-6 Heating Circulator. The high-pressure CO_2 was subsequently injected into the absorption chamber, and constant pressure was achieved using a syringe pump (260D, ISCO). At the first stage of CO_2 dissolution in the PC sample, the typical sorption uptake curve (due to weight gain) was observed. When the saturation condition was reached, the CO_2 gas stopped permeating into the PC sample. Maximum weight gain was attained when the weight of the PC sample leveled off. As the sorption of high-pressure CO_2 in PC took place below the melting temperature of PC ($\sim 267°C$),[1] the dissolved CO_2 in the PC matrix significantly improved the mobility of PC's molecular chains and lowered the T_g. It is believed that the mobility of the molecular chain is improved by the plasticizing effect of dissolved CO_2,[1] which induces crystallization. During crystallization, the molecular chains folded to form crystallites,[14] which expelled or squeezed out the initially dissolved CO_2 molecules in the amorphous region. The loss of the initially dissolved CO_2 molecules in the PC matrix directly resulted in a weight loss observed in the sorption uptake curve. As the crystallization rate of PC is very slow compared with the overall saturation time of CO_2 in PC, it is reasonable to assume that crystallization will not occur until the completion of CO_2 sorption in PC. At a higher degree of crystallinity, a greater weight loss was observed, which indicated that more CO_2 was being expelled.

Using the MSB apparatus to gauge the sorption of CO_2 in PC, weight gain information was derived from the sorption measurements. This data was then applied to yield an analysis of the crystallization process. The crystallization kinetics information was extracted from the sorption uptake curve in this manner.

Differential scanning calorimetry

The thermal behavior of the isothermally crystallized PC under high-pressure CO_2 was investigated by differential scanning calorimetry using a TA DSC-2910 instrument, which was operated at a scanning rate of 10°C/min under a nitrogen environment.

XRD

The crystalline pattern of the isothermally crystallized PC under high-pressure CO_2 was determined by an X-ray diffraction (XRD) measurement, performed with a Bruker AXS D8 microdiffractometer. The system was equipped with a Cu-Kα high powder point focus X-ray tube and a graphite primary monochromator. The diffraction image plate was a 2D GADDS[TM] area detector. No correction for air scattering was applied.

RESULTS AND DISCUSSION

### High-pressure CO_2 induced crystallization in PC

The high-pressure CO_2 induced crystallization phenomenon was observed during the sorption experiment. The crystalline structure of PC was detected afterward with DSC (Fig. 1) and XRD (Fig. 2). The heat of fusion adopted for the pure crystalline phase (ΔH_m^0) of PC was 26.2 cal/g.[2] The degree of crystallinity (X) of the CO_2-treated PC sample was, therefore, calculated with the following formula: Degree of crystallinity (X) % = Measured $\Delta H_m / \Delta H_m^0$. and listed in Table I. Figure 1(a) shows that under the same sorption temperature (160°C), using a higher CO_2 pressure increased the degree of crystallinity of PC from 13.61% at 10.34 MPa to 17.81% at 17.58 MPa. As the CO_2 pressure was increased, the dissolved CO_2 content in the polymer increased accordingly. It has been surmised that the significant plasticizing effect caused by the dissolved CO_2 content in
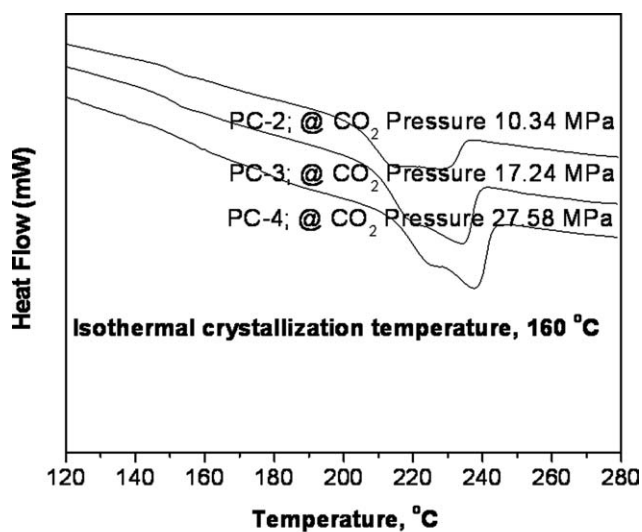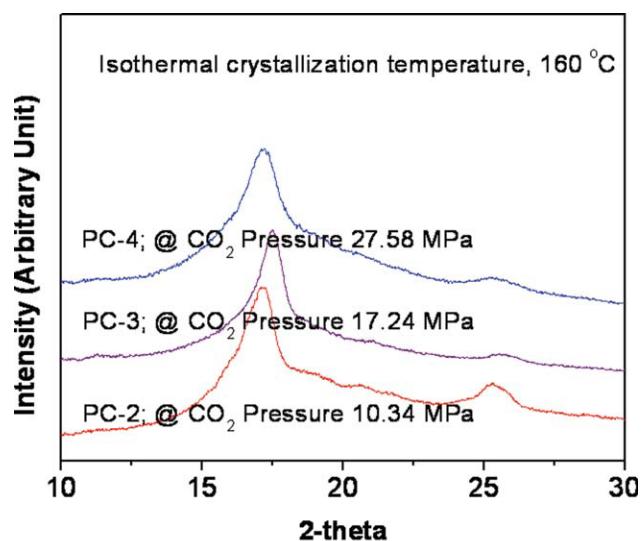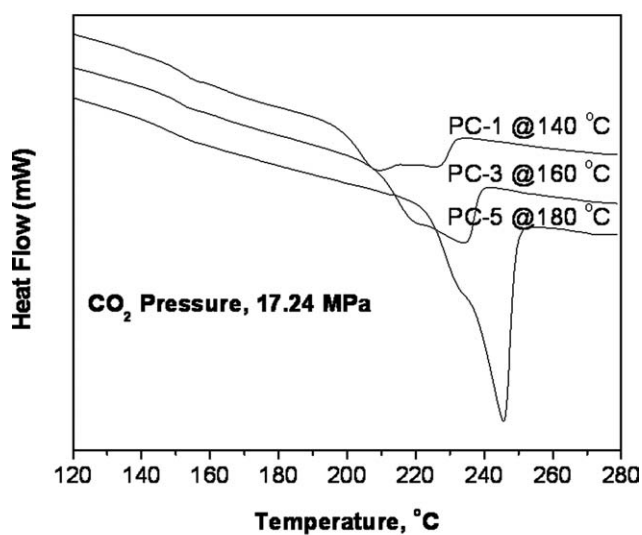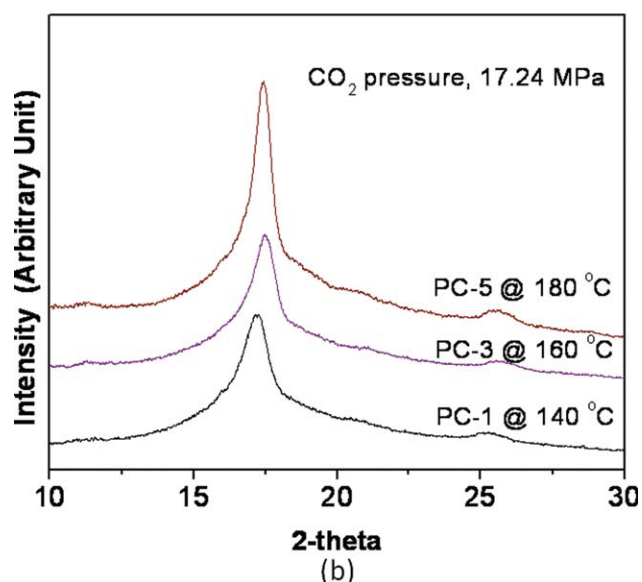
Figure 1 (a) DSC results of PC isothermally crystallized at 160°C under pressurized CO_2 at pressures from 10.34 MPa to 27.58 MPa. (b) DSC results of PC isothermally crystallized at temperatures from 140°C to 180°C under a pressurized CO_2 at 17.24 MP.

Figure 2 X-ray diffraction (XRD) results in high-pressure CO_2-treated PC samples: (a) CO_2 pressure effect. (b) Isothermal crystallization temperature effect. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the PC matrix significantly improved the mobility of the molecular chains. In turn, a higher degree of crystallinity and a more perfect crystalline structure (i.e., a higher T_m) could be achieved with a higher dissolved CO_2 content. This result was also compared with and confirmed by the XRD results, as illustrated in Figure 2(a).

To ascertain the effects of temperature on the gas-induced crystallization of PC, the sorption experiments of CO_2 in PC were conducted in isobaric conditions at three different saturation temperatures: 140, 160, and 180°C. Figure 1(b) and 2(b) provide evidence of the fact that temperature played a more significant role than CO_2 pressure in the CO_2-

induced crystallization of PC. Table I illustrates that under the same CO_2 saturation pressure (i.e., 17.24 MPa), the PC sample crystallized at 180°C exhibited

TABLE I
Degree of Crystallinity and Melting Temperature (T_m) on Crystalline PC Samples

Sample	Sorption temperature (°C)	CO_2 Pressure (MPa)	T_m (°C)	X (%)
PC-1	140	17.24	208.66	14.43
PC-2	160	10.34	215.06	13.61
PC-3	160	17.24	233.47	15.75
PC-4	160	27.58	237.56	17.81
PC-5	180	17.24	245.62	21.60

the highest degree of crystallinity (21.6%), compared with 15.75% at 160°C and 14.43% at 140°C, respectively. Furthermore, the increase of isothermal crystallization temperature from 140°C to 160°C and subsequently to 180°C led to a shift in maximum melting temperatures of crystallized PC; they reached higher temperatures of 208.66, 233.47, and 245.62°C, respectively. As with higher supercritical CO_2 pressure, higher isothermal crystallization temperature improved PC molecular chain mobility, which increased the amount of induced crystallization and produced an improved crystalline structure (i.e., a higher degree of crystallinity/T_m). It was concluded that under the given measurement conditions (temperature and pressure) in this study, molecular chain mobility was the dominant factor in the CO_2-induced crystallization of PC. With the enhanced mobility of the molecular chains (either improved by the plasticizing effect or the higher temperature), a better crystalline structure can therefore be obtained.

Double melting peaks of crystallized PC

The double melting peak behavior of isothermally crystallized PC under high-pressure CO_2 was observed from the DSC scanning results shown in Figure 1. As reported by Sohn et al.,[15] a low temperature endothermic melting peak was typically associated with the secondary crystal population; whereas a high temperature endothermic melting peak characterized the primary crystal population. The two distinct populations of crystals have different thermal stabilities and are both present in the crystallized PC.[15] Unlike Sohn et al.'s study,[15] this experiment examined PC that was isothermally crystallized under high-pressure CO_2. It was found that the isothermal crystallization temperature and the CO_2 saturation pressure affected the fraction and perfection of both the secondary and primary crystals. A higher CO_2 saturation pressure, as well as a higher isothermal crystallization temperature, increased the fraction of primary crystals in the overall crystal population, which led to a shift in the melting peaks; both peaks reflected a move toward higher temperatures.

Investigation of the crystallization kinetics

As explained in the experimental section, the crystallization kinetics data was derived from the sorption uptake curves generated by sorption experiments using an MSB. Figure 3 shows the typical uptake curve for the sorption of CO_2 in PC. Again, we observed that the overall saturation time of CO_2 in PC is much shorter than the crystallization time. We can assume with confidence that the crystallization will not occur until the completion of CO_2 sorption
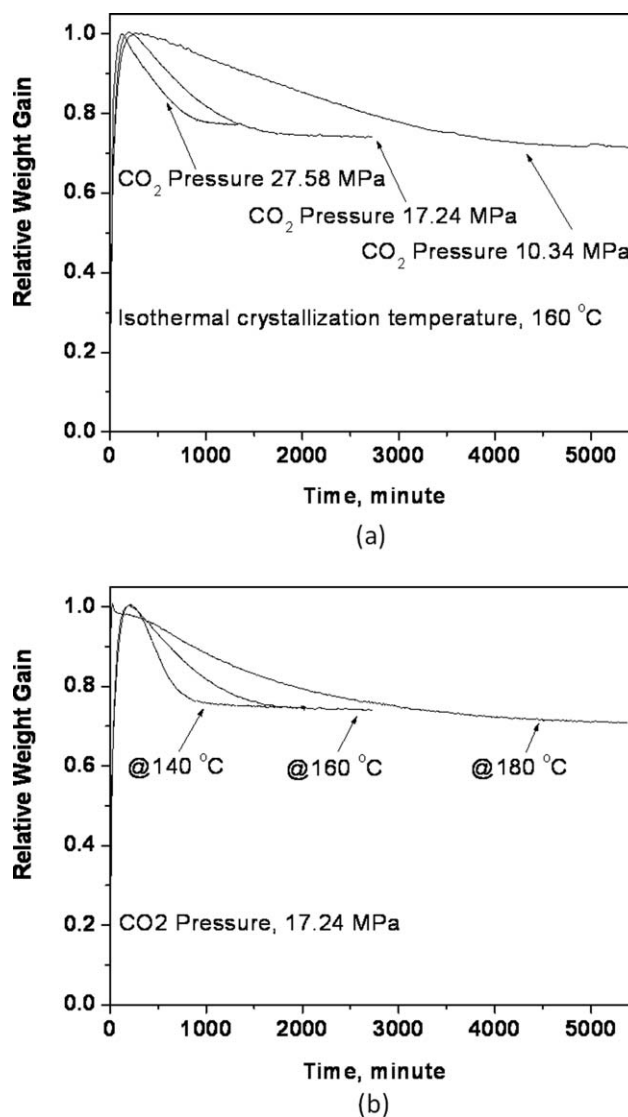

Figure 3 Sorption uptake curve measured from high-pressure CO_2 sorption in PC with an MSB (a) CO_2 pressure effect. (b) Isothermal crystallization temperature effect.

in PC. The absolute weight gain was first normalized and converted to the relative weight gain (W). From the uptake curve, it was observed that the weight gain of the PC sample increased early on after the high-pressure CO_2 was introduced into the measuring cell, and that sorption continued until saturation was achieved. At the saturation point, the maximum weight gain was achieved. Using the definition of relative weight gain, the maximum relative weight gain (W_{max}) was defined as one: $W_{max}=1$. Following saturation, a gradual weight loss was observed. The weight loss that transpired during the sorption measurements marked the onset of crystallization in the PC, which was induced by the dissolved supercritical CO_2. With the development of crystalline domains in the PC matrix during the crystallization process, the chain molecules were
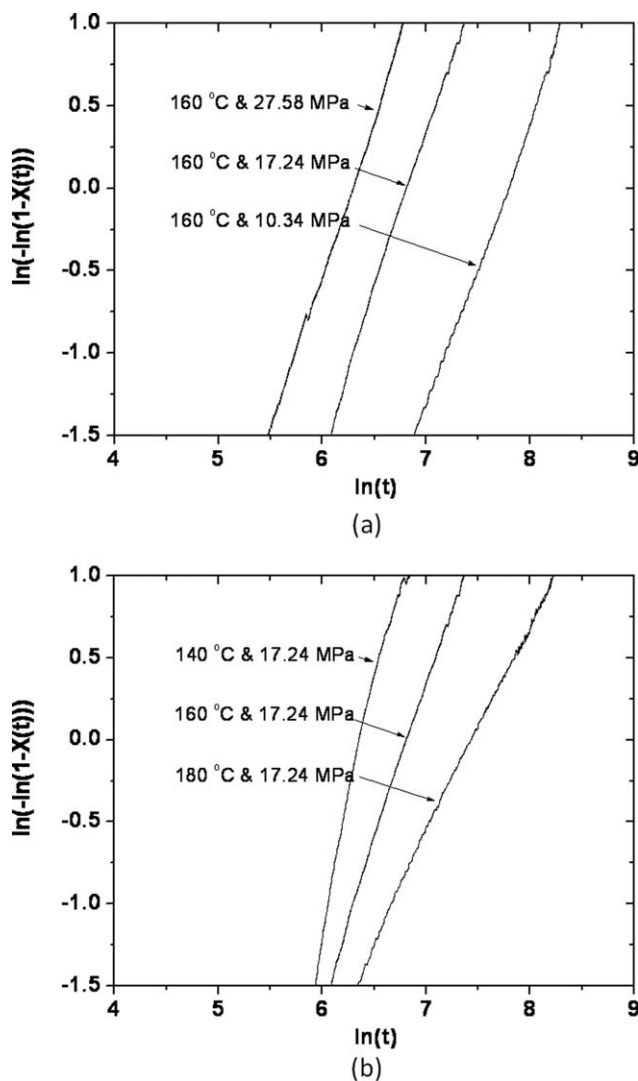
Figure 4 Avrami's plots for kinetics of pressurized CO_2 induced crystallization in PC (a) CO_2 pressure effect. (b) Isothermal crystallization temperature effect.

converted from random coil conformations to folded lamellar crystals.[14] The newly developed crystalline structure could no longer accommodate CO_2 and was, therefore, forced to expel the initially dissolved CO_2 out of the PC crystalline domain. As a result, we observed a significant weight loss in the sorption uptake curve after the relative weight gain reached W_{max}. The relative weight loss, $\Delta W(t)$, is defined in eq. (1).

$$\Delta W(t) = W_{max} - W(t) = 1 - W(t) \qquad (1)$$

Based on our data, we determined that the degree of crystallinity (X) is proportional to the relative weight loss (ΔW); a greater degree of crystallinity was obtained when larger amounts of weight were shed. In this study, the fractional crystallinity, $X_c(t)$, at time (t), was calculated from the ratio of relative weight loss at time (t) to that at infinite time (∞), as depicted in eq. (2):

$$X_c(t) = \frac{X(t)}{X_\infty} = \frac{\Delta W(t)}{\Delta W_\infty} \qquad (2)$$

Avrami's theory was applied to analyze the crystallization kinetics in PC and is shown in eq. (3):

$$-\ln(1 - X_c(t)) = kt^n \qquad (3)$$

where k is the crystallization kinetic constant, and n is the Avrami exponent, which reflects the mechanisms of crystal nucleation and growth.[6] Avrami's Equation is an accurate expression of crystallization kinetics in PCs. Using this expression for $X_c(t)$ and the data obtained in this study, Figure 4 was created to show the Avrami double-log plots of PC. The Avrami exponent (n), the half-time of crystallization $(t_{1/2})$, and the crystallization kinetic constant (k) are all summarized in Table II.

It can be observed from Figure 3(a) that at a fixed temperature (i.e., 160°C), the relative weight gain that corresponds the overall crystallization rate increased significantly as the supercritical CO_2 pressure was also raised. The results of the analysis shown in Table II indicate that $t_{1/2}$ decreased with the increase of CO_2 pressure, whereas the Avrami exponent (n) remained almost the same (1.75–1.89) for PC-2, PC-3, and PC-4. We suspect that the enhanced mobility of the molecular chains, caused by a larger amount of dissolved CO_2, brought about an increase in the crystal growth rate (k). Nevertheless, the dimensionality of crystal growth (n) caused by gas-induced crystallization in the PC remained unchanged, regardless of the CO_2 saturation pressure change, so long as the same isothermal saturation temperature was applied.

The effects of saturation temperature on crystallization rate were also considered. It was found that the highest overall crystallization rate $(t_{1/2})$ was obtained at the lowest temperature (140°C). A more detailed analysis was performed and is found in Table II. Table II shows that the actual crystal growth rate (k) increased as the temperature was increased. It was easy to recognize that the higher temperature improved the molecular chain mobility and thus

TABLE II
Avrami Exponent (n), Crystallization Rate (k), and Half-Time of Crystallization ($t_{1/2}$) of Crystalline PC Samples

Sample	Sorption temperature (°C)	CO_2 Pressure (MPa)	n	k	$t_{1/2}$ (min)
PC-1	140	17.24	2.710	3.02×10^{-8}	520.1
PC-2	160	10.34	1.751	1.23×10^{-6}	1921.3
PC-3	160	17.24	1.883	2.64×10^{-6}	755.4
PC-4	160	27.58	1.889	7.02×10^{-6}	440.2
PC-5	180	17.24	1.265	8.12×10^{-5}	1281.4

augmented the crystal growth rate. However, the Avrami exponent (n) changed according to the temperature; its values decreased as the temperature was raised: the exponent was 2.71 at 140°C and became 1.26 at 180°C. This suggested that under presumed conditions of heterogeneous nucleation, the crystal growth changed from a 3D to a 1D configuration when the temperature was increased from 140°C to 180°C. Thus, we concluded that the higher isothermal saturation temperature ultimately enhanced the crystal growth rate (k) but decreased the Avrami exponent (n). Therefore, the overall crystallization rate decreased as the temperature was increased, despite the higher mobility of the molecular chain.

CONCLUSIONS

In this article, we present the results of our investigations into inducing PC crystallization with high-pressure CO_2 at various temperatures. It is the first time that an approach based on the sorption measurements derived from an MSB for the purpose of studying gas-induced crystallization kinetics has been proposed. The crystalline structure of isothermally crystallized PC precipitated under the introduction of high-pressure CO_2; this was further explored and verified. It was observed that either a higher content of dissolved CO_2 or raising the crystallization temperature could successfully promote the increased mobility of the molecular chains. Consequently, the degree of crystallinity, the melting temperature, and the crystal growth rate were all increased. With the augmentation of isothermal crystallization temperature from 140°C to 160°C to 180°C, the Avrami exponent (n) decreased incrementally from 2.71 to 1.88 to 1.26, respectively, indicating that the crystal growth changed from a 3D to 1D configuration.

References

1. Beckman, E.; Porter, R. S. J Polym Sci Part B 1987, 25, 1511.
2. Gross, S. M.; Roberts, G. W.; Kiserow, D. J.; Desimone, J. M. Macromolecules 2000, 33, 40.
3. Liao, X.; Wang, J.; Li, G.; He, J. J Polym Sci Part B 2004, 42, 280.
4. Takada, M.; Hasegawa, S.; Ohshima, M. Polym Eng Sci 2004, 44, 186.
5. Takada, M.Ohshima, M. Polym Eng Sci 2003, 43, 479.
6. Takada, M.; Tanigaki, M.; Ohshima, M. Polym Eng Sci 2001, 41, 1938.
7. Handa, Y. P.; Zhang, Z. J Polym Sci Part B 2000, 38, 716.
8. Naguib, H. E.; Song, S. W.; Byon, Y. J.; Park, C. B. Annu Tech Conf Soc Plast Eng 2000, 58, 1867.
9. Kleinrahm, R.; Wagner, W. J Chem Thermodyn 1986, 18, 739.
10. Li, G.; Li, H.; Wang, J.; Park, C. B. Annu Tech Soc Plast Eng 2005, 63, 2332.
11. Sato, Y.; Takikawa, T.; Takishima, S.; Masuoka, H. J Supercrit Fluids 2001, 19, 187.
12. Sato, Y.; Takikawa, T.; Yamane, M. Fluid Phase Equilib 2002, 194, 847.
13. Areerat, S.; Hayata, Y.; Katsumoto, R.; Kegasawa, T.; Egami, H.; Ohshima, M. J Appl Polym Sci 2002, 86, 282.
14. Cheng, S. Z. D.; Lotz, B. Polymer 2005, 46, 8662.
15. Sohn, S.; Alizadeh, A.; Marand, H. Polymer 2000, 41, 8879.