



The effect of prepolymer crystallinity on solid-state polymerization of poly(bisphenol A carbonate)

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ARTICLE INFO

Article history:

Received 21 December 2009

Received in revised form

24 March 2010

Accepted 27 March 2010

Available online 7 April 2010

Keywords:

Solid-state polymerization

Poly(bisphenol A carbonate)

Prepolymer crystallinity

ABSTRACT

The effect of prepolymer crystallinity on the solid-state polymerization (SSP) of poly(bisphenol A carbonate) was examined using nitrogen as a sweep fluid. A low-molecular-weight prepolymer was synthesized by melt transesterification and prepolymers with different crystallinities (11.7%, 23.3%, 33.7%) were prepared with supercritical carbon dioxide treatment. SSP of the three prepolymers was then carried out at reaction temperatures in the range of 150–190 °C, with a prepolymer particle size of 75 µm and a N₂ flow rate of 1600 ml/min. The glass-transition temperature (T_g), absolute weight-average molecular weight (M_n), and percent crystallinity were measured at various times during each SSP. At each reaction temperature, SSP of the lower crystallinity prepolymer (11.7%) always resulted in higher-molecular-weight polymers, compared with the polymers synthesized using the higher crystallinity prepolymer (23.3% and 33.7%). The crystallinity of the polymers synthesized from the high crystallinity prepolymer was significantly higher than for those synthesized from the low crystallinity prepolymer. Higher crystallinity of the prepolymer and the synthesized polymers may lower the reaction rate by reducing chain-end mobility or/and by inhibiting byproduct diffusion.

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1. Introduction

Solid-state polymerization (SSP) is a potential environmentally-friendly alternative to conventional production methods for poly(bisphenol A carbonate) (BPA-PC), including interfacial polymerization of bisphenol A (BPA) and phosgene, and melt transesterification of bisphenol A (BPA) and diphenyl carbonate (DPC) [1–4]. Phosgene is an extremely toxic and highly regulated chemical, and the interfacial polymerization process generates a large amount of organic and aqueous waste. The viscosity of the polymer melts in the melt transesterification process can be extremely high (e.g. 8000–20000 poise at 280 °C depending on the molecular weight) [5]. These high viscosities cause difficulty in removing the reaction condensate (phenol), which often limits the final molecular weight of the polymer. In contrast, high-quality, high-molecular-weight BPA-PC can be obtained with SSP at relatively low

temperatures of 165–240 °C without generating organic/aqueous wastes [6–11]. In a typical SSP process, a low-molecular-weight polymer (or prepolymer), prepared by melt transesterification at low temperatures, is partially crystallized, and is then heated to temperatures between its glass-transition temperature (T_g) and its melting temperature (T_m). The reaction byproduct, phenol, is removed by flowing a sweep fluid (an inert gas [7,10] such as N₂ or scCO₂ [7,8,11]) or by applying vacuum [6]. Therefore, the high melt viscosities and high reaction temperatures associated with melt transesterification, along with the use of toxic chemicals/solvents and the generation of waste chemicals associated with interfacial polymerization, can be avoided in SSP of BPA-PC. Beyond BPA-PC, SSP has been widely used to produce various step-growth polymers including poly(butylene terephthalate) [12], Nylon 6 [13], poly(ethylene naphthalate) [14], poly(sulphur nitride) [15] and poly(ethylenedioxythiophene) [16]. Modeling works to get better insight into SSP behaviors have also been studied in industrially relevant polymer such as BPA-PC [17–19], Nylon [20] and PET [21–23].

The overall reaction rate of SSP depends on the rates of the following steps: (1) end-group diffusion in the polymer matrix; (2) the intrinsic kinetics of the chain-extension reaction; (3) internal diffusion of the byproduct from the polymer matrix to the polymer

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surface, and; (4) external diffusion of the byproduct from the polymer surface into the sweep fluid phase. Depending on prepolymer properties such as particle size, molecular weight, crystallinity, and catalyst concentration, and on the reaction conditions such as sweep fluid flow rate, temperature, and pressure, the rate of SSP and the obtainable molecular weight are controlled by one or more of these steps.

Although SSP of BPA-PC potentially has many advantages over the current polymerization methods, there are only a few fundamental studies of this process. Shi et al. measured the forward reaction constants and activation energies for the SSP of BPA-PC by carefully adjusting experimental conditions, such as particle size and sweep gas flow rate, to eliminate the influence of both internal and external phenol diffusion on reaction kinetics [8,10]. However, these studies suffered from the use of extremely high catalyst concentration (~ 700 ppm based on the weight of BPA) and overestimation of the absolute number-average molecular weight of the polymers [9]. Kim et al. studied the effect of prepolymer molecular weight on the SSP of BPA-PC using nitrogen as a sweep gas [9]. At SSP temperatures of 150–190 °C, higher-molecular-weight polymers always resulted from SSP of higher-molecular-weight prepolymer ($M_n = 3800$ g/mol), compared with the polymers obtained by SSP of the lower-molecular-weight prepolymer ($M_n = 2400$ g/mol). At comparable SSP conditions, the crystallinity and lamellar thickness of the polymers formed from the lower-molecular-weight prepolymer were larger, and this may lower the reaction rate by reducing chain-end mobility, thus effectively reducing the rate constant for the reaction of end groups.

Typically crystallization of a prepolymer is carried out prior to SSP to avoid particles sticking and agglomeration problem in the SSP reactor. Prepolymer crystallinity may have a significant effect on the reaction rate, by influencing one or more of the rate-limiting steps including end-group diffusion, internal byproduct diffusion and the intrinsic kinetics of the chain-extension reaction. Previous experimental and modeling studies suggest that crystallinity can have two contradictory effects on the SSP rate. High initial prepolymer crystallinity might increase SSP rate by increasing the concentration of reactive end groups in the amorphous phase that are rejected from the crystalline phase. On the other hand, crystallinity can decrease the SSP rate by limiting byproduct diffusion and chain-end mobility. Clearly, the negative effect of crystallinity on SSP rate can be more dominant when the particle size is large, and the reaction rate is determined by the internal diffusion step. Beyond this, published studies are inconclusive. Duh reported that SSP rate of poly(ethylene terephthalate) (PET) powder (80–100 mesh size, particle size = 0.15 mm) increased from 0.086 to 0.200 dL/g/h when the polymer crystallinity increased from 51.6 to 59.8% [24]. When the crystallinity was controlled by heat treatment, the prepolymer intrinsic viscosity increased from 0.56 dL/g to 0.82 dL/g, indicating prepolymer molecular weight increase. Thus the crystallinity effect and prepolymer molecular weight effect may be not decoupled. Medellin-Rodriguez et al. examined the SSP of PET with two prepolymers of similar molecular weights, but different crystallinities (16.87% crystallinity and M_w of 67,800 g/mol; 22.02% crystallinity and M_w of 60,800 g/mol; information on particle size was not presented) [25]. The higher crystallinity prepolymer resulted in slightly higher-molecular-weight (74,900 g/mol) after SSP than those obtained from the lower crystallinity prepolymer (73,000 g/mol). Li et al. simulated SSP rates of Nylon 6,6 and showed that higher-molecular-weight polymer can be obtained beginning with higher crystallinity prepolymer [26]. Kuran et al. reported that higher-molecular-weight BPA-PC resulted when a prepolymer with long crystallization time was solid-state polymerized [27]. However, other important prepolymer characteristics including crystallinity, particle size and prepolymer

molecular weight were not presented in their study. Through modeling of PET SSP, Kang et al. showed that high initial crystallinity retarded the SSP rate [28]. Xu et al. solid-state synthesized six poly(L-lactic acid) prepolymer samples with crystallinities ranging from 22.8 to 26.9% and reported that SSP of medium crystallinity prepolymer (25.3%) resulted in high-molecular-weight polymer (M_w of 80,000 g/mol) while SSP of high crystallinity sample (26.9%) resulted in low-molecular-weight polymer (M_w of 65,000 g/mol) [29]. However, the molecular weights of prepolymers with different crystallinities were not the same. Thus, the effects of crystallinity and prepolymer molecular weight were not decoupled.

In this paper, the effect of prepolymer crystallinity on the SSP of BPA-PC was studied using nitrogen as a sweep gas. Prepolymer with absolute weight-average molecular weight of 5500 g/mol was synthesized by melt transesterification. The prepolymer was crystallized to 11.7%, 23.3%, and 33.7% in supercritical carbon dioxide at different temperatures and periods. The prepolymer molecular weights after the crystallization were in the range of 5300–5500 g/mol, so that the effect of prepolymer molecular weight can be isolated. As the SSP of each polymer was carried out, absolute weight-average molecular weights of the polymers were measured using gel permeation chromatography with a light scattering detector. It is noted that the absolute weight-average molecular weight values are only 0.35–0.55 times the relative molecular weight values determined by comparison with polystyrene standards [9]. The polymer properties, including glass-transition temperature (T_g), melting temperature (T_m), and heat of fusion (ΔH_f), were measured, and crystallinity was estimated using differential scanning calorimetry (DSC). The end-group ratios of the polymers were determined using high-resolution (125.76 MHz) ^{13}C NMR spectroscopy [30].

2. Experimental section

2.1. Materials

Bisphenol A (BPA, >98%) was purchased from Junsei Chemical (Tokyo, Japan). Diphenyl carbonate (DPC, >99%), and lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, >99.995%) were purchased from Sigma-Aldrich (St. Louis, MO). Methanol (HPLC grade), tetrahydrofuran (THF, HPLC grade), and deionized ultrafiltered (DIUF) water were purchased from Daejung Chemicals & Metals (Siheung, Korea). Deionized ultrafiltered (DIUF) water was prepared using a Milli-Q Ultrapure water purification system with a 0.22 μm filter (Billerica, MA). BPA and DPC were recrystallized prior to use. Details of recrystallization were described previously in ref. [30]. $\text{LiOH}\cdot\text{H}_2\text{O}$ was used as received. The nitrogen (purity of 99.9999%) and carbon dioxide (purity of 99.999%) were purchased from Shinyang Sanso (Seoul, Korea). The carbon dioxide was passed through a high-pressure moisture trap filled molecular sieve and the nitrogen was passed through a moisture trap (Model 20686, Restek, Inc., Bellefonte, PA) and an oxygen trap (Model 20601, Restek, Inc., Bellefonte, PA) before introducing it to a reactor.

2.2. Prepolymer synthesis and crystallization

Prepolymer was synthesized by the melt transesterification of BPA (0.8 mol) and DPC (0.824 mol) using an aqueous solution of $\text{LiOH}\cdot\text{H}_2\text{O}$ (0.001 g/ml) as the catalyst. Eighteen ppm $\text{LiOH}\cdot\text{H}_2\text{O}$ based on the BPA weight was used. The melt polymerization was carried out in a 1200 cm^3 reactor with a nitrogen flow rate of 580 ml/min. The reactor temperature was maintained at 160 °C with 900 rpm stirring for 15 min and then 18 ppm (based on the BPA weight) of $\text{LiOH}\cdot\text{H}_2\text{O}$ was introduced into the reactor through an injection port. The reactor temperature was increased stepwise 20° until 240 °C. Before being solid-state polymerized, the

prepolymers were ground to a particle size of less than 75 μm using a mortar and a pestle (the grinder). The ground prepolymers were then crystallized using scCO_2 at various conditions. The crystallized prepolymers, PCP1, PCP2, and PCP3, were then ground to a particle size of less than 75 μm .

2.3. Solid-state polymerization

A schematic of the solid-state polymerization apparatus is shown in Fig. 1. The apparatus consists of a reactor (6), a glass coil (5), two gas purifiers (2 and 3), a flow rate controller (4), a heat bath (8), isolation valves (10), and a nitrogen source (1). The reactor (6) was a glass tube with an internal diameter of 1.3 cm and a glass frit to hold the polymer particles in position. The reactor and the glass preheater coil (5) were immersed in the heating bath (8), which contained a silicone oil (Dow Corning® 710 FLUID). The temperature of the reactor was controlled using the heat bath (8, Daepoong, Co., Gimpo, Korea) and the oil agitator (11, Hanyang Precision Co., Seoul, Korea). Each step in increasing temperature lasted 5–10 min. The temperature during SSP was controlled to within $\pm 0.5^\circ\text{C}$ of the desired temperature. The temperature was monitored using a Type K thermocouple (7, Omega Engineering, Inc., Stamford, CT) inserted in the reactor. The nitrogen was passed through a gas dehumidifier (2, Model 20686, Restek, Inc., Bellefonte, PA) and an oxygen trap (3, Model 20601, Restek, Inc., Bellefonte, PA). The nitrogen flow rate was controlled using a precision rotameter (4, Model 603, Matheson Tri-Gas®, Inc., Basking Ridge, NJ). A detailed SSP experimental procedure is given in a previous paper [9].

2.4. Characterization

The quantification of phenolic and phenyl end groups and the calculation of end-group ratios were carried out using a Bruker Avance 500 MHz Spectrometer equipped with an Oxford narrow bore magnet, a RedHat Linux host workstation, and XwinNMR software (version; 3.6). Molecular weights of the prepolymer and solid-state polymerized BPA-PC were measured using a Waters Alliance GPC System (Waters Corporation, Milford, MA) with tetrahydrofuran (THF) as a mobile phase. Note that *absolute* weight-average molecular weights, measured using a light scattering detector, are reported in this study, in contrast to number-average molecular weights *relative* to a polystyrene standard. The thermal properties of the polymers were measured using a Q1000 differential scanning calorimeter equipped with a refrigerated cooling system (RCS90), manufactured by TA Instruments (New Castle, DE).

Details on NMR, GPC, and TGA measurements were provided previously in ref. [30].

3. Results and discussion

3.1. Prepolymer crystallization in supercritical carbon dioxide

Fig. 2 shows the melting behavior of the prepolymers crystallized in supercritical carbon dioxide (scCO_2) at various conditions. CO_2 -induced T_g depression and crystallization of polymers have been observed in various polymers including poly(ether ether ketone) (PEEK) [31], BPA-PC [32,33], poly(phenylene sulfide) (PPS) [34], and poly(vinylidene fluoride) (PVDF) [35]. Table 1 lists the crystallization conditions and the prepolymer properties, including weight-average molecular weight (M_w), glass-transition temperature (T_g), onset melting temperature ($T_{m, \text{onset}}$), melting temperature (T_m), crystallinity, and end-group ratio, before and after the crystallization. No crystallinity was observed in the neat prepolymer prior to crystallization, indicating that the small amount of catalyst used in this study did not cause crystal nucleation in the polymer matrix [10,36,37]. Conventional BPA-PC crystallization is carried out by thermal annealing, by solvent-induced crystallization, or by dissolution of the prepolymer in a solvent followed by precipitation in a non-solvent. It is well known that pure BPA-PC is not easily thermally crystallized [37], which is caused by the low mobility of its rigid chains. Typically, annealing for several days at temperatures of 190°C or higher is required to impart a moderate crystallinity [38]. As a result, the thermal annealing method suffers from long crystallization period, large energy consumption, and low degree of crystallinity. The solvent-induced crystallization and the non-solvent methods are based on the use of toxic organic solvents, such as acetone and methylene chloride, which are undesirable environmentally and generate large quantities of organic wastes when applied on an industrial scale. Crystallization of BPA-PC in scCO_2 is an environmentally benign, efficient alternative to the conventional methods [32,33,39]. Supercritical carbon dioxide can plasticize amorphous regions of BPA-PC, resulting in a significant decrease in T_g (down to 75°C with scCO_2 at 80 bar [40]) and an increase in free volume of the amorphous region and in chain mobility. This leads to the nucleation and growth of a crystalline phase at relatively low temperatures. It can be seen in Table 1 that at a low temperature of

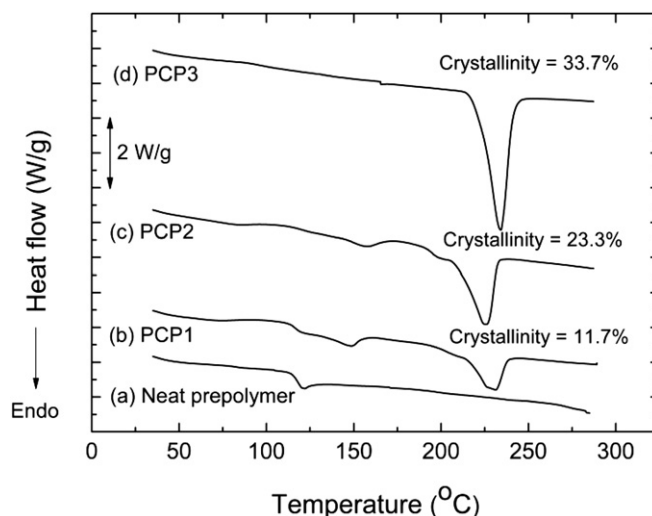


Fig. 2. Melting isotherms for prepolymers crystallized in scCO_2 at various conditions. (a) neat prepolymer, (b) prepolymer crystallized at 207 bar, 70°C and 20 min (PCP1), (c) prepolymer crystallized at 207 bar, 180°C and 1 h (PCP2), and (d) prepolymer crystallized at 207 bar, 180°C and 1 h (PCP3).

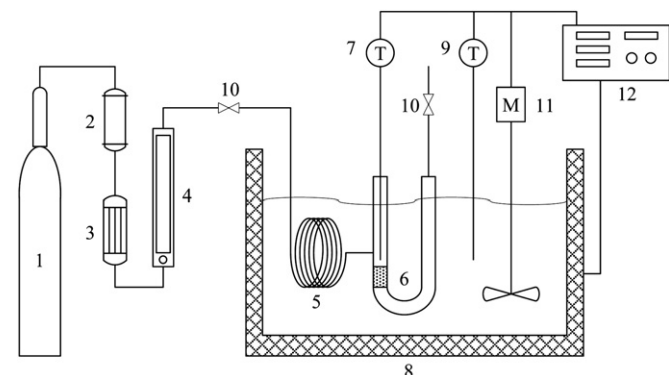


Fig. 1. Schematic of the solid-state polymerization apparatus. 1-Nitrogen source tank, 2-gas dehumidifier, 3-oxygen trap, 4-flow rate controller, 5-glass coil preheater, 6-SSP reactor, 7,9-(T)-thermocouple, 8-heat bath, 10-isolation valves, 11-mechanical stirrer, 12-temperature controller.

Table 1Absolute weight-average molecular weights (M_w), T_g , T_m , onset, T_m , crystallinity, and end-group ratio of prepolymers before and after crystallization.^a

	Crystallization conditions	M_w (g/mol)	T_g (°C)	T_m , onset (°C)	T_m (°C)	Crystallinity ^d (%)	C ₆ H ₅ /OH end-group ratio
PCP ^b	—	8700	118	—	—	0	0.85
PCP1 ^c	207 bar, 60 °C, 20 min	8700	119	197	227	11.7	0.83
PCP2 ^c	207 bar, 70 °C, 1 h	8400	120	196	226	23.3	0.84
PCP3 ^c	207 bar, 180 °C, 1 h	8500	119	215	234	33.7	0.85

^a For a typical crystallization, the prepolymer (20 g) was placed in a high-pressure vessel (50 ml). The vessel was purged with CO₂ at a pressure of 7 bar for 5 min, after which the crystallization was carried out in scCO₂.

^b PCP is the prepolymer before crystallization.

^c PCP1, PCP2 and PCP3 are the prepolymers after crystallization in scCO₂ at different conditions.

^d Crystallinity of the prepolymer was determined by measuring the heat of fusion (ΔH_f , sample) of the polymer using DSC. The crystallinity was calculated using $\text{Crystallinity} = \Delta H_{f, \text{sample}} / \Delta H_f^\circ \times 100$, where ΔH_f° is the heat of fusion of the standard state for BPA-PC (109.62 J/g).

60 °C and a very short crystallization period of 20 min, crystallinity of ~12% can be obtained with scCO₂ (PCP1). Moreover, the polymer crystallinity can be easily controlled by adjusting crystallization conditions such as temperature, pressure and crystallization period. As shown in Fig. 2 and listed in Table 1, prepolymers with higher crystallinity (23.3%, PCP2; 33.7%, PCP3) were obtained at longer crystallization times or at higher temperatures. The relatively sharp melting peak of PCP3 shown in Fig. 2 indicates that more uniform size crystals were present compared to those in PCP1 and PCP2.

As listed in Table 1, there was very little change in either M_w or T_g after the crystallization. This indicates that chain-extension reactions did not occur during crystallization. In addition, the phenolic and phenyl chain-end-group ratios of the three prepolymers are quite similar. Thus the effect of crystallinity on SSP that is examined in this study is decoupled from the effect of prepolymer molecular weight effect and from the end-group ratio effect, since essentially no chain-extension reactions and changes in the end-group ratio occurred during the crystallization step.

3.2. Prepolymer crystallinity effects

Fig. 3 shows the effect of reaction temperature on molecular weight evolution during SSP of PCP1, PCP2 and PCP3. At the lowest temperature of 150 °C, higher-molecular-weight polymers were obtained from the prepolymer with the lowest crystallinity (Fig. 3a). The molecular weight increased substantially, from 8700 to 13,600 g/mol, when this prepolymer (PCP1) was SSP'd. The molecular weight increased only marginally, from 8500 to 8900 g/mol, when the highest crystallinity prepolymer (PCP3) was solid-state polymerized. The molecular weight of polymers SSP'd using the medium crystallinity prepolymer (PCP2) were higher than those SSP'd from the highest crystallinity prepolymer (PCP3), but lower than those obtained from the lowest crystallinity prepolymer (PCP1).

At higher temperatures of 170–190 °C, the molecular weight increased sharply during the first 1–4 h of reaction and appeared to reach an asymptotic value (Fig. 3b–c). The asymptotic value increased with increasing SSP temperature. At each temperature, the molecular weights of the polymer synthesized from PCP1 are higher than those of the polymers synthesized from PCP2 and PCP3. In contrast to the reaction temperature of 150 °C, the molecular weights of the polymers SSP'd from PCP2 were almost identical to those SSP'd from PCP3. This difference will be discussed later. Fig. 3 shows that there was very little increase in the molecular weight after 3 h. The asymptotic molecular weight behavior at long SSP time is probably because the reaction temperature is not high enough to induce rapid end-group diffusion and chain-extension [9]. Stated differently, the glass-transition temperature of the polymer being SSP'd increases as the molecular weight increases, and eventually approaches the reaction temperature so closely that the kinetics of SSP becomes quite slow.

Fig. 4 is a plot of the difference between the reaction temperature and the glass-transition temperature ($T_r - T_g$) versus reaction time as

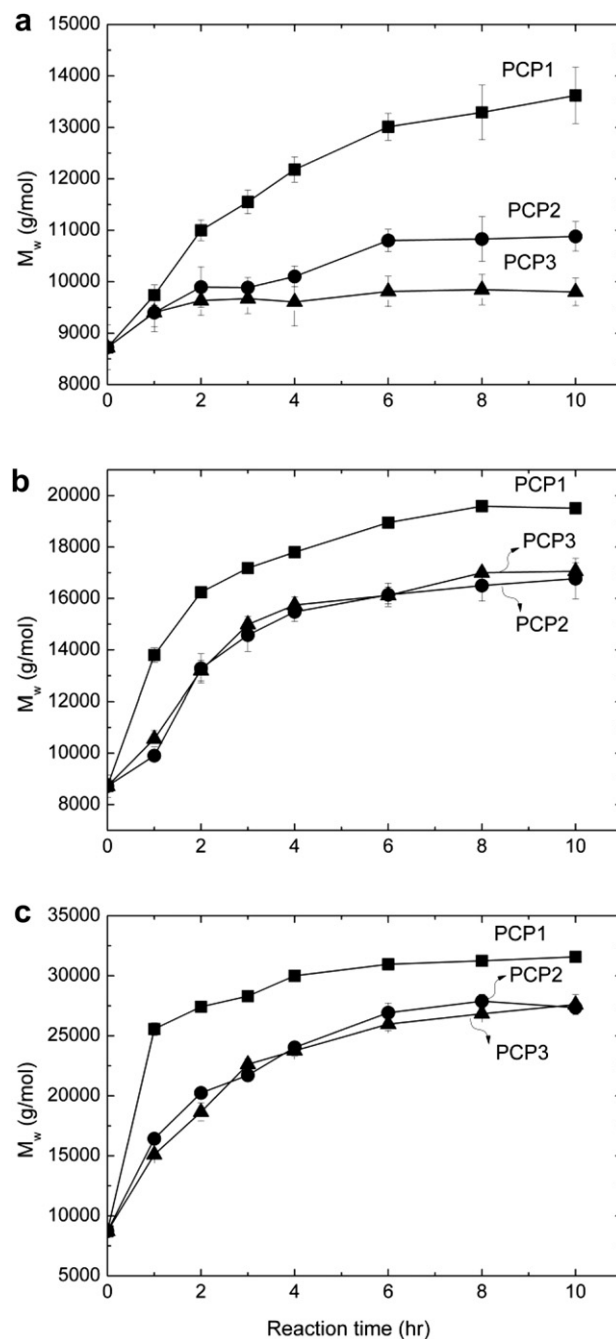


Fig. 3. Effect of temperature on molecular weight evolution during SSP of PCP1 (crystallinity = 11.7%), PCP2 (crystallinity = 23.3%), and PCP3 (crystallinity = 33.7%) at reaction temperatures of (a) 150 °C, (b) 170 °C, and (c) 190 °C.

PCP1 was solid-state polymerized. Similar ($T_r - T_g$) behaviors were observed when PCP2 and PCP3 were used (see Fig. S1 in the Supplementary Material). At a reaction temperature of 150 °C, ($T_r - T_g$) decreased slowly during the first 3 h of SSP, reaching a plateau of ~13 °C at times greater than about 3 h. When the reaction temperature was 170 °C, ($T_r - T_g$) decreased rapidly during the first hour of SSP, reaching a plateau of ~26 °C at times greater than about 2 h. At 190 °C, similar behavior was observed. The glass-transition temperature of the polymers obtained from PCP2 and PCP3 approached those of a typical, high-molecular-weight BPA-PC (~150 °C) and $T_r - T_g$ approached an asymptote of ~40 °C.

As described previously, the asymptotic molecular weights of polymers synthesized from PCP1 are greater than those synthesized from PCP2 and PCP3, at the same reaction conditions (prepolymer particle size, temperature, N₂ flow rate). The causes of the molecular weight difference can be associated with prepolymer properties including molecular weight, crystallinity and end-group ratio. As listed in Table 1, the molecular weights and end-group ratios of the prepolymers are similar. Therefore the prepolymer molecular weight and end-group ratio cannot account for the higher molecular weights obtained by SSP of the lowest crystallinity polymer.

The glass-transition temperature, the melting temperature, and the crystallinity of the polymers were measured at each reaction time to explore the cause of the molecular weight difference for the PCP1, PCP2 and PCP3 polymers. Fig. 5 shows the dependence of T_g on reaction time for a reaction temperature of 170 °C. When PCP1 was used, T_g increased rapidly during the first hour of SSP and approached an asymptotic value of ~145 °C. In contrast, T_g of the polymers SSP'd with the higher crystallinity prepolymers (PCP2 and PCP3) increased relatively slowly during the first 4 h. Similar T_g trends were observed at the reaction temperatures of 150 °C and 190 °C (see Fig. S2 in the Supplementary Material). The higher T_g values of the polymers SSP'd using PCP1, compared to those using PCP2 and PCP3, agree well with the molecular weight results.

The melting behavior of the prepolymers and the solid-state polymerized polymers at various reaction temperatures is shown in Supplementary Material (Figs. S3–S5). The polymers SSP'd using PCP1 showed two melting peaks at each reaction temperature (Figures S3). The lower-temperature melting peak became more dominant when the reaction period increased at temperatures of 150–170 °C, while larger melting peaks at lower T_m 's were observed after the first hour of SSP in the polymers synthesized at 190 °C. As shown in Figs. S2 and S3, the polymers SSP'd using PCP2 and PCP3 at

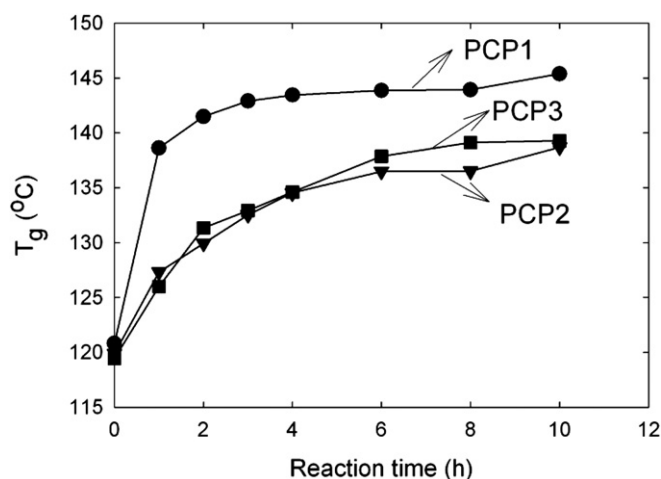


Fig. 5. Dependence of glass-transition temperature (T_g) on reaction time at a reaction temperatures of 170 °C. PCP1 (crystallinity = 11.7%), PCP2 (crystallinity = 23.3%), and PCP3 (crystallinity = 33.7%).

150 °C showed marginal changes in the melting isotherms while at 190 °C the melting peaks became sharp and the melting temperature shifted to higher temperatures as the reaction period increased. The increase of the melting peak sharpness is associated with chain extension during SSP, indicating crystallinity and lamellar thickness increase as BPA-PC chains extend via SSP [9].

The double melting peaks of BPA-PC have been observed in polymers that were crystallized via thermal annealing [38,41], or via treatment with supercritical carbon dioxide [39], as well as in the SSP [9,42]. The double melting behavior is attributed either to lamellar thickening and crystal perfection of pre-existing crystals (melting-recrystallization–remelting process), or to formation of new crystalline phases caused by secondary crystallization (melting of crystals with different stability) [43]. In order to gain a better insight into the double melting behavior during the SSP of BPA-PC, the solid-state synthesized polymers were examined using DSC with different heating rates. If the double melting behavior is caused by the melting-recrystallization–remelting process, then an increase in heating rate should shift the higher melting peak to lower temperatures because a short residence time does not provide enough time for the polymers to be recrystallized [41]. As shown in Fig. 6, the lower T_m increased from 238.5 °C to 244.8 °C and the higher T_m increased from 248.4 °C to

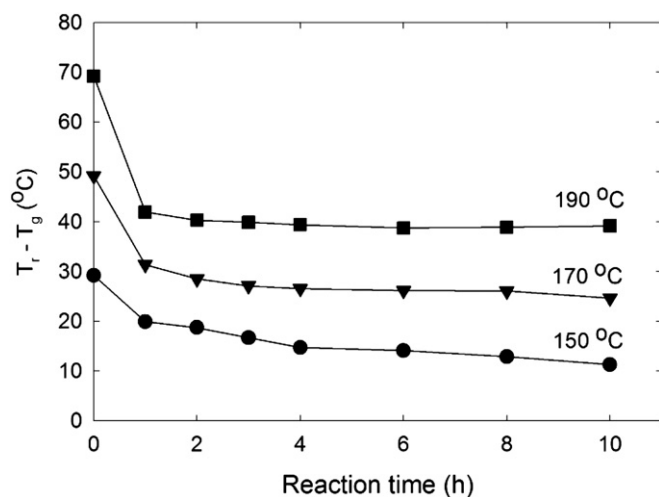


Fig. 4. Dependence of the difference between reaction temperature and glass-transition temperature ($T_r - T_g$) of the polymers SSP'd from PCP1 (crystallinity = 11.7%) on reaction time at reaction temperatures in the range 150–190 °C.

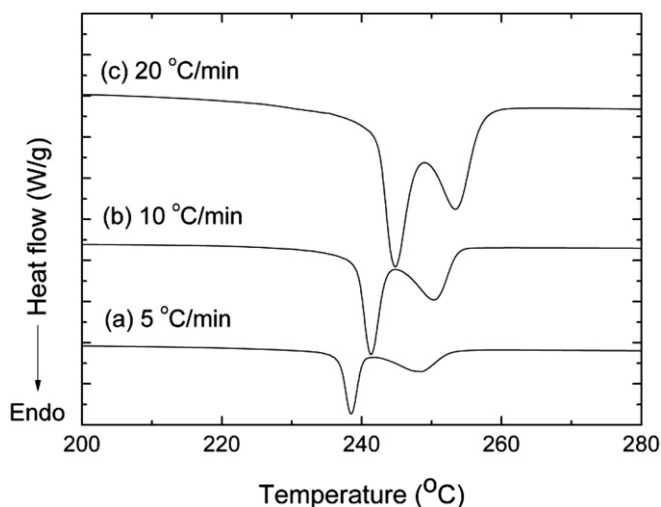


Fig. 6. Effect of heating rate on the melting behavior of SSP'd PC from PCP3 (crystallinity = 33.7%) at 150 °C for 10 h.

253.2 °C when the heating rate increased from 5 °C to 20 °C. This indicates that the double melting behavior of the SSP'd BPA-PC is due to the formation of a new crystalline phase during the reaction. Thus the thermal stabilities of the crystals are different.

Fig. 7 shows the crystallinity of the synthesized polymers as a function of reaction time. At the low temperature of 150 °C, no significant crystallinity changes were observed in the polymers after SSP (Fig. 7a). At 170 °C, the crystallinity of the polymers SSP'd using PCP1 increased from 11.7% to 26.3% while the crystallinity of the polymers SSP'd from PCP2 and PCP3 increased only marginally (Fig. 7b). The crystallinity of SSP'd PCP1 for 1 h is similar to that of

PCP2. Even in this case, further SSP of PCP1 did not mirror the crystallinity of PCP2. This may be because the higher molecular weight of the SSP'd PCP1 after 1 h (13,800 g/mol) compared to that of PCP2 (8400 g/mol) retard the crystallinity increment. At the high temperature of 190 °C, crystallinity of all the synthesized polymers increased. The crystallinity increased sharply during the first hour of SSP and rapidly reached an asymptotic value (Fig. 7c). An increase in crystallinity with an increase in SSP time has also been observed during the synthesis of BPA-PC using a disodium salt of BPA as a catalyst [6], using a prepolymer crystallized with a spray method [42], and for poly(L-lactic acid) (PLA) [29,44], poly(ethylene terephthalate) (PET) [45], and Nylon 6,6 [26]. The final crystallinity of the polymers after SSP increased in the order of polymers from PCP1 polymers < PCP2 polymers < PCP3 polymers at each reaction temperature.

The higher crystallinity of the PCP2 or PCP3 may be responsible for the fact that these prepolymers yield lower-molecular-weight polymers than those derived from PCP1. The higher crystallinity may reduce the SSP rate by inhibiting the mobility of polymer chains in the amorphous phase or/and by hindering byproduct diffusion throughout the polymer particles. Therefore, low crystallinity prepolymers are desirable when using SSP to achieve high-molecular-weight BPA-PC. Lastly, as discussed earlier, the molecular weight of the polymers from PCP2 is higher than those from PCP3 at 150 °C while the molecular weights of the polymers from PCP2 and PCP3 are quite similar at higher temperatures of 170–190 °C. This may imply that end-group diffusion and chain extension is faster in polymers synthesized from the lower crystallinity prepolymer (PCP2) at 150 °C while the difference in end-group diffusion and chain-extension rate are negligible at higher temperatures of 170–190 °C. A borderline crystallinity may exist above which SSP rate does not seem to be dependent on the prepolymer crystallinity at higher reaction temperatures. At above the borderline crystallinity, the negative effect of crystallinity on SSP rate, limitation of byproduct diffusion and chain-end mobility, may not significantly affect the SSP rate at higher reaction temperatures.

4. Conclusions

The effect of initial crystallinity on the solid-state polymerization of poly(bisphenol A carbonate) was studied at reaction temperatures in the range of 150–190 °C using prepolymers with three different crystallinities. The effect of crystallinity on SSP was decoupled from other prepolymer effects including molecular weight, end-group ratio and particle size. At a given temperature and reaction time, the molecular weights of the polymers synthesized from PCP1 (crystallinity of 11.7%) were always larger than those of the polymers synthesized from PCP2 (crystallinity of 23.3%) and PCP3 (crystallinity of 33.7%). The crystallinity of the polymers synthesized from the highest crystallinity prepolymer is always larger than those of the polymers synthesized from the lower crystallinity prepolymer. The larger crystallinity may result in decreased chain mobility, thus hindering the development of high-molecular weights.

Acknowledgement

This research was supported by the Korea Evaluation Institute of Industrial Technology funded by the Ministry Knowledge Economy.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2010.03.054.

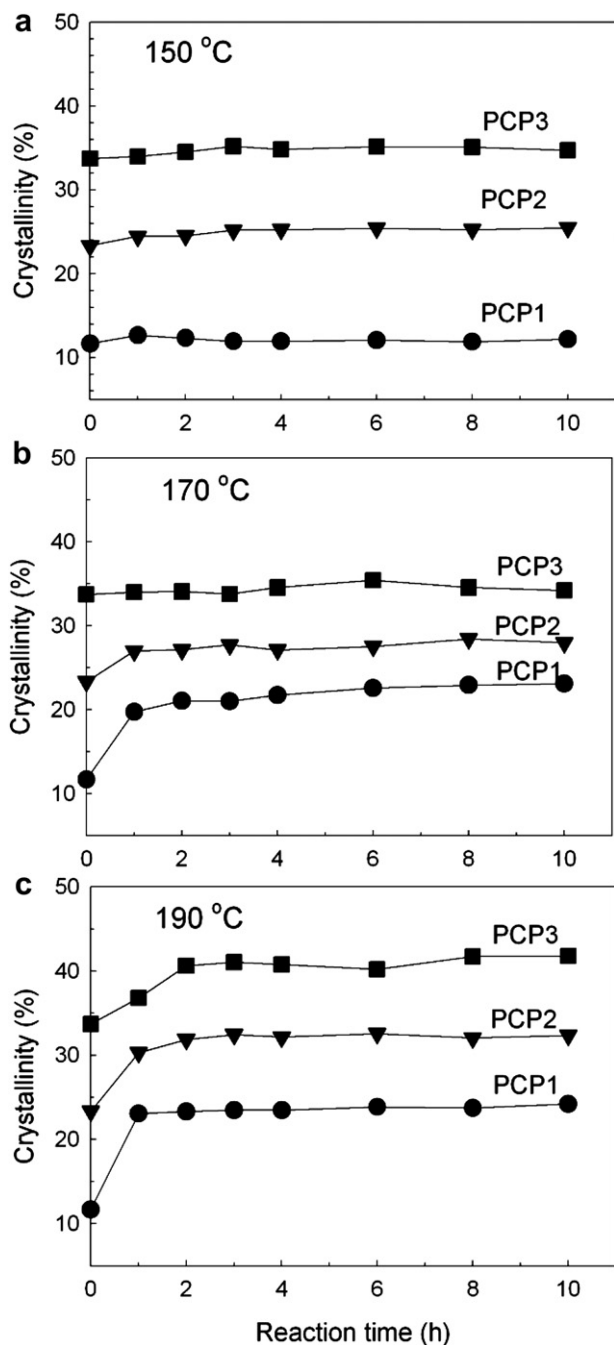


Fig. 7. Dependence of crystallinity of polymers solid-state polymerized using PCP1 (crystallinity = 11.7%), PCP2 (crystallinity = 23.3%) and PCP3 (crystallinity = 33.7%) on reaction time at reaction temperatures of 150–190 °C.

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