Complex Effects of the Sweep Fluid on Solid-State Polymerization: Poly(bisphenol A carbonate) in Supercritical Carbon Dioxide

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ABSTRACT: The effects of the sweep fluid on solid-state polymerization (SSP) of poly(bisphenol A carbonate) (BPA-PC) were investigated. Prepolymers with two different number-average molecular weights, PCP6C (M_n = 3800 g/mol) and PCP9C (M_n = 2400 g/mol), were synthesized using melt transesterification. Solid-state polymerization of these prepolymers was carried out at temperatures in the range of 150–190 °C with supercritical carbon dioxide ($scCO_2$) and N_2 as the sweep fluids. It was found that $scCO_2$ at 207 bar could either increase or decrease the rate of SSP relative to the rate in atmospheric N_2, depending on the prepolymer molecular weight. At 190 °C, the molecular weights of the polymers synthesized from the higher-molecular-weight prepolymer (PCP6C) were higher with $scCO_2$ as the sweep fluid compared to those of the polymers synthesized with N_2. In contrast, at the same temperature of 190 °C, the molecular weights of the polymers synthesized from the lower-molecular-weight prepolymer (PCP9C) were lower with $scCO_2$ compared to those of the polymers synthesized with N_2. This apparently contradictory effect can be understood in terms of competition between rate-increasing effects of $scCO_2$, such as greater chain mobility and a higher byproduct diffusion coefficient caused by plasticizing of the polymer by $scCO_2$, and rate-diminishing effects associated with $scCO_2$, such as lamellar thickening, higher crystallinity, and perhaps increased occlusion of end groups in crystalline regions.

1. Introduction

Poly(bisphenol A carbonate) (BPA-PC) is an important engineering plastic that is used in products for the optical recording, electronic and electrical, architecture, automotive, health and medical, and leisure and safety industries.[1] The polymer is produced commercially either by interfacial polymerization of bisphenol A (BPA) and phosgene or by melt transesterification of BPA and diphenyl carbonate (DPC). High-quality, high-molecular-weight BPA-PC can be obtained via interfacial polymerization. However, phosgene, a highly toxic and regulated chemical, is a raw material in this process, and large quantities of organic and aqueous wastes are generated. Melt transesterification is a solvent-free, potentially phosgene-free route to BPA-PC. However, low-quality, low-molecular-weight BPA-PC is often obtained due to extremely high melt viscosity and side reactions at typical, high reaction temperatures (ca. 280–310 °C). In order to obtain high-quality, high-molecular-weight PC with melt transesterification, a specially designed reactor (such as a rotating disk reactor) and a multistage reaction must be used to remove the byproduct efficiently from the high-viscosity polymer melt.[2] Therefore, considerable effort has been devoted to developing more environmentally friendly and lower-cost techniques to produce high-quality BPA-PC.[3]

Solid-state polymerization (SSP) is a solvent-free, environmentally benign alternative route to high-quality, high-molecular-weight BPA-PC.[4,5] In a typical SSP process, a low-molecular-weight polymer (prepolymer) is synthesized using melt transesterificaton. The solid prepolymer then is heated to a temperature above its glass transition temperature (T_g) and below its melting temperature (T_m). At these conditions, the transesterification reaction continues and the molecular weight of the polymer increases. The reaction byproduct, phenol, is removed by flowing a sweep fluid (an "inert" gas[5,6] such as N_2 or supercritical carbon dioxide ($scCO_2$[5,7])) through the solid particles or by applying vacuum.[4] Recent studies have shown that high-quality, high-molecular-weight BPA-PC can be obtained via SSP at relatively low temperatures of 165–240 °C.[4–6] Therefore, the drawbacks associated with the high temperatures of conventional melt-transesterification processes, along with the use of toxic chemicals and the generation of toxic wastes, can be avoided by using SSP to prepare BPA-PC.

The overall rate of SSP depends on the rates of the individual steps which make up the reaction: (1) end-group diffusion in the polymer matrix, (2) the intrinsic kinetics of the chain extension reaction, (3) the internal diffusion of the condensate molecule (reaction byproduct) through the polymer to the particle surface, and (4) the external diffusion of the condensate molecule from the polymer surface to the sweep fluid. Depending on prepolymer properties (particle size, prepolymer molecular weight, crystallinity, and catalyst concentration) and reaction conditions (sweep fluid flow rate, temperature, and pressure), the rate of SSP and the obtainable molecular weight can be controlled by the rate of one or more of these steps.

It has been shown that using $scCO_2$ as the sweep fluid can increase the rate of SSP of BPA-PC;[5,7,8] e.g., the molecular weights of BPA-PC SSP'd in $scCO_2$ are higher at a given temperature and reaction time than the molecular weights of the same prepolymer SSP'd in atmospheric N_2. For example, Shi et al. reported that the number-average molecular weight of BPA-PC relative to polystyrene increased from 4300 to 7000 g/mol with N_2 and increased to 10 000 g/mol with $scCO_2$ (345 bar), at 120 °C and a 10 h reaction time.[7] This beneficial effect of $scCO_2$ can result from several phenomena. It has been established that $scCO_2$ can plasticize amorphous regions of BPA-PC, resulting in a significant decrease in T_g. For example, the T_g of BPA-PC decreased by 75 °C when the polymer was equilibrated with $scCO_2$ at 80 bar.[9] The resulting increase in

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Table 1. Number-Average Molecular Weight (M_n), Glass-Transition Temperature (T_g), Onset Melting Temperature ($T_{m,\ onset}$), Melting Temperature (T_m), Crystallinity, and End-Group Ratio of Prepolymers before and after Crystallization

	M_n (g/mol)	PDI	T_g (°C)	$T_{m,\ onset}$ (°C)	T_m (°C)	crystallinity (%)[c]	C_6H_5/OH end-group ratio
PCP6[a]	3800	1.47	118			0	0.76
PCP6C[b]	3800	1.45	115	195	223	20	0.73
PCP9[a]	2400	1.32	93			0	1.01
PCP9C[b]	2300	1.35	96	191	216	23	0.99

[a] PCP6 and PCP9 are the prepolymers before crystallization. [b] PCP6C and PCP9C are the prepolymers after crystallization in $scCO_2$. The crystallization conditions were 4000 psi, 70 °C, and 6 h. [c] Crystallinity of the prepolymer was determined by measuring heat of fusion ($\Delta H_{f,sample}$) of the polymer using DSC. The crystallinity was calculated using crystallinity = $\Delta H_{f,sample}/\Delta H_f^\circ \times 100$, where ΔH_f° is heat of fusion of the standard state for BPA-PC (109.62 J/g).[18]

free volume of the amorphous region increases chain end mobility, leading to a higher rate constant for the chain extension reaction. The increase in free volume caused by dissolved CO_2 also increases the diffusion coefficient of phenol in the polymer. For example, the diffusion coefficient of phenol in BPA-PC is about 1.6 times larger with $scCO_2$ (207 bar) than with atmospheric N_2 as the sweep fluid.[10] Finally, the solubility of phenol in $scCO_2$ is very high, e.g., 2.4 wt % at 90 °C and 275 bar.[11] This increases the driving force for the external transport step.

Herein we report that the effect of the sweep fluid on the rate of SSP is more complex than suggested by previous research. In particular, the use of $scCO_2$ does not *always* increase the rate of SSP of BPA-PC. The molecular weight of the BPA-PC prepolymer has a significant influence on whether the SSP rate is higher in atmospheric N_2 or in $scCO_2$. In the sections that follow, the interactions between the choice of sweep gas and the properties of the BPA-PC prepolymer are explored.

2. Experimental Section

2.1. Materials. Bisphenol A (BPA, >99%), diphenyl carbonate (DPC, >99%), and lithium hydroxide monohydrate ($LiOH \cdot H_2O$, >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 Fisher Scientific (Pittsburgh, PA). BPA was recrystallized from a mixture of methanol and DIUF water (2/1 by volume) and dried in a vacuum at 60 °C for at least 2 days. DPC was recrystallized from methanol and dried in a vacuum at 40 °C for at least 2 days. $LiOH \cdot H_2O$ was used as received. The nitrogen was Ultra High Purity (purity of 99.999%), obtained from National Welders (Charlotte, NC). The carbon dioxide was Coleman grade (purity of 99.99%), obtained from National Welders (Charlotte, NC). Carbon dioxide was passed through three inline high-pressure oxygen traps (Alltech Associates, Inc., Deerfield, IL), and nitrogen was passed through a gas purifier (Drierite, Xenia, OH) and an oxygen trap (Model 1000, Chromatography Research Supplies, Louisville, KY) before they were introduced into a reactor.

2.2. Prepolymer Synthesis and Crystallization. BPA-PC prepolymers were synthesized by melt transesterification of BPA and DPC using an aqueous solution of $LiOH \cdot H_2O$ (0.001 g/mL) as the catalyst. 18 ppm of $LiOH \cdot H_2O$, based on the BPA weight, was used. A detailed description of prepolymer synthesis is given in a previous work.[12] Two prepolymers with different number-average molecular weights, PCP6 (3800 g/mol) and PCP9 (2400 g/mol), were used in the present study. The prepolymers were crystallized using $scCO_2$, as described in a previous publication.[13] The crystallized prepolymers were then ground to a particle size of 20−45 μm. Table 1 lists the prepolymer properties, including number-average molecular weight (M_n), polydispersity index (PDI), glass transition temperature (T_g), onset melting temperature ($T_{m,onset}$), melting temperature (T_m), crystallinity, and end-group ratio, both before and after crystallization. The number-average molecular weight (M_n) and PDI were determined using gel permeation chromatography (GPC), as described in section 2.4. The T_g, $T_{m,onset}$, T_m, and heat of fusion (ΔH_f) were determined using differential scanning calorimetry (DSC). The crystallinity was calculated from ΔH_f, as indicated in Table 1. The end-group ratio was determined using a recently developed procedure based on nuclear magnetic resonance (NMR) spectroscopy.[12] This technique is a major advance over existing methods for analysis of end-group ratios in BPA-PC.

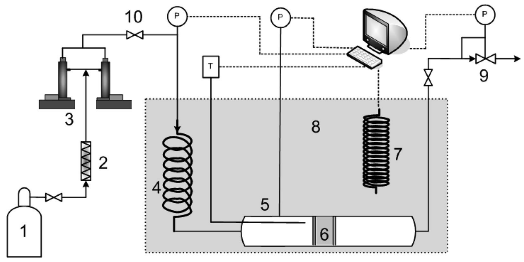

Figure 1. Schematic of the solid-state polymerization apparatus used with $scCO_2$ as a sweep fluid: 1, carbon dioxide source tank; 2, high-pressure oxygen trap; 3, dual-syringe ISCO pumps; 4, coil preheater; 5, tubular SSP reactor; 6, prepolymer particles; 7, heat circulator; 8, heating oil bath; 9, back-pressure regulator; 10, isolation valve; P, pressure transducer; T, thermocouple.

As shown in Table 1, M_n and T_g of the prepolymer changed only marginally during crystallization. This indicates that no chain extension reactions occurred during this step. No crystallinity was observed in either PCP6 or PCP9, indicating that the small amount of catalyst used in the melt transesterification did not cause crystal nucleation in the polymer matrix.[6,14,15]

The measured end-group ratio of PCP6C is lower than that of PCP9C. However, the M_n of PCP6C is higher than that of PCP9C. If the end-group ratio of a linear step-growth polymer deviates at all from 1.0, that ratio will decrease or increase as polymerization proceeds. In order to isolate the effect of end-group stoichiometry, the apparent ratio of the phenyl and hydroxyl end groups at the start of polymerization was calculated from the measured ratios and molecular weights, as given in Table 1. For both prepolymers, the apparent initial end-group ratio was between 0.99 (PCP6C) and 1.00 (PCP9C). Therefore, the differences in SSP behavior between these two prepolymers, as described below, can be ascribed to the effect of molecular weight per se. The lower end-group ratio for PCP6C shown in Table 1 is a consequence of its higher degree of polymerization, given the very slight initial stoichiometric imbalance of the end groups (ratio = 0.99).

2.3. Solid-State Polymerization (SSP). The experimental apparatus for carrying out solid-state polymerization with N_2 as the sweep gas was described in a previous publication.[13] The equipment for SSP with $scCO_2$ as the sweep fluid is shown schematically in Figure 1. The apparatus consists of a reactor (5), a preheating tube (4), high-pressure oxygen traps (2), ISCO dual syringe pumps (3), a heat circulator (7), a heating bath (8), a back-pressure regulator (9), isolation valves (10), and a carbon dioxide source (1). The SSP reactor (5) was a tubular SS316 microreactor purchased from High Pressure Equipment Co. (Erie, PA). The internal diameter and the length of the reactor were 0.48 and 10 cm, respectively. The 15 m long preheating tube (4) was connected to the inlet portion of the reactor. The reactor and the preheating tube 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 circulator (7) (Haake Phoenix II P2-H70) manufactured by Thermo Electron Corp., Inc. (Newington, NH). The temperature during SSP was within ±0.5 °C of the desired temperature. The temperature was monitored using a type J thermocouple (T) (Omega Engineering, Inc., Stamford, CT) inserted inside the reactor.

The pressure during SSP was controlled to within ±1 bar of the desired pressure using an automated back-pressure regulator (9) (Model BPR-200A, Thar Designs, Pittsburgh, PA) and ICM software (Thar Designs). The pressures of the reactor and the preheating coil were monitored using a high-accuracy pressure transducer (±0.01 bar) (P) (Model PX010C0-7.5KG5T) manufactured by Omega Engineering, Inc.

The $scCO_2$ was pumped into the reactor using an ISCO dual syringe pump (3) (Model 500 D, Lincoln, NE) equipped with pneumatic flow control valves. The temperature of the syringes was controlled by circulating a heat-transfer fluid to a heating/cooling jacket around the syringes using a Model 1140S bath circulator manufactured by VWR (West Chester, PA). The temperature was set at 4 °C. The flow rate of $scCO_2$ was controlled using the ISCO pumps in a constant flow rate mode. The CO_2 was passed through three parallel high-pressure oxygen traps (2) (Alltech Associates, Inc., Deerfield, IL).

For SSP experiments, the crystallized prepolymers were ground to a particle size of 25−45 μm. About 0.4 g of the ground prepolymer was loaded into the reactor and held in position using glass wool (item 6, Figure 1). The reactor was then purged with 200 psi of CO_2 for 10 min. After purging, the reactor was vented back to atmospheric pressure and was isolated by closing the isolation valves. The reactor was then immersed into the heating bath, the temperature of which was preset at the desired SSP temperature. A 5−10 min stabilization time was required for the reactor to reach the SSP temperature. When the temperature was 5 °C below the SSP temperature, the reactor was pressurized slowly with CO_2 to the desired pressure. When the pressure and temperature of the reactor reached the desired values, SSP was initiated by flowing 20 mL/min CO_2 (at the conditions of the ISCO pumps) through the reactor, and reaction time was recorded. After each experiment was completed, the CO_2 flow was stopped and the reactor was vented back to atmospheric pressure. The reactor was then removed from the heating bath and cooled with a fan. SSP was typically carried out for 10 h, and samples were removed every 1−2 h for analyses.

The CO_2 and N_2 flow rates and the prepolymer particle size were chosen because earlier studies had shown that neither internal nor external transport influenced the rate of SSP of BPA-PC at these conditions.[6,7] However, the present research extended to higher temperatures and utilized higher-molecular-weight prepolymers. Therefore, the possibility that the SSP rates measured in this study were influenced to some extent by internal and/or external transport cannot be excluded.

2.4. Characterization. The quantification of phenolic and phenyl end groups was 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 Corp., Milford, MA) with tetrahydrofuran (THF) as a mobile phase. The eluent from the GPC was measured with a light scattering detector (miniDAWN Tristar Model WTR-02, Wyatt Technology, Santa Barbara, CA) and with a refractive index detector (Optilab rEX, Wyatt Technology, Santa Barbara, CA). 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 of the NMR, GPC, and DSC were provided previously.[12,13] With the light scattering detector, *absolute* weight-average molecular weights are obtained. Values of M_n were calculated from the combined responses of the light-scattering and refractive index detectors using the ASTRA software (Wyatt Technology, Santa Barbara, CA). Analysis of multiple samples showed that M_w measurements were reproducible to ±200 over the range of M_w's in this research.

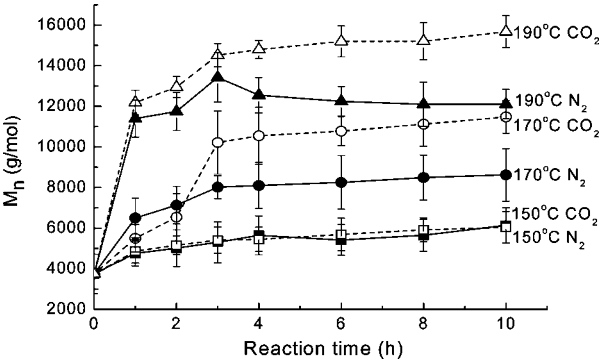

Figure 2. Effect of temperature on molecular-weight evolution during SSP of PCP6C ($M_n = 3800$ g/mol) with N_2 (filled symbols) and $scCO_2$ (207 bar) (open symbols) as sweep fluids at reaction temperatures of 150−190 °C. The prepolymer particle size was 20−45 μm; N_2 flow rate was 1600 mL/min; $scCO_2$ flow rate was 20 mL/min. The error bars are generated by the ASTRA software; they reflect the variation of M_w over a single chromatogram.

3. Results and Discussion

Figure 2 shows the effect of temperature on molecular-weight evolution during SSP of PCP6C ($M_n = 3800$ g/mol) with either N_2 or $scCO_2$ (207 bar) as the sweep fluid. When the reaction temperature was 150 °C, the molecular weights of the polymers synthesized in N_2 were similar to those of the polymers synthesized in $scCO_2$. After 10 h, the number-average molecular weight (M_n) had increased only marginally, from 3800 to 6100 g/mol with N_2 and to 6500 g/mol with $scCO_2$. At the highest temperature of 190 °C, the molecular weight increased substantially during the first hour of SSP and reached an asymptotic value after about 3 h. At 190 °C, higher-molecular-weight polymers resulted when $scCO_2$ was used as the sweep fluid. After 10 h, the molecular weight had increased to 12 100 g/mol with N_2 and to 15 700 g/mol with $scCO_2$.

Interestingly, at 170 °C, the molecular weight was lower during the first 2 h of SSP with $scCO_2$ as the sweep fluid, and higher during hours 3 through 10, compared to the molecular weights of the polymers synthesized with N_2 at identical times. Because of the unusual behavior of the M_n at short times with $scCO_2$ as the sweep fluid, the first 2 h of this experiment were repeated. The M_n after 1 h was slightly less (−400) than the original value. The M_n after 2 h was slightly higher (+400) than the original value. These results confirmed the slow initial rate of molecular-weight development at 170 °C in $scCO_2$ relative to SSP in N_2 at 170 °C. A possible explanation of this behavior will be provided later.

The asymptotic behavior of the molecular weight at long reaction times was discussed in a previous publication.[13] The asymptote does not result from the depletion of one (or both) end groups. In fact, when the polymer SSP'd at 190 °C with N_2 was further SSP'd at 230 °C for 6 h, the molecular weight increased from 12 100 to 25 300 g/mol.[13] The asymptotic molecular weight appears to be a consequence of the fact that the glass-transition temperature (T_g) and the crystallinity increase, and the lamellar thickness of the crystalline regions often increases, during SSP. These increases may reduce the mobility of the unreacted end groups and eventually lead to a negligibly small reaction rate. The higher the SSP temperature, the farther the reaction will go before these effects cause the rate to become insignificant.[13]

The molecular-weight evolution of polymers synthesized by SSP using the lower-molecular-weight prepolymer (PCP9C, 2400 g/mol) is different in some respects from that of the polymers synthesized using the higher-molecular-weight prepolymer (PCP6C, 3800 g/mol). Figure 3 shows the effect of

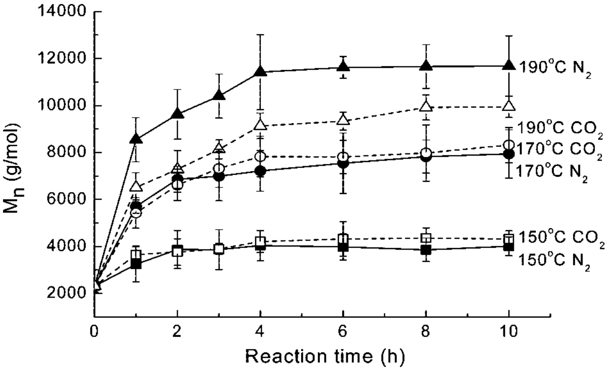

Figure 3. Effect of temperature on molecular-weight evolution during SSP of PCP9C (M_n = 2300 g/mol) with N_2 (filled symbols) and $scCO_2$ (207 bar) (open symbols) as sweep fluids at reaction temperatures of 150 (squares), 170 (circles), and 190 °C (triangles). The prepolymer particle size was 20−45 μm; N_2 flow rate was 1600 mL/min; $scCO_2$ flow rate was 20 mL/min. The error bars are generated by the ASTRA software; they reflect the variation of M_w over a single chromatogram.

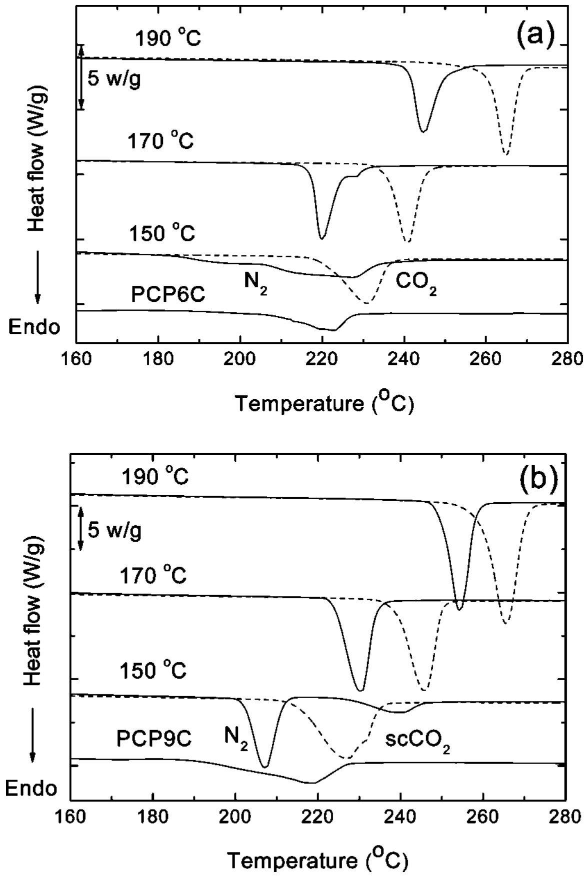

Figure 4. Melting isotherms for polymers solid-state polymerized using (a) PCP6C (M_n = 3800 g/mol) and (b) PCP9C (M_n = 2300 g/mol) with N_2 (solid lines) and $scCO_2$ (207 bar) (dashed lines) as sweep fluids at reaction temperatures of 150, 170, and 190 °C and a reaction time of 10 h.

temperature on the molecular weight during SSP of PCP9C with N_2 and $scCO_2$ (207 bar) as the sweep fluids. At a temperature of 150 °C, the molecular weights increased only marginally, from 2300 to about 4200 g/mol. At 170 °C, the molecular weight increased to about 8200 g/mol. The molecular weights of the polymers synthesized with N_2 are similar to those of the polymers synthesized with $scCO_2$ at these two temperatures. At the highest SSP temperature of 190 °C, the molecular weight of the polymers synthesized with $scCO_2$ is lower than that of the polymers synthesized with N_2. The molecular weight of the polymer synthesized with N_2 increased to an asymptotic value of 11 700 g/mol after 10 h, while the molecular weight of the polymer synthesized with $scCO_2$ increased to 9900 g/mol at the same time. This is in sharp contrast to the behavior of the high-molecular-weight prepolymer (PCP6C).

It has previously been reported that the use of $scCO_2$ as a sweep gas increases the rate of SSP of BPA-PC SSP relative to the rate obtained with atmospheric N_2.[5,7,8] In the absence of internal or external transport limitations, the intrinsic kinetics of the chain extension reaction were observed to be faster with $scCO_2$ as a sweep gas.[7] This effect was ascribed to swelling of the amorphous regions of the BPA-PC, leading to increased chain mobility and lower T_g. It was also determined that the diffusion coefficient of phenol in BPA-PC was higher in the presence of $scCO_2$ than with atmospheric N_2, again presumably because of swelling of the polymer matrix by $scCO_2$.[10] The higher molecular weights of the polymers synthesized from PCP6C at 190 °C with $scCO_2$, relative to the molecular weights of the polymers synthesized with N_2, agree with the conclusions from these previous studies.[5,7,8] However, when the lower-molecular-weight prepolymer (PCP9C) was used at the same temperature, the molecular weights of the polymers synthesized with N_2 were significantly higher than those synthesized with $scCO_2$. This behavior will be discussed later.

The molecular weights of the polymers synthesized from the lower-molecular-weight prepolymer (PCP9C) are consistently smaller at the same time and temperature, and with the same sweep gas, compared to the molecular weights of the polymers synthesized from the higher-molecular-weight prepolymer (PCP6C). This behavior has been attributed to the fact that longer chains exhibit less tendency for crystallization and for lamellar thickening during SSP, resulting in higher chain-end mobility.[13]

The polymer thermal properties, including melting temperature and crystallinity, were measured to explore the reason(s) for the molecular-weight differences between the polymers synthesized with N_2 and with $scCO_2$. Figure 4 shows the melting behavior of the prepolymers and the polymers after solid-state polymerization for 10 h. In both sweep fluids, the melting endotherms shifted to higher temperatures, and the melting peaks became sharper as the reaction temperature increased. The increase of melting peak sharpness is probably because crystal perfection increases when the polymer chains are extended via SSP.[13] The polymers SSP'd in $scCO_2$ had higher melting temperatures at a given reaction temperature than the polymers synthesized with N_2 as the sweep fluid. For example, T_m of the polymer synthesized at 190 °C from PCP6C with N_2 increased to 244 °C while T_m of the polymer synthesized at 190 °C from PCP6C with $scCO_2$ increased to 266 °C (Figure 4a). This suggests that $scCO_2$ plasticizes the amorphous regions of the polymer, thus allowing the polymer chains to rearrange into a more energetically favorable crystalline state during SSP.

The melting isotherm of the polymer synthesized from PCP6C with N_2 at 150 °C is very broad while that of the polymer synthesized from PCP9C with N_2 at 150 °C is much sharper (Figure 4a,b). This may be because shorter chains are more mobile and it is easier for the shorter chains to become incorporated into the crystal lattices. Two melting transitions are observed in the polymer synthesized from PCP9C with N_2 at 150 °C. As shown in Figure 4b, there is a larger melting transition at 207 °C and a smaller one at 240 °C. The T_m of the larger melting transition is lower than T_m of the prepolymer (216 °C). A similar trend was found in the polymers synthesized from PCP6C with N_2 at 170 °C (Figure 4a), with a larger melting transition at 220 °C and smaller transition at 229 °C. The T_m of the larger melting transition is lower than T_m of the prepolymer

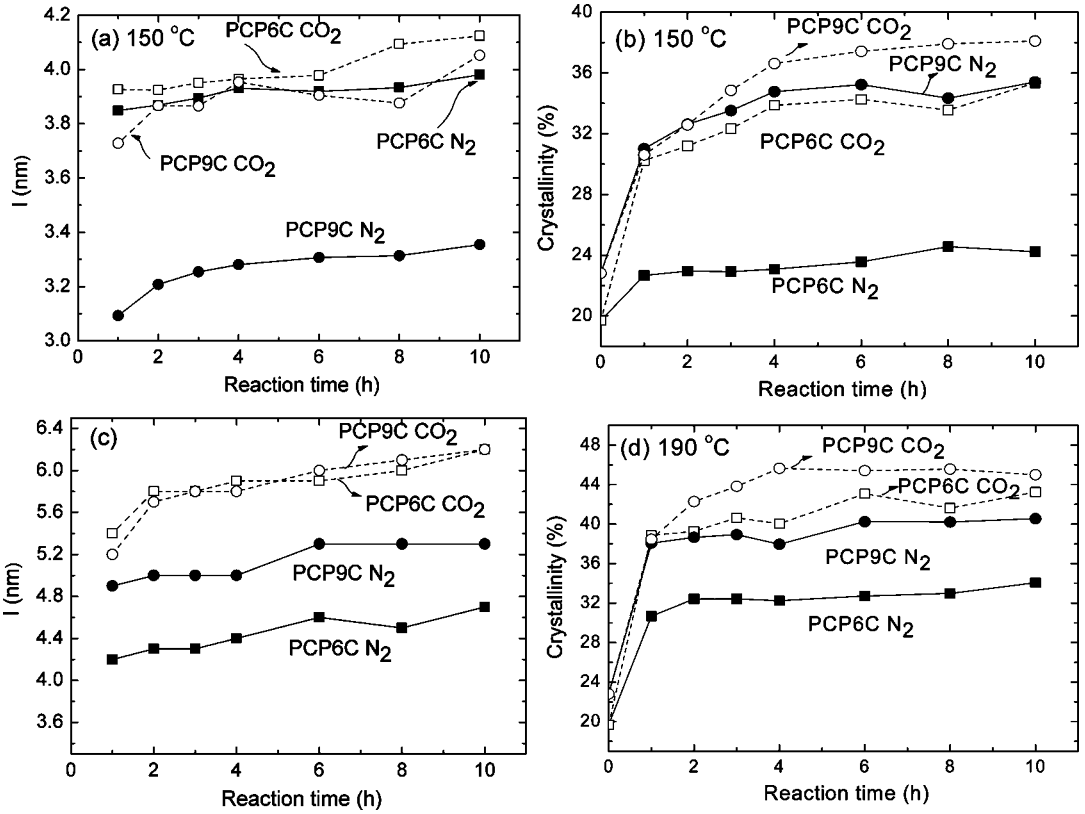

Figure 5. Dependence of lamellar thickness (l) and crystallinity on reaction time for polymers solid-state polymerized using PCP6C (M_n = 3800 g/mol) and PCP9C (M_n = 2300 g/mol): (a) lamellar thickness, reaction temperature 150 °C; N_2, filled symbols; $scCO_2$, unfilled symbols; (b) crystallinity, reaction temperature 150 °C; N_2, filled symbols; $scCO_2$, unfilled symbols; (c) lamellar thickness, reaction temperature 190 °C; N_2, filled symbols; $scCO_2$, unfilled symbols; (d) crystallinity, reaction temperature 150 °C; N_2, filled symbols; $scCO_2$, unfilled symbols.

(223 °C). This suggests a heterogeneity of the crystal structure that disappears at higher SSP temperatures. However, the melting peaks of both prepolymers are quite broad, making it difficult to estimate a T_m with any precision.

The lamellar thickness (l) and crystallinity of the polymers synthesized from PCP6C and PCP9C are shown in Figure 5. The lamellar thickness was estimated using the Gibbs−Thomson equation[16]

$$T_m = T_m^{\circ}\left(l - \frac{2\sigma_e}{l\Delta H_f^{\circ}}\right) \tag{1}$$

where T_m is the melting temperature, T_m° is the equilibrium melting temperature of BPA-PC (335 °C),[17] σ_e is the fold surface free energy (70 mJ/m^2),[17] and ΔH_f° is the enthalpy of fusion for a perfect crystal (109.62 J/g).[18] Figure 5 shows that lamellar thickness and crystallinity strongly depend on SSP temperature, prepolymer molecular weight, and the sweep gas. When two melting peaks were present, the lamellar thickness was estimated from the T_m of the larger peak. The lamellar thickness of the prepolymers is not shown because of the uncertainty of their T_m's. At 150 °C, the lamellar thickness changes of the polymers synthesized from both prepolymers in both sweep fluids were similar; the lamellar thickness increased modestly, by several tenths of a nanometer, as SSP proceeded (Figure 5a). The lamellar thicknesses of the polymers from PCP9C with N_2 are lower than those of the other polymers because they were calculated from the T_m of the strong, low-temperature melting peak shown in Figure 4b.

The crystallinity of the polymers SSP'd with $scCO_2$ is consistently larger than that of the polymers SSP'd with N_2. As shown in Figure 5b, the crystallinity of the polymer synthesized from PCP6C with N_2 increased slightly from 20% to 24% over 10 h at 150 °C, while that of the polymer synthesized with $scCO_2$ at 150 °C increased significantly to 35%. When PCP9C was used, the crystallinity of the polymers synthesized with N_2 increased significantly from 23% to 35% over 10 h at 150 °C, while the crystallinity of the polymers synthesized with $scCO_2$ increased to 38%. Figure 5b shows that the crystallinity of the polymers synthesized from the lower-molecular-weight prepolymer (PCP9C) is consistently higher than that of the polymers derived from the higher-molecular-weight prepolymer (PCP6C) at 150 °C.

At the highest temperature of 190 °C, both the lamellar thickness and crystallinity increased sharply during the initial few hours of SSP and reached asymptotic values (Figure 5c,d). The lamellar thickness of the polymers synthesized from PCP6C with N_2 increased from 4.2 to 4.7 nm while that of the polymers synthesized from PCP9C with N_2 were significantly higher after the first hour of SSP but increased only modestly thereafter. When $scCO_2$ was used, similar lamellar thickening was observed in the polymers from both of the prepolymers. The final lamellar thickness of the polymers synthesized with $scCO_2$ (ca. 6.2 nm) is larger than that of the polymers synthesized with N_2 (4.7−5.3 nm).

Figure 5d shows that, at 190 °C, the crystallinity of the polymers derived from PCP6C with N_2 (34%) and $scCO_2$ (43%) are smaller than that of the polymers synthesized from PCP9C with N_2 (41%) and $scCO_2$ (45%). The crystallinity of the polymers synthesized with N_2 is smaller than that of the polymers synthesized with $scCO_2$. Similar trends of lamellar thickness and crystallinity with prepolymer molecular weight and sweep fluid were observed at a lower reaction temperature of 170 °C. The increase in crystallinity with increased SSP time has also been found during the synthesis of BPA-PC using a disodium salt of BPA as a catalyst[4] and for poly(L-lactic acid)

(PLA),[19,20] poly(ethylene terephthalate) (PET),[21] and nylon-6,6.[22]

In previous work, we discussed the effect of prepolymer molecular weight on SSP of BPA-PC with N_2 as the sweep fluid.[13] Higher-molecular-weight BPA-PC was obtained when the higher-molecular-weight prepolymer (PCP6C) was used. This was attributed to the lower lamellar thickness and the lower crystallinity of the polymers derived from PCP6C compared to those of the polymers from PCP9C. We speculate that end-group mobility and byproduct diffusion in the polymers synthesized from the higher-molecular-weight prepolymer (PCP6C) are less constrained relative to those of the lower-molecular-weight prepolymer (PCP9C). The larger lamellar thickness and higher crystallinity of the polymers synthesized from PCP9C with $scCO_2$, compared with those of the polymers synthesized with N_2 (Figure 5c,d), may account for the lower molecular weight of the polymers synthesized with $scCO_2$ at 190 °C (Figure 3). However, lamellar thickness and crystallinity do not account for the higher molecular weight of the polymers synthesized with $scCO_2$, compared to the polymers synthesized with N_2, when PCP6C was used, The lamellar thickness and crystallinity of the polymers synthesized from PCP6C with $scCO_2$ are larger than those of the polymers with N_2 (see Figure 5c,d) while the molecular weights of the polymers with $scCO_2$ are larger than those of the polymers with N_2 at 190 °C (Figure 2). We speculate that this complex effect of $scCO_2$ on the rate of SSP may result from a balance between the rate-enhancing effects (increased chain mobility and higher byproduct diffusion coefficient) and the rate-diminishing effects (lamellar thickening and crystallization) of $scCO_2$. With the higher-molecular-weight prepolymer (PCP6C), the rate-enhancing effects may be dominant while with the lower-molecular-weight prepolymer (PCP9C), the rate-diminishing effects may be dominant at 190 °C. The similar molecular weights of the polymers with N_2 and $scCO_2$ at 150 °C when PCP6C was used, and at 150 and 170 °C when PCP9C was used, may be due to a similar balance.

Earlier, during the discussion of Figure 2, it was noted that with PCP6C, lower-molecular-weight polymers resulted during the first 2 h of SSP at 170 °C when $scCO_2$ (207 bar) was the sweep gas, compared to the same conditions with N_2 as the sweep gas. At longer SSP times, higher-molecular-weight polymers resulted with $scCO_2$ than with N_2. Figure 6a shows gel permeation chromatograms of PCP6C prepolymer, of polymers synthesized from PCP6C with N_2 and $scCO_2$ (207 bar), and of polymer synthesized from PCP9C with $scCO_2$ (276 bar). The last three chromatograms are for polymers that had been SSP'd for 1 h. As indicated by the arrows in Figure 6a, lower-molecular-weight shoulders were observed at an elution time of 33 min in the three polymers that had been SSP'd, but not in the PCP6C prepolymer. The prominence of these shoulders during the early stage of SSP suggests that some of the end groups in the lower-molecular-weight portion of the prepolymer may not participate in the chain extension reaction to the same extent as the other end groups. These "less-reactive" end groups may be trapped in the crystalline phase or immobilized and inactivated by the crystalline structure.[23]

The gel permeation chromatogram peaks were deconvoluted to quantify the lower-molecular-weight polymer fractions. Figure 6b,c shows representative deconvolution results of the polymers from PCP6C synthesized at 170 °C with N_2 at reaction times of 1 and 10 h. The overall distribution was well described as the summation of three separate peaks. It can be seen that the lowest-molecular-weight peak, with an elution time of 33 min, decreased with reaction time.

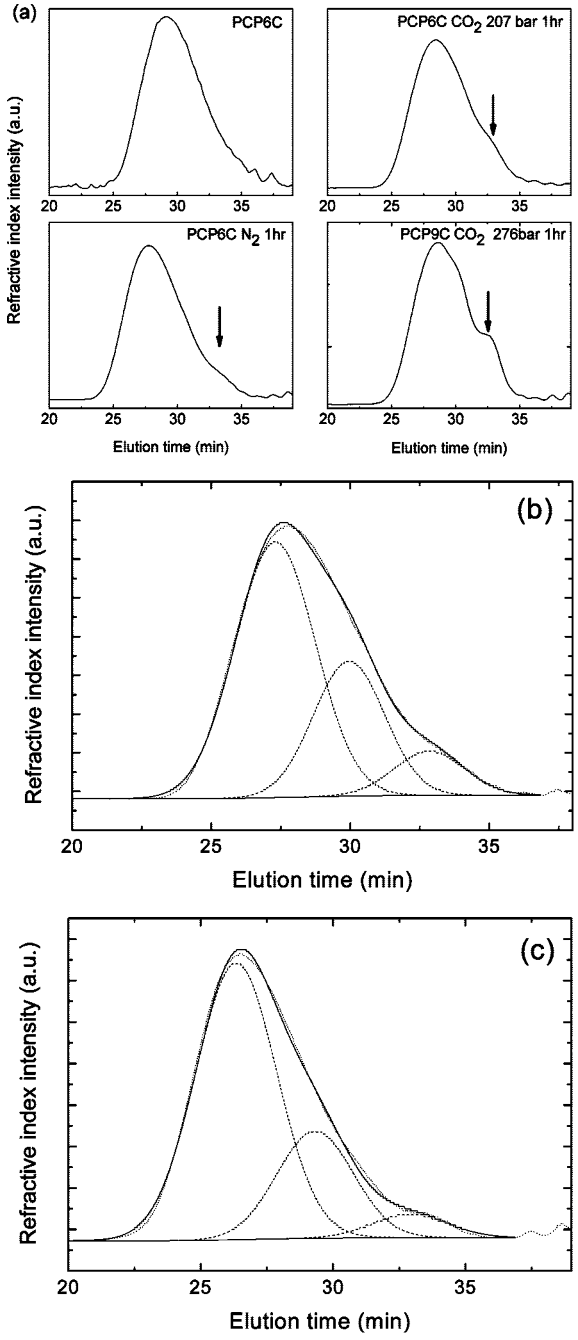

Figure 6. (a) Gel permeation chromatograms of PCP6C (M_n = 3800 g/mol), of polymers synthesized from PCP6C with N_2 and $scCO_2$ (207 bar) as sweep fluids, and of polymer synthesized from PCP9C (M_n = 2300 g/mol) with $scCO_2$ (276 bar) as the sweep fluid. For the last three polymers, reaction temperature = 170 °C and reaction time = of 1 h; (b) deconvolution of chromatogram for PCP6C after 1 h SSP time at 170 °C in N_2; (c) deconvolution of chromatogram for PCP6C after 10 h SSP time in N_2 at 170 °C.

Table 2 lists molecular weights, crystallinity, lamellar thickness, and estimated lowest-molecular-weight polymer fraction (at 33 min elution time) for the polymers synthesized with N_2 and $scCO_2$ (207 bar) at 170 °C. When N_2 was used as the sweep fluid, the lowest-molecular-weight polymer fraction after 1 h SSP was 9%. This fraction decreased to 5% after 10 h SSP. In contrast, with $scCO_2$ as the sweep fluid, a much higher amount of the lower-molecular-weight polymer fraction (ca. 20%) was observed after 1 h of SSP. However, this fraction decreased significantly to 4% after 10 h of SSP. It may be that a large number of the end groups were trapped by the crystalline phase during the early stages of SSP in $scCO_2$ due to the enhanced crystallization effects associated with $scCO_2$. This may have led to a lower average molecular weight with $scCO_2$ (5200 g/mol) than with N_2 (6500 g/mol) when the reaction time was

Table 2. Number-Average Molecular Weight (M_n), Crystallinity, Lamellar Thickness, and Lower-Molecular-Weight Polymer (LMP) Fractions of the Polymers Solid State Polymerized with N_2 and $scCO_2$ at 207 bar at 170 °C for 1 and 10 h (PCP6C Prepolymer Was Used)

	M_n (g/mol)	crystallinity (%)	lamellar thickness (nm)	LMP fractions (at 33 min) (%)
PCP6C−N_2−1 h	6500	30	3.5	9
PCP6C−N_2−10 h	8600	30	3.7	5
PCP6C−CO_2 (207 bar)−1 h	5500	32	4.1	20
PCP6C−CO_2 (207 bar)−10 h	11500	36	4.6	4

1 h. As SSP proceeded, the trapped end groups appear have been rejected into the amorphous phase, perhaps as a result of crystal perfection caused by $scCO_2$. Thus, end groups that are initially occluded in crystalline regions become available for the chain-extension reaction at longer reaction times. Although the crystallinity and lamellar thickness of the polymers synthesized with $scCO_2$ are larger than those of the polymers synthesized with N_2 after 10 h, higher-molecular-weight polymer was obtained with $scCO_2$ (11 500 g/mol) compared with that of the polymer synthesized with N_2 (8600 g/mol). This suggests that the rate-increasing effects associated with $scCO_2$ were dominant in the latter stages of SSP.

The effects of $scCO_2$ pressure on molecular weight evolution, crystallinity, and lamellar thickness are shown in Figure 7and listed in Table 3. Figure 7 shows the effect of CO_2 pressure on molecular-weight evolution during SSP of PCP9C at 170 °C with $scCO_2$ at 207 and 276 bar. The molecular weights of the polymers synthesized at 276 bar are smaller than those of the polymers synthesized at 207 bar over the whole 10 h reaction period. Table 3 shows that the crystallinity and lamellar thickness of the polymers synthesized with $scCO_2$ at 207 and 276 bar are similar after 1 and 10 h and probably cannot account for the significantly lower molecular weights of the polymers SSP'd at the higher $scCO_2$ pressure. However, the lower-molecular-weight fractions of the polymers synthesized at the higher $scCO_2$ pressure of 276 bar (32% after 1 h SSP and 13% after 10 h SSP) are larger than those of the polymers synthesized with the lower $scCO_2$ pressure of 207 bar (25% after 1 h SSP and 10% after 10 h SSP). This suggests that a larger number of end groups are occluded by the crystalline phase at the higher $scCO_2$ pressure, leading to lower-molecular-weight polymers at the higher $scCO_2$ pressure.

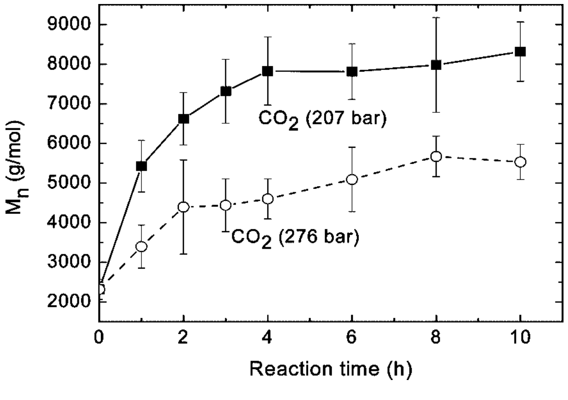

Figure 7. Effect of pressure on molecular-weight evolution during SSP of PCP9C (M_n = 2300 g/mol) with $scCO_2$ (207 and 276 bar) as sweep fluid at reaction temperature of 170 °C. The prepolymer particle size was 20−45 μm; N_2 flow rate was 1600 mL/min; $scCO_2$ flow rate was 20 mL/min.

The rate-diminishing effects (crystallinity, lamellar thickness, and inactive end groups) associated with $scCO_2$ were more significant when the lower-molecular-weight prepolymer (PCP9C) was solid state polymerized with $scCO_2$ (compare PCP9C with PCP6C in Tables 2 and 3). This suggests that shorter polymer chains are more easily occluded by the crystalline phase and that the end groups attached to the shorter chains are more easily trapped in the crystalline phase. In addition, the end groups attached to the shorter chains appear to be rejected from the crystalline phase more slowly. Therefore, high-molecular-weight prepolymers are desired when using SSP to synthesize high-molecular-weight BPA-PC, especially when attempting to exploit the rate-enhancing effects associated with $scCO_2$.

Finally, it is important to reconcile the present results with those of a previous study of the SSP of BPA-PC with $scCO_2$ and atmospheric N_2 as the sweep fluids.[6] In the earlier research, a prepolymer with M_n = 4300 g/mol *relative to polystyrene* was used. Based on the present studies using GPC with light scattering and refractive index detectors, the *absolute* M_n of this prepolymer is estimated to be about 1900 g/mol, less than that of PCP9C. Consistent with a lower M_n, the T_g and T_m of the earlier prepolymer were substantially lower than those of PCP9C (T_g = 69 °C vs 96 °C for PCP9C; T_m = 197 °C vs 216 °C for PCP9C). Moreover, the concentration of the $LiOH \cdot H_2O$ catalyst in the earlier prepolymer was much higher than in PCP9C (397 ppm vs 18 ppm for PCP9C, based on BPA). Because of the lower T_g and T_m of the earlier prepolymer, the SSP experiments with this material had to be conducted at lower temperatures, in the range of 90−135 °C. At these conditions, the SSP rate in $scCO_2$ was always greater than in atmospheric N_2. The type of SSP behavior observed with PCP9C, where $scCO_2$ had either no significant effect or decreased the SSP rate, was not observed. At this point, we can only speculate that SSP temperature per se may also contribute to determining the balance between rate-increasing and -decreasing effects.

4. Conclusions

The effects of using $scCO_2$ as a sweep gas for the solid-state polymerization of poly(bisphenol A carbonate) were examined at temperatures in the range 150−190 °C. Two different prepolymers with different molecular weights were studied. When the higher-molecular-weight prepolymer (M_n = 3800) was used, the rate of SSP was always faster in $scCO_2$ at 207 bar than in atmospheric N_2, presumably due to higher chain-end mobility and a higher phenol diffusion coefficient. However,

Table 3. Number-Average Molecular Weights (M_n), Crystallinity, Lamellar Thickness, and Lower-Molecular-Weight Polymer (LMP) Fractions of the Polymers Solid-State Polymerized with N_2 and $scCO_2$ at 207 and 276 bar at 170 °C for 1 and 10 h (PCP9C Prepolymer Was Used)

	M_n (g/mol)	crystallinity (%)	lamellar thickness (nm)	LMP fractions (at 33 min) (%)
PCP9C−CO_2−1 h−207 bar	5100	38	4.3	25
PCP9C−CO_2−10 h−207 bar	8300	42	4.8	10
PCP9C−CO_2−1 h−276 bar	3400	35	4.4	32
PCP9C−CO_2−10 h−276 bar	5500	41	4.7	13

when the lower-molecular-weight prepolymer ($M_n = 2400$) was used, the rate of solid-state polymerization was not always higher in $scCO_2$. Supercritical CO_2 can cause thicker crystal lamella, higher crystallinity, and end-group occlusion in crystalline regions, all of which retard the rate of SSP. Thus, high-molecular-weight prepolymer should be solid-state polymerized in order to obtain the highest molecular weight of BPA-PC at a given set of conditions, especially if $scCO_2$ is used as the sweep fluid.

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