

Complex Effects of the Sweep Fluid on Solid-State Polymerization:

Poly(bisphenol A carbonate) in Supercritical Carbon Dioxide

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ABSTRACT

Solid-state polymerization (SSP) of Poly(bisphenol A carbonate) was carried out with both N₂ and supercritical carbon dioxide (scCO₂) as the sweep fluids. ScCO₂ had both beneficial and detrimental effects on SSP, depending on prepolymer molecular weights. When a high molecular weight prepolymer was used, scCO₂ effectively plasticizes the amorphous region of the polymer, thus significantly increased the SSP reaction rate by increasing chain mobility and facilitating condensate removal. When a low molecular weight prepolymer was used, scCO₂ significantly increased crystallinity and lamellar thickness of the polymer, thus decreased the SSP reaction rate by decreasing chain mobility and by retarding condensate removal.

INTRODUCTION

Poly(bisphenol A carbonate) (BPA-PC) is an important engineering polymers and used in numerous commercial applications including optical recording, electronic and electrical, architecture, automotive, health and medical, and leisure and safety industries. Current industrial process produces BPA-PC either by interfacial polymerization with monomers of bisphenol A and phosgene or by melt transesterification with monomers of bisphenol A and diphenyl carbonate. The interfacial polymerization generates huge amount of organic and aqueous wastes. The melt transesterification often produces low quality, low molecular weight polymers due to extremely high viscosity of polymer melts. Solid state polymerization (SSP) is a solvent-free, environmentally benign alternative route to produce high-quality, high molecular weight BPA-PC. In a typical SSP process, a low molecular weight polymer (or prepolymer), synthesized using the melt transesterification, is heated below a melting temperature (T_m), but above a glass transition temperature (T_g). The removal of

reaction byproduct, phenol, is facilitated by flowing sweep fluids (N_2 or $scCO_2$). The rate of SSP depends on one of the following rate-determining steps; (1) chain end-groups diffusion, (2) intrinsic kinetics of the forward reaction, (3) phenol diffusion through the polymer matrix to the exterior surface (internal mass transfer), and (4) phenol diffusion from the exterior surface of the particle to the sweep fluid phase (external mass transfer). Figure 1 shows transesterification reaction during SSP of BPA-PC.

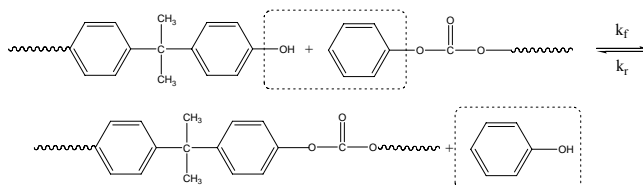


Figure 1. Transesterification during SSP

In the previous works, it has been shown that $scCO_2$ effectively plasticizes the amorphous region of the polymer, thus significantly increases the SSP reaction rate by increasing chain mobility and facilitating condensate removal [1,2]. Thus higher molecular weight BPA-PC resulted when $scCO_2$ was used as the sweep fluid compared with molecular weights of BPA-PC synthesized with N_2 as the sweep fluid at the same reaction temperature.

Herein we report that $scCO_2$ does *not always* enhance SSP rate of BPA-PC. It will be shown that the SSP rate enhancing effects associated with $scCO_2$ is effective when a higher molecular weight prepolymer was used. In the sections that follow, the prepolymer molecular effects and the sweep gas fluid effects for the SSP of BPA-PC with N_2 and $scCO_2$ as the sweep fluids were investigated. Prepolymers with number average molecular weights of 3,800 g/mol and 2,400 g/mol were synthesized using melt transesterification of BPA and DPC. The *absolute* molecular weights of the polymers were directly measured using gel permeation chromatography with a light scattering detector. The polymer properties, including melting temperatures (T_m), and heat of fusion (ΔH), were measured and crystallinity and lamellar thickness were estimated using differential scanning calorimetry (DSC).

MATERIALS AND METHODS

Prepolymer Synthesis and Crystallization

The prepolymers were synthesized by melt transesterification of Bisphenol A and diphenyl carbonate using an aqueous solution of $LiOH \cdot H_2O$ (0.001 g/ml) as a catalyst. 18 ppm of $LiOH \cdot H_2O$ based on the BPA weight was used. The prepolymers were then crystallized using $scCO_2$ at 276 bar $70^\circ C$, and 6 h. The crystallized prepolymers, namely PCP6C and PCP9C, were then ground with a particle size of 20-45 μm . Table 1 lists the prepolymer properties including 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 before and after crystallization. M_n was determined using gel permeation chromatography (GPC), T_g , $T_{m,onset}$, T_m , crystallinity were determined using differential scanning calorimeter (DSC), and end group ratio was determined using nuclear magnetic resonance (NMR) spectroscopy. As shown in Table 1, M_w and T_g of the prepolymer were marginally changed after the crystallization. This indicates that no chain extension reaction occurred during the crystallization.

A schematic of solid-state polymerization apparatus is shown in Figure 2. The apparatus consists of a CO₂ source (1), high-pressure oxygen traps (2), dual ISCO pumps (3), a preheating tubing (4), a SSP tubular reactor (5), a heat circulator (7), a heat bath (8), and a back-pressure regulator (9). The polymer particles (6) were fixed in the middle of the reactor using glass wool.

Table 1. Number average molecular weights (M_n), T_g , $T_{m,onset}$, T_m , crystallinity, and end group ratio of the prepolymers before and after crystallization

	M_n (g/mol)	T_g (°C)	$T_{m,onset}$ (°C)	T_m (°C)	Crystallinity (%) ^c	C ₆ H ₅ /OH end group ratio
PCP6 ^a	3,800	118	-	-	0	0.76
PCP6C ^b	3,800	115	195	223	20	0.73
PCP9 ^a	2,400	93	-	-	0	1.01
PCP9C ^b	2,400	96	191	216	23	0.99

^cCrystallinity of the prepolymer was determined by measuring heat of fusion ($\Delta H_{f,sample}$) of the polymer from DSC. The crystallinity was calculated

$Crystallinity = \Delta H_{f,sample} / \Delta H_f^o \times 100$, where ΔH_f^o is heat of fusion of the standard state for BPA-PC (109.62 J/g) [3].

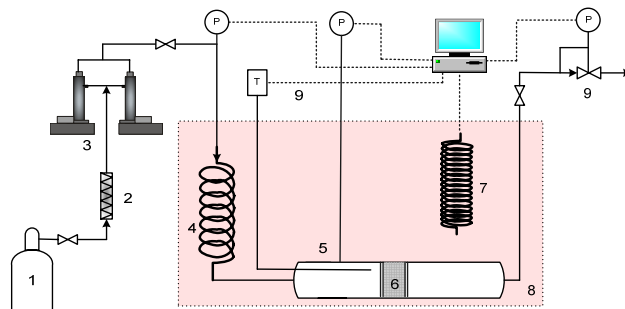


Figure 2. Experimental equipment for SSP with scCO₂ as the sweep fluid

For SSP experiments, the prepolymers were ground with particle size of 25-45 μm . A 0.4 g of the ground prepolymer was loaded into the reactor and then the reactor was purged with 6.9 bar CO₂ for 5 min. After stop purging and decrease pressure, the reactor was isolated with CO₂ atmosphere and was immersed into the heat bath. The temperature of heat bath was preset to a desired SSP temperature. A 5-10 min stabilization time was required to reach for the reactor to the SSP temperature. When the temperature was 5 °C below the SSP temperature, the reactor was pressurized slowly with CO₂ to the experimentally desired pressure. When the pressure and temperature of the

reactor reached the desired pressure and temperature, SSP was initiated by flowing 20 ml/min CO₂ (flow rate in the ISCO pumps) through the reactor and reaction time was recorded. After each SSP was completed, the CO₂ flow was stopped and the reactor was vented back to atmospheric pressure. The reactor was then removed from the heat bath and cooled with a fan. SSP was typically carried out for 10 h and the polymerized samples were taken out every 1-2 h for analyses. When N₂ was used as the sweep fluid, U-tube glass reactor was used. The flow rate of N₂ was 1600 ml/min. Details on the SSP apparatus with N₂ as the sweep fluid was described in the previous paper [4].

The quantification of phenolic and phenyl end group and calculation of end group ratio were carried out using a Bruker Avance 500 MHz. Molecular weights of the prepolymer and the solid-state polymerized BPA-PC were measured using Waters Alliance GPC system (Waters Corporation, Milford, MA) with tetrahydrofuran (THF) as a mobile phase. It is noted that *absolute* molecular weights measured using a light scattering detector (in contrast to molecular weights *relative* to polystyrene standard) are reported in this study. 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.

RESULTS

Figure 3 shows effect of temperature on molecular weight evolution during SSP of PCP6C ($M_n = 3,800$ g/mol) at reaction temperatures ranging 150-190 °C with two different sweep fluids, scCO₂ at 207 bar and N₂.

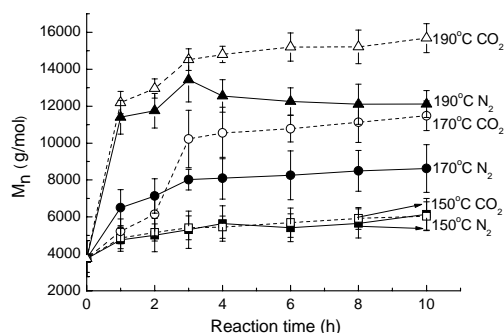


Figure 3. Effect of temperature on molecular weight evolution during SSP of PCP6C ($M_n = 3,800$ g/mol) with scCO₂ at 207 bar and N₂.

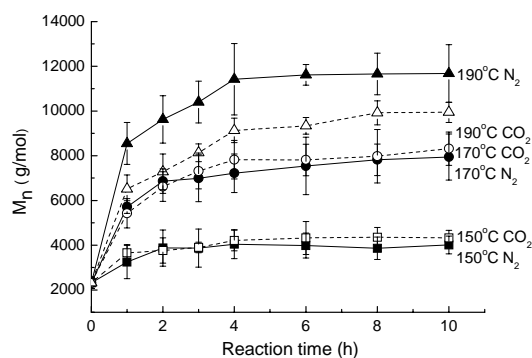


Figure 4. Effect of temperature on molecular weight evolution during SSP of PCP9C ($M_n = 2,400$ g/mol) with scCO₂ at 207 bar and N₂.

At 150 °C, the molecular weight of the polymer synthesized using scCO₂ is similar to the molecular weights of the polymer synthesized using N₂. At higher temperatures of 170-190 °C, higher molecular weight polymers resulted when scCO₂ was used as the sweep fluid. Thus the presence of scCO₂ increases the SSP reaction rate and increases asymptotic molecular weight of the polymers.

This indicates that scCO₂ effectively plasticizes the amorphous region of the polymer, thus significantly increases the SSP reaction rate by increasing chain mobility and facilitating condensate removal.

When SSP was carried out with the lower molecular weight prepolymer, PCP9C ($M_n = 2,400$ g/mol), scCO₂ effects on the SSP rate are different compared with the scCO₂ effects when the higher molecular weight prepolymer (PCP6C) was used. Figure 4 shows effect of temperature on molecular weight evolution during SSP of PCP9C.

Figure 4. Effect of temperature on molecular weight evolution during SSP of PCP9C ($M_n = 2,400$ g/mol) with scCO₂ at 207 bar and N₂.

At 150-170 °C, molecular weights of the polymer from scCO₂ are similar to those of the polymers synthesized from N₂. At 190°C, however, the molecular weights of the polymer from scCO₂ are significantly lower than those from N₂.

Figure 5 shows lamellar thickness and crystallinity of the polymer from PCP6C and PCP9C at 170 °C with scCO₂ (207 bar) and N₂ as the sweep fluids.

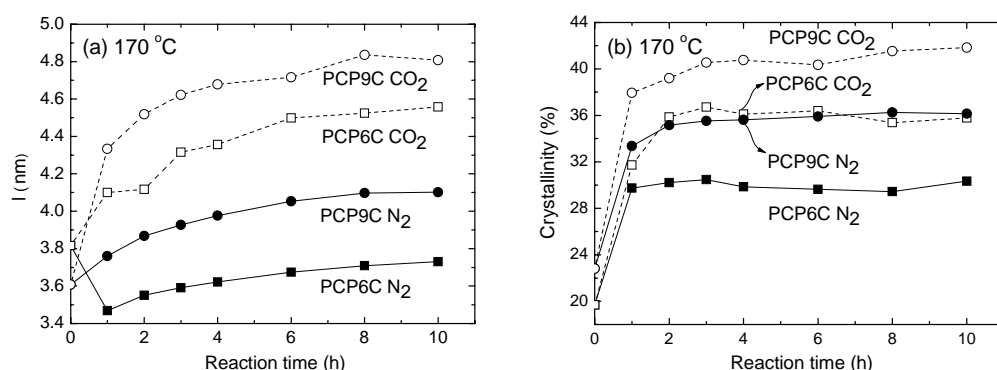


Figure 5. Lamellar thickness, and crystallinity of the polymers synthesized by SSP at 170 °C with scCO₂ (207 bar) and N₂ as the sweep

fluids. Lamellar thickness was calculated using Gibbs-Thomson equation, $T_m = T_m^0 \left(1 - \frac{2\sigma_e}{l\Delta H_f}\right)$, where T_m^0 is the equilibrium melting

temperature (335 °C) [5], σ is the fold surface free energy (70 mJ/m²) [5], and ΔH_f is the heat of fusion.

The lamellar thickness and crystallinity of the polymer synthesized from PCP9C with N₂ is larger than those of the polymer from PCP6C with N₂. The larger lamellar thickening and the larger crystallinity of the polymer from PCP9C may be associated with smaller molecular weight of the prepolymer. It would be easier for shorter chains to fit into the crystal lattices. As a result, the polymer chains become rigid and chain end mobility is more inhibited. Thus end-group diffusion and byproduct diffusion of the polymers synthesized from the lower molecular weight prepolymer (PCP9C) is more inhibited relative to those of the lower molecular weight prepolymer (PCP6C). As

a result, molecular weights of the polymers from PCP9C are smaller than those from PCP6C when N₂ was used as the sweep fluid.

It can be seen in Figure 5 that the lamellar thickness and the crystallinity of the polymers synthesized with scCO₂ as the sweep fluid are larger than those of the polymers synthesized with N₂. The lamellar thickness and the crystallinity of the polymers from PCP6C are smaller than those of the polymers from PCP9C when scCO₂ was used as the sweep fluid. The molecular weights of the polymers synthesized with scCO₂ are larger than those of the polymers synthesized with N₂ when PCP6C was used (Figure 3). This suggests that the molecular weight enhancing effects associated with scCO₂ is dominant when the higher molecular weight prepolymer (PCP6C) was used. In contrast, molecular weight of the polymers synthesized with scCO₂ is similar (at 170 °C) or lower (at 190 °C) than the molecular weight of the polymers synthesized with N₂ when PCP9C was used (Figure 4). This indicates that scCO₂ has detrimental effects on the SSP rate when PCC9C was used. This may be because shorter chains are easier to fit into the crystal lattices and more of the end-groups are become inactive by the crystalline phase.

CONCLUSION

BPA-PC was solid-state polymerized with N₂ and scCO₂ as the sweep fluids. Supercritical carbon dioxide did not always enhance SSP rate of BPA-PC. When the lower molecular weight prepolymer was used, crystallinity and lamellar thickness of the polymers during SSP with scCO₂ is more significantly increased, which retard chain extension reaction by increasing chain mobility and byproduct diffusion. This results in the similar or lower molecular weight polymers compared with the polymers synthesized with N₂. Therefore, high molecular weight prepolymers are desired when using SSP in order to achieve high molecular weight BPA-PC by exploiting molecular weight enhancing effects associated with scCO₂.

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