Crystallization and Solid-State Polymerization of Poly(bisphenol A carbonate) Facilitated by Supercritical CO_2

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ABSTRACT: Poly(bisphenol A carbonate) was synthesized by solid-state polymerization (SSP) using supercritical CO_2 to induce crystallinity in low molecular weight polycarbonate beads. The CO_2-induced crystallization was studied as a function of time, temperature, molecular weight, and pressure. There was an optimum temperature for crystallization which depended on the molecular weight of the polymer. The molecular weight and percent crystallinity of the polymer produced by SSP were determined as a function of time and radial position in the bead. The molecular weight and percent crystallinity were strong functions of the particle radius, probably because of the slow diffusion of phenol out of the polymer particles. Nitrogen and supercritical CO_2 were used as sweep fluids for the SSP process. The polymerization rate was always higher in supercritical CO_2 at otherwise comparable conditions. We hypothesize that supercritical CO_2 plasticizes the amorphous regions of the polymer, thereby increasing chain mobility and the rate of phenol diffusion out of the polymer. This permits the reaction temperature to be reduced, thereby suppressing side reactions that lead to color body formation. These advantages result in higher molecular weight product with good optical clarity when supercritical CO_2 is the sweep fluid.

Introduction

Polycarbonates are used in numerous commercial applications including compact disks, automotive parts, and other goods. Polycarbonates are produced at a rate of about 3 billion pounds per year, with an expected increase of 7−10% a year for the next decade as DVDs and polycarbonate windows become commonplace.[1] Two industrially suitable synthetic routes were developed virtually simultaneously by Bayer A. G.[2] and General Electric Co:[3] an interfacial reaction between phosgene and bisphenol A in a biphasic reaction system of methylene chloride and alkaline water (GE) or by a melt phase transesterification between a bisphenol and a diaryl carbonate (Bayer).

The interfacial route typically results in high molecular weight polymer with excellent optical properties. However, this method uses phosgene and produces an aqueous waste stream and a methylene chloride waste stream. The melt phase condensation reaction between bisphenol A and diphenyl carbonate is a solvent-free process; phenol is produced as a byproduct and must be recovered and recycled. This method also offers the possibility of a phosgene-free synthesis once a viable non-phosgene synthesis of diphenyl carbonate is developed. The drawback of the melt phase process arises from the high viscosity of the melt which limits the rate of phenol removal and the rate at which chain extension reactions can occur. Higher temperatures are required for the melt phase reaction which leads to an increase in the rates of the side reactions that produce color bodies that reduce the optical quality of the polymer product.

Because of the abundant demand for this polymer, it is increasingly important that an environmentally friendly synthesis is developed. In an attempt to devise a phosgene-free and solvent-free synthesis of poly(bisphenol A carbonate), solid-state polymerization (SSP) of the polymer was explored. Unlike PET, polycarbonate does not thermally crystallize; it undergoes solvent-induced crystallization by organic solvents[6] and by the addition of nucleating agents.[7] The solvents known to induce crystallinity (e.g., acetone) are difficult to handle in a world-scale commercial plant and are undesirable environmentally. Additionally, it is very difficult to remove all the organic solvent from the polymer after crystallinity is induced. Even after vacuum was applied for 24 h at temperatures above 150 °C, solvent remained in the polymer.[6,8] Currently, the SSP of poly(bisphenol A carbonate) is not practiced commercially despite the fact that SSP is the method of choice for large-volume step-growth polymers such as “bottle-grade” poly(ethylene terephthalate) (PET).[4,5]

Recently, it was shown that thin films of polycarbonate can undergo crystallization upon exposure to CO_2 at elevated pressures and temperatures.[9] CO_2 rapidly degassed from the polymer after the crystallization process when the pressure was released from the high-pressure vessel. Herein we report the extension of the crystallization process with supercritical CO_2 to granules or beads of low molecular weight polycarbonate in an effort to create a material that can undergo solid-state polymerization without using toxic organic solvents.

For SSP processing, it is advantageous to have the polymer in pelletized form. However, for the solid-state polymerization of large particles, a molecular weight gradient between the center and surface may exist depending on the process conditions.[10−13] This gradient is due to the fact that the condensate molecule must

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diffuse out of the interior of the particle before the molecular weight can increase in that region. Under some circumstances, the molecular weight increase in the center of the particle can be controlled by the diffusion of the byproduct. Additionally, the morphological characteristics of the polymer particle may vary with position. It has been reported that polycarbonate undergoes a crystallization that is induced by the solid-state polymerization.[14−16] If the particle surface is undergoing chain extension reactions at a greater rate than the particle interior, it is likely that the surface would have a greater degree of crystallinity.

In addition to inducing crystallinity in the prepolymer, CO_2 can also play a key role in facilitating the removal of the condensate. In SSP processes, a sweep fluid is passed through the bed of polymer particles in order to remove the condensate from the reactor. With supercritical CO_2 as the sweep fluid, the solid-state polymerization of polycarbonate can be viewed as a supercritical fluid extraction of phenol from the polymer particle. Since phenol is very soluble in supercritical CO_2, this process should be greatly enhanced.[18] Moreover, supercritical CO_2 plasticizes the amorphous regions of the polycarbonate sample and should give the chains increased mobility for chain extension reactions and should increase the diffusion coefficient of phenol in the polymer particles. The use of supercritical CO_2 as the sweep fluid should also allow lower reaction temperatures due to the fact that it greatly depresses the T_g of the polymer. This should lead to a product with better optical quality since the side reactions that lead to color body formation occur above 150 °C in the presence of alkali catalyst.[2] A number of step-growth processes could benefit from the use of supercritical CO_2 as a processing aid if the mechanism of polymerization is compatible with CO_2. It has been previously demonstrated that the polymerization of poly(bisphenol A carbonate) is compatible with the use of CO_2.[16,17]

Experimental Section

Reagents and Prepolymer Synthesis. Bisphenol A (BPA) was recrystallized from methanol/water (1/1 by volume) and dried in a vacuum at 60 °C. Diphenyl carbonate (DPC) was recrystallized from hot methanol and dried in a vacuum at room temperature. $LiOH{\cdot}H_2O$ from Aldrich was used as received. Prepolymer was synthesized by the step-growth polymerization of bisphenol A and diphenyl carbonate using an aqueous solution of LiOH as the initiator. The molecular weight of the prepolymer depended on the removal of phenol (bp 181 °C) which was accomplished either by using a vacuum or by flowing an inert gas (argon or nitrogen) through the reaction system. At the end of the polymerization, prepolymer was poured into a hot glass syringe. The prepolymer dripped from the hot syringe under its own weight into a beaker of room-temperature water, forming uniform sized beads. The beads had an average mass of 40 mg and had an average diameter of 3.6 mm.

Solvent-Induced Crystallization. The solvent-induced crystallization of poly(bisphenol A carbonate) was studied as a function of pressure (100−340 bar), temperature (range is dependent on M_w), and time (up to 12 h). Data were collected for polycarbonate of three different molecular weights, 4.4×10^4, 1.8×10^4, and 2.5×10^3 g/mol. A typical crystallization experiment involved placing amorphous polycarbonate beads in a high-pressure vessel. The cell was heated to the crystallization temperature, and CO_2 was subsequently added to the vessel. Once the desired pressure was reached, the time measurement began. At the end of the experiment, CO_2 was slowly vented from the vessel, and the polymer beads were collected. Differential scanning calorimetry (DSC) measurements were made to determine the amount of crystallinity induced in the polymer sample.

SSP Using N_2 as a Sweep Fluid. In a typical experiment, 1 g of a 19% crystalline prepolymer with an M_w of 2.5×10^3 g/mol was placed in a solid-state polymerization vessel at 160 °C (3 deg below the onset of melting) as nitrogen was passed through the vessel. Approximately 0.25 g of prepolymer was removed from the vessel after the polymerization had run for 2, 4, 6, and 12 h. Since it was observed that the T_m increased during the polymerization, a polymerization was run where the temperature was raised with time, i.e., 180 °C for 2 h, then 205 °C for 2 h, then 230 °C for 2 h, and finally 240 °C for an additional 6 h.

Gradient Measurements. The molecular weight and thermal properties of polycarbonate beads were studied as a function of radial position. The sample studied was polymerized at 180 °C for 2 h, then 205 °C for 2 h, then 230 °C for 2 h, and finally 240 °C for an additional 6 h using nitrogen as the sweep gas. The polycarbonate beads were carefully dissected with a razor, and the distance from the core was monitored using a micrometer. The beads were dissected into three different regions. These regions are a core region (0.0−0.4 mm from the center), an intermediate region (0.4−1.4 mm from the center), and a surface region (1.4−1.8 mm from the center). The samples were analyzed by gel permeation chromatography (GPC) to determine molecular weight and by DSC to determine the percent crystallinity and T_m of the polymer.[19,20]

SSP Using Supercritical CO_2 as the Sweep Fluid. Polycarbonate beads were prepared and crystallized by the method described above. Fifteen percent crystalline prepolymer beads with an M_w of 2.5×10^3 g/mol were placed in a high-pressure vessel and were packed in place by glass wool. The pressure and flow rates were controlled by a back-pressure regulator and Isco syringe pump, respectively. A temperature controller was used to maintain the temperature of a probe at the center of the vessel. The sample was heated to the reaction temperature, and supercitical CO_2 was allowed to flow through the vessel at 2 mL/min at a constant pressure.

Results and Discussion

Solvent-Induced Crystallization. Solid-state polymerization must be carried out between the T_g and T_m of the polymer. Poly(bisphenol A carbonate) is amorphous after synthesis, thereby not lending itself to solid-state polymerization in its virgin state. The most direct method for determining the crystallinity of the polymer in the current system is DSC. The percent crystallinity (P) can be calculated using the following equation with a value of 26.2 cal/g for the $\Delta H_f°$ of bisphenol A polycarbonate:[21]

$$P = \Delta H_f(\text{sample})/\Delta H_f° \qquad (1)$$

Figures 1 and 2 show the results of the solvent-induced crystallization experiments as a function of temperature, pressure, and time on a sample with an M_w of 4.4×10^4 g/mol. As seen in Figure 1, the highest percent crystallinity for each time occurs at approximately 140 °C. During the crystallization process the polymer is plasticized by supercritical CO_2. At some temperature below the maximum temperature for crystallization, small crystallites (presumably spherulites) develop and grow with time until impingement occurs. We speculate the crystalline growth rate increases with temperature below the maximum temperature for crystallization. Supercritical CO_2 enables this crystallization since it increases the free volume of the amorphous regions of the polymer. This allows the ordinarily rigid chains to rearrange into a more energetically favored state. However, as the temperature is increased past

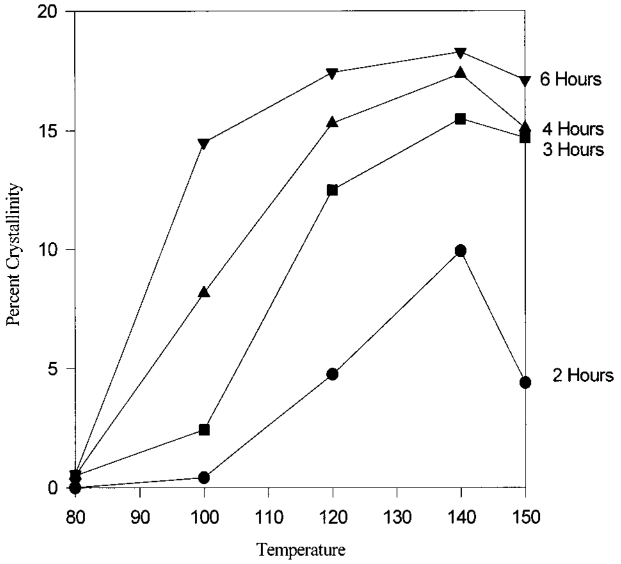

Figure 1. Percent crystallinity induced by supercritical CO_2 in poly(bisphenol A carbonate) (MW = 4.4 × 10^4 g/mol) as a function of temperature at 204 bar.

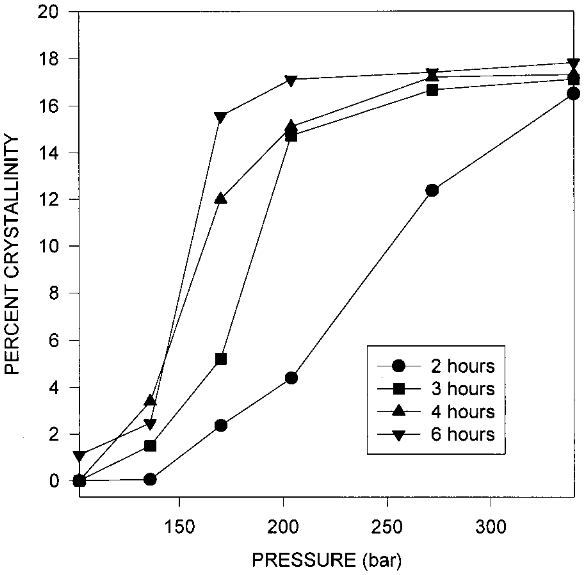

Figure 2. Percent crystallinity induced by supercritical CO_2 in poly(bisphenol A carbonate) (MW = 4.4 × 10^4 g/mol) as a function of pressure at 150 °C.

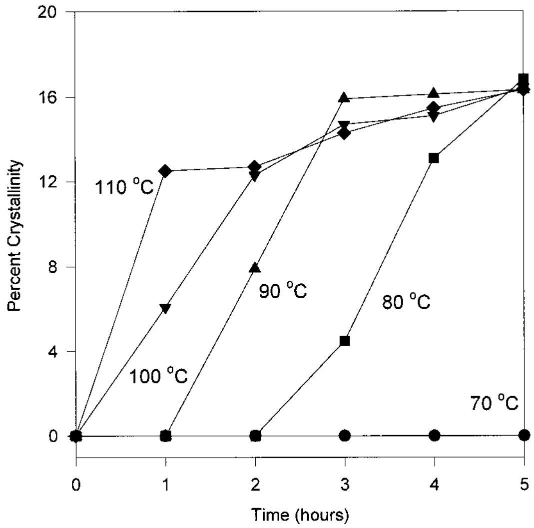

Figure 3. Percent crystallinity induced by supercritical CO_2 in poly(bisphenol A carbonate) (MW = 1.8 × 10^4 g/mol) as a function of temperature at 204 bar.

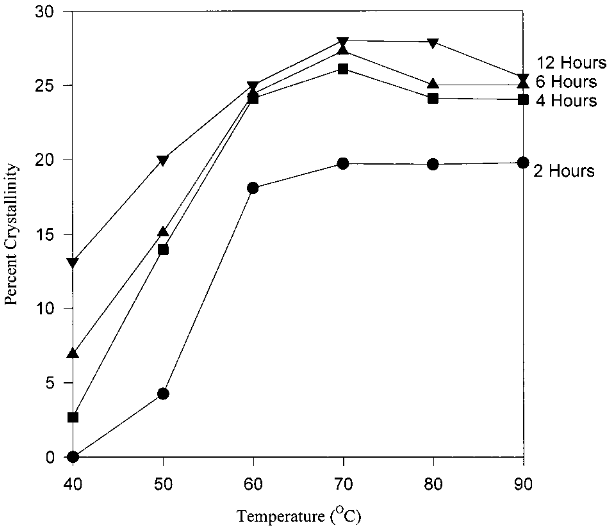

Figure 4. Percent crystallinity induced by supercritical CO_2 in poly(bisphenol A carbonate) (MW = 2.5 × 10^3 g/mol) as a function of temperature at 204 bar.

the maximum temperature for crystallization, we suspect that the smaller imperfect crystallites begin to melt. In crystallization experiments run at too a high a temperature (close to what the induced T_m of this process would be), crystallization was not seen over the course of hours. There was no crystallinity induced in the sample at 180 °C over 6 h. Therefore, it is important to understand from a processing point of view the most efficient conditions for crystallization.

In Figure 2, it is seen that the crystallization rate increases with pressure up to 340 bar when run at 150 °C. Crystallization occurs at much slower rates between 100 and 170 bar. At this M_w, the data show that there is a maximum amount of crystallinity of approximately 18% that is induced by supercritical CO_2.

Figure 3 shows the percent crystallinity as a function of time at 204 bar for a polycarbonate sample with an M_w of 1.8 × 10^4 g/mol, at different crystallization temperatures. This experiment shows that a sample of intermediate molecular weight has a maximum induced crystallization of approximately 18%. Looking closer at these data reveals some interesting facts about the temperature effects on inducing crystallinty. At lower temperatures, it takes considerably longer to induce crystallinity than at higher temperatures. At 80 °C, 2 h pass before crystallinity is detected by DSC measurements. However, experiments run at 110 °C show that a significant degree of crystallinity can be induced on a sample of this M_w relatively quickly. It is also interesting to note that, once crystallization occurs for samples at any temperature, the maximum is rapidly approached. Once the maximum crystallinity level is approached, the crystallization rate rapidly drops off. Currently, wide-angle X-ray diffraction (WAXD) studies are under way to investigate the exact nature of the crystallization process.

Figure 4 shows the crystallinty induced in a polycarbonate sample with an M_w of 2.5 × 10^3 g/mol at 204 bar as a function of temperature at different time lengths. This figure shows that a polycarbonate sample of very low molecular weight has a higher degree of

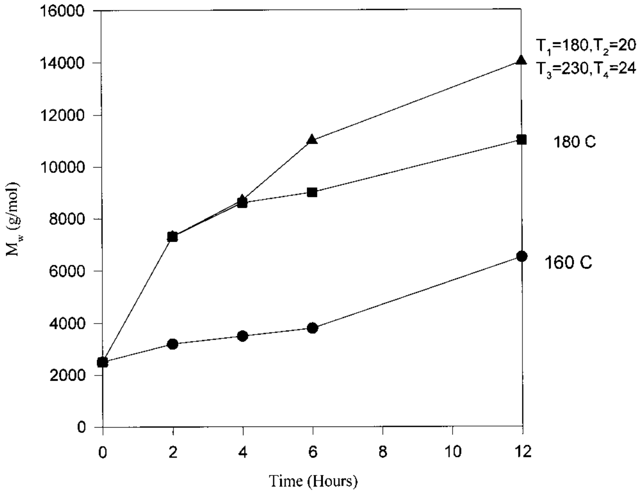

Figure 5. Increase in M_w for three samples of poly(bisphenol A carbonate) with an initial M_w of 2.5 × 10^3 g/mol from solid-state polymerization at different temperatures over 12 h. The time–temperature profile for the reaction was 180 °C for 2 h, 205 °C for 2 h, 230 °C for 2 h, and finally 240 °C for an additional 6 h.

crystallization induced and a different temperature range for crystallization. The result that a higher level of crystallinity is attained for lower molecular weight polymers has previously reported by other investigators.[24,25]

SSP Using N_2 as the Sweep Fluid. Initially, amorphous polycarbonate beads with a M_w of 2.5 × 10^3 g/mol were exposed to supercritical CO_2 and were crystallized to 19% crystalline with a resulting T_m of 197 °C. There was no chain extension during the crystallization process as confirmed by GPC. Figure 5 shows the M_w increases with increasing reaction temperature. For the sample polymerized at 160 °C, the final M_w was 6.5 × 10^3 g/mol after 12 h, while for the sample polymerized at 180 °C, the final M_w was 1.1 × 10^4 g/mol after the same time. In a polymerization where the temperature was increased over time, the final M_w was 1.4 × 10^4 g/mol. The observed increase in molecular weight demonstrates that the use of supercritical CO_2 to induce crystallinity is compatible with the solid-state polymerization of polycarbonates. As the polymerization proceeded, the samples became progressively more crystalline and the T_m increased significantly.[16] An increase in crystallinity with chain extension during solid-state polymerization has been previously observed by Sivaram et al.[14,15] This phenomenon was explained by the fact that the polymer was greatly reorganized in the solid phase, leading to the development of more perfect crystallites.[22]

Gradient Measurements. The step-growth polymerization of nearly all polyesters is limited by the removal of the byproduct produced in the process. In fact, the equilibrium constant K_{eq} is very low, with 1–10 being common values.[23] These low K_{eq} values show the importance of removing the byproduct. It follows then that in the solid-state polymerization of poly(bisphenol A carbonate) the removal of phenol could limit the molecular weight. Since the mechanism of phenol removal for solid-state polymerization is to pass a sweep fluid past the surface of the bead, a gradient in phenol concentration may develop radially across the bead. The lowest concentration of phenol will be at the bead surface, and the highest concentration of phenol should be at the center. To determine what effect the phenol gradient would have on molecular weight, percent crystallinity, and T_m of the polymer, the beads were dissected into three regions as described earlier.

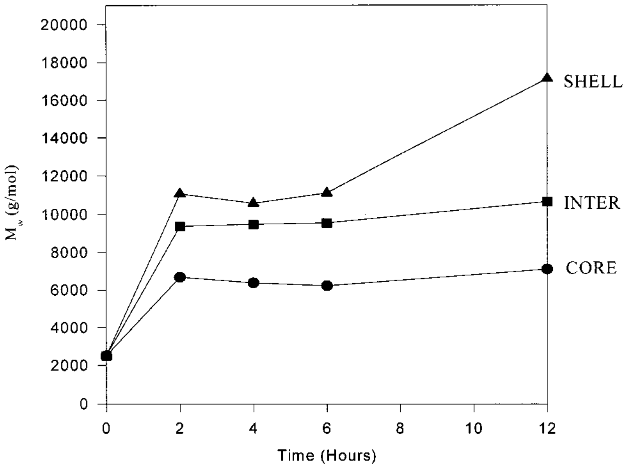

Figure 6. M_w measurements for three regions (core, intermediate, and shell) of a polycarbonate bead (initial M_w of 2.5 × 10^3 g/mol) from a solid-state polymerization over 12 h using a time–temperature profile of 180 °C for 2 h, 205 °C for 2 h, 230 °C for 2 h, and finally 240 °C for an additional 6 h.

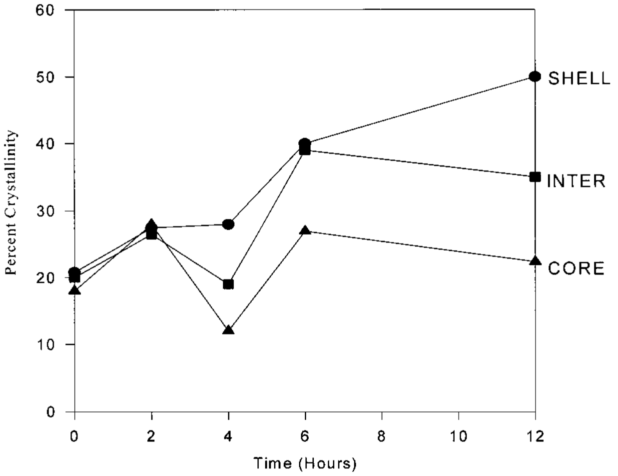

Figure 7. Percent crystallinity measurements for three regions (core, intermediate, and shell) of a polycarbonate bead (initially 19% crystalline) from a solid-state polymerization over 12 h using a time–temperature profile of 180 °C for 2 h, 205 °C for 2 h, 230 °C for 2 h, and finally 240 °C for an additional 6 h.

Figure 6 shows the molecular weight buildup as a function of time for the three different regions of the polycarbonate bead. The shell of the bead had the greatest chain extension over the course of the reaction and reached the highest molecular weight. The intermediate and core regions also underwent chain extension reactions, but to a lesser extent, with lower molecular weights. Figure 7 shows the percent crystallinity as a function of time for the three different regions of the bead. The shell has the highest degree of crystallinity at the end of the experiment. The T_m was also measured as a function of time for the three different regions of the particle. It was previously shown that the T_m increases as the molecular weight increases in the particle.[17] It was found that the increase or decrease in T_m paralleled the increase or decrease in crystallinity in the different regions of the particle. The percent crystallinity and T_m measurements were made on beads

Table 1. Increase in M_w for a Sample That Was Initially 2.5×10^3 g/mol Is Reported for Solid-State Polymerizations Using Supercritical CO_2 as the Sweep Fluid at 2 mL/min

sample	temp (°C)/ time (h)	press. (bar)/ time (h)	M_w (g/mol)	control M_w (g/mol) N_2 flow
1	120/2	340/2	4.6×10^3	3.2×10^3
2	140/2	136/2	4.8×10^3	3.3×10^3
3	140/2	340/2	5.6×10^3	3.3×10^3
4	140/4	136/4	6.9×10^3	3.5×10^3
5	140/4	136/2 340/2	1.0×10^4	3.5×10^3
6	140/2 160/2	136/4	1.1×10^4	3.6×10^3
7	140/8	136/2 340/6	1.4×10^4	5.1×10^3
8	140/2 150/2 160/4	136/8	1.5×10^4	5.8×10^3
9	140/12	136/8	1.9×10^4	5.9×10^3

that were not heated isothermally, but rather from an experiment in which the temperature increased with time. This experimental condition leads to different morphological effects in different regions of the particle over time. For example, in Figure 7, the percent crystallinity decreases with time from 2 to 4 h and from 6 to 12 h in the core and intermediate regions of the particle. We speculate that the higher reaction temperatures melt the smaller imperfect crystallites in these regions.

The molecular weight, percent crystallinity, and T_m of each region play an important role in the phenol concentration gradients that develop. The highly crystalline shell of the bead should lower the rate of phenol diffusion out of the particle. Crystallization creates a torturous path for phenol to diffuse out of the particle that would limit the molecular weight increase in the interior of the particle. The gradient in crystallinity is not surprising due to the solid-state polymerization-induced crystallization observed in the SSP experiment with nitrogen as the flow gas.[17] Since the shell undergoes the greatest degree of polymerization, it follows that it is more crystalline than the other regions. The increase in T_m with molecular weight is likely due to the fact that more perfect crystallites are forming during the chain extension reactions. This is likely due to the fact that there are a greater number of crystallites with a less perfect structure in these regions than in the surface region of the particle. As the temperature is increased, it is likely that these less perfect crystallites melt in the interior regions. A more in depth study using WAXD is underway to provide insight into the nature of the crystallization change occurring during the solid-state polymerization process in this system.

SSP Using Supercritical CO_2 as the Sweep Fluid. A number of solid-state polymerization experiments were run at different reaction conditions with supercritical CO_2 as the sweep fluid. Initially, experiments were run at 160 and 180 °C (below the onset of melting) with the supercritical CO_2 flowing at a rate of 2 mL/min at 136 bar. However, the particles became distorted and lost their shape at these temperatures. This is likely due to the fact that the amorphous regions of the pellets are plasticized to such a great degree at these temperatures and pressures that the sample flows. Compared to the N_2 sweep fluid experiments, the polymerizations run in the presence of CO_2 at 160 or 180 °C are up to 100 °C higher than the T_g of the polymer sample. Since the samples are approximately 85% amorphous, the sample begins to flow, and the reaction is no longer taking place in the solid state. As a result, the experiments were run at lower temperatures to prevent the particles from flowing.

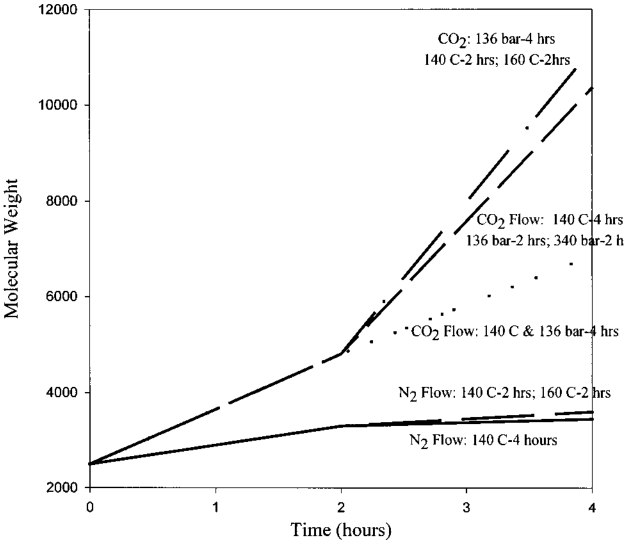

Figure 8. Increase in M_w of five samples of poly(bisphenol A carbonate) with an initial M_w of 2.5×10^3 g/mol from solid-state polymerization at different temperatures over 4 h. The time–temperature–pressure profile and type of sweep fluid for each reaction are noted.

The exact conditions and results from these experiments are listed in Table 1. Control experiments were run with a nitrogen flow at the same reaction temperature and time length. These results show that using supercritical CO_2 as the sweep fluid leads to a higher molecular weight polymer as opposed to using N_2 at these processing conditions. Figure 8 shows the rate enhancement of this process for a number of these experiments over time. There is very little molecular weight buildup at these low temperatures when N_2 is used as the sweep fluid. There is a much greater molecular weight buildup when supercritical CO_2 is used as the sweep fluid, especially when the pressure is stepped up to 340 bar or the temperature is increased to 160 °C after 2 h. This increase in rate is likely due to a few reasons. First, there should be enhanced phenol removal by the supercritical CO_2 due to the solubility of the condensate in the sweep fluid. Second, the reactions that lead to chain extension should be enhanced by the increased chain mobility in the amorphous regions afforded by the supercritical CO_2-induced plasticization. Third, we speculate a higher diffusion coefficient of phenol in polycarbonate in the presence of supercritical CO_2.

Conclusions

The use of supercritical CO_2 is advantageous in the synthesis of poly(bisphenol A carbonate). Supercritical CO_2 is compatible with the mechanism of polymerization and can be used to render the prepolymer in a suitable morphology for solid-state polymerization. Optimum conditions were determined for the crystallization process for polycarbonate samples with different molecular weights. Polymer molecular weight increased as the reaction temperature increased in solid-state polymerizations using nitrogen as the sweep fluid. The molecular weight, percent crystallinity, and T_m were strong functions of the particle radius, probably because of the slow diffusion of phenol out of the polymer particles.

Solid-state polymerizations using supercritical CO_2 as the sweep fluid provided an enhancement in the reaction rate as opposed to experiments that used nitrogen as the sweep fluid under similar reaction conditions. Polymerizations performed with supercritical CO_2 as the sweep fluid can be run at lower temperatures due to the plasticization of the amorphous regions. Reactions run at lower temperatures provide a high-quality product since the color body forming side reactions associated with the traditional melt condensation reaction are suppressed at lower temperatures.

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