Synthesis of High Molecular Weight Polycarbonate by Solid-State Polymerization

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ABSTRACT: The solid-state polymerization (SSP) of small particles (20 μm) of poly(bisphenol A carbonate) resulted in high molecular weight material (M_w of 36 000 g/mol). Molecular weight distribution broadening was not observed in polycarbonate in the form of small granulated powders but did occur in large polycarbonate beads (3.6 mm diameter). We hypothesize that this broadening is due to slow diffusion of phenol inside the larger polymer particles. A systematic investigation of the role of CO_2 pressure and temperature was performed. It was found that the increase in molecular weight was a strong function of CO_2 pressure and temperature. Additionally, the chain extension reactions occurred faster at higher supercritical CO_2 flow rates. The SSP of polycarbonate in the presence of supercritical CO_2 can be accomplished at temperatures as low as 90 °C, which is 60 °C lower than the T_g of polycarbonate at normal conditions. This should suppress the side reactions that lead to color body formation, thereby resulting in a product with good optical clarity and color.

Introduction

Poly(bisphenol A carbonate) is an important thermoplastic. Bisphenol A based polycarbonates display exceptional toughness, electrical properties, thermal stability, and structural properties, making them appropriate for engineering and durable goods applications.[1] An extremely large market (1997 global consumption was 2.7 billion pounds) with numerous applications has been developed for these materials.[2] Bisphenol A polycarbonate resins are extensively utilized in the digital recording, electronic, electrical, automotive, and architectural industries.

Two industrially significant syntheses of poly(bisphenol A carbonate) were developed in the early 1960s. These processes have proven to be the only relatively inexpensive routes to producing superior polymer resin. The first process, developed by Bayer in 1962, is a two-phase interfacial reaction.[3] In this process, bisphenol A is added first to the reactor in methylene chloride (with a monohydroxylic phenol to control molecular weight). Subsequently, phosgene is added to the reactor, along with aqueous sodium hydroxide (HCl scavenger), to produce a biphasic liquid−liquid system.[1] This synthetic route advantageously leads to high molecular weight polymer with excellent optical clarity and color. The major disadvantage of this process is that it uses phosgene, which is a highly regulated hazardous chemical. Additionally, it is necessary to treat or dispose of an extremely large amount of wastewater and methylene chloride. The second process, developed by GE in 1964, is a melt transesterification reaction of diphenyl carbonate and bisphenol A in the bulk.[4] This synthetic route is solvent-free and avoids the direct use of phosgene. However, the high viscosity of the melt decreases the diffusion of a condensation byproduct phenol, which limits the final molecular weight of the polymer. Additionally, the thermal instability of bisphenol A at high temperatures in the presence of hydroxide anion can result in the discoloration of the final product.[5]

It is increasingly important that an environmentally friendly synthesis of poly(bisphenol A carbonate) 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. 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).[6,7] Unlike PET, polycarbonate does not thermally crystallize; it undergoes solvent-induced crystallization by organic solvents[8] and by the addition of nucleating agents.[9] However, 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.[8,10]

It was shown that thin films of polycarbonate could undergo crystallization upon exposure to CO_2 at elevated pressures and temperatures.[11] It was found that CO_2 could be rapidly degassed from the polymer after the crystallization process upon the release of pressure. Herein we report the extension of our previous work of the crystallization process with supercritical CO_2 to extremely small particles of low molecular weight polycarbonate in an effort to create a material that can undergo solid-state polymerization without using toxic organic solvents.[12,13]

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From a processing standpoint, 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.[12,14–16] This gradient is due to the fact that the condensate molecule must diffuse out of the interior of the particle before the molecular weight can increase in that region. Slow diffusion can limit the molecular weight that is obtained in the final product. Additionally, the morphological characteristics of the polymer particle may vary with position.[12] It has been reported that polycarbonate undergoes a crystallization that is induced by the solid-state polymerization.[12,13,17–19] The particle surface, which undergoes chain extension reactions at a greater rate than the particle interior, becomes significantly more crystalline than the interior of the bead. This presumably creates an extremely tortuous diffusion path for the phenol escaping from the polymer bead. The use of significantly smaller polymer particles for SSP should result in polymer with a greater final molecular weight, because phenol will have a shorter distance to diffuse from smaller particles. Additionally, the greater surface area of a smaller particle will allow for more efficient transfer of phenol from the polymer particle into the surrounding gas.

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 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 particles, since phenol is very soluble in supercritical CO_2.[20] Moreover, supercritical CO_2 plasticizes the amorphous regions of the polycarbonate. This should give the chains increased mobility for chain extension reactions and should increase the diffusion coefficient of phenol in the polymer particles. The SSP of poly(bisphenol A carbonate) can be achieved at lower reaction temperatures when facilitated with supercritical CO_2 as the sweep fluid.[12] Since supercritical CO_2 greatly depresses the T_g of the polymer (by ~75 °C), the window of reaction temperatures for the SSP changes. 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.[5] A number of step growth processes might benefit from the use of supercritical CO_2 as a processing aide 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.[12,13,20]

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, the prepolymer was collected and ground into small particles using a mortar and pestle. The size of the particles was determined using a scanning electron microscope. By measuring the average of 100 particles, it was determined that the particles were 20 ± 5 μm in size.

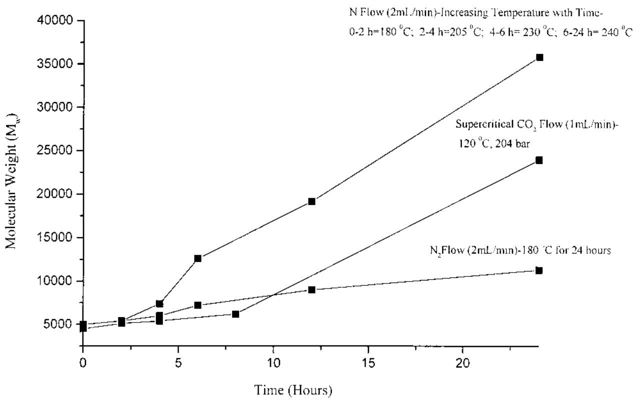

Figure 1. Increase in M_w for three samples of poly(bisphenol A carbonate) from solid-state polymerization under different reaction conditions. The time–temperature profiles, sweep fluid type, and flow rate are noted.

Solvent-Induced Crystallization. To render the poly(bisphenol A carbonate) prepolymer in a suitable morphology for SSP, prepolymer particles were treated with supercritical CO_2 to induce crystallization. A typical crystallization experiment involved placing amorphous polycarbonate powder in a high-pressure vessel. The cell was heated to the crystallization temperature (65 °C), and CO_2 was subsequently added to the vessel (200 bar). At the end of the experiment, CO_2 was slowly vented from the vessel, and the semicrystalline polymer powder was collected. Differential scanning calorimetry (DSC) measurements were made to determine the amount of crystallinity in the polymer sample.[12,21]

Characterization. Thermal analysis measurements were measured by differential scanning calorimetry using a Seiko Haake (DSC 220) in a N_2 atmosphere at a rate of 10 °C/min. Molecular weight measurements were made using a Waters 150-CV gel permeation chromatograph using a THF mobile phase and polystyrene standards.

SSP Using N_2 as a Sweep Fluid. In a typical experiment, 2 g of a 18% crystalline prepolymer with an M_w of 2.5×10^3 g/mol was placed in a vessel at 180 °C (3 deg below the onset of melting) as nitrogen was passed through the vessel. Approximately 0.40 g of prepolymer was removed from the vessel after the polymerization had run for 2, 4, 6, 12, and 24 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 18 h.

SSP Using Supercritical CO_2 as the Sweep Fluid. Polycarbonate powder was prepared and crystallized by the method described above. Crystalline prepolymer (18%) with an M_w of 4.5×10^3 g/mol was placed in an Isco supercritical fluid extractor. An Isco syringe pump controlled the pressure and an Isco heated adjustable flow restrictor needle controlled the flow rates. The Isco extractor module controlled the temperature. The sample was heated to the reaction temperature, and supercritical CO_2 was introduced into the extractor at a constant pressure (100–340 bar) and a constant flow rate (1 or 2 mL/min).

Results and Discussion

Solid-State Polymerization Using N_2 as the Sweep Fluid. Initially, amorphous polycarbonate powder (20 μm) with a M_w of 2.5×10^3 g/mol was exposed to supercritical CO_2 and was rendered 18% crystalline with a resulting T_m of 197 °C. There was no chain extension during the crystallization process as confirmed by GPC. Figure 1 shows that M_w increases with increasing reaction temperature. For the sample polymerized at 180 °C, the final M_w was 12 000 g/mol after

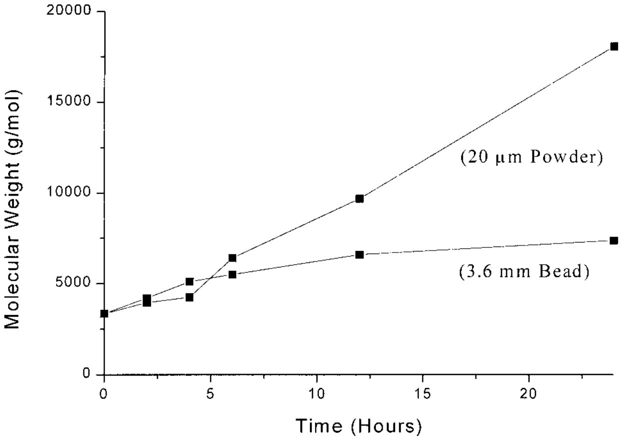

Figure 2. Increase in M_w for two different sized samples (3.6 mm and 20 μm) of poly(bisphenol A carbonate) with an initial M_w of 2.5 × 10^3 from solid-state polymerization at different temperatures over 24 h. The time−temperature profiles are noted. The sweep fluid was nitrogen at a flow rate of 2 mL/min.

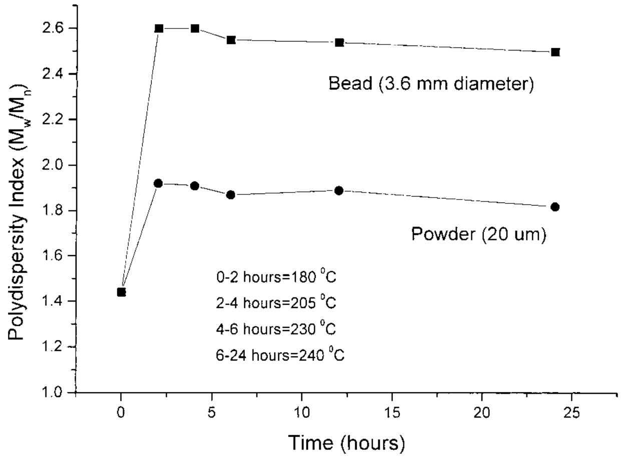

Figure 3. Polydispersity index (M_w/M_n) vs time for two different sized polycarbonate samples (20 μm and 3.6 mm) following solid-state polymerization. The time−temperature profile is noted. The sweep fluid was nitrogen at a flow rate of 2 mL/min.

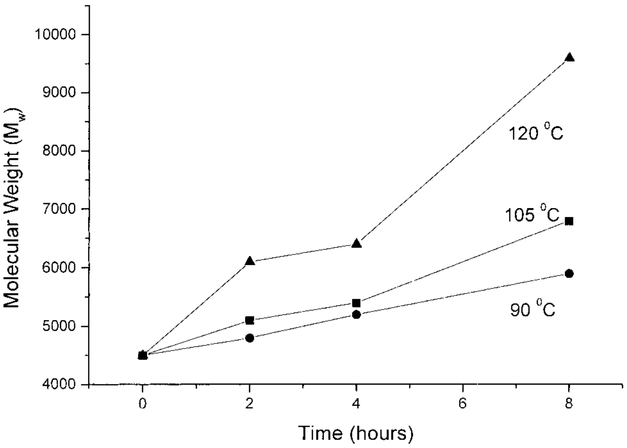

Figure 4. Increase in the M_w of three samples of poly(bisphenol A carbonate) with an initial M_w of 4.5 × 10^3 and a particle size of 20 μm. Supercritical CO_2 was used as the sweep fluid at 340 bar with a flow rate of 1 mL/min at 90, 105, or 120 °C.

Table 1. Increases in M_w for Samples (20 μm) that Were Initially 4.5 × 10^3 g/mol for Solid-State Polymerizations Using Supercritical CO_2 as the Sweep Fluid at 1 mL/min

sample	temp (°C)	press. (bar)	M_w (g/mol) after 2 h	M_w (g/mol) after 4 h	M_w (g/mol) after 8 h
1	90	102	4.7 × 10^3	4.9 × 10^3	5.0 × 10^3
2	90	204	4.8 × 10^3	4.9 × 10^3	5.1 × 10^3
3	90	340	4.8 × 10^3	5.2 × 10^3	5.9 × 10^3
4	105	102	4.9 × 10^3	5.1 × 10^3	5.8 × 10^3
5	105	204	5.0 × 10^3	5.2 × 10^3	6.0 × 10^3
6	105	340	5.1 × 10^3	5.4 × 10^3	6.8 × 10^3
7	120	102	4.9 × 10^3	5.1 × 10^3	5.9 × 10^3
8	120	204	5.1 × 10^3	5.4 × 10^3	6.2 × 10^3
9	120	340	6.1 × 10^3	6.4 × 10^3	9.6 × 10^3

24 h. In the polymerization where the temperature was increased over time, the final M_w was 36 000 g/mol. As the polymerization proceeded, the samples became progressively more crystalline and the T_m increased significantly. The increase in crystallinity and T_m was expected and on the same order of magnitude as described in earlier work.[12,13]

Large poly(bisphenol A carbonate) beads with a diameter of 3.6 mm were used in our previous SSP work. It was found that molecular weight increase was relatively slow with the large polycarbonate beads.[12,13] Figure 2 shows the effect of particle size on number-average molecular weight. In addition, the molecular weight was a strong function of particle radius. The surface of the particle had a higher molecular weight than the interior.

In the previous work, the polymer beads had a significantly greater polydispersity index (M_w/M_n) than expected by theory. This broadening in molecular weight was likely due to the slow diffusion of phenol from the interior of the larger polymer particle. Locally, the PDI was close to theoretical maximum of 2; however, the overall particle itself exhibited a PDI of 2.6. In Figure 3, the polydispersity index for polycarbonate beads and polycarbonate powder after solid-state polymerization are compared as a function of time under similar reaction conditions. The polymerization temperature was increased over time (180 °C for 2 h, then 205 °C for 2 h, then 230 °C for 2 h, and finally 240 °C for an additional 18 h). The polydispersity of the powder remained just below 2.0; however, the polydispersity of the bead was as high as 2.6.

Solid-State Polymerization Using Supercritical CO_2 as the Sweep Fluid. A systematic study of the effect of CO_2 pressure and temperature on the solid-state polymerization process was carried out. Amorphous polycarbonate powder with a M_w of 4.5 × 10^3 g/mol was exposed to supercritical CO_2 and was rendered 18% crystalline with a resulting T_m of 197 °C. There was no chain extension during the crystallization process as confirmed by GPC. The results of this study can be seen in Table 1. The reaction temperature was varied from 90 to 120 °C. In Figure 4, it can be seen that a greater degree of polymerization occurs in the presence of higher temperature CO_2 under isobaric conditions (340 bar). The greater reaction rates at higher temperatures under isobaric conditions are likely due to a combination of effects. The phenol should have a greater diffusivity at higher temperatures. Additionally, the end groups should have greater mobility at higher reaction temperatures, which should lead to an increase in the rate of chain extension reactions. Because of the fact that the polymer is significantly plasticized by supercritical CO_2, we wanted to explore the boundaries of where these chain extension reactions could occur. It would be advantageous from an economic

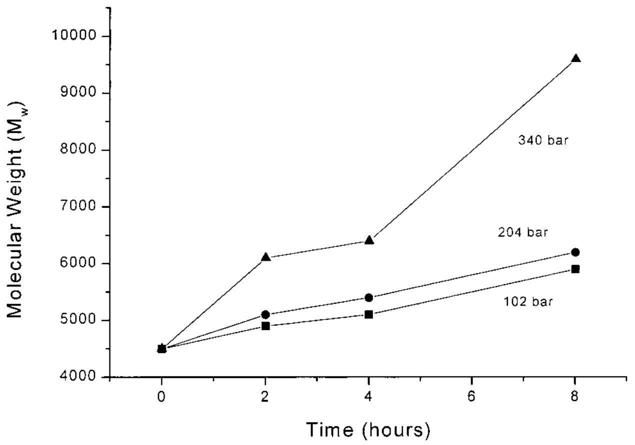

Figure 5. Increase in the M_w of three samples of poly(bisphenol A carbonate) with an initial M_w of 4.5×10^3 and a particle size of 20 μm. Supercritical CO_2 was used as the sweep fluid at 102, 204, or 340 bar with a flow rate of 1 mL/min at 120 °C.

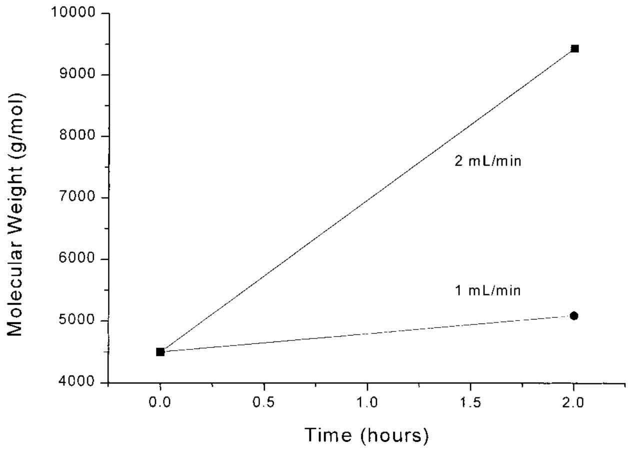

Figure 6. Increase in the M_w of two samples of poly(bisphenol A carbonate) with an initial M_w of 4.5×10^3 and a particle size of 20 μm. Supercritical CO_2 was used as the sweep fluid at 204 bar with a flow rate of 1 or 2 mL/min at 120 °C.

standpoint to work at as low of a temperature as possible. Additionally, it is advantageous to work at lower temperatures because the side reactions that lead to color body formation should only occur at temperatures greater than 150 °C.[5] It can be seen in Figure 1 that high molecular weight polymer can be obtained at 120 °C using supercritical CO_2 as the sweep fluid for 24 h.

A range of CO_2 pressures was also studied under isothermal conditions. As seen in Figure 5, a greater degree of polymerization results as the pressure increases in the presence of CO_2 at 120 °C. The increase in pressure probably accelerated the chain extension reactions for several reasons. Phenol should have a higher solubility in supercritical CO_2 at higher pressures under isothermal conditions.[22] This should drive the reaction to a higher degree of polymerization. Additionally, the amorphous regions should be swollen to a greater degree as the pressure is increased.[20] With this increase in free volume in the amorphous domains of the polymer, the end groups should have a greater mobility, resulting in a greater rate for chain extension reactions. Also, the increase in free volume should allow the phenol to diffuse through a less entangled pathway in order to escape from the polymer particle.

It was also observed that the flow rate of the supercritical CO_2 can influence the rate of solid-state polymerization of polycarbonate. As seen in Figure 6**,** the chain extension reactions in a solid-state polymerization at 120 °C and 200 bar occurred to a much greater degree when the CO_2 was flowed through the reactor at 2 mL/as opposed to 1 mL/min. The flow rate of CO_2 allows for more efficient mass transfer of the phenol from the surface of the polymer particle to the sweep fluid.

Conclusions

The use of smaller polymer particles for the solid-state polymerization of poly(bisphenol A carbonate) is advantageous for synthesizing high molecular weight material. Solid-state polymerization of polycarbonate powder with nitrogen as the sweep fluid resulted in polymer with a M_w greater than 35 000 g/mol and a polydispersity index of approximately 2. The polymer molecular weight increased as the reaction temperature increased for this process. It was found that greater molecular weights were obtainable using smaller polymer particle size. Additionally, the molecular weight distribution broadening that occurs in the larger polymer beads (3.6 mm diameter) does not occur in the smaller polymer particles.

Solid-state polymerizations using supercritical CO_2 as the sweep fluid were studied as a function of CO_2 pressure and temperature. The chain extension reactions occurred to a greater degree in the presence of higher temperature and higher pressure CO_2. Additionally, the chain extension reactions occurred to a greater degree when the CO_2 was flowed through the reactor at a greater rate. Future efforts of these polymerizations will focus on the optimization of the solid-state polymerization process using supercritical CO_2 as the sweep fluid. Reactor design, monomer type, catalyst type, and sweep fluid flow rate are all variables that can still be optimized for this process.

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