Synthesis and Swelling of Poly(bisphenol A carbonate) Using Supercritical CO_2

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Introduction. Among the advantages of traditional melt-phase polymerization processes is the potential to produce a high molecular weight polymer without the use of solvent. While solvent-free melt-phase polymerization methods avoid the use of environmentally detrimental solvent mixtures, it would be convenient to mediate the high viscosity of the polymer melt associated with the attainment of high molecular weight polymer, especially near the end of the polymerization. It has been noted previously that the condensate associated with certain step-growth polymerizations can be removed more effectively by swelling or plasticizing the polymer melt in some manner, thus increasing both chain mobility and free volume in the melt phase.[1] Swelling agents should improve polymerization rates of step-growth polymerization processes by increasing the surface area available for condensate removal, but such a technique is not an advantage from a processing standpoint if it introduces to the reaction a swelling agent that is toxic, costly, or difficult to separate from the end product. Since many step-growth polymers are used for food and beverage packaging applications, absolute safety of any additive to the melt phase is imperative.

Polycarbonates are an important class of polymers due primarily to their toughness and optical clarity. Two different, industrially suitable, synthetic routes were developed virtually simultaneously by Bayer A.G. and General Electric Co.[2] The first route involves an interfacial reaction between 4,4′-isopropylidene bisphenol (bisphenol A) and phosgene using a biphasic system of methylene chloride and an alkaline aqueous phase with a phase-transfer catalyst. The other route involves a melt transesterification between a bisphenol and a diaryl carbonate, typically diphenyl carbonate. The former has become the predominant industrial route despite the drawbacks of the use of both phosgene and methylene chloride. The difference in pK_a of various bisphenols, their partitioning between the two phases, and interaction with the phase-transfer catalyst reduce the utility of this route for producing a wide range of statistical copolymers.[3] For this reason, as well as both the ease of synthesis of the monomer and satisfactory properties of the derived polymer, the industry has centered on the use of bisphenol A. Melt transesterification provides a useful route to a wide range of statistical copolymers, but the high viscosity of the melt limits the molecular weight that can practically be achieved. The high viscosity, which, for example, can reach 10^6 P for poly(4,4′-cyclohexylidene bisphenol) carbonate at the reaction/processing temperature of 280 °C, is the result of the polymer chain stiffness which also provides the desirable mechanical properties. Such viscosities necessitate the use of high temperatures, which, in turn, can lead to discoloration in the final product.

Although CO_2 is a nonsolvent for most polymers (exceptions include many fluoropolymers and silicones), CO_2 has been found to be an excellent plasticizing agent.[4−7] Thus, if the mechanism of a given polymerization process is compatible with CO_2, many mass/bulk polymerization processes could benefit from the plasticization afforded by CO_2. Recent work using liquid or supercritical carbon dioxide as a solvent medium has shown that supercritical CO_2 is compatible with a number of polymerization types, including free radical,[8] cationic,[9] ring opening,[10] and oxidative coupling.[11] A number of small molecules display significant solubility in liquid or supercritical CO_2, including a number of step-growth reaction byproducts. Although water has a low solubility in supercritical CO_2, other common condensates, such as acetic acid, neopentyl glycol, and phenol, have the potential to be extracted from a reaction melt using supercritical fluid extraction methods that would drive the reaction to completion. Conventional methods of melt-phase step-growth polymerizations use vacuum techniques to remove condensates, but extraction of condensates using a SCFE method with CO_2 has the added benefit of introducing a swelling agent into the polymer melt. In addition, the commercial scale use of vacuum methods requires tedious process controls and extensive capital investment in order to maintain vacuum integrity for extended periods of time (years) with little maintenance. The use of low-pressure CO_2 as a continuous phase for bulk-phase polymerizations of polyesters and polyamides has been proposed,[12] but the issue of the potential plasticization of the melt phase afforded by high-pressure CO_2 has only been recently demonstrated.[13] We are currently investigating the effects of CO_2 as the swelling medium for melt-phase step-growth polymerizations. If the mechanism of polymerization is compatible with CO_2, we anticipate that the swelling of the polymer melt by supercritical CO_2 will lead to a reduction in the melt viscosity, which, in turn, may lead to increased reaction rates and increased production quality (color, higher purity lower residual monomer, etc.).

Polymer Swelling Measurements. Measurements of polymer swelling with CO_2 was performed in a specially designed high-pressure view cell, constructed of 316 stainless steel. The window of the cell consists of a steel plug in series with a brass O-ring, a 1 in. o.d., 0.5 in. thick sapphire window and a 0.002 in. thick Teflon gasket. High-pressure CO_2 was introduced to the cell using a syringe pump (Isco 260D). A digital camera (Pulnix TM-7CN) outfitted with a 50 mm lens (Nikon f/1.4D) was used to view and record the swelling kinetics

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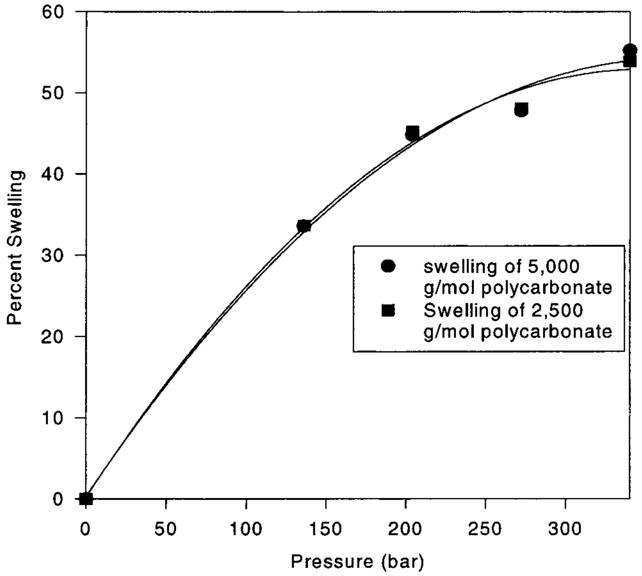

Figure 1. Percent swelling of polycarbonate (M_n of 2500 and 5000 g/mol) at 235 °C at various pressures.

of the polymer/CO_2 system in real time. The feed from the digital camera was captured using a frame grabber board (Scion Corp LG3) and NIH imaging software.

At the beginning of each experimental run the cell was thoroughly cleaned with THF and acetone, dried with compressed air, and purged several times with high-pressure CO_2. Approximately 0.50 g of the polycarbonate was added to the cell. The system was allowed to reach thermal equilibrium. The digital camera in conjunction with the NIH imaging software captures a series of images at a constant interval of time as the sample is exposed to supercritical CO_2. When the polycarbonate has absorbed the equilibrium amount of CO_2 and no further swelling is detected, the images are stopped. Using the imaging software, the number of pixels corresponding to the height of polycarbonate melt is measured for each individual picture.

Swelling experiments were run on low molecular weight poly(bisphenol A carbonate) samples with an M_n of 2500 and 5000 g/mol, respectively. The percent swelling was determined by the following equation:

$$\% \text{ SW} = [(V_t - V_0)]/(V_0) \times 100$$

where V_0 is the volume of the polymer at the beginning of the experiment prior to the introduction of CO_2 and V_t is the volume of the polymer after the equilibrium amount of CO_2 had been reached. Figure 1 shows the results of the in-situ swelling measurements run at 235 °C at various pressures.

Swollen Melt-Phase Polymerization 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 methanol and dried in a vacuum at room temperature. Tetraphenylphosphonium tetraphenylborate (TPP-TPB) was prepared from tetraphenylphosphonium bromide and sodium tetraphenylborate. Carbon dioxide (SCF/SCE grade with a helium head pressure) was provided by Air Products and Chemicals and was used as received. Melt-phase polymerizations were carried out in a 100 mL Autoclave high-pressure, high-temperature reaction vessel, shown in Figure 2. The CO_2 was pressurized by an Isco 500D or 260D pump. Constant pressure extraction was obtained by balancing the flow through the micrometering valve (A in Figure 2) with the CO_2 delivery rate afforded by the Isco pump. The phenol byproduct was collected as a solid in a dry ice trap.

A typical reaction involved charging the reactor with the following reagents: 29.68 g (0.13 mol) of BPA, 27.99 g (0.131 mol: 1.005 equiv/BPA) of DPC, and 2 mg of TPP-TPB. The reactor was heated using a three-step variable time−temperature profile. The first two steps involved the formation of prepolymer. The third step involved a constant pressure extraction to drive the product to higher molecular weight. Initially the reactor was heated to 150 °C to melt the reagents while argon gas was continuously passed slowly through the reactor. The variable time−temperature profile was then implemented as the reactor was heated to 160 °C and held there for 10 min, and then the temperature was raised to 270 °C gradually and held at 270 °C for 1 h. Phenol was removed by the initial process using a continuous flow of argon. In the third step, CO_2 was then introduced to the reactor, and the pressure was raised to 34.5 bar for 2 h and 300 bar for 4 h. In the supercritical fluid extraction, CO_2 was continuously flowed through the reactor at a rate of 1−2 mL/min. As shown in Figure 1, the CO_2 was vented through a line that ran through a cold trap where the phenol was collected. After the extraction, the reactor was cooled to ambient temperature. The reactor was opened, and the product was

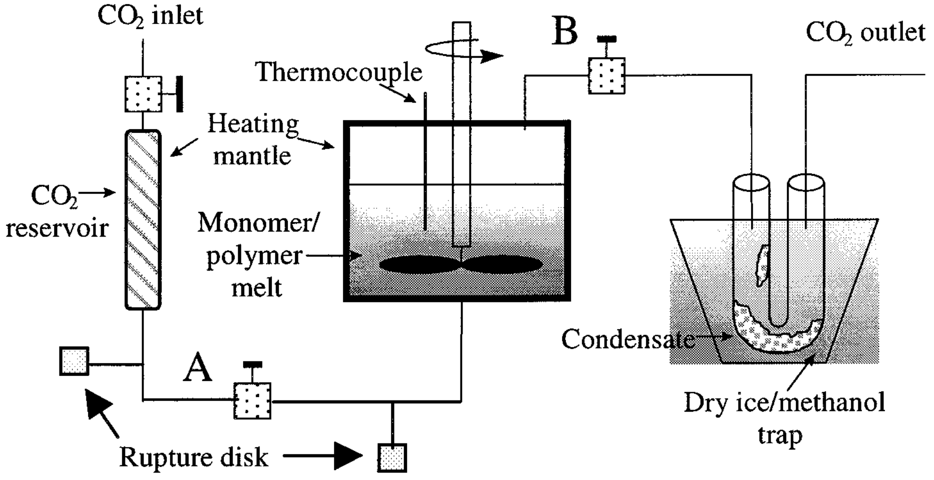

Figure 2. Supercritical fluid extraction reactor for the melt-phase polymerizations.

Table 1. Reaction Conditions for the SCFE and Control Experiments

time/temp profile (min at °C) step 1	step 2	extraction step 3 (h at °C)	press. of extraction (bar)	M_n (g/mol)	M_n control (Ar flow in place of SCFE)
60 at 180	60 at 270	4 at 270	310	3.0×10^3	2.2×10^3
120 at 160	120 at 220	7 at 220	240	9.0×10^3	5.1×10^3
10 at 160	30 at 270	6 at 270	300	1.1×10^4	7.6×10^3
10 at 260	60 at 270	6 at 270	300	1.3×10^4	8.0×10^3

quantitatively removed from the reactor by dissolving it in 50 mL of methylene chloride; the solution was precipitated into 600 mL of acetone, collected by filtration, washed with acetone, and then dried in a vacuum at room temperature for 15 h.

Control experiments were also run using the same time–temperature profile as the extractions. In the control experiment, argon was continuously flowed through the reactor through the first two steps of the time–temperature profile. In step 3, there was no CO_2 introduced. Instead, argon was continuously flowed through the system. The results of both the extractions and the control experiments can be seen in Table 1.

Several polymerization variables were investigated to determine their impact on the polymerization (see Table 1). It was shown that by varying the temperature, pressure, and time length of the extraction that the optimal conditions can be determined for the supercritical fluid extraction process. It was determined that in the low molecular weight polycarbonate samples that the polymer was swollen significantly by the CO_2 at 235 °C. Both samples were swollen over 33% at 136 bar and over 50% at 340 bar. Molecular weight did not seem to have an important effect on swelling on these two samples. The swelling in this system should be rapid due to the mixing of the polymer melt. This swollen melt-phase polymer system displayed enhanced reaction rates as reflected by the higher resulting M_n of the polymer synthesized by the supercritical fluid extraction.

In summary, we found that CO_2 is compatible with the mechanism associated with the synthesis of poly(bisphenol A carbonate) from bisphenol A and diphenyl carbonate. Many additional experiments are now underway, and we believe that significant advantages will result from the reduction in viscosity of the melt-phase swollen with CO_2, which may offer new opportunities in the production/processing costs and improved materials (e.g., optical clarity).

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