Reaction Kinetics of the Solid-State Polymerization of Poly(bisphenol A carbonate) Facilitated by Supercritical Carbon Dioxide

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ABSTRACT: The kinetics of solid-state polymerization (SSP) of poly(bisphenol A carbonate) was investigated with supercritical CO_2 ($scCO_2$) as the sweep fluid. The CO_2 flow rate and polymer particle size were chosen to ensure that the kinetics was controlled by the rate of the forward transesterification reaction, i.e., so that both external and internal phenol diffusion limitations were negligible. The forward reaction rate constants were determined between 90 and 135 °C, at CO_2 pressures of 138, 207, and 345 bar. At a given temperature, the reaction rate was higher with $scCO_2$ as the sweep fluid than with N_2, especially at lower temperatures. The rate constant for the forward transesterification reaction increased with increasing CO_2 pressure up to about 207 bar, at which point the rate constant was no longer sensitive to CO_2 pressure. The activation energy decreased from 23.9 kcal/mol in N_2 to 15.5, 11.6, and 11.4 kcal/mol at CO_2 pressures of 138, 207, and 345 bar, respectively. The effect of $scCO_2$ on the rate of polymerization can be understood in terms of the solubility of CO_2 in the polymer.

Introduction

Poly(bisphenol A carbonate) (BPA-PC) is an important thermoplastic that is used in many applications due to its excellent mechanical and optical properties. Currently, BPA-PC is synthesized industrially by one of two major processes: interfacial phosgenation of bisphenol A (BPA) and melt polymerization of BPA and diphenyl carbonate (DPC).[1] In the first process, phosgenation of bisphenol A occurs at the interface between methylene chloride and an aqueous solution of sodium hydroxide. High-molecular-weight, high-quality polymer can be produced at low reaction temperatures (typically 40 °C). After the reaction is complete, the polymer is collected and washed. It is then dried and melt-stabilized to prevent color development and a lowering of molecular weight during subsequent processing.[1] The process generates large amounts of organic, aqueous, and solid waste and uses toxic and hazardous chemicals such as phosgene.

The base-catalyzed, melt-phase condensation polymerization of BPA with DPC is a solvent-free alternative process to synthesize polycarbonate. A high temperature is required to ensure that monomers, oligomers, and polymers remain molten during the reaction. Condensate (phenol) removal becomes more difficult as the molecular weight builds up due to the increasingly high viscosity of the melt. Since the transesterification reaction is highly reversible,[2] the obtainable molecular weight is limited by the ability to remove the condensate from the melt. High reaction temperature facilitates phenol removal but also leads to color body formation.[3]

Solid-state polymerization (SSP) of BPA-PC might provide a means to obtain high molecular weights at relatively low reaction temperatures. Solid-state polymerization currently is used to produce high-molecular-weight poly(ethylene terephthalate) (PET) and nylon.[4−8] Polymer chips or fibers (postextrusion SSP) are heated to a temperature higher than the glass transition temperature (T_g) but lower than the onset of melting to make end groups mobile enough to react. The polymer must have some crystallinity to prevent the chips or fibers from sticking during the SSP process. The polymer molecular weight can be significantly increased via SSP, and side reactions are minimized at such low reaction temperatures. However, the low temperature makes SSP slow relative to melt phase polymerization, and condensate diffusion can slow the reaction even further if the particle size is too large.

High-molecular-weight BPA-PC can be generated via SSP, starting with a low-molecular-weight, semicrystalline “prepolymer” synthesized via melt polycondensation.[3,9−13] The solid-state polymerization is carried out with a continuous flow of an inert sweep fluid (e.g., N_2) to facilitate phenol removal. Poly(bisphenol A carbonate), typically an amorphous polymer, can be partially crystallized either thermally or in the presence of a plasticizer (e.g., supercritical carbon dioxide).[9,11,14] In addition, certain transesterification catalysts appear to serve as chemical nucleating agents and render the resulting polycarbonates crystalline.[11,15,16] Compared to high-molecular-weight polycarbonate, which has a very slow crystallization rate, low-molecular-weight polymers crystallize more rapidly.[3] We took advantage of this tendency in this research.

To increase the rate of SSP, swollen-state polymerization of PET has been investigated.[17,18] An organic solvent or solvent mixture was used to swell PET polymer chips, and an increased rate of molecular weight buildup was observed. However, it is impossible to tell whether the solvent increased the intrinsic reaction kinetics, via enhanced end group mobility, and/or facilitated condensate removal. In any event, the use of an organic swelling agent has a detrimental environ-

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mental impact, and the product inevitably is contaminated by the solvent.

Recent research has demonstrated that dense carbon dioxide exhibits substantial solubility in both amorphous and semicrystalline polymers, including polycarbonate, and effectively plasticizes these polymers by increasing their free volume.[19−21] By utilizing supercritical CO_2 ($scCO_2$) as the sweep fluid for SSP of BPA-PC, the polymerization rate can be increased, presumably through this plasticization effect.[9]

The kinetics of the SSP of poly(bisphenol A carbonate) in $scCO_2$ has never been studied in detail. However, we recently published a study of the intrinsic kinetics of the forward transesterification reaction in atmospheric N_2.[10] That study provides a baseline against which to compare the present results.

The rate of solid-state polycondensation depends on both chemical and physical processes. The possible rate-determining steps are (1) intrinsic kinetics of the forward (condensation) reaction, (2) phenol diffusion through the solid polymer to its exterior surface, and (3) phenol diffusion from the exterior surface of polymer particle into the sweep fluid. Depending on polymer properties (e.g., crystallinity, particle size) and operating conditions (e.g., temperature, pressure, sweep fluid flow rate), the rate of molecular weight increase is controlled by one or more of these steps.

In this research, experimental conditions were adjusted to eliminate the influence of phenol transport on reaction kinetics. The forward reaction rate constants were determined between 90 and 135 °C, at pressures of 138, 207, and 345 bar. The respective activation energies were derived for these reaction pressures. The rate constants and activation energies were compared with those for SSP using N_2 as the sweep gas. A qualitative explanation for the higher observed reaction rates in $scCO_2$ is proposed.

Experimental Section

Materials. Bisphenol A (BPA, 99.9+%, Aldrich) was recrystallized from methanol and water (1:1 v/v) and dried under vacuum at 60 °C. Diphenyl carbonate (DPC, 99%, Aldrich) was recrystallized from methanol and dried under vacuum at room temperature. Lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, 99.9+%, Aldrich) was used as received. Nitrogen (Ultra High purity, 99.999%, National Specialty Gases) was passed through a drying tube containing anhydrous calcium sulfate before entering the reactor. Carbon dioxide (Instrument/Coleman Grade, 99.99%, National Specialty Gases) was used as received.

Prepolymer Synthesis. Poly(bisphenol A carbonate) prepolymer was synthesized by melt polymerization as described previously.[10] In a typical experiment, 27.36 g of BPA (0.12 mol) and 26.96 g of DPC (0.126 mol, DPC:BPA molar ratio = 1.05) were added to an agitated, stainless steel reactor and heated to 160 °C under N_2. After the monomers melted, 200 ppm (based on monomer weight) of $LiOH{\cdot}H_2O$ was injected as an aqueous solution. The reaction temperature was kept at 160 °C for 0.5 h and then increased to 180 °C for 1 h, to 190 °C for 1 h, and then to 230 °C for 0.5 h. Finally, the reactor was held under vacuum (less than 1 Torr) for 0.5 h to remove phenol. The melt was cooled to room temperature in the reactor overnight, and a low-molecular-weight prepolymer was collected as a solid.

The prepolymer was ground to powder and separated into different sizes by sieving. The prepolymer had a starting number-average molecular weight (M_n) of 4300 g/mol based on a polystyrene standard, as determined by gel permeation chromatography (GPC). Differential scanning calorimetry (DSC) measurements showed that the prepolymer had a T_g of 69 °C and a T_m of 197 °C. The crystallinity of the prepolymer was 24.3%, calculated from the area of the DSC melting peak using a value of 26.2 cal/g for the heat of fusion of crystalline BPA-PC.[9]

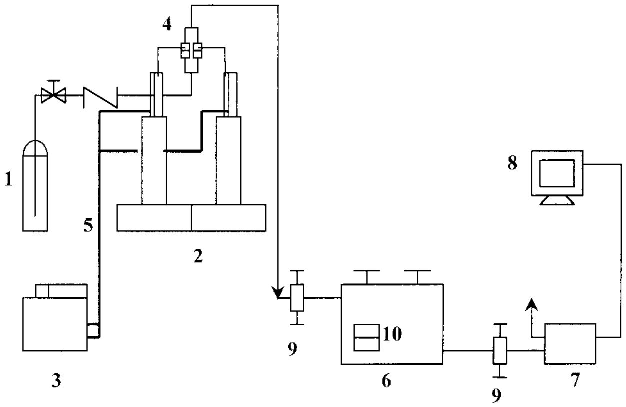

Figure 1. Experimental equipment for solid-state polymerization of BPA-PC with supercritical CO_2 as the sweep fluid. Equipment description: 1, CO_2 cylinder; 2, dual-barrel CO_2 pump; 3, chiller; 4, electronic control valve for the dual-barrel CO_2 pump; 5, cooling/heating tubing for each pump; 6, reactor chamber with built-in temperature controller (reactor internal diameter $^1/_4$ in.); 7, automated back-pressure regulator (BPR); 8, computer used to control BPR; 9, valves; 10, temperature controller.

A higher-molecular-weight prepolymer (M_n = 6100 g/mol, based on a polystyrene standard) was synthesized by solid-state polymerizing the original prepolymer for 4 h in CO_2 at 105 °C and 345 bar. The T_g and T_m increased to 102 and 223 °C, respectively, and the crystallinity increased to 36%. The higher T_m of this second prepolymer permitted it to be used at SSP conditions (temperatures higher than 120 °C and CO_2 pressures higher than 207 bar) where the lower-molecular-weight prepolymer could not be used directly because the particles fused together during SSP.

Solid-State Polymerization. The experimental setup for solid-state polymerization with N_2 as the sweep gas has been described previously.[10] Some additional high-temperature experiments (220 °C) with N_2 as the sweep gas were carried out in the same equipment to confirm end group stoichiometry.

The reaction system for SSP with $scCO_2$ as the sweep fluid is shown schematically in Figure 1. An Isco SFX 2-10 dual chamber supercritical extractor with a built-in temperature controller rated to ±0.5 °C was used as the SSP reactor. One of the two stainless steel extraction chambers (internal diameter $^1/_4$ in.) in this device was connected to the pump and back-pressure regulator and actually used as the SSP reactor. In a typical experiment, 50 mg of polymer particles of a certain size range was added to the reactor and held in position by the sintered stainless steel filter. The reactor was then put into the constant temperature extraction chamber. The temperature stabilized after 1 h, and then CO_2 was pumped continuously by the Isco dual syringe pumps (260D with electronic control valve) in the constant flow mode. The $scCO_2$ was heated in the stainless steel coil before entering the reactor in downward flow through the polymer particles. The reaction pressure was adjusted by an automated back-pressure regulator (Thar Designs, BPR-200A) and controlled to ±1 bar with the ICM software (Thar Designs) in a computer. After about 5 min, the pressure stabilized and timing was begun for the SSP. The reaction was carried out continuously for the desired reaction time, without sampling during reaction. Therefore, each data point in Figures 2−6 represents a separate experiment. Control experiments showed that there was no molecular weight increase during the initial pressure stabilization and final depressurization stages.

Polymer Molecular Weight Determination and Thermal Analyses. The polymer molecular weight was determined with a Waters 150-CV gel permeation chromatography (GPC) with Ultrastyragel columns of 100, 500, 10^3, 10^4, and 10^5 Å porosities. Tetrahydrofuran (THF) was used as the mobile phase, and polystyrene standards (Showa Denko, Polysciences) were used for the calibration. For quantitative kinetic calculations, the number-average molecular weights relative to polystyrene, as determined by GPC (M_n), were converted to absolute BPA-PC molecular weights, denoted $M_{n,PC}$, as described previously.[10] This conversion gives the relationship between $M_{n,PC}$ and M_n as $M_{n,PC} = 0.714M_n$. A Seiko Haake DSC 220 was used to determine the T_g, T_m, and crystallinity of the polymer in a N_2 atmosphere at a heating rate of 10 °C/min.

Results and Discussion

For SSP of BPA-PC, the overall reaction rate can be affected by both intrinsic reaction kinetics and phenol transport.[5−7] The latter includes phenol diffusion inside the polymer particles and from the particle surface to the sweep fluid. Therefore, to obtain intrinsic forward reaction rate constants, small prepolymer particles were used to eliminate the influence of internal diffusion, and the CO_2 flow rate was adjusted to remove any external mass transfer influence.

In atmospheric N_2, SSP could be carried out a reaction temperature as high as 165 °C starting with the low-molecular-weight prepolymer ($M_n = 4300$ g/mol). However, the highest reaction temperature that could be used with this prepolymer when $scCO_2$ was the sweep fluid was about 120 °C, if the CO_2 pressure was higher than 207 bar. Attempts to run at higher temperatures resulted in coalesced polymer samples with minimal molecular weight increase. This behavior is attributed to lowering of T_m by CO_2 dissolved in the polymer.

The highest permissible SSP temperature was influenced by both the CO_2 pressure and the prepolymer properties. Experiments were possible with the low-molecular-weight prepolymer at 135 °C and 138 bar of CO_2. At the same temperature and 345 bar, SSP could not be carried out with the low-molecular-weight prepolymer because the particles became fused during the polymerization. However, the high-molecular-weight prepolymer ($M_n = 6100$) could be used without fusion or coalescence of the particles at these conditions. These differences probably are due to depression of both T_m and T_g by supercritical CO_2. It is known that dissolved $scCO_2$ functions to lower the temperature needed for the solid−liquid to liquid transition.[22,23]

CO_2 Flow Rate. The effect of CO_2 flow rate was studied with the low-molecular-weight prepolymer at 120 °C and 345 bar, the reaction conditions that gave the highest polymerization rate. The size of the prepolymer particles was in the range 75−125 μm. Figure 2 shows the molecular weight increase with time at different CO_2 flow rates (10−30 mL/min). At a given time, higher flow rate always resulted in a slightly higher molecular weight. However, the effect of flow rate was small. At 20 mL/min, the SSP experiments could be carried out conveniently, without having to switch CO_2 cylinders frequently, and the effect of external mass transfer was negligible. Therefore, a 20 mL/min flow rate was used in subsequent experiments. At lower temperatures and CO_2 pressures, the polymerization rates, and hence the phenol generation rates, are lower than at 120 °C and 345 bar. This should ensure that no external phenol removal limitation existed during the experiments with the low-molecular-weight prepolymer.

Internal Mass Transfer Effects. To determine the appropriate particle size for SSP in CO_2, such that the polymerization rate is not influenced by diffusion of phenol inside the polymer particles, SSP was carried out at 120 °C and 345 bar with three different particle sizes: 45−75, 75−125, and 125−180 μm. The results are shown in Figure 3. In the range of particle sizes studied, there is little or no effect of particle size on reaction rate. This indicates that phenol diffusion inside the polymer particles does not influence the overall reaction rate. A particle size of 75−125 μm was chosen for subsequent experiments.

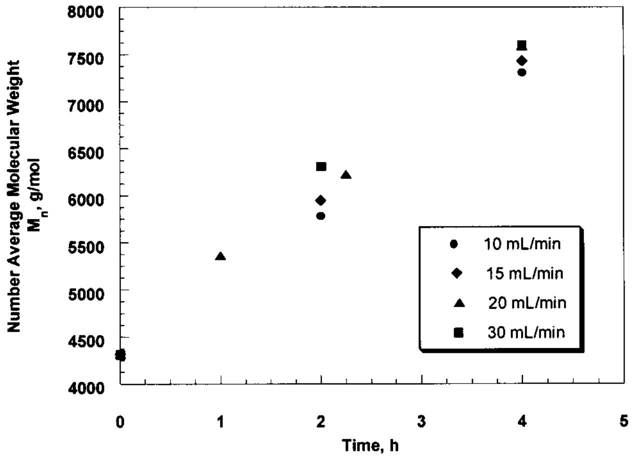

Figure 2. Effect of CO_2 flow rate on molecular weight evolution during SSP of BPA-PC at 120 °C and 345 bar (particle size = 75−125 μm).

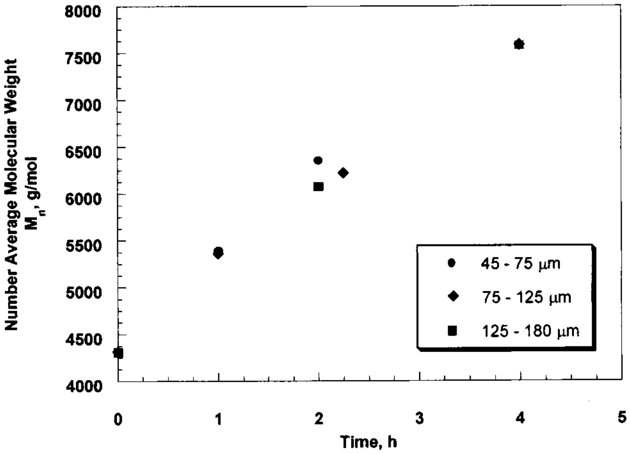

Figure 3. Effect of particle size on molecular weight evolution during SSP of BPA-PC at 120 °C and 345 bar (CO_2 flow rate = 20 mL/min).

Rate Constant Derivations. When the rate of SSP is controlled by the kinetics of the transesterification reaction between hydroxyl and phenyl end groups, the reaction rate is given by eq 1:[10]

$$-\frac{dC_{OH}}{dt} = C_{OH,0}\frac{dx}{dt} = kC_{OH}C_{phenyl} = kC_{OH,0}^2(1-x)(1+\epsilon-x) \quad (1)$$

where C_{OH} and C_{phenyl} are the concentrations of hydroxyl and phenyl end groups, respectively, $C_{OH,0}$ is the initial hydroxyl end group concentration in the monomer melt from which the prepolymer was produced, x is the fractional conversion of the stoichiometrically deficient end group, ϵ is the fractional molar excess of the other end group, and t is the SSP time. The concentrations C_{OH} and C_{phenyl} are the concentrations in the polymer particle as a whole, not just in the amorphous region.

A correction of the reation rate to account for the variation of crystallinity with time has been proposed for SSP of PET.[7] However, DSC measurements revealed that the crystallinity of the low-molecular-weight prepolymer increased rapidly from about 24% to 33% during the first hour of SSP (both in N_2 and in CO_2) and was almost constant thereafter. Therefore, crystallinity was not accounted for in the present analysis. The values of the rate constants will change if they are based only on the amorphous region. However, the activation energies will not be affected.

Equation 1 suggests that phenyl end groups are in excess, which is reasonable since a 5 mol % excess of DPC was used in the prepolymer synthesis. However, the following analysis does not depend on which end group is in excess. The value of ϵ previously was determined to be 0.025 from the asymptotic molecular weight for SSP in N_2 at 165 °C.[10] Additional experiments at 180 and 220 °C in N_2, using polymer that had been polymerized previously at 165 °C, revealed no further increase in molecular weight, confirming that the obtainable molecular weight at 165 °C in N_2 was limited by end group stoichiometry, not by reaction kinetics.

Integrating eq 1 from the start of solid-state polymerization ($t = 0$, $x = x_0$) for a constant, nonzero value of ϵ gives

$$A = \frac{1}{\epsilon}\left(\ln\frac{1+\epsilon-x}{1-x} - \ln\frac{1+\epsilon-x_0}{1-x_0}\right) = kC_{\mathrm{OH},0}t = k_f t \tag{2}$$

In eq 2, $kC_{\mathrm{OH},0}$ is treated as an apparent forward reaction rate constant (k_f), with units of h^{-1}. The conversion x in eq 2 can be determined at any reaction time from the relationship[24]

$$\frac{M_{\mathrm{n,PC}}}{127} = \frac{2+\epsilon}{2+\epsilon-2x} \tag{3}$$

The initial conversion x_0 at the start of SSP can be determined from eq 3 by substituting the absolute number-average molecular weight of the prepolymer. When the prepolymer molecular weight (M_n) is 4300 g/mol, x_0 is 0.971. For the prepolymer with a molecular weight (M_n) of 6100 g/mol, x_0 was 0.983.

If the kinetic model of eq 1 fits the experimental data, a plot of the left-hand side (expression A) of eq 2 vs time should give a straight line through the origin. The slope of the line is the apparent forward reaction rate constant, k_f.

Plots of M_n vs t at different temperatures and pressures (Figures 4−6) show that the molecular weight increases almost linearly initially and that the rate of molecular weight increase slows at longer reaction times. When the reaction was carried out for a sufficiently long period of time, e.g., the experiment at 120 °C and 345 bar of CO_2 shown in Figure 4, the molecular weight reached an asymptotic value. The asymptotic molecular weight at 120 °C and 345 bar ($M_n = 10\,000$) is lower than the asymptotic value for SSP of the same prepolymer in N_2 at 165 °C ($M_n = 14\,600$). It was shown previously[10] that end group stoichiometry limits the obtainable molecular weight for the experiment in N_2 at 165 °C. In that study, it also was shown that M_n can reach an apparent asymptotic value that is lower than the asymptotic value associated with end group stoichiometry. This behavior appears to be the result of an increase in T_g during SSP, such that T_g approaches the SSP reaction temperature[10] and the mobility of the end groups becomes so low that the reaction appears to stop.

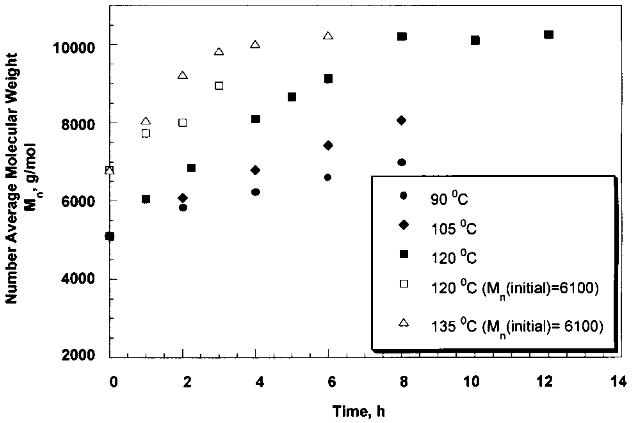

Figure 4. Effect of temperature on molecular weight evolution during SSP of BPA-PC at 345 bar (CO_2 flow rate = 20 mL/min; particle size = 75−125 μm). The unfilled markers represent data for the high-molecular-weight prepolymer (M_n = 6100).

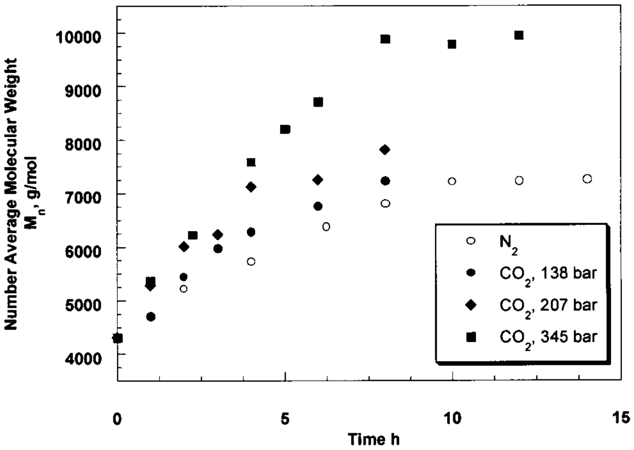

Figure 5. Effect of pressure on molecular weight evolution during SSP of BPA-PC at 120 °C (CO_2 flow rate = 20 mL/min; particle size = 75−125 μm). The unfilled circles represent molecular weight changes during SSP with N_2 as the sweep gas[10] (N_2 flow rate = 1533 mL/min; particle size = 75−125 μm).

The presence of supercritical CO_2 can increase the SSP reaction rate significantly and can increase the asymptotic molecular weight at a given reaction temperature. This can been seen clearly in Figure 5. During the initial period of SSP at 120 °C, the rates of molecular weight increase are higher at 207 and 345 bar of CO_2 than in N_2. Moreover, the final molecular weights at 207 and 345 bar of CO_2 are higher than those for SSP in N_2.

In Figure 6, the close agreement between the filled and unfilled squares, which represent two different particle sizes, indicates that the SSP was not limited by internal diffusion of phenol, even at 135 °C and 345 bar. This temperature is 15 °C higher than that used for the particle size study shown in Figure 3.

A plot of the data at each temperature, in the form of eq 2, is shown in Figure 7 for a CO_2 pressure of 345 bar. Only the data at short reaction times are included. The linearity of these plots supports the kinetic model of eq 1. The forward reaction rate constant, k_f, was calculated from the slope of the line at each temperature.

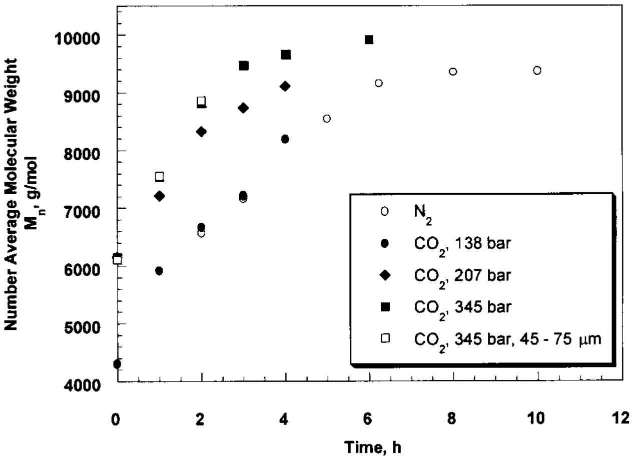

Figure 6. Effect of pressure on molecular weight evolution during SSP of BPA-PC at 135 °C (CO_2 flow rate = 20 mL/min; particle size = 75−125 μm). The unfilled circles represent molecular weight changes during SSP with N_2 as the sweep gas (N_2 flow rate = 1533 mL/min; particle size = 75−125 μm).[10] The unfilled squares indicate the molecular weight increase at 345 bar with a particle size of 45−75 μm.

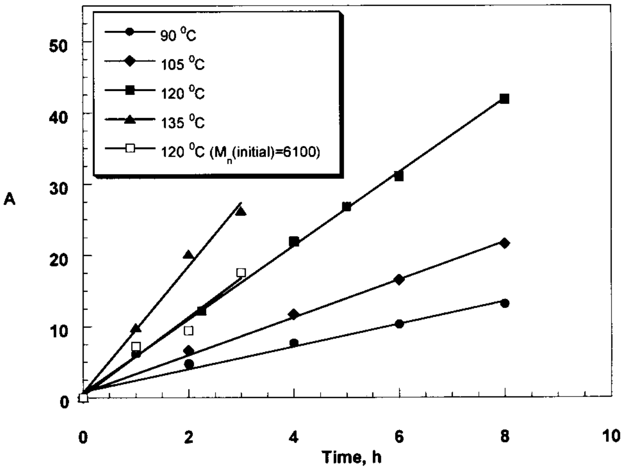

Figure 7. Test of eq 2 for SSP of BPA-PC at short reaction times at different temperatures and a CO_2 pressure of 345 bar. The parameter A was calculated with $\epsilon = 0.025$. For 120 (solid squares), 105, and 90 °C, $x_0 = 0.971$ (M_n(prepolymer) = 4300); for all others, $x_0 = 0.983$ (M_n(prepolymer) = 6100). The unfilled squares indicate A values at 120 °C for the high-molecular-weight prepolymer (M_n = 6100).

The unfilled points in Figure 7 denote experimental results obtained with the high-molecular-weight prepolymer. The unfilled squares fall on essentially the same line as the filled squares, obtained with the low-molecular-weight prepolymer. This shows that the SSP kinetics are independent of the initial molecular weight, as long as the reaction temperature is much higher than T_g. The correspondence between the filled and unfilled points also justifies use of the kinetic data at 135 °C, 207 and 345 bar, in the calculation of the activation energy. These data were obtained exclusively with the high-molecular-weight prepolymer.

Plots of A vs time also were constructed at the other CO_2 pressures, 138 and 207 bar. The data at short reaction times were linear at these pressures, and the rate constants were calculated from the slope of the lines.

An Arrhenius plot at each CO_2 pressure is shown in Figure 8. The Arrhenius plot for SSP in N_2[10] is shown for comparison. The regression at 138 bar was carried out with the rate constants for the three highest temperatures: 105, 120, and 135 °C. The rate constant at 90 °C and 138 bar is plotted but was not included in the regression since the uncertainty in molecular weight measurement could induce a large uncertainty in the calculated activation energy when the reaction rate is so low.

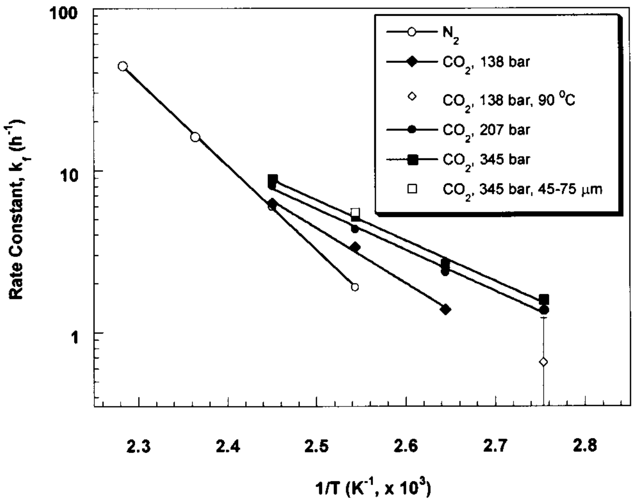

Figure 8. Arrhenius plot for SSP of BPA-PC at temperatures between 90 and 135 °C at pressures of 138, 207, and 345 bar. The Arrhenius plot for SSP with N_2 as the sweep gas (between 120 and 165 °C) was plotted in the same figure for comparison. Concentration of LiOH catalyst = 200 ppm.

Figure 8 shows that supercritical CO_2 can enhance the SSP reaction rate significantly, especially at lower reaction temperatures. At a fixed temperature, the rate constant increased as the pressure was increased, up to a pressure of about 207 bar. The SSP of BPA-PC with N_2 as the sweep gas has an activation energy of 23.9 kcal/mol, which is very close to the activation energy for the melt synthesis (23.4 kcal/mol).[25] The activation energy in the presence of $scCO_2$ was about half of the value in N_2. The activation energies for SSP in CO_2 were 15.5, 11.6, and 11.4 kcal/mol for pressures of 138, 207, and 345 bar, respectively. These values are comparable to the activation energy observed for simple transesterification[26] and for melt synthesis of high-molecular-weight polycarbonate from cyclic oligomers.[25] The complete Arrhenius equations for SSP in N_2 and SSP in CO_2 at the three pressures and with a 200 ppm concentration of LiOH catalyst are

$$N_2\text{:}\quad k_f = 3.36 \times 10^{13} \exp\left(\frac{-99600}{RT}\right)\ h^{-1} \tag{4}$$

$$CO_2\text{, 138 bar:}\quad k_f = 1.31 \times 10^{9} \exp\left(\frac{-64900}{RT}\right)\ h^{-1} \tag{5}$$

$$CO_2\text{, 207 bar:}\quad k_f = 1.21 \times 10^{7} \exp\left(\frac{-48400}{RT}\right)\ h^{-1} \tag{6}$$

$$CO_2\text{, 345 bar:}\quad k_f = 1.15 \times 10^{7} \exp\left(\frac{-47800}{RT}\right)\ h^{-1} \tag{7}$$

The behavior of the SSP of BPA-PC in $scCO_2$ can be explained by the plasticizing effect of dissolved CO_2 on the polymer. At reaction conditions, CO_2 molecules dissolve in the rubbery region of the polymer and serve as a diluent, effectively increasing the mobility of the polymer end groups by increasing the polymer free volume. The macroscopic result is the lowering of the glass transition temperature (T_g depression).

If the observed rate enhancement is a result of CO_2 dissolved in the polymer, conditions that affect CO_2 solubility would be expected to affect the reaction rate. Mallon and co-workers[27] studied the effect of the purge gas on the SSP of PET. At atmospheric pressure, the rate of SSP with CO_2 as the sweep gas was the same as with N_2 and He. Results from the present research are consistent with this finding. Figures 5 and 6 show that the reaction rate was increased significantly only when the CO_2 pressure was substantially above atmospheric, presumably as a result of increased solubility of CO_2 in the polymer. However, once the CO_2 pressure reached about 207 bar, a further increase of pressure to 345 bar only gave a marginal increase in reaction rate. Chang and co-workers[28] measured the solubility of $scCO_2$ in glassy polycarbonate at 35 °C. When the pressure was increased from 200 to 300 bar, the increase in CO_2 solubility was minimal. Although that work was carried out below T_g, with a polycarbonate sample that probably was amorphous initially, the trend in CO_2 solubility with pressure is consistent with the present kinetic results.

When the pressure is fixed and the temperature is increased, the CO_2 solubility is expected to decrease, causing a decrease in the extent of plasticization of the polymer. Above the T_g of a polymer, dissolution of a fluid occurs primarily by a Henry's law mechanism.[29] Both Chan and Paul[30] and Holl et al.[31] have shown that the Henry's law constant for CO_2 in polycarbonate decreases with temperature, at temperatures in the vicinity of those used in this study. The fact that the difference between the measured rate constants in CO_2 and those in N_2 decreases as temperature is increased is consistent with a decrease in CO_2 solubility with temperature. The Arrhenius plots for the rate constants in CO_2 intersect the Arrhenius plot for the rate constants in N_2 at a temperature of about 145 °C. At this point, CO_2 pressure has no effect on the SSP rate constant. We speculate that the rate constants are essentially equal at this temperature because the solubility of CO_2 in the polymer has become negligible.

Finally, the difference between the activation energy in N_2 and that in CO_2 is approximately 12 kcal/mol. The enthalpy of dissolution for CO_2 in polycarbonate reported by Chan and Paul[30] is about 4 kcal/mol, and a value of about 6 kcal/mol can be extracted from the Henry's law constants reported by Holl et al.[31] Thus, the influence of temperature on the solubility of CO_2 in polycarbonate can account for about $^1/_3$ to $^1/_2$ of the activation energy difference between the rate constants in N_2 and those in CO_2.

In view of the potential importance of fluid solubility on SSP kinetics, we have begun to measure the solubility of $scCO_2$ in poly(bisphenol A carbonate) at the temperatures and pressures of this study.

As mentioned previously, the molecular weights achieved in this study were limited by end group stoichiometry. There was approximately a 2.5% molar excess of one end group, presumably phenoxy, over the other, hydroxyl. To put the issue of end group stoichiometry into perspective, the measured rate constants were used to calculate the course of a polymerization in which the concentrations of the two end groups were exactly equal. Two cases were considered: (1) an SSP temperature of 165 °C with atmospheric N_2 as the sweep gas and (2) an initial SSP temperature of 120 °C, with an instantaneous increase to 135 °C when $M_{n,PC}$ reached 4400, with $scCO_2$ at 207 bar as the sweep fluid.

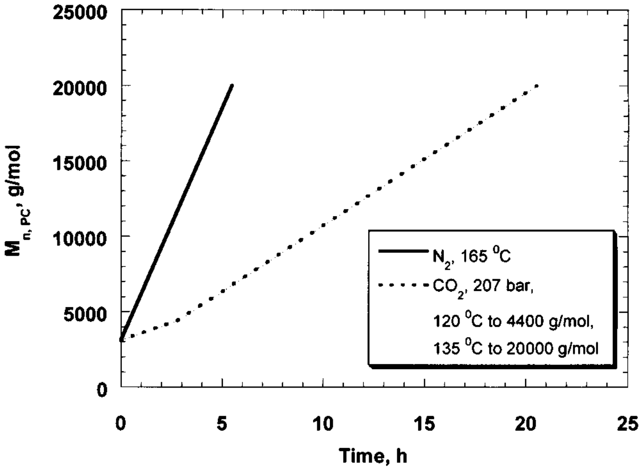

Figure 9. Calculated absolute number-average molecular weight ($M_{n,PC}$) vs time for solid-state polymerization of a prepolymer with $M_{n,PC} = 3070$. Solid curve: temperature = 165 °C, atmospheric N_2 sweep gas. Dashed curve: initial temperature = 120 °C, temperature increased to 135 °C when $M_{n,PC}$ reached 4400, $scCO_2$ at 207 bar.

The first case is based on the highest temperature that can be used with a prepolymer whose $M_{n,PC}$ is 3070 ($M_n = 4300$), with N_2 at atmospheric pressure as the sweep gas. In N_2, particles of this prepolymer became fused at temperatures higher than 165 °C, presumably because the onset of melting is only slightly greater than this temperature. Figure 9 shows that a molecular weight ($M_{n,PC}$) of 20 000 can be achieved in about 5 h for this case.

The second case in Figure 9 is a low-temperature SSP with $scCO_2$ as the sweep fluid. Once again, the prepolymer has a molecular weight, $M_{n,PC}$, of 3070. The SSP temperature begins at 120 °C. As noted earlier, this prepolymer could be used directly in $scCO_2$, with no fusion of the prepolymer particles, if the temperature was 120 °C or lower. The temperature changes to 135 °C after about 3 h, at the point that M_n has increased to 6100 ($M_{n,PC} = 4400$). This is the molecular weight of the higher-molecular-weight prepolymer that was used to carry out experiments in $scCO_2$ at 135 °C. At these temperatures, $scCO_2$ has a kinetic advantage over atmospheric N_2. Figure 8 shows that the rate constant in $scCO_2$ is greater than in atmospheric N_2, as long as the SSP temperature is less than about 145 °C.

The dashed curve in Figure 9 shows that an $M_{n,PC}$ of 20 000 can be achieved in about 20 h with a sweep fluid of $scCO_2$ at 207 bar and with a temperature that never exceeds 135 °C. Although much more time is required to reach $M_{n,PC} = 20\ 000$ at the second set of conditions, the maximum temperature for this case is 30 °C lower than for the first case.

Finally, it is important to emphasize that the calculations of Figure 9 contain two important assumptions: (1) the rate of solid-state polymerization is controlled by the intrinsic kinetics of the forward transesterification reaction, and (2) the two end groups are present in a 1:1 ratio throughout the polymerization.

Conclusions

Solid-state polymerization of poly(bisphenol A carbonate) was carried out with supercritical carbon dioxide as the sweep fluid. External diffusion influence was eliminated by using a sufficiently high CO_2 flow rate. Internal diffusion influence was eliminated by using small particle sizes. End group stoichiometry limited the obtainable molecular weight for SSP in both N_2 and CO_2. The reaction rate for SSP in $scCO_2$ was significantly higher than in atmospheric N_2, and the molecular weight of the polymer reached a higher asymptotic value at a given temperature. The rate constant increased as the CO_2 pressure increased at a fixed temperature, up to about 207 bar. Further pressure increase resulted in only a marginal increase in the rate constant. At a constant pressure, the effect of CO_2 on the rate constant decreased with increasing temperature. The activation energy in $scCO_2$ was much lower than in N_2. The activation energies were 15.5, 11.6, and 11.4 kcal/mol for 138, 207, and 345 bar of CO_2, respectively, compared to 23.9 kcal/mol for SSP in atmospheric N_2. The reaction rate enhancement by $scCO_2$ appears to be a consequence of increased end group mobility due to plasticization of the polymer by dissolved CO_2.

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