

# SOLID STATE POLYMERISATION IN THE PRESENCE OF SUPERCRITICAL CARBON DIOXIDE: MECHANISMS OF REACTION RATE ENHANCEMENT

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When solid state polymerization (SSP) is carried out in the presence of supercritical carbon dioxide (scCO<sub>2</sub>), the overall rate of polymerization is significantly higher than when the polymerization is carried out in the presence of N<sub>2</sub>. During SSP, the reaction rate depends on both chemical and physical processes. The SSP of poly(bisphenol A carbonate) has been used as a model reaction to investigate the SSP kinetics and determine important physical parameters such as the forward reaction rate constant and the diffusivity of the condensate molecule, phenol, that is produced in the SSP reaction. The results with scCO<sub>2</sub> as the sweep fluid were compared with those with N<sub>2</sub> as the sweep gas. Supercritical CO<sub>2</sub> increased both the reaction rate constant and the condensate diffusivity. The magnitude of the increase depended on temperature and on the pressure of the scCO<sub>2</sub>. By comparing the activation energies for chemical reaction and condensate diffusion, it was deduced that the SSP of poly(bisphenol A carbonate) shifts from diffusion control at low temperatures to chemical reaction control at high temperatures.

## INTRODUCTION

Although carbon dioxide is a nonsolvent for most polymers except certain fluoropolymers, silicones, and poly(ether carbonates)<sup>[1-3]</sup>, it exhibits substantial solubility in both amorphous and semicrystalline polymers, and effectively plasticizes these polymers by increasing their free volume<sup>[4-7]</sup>. It was demonstrated that polycarbonate, a polymer with an extremely slow crystallization rate due to its chain stiffness, can undergo fast crystallization upon exposure to CO<sub>2</sub> at elevated pressures and temperatures due to this plasticization<sup>[8,9]</sup>. For example, poly(bisphenol A carbonate) with a molecular weight of 44000 g/mol obtained a crystallinity of 18 % after 6-hour treatment in CO<sub>2</sub> at 340 bar and 150 °C<sup>[9]</sup>. In our investigation of a more environmentally-benign synthesis of poly(bisphenol A carbonate), we have carried out solid state polymerization (SSP) with supercritical carbon dioxide as the sweep fluid to remove reaction condensate, phenol. Solid state polymerization has been used extensively to synthesize high-molecular-weight condensation polymers, such as bottle-grade poly(ethylene terephthalate) (PET), and high-modulus nylon<sup>[10,11]</sup>. Typically, a low-molecular-

weight prepolymer was heated to a temperature well above the glass transition temperature ( $T_g$ ), but about 10-20 °C lower than the melting temperature ( $T_m$ ) to prevent particle sticking. At such a temperature, additional condensation reactions occur. A high-molecular-weight polymer can be obtained when the condensate can be effectively removed by flowing an inert gas stream through the polymer or by applying vacuum. To synthesize high-molecular-weight polycarbonate via SSP, a low-molecular-weight prepolymer was synthesized first by melt transesterification between bisphenol A (BPA) and diphenyl carbonate (DPC) and rendered semicrystalline, a morphology suitable for SSP, either thermally or by exposure to scCO<sub>2</sub>. When scCO<sub>2</sub> was used as the sweep fluid for SSP, high-molecular-weight polycarbonate could be synthesized at a lower reaction temperature and/or a shorter reaction time when compared with using N<sub>2</sub> as the sweep gas<sup>[9,12]</sup>. Measurements of the reaction rate constants and phenol diffusivities in the polymer during SSP are presented in this manuscript. The results for SSP in scCO<sub>2</sub> are compared with those for SSP in N<sub>2</sub>, and the mechanism of reaction rate enhancement is discussed.

## MATERIALS AND METHODS

**Prepolymer Synthesis.** The prepolymer was synthesized by melt polymerization of bisphenol A (99.9+%, Aldrich, recrystallized from methanol and water (1:1 v/v) and dried under vacuum at 60 °C) and diphenyl carbonate (99%, Aldrich, recrystallized from methanol and dried under vacuum at room temperature), with 200 ppm LiOH·H<sub>2</sub>O (99.9+%, Aldrich, based on monomer weight) as the catalyst. For the study of intrinsic reaction kinetics, the prepolymer melt was allowed to cool slowly overnight, ground to powder, and separated into different size ranges by sieving. The prepolymer powder had a crystallinity of 24%. To investigate phenol diffusion, prepolymer melt was poured into a hot metal syringe. The prepolymer dripped from the hot syringe under its own weight into cold water to form transparent beads with an average diameter of 2 mm. The amorphous beads were then exposed to scCO<sub>2</sub> to obtain a crystallinity of 22%.

**Solid State Polymerization.** For SSP in scCO<sub>2</sub>, a supercritical fluid extractor with built-in temperature control was used as the reactor (I.D: ¼", rated up to 400 bar). Carbon dioxide (Instrument/Coleman Grade, 99.99%, National Specialty Gases) was pressurized in a dual-barrel pump (Isco, Inc.) and flowed through the reactor in a constant downward flow. The reaction pressure was controlled by an automated back pressure regulator (Thar Designs, Inc.). Control experiments with N<sub>2</sub> as the sweep gas were carried out according to the procedure described elsewhere<sup>[13]</sup>.

**Instrumentation and Analysis.** The SSP was allowed to run for a specific period of time. The resulting polymer molecular weight was determined on a Waters 150-CV GPC using a THF mobile phase and polystyrene standard. Universal calibration was carried out to convert the  $M_n$  relative to polystyrene to the absolute polycarbonate  $M_{n,PC}$ . A simple coefficient was introduced for the conversion:  $M_{n,PC}=0.714M_n$ <sup>[13]</sup>. A Seiko Haake DSC 220 was used to determine the  $T_g$ ,  $T_m$ , and crystallinity of the polymer in a N<sub>2</sub> atmosphere at a heating rate of 10 °C.

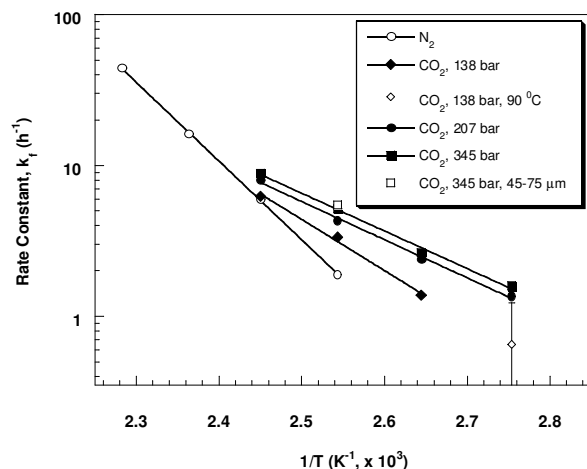
## RESULTS AND DISCUSSION

The SSP of BPA-PC involves a reaction between two dissimilar end groups. As a result, the end group stoichiometry has a strong effect on both the obtainable molecular weight of the polymer and the reaction kinetics. In our research, the ratio of the end groups in

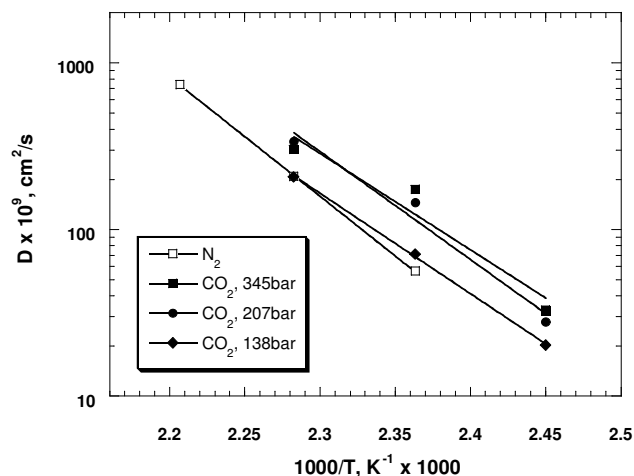
the prepolymer was determined via  $^1\text{H}$  and  $^{13}\text{C}$  NMR to be 1.014 (phenyl/hydroxyl). To study the intrinsic reaction kinetics, experimental conditions (prepolymer particle size and sweep fluid flow rate) were adjusted to eliminate any influence of phenol transport on reaction kinetics. The rate of SSP was assumed to be first order with respect to each end group (hydroxyl and phenyl) concentration. The reaction between these two end groups was assumed to be the only reaction taking place. Forward reaction rate constants were calculated by fitting the kinetic model to the experimental data of MW evolution versus SSP time.

To determine the phenol diffusivity during reaction, large prepolymer beads ( $2.0\pm 0.2\text{mm}$ ) were used for SSP. High sweep fluid flow rates were chosen to eliminate any effect of external phenol transport. As a result of the large polymer beads used for SSP, phenol diffusion inside the polymer particle was the rate-limiting step for the overall reaction. Therefore, the intrinsic chemical reaction could be assumed to reach local equilibrium instantaneously. A mathematical model was developed<sup>[14]</sup> to fit the experimental data of average MW increase with time, with phenol diffusivity as the only fitting parameter<sup>[15]</sup>. Phenol diffusivities were determined at different SSP temperatures and  $\text{CO}_2$  pressures.

The forward reaction rate constants and phenol diffusivities are plotted according to the Arrhenius relationship in Figure 1 and Figure 2, respectively. As can be seen from these figures, both the reaction rate constant and phenol diffusivity in the polymer were significantly higher in  $\text{scCO}_2$  than in atmospheric  $\text{N}_2$ . It is also observed that the rate-enhancing effect of  $\text{CO}_2$  depends strongly on the SSP temperature and pressure. At a fixed pressure, the effect of  $\text{CO}_2$  on the rate constant decreased with increasing temperature, indicating that the hydrostatic pressure alone is not the reason for the enhancements in the rate constant and phenol diffusivity. This conclusion is further supported by the fact that the same molecular weight evolution profile was observed during SSP in  $\text{N}_2$  at 207 bar and in atmospheric  $\text{N}_2$  at  $180^\circ\text{C}$  (data not shown). There exists an optimal  $\text{CO}_2$  pressure near 207 bar where  $\text{CO}_2$  has a maximum effect on the reaction rate and phenol diffusivity. The changes in reaction rate and phenol diffusivity with temperature and  $\text{CO}_2$  pressure are similar and may possibly be correlated with  $\text{CO}_2$  solubility in the polymer, which in turn may result in different degrees of polymer plasticization or  $T_g$  depression during SSP. Preliminary measurements of  $\text{CO}_2$  sorption in polycarbonate at 138 bar indicated that equilibrium was achieved within 2 hours, and that the equilibrium sorption level decreased significantly as temperature increased. Previous research showed that  $\text{CO}_2$  solubility in amorphous polycarbonate increases as the pressure increases<sup>[16]</sup>. However, at much higher pressures, there is not much further increase in  $\text{CO}_2$  solubility in the polymer<sup>[17]</sup> and the static pressure tends to increase polymer  $T_g$ <sup>[18]</sup>.



**Figure 1** Arrhenius plot for the forward reaction rate constant during SSP of poly(bisphenol A carbonate) with  $N_2$  and  $scCO_2$  as the sweep fluid.



**Figure 2** Arrhenius plot for phenol diffusivities during SSP of poly(bisphenol A carbonate) with  $N_2$  and  $scCO_2$  as the sweep fluid.

The activation energies for the forward reaction rate constant ( $E_k$ ) and for phenol diffusivity ( $E_D$ ) were calculated from the Arrhenius plots and are tabulated in Table 1. The activation energy for diffusion is always larger than that for the forward chemical reaction. As a result, for a constant crystallinity, increasing the SSP temperature increases the diffusion rate more than the intrinsic chemical reaction rate. This means that the overall SSP reaction will tend to shift from diffusion-controlled at lower temperatures to chemical-reaction-controlled at higher temperatures.

Table 1. The activation energies ( $E_k$ ) for the forward reaction rate constant and for phenol diffusivity ( $E_D$ ) during SSP of BPA-PC in atmospheric  $N_2$  and in  $scCO_2$ .

	Diffusion Coefficient	Forward Rate Constant
	$E_D$ (kcal/mol)	$E_k$ (kcal/mol)
$N_2$	32.8	23.9
138 bar $CO_2$	27.4	15.5
207 bar $CO_2$	29.7	11.6
345 bar $CO_2$	26.3	11.4

## CONCLUSION

The reaction kinetics for the solid state polymerization of poly(bisphenol A carbonate) using  $scCO_2$  as the sweep fluid was investigated and compared with kinetics using  $N_2$  as the sweep gas. Both the forward chemical reaction rate constant and the phenol diffusion coefficient inside the polymer particle during SSP were significantly higher in  $scCO_2$  than in atmosphere  $N_2$ . Therefore, the higher overall rates of SSP in  $scCO_2$  appear to be caused by a combination of higher rate constant and higher phenol diffusivities. The rate enhancement by  $scCO_2$  depends strongly on the reaction temperature and  $CO_2$  pressure, and appears to be a consequence of increased end group mobility and free volume due to the plasticization of the polymer by dissolved  $CO_2$ . By comparing the activation energies for chemical reaction and condensate diffusion, it appears that the SSP reaction will shift from diffusion control at low temperatures to chemical reaction control at high temperatures.

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