Macromolecules **1999,** *32,* 3167−3169

Solid-State Polymerization of Polycarbonates Using Supercritical CO_2

**Stephen M. Gross,[†] Devin Flowers,[†]
George Roberts,[‡] Douglas J. Kiserow,[§] and
Joseph M. DeSimone*[,†,‡]**

Venable and Kenan Laboratories, CB# 3290, Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905, Chemical Sciences Division, Army Research Office, PO Box 12211, Research Triangle Park, North Carolina 27709-2211

Received September 2, 1998
Revised Manuscript Received February 8, 1999

Polycarbonates are a commercially 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.[1] and General Electric Co.[2] Traditionally, high molecular weight polycarbonates have been synthesized by either an interfacial reaction between phosgene and bisphenol A in a biphasic reaction system of methylene chloride and alkaline water, or by a melt-phase transesterification between a bisphenol and a diaryl carbonate. An important drawback of the melt-phase process is the high reaction temperatures needed to remove phenol from the melt which leads to the formation of color bodies that reduce the optical clarity of the polymer. Conventional methods of melt-phase step-growth polymerizations use vacuum techniques to remove condensates; however, the commercial scale use of vacuum requires tedious process controls and extensive capital investment in order to maintain vacuum integrity for extended periods of time (years) with little maintenance. The solid state polymerization (SSP) of poly(bisphenol A carbonate) is not commercially practical despite the fact that SSP is the method of choice for large volume step-growth polymers such as “bottle-grade” poly(ethylene terephthalate) (PET).[3] The reaction temperature of the SSP process needs to be above the T_g of the polymer in order to have enough chain mobility for the chain extension reactions to take place. To operate above T_g, the polymer must be precrystallized to prevent sticking or coalescence of the particles. Even so, the temperature must be below the T_m so that the crystallized granules do not stick or coalesce.

Unlike PET, polycarbonate only undergoes solvent-induced crystallization by organic solvents[4] and by the addition of nucleating agents.[5] The solvents normally known to induce crystallinity (e.g., acetone, methylene chloride) are difficult to handle in a world-scale commercial plant and are undesirable in that they raise potential environmental risks. Recently it has been shown that thin films of polycarbonates can undergo crystallization upon exposure to CO_2 at elevated pressures and temperatures.[6] 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.

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 methanol and dried in a vacuum at room temperature. LiOH 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. Control of 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 uniformly sized beads. The beads had an average mass of 40 mg and had an average diameter of 3.6 mm.

Crystallization. The polycarbonate prepolymer beads were crystallized by treatment with supercritical CO_2. The resulting samples lose their transparency and become white and opaque. The solvent-induced crystallization of low molecular weight polycarbonate (2500) was studied as a function of time and temperature. T_g and T_m were measured by differential scanning calorimetry (DSC) using a Seiko Haake instrument (DSC 220) in a N_2 atmosphere at a rate of 10 °C/min. The degree of crystallinity can be determined by measuring the enthalpy of fusion, ΔH_f, of the polymer sample. The percent crystallinity (P) was calculated from

$$P = \Delta H_f\,(\text{sample})/\Delta H_f^\circ \qquad (1)$$

where ΔH_f° is the heat of fusion for the standard state, which for poly(bisphenol A carbonate) has been determined to be 26.2 cal/g.[7] Figure 1 indicates that the maximum rate of crystallization occurs between 70 and 90 °C and that the maximum crystallinity induced was 28% at 208 bar. The rate of solvent-induced crystallization passes through a maximum between the T_g and the T_m of the polymer.

Solid State Polymerization. In a typical experiment, 1 g of crystallized prepolymer was placed in a solid-state polymerization vessel at 160 ˚C (3 °C below the onset of melting) as nitrogen was passed through the vessel. Approximately 0.25 g of prepolymer were removed from the vessel after the polymerization had run for 2, 4, 6 and 12 h. The M_w of the polymer samples run at 160 and 180 °C are shown in Figure 2. Because it was observed that the T_m increased during the polymerization, we also ran a polymerization 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 6 h. The results of this experiment are also in Figure 2.[8] Solid-state polymerization was also run on prepolymer with a molecular weight of 5000 at the same temperature−time profile. The result of this experiment, which explores the effect of initial molecular weight on solid-state polymerization under these reaction conditions, can also be seen in Figure 2.

---

* To whom correspondence should be addressed.
[†] University of North Carolina at Chapel Hill.
[‡] North Carolina State University.
[§] Army Research Office.

10.1021/ma981395y CCC: $18.00

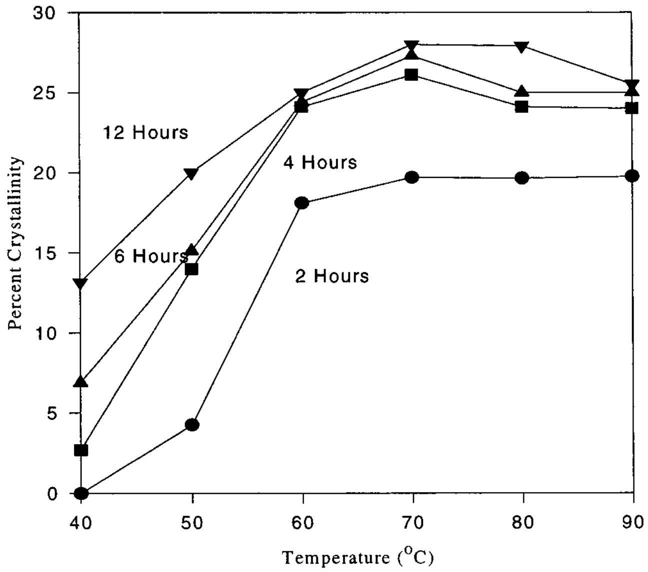

Figure 1. Percent crystallinity induced by supercritical CO_2 in poly(bisphenol A carbonate) (MW = 2500) as a function of temperature at 204 bar.

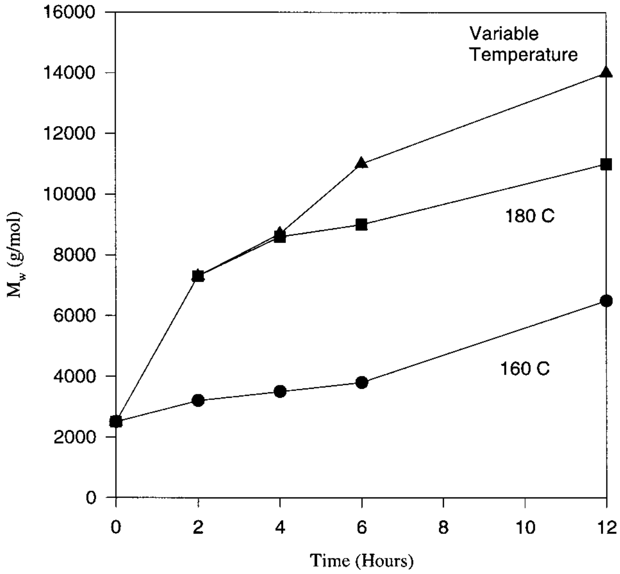

Figure 2. Increase in M_w of 3 samples of poly(bisphenol A carbonate) with a M_W = 2500) from solid-state polymerization at different temperatures over 12 h. The increase in M_w of a sample of initially MW = 5000 is also included. The time–temperature profile for the reaction was 180 °C for 2 h, then 205 °C for 2 h, then 230 °C for 2 h, and finally 240 °C for 6 h.

Results and Discussion. Initially, the amorphous polycarbonate beads with an M_w of 2500. The beads were exposed to supercritical CO_2 and were rendered 19% crystalline with a T_m of 197 °C. There was no chain extension during crystallization. As seen in Figure 2, the M_w increased a greater amount at higher reaction temperatures. For the sample polymerized at 160 °C, the M_w increased to 6500 over 12 h. The sample polymerized at 180 °C increased in M_w to 11 000. In the polymerization where the temperature was increased over time, the M_w increased to 14 000. The observed increase in molecular weight demonstrated that the use of supercritical CO_2 to induce crystallinity was compatible with the process of solid-state polymerization for polycarbonates.

As the polymerization proceeded, the samples became progressively more crystalline, as seen in Figure 3.

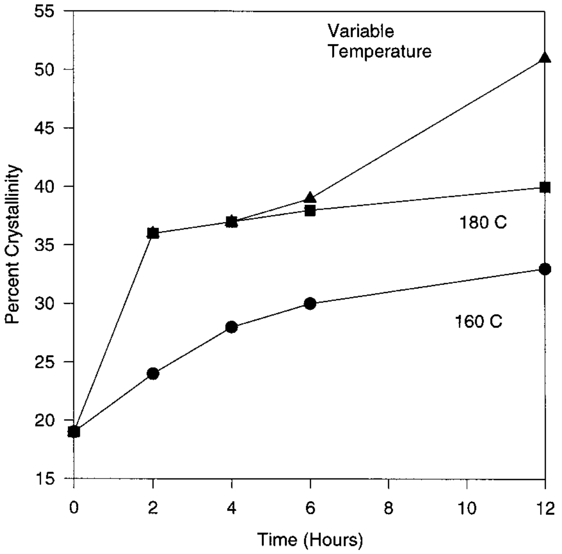

Figure 3. Increase in percent crystallinity of poly(bisphenol A carbonate) (MW = 2500) from solid-state polymerization at different temperatures over 12 h. The time–temperature profile for the reaction was 180 °C for 2 h, then 205 °C for 2 h, then 230 °C for 2 h, and finally 240 °C for 6 h.

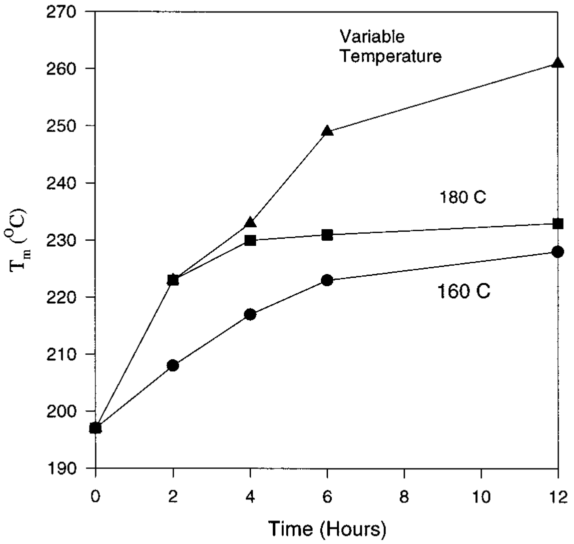

Figure 4. Increase in the T_m of poly(bisphenol A carbonate) (MW = 2500) from solid-state polymerization at different temperatures over 12 h. The time–temperature profile for the reaction was 180 °C for 2 h, then 205 °C for 2 h, then 230 °C for 2 h, and finally 240 °C for 6 h.

Additionally, the T_m increased significantly with time, as seen in Figure 4.[9] An increase in crystallinity with chain extension during solid-state polymerization has been previously observed by Sivaram et al.[10,11] This phenomena was explained by the fact that the polymer was greatly reorganized in the solid phase, leading to the development of more perfect crystallites.[12] As seen in Figure 2, the polymerization rates decrease significantly over time for samples of both molecular weights. Although this is true for the conditions of this study, it is likely that the relationship between the molecular weight of the oligomer and the polymer product would change if a number of processing steps were changed (e.g., particle shape and size).

The observed change in rate is a composite of a number of effects including the increase in reaction temperature and polymer crystallinity along with a decrease in endgroup concentration. The increase in reaction temperature should lead to an increase in reaction rate because both endgroup mobility and the diffusivity of phenol should increase with temperature. The role of polymer crystallinity is 2-fold. An increase in polymer crystallinity should concentrate the endgroups in the amorphous regions of the polymer, leading to an increased reaction rate. However, the great increase in crystallinity with time should decrease the rate of diffusion of phenol from the polymeric bead, which may limit the molecular weight that can be achieved in a given time. Additionally, the decrease in endgroup concentration with time should decrease the reaction rate. We are currently investigating these issues in greater detail.

In addition to the standard solid-state polymerization processes (e.g., SSP of PET) that use nitrogen at low pressure as a sweep gas, we are currently investigating the use of high pressure (SCF) CO_2 as the carrier gas. Supercritical CO_2 is known to plasticize the amorphous regions of the polymer and may facilitate the removal of phenol. The fact that phenol is soluble in supercritical CO_2 may lead to an enhancement in the reaction rates in this step-growth polymerization by driving the reaction to completion. Further studies will investigate the effect of morphology of the polycarbonate sample on MW. Samples that have an amorphous core and a crystalline shell can be prepared using supercritical CO_2. The solid state polymerization of these samples will be compared to samples that are uniformly crystalline throughout. Determining if the increase in molecular weight by solid-state polymerization changes with sample morphology can provide useful information for understanding this process.

Acknowledgment. We gratefully acknowledge financial support from the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing and Summer Pre-Graduate Research Experience for a summer internship.

References and Notes

(1) Schnell, H. *Chemistry and Physics of Polycarbonates*; John Wiley: New York, 1964.

(2) Tangle, L. H.; Diaz, F. R. *Eur. Polym. J.* **1987**, *23* (2), 109−112.

(3) (a) Schulz, J. M.; Fakirov, S. *Solid State Behavior for Linear Polyesters and Polyamides*; Prentice Hall: Englewood Cliffs, NJ, 1990. (b) Pilati, F. In *Comprehensive Polymer Science*; Bevington, J. C., Allen, G. C., Eds.; Pergamon: Oxford, U.K., 1989; Vol. 5, p 201.

(4) Mercier, J. P. *J. Polm. Sci., Polym. Symp.* **1967**, *16*, 2059.

(5) Legras, R.; Mercier, J. P.; Nield, E. *Nature* **1983**, *304*, 432.

(6) Beckman, E.; Porter, R. S. *J. Polym. Sci.: Part B: Polym. Phys.* **1987**, *25*, 1511−1517.

(7) Mercier, J. P.; Legras, R. *J. Polym. Sci. Polym. Lett. Ed.* **1970**, *8*, 645.

(8) Molecular weight measurements were made using a Waters 150-CV gel permeation chromatograph using a THF mobile phase and polystyrene standards.

(9) Thermal analysis measurements were measured by DSC using a Seiko Haake (DSC 220) in a N_2 atmosphere at a rate of 10 °C/min.

(10) Iyer, V. S.; Sehra, J. C.; Ravindranath, K.; Sivaram, S. *Macromolecules* **1993**, *26*, 1186.

(11) Radhakrishnan, S.; Iyer, V. S.; Sivaram, S. *Polymer* **1994**, *35*, 3789.

(12) Richardson, M. J. In *Developments in Polymer Characterization;* J. V. Dawkins, Ed.; Applied Science Publishers: London, 1978; p 205.

MA981395Y