Reaction Kinetics of the Solid State Polymerization of Poly(bisphenol A carbonate)

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ABSTRACT: The kinetics of solid-state polymerization (SSP) of poly(bisphenol A carbonate) was investigated with N_2 as the sweep gas. The N_2 flow rate and prepolymer particle size were chosen to eliminate the influence of both external and internal phenol diffusion, and to ensure that the kinetics was controlled by the rate of the forward transesterification reaction. The forward reaction rate constants were evaluated at different temperatures between 120 and 165 °C, and the activation energy for SSP of poly(bisphenol A carbonate) with N_2 as the sweep gas was determined to be 99.6 kJ/mol. At each temperature, the polymer molecular weight increased with time, eventually reaching an asymptotic value. The asymptotic molecular weight increased with temperature. The glass transition temperature (T_g) of the polymer increased as the molecular weight increased. At lower reaction temperatures, T_g approaches the reaction temperature as the polymerization proceeds, and the achievable molecular weight appears to be limited by decreased end group mobility. At the highest reaction temperature, which was well above the final T_g of the polymer, the stoichiometric ratio of the two end groups appears to determine the achievable molecular weight.

Introduction

Aromatic polycarbonates are used in many commercial applications, including safety glasses, medical devices, and compact discs, due to their unusual mechanical and optical properties.[1] High molecular weight, high quality polycarbonates can be produced by interfacial phosgenation of bisphenol A. However, this process generates both organic and aqueous waste streams that can cause serious environmental problems. Melt polymerization is an environmentally benign alternative route for polycarbonate production. The major drawback of the melt polymerization process is the viscosity increase that occurs as the molecular weight of the polymer increases. High viscosity limits removal of phenol, the condensate molecule, and hence also limits the obtainable molecular weight. High reaction temperatures will reduce melt viscosity and facilitate phenol removal, but these high temperatures lead to poor product quality.

Recent research has demonstrated that high molecular weight poly(bisphenol A carbonate) can be generated through solid-state polymerization (SSP).[2,3] Low molecular weight prepolymer first was synthesized by melt polymerization from bisphenol A (BPA) and diphenyl carbonate (DPC) and was partially crystallized, either thermally[2] or with the aid of a penetrant or nucleating agent (e.g., supercritical carbon dioxide[3]), to prevent particle agglomeration during SSP. The semicrystalline prepolymer subsequently was heated to a temperature between the glass transition temperature (T_g) of the amorphous polymer and the melting point (T_m) of the crystallites. At such a temperature, the end groups are mobile enough for the reaction to occur, yet the growing polymer remains solid, without melting or agglomerating. The polymerization is typically carried out with a continuous flow of an inert or sweep fluid (e.g., N_2 or supercritical CO_2) to facilitate phenol removal.

For solid-state polycondensation, the reaction rate depends on both chemical and physical processes. The possible rate-determining steps are as follows:

1. Intrinsic kinetics of the forward (condensation) reaction.
2. Phenol diffusion through the solid polymer to its exterior surface.
3. Phenol diffusion from the surface of the polymer particle into the sweep fluid.

Depending on the prepolymer 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.

The kinetics of the SSP of poly(bisphenol A carbonate) never has been studied in detail. Important parameters such as reaction rate constants, equilibrium constants, and phenol diffusion coefficients have not been measured under SSP conditions. Moreover, no reliable data are available for melt polymerization of poly(bisphenol A carbonate). Among the few studies, Choi and coworkers obtained forward reaction rate constants and equilibrium constants for both uncatalyzed and catalyzed melt polymerizations of BPA and DPC with $LiOH \cdot H_2O$ as the catalyst in a batch reactor.[4−6] Their experi-

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mental results showed that the uncatalyzed reaction is exothermic while the catalyzed reaction is endothermic, which is thermodynamically inconsistent.

In this research, we investigated the kinetics of the SSP of poly(bisphenol A carbonate) with N_2 as the sweep gas. Experimental conditions were adjusted to eliminate any influence of phenol transport on reaction kinetics. The forward reaction rate constants were determined between 120 and 165 °C, and the corresponding activation energy was derived.

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 was passed through a drying tube containing anhydrous calcium sulfate before entering the reactor.

Prepolymer Synthesis. Poly(bisphenol A carbonate) prepolymer was synthesized by melt polymerization. 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 the stainless steel reactor, which was equipped with an overhead stirrer. The excess of DPC was used in an attempt to compensate for vaporization during the melt polymerization. Nitrogen was purged through the reactor while the monomers were heated to 160 °C under stirring. After the monomers were melted, 200 ppm (based on monomer weight) of $LiOH{\cdot}H_2O$ (333 μL of 1.425 g of $LiOH{\cdot}H_2O$ in 25 mL of DI water stock solution) was injected as a catalyst. 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 kept under vacuum (less than 1 Torr) for 0.5 h to remove phenol. The polymer was cooled to room temperature in the reactor overnight and then collected as a solid.

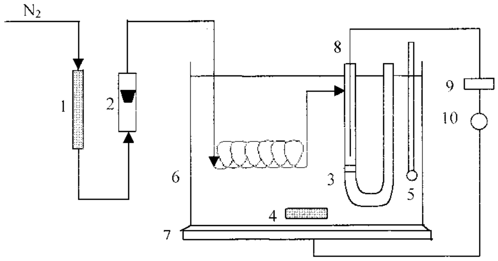
Solid State Polymerization. The prepolymer used for solid-state polymerization was ground to powder and separated into different sizes by sieving. Two different particle sizes were used in these experiments: 75−125 and <45 μm. The prepolymer had a starting number-average molecular weight (M_n) of 4300 relative to polystyrene, as determined by gel permeation chromatography (GPC). Differential scanning calorimetry (DSC) measurements showed that the prepolymer had a T_g of 69 °C, a T_m of 197 °C, and an onset temperature of melting of 167 °C. The weight percent crystallinity (P) was determined to be 24.3% using eq 1 with $\Delta H_f{}^0 = 26.2$ cal/g for poly(bisphenol A carbonate).[7]

$$P = \frac{\Delta H_{\mathrm{f,sample}}}{\Delta H_f^0} \qquad (1)$$

A crystallinity of 20−30% for the prepolymers was obtained repeatedly in similar syntheses. This may be due to the nucleating effect of the catalyst, which has been observed by several other research groups.[2,8,9]

The experimental setup for solid-state polymerization with N_2 as the sweep gas is shown in Figure 1. The whole reactor was made of glass. In one arm of the U-tube reactor (internal diameter 1/2 in.) there was a medium frit to hold polymer particles (500 mg) in position. The reactor was immersed in an oil bath at the reaction temperature. Nitrogen was passed through the drying tube, metered by a flowmeter, and heated in the glass coil before entering the reactor. The reaction temperature was monitored through a thermocouple inserted in the thermowell and controlled to within 1 °C of the set reaction temperature. The solid state polymerization was typically carried out for 10 h and samples were taken every 1−2 h.

Polymer Molecular Weight Determination and Thermal Analyses. The polymer molecular weight was determined on a Waters 150-CV gel permeation chromatograph using a THF mobile phase and polystyrene standards. The number-average molecular weights determined in this manner are denoted M_n and are relative to polystyrene. For quantitative calculations, these relative molecular weights were converted to absolute polycarbonate molecular weights, denoted $M_{n,PC}$. The conversion procedure is described below.



1. drying tube
2. flowmeter
3. SSP reactor with preheating coil and medium frit in arm of the U–tube reactor (internal diameter 1/2″)
4. stirring bar
5. thermometer
6. oil bath
7. hot plate
8. thermocouple
9. temperature controller
10. power autotransformer

Figure 1. Experimental setup for solid-state polymerization of poly(bisphenol A carbonate) with N_2 as the sweep gas.

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. The T_g of the polymer also was measured by thermal mechanical analysis (TMA) with a Seiko TMA/SS 120C at a load rate of 5 g/min and a heating rate of 2 °C/min. The T_g measured by TMA generally was about 5 °C higher than the T_g determined by DSC.

Results and Discussion

N_2 Flow Rate Effects. The rate of solid-state polymerization can be affected by mass transfer of condensate, as well as by the intrinsic reaction kinetics.[10−12] For SSP of poly(bisphenol A carbonate), the mass transfer effects include both internal mass transfer of phenol within the polymer particles and external mass transfer from the particle surface to the sweep gas. Therefore, to obtain intrinsic forward reaction rate constants, small prepolymer particles were used to eliminate the influence of internal mass transfer, and the N_2 flow rate was adjusted to remove any external mass transfer influence.

The N_2 flow rate effect was studied at the highest SSP temperature, 165 °C, which was only about 2 °C below the onset of melting for the prepolymer and which gave the highest polymerization rates of those temperatures studied. The size of the prepolymer particles was in the range 75−125 μm. A plot of the number-average molecular weight (M_n) vs time at different N_2 flow rates (20−1533 mL/min) is shown in Figure 2. Typically, for all of the flow rates studied, the molecular weight increased rapidly with time during the first 2 h of reaction, after which the rate of increase slowed significantly. At long times, the molecular weight approached an asymptotic value. Although the molecular weight at a given time always was highest for the 1533 mL/min of N_2 flow rate, the effect of flow rate was quite small within the wide range studied. Therefore, a flow

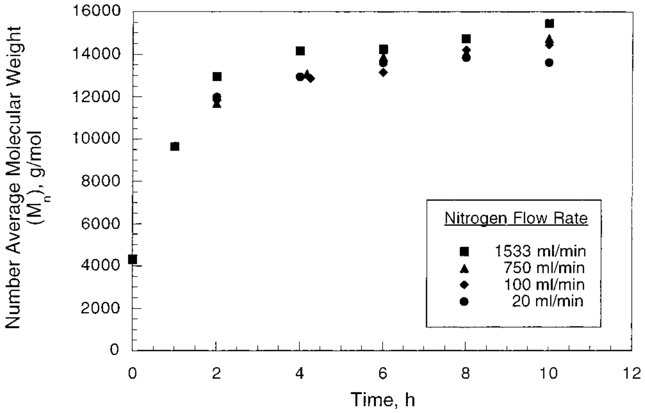


Figure 2. Effect of N_2 flow rate on molecular weight evolution during SSP of poly(bisphenol A carbonate) at 165 °C (particle size = 75−125 μm). The point at zero time represents the starting prepolymer.

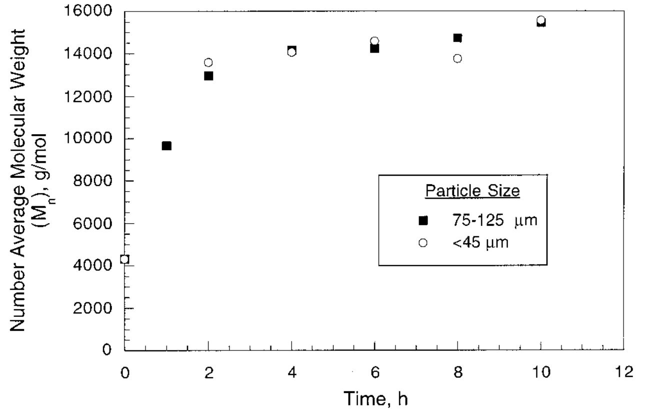


Figure 3. Effect of particle size on molecular weight evolution during SSP of poly(bisphenol A carbonate) at 165 °C (N_2 flow rate = 1533 mL/min). The point at zero time represents the starting prepolymer.

rate of 1533 mL/min appears to be sufficient to eliminate any effect of external mass transfer at the highest reaction temperature, 165 °C. At lower temperatures, where the polymerization rate and the phenol generation rate are lower, the 1533 mL/min flow rate also should be adequate to ensure that no external phenol removal limitation exists. In subsequent experiments, the N_2 flow rate always was kept at 1533 mL/min.

Internal Mass Transfer Effects. To determine whether the solid-state polymerization was influenced by phenol diffusion inside the polymer particles with the 75−125 μm particle size, the SSP was carried out at 165 °C and a N_2 flow rate of 1533 mL/min with a smaller particle size, <45 μm. The molecular weight increase with time was compared with that for the 75−125 μm particle size. The results are shown in Figure 3. The molecular weight increase with time was not affected by decreasing the particle size from 75−125 to <45 μm. This indicates that phenol diffusion inside the polymer particles does not influence the overall reaction rate, at any of the conditions used in this study. Subsequent experiments were done with particle sizes in the range 75−125 μm.

Forward Reaction Rate Constant Derivations. By elimination of both external and internal phenol transport influences, the rate of solid state polymerization is controlled solely by reaction between end groups in the amorphous region of the semicrystalline polymer. The main transesterification occurs between phenyl carbonate and hydroxyl end groups to form poly(bisphenol A carbonate), in the presence of $LiOH \cdot H_2O$ as a catalyst.

Assuming an elementary reaction, the intrinsic reaction rate is

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

where C_{OH} and C_{phenyl} are the concentrations of hydroxyl and phenyl end groups respectively, $C_{OH,0}$ is the hydroxyl end group concentration in the starting monomer melt from which the prepolymer is 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.

Equation 2 suggests that phenyl end groups are in excess. This is reasonable in view of the fact that DPC initially was present in 5 mol % excess. However, the following analysis does not depend on which end group is in excess. The value of ϵ is assumed to be that at the end of the melt polymerization, and is assumed to be constant throughout the SSP. If the asymptotic value of the number-average molecular weight is determined solely by the stoichiometric excess, ϵ can be calculated using the equation[13]

$$X_n = \frac{M_{n,PC}}{127} = \frac{2+\epsilon}{\epsilon} \qquad (3)$$

In eq 3, X_n is the asymptotic number-average degree of polymerization and 127 is the molecular weight of the structural unit for poly(bisphenol A carbonate). As noted earlier, the symbol $M_{n,PC}$ denotes the absolute number-average molecular weight for polycarbonate. This molecular weight was calculated from M_n, the molecular weight relative to polystyrene as measured by GPC, using the relationship[14]

$$[\eta]_{PS}M_n = [\eta]_{PC}M_{n,PC} \qquad (4)$$

The Mark−Houwink equations for polystyrene and poly(bisphenol A carbonate) are, respectively[15]

$$[\eta]_{PS} = 1.4 \times 10^{-2}M_w{}^{0.70} = 1.4 \times 10^{-2}(2.1M_n)^{0.70}\ \text{mL/g} \qquad (5)$$

$$[\eta]_{PS} = 3.14 \times 10^{-2}M_{w,PC}{}^{0.70} = 3.14 \times 10^{-2}(1.5M_{n,PC})^{0.70}\ \text{mL/g} \qquad (6)$$

The weight-average molecular weights (M_w) in eqs 5 and 6 have been converted to number-average molecular weights using the average polydispersities of the samples from which the Mark−Houwink constants were derived.[15] From eqs 4−6, the relationship between $M_{n,PC}$ and M_n is

$$M_{n,PC} = 0.714M_n \qquad (7)$$

After M_n is converted to $M_{n,PC}$, ϵ can be calculated from eq 3. The conversion x at any time of SSP then can be calculated from eq 8.[13]

$$\frac{M_{n,PC}}{127} = \frac{2 + \epsilon}{2 + \epsilon - 2x} \tag{8}$$

Integrating eq 2 from the start of solid-state polymerization ($t = 0$, $x = x_0$) for a nonzero value of ϵ gives

$$A = \frac{1}{\epsilon}\left(\ln\frac{(1 + \epsilon - x)}{(1 - x)} - \ln\frac{(1 + \epsilon - x_0)}{(1 - x_0)}\right) = kC_{OH,0}t = k_f t \tag{9}$$

In the following derivation, $kC_{OH,0}$ is treated as an apparent forward reaction rate constant (k_f), with units of h^{-1}. If the kinetic model of eq 2 fits the experimental data, a plot of the left-hand side (expression A) of eq 9 vs time should give a straight line through the origin. The slope of the line is k_f. However, the values of ϵ and x_0 must be obtained before eq 9 can be tested against the experimental data, and the value of k_f can be determined.

Examination of plots of M_n vs t at different temperatures (Figure 4) reveals an initial, rapid molecular weight increase. However, as the SSP continues, the rate of molecular weight increase slows. Moreover, the molecular weights reach different asymptotic values at different reaction temperatures. A simple stoichiometric imbalance associated with the prepolymer cannot account for the fact that the asymptotic molecular weights are different at different SSP temperatures.

We hypothesize that the asymptotes at the low reaction temperatures (≤150 °C) are caused by an increase of the glass transition temperature, T_g, as the molecular weight increases during SSP, as shown in Figure 5. As T_g approaches the actual SSP reaction temperature, the mobility of the end groups decreases and the reaction rate decreases accordingly. Eventually, the end groups are no longer very mobile, so that the SSP appears to stop and the molecular weight appears to reach an asymptotic value. It has been observed that at temperatures just above T_g (from T_g to T_g + 30 °C), polymer chain segment movement, and therefore end group mobility, are rather low.[16] This may explain why the SSP of poly(bisphenol A carbonate) appears to stop somewhat before the T_g of the polymer actually reaches the reaction temperature. Thermal analysis by DSC showed that the polymer crystallinity increased to a constant value of about 35% within the first hour of reaction at each SSP temperature, and therefore cannot account for the greatly decreased reaction rates at long times.

At the highest SSP temperature, 165 °C, the reaction temperature always was much higher (>30 °C) than the measured T_g of the growing polymer. The limiting value of T_g is about 148 °C for poly(bisphenol A carbonate), as determined by DSC at a 10 °C/min heating rate.[15] Therefore, at 165 °C, it is reasonable to argue that decreased end group mobility no longer accounts for the plateau in the molecular weight at long reaction times. At 165 °C, the asymptotic value of the molecular weight should be determined by the stoichiometric ratio of end groups in the polymer. This hypothesis was tested by carrying out SSP at 180 °C, using the polymer that had been polymerized previously in the solid state at 165 °C. No molecular weight increase was observed over a period of 10 h. This experiment supports the conclusion that a stoichiometric imbalance, rather than end group mobility, limits the molecular weight at higher SSP temperatures.

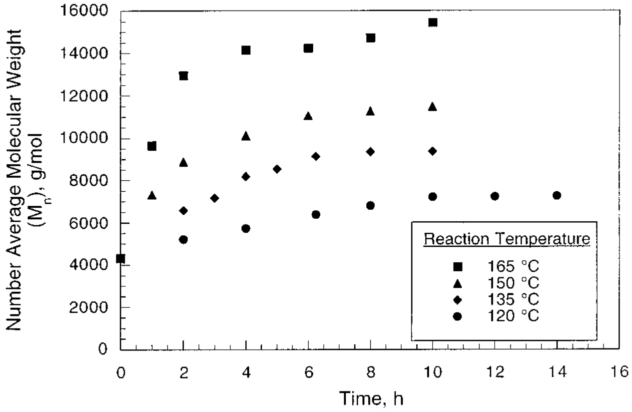


Figure 4. Effect of temperature on molecular weight evolution during SSP of poly(bisphenol A carbonate). (N_2 flow rate = 1533 mL/min; particle size = 75−125 μm). The point at zero time represents the starting prepolymer.

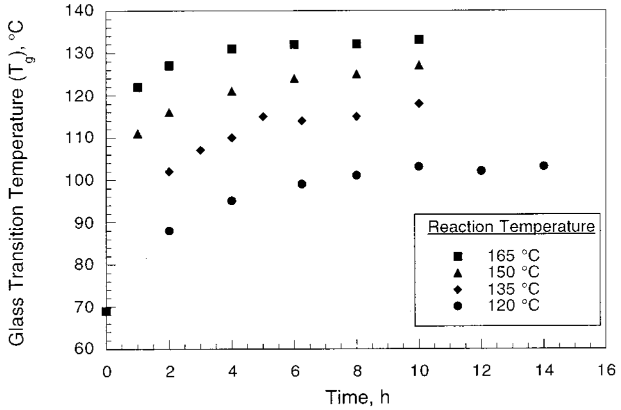


Figure 5. Glass transition temperature increase during SSP of poly(bisphenol A carbonate) at different temperatures. (N_2 flow rate = 1533 mL/min; particle size = 75−125 μm). The point at zero time represents the starting prepolymer.

The last four $M_{n,PC}$'s at 165 °C were averaged to give an asymptotic molecular weight of 10 400. The molar end group excess, ϵ, then was calculated to be 0.025 using eq 3. Since the same batch of prepolymer was used at the four different temperatures, this value of ϵ was used in eq 8 to calculate conversions. The initial conversion of the prepolymer was calculated to be $x_0 = 0.971$.

A plot of the data at each temperature, in the form of eq 9, is shown in Figure 6. Only the data at short reaction times is included. The linearity of these plots supports the kinetic model of eq 2. A value of the rate constant, k_f, at each temperature was calculated from the slope of each line.

The corresponding Arrhenius plot is shown in Figure 7. The activation energy for solid-state polymerization of poly(bisphenol A carbonate) with 200 ppm LiOH as a catalyst and with N_2 as the sweep gas is 99.6 kJ/mol or 23.8 kcal/mol. The complete Arrhenius equation is

$$k_f = 3.36 \times 10^{13} \exp\left(\frac{-99\,600}{RT}\right) h^{-1} \tag{10}$$

Choi and co-workers reported an activation energy of 25.3 kcal/mol for the uncatalyzed melt transesterification of BPA and DPC,[4] and activation energies of 14.2[4] and 21.0 kcal/mol[6] for the melt transesterification catalyzed with 9.1×10^{-5} mol/L and 25−100 ppm (based on weight) of LiOH, respectively.

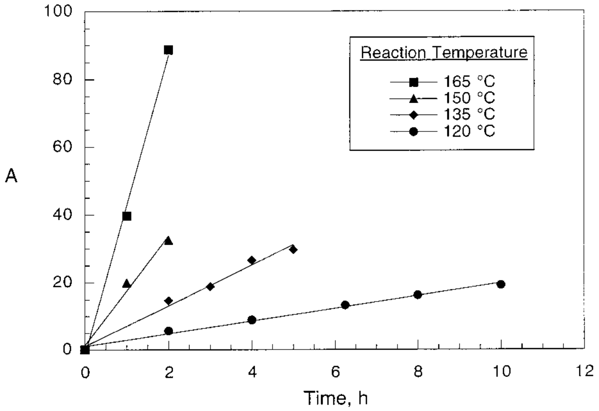


Figure 6. Test of eq 9 for SSP of poly(bisphenol A carbonate) at short reaction times and different temperatures. The apparent rate constant, k_f, is the slope of the lines. The parameter A is defined by eq 9 with $x_0 = 0.971$ and $\epsilon = 0.025$.

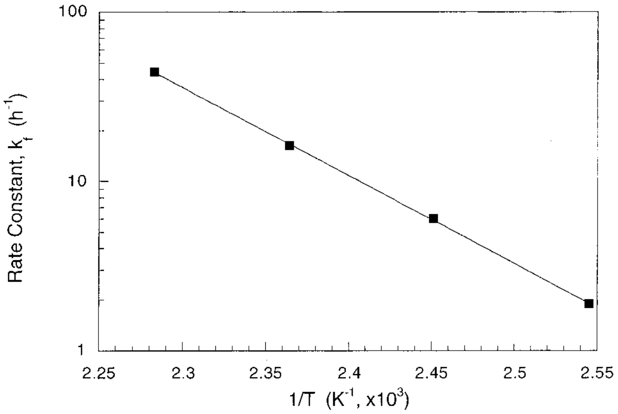


Figure 7. Arrhenius plot for SSP of poly(bisphenol A carbonate) at temperatures between 120 and 165 °C. Concentration of LiOH catalyst = 200 ppm.

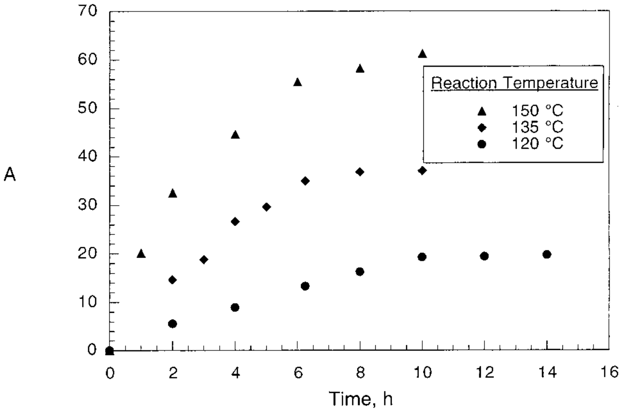


Figure 8. Plot of A vs SSP time at 120, 135, and 150 °C. The parameter A is defined by eq 9 with $x_0 = 0.971$ and $\epsilon = 0.025$. The apparent rate constant, k_f, is the slope of the plot of A vs time, which decreases at longer reaction times.

Figure 8 shows the value of A at temperatures of 120, 135, and 150 °C for the whole range of times covered by Figure 4. After the initial linear portion, as shown in Figure 6, the slope of the curve decreases with time; i.e., the apparent value of k_f decreases as the polymerization proceeds. This decrease is consistent with the earlier hypothesis that end group mobility decreases as T_g approaches the reaction temperature.

Conclusions

Solid-state polymerization of poly(bisphenol A carbonate) was carried out with N_2 as the sweep gas. External diffusion influence was removed by using a high N_2 flow rate. Internal diffusion influence was removed by using small particle sizes. As the molecular weight increased, the glass transition temperature of the polymer also increased. As a result of this T_g increase, end group mobility appeared to decrease, at a constant reaction temperature. The reaction rate decreased as a consequence. Eventually, the reaction appeared to almost stop when T_g rose to within about 25 °C of the SSP temperature. At reaction temperatures much higher than the T_g of the polymer, a stoichiometric imbalance of end groups limited the achievable molecular weight. Forward reaction rate constants were derived for SSP at 120, 135, 150, and 165 °C. The activation energy for solid-state polymerization of poly(bisphenol A carbonate) with N_2 as the sweep gas is 99.6 kJ/mol (23.8 kcal/mol).

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