Melt Transesterification of Diphenyl Carbonate with Bisphenol A in a Batch Reactor

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Synopsis

The kinetics of the melt transesterification of diphenyl carbonate with 4,4-dihydroxydiphenyl–2,2-propane has been studied in a batch reactor with $LiOH \cdot H_2O$ as a catalyst in the temperature range of 150–180°C. The third-order forward and backward rate constants were determined experimentally and a linear dependence of the transesterification rate on the catalyst concentration was observed. The product oligomer concentration distribution has also been measured experimentally and estimated by the molecular species model which describes the progress of the melt transesterification.

INTRODUCTION

Polycarbonates, polyesters derived from the reaction between a diol and a carbonate ester, are an important class of thermoplastic engineering polymers. There are three major industrial processes used to produce aromatic polycarbonates: a solution phosgenation, an interfacial phosgenation, and a melt transesterification. In the melt process, the prepolymer is produced by transesterifying diphenyl carbonate (DPC) with a 4,4-dihydroxydiphenyl–2,2-propane (bisphenol A, BPA) in the presence of a catalyst to produce oligomers initially through the formation of the monophenyl carbonate of bisphenol A. The oligomers having phenoxy and hydroxyl end groups are formed along with phenol, which is split out during the transesterification reactions. The oligomers are then further polycondensed to produce high molecular weight polycarbonate by employing high temperature (270–300°C) and low pressure ($\sim$ 1 mm Hg) with the splitting out of more phenol, and even diphenyl carbonate. Bisphenol A polycarbonate is an amorphous, high glass transition ($T_g = 145°C$), thermoplastic polycondensate characterized by an exceptional toughness.

The melt transesterification method offers many advantages. For example, polycarbonates produced by the melt process are pure due to the absence of any solvents in the reactor, the polymerization reactor can be operated continuously, and the polymers from the reactor can be directly pelletized. However, it has also been known that high molecular weight polycarbonates are more difficult to obtain in the transesterification process than in other processes because the viscosity of the polymer melt increases significantly as the polymer molecular weight increases and thermal degradation reactions occur at high reaction temperatures (e.g., 300°C). Like other melt polycondensation processes [e.g., poly(ethylene terephthalate)], specially designed finishing reactors providing a large surface area for the removal of the condensation byproduct (phe-

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nol) are required to deal with the highly viscous polymer melt and to obtain a high polymer molecular weight.

Considering the fact that a precise control of polymer properties and process productivity is one of the key issues in designing or optimizing the melt transesterification processes, one needs to develop a deep understanding of polymerization kinetics and associated physicochemical phenomena, and the reactor behavior. Unfortunately, however, there is a dearth of open literature on the kinetics of the melt transesterification of aromatic polycarbonates. In this work, the first stage of the batch melt transesterification of diphenyl carbonate and BPA is studied and the relevant kinetic parameters are estimated.

In conducting the melt transesterification, basic compounds are very effective in promoting the transesterification to a great degree. Examples of basic catalysts include alkali, alkaline earth metals and their oxides, hydroxides, and phenolates. Although numerous catalyst systems are known to be usable for the melt transesterification, few reports are available on the reaction kinetics and mechanism with these catalysts. Some workers[1-3] studied the melt transesterification of DPC with BPA in semibatch type reactors using zinc oxide as a catalyst. However, in the experimental studies reported in the literature, the reverse reaction was not included in their kinetic scheme. Therefore, no equilibrium reaction data have been reported. Since the transesterification reaction occurs reversibly and the overall reaction becomes mass transfer controlled at high monomer conversion, it is necessary to quantify the equilibrium reaction kinetics for a given catalyst system.

In this paper, we shall present experimental data along with a theoretical kinetic modeling study of the first stage in the melt transesterification of DPC with BPA for the polymerization of polycarbonates. The experiments were conducted at 150–180°C and ambient pressure using a batch reactor with lithium hydroxide monohydrate ($LiOH \cdot H_2O$), which is a more efficient transesterification catalyst than zinc oxide, as a catalyst.

EXPERIMENTAL

The batch melt transesterification experiments were carried out by using an 100-mL round-bottom glass reactor equipped with a stirrer. The glass reactor was submerged in an oil bath for heating. The standard reaction recipe for the batch experiment uses a 1.06 mol ratio of diphenyl carbonate (Aldrich) to bisphenol A (Aldrich) (e.g., 0.2334 mol DPC and 0.2202 mol BPA). After these reactants were weighed and added to the reactor, the reactor was evacuated and purged with nitrogen. The reactor was then heated to the desired reaction temperature while the stirrer was activated. The diphenyl carbonate melted first at around 90°C followed by bisphenol A around 140°C. When the reaction medium reached the desired temperature, a predetermined amount of lithium hydroxide catalyst (Aldrich) was added. Small amounts of samples of the reaction mixture were taken at different times during the experiment and analyzed to determine the degree of reaction and the product composition. More details of the experimental procedure can be found in Ref. 4.

The concentrations of the various reaction products and reactants were measured by an HPLC with a refractive index (RI) detector and tetrahydrofuran

(THF) as a solvent. Four Ultrasyragel columns (Waters, 100 Å, two 500 Å, one linear column) were used and very satisfactory separation of the reaction mixture was obtained. Syrene was used as an internal standard and the universal calibration method was used to calibrate the columns with polystyrene standards of narrow molecular weight distributions. When the sample was injected into the columns, the polymer (oligomers) was separated out first, followed by a bisphenol A peak, a diphenyl carbonate peak, a phenol peak, and lastly a styren peak.

REACTION MODELS

The main transesterification reaction occurs between the phenyl carbonate group and the hydroxyl group in the presence of lithium hydroxide catalyst. In the absence of side reactions (e.g., Kolbe–Schmitt type), these two functional groups can only react reversibly in one way:
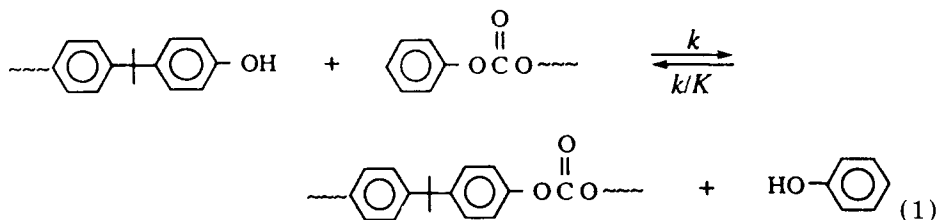
In the analysis of this reaction, the following short hand notation is used to denote various species present in the reaction mixture:
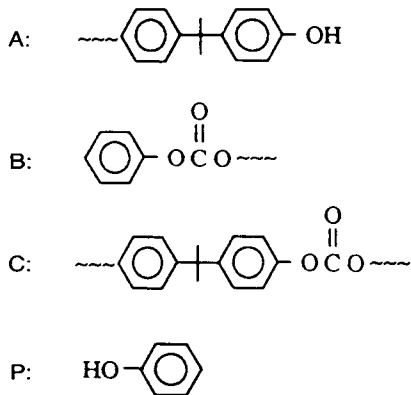
Then, the stoichiometric equation takes the form

$$A + B \underset{k/K}{\overset{k}{\rightleftharpoons}} C + P \tag{2}$$

The initial concentrations of A and B (i.e., $[A]_0$ and $[B]_0$) are twice the initial concentration of bisphenol A and diphenyl carbonate, respectively.

The reaction rate expression, assuming that the above reaction is an elementary reaction, is given by

$$r = k'[A][B] - \frac{k'}{K}[C][P] \qquad (\text{mol/mL min}) \qquad (3)$$

where

$$k' = k[C^*] = kn_{cat}/V \qquad (\text{mL}^2/\text{mol}^2 \text{ min})$$

$[C^*]$ is the catalyst concentration, and n_{cat} is the number of moles of catalyst added to the reactor. It is assumed that the volume of reaction mixture (V) is constant during the transesterification. If the reaction is started with only bisphenol A and diphenyl carbonate, the above rate equation can be rewritten in terms of phenol concentration ($[P]$) as follows:

$$\frac{d[P]}{dt} = k'\left\{([A]_0 - [P])([B]_0 - [P]) - \frac{[P]^2}{K}\right\} \qquad (4)$$

At equilibrium,

$$K = \frac{[P]_e^2}{([A]_0 - [P]_e)([B]_0 - [P]_e)} \qquad (5)$$

where $[P]_e$ is the phenol concentration at equilibrium.

The effective forward reaction rate constant (k') can be determined experimentally by measuring the initial reaction rate r_0:

$$r_0\left(= \left.\frac{d[P]}{dt}\right|_{t=0}\right) = k'[A]_0[B]_0 \qquad (6)$$

With both K and k' values determined experimentally, the backward rate constant can be obtained. By conducting batch transesterification experiments at different temperatures and catalyst concentrations, one can also find the temperature dependence and the catalyst dependence of the rate constants, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the concentration profiles of phenol in the reaction mixture for three different catalyst concentrations, i.e., 0.01, 0.005, and 0.0025 wt %, at 150°C. The concentration of phenol was measured by HPLC and all the experimental data points are the averages of replicated experiments. Note that at $[C^*] = 0.01$ wt % the transesterification reaction reaches an apparent equilibrium in about 30 min. The equilibrium conversion measured in (phenol produced)/(theoretical amount of phenol produced at the completion of the transesterification) is 38.7% (average). From these experiments, the following rate constant values have been obtained at 150°C:
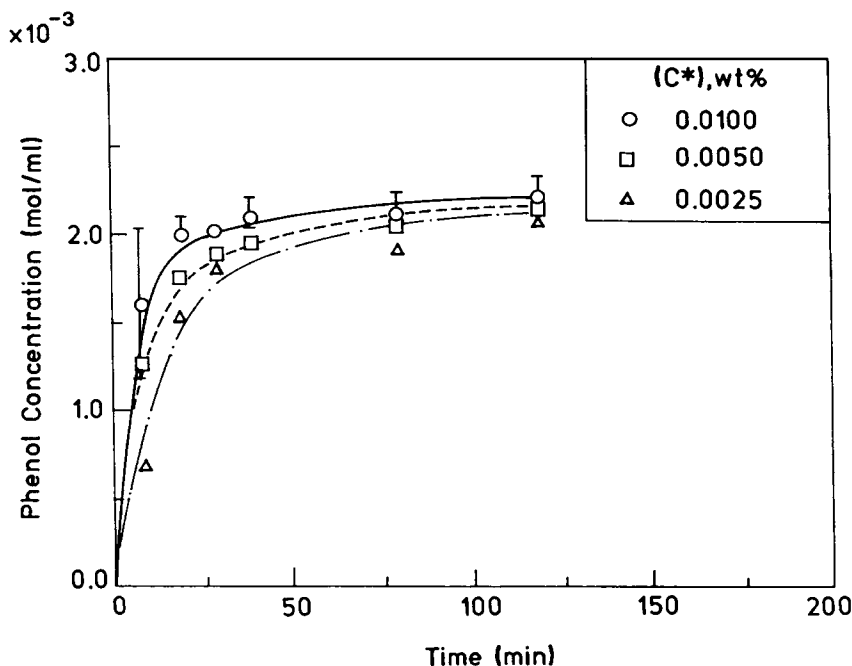
Fig. 1.   Phenol concentration vs. reaction time in a batch melt transesterification of DPC with BPA: 150°C, [C*] (wt %): (○) 0.0100; (□) 0.0050; (△) 0.0025.

$$k = (7.024 \pm 0.280) \times 10^6 \qquad \mathrm{mL}^2/\mathrm{mol}^2 \, \mathrm{min}$$

$$(\text{or } k' = 11.495 \qquad \mathrm{mL}/\mathrm{mol} \, \mathrm{min})$$

$$K = 0.420 \pm 0.032$$

It should be noted that, in estimating the reaction rate, the presence of phenol vapor in the reactor (e.g., less than 0.5 mol % of the total amount of phenol liberated) was ignored in the calculation. Figure 2 shows the variation of the initial reaction rate at 150°C with catalyst concentration. Notice that the reaction rate is first order with respect to the catalyst concentration in the catalyst concentration range studied.

Similar experiments have been carried out at 165 and 180°C for the catalyst concentration of 0.0025 and 0.0018 wt %, respectively. The use of high catalyst concentration (e.g., 0.0025 wt %) at 180°C resulted in a vigorous liberation of phenol vapor and a significant decrease in reaction temperature due to evaporative cooling. Thus lower catalyst concentration was used at 180°C. Figure 3 shows the Arrhenius plot for the forward reaction rate constant (k) and the backward reaction rate constant (k_{-1}). From this plot, k and k_{-1} have been determined:

$$k = 4.890 \times 10^{17} \exp(-21{,}048/RT) \qquad \mathrm{mL}^2/\mathrm{mol}^2 \, \mathrm{min}$$

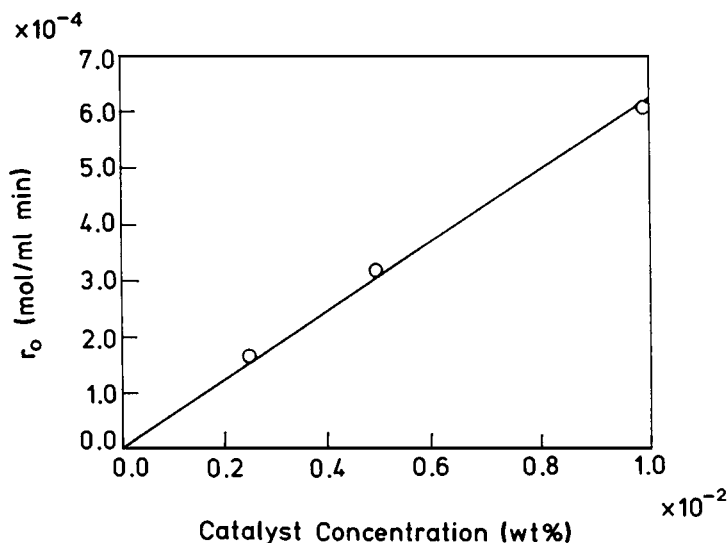$$k_{-1} = 8.180 \times 10^{15} \exp(-16{,}884/RT) \qquad \mathrm{mL}^2/\mathrm{mol}^2 \, \mathrm{min}$$

Fig. 2.   The variation of the initial reaction rate with catalyst concentration at 150°C.

Note that the equilibrium constant (K) increases slightly with temperature and is less than unity [e.g., $K = 0.420(150°C)$, $0.514(165°C)$, $0.581(180°C)$] and hence unfavorable for the forward reaction (transesterification). Quite obviously, the reaction byproduct (phenol) must be removed from the reactor in order to promote the forward reaction and to obtain a high polymer molecular weight. The rate constant value obtained in our work for the lithium hydroxide monohydrate catalyst system is much larger than the rate constant reported by Turska and Wrobel[3] for the zinc oxide catalyst system ($k = 6.73 \times 10^{11}$ $\exp(-14{,}450/RT \text{ mL}^2/\text{mol}^2 \text{ min})$).

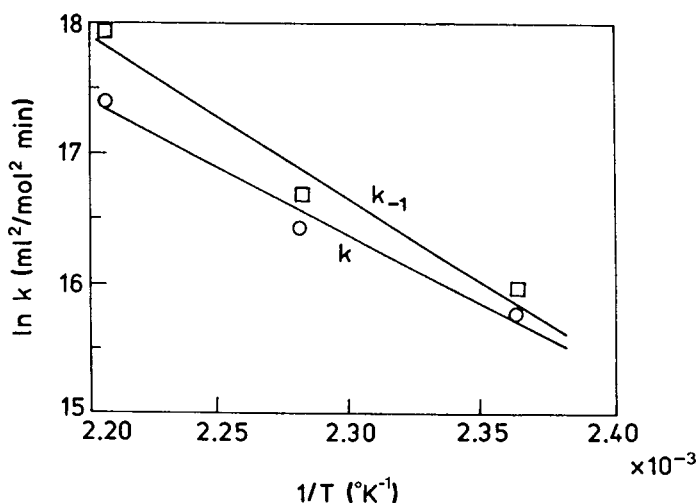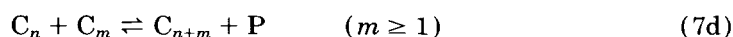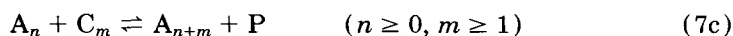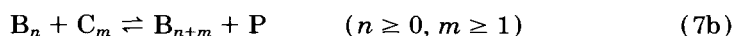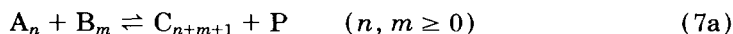The simple functional group model which was used above to estimate

Fig. 3.   The Arrhenius plot for the forward reaction rate constant (k) and the backward reaction rate constant (k_{-1}).

the forward and backward rate constants has a limitation in that complete product distributions are not obtainable. The molecular species model[5,6] tracks every component in the reaction medium as well as the molecular weight of each macromolecule and the average molecular weight of the whole polymerizing mixture. Since there are only two functional end groups and only one way for them to react in the absence of side reactions (e.g., Kolbe–Schmitt type), the following relatively simple sequence of reactions constitute the molecular species model for the melt transesterification of DPC with BPA:

$$A_n + B_m \rightleftharpoons C_{n+m+1} + P \qquad (n, m \geq 0) \tag{7a}$$

$$B_n + C_m \rightleftharpoons B_{n+m} + P \qquad (n \geq 0, m \geq 1) \tag{7b}$$

$$A_n + C_m \rightleftharpoons A_{n+m} + P \qquad (n \geq 0, m \geq 1) \tag{7c}$$

$$C_n + C_m \rightleftharpoons C_{n+m} + P \qquad (m \geq 1) \tag{7d}$$

where A_n = an oligomer with 2 hydroxyl end groups with n repeating units, B_n = an oligomer with 2 phenyl carbonate end groups with n repeating units, C_n = an oligomer with 1 hydroxyl end group and 1 phenyl carbonate end group with n repeating units, and P = phenol. Note that A_0 and B_0 represent bisphenol A and diphenyl carbonate, respectively, and C_1 is the monophenyl carbonate of bisphenol A. The repeating unit is
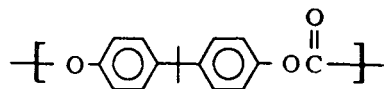
Assuming that the reactivities of the functional end groups are independent of the chain length, one can derive the component material balances for isothermal reaction conditions as follows:

$$\frac{dA_0}{dt} = n_{\text{cat}} \frac{1}{V^2} \left(-4kA_0B_0 - 4kA_0 \sum_{m=1}^{\infty} B_m \right.$$
$$\left. + k_{-1}P \sum_{m=1}^{\infty} C_m - 2kA_0 \sum_{m=1}^{\infty} C_m + 2k_{-1}P \sum_{m=1}^{\infty} A_m \right) \tag{8a}$$

$$\frac{dB_0}{dt} = n_{\text{cat}} \frac{1}{V^2} \left(-4kA_0B_0 - 4kB_0 \sum_{m=1}^{\infty} A_m \right.$$
$$\left. + k_{-1}P \sum_{m=1}^{\infty} C_m - 2kB_0 \sum_{m=1}^{\infty} C_m + 2k_{-1}P \sum_{m=1}^{\infty} B_m \right) \tag{8b}$$

$$\frac{dC_1}{dt} = n_{\text{cat}} \frac{1}{V^2} \left(4kA_0B_0 - k_{-1}PC_1 - 2kC_1B_0 \right.$$
$$- 2kC_1 \sum_{m=1}^{\infty} B_m + 2k_{-1}P \sum_{m=1}^{\infty} B_m - 2kC_1A_0 - 2kC_1 \sum_{m=1}^{\infty} A_m$$
$$\left. + 2k_{-1}P \sum_{m=1}^{\infty} A_m - 2kC_1 \sum_{m=1}^{\infty} C_m + 2k_{-1}P \sum_{m=2}^{\infty} C_m \right) \tag{8c}$$

$$\frac{dP}{dt} = n_{\text{cat}} \frac{1}{V^2} \Bigg[4kA_0 B_0 + 4kA_0 \sum_{m=1}^{\infty} B_m + 4kB_0 \sum_{m=1}^{\infty} A_m$$

$$+ 4k \sum_{m=1}^{\infty} A_m \sum_{j=1}^{\infty} B_j - k_{-1}P \sum_{m=1}^{\infty} mC_m + 2kB_0 \sum_{m=1}^{\infty} C_m + 2k \sum_{m=1}^{\infty} B_m \sum_{j=1}^{\infty} C_j$$

$$- 2k_{-1}P \sum_{m=1}^{\infty} mB_m + 2kA_0 \sum_{m=1}^{\infty} C_m + 2k \sum_{m=1}^{\infty} A_m \sum_{j=1}^{\infty} C_j - 2k_{-1}P \sum_{m=1}^{\infty} mA_m$$

$$+ k \sum_{m=1}^{\infty} C_m \sum_{j=1}^{\infty} C_j - k_{-1}P \sum_{m=2}^{\infty} (m-1)C_m \Bigg] \qquad (8d)$$

$$\frac{dA_n}{dt} = n_{\text{cat}} \frac{1}{V^2} \Bigg(-4kA_n B_0 - 4kA_n \sum_{m=1}^{\infty} B_m$$

$$+ k_{-1}P \sum_{m=n+1}^{\infty} C_m - 2kA_n \sum_{m=1}^{\infty} C_m + 2kA_0 C_n + 2k \sum_{m=1}^{n-1} A_m C_{n-m}$$

$$- 2k_{-1}PnA_n + 2k_{-1}P \sum_{m=n+1}^{\infty} A_m \Bigg) \qquad (n \geq 1) \quad (8e)$$

$$\frac{dB_n}{dt} = n_{\text{cat}} \frac{1}{V^2} \Bigg(-4kB_n A_0 - 4kB_n \sum_{m=1}^{\infty} A_m$$

$$+ k_{-1}P \sum_{m=n+1}^{\infty} C_m - 2kB_n \sum_{m=1}^{\infty} C_m + 2kB_0 C_n + 2k \sum_{m=1}^{n-1} B_m C_{n-m}$$

$$- 2k_{-1}PnB_n + 2k_{-1}P \sum_{m=n+1}^{\infty} B_m \Bigg) \qquad (n \geq 1) \quad (8f)$$

$$\frac{dC_n}{dt} = n_{\text{cat}} \frac{1}{V^2} \Bigg[4k \sum_{m=0}^{n-1} A_m B_{n-m-1} - k_{-1}PnC_n - 2kC_n B_0$$

$$- 2kC_n \sum_{m=1}^{\infty} B_m + 2k_{-1}P \sum_{m=n}^{\infty} B_m - 2kC_n A_0 - 2kC_n \sum_{m=1}^{\infty} A_m$$

$$+ 2k_{-1}P \sum_{m=n}^{\infty} A_m - 2kC_n \sum_{m=1}^{\infty} C_m + k \sum_{m=1}^{n-1} C_m C_{n-m} - k_{-1}P(n-1)C_n$$

$$+ 2k_{-1}P \sum_{m=n+1}^{\infty} C_m \Bigg] \qquad (n \geq 2) \quad (8g)$$

In the above equations, the italic capital letters represent the concentration of that particular component.

The above equations can be solved either by integrating them directly with given initial conditions and prespecified n value or by using the molecular weight moments defined as

$$\alpha_k = \sum_{n=1}^{\infty} n^k A_n \qquad (9a)$$

$$\beta_k = \sum_{n-1}^{\infty} n^k B_n \qquad (9b)$$

$$\gamma_k = \sum_{n=1}^{\infty} n^k C_n \qquad (9c)$$

where α_k, β_k, and γ_k represent the kth moment of A_n, B_n, and C_n species, respectively. Since the batch prepolymerization or transesterification is conducted at low temperature (150–200°C) and ambient pressure or slightly reduced pressure, the degree of oligomerization (n) is not expected to be high. Therefore, one can specify the n value *a priori* and integrate ($3n + 3$) equations to obtain the concentration of each polymeric species. In what follows, we shall present the results obtained by integrating the component mass balance equations for a finite value of n ($n = 3$), which is chosen from the experimental analysis of the oligomer composition distribution.

For the calculation of the concentrations of the volatile species (e.g., phenol) in the reaction mass and in the vapor phase, a quasisteady state assumption is used for the vapor–liquid equilibrium in small increments of time. The vapor phase is assumed to follow the ideal gas law and in the liquid phase, the Flory–Huggins modes is used. Under vapor–liquid equilibrium, the partial pressure of the volatile species in the liquid phase can be represented as

$$P_i = \gamma_i P_i^{\text{sat}} x_i \qquad (10)$$

where P_i is the partial pressure of species i. γ_i, P_i^{sat}, and x_i are the activity coefficient, saturated vapor pressure, and mole fraction of component i, respectively. At the reaction temperatures used in our experimental study, the vapor pressure for bisphenol A and diphenyl carbonate are very small and can be neglected. Therefore, only phenol is assumed to be present in the vapor phase. The temperature dependence of the vapor pressure of phenol is given in the Antoine equation[7]:

$$\ln P^{\text{sat}} = 16.4279 - \frac{3,490.89}{T - 98.59} \qquad (P \text{ in mm Hg}, T \text{ in K}) \qquad (11)$$

The activity coefficient of phenol (γ_1) for the Flory–Huggins model is given by[8]

$$\ln \gamma_1 = \ln[1 - (1 - 1/m)(1 - \Phi_1)]$$
$$+ (1 - 1/m)(1 - \Phi_1) + \chi_1(1 - \Phi_1)^2 \qquad (12)$$

where m is the ratio of molar volumes of polymer and sovent (phenol), Φ_1 is the volume fraction of phenol, and χ_1 is the Flory interaction parameter. A detailed implementation procedure of the vapor–liquid equilibrium equations into the kinetic models is described in Ref. 4.

Figure 4 shows the chromatograms of the samples produced from the batch experiments at 180°C and a catalyst concentration of 0.0018 wt %. First note that low molecular weight oligomers are produced during the early reaction
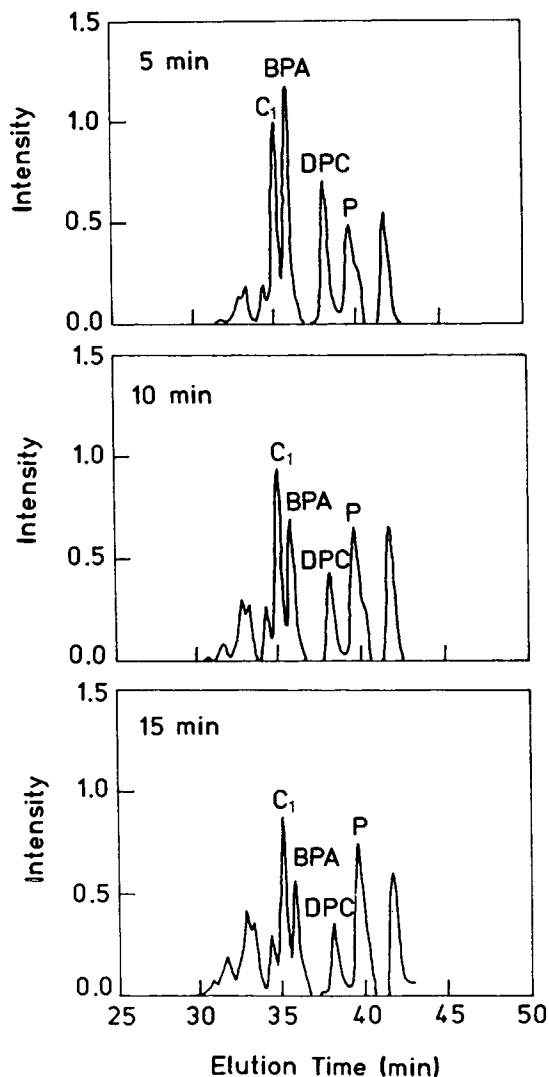
Fig. 4. HPLC chromatograms from batch experiments at 180°C and a catalyst concentration of 0.0018 wt %.

period and, as the reaction proceeds, higher molecular weight oligomers are produced. At the same time the total oligomer concentration decreases while the concentrations of bisphenol A and diphenyl carbonate decrease. It was observed that the product distribution became essentially constant after 30 min, indicating that the reaction had reached an equilibrium (cf. Fig. 1). Figure 5 also illustrates that the rate of change in the phenol concentration levels off after about 30 min of reaction. Note that C_1 (monophenyl carbonate of bisphenol A) which is the first oligomer with one hydroxyl end group and one phenyl carbonate end group has the lowest molecular weight of all the oligomers, but has a higher molecular weight than the monomers (BPA and DPC) and phenol.
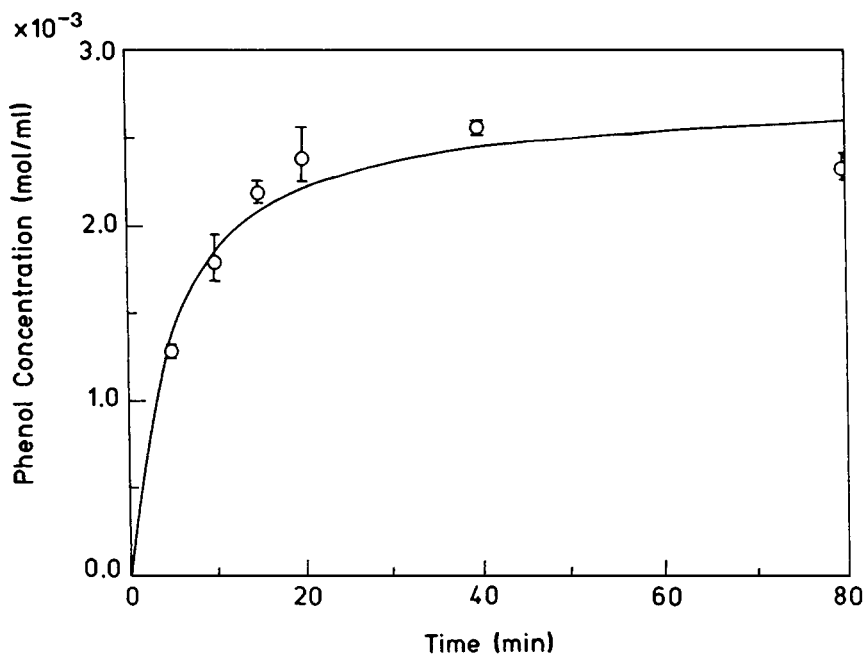
Fig. 5.   Phenol concentration in the reaction mixture: 180°C, $[C^*] = 0.0018$ wt %.

Figure 6 shows the phenol conversion [i.e., (phenol produced)/(theoretical amount of phenol produced at the completion of the transesterification)], BPA concentration, and DPC concentration profiles at 180°C and $[C^*] = 0.0018$ wt % observed experimentally. The solid lines are the model predictions. Note that the predicted concentration profiles show very good agreement with experimental data, albeit with slight overestimation at higher conversion to phenol.

Typical oligomer concentration profiles are illustrated in Figure 7. As was observed in Figure 4, the concentration of monophenyl carbonate of bisphenol A (C_1) increases sharply to a maximum in about 20 min and there is only a slight amount of dimers and trimers of the three oligometric species. These diagrams also indicate that C_n-type species are the dominant species in the reaction mixture. A similar behavior was reported in Ref. 9. Figure 8 shows the average molecular weight profiles of the reaction mixture measured experimentally and estimated by the model. The predicted molecular weight profile is in very close agreement with that predicted by the model.

CONCLUDING REMARKS

In this paper we have presented the reaction rate parameters for the batch melt transesterification of diphenyl carbonate with bisphenol A in the presence of lithium hydroxide monohydrate as a catalyst. The transesterification reaction is first order in the catalyst concentration, and the third-order forward and backward reaction rate constants obtained are
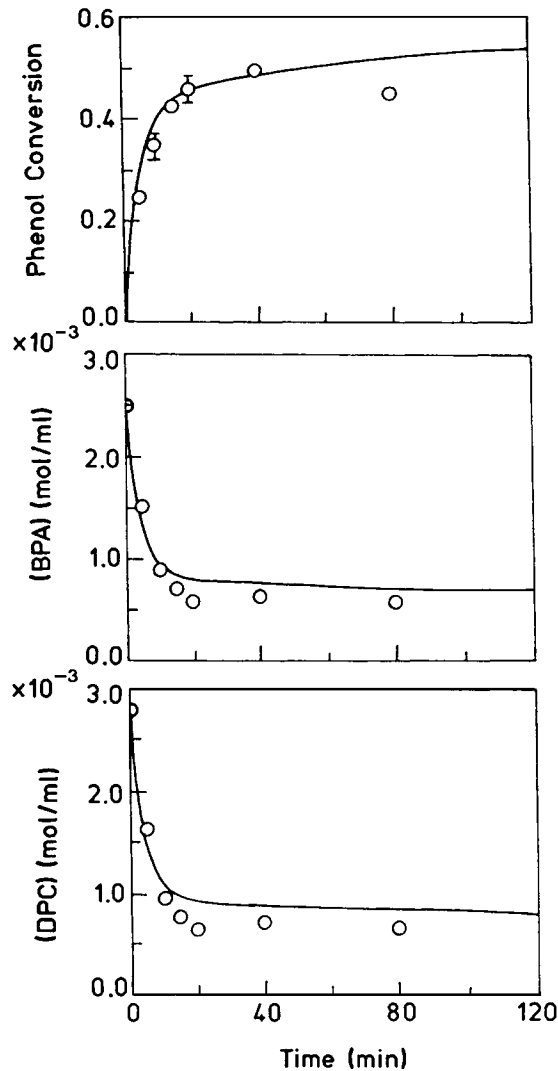
Fig. 6. Batch melt transesterification: (—) model simulation; (○) experimental data; 180°C, [C*] = 0.0018 wt %.

$$k = 4.890 \times 10^{17} \exp(-21{,}048/RT) \qquad mL^2/mol^2 \ min$$

$$k_{-1} = 8.180 \times 10^{15} \exp(-16{,}884/RT) \qquad mL^2/mol^2 \ min$$

It was also found that, for the reaction conditions used in our experiments, bisphenol A monophenyl carbonate and the oligomers capped by a hydroxyl end group and a phenyl carbonate group are the predominant species present in the reaction mixture. The progress of the transesterification reaction predicted by the molecular species model developed was also in good agreement with experimental data. The results obtained in this work will be useful in
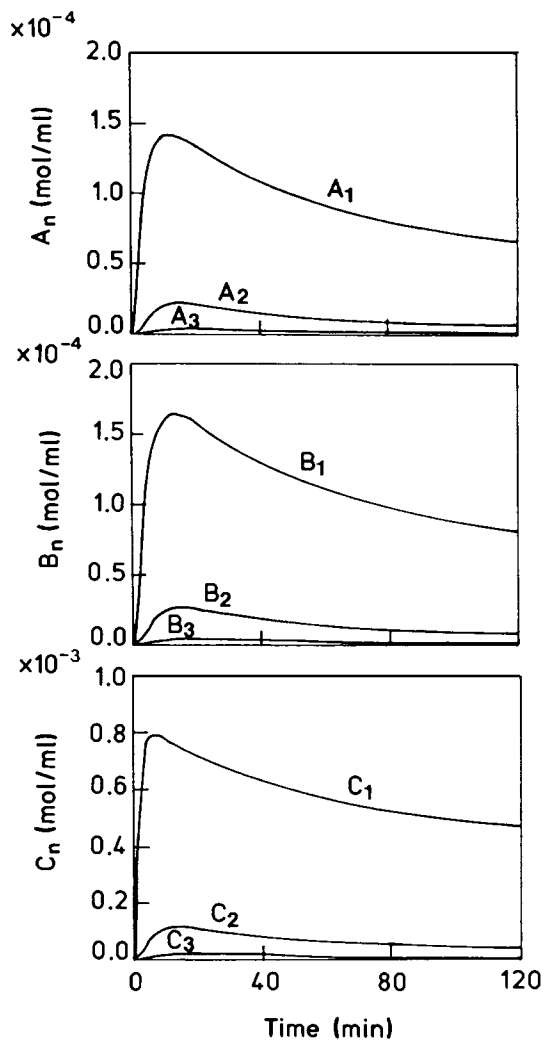
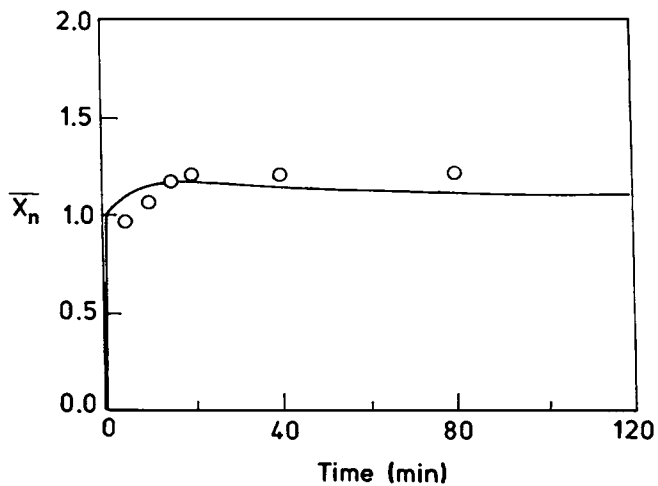Fig. 7. Oligomer concentration profiles at 180°C, $[C^*] = 0.0018$ wt %.

Fig. 8. Number average degree of oligomerization of the reaction mixture, 180°C, $[C^*] = 0.0018$ wt %.

studying the melt transesterification at high temperatures and low pressures (e.g., second stage polymerization). The melt transesterification in a semibatch reactor at elevated temperature and reduced pressure will be reported in our forthcoming paper.

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