

Reaction Kinetics of Interfacial Polycondensation of Polyarylate

INTRODUCTION

In a previous paper,¹ the kinetics of interfacial polycondensation of bisphenol A with isophthaloyl chloride and terephthaloyl chloride in dichloromethane with TEBAC (triethylbenzylammonium chloride) as the catalyst was presented. The reaction kinetics was found to be second order with respect to bisphenolate concentration in the aqueous phase for equal molar ratio of bisphenol A to diacid chlorides. The effect of stirring speed, amount of TEBAC added, and reaction temperature on rate constant was described.

Brzozowsky and co-workers² also presented rough kinetic data of interfacial polycondensation of polyarylates in the presence of two different catalysts (TEBAC and tetrabutylammonium hydroxide). They studied the kinetics through analysis of diacid chloride concentration vs. reaction time relationship by determining the concentration of sodium chloride titrated with silver nitrate. A second-order reaction with respect to diacid chloride concentration was suggested. They also showed that the diffusion of bisphenolate was the rate-determining step at stirring speed up to 3000 rpm.

Brzozowsky and co-workers suggested a second-order reaction with respect to diacid chloride concentration, while a second-order reaction with respect to bisphenolate concentration in the aqueous phase was found in our results. As described previously,¹ the rate equation may be first order with respect to bisphenolate concentration in the aqueous phase and also first order with respect to diacid chlorides concentration in the organic phase. Since the molar ratio of bisphenol A to diacid chlorides was equal to 1 in the previous work, and the interfacial polycondensation under that condition was a diffusion-controlled reaction, the concentration of bisphenolate in the aqueous phase was proportional to that of diacid chlorides in the organic phase. Thus, a second-order reaction with respect to bisphenolate concentration in the aqueous phase was found. The situation will be interesting if the molar ratio of bisphenol A to diacid chloride is other than 1. In this paper, the molar ratio of bisphenol A to isophthaloyl chloride was varied, and the kinetic data were determined to interpret the rate equation of interfacial polycondensation.

EXPERIMENTAL

The reagents used were described in a previous paper.³ The reaction with equal molar ratio of bisphenol A to isophthaloyl chloride was carried out as follows. A solution of 20.3 g (0.1 mol) of isophthaloyl chloride in 250 mL of dichloromethane was prepared, and 22.8 g (0.1 mol) of bisphenol A, 8.8 g of sodium hydroxide, and 0.141 g (6.2×10^{-4} mol) of TEBAC were dissolved in 500 mL of distilled water. The reaction was carried out by mixing the two solutions at 20°C at stirring speed of 500 rpm. At each time interval, 20 mL of reaction mixture was taken out, and the bisphenolate concentration in the aqueous phase was determined as described previously.³

For the reaction with molar ratio of bisphenol A to isophthaloyl chloride equal to 1.1, 25.1 g (0.11 mol) of bisphenol A and 9.7 g of sodium hydroxide were used. For the reaction with molar ratio equal to 0.9, 20.6 g (0.09 mol) of bisphenol A and 7.9 g of sodium hydroxide were used.

RESULTS AND DISCUSSION

Bisphenolate Concentration vs. Reaction Time

The bisphenolate concentration in the aqueous phase at each time interval for the three interfacial polycondensation reactions was determined. The results are shown in Figure 1.

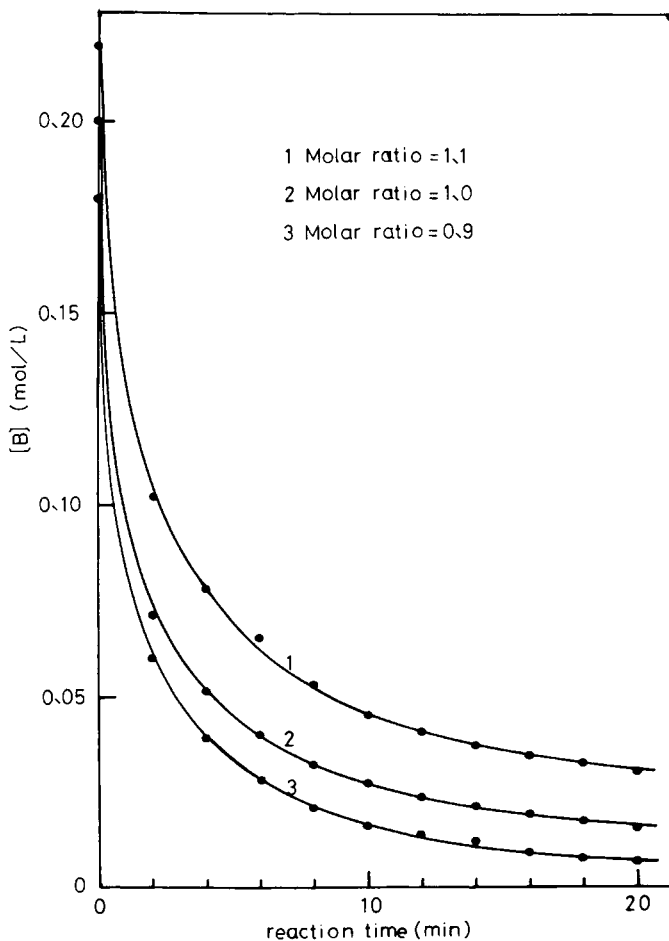


Fig. 1. The bisphenolate concentration in the aqueous as a function of reaction time for the reactions with different molar ratio of bisphenol A to isophthaloyl chloride.

Integrated Form of Rate Equation

The rate equation may be first order with respect to bisphenolate concentration in the aqueous phase and first order with respect to diacid chloride concentration in the organic phase, that is,

$$R = -\frac{d[B]}{dt} = k[B][I] \quad (1)$$

where R is the decrease rate of bisphenolate concentration in the aqueous phase, k is the rate constant, $[B]$ is the concentration of bisphenolate in the aqueous phase, and $[I]$ is the concentration of diacid chloride in the organic phase.

The interfacial polycondensation was a diffusion-controlled reaction under the condition we studied. For the reaction with equal molar ratio of bisphenol A isophthaloyl chloride, $[B]$ is proportional to $[I]$. The volume of the aqueous phase (500 mL) was double of that of the organic phase (250 mL), thus $[I] = 2[B]$. The rate equation becomes

$$R = -\frac{d[B]}{dt} = 2k[B]^2 \quad (2)$$

The integrated form is

$$\frac{1}{[B]} - \frac{1}{[B]_0} = 2kt \quad (3)$$

where $[B]_0$ is the bisphenolate concentration in the aqueous phase before reaction.

For the reaction with molar ratio of bisphenol A to isophthaloyl chloride other than 1, the molar ratio (S) can be calculated from the initial concentrations of reactants:

$$S = 2[B]_0/[I]_0 \quad (4)$$

where $[I]_0$ is the concentration of diacid chloride in the organic phase before reaction.

Since a diffusion-controlled reaction is considered, the molar number of bisphenolate (in the aqueous phase) that has disappeared is equal to that of diacid chloride in the organic phase. From mass balance,

$$N_{0,B} - N_B = N_{0,I} - N_I \quad (5)$$

where $N_{0,B}$ and $N_{0,I}$ are the molar number of bisphenolate and diacid chloride, respectively, before reaction, and N_B and N_I are the molar number of bisphenolate and diacid chloride remaining in each own phase at time t . Converting Eq. (5) into the form of concentration gives

$$[B]_0 - [B] = ([I]_0 - [I])/2 \quad (6)$$

From eqs. (4) and (6), $[I]$ can be related to $[B]$:

$$[I] = 2\left(\frac{1-S}{S}[B]_0 + [B]\right) \quad (7)$$

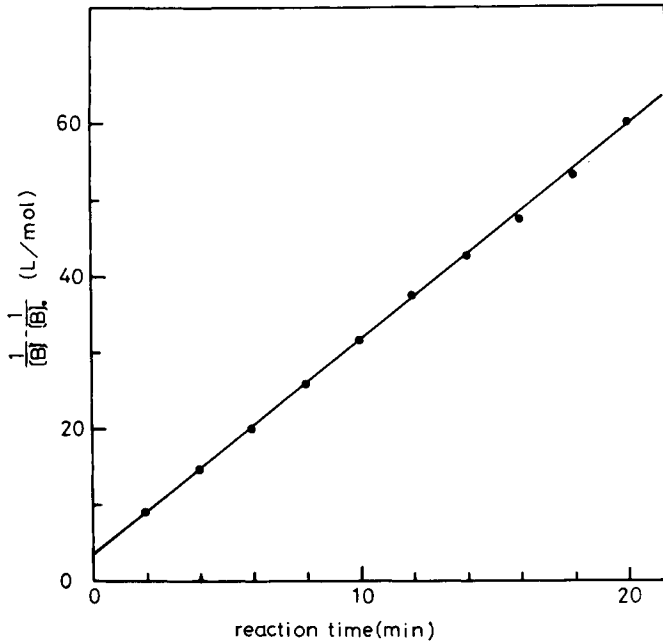


Fig. 2. The kinetic plot of the reaction with equal molar ratio of bisphenol A to isophthaloyl chloride.

and

$$-\frac{d[B]}{dt} = k[B][I] = 2k[B]\left(\frac{1-S}{S}[B]_0 + [B]\right)$$

After integration

$$\ln\left\{\frac{[B]}{[B] + [(1-S)/S][B]_0}\right\} = -2k\frac{1-S}{S}[B]_0t + C$$

The boundary condition is $t = 0$, $[B] = [B]_0$. The integrated form becomes

$$\ln\left\{\frac{[B]}{[B] + [(1-S)/S][B]_0}\right\} - \ln\left\{\frac{[B]_0}{[B]_0 + [(1-S)/S][B]_0}\right\} = -2k\frac{1-S}{S}[B]_0t \quad (8)$$

Substituting eq. (7) into eq. (8) gives

$$\ln\left(\frac{2[B]}{[I]}\right) - \ln\left(\frac{2[B]_0}{[I]_0}\right) = (2[B]_0 - [I]_0)kt \quad (9)$$

Thus, the plot of $\ln(2[B]/[I])$ vs. t would give a straight line with slope of $(2[B]_0 - [I]_0)k$ for the reaction with unequal molar ratio of bisphenol A to isophthaloyl chloride.

Kinetic Plots

For the reaction with equal molar ratio of bisphenol A to isophthaloyl chloride, eq. (3) is used here to treat the kinetic data. The plot of $1/[B] - 1/[B]_0$ vs. reaction time gives a straight line as shown in Figure 2. The slope is equal to 2.8 L/mol min, and the rate constant defined by eq. (1) is equal to 0.0233 L/mol s.

Equation (9) is used to treat the kinetic data of the other two reactions with molar ratio of bisphenol A to isophthaloyl chloride other than 1. For the reaction with molar ratio equal to 1.1,

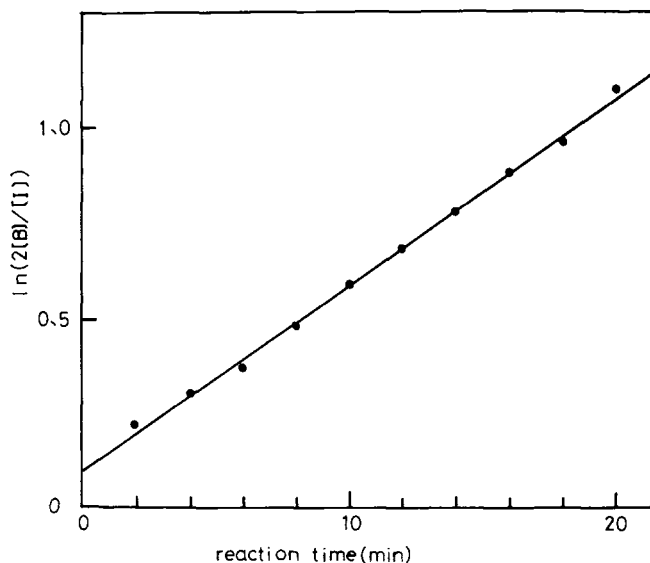


Fig. 3. The kinetic plot of the reaction with molar ratio of bisphenol A to isophthaloyl chloride equal to 1.1.

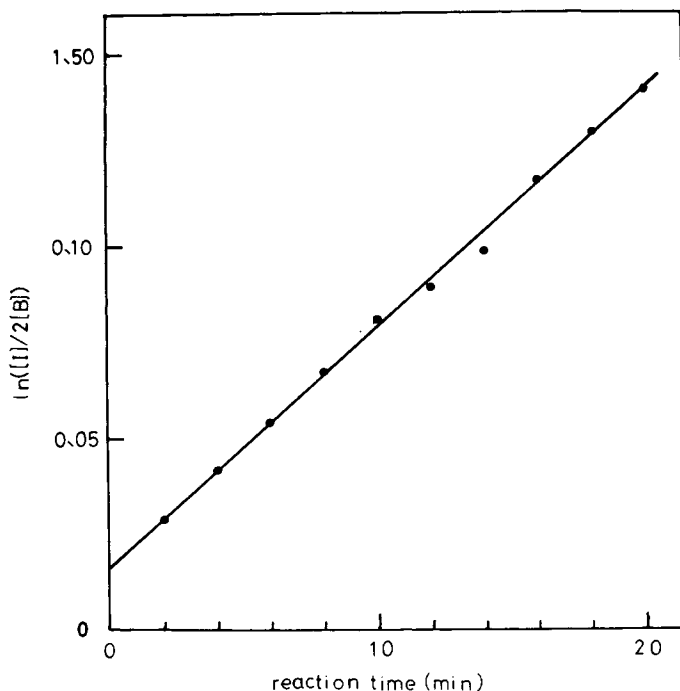


Fig. 4. The kinetic plot of the reaction with molar ratio of bisphenol A equal to 0.9.

[I] can be calculated by $[I] = 2([B] - 0.02 \text{ mol/L})$. The plot of $\ln(2[B]/[I])$ vs. reaction time is shown in Figure 3. Obviously, a straight line was obtained. This means that the kinetic data fit the rate equation (1). The slope is equal to 0.049 1/min. Since $2[B]_0 - [I]_0 = 0.04 \text{ mol/L}$, the rate constant is equal to 0.0204 L/mol s.

For the reaction with molar ratio equal to 0.9, $[I] = 2([B] + 0.02 \text{ mol})$. The plot of $\ln([I]/2[B])$ vs. reaction time also gives a straight line as shown in Figure 4. The slope is equal to 0.062 1/min and the rate constant is equal to 0.0258 L/mol s.

Table I lists the determined rate constants for the reactions with different molar ratio. The values of the rate constants are close to each other. Two effects may have contributed to the difference in the rate constants for the different molar ratio reactions.

Considering the reaction in the organic phase, the reactivity of $-\text{COCl}$ groups for isophthaloyl chloride (monomer) is higher than that of reacted ones (oligomers). The rate constant of reaction of bisphenolate with the former $-\text{COCl}$ groups (K_1) is greater than the latter (K_2). In the case of the reaction of molar ratio of bisphenol A to isophthaloyl chloride equal to 0.9, isophthaloyl chloride was in stoichiometric excess; there was more amount of isophthaloyl chloride at a given reaction time as compared with other two reactions. Thus the contribution of K_1 would be more in this case, and the overall rate constant was raised to some extent.

TABLE I
Rate Constant of the Three Reactions with Different Molar Ratio
of Bisphenol A to Isophthaloyl Chloride

Molar ratio	Rate constant (L/mol s)
1.1	0.0204
1	0.0233
0.9	0.0258

The diffusion of bisphenolate from the aqueous phase to the organic phase would be altered as the amount of bisphenol A was different. As described in a previous paper,¹ the presence of TEBAC was to enhance the transfer rate of bisphenolate, and the rate constant increased as the amount of TEBAC increased with the amounts of other reagents being held constant. The amount of TEBAC was held constant in the three reactions. In the case of the reaction with molar ratio equal to 0.9, the amount of bisphenol A was less than that of other two reactions. In other words, the relative amount of TEBAC of the reaction with molar ratio equal to 0.9 was more than that of two other reactions based on the same amount of bisphenol A. Then, the diffusion rate constant would be greater and the overall rate constant was increased.

The net result was that the rate constant was greater for the reaction with molar ratio of bisphenol A to isophthaloyl chloride equal to 0.9. For the same reasons, the rate constant was smaller for the reaction with molar ratio equal to 1.1.

CONCLUSION

The kinetic data of interfacial polycondensations with different molar ratio of bisphenol A to isophthaloyl chloride were determined. The rate equation was predicted to be $R = -d[B]/dt = k[B][I]$. The integrated form of rate equation for reactions with molar ratio of bisphenol A to isophthaloyl chloride other than 1 was derived. It was found that the kinetic data fit the rate equation well.

References

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