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Kinetics of Interfacial Polycondensation of Bisphenols with Isophthaloyl Chloride

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ABSTRACT

Reaction rates of interfacial polycondensation of bisphenol A and chlorobisphenol II with isophthaloyl chloride were investigated. Rate constants and activation energies were determined The reaction rate was found to depend on stirring speed, catalyst, type of bisphenol, and temperature.

INTRODUCTION

Up to the present date, few attempts have been made to investigate the kinetics of interfacial polycondensation. Morgan [1] estimates that the rate constants of the reaction of aliphatic diamines and aliphatic diacid chlorides lie in the range of 10^2-10^6 liter/mole-sec. Fainberg and Mikhailov [2] investigated the kinetics of interfacial polycondensation of diamines and diacid chlorides by following the changes in conductivity of the aqueous phase containing the diamine.

Evseev [3] determined interfacial polycondensation rates for terephthaloyl chloride and bisphenol A by measuring the power input required for stirring.

Carraher [4] investigated the interfacial polymerization of dialkalosilane compounds with diols and found the expression for the reaction rate to be.

$$\text{rate} = k\,[\text{ethylene glycol}]^{2/3}\,[\text{silane}]$$

and the rate constant $k = 1.4 \times 10^{-4}$ liter$^{2/3}$/mole$^{2/3}$-sec.

The interfacial polymerization of terephthaloyl chloride and C. I. Direct Violet 12 was found by Ogawa [5] to be controlled by the rate of diffusion.

This paper, together with a paper dealing with the mechanism of catalyst action in interfacial polycondensation of bisphenols and isophthaloyl chloride [6] is a continuation of the work on aromatic polyesters being carried out at Warsaw Polytechnic [7-9].

EXPERIMENTAL

Materials

2,2-Bis(4-hydroxyphenyl)propane (bisphenol A) was technical bisphenol A purified by recrystallization from methanol, mp 156-157°C. 2,2-Bis(4-hydroxyphenyl)-1,1-dichloroethane (CBP II) was obtained as described in the literature [10], mp 214-215°C. Isophthaloyl chloride was obtained from Fluka AG and purified by vacuum distillation. Triethylamine was purified by distillation over zinc dust, bp 89-90°C.

Triethylbenzylammonium chloride (TEBA) was obtained from 12.6 g of benzyl chloride and 10 g of triethylamine. The crystals formed after 24 hr were filtered off, washed with a small amount of benzene, and dried at room temperature in a vacuum desiccator. Tetra-n-butylammonium hydroxide was obtained from BDH Chemicals Ltd.

Reaction Procedure

Interfacial polycondensation of bisphenol A, CBP II, and isophthaloyl chloride was carried out by the method described by Brzozowski [7-9]. Two series of syntheses were carried out at different stirring speeds in the range of 760-4500 rpm, both with the addition of a catalyst (TEBA) and without. The polymer solutions were dropped into

TABLE 1. Composition of Reaction Mixture

Component	Amt
2,2-Bis(4-hydroxyphenyl)propane (bisphenol A)	18.24 g
2,2-Bis(4-hydroxyphenyl)-1,1-dichloroethane (CBP II)	22.48 g
Isophthaloyl chloride	32.48 g
Triethylbenzylammonium chloride	1.816 g
Sodium hydroxide	16.0 g
Methylene chloride	800 ml
Distilled water	1600 ml

methanol and the precipitated polymers filtered, washed with methanol, and dried. The molecular weights of the polymers were determined by a viscometric method according to the following expression:

$$[\eta] = 2.7 \times 10^{-4} M^{0.71}$$

where $[\eta]$ is the intrinsic viscosity and M is the average molecular weight of the polymer.

Kinetic Measurements

The kinetics of interfacial polycondensation of bisphenols with isophthaloyl chloride were investigated by measuring the changes in concentration of one of the reaction products–sodium chloride. All the reactions were carried out in a 3-liter flask with a metal stirrer, thermometer, condenser, and tap for taking samples. The composition of the reaction mixture is presented in Table 1. A solution of isophthaloyl chloride in CH_2Cl_2 was added carefully to the bisphenol and TEBA dissolved in aqueous sodium hydroxide in such a way as not to mix the two phases. Next the stirrer was started and samples were taken.

The rate of increase of chloride ion concentration was followed by titrating samples of the reaction mixture with a 0.1 N solution of silver nitrate by the Mohr method. Before titration the samples were treated with acetic acid (1:1) to stop the reaction and then neutralized with aqueous sodium hydroxide in the presence of phenolophthalein.

The values of isophthaloyl chloride concentration were calculated from the following expression:

$$[A] = [A]_0 - {}^1/_2\,([Cl^-] - [Cl^-]_0)$$

where $[A]$ and $[A_0]$ are isophthaloyl chloride concentration at time of sampling and initially, respectively, and $[Cl^-]$ and $[Cl^-]_0$ are concentration of chloride anions at time of sampling and before addition of organic phase, respectively.

Influence of Catalyst, Bisphenol, Stirring Rate, and Temperature upon Reaction Rate

Several reactions were carried out in the manner described above under various conditions. The parameters of the reactions are presented in Table 2. The change in isophthaloyl chloride concentration during the course of the reaction was determined as described above.

RESULTS AND DISCUSSION

Rate-Determining Step

The presence of a phase boundary in interfacial polycondensation makes it necessary to determine whether we are measuring the actual rate of the reaction or only the rate of diffusion of molecules to the phase boundary. By increasing the stirring speed one increases the area of the interface boundary, simultaneously increasing the rate of diffusion. In certain cases it is possible to reach a point where the reaction rate is slower than the diffusion rate, or in other words, where the chemical reaction is the rate determining step. In the case of polycondensation, the rate-determining step may be found by determining the dependence of the molecular weight of the polymer upon stirring speed. Such a dependence for the reaction of bisphenol A, CBP II and isophthaloyl chloride is presented in Fig. 1.

The molecular weight of the polymer shows a marked dependence on stirring speed up to about 3000 rpm. At higher stirring rates the molecular weight of the polymer decreases. This is most probably the result of an increase in the rate of a side reaction, i. e., the hydrolysis of -COCl groups located at the ends of polymer chains, and their consequent deactivation. This increase in the rate of hydrolysis could be explained in the following manner.

The hydrolysis of -COCl groups is, in general, a faster reaction than their esterification. However, in the interfacial process, at low stirring speeds, diffusion of the hydroxyl anion is slower than diffusion of the bisphenolate anion, which is assisted by the triethylbenzylammonium cation of the catalyst. This catalyst activity is shown in Fig. 1 by the marked difference in molecular weights of

TABLE 2. Reaction Parameters

No.	Bisphenol	Catalyst	Temperature (°C)	Stirring rate (rpm)
1	Bisphenol A + CBP II, 1:1	None	25	5000
2	"	TEBA	25	5000
3	"	TBA	25	5000
4	Bisphenol A	TEBA	25	5000
5	CBP II	TEBA	25	5000
6	Bisphenol A + CBP II (1:1)	"	2	5000
7	"	"	11	5000
8	"	"	23	5000
9	"	"	30	5000
10	"	None	2	5000
11	"	"	11	5000
12	"	"	23	5000
13	"	"	30	5000
14	"	TEBA	25	1000
15	"	"	25	3000
16	"	"	25	4000
17	"	"	25	5000
18	"	"	25	7000
19	"	"	25	9000

polymers obtained in the presence of TEBA and without TEBA at low stirring speeds. At higher stirring rates, above 3000 rpm, diffusion ceases to limit the rate of the process and hydrolysis of -COCl groups, as the kinetically faster reaction is predominant. Therefore, the molecular weight of the polymer drops very rapidly with increasing stirring rates. So, taking into account the general shape of the curve presented in Fig. 1, one may assume that above 3000 rpm only the reaction rate determines the rate of polymer formation.

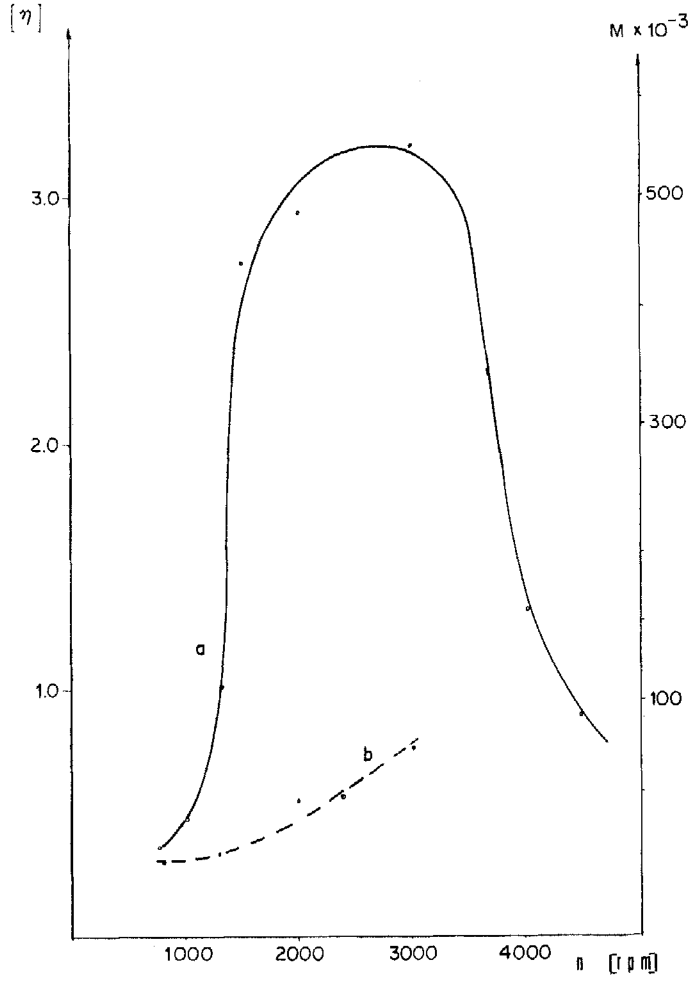

FIG. 1. Dependence of molecular weight of polymer upon stirring speed: (a) reaction catalyzed by triethylbenzylammonium chloride; (b) uncatalyzed reaction.

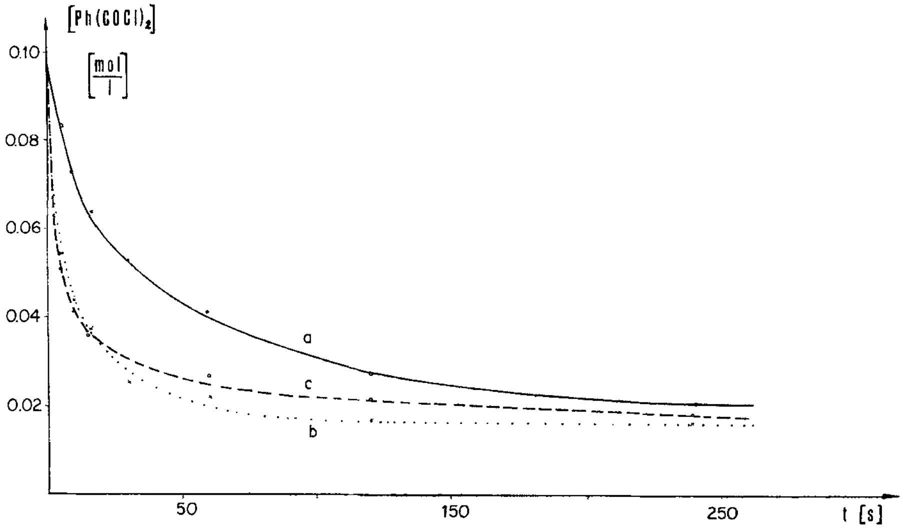

FIG. 2. Change of isophthaloyl chloride concentration with time for interfacial polycondensation of bisphenol A, CBP II, and isophthaloyl chloride: (a) uncatalyzed reaction; (b) reaction catalyzed by triethylbenzylammonium chloride; (c) reaction catalyzed by tetrabutylammonium hydroxide (TBA).

Influence of Catalyst upon Reaction Rate

Figure 2 presents kinetic curves for reactions carried out (a) without a catalyst, (b) in the presence of TEBA, and (c) in the presence of TBA. By comparing the slopes of the curves during the first part of the reaction one finds that TEBA increases the reaction rate approximately five times. The more lipophilic TBA gives a similar reaction rate to TEBA.

Influence of Bisphenol on Reaction Rate

Figure 3 presents kinetic curves for reactions carried out with two different bisphenols, namely bisphenol A and CBP II. Once again, by comparing the slopes of the curves during the first minute of the reaction, one finds that bisphenol A reacts nearly twice as fast with isophthaloyl chloride as does CBP II. This is in agreement with the greater nucleophility of the bisphenolate A dianion as compared to that of the dianion formed from CBP II.

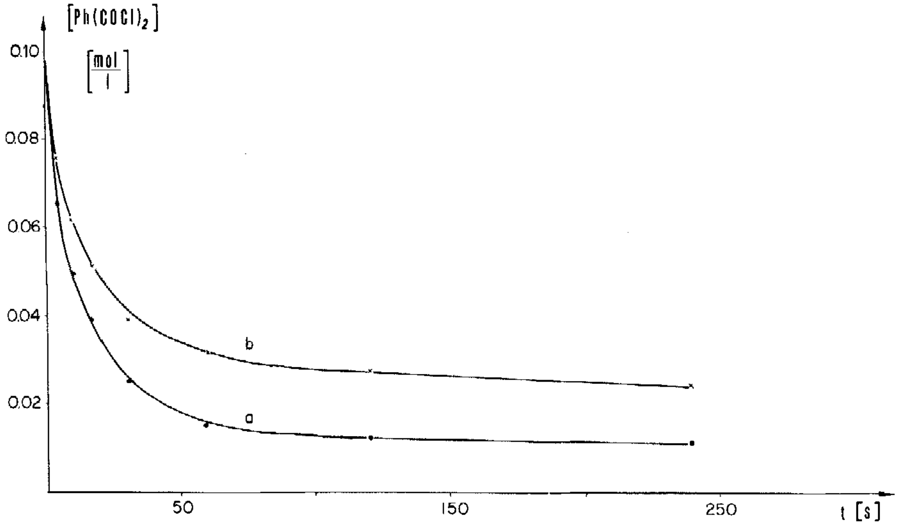

FIG. 3. Change of isophthaloyl chloride concentration with time for interfacial polycondensation of isophthaloyl chloride with (a) bisphenol A and (b) CBP II.

Reaction Rate Constant

Reaction rate constants calculated from an integrated second order kinetic equation are presented in Table 3. The reaction rate may therefore be given as

$$\text{rate} = k\,[\text{isophthaloyl chloride}][\text{bisphenol}]$$

The rate constant for the uncatalyzed polycondensation at 22°C is of the order 3×10^{-1} liter/mole-sec.

Dependence of Reaction Rate upon Temperature

Reactions 6-13 (Table 2) were carried out at different temperatures. Reaction rate constants were calculated according to integrated kinetic equations for a second-order reaction. The natural logarithm, ln k is plotted against the reciprocal of temperature in Fig. 4 for both the catalyzed and uncatalyzed reactions. The activation energy calculated

TABLE 3. Second-Order Reaction Rate Constants

Reaction no. (from Table 2)	Time (sec)	$Ph(COCl)_2$ (mole/liter)	Rate constant (liter/mole-sec)
1	0	0.0975	
	5	0.0827	0.30
	10	0.0718	0.33
	15	0.0639	0.33
	30	0.0531	0.27
	60	0.0412	0.23
	120	0.0274	0.22
10	0	0.0975	
	5	0.0927	0.10
	10	0.0869	0.12
	15	0.0803	0.15
	30	0.0684	0.15
	60	0.0549	0.13
	120	0.0398	0.12
	240	0.0282	0.11

from the slope of this line equals 6.7 kcal/mole for the uncatalyzed reaction and 2.2 kcal/mole for polycondensation in the presence of TEBA.

Dependence of Rate upon Stirring Speed

Reactions 14-19 (Table 2) were carried out at different stirring speeds in the range of 1000-9000 rpm. Process rate constants k were calculated according to the equation:

$$(1/[A]) - (1/[A]_0) = kt$$

The values of k are plotted against stirring speed on Fig. 5.

The shape of the curve in Fig. 5 is in agreement with the assumption that the reaction is diffusion-controlled at lower stirring speeds

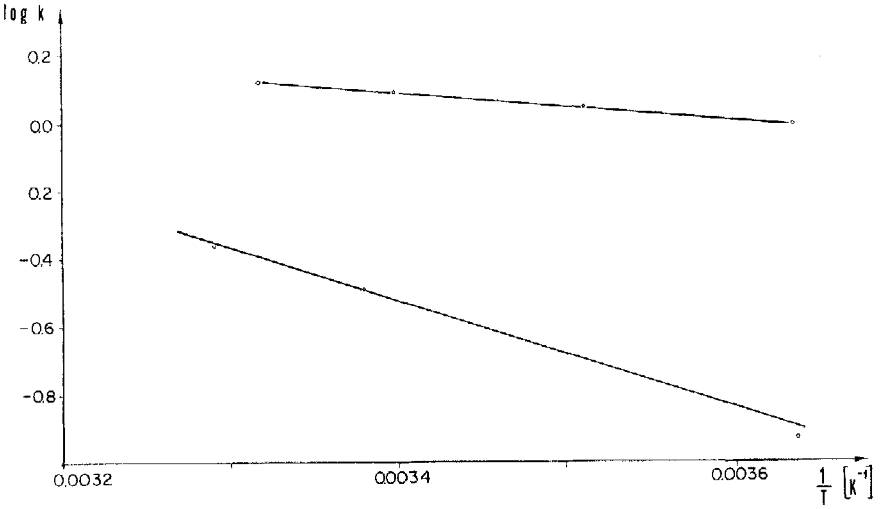

FIG. 4. Dependence of reaction rate upon temperature: (a) reaction catalyzed by TEBA; (b) uncatalyzed reaction.

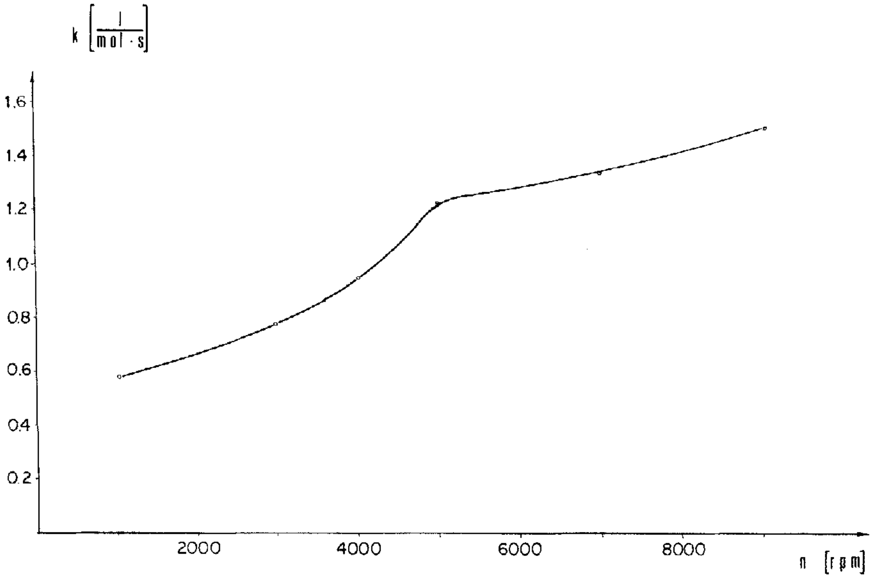

FIG. 5. Dependence of reaction rate upon stirring speed.

and kinetically controlled at higher stirring speeds. However, the boundary between these two areas seems to lie higher, at 5000 rpm, than was determined from molecular weight values from Fig. 1. This difference could possibly be due to the different geometry of the reactor in which the first batch of reactions was carried out. The slope of the line above 5000 rpm is a measure of the dependence of the reaction rate upon interface area.

Limitations of the Method

The high rate of the reaction, presence of an interfacial boundary, and changing viscosity of the organic solvent make kinetic measurements extremely difficult. The half time of the reaction was less than a minute, which made the intervals between taking samples very short. A significant exothermic effect made it difficult to maintain a constant temperature. Therefore, the data presented in this paper must be treated as an approximation and guide to further investigations in this field.

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