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Copolymerization of 2-Hydroxy-(2,3-epoxypropoxy)benzophenone with Phthalanhydride Catalyzed by Tertiary Amine

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ABSTRACT

The copolymerization of an epoxide, 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone, with cyclic anhydride catalyzed by tertiary amine in different solvents was studied. The copolymerization curves are sigmoidal in character with an induction period. In the region following the induction period, the loss in epoxide or anhydride may be correlated with the kinetic equation of the first order reaction provided the monomers are present in equimolar ratio or anhydride is in excess with respect to epoxide. The rate constant found experimentally after the induction period depends on the first power of the concentrations of amine, epoxide, and anhydride. The activation energy of copolymerization in *o*-xylene is 58.2 kJ/mole (13.9 kcal/mole) and $\log A = 3.6$. The rate of copolymerization depends on polarity of the solvent and increases with dielectric constant. A reaction scheme has been proposed for the copolymerization of epoxides with cyclic anhydrides catalyzed by tertiary amines which involves the formation of a catalytic center of ionic character by isomerization of epoxide into a derivative of allyl alcohol and its subsequent interaction with tertiary amine and anhydride in equilibrium reactions. In this way, an active center

of the carboxylic anion type is formed which reacts with epoxide to give alkoxide anion. This alkoxide anion reacts with anhydride to yield carboxylic anion. By interchange of these reactions, an alternating copolymer-polyester arises. The termination involves the decay of the active center into tertiary amine and carboxylic or hydroxylic endgroups. The kinetic solution of this scheme is in agreement with the experimental results of kinetic measurements and the rate of copolymerization is governed by the equation: $-d[\text{epoxide}]/dt = k_p [\text{amine}]_0 [\text{epoxide}]_0 [\text{anhydride}]_0 [\text{epoxide}]$.

INTRODUCTION

The greatest importance of the copolymerization of cyclic ethers with cyclic anhydrides consists in its use for curing epoxide resins [1, 2]. The preparation of linear polyesters by this reaction served mostly for elucidation of the processes which take place during cure. The cure may proceed as a noncatalyzed reaction or it may be catalyzed by basic or acid catalysts. Most attention has been paid to the copolymerization catalyzed by tertiary amines. Many authors have presented different kinetic equations for this reaction, and there are different opinions about the mechanism of this copolyaddition reaction. Malavašič et al. [3] determined a half reaction order for curing epoxide resins with cyclic anhydrides while they considered the reaction to be of the first order in advanced stages of copolymerization. The first order of the curing and copolymerization reaction was also ascertained by other authors [4-8]. Tanaka and Kakiuchi [9] determined a second reaction order for the region of initiation and a first reaction order for the region of maximum rates. Antipova et al. [10] and Sorokin et al. [11], too, determined a second reaction order, whereas Tanaka and Kakiuchi tend to believe [12] that the cure of resins is a third-order reaction.

From the viewpoint of polymerization mechanism, the views on the mode of formation and character of the reaction center are not consistent. Fischer [4], Tanaka and Kakiuchi [12], and Feltzin [5] assume anionic character of the end of the growing chain, whereas a catalytic effect of the tertiary amine in the transition state in a ternary complex is suggested in another paper [9]. Fischer [4] assumes that the active center is formed by direct interaction between tertiary amine and anhydride and exhibits a betainelike structure. This mechanism is modified in the presence of proton-donating compounds. In this connection, Tanaka and Kakiuchi [12] presumed the formation of an associated complex consisting of tertiary amine and

proton-donating compound. This complex opens the anhydride ring to give the betaine structure, which is stabilized by a hydrogen bond to the proton-donating compound. Feltzin et al. explained the activation of tertiary amine by a proton-donating compound which is present in the reaction mixture as an impurity on the basis of the formation of a quaternary ammonium salt [5], while Tanaka and Kakiuchi [9] assumed a ternary complex of nonionic character to be formed from epoxide, tertiary amine, and proton-donating compound.

These inconsistent views stimulated us to study further the kinetics and mechanism of copolymerization of epoxides with cyclic anhydrides in the presence of tertiary amines. The copolymerization of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPBP) was chosen as the object of this study and high-boiling tri-*n*-hexylamine (THAm) was used as a catalyst.

EXPERIMENTAL

Chemicals

2-Hydroxy-4-(2,3 epoxypropoxy)benzophenone was prepared from 2,4-dihydroxybenzophenone and epichlorohydrin in a one-step process according to the literature [13, 14]. The melting point of the product used for polymerization was 100-100.5°C (99-100°C [15]). Phthalanhydride (Lachema, N. E., Brno, ČSSR) was purified either by sublimation in a stream of nitrogen or by crystallization from benzene (mp 130-131°C). Tri-*n*-hexylamine (Fluka, A. G., Switzerland) was purified by distillation under reduced pressure. The solvents were purified by the usual methods [16].

Methods

The polymerization was carried out in solution in a three-necked flask equipped with a thermometer, stirrer, and nitrogen inlet and outlet. Calculated amounts of epoxide and anhydride were weighed into a graduated flask which was filled to the mark with solvent. The contents of this flask were warmed, dissolved, and transferred into a polymerization flask flushed with a strong stream of nitrogen at the temperature of polymerization. On thermostating the polymerization solution a moderate flow of nitrogen was bubbled through, and the catalyst was added. For rinsing the graduated flask and scavenging the catalyst, the amount of solvent used was such that the required molar concentrations of components could be obtained. The polymerization time was calculated from the moment when the catalyst was

added. The temperature of the polymerization solution was held constant to $\pm 0.1^\circ\text{C}$. After the addition of catalyst, the samples for the determination of the content of epoxide or anhydride were taken at convenient time intervals.

On acidifying with a solution of hydrogen chloride in dioxane, the content of epoxide was determined according to Vorobjov [17, 18] by mercurimetric titration of the unconsumed hydrogen chloride using diphenylcarbazone as an indicator. The content of the unconsumed epoxide relative to the original 100% concentration or to the molar content of epoxide used at the outset of polymerization was calculated from the decrease in the epoxide groups.

The content of anhydride was estimated by infrared spectroscopy of the absorption band $\nu = 1853\text{ cm}^{-1}$ [19] which did not interfere with the new ester band. The carbonyl band of benzophenone $\nu = 1625\text{ cm}^{-1}$ which did not change during polymerization was used as an internal standard. The content of anhydride was calculated from the calibration plot $A_{1853}/A_{1625} = f(c)$ which obeyed the Lambert-Beer law.

RESULTS

Polymerization in a solution of *o*-xylene was used for kinetic investigation of the copolymerization of HEPBP with FA catalyzed by THAM. The conversion curves had a sigmoidal shape with a distinct induction period (Fig. 1); while the loss in epoxide and in anhydride at equimolar ratios was governed by an equal relationship.

By analyzing this curve, it may be ascertained that the temporal course of the reaction outside the induction period may be described by Eq. (1):

$$\log [\text{HEPBP}] = \log [\text{FA}] = a - kt \quad (1)$$

where $k = k_{\text{exp}}/2.303$ is the slope of this linear equation and k_{exp} is the rate constant of the reaction (Fig. 2). This means that the copolymerization at equimolar ratio of epoxide to anhydride is a first order reaction with respect to either monomer.

The experimental verification was carried out by changing the concentrations of epoxide and anhydride at equimolar ratio. The results are given in Table 1. The dependence of the slope on initial concentrations of the monomer shows the exponential character, and the logarithmic expression,

$$\log k_{\text{exp}} = f \{ \log([\text{HEPBP}]_0 [\text{FA}]_0) \}$$

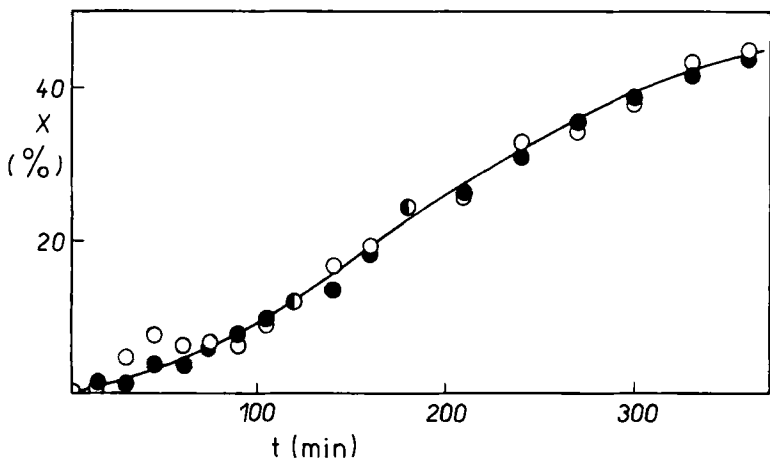


FIG. 1. Conversion curves of the copolymerization of HEPBP (0.5 mole/liter) with FA (0.5 mole/liter) catalyzed by THAm (0.01 mole/liter) in *o*-xylene at 120°C: (○) anhydride; (●) epoxide.

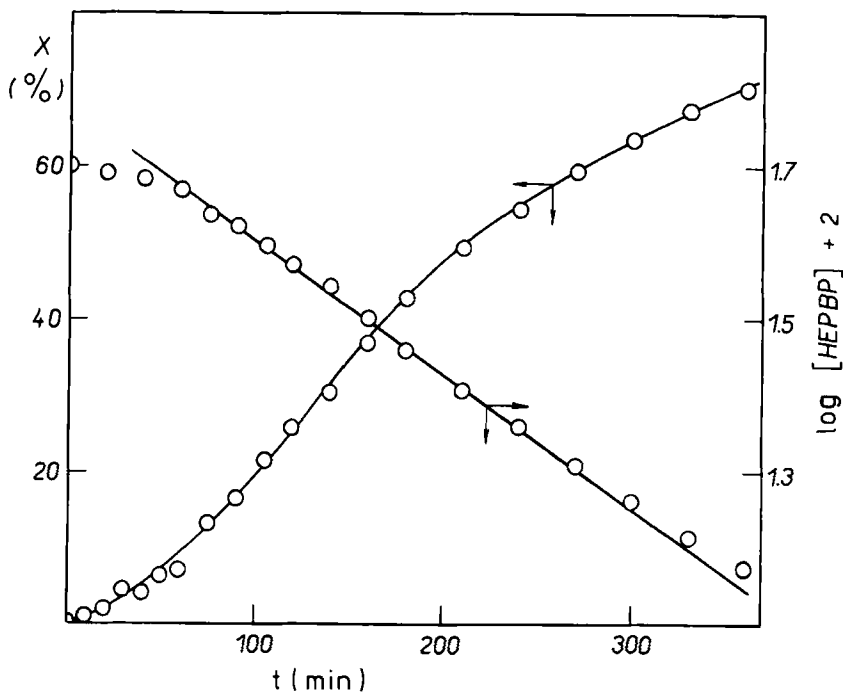


FIG. 2. Course of the copolymerization of HEPBP (0.5 mole/liter) with FA (0.5 mole/liter) in *o*-xylene at 120°C, catalyzed by THAm (0.025 mole/liter).

TABLE 1. Influence of Conditions on the Experimental Rate Constant of the Copolymerization of 2-Hydroxy-4-(2,3-epoxypropoxy)-benzophenone (HEPBP) with Phthalanhydride Catalyzed by Tri-n-hexylamine (THAm)

n	[HEPBP] ₀ (mole/ liter)	[FA] ₀ (mole/ liter)	[THAm] ₀ (mole/ liter)	Solvent	T (°C)	k _{exp} × 10 ⁵ (sec ⁻¹) ^a
1	0.2	0.2	0.025	o-Xylene	120	1.2
2	0.3	0.3	0.025	"	"	2.3
3	0.4	0.4	0.025	"	"	3.7
4	0.5	0.5	0.025	"	"	6.5
5	0.6	0.6	0.025	"	"	7.2
6	0.7	0.7	0.025	"	"	10.6
7	1.0	1.0	0.025	"	"	24.5
8	0.5	1.0	0.025	"	"	12.5
9	0.6	1.0	0.025	"	"	14.5
10	0.7	1.0	0.025	"	"	17.9
11	0.8	1.0	0.025	"	"	20.7
12	0.9	1.0	0.025	"	"	23.0
13	0.5	0.4	0.025	"	"	5.6
14	0.5	0.6	0.025	"	"	8.5
15	0.5	0.7	0.025	"	"	9.3
16	0.5	0.8	0.025	"	"	10.3
17	0.5	0.5	0.005	"	"	1.2
18	0.5	0.5	0.01	"	"	2.6
19	0.5	0.5	0.015	"	"	5.2
20	0.5	0.5	0.02	"	"	6.7
21	0.5	0.5	0.030	"	"	7.9
22	0.5	0.5	0.035	"	"	8.8
23	0.5	0.5	0.04	"	"	9.1
24	0.5	0.5	0.05	"	"	12.9

TABLE 1. (cont.)

n	[HEPBP] ₀ (mole/ liter)	[FA] ₀ (mole/ liter)	[THAm] ₀ (mole/ liter)	Solvent	T (°C)	k _{exp} × 10 ⁵ (sec ⁻¹) ^a
25	0.5	0.5	0.07	o-Xylene	120	17.1
26	0.5	0.5	0.025	"	90	1.3
27	0.5	0.5	0.025	"	100	2.5
28	0.5	0.5	0.025	"	110	4.5
29	0.5	0.5	0.025	"	130	9.4
30	0.5	0.5	0.025	Chloro- benzene	120	6.4
31	0.5	0.5	0.025	o-Dichlo- robenzene	120	11.0
32	0.5	0.5	0.025	Aceto- phenone	120	11.0
33	0.5	0.5	0.025	Nitro- benzene	120	20.4

^a Found by the use of 2-10 values.

gives a straight line with slope 2 (Fig. 3). Hence, k_{exp} increases with the second power of the monomer concentrations if initial concentrations of epoxide and anhydride are raised and $[\text{HEPBP}]_0 = [\text{FA}]_0$.

At nonequimolar ratio, the excess of anhydride does not influence the chemical composition of the polymer [20] while various homopolymerization, isomerization, and other side reactions take place in the presence of excess epoxide, which means the reactions of the phenolic groups [20, 21] in case of the polymerization of HEPBP. The course of the copolymerization of HEPBP with FA in the presence of excess epoxide is illustrated in Fig. 4. After the induction period, Eq. (1) is valid under these conditions until anhydride is consumed. Analysis of the further course of polymerization and comparison of the rates of both processes which could reveal the specificity of copolymerization, as suggested by Alvey [22], were not performed.

Notwithstanding, the influence of the concentration of epoxide on the

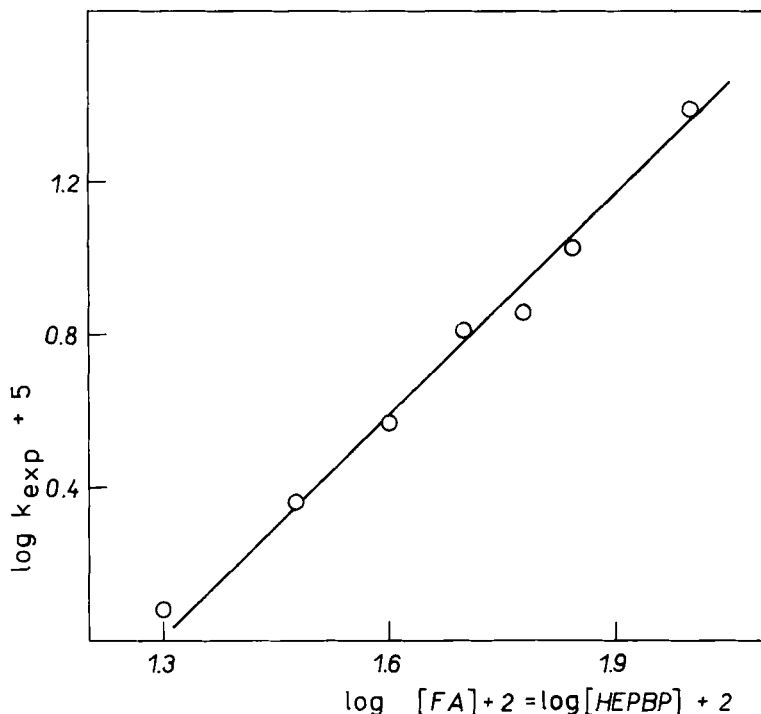


FIG. 3. Effect of the concentrations of monomers on the copolymerization of HEPBP with FA in *o*-xylene at 120°C, catalyzed by THAm (0.025 mole/liter).

course of this reaction at constant concentrations of anhydride and catalyst as well as the influence of the concentration of anhydride at constant concentrations of epoxide and catalyst in *o*-xylene were investigated at 120°C for $[HEPBP]_0/[FA]_0 \leq 1$. The results are given in Table 1. According to these results, k_{exp} increases linearly with the concentration of epoxide or anhydride. The first reaction order with respect to the concentration of epoxide was verified by using the plot $\log k_{\text{exp}} = f(\log [HEPBP]_0)$. This plot is a straight line (Fig. 5) the slope of which equals one. In the same way, the first reaction order with respect to the concentration of anhydride was verified by using the plot $\log k_{\text{exp}} = f(\log [FA]_0)$. This plot, too is a straight line and its slope equals one (Fig. 6).

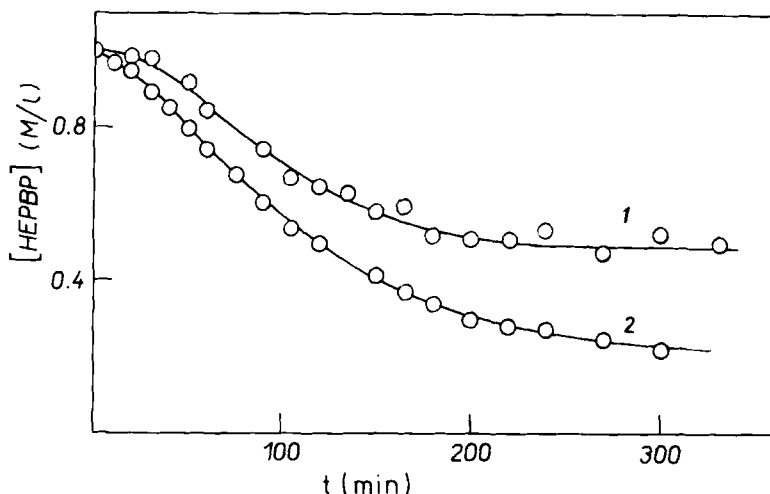


FIG. 4. Conversion curves of the copolymerization of HEPBP (1 mole/liter) with FA in *o*-xylene at 120°C, catalyzed by THAm (0.025 mole/liter): (1) $FA_0 = 0.5$ mole/liter; (2) $FA_0 = 0.8$ mole/liter).

The influence of concentration of the THAm catalyst was investigated in the range from 0.005 mole/liter to 0.07 mole/liter for constant concentrations of HEPBP and FA (0.5 mole/liter) in *o*-xylene at 120°C. The experimental data in Table 1 demonstrate that k_{exp} is a linear function of the concentration of THAm. By plotting the function $\log k_{\text{exp}} = f(\log [\text{THAm}]_0)$, we obtain a straight line the slope of which equals one (Fig. 7).

The activation energy of the copolymerization of HEPBP with FA catalyzed by THAm in *o*-xylene was determined in the temperature range from 90°C to 130°C (Table 1). The activation energy calculated from the data in Fig. 8 is equal to 58.2 kJ/mole (13.9 kcal/mole) and $\log A = 3.6$.

The effect of solvent on the rate of the copolymerization of HEPBP with FA catalyzed by THAm is shown in Table 1. These data show that the rate of copolymerization increases with dielectric constant (Fig. 9), though the selection of suitable solvents was limited because of the relatively high temperature of polymerization.

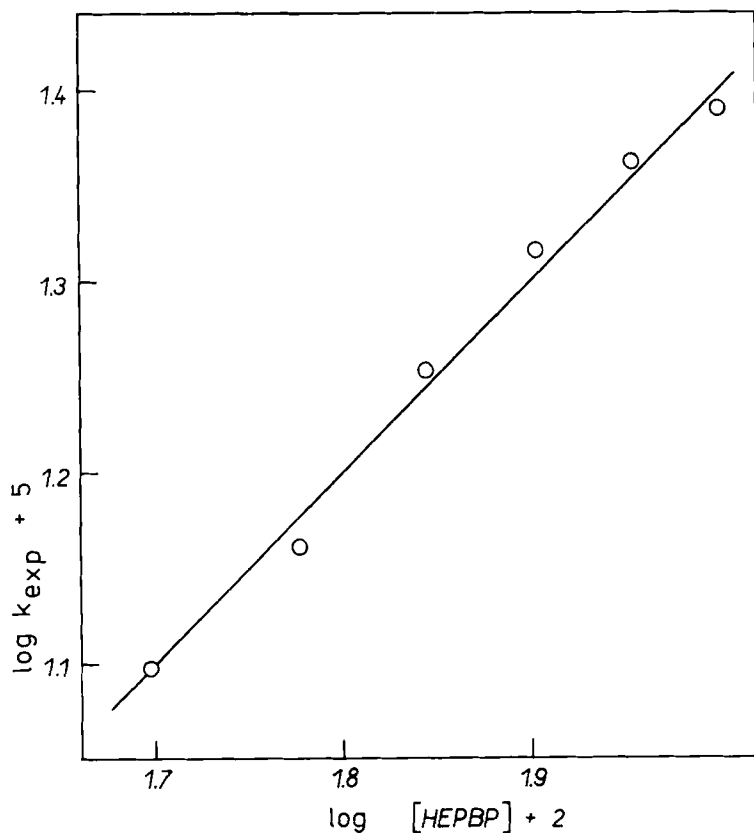


FIG. 5. Effect of the concentration of HEPBP on the copolymerization with FA (1 mole/liter) in *o*-xylene at 120°C, catalyzed by THAm (0.025 mole/liter).

DISCUSSION

The conversion curves obtained for the copolymerization of HEPBP with FA catalyzed by tertiary amine show a sigmoidal shape with the region of induction period in which the rate of copolymerization rises (Fig. 1). For a slow polymerization, e. g., at lower concentrations of catalysts in solution, equal character of copolymerization was observed by other authors [9, 12, 23]. The induction period at the outset of polymerization can be explained by the gradual increase in concentration of the active centers [9], and the rate of loss of epoxide

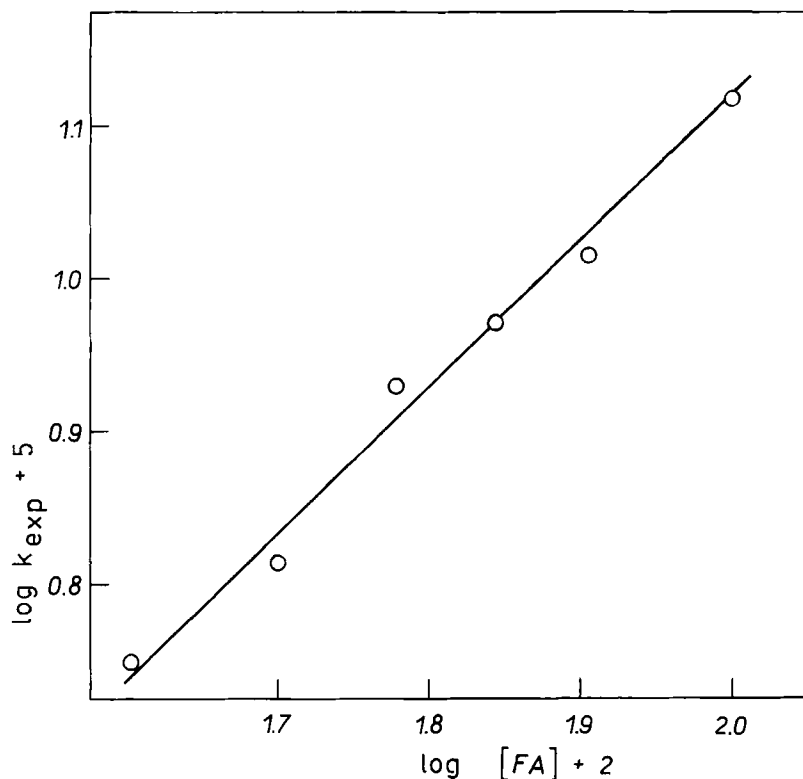


FIG. 6. Effect of the concentration of FA on the copolymerization with HEPBP (0.5 mole/liter) in *o*-xylene at 120°C, catalyzed by THAm (0.025 mole/liter).

and anhydride is equal for equimolar initial ratio of the components (Fig. 1). From the conductivity measurements of the components of the polymerization system and their binary mixtures it is seen that a convenient increase in conductivity appears only in the ternary system of all components—epoxide, anhydride, and tertiary amine [24]. This means that a formation and dissociation of ion pairs takes place in ternary system which indicates ionic character of the polymerization process. From the increase in content of the hydroxyl groups and double bonds during copolymerization [9], we may infer that the hydroxyl groups participate in the process of polymerization. On the basis of these experimental results, the reaction scheme shown in Eqs. (2)-(9) has been proposed.

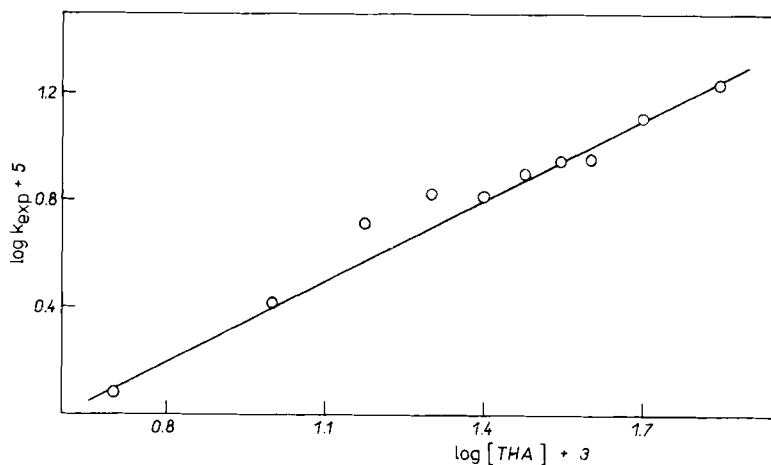
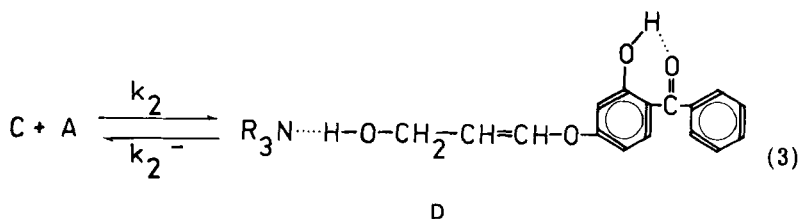
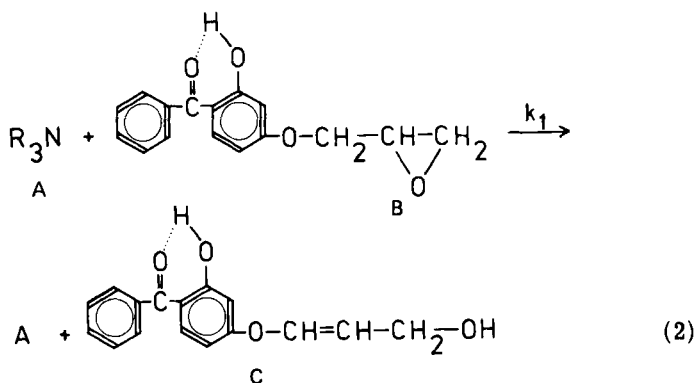


FIG. 7. Effect of the concentration of THAm on the copolymerization of HEPBP (0.5 mole/liter) with FA (0.5 mole/liter) in o-xylene at 120°C.



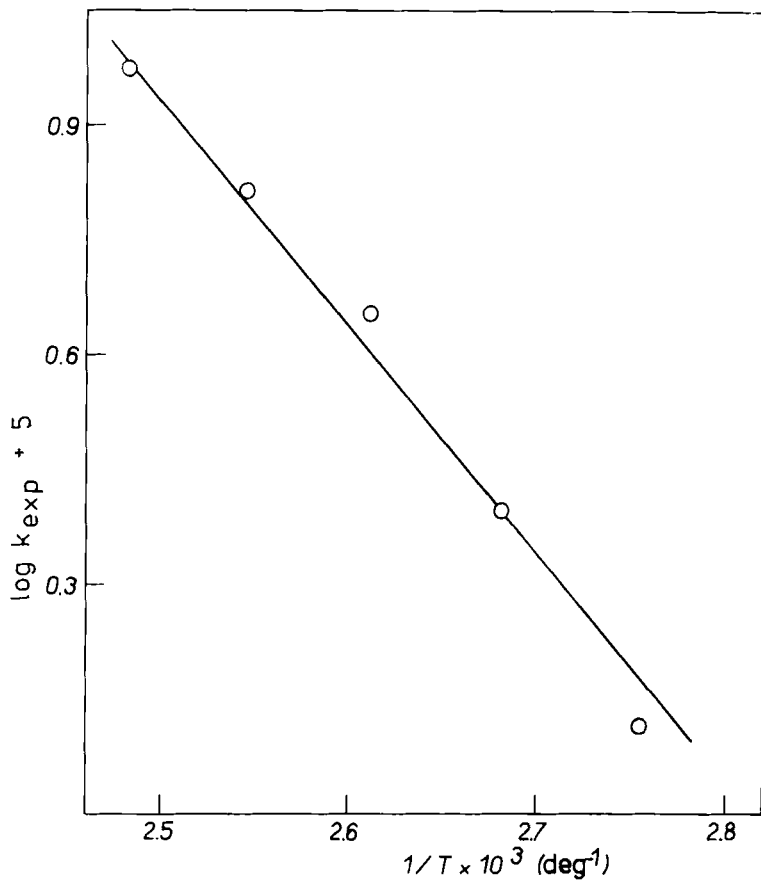
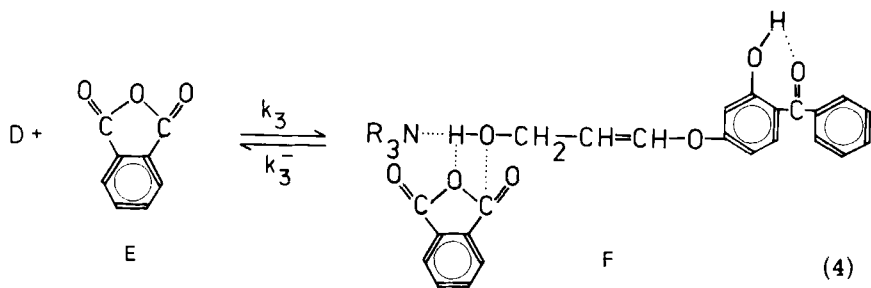


FIG. 8. Arrhenius plot of the copolymerization of HEPBP (0.5 mole/liter) with FA (0.5 mole/liter) in *o*-xylene, catalyzed by THAm (0.025 mole/liter).



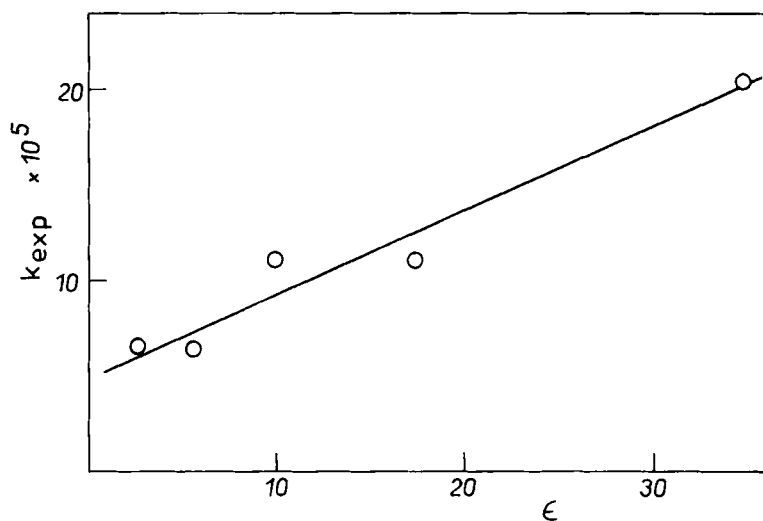
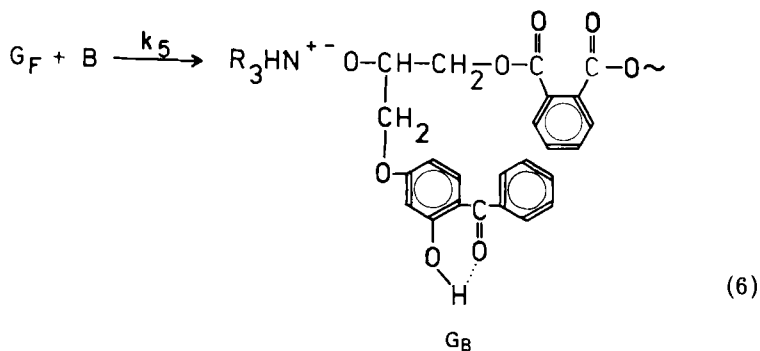
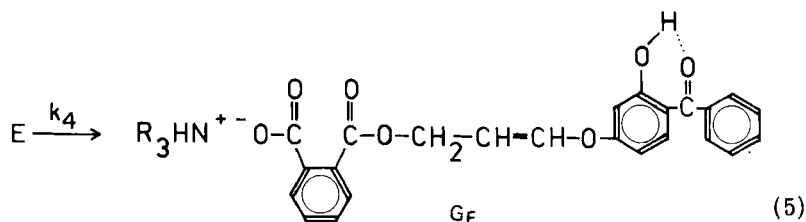
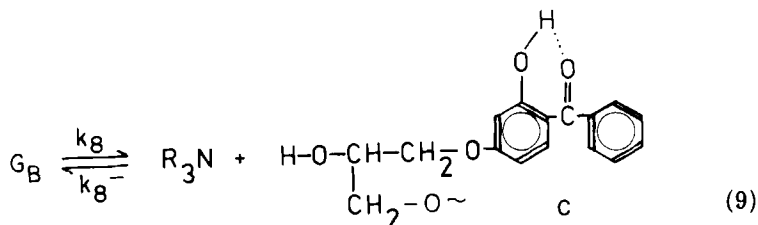
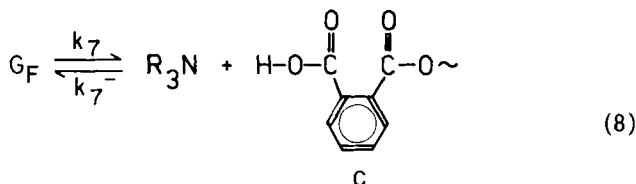
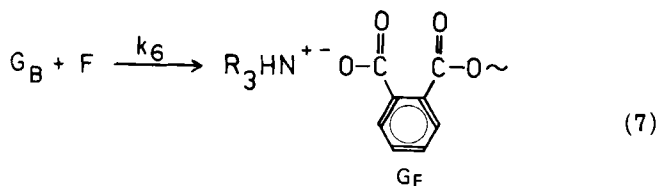


FIG. 9. Effect of dielectric constant ϵ of the solvent on the copolymerization of HEPBP (0.5 mole/liter) with FA (0.5 mole/liter) at 120°C, catalyzed by THAm (0.025 mole/liter).





Equation (2) describes the base-catalyzed isomerization of HEPBP yielding a derivative of allyl alcohol. This isomerization reaction was suggested by Tanaka and Kakiuchi [9]. On the basis of this reaction, the increase in content of the double bonds and hydroxyl groups during copolymerization is to be explained. This isomerization which is catalyzed by basic and acidic catalysts, is well known [25-32], though further polymerization of the epoxide groups must take place at relatively high temperatures in case of the catalysis by tertiary amines. Only at low reaction temperatures and equimolar ratio of tertiary amine to epoxide, Burness [33] isolated the ammonium salt of a derivative of allyl alcohol as a reaction product of isomerization. In this reaction, we must assume the intermediary formation of an epoxide which, by the effect of the catalysis by tertiary amine, isomerizes to give a derivative of allyl alcohol. The rate of reaction and isomerization depends on the structure and basicity of tertiary amine [33, 34]. The rate of isomerization increases considerably with temperature [34]. The isomerization of ethylene oxide which does not contain any α -hydrogen atoms continues to proceed in the presence of tertiary amines as catalysts and even yields acetaldehyde [35]. Since it is obvious from spectral measurements that the extinction coefficients do not decrease during the

copolymerization of HEPBP with FA, which indicates that the intramolecular hydrogen bond has not been impaired [20], the portion of the phenolic groups of HEPBP consumed in initiation reactions must be insignificant.

Equations (3) and (4) describe the gradual formation of the ternary complex of tertiary amine, proton-donating compound, and anhydride which precedes the formation of the proper active center [Eq. (5)]. The interaction between proton-donating compounds and tertiary amines is well known [36, 37], and the formation of hydrogen bonds is an intermediary reaction in the generation of ion pairs. The magnitude of interaction is dependent on the rate of diffusion, strength of base, strength of proton donating compound, and kind of solvent [36-38]. As the acids which are weaker than substituted phenols form complexes bonded only by hydrogen bonds that do not produce any ion pairs [38], the formation of a binary complex in a given system according to Eq. (3) must be assumed. While Eqs. (2) and (3) were already suggested by Tanaka and Kakiuchi, their reaction scheme assumes only the three-component complex tertiary amine-proton donating compound-epoxide to be the active center. The interaction of the binary complex tertiary amine-proton donating compound with anhydride is assumed on the basis of the fact that the binary system does not cause any convenient increase in conductivity under the reaction conditions used. The increase in conductivity appears only in a ternary system containing anhydride [24] which makes possible the origination of the ternary complex according to Eq. (4). The origination of the ternary complex is an intermediary stage in the formation of the proper active center which exhibits ionic character [24]. As is obvious from Eq. (5), the active center is a kind of ammonium salt. This species is more or less dissociated according to dielectric properties of the solution which manifest itself in the values of conductivity found in different solvents. By comparing the maximum conductivities of the copolymerization solutions with the rate constants of copolymerization, it has been ascertained that there is no correlation between these data. Therefore, it appears that the copolymerization of epoxides with anhydrides is catalyzed by the active center in both dissociated and nondissociated form [24]. A certain relationship may be found only between dielectric constant of the solvent and the rate constants (Fig. 9) which, however, must be accepted with reserve owing to small number of experimental data.

The growth reactions are described by Eqs. (6) and (7). The interaction between the primary carboxyl anion and the epoxide groups [Eq. (6)] results in the formation of an alkoxide anion which subsequently reacts with anhydride to give the carboxyl anion [Eq. (7)]. By interchanging both propagation reactions, the chain grows and polyester arises. Such a growth of chain manifests itself

by equal loss of epoxide and anhydride during copolymerization (Fig. 1) which has been also observed with other epoxides [4, 12, 23] as well as by equal content of both component in the polyester [39]. Therefore, no polyether sequences arise if tertiary amines are used as catalysts, and Eq. (10) is not valid.



The termination is caused by the decay of the active center of the growing chain which involves the abstraction of hydrogen atom from the ammonium ion by the effect of the basic alkoxide or carboxyl anion according to Eqs. (8) and (9). In this process, a molecule of catalyst is liberated and the terminal carboxyl or hydroxyl groups are formed. These groups however, take part in the initiation reaction again. The carboxyl group interacts directly with tertiary amine to give an ion pair [40], while the hydroxyl group is subjected to reactions (3)-(5) of the above scheme. Therefore, both reactions are referred to as reversible reactions. It may be assumed that the reinitiation according to Eq. (8) which follows the induction period gains dominant importance.

In the reaction scheme, we may combine Eqs. (2) and (3) to obtain an equilibrium equation describing the formation of complex D:



Then the rates of the consumption of individual components may be expressed by Eqs. (12)-(19).

$$-dA/dt = k_2AB - k_{\bar{2}}D - k_7G_F + k_{\bar{7}}CA - k_8G_B + k_{\bar{8}}CA \tag{12}$$

$$-dB/dt = k_2AB - k_{\bar{2}}D + k_5G_F B \tag{13}$$

$$-dC/dt = -k_7G_F + k_{\bar{7}}CA - k_8G_B + k_{\bar{8}}CA \tag{14}$$

$$-dD/dt = -k_2AB + k_{\bar{2}}D \tag{15}$$

$$-dE/dt = -k_3DF + k_{\bar{3}}E + k_4E \tag{16}$$

$$-dF/dt = k_3DF - k_{\bar{3}}E + k_6G_B F \quad (17)$$

$$-dG_F/dt = -k_4E + k_5G_F B - k_6G_B F + k_7G_F - k_{\bar{7}}CA \quad (18)$$

$$-dG_B/dt = -k_5G_F B + k_6G_B F + k_8G_B - k_{\bar{8}}CA \quad (19)$$

Supposing a stationary state, the concentration of active centers G_F and G_B and free amine in the region following the induction period may be considered to be constant:

$$-dA/dt = -dG_F/dt = -dG_B/dt = 0 \quad (20)$$

A stationary concentration of active centers gradually arises at the end of the induction period at a low conversion of reacting components, and therefore it may be assumed that the concentration of intermediary complexes is proportional to the initial concentration of monomers and catalyst. Then it follows from Eqs. (9) and (11) that

$$D = K_D A_0 B_0 \quad (21)$$

and

$$E = K_E DF_0 = K_D K_E A_0 B_0 F_0 \quad (22)$$

where K_D and K_E are the equilibrium constants of the formation of complexes D and E. Thus we can calculate the concentration of active centers G_B and G_F from Eqs. (12), (18), (19), and (22):

$$G_B = k_B A_0 B_0 F_0 \quad (23)$$

where

$$k_B = \frac{k_4(k_{\bar{7}} + k_{\bar{8}}) K_D K_E}{k_8(k_{\bar{7}} - k_{\bar{8}})}$$

$$G_F = k_F A_0 B_0 F_0 \tag{24}$$

where

$$k_F = \frac{k_4(k_7 + k_8) K_D K_E}{k_7(k_7 - k_8)} \tag{24}$$

Hence, by using Eqs. (23) and (24), the rate of copolymerization according to Eqs. (13) and (17) is defined for a stationary state by Eqs. (25) and (26):

$$-dB/dt = k_p A_0 B_0 F_0 B \tag{25}$$

where $k_p = k_5 k_F$, and

$$-dF/dt = k_p' A_0 B_0 F_0 F \tag{26}$$

where $k_p' = k_6 k_B$.

As k_p and k_p' are defined by elementary rate constants of individual reaction steps, they represent the complex rate constants of copolymerization.

By integrating Eqs. (25) and (26) and rearranging, we obtain:

$$\log B = \log B_0 - (k_p/2.303) A_0 B_0 F_0 t \tag{27}$$

$$\log F = \log F_0 - (k_p'/2.303) A_0 B_0 F_0 t \tag{28}$$

The experimental results of kinetic measurements have shown that the loss in epoxide and anhydride after the induction period obeys the kinetic equation of the first order reaction and the experimental rate constant k_{exp} depends on the initial concentration of amine (Table 1, Fig. 7), epoxide, and anhydride (Table 1, Figs. 3, 5, 6). Therefore, the following equation must be valid:

$$k_{exp} = k_p [A]_0 [B]_0 [F]_0 \tag{29}$$

TABLE 2. Calculated and Experimental Values of k_{exp} in o-Xylene for Different Initial Concentrations of the Components in the Reaction Mixture at 120°C

[HEPBP] ₀ (mole/ liter)	[FA] ₀ (mole/ liter)	[THAm] ₀ (mole/ liter)	$k_{\text{exp}} \times 10^5 \text{ (sec}^{-1}\text{)}$	
			Calculated	Found
0.3	0.3	0.025	2.33	2.3
0.5	0.5	0.025	6.47	6.5
1.0	1.0	0.025	25.88	24.5
0.5	1.0	0.025	12.94	12.5
0.6	1.0	0.025	15.53	14.5
0.5	0.7	0.025	9.06	9.3
0.5	0.5	0.010	2.59	2.6
0.5	0.5	0.035	9.06	8.8
0.5	0.5	0.070	18.11	17.1

By comparing Eqs. (1), (27), (28), and (29) it may be stated that the solution of the reaction scheme is consistent with experimental results. The term a in Eq. (1) corresponds formally to $\log [B]_0$.

Nevertheless, as the rate of polymerization is lower in the induction period, section a corresponds to $\log [B]_0$ for a stationary state after the induction period. In other words, the rate of polymerization depends on the concentration of active centers, which is a function of the initial concentration of amine, epoxide, and anhydride in the sense of Eq. (29).

From the experimental data listed in Table 1 the value of the overall rate constant k_p has been calculated for o-xylene and 120°C ($k_p = 1.035 \times 10^{-2}$ liter³/mole-sec). The experimental rate constants found for different concentration ratios of the reacting components have been correlated with the values calculated by means of the overall constant. The results are given in Table 2. It is obvious that the calculated values are in good agreement with the experimental values of k_{exp} . Thus the rate of polymerization of HEPBP with FA in o-xylene at 120°C is governed by Eq. (30):

$$-d[\text{HEPBP}]/dt = 1.035 \times 10^{-2} [\text{THAm}]_0 [\text{HEPBP}]_0 [\text{FA}]_0 [\text{HEPBP}] \quad (30)$$

The suggested reaction scheme is in agreement with the experimental results of polymerization. Formally, the copolymerization obeys the equation of the first order reaction and the rate of copolymerization is proportional to the concentration of active centers and of epoxide or anhydride. The concentration of active centers is constant in the region after the induction period and depends on the initial concentrations of all components in the polymerization system. The equilibrium character of the equations expressing the origination and decay of active centers is responsible for low molecular weights of the polyesters prepared by the copolymerization of epoxides with anhydrides [39] and for a low frequency factor of copolymerization.

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