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Copolymerization of Epoxides with Cyclic Anhydrides Catalyzed by Tertiary Amines in the Presence of Proton-Donating Compounds

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ABSTRACT

This paper deals with the copolymerization of epoxide [2-hydroxy-4-(2,3-epoxypropoxy)benzophenone] with cyclic anhydride (phthalic anhydride) catalyzed by tertiary amine (tri-n-hexylamine) in the presence of proton-donating compounds in o-xylene solution at 393°K (120°C). On the basis of kinetic investigations performed in the presence of benzoic acid, a reaction scheme has been put forward for the copolymerization. This scheme involves the assumption that the primary active center of ionic character may arise by interaction of acid with amine as well as by initiation mechanism in the absence of proton-donating compound. In the growth stage, alternating reactions of the carboxylate or alkoxide reaction center with epoxide or anhydride take place to give polyester. The termination involves a monomolecular decomposition of the active centers giving rise to intermediates with alcoholic and carboxylic terminal groups which participate again in reinitiation of the copolymerization. By comparing the effect of different proton-donating compounds of various types (alcohol, phenol, or acid), it may be deduced that the acceleration of copolymerization depends not only on the proton-donating power of the compound but also on its behavior in esterification reactions.

INTRODUCTION

As regards the polymerization of epoxides catalyzed by tertiary amines, it is assumed [1, 2] that the presence of a hydroxyl group is indispensable for initiation of the polymerization reaction. The hydroxyl groups continue to arise during the polymerization [3], and their presence was experimentally proved by infrared spectra [1-4]. Similarly, it was established that the content of double bonds and hydroxyl groups [5] increased during the copolymerization of epoxides with cyclic anhydrides catalyzed by tertiary amines. Furthermore, it was found that proton-donating compounds (alcohols, phenols, and acids) have a cocatalytic effect on the curing of epoxide resins with cyclic anhydrides catalyzed by tertiary amines [6, 7] and it was suggested that these substances eliminated the induction period and raised the overall rate of copolymerization [5]. On the other hand, it was found that the induction period in the copolymerization system was not eliminated but merely shortened [8].

In our preceding paper [9], a copolymerization scheme was proposed for the model copolymerization of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEB) with phthalic anhydride (PA) catalyzed by tri-n-hexylamine (THA). This paper is concerned with the effect of different proton-donating compounds and with the kinetics of the above copolymerization in the presence of benzoic acid (BA).

EXPERIMENTAL

Preparation of monomers, their purification and polymerization, and analytical procedures were described in the preceding paper [9]. The acids, alcohol, and phenol were analytical grade chemicals (Lachema, Czechoslovakia) and were used without any further purification. 4-Hydroxybenzophenone was prepared by rearrangement of phenyl benzoate [10]. The solvents were purified by usual procedures [11].

RESULTS

The copolymerization of HEB with PA catalyzed by THA in the presence of proton-donating compounds (PDC) was carried out in the

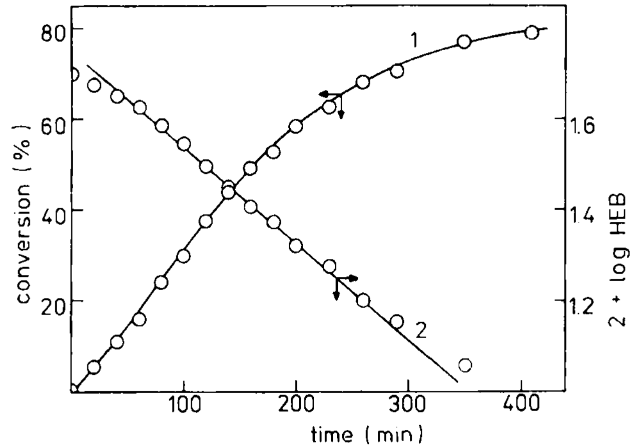


FIG. 1. Copolymerization of 2-hydroxy-4-(2,3-epoxypropoxy)-benzophenone (0.5 mole/liter) with phthalic anhydride (0.5 mole/liter) catalyzed by tri-n-hexylamine (0.025 mole/liter) in the presence of benzoic acid (0.015 mole/liter) in o-xylene at 393°K (120°C): (1) conversion curve of epoxide; (2) functional relationship according to Eq. (1).

solution of o-xylene. The conversion curves expressing the loss of epoxide show sigmoidal form like the curves obtained for analogous copolymerization in the absence of proton-donating compounds [9], but the induction period is shorter. The conversion of epoxide (Fig. 1) may be correlated with the semilogarithmic relationship valid for reactions of the first order

$$\log [\mathrm{HEB}] = a - kt \qquad (1)$$

where $k = k_{exp}/2.303$ is the slope of linear function following the induction period and k_{exp} is the experimental rate constant of the first-order reaction.

In Table 1 the influence of various proton donors on the rate constant is presented, and it is obvious that these proton-donating compounds have an accelerating effect on the copolymerization of epoxide with cyclic anhydride catalyzed by THA.

The influence of benzoic acid functioning as a proton donor in the copolymerization system HEB-PA in o-xylene was thoroughly investigated at 393°K (120°C). The values of rate constants k_{exp} found for

TABLE 1. Influence of Various Proton-Donating Compounds (0.025 mole/liter) on the Value of k_{exp} for the Copolymerization of 2-Hydroxy-4-(2,3-epoxypropoxy)benzophenone (0.5 mole/liter) with Phthalic Anhydride (0.5 mole/liter) Catalyzed by Tri-n-hexylamine (0.025 mole/liter) in o-Xylene at 393°K (120°C)

n	Proton-donating compound	$k_{exp} \times 10^5$ (sec^{-1})	pK_a[a]
1	-	6.5[b]	-
2	Phthalic acid	13.4	2.95; 5.41
3	Benzoic acid	12.6	4.18
4	Trimethylacetic acid	10.4	5.05
5	Trichloroacetic acid	11.6	1.66
6	Cyclohexanol	10.5	-
7	Phenol	7.4	10.0
8	4-Hydroxybenzophenone	7.8	7.85[c]

[a] In aqueous solutions [12].
[b] Value according to previous paper [9].
[c] In aqueous ethanolic solution [13].

the copolymerization of equimolar monomer mixture at different concentrations of BA and tertiary amine are listed in Table 2. The results presented in Table 2 and Fig. 2 also illustrate the influence of initial monomer concentrations on the rate constant k_{exp} at a constant concentration of catalytic components.

The curves in Fig. 2 show clearly that the rate constant of the first-order reaction k_{exp} is at a constant concentration of BA a linear function of the initial concentrations of tertiary amine (curve 1), anhydride (curve 2), and epoxide (curve 3). But the dependence of this constant on the concentration of BA as a cocatalytic component is not linear at constant concentrations of monomers and tertiary amine (curve 4). According to the results published in our preceding paper [9], the curves obtained in the absence of BA (curves 1', 2', and 3') are also presented in Fig. 2. It is obvious from the course of linear functions 2 and 2' or 3 and 3' in Fig. 2 that an addition of BA as cocatalytic component (0.025 mole/liter) results in the fact that the rate constant k_{exp} increases by an equal value. By using a constant concentration of catalyst and BA, the rate constant found experimentally for the above copolymerization systems k_{exp} obeys Eq. (2):

TABLE 2. Influence of Concentration of the Components on the Value of k_{exp} for the Copolymerization of 2-Hydroxy-4-(2,3-epoxypropoxy)-benzophenone (HEB) with Phthalic Anhydride(PA) Catalyzed by Tri-n-hexylamine (THA) in the Presence of Benzoic Acid (BA) in o-Xylene at 393°K (120°C)

					$k_{exp} \times 10^5$ (sec^{-1})		
n	HEB_0 (mole/ liter)	PA_0 (mole/ liter)	THA_0 (mole/ liter)	BA_0 (mole/ liter)	Found	Calculated	In the absence of BA[a]
1	0.5	0.5	0.025	0.005	8.1	8.2	6.5
2	0.5	0.5	0.025	0.01	9.8	9.5	
3	0.5	0.5	0.025	0.025	12.6	12.5	
4	0.5	0.5	0.025	0.035	14.3	14.0	
5	0.5	0.5	0.025	0.05	16.2	16.3	
6	0.5	1.0	0.025	0.025	18.0	18.8	12.5
7	0.6	1.0	0.025	0.025	19.6	21.4	14.5
8	0.7	1.0	0.025	0.025	22.6	23.0	17.9
9	0.8	1.0	0.025	0.025	25.0	26.6	20.7
10	1.0	1.0	0.025	0.025	29.9	31.8	24.5
11	0.5	0.5	0.005	0.025	2.7	2.5	1.2
12	0.5	0.5	0.01	0.025	4.8	5.0	2.6
13	0.5	0.5	0.015	0.025	6.8	7.5	4.2
14	0.5	0.6	0.025	0.025	13.3	13.7	8.5
15	0.5	0.7	0.025	0.025	15.4	15.0	9.3
16	0.5	0.8	0.025	0.025	16.6	16.3	10.3

[a] Values of k_{exp} according to the literature [9], measured in the absence of BA.

$$k_{exp} = k_{exp}^{0} + b \tag{2}$$

where k_{exp}^{0} is the rate constant of the first-order reaction in the absence of BA and b = 5.9 × 10^{-5}/sec provided it holds $[THA]_0 = [BA]_0 = 0.025$ mole/liter (Fig. 2).

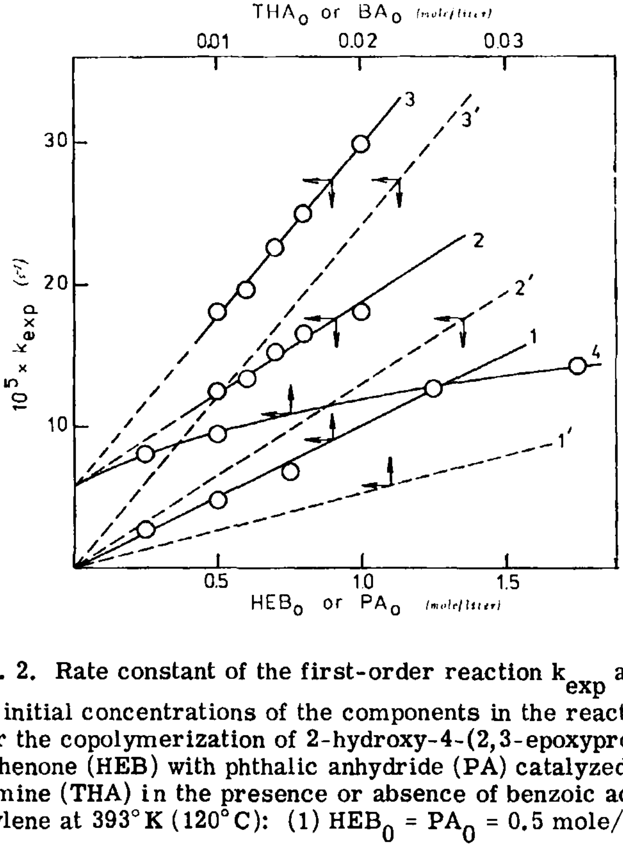


FIG. 2. Rate constant of the first-order reaction k_{exp} as a function of initial concentrations of the components in the reaction system for the copolymerization of 2-hydroxy-4-(2,3-epoxypropoxy)-benzophenone (HEB) with phthalic anhydride (PA) catalyzed by tri-n-hexylamine (THA) in the presence or absence of benzoic acid (BA) in o-xylene at 393°K (120°C): (1) $HEB_0 = PA_0 = 0.5$ mole/liter, $BA_0 = 0.025$ mole/liter; (1') the same as (1) except $BA_0 = 0$; (2) $HEB_0 = 0.5$ mole/liter, $THA_0 = BA_0 = 0.025$ mole/liter; (2') the same as (2) except $BA_0 = 0$; (3) $PA_0 = 1.0$ mole/liter, $THA_0 = BA_0 = 0.025$ mole/liter; (3') the same as (3) except $BA_0 = 0$; (4) $HEB_0 = PA_0 = 0.5$ mole/liter, $THA_0 = 0.025$ mole/liter.

As is evident from Fig. 2 (curve 1), the value of k_{exp} is proportional to the concentration of catalyst if a constant initial concentration of monomers (0.5 mole/liter) and BA (0.025 mole/liter) has been used:

$$k_{exp} = k_a \, [\mathrm{THA}]_0 \qquad (3)$$

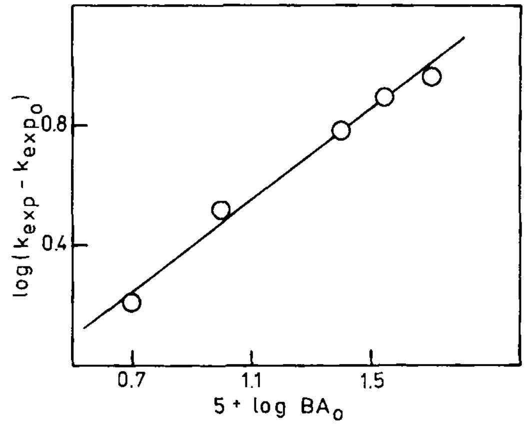


FIG. 3. Influence of the benzoic acid (BA) concentration on acceleration of the copolymerization of 2-hydroxy-4-(2,3-epoxypropoxy)-benzophenone (0.5 mole/liter) with phthalic anhydride (0.5 mole/liter) catalyzed by tri-n-hexylamine (0.025 mole/liter) in o-xylene at 393°K (120°C). The effect is expressed as a dependence of the difference between rate constants of the cocatalyzed reaction k_{exp} and the non-accelerated reaction k_{exp}^0 on initial BA concentration.

where k_a from Fig. 2 is 5.0×10^{-3} liter/mole-sec. The value of this constant for an analogous copolymerization system without BA is 2.7×10^{-3} liter/mole-sec (curve 1').

As k_{exp}^0 is a linear function of the initial concentration of THA [9], it results from Eq. (3) that the quantity b in Eq. (2) is also a function of this concentration. Therefore, we may write:

$$k_{exp} = k_{exp}^0 + [\mathrm{THA}]_0\, c \tag{4}$$

The form of curve 4 in Fig. 2 shows clearly that k_{exp} is an exponential function of the concentration of BA, from which it follows for the quantity c in Eq. (4),

$$c = f([\mathrm{BA}]^x)$$

The exponent x reflects the influence of the concentration of BA. By using the relationship $\log (k_{exp} - k_{exp}^0) = f(x \log [BA])$ represented in Fig. 3, it has been found that the value of x is 0.74.

DISCUSSION

The cocatalytic effect of different proton-donating compounds added into the reaction system (Table 1) manifests itself in the copolymerization of HEB with PA catalyzed by THA in o-xylene. In contrast to the results of Tanaka and Kakiuchi [5, 7], it has been found that the induction period, which is regarded as the stage of gradual increase in concentration of the active centers [5, 9], is not fully eliminated in the concentration range of the catalytic system used (Fig. 1). The reduction of induction period by the cocatalytic effect of proton-donating compounds is considerable, owing to which the time interval necessary for reaching a stationary concentration of the active centers decreases. Furthermore, the initial stage of copolymerization up to the end of induction period is identical with the time interval necessary for reaching the maximum conductivity in equal systems [8]. After the induction period, the course of copolymerization fulfills the kinetic condition of a first-order reaction even in the presence of proton donors exhibiting a cocatalytic effect.

The results obtained by evaluating the cocatalytic effect described by the experimental relationship [Figs. 2 and 3, Eq. (3) and (4)] show that the value of the rate constant k_{exp} may be expressed in terms of the Eq. (5):

$$k_{exp} = k_{exp}^0 + k_c [THA]_0 [BA]_0^{3/4} \qquad (5)$$

The experimental conditions were so chosen that the ratio anhydride/epoxide ≥ 1 was valid owing to which some isomerization and homopolymerization side reactions that could proceed at an excess of epoxide [5] were eliminated.

In the preceding paper [9] a scheme was put forward for the copolymerization of epoxides with cyclic anhydrides catalyzed by tertiary amines in the absence of proton donors. This scheme involves a catalyzed isomerization of epoxides giving rise to a derivative of allyl alcohol from which a binary complex arises by interaction with tertiary amine. The interaction of this complex with anhydride yields a ternary complex which provides the proper active center of ionic character. The rate constant of the first-order copolymerization reaction k_{exp}^0 in the absence of a proton donor is a linear function of initial concentrations of the monomers and catalyst:

$$k_{exp}^{0} = k_p[\mathrm{THA}]_0[\mathrm{HEB}]_0[\mathrm{PA}]_0 \qquad (6)$$

In the presence of a proton donor, a direct interaction between the tertiary amine and proton-donating compound should be taken into consideration. If an organic acid (BA) is used as the proton donor, the suggested scheme of this interaction is as follows [14]:

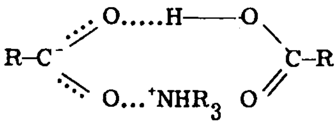
$$\mathrm{RCOOH} + \mathrm{NR_3} \rightleftharpoons \mathrm{RCOOH...NR_3} \rightleftharpoons \mathrm{RCOO^-...^+NHR_3} \rightleftharpoons$$

$$\mathrm{RCOO} \;\; + \mathrm{^+NHR_3}$$

where $\mathrm{RCOOH...NR_3}$ is a simple complex bonded by a hydrogen bond and $\mathrm{RCOO^-...^+NHR_3}$ is a proton-transfer (PT) complex (ion-pair formed by the transfer of a proton).

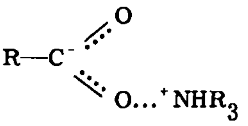
The formation of PT complexes (ion pairs) is dependent on the values of dissociation constants of amine and acid in the sense of the Huyskens Zeegers-Huyskens model [15] of PT complexes.

From the view-point of stoichiometry, the adducts in which the ratio of acid to tertiary amine is 2:1 are the first to arise. The suggested structure [16] of this adduct is I:

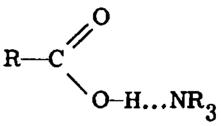


I

and only in the presence of an excess of tertiary amine are the 1:1 complexes of the structures (II or III) formed.



II

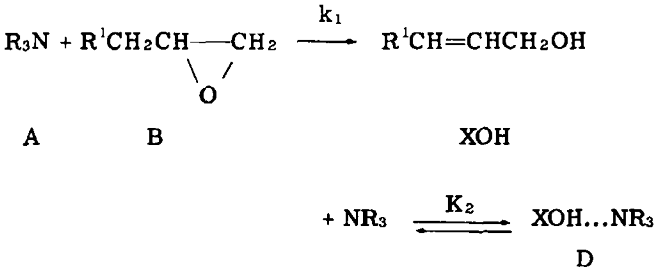


III

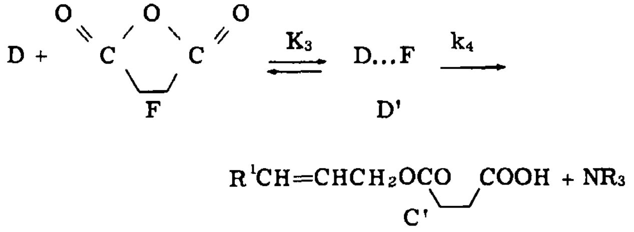
If we complete the previously described scheme [9] in this sense, we may consider the formation of PT complexes or their dissociated parts which both are in operation as active centres in the copolymerization [8] to be the primary initiating step. On the basis of experimental results and the mechanism suggested for nonaccelerated copolymerization in preceding paper [9], we may put forward the reaction pathways shown in Eqs. (7)-(14).

Initiation:

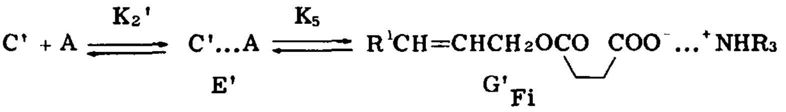
Formation of primary active centers by interactions among amine, epoxide, and anhydride in the absence of PDC:



(7)



(8)

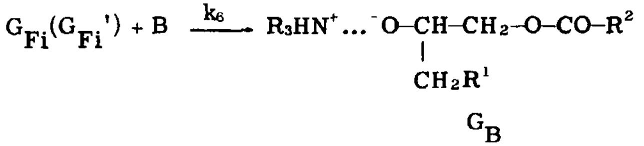


(9a)

Formation of primary active centers by the effect of PDC:

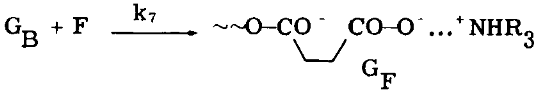
$$\underset{C}{C_6H_5COOH} + A \overset{K_2'}{\rightleftharpoons} \underset{E}{C_6H_5COOH...NR_3} \overset{K_5}{\rightleftharpoons} \underset{G_{Fi}}{C_6H_5COO^-...^+NHR_3} \quad (9b)$$

Formation of the propagation active centers:

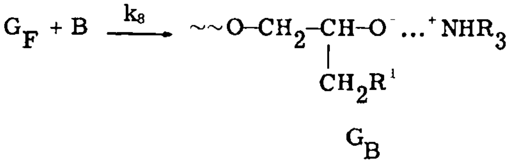


$$G_{Fi}(G_{Fi}') + B \xrightarrow{k_6} \underset{G_B}{R_3HN^+...^-O\text{–}\underset{CH_2R^1}{\underset{|}{CH}}\text{–}CH_2\text{–}O\text{–}CO\text{–}R^2} \quad (10)$$

Propagation:

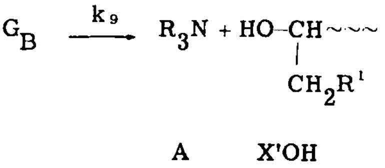


$$G_B + F \xrightarrow{k_7} \underset{G_F}{\sim\sim O\text{-}CO^- \;\; CO\text{-}O^- \ldots {}^+NHR_3} \qquad (11)$$



$$G_F + B \xrightarrow{k_8} \underset{G_B}{\sim\sim O\text{-}CH_2\text{-}\underset{\substack{|\\ CH_2R^1}}{CH}\text{-}O^- \ldots {}^+NHR_3} \qquad (12)$$

Termination:



$$G_B \xrightarrow{k_9} \underset{A}{R_3N} + \underset{X'OH}{HO\text{-}\underset{\substack{|\\ CH_2R^1}}{CH}\sim\sim\sim} \qquad (13)$$

$$G_F \overset{K_5}{\rightleftharpoons} E \overset{K_2'}{\rightleftharpoons} \underset{A}{R_3N} + \underset{C'}{HOOC \sim\sim} \qquad (14)$$

As evident from this reaction scheme, the proper active polymerization center G_B is formed in the reaction of the primary center G_{Fi} or G_{Fi}' with epoxide (B) and subsequently it is subject to the reaction with anhydride [Eq. (11)] in which the carboxylate type of the propagation center is regenerated. According to Eq. (9b), the formation of the primary initiating active centers G_{Fi} is affected by the proton donor added to the copolymerization system while the analogous centers G_{Fi}' originate from the starting components of the reaction system by reactions (7), (8), and (9a). The reactivities of primary centers G_{Fi} and G_{Fi}' may be assumed to be comparable (similarly C and C' and of their complexes E and E') and they will be, therefore, regarded as identical in subsequent considerations.

As evident from the copolymerization scheme, the alkoxide anion G_B reacts with anhydride F in the propagation stage [Eq. (11)] to form the carboxyl anion G_F which opens the epoxide ring in the reaction with monomer B to give the alkoxide anion G_B [Eq. (12)]. The repetition of these reactions brings about a growth of the chain and results in the formation of alternating copolymer-polyester. According to Eq. (13) and (14), the termination reactions involve a monomolecular decomposition of the active centers [17] to give amine and PDC. These intermediates take part in reinitiation of the copolymerization.

According to the above scheme, the rate of copolymerization depends on the rate of monomer consumption in the dominating propagation reactions [Eqs. (11) and (12)], while the rate of monomer consumption is proportional to the concentration of propagation active centers and instantaneous concentration of monomers:

$$- dF/dt = k_7[G_B][F] \tag{15}$$

$$- dB/dt = k_8 [G_F][B] \tag{16}$$

On supposing a stationary state, the concentration of the propagation centers G_B and G_F is constant, which implies a constant concentration of the PT complexes as well.

The primary active centers G_{Fi} gradually arise in the induction period according to Eqs. (7), (8), and (9a) and the formation of further primary centers G_{Fi} is affected according to Eq. (9b) by BA added to the reaction system as proton donor and by tertiary amine. It follows from the reduction of induction period that the interaction of tertiary amine with acid according to Eq. (9b) prevails in the primary initiation. Thus, the total concentration of the primary active centers must be:

$$[G_i] = [G_{Fi}] + [G_{Fi}'] \tag{17}$$

According to the results published in the preceding paper [9], the concentration of active centers in the absence of a proton donor depends on initial concentrations of monomers and tertiary amine and the stationary concentrations of active centers is established at the end of the induction period:

$$G_{Fi}' = k_p' A_0B_0F_0 \tag{18}$$

where the rate constant k_p' is defined by the rate constants and equilibrium constants of initiation and termination reactions.

According to Eq. (9b) stating the equilibrium character of the reaction, the concentration of active centers G_{Fi} in the induction period may be expressed by Eq. (19).

$$G_{Fi} = K_5C_0A_0/(1 + K_5C_0) \cong k_c' A_0 C_0^x \tag{19}$$

At the beginning of copolymerization BA is gradually consumed, but we may assume the establishment of a stationary concentration of the reaction intermediates C' with terminal hydroxyl groups in this process.

With respect to Eq. (16)-(19) Eq. 20 holds for the reaction rate calculated from the loss of epoxide:

$$dB/dt = (k_pA_0B_0F_0 + k_cA_0C_0^x)\,B \tag{20}$$

where

$$k_p = k_8\, k_p'$$

and

$$k_c = k_8\, k_c'$$

On integrating Eq. (20), we obtain:

$$\ln B = \ln B_0 - (k_pA_0B_0F_0 + k_cA_0C_0^x)\,t \tag{21}$$

By using Eq. (1) and (5) and experimental results, Eq. (21) may be written in the form:

$$\log HEB = \log HEB_0 - (k_pHEB_0PA_0THA_0 + k_cTHA_0BA_0^{3/4})\,t/2.303 \tag{22}$$

The values of k_p and k_c in Eq. (22) were derived from experimental results. They are: $k_p = 1.035 \times 10^{-2}$ liter^3/mole^3-sec and $k_c = 3.74 \times 10^{-2}$ liter$^{1.75}$/mole$^{1.75}$-sec.

The proposed reaction scheme is in a good agreement with experimental results. In the presence of the catalytic system tertiary amine-proton donor, the copolymerization of epoxide with cyclic anhydride formally obeys the equation of the first-order reaction. The rate constant of the first-order reaction (effective) found experimentally k_{exp} is proportional to the concentration of active centers and may be expressed by Eq. (23).

$$k_{exp} = 1.035 \times 10^{-2}\ HEB_0PA_0THA_0 + 3.74 \times 10^{-2}\ THA_0BA_0^{3/4} \quad (23)$$

The values of k_{exp} calculated according to Eq. 23 are listed in Table 2. They are in a good agreement with the values found experimentally.

The experimental results given in Table 1 and the limited section of the proton donor compound used do not allow any correlation between the acidity of the proton donor and k_{exp}. A qualitative comparison gives the accelerating effect in the order: acids > alcohols > phenols, which is in agreement with the experimental results obtained by Tanaka and Kakiuchi [7], but to a certain degree in contrast to the intensity of the interactions (PT complexes, hydrogen bonds) between tertiary amines and proton donors because the magnitude of these interactions decreases in the order: acid > phenol > alcohol. This apparent contradiction may be explained from the point of view of mechanism of the initiation. If an organic acid is used as proton donor, the initiation may be explained by the reaction of an ion-pair or free carboxyl anions with epoxide group [Eq. (10)] which gives rise to a propagation active center. If alcohol or phenol is used as proton donor, we may apply the scheme of copolymerization in the absence of proton donor [9] in which it is assumed that alcohol originates from the catalyzed isomerization of epoxide and the proper active center of anionic character is formed by interaction with anhydride through a transient ternary complex. In either case, an ester is involved in the origination of active center and it may be stated that not only the acidity of the proton donor but also its character with respect to esterification reactions is of decisive importance for the copolymerization of epoxides with cyclic anhydrides catalyzed by tertiary amines in the presence of a proton donor. A higher acidity of phenol in comparison with alcohol is responsible for its lower acceleration effect in the copolymerization of epoxide with cyclic anhydride.

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