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Polymeric UV Absorbers of the 2-Hydroxybenzophenone Type. III. Tertiary Amine Catalyzed Polymerization of 2-Hydroxy-4(2,3-epoxypropoxy)benzophenone

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Polymeric UV Absorbers of the 2-Hydroxybenzophenone Type. III. Tertiary Amine Catalyzed Polymerization of 2-Hydroxy-4(2,3-epoxypropoxy)benzophenone

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ABSTRACT

The tertiary amine catalyzed polymerization of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPBP) in melt and *o*-xylene solution was studied. UV, IR, and NMR spectra of the polymer thus obtained were evaluated and its molecular weight was determined. In order to elucidate the polymerization of HEPBP, the model reaction of 2-hydroxybenzophenone with 4-(2,3-epoxypropoxy)benzophenone at an equimolar ratio as well as the reaction of HEPBP with 2,4-dihydroxybenzophenone at a molar ratio of 2:1 was investigated. A reaction mechanism was suggested for the polymerization of HEPBP on the basis of the results obtained. According to this mechanism, a catalytic center originates during initiation, and that center affords phenoxyl anion by reacting with HEPBP. In the following step phenoxyl anion opens the epoxide ring and an alkoxide anion arises. The basic alkoxide anion is stabilized by a proton transfer of a phenolic group. The successive recurrence of these reactions results in the growth of the polymer chain.

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The reactions of *o*-phenolic groups taking place during the polymerization of HEPBP impair the polymer functioning as a UV absorber.

INTRODUCTION

In the previous paper, which was concerned with the polymerization of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPBP) with phthalic anhydride at a nonequimolar ratio of both compounds, we revealed by UV spectral analysis that an excess of HEPBP with respect to phthalic anhydride resulted in a deformation of the UV spectra [1]. The absorption band at 328 nm vanished and a shoulder at 305 nm appeared. Equal results were obtained when tri-*n*-hexylamine or potassium benzoate was used as the catalyst. We found that a molar excess of phthalic anhydride did not influence the course of the copolyaddition reaction taking place during the synthesis of UV absorbers of the 2-hydroxybenzophenone type, while an excess of HEPBP brought about some reactions which resulted in a decrease in the UV stabilization effect. We suggested that the reactions of *ortho*-phenolic groups were involved in this process. Tanaka and Kakiuchi [2] investigated the copolymerization of the substituted phenyl glycidyl ethers with hexahydrophthalic anhydrides and assumed that some isomerizations and other reactions might take place, provided the epoxide compound was in excess. The aim of this study was to clear up the mechanism of the polymerization of HEPBP, especially as it concerns the part the *ortho*-phenolic groups of HEPBP play in this process which results in an impairment of the compounds thus prepared and used as UV stabilizers.

EXPERIMENTAL

HEPBP was prepared according to Ref. 3. 2-Hydroxybenzophenone (2-HBP) and 4-hydroxybenzophenone (4-HBP) were prepared by the rearrangement of phenyl benzoate with AlCl_3 and then by the distillation of 2-HBP with water vapor [4]. 4-(2,3-Epoxypropoxy)benzophenone (EPBP) was prepared from 4-HBP according to Ref. 3. 2,4-Dihydroxybenzophenone (DBP) was a commercial product of CHZJD, Bratislava, Czechoslovakia, which was recrystallized from benzene before use (mp 145°C). Other chemicals and solvents were commercial analytical grade chemicals used without any purification.

The determination of epoxy groups was performed according to Vorobjov [5]. UV spectra were measured on a Unicam SP 700 A

recording instrument while IR spectra were taken on a Perkin-Elmer 457 recording instrument. NMR spectra were recorded on a Tesla BS 487 B instrument at 80 MHz either at room temperature (HEPBP) or at 60°C [poly(HEPBP)]. All spectral measurements were performed with chloroform solutions of the samples, and TMS was used as an internal standard for NMR. The molecular weights of polymers were determined with a high-speed membrane osmometer, model 502 (Hewlett-Packard). The bulk polymerizations and reactions were carried out in sealed glass ampules in nitrogen atmosphere or in open systems. The use of open systems enabled us to remove aliquots for the determination of epoxy groups or to measure the UV spectra easily. The polymerizations of *o*-xylene were performed in a three-neck flask equipped with a stirrer, device for inlet and outlet of nitrogen, thermometer, and tube for sampling.

RESULTS

The polymerization of HEPBP in melt was performed in sealed glass ampules at 130°C. Triethylamine (10 mole %) was used as a catalyst, and the duration of polymerization was 3 hr. When the polymerization finished, the product was dissolved in acetone and precipitated into an excess of water. A white powdered polymer of molecular weight 15,600 was isolated.

The UV spectrum of this polymer, together with the spectrum of HEPBP, is presented in Fig. 1. The spectrum of HEPBP shows two absorption bands at 285 and 328 nm in the near-UV region. It is evident that the UV spectrum of poly(HEPBP) is deformed similarly as found for the copolymerization of HEPBP with phthalic anhydride in an excess of HEPBP [1]. The absorption band at 328 nm, which corresponds to the derivatives of 2-hydroxybenzophenone, vanishes and a shoulder appears at 305 nm. At the same time the extinction coefficient of the band at 285 nm decreases.

The IR spectrum of poly(HEPBP) in the 1400-1800 cm^{-1} region, as well as the spectra of HEPBP and EPBP, are presented in Fig. 2. The spectrum of HEPBP shows three bands in this region, i.e., the vibrations of the benzene ring at 1580 and 1605 cm^{-1} and the band of the hydrogen-bonded carbonyl group at 1620 cm^{-1} , which is typical for the derivatives of 2-HBP. The spectrum of poly(HEPBP) differs from the spectrum of HEPBP. The ring vibrations of benzene remain and a new band of the free carbonyl group appears at 1660 cm^{-1} . This spectrum is practically equal to the spectrum of EPBP. This means that some phenolic groups of 2-HBP have been lost during the polymerization of HEPBP. This fact is also confirmed by the NMR spectra of HEPBP and poly(HEPBP) shown in

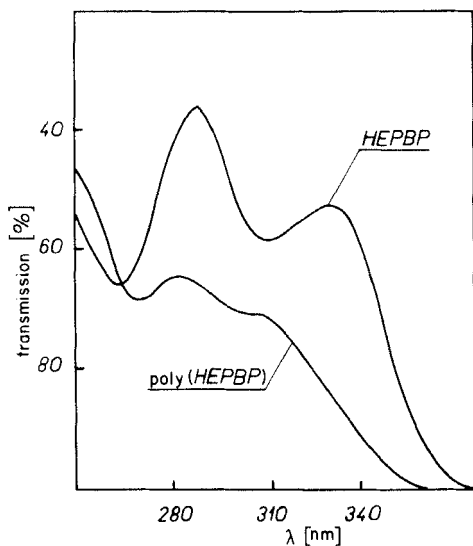


FIG. 1. UV spectra of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPBP) and its polymer [poly(HEPBP)] in chloroform. Concentration, 5×10^{-5} M/liter; $d = 0.5$ cm.

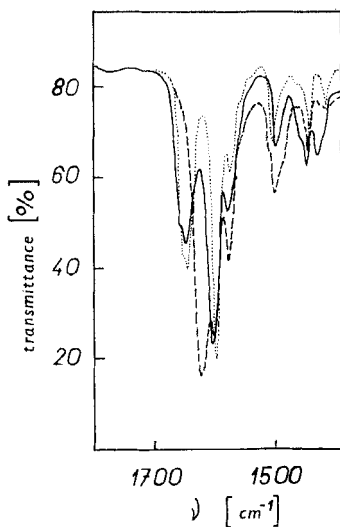


FIG. 2. IR spectra of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPBP) (---), 4-(2,3-epoxypropoxy)benzophenone (EPBP) (···), and poly(HEPBP) (—) in the region from 1400 to 1800 cm^{-1} in chloroform.

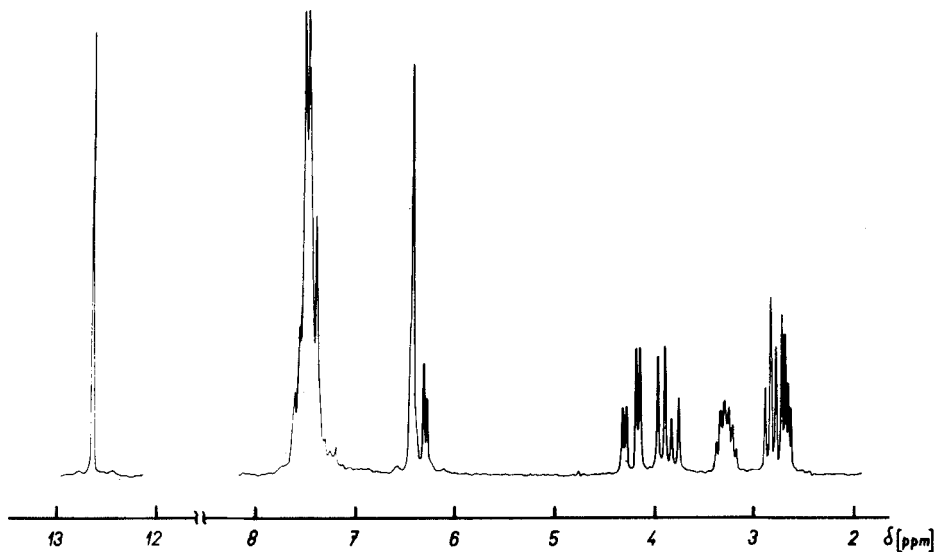


FIG. 3. NMR spectrum of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPBP) in chloroform-d at room temperature.

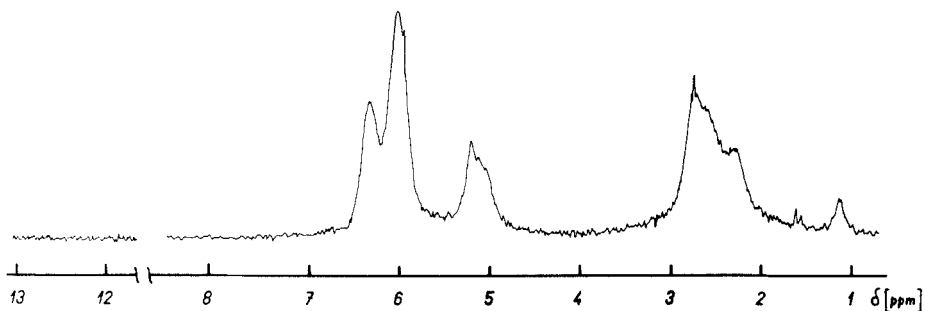


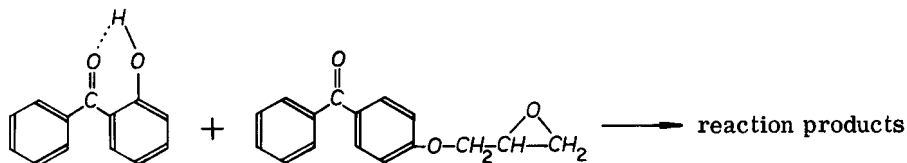
FIG. 4. NMR spectrum of the polymer of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone in chloroform-d at 60°C.

Figs. 3 and 4, respectively. The NMR spectrum of HEPBP (Fig. 3) consists of the following signals: at δ 12.65 (1 proton singlet) of the hydrogen-bonded phenolic group; at δ 7.50 (6 proton multiplet), corresponding to the nonsubstituted phenyl ring and H-6 substituted phenyl ring; at δ 6.41 (1 proton doublet), corresponding to the H-3 substituted benzene ring; and at δ 6.36 (1 proton quartet), corresponding to the H-5 substituted benzene ring. The signals at δ 4.22 (1 proton

quartet) and $\delta 3.86$ (1 proton quartet) correspond to the protons bounded to C_1 in the aliphatic chain, and the signals at $\delta 3.30$ (1 proton multiplet), $\delta 2.82$ (1 proton triplet), and $\delta 2.66$ (1 proton quartet) correspond to the protons in the CH and CH_2 groups of epoxide chain. It is obvious from the NMR spectrum of poly(HEPBP) in Fig. 4 that the signal of the ortho-phenolic group vanished, which gives evidence that a proton of the phenolic group underwent reaction. The distribution of the signals of aromatic protons remains unchanged and is equal to that found with the model substance. The protons of the aliphatic chain appear as a multiplet from $\delta 3.00$ to $\delta 4.15$. The disappearance of protons at $\delta 2.82$ and $\delta 2.66$ on the primary carbon of the epoxide ring indicates a cleavage of the epoxide ring. We did not identify the small peak at $\delta 2.44$.

Equal changes in the UV and IR spectra appear during the polymerization of HEPBP with other catalysts under the conditions stated in Table 1. The extinction coefficients of the shoulder at 305 nm as well as the molecular weights of poly(HEPBP) are also given in Table 1.

The reaction of 2-HBP with EPBP at an equimolar ratio, which is a model reaction for the polymerization of HEPBP, was performed without any solvent in the melt of the reaction mixture at 145°C by using tri-*n*-hexylamine (2 mole %) as the catalyst:



The course of the reaction was followed by the decrease of epoxide groups, and simultaneously the samples were taken for UV spectra. Under these conditions, 95% of epoxide groups was consumed in 1 hr. The UV spectra of the samples of reaction mixture taken in the time interval between 0 and 60 min, as well as the spectra of 2-HBP and EPBP, are presented in Fig. 5. It is evident from this Fig. 5 that the absorption band at 340 nm, corresponding to the derivatives of 2-HBP, vanishes, which means that the ortho-phenolic groups are subject to reaction.

Similarly, when HEPBP is reacted with DBP in the melt at a molar ratio of 2:1 at 145°C in the presence of tri-*n*-hexylamine (THAm) (0.25 mole %) as the catalyst, the epoxide groups of HEPBP were consumed in 1.5 hr (Fig. 6). For both these systems the time decrease of the glycidyl derivatives of benzophenone corresponds to a first-order reaction up to 70% conversion.

TABLE 1. Polymerization of 2-Hydroxy-4-(2,3-epoxypropoxy)benzophenone in the Melt at 130°C

n	HEPBP (g)	Catalyst		Polymerization time (hr)	Yield ^a (%)	ϵ_{305} [liter/(M)(cm)]	Molecular weight
		Kind	Weight (g)				
1	1.35	TEtAm ^b	0.08	2.5	100	6710	15600
2	5.4	TEtAm ^c	0.15	4	98	-	12300
3	2.7	CaO	0.011	2	98	5680	-
4	2.7	BaO	0.031	4	99.5	6020	-
5	1.95	NaOH	0.031	4	99	6840	-

^a Isolation was performed by precipitating the acetone solution into an excess of water.

^b TEtAm = triethylamine.

^c TEtAm = triethanolamine.

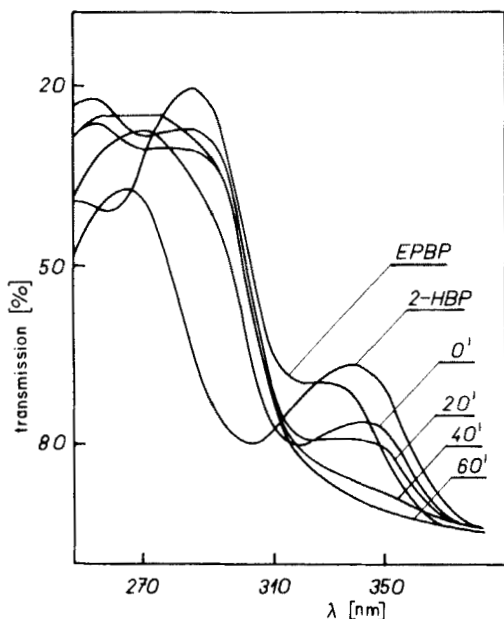


FIG. 5. UV spectra of 2-hydroxybenzophenone (2-HBP), 4-(2,3-epoxypropoxy)benzophenone (EPBP) and of the products of the reaction of these compounds at a molar ratio of 1:1 taken at intervals from 0 to 60 min in chloroform.

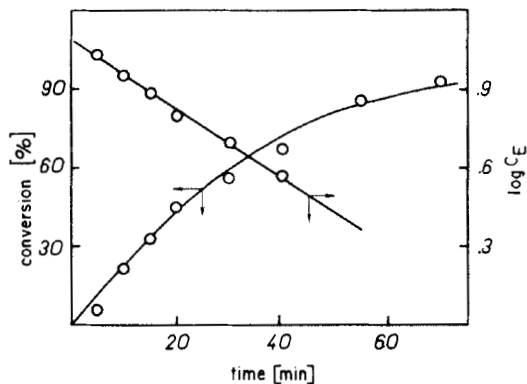


FIG. 6. The course of the reaction of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPBP) with 2,4-dihydroxybenzophenone (DBP) at a molar ratio of 2:1 in the melt at 145°C catalyzed by 0.25 mole % of tri-n-hexylamine.

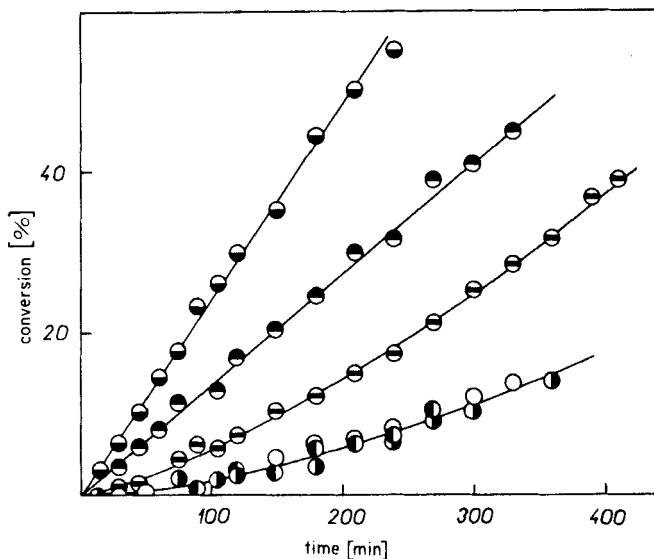


FIG. 7. The polymerization of 2-hydroxy-4-(2,3-epoxypropoxy) benzophenone (HEPBP) [1 mole/liter] in *o*-xylene catalyzed by tri-*n*-hexylamine [0.1 mole/liter] at 110°C in the presence or absence of various hydroxy-compounds: (O) without any hydroxy-compound, (●) 2-hydroxy-4-*n*-octyloxybenzophenone [0.1 mole/liter], (⊙) cyclohexanol [0.1 mole/liter], (⊖) 2-hydroxybenzophenone [0.1 mole/liter], (⊕) 4-hydroxybenzophenone [0.5 mole/liter], and (⊗) 4-hydroxybenzophenone [0.1 mole/liter].

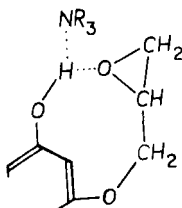
The course of the polymerization of HEPBP in *o*-xylene (1 mole/liter) catalyzed by THAm (0.1 mole/liter) at 110°C is shown in Fig. 7, together with the curves which illustrate the effect of various compounds with active hydrogen on the polymerization of HEPBP catalyzed by tertiary amines. It is obvious from Fig. 7 that the polymerization of HEPBP shows an autocatalytic character. An induction period appears at the beginning of polymerization. Afterwards the rate of polymerization increases because the concentration of active centers increases. The cocatalytic effect of secondary alcoholic groups was modeled by means of cyclohexanol added in the amount of 10 mole %, while the effect on polymerization of phenolic groups bound by hydrogen bonds was ascertained by means of 2-hydroxy-4-*n*-octyloxybenzophenone added in the amount of 10 mole % with respect to HEPBP. The corresponding two curves presented in Fig. 7 have the same pattern as the kinetic curve obtained for the polymerization of HEPBP in the absence of these admixtures, i.e., the induction period remains, the cocatalytic

effect does not appear, and the reaction is of an autocatalytic character. The addition of 2-HBP does not eliminate the induction period completely, but this period is reduced and the autocatalytic character of polymerization remains. However, the rate of polymerization is higher than the rate of polymerization catalyzed only by THAm. The induction period may be eliminated by the cocatalytic effect of free phenolic groups modeled by 4-HBP when they are added in an equimolar ratio or even in a lower concentration with respect to THAm. At the same time, an increase in the rate of HEPBP polymerization proportional to the concentration of 4-HBP is observed (Fig. 7).

DISCUSSION

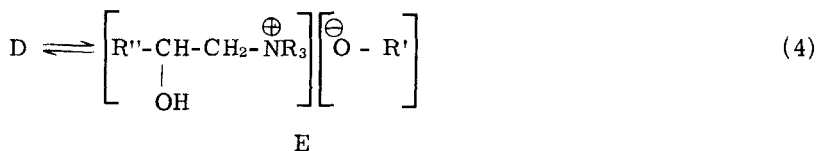
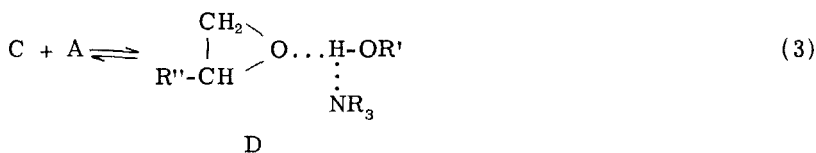
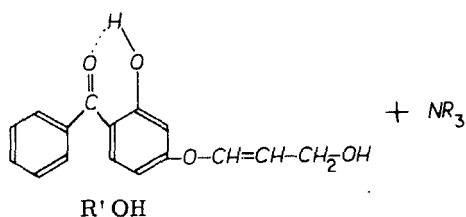
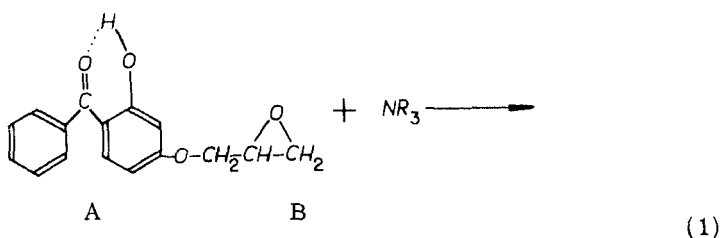
HEPBP contains both epoxide and phenolic groups which are able to take part in the polymerization reactions of this monomer. Only the epoxide group reacts selectively in the copolymerization of HEPBP with phthalic anhydride at an equimolar ratio of both monomers. The 2-phenolic group, which forms hydrogen bond with carbonyl group [6], remains [3] and does not participate in the initiation reaction which is made possible, according to Tanaka and Kakiuchi [2], by the formation of a ternary complex epoxide-tertiary amine-hydroxy compound. The polymerization curves of the copolymerization of HEPBP with phthalic anhydride show an induction period at the beginning of polymerization [7] and therefore are equal to the curves describing the polymerization of glycidyl ethers which do not contain any phenolic groups [2]. A gradual rearrangement of glycidyl ethers takes place in the induction period and an unsaturated alcohol is formed. This product is responsible for the formation of the catalytic center [2]. It is possible to eliminate the induction period by adding a catalyst with an active hydrogen. From the existence of the induction period of the copolymerization of HEPBP with phthalic anhydride [7] it may be concluded that the formation of a complex of a tertiary amine with a 2-phenolic group is negligible. If HEPBP is in excess with respect to phthalic anhydride, the limiting case of which is the homopolymerization of HEPBP in the absence of phthalic anhydride, the conditions are changed due to the impairment of the 2-HBP structural elements with an UV stabilization effect. The course of the reaction between 2-HBP and EPBP, as well as the deformation of the UV spectra of the product of this reaction (Fig. 5) which are comparable to the spectra of poly(HEPBP) (Fig. 1) confirms the existence of reactions of 2-phenolic groups during the polymerization of HEPBP. The NMR spectrum of poly(HEPBP) (Fig. 4)

and the disappearance of the absorption band in the UV spectrum of poly(HEPBP) (Fig. 1) gives direct evidence that the 2-phenolic group of benzophenone is subject to reaction. As is evident from Fig. 2, during the polymerization of HEPBP a band of the free carbonyl group appears and no reaction or isomerization between the phenolic and carbonyl groups takes place. These results indicate that a reaction with the epoxide group is responsible for the disappearance of the phenolic group bound by a hydrogen bond. According to the results obtained by Shode et al. [8], the reaction between the epoxide and phenolic groups as catalyzed by a tertiary amine proceeds through a transition complex which consists of tert-amine, epoxide, and phenol [8]. In this case there are two possible reactions, i.e., an intramolecular reaction and an intermolecular reaction. As for the intramolecular reaction, a 9-membered ring should arise:



the formation of which is unprobable because of steric reasons. Besides, as is evident from Fig. 7, the hydrogen bonded phenolic group of 2-hydroxy-4-n-octyloxybenzophenone does not participate significantly in the initiation reaction. Therefore, in the polymerization of HEPBP catalyzed by tert-amine the intermolecular reaction between phenolic group and epoxide group has priority. It must also be taken into consideration that a product of relatively high molecular weight is formed in the polymerization of HEPBP, which confirms the intermolecular mechanism of the consecutive reactions which lead the polymer.

On the basis of these results as well as the information in papers concerned with the polymerization of epoxides and the effect of tertiary amines [8-15], we put forward a scheme for the polymerization of HEPBP, i.e., a compound with epoxide and phenolic groups. Equations (1) to (4) describe the formation of catalytic centers during the initiation of the polymerization of HEPBP, as well as a suggested mechanism of initiation which is applicable to other epoxide compounds.



The substituent R' in Eqs. (3) and (4) represents the 2-hydroxy-4-methylenoxybenzophenone group.

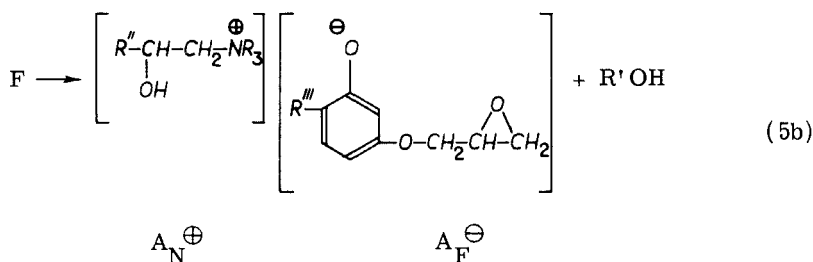
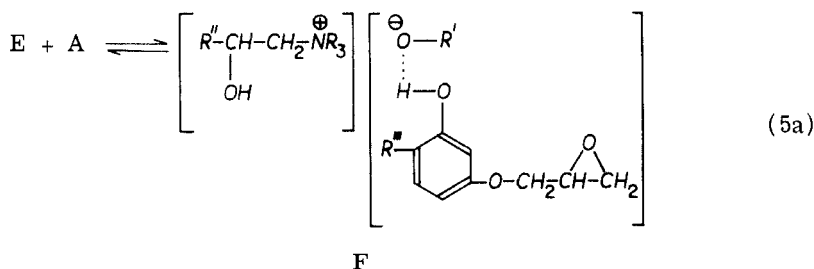
Equation (1) describes the rearrangement of the 4-glycidyl ether of 2-hydroxybenzophenone catalyzed by THAM which yields a derivative of allyl alcohol. According to Sorokin et al. [9] and Tanaka and Kakiuchi [10], the presence of hydroxyl groups is a necessary condition for the polymerization of epoxides. Hydroxyl groups as well as unsaturated groups are incessantly formed during the polymerization [11] and their presence was proved experimentally by IR spectra [9-12]. Such rearrangement of epoxide derivatives

in basic or acid medium is well known [16-22], and it has been found that aldehydes and ketones [17-21] may arise in addition to unsaturated alcohols. It is obvious that the basicity of the medium where the polymerization of HEPBP is initiated is not able to loosen the hydrogen bound to a carbonyl group by the primary effect of the tert-amine (Fig. 7). Therefore, the isomerization reaction of HEPBP according to Eq. (1) must be the major source of the cocatalytic component.

A further stage in the formation of an active center is the interaction between the tert-amine and the hydroxyl group of isomerized HEPBP. Caldin et al. [23-25] and Ivin et al. [26] studied the formation of hydrogen bonds through ion-pairs in the reaction between substituted phenols containing electron-withdrawing substituents and tert-amines. The rate of ion-pair formation in the equilibrium reaction is fairly high, and the equilibrium constants indicate a shift of equilibrium toward the formation of ion-pairs. The formation of hydrogen bonded complexes is a transition stage of this reaction. The rate constants are not limited by an energy barrier to proton transfer, but mainly by the rate of diffusion [23], and they show a good inverse correlation with the viscosity of solvent [25]. These reactions are dependent on the kind of base used [25], and for aliphatic amines the rate of forward reaction decreases with the length of the aliphatic chains. In the polymerization of phenyl glycidyl ether the rate of initiation reaction is also decreased due to the steric effects of the substituents bonded to tert-nitrogen [12]. In the case of amines the magnitude of interaction, however, depends on the strength of base [24]. As for hydroxyl compounds, the magnitude of interaction depends on the pK of the hydroxyl compound. Some acids weaker than substituted phenols with tert-amines in carbon tetrachloride form hydrogen-bonded complexes which do not pass into ion-pairs [27]. Since the energy barrier of the hydrogen bonded phenolic group in a molecule of HEPBP hinders interaction with the catalyst, the alcoholic group of the compound R'OH, which arises by rearrangement according to Eq. (1), must react preferentially with the tert-amine and yield complex C according to Eq. (2).

Equation (3) represents a further stage of the initiation reaction, i.e., the formation of the ternary complex which consists of epoxide group, alcohol, and tert-amine. This step is certainly necessary from the point of view of the formation of an ion-pair according to Eq. (4). It is accompanied by the cleavage of the epoxide ring, proton transfer, and formation of an alkoxide anion while simultaneously a quaternary nitrogen cation is formed. A successive increase in the concentration of active centers during polymerization according to Eqs. (1) to (4) is responsible for the induction period at the beginning of reaction as well as the autocatalytic character of polymerization. The formation of quaternary ammonium salts

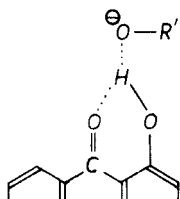
was proved analytically by Sorokin et al. [28]. When the polymerization of phenyl glycidyl ether took place in the presence of dimethylhexylamine and butanol, more than 15% of the amine was transformed into the form of quaternary ammonium salt. The stoichiometric equation put forward by Sorokin et al. [28] is equivalent to Eq. (4) in our scheme. Another type of quaternary salt is assumed to occur in the reaction between carboxylic acids and epoxides catalyzed by tert-amines according to Pirozhnaya and Gromov [13]. For the reaction between phenol and epoxide catalyzed by tert-amines, Patat and Erlmeier [14, 15] assume merely the formation of ternary complex, and so also do Tanaka and Kakiuchi [2] in the case of the copolymerization of phenyl glycidyl ethers with cyclic anhydrides. As to the mechanism of initiation, these reactions are similar and correspond to Eq. (3) of the above scheme. Evidently, an ionic structure of the initiation center is necessary for the abstraction of a hydrogen atom from the phenolic group of HEPBP according to Eqs. (5a) and (5b).



In Eq. (5a), R''' represents the benzoyl group, A_N^{\oplus} in Eq. (5b) denotes a cation with a quaternary nitrogen, and A_F^{\ominus} denotes a phenoxy anion.

Equations (5a) and (5b) depict the first step of the polymerization reaction. Equation (5a) describes the intermediate stage of the propagation reaction when the interaction between alkoxide anion

and the hydrogen of phenolic group sets in. The transient structure of this complex may be represented as



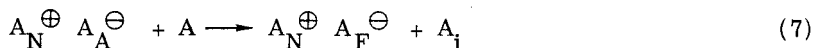
In the subsequent step (Eq. 5b) a proton is abstracted from the phenolic group and thus the alkoxide anion is stabilized. In this way a phenoxyl anion is formed and an unsaturated alcohol is made free. The basicity of the alkoxide anion is evidently sufficient to overcome the energy barrier of the hydrogen bond. The existence of these reactions is confirmed by a gradual decrease in the 2-phenolic groups during the polymerization of HEPBP which is demonstrated for the model reaction between 2-HBP and EPBP (Fig. 5), and by a full disappearance of the signal of the bonded phenolic group in the NMR spectrum (Figs. 3 and 4). The derivative of allyl alcohol $R'OH$ which is produced in Reaction (5b) can enter subsequently into initiation or transfer reactions.

In the following step the phenoxyl anion reacts with the epoxide group of HEPBP according to



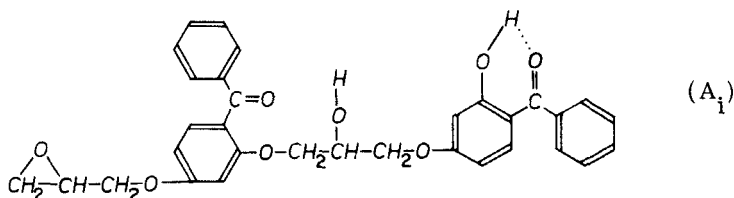
where A_A^{\ominus} stands for the anion with a charge on the alkoxide group.

This reaction is beyond doubt preceded by the interaction between the phenoxyl anion and the carbon of the epoxide ring. In this reaction the epoxide ring is opened by the effect of the phenoxyl anion which manifests itself in the loss of epoxide groups during the polymerization (Fig. 7). Subsequently the alkoxide anion reacts again with the phenolic group according to

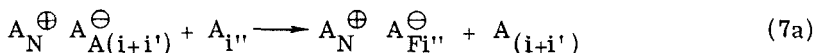
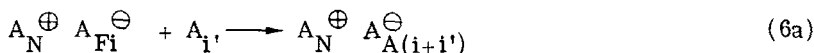


In this reaction the phenoxyl anion A_F^{\ominus} is again produced by the proton transfer of the phenolic group to the strongly basic alkoxide

anion, and thus compound A_i with a secondary hydroxyl group is formed. This compound arises according to Eq. (7) and corresponds to a dimeric addition product ($i = 2$) to which the following formula may be attributed:



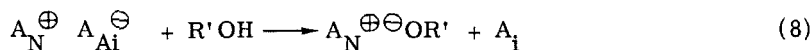
From the structure of compound A_i it is obvious that a bifunctional product with phenolic and epoxide groups has arisen. This species takes part in subsequent reactions according to



The character of Reactions (6a) and (7a) accounts for the formation of a polymer with relatively high molecular weight (Table 1).

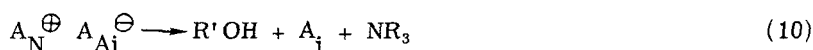
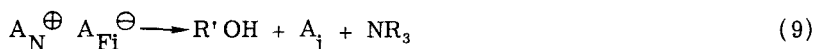
The transfer reactions are characteristic of the polymerization of epoxides catalyzed by tert-amines and give polyethers of low molecular weight [10, 12]. For the products of the polymerization of phenyl glycidyl ether, Sorokin et al. [9, 12] determined the average polymerization degree which was approximately equal to 5. Analogous results were also obtained by Tanaka et al. [10] for the polymerization of substituted phenyl glycidyl ethers. As is obvious from Table 1, for the polymerization of HEPBP catalyzed by tert-amines the molecular weight of poly(HEPBP) corresponds to an average degree of polymerization of about 50. Such an increase in the value of the degree of polymerization is hardly to be explained by a reduction of the transfer constant. However, it may be easily explained by the existence of Reactions (6a) and (7a).

In the reaction scheme a transfer to the unsaturated alcohol $R'OH$ may also be taken into account:



The secondary alcoholic groups in the products A_1 , the acidity of which is lower than that of unsaturated alcohol, are not likely to take a significant part in the transfer reactions. For the polymerization of HEPBP catalyzed by tert-amines, no cross-linked polymer was observed among the products, and this indicates that the extent of the reactions of the secondary alcoholic groups is negligible. The course of these reactions depends on the selectivity of the catalyst used [29, 30] and is also evidently dependent on the acidity of phenol.

During polymerization in a steady-state, thermal decomposition of the catalytic center must proceed in some other way than as expressed by equilibrium Eq. (4). This decomposition might obey



By the decay of the ion-pair, tert-amine is liberated from the cation and unsaturated alcohol regenerates while the anion reacts with the free proton produced by the decay of cation in a chain-breaking reaction. Thus the bifunctional product A_1 is formed again. This product can react in an arbitrary reaction according to Eqs. (6a) and (7a). A similar kind of decomposition was suggested by Pirozhnaya [11]. By this reaction mechanism it is possible to explain the increase in the content of unsaturated groups which was observed during the polymerization of epoxide compounds [9, 11].

It ensues from the above scheme that the polymerization of HEPBP catalyzed by tert-amines differs from the polymerization of other epoxide compounds. While the epoxide group polymerizes in the case of other epoxide compounds, the growth reactions taking place during the polymerization of HEPBP represent a sequence of consecutive reactions of epoxide groups and hydrogen-bonded phenolic groups. A phenoxyl anion is formed by an ionic mechanism. This anion opens the epoxide ring with the formation of an alkoxide anion which is stabilized by the proton-transfer of the phenolic group. Since a bifunctional species arises again in the transfer reactions, the chain grows in the reactions which follow and the average polymerization degree is increased in comparison with a polymerization of other epoxides.

The reactions of phenolic groups taking place during the polymerization of HEPBP explain why the polymers prepared from HEPBP in the presence of tert-amines as catalysts either

show no stabilizing efficiency or a reduced stabilizing efficiency [1] in the case of polymerization with a smaller amount of phthalic anhydride.

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