

Polymerization of Epoxides in the Presence of Tertiary Amino Alcohols

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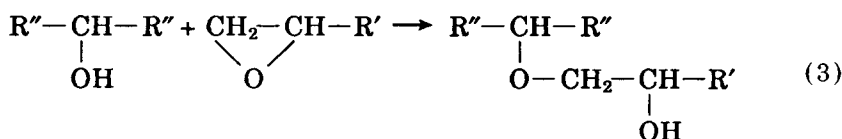
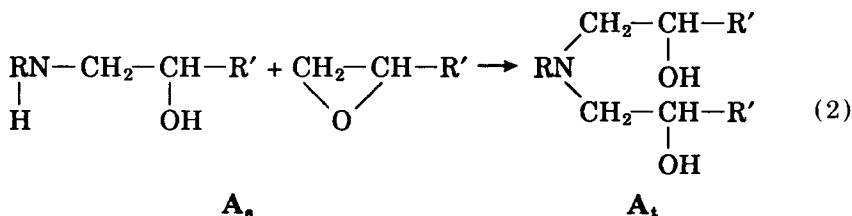
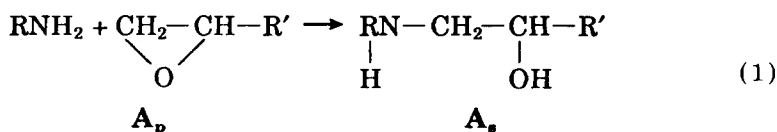
Synopsis

Polymerizations of phenyl glycidyl ether (PGE) and the diglycidyl ether of Bisphenol A (DGEBA) were initiated with tertiary amino alcohols. The reaction was followed by means of HPLC and IR spectroscopy. The main products isolated from the reaction mixture were identified by using mass spectrometry. The sol fraction and the critical conversion at the gel point were determined for the crosslinking polymerization of DGEBA.

Three series of oligomers arise from three initiating centers during the polymerization of PGE. In addition to the amino alcohol—a product of the secondary amine addition to the epoxy group—the phenol arising in the reaction mixture also acts as an initiator. The third oligomer series propagates by an anionic mechanism from a quaternary ammonium base originating from the reaction of PGE with the amino alcohol. Formation of the new initiating centers during the reaction results in a decrease in the molecular weight of the polymer relative to the value predicted from the amount of initiator initially added. The relative content of products of the particular oligomeric series in the reaction mixture depends on temperature and on the concentration of the initiator.

INTRODUCTION

The following reactions take place during curing of epoxides with amines:



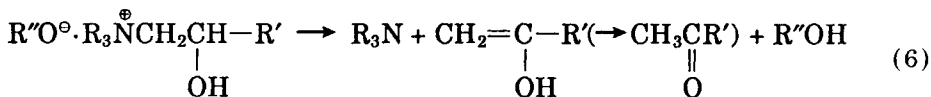
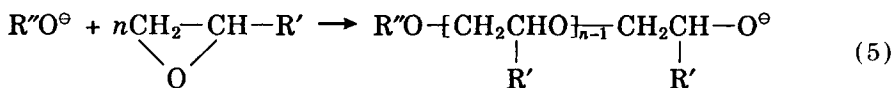
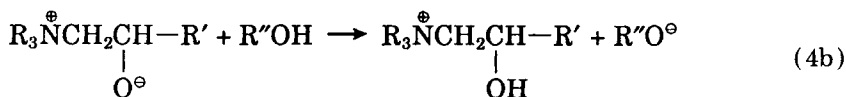
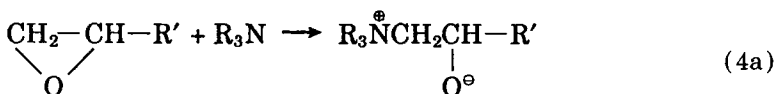
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where A_p , A_s , and A_t are, respectively, the primary, secondary, and tertiary amines.

The addition of an amine to the epoxy ring [eqs. (1) and (2)] is, in the absence of a catalyst, substantially faster than the polyetherification or homopolymerization of an epoxide [eq. (3)]. In the literature, etherification is usually considered as the reaction of an epoxide with an OH group and homopolymerization is regarded as the anionic polymerization of an epoxide. In this paper, the term polymerization involves both these reactions. The build-up of the network structure is mainly brought about by reactions (1) and (2). The proportion of epoxide chain growth polymerization in the total reaction mechanism during curing depends on the structure of the amine and epoxide and on the catalyst, molar ratio of amine to epoxide, and temperature. The amount of polymerization is considerable in systems with an excess of epoxide and in curing at higher temperature (over 150°C). Lewis acids (e.g., BF_3 -amine complexes¹⁻³) and tertiary amines⁴⁻⁸ are effective catalysts of the polymerization.

The mechanism of tertiary amine catalysis of epoxide polymerization is very complex and has been discussed in detail in reviews by Rozenberg⁶ and Fedtke.⁷ Equations (4)–(6) present a description of the reaction paths. Traces of a proton donor compound are likely necessary to initiate the anionic polymerization of the epoxide group [eqs. (4) and (5)]. Termination occurs, e.g., by splitting of a bond, which results in the formation of oligomers with a double bond [eq. (6)].



Excess of epoxide is often employed in systems of practical interest; consequently, the knowledge of etherification or homopolymerization is important. Inclusion of etherification into the theory of network formation⁹⁻¹³ is necessary for a theoretical calculation of the build-up of the polymer structure. So far, these theoretical approaches have assumed a simple etherification mechanism. The formation of an ether bond is considered either as a random stepwise reaction of epoxy and OH groups, or as a reaction initiated by the aminoalcohols formed in steps (1) and (2).

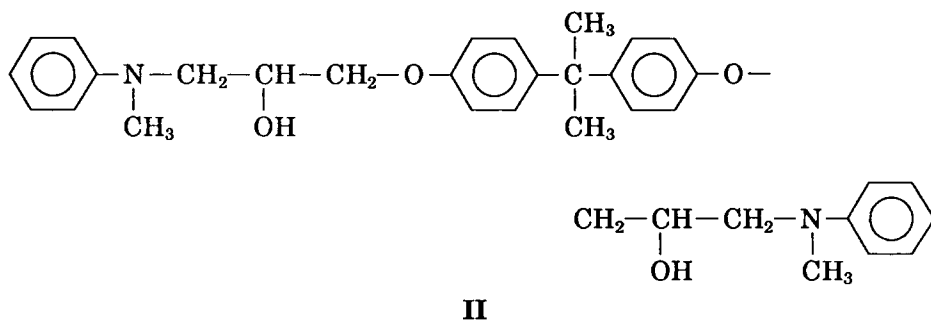
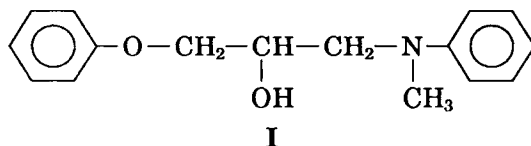
The goal of this article is to elucidate the polymerization mechanism of epoxide groups during the cure of epoxy resins with primary amines. The influence of reaction conditions on the course of polymerization and structure of homopolymers was another object of the study. Usually no catalyst is used to

crosslink epoxides with amines, because both the amine-epoxide addition reaction and the epoxide polymerization are catalyzed by the amine-epoxide reaction products.

It is known^{7,8,14} that the tertiary amino alcohol formed by reaction (2) is a more effective catalyst for epoxide polymerization than is a tertiary amine. Therefore, we were engaged in the study of formation of ether bonds from epoxides initiated by the tertiary amino alcohol.

We first studied the polymerization mechanism of the model system—phenylglycidyl ether (PGE)—in the presence of the initiator 1-(*N*-methylanilino)-3-phenoxy-2-propanol (**I**). The influence of the reaction temperature and concentration of the catalyst on the course of the reaction was determined. The reaction was followed by means of liquid chromatography (HPLC) and IR spectroscopy. Mass spectrometry was used to identify the products. Žorina et al.¹⁴ had studied the same system. However, she was interested only in the overall kinetics and not in the reaction mechanism.

The second part of our work concerns the study of network formation during the polymerization of difunctional epoxide—diglycidyl ether of Bisphenol A (DGEBA) in the presence of the tertiary aminoalcohols **I** or 2,2-bis [4-(3-(*N*-methylanilino)-2-hydroxypropoxy)phenyl]propane (**II**).



EXPERIMENTAL

Diglycidyl ether of Bisphenol A was recrystallized from a 4 : 1 methanol : acetone mixture. The epoxy equivalent (171 g/mol), which corresponds to 99.4% purity of DGEBA, was determined by titration. The purity of phenylglycidyl ether (PGE) (Fluka) was 98% by HPLC analysis. Tertiary aminoalcohols **I** and **II** were prepared by the reaction of an equimolar mixture of PGE with *N*-methylaniline (NMA) at 110°C for 18 h and DGEBA with NMA in the molar ratio 1 : 2 at 110°C for 12 h. Their purity was 92 and 98%, respectively (HPLC).

PGE was polymerized without any solvent in the presence of 5–30 mol % of the catalyst **I** at 140–170°C. Reactions were performed in sealed ampoules under nitrogen and samples were analyzed by HPLC and IR spectroscopy. The

reaction products corresponding to the HPLC peaks P_1 , P_2 , and P_3 (see below) were isolated from the reaction mixture by semipreparative HPLC and identified by mass spectrometry.

The content of epoxy groups in reaction systems containing DGEBA was determined by means of IR spectroscopy using the band at 914 cm^{-1} . Samples were measured in dimethylformamide solution or in KBr pellets with a Perkin-Elmer 580 B spectrometer. The critical conversion of the epoxy groups, α_c , corresponds to the conversion at the reaction time, t_c , when formation of a gel sets in. The time, t_c , was determined by an extrapolation of the reaction time dependence of the sol fraction w_s to a w_s value of 1 (cf. Fig. 8, later—hatched area). The sol fraction was determined by extraction of a sample with dimethylformamide.

HPLC analyses were performed on a Spectra physics SP 8100 chromatograph with a CGC ($150 \times 3\text{ mm}$) glass column packed with the reverse phase Separon C18; particle size was $5\text{ }\mu\text{m}$. The samples were injected ($5\text{ }\mu\text{L}$) as ca 0.2% solutions in methanol. The analysis was performed by gradient elution with a methanol–water mixture starting with 40% and ending with 100% methanol at a flow rate of 0.5 mL/min . UV detection was used at the wavelengths $\lambda = 254$ and/or 270 nm . The reaction products were isolated by repeated separation in a column ($250 \times 8\text{ mm}$) packed with the reverse phase Separon C18 of particle size $10\text{ }\mu\text{m}$. The fractions were detected at $\lambda = 270\text{ nm}$.

Identification of the products was performed by means of an AEI MS 902 mass spectrometer with direct inlet, source temperature 160°C , ionization energy 70 eV , emission 100 mA , and accelerating voltage 6 kV .

Molecular weight, M_n , was determined by vapor pressure osmometry (VPO) using the apparatus Hitachi Perkin-Elmer Model 115. Benzil was used as a low-molecular-weight calibration standard.

RESULTS AND DISCUSSION

In the polymerization of PGE, amino alcohol **I** serves as an initiator and remains in the reaction mixture partly unreacted even at full conversion of epoxy groups (cf. Fig. 1). Formation of the three main products during the reaction was followed by HPLC. They are characterized by the HPLC peaks P_1 , P_2 , and P_3 (see Fig. 2). Furthermore, a small amount of phenol was detected in the reaction mixture (cf. Fig. 2) especially at higher temperatures. IR spectroscopy reveals an increase in the content of OH groups (band at $3400\text{--}3500\text{ cm}^{-1}$), ethers (1120 cm^{-1}), and C=C bonds (1640 and 1670 cm^{-1}), and the formation of traces of C=O (1720 cm^{-1}) during the reaction. The concentration of OH groups and C=C bonds increases with increasing temperature and concentration of the initiator.

The course of the polymerization and the structure of oligomers formed are determined primarily by the mechanisms of initiation, transfer and termination. The approximate expression (7) holds for the number average degree of polymerization P_n of the polymer formed. This assumes a simple "living" polymerization mechanism of initiation without transfer or termination. In addition, propagation must not be much faster than initiation:

$$P_n \sim \Delta C_E / \Delta C_I \quad (7)$$

where $\Delta C_E = C_E^0 - C_E$ and $\Delta C_I = C_I^0 - C_I$ are changes in the concentration of the epoxide and initiator, respectively, while C_E^0 and C_I^0 are the respective initial concentrations.

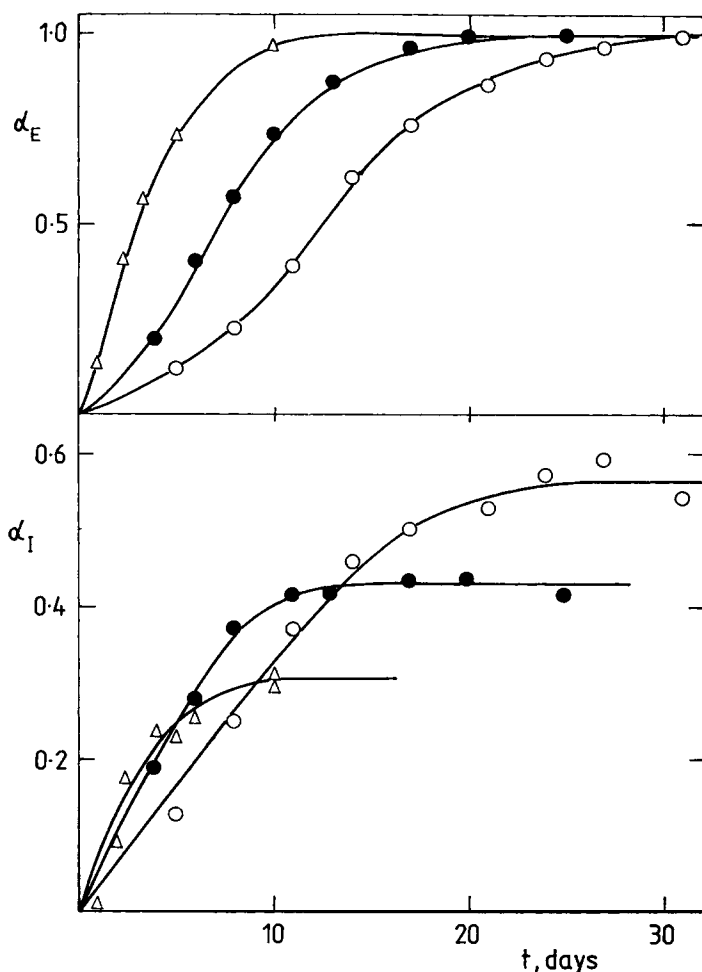


Fig. 1. Dependence of conversion on time for: (a) PGE (α_E), (b) amino alcohol I (α_I) in the polymerization of PGE in the presence of I; $T = 140^\circ\text{C}$, $C_I^0/C_E^0 = 0.05$ (○), 0.10 (●), 0.30 (△); C_I^0 , C_E^0 = initial molar concentration of I and PGE, respectively.

The ratio of the decrease in the concentration of PGE to the decrease in the concentration of catalyst I during polymerization as a function of conversion of PGE, is shown in Figure 3. One can see the influence of temperature and concentration of the initiator on the course of polymerization. The ratio $\Delta C_E / \Delta C_I$ characterizes the number of PGE molecules that have reacted with respect to one reacted molecule of I. This ratio increases with decreasing content of initiator, and surprisingly also with increasing temperature. It reaches the value 10–35 at full conversion of PGE, which would correspond to the molecular mass $M_n \sim 1500$ –5000. The determination of M_n by VPO, however, reveals a significantly lower molecular mass of the reaction mixture at full conversion of PGE; $M_n \sim 400$. Berger and Lohse⁸ also found very low values of P_n in the polymerization of cresylglycidyl ether initiated with benzyldimethylamine (BDMA); $P_n < 4.0$. The presence of an alcohol resulted in a further decrease in P_n .

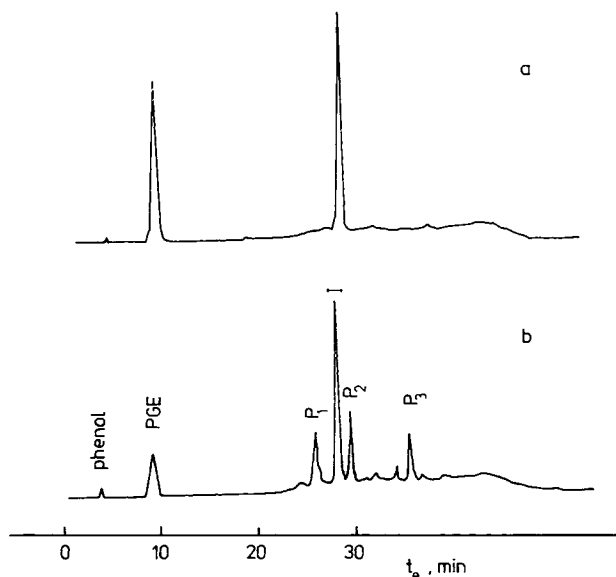
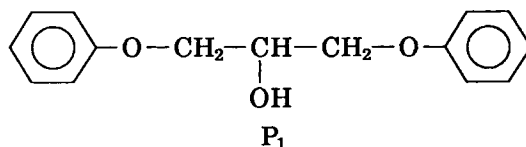


Fig. 2. HPLC record of the reaction mixture of PGE with I: (a) reaction time $t = 0$, (b) $t = 5$ days. $C_I^0/C_E^0 = 0.3$, $T = 150^\circ\text{C}$. t_e = time of elution, detection at $\lambda = 270$ nm.

The ratio of areas of HPLC peaks P_1 , P_2 , and P_3 for the given reaction mixture depends on the wavelength of UV detection. It was found that the peak P_3 is much more intense and the peaks P_1 , P_2 are weaker in the case of UV detection at 254 nm, compared with detection at 270 nm. UV chromophores --O-- and $\text{--N(CH}_3\text{)--}$ originating from PGE and the initiator, respectively, are expected in the oligomers formed in addition to weak C=C chromophores. While the UV spectrum of PGE shows a maximum at 270 nm, the maximum of absorption by the initiator is located at 254 nm (cf. Fig. 4). At 254 nm, one can expect a more intense response for the products containing $\text{--N(CH}_3\text{)--}$, and at 270 nm for the products with the chromophore --O-- only. However, this conclusion holds only for the shortest oligomers, in which the contribution by the initiating group is not negligible. Consequently, it is likely that the product P_3 contains the structural group $\text{--N(CH}_3\text{)--}$, i.e., involves a molecule of the initiator in contrast to the products P_1 and P_2 .

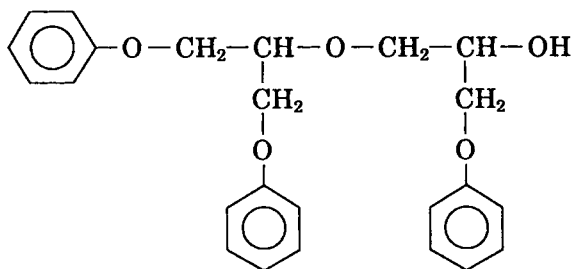
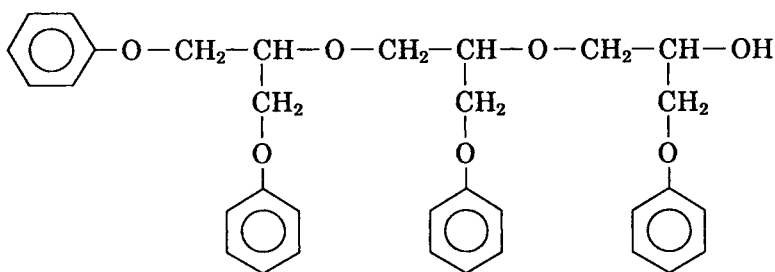
Fractions of P_1 , P_2 , and P_3 were isolated and identified by mass spectrometry.

The spectrum of the fraction P_1 shows the molecular ion $M^+ = 244$ and intense peaks of fragments with $m/z = 150, 133, 94$ and 77 . The structure P_1 corresponds to this fragmentation. Its formation was shown earlier.^{7,8}

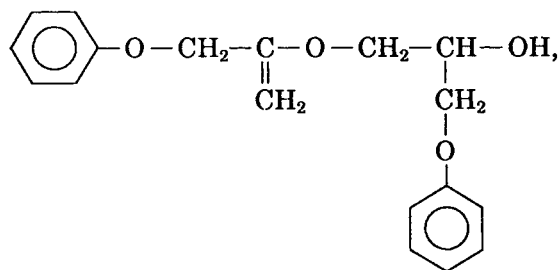


The appearance of P_1 in the polymerization of PGE was shown by comparing an HPLC scan of a mixture PGE/initiator (Fig. 5a) with an HPLC scan of a reaction mixture of equimolar quantities of PGE and phenol containing 1,3-

diphenoxy-2-propanol (P_1) (cf. Fig. 5b). Also, higher etherification products of the PGE-phenol reaction, P_{11} and P_{12} , were found in small amounts in the polymerization mixture.

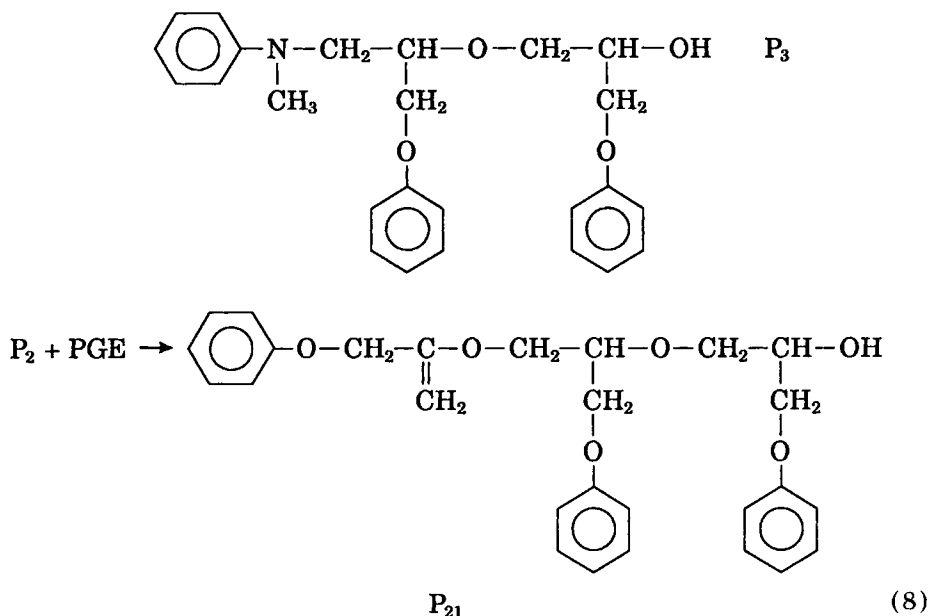
 P_{11}  P_{12}

The following fragmentation was determined for the fraction of P_2 : molecular ion $M^+ = 300$ and fragments $m/z = 193, 150, 133, 107, 94$ and 77 . The most probable structure conforming to this fragmentation is:

 P_2

which is also in accordance with the literature.^{1,6-8}

The isolated fraction of P_3 represents a mixture of two compounds with the molecular ions $M^+ = 450$ and 407 . These ions are not derived from the same compound, because the relative intensities of the peaks change with time, temperature and ionizing energy. The spectrum has the following fragmentation of ions; $m/z = 223, 205, 193, 163, 149, 120, 107, 94$, and 77 . We assume that the structure of P_3 , formed by the reaction of PGE with the initiator, corresponds to the molecular ion $M^+ = 407$. The molecular ion $M^+ = 450$ is assigned to the structure of P_{21} [see eq. (8)]:



The suggested structures are in agreement with the finding that P_3 contains a molecule of the initiator in contrast to the products P_1 and P_2 . Chromatographic peaks P_1 and P_2 were observed even in the polymerization of PGE catalyzed with BDMA in the absence of **I**.

The relative ratio of concentrations of these three products in the reaction mixture strongly depends on the reaction temperature and concentration of the initiator, as is obvious from Figures 6 and 7. Only a relative content of products, characterized by the area of the chromatographic peaks, is given, because a quantitative calibration is not available. The figures show the dependence of the areas of the HPLC peaks P_1 , P_2 , and P_3 on conversion of PGE during polymerization. An increase in the reaction temperature from 140 to 170°C promotes formation of the P_1 product, while the content of P_3 decreases (cf. Fig. 6). On the other hand, formation of P_2 especially is enhanced by an increase in the concentration of the initiator from 5 to 30 mol% with respect to PGE (Fig. 7).

The three main products are already detectable at the beginning of the reaction. Therefore, we suppose the formation of three active centers that initiate the propagation of three series of the oligomers P_{1n} , P_{2n} and P_{3n} according to Scheme 1 (cf. Ref. 7). This scheme does not show the detailed path of the reaction but only the intermediate products that were identified. It is likely that the mechanism is anionic and that the polymerization is initiated by alkoxide ions.

The results reveal the presence of phenol in the reaction mixture, formation of which was interpreted by Fedtke⁷ as being a result of the thermal splitting of PGE catalyzed with a tertiary amine (acrolein being the other product). However, the occurrence of phenol in the reaction mixture can be explained also, e.g., by its splitting off from some of the reaction products. The coproduct (possibly acrolein) is indicated as X in the scheme. Phenol acts as an initiator of the polymerization of PGE, resulting in the formation of the product P_1 and

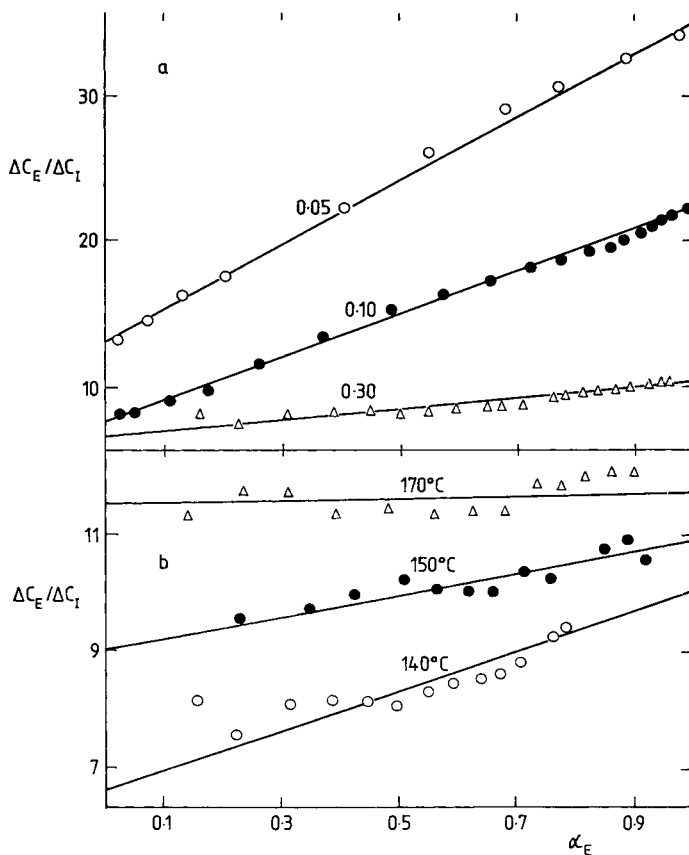


Fig. 3. Dependence of the decrease in relative concentration of PGE and amino alcohol I ($\Delta C_E / \Delta C_I$) on the conversion α_E of PGE during the polymerization: (a) $T = 140^\circ\text{C}$, $C_I^0 / C_E^0 = 0.05$ (○), 0.10 (●), 0.30 (Δ); (b) $C_I^0 / C_E^0 = 0.30$, $T = 140^\circ\text{C}$ (○), 150°C (●), 170°C (Δ).

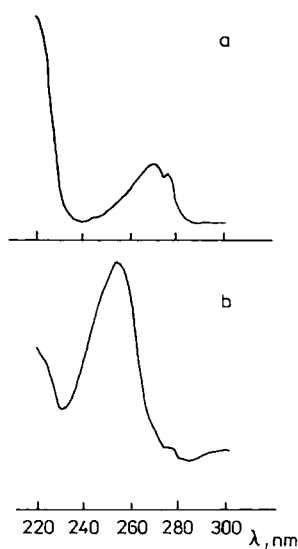


Fig. 4. UV spectrum of (a) PGE and (b) amino alcohol I.

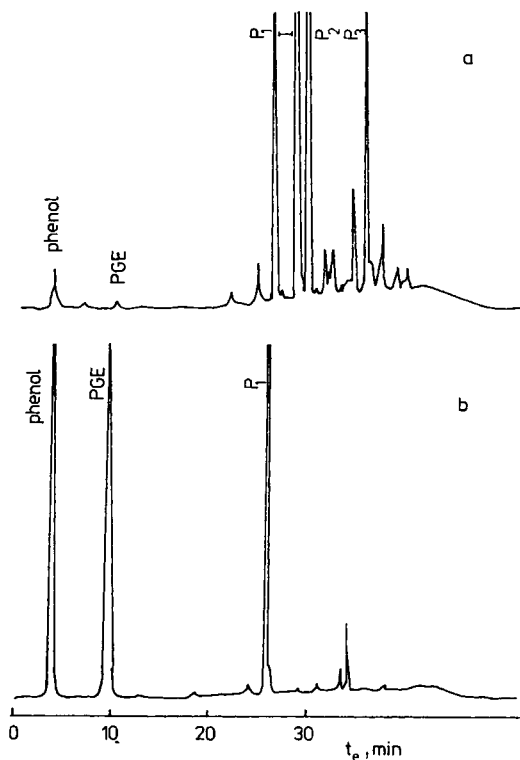


Fig. 5. HPLC scans of the reaction mixtures heated at 170°C for time t : (a) PGE + **I** = 1 : 0.3; t = 4 days, (b) PGE + phenol = 1 : 1; t = 4 h; detection at λ = 270 nm.

the series of oligomers P_{1n} . This series corresponds to oligomers of the B type described by Fedtke⁷ for the polymerization of an epoxide by BDMA. The product P_2 may possibly result from the formation of a quaternary ammonium base by the reaction of PGE with amino alcohol **I**, followed by an elimination termination^{1,6,7} (cf. Scheme 1). It does not arise from heating the mixture of PGE with phenol or PGE alone. The series P_{2n} then propagates by anionic polymerization. This series corresponds to the oligomers of the A type for the polymerization of PGE by BDMA according to Fedtke.⁷ The product P_3 and the series P_{3n} arise by a direct reaction of PGE with the initiator.

The experimental results reveal that the formation of phenol is promoted at elevated temperatures. P_1 and the oligomers P_{1n} are the dominant products under these conditions, because PGE then reacts faster with phenol to form P_1 than with **I** to give rise to P_3 . On the contrary, P_2 and the oligomers P_{2n} predominate in the reaction mixture with higher concentrations of the initiator.

Molecular weight M_n of a system measured by VPO was found to be below that predicted by eq. (7). This is a result of the existence of additional types of initiation centers and of the increasing content of "initiators" during the reaction. In this case, $\Delta C_E/\Delta C_I$ does not characterize the kinetic length of a chain, because PGE is consumed not only by propagation, but also by the formation of new active centers. The increase in $\Delta C_E/\Delta C_I$ with increasing temperature [cf. Fig. 3(b)] indicates a higher extent of side reactions of PGE to form the initiating centers at higher temperature.

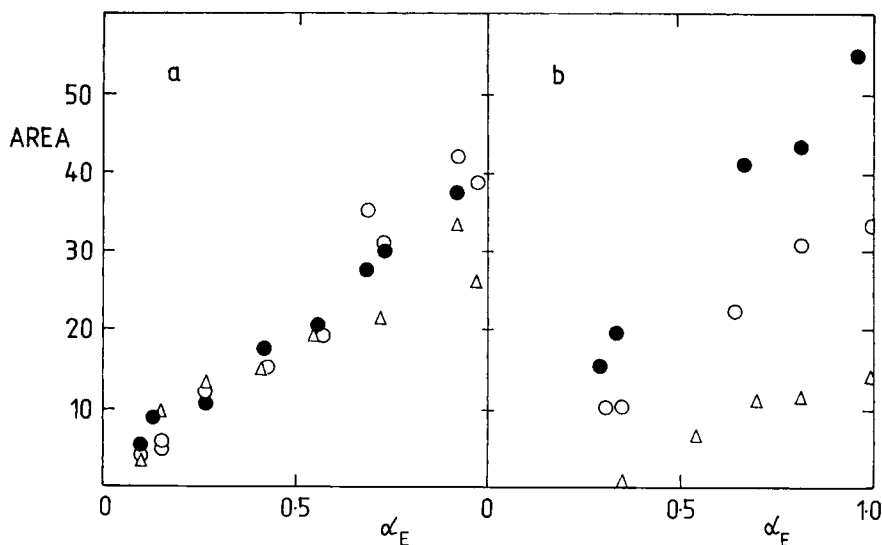


Fig. 6. Area of the HPLC peaks P_1 , P_2 , and P_3 as a function of PGE conversion α_E , $C_1^0/C_E^0 = 0.30$: (a) $T = 140^\circ\text{C}$, (b) $T = 170^\circ\text{C}$; (●) P_1 , (○) P_2 , (△) P_3 , detection at $\lambda = 270\text{ nm}$.

A branched and crosslinked structure is formed by the polymerization of a difunctional epoxide. Buildup of a network depends on the polymerization mechanism. Therefore, we studied the polymerization of DGEBA and determined both the sol fraction, w_s , of samples during polymerization and the critical conversion of the epoxy groups, α_c . The critical conversion corresponds to the conversion at the instant of gel formation, and the critical region is indicated

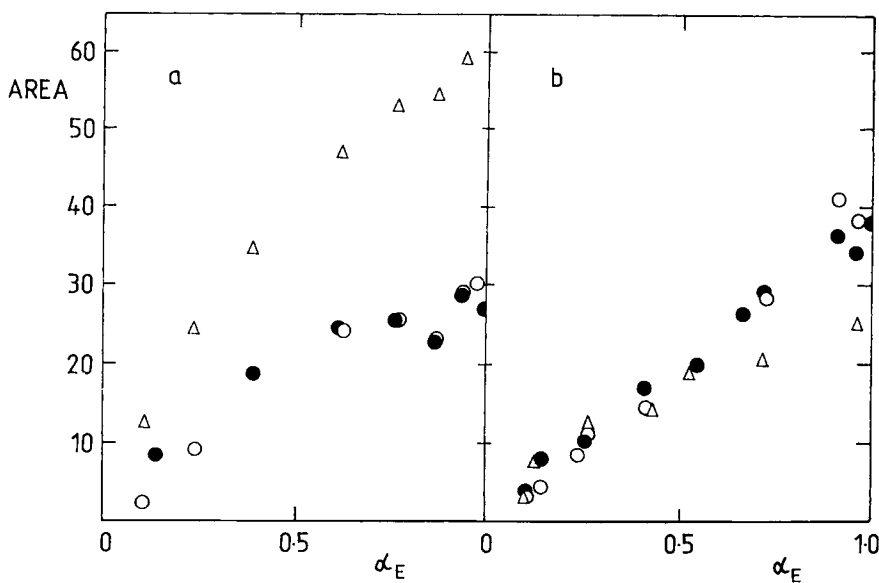


Fig. 7. Area of the HPLC peaks P_1 , P_2 , and P_3 as a function of PGE conversion at 140°C : (a) $C_1^0/C_E^0 = 0.05$, (b) $C_1^0/C_E^0 = 0.30$; (●) P_1 , (○) P_2 , (△) P_3 , detection at $\lambda = 270\text{ nm}$.

in Figure 8 by the hatched area. The reaction was initiated by monofunctional amino alcohol **I** or difunctional initiator **II**. The rate of gel formation rises with increasing concentration of the initiator. Figure 9 shows the dependence of the values of (1) critical conversion and (2) the sol fraction at complete epoxide group conversion, on the relative molar concentration of the initiator with respect to DGEBA, C_I/C_E . It is obvious that α_c and w_s increase with growing concentration of the initiator. The critical conversion and w_s are lower if the difunctional initiator **II** is used, in comparison with a system polymerized with monofunctional **I**. This result is due to the formation of oligomers having doubled molecular weight, in an ideal case, if the difunctional initiator is employed.

The crosslinked samples were analyzed by IR spectroscopy. An increase in the content of OH groups (band at 3480 cm^{-1}) and of C = C bonds (bands at 1640 and 1670 cm^{-1}) was observed during polymerization. The intensity of the bands at 3480 and 1670 cm^{-1} increases with increasing reaction temperature and concentration of the initiator.

The results obtained for PGE and DGEBA are consistent. The decrease in $\Delta C_E/\Delta C_I$ in the polymerization of PGE in the presence of a higher initiator/PGE ratio implies either a decrease in M_n and/or a smaller extent of side reactions of PGE in the initiation stage. The occurrence of values of $\Delta C_E/\Delta C_I$ higher than those predicted confirms a significant extent of formation of new initiation centers during polymerization, resulting in a substantial decrease in molecular weight. The increase in α_c and w_s with increasing concentration of the initiator in the polymerization of DGEBA is consistent with results in the linear polymerization of PGE.

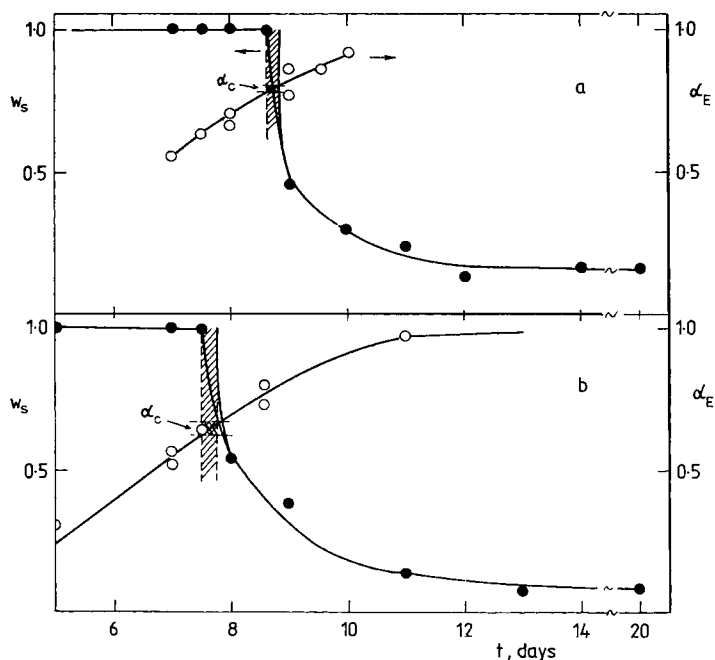


Fig. 8. Sol fraction w_s (●) and degree of epoxy group conversion α_E (○) during the polymerization of DGEBA in the presence of initiator **I** (a) and initiator **II** (b); $T = 140^\circ\text{C}$, $C_I^0/C_E^0 = 0.10$, α_c = critical conversion of the epoxy groups.

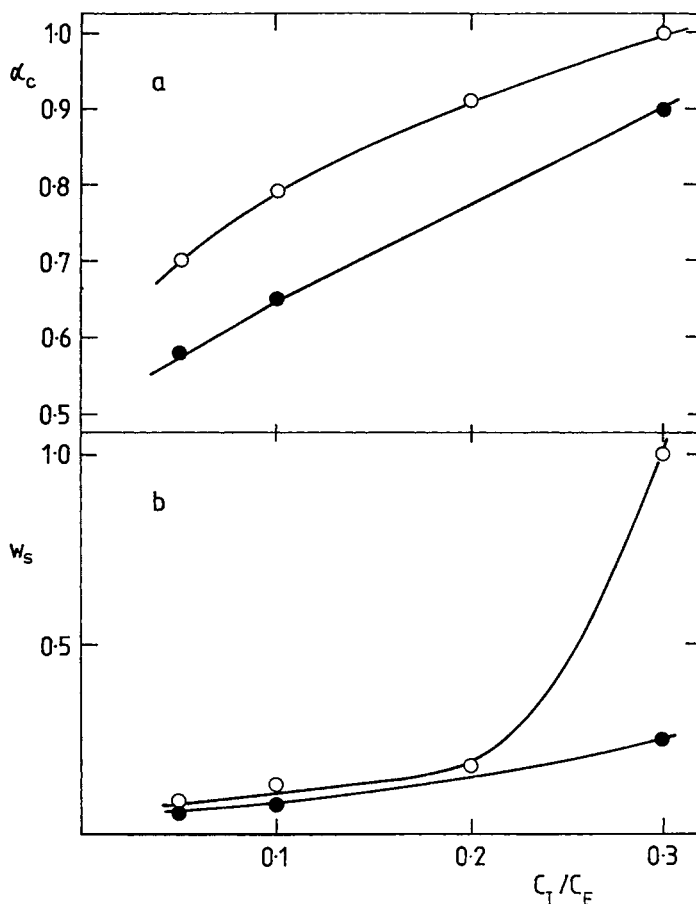


Fig. 9. The critical conversion of the epoxy groups α_c (a) and the sol fraction w_s (b) as a function of the relative concentration of the initiator C_I^0/C_E^0 in the polymerization of DGEBA in the presence of initiator I (○), II (●), $T = 140^\circ\text{C}$.

CONCLUSION

Polymerization of PGE in the presence of tertiary amino alcohol I proceeds by an anionic mechanism and results in the formation of three series of oligomeric products, similarly to polymerization initiated by a tertiary amine.⁷ The series P_{1n} and P_{2n} are typical of the products of polymerization with a tertiary amine, and arise also in initiation by BDMA. P_{1n} oligomers are initiated with phenol or phenolate ion formed in the reaction mixture of PGE with amino alcohol. P_{2n} oligomers derive from a quaternary ammonium intermediate (see Scheme 1). The series P_{3n} is initiated by amino alcohol I. The formation of initiating centers during polymerization is a reason for the very low molecular weights of the oligomers formed. The average molecular weight of the system decreases with increasing temperature and concentration of the initiator, because formation of new initiating centers then becomes more facile.

For the same reason, the sol fraction and the critical conversion in the cross-linking polymerization of DGEBA increase with increasing concentration of the initiator.

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