Polymerization of 3,6-Dibromo-9-(2,3-Epoxypropyl)Carbazole with Lewis Acids

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ABSTRACT

The kinetics of polymerization of 3,6-dibromo-9-(2,3-epoxypropyl)carbazole with stannic chloride and boron trifluoride etherate were studied by a microcalorimetric technique. Complex kinetics of the polymerization rate were observed. A spontaneous increase of the reaction rate was recorded after it decreased and after polymerization for some time at the minimal rate. This effect is explained by a change in the mechanism of polymerization. At the high enough degree of conversion, transition from an active chain end mechanism to an activated monomer mechanism takes place.

INTRODUCTION

Because of their high photoconductivity and good film-forming properties, carbazolyl-containing oligoethers, obtained by ionic polymerization of the corresponding epoxides, are of great interest as organic photoconductors [1–3]. In previous work [4], cationic polymerization of 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane (ECOH) was studied by a microcalorimetric technique. This technique is the most suitable method for investigating the kinetics of oligomerization of such monomers. Microcalorimetry measures the reaction rate continuously and directly, independent of the physical state of the sample and requires only one sample for the entire conversion range. The accuracy and sensitivity of this method are better than those achieved with other continuous methods. Microcalorimetry enabled us to observe

the complex kinetics of polymerization of ECOH with Lewis acids. It has been stated [4] that the active species of the final stage of polymerization are different from those of the initial stage. However, the origin of the active centers of the final stage, when acceleration of polymerization occurred, was not established. The aim of this work was to investigate the polymerization of 3,6-dibromo-9-(2,3-epoxypropyl)carbazole (DBEPC) with Lewis acids, which can be represented by the following reaction:

the complex kinetics of polymerization of ECOH with Lewis acids. It has been
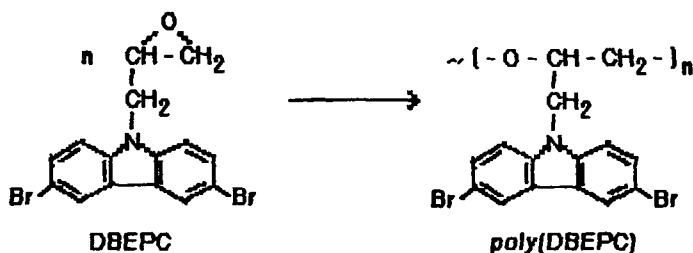
Oligomeric poly(DBEPC) as a photoconductor is superior to its unbrominated counterpart, poly[9-(2,3-epoxypropyl)carbazole], which is a widely used organic photoconductor, as well as to other photoconductive polymers containing unbrominated carbazole [3, 5]. Since the kinetics of polymerization of DBEPC with Lewis acids are similar to those of the polymerization of 9-(2,3-epoxypropyl)carbazole (EPC) ECOH, and other carbazolyl-containing epoxides, the results obtained in this work will be useful in studying the mechanism of catonic polymerization of ether epoxy monomers of this kind.

EXPERIMENTAL

Monomeric DBEPC was synthesized in the Department of Organic Chemistry, Kaunas University of Technology, by bromination of 9-(2,3-epoxypropyl)carbazole with N-bromosuccinimide [6]. It was purified by recrystallization from toluene, mp 141–142°C. EPC (from Biolar, Latvia) was recrystallized twice from ethanol, mp 110–111°C. Polymerization of DBEPC was carried out in 1,2-dichloroethane which was purified by the conventional procedure [7]. Boron trifluoride etherate (BF_3Et_2O) and stannic chloride $(SnCl_4)$ were used as catalysts. BF_3Et_2O was purified by refluxing over calcium hydryde with the following fractional distillation (bp 126–126.5°C). $SnCl_4$ was dried over P_2O_5, then distilled (bp 113–114°C). Only fresh samples of catalysts were used for the initiation of polymerization.

The kinetics of DBEPC polymerization were investigated by microcalorimetry under isothermal conditions by using a differential automatic microcalorimeter DAK 1-1A (Chernogolovka, Russia). The total heat of the reaction of polymerization was estimated by integration of the area under the calorimetric curve expressing the heat flow rate versus time function. Integrated heat flow rate versus time curves were transformed into the kinetic curves of polymerization (conversion versus time) by evaluating the heat of polymerization of DBEPC. The value of the heat of polymerization of DBEPC was established from the relation of the total thermal

energy of reaction and the number of moles of converted monomer. The heat of polymerization of DBEPC determined for the system DBEPC-BF$_3$Et$_2$O-1,2-dichloroethane was found to be 95.4 $\pm$ 0.33 kJ·mol^{-1} [8]. Conversion of the monomer was determined by GPC from the relation of the integral area under the elution curves of the oligomer and that of the oligomer plus monomer. A column packed with Sephadex LH-20 gel was used for the GPC experiments, using dimethylformamide as eluent. A method of self-calibration was used to determine the molecular weights and molecular weight distributions (M_w/M_n) of poly(DBEPC). The kinetic parameters of polymerization of DBEPC were determined by the method of optimization of the experiment [9]. The total factor experiment was carried out with respect to three factors ($1/T$, lg M, lg c) connected by the linear function

$$\lg W = (\lg A - E/R)(1/T) + x \lg M + y \lg c$$

where W is the initial polymerization rate, A and E are the constants, R is the gas constant, T is the absolute temperature, M is the initial concentration of a monomer, c is the initial concentration of a catalyst, x is the reaction order with respect to the concentration of monomer, and y is the reaction order with respect to the concentration of catalyst.

RESULTS AND DISCUSSION

Investigation of the kinetics of polymerization of DBEPC with BF$_3$Et$_2$O and SnCl$_4$ revealed that initiation occurs instantaneously. However, shortly after initiation a large decrease in the polymerization rate was observed. Such a quick decrease in the polymerization rate obviously cannot be caused only by the decrease in the concentration of the monomer. Deviation from a linear dependence of the logarithm of the ratio of initial and present concentrations of DBEPC on time indicates an intensive termination process (Fig. 1).

As the temperature increases from 30 to 60°C, the reaction rate increases 1.34–1.38 times for initiation with BF$_3$Et$_2$O and 1.30–1.34 times for initiation with SnCl$_4$. As the temperature increases, the molecular weight decreases slightly, and the ratio $N = \overline{M}_w/\overline{M}_n$ is almost constant (see Table 1).

The low degree of polymerization (low molecular weight) is not a result of high concentration of catalyst, because when the ratio C_{cat}/C_m decreases, the molecular weight increases slightly and conversion decreases considerably (see Table 2).

When a low concentration ratio of a catalyst and the monomer was used ($c = 0.0125$ mol/L, $M = 0.4$ mol/L), complete cessation of polymerization was observed before conversion of the monomer reached 50%. In the case of initiation with SnCl$_4$ the conversion limit was a little higher. SnCl$_4$ also gave a higher initial polymerization rate relative to that observed with BF$_3$Et$_2$O. The introduction of a new quantity of catalyst after the cessation of polymerization leads to resumption of the reaction, which shows that deactivation of active centers is the reason for the termination of polymerization. When the monomer/catalyst concentration ratio is above a certain limit (~ 0.125), high conversion of DBEPC (60–90%) can be easily achieved (cf. Fig. 1, Curves 3 and 4), and no complete cessation of polymerization is observed. After a certain period of time (the kinetics of change of the polymeriza-
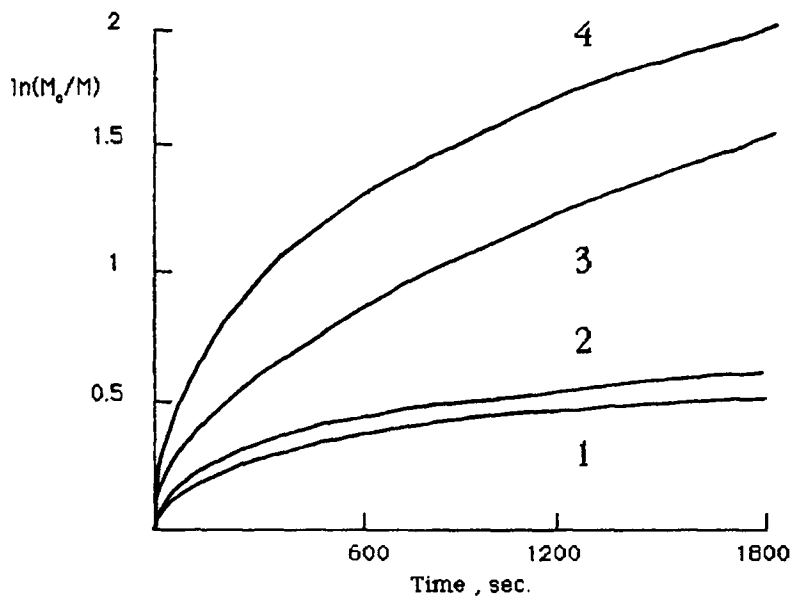
FIG. 1. Dependence of the logarithm of the ratio of initial and moment concentrations of DBEPC on the time for polymerization of DBEPC with BF_3Et_2O (Curves 1 and 3) and $SnCl_4$ (Curves 2 and 4) at 60°C. Concentration of catalysts: 0.0125 (Curves 1 and 2) and 0.05 (Curves 3 and 4) mol/L.

TABLE 1.

| | Polymerization[a] temperature, °C | | | |
| | 18 | | 60 | |
Catalyst	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$
BF_3Et_2O	1550	1300	1350	1150
$SnCl_4$	1650	1600	1650	1400

[a]0.4 M DBEPC, 0.05 M catalyst.

TABLE 2.

| | Catalyst | | | |
| | BF_3Et_2O | | $SnCl_4$ | |
Ratio, C_{cat}/C_m[a]	0.125	0.025	0.125	0.025
$\overline{M}_n$	1150	1200	1400	1200
Conversion, %	100	25	100	30

[a]C_m = 0.4 mol/L, 60°C.

tion rate will be discussed in more detail below), complete conversion of the monomer can be achieved.

The following range of parameters was chosen to obtain the quantitative dependence of the initial polymerization rate upon these parameters: Temperature from 30 to 60°C, concentration of DBEPC from 0.1 to 0.4 mol/L, concentration of catalyst from 0.0125 to 0.05 mol/L. For DBEPC polymerization with BF_3Et_2O under the above described conditions, this dependence can be presented by the following equation:

$$W = K_1 M^{0.592} c^{0.637} \qquad mol \cdot L^{-1} \cdot s^{-1}$$

where $K_1 = 10^{-0.0798-(448.7)/T}$.

For polymerization with $SnCl_4$, this equation is

$$W = K_2 M^{0.592} c^{0.703} \qquad mol \cdot L^{-1} \cdot s^{-1}$$

where $K_2 = 10^{-0.0932-(405.7)/T}$. At 45°C, $K_1 = 0.0323$, $K_2 = 0.0428$.

It is evident that $SnCl_4$ is a more effective catalyst of this reaction. In both cases the reaction order with respect to monomer and catalyst are lower than 1. This indicates the complexity of processes of the generation of active centers as well as of chain growth.

Initiation and propagation apparently occur via the formation of active centers which have the structure of amphions [10]:
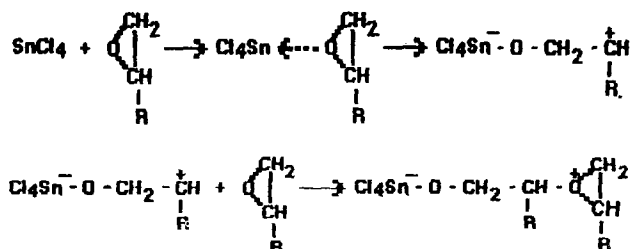
where R is methylene-9-(3,6-dibromocarbazolyl).

Active centers with the structure of oxonium salts can also be formed via autoionization of the Lewis acid [11]:
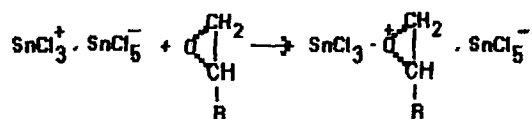
As was mentioned above, when the c/M ratio is high enough, no cessation of polymerization is observed and complete conversion of the monomer can be achieved. Figure 2 shows the change of the reaction rate during the process of DBEPC polymerization with BF_3Et_2O ($c/M = 0.125$). A similar behavior of the polymerization rate was observed in polymerization with $SnCl_4$ at similar conditions. With respect to a change of the reaction rate, polymerization of DBEPC can be roughly divided into two periods: a fast one and a slow one. The fast period is very short, and the microcalorimetric technique enables a dramatic decrease of the
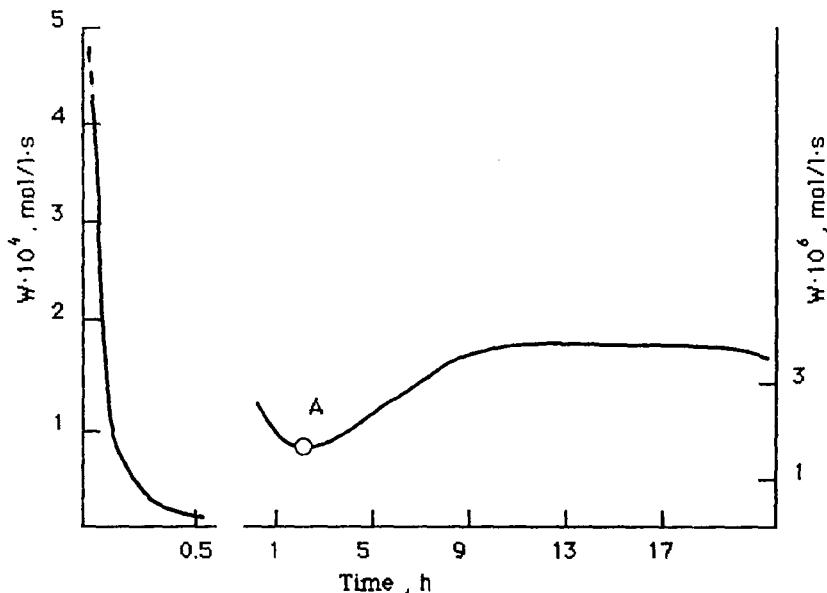
FIG. 2.   Rate of polymerization versus time curve for the polymerization of DBEPC in 1,2-dichloroethane with BF_3Et_2O at 60°C. $[DBEPC]_0 = 0.4$ mol/L, $[BF_3Et_2O]_0 = 0.05$ mol/L.

polymerization rate up to a certain minimal value to be recorded. The period of slow polymerization can be roughly divided into four stages. The minimal polymerization rate stage lasts for approximately 0.5–1 hour, then a gradual increase of the polymerization rate occurs (Stage 2). After reaching a definite value, the polymerization rate remains almost constant for 15–30 hours (Stage 3), followed by a decrease of the polymerization rate (Stage 4) which is determined by exhaustion of the monomer. A similar behavior of the polymerization rate was observed for the polymerization of ECOH with Lewis acids {4}. However, the reasons of such complex kinetics of polymerization were not completely disclosed. It should be noted that the increase of polymerization rate in the slow period depends on temperature. With a decrease of the temperature of reaction, this autoacceleration effect is less clearly expressed. The temperature dependence of this effect is more distinct in the polymerization with BF_3Et_2O than in the polymerization with $SnCl_4$.

Increases of molecular weight and molecular weight distribution of the oligomer were observed in Stage 2 (Figs. 3 and 4). It is evident from Fig. 3 that the increase of molecular weight is due to the increase in the high-molecular fraction share. Since the relative share of low-molecular fractions decreases in the period of slow polymerization, it can be presumed that the increase of polymerization rate in Stage 2 is not determined by regeneration of active centers identical to the initial ones. Figure 4 shows that up to a certain monomer conversion, $\overline{M}_n$ remains almost constant, and only after ~ 80% monomer conversion is reached is a linear increase of $\overline{M}_n$ with conversion observed. It should be noted that the onset of the increase of molecular weight of poly(DBEPC) coincides approximately with the onset of the
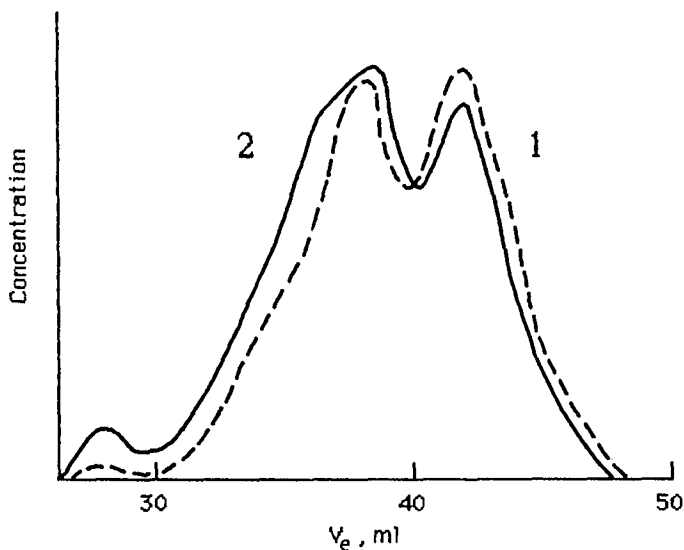
FIG. 3. Normalized elution curves of the reaction mixture of polymerization of DBEPC in 1,2-dichloroethane with $SnCl_4$ at 60°C. (Concentration of the monomer and catalyst as in Fig. 2.) Polymerization time: 2 hours (Curve 1) and 24 hours (Curve 2). Peak of DBEPC is not shown.

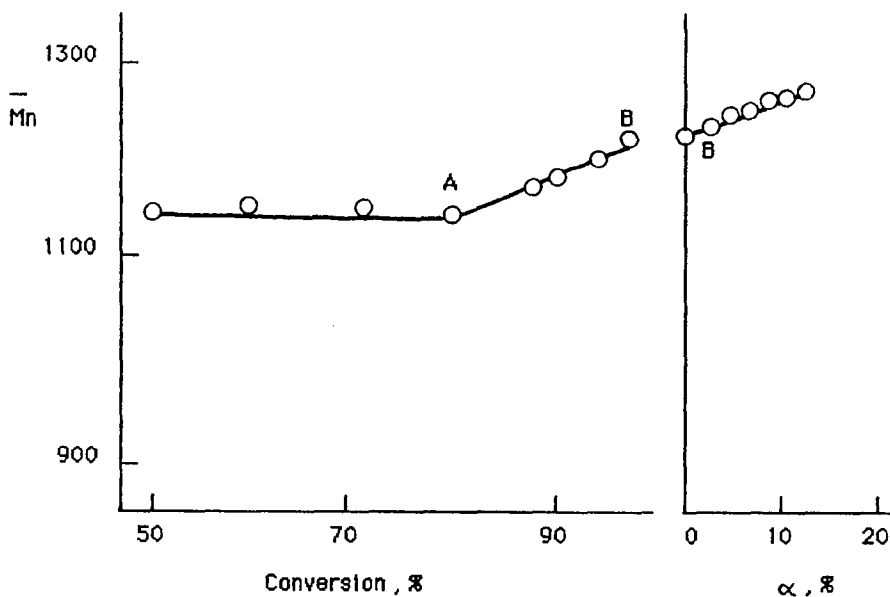FIG. 4. M_n versus conversion curves for the polymerization of DBEPC in 1,2-dichloroethane at 60°C. $[DBEPC]_0 = 0.4 \, mol/L$, $[BF_3Et_2O]_0 = 0.05 \, mol/L$. α is the amount of the newly introduced monomer (% from the converted monomer).

spontaneous increase of the polymerization rate (cf. Point A in Figs. 2 and 4). Figure 4 also shows the dependence of oligomer molecular weight on the amount of monomer introduced into the reaction mixture. The addition of monomer was in small portions (1–2% from the converted monomer every 10–20 minutes). The first new portion of the monomer was added when 97–99% conversion was achieved. It is evident that the addition of monomer after complete conversion was almost reached leads to an increase of $\overline{M}_n$. The function $\overline{M}_n$ versus the amount of added monomer is again close to linear. If a large quantity of the monomer (25–30% from the converted monomer) is introduced into the system as a unit, no increase in molecular weight is observed.

It can be concluded from the above data that a change in the mechanism of polymerization takes place in the slow polymerization period.

It is known that cationic polymerization leads to the formation of a certain amount of hydroxyl-containing molecules. Absorption bands at 3200–3600 cm^{-1}, corresponding to hydroxyl end-groups, have been observed in the IR spectra of poly(DBEPC) obtained in this reaction. We have studied the kinetics of formation of hydroxyl groups in the polymerization of DBEPC with Lewis acids. Figure 5 shows the dependence of the relative concentration of hydroxyl groups in the system on time for the polymerization of DBEPC with BF$_3$Et$_2$O. The conversion versus time curve recorded under the same conditions is also presented. The similar characteristics of the curves in the time period corresponding to fast polymerization is evident. In the slow period of polymerization, where a linear increase of the molecu-
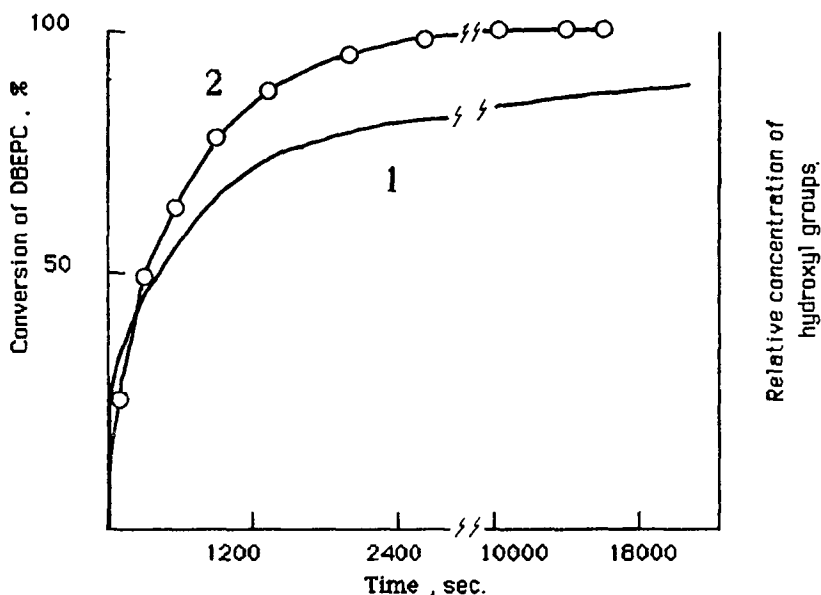

FIG. 5. Conversion versus time (Curve 1) and relative concentration of hydroxyl groups versus time (Curve 2) for the polymerization of DBEPC with BF$_3$Et$_2$O at 60°C. [DBEPC]$_0$ = 0.4 mol/L, [BF$_3$Et$_2$O]$_0$ = 0.5 mol/L.

lar weight was observed, no change of hydroxyl group concentration was recorded. This observation also shows that the mechanism of polymerization in the late stage of the reaction is different from that in the initial stage.

The presence of hydroxyl-containing molecules in the system, as well as the character of the $\overline{M}_n$ function versus conversion in the slow polymerization period, shows that the reaction in this period is by the activated monomer (AM) mechanism described in detail by Polish authors [11–13]. When the instantaneous ratio of concentrations, $[\text{monomer}]_{inst}/[\text{OH}]_{inst}$, becomes low enough, the transition of polymerization from the active chain end (ACE) mechanism to the AM mechanism apparently takes place. Such a transition is possible only when the initial concentration of a catalyst is large enough. A high ratio of the initial concentrations, $[\text{monomer}]_0/[\text{catalyst}]_0$, is presumably necessary to produce a sufficient amount of hydroxyl groups.

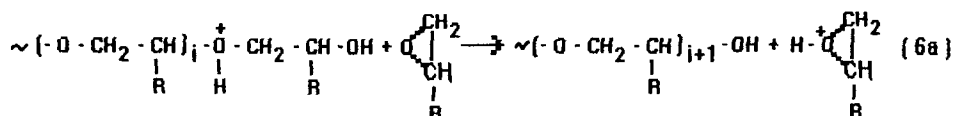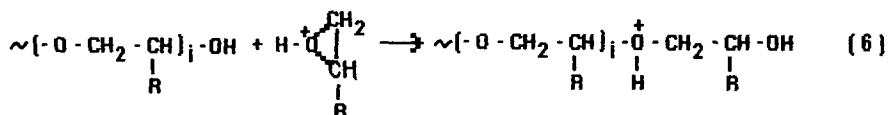Activated (protonated) monomer and hydroxyl end-groups apparently appear in the system owing to a chain transfer reaction with the participating of a monomer by the conventional mechanism of proton transfer from the active centers to the molecules of DBEPC:

(3)

(4)
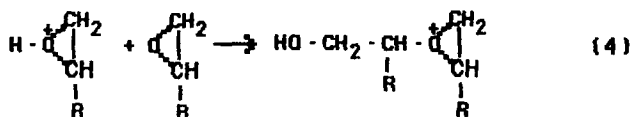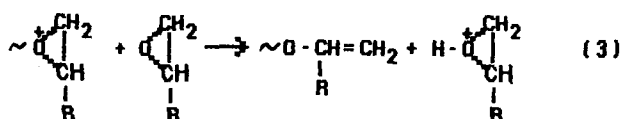
Protonation of the monomer can also take place if the formation of cyclic end-groups occurs by the mechanism proposed by Getmanchuk et al. [14]:
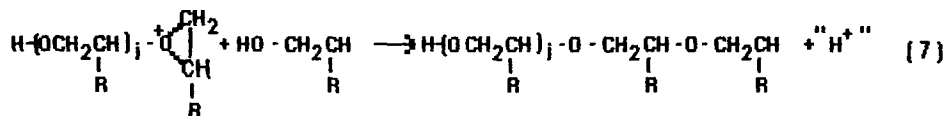
(5)

(5a)
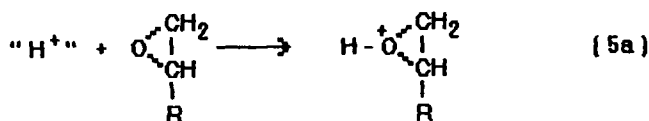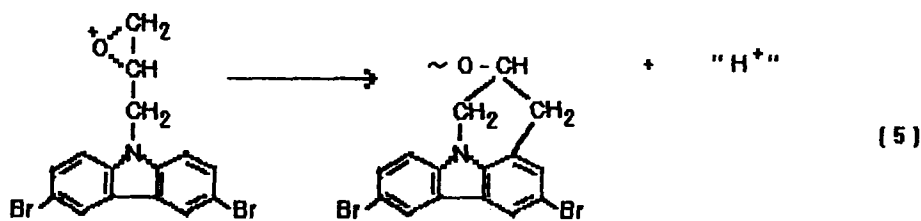
The essence of the AM mechanism lies in the stronger inclination of the protonated monomer to react with a hydroxyl-containing molecule than with a monomer (the nucleophilicity of ROH is higher than that of the epoxy monomer). When the concentration of the hydroxyl-containing molecules is close to the concentration of the monomer, i.e., at a high degree of conversion, the following reaction will compete with Reaction (4):

$$\sim[\text{-}O\text{-}CH_2\text{-}CH]_i\text{-}OH + H\text{-}\overset{+}{\underset{\overset{|}{CH}}{C}}\overset{CH_2}{\underset{\overset{|}{R}}{}} \longrightarrow \sim[\text{-}O\text{-}CH_2\text{-}CH]_i\text{-}\overset{+}{O}\text{-}CH_2\text{-}CH\text{-}OH \qquad (6)$$

$$\sim[\text{-}O\text{-}CH_2\text{-}CH]_i\text{-}\overset{+}{O}\text{-}CH_2\text{-}CH\text{-}OH + C\overset{CH_2}{\underset{\overset{|}{R}}{CH}} \longrightarrow \sim[\text{-}O\text{-}CH_2\text{-}CH]_{i+1}\text{-}OH + H\text{-}\overset{+}{C}\overset{CH_2}{\underset{\overset{|}{R}}{CH}} \qquad (6a)$$

The reproduced protonated monomer can take part in further acts of step-by-step addition of the activated monomer to the macromolecular alcohol. If the instantaneous concentration of the monomer does not exceed the instantaneous concentration of hydroxyl-containing molecules, polymerization will be by a pure AM mechanism. The inclination of DBEPC to cationic polymerization by the AM mechanism is proved by the fact that in the presence of propandiol-1,3, the initial concentration of which is half that of the monomer, the linear dependence of M_n versus conversion is observed from 25% conversion of DBEPC [15]. Obviously the hydroxyl-containing oligomers–monomer system is more complex than the alkanediol–monomer system.

Presumably in the initial fast period of reaction polymerization is by the ACE mechanism where the reactions presented in the Eqs. (3) and (4) play an important part. In the "slow" period of polymerization where the monomer concentration decreases and the concentration of hydroxyl-containing molecules increases, propagation via oxonium ions is problematic and the probability of termination leading to proton expulsion [12] increases:

$$H\text{-}[OCH_2CH]_i\text{-}\overset{+}{C}\overset{CH_2}{\underset{\overset{|}{R}}{CH}} + HO\text{-}CH_2CH \longrightarrow H\text{-}[OCH_2CH]_i\text{-}O\text{-}CH_2CH\text{-}O\text{-}CH_2CH + "H^+" \qquad (7)$$

The increase of the polymerization rate in Stage 2 (cf. Fig. 2) can apparently be partially explained by intensification of the process presented in Eqs. (6) and (7). In addition, the explanation of the autoacceleration of the reaction can be based on the results obtained in the investigation of ethylene oxide polymerization by the AM mechanism [13]. It was established that the rate of addition of protonated monomer to the HO-terminated macromolecule increases with conversion. The assumption was made that the ether groups within a chain can also contribute to chain growth. Obviously, their number increases with conversion.

Polymerization of carbazolyl-containing epoxides by a "pure" AM mechanism

offers new possibilities for the synthesis of telechelic photoconductive oligomers and block co-oligomers distinguished by low glass-transition temperatures and good film-forming properties.

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