

The Kinetics of the Trimethoxyboroxine-Induced Thermal Polymerization of Phenyl Glycidyl Ether

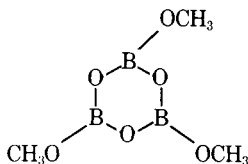
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Synopsis

The kinetics of the bulk thermal polymerization of phenyl glycidyl ether induced by trimethoxyboroxine were investigated. Infrared absorption spectroscopy and gel permeation chromatography were used to follow the course of polymerization, while proton and boron-11 NMR spectroscopy were used to support the kinetic model developed. The postulated mechanism involves a fast-initiated, nonstationary cationic polymerization with five elementary steps, including spontaneous and monomer transfer as well as a termination reaction. The trimethoxyboroxine was found to be incorporated into the structure of the cured polymer. The polymerization was followed at several temperatures and with several ratios of initial concentrations of trimethoxyboroxine to phenyl glycidyl ether.

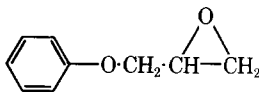
INTRODUCTION

We are interested in studying the high-temperature behavior of diglycidyl ether resins cured with the novel curing agent trimethoxyboroxine (TMB)



TMB

as a follow-up to a prior paper¹ in which the thermal properties of the cured diglycidyl ethers were related to the actual chemical structure of the cured polymer. An understanding of the structure of the polymer produced when the diglycidyl ethers are polymerized with TMB might be obtained by studying the polymerization kinetics. However, the diglycidyl ethers themselves are intractable for such an investigation because of crosslinking reactions which produce a three-dimensional gel network structure early in the cure cycle. Therefore, to simulate the reactions observed with the diglycidyl ethers, we have chosen phenyl glycidyl ether (PGE)



PGE

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as a model compound for investigation. Since the monomer is bifunctional in the case of PGE, crosslinking reactions during polymerization are averted, thereby simplifying analysis of the kinetics.

Our kinetic investigation of the bulk-thermal polymerization of PGE induced by TMB has revealed the following: (i) TMB is not a true catalyst for the polymerization, but becomes covalently bonded into the structure of the polymer itself. (ii) Polymerization occurs by a cationic mechanism. (iii) Only low molecular weight epoxy-based polyethers are obtained. (iv) Approximate rate constants are given which show properties of the model developed to explain the polymerization.

EXPERIMENTAL

Materials

PGE (Shell Chemical Company) was dried with BaO and fractionally distilled under reduced pressure (~ 60 torr). The heart cut, boiling at 130°C , was collected ($n_D^{20} = 1.5307$).² TMB (Stauffer Chemical Company) was dried overnight with BaO prior to use.

Kinetic studies were performed on purified reagents as well as on reagents as received, and we found that purification of PGE and TMB as described above had no effect whatsoever on the kinetics of polymerization. This implied that impurities removed from PGE by fractional distillation, and the water removed by drying, had no influence on the rate constants of polymerization. Moreover, no flakes of B_2O_3 , one of the products of hydrolysis, were observed in TMB as received, and gel permeation chromatography of the unpurified TMB revealed it to be pure. Consequently, PGE and TMB were used as received for all the kinetic studies described herein.

Apparatus

The infrared spectra were obtained on a Perkin-Elmer Model 521 grating infrared spectrophotometer operating in the range of 4000 to 500 cm^{-1} . The spectra of films were taken by casting the film directly on an NaCl plate; the solution spectra were obtained with a liquid cell having NaCl windows.

The molecular weight determinations were made using a Waters Associates Model 200 gel permeation chromatograph. Three columns were used in series to effect the separations: 5×10^2 , 3×10^3 , and 5×10^4 Å crosslinked polystyrene gels. The solvent used was tetrahydrofuran (Baker Analyzed Reagent, stabilized with 0.025% butylated hydroxytoluene). All chromatograms were obtained at ambient temperature on $\sim 1\%$ solutions (using the differential refractometer) at a flow rate of $1\text{ cm}^3/\text{min}$.

The calibration curve for the gel permeation chromatograph (GPC) was obtained by using narrow molecular weight-range polystyrene standards for the high molecular weight end, and polyglycol standards for the low molecular weight range.

Proton (^1H) NMR spectra were recorded on a Varian Associates HA-100D spectrometer operating at 100 MHz at 31°C in CCl_4 or DMSO-d_6 , using TMS (tetramethylsilane) as an internal reference. Boron-11 (^{11}B) NMR spectra were

recorded on another HA-100D spectrometer operating at 32 MHz at ambient temperature in 1,4-dioxane, using trimethylborate, $B(OCH_3)_3$, as an external reference.

Procedure

The bulk polymerization was carried out in aluminum sample cups placed in an oven set at a preselected temperature (and maintained at that temperature $\pm 1^\circ$) and flushed with dry N_2 for at least 1 hr prior to introducing the sample. The polymerizations were conducted at four temperatures: 102, 112, 125, and 154°C. The polymerization at 112° was investigated at three initial concentrations of TMB: 0.06*M*, 0.13*M*, and 0.19*M*. The initial concentration of PGE used in each case was 7.36*M*. These concentrations were calculated by assuming no volume change on addition of TMB to PGE.

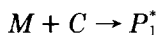
During polymerization, the epoxide ring is opened and converted into an aliphatic ether linkage which we were able to follow by observing the disappearance of the epoxide infrared absorption band at 920 cm^{-1} ($10.95\ \mu$).³ The polymerization was actually monitored by dissolving identical amounts of the polymerizing mixture in spectral quality benzene (Aldrich Chemical Company, Inc.) and scanning the spectrum of this solution. A quantitative relationship was determined with standards between the amount of epoxide in the solution (i.e., the amount of unreacted PGE) and the ratio of the absorbance at 920 cm^{-1} (due to an asymmetric stretching mode of the oxirane group) to the absorbance at 750 cm^{-1} (assigned to an out-of-plane bending mode of the phenyl group).

The molecular weights were calculated from the gel permeation chromatographs obtained on "completely cured" resins. Infrared spectroscopy revealed no epoxide group absorptions in the completely cured systems, and, moreover, the IR spectrum remained unchanged with an additional 24 hr of cure.

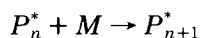
RESULTS AND DISCUSSION

The amount of PGE remaining after different periods of time (in the early stages of the reaction) at several initial concentrations of TMB at 112°C is shown in Figure 1. As is apparent, a steady-state condition is not observed during the bulk thermal polymerization of PGE by TMB; that is, the rate of polymerization does not attain a constant value. Burton and Pepper⁴ interpreted this type of reaction kinetics in terms of a fast-initiated, nonstationary polymerization, i.e., one in which the rate constant for the initiation step is much larger than the rate constant for the propagation step. The Burton and Pepper scheme envisions the following five basic steps (symbols being used: M = monomer (PGE), C = initiator (TMB), P_n^* = growing polymer of n monomer units, P_n = "dead" polymer of n monomer units):

- (i) Initiation with rate constant k_i :



- (ii) Propagation with rate constant k_p :



- (iii) Spontaneous transfer with rate constant k_{ST} :

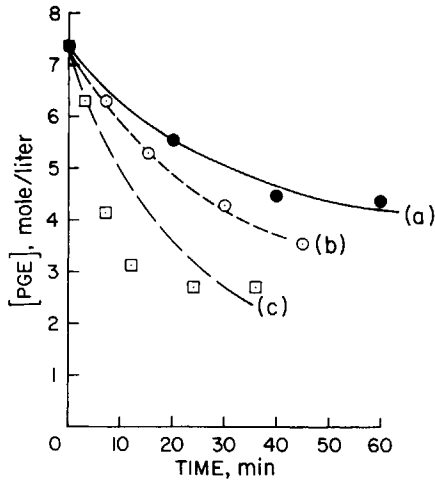


Fig. 1. Concentration of PGE as a function of time (112°) at several initial concentrations of TMB: (a) $[TMB]_0 = 0.06M$; (b) $[TMB]_0 = 0.13M$; (c) $[TMB]_0 = 0.19M$.

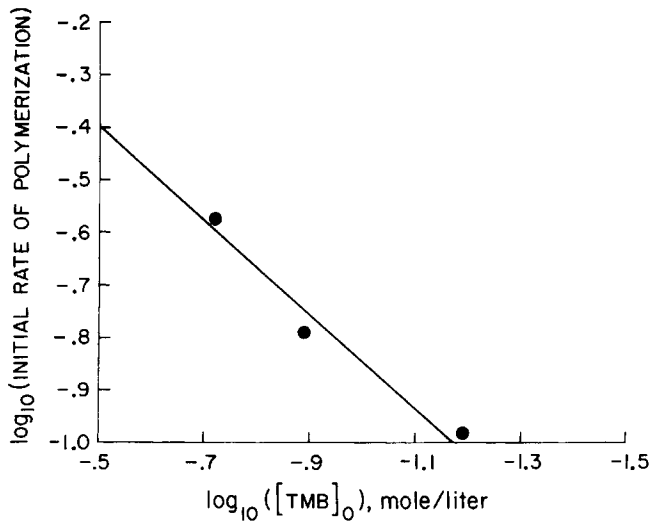
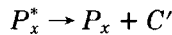
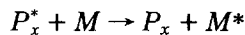


Fig. 2. Plot of \log_{10} (initial rate of polymerization), mole/liter/min, at 112°C vs. \log_{10} (initial concentration of TMB); slope = TMB reaction order.



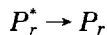
where C' may be the initiator or any other species capable of continuing the polymerization.

(iv) Monomer transfer with rate constant k_{TM} :



where $M^* = P_1^*$.

(v) Termination with rate constant k_t :



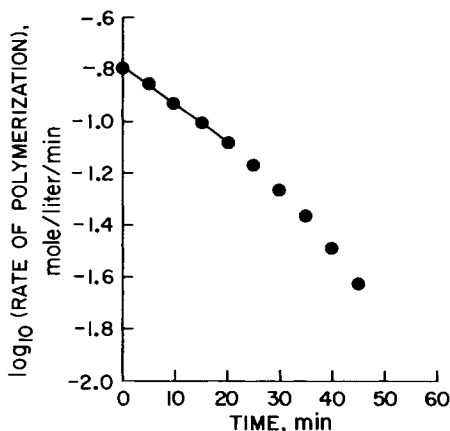


Fig. 3. Plot of \log_{10} (rate of polymerization), mole/liter/min, at 112° vs. time, min.

The order of reaction with respect to TMB can be found from a log-log plot of the initial rate of polymerization against the initial concentration of TMB; from Figure 2, a reaction which is approximately first order (~ 0.9) is found in TMB.

In order to determine the reaction order in PGE, we turn to a rate equation derived by Burton and Pepper⁴ which is applicable to our current polymerization:

$$\begin{aligned} \text{rate of polymerization} &= \frac{-d[\text{PGE}]}{dt} \\ &= (k_p + k_{TM})[\text{TMB}]_0[\text{PGE}]e^{-k_{it}} + k_{ST}[\text{TMB}]_0e^{-k_{it}} \end{aligned} \quad (1)$$

We shall examine two extreme cases for the dependence of the rate of polymerization on the concentration of PGE: Case I assumes that $k_{ST} \gg (k_p + k_{TM})[\text{PGE}]$, while case II assumes the converse, i.e., $(k_p + k_{TM})[\text{PGE}] \gg k_{ST}$. If case I is found to prevail for the polymerization of PGE by TMB, then a semilogarithmic plot of the rate of polymerization against time would give a straight line. On the other hand, case II yields a straight line from a semilogarithmic plot of the rate of polymerization/[PGE] versus time. Figure 3 shows that a semilog plot of rate versus time for the polymerization of PGE at 112°C with an initial concentration of TMB of $0.13M$ approximates a straight line, at least in the early part of the reaction (before volume changes become appreciable). On the other hand, a plot corresponding to case II is V-shaped in the early part of the reaction, instead of being linear. Thus, we conclude that the polymerization is approximately zero order in PGE, i.e.,

$$\text{rate of polymerization} = \frac{-d[\text{PGE}]}{dt} \cong k_{ST}[\text{TMB}]_0e^{-k_{it}} \quad (2)$$

Although the polymerization envisioned by eq. (1) is a five-step process, the rate constant for the initiation reaction (k_i) cannot be determined. The only information that we have concerning this rate constant is that it is much larger in magnitude than k_p , since a stationary rate of polymerization is not observed.

The activation energy for the rate of polymerization was determined for reaction systems containing an initial concentration of TMB of $0.06M$ at four

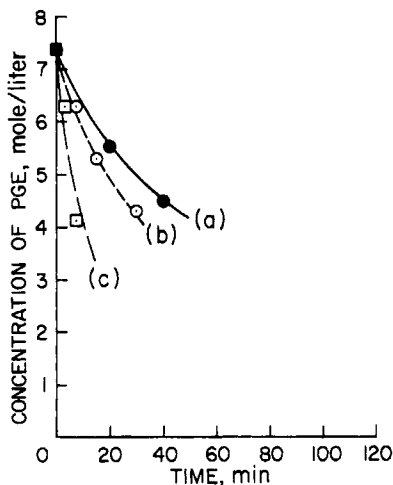


Fig. 4. Concentration of PGE as a function of time at several temperatures for $[TMB]_0 = 0.06M$: (a) $T = 102^\circ$; (b) $T = 125^\circ$; (c) $T = 154^\circ$.

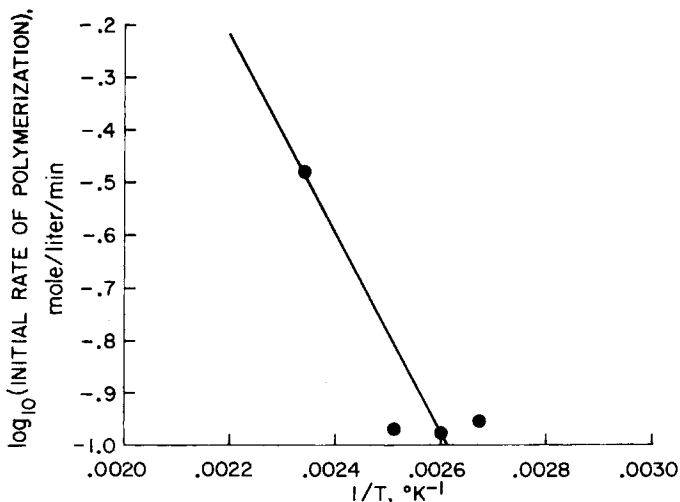


Fig. 5. Arrhenius plot for rate of polymerization of PGE, mole/liter/min, with $[TMB]_0 = 0.06M$; slope = $-E_R^{act}/4.57$.

temperatures. The initial rates of polymerization, as determined from Figure 4, along with the data shown in Figure 1 for the run at 112° , were used to construct the Arrhenius plot shown in Figure 5. From the latter plot, an activation energy of $+8.7$ kcal/mole for the rate of polymerization (E_R^{act}) was determined.

In order to verify the presence of the transfer and termination reactions implied in eq. (1), we investigated the dependence of the number-average degree of polymerization (\overline{DP}_n) on the ratio of the initial concentration of TMB to that of PGE. The degree of polymerization of the completely cured resin was calculated from the number-average molecular weight as determined by GPC. Figure 6 shows the GPC curves for several different $[TMB]_0/[PGE]_0$ ratios, with the pertinent results summarized in Table I. As shown in Figure 7, the Mayo plot

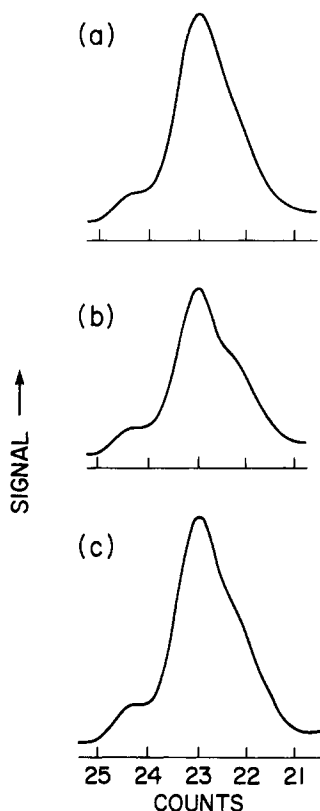


Fig. 6. Gel permeation chromatographs of cured polymer: signal vs. counts from sample introduction for several $[\text{TMB}]_0/[\text{PGE}]_0$ ratios. All polymerizations were conducted at 112° : (a) $[\text{TMB}]_0/[\text{PGE}]_0 = 0.00879$; (b) $[\text{TMB}]_0/[\text{PGE}]_0 = 0.0177$; (c) $[\text{TMB}]_0/[\text{PGE}]_0 = 0.0264$.

of inverse \overline{DP}_n versus $[\text{TMB}]_0/[\text{PGE}]_0$ gives a straight line the intercept of which has a value of 0.272. Using an expression analogous to that of Burton and Pepper⁴ for the \overline{DP}_n for a fast-initiated, nonstationary polymerization, we have

$$\frac{1}{\overline{DP}_n} = \left(\frac{k_{TM}}{k_p + k_{TM}} \right) + \frac{k_p k_{ST} + k_t(k_p + k_{TM})}{k_t(k_p + k_{TM})} \cdot \frac{[\text{TMB}]_0}{[\text{PGE}]_0 - [\text{PGE}]_\infty} \quad (3)$$

Since, in our polymerization, infrared spectroscopy revealed no unreacted PGE in the completely cured resin, the $[\text{PGE}]_\infty$ term in the denominator drops out.

TABLE I
 \overline{DP}_n as a Function of $[\text{TMB}]_0$ at Several Temperatures

Initial concentration $[\text{TMB}]_0$	\overline{DP}_n		
	102°C	112°C	154°C
0.06M	3.440	3.482	3.613
0.13M		3.494	
0.19M		3.515	
0.26M		3.175	

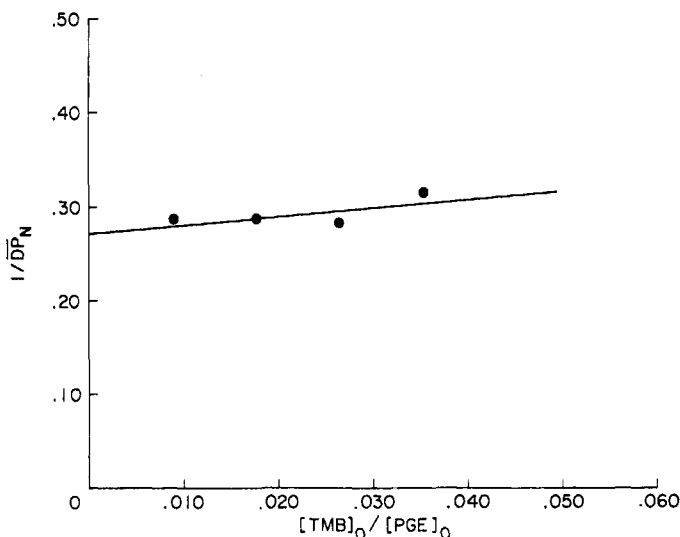


Fig. 7. $1/\overline{DP}_n$ vs. $[\text{TMB}]_0/[\text{PGE}]_0$ with intercept = $k_{TM}/(k_p + k_{TM})$.

Thus, from the data shown in Figure 7 and eq. (3), we find that

$$\frac{k_{TM}}{(k_p + k_{TM})} = 0.272 \quad (4)$$

From eq. (2), we see that a plot of \ln (rate of polymerization) versus time will give a straight line with a slope of $-k_t$ and an intercept of $\ln(k_{ST}[\text{TMB}]_0)$. Drawing the best straight line through the first five data points of Figure 3 (representing approximately the first third of the reaction), we find values of $k_t^{112^\circ} \cong 3.4 \times 10^{-2} \text{ min}^{-1}$ and $k_{ST}^{112^\circ} \cong 1.3 \text{ min}^{-1}$. Note that these are only approximate values, true in the limit $k_{ST} \gg (k_p + k_{TM})[\text{PGE}]$.

These results may now be combined with eqs. (1) and (4) to give

$$\begin{aligned} \text{rate of polymerization} &= \frac{-d[\text{PGE}]}{dt} \\ &\cong 1.374k_p[\text{TMB}]_0[\text{PGE}]e^{-k_t t} + k_{ST}[\text{TMB}]_0e^{-k_t t} \end{aligned}$$

so that, at $t = 0$, this becomes

$$\text{initial rate of polymerization} \cong 1.374k_p[\text{TMB}]_0[\text{PGE}]_0 + k_{ST}[\text{TMB}]_0 \quad (5)$$

Using this equation, together with the data in Figure 1 for the case where $[\text{TMB}]_0 = 0.13M$, we find a value of $k_p^{112^\circ} \cong 2.1 \times 10^{-2} \text{ mole}^{-1} \cdot \text{liter} \cdot \text{min}^{-1}$; when this value of k_p is substituted into eq. (4), we obtain $k_{TM}^{112^\circ} \cong 7.8 \times 10^{-3} \text{ mole}^{-1} \cdot \text{liter} \cdot \text{min}^{-1}$. Table II summarizes these results for the elementary-step rate constants; these values for the rate constants display the properties of the Burton-Pepper model.⁴

An activation energy for chain growth (E_{DP}^{act}) of +2.2 kcal/mole is obtained from the Arrhenius plot of \overline{DP}_n against T^{-1} (Fig. 8).

On the basis of the above kinetic parameters, a five-step polymerization mechanism is postulated:

(i) Initiation, involving attack (most likely nucleophilic) by the epoxide oxygen

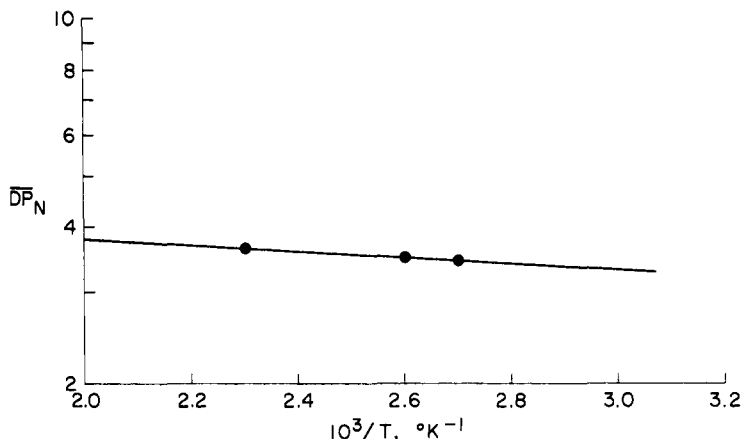
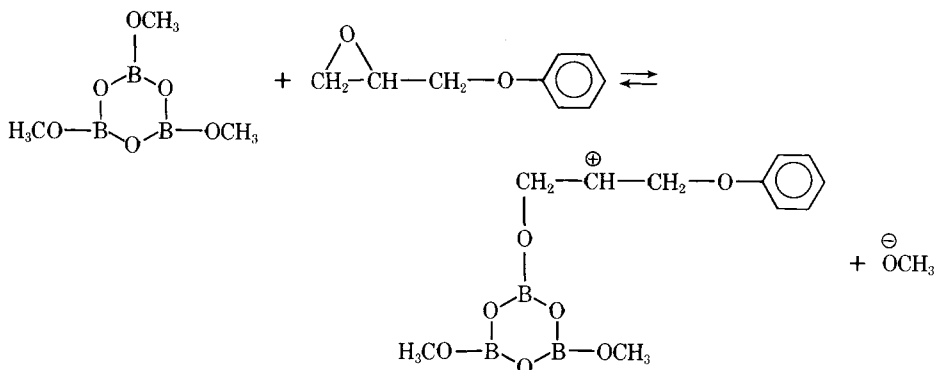


Fig. 8. Plot of \overline{DP}_n vs. T^{-1} ($^\circ\text{K}^{-1}$) for $[\text{TMB}]_0 = 0.06M$; slope = $-E_{DP}^\ddagger/4.57$.

atom on a boron atom with simultaneous displacement of a methoxide anion:



Although likely to be an equilibrium, the reaction will be displaced to the right as a result of the polymerization. Also, as written above, the propagating species is represented as a free carbonium ion; actually, the data are insufficient to distinguish between ion-pair, free-ion, and/or simultaneous propagation. Our initiation reaction merely represents cationic polymerization of PGE by TMB.

Supporting evidence for the initiation step was obtained from NMR studies. Figure 9 shows the ^{11}B NMR spectrum of TMB. As can be seen, the resonances of TMB and trimethylborate, $\text{B}(\text{OCH}_3)_3$, are identical. The reason for this is that in both compounds each boron atom is surrounded by three oxygen atoms in a trigonal arrangement, and the location of the oxygen atoms plays a key role in determining the position of the boron resonance. Figure 9 also shows the ^{11}B NMR spectrum of the polymer produced by polymerizing PGE with 16 wt-% TMB. Again, the ^{11}B resonance occurs at the same chemical shift in the polymeric resin as in the reference compound. Hence, either TMB serves as a true catalyst in the thermal polymerization of PGE (i.e., is regenerated after initiating polymerization), or it reacts with PGE in such a way that the trigonal arrangement of the oxygen atoms around each boron atom is retained during cure.

It has been shown that TMB is not serving as a true catalyst on the basis of the following evidence. The ^1H NMR spectrum of TMB dissolved in deuterated

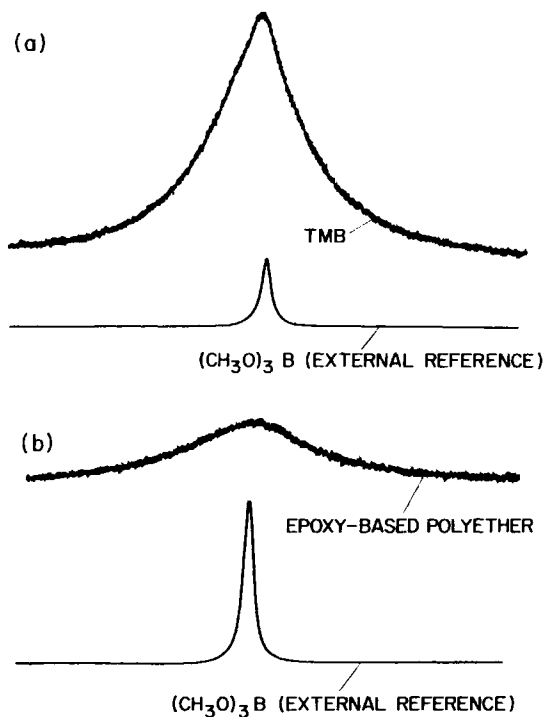


Fig. 9. Boron-11 (^{11}B) NMR spectra: (a) TMB and external reference (trimethylborate); (b) Polymer cured with 16 wt-% TMB and external reference (trimethylborate).

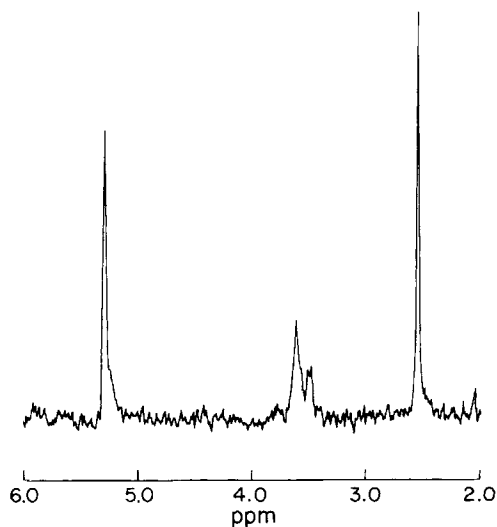


Fig. 10. Proton (^1H) NMR spectrum of decomposed TMB. TMB was heated at 90° for 3 hr; TMS was used as the internal reference.

dimethylsulfoxide (Stohler Isotope Chemicals) shows a major peak at a chemical shift of 3.42 ppm (using TMS as an internal reference). Figure 10 shows the ^1H spectrum obtained under the same conditions after heating TMB at 90°C for several hours. There are now four resonances instead of just one: 2.56, 3.49,

TABLE II
Elementary Step Rate Constants (112° C)

Elementary step	Rate constants
Initiation	$k_i \gg k_p$
Propagation	$k_p \cong 2.1 \times 10^{-2} \text{ mole}^{-1} \text{ liter min}^{-1}$
Spontaneous transfer	$k_{ST} \cong 1.3 \text{ min}^{-1}$
Monomer transfer	$k_{TM} \cong 7.8 \times 10^{-3} \text{ mole}^{-1} \text{ liter min}^{-1}$
Termination	$k_t \cong 3.4 \times 10^{-2} \text{ min}^{-1}$

3.62, and 5.30 ppm. This is attributed to thermal disproportionation of TMB;⁵ since the disproportionation occurs at a temperature lower than that used to polymerize PGE, if TMB were a true catalyst it would also undergo thermal disproportionation after effecting polymerization. Since the ¹¹B NMR spectrum of the polymerized resin does not show the effects of disproportionation, there must be a reaction between PGE and TMB which stabilizes the boroxine ring (i.e., our proposed initiation reaction).

Note that there are three boron atoms per TMB molecule at which reaction may occur; consequently, the trimethoxyboroxine molecule itself may serve as a crosslink during polymerization.

(ii) The propagation step:

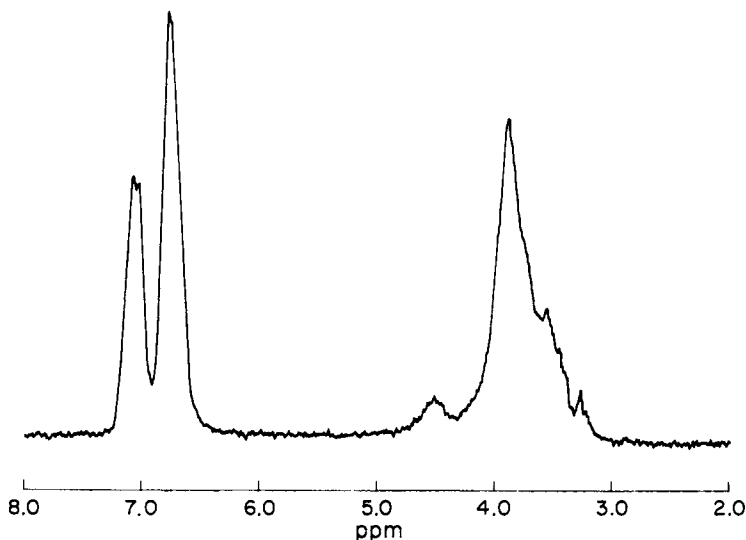
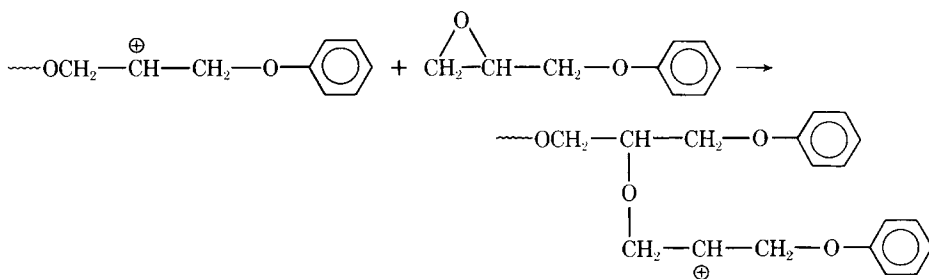
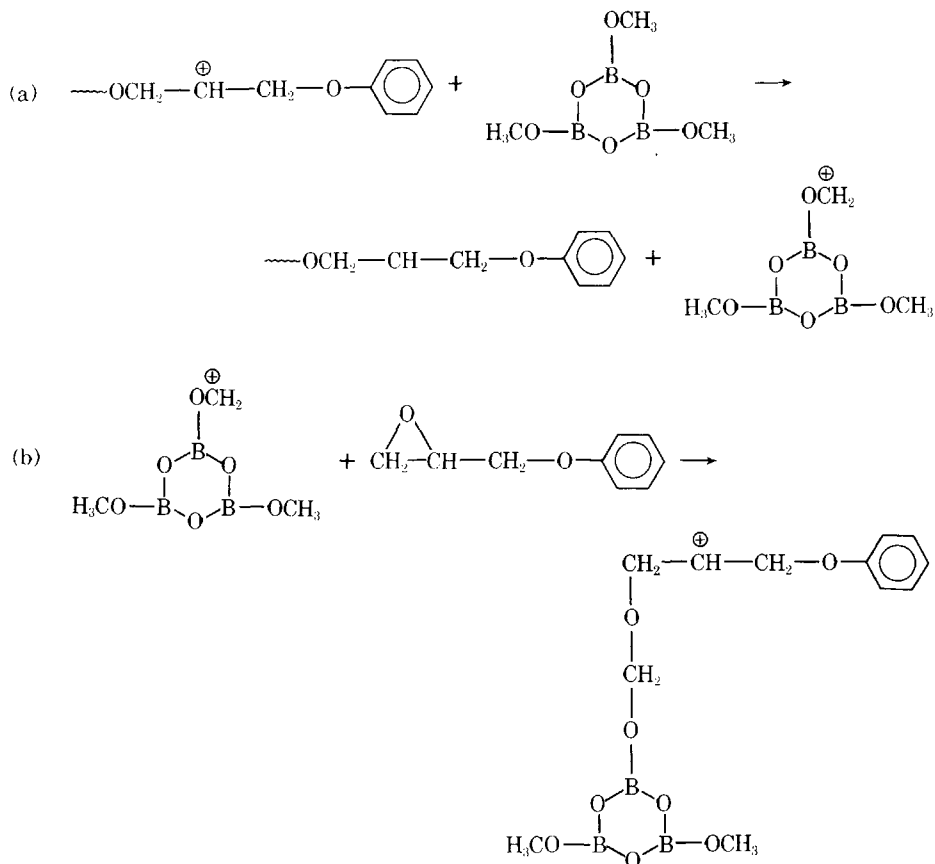


Fig. 11. Proton (¹) NMR spectrum of polymer cured with 16 wt-% TMB. TMS was used as the internal reference.

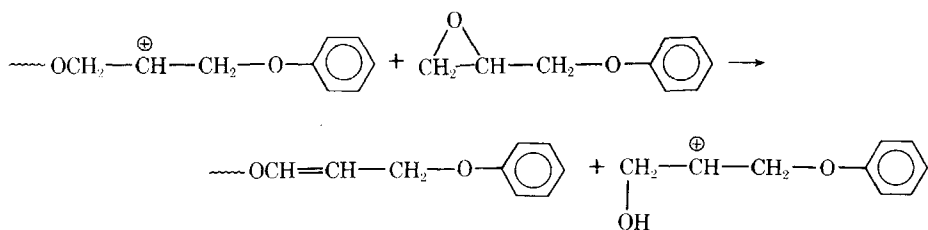
This involves a nucleophilic attack of the epoxide oxygen atom on the carbonium ion of the growing chain, and a secondary carbonium ion is regenerated. The magnitude of the propagation rate constant given in Table II is consistent with the values usually observed in cationic polymerizations.⁶

(iii) Spontaneous transfer is postulated as



We postulate this reaction as the spontaneous transfer primarily because it is consistent with the magnitude of the rate constant for this step, as given in Table II. As can be seen, k_{ST} is the largest rate constant observed, and since the reaction postulated above would involve a primary carbonium ion on TMB, it should be exceedingly rapid, indeed. Furthermore, it seems unlikely that the transfer could involve an agent other than TMB itself since drying and fractional distillation had no effect whatsoever on the polymerization.

(iv) Monomer transfer involves a proton shift:



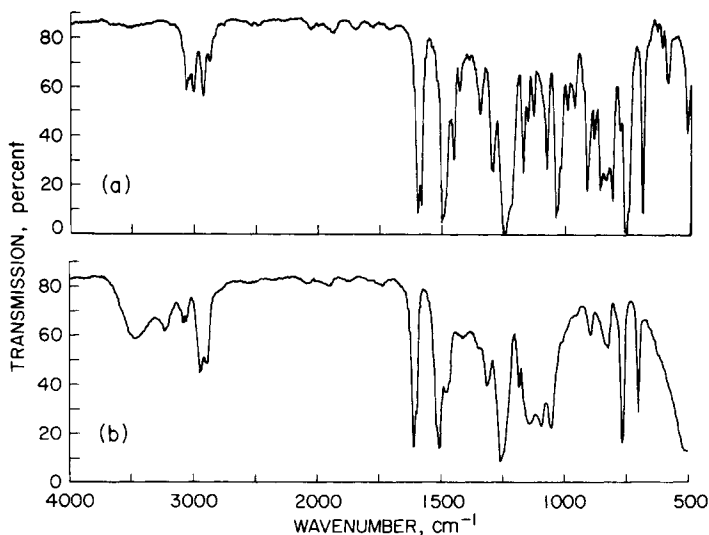
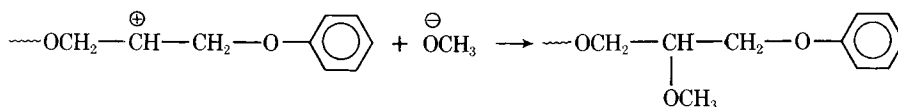


Fig. 12. Infrared absorption spectra (film samples) from 4000 to 500 cm^{-1} : (a) PGE, uncured; (b) Polymer cured with 16 wt-% TMB.

Proton NMR studies and IR spectroscopy lend support to this scheme. Figure 11 shows the ^1H NMR spectrum of the polymer produced by polymerizing PGE with 16 wt-% TMB. The weak resonance at 4.50 ppm can be assigned to the protons attached to a carbon-carbon double bond. Furthermore, the infrared spectrum of the cured epoxy-based polyether resin shown in Figure 12 indicates strong, broad absorption in the 3200 to 3500 cm^{-1} range, which is the region of hydroxyl-group absorption. Figure 12 also shows the IR absorption spectrum of PGE with the complete absence of the characteristic hydroxy bands. Thus, while the various spectroscopic results are not conclusive, they are at least in agreement with our postulated transfer reactions.

(v) The termination reaction involves ion recombination:



In view of the evidence presented for the initiation and propagation reaction, it appears that this is a likely method of terminating the growing chain. Furthermore, the ^1H NMR spectrum of the cured resin shown in Figure 11 displays several resonances in the range of 2.8–4.0 ppm. This is in the range expected for $-\text{OCH}_3$ groups; moreover, since we were unable to remove either TMB or any of its disproportionation products after polymerization, it is unlikely that the methoxy resonance is due to either unreacted TMB or its reaction products.

CONCLUSIONS

As a result of our investigation into the kinetics of the bulk-thermal polymerization of PGE induced by TMB, we have reached the following conclusions:

(i) Polymerization proceeds by a cationic, fast-initiated, nonstationary mechanism.

(ii) The polymerization occurs in five steps, including spontaneous transfer, monomer transfer, and termination reactions.

(iii) The boroxine ring remains intact in the cured polymer; in fact, the boroxine ring is covalently bonded into the structure of the cured resin, and can itself serve as a crosslinking agent.

(iv) Only low molecular weight oligomers are produced due to the extremely fast spontaneous transfer reaction.

(v) The overall activation energies for both chain growth and rate of polymerization are positive, with the former observation being somewhat unusual for epoxide polymerizations.⁶

A mechanism consistent with our observations is postulated for this polymerization reaction.

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