

Curing Reactions in Elastomers. II. Carboxy-Terminated Polybutadiene

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Synopsis

Attempts have been made to understand the curing reactions in carboxy-terminated polybutadiene (CTPB), which happens to be the most practical binder in advanced solid composite propellants. The curing of CTPB has been studied for different ratios of curing agents (MAPO and Epoxide) by gel content, molecular weight, crosslink density, and penetration temperature measurements, and the optimum composition of curators for effective curing of CTPB has been determined. Activation energy calculations on the curing of CTPB with 9.5% epoxide and 0.5% MAPO in the temperature range 75–100°C gave 14.1 kcal/mol for which a diffusion-controlled or acid-catalyzed epoxide ring opening mechanism has been suggested for the curing process in CTPB.

INTRODUCTION

A thorough understanding of the curing of binder in solid composite propellant is of great importance for getting desirable mechanical and ballistic properties. Recently,¹ we have studied in detail the curing reactions of thermoplastic binder (polystyrene) and corresponding propellant system to understand the mechanism of physical curing. Through this paper we are attempting to understand the curing of a chemically cured polymer, i.e., carboxy-terminated polybutadiene (CTPB), which happens to be the most practical binder in advanced solid composite propellants. In the case of CTPB, either aziridines like MAPO [tris-(methyl aziridinyl phosphine oxide)] or epoxides or both are used for curing. When MAPO alone is used as curing agent, it is found that it undergoes side reactions such as homopolymerization and rearrangement to oxazolines.² Another disadvantage in using MAPO alone as a curing agent in CTPB-based ammonium perchlorate (AP) propellant is that higher concentrations of AP (84.5%) with a finer particle size of AP and mixing action increased the extent of the formation of the oxazolines,³ which adversely affect the mechanical properties of the propellant. Further, the polymer network formed with MAPO is not very stable, leading to softening due to the presence of 3P—N bonds, which cleave at high temperatures. CTPB gets cured with difficulty with epoxide alone,⁴ but the side reactions are much less compared to the MAPO—CTPB system. For this reason a combination of MAPO—epoxide is employed for CTPB curing. However, the optimum ratio in which the two curators bring about the most effective curing is not precisely known. In the present investigation an attempt has been made to study the optimum MAPO/epoxide ratio for effective curing of CTPB. The rate of curing has been followed by measuring the gel content and by measuring the crosslink density using thermal mechanical analyzer.

EXPERIMENTAL

Sample Preparation and Method of Curing

CTPB (Butarez CTL), MAPO (Arsynco Inc., USA) and Gy 252 epoxy resin (Ciba-Giegy) were employed in this study. Samples of CTPB with different ratios of MAPO and epoxide (both together 10% by weight of CTPB) were prepared by stirring well to get a homogeneous blend and then placing at 75°C in an air oven for curing. Temperature accuracy was within $\pm 1^\circ\text{C}$. Samples were taken out at different intervals of time, and the curing process was followed by the analysis of sol portion and gel content.⁵ Samples were extracted by swelling with AR benzene to dissolve the sol portion. The residual gel was washed with benzene a number of times, dried under vacuum, and the percentage of the gel content was determined. The benzene solvent was removed from the sol by evaporation under reduced pressure, and the sol portions were analyzed for the intrinsic viscosity determination in AR toluene at 30°C, using an Ubbelohde viscometer. The influence of temperature on the rate of curing was determined by carrying out similar curing experiments on CTPB at different temperatures (75°C, 82°C, 90°C, and 100°C).

Measurement of Penetration Temperature and Crosslink Density

The measurements were carried out in a DuPont 943 Thermal Mechanical Analyzer (TMA) provided with a penetration probe 0.635 mm in diameter and a two-pen recorder (DuPont 990 X-Y Recorder) for the probe displacement and temperature. The method of obtaining crosslink density and penetration temperature from TMA is described elsewhere.⁶

For crosslink density measurements samples cured at 75°C to the maximum gel content were employed. A decrease in thickness of the sample by applying force (5 g) on the probe was recorded at room temperature from which crosslink density can be calculated.

IR Spectra

IR spectra were taken for CTPB samples just before the attainment of measurable gel content using a UR 10 Infrared Spectrophotometer.

RESULTS AND DISCUSSION

Curing at 75°C

Curing of CTPB involves the reaction of COOH groups with the curing agents (epoxide and MAPO) to form an ester followed by crosslinking. This is evident from the IR spectra (Fig. 1) taken for the samples (A) CTPB alone, (B) a mixture of CTPB 9.5% epoxide and 0.5% MAPO, and (C) CTPB with curators (9.5% epoxide + 0.5% MAPO), which was removed from the oven just before the attainment of measurable gel content. As the curing proceeds, —COOH group intensity (1710 cm^{-1}) is reduced with reference to C=C (1640 cm^{-1}), and a shoulder corresponding to the formation of ester at 1740 cm^{-1} develops.

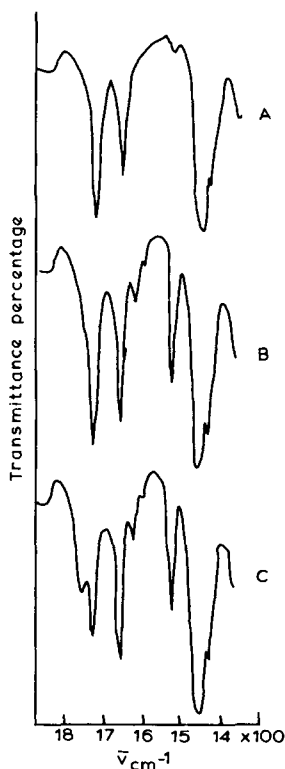


Fig. 1. IR spectra of: (A) pure CTPB; (B) mixture of CTPB, 9.5% epoxide and 0.5% MAPO; (C) CTPB + 9.5% epoxide + 0.5% MAPO kept at 75°C for 110 h.

The relation between gel content and curing time for different ratios of curators is shown in Figures 2 and 3. A general trend in all the cases is that the percentage gel content increases first with curing time and finally attains a constant value indicating the completion of curing. Curing of CTPB with epoxide [Fig. 3(D)] was not complete even after 700 h.

During the curing the intrinsic viscosity $[\eta]$ of the sol portions were determined by viscometric measurements, and the viscosity values were plotted against curing time for all the composition of curators in Figures 4 and 5. $[\eta]$ of all the sol portions increases, first reaching a maximum and then falling down as the curing time is increased; i.e., initially curing of CTPB produces larger molecules by chain extension, and it is interesting to find that the molecular weight in the sol starts decreasing after the attainment of the maximum gel content. This indicates that the larger molecules become crosslinked and are taken out of the sol fraction to form the gel.

In order to obtain the best composition of the curing agents, the maximum gel content and maximum $[\eta]$ obtained in the sol portion were plotted against the percentage composition of the epoxide in the curing mixture (Fig. 6). The maximum gel content obtainable for curing of CTPB is not affected very much by change in the composition of the curators, but the molecular weight, i.e., $[\eta]$ of sol portion is found to increase as the composition of epoxide in the curing

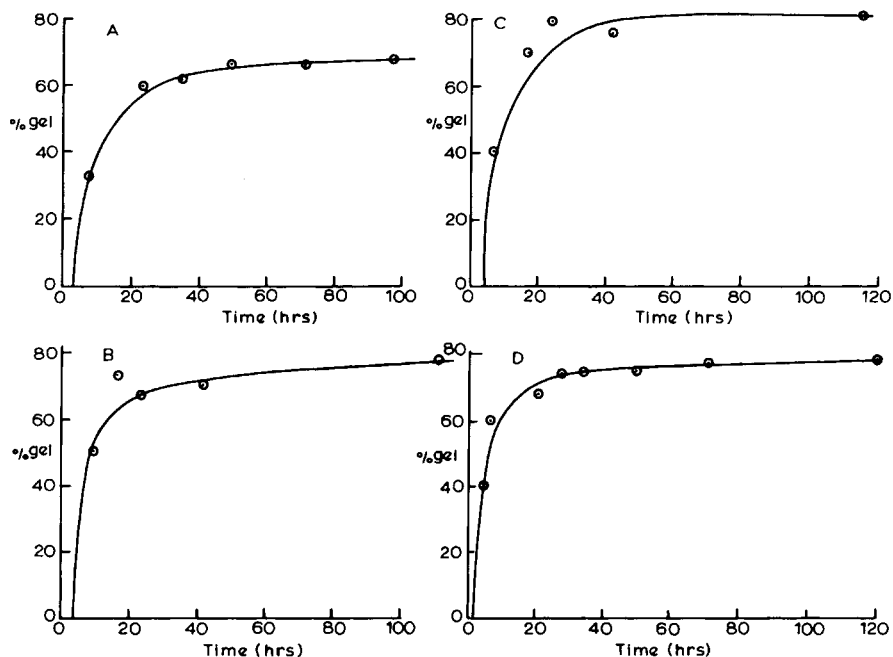


Fig. 2. Plots of % gel vs. curing time for CTPB with epoxide and MAPO curing agents: (A) 10% MAPO; (B) 8% MAPO + 2% epoxide; (C) 6% MAPO + 4% epoxide; (D) 4% MAPO + 6% epoxide. Temp = 75°C.

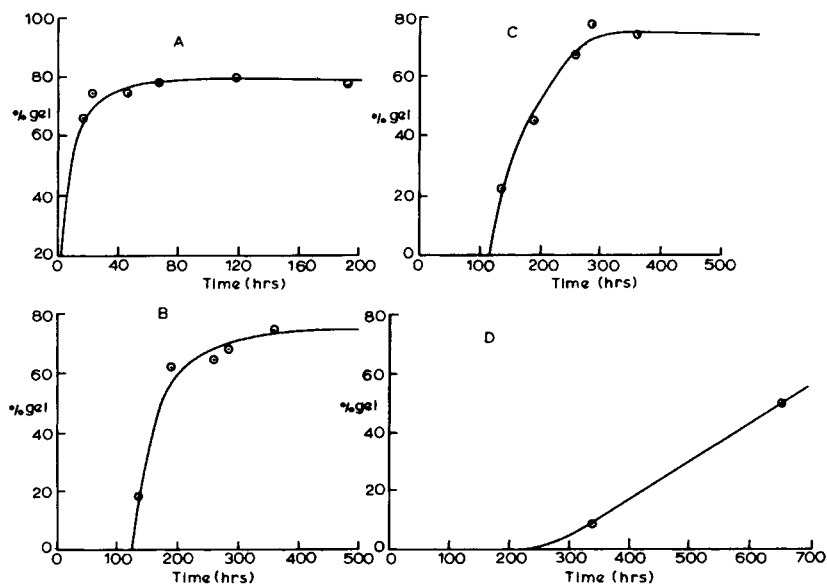


Fig. 3. Plots of % gel vs. curing time for CTPB with epoxide and MAPO curing agents: (A) 2% MAPO + 8% epoxide; (B) 1% MAPO + 9% epoxide; (C) 0.5% MAPO + 9.5% epoxide; (D) 10% epoxide. Temp = 75°C.

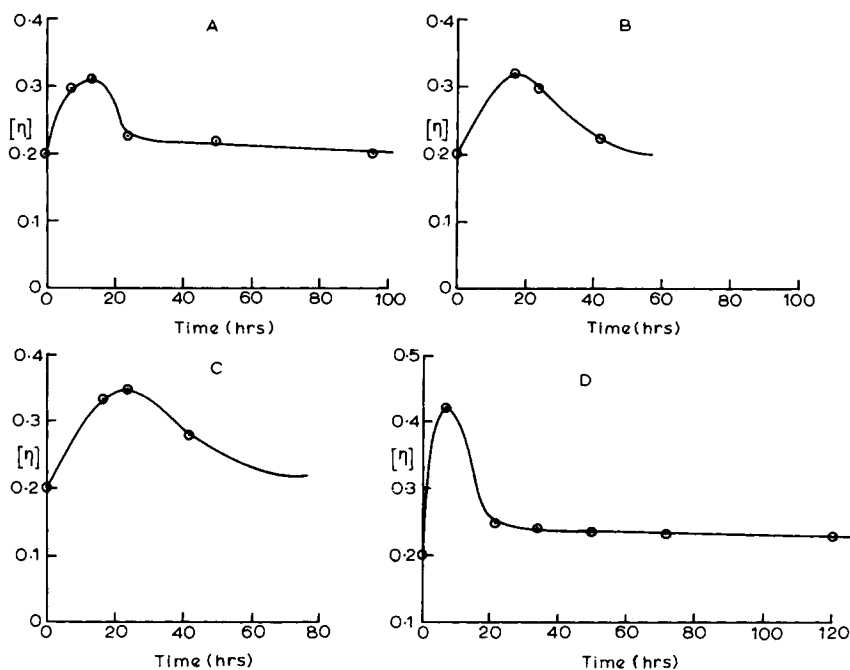


Fig. 4. $[\eta]$ of sol fraction as a function of curing time for CTPB with MAPO and epoxide curing agents: (A) 10% MAPO; (B) 8% MAPO + 2% epoxide; (C) 6% MAPO + 4% epoxide; (D) 4% MAPO + 6% epoxide.

agents mixture is increased. Further, while epoxide alone could not cure CTPB completely [Fig. 3(D)], addition of even a small percentage (5%) of MAPO is sufficient to give gel content and high molecular weight of the sol, but the time taken for curing is comparatively larger. A plot of gel content versus $[\eta]$ of sol for the curing of CTPB with different ratios of curators (Fig. 7) shows that 5% MAPO and 95% epoxide will give better curing conditions.

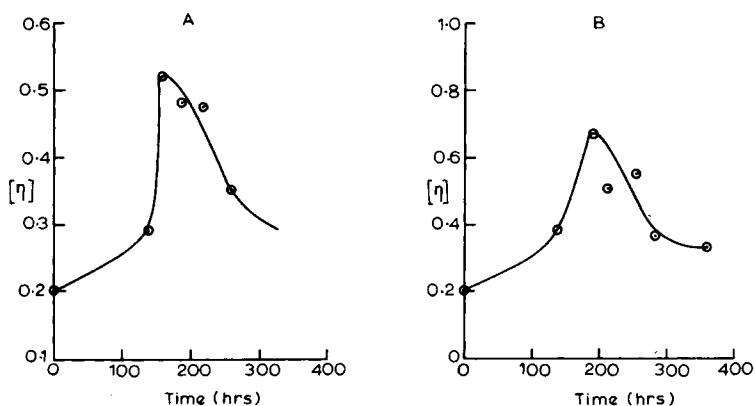


Fig. 5. $[\eta]$ of sol fraction against curing time for CTPB with MAPO and epoxide curing agents: (A) 1% MAPO + 9% epoxide; (B) 0.5% MAPO + 9.5% epoxide.

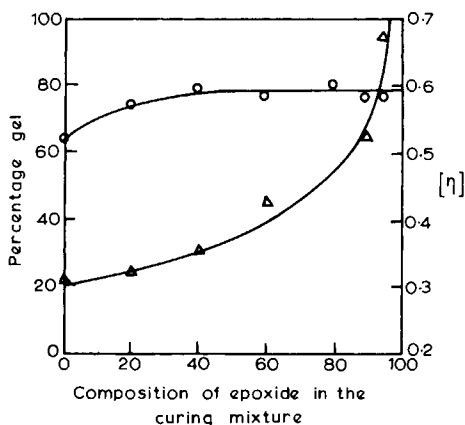


Fig. 6. Percentage gel (O) and intrinsic viscosity (Δ) as a function of percentage composition of epoxide in the curing agents mixture.

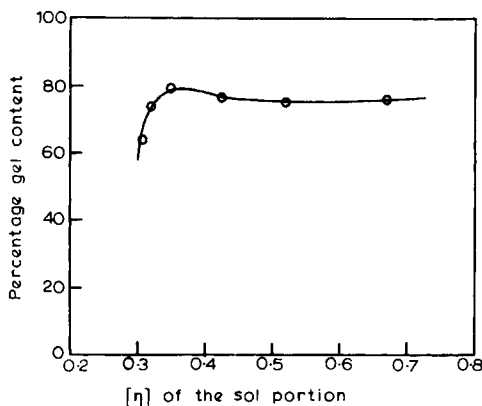


Fig. 7. Percentage gel content as a function of $[\eta]$ of sol fraction for different composition of curators.

Crosslink Density and Penetration Temperature

Samples of CTPB cured at 75°C by using different ratios of MAPO and epoxide to maximum gel content were employed for penetration temperature and crosslink density determinations in DuPont 943 TMA. In our recent work⁶ on the measurement of crosslink density of CTPB by using Cluff's swollen gel method and unswollen TMA method, it has been shown that the crosslink density values obtained by the two methods show a similar trend, although the actual numbers differ to some extent. However, since we are only using the crosslink density data for comparative purposes, the unswollen TMA technique offers a rapid and reliable method for the purpose. Crosslink density (i.e., the number of moles of crosslinks per unit volume) is given by the following equation:

$$\frac{N}{V} = \frac{F/A}{RT(\alpha - 1/\alpha^2)}$$

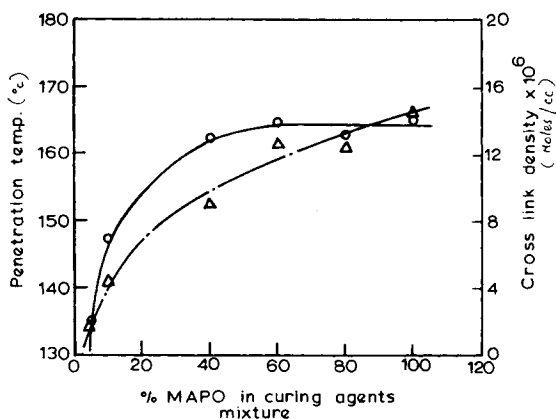


Fig. 8. Crosslink (Δ) and penetration temperature (\circ) as a function of percentage composition of epoxide in the curing agents mixture.

where F is the compression force (dyn), A is the area (cm^2) of the penetration probe, R is the gas constant ($\text{ergs}/^\circ\text{C}\cdot\text{mol}$), T is the temperature ($^\circ\text{K}$), and $\alpha = 1 - \epsilon$, ϵ being the penetration ratio given by $\Delta l/l$, Δl being the change in thickness by the application of force F and l the original thickness of the sample. Crosslink density measurements were made at room temperature. Penetration temperature (the temperature at which penetration of the sample by the probe occurs) was measured at a heating rate of $10^\circ\text{C}/\text{min}$. Figure 8 shows the influence of composition of the curing agents on penetration temperature and crosslink density. As the composition of epoxide is increased, both the penetration temperature and crosslink density decrease. These results are in good agreement with the molecular weight change in the system with the change in composition of curators.

Mechanism of Curing of CTPB

In order to determine the rate-controlling step, the curing of CTPB was carried out with 9.5% epoxide and 0.5% MAPO, at temperatures 75°C , 82°C , 90°C , and 100°C . As described earlier, the curing process was followed by observing the change in gel content with time. Figure 9 gives the plot of percentage gel content against curing time at temperatures 82°C , 90°C , and 100°C . From this plot the rate of curing, i.e., the inverse of time taken to attain different gel content was determined at all four temperatures. Activation energy (E) calculations were made using the Arrhenius equation by plotting \ln (rate of curing) against inverse of temperature (Fig. 10), and E was found to be in the order of 14–15 kcal/mol.

From Figures 2(A) and 3(D), it is evident that the slower process in the curing of CTPB is the reaction of $-\text{COOH}$ with epoxide, compared to that with MAPO. Moreover, in the optimum mixture of curatives used (for which E has been estimated), MAPO is present in a very small proportion as compared with epoxide. Now the rate-controlling step in the curing of CTPB can be either the breaking of the $\text{C}-\text{O}$ bond in order to open up the epoxide ring or the diffusion of epoxide towards CTPB. In the literature,⁷⁻¹¹ we find that E values of many epoxide

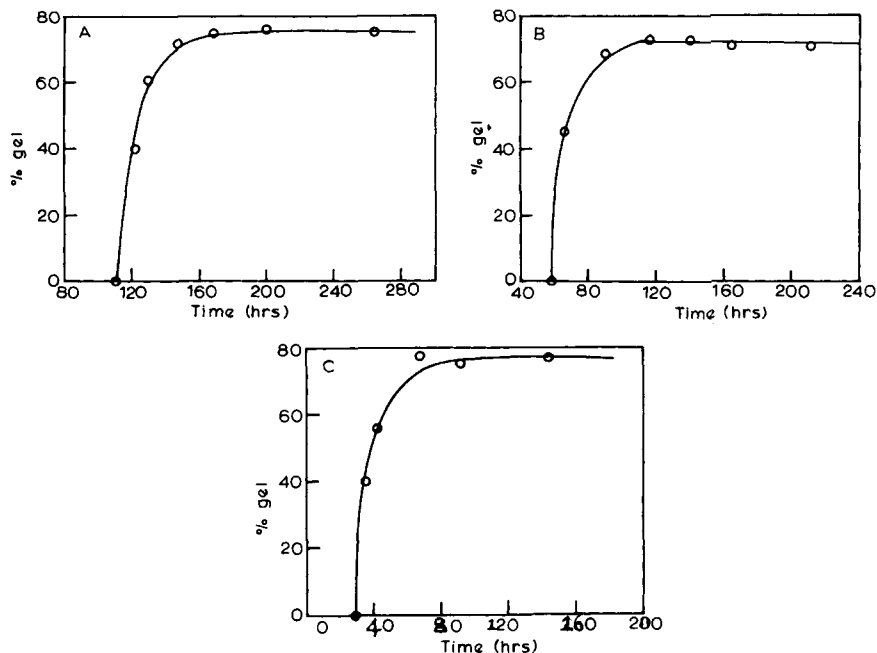


Fig. 9. Percentage gel content vs. time for curing of CTPB with 9.5% epoxide and 0.5% MAPO at (A) 82°C, (B) 90°C, and (C) 100°C.

hardener systems (Table I) have been reported in the range of 13–20 kcal/mol, but no specific mechanism has been attributed for these E values. In the present work also we get E of the order 14–15 kcal/mol, which falls in the same range.

In order to test whether the rate controlling step corresponds to the breaking

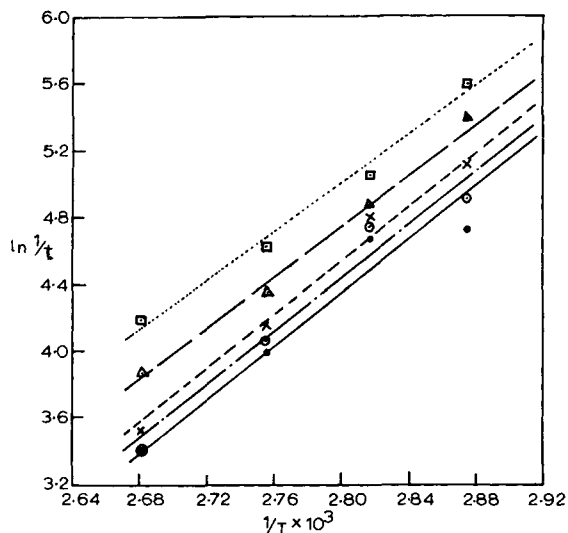


Fig. 10. Arrhenius plot of \ln (rate of curing) versus $1/T$. Gel content: (□) maximum; (⊙) 20%; (×) 40%; (Δ) 60%; (●) close to 0%.

TABLE I
Literature Data on the E of Epoxide Curing

System	Method	Activation energy (kcal/mol)	Ref. no.
Glycidyl ether-amine	Gel time	14-16	7
Phenyl glycidyl ether-butyl amine	Reaction rate	13.9	8
Shell Epon 828-diamine	IR	11.0	9
DER 332-amine	Gel time	13.6	10
X-102-anido amine	Calorimetric	9.3, 13.7, 22.8	11
X-102-ducyan diamide	Calorimetric	18.8, 20.9, 19.2	11
X-102-diamine	Calorimetric	19.2, 18.7, 19.2	11
C-24-diamide	Calorimetric	14.7, 19.8, 17.8	11
C-24-dicyandiamide	Calorimetric	16.3, 20.3, 17.8	11

of the C—O bond for epoxide ring opening, reference was made to a recent calculation¹² where 24 kcal/mol has been mentioned as the energy required for the breaking of the C—O bond in an uncatalyzed epoxide ring. Since CTPB can act on a hydrogen bond donor, the epoxide ring opening could be considered as an acid-catalyzed process. The activation energy for the hydrogen-ion-catalyzed epoxide ring opening has been reported^{8,13} to be 13 ± 2 kcal/mol. This activation energy tallies with our experimental E for the curing reaction, and therefore one may conclude that E corresponds to the acid-catalyzed epoxide ring rupture.

There are several other references in the literature,¹⁴⁻¹⁷ where the rate-controlling step for the reaction of epoxide and amines has been attributed to a diffusion-controlled process with an associated E of 13 ± 1 kcal/mol. Since the present E of the curing process is also of the similar order, it may be said that the rate controlling step involves a diffusion-controlled mechanism. Thus, considering both the epoxide ring breaking and the diffusion of macromolecules, it is very difficult to decipher in favor of one among these mechanisms, and it requires much deeper study. It may therefore be concluded that the rate-controlling step of CTPB curing (in presence of a large excess of epoxide compared to MAPO) could involve either ring opening of epoxide or diffusion of the macromolecules.

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