Assessment of Cyclization and Network Defects in Glycidylamine-Based Epoxy Networks by Selective Degradation

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ABSTRACT: A special model system based on trimethylene glycol di(*p*-aminobenzoate) and its glycidyl derivative was evaluated to study the extent of cyclization in glycidylamine epoxies. The cured resins were degraded by alkaline hydrolysis, which left the cycles unaffected. The cycle concentration obtained by high-performance liquid chromatography was 15%. The oligomer distribution of the degradation products strongly indicated that up to 40% of the epoxy groups were lost to side reactions, and this resulted in a large number of structural defects in the network. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3951–3956, 2003

Key words: networks; degradation; crosslinking thermosets

INTRODUCTION

Cyclization reactions during network formation are common features of many crosslinking polymers. Their extent depends primarily on structural peculiarities and the mechanism of network formation and can vary widely. In the case of epoxies designed for use in structural materials and molding compounds, these side reactions are important because they affect both the processing behavior and the final properties of the cured resin.

With epoxies, a variety of reactions leading to cyclic structures can occur during resin synthesis and cure (Fig. 1). They include six- and eight-membered rings, such as morpholines and quinolines, from etherification reactions and cyclics from the ring closure of adjacent glycidyl units with amino groups from the curing agent. Of special interest is their dependence on the structure of the resin. It was first reported that bisphenol A based epoxies exhibited no tendency to cyclize when cured by amines.[1] Cyclics were found only under special conditions at high dilution, not in bulk reactions.[2]

The situation changes when adjacent groups are in close proximity. Epoxies based on *o*-phthalic acid or pyrocatechol yield some 25% cyclics when cured by amines.[3,4] This is most critical in cases in which two glycidyl units are located at the same atom; for example, a variety of reactions have been identified for tetraglycidyl diaminodiphenylmethane (Fig. 1) that lead to several cyclic structures.[5–15]

In addition to etherification reactions that occur preferentially during late curing stages at high temperatures,[5] the eight-membered ring (**1**) in Figure 1 is especially interesting. It is generated during curing by direct cyclization between the resin and curing agent, thereby reducing the effective crosslink density of the cured resin. Here the model reaction between *N*-diglycidyl aniline and aniline provides an elegant method for testing for cyclization.[3,4] It leads to a linear polymer with cyclics as byproducts so that a normal molecular weight distribution with a well-separated peak from the cycles at the low molecular end is obtained. Fairly high amounts of cyclic products, around 25–30%, were reported with this model system.[3,4,6] Another study with the same model reactions claimed a range of 15–45% that depended on structural factors.[7]

The results of networks from *N,N′*-tetraglycidyl diaminodiphenylmethane (TGDDM) and aromatic diamines such as diaminodiphenylsulfone (DDS) were somewhat different. From the critical ratio, necessary for the gelation of nonstoichiometric systems, the amount of cyclization was reported to be around 15%.[8] This was in close agreement with results from spectroscopic studies of cured resins reported elsewhere.[9] However, the same group also claimed an overall degree of cyclization, including etherification reactions, of around 50–65%.[5,10,11] For the resolution of these uncertainties, a study was performed with a special degradation technique by which the network was cleaved after curing and the amount of cycles was determined from the fragments.

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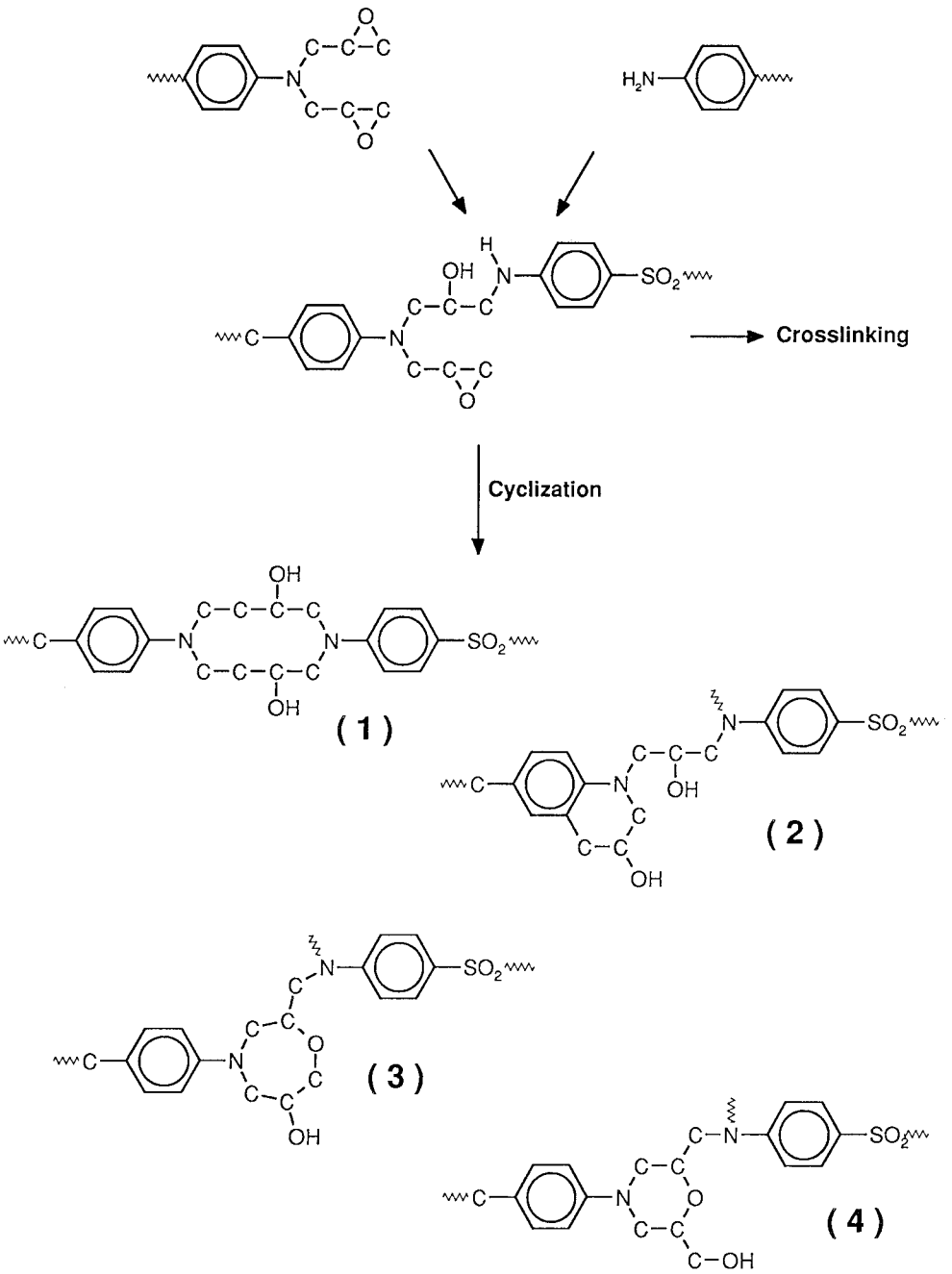


Figure 1 Cyclization reactions in glycidylamine epoxies.

PRINCIPLE OF NETWORK CLEAVAGE

The basic principle of cleaving a network and retaining the cyclic structures is outlined in Figure 2.

Curing TGDDM with DDS results in a purely tetrafunctional network consisting of an alternating arrangement of units of the resin and curing agent with some cycles. If the network is cut just between the phenylene rings of both the resin and curing agent, the network is cut into linear polymers and cycles that remain unaffected and can be analyzed. The situation is the same as the model reaction of diglycidylaniline and aniline. The concentration of cycles can then be determined by chromatographic characterization.

There are some additional requirements. The cleavage reaction must be highly selective and lack side reactions under the conditions used. In addition, both the resin and curing agent should have the same structural unit so that complications in the interpretation of chromatographic data will be prevented.

Trimethylene glycol di(*p*-aminobenzoate) (TMAB) fulfills all these requirements. It is commercially available and is recommended as a nontoxic and slowly

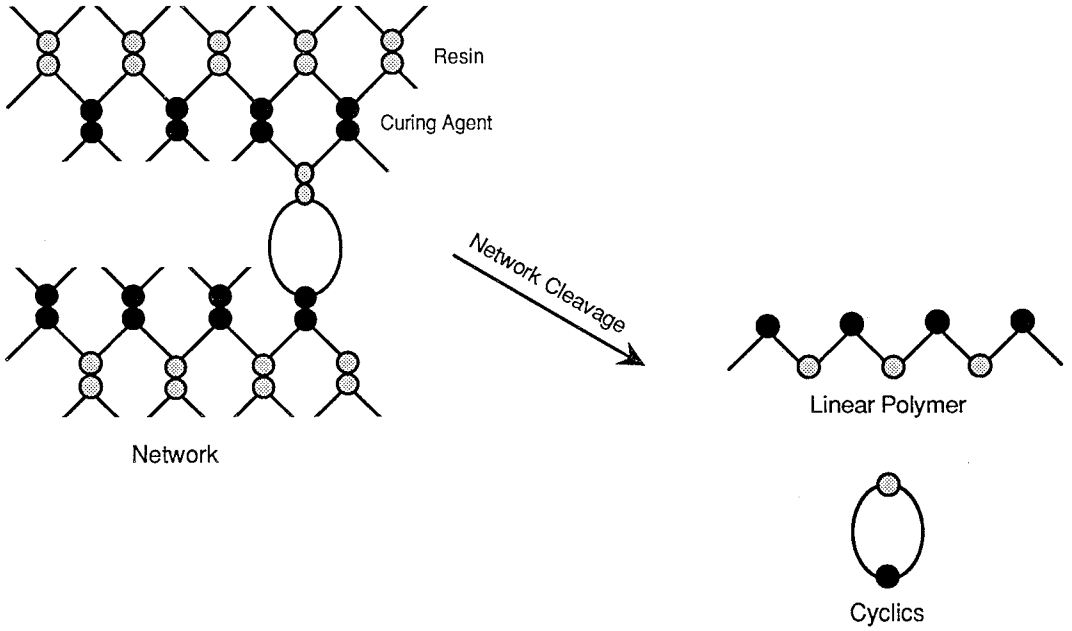


Figure 2 Schematic representation of network degradation with the retention of cyclic structures.

reacting component for polyurethanes and epoxies. It can be reacted with epichlorohydrin to give the corresponding tetraglycidyl derivative and can be used as received as a curing agent (Fig. 3). Network cleavage is performed by the alkaline hydrolysis of the ester groups.

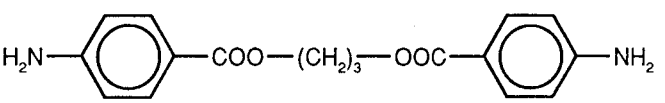
EXPERIMENTAL

Raw materials

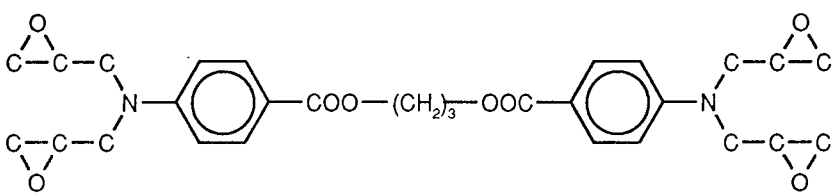
TMAB (Versalink 740M, Air Products) was used as received without further purification. It was an off-white crystalline powder with a melting range of 125–128°C. The corresponding tetraglycidyl derivative (TG-TMAB) was synthesized by the reaction of TMAB with epichlorohydrin and subsequent dehydrochlorination with powdered NaOH. Its epoxy content was 5.0×10^{-3} equiv/g.

Curing

The components were mixed in stoichiometric equivalent ratios at 120°C *in vacuo* for 5 min until a homogeneous solution was obtained, and the solution was



Trimethyleneglycol-di(p-aminobenzoate) **(TMAB)**



Tetraglycidyl-[trimethyleneglycol-di(p-aminobenzoate)] **(TG-TMAB)**

Figure 3 Constituents of a degradation model system suitable for the determination of cyclic structures.

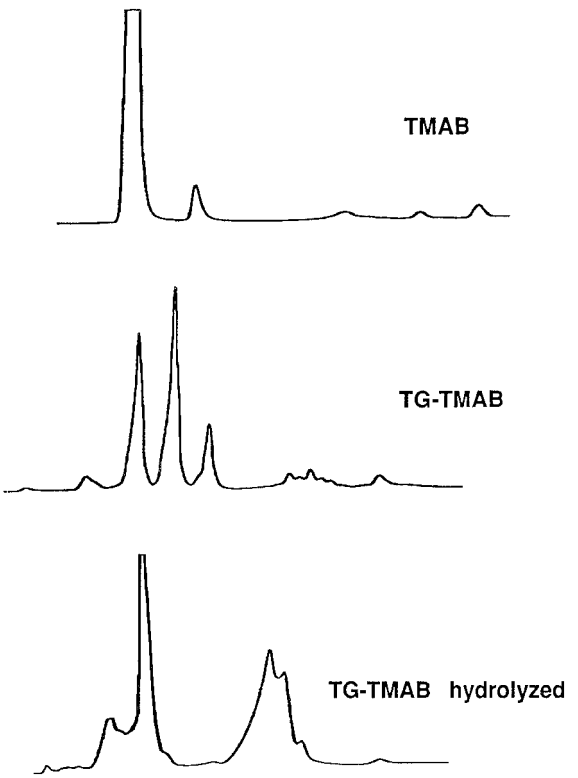


Figure 4 Chromatographic characterization of the raw materials.

then cast onto 4-mm plates with thermostated steel molds and cured. Three samples were prepared with the following curing conditions: sample A, 3 h at 120°C and 5 h at 150°C; sample B, 3 h at 120°C and 5 h at 180°C; and sample C, 3 h at 120°C, 5 h at 150°C, and 3 h at 210°C.

Network cleavage

Network cleavage was achieved by the refluxing of ground resins with an alcoholic KOH solution (5% KOH in 1/1 v/v water/ethanol) for 2 h until the resin was completely dissolved. The solution was then neutralized with sulfuric acid and filtered for the removal of precipitated K_2SO_4, and the solvents were stripped off at 60°C *in vacuo*. The residue was analyzed by high-performance liquid chromatography. The residual K_2SO_4 did not disturb the chromatographic characterization.

Chromatographic characterization

The chromatographic characterization was performed by reverse-phase high-performance liquid chromatography with a Lichrosorb RP-8 250-4 column (5 μ) at 40°C. The eluent was water/acetonitrile with a gradient of 15–65% acetonitrile. An ultraviolet detector at 270 nm was used for detection.

RESULTS AND DISCUSSION

First, the raw materials were characterized (Fig. 4). The commercial TMAB had a major peak (93%) and four additional small peaks at higher retention times. The corresponding epoxy (TG-TMAB) exhibited three major peaks (80%), probably oligomers. A series of additional peaks present at both lower and higher retention times at concentrations of around 3–5% each were probably byproducts.

This epoxy was hydrolyzed under the same conditions used for the cured resins. The hydrolyzed product showed essentially two groups of peaks, one with 51% and the other with 46%. This indicated that the resin consisted of approximately equal amounts of monomer and higher oligomers, which also corresponded to its epoxy content. Because the higher oligomers did not interfere with the determination of the cyclics, no effort was made to prepare resins of higher purities.

The cured resins were characterized for the residual epoxy content, glass temperature, and amount of solubles (Table I). These networks were cleaved and analyzed.

The chromatograms (Fig. 5) consisted essentially of a series of groups of peaks with increasing retention times (probably higher oligomers) depending on the curing temperature. At 150°C, only the low oligomers were present; the higher appeared only at higher curing temperatures.

Although these chromatograms were rather complicated, it was possible to identify the cycles by a comparison with hydrolyzed TG-TMAB in Figure 4. Hydrolyzed TG-TMAB exhibited two groups of peaks, and the region between them was void. These peaks were also found in the cured resins. However, all the chromatograms of the degraded networks exhibited two additional peaks labeled C1 and C2 (cyclic structures) just between the monomer peaks.

Although it was not possible to isolate and identify these peaks because of chromatographic instabilities, it was most likely that these two peaks were the cycles from each half of a structural unit of the resin and curing agent. This was also supported by model reactions with diglycidylaniline/aniline, the peak patterns of which were similar and the cycles of which could be identified. This also compared favorably with data in

TABLE I
Analytical Data of the Cured Resins

Cunag temperature	Sample A	Sample B	Sample C
(°C)	150	180	210
Residual epoxy (%)	17	8	ϕ
Soluble weight fraction	0.021	0.048	0.051
Glass temperature (°C)	Not applicable	179	198

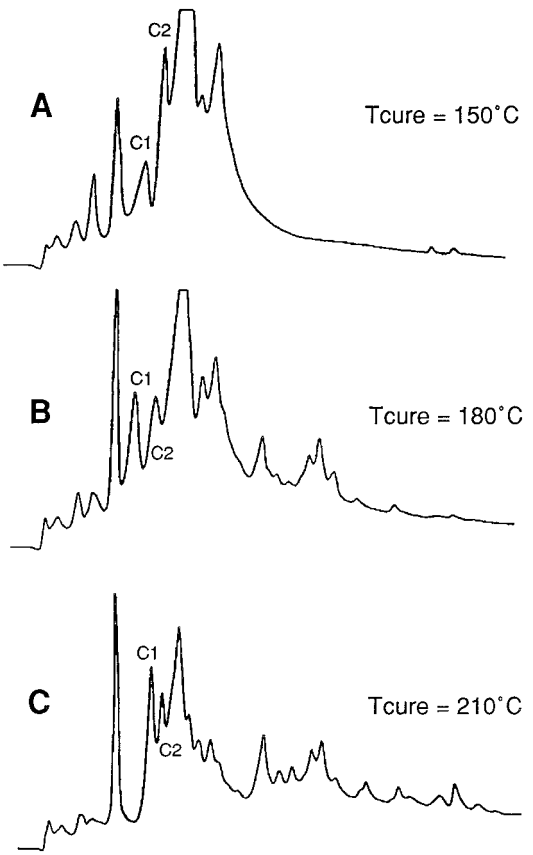


Figure 5 Oligomer distribution of the degradation products of resins cured at (A) 150, (B) 180, and (C) 210°C.

the literature,[6,7] in which two peaks were also found that were identified as isomers of cycles.

The average cycle concentration was 15%, with no clear dependence on the final curing temperature. This was somewhat unexpected because the number of cycles should increase with the temperature,[6] but it may be the result of the small span in the degree of cure. The difference in the effective degree of cure at 150 and 210°C was only a few percent, as shown by the glass temperatures.[16]

Therefore, the results from the network and model reactions were quite comparable. The extent of cyclization found here was also supported by the results of gelation experiments.[8]

Also interesting in this context are the oligomer distributions of the cured resins and their relationship with the analytical data in Table I. The residual epoxy content vanished at high curing temperatures (>180°C), and this indicated a full cure. Therefore, the oligomer distribution after network cleavage should be shifted to higher molecular weights comparable to those obtained from diglycidylaniline/aniline model reactions.[3,4,6,7,17]

The chromatograms of the degradation products, however, were quite different. In all cases, the majority of the oligomers was centered at low molecular weights, with only minor amounts of higher oligomers. This was found even after curing at 210°C, at which point all epoxy groups were consumed. The complete conversion of epoxy groups in comparable systems was also reported elsewhere.[18]

These results indicated that the effective degree of cure was much lower than that what would be expected from the residual epoxy content, at least at high curing temperatures. It was most likely that this was the result of side reactions of epoxy groups and thermal degradation of the resin that superposed the curing reaction. The net result was an appreciable deficiency of the crosslink density and networks with large numbers of structural defects.

This conclusion was also supported by the analytical data presented in Table I. Because the glass temperature and the amount of solubles were characteristic of the actual state of the network,[16,19] whereas the epoxy content characterized the overall conversion of the functional groups, these data could also be used together to characterize the actual cure state of the network. They could be used to check whether the cure reaction was complete or was superposed by side reactions or thermal degradation during curing.

The relatively large amounts of solubles listed in Table I show that these resins were still far from being fully cured. In addition, the increasing amount of solubles along with the decreasing epoxy content at higher curing temperatures clearly indicated that there was some interference of the curing reaction by thermal degradation and side reactions of the epoxy groups at high curing temperatures.

The effect of side reactions is especially evident in Figure 6, in which the influence of catalysis is considered. Here a BF_3 amine catalyst was used to accelerate

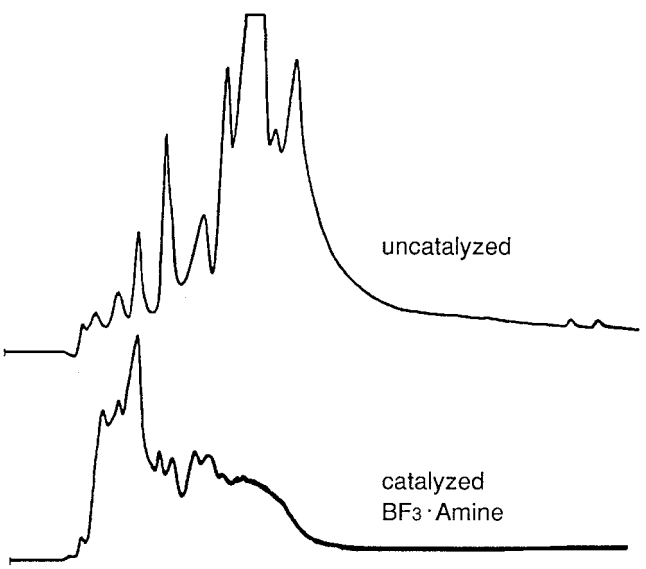


Figure 6 Influence of a BF_3 catalyst on the oligomer distribution.

the curing reaction.

The catalyzed sample showed a shift of the chromatogram to the lower oligomers, although the residual epoxy content was lower than that of the noncatalyzed sample. This may have been due to side reactions, which were accelerated by the catalyst, leading to dead chain ends and lower effective degrees of cure. The decrease in the glass temperature, which was known especially from BF_3-accelerated resins, also supported this conclusion.

It follows from branching theory[19] that for the system discussed here, 5% solubles corresponded to an effective degree of cure of 0.59. This was in good agreement with the corresponding value from the glass temperature. Because the glass-temperature/cure-conversion curves of A_4B_4 systems (where A_4 is a tetrafunctional curing agent and B_4 is a tetrafunctional resin) were similar in the final cure states, literature data of TGDDM/DDS[16] were also used for an assessment of the effective degree of cure. Considering again the sample fully cured at 210°C, we found that its glass temperature of 198°C corresponded to an effective degree of cure of 0.62. This was in good agreement with the value obtained from the amount of solubles. The experimental oligomer distribution in Figure 5 is also in fair agreement with the expected theoretical distribution for a degree of cure of 0.6 obtained by Monte Carlo simulations.

Therefore, it can be concluded from the results obtained here that in glycidylamine-based epoxies, the degree of cyclization from ring closure of adjacent glycidyl units with a primary amino group of the curing agent does not exceed 15%. This is consistent with literature data from both model reactions and gelation experiments.

According to both the analytical data of the cured resins and the oligomer distributions of the hydrolyzed samples, the effective degree of cure was only around 0.6, although no residual epoxy was detected by Fourier transform infrared spectroscopy (FTIR). It was most likely that the loss of epoxy groups was the result of side reactions that occurred, especially at temperatures greater than 150°C. At high curing temperatures, there was also some interference by thermal degradation of the network. Both reduced the effective crosslink density and the available degree of cure. The final result was networks with large numbers of structural defects.

The cycles generated by etherification reactions (e.g., structures **3** and **4** in Fig. 1) are another aspect to be considered. It was reported that large amounts of cyclic ethers could be formed in glycidylamine-based epoxies.[5] However, these ethers were generated primarily in nonstoichiometric resins with an excess of epoxy groups and only in the very final curing stages at temperatures well above 200°C, at which thermal degradation occurred. It is also known that the formation of cyclic ethers is significant only at high temperatures and with excess epoxy.[6] This was confirmed during this study by FTIR. Some ether groups were already present in the raw materials, but their concentration did not increase during the cure. In addition, most of the etherification reactions did not contribute to the crosslink density and so had to be intramolecular.[18]

In summary, the network defects in glycidylamine-based epoxies from cyclization are far fewer than those resulting from side reactions, a limited degree of cure, and thermal degradation.

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