

# Cure of Epoxy Resins with a New Dicarboxy-bis-Azomethine

## INTRODUCTION

The synthesis and evaluation of polymeric azomethines have been reported in the literature in a number of papers.<sup>1-11</sup> These polymers display high thermal stability and high glass transition temperatures; however, they are infusible, intractable, and insoluble in common solvents and thus cannot be processed into films, fibers, or other desired shapes.<sup>12,13</sup> In a recent report, ring substitution, copolymerization, and introduction of in-chain flexible units were shown to lower the melting points of the azomethine polymers.<sup>14</sup> These modified polymers produce optically anisotropic melts which provide structurally ordered fibers with high tensile strength properties. In this report we describe the synthesis of a new conjugated dicarboxy-bis-azomethine and its reaction with epoxy resins to introduce this stiff azomethine structure into the polymer network.

## EXPERIMENTAL

Reagent grade dimethylformamide and ethanol were used as solvents. Terephthalaldehyde and *p*-aminobenzoic acid were obtained from Aldrich Chemical Co. and were used without further purification. The epoxies investigated were bisphenol-A diglycidyl ether (EPON resin 828, Shell Chemical Co.) (I) and triglycidyl *p*-aminophenol (epoxy resin 0510, Ciba-Geigy) (II):

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Thermal decomposition of the polymers was studied in Argon (40 mL/min) with a DuPont 990A thermal gravimetric analyzer and the softening points were determined with a DuPont Model 943 thermal mechanical analyzer by employing the penetration mode with a heating rate of 10°C/min.

**Preparation of 4,4'-Dicarboxyphenyl-Bis-Azomethinexylelidene III.** Terephthalaldehyde (13.4 g, 0.1 mol) was dissolved in a mixture of 100 mL ethanol and 15 mL dimethylformamide. In a separate flask 27.4 g (0.2 mol) *p*-aminobenzoic acid was dissolved in 100 mL ethanol and 15 mL dimethylformamide. The two solutions were heated to 50°C and then mixed at that temperature. A yellow color appeared immediately and within minutes the product separated as light yellow crystals. The solid was collected by filtration and dried under vacuum to yield 24.9 g of product. The product did not show any melting up to 300°C.

**Curing of the Epoxies with 2,4,6-tris-(Dimethylaminomethyl)phenol.** Five grams of epoxy, as shown in Table I, was mixed with a catalytic amount of the amine with stirring and heating. The mixture was placed in an aluminum pan, and a small amount of the mixture was drawn on a sodium chloride plate to record an infrared spectrum. The aluminum pan and the salt plate were

TABLE I  
Cure of Epoxies with Dicarboxyazomethine III

Comp.	Amount of epoxy (g)		Amount of acid		Acid/epoxy equiv. ratio	Softening points ΣC
	Epon 828	Epoxy resin 0510	g	%		
A	5.0	—	0	0	0	66
B	9.5	—	2.1	18.1	0.238	114
C	13.3	—	5.0	27.3	0.405	133
D	10.0	—	5.2	34.2	0.559	159
E	—	5.0	0	0	0	154
F	—	10.9	1.8	14.2	0.0986	188
G	—	18.0	4.5	20.0	0.148	195
H	—	12.0	4.2	25.9	0.207	220

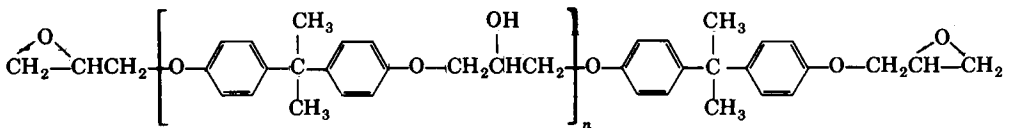
placed in an oven at 180°C for 2 h. The samples were allowed to cool to room temperature and were subjected to infrared and thermal mechanical analysis (TMA).

**Curing of Epoxies with Diacid III.** General: The epoxy and the diacid, as shown in Table I, were mixed in a beaker, and the mixture was placed on a hot plate at about 150°C. The mixture was stirred with a magnetic stirrer until the diacid completely dissolved in the epoxy. The solution was then placed in an aluminum pan, and part of the solution was drawn on a sodium chloride plate. The aluminum pan and the salt plate were placed in an oven at 180°C for 2 h. After cooling to room temperature, infrared and TMA were carried out.

In calculating the stoichiometry of the reactants, the equivalent weights of EPON resin 828, epoxy resin 0510, and the azomethinediacid III were assumed to be 200, 110, and 186 respectively.

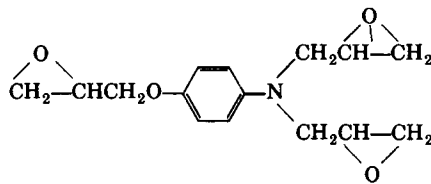
## RESULTS AND DISCUSSION

In the preparation of azomethine diacid III, 2 mol of *p*-aminobenzoic acid were allowed to react with 1 mol of terephthalaldehyde to produce the desired structure III as shown in Scheme I:

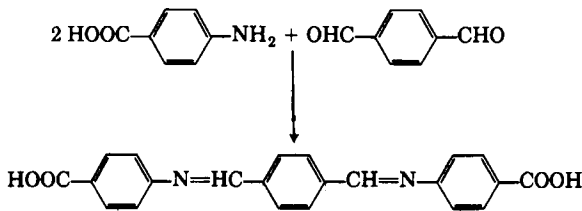


where  $n$  is less than 1,

I



II



III

Scheme I.

Since bisazomethine III has a conjugated, rodlike structure, it has very low solubility even in polar solvents and crystallizes out immediately from the reaction solvent. The conjugated, rodlike structure also renders this material high melting. The presence of carboxylic acid groups and their probable association with the amino moieties would be expected to further raise the melting point

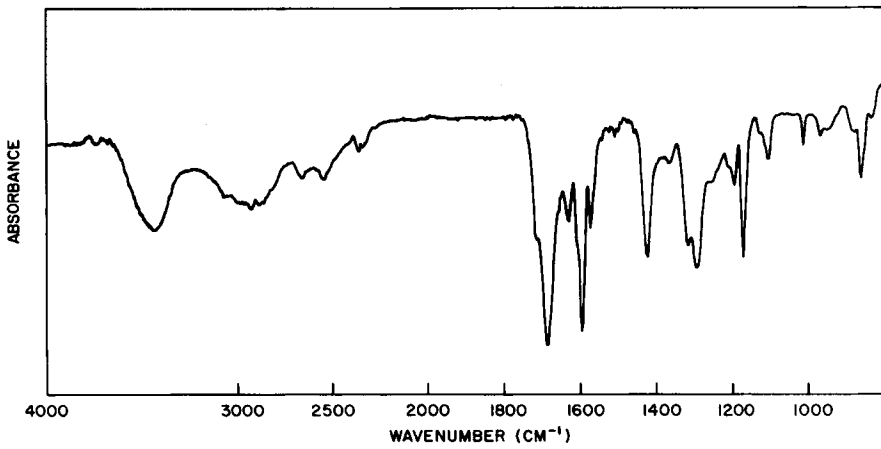


Fig. 1. Infrared spectrum of bisazomethine diacid III.

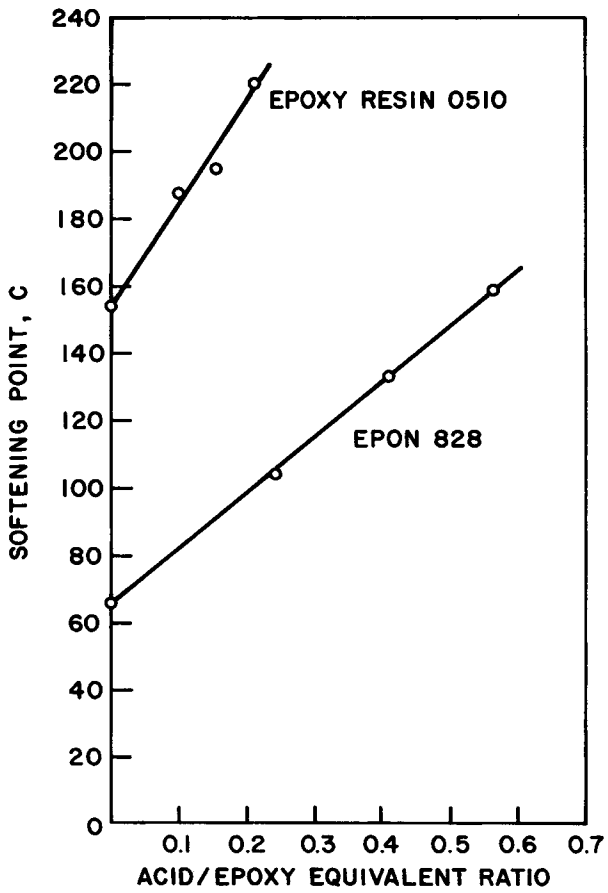


Fig. 2. Softening point vs. acid/epoxy equivalent ratios.

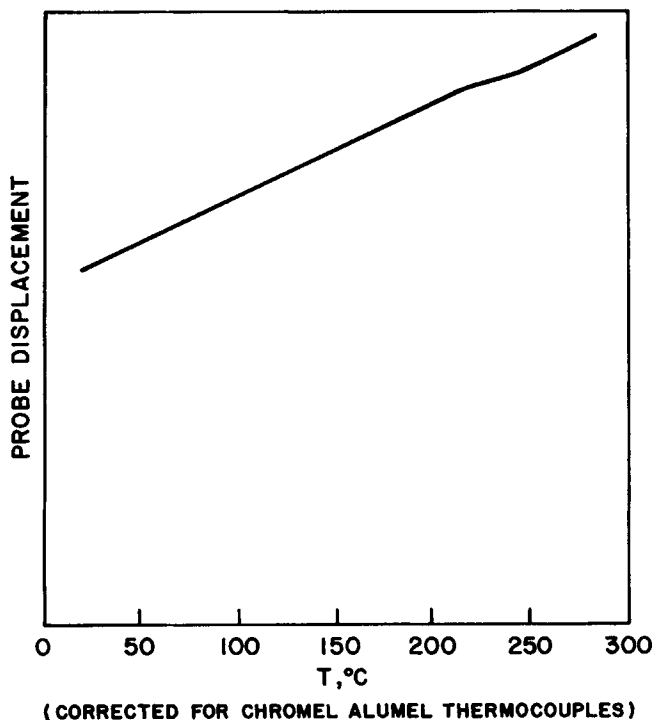


Fig. 3. Thermal mechanical analysis of composition H (Table I).

of this compound; no melting was observed up to 300°C. The structure of azomethine III is supported by its infrared spectrum. The strong absorption at  $1595\text{ cm}^{-1}$  is assigned to the C=N bonds and the band at  $1685\text{ cm}^{-1}$  to the carboxylic acid groups (Fig. 1).

In the reaction of diacid with epoxy I, the carboxylic groups react with epoxides to produce essentially linear oligoesters with pendant hydroxy and epoxy functionalities. Upon further heating, the hydroxy and epoxide functionalities react to produce a crosslinked network. The crosslinking takes place through formation of ether linkages. The reaction of diacid III with epoxy II produces branched polymers and crosslinked networks by the reaction of the acid groups with epoxide moieties. Upon further heating, additional crosslinking takes place through ether linkage formation resulting from the reaction of hydroxy with epoxide groups.<sup>16</sup> In the amine catalyzed curing of epoxies I and II, all the polymerization takes place through ether linkage formation. The complete absence of an absorption at  $910\text{ cm}^{-1}$  in the infrared spectra of the cured compositions, indicated the disappearance of the epoxide functionality and presence of the absorption band at  $1595\text{ cm}^{-1}$  indicated that the C=N bonds did not participate in the curing of these compositions.

Compositions A–D contain difunctional epoxy I. Composition A, which contains no rigid azomethine segments, has the lowest softening point (Table I). Compositions B–D exhibit increased softening points as the percentage of acid in the total composition increases. Similarly, with the trifunctional epoxy II, as the percentage of rigid segments increases, there is a corresponding increase in the softening point (E–H, Table I). The composition E, which contains no rigid azomethine segments, has the lowest softening point. The relationship between the increase in the softening point and the increase in ratio of azomethine to epoxy is essentially linear (Fig. 2). A typical softening point curve for these crosslinked compositions is shown in Figure 3. Higher ratios of azomethine III/epoxy than those in D and H (Table I) could not be applied because of the limited solubility of III in epoxies I and II. Thermal gravimetric analysis of all new compositions show no decomposition below 300°C; TGA curves for two of the compositions are shown in Figure 4.

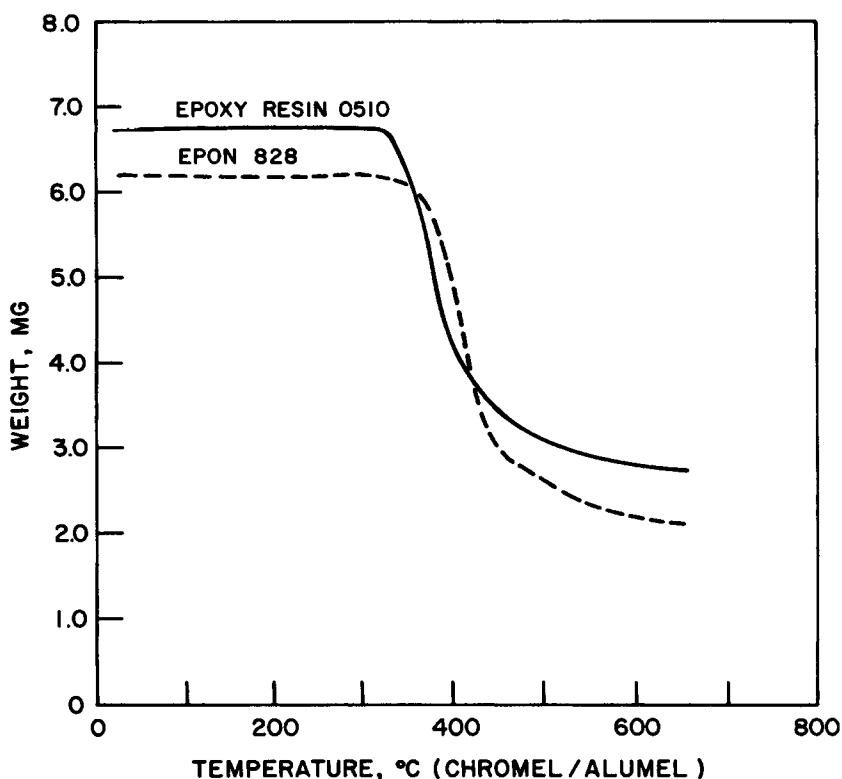


Fig. 4. Thermal gravimetric analyses of compositions D and H (Table I).

### CONCLUSIONS

Structurally rigid dicarboxyazomethine can be prepared by the reaction of *p*-aminobenzoic acid with terephthalaldehyde. When the azomethine is heated with epoxy resins, the carboxy moieties react with epoxy groups to introduce stiff conjugated azomethine segments into the epoxy matrix. Increasing amounts of the rigid segments produce thermoset epoxy compositions with enhanced glass transition temperatures. However, an amount of carboxy azomethine equivalent to that of the epoxy cannot be employed due to its lack of solubility in the epoxy resins. The limited miscibility of the carboxy azomethine with the epoxy resins make these compositions rather difficult to process.

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