

# Reversible Crosslinking in Epoxy Resins.

## II. New Approaches

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### Synopsis

Epoxy resins of varying epoxy equivalent weight were crosslinked with 4,4'-dithiodianiline (DTDA) at a 2/1 mole ratio. Resin of equivalent weight 190 (Epon 828) was cured with DTDA at mole ratios varying from 2/1 to 1.25/1. Properties of cured resins were evaluated and their reduction was investigated. Under the conditions used, reduction to the point of complete solubilization was possible providing crosslink density did not exceed a threshold value tentatively established as  $M_c = 400 - 500$ . Recurring of reduced resins was accomplished by oxidation and by reaction of thiol groups with polyfunctional reagents, including bismaleimides and polyepoxides.

### INTRODUCTION

In Part I of this series, we have reported results obtained when a prototype epoxy resin (Epon 828, Shell) was crosslinked with disulfide-containing curing agents: Disulfide bonds in the cured resins were reduced to the point of complete solubilization, and then reformed by oxidation. In the present paper, we describe and discuss results obtained with dithiodianiline as curing agent, by varying the epoxy equivalent weight of the resin employed and also at varying mole ratios of epoxy to amine in the curing reaction. Modifications of the experimental resins after reduction have also been investigated in addition to the reformation of disulfide crosslinks by oxidation. The results reported here expand the scope of the approach previously described and also demonstrate that novel resins exhibiting a broad spectrum of properties may be obtained by curing epoxy resins with dithiodianiline (DTDA), reducing the cured resins, and subsequently reacting the thiol groups formed with polyfunctional reagents. The use of DTDA or related crosslinking agents for curing of epoxy resins provides a viable approach to the recovery and reuse of cured polymers, and is also suitable for the preparation of modified resins in which the thiol groups obtained by reduction of disulfide bonds are reacted with selected polyfunctional reagents.

A comparative evaluation of mechanical properties of epoxy resins fully cured with DTDA and with MDA is currently in progress and will be reported elsewhere.

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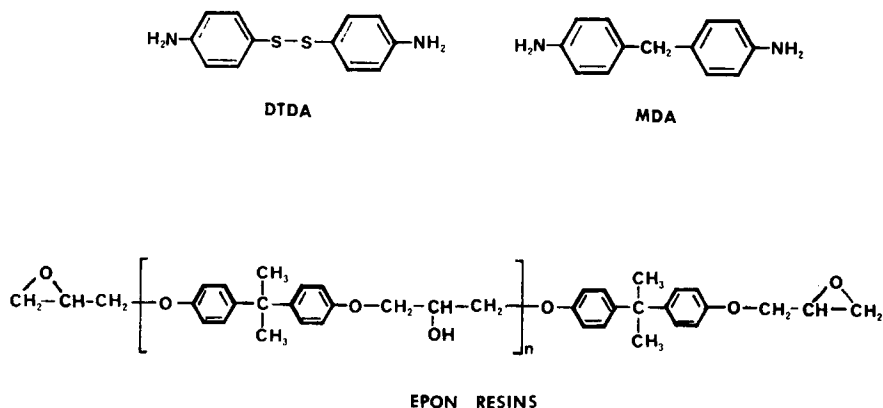


Fig. 1. Structures of monomers.

## EXPERIMENTAL

### Materials

Methylene dianiline (MDA) and 4,4'-dithiodianiline (DTDA) (both Aldrich) were recrystallized from aqueous methanol. Methylene dianiline bismaleimide (MDABM), paraphenylenediamine bismaleimide (PPDABM), tri-*n*-butyl phosphine (Bu<sub>3</sub>P), iodine crystals, diglyme, HPLC grade tetrahydrofuran (all Aldrich), Epon 828 (Polysciences), Epon 834, Epon 836, and Epon 1001F (all Shell) were used as received. Triethylamine (TEA) (Aldrich) was freshly distilled over LiAlH<sub>4</sub>, and *m*-cresol (Aldrich) was freshly distilled before use. All other solvents were used as received. Structures of curing agents and epoxides are given in Figure 1.

### Methods

Differential scanning calorimetry (DSC) was performed on a DuPont 910 instrument under nitrogen at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was carried out on a DuPont 951 analyzer under nitrogen at a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) was done on a DuPont 982 analyzer at a heating rate of 5°C/min.

Gel permeation chromatography (GPC) was carried out on a Waters GPC I, Model 590, liquid chromatograph, using the refractive index detector and narrow molecular weight polystyrene standards for the calibration curve. Tetrahydrofuran was the eluant at a flow rate of 0.8 mL/min using Waters  $\mu$ -styragel columns of 10<sup>4</sup>, 10<sup>3</sup>, and 500 Å in series.

FT-IR spectra were measured on a Bio-Rad FTS 60 spectrophotometer. Chemical analysis of cure kinetics and epoxide conversion was according to Bell<sup>1</sup> and Lee and Neville.<sup>2</sup> Determination of thiol groups after reduction (using DMF as the solvent) was by the method of Bald.<sup>3</sup> Elemental analysis was performed by Microlytics, South Deerfield, MA.

TABLE I  
Resin Designations

Resin (diamine/ <i>x</i> mol-Epon resin)	Designation			
	Fully cured	Reduced	Reoxidized	Modified
DTDA/2-Epon 828	1	1R	1RO	—
DTDA/2-Epon 834	2	2R	2RO	—
DTDA/2-Epon 836	3	3R	3RO	—
DTDA/2-Epon 1001F	4	4R	4RO	—
MDA/2-Epon 828	5	—	—	—
DTDA/1.75-Epon 828	6	6R	6RO	6MO
DTDA/1.5-Epon 828	7	—	—	—
DTDA/1.25-Epon 828	8	—	—	—
MDA/1.75-Epon 828	9	—	—	—

### Cure, Reduction, and Reoxidation of DTDA and Epon Resins in Stoichiometric Ratios

In a typical experiment, stoichiometric ratios of reagents (i.e., a 1:2 molar ratio diamine/diepoxide) were accurately weighed in a Teflon beaker and mixed well. The beaker was then put in an oven at 60°C (for Epon 828 and Epon 834) or 80°C (for Epon 836 and Epon 1001F) till the diamine completely dissolved. The resins were then cured at 100°C for 2 h followed by 150°C for another 2 h. The cure profile for the MDA cured resin 5 was 80°C for 2 h and 100°C for 2 h (after dissolving the diamine at 60°C). Resin designations are given in Table I, DSC cure temperatures in Table II, and properties of the fully cured resins 1–5, 6, and 9 are shown in Table III.

For the reduction reaction, the fully cured resins were ground to 600- $\mu$ m-sized particles with liquid nitrogen after the first stage of the cure cycle, and then cured at 150°C for 2 h. Reduction conditions are shown in Table IV. The solubilized polymers were then poured into excess methanol. The solid so obtained was washed with methanol, filtered, and dried in a vacuum desiccator at room temperature to constant weight.

Reoxidation of the dry, soluble, thiol-containing polymers 3R and 4R was carried out by dissolving 0.5 g of the reduced resin in 20 mL diglyme. A 10% iodine solution in diglyme was then added dropwise with constant stirring until the iodine color persisted. The solution was warmed to 60°C and a few more drops of iodine added until the iodine color persisted. The solution was stirred for an additional 30 min and cooled to room temperature. The

TABLE II  
DSC Cure Temperatures and Heats of Cure

Resin	Onset (°C)	Peak (°C)	Heat of cure (J/g)
1	140.3	170.8	241
5	116.4	146.2	410
6	154.4	188.9	366
9	131.7	163.6	420

TABLE III  
 Properties of Fully Cured Resins

Resin	Monomers			Fully cured resins			
	Epon Resin	Epoxide eq wt	Diamine	$T_g^a$ (°C)	$M_c^a$	$M_c$ (theoretical)	$T_D^b$ (°C)
1	828	190	DTDA	176	370	336	336.5
2	834	250	DTDA	150.5	393	416	344.8
3	836	310	DTDA	152.5	550	496	354
4	1001F	545.5	DTDA	124	908	810	369.8
5	828	190	MDA	167	357	319	401
6	828	190	DTDA	167	470	—	332.9
9	828	190	MDA	174.5	491.5	—	388.1

<sup>a</sup>DMA, 5°C/min.

<sup>b</sup>TGA, N<sub>2</sub>, 20°C/min.

insoluble material was then filtered, washed with diglyme and methanol, and dried overnight in a vacuum oven at 100°C. Thermal properties of the reoxidized resins 3RO and 4RO are given in Table IV.

#### Curing of Epon 828 with DTDA and MDA in Differing Molar Ratios

In a typical experiment, diamine and diepoxide in appropriate molar ratios (diamine/diepoxide) were mixed well in a Teflon beaker and placed in an oven at 60°C till the diamine just dissolved. Cure profiles were:

- (i) 100°C, 2 h; 150°C, 2 h for resins 6–8
- (ii) 80°C, 2 h; 150°C, 2 h for resin 9

Properties of the cured resins are given in Table V.

Elemental analysis	Calcd (%)	Anal (%)
Resin 1	N 2.77, S 6.34	N 2.72, S 6.34
Resin 6	N 3.1, S 7.0	N 4.16, S 7.03

#### Reduction and Reoxidation of 6 (DTDA/Epon 828 at 1 / 1.75)

For the reduction reaction, the resin was ground to 600- $\mu$ m-sized particles as described above. One gram of 6 was accurately weighed in a 100 mL round-bottomed flask. Diglyme (25 mL) was added, followed by five drops of dilute HCl (from a stock solution of 15 mL water containing two drops concd HCl). Tributyl phosphine (1.5 mL) was then added and the solution was refluxed under nitrogen for 55 min till all the resin just dissolved. The reaction was cooled and poured into excess methanol. The solid so obtained was washed again with methanol and dried in a vacuum desiccator to constant weight, to obtain quantitative yields of the reduced polymer 6R, the properties of which are given in Table VI.

TABLE IV  
 Reduction and Reoxidation of Fully Cured Resins 1-4

Fully cured resin	Reduction			Reoxidation				
	Designation	Reduction to complete solubility	Conditions	—SH content (meq/g)	Designation	Conditions	$T_g^a$ (°C)	$T_D^b$ (°C)
1	1R	No	Bu <sub>3</sub> P, diglyme	—	1RO	—	—	—
2	2R	No	Bu <sub>3</sub> P, diglyme	—	2RO	—	—	—
3	3R	Yes	1.5 g resin, 20 mL diglyme, 2 mL Bu <sub>3</sub> P, 3 drops dil. HCl, reflux, N <sub>2</sub> , 4 h	0.51	3RO	I <sub>2</sub> /diglyme	106.3	268
4	4R	Yes	1.0 g resin, 15 mL diglyme, 2 mL Bu <sub>3</sub> P, 3 drops dil. HCl, reflux, N <sub>2</sub> , 1 h	0.395	4RO	I <sub>2</sub> /diglyme	69.3	327.9

<sup>a</sup>DSC, N<sub>2</sub>, 10°C/min.

<sup>b</sup>TGA, N<sub>2</sub>, 20°C/min.

TABLE V  
 Properties of Fully Cured Resins with Varying DTDA/Epon 828 Molar Ratios

Resin	$T_g^a$ (°C)	$M_c^a$	$\tan \delta_{\max}^a$	$T_g^b$ (°C)
1	176	370	0.0775	160
6	167	470	0.094	140
7	152	736	0.127	133
8	134	1172	0.148	111

<sup>a</sup>DMA, 5°C/min.<sup>b</sup>DSC, N<sub>2</sub>, 10°C/min.
 TABLE VI  
 Properties of Reduced, Reoxidized, and Modified Resins of 6

	Designation	Conditions	$T_D^a$ (°C)	$T_g^b$ (°C)	$M_c^c$	—SH Content (meq/g)	MW
Fully cured resin	6	100°C, 2 h 150°C, 2 h	332.9	139.9	470	—	—
Reduction	6R	Bu <sub>3</sub> P, diglyme, reflux, N <sub>2</sub> , 55 min	182	49.9	—	0.955	$\bar{M}_n = 2400$ $\bar{M}_w = 3600$
Reoxidation	6RO-1	I <sub>2</sub> /dioxane	285	126.8	800 <sup>d</sup>		
	6RO-2	Air, 160°C, 24 h	313.5	109.9	1180 <sup>d</sup>		
Modification	6MO-1	PPDABM, TEA (cat) <i>m</i> -cresol, 105°C, 3 h	340.6	147	—		
	6MO-2	MDABM, TEA (cat) <i>m</i> -cresol, 105°C, 3 h	345	135	—		
	6MO-3	10% (by wt) Epon 828, TEA (cat), DMF, 105°C, 1.5 h	332.6	72.3	—		
	6MO-4	20% (by wt) Epon 828, TEA (cat), DMF, 105°C, 1.5 h	345	118.7	—		

<sup>a</sup>TGA, N<sub>2</sub>, 20°C/min.<sup>b</sup>DSC, N<sub>2</sub>, 10°C/min.<sup>c</sup>DMA, N<sub>2</sub>, 5°C/min.<sup>d</sup>Extrapolated values.

Reoxidation of 6R was carried out by dissolving 0.4 g of the polymer in 15 mL dioxane and adding to it a 10% iodine solution in dioxane dropwise with constant stirring. A precipitate gradually formed. The mixture was warmed to 60°C. When the iodine color disappeared, a few additional drops were added till the color just persisted. The solution was stirred for an additional 30 min, cooled to room temperature, and the solid filtered and washed with dioxane and several times with methanol. The reoxidized resin 6RO-1 was dried in a vacuum oven overnight at 100°C.

Air reoxidation of 6R was done by weighing 0.5 g 6R in a Teflon beaker and placing it in an air oven at 160°C for 24 h. The dark solid 6RO-2 was cooled and thermal properties were measured. Properties of reoxidized resins 6RO-1 and 6RO-2 are given in Table VI.

### Percent Conversion of Epoxide and Percent Gel in the Curing of 6

A total of 15 g of reactants (DTDA and Epon 828 in a 1 : 1.75 molar ratio diamine/diepoxide) was accurately weighed in a Teflon beaker, mixed well, and placed in an oven at 60°C till the diamine just dissolved. The beaker was then placed at the appropriate isothermal temperature of cure and 1-g samples removed at various intervals of time. The samples were analyzed for epoxide conversion and the glass transition temperature of the reaction mixture was measured. Cure temperatures of 60, 80, 100, 120, 140, and 160°C were employed.

$$\% \text{ epoxide conversion} = \frac{E_0 - E_t}{E} \times 100$$

where  $E_0$  = epoxide content at time  $t_0$  and  $E_t$  = epoxide content at time  $t$ .

About 0.5 g of the above sample was accurately weighed in a 100 mL round-bottomed flask and 25 mL dioxane added. The solution was refluxed for 3 h and filtered while hot. The solid was washed with dioxane and dried well in a vacuum oven at 100°C, accurately weighed and gel content calculated.

$$\% \text{ gel} = \frac{\text{solid after extraction}}{\text{initial resin}} \times 100$$

### Analysis of the Reduction Reaction of 6

About 1 g of fully cured 6 (finely ground 600  $\mu\text{m}$  particles) was accurately weighed in a 100 mL round-bottomed flask. To it was added 25 mL diglyme and five drops dilute HCl (from the stock solution described above).  $\text{Bu}_3\text{P}$  (1.5 mL) was then added and the mixture refluxed under nitrogen. Six different samples were prepared in this manner. Refluxing was continued for various lengths of time. At the specified time, the solution was filtered while hot, the gel was washed with a minimal amount of diglyme followed by 5 mL of methanol, and dried to constant weight, and percent gel was calculated. The filtrate was poured into excess water. A soft solid was obtained. The liquid was decanted and the solid transferred to an accurately weighed vial. The solid was dried in a vacuum oven at 100°C overnight and percent sol calculated. Profiles with time are shown in Figure 10. The glass transition temperatures of the gels were also measured by DSC and plotted against time (Fig. 11).

### Modification of 6R with Bismaleimides

Modification reactions were run on a sample of 6R having a thiol content of 1.04 meq/g. The method of White and Scaia<sup>4,5</sup> was followed using exact stoichiometric amounts of bismaleimide.

#### *With Paraphenylenediamine Bismaleimide (PPDABM)*

In a 50-mL round-bottomed flask with a magnetic stirrer was added 0.5015 g 6R and 7 mL diglyme. Once the resin had dissolved, 5 mL *m*-cresol was added, followed by 0.0704 g PPDABM and five drops of triethylamine.

The flask was fitted with a reflux condenser and immersed in an oil bath kept at  $105 \pm 3^\circ\text{C}$ . A precipitate started forming after 30 min. The reaction was continued for a total of 3 h. The solution was then cooled, and the solid filtered, washed with diglyme, and methanol, and dried at  $100^\circ\text{C}$  in a vacuum oven overnight to give 0.516 g (98.1%) of 6MO-1. Thermal properties are shown in Table VI.

#### *With Methylenedianiline Bismaleimide (MDABM)*

The procedure used for 6MO-1 was followed using 0.5085 g of 6R and 0.0947 g MDABM to give 0.598 g (99.2%) of modified polymer 6MO-2. Thermal properties are given in Table VI.

### **Modification of 6R with Epon 828**

The method of Iwakura et al. was followed.<sup>6</sup>

#### *Using 10% by Weight Epon 828*

To 0.0412 g Epon 828 and 0.412 g 6R in a 50-mL round-bottomed flask with a magnetic stirrer was added 15 mL DMF. Once the solids had dissolved, 15 drops of triethylamine catalyst was added. The flask was fitted with a reflux condenser and immersed in an oil bath at  $105 \pm 3^\circ\text{C}$  for 1.5 h, during which time an insoluble polymer formed. The solution was cooled and the solid filtered, washed with DMF and methanol, and dried at  $100^\circ\text{C}$  in a vacuum oven overnight to give 0.45 g (99.5%) of 6MO-3. Thermal properties are given in Table VI.

#### *Using 20% by Weight Epon 828*

The procedure for 6MO-3 was repeated using 0.1032 g Epon 828 and 0.516 g 6R to give 0.6 g (97%) crosslinked polymer 6MO-4. Thermal properties are given in Table VI.

## **RESULTS AND DISCUSSION**

Initial studies were performed on fully cured resins of DTDA and epoxy resins (Fig. 1) of varying epoxide equivalent weights (EEW). Resins 1–5 (Table I) were cured using stoichiometric ratios of reactants (i.e., 1 : 2 molar ratio diamine/diepoxyde). The synthesis of resin 5 with MDA as a reference curing agent served a twofold purpose: the first, to compare its resin properties with 1, and, the second, to validate results obtained in our laboratories with those reported in the literature.<sup>1,7,8</sup>

The standard cure profile of  $80^\circ\text{C}$  for 2 h followed by  $150^\circ\text{C}$  for 2 h was employed for resin 5.<sup>1,8</sup> DSC analysis (Table II) and cure kinetics of DTDA and MDA with Epon 828<sup>9</sup> showed that DTDA had a lower reactivity than MDA. A cure temperature of  $100^\circ\text{C}$  for 2 h was found to be a more appropriate temperature for the first stage of the cure profile followed by  $160^\circ\text{C}$  for resin 1 and  $150^\circ\text{C}$  for resins 2–4. Properties of the fully cured resins are given in Table III.



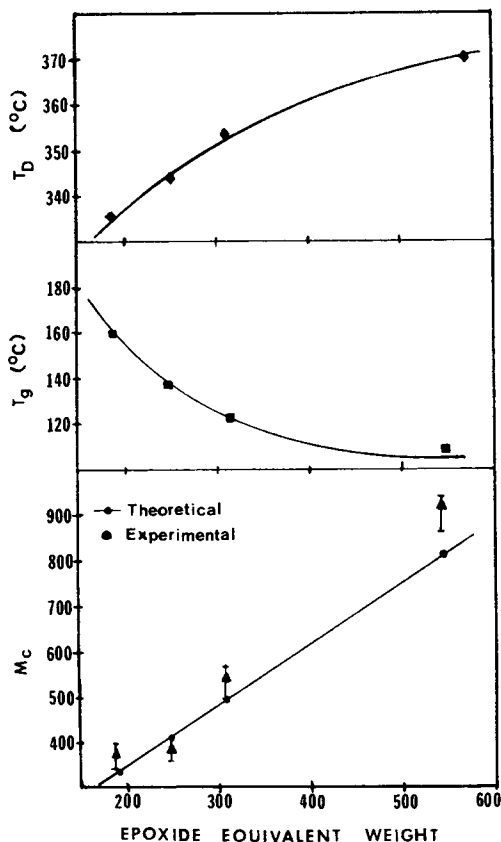


Fig. 2. Variation of  $M_c$  (from DMA),  $T_g$  (from DSC), and  $T_D$  (from TGA) with epoxide equivalent weight for resins 1-4.

Epoxide equivalent weights ranged from 190 to 545.5 and corresponded to a range of physical, thermal, and mechanical properties for the cured resins. Figure 2 illustrates the variation of some of these properties with epoxide equivalent weight. The average molecular weight between crosslinks ( $M_c$ ) increases with increasing EEW. Experimental values are in close agreement with theoretically calculated values.<sup>1,8</sup> The increase in  $M_c$  is reflected in the corresponding decrease in the glass transition temperature ( $T_g$ ). The higher aromatic content of Epon resins with higher EEW gives the cured resins a higher onset of decomposition ( $T_D$ ). The  $T_D$  of 1 is, however, lower than that of 5 (Table III) due to the thermal lability of the disulfide bond.

Reduction of resins 1 and 2 by cleavage of the disulfide bonds<sup>10,11</sup> did not yield soluble polymers under the conditions studied. A resin with a higher  $M_c$  (i.e., a lower crosslink density) was thus needed to facilitate reduction to complete solubility. This was achieved for resins 3 ( $M_c = 550$ ) and 4 ( $M_c = 908$ ), the latter being solubilized in a shorter reaction time (Table IV). All reductions were carried out on samples with particle sizes of 600  $\mu\text{m}$  to provide a larger surface area and thus facilitate access of  $\text{Bu}_3\text{P}$  to the disulfide bonds. Reoxidation of 3R and 4R with a 10% iodine solution gave resins 3RO and 4RO, respectively, whose thermal properties approached that of the

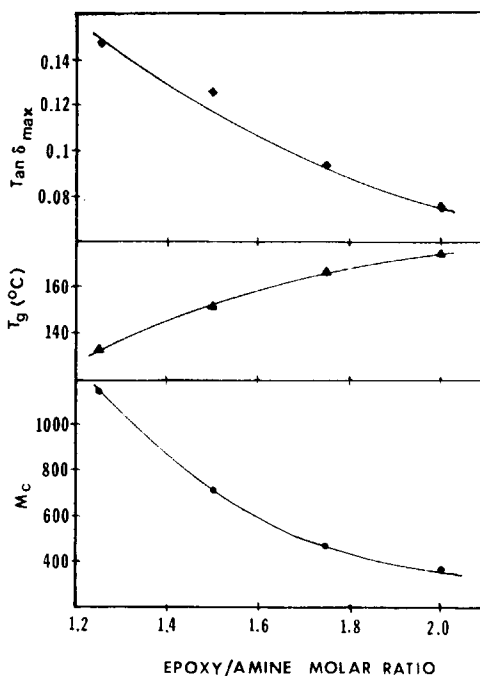


Fig. 3. Variation of  $M_c$ ,  $T_g$ , and  $\tan \delta_{\max}$  (all from DMA) with epoxy/amine molar ratio for resins 1, 6, 7, and 8.

parent resins 3 and 4 (Table IV). This study showed that the  $M_c$  of the cured resin needs to approach a threshold value of 400–500 in order to cleave the disulfide bonds and obtain a soluble polymer under the conditions evaluated.

A series of resins of DTDA and Epon 828 in varying diamine/diepoxy molar ratios were then synthesized (resins 1, 6, 7, 8, Table I), in order to compare their crosslink densities and thermal properties (Table V). Figure 3 illustrates the trends of  $M_c$ ,  $T_g$ , and  $\tan \delta_{\max}$  with the epoxy/amine molar ratio. All values were obtained from dynamic mechanical analysis. An equimolar epoxy/amine ratio yields a polymer with a linear structure and an  $M_c$  value approaching infinity (assuming exact stoichiometry and no crosslinking side reactions). An epoxy/amine molar ratio of 2 gives the tightest crosslinked network and a low  $M_c$  value. Increased crosslinking also increases the  $T_g$  but decreases the energy dissipation of the network, lowering the  $\tan \delta_{\max}$  value<sup>8</sup> (Fig. 3). Glass transition temperatures obtained from DSC can be correlated to corresponding  $T_g$  values obtained from DMA, which in turn can be plotted against values for  $M_c$  (Fig. 4). Extrapolated values for molecular weight between crosslinks can thus be obtained by measuring the  $T_g$  of the resin by simple DSC.

A preliminary reduction study of resin 6<sup>9</sup> showed that complete solubility could be achieved. The  $M_c$  value of 470 confirmed the validity of the hypothesis that a threshold value ( $M_c \sim 400$ –500) needs to be reached before complete dissolution by reduction can be attained. A more detailed study of the cure, reduction, and reoxidation of 6 was undertaken. MDA (resin 9) was

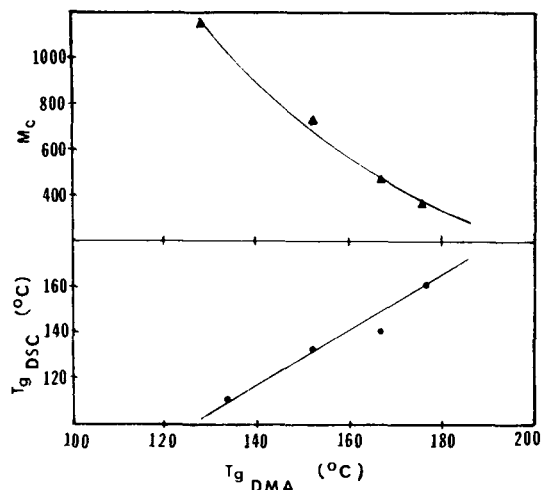


Fig. 4. Plots of  $T_g$  (from DMA) vs.  $T_g$  (from DSC) and  $M_c$  (from DMA) for resins 1, 6, 7, and 8, for calculation of extrapolated  $M_c$  values from simple DSC measurements.

once again used as the reference curing agent in the same molar ratios as that of 6.

DSC cure profiles of MDA and DTDA with Epon 828 in a 1:1.75 molar ratio diamine/diepoxy are shown in Figure 5. DTDA has a lower reactivity (onset of cure 154.4°C, Table II) than MDA (onset of cure 131.7°C). Due to this lower reactivity, the two stage cure profile (80°C, 2 h; 150°C, 2 h)<sup>1</sup> established for MDA/Epon 828 systems may not be appropriate for the first stage of the DTDA/Epon 828 system. Epoxide conversion<sup>1,2</sup> was thus analyzed at different isothermal temperatures of cure with time, for both MDA

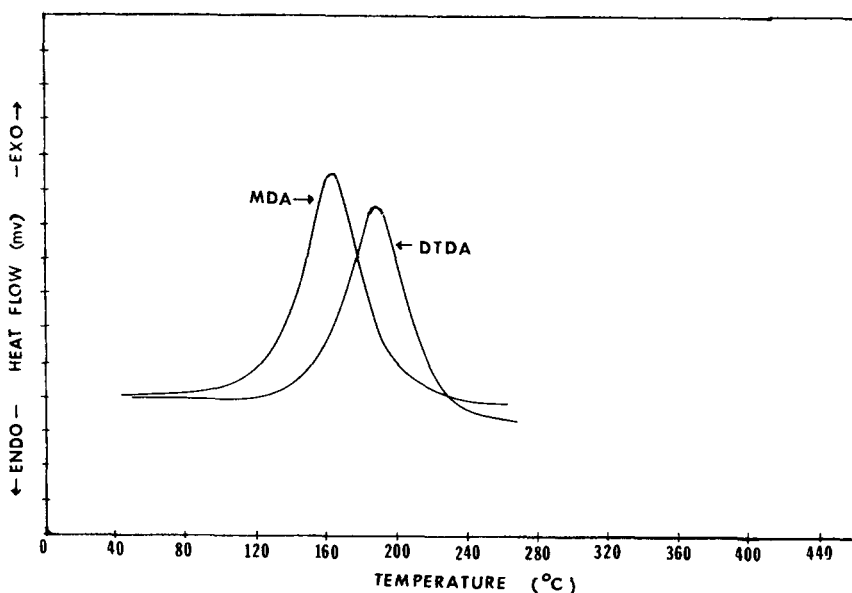


Fig. 5. DSC cure thermograms of resins 6 and 9.

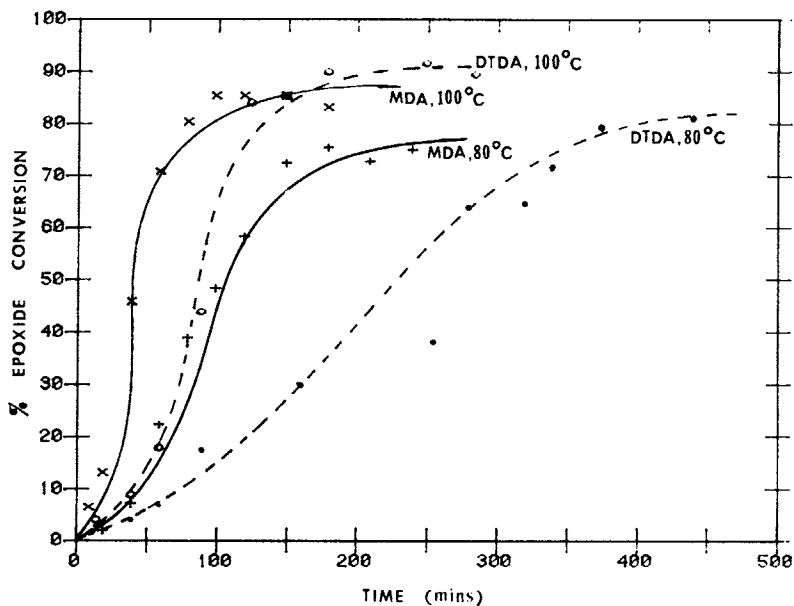


Fig. 6. Cure kinetics of resins 6 and 9 at 80 and 100°C.

and DTDA (Fig. 6). The reaction of DTDA with Epon 828 is extremely slow, and at 100°C, 57.1% of the epoxy groups (i.e., reaction of all primary amine)<sup>1</sup> were consumed after 94 min and was comparable to the cure of MDA at 80°C (57.1% epoxide consumed after 118 min). A cure profile of 100°C for 2 h followed by 150°C for 2 h was selected for this system. Properties of the fully cured resins are given in Table III. The onset of decomposition for 6 ( $T_D = 332.9^\circ\text{C}$ ) is lower than that of 9 ( $T_D = 338.1^\circ\text{C}$ ) due to the thermal lability of the disulfide link.

Intermediate stages of cure were analyzed for epoxy content and correlated with their glass transition temperatures obtained by DSC (Fig. 7). As the  $T_g$  rises, indicating further amine/epoxy reaction, the epoxide conversion correspondingly increases. Complete conversion is approached at the  $T_g$  of the fully cured resin. Consistency of the results is reflected in the fact that data obtained from different isothermal cure temperatures fall on the same curve.

Percent gel of the above samples were also measured and plotted against  $T_g$  (Fig. 8). Below a  $T_g$  of 41°C the resin is completely soluble. This is the point of incipient gelation. At a glass transition temperature of 105°C the resin is completely gelled.

The time-temperature-transformation (TTT) isothermal cure diagram described by Gillham<sup>12,13</sup> is used to interpret and compare the curing behavior and physical properties of the system (Fig. 9). Times to gelation and vitrification were computed from isothermal curing studies. Higher isothermal cure temperatures induce gelation significantly earlier than the vitrification of the resin.

Reduction of 6 with tributylphosphine,<sup>14</sup> in refluxing diglyme to the point of just complete solubilization, was accomplished in 55 min. The use of tributylphosphine instead of triphenylphosphine<sup>10,11</sup> has the added advantage

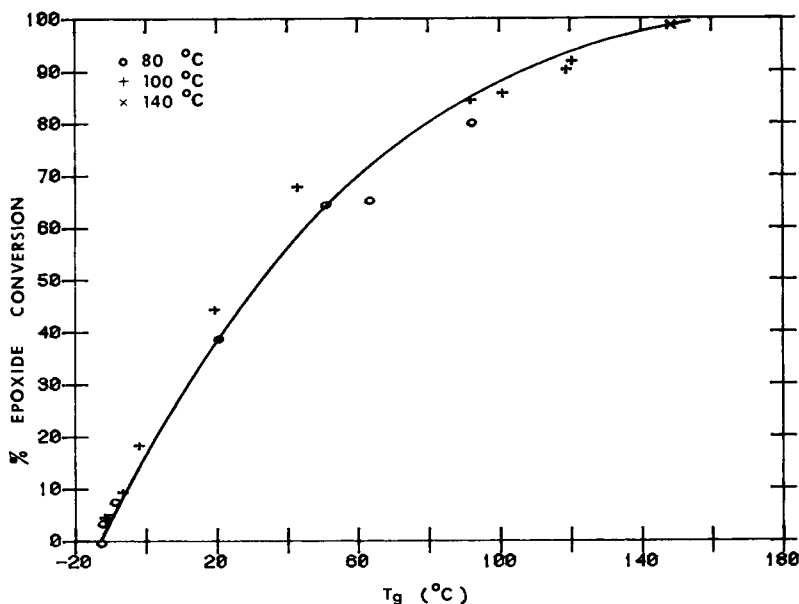


Fig. 7.  $T_g$  vs. percent epoxide conversion for 6.

of being soluble in methanol and can thus be removed from the reduced polymer during its precipitation in and washing with methanol. The reduction reaction was analyzed for percent sol and gel with time to the point of complete solubility (Fig. 10). The reduction rate during the first 10 min is very fast, after which the rate is more gradual. The  $T_g$  of the gels were also measured and plotted vs. time (Fig. 11).

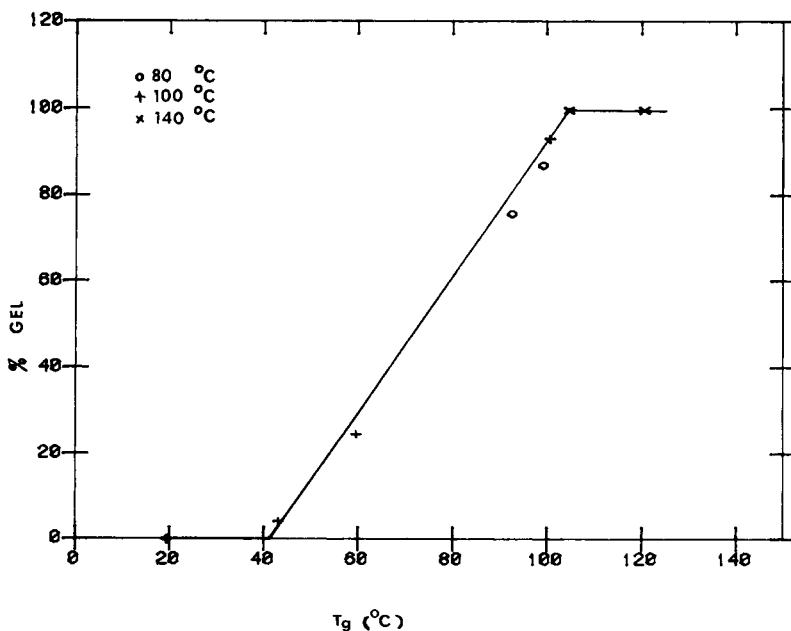


Fig. 8.  $T_g$  vs. percent gel during the cure cycle of 6.

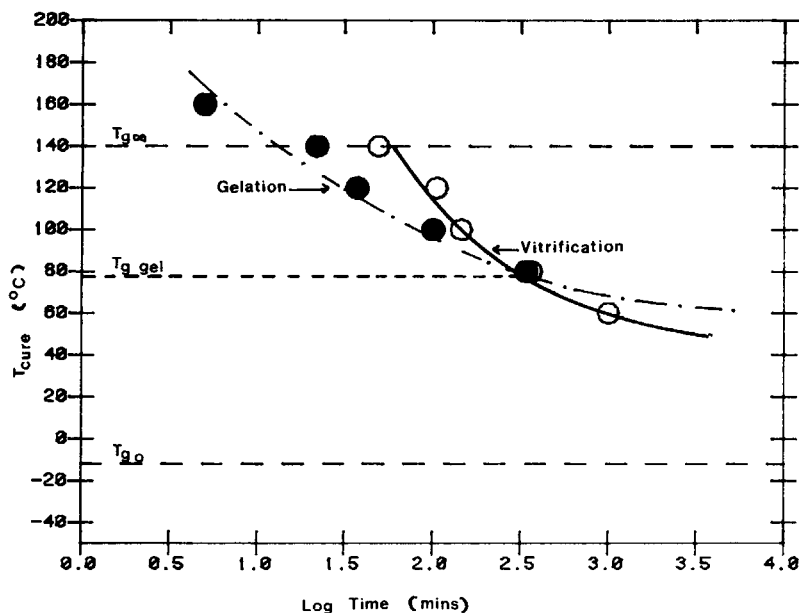


Fig. 9. TTT isothermal cure diagram of resin 6.  $T_{g0}$  = glass transition temperature of unreacted mixture;  $T_{g\infty}$  = glass transition temperature of fully cured resin;  $T_{g\text{ gel}}$  = glass transition temperature of the gel.

The  $T_g$  of the gel decreases with time, indicating cleavage of crosslinks during reduction. It then plateaus to a value of  $40^\circ\text{C}$  below which there is only soluble material. This threshold glass transition temperature is in direct correlation with the  $T_g$  of  $41^\circ\text{C}$  of resin 6 at incipient gelation (Fig. 8) during the cure cycle. This could be due to the similar network structures obtained during both the cure and reduction of 6.

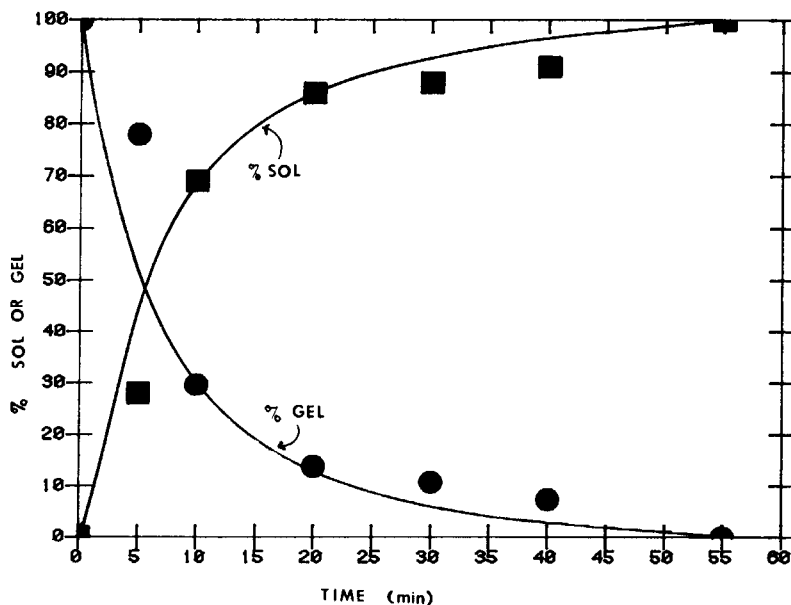


Fig. 10. Change of percent sol and gel with time during the reduction of 6.

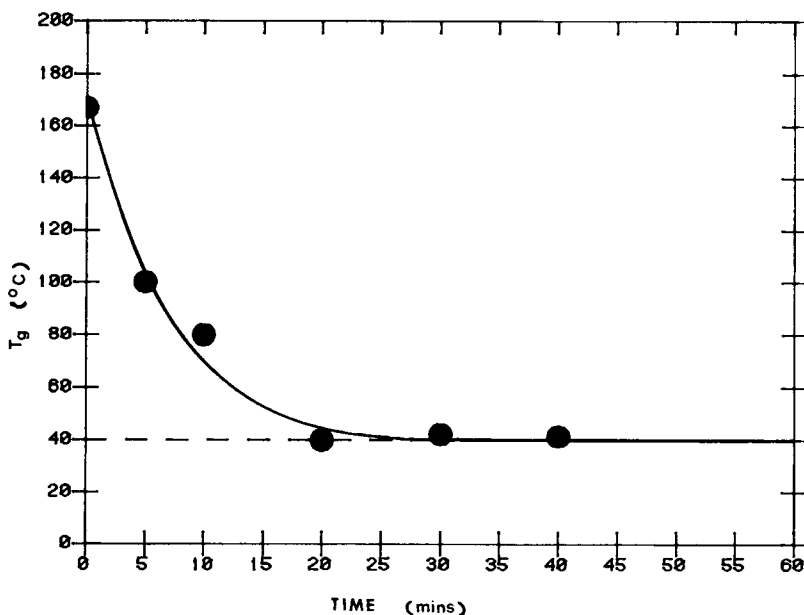


Fig. 11. Variation of  $T_g$  of unreduced gel (insolubles) with time during the reduction of 6.

Properties of the reduced resin 6R are given in Table VI. The polymer had a significantly lower  $T_g$  and  $T_D$  than the parent resin 6. GPC analysis gave a  $M_w$  of 3600 and  $M_n$  of 2400 against a polystyrene calibration curve. Dispersity of the resin ( $M_w/M_n = 1.5$ ) was low and a degree of polymerization of  $DP_w = 3.94$  is obtained (assuming a 1–1.75 per molecular weight of 913). The percentage sulfur as thiol groups in 6R was 47.85%—calculated by dividing the —SH content of 6R (Table VI) by the total amount of sulfur obtained from elemental analysis.

Two methods of reoxidizing the free thiol groups back to disulfide bonds were employed. The first was a solution oxidative-coupling reaction with iodine.<sup>15,16</sup> Reaction was immediate and the reoxidized polymer easily precipitated from the clear solution. Thermal properties of the reoxidized polymer 6RO-1 (Table VI) showed a 48°C lower  $T_D$  and a 13°C lower  $T_g$  compared to 6. The extrapolated molecular weight between crosslinks ( $M_c = 800$ ) from the DSC analysis of  $T_g$  was obtained from Figure 4. Totally efficient coupling does not occur due to the restricted mobility of the free thiol groups in the partially crosslinked, precipitated polymer.

The second reoxidation method was with air (Table VI) on solid resin 6R, above its glass transition temperature in order to enhance the mobility of the reacting functionalities. The reoxidized material 6RO-2 had comparable thermal stability to 6 [ $T_D(6RO-2) = 313.5^\circ\text{C}$ ;  $T_D(6) = 332.9^\circ\text{C}$ ] but a 30°C difference in  $T_g$  corresponding to a very low crosslink density (i.e., high  $M_c$  value). Though thiol coupling was poor, the comparable  $T_D$  values indicate that air oxidation of 6R to 6RO-2 produces a thermally stable oxidized material. Analysis of this “oxidized” state was not investigated.

In addition to the reoxidation of 6R the free thiol groups can also be reacted with other bifunctional compounds to obtain modified resins of comparable or improved properties than the fully cured parent resin. Thiols

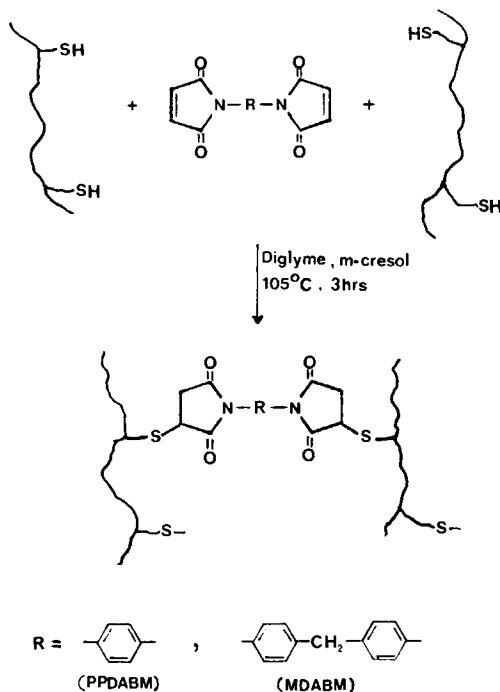


Fig. 12. Schematic of bismaleimide modification of 6R.

can be reacted with bismaleimides in polar solvents and a base catalyst, via the Michael addition reaction, to give polyimidosulfides.<sup>4,5</sup> These polymers possess higher glass transition temperatures than the polyaspartimides<sup>17,18</sup> obtained via the Michael addition of a bismaleimide and a diamine.

The reduced, soluble polymer 6R was modified with two aromatic bismaleimides—paraphenylenediamine bismaleimide (PPDABM) and methylene dianiline bismaleimide (MDABM)—schematically shown in Figure 12. Reaction was carried out in *m*-cresol, with triethylamine as the base catalyst to initiate thiolate formation. Stoichiometric equivalent amounts of bismaleimide were used for every —SH equivalent of 6R. Properties of PPDABM (6MO-1) and MDABM (6MO-2) modified resins are given in Table VI. The high thermal stability and rigidity of the aromatic-imide condensed ring structures incorporated into the epoxy system are reflected in the higher onset of decomposition temperatures as compared to the parent resin 6. The rigid wholly aromatic imide PPDABM modification gives a resin with a 12°C higher  $T_g$  than the MDABM modification due to the relatively more flexible MDABM structure. The TGA spectrum of 6MO-1 compared to 6 and 6R is shown in Figure 13. Reduced polymer 6R shows decreased thermal stability with weight loss starting at 182°C. Thermal stability is regained in the imide modified resin 6MO-1. Figure 14 compares the FTIR spectra of resins 6, 6R, 6MO-1, and 6MO-2. The —SH band of the thiol at 2555  $\text{cm}^{-1}$  in 6R is weak and disappears in the modified resins, which show the characteristic imide carbonyl stretches at 1780 and 1720  $\text{cm}^{-1}$ .



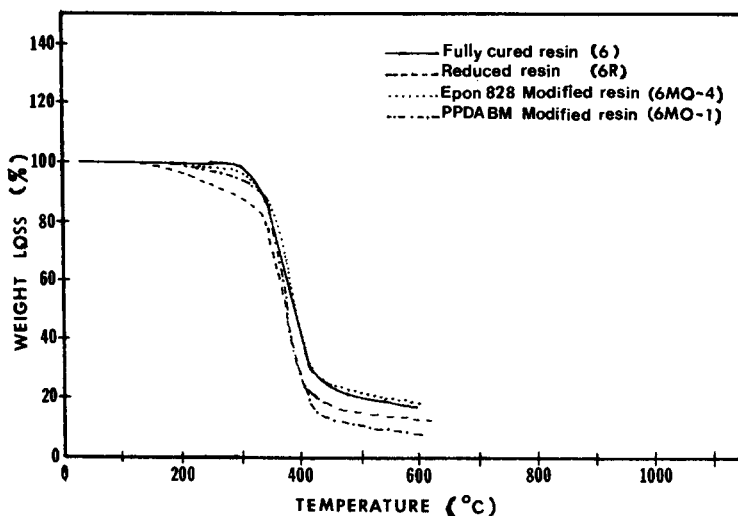


Fig. 13. TGA thermograms of 6, 6R, 6MO-1, and 6MO-3.

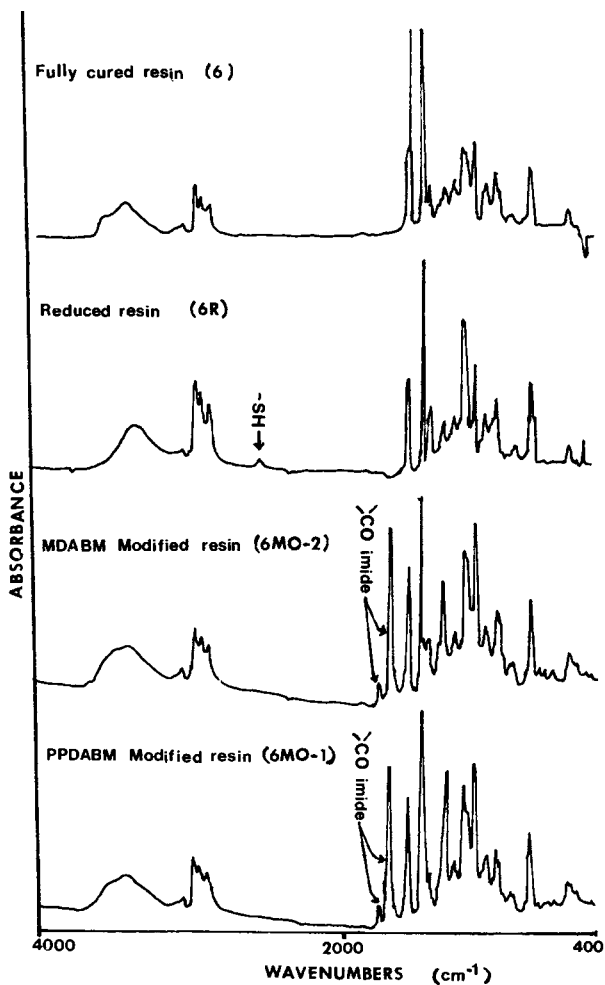


Fig. 14. FTIR spectra of 6, 6R, 6MO-1, and 6MO-2.

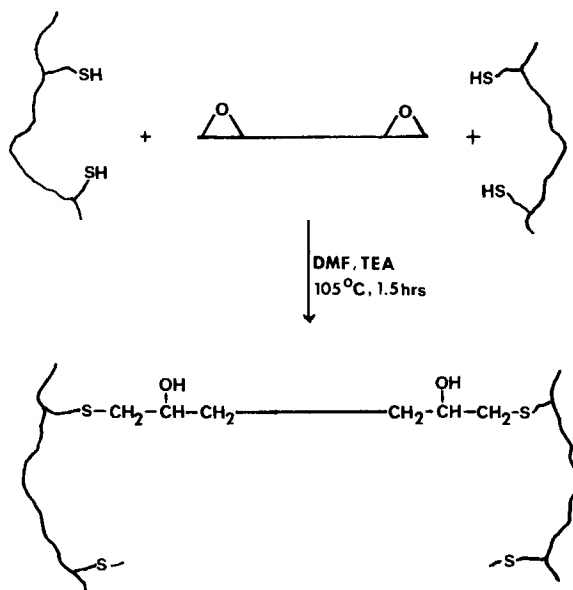


Fig. 15. Schematic of epoxy modification of 6R.

Thiols can also be reacted with epoxides in the presence of a base<sup>5</sup> to give thioether-polyols. Two ratios of Epon 828 were used in the modification whose reaction is schematically shown in Figure 15. Resin 6MO-3 was modified using a 49.4% deficient amount of epoxide to thiol (i.e., there was a 49.4% equivalent excess of  $-\text{SH}$ ). A slight equivalent excess (1.2%) of epoxide was used for resin 6MO-4. The latter resin has a higher  $T_g$  (more reacted  $-\text{SH}$ ) and a higher  $T_D$  (Table VI). The absence of the thermally labile  $\text{S}-\text{S}$  bond and the introduction of aromatic groups gives resin 6MO-4 a higher  $T_D$  compared to 6 (Fig. 13) but a lower  $T_g$  [ $T_g(6\text{MO-4}) = 118.7^\circ\text{C}$ ;  $T_g(6) = 139.9^\circ\text{C}$ ] due to the flexible spacer between disulfide links in effect "increasing" the molecular weight between crosslinks.

### SUMMARY AND CONCLUSIONS

A continuing investigation of disulfide-containing compounds, and specifically of 4,4'-dithiodianiline (DTDA) as curing agents for epoxy resins, has shown that fully cured resins of properties comparable to those of resins cured with methylenedianiline (MDA) can be obtained. Disulfide bonds in resins cured with DTDA can be reduced to the point of complete solubilization, provided that the crosslink density does not exceed a threshold value tentatively established as  $M_c = 400-500$ . Control of the molecular weight between crosslinks ( $M_c$ ) can be attained by varying the epoxy equivalent weight of the resin and/or the ratio of epoxy to amine functional groups in the curing reactions.

Reduction of resins cured with DTDA yields soluble thiol-containing polymers that can be crosslinked anew by oxidation or by reaction with thiol-reactive polyfunctional compounds. The properties of recured resins can be modified by appropriate selection of crosslinking reagents employed for the

recurring reaction, and incorporated in the final product. In one such modification, resin solubilized by reduction of disulfide bonds can be blended with varying ratios of virgin epoxy resin.

The viability of reprocessing and reuse of epoxy resins cured with DTDA has been demonstrated by the work reported.

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