

The Synthesis and Properties of Tetrafunctional Epoxy Resins

WEN-LIANG LIU, ELI M. PEARCE, and T. K. KWEI *Polymer Research Institute, Polytechnic Institute of New York, Brooklyn, New York and Materials Research Laboratory, Industrial Technology Research Institute, Hsinchu, Taiwan, Republic of China*

Synopsis

N,N,N,N'-tetraglycidyl-4,4'-diaminodiphenylalkane epoxy resins with alkyl substituents on the methylene carbon were synthesized and characterized. The thermal and dynamic mechanical properties of these resins when cured with diaminodiphenylsulfone were compared with those of the cured unsubstituted epoxy resin. Although the resins have similar structures, the cured resin from the unsubstituted epoxy has the higher polymer decomposition temperature and glass transition temperature. The substituted epoxy resins have higher dynamic Young's moduli and loss moduli.

INTRODUCTION

Epoxy resins containing *N,N,N,N'*-tetraglycidyl methylene dianiline (TGDDM) are widely used in the manufacturing of fiber-reinforced structures for aerospace applications. However, little is known about the physical properties of the cured resins if the methylene group of the TGDDM is replaced by other alkyl groups.¹ In this paper, we wish to report the results of our study on the effect of alkyl substitution on the methylene carbon of TGDDM on the curing behavior of the resins when reacted with diaminodiphenylsulfone (DDS) and on the thermal stabilities of the cured resins.

EXPERIMENTAL

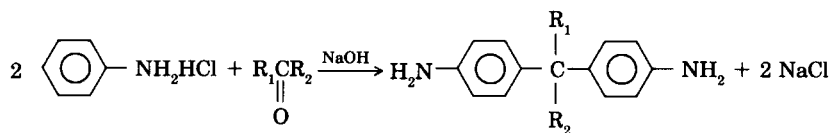
Materials

Aniline hydrochloride was purified by crystallization from aniline and hydrochloric acid. Acetone (Aldrich), methyl ethyl ketone (Aldrich), 2-pentanone (Fluka), 2-heptanone (Aldrich), diethyl ketone (Fluka), acetophenone (Aldrich) were purified by distillation under normal pressure or reduced pressure (30 mm Hg). Epichlorohydrin, toluene, 95% ethanol, and diaminodiphenylsulfone were obtained from Aldrich Co. and Fluoro-release agent All #30 from Airtech Corp. Tetraglycidyl 4,4'-diaminodiphenyl methane was obtained as a courtesy from Ciba-Geigy Co. and used without further purification.

Synthesis of 4,4'-Diaminodiphenyl Alkanes

The synthesis of TGDDM involves the reaction between 4,4'-diaminodiphenylmethane (DDM) and epichlorohydrin in suitable solvents.^{2,3} Similarly, the synthesis of *N,N,N,N'*-tetraglycidyl-4,4'-diaminodiphenyl alkane

requires the synthesis of *p,p*-diaminodiphenylalkane as the first step. There are several patents⁴⁻⁷ describing the synthesis of 4,4'-diaminodiphenylalkane from aniline hydrochloride and different ketones, and the reaction can be described as follows;



R₁, R₂: alkyl group

The molten-amine method employs complicated instruments which allows the ketone vapor to react with the molten aniline between 180 and 200°C. Yields of 50–60% have been reported by the use of the high pressure bomb method, but this technique requires special design to sustain high vapor pressure at 200°C. A modified high pressure method involves the use of a glass bottle to obtain yields of ~50%, and has the advantage of being simpler, easier to handle, and less expensive. The only drawback is that the reaction times are longer (~1 week) at 140°C.

In the above reaction the hydrochloride salt of aniline prevents the formation of spontaneous condensation products. The molar ratio of aniline hydrochloride salt to ketone is usually between 2.2:1 to 2.6:1, but there are little differences in the yields. A molar ratio of 3.5 for water to aniline hydrochloride salt was recommended by the patent.⁵

A typical procedure for the synthesis of 4,4'-diaminodiphenyl alkanes is as follows: 56 g of aniline hydrochloride was dissolved in 25 g of water prepurged by nitrogen gas. The solution, together with 10.4 g acetone, was introduced into a 200 ml Wheaton pressure bottle. The temperature of the reaction mixture was raised to 145°C in a period of 1 h and kept at this temperature for 8 days. The contents of the bottle were then cooled under a stream of cold water. The product was neutralized with 60 g of a 30% aqueous caustic soda solution and filtered. The organic layer was separated by decantation, and then washed twice with 500 mL of water. Excess aniline was separated from this organic layer by distillation in vacuum (10⁻³ mm Hg) and the residue was washed with carbon tetrachloride. After filtration and drying, 21.2 g of 2,2-*p,p'*-diaminodiphenylpropane was obtained, corresponding to a yield of 52% based on reacted acetone (Table I). The structure of this compound was confirmed by IR and H¹-NMR spectra.

TABLE I
Synthesis of Different *p,p'*-Diaminodiphenyl Alkanes^a

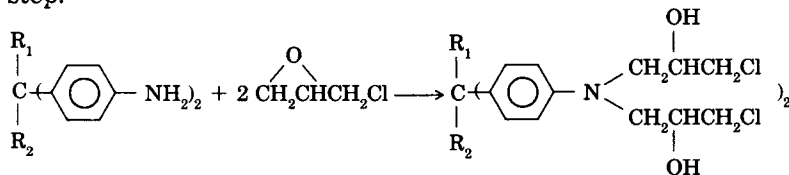
Compound		Molar ratio		Temp (°C)	Time (h)	Yield (%)
		<i>a</i>	<i>b</i>			
R ₁ =CH ₃	R ₂ =CH ₃	2.3	3.5	140	216	52
R ₁ =CH ₃	R ₂ =C ₂ H ₅	2.2	3.5	130	184	50
R ₁ =CH ₃	R ₂ =C ₃ H ₇	2.5	3.5	140	184	50
R ₁ =CH ₃	R ₂ =C ₅ H ₁₁	2.5	3.5	142	188	49
R ₁ =CH ₃	R ₂ =C ₆ H ₅	2.6	3.5	140	356	46
R ₁ =C ₂ H ₅	R ₂ =C ₂ H ₅	2.6	3.5	140	336	47

^a *a* = PhNH₂HCl/R₁COR₂, *b* = H₂O/PhNH₂HCl.

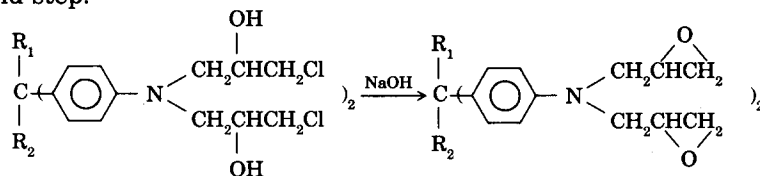
Synthesis of *N,N,N',N'*-Tetraglycidyl-4,4'-Diaminodiphenyl Alkane

The reaction from 4,4'-diaminodiphenyl alkane to *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylalkane takes place in two steps.

First step:



Second step:



Eleven grams of 2,2-*p,p'*-diaminodiphenylpropane was dissolved at room temperature in a mixture of 90 g epichlorohydrin, 40 g 95% ethanol, and 4 g water in a 200 ml three neck flask with nitrogen gas purge. The solution was then heated to, and held at, 65°C for 65 h. After the reaction mixture was allowed to cool to 60°C, 30 g of 30% NaOH (0.225 mol) was added over a period of 1.5 h at that temperature. The contents were held for an additional 30 min at 60°C, then stripped under vacuum at 65°C/30 mm Hg. Then 30 g of toluene was added to the residue, and this solution was washed three times with 100 ml portions of water. The water layer was removed by decantation and the organic layer was distilled under vacuum at 70°C/10⁻² mm Hg. A yield of 15 g of an amber, viscous liquid was obtained (Table II).

The epoxy value was determined by titration of 0.3 g epoxy resin in 25 mL hydrogen chloride-acetone solution (2.8 ml 36.5% HCl in 140 ml of acetone) by 0.1*N* sodium hydroxide solution and methyl red was used as the indicator.

TABLE II
Synthesis of Tetrafunctional Epoxy Resins

	Temp (°C)	Time (h)	Epoxy resin		Yield (%)	EEW ^b	Epoxy content % (theoretical)
			R ₁	R ₂			
1	65	65	CH ₃	CH ₃	78	149	76
2	20	70	CH ₃	CH ₂ H ₅	85	143	81
3	16	72	CH ₃	C ₃ H ₇	75	154	77
4	16	72	CH ₃	C ₅ H ₁₁	75	154	82
5	16	80	CH ₃	C ₆ H ₅	77	193	67
6	18	68	C ₂ H ₅	C ₂ H ₅	80	154	77
7 ^a			H	H		128	82

^a Ciba-Geigy's Araldite MY720 epoxy resin.

^b EEW = epoxy equivalent weight.

Gel Permeation Chromatography (GPC)

A Waters instrument Model 440 with microstrogel columns of 10^1 , 10^3 , and 10^4 Å was utilized at room temperature. Tetrahydrofuran solvent was used together with a refractive index (RI) detector. The concentration of the epoxy in THF was 2–5 mg/mL and the flow rate was 1 mL/min. The major purpose of using GPC is to check the purity of epoxy resins.

H^1, C^{13} -NMR Investigations

H^1 -NMR spectra were recorded on a Varian A-60 NMR spectrometer, C^{13} -NMR spectra were recorded on a JEOL FX-90Q FT-NMR spectrometer. The chemical shift (δ) was given in parts per million (ppm) with tetramethylsilane as the internal standard, and chloroform-d as solvent.

Differential Scanning Calorimetry (DSC) and Thermogravimeter Analysis (TGA)

Thermal analysis measurements via DSC and TGA were utilized both to follow the curing reaction and to characterize the network materials, and were performed on a DuPont 990 thermal analysis system. The former measurement was made at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen at a flow rate of 150 ml/min. In the latter, the heating rate was $20^\circ\text{C}/\text{min}$ in nitrogen at the same flow rate. In the determination of the glass transition temperature of the cured resin by DSC. The temperature (extrapolated) at which a step-jump in specific heat capacity occurs is taken as T_g .

Infrared Spectroscopy

IR spectra were recorded on a Perkin-Elmer 360 IR spectrometer and a Digilab Inc., FT IR spectrometer, Model FTS-20B on KBr plates to observe absorption peaks which are characteristic of the synthesized amines and epoxy resins.

The Curing of Epoxy Resins and the Characterization of Cured Resins

0.02 mol premelt diaminodiphenyl sulfone (DDS) was added to 0.039 mol epoxy resin at 135°C under vigorous stirring for 6 min. The mixture was then placed into a vacuum oven for 15 min to remove gaseous bubbles. The void-free mixtures were used to perform DSC studies of homopolymerization and DDS curing.

For thermogravimetric analysis and measurement of dynamic mechanical properties the epoxy samples were cast in a mold of 1 mm thickness and cured⁸ for 2 h at 80°C , plus 1 h at 100°C , plus 4 h at 150°C followed by post-cure for 7 h at 200°C in a vacuum oven.

Dynamic Mechanical Spectrometer

Dynamic mechanical modulus was measured in forced torsion using a Rheometrics Mechanical Spectrometer (RMS 605). Storage (G') and loss (G'') moduli and $\tan \delta = G''/G'$ were recorded as a function of temperature

from 60°C to 250°C and measurements were made every 10°C. The sample was subjected to a oscillatory strain of 0.2% at a fixed frequency of 1 Hz.

RESULTS AND DISCUSSION

Chemical Structure of the Epoxy Resins

It ought to be pointed out at the outset that the epoxy resins synthesized in this study all have, on the average, less than four epoxide groups per molecule (Table II). With the exception of methyl-phenyl substituted resin which has a functionality of only 2.68, the other resins have average functionalities between 3.04 and 3.38 per formula weight. The unsubstituted resin obtained commercially has an average functionality of 3.28.

The chemical structures of these resins were confirmed by C^{13} -FTNMR and FTIR spectra. The peak positions of the different carbon atoms in the NMR spectra are listed in Table III.

The FTIR spectra of the seven epoxy resins are displayed in Figure 1. The absorption bands are similar for the seven resins except in the region of 1300–1500 cm^{-1} due to $-CH_2$ and $-CH_3$ absorptions of the different alkyl substituents. Epoxide group absorption at 905 cm^{-1} and hydroxyl group absorption at 3350 cm^{-1} are noted in all resins. The hydroxyl absorption suggests that some of the epoxide rings may have reacted as in the commercial grade diglycidylether of bisphenol A. This may account, at least in part, for the decrease in average functionality.

Heat of Reaction

In our study of the epoxy–DDS curing reactions, a molar ratio of 1.95 to 1 of epoxy resin to DDS was used. This ratio was chosen so that the composition of the mixture containing the unsubstituted resin corresponds closely to that of a commercial system. The heats of reaction of each of the epoxy–DDS mixtures, as determined by DSC scan at a rate of 10°C/min, are shown in Table IV. Except for the low value of 22.9 kcal/mol eq epoxide groups for the mixture containing the methyl/phenyl substituted resin, the heats of epoxy–DDS reaction range from 24.6 to 27.3 kcal/mol. The low ΔH value for sample 5 and the low functionality of the methyl/phenyl-substituted resin suggest that the cured polymer has a lower crosslink density than the other polymers. The peak temperatures of the exotherms, T_{exo} , occur between 257 and 270°C.

The heats of reaction for the thermal polymerization of the epoxy resins were also determined by differential scanning calorimetry. Most of the ΔH values range from 25.0 to 26.9 kcal/mol eq epoxide groups. But sample 6 has a low value of 21.2 and sample 3 a high value of 30.4, for reasons not known to us at present. The T_{exo} values vary between 299 and 317°C. This exotherm was believed to be due mainly to the isomerization of the epoxide group and to epoxide–epoxide polymerization.^{9,10}

The principal reactions in the amine cured epoxy resins are (1) the primary amine–epoxide reaction, (2) the secondary amine–epoxide reaction, (3) the hydroxyl–epoxide reaction, and (4) the epoxide–epoxide reaction. All

TABLE III
Major C^{13} -FTNMR spectrum of Tetrifunctional Epoxy Resins (ppm)

Epoxy	Carbon no.													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<p>(1)</p>	146.1	139.9	127.6	111.9	53.1	50.6	45.4	41.0	30.9					
<p>(2)</p>	146.9	139.0	128.5	112.6	53.6	50.9	45.5	45.0	27.5	37.4	9.6			
<p>(3)</p>	145.9	139.1	128.1	111.9	53.1	50.6	45.4	44.6	27.7	44.4	18.1		14.8	

<p>(4)</p>	147.1	139.3	128.5	112.7	53.8	51.0	45.4	42.8	28.3	44.8	33.3	25.2	23.2	14.4
	<p>(5)</p>	146.2	138.2	128.2	111.7	53.1	50.8	45.5	50.6	30.4				
<p>(6)</p>	147.0	137.9	129.3	112.6	53.8	51.0	45.4	48.6	29.9	8.8				

^a CDCl₃ as solvent, TMS as internal standard.

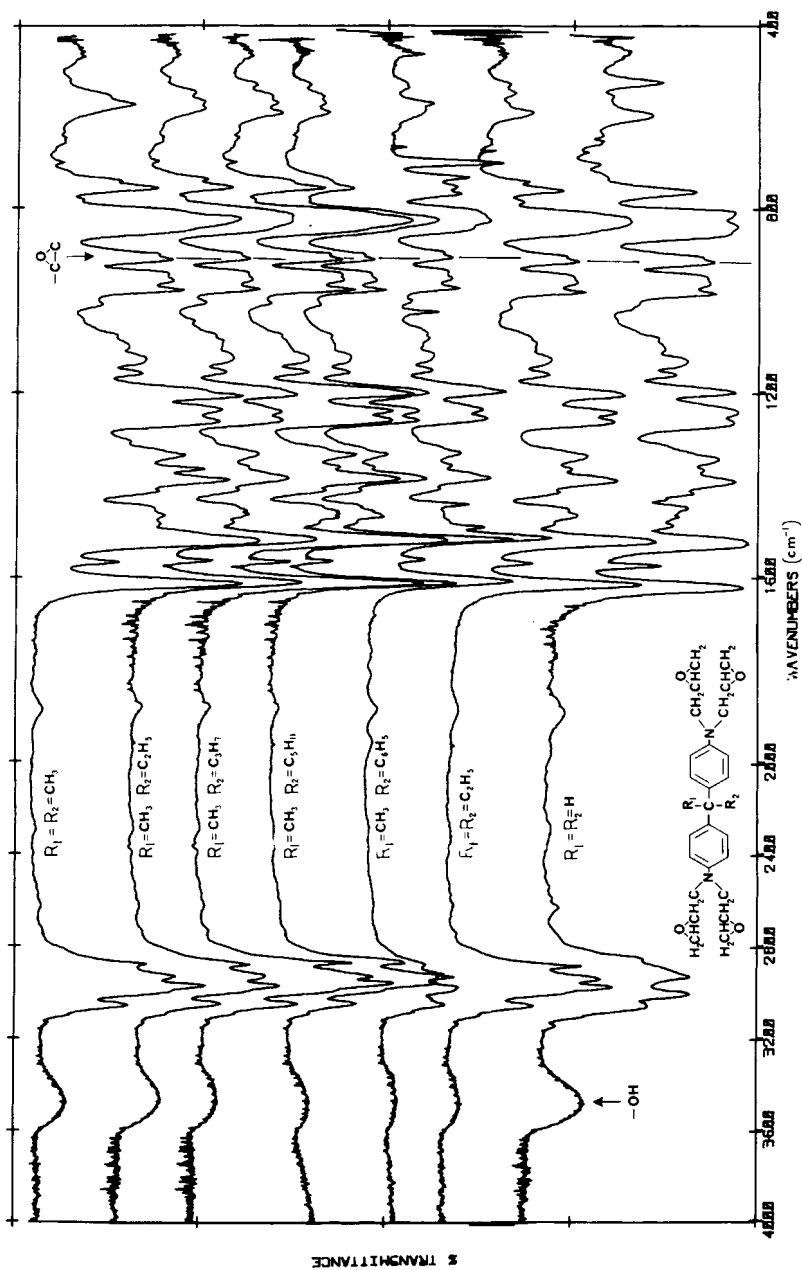


Fig. 1. FT-IR spectra of tetrafunctional epoxy resins.

TABLE IV
Thermal Analysis of the Epoxy-DDS Curing Reaction and the Thermal Polymerization of Epoxy Resins

Epoxy	Epoxy-DDS curing reaction		Thermal polymerization	
	$-\Delta H$ (kcal/mol eq epoxide)	T_{exo} (°C)	$-\Delta H$ (kcal/mol eq epoxide)	T_{exo} (°C)
1	26.7	257	25.0	297
2	24.6	260	25.7	299
3	27.3	268	30.4	308
4	24.9	270	26.7	314
5	22.9	264	26.9	304
6	25.8	259	21.2	305
7	25.1	268	26.4	317

four reactions can take place during thermal scan because there are about 1.5 epoxide group per active amine hydrogen in each of the curing mixtures. The primary amine-epoxide reaction has the largest rate constant. The rate constants of the secondary amine-epoxide reaction¹¹ and the hydroxyl-epoxide reaction¹² are about 1/10 that of the primary amine-epoxide reaction and the rate constant of the epoxide-epoxide reaction about 1/200 th.¹³ The latter reaction proceeds at a significant rate only at high temperatures, as indicated by the high peak exotherm temperatures shown in Table IV. The heat of reaction of amine addition to epoxy has been reported to be 24–26 kcal/mol epoxide group.^{14,15} The heat of reaction of epoxide-epoxide addition is about 25–27 kcal/mol according to our study. Although we do not have information about the heat generated in the hydroxyl-epoxide reaction, the overall heats of reaction of 24.6–27.3 kcal/mol found in this study for the epoxy-DDS mixtures appear to be reasonable in magnitude.

Thermal Decomposition and Char Formation

The thermal decomposition temperature of the polymer (PDT) was determined by the intersection of the tangent to the steepest portion of the TGA curve with the straight line portion of the same curve prior to any significant weight loss. The PDT values of the cured resins are arranged in the following order (Fig. 2):

$R_1, R_2;$	$H, H >$	$CH_3,$	$C_5H_{11} >$	$C_2H_5,$	$C_2H_5 >$
$CH_3,$	$C_3H_7 \approx CH_3,$	$C_6H_5 \approx CH_3,$	$C_2H_5 >$	$CH_3,$	CH_3
PDT (°C)	353	339		330	
	322	321	320		313

The thermal decomposition of cured epoxy resins involves a number of simultaneous and/or sequential reactions, and a mechanistic interpretation of the relative stabilities of these resins is beyond the scope of this study. Nevertheless, it is instructive to cite the results by Lin, Bulkin, and Pearce¹⁶ on the thermal degradation of trimethoxyboroxine cured diglycidyl ether

of bisphenol A by FTIR. According to these authors, the thermal stabilities of the functional groups can be ranked as follows:

methyl > benzene ring > methylene > *p*-phenylene
> ether > isopropylidene

Both the dissociation of the aryl-isopropylidene bond and the loss of methyl group have been observed by Paterson-Jones¹⁷ for an amine-cured DGEBA resin. It has also been reported in other studies¹⁸⁻²⁰ that methane is a product of pyrolysis. The low bond energy of the C—CH₃ bond in the isopropylidene group, about 50 kcal/mol is probably responsible for its susceptibility to thermal dissociation.¹⁶ The low stability of the CH₃,CH₃-substituted resin found in this study is in agreement with earlier observations. The substituents R₁ and R₂ on the central carbon of —φ—C(R₁R₂)—φ change the stabilities of the radicals formed by the cleavage of the C—R bond and the observed decomposition temperatures reflect these differences.

The char yields of the cured resins at 700°C are

R ₁ ,R ₂ :	H,H ≈	CH ₃ , CH ₃ >	CH ₃ , C ₂ H ₅ >
	C ₂ H ₅ , C ₂ H ₅ ≈	CH ₃ , C ₃ H ₇ ≈	CH ₃ , C ₅ H ₁₁ >
	CH ₃ , C ₆ H ₅		
Char yield (%)	27.1	25.7	21.2
	18.8	17.8	16.2
	13.7		

The TGA curves for diethyl- and methyl, pentyl-substituted resins indicate degradation taking place in two stages while the curves for the five other resins have a conventional single stage.

Glass Transition Temperatures and Dynamic Mechanical Moduli

The glass transition temperatures of the cured resins measured by DSC are listed in Table V, together with the temperatures of the tangent DSC maximum determined in the measurements of dynamic mechanical properties. Both *T_g* and *T_{max}* follow the same trend as R₁ and R₂ vary.

TABLE V
T_g and *T_{max}* of Cured Resins^a

R ₁ , R ₂	<i>T_g</i> (°C)	<i>T_{max}</i> (°C)
H, H	220	265
CH ₃ , C ₃ H ₇	191	230
CH ₃ , C ₆ H ₅	186	217
CH ₃ , CH ₃	182	212
CH ₃ C, C ₅ H ₁₁	177	—
CH ₃ , C ₂ H ₅	175	206
C ₂ H ₅ , C ₂ H ₅	168	205

^a *T_g* measured by first onset point.

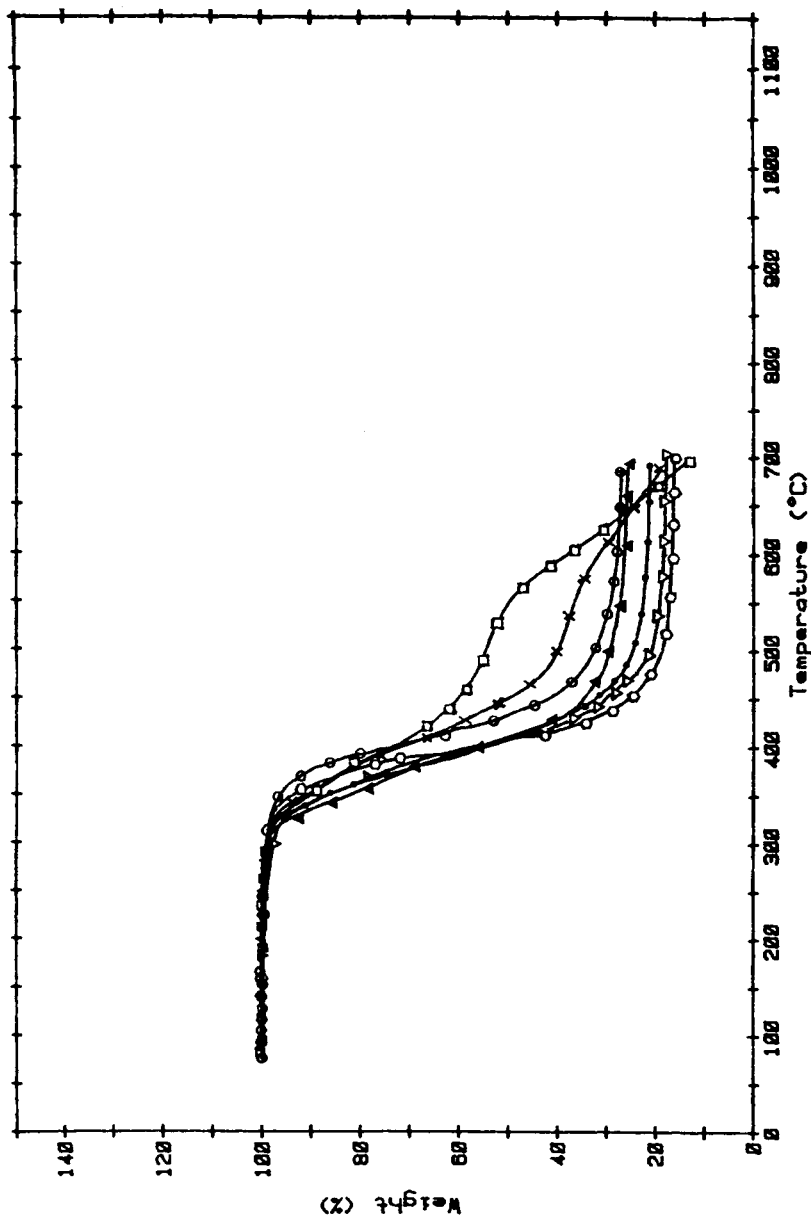


Fig. 2. TGA thermograms of epoxy resins cured with DDS; N₂, 20°C/min: (▲—▲—▲) (1); CH₃CC₆H₃ (●—●—●) (2); CH₃CC₂H₆ (▽—▽—▽) (3); CH₃CC₃H₇ (○—○—○) (4); CH₃CC₂H₁₁ (□—□—□) (5); CH₃CC₆H₅ (x—x—x) (6); C₂H₅CC₂H₅ (●—●—●) (MY 720) HCH.

Although the nature of the large scale segmental motion giving rise to the glass transition in the cured epoxy resin is still open to discussion, the substituents on the central carbon influence segmental motion in at least

two ways. A bulky substituent is expected to stiffen the $\phi - \overset{\text{R}_1}{\underset{\text{R}_2}{\text{C}}} - \phi$ chain and

decrease segmental mobility. On the other hand, the bulkiness of the substituent may have an adverse effect on the packing of chains and induces a large free volume in the polymer. The complex interplay of the two opposing contributions renders the interpretation of the T_g data at best speculative. But the trend of T_g values for $\text{R}_1, \text{R}_2 = \text{H, H}; \text{CH}_3, \text{CH}_3; \text{CH}_3, \text{C}_5\text{H}_{11}; \text{CH}_3, \text{C}_2\text{H}_5$; and $\text{C}_2\text{H}_5, \text{C}_2\text{H}_5$ can be rationalized by invoking the effect of decreased packing density upon substitution. The methyl, phenyl-substituted resin would probably have a higher T_g if the crosslink density were higher.

The substituted resins have higher dynamic Young's moduli than the unsubstituted resin (Fig. 3). Since the $\tan \delta$ values for all the resins are similar in magnitude, the loss moduli of the substituted resins are also higher.

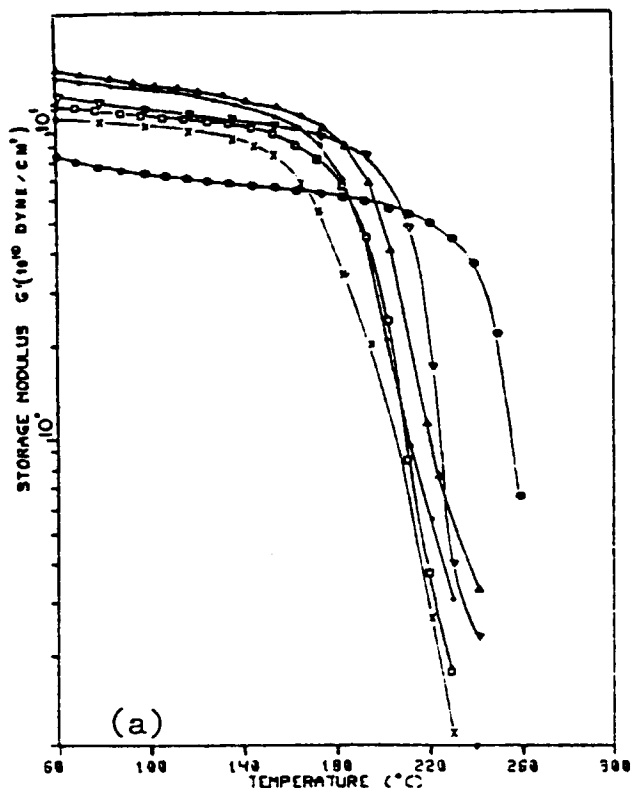


Fig. 3. Storage modulus (a), loss modulus (b), and $\tan \delta$ (c) of DDS-cured epoxy resins:

($\blacktriangle - \blacktriangle - \blacktriangle$) (1); CH_3CCH_3 ($\bullet - \bullet - \bullet$) (2); $\text{CH}_3\text{CC}_2\text{H}_5$ ($\nabla - \nabla - \nabla$) (3); $\text{CH}_3\text{CC}_3\text{H}_7$ ($\square - \square - \square$) (5); $\text{CH}_3\text{CC}_6\text{H}_5$ ($x - x - x$) (6); $\text{C}_2\text{H}_5\text{CC}_2\text{H}_5$ ($\odot - \odot - \odot$) (MY 720) HCH.

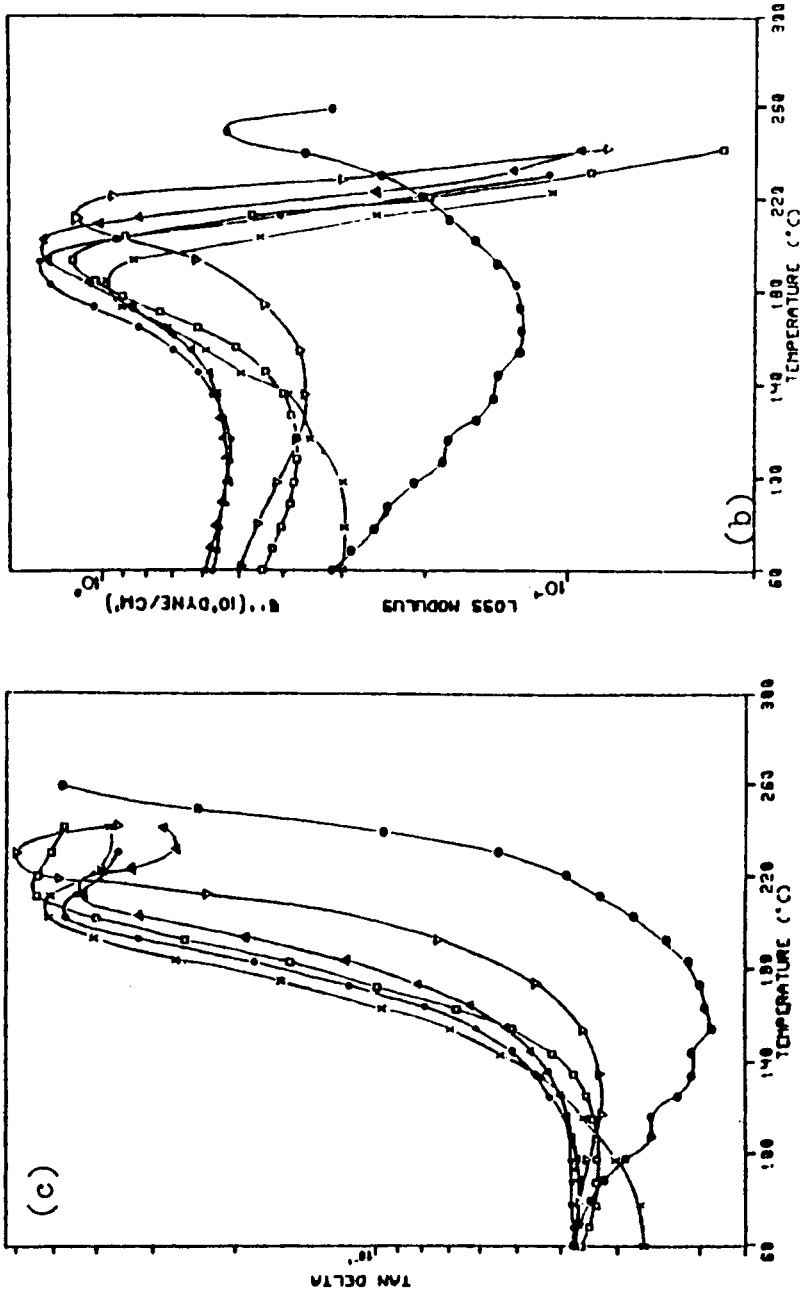


Fig. 3. (continued from previous page)

References

1. I. M. Ward, *Mechanical Properties of Solid Polymers*, 2nd ed., Wiley, New York, 1983, pp 168-170.
2. N. H. Reinking, U. S. Pat. 2,915,822 (1960).
3. R. Wegier and G. Frank, U. S. Pat. 2,884,406 (1959).
4. H. Krimm, A. Botta, and H. Schneill, U. S. Pat. 3,670,024 (1972).
5. S. Rhodiaceta, Fr. Pat. 1,555,580 (1967).
6. E. L. Powers and I. B. VanHorn, U. S. Pat. 3,260,751 (1966).
7. E. L. Powers, U. S. Pat. 3,277,139 (1966).
8. Ciba-Geigy Corp. Product Data No. CR725A5M82.
9. R. S. Bauer, *Epoxy Resins Chemistry 2*, ACS Symposium Series 221, Am. Chem. Soc., Washington, DC, 1983, p. 206.
10. H. C. Anderson, *Anal. Chem.*, **32**, 1592 (1960).
11. J. P. Bell, *J. Polym. Sci.*, **A2**, 417 (1970).
12. J. Moacanin, M. Cizmecioglu, F. Tsay and A. Gupta, *Org. Coatings Appl. Polym. Sci., Proc. Am. Chem. Soc.*, **47**, 587 (1982).
13. E. T. Mones and R. J. Morgan, *Polym. Mater. Sci. Eng. Proc.*, Am. Chem. Soc., **51**, 430 (1984).
14. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci., Polym. Chem. Ed.*, **8**, 1357 (1950).
15. S. Sourour and M. R. Kamal, *Thermochim. Acta*, **14**, 41 (1976).
16. S. C. Lin, B. J. Bulkin, and E. M. Pearce, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 3121 (1979).
17. J. C. Paterson-Jones, *J. Appl. Polym. Sci.*, **19**, 1539 (1974).
18. D. P. Bishop and D. A. Smith, *J. Appl. Polym. Sci.*, **14**, 205 (1970).
19. J. M. Stuart and D. A. Smith, *J. Appl. Polym. Sci.*, **9**, 3195 (1965).
20. L. H. Lee, *J. Polym. Sci.*, **A3**, 859 (1965).

Received October 18, 1984

Accepted November 30, 1984