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ROOM TEMPERATURE CURING POLYMERS

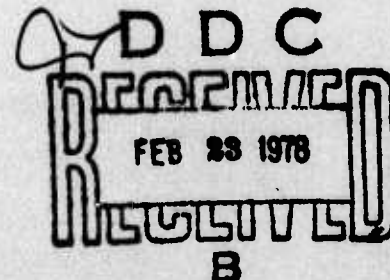
ACUREX CORPORATION/AEROTHERM DIVISION
485 CLYDE AVENUE
MOUNTAIN VIEW, CALIFORNIA 94042

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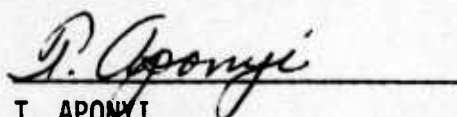
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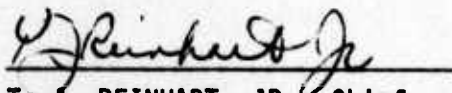
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This technical report has been reviewed and is approved for publication.



T. APONYI
Project Monitor
FOR THE COMMANDER



T. J. REINHART, JR., Chief
Composite and Fibrous Materials Branch
Nonmetallic Materials Division

62102F

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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) A rationale is presented for the development of room temperature curing polymers with the potential for 350°F performance. Such a polymer system must have a glass transition temperature (T _g) near room temperature, yet be highly crosslinked for good modulus retention at elevated temperatures. In order to test the hypothesis, epoxy resins have been prepared and used in room temperature cure studies directed to the development of polymer systems which will exhibit elevated temperature (350°F) performance.		

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Pure aliphatic diglycidyl ethers and esters were prepared and cured with aliphatic and aromatic amines to give materials with Tg's near room temperature. The moduli of the room temperature cured materials on the rubbery plateau above Tg were $\cong 10^8$ dynes/cm² indicative of highly crosslinked systems. At temperatures above Tg the strength of the room temperature cured materials and other epoxy systems tested was low, suggesting crosslink inhomogeneity. The experimental results obtained indicate the approach is valid, however the polymerization mechanism and/or the products formed during the cure of aliphatic glycidyl materials appear to lead to highly crosslinked "gel balls". Other widely used epoxy resin systems also were found to have low strength above their Tg.

FOREWORD

This Interim Technical Report was prepared by the Aerotherm Division, Acurex Corporation, Mountain View, California 94042, under USAF Contract No. F33615-76-C-5097, "Room Temperature Curing Polymers". This development effort was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBC), Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433, with Mr. T. J. Aponyi (AFML/MBC) as Project Monitor. This contract was initiated under Project No. 7340 "Nonmetallic Structural Materials," and Task No. 734004, "Polymers Synthesis and Characterization."

The effort at Aerotherm was conducted within the Materials department under the direction of Mr. R. M. Washburn. Mr. C. B. Delano was the Program Manager and Dr. B. J. Burreson was the Principal Investigator. Ms. J. H. Hurst provided chemical synthesis support.

This report covers work performed during the period of 2 February 1976 through 1 February 1977.

The report was submitted by the authors on 28 February 1977.

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SECTION 1

INTRODUCTION

A known maxim of polymer behavior is that a polymer system cannot be used in structural applications much above its cure temperature. This rule applies primarily to rigid glassy systems because the cure of such resins stops when the material vitrifies^{1,2}. When a material is heated above the cure temperature, the material softens and the cure continues until it vitrifies again or the glass transition temperature (T_g)* of the completely cured system is reached. A rigid material obviously loses its desirable mechanical properties if it softens, resulting in a practical correlation between use and cure temperature. Also, the ultimate mechanical properties of a material are not usually achieved unless cure is complete, so in practice, materials are heated to temperatures above the T_g to ensure cure.

Low modulus polymers such as the silicone rubbers are successful in applications requiring room temperature cure and 350°F performance. Silicone polymers typically have brittle temperatures (assume brittle temperature $\cong T_g$) below room temperature which allows for the cure to proceed at room temperature.

High modulus, room temperature curing systems are marketed today, however our examination of one system, EA 934, led to our concluding that cure was incomplete at room temperature. It appears as if its cure rate is sufficiently rapid that in normal laboratory exposure times for elevated temperature testing additional cure occurs and the adhesive stiffens prior

*Since this report is concerned primarily with crosslinked polymers and the glass transition temperature, T_g is defined for linear amorphous polymers, references to the glass transition temperature will mean apparent glass transition temperature.

to testing. Such a material will retain structural integrity only so long as the curing polymer does not experience load during heat up. However, this does not achieve the goal of structural performance above the cure temperature.

The basic objective of the work described in this report is to synthesize and characterize resin systems which can be cured at room temperature or at slightly elevated temperatures [100°F (38°C)] which will exhibit good performance characteristics over a range of -65°F to 350°F. The applications for such resin systems as adhesives or matrices for composites dictate that they must be free of solvent.

SECTION 2

TECHNICAL DISCUSSION

2.1 APPROACH

Since polymer cure in the glassy state (below T_g) is essentially nonexistent, polymerizations which lead to vitrified products at room temperature will be incompletely cured and will have T_g 's near room temperature. Generally, such a system is not capable of 350°F mechanical performance without further cure.

These results have been demonstrated experimentally for a state-of-the-art epoxy adhesive, EA 934. The T_g of the EA 934 system, cured 6 months at room temperature, is 44°C (111°F) as determined using thermomechanical analysis (TMA) at a 5°C/min heating rate. After the 6 months aging at room temperature residual cure exotherm is detectable by DSC. After a brief cure at 204°C (400°F) the T_g was raised to 115°C (265°F) and residual exotherm absent. The observed final T_g is consistent with the manufacturer's data for tensile shear strength as a function of temperature, (Figure 1) which shows maximum strength values below 100°F (38°C) and softening as the T_g is approached.

The results demonstrate that for a system to cure completely at room temperature it must have a T_g near room temperature.

Realizing the difficulties of developing a room temperature curing — 350°F performing polymer system Aerotherm selected the approach described below.

Consider the familiar shear modulus, G vs. temperature curves for typical crosslinked rubbers. Figure 2 provides the softening behavior of 1,4 butadiene rubbers with increasing crosslink densities. The polymers

exhibit a glassy region ($G > 10^{10}$ dynes/cm²), a transition region ($G = 10^8 \rightarrow 10^{10}$ dynes/cm²) and a rubbery plateau region ($G < 10^8$ dynes/cm²). The slight plateau seen for the uncrosslinked polymers at $G \sim 10^7$ dynes/cm² is attributed to chain entanglements.

The modulus of the crosslinked rubbers on their rubbery plateaus is seen to increase slightly with increasing temperature and the plateaus moduli increase with higher crosslink densities at a specified temperature.

The T_g of the sulfur cured rubber shifts to higher temperatures with increasing sulfur contents and also higher crosslink densities. This shift is attributed to the increasing sulfur content of these systems. Only a very slight T_g shift is seen for the radiation cured 1,4 polybutadienes with increasing crosslink densities.

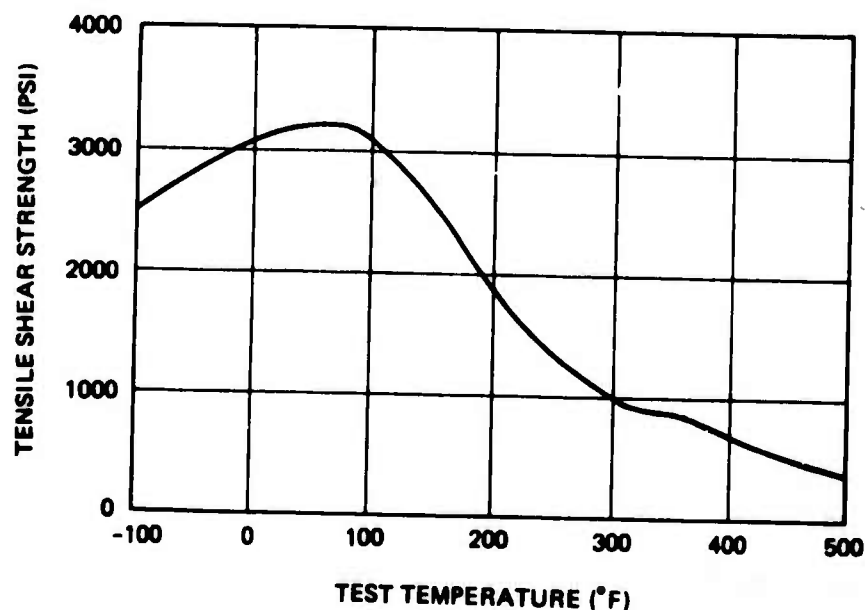


Figure 1. Typical tensile shear strength vs. test temperature for EA 934. (Aluminum adherends-thermocoupled specimens with 10 min. hold at test temperature).

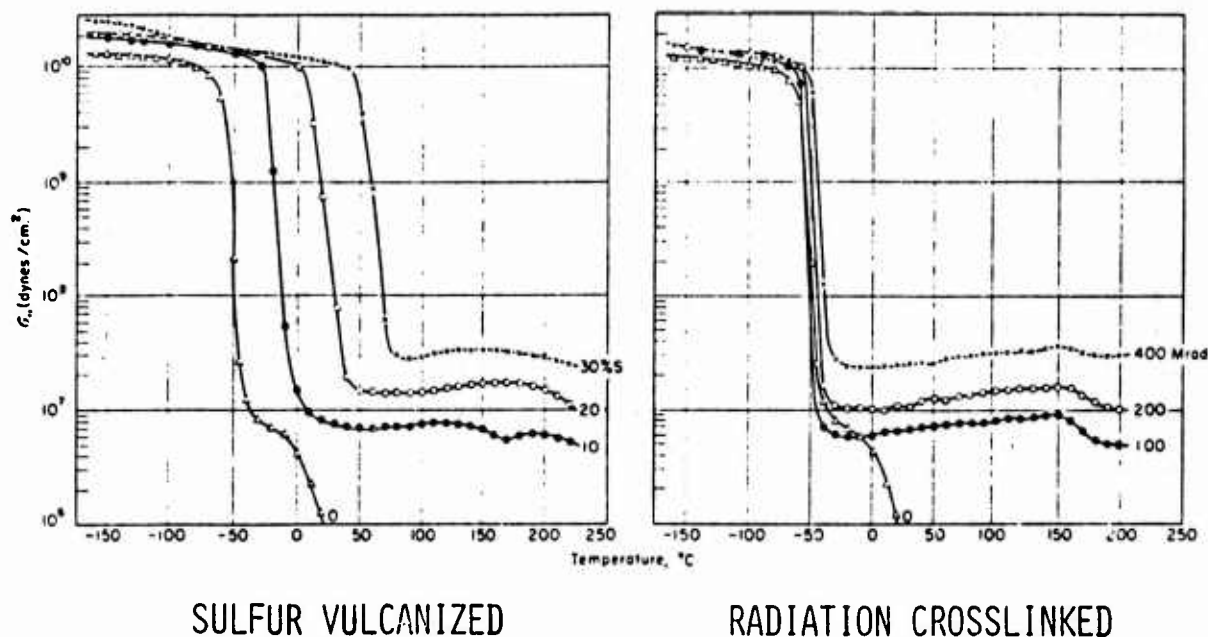


Figure 2. Shear modulus, G -temperature curves for crosslinked 1,4 polybutadiene

The kinetic theory of rubber^{3,4-6} relates the equilibrium elastic shear modulus at temperatures well above T_g to the density of crosslinks by

$$G = \left(\frac{\bar{r}^2}{\bar{r}_0^2} \right) \frac{\rho RT}{M_c} \left(1 - \frac{2M_c}{M_n} \right) \quad \text{Equation (1)}$$

where G is the shear modulus of elasticity, $\bar{r}^2/\bar{r}_0^2$ is the ratio of the mean-square distance between network junctures to the mean-square end-to-end distance of network chains in free space, ρ is the density, R is the gas constant, T is the absolute temperature, M_c is the average molecular weight between crosslinks and M_n is the molecular weight of uncross-linked polymer.

The term $\bar{r}^2/\bar{r}_0^2$ is usually often neglected since this ratio is generally about 1.0. Equation (1) applies fairly well for crosslinked rubbers if the measurements are carried out slowly enough that near equilibrium is achieved. For fast measurements, especially those on very lightly crosslinked rubbers, the measured modulus values are greater than those predicted by equation (1). At least part of this higher value is due to chain entanglements, which act as temporary crosslinks. The term $2M_c/M_n$ is a correction for polymer chain ends not effectively tied into the network; if M_n is large or if the degree of crosslinking is moderate, this term is neglected. Variance of shear moduli predicted by equation (1) from those observed experimentally have been investigated by several people, including Tobolsky.⁷

The theory assumes tetrafunctional crosslinks shown schematically in Figure 3 as only one of the few possible crosslink geometries that might be expected. Networks can be regular, highly irregular, tightly crosslinked, loosely crosslinked, highly imperfect with intramolecular loops and many free ends and molecules trapped in the network but unattached to it, or combinations of the above. The crosslink junctures can be trifunctional or tetrafunctional. Thus, compared to the characterization of the distribution in molecular weights of a linear polymer, the characterization of the structure of a crosslinked polymer is much more complex and difficult.

Equation (1) is simplified to $G = \rho RT/M_c$ and used to estimate M_c as follows. If a crosslinked rubber exhibits a shear modulus of 10^7 dynes/cm² at 298°K and has a density of 1.0 g/cc at 298°K using 8.316×10^7 ergs/°K mole for the gas constant, its M_c would be estimated to be 2478 molecular weight units as shown below:

$$M_c = \frac{\rho RT}{G} \quad \text{Equation (2)}$$

$$M_c = \frac{1.0 \text{ g/cm}^3 \times 8.316 \times 10^7 \text{ ergs/}^\circ\text{K mole} \times 298^\circ\text{K}}{10^7 \text{ dynes/cm}^2}$$

$$M_c = 2478$$

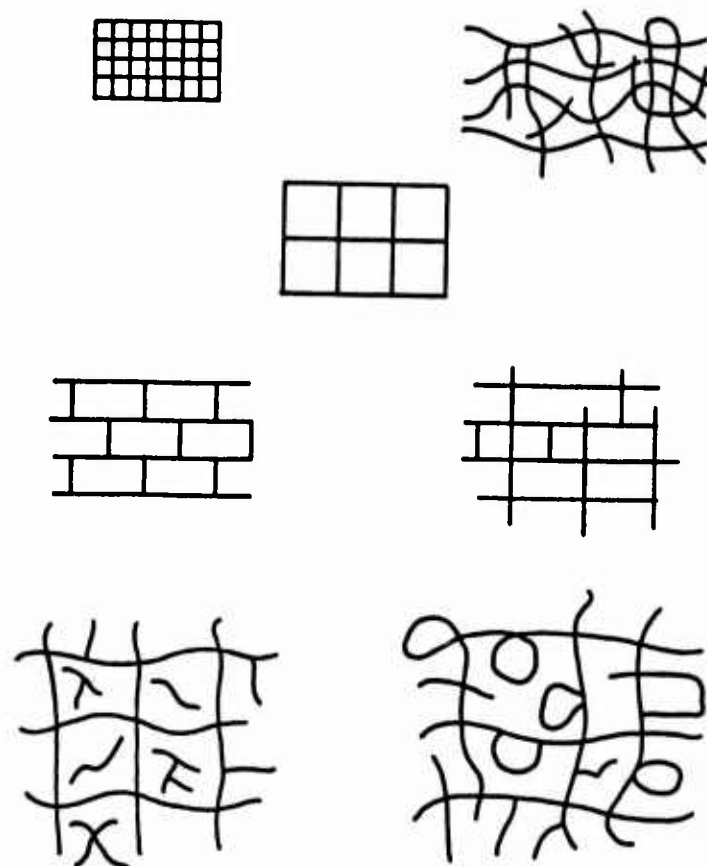


Figure 3. Schematic diagram of some different types of crosslinked networks

Modified forms of equation (1) are employed to great advantage to approximate the number of moles of crosslinks per cubic centimeter, ρ/M_c in the rubber by simply measuring the force necessary to maintain a rubber sample of original length in a stretched state of new length. Since most rubbers are produced by chemical crosslinking (procedures that are not quantitative), adapted forms of equation (1) provide a very important method for characterizing rubber networks. When crosslinking is produced by high energy radiation, such a procedure may be the only way to estimate M_c .

The calculated and observed shear rubbery moduli of crosslinked systems below 10^8 dynes/cm² are usually in good agreement. When the plateau moduli are much greater than 10^8 dynes/cm², such accord is no longer found. Even though "plateau" behavior is observed for crosslinked systems with shear moduli above 10^8 dynes/cm², kinetic rubber theory and modifications to the theory have not been totally successful to date. Tobolsky in attempts to understand the behavior of systems with plateaus greater than 10^8 dynes/cm² investigated several highly crosslinked systems. The modulus temperature curves for copolymers of ethyl acrylate and ethylene glycol dimethacrylate are shown in Figure 4.^{7,8}

The copolymer's "rubbery" plateaus exhibit nonsoftening behavior up to very high temperatures, $\sim 200^\circ\text{C}$. This behavior sought for a room temperature curing system is the basis of Aerotherm's approach. Specifically, a resin developed to have shear modulus of 10^9 dynes/cm² (14,500 psi) would be sufficiently stiffer than more familiar rubbery material to be structurally useful. Further, such a system should show little initial modulus loss to very high temperatures.

The more familiar Young's modulus is related to the bulk and shear moduli of materials through Poisson's ratio¹¹ as follows:

$$E = 3B(1-2\sigma) = 2(1+\sigma)G$$

Where E is Young's modulus, B is Bulk Modulus, σ is Poisson's ratio, and G is shear modulus. The variation of E/G with Poisson's ratio for various permissible values of σ is given below in Table 1.

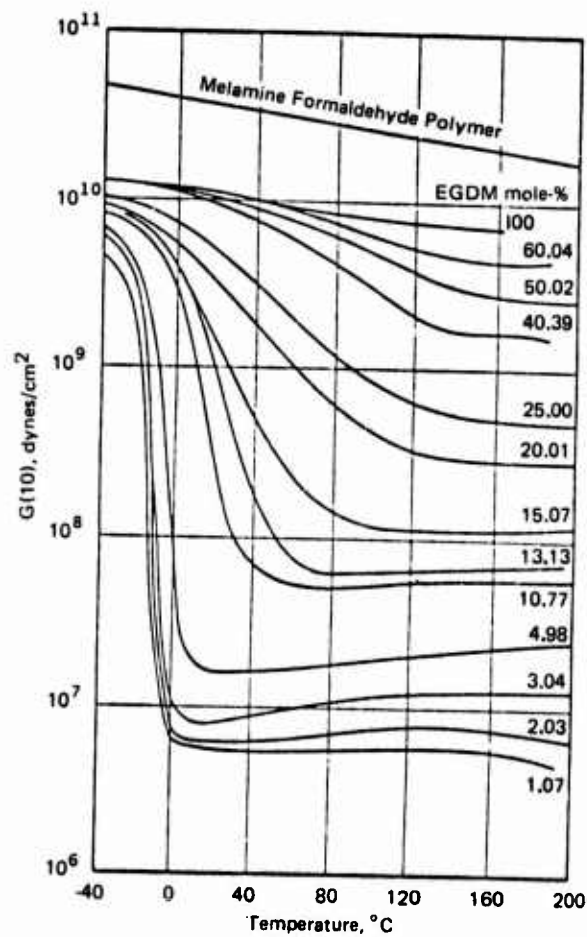


Figure 4. Dependence of 10-second stress-relaxation moduli^{9,10} on temperature for copolymers of ethyl acrylate and ethylene glycol dimethacrylate and of a melamine-formaldehyde polymer.

TABLE 1. E/G VERSUS POISSON RATIO, σ

σ	E/G	Remarks
0.00	2	
0.10	2.2	
0.20	2.4	} Range for crystalline materials and glasses
0.25	2.5	
0.30	2.6	
0.333	2.666	
0.40	2.8	
0.4996	2.9992	} Range for rubbery materials
0.4997	2.9994	
0.4998	2.9996	
0.4999	2.9998	
0.49995	2.9999	
0.50	3.00	

Since rubbery materials have a Poisson's ratio very close to 0.50, Young's modulus will be very close to three times the value of the shear modulus.

Accordingly, a "rubbery" material with a shear modulus of 10^9 dynes/cm² (14,500 psi) would have a Young's modulus close to 3×10^9 dynes/cm² (43,500 psi). Young's moduli (tensile) as high as 440,000 psi are reported for Epi-Rez 508 (Bisphenol A diepoxy) cured with 30 parts of Epi-Cure 8771 (Lewis acid) after two weeks at room temperature.¹² The attainment of a useful Young's modulus appears to be easily within reach of room temperature curing resin systems.

Thus to achieve nonsoftening behavior to high temperatures, the need for a highly crosslinked system is clearly seen. Using the relationship shown in equation (2) for a polymer with a density of 1.2g/cc, one must specify an M_c of no more than ~ 300 molecular weight units to achieve a "rubbery" plateau modulus of 10^9 dynes/cm² at room temperature.

M_c , the molecular weight between crosslinks, is defined from rubber theory by the relationship given by equation (2) and is calculated from the observed modulus of the rubbery plateau. Reversing this calculation procedure provides the polymer chemist with a method for monomer selection. For instance, the combination of 1,4-butane diglycidyl ether with Shell Z ($M_c = 354$) would provide a higher crosslink density than a similar system from higher molecular weight diepoxides and/or diamines. Assuming the described system reacted quantitatively to give the theoretical structure, one would expect to obtain shear modulus, G of approximately 1.14×10^8 dynes/cm² at 298°K if the density of the cured polymer were 1.22g/cc. This calculation is shown below.

$$G = \frac{\rho RT}{M_c}$$

$$G = \frac{1.22\text{g/cc} \times 8.316 \times 10^7 \text{ ergs/}^\circ\text{K mole} \times 398^\circ\text{K}}{354}$$

$$G = 1.14 \times 10^8 \text{ dynes/cm}^2$$

To calculate the M_c , based on the theoretical structure of a crosslinked polymer, the molecular weight of the repeating unit and the number of bonds to each repeat unit are first calculated. Two bonds are subtracted for polymer linearity and the remaining number of bonds (crosslink bonds) divided into the repeating unit molecular weight to provide an estimation of the M_c which could be achieved from the monomers. Monomer purities must also be taken into account. This calculation is shown below for the 1,4-butane diglycidyl ether cured with Shell Z system cited above.

$$\begin{aligned} M_c &= \frac{\text{mer molecular weight}}{2 \text{ crosslink bonds}} \\ &= \frac{4 \times (\text{EEW of Diepoxy}^* + \text{Eq. Wt. of Diamine}^{**})}{2} \\ &= \frac{4 \times (134 + 43)}{2} \\ &= 354 \end{aligned}$$

*Butane diglycidyl ether; epoxy equivalent weight (EEW) of 134 (theor. 101)

**Shell Z, equivalent weight of 43

Although the actual attained M_c is influenced by cure statistics (typically at least 10% not reacted in a fully cured system), intramolecular looping and similar considerations, we did not attempt to modify our simplified calculation to account for these items. Further, ignoring segment end to end distances, four bonds per crosslink and other theoretical considerations as shown later, the fit of the simplified M_c calculation to the M_c calculated from the observed modulus of the rubbery plateau is acceptable.

Inspection of Figures 2 and 4 indicates a T_g shift to higher temperatures with increasing crosslink densities. Although T_g cannot be obtained precisely from modulus-temperature curves, the intercept of the glassy curve with the softening curve is usually within a few degrees of the T_g . Such intercepts can be clearly pictured for the 1,4-butadiene polymers shown in Figure 2. In Figure 4 the curves become more difficult to interpret as the moduli of the plateaus increase. The mechanical T_g is usually considered¹³ represented by a shear modulus of 10^9 dynes/cm².

The key question is: "When in a room temperature curing crosslinked system will the system vitrify and the cure halt?" It is known that bisphenol A diepoxies cured at room temperature with aromatic diamines vitrify (B stage) and are remelted at higher temperatures allowing the cure to proceed. This is attributed to the structures of the prepolymers formed. High temperatures are required to complete the cure and resin systems with T_g s of $\sim 100^\circ\text{C}$ or higher are obtained. Thus, even though the chemistry of such systems is favorable for room temperature cure, vitrification occurs at room temperature and the cure halts.

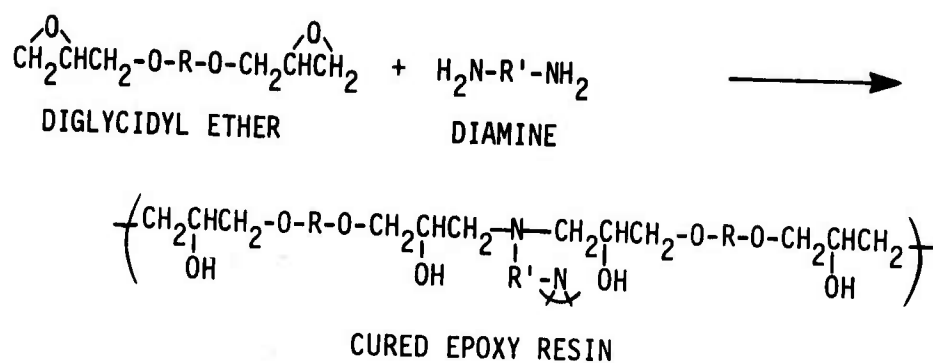
To satisfy the room temperature cure and 350°F heat stability requirements, amine cured glycidyl epoxy resin systems were selected as the basic chemical structure. In order to lower the Tg to room temperature, it was concluded that flexible segments would be required. The segments chosen for investigation include polymethylene (Tg=-90°C), polydimethyl siloxane (Tg=-123°C), and polyaliphatic ether (Tg=-84°C)¹⁴ (Figure 5). Using these flexible low Tg segments, an epoxy system should be feasible which would have a Tg near room temperature, yet be highly crosslinked for elevated temperature performance.

2.2 MONOMER SYNTHESIS

2.2.1 Synthesis of Diglycidyl Ethers

The initial synthetic route to aliphatic diglycidyl ethers was the boron trifluoride catalyzed reaction of an aliphatic diol with epichlorohydrin as depicted in Figure 6. This procedure was used for 1,2-ethylene glycol and 1,4-butanediol and the diglycidyl ethers of these diols were purified by vacuum distillation from polymeric products in yields below 50 percent. Purity was in the 75-95 percent range, as indicated by epoxy equivalent weight determination, and was dependent on the distillation method employed. The infrared (IR) spectra (Figure 14) of these epoxies had weak hydroxyl peaks indicating some impurity in these products, but the nuclear magnetic resonance (NMR) spectra (Figure 15) were consistent with the expected products. 1,4-Butane diglycidyl ether is commercially available and this material was acceptable when distilled. Table 2 summarizes the data for diglycidyl ether synthesis.

For longer chain diols, the diol-epichlorohydrin reaction used did not provide good yields of the expected products whether boron trifluoride catalyzed or with base. Attempted purification with high vacuum distillation resulted in only low yields of impure material. The reasons for this can be seen from the equations in Figure 6. The reaction of a diol and epichlorohydrin to give a diglycidyl ether proceeds in two steps. In the first step, a boron trifluoride catalyzed reaction of a diol with epichlorohydrin is performed to give a chlorohydrin, which is then treated with sodium hydroxide in step two to yield the diglycidyl ether (Route 1).



FLEXIBLE SEGMENT	T _g , °C	
$\text{R} = \left(\text{CH}_2 \right)_n$	-90	Polymethylene
$\text{R} = \text{O}-\text{C}(\text{O})-(\text{CH}_2)_n-\text{C}(\text{O})-\text{O}$	-90	Polyaliphatic ester
$\text{R} = \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{Si}-\text{O} \\ \\ \text{CH}_3 \end{array} \right)_n - \text{Si} \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	-123	Polydimethyl siloxane
$\text{R} = \left(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-O} \right)_n \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$	-84	Polyaliphatic ether
$\text{R}' = \left(\text{CH}_2 \right)_n$	-90	Polymethylene
$\text{R}' = \left(\begin{array}{c} \text{CH}_2\text{CH-O} \\ \\ \text{CH}_3 \end{array} \right)_n \text{CH}_2\text{CH-}$	-75	Polyoxypropylene

Figure 5. Candidate epoxy resin systems.

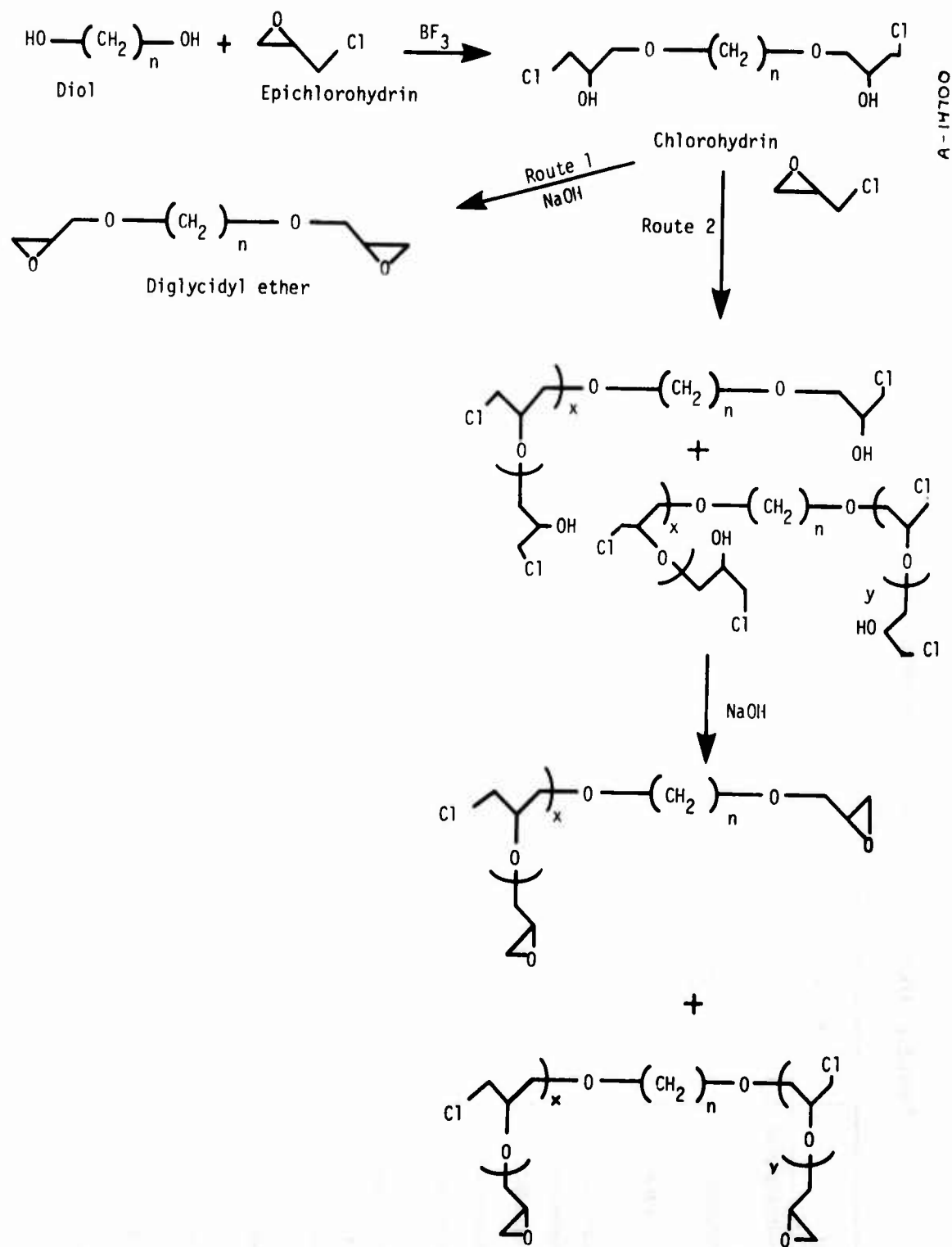


Figure 6. Reaction of a diol with epichlorohydrin.

TABLE 2. DIOL DIGLYCIDYL ETHER EPOXY EQUIVALENT WEIGHTS (EEW)
Summary of Diol Diglycidyl Ether Syntheses

Diol	Preparation Method/Source	Purification	Epoxy Equivalent Weight (EEW)
1,2-ethylene glycol	diol + epichlorohydrin + boron trifluoride	distillation	101 (theory 87)
1,4-butanediol	diol + epichlorohydrin + boron trifluoride	none	185 (theory 101)
1,4-butanediol	diol + epichlorohydrin + boron trifluoride	distillation	104-134 (75-97%)
1,4-butanediol	Ciba-Geigy RD-2	none	176
1,4-butanediol	Ciba-Geigy RD-2	distillation	124-134
neopentanediol	Ciba-Geigy XU-197	none	140 (theory 108)
neopentanediol	Ciba-Geigy XU-197	distillation	114 (95%)
1,6-hexanediol	diol + epichlorohydrin + boron trifluoride	none	754 (theory 115)
1,6-hexanediol	diol + epichlorohydrin + sodium hydroxide	none	535
1,6-hexanediol	1) diol + allyl bromide 2) peracetic acid	none	200
1,6-hexanediol	1) diol + allyl bromide 2) peracetic acid	distillation	134
1,8-octanediol	diol + epichlorohydrin boron trifluoride	none	600-900 (theory 129)
1,10-decanediol	1) diol + allyl bromide 2) m-chloroperbenzoic acid	none	158 (theory 143)
1,10-decanediol	1) diol + allyl bromide 2) peracetic acid	none	205

However, once the chlorohydrin is formed, the hydroxy in this molecule can react just as the diol starting material, resulting in larger molecular weight chlorohydrin molecules (Route 2). This reaction repeats itself as shown in Figure 6 and eventually results in products which have much higher than theoretical epoxy equivalent weights.

A more satisfactory method of preparing long chain aliphatic diglycidyl ethers was found to be the preparation of a diol diallyl ether followed by epoxidation with a peracid (Figure 7). For example, a one mole reaction of 1,10-decanediol and sodium hydride in tetrahydrofuran gave the disodium salt of the diol which was then treated with allyl bromide to give the diallyl ether in 77 percent yield. 1,10-Decane diallyl ether was free of alcohol by IR (Figure 16) and had a bromine number near theoretical, 121 (Theory 126) using the procedure in Appendix B. The NMR spectrum (Figure 17) was as expected for pure diallyl ether. Epoxidation reactions were performed with excess *m*-chloroperbenzoic acid to give 1,10-decane diglycidyl ether, EEW 158 (Theory 143) which required no further purification. This procedure was most useful for preparing glycidyl ethers from aliphatic alcohols and was successful in a number of cases. Products (Figure 18) from this reaction which have high epoxy equivalents usually contain unreacted allyl ether by NMR spectroscopy (Figure 19) and need to be treated with additional *m*-chloroperbenzoic acid to give pure product.

The diallyl ethers were also oxidized to epoxides with buffered 40 percent peracetic acid in acetic acid. However, epoxy equivalents greater than theoretical resulted from these reactions and the products needed purification. For example, the reaction of 1,10-decane diallyl ether treated with peracetic acid at 0°C gave essentially no reaction, while at room temperature a product with an EEW of 205 (Theory 143) was obtained. The product from this latter reaction had bands due to hydroxyl and ester carbonyl groups in the infrared spectrum, indicating that acetic acid reacts with the epoxide ring of the glycidyl ether.

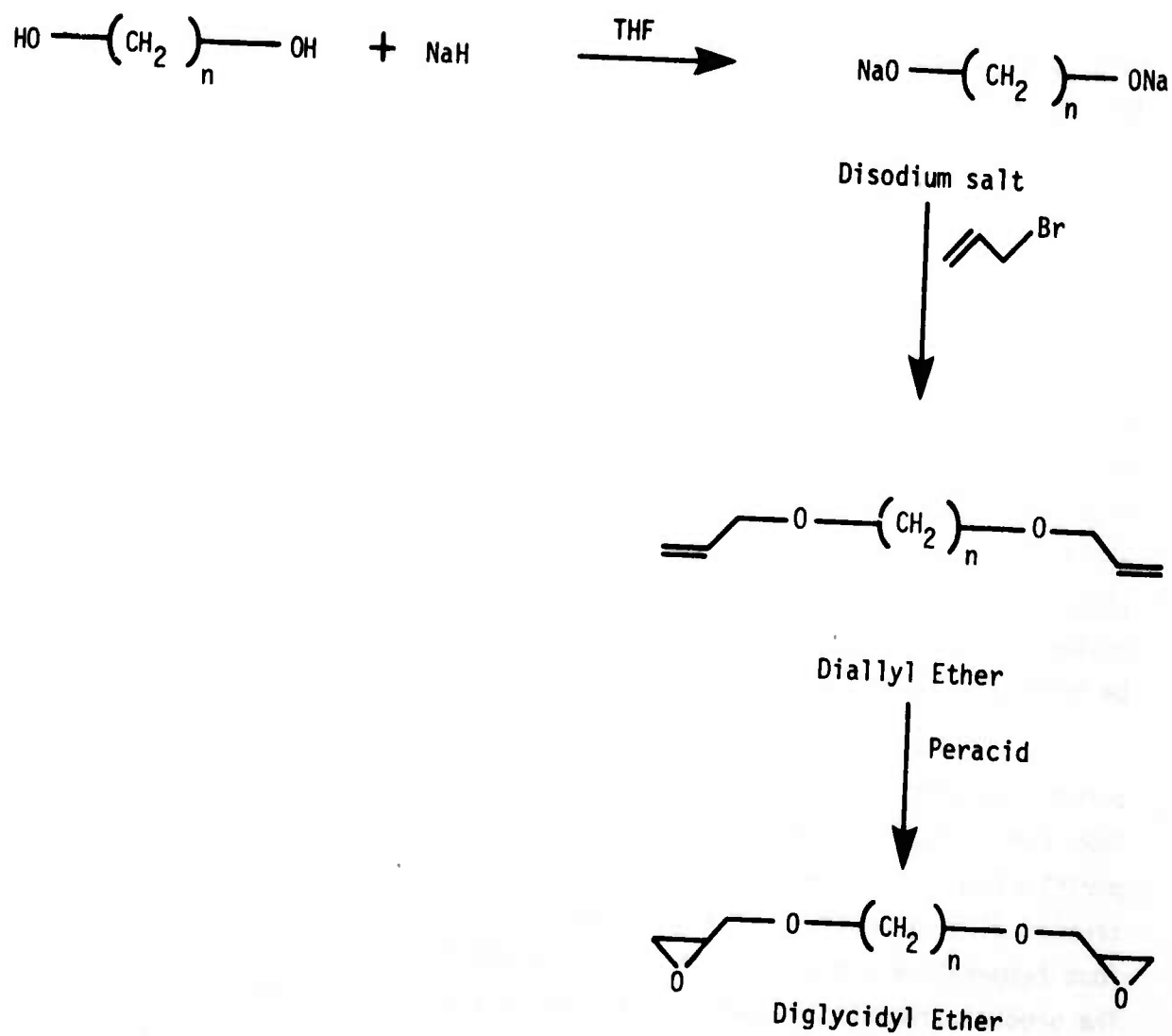


Figure 7. Preparation of diglycidyl ethers from diallyl ethers.

2.2.2 Synthesis of Diglycidyl Esters

Several long chain diglycidyl esters were synthesized by the method of Maerker¹⁵ as shown in Figure 9. This procedure involves the reaction of the diacid disodium salt with excess epichlorohydrin. The possibility of multiple reaction with epichlorohydrin, as outlined in Figure 6 for a diol, exists here also, but is diminished. Because the diglycidyl esters are low melting solids, they are easily purified by recrystallization. Both diglycidyl adipate and sebacate were prepared in 88 percent yields. The latter was found to have an EEW of 175 (theory 143).

2.3 POLYMERIZATIONS

The aliphatic diglycidyl ethers and esters were cured with stoichiometric amounts of diamine. Although all the systems investigated are capable of room temperature cure, in most cases a cure temperature of 220°F was used to shorten the time required for cure, enabling faster determination of the ultimate properties. The degree of cure at room temperature was demonstrated equivalent to elevated temperature cure for systems with Tg's near room temperature by comparing the Tg's and mechanical properties of materials resulting from cure at both temperatures.

The cured epoxy resins from aliphatic diglycidyl ethers or esters and aliphatic diamines are flexible materials with apparent Tg's below room temperature (Tables 3,4,5) as determined by linear expansion (Figure 9). The cure was monitored by observing the disappearance of epoxide bands in the infrared (IR) spectrum at 1250, 970 and 850 cm⁻¹. At room temperature the resins gelled in a few hours and were cured on standing overnight or heating at 220°F for 2 hours. In addition, information pertaining to the cure was obtained by observing the Tg development of a sample with increased cure temperatures. Polymer systems with Tg's below room temperature did not have significant Tg increase after heating, indicating complete reaction at

room temperature. For instance, the Tg of 1,4-butane diglycidyl ether cured with 1,8-octanediamine increased 7 degrees from -17 to -10°C on heating at 220°F for one hour.

Tables 3 and 4 demonstrate the expected trend in increasing Tgs with increasing crosslink density for the resin systems shown. The shorter the aliphatic chain in the amine and/or glycidyl ether or ester, the higher the apparent Tg. Calculation of the molecular weight between crosslinks (Mc) gives a Mc of 416 for the epoxy resin from 1,12-dodecanediamine and 1,10-decane diglycidyl ether which had an apparent Tg of -38°C. In contrast,

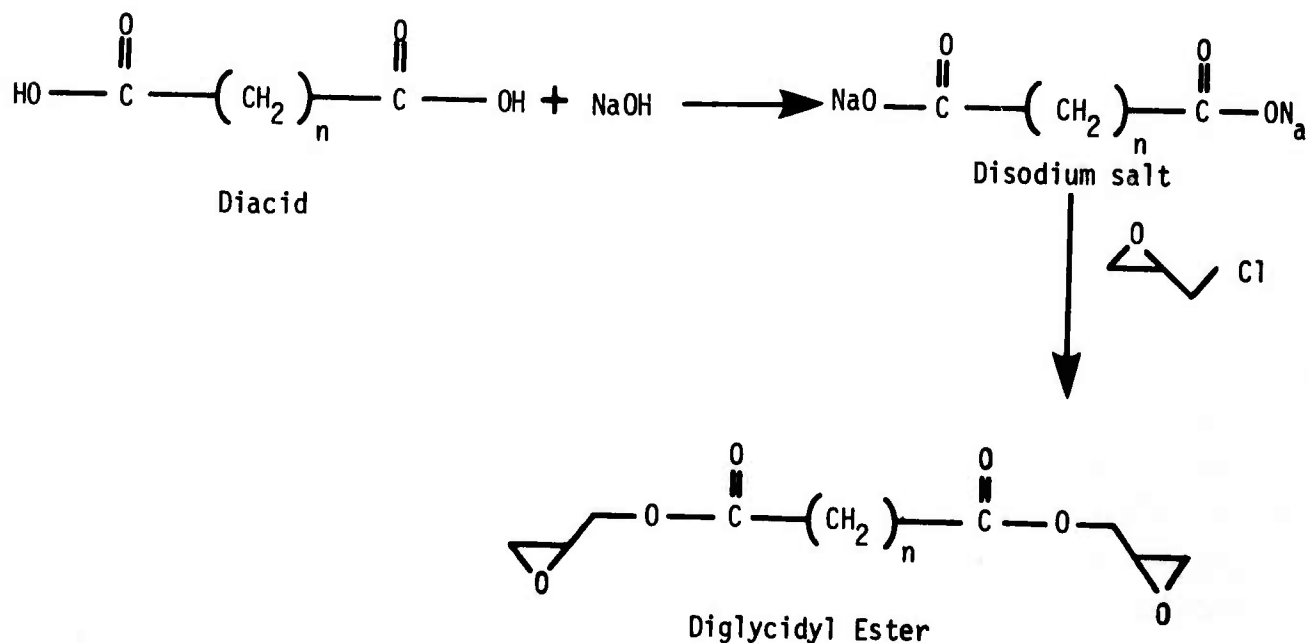


Figure 8. Preparation of diglycidyl esters.

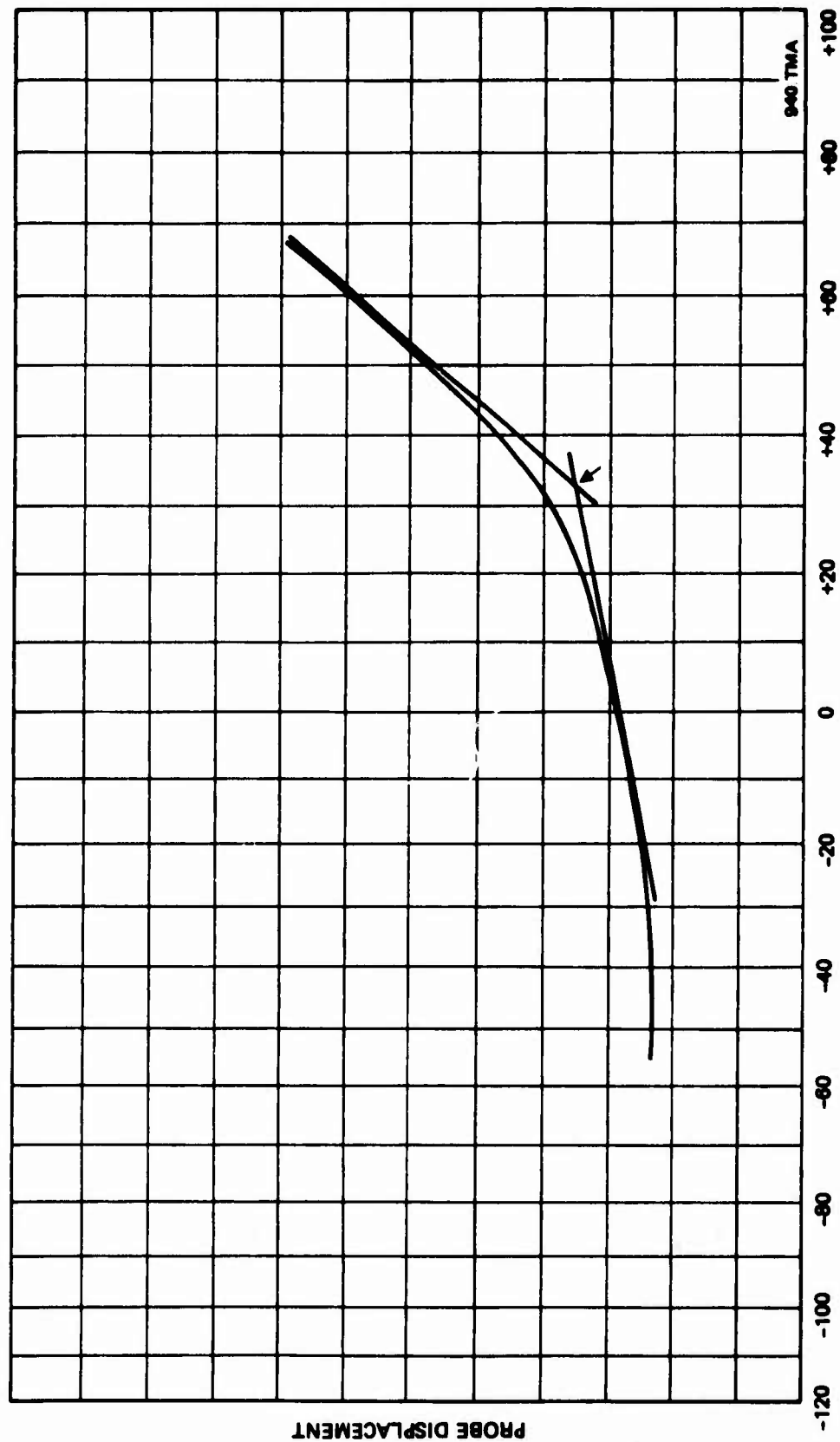
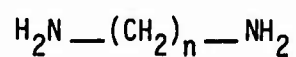
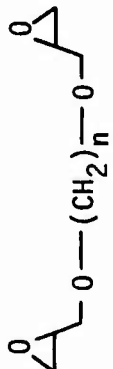


Figure 9. Linear expansion of 1,4-butane diglycidyl ether/Shell Z.

TABLE 3. APPARENT T_g OF ALIPHATIC GLYCIDYL ETHER/AMINE EPOXIES^a



		n = 4	6	8	12
	n = 4 ^b	-8°C	-11°C	-11°C	-9°C
	6 ^c	—	—	-30°C	—
	10 ^d	—	-20°C	—	-38°C

^acure: 2 hours at 220°F; ^bEEW 128 (Theor. 101); ^cEEW 134 (Theor. 115);
^dEEW 158 (Theor. 142)

TABLE 4. APPARENT T_g OF DIGLYCIDYL ADIPATE^a
 CURED WITH ALIPHATIC DIAMINES^b

DIAMINE	APPARENT T _g	DSC MAX. (°C)
1,6-Hexane	+7°C	84
1,8-Octane	-12°C	—

^aEEW 125 (Theor. 115); ^bcure = 2 hours at 220°F

TABLE 5. CURE OF 1,4-BUTANE DIGLYCIDYL ETHER^a WITH DIAMINES

Diamine ^b	Catalyst	Apparent ^c T _g (°C)	DSC Max. (°C)
1,4-butanediamine	—	- 8	102
1,4-butanediamine	tin octoate	-12	
1,6-hexanediamine	—	-11	
1,8-octanediamine	—	-17	
1,8-octanediamine	tin octoate	-11	
1,8-octanediamine	BF3-MEA	-16	

^a Epoxy equivalent weight 128

^b Stoichiometric amount of amine was used; cured 24 hr. at 23°C

^c Determined by thermal expansion with a DuPont 900 thermal analyzer

a system with a lower molecular weight between crosslinks (higher crosslink density) such as the resin from 1,4-butanediamine and 1,4-butane diglycidyl ether has an apparent T_g of -8°C (M_c=246).

The apparent T_g of even the short chain all aliphatic epoxy systems were quite low and some work was done to incorporate aromatic groups into the aliphatic systems to increase the T_g to nearer room temperature. One method used was the cure of aliphatic diglycidyl ethers with the aromatic amine Shell Z (a eutectic mixture of methylene dianiline and m-phenylenediamine). The Shell Z cured resins had apparent T_g's near room temperature (Table 6), but several of the shorter chain glycidyl ethers gave materials with T_g's too high for them to cure properly without slight heating. The second method employed to prepare epoxy resins with T_g's near room temperature was to add an aromatic epoxy resin such as Epon 828 (based on bisphenol A diglycidyl ether) to the aliphatic epoxy. Very long flexible amine curing agents like polyoxypropylene diamines with molecular weights of 200-400 were used with these systems to keep the T_g near ambient. As seen in Tables 6 and 7 several formulations resulted in materials with T_g's near room temperature.

TABLE 6. APPARENT T_g OF ALIPHATIC DIGLYCIDYL ETHERS AND ESTERS CURED WITH SHELL Z^a

Diglycidyl ether	Apparent T _g °C
1,4-butane ^b	+30 ^a
1,6-hexane ^c	+14
1,10-decane ^d	+14
neopentane ^e	+61
75/25 neopentane/1,6-hexane	+29
1,2-Ethane	+40
Diglycidyl ester	
Diglycidyl adipate ^f	+42
Diglycidyl sebacate ^g	+27

^acure: 2 hours at 220°F; ^bEEW 128; ^cEEW 134; ^dEEW 167; ^eEEW 115 (Theor. 108); ^fEEW 125 (Theor. 115); ^gEEW 171 (Theor. 143)

TABLE 7. DIGLYCIDYL ETHER MIXTURES CURED WITH POLYETHER DIAMINES^a

Diglycidyl ether	Diamine	Apparent T _g °C
1,6-hexane/Epon 828 25/75	Jeff. D-230 ^b	+34
1,6-hexane/Epon 828 25/75	Jeff. D-400 ^c	+22
1,4-butane/Epon 828 25/75	Jeff. D-400	+17
1,4-butane/Epon 828 25/75	Jeff. D-230	+50

^aCure: 2 hours at 220°F; ^bPolyoxypropylene diamine MW ~ 230; ^cPolyoxypropylene diamine MW ~ 400.

2.4 TESTING OF CURED RESINS

2.4.1 Mechanical and Dynamic Mechanical

Selected resin compositions were subjected to mechanical strength and modulus determination. The low strengths of the polymers whose Tg's were below room temperature were unexpected. In particular the tear strength* of these systems is very low. High tear strength of course, is the result of high tensile strength in combination with good tensile elongation or good tensile strength in combination with high tensile elongation.

A number of experiments were performed toward the goal of improving the tear strength characteristics of the cured rubbery resins. Investigation of additional thermal treatments in some cases to near destruction failed to improve the measured Tg's or strengths. Rigorous exclusion of moisture did not improve the strength properties of the 1,4-butane diglycidyl ether/1,6-hexanediamine system. The effect of epoxide purity on the strength of this resin system was also investigated. A sample of very pure 1,4-butane diglycidyl ether of EEW 104 (theory 101) was prepared to determine the effect of epoxide purity on the polymer. However, castings from this material cured with 1,6-hexanediamine had properties very similar to those made with the less pure 1,4-butane diglycidyl ether (EEW 128).

We concluded that the polymerizations were indeed giving the expected reactions; however, a continuous homogeneous crosslinked network was not being formed (discussed in Section 2.6 below).

The resins prepared containing aromatic groups with Tg's slightly above room temperature seemed qualitatively to have higher strength and modulus than the low Tg all aliphatic compositions. These materials had good tear strength at room temperature. Some of these systems were cast into 3" x 1" x 1/16" specimens for tensile strength and modulus determination. The results of the tests are shown in Table 8. The castings were cured at 220°F, except for sample No. 2, to expedite the sample testing. At room temperature, the tensile strengths of these systems were in the 3300-7500 psi range with 20-43 percent elongation.

The number 4 system shown in Table 8 was tested with an extensometer attached to the test area. Its initial tensile modulus was observed to

*Tear strength of rubbers is related to the area under the stress-strain curve (toughness) of structural plastics.

TABLE 8. TENSILE DATA OF ALIPHATIC EPOXY RESINS^g

Aliphatic Diglycidyl Ether or Ester	Amine (phr)	Apparent T _g °C	M _c	Ultimate Strength psi	Initial Modulus psi x 10 ⁴ , k.i.	Elongation (%)
1. 1,4 Butane diglycidyl Ether ^a /Epon 828 25/75	Jeff. D-230 ^{e,h} (33)	50	332	6820	—	30
2. 1,4 Butane diglycidyl Ether ^a /Epon 828 25/75	Jeff. D-230 ^f (33)	32	332	7170	—	37
3. 1,4 Butane diglycidyl Ether ^a	Shell Z ^e (32)	34	354	4950	—	25
4. 1,4 Butane diglycidyl Ether	Shell Z ^e (32)	34	354	3300 ⁱ	19.0 ^j	21
5. 1,4 Butane diglycidyl Ether ^a / Neopentane diglycidyl Ether ^b 25/75	Shell Z ^e (36)	47	323	6450	—	21
6. 1,6 Hexanediglycidyl Ether ^c /Epon 828 25/75	Jeff. D-230 ^e (31)	34	335	7530	—	43
7. Neopentane diglycidyl Ether ^b	Shell Z ^e (38)	61	314	4210 ^j	—	24
8. Diglycidyl Adipate ^d	Shell Z ^e (30)	42	374	6690	—	31

Epoxy Equivalent Weights (EEW)

- ^aEEW = 134 (Theor. 101)
^bEEW = 114 (Theor. 108)
^cEEW = 141 (Theor. 115)
^dEEW = 144 (Theor. 115)

Cure Schedule

- ^e2 hours at 220°F
^f1 week at 70°F

^gTested at 70°F, two specimen average

^hPolyoxypropylene diamine MW 230

ⁱDog bone specimens with extensometer (average of 3 tests)

^jOne specimen test

^kYoung's modulus

^lOnly extensometer data is reported

be 190,000 psi which is consistent with the modulus obtained by Rheovibron discussed below.

The effectiveness of a room temperature cure for amine cured aliphatic epoxy resins is demonstrated by system 2 in Table 8 (room temperature cured), which has essentially the same properties as system 1, the same composition cured at 220°F.

When attempts were made to test the materials in Table 8 containing aromatic groups at 200°F, it was found that the specimens had become very rubbery and had low tear strength much like the all aliphatic systems at room temperature. For example, at 200°F a tensile specimen of 1,4-butane diglycidyl ether/Shell Z under a small load (about 200 psi) elongated about 10 percent and then failed by tearing perpendicular to the load. Other materials in Table 8 behaved similarly.

Dynamic* mechanical testing of 1,4-butane diglycidyl ether/Shell Z films cured at 165°F and 400°F was done from -100°C to 150°C at 3.5 Hz on a Rheovibron Viscoelastometer. The modulus vs. temperature curve is shown in Figure 10 and the loss tangent vs. temperature is shown in Figure 11. The low temperature secondary relaxation peaks (Figure 11) for these samples appear to be unaffected by cure, both being near -50°C. The high temperature loss peaks in the loss tangent plot indicate that the primary loss peak is at 60°C for the 165°F cured sample, but is increased to 80°C for the 400°F cured sample. The former retained mechanical rigidity up to 150°C, but the latter shows evidence of the onset of flow above 110°C. This loss of modulus could be due to degradation at the 400°F cure temperature or mechanical failure of the thin film used in the test.

From the storage moduli (E') plot (Figure 10), the rubbery moduli for both samples are slightly greater than 10^8 dynes/cm². This indicates they are extensively crosslinked with estimated M_c from equation (2) of about 614.* This agrees well with the calculated M_c of 354 and substantiates the modulus approach to the design of room temperature curing 350°F performing resin systems.

*The measurements and analysis were performed by Professor Mitchel Shen, Department of Chemical Engineering, University of California at Berkeley (Appendix C).

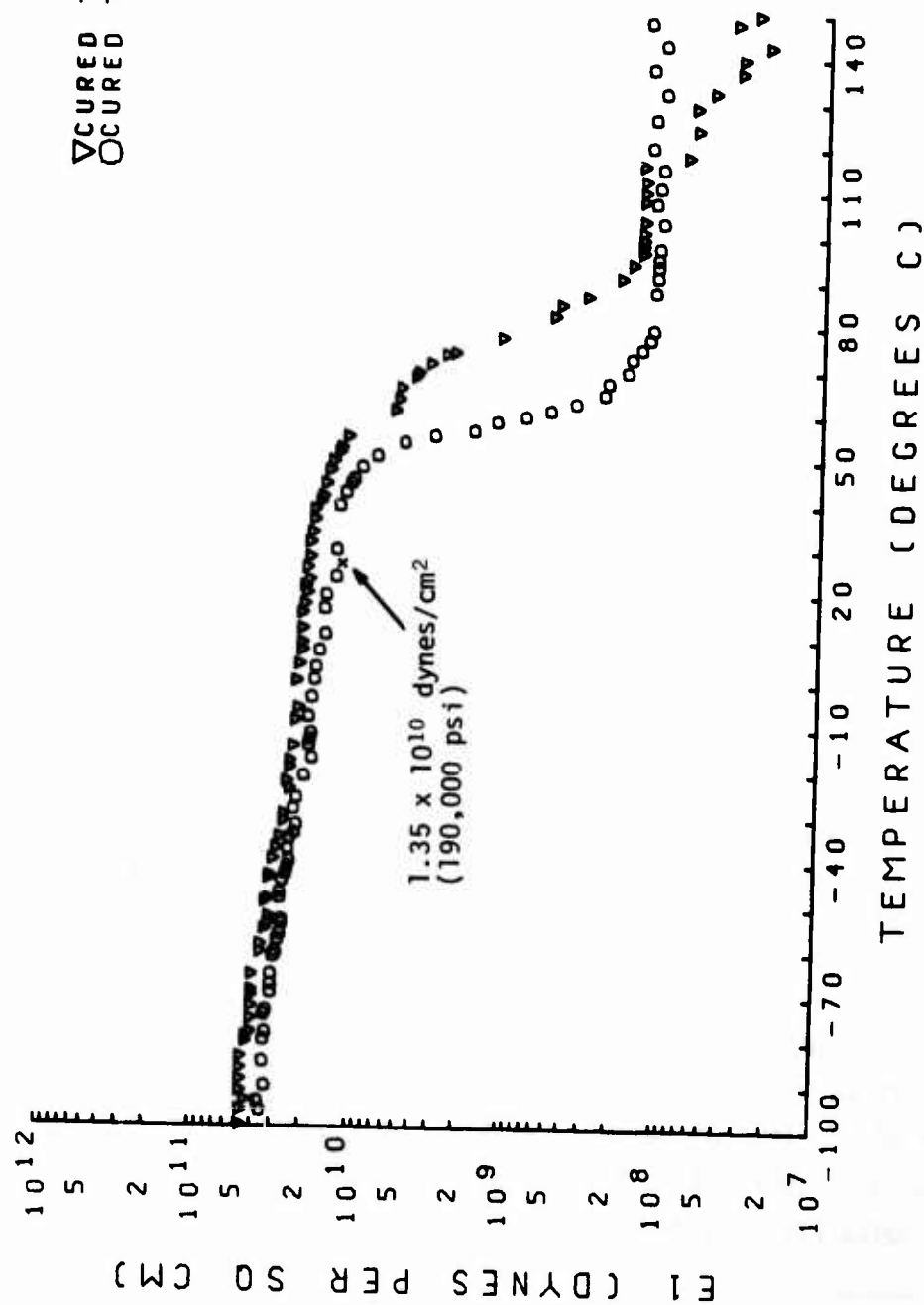


Figure 10. Modulus vs. temperature for 1,4-butane diglycidyl ether/Shell Z.

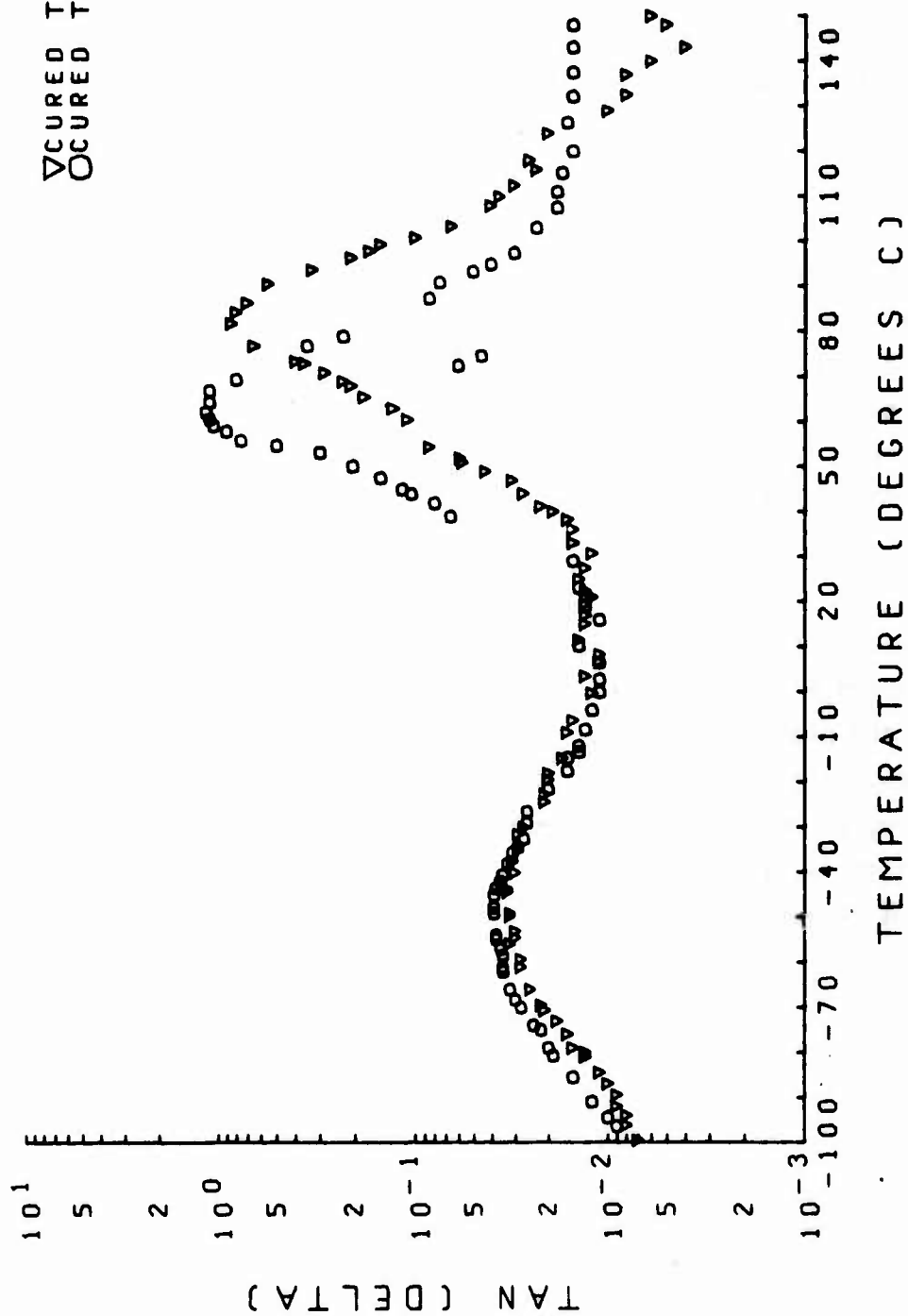


Figure 11. Loss tangent vs. temperature for 1,4-butane diglycidyl ether/Shell Z.

The Young's (tensile) modulus of Resin System No. 4 in Table 8 of 190,000 psi corresponds to 1.35×10^{10} dynes/cm². This can be seen to be in good agreement with the storage modulus curves seen in Figure 10 at 25°C for the same composition.

Figure 10 provides mechanical Tg (10^9 dynes/cm²) temperatures for the 1,4-butane diglycidyl ether cured at 165°F and 400°F of about 60°C and 75°C respectively. The expansion Tg seen in Figure 9 for this polymer is 34°C. The relationship of Tg to dynamic mechanical properties is discussed in Appendix C.

In summary, the low tensile strength of epoxy polymers on the rubbery plateau was unexpected as chemically they demonstrated cure and should form a continuous network. Since the modulus of the rubbery plateau increases with decreasing M_c the force required to deform samples with increasing modulus also increases. This must be interpreted to mean that lower M_c 's should result in higher strength. This may be demonstrable in compressive testing however in tensile testing the polymer must be capable of elongating without failure to sustain the increasing loads. If premature failure occurs due to flaws or other reasons the material's potential strength is not realized.

The tensile elongation is expected to decrease as the polymer chains are restricted by crosslinking and the modulus of the rubbery plateau increases. The elongation of the systems seen in Table 8 is 20 to 40 percent. Since these systems are very near or only slightly below their Tg at room temperature, an increase in tensile elongation would be expected as the modulus of the system is decreased. This is not consistent with the low elongations observed in our systems when they are on the rubbery plateau.

2.4.2 Swelling

Since solvent swelling of polymer systems is relatable to the cross-link density, attempts were made to study the degree of swelling in the cured aliphatic epoxy systems. However, after only a few days in chloroform, samples of polymers such as 1,4-butane diglycidyl ether cured with 1,6-hexanediamine, partially disintegrated into a number of small pieces. It was desirable to compare these results with the swelling of more standard epoxy systems. Because solvent swelling is very slow for glassy substances, it was necessary to perform the experiments at elevated temperatures, above the T_g of the polymer. Thus, a sample of Epon 828 cured with 1,8-octanediamine was refluxed in chloroform, and Epon 828 cured with Versamide 125 (1:1) refluxed in dioxane. In both cases the materials fell apart into several pieces after several hours much like was observed for the aliphatic systems at room temperature.

2.5 DISCUSSION

The low mechanical strength of epoxy resins on the rubbery plateau and the lack of solvent resistance at these temperatures indicate that the structure of most of these polymers is not the regular, continuous network often postulated. Rather the structure must be non-homogeneous and have areas of high and low crosslink density with the low crosslinked areas leading to poor tear strength and resistance to dissolution solvents. Inhomogeneities have been advocated by Labana, Newman and Chompff¹⁶ to explain the properties of several crosslinked systems. They also found that crosslink density inhomogeneity can exist at high degrees of cure in epoxy resins below their T_g . These authors observed the presence of "gel balls" 100 Å in diameter in epoxy resins by scanning electron microscopy. They represent a gel ball as in Figure 12, where a large amount of intramolecular reaction has taken place leading to crosslinked regions which are poorly connected with each other. This hypothesis may provide the explanation for the poor strength of our rubbery materials and the destruction of these polymers by solvent.

Figure 12 shows a "gel ball" at the center, loosely tied to six similar regions around it. Also of note is the use of four molecular segments

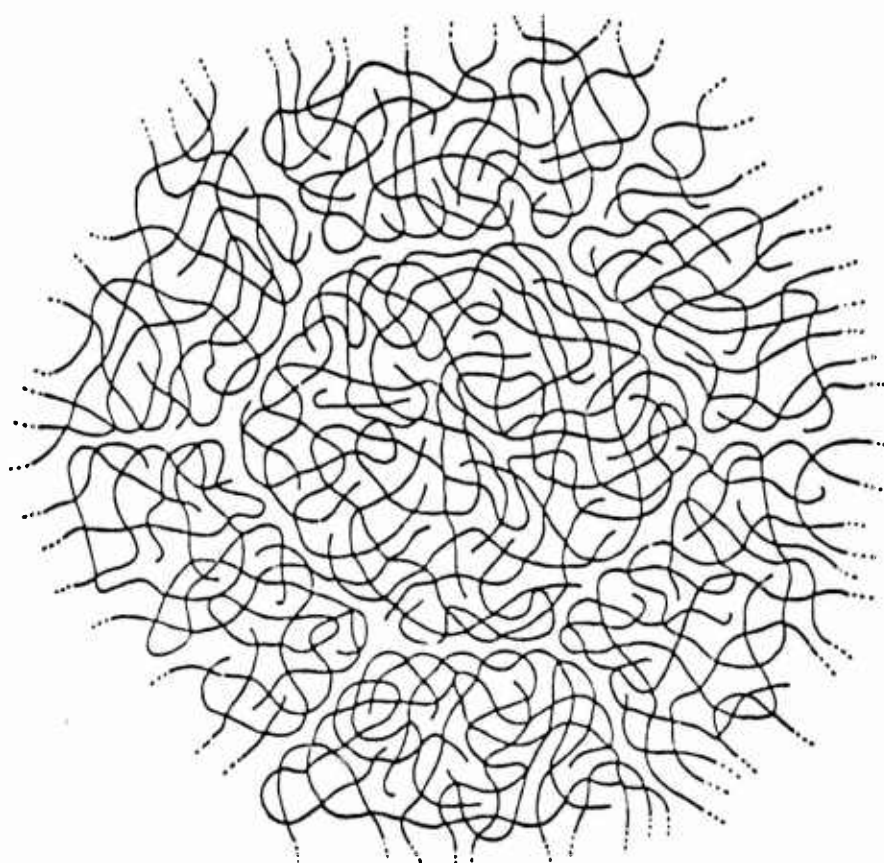


Figure 12. Two-dimensional schematic representation of crosslink density inhomogeneities.

emanating from each crosslink (rubber theory), a few covalent links to other gell balls and the presence of intramolecular looping which the theory for reacting multifunctional monomers together prescribes.

Apparently, the toughness observed at room temperature for the Shell Z cured aliphatic epoxies is due to the response of the material at that particular temperature rather than an inherent toughness in the molecular structure. In other words the toughness of the aliphatic epoxy/Shell Z material is dependent on their location on the modulus/temperature curve rather than on differences in chemical composition. This is illustrated for 1,4-butane diglycidyl ether/Shell Z with a T_g of $+34^\circ\text{C}$ in Figure 13. At room temperature, the material is slightly below the T_g , as suggested by the thermal expansion curve (Figure 9), and the modulus has dropped slightly from that in the glassy region. At 200°F (93°C) the material is on the

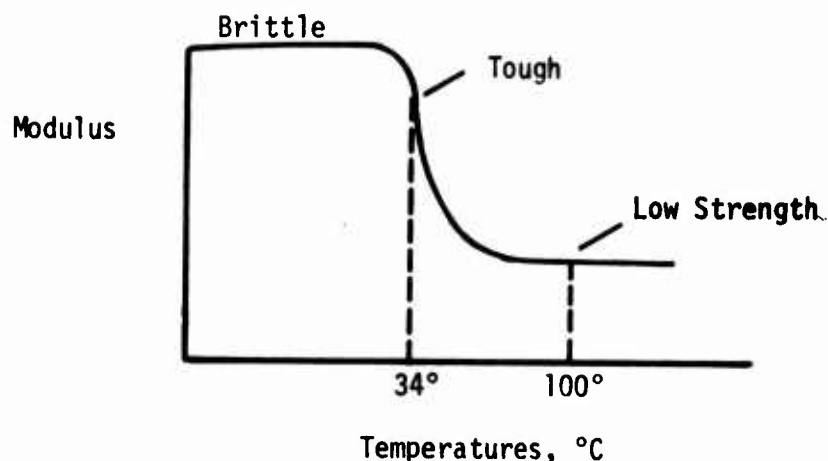


Figure 13. Modulus/temperature curve for 1,4-butane diglycidyl ether cured with Shell Z.

rubbery plateau and was expected to be tough but instead demonstrated low tear strength.

Lebana, et al's, representation of the morphology of highly cross-linked systems appears to fit several experimental facts. The key question then becomes: "Can the morphology be changed to provide high strength, highly crosslinked rubbers?" Restated: Can the polymer chemist design monomers which upon reaction will not result in gel ball formation?

The achievement of equilibrium solvent swelling measurements as contrasted to our observed disintegrations is the result of the postulated regular, continuous network having been attained. Typically, classical crosslinked rubbers result from crosslinking of high molecular weight linear prepolymers. Lebana (et al) used low molecular weight polyglycidyl methacrylate prepolymers in combination with methylene dianiline in their studies. Further, the authors predict that the use of intermediate molecular weight prepolymers will only result in larger gel balls. These conclusions are based on the reasonable assumption that the forming prepolymer rapidly obtains its equilibrium conformations after each reaction with the curing agent.

Accordingly, the successful development of a room temperature curing, 350°F performing resin system appears to lie with the development of a monomer system which upon reaction will provide a high molecular weight precursor with unreacted functionality suitable for subsequent crosslinking such as the 1,4 polybutadienes.

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

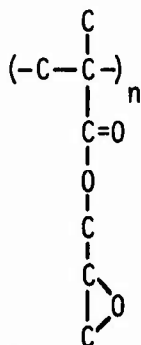
3.1 CONCLUSIONS

1. It is concluded that crosslinked epoxy resins will exhibit a rubbery plateau. Its modulus will be relatable to the $G = \rho RT/M_c$ relationship.
2. Without detail knowledge of the cure statistics, M_c can be calculated from the measured purities and molecular weights of the monomers.
3. Most epoxy resins when on rubbery plateau will exhibit low strength characteristics. We attribute this to the theory of the reaction of multifunctional monomers and gel ball formation.
4. Cure will proceed to completion at room temperature if the T_g is below or near room temperature. If the T_g is much higher than room temperature, the cure will cease leaving the reaction incomplete until heat is applied.
5. Aliphatic epoxy resin systems, even highly crosslinked, provide cured systems whose T_g is below room temperature.
6. Toughness is a property of resin systems near their glassy state. This toughness is characteristic of both linear and crosslinked systems and its origin is related to phenomena of the glassy state not the rubbery state.
7. Real solutions to the development of a room temperature curing 350°F performing resin appear to exist. The present efforts as well as Tobolsky's work leave little doubt that initial modulus

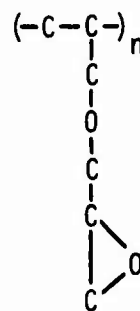
can be retained to very high temperatures. This, in combination with Young's moduli greater than 300,000 psi being attained by available room temperature curing epoxies suggests that highly crosslinked monomer systems can be designed to provide room temperature cure and 350°F performance.

3.2 RECOMMENDATIONS

1. It is recommended that the development of monomers which will provide a linear polymer with suitable functionality for subsequent crosslinking continue. Mixed radical-epoxy cured systems may provide such systems. Two epoxy prepolymers of this type are poly(glycidyl methacrylate) and poly(allyl glycidyl ether) and are shown below.



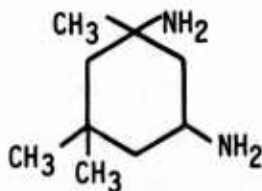
poly(glycidyl methacrylate)



poly (allyl glycidyl ether)

Their subsequent crosslinking step would be with amines, bisphenols or similar which would be slower than the radical reaction.

2. Consistent with the different reactivities suggested above another approach might include diamines of differing reactivities. Such an amine might be isophorone diamine as shown below.



Its reaction with 1,4-butane diglycidyl ether did not provide the sought results.

Other diamines could be sought or other functionalities investigated such as one would have with a dimercapto monoamine curing agent.

This approach does not appear as attractive as the first one unless epoxy resins of different reactivities could be used in combination with the curing agents. The preferred product for a dimercapto amine with an epoxy resin with only one type of reactivity would be the epoxy-end-capped moiety and not a high molecular weight prepolymer.

3. Another known approach for increasing the strength of systems on their rubbery plateau is the use of fillers 500 Å in diameters which are known to increase the strength of noncrystallizing rubbers.³

SECTION 4

EXPERIMENTAL

Melting points were performed on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-10 instrument as neat films or nujol mulls. NMR spectra were recorded on a JEOL 100 MHz instrument in CDCl_3 using tetramethyl silane as internal reference with $\delta = 0$; s, singlet; d, doublet; t, triplet; m, multiplet.

1,2-Ethane Diglycidyl Ether

To epichlorohydrin (277.5 g, 3 moles) and ethylene glycol (62.1 g, 1 mole), six drops of boron trifluoride etherate were added and the mixture stirred for 5 hours. Sodium hydroxide (80 g, 2 moles) dissolved in water was added to the mixture. After 1 hour benzene and water were added and the mixture was stirred until the salt was dissolved. The organic layer was then separated and dried (MgSO_4) and the benzene and excess epichlorohydrin removed under reduced pressure. Kugelrohr distillation of the crude product resulted in 25 g of product with an epoxy equivalent weight (EEW) of 101 (Theory 87). The method used to determine EEW is described in Appendix A.

1,4-Butane Diglycidyl Ether

1,4-butane diglycidyl ether was prepared in the manner described for the preparation of 1,2-ethane diglycidyl ether. Distillation (120°C, 0.1 mm) of 95 g of crude product with an EEW 185 yielded 15 g of distilled product with an EEW of 134 (Theory 101).

Two commercial products Ciba-Geigy Araldite RD-2 and Aldrich BDGE were Kugelrohr distilled.

The epoxy equivalent weight of crude Araldite RD-2 was 176. Kugelrohr distillation (120°, 0.1 mm) of 200 g resulted in 50 g of product with an EEW of 114. The IR and NMR spectra of this material are shown in Figures 14 and 15.

Aldrich, 1,4-butane diglycidyl ether had an epoxy equivalent weight of 274. Distillation (110°C, 0.1 mm) resulted in 5 g of product with an EEW of 104.

1,10-Decane Diallyl Ether

1,10-decanediol (174 g, 1 mole) was added to sodium hydride (96 g, 2 mole) 54% in mineral oil, suspended in THF (1500 ml) under nitrogen and the mixture was stirred and heated at reflux for 16 hours. The mixture was filtered and the unreacted sodium hydride in the filter cake was destroyed with methanol. The THF in the filtrate was removed with reduced pressure in a rotary evaporator and the residue was distilled to yield 195 g (77%) of 1,10-decane diallyl ether bp 120° (0.5 mm). The IR spectrum had bands at 3090, 1650, 990 and 920 cm^{-1} due to the allyl group and no band in the 3500 cm^{-1} hydroxyl region. The bromine number was found to be 121 (Theory 125) by the method in Appendix B.

1,10-Decane Diglycidyl Ether

1,10-decane diallyl ether (25.4 g, 0.1 mole) and m-chloroperbenzoic acid (65 g, 0.3 mole) were stirred 16 hours in methylene chloride (300 ml) at room temperature. The white precipitate was filtered and the filtrate extracted with saturated sodium bicarbonate solution, saturated ferrous sulfate solution, and sodium bicarbonate again, then dried over potassium carbonate. The solvent was removed and the residue, 22 g, was >90% decane diglycidyl ether, EEW 158 (Theory 143). The IR spectrum has epoxide bands at 1250, 920 and 850 cm^{-1} .

Peracetic acid was also used to prepare 1,10-decane diglycidyl ether. In this preparation a mixture of 1,10-decane diallyl ether (25.4 g, 0.1 mole), 40% peracetic acid in acetic acid (60 g, 0.4 mole) and sodium acetate (2 g) in chloroform (200 ml) was stirred 16 hours at room temperature. The solution was extracted with water, saturated sodium carbonate solution, saturated ferrous sulfate solution, and saturated sodium carbonate solution a second time

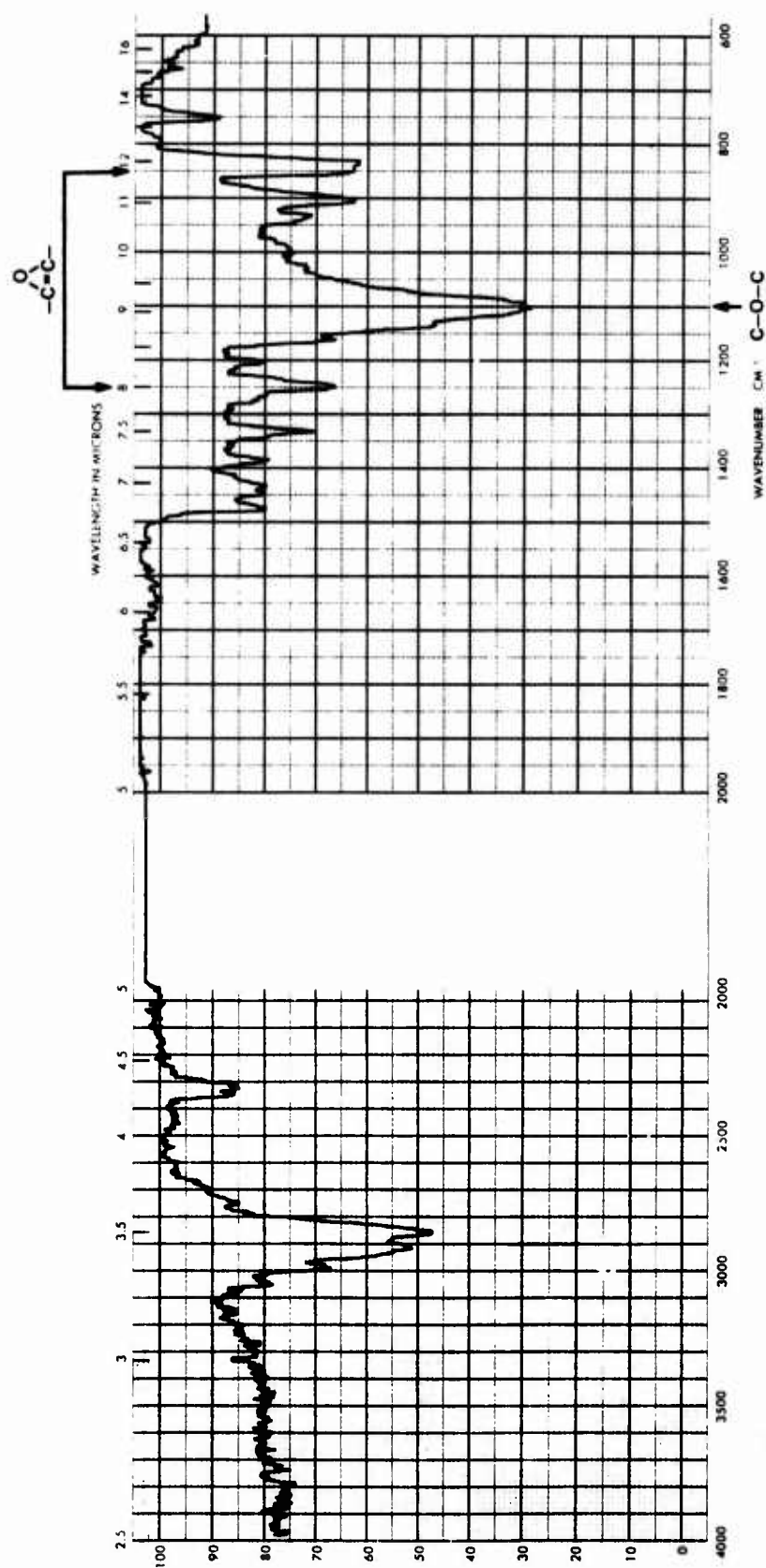


Figure 14. Infrared spectrum of 1,4-butane diglycidyl ether EEW 114.

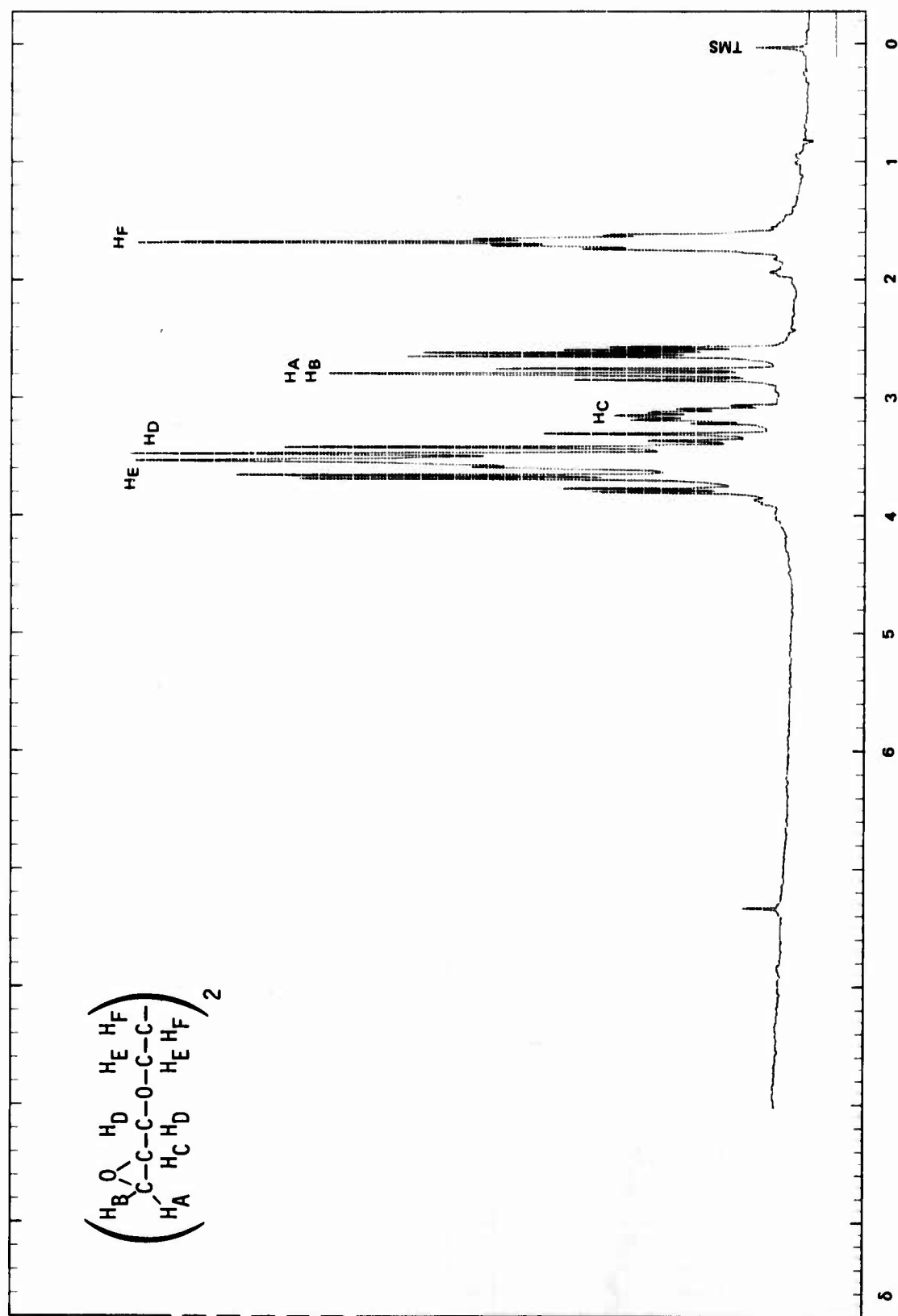


Figure 15. NMR spectrum of 1,4-butane diglycidyl ether EEW 114.

then dried over sodium carbonate. The solvent was removed to give impure 1,10-decane diglycidyl ether EEW 200 (Theory 143). The IR spectrum had bands at 3500, 1740, 1250, 920 and 850 cm^{-1} .

1,6-Hexane Diallyl Ether

This compound was prepared in 83% yield by the same method used for 1,10-decane diallyl ether, bp 60° (0.5 mm). The IR spectrum had bands at 3090, 1650, 990 and 920 cm^{-1} (Figure 16). The NMR spectrum had: δ 1.4 m, 8 protons; δ 3.38 t, J = 66 Hz, 4 protons; 3.92 J = 6 Hz, 4 protons; 5.2 m 4 protons; and 5.84 m 2 protons. The bromine number (Appendix B) of the product seen in Figure 17 was found to be 156 (Theory 163).

1,6-Hexane Diglycidyl Ether

This compound was prepared using the peracetic acid method described for 1,10-decanediol diglycidyl ether. The crude product had an EEW of 200 and distillation (bp 80°, 0.5 mm) resulted in material with EEW 134 (Theory 115). The IR spectrum of the crude material (Figure 18) had bands at 3500 (hydroxyl), 1740 (ester carbonyl) and 1260, 920 and 850 cm^{-1} (epoxide). The NMR spectrum of 1,6-hexane diglycidyl ether had peaks at δ 1.5 m, 8 protons; 2.59, dd J = 5,2 Hz, 2 protons; 2.79, t J = 5 Hz 2 protons; 3.14 m, 2 protons; and 3.5 m, 8 protons. The NMR spectrum of this material had small peaks due to unreacted allyl groups (Figure 19).

Other attempts were made to prepare 1,6-hexane diglycidyl ether by treatment of 1,6-hexanediol with epichlorohydrin.

A mixture of 1,6-hexanediol (11.8 g, 0.1 mole) in toluene (200 ml) was heated to reflux and sodium (4.6 g, 0.2 mole) added in small pieces to the stirred mixture under nitrogen. The mixture was allowed to reflux 12 hours. Epichlorohydrin (92.5 g, 1 mole) was added and the mixture allowed to cool. The mixture was then filtered and the solvent removed under vacuum. The residue had EEW 418.

1,6-Hexane Diglycidyl Ether

1,6-hexane diglycidyl ether was prepared from 1,6-hexanediol and epichlorohydrin in the manner described for the preparation of 1,2-ethane

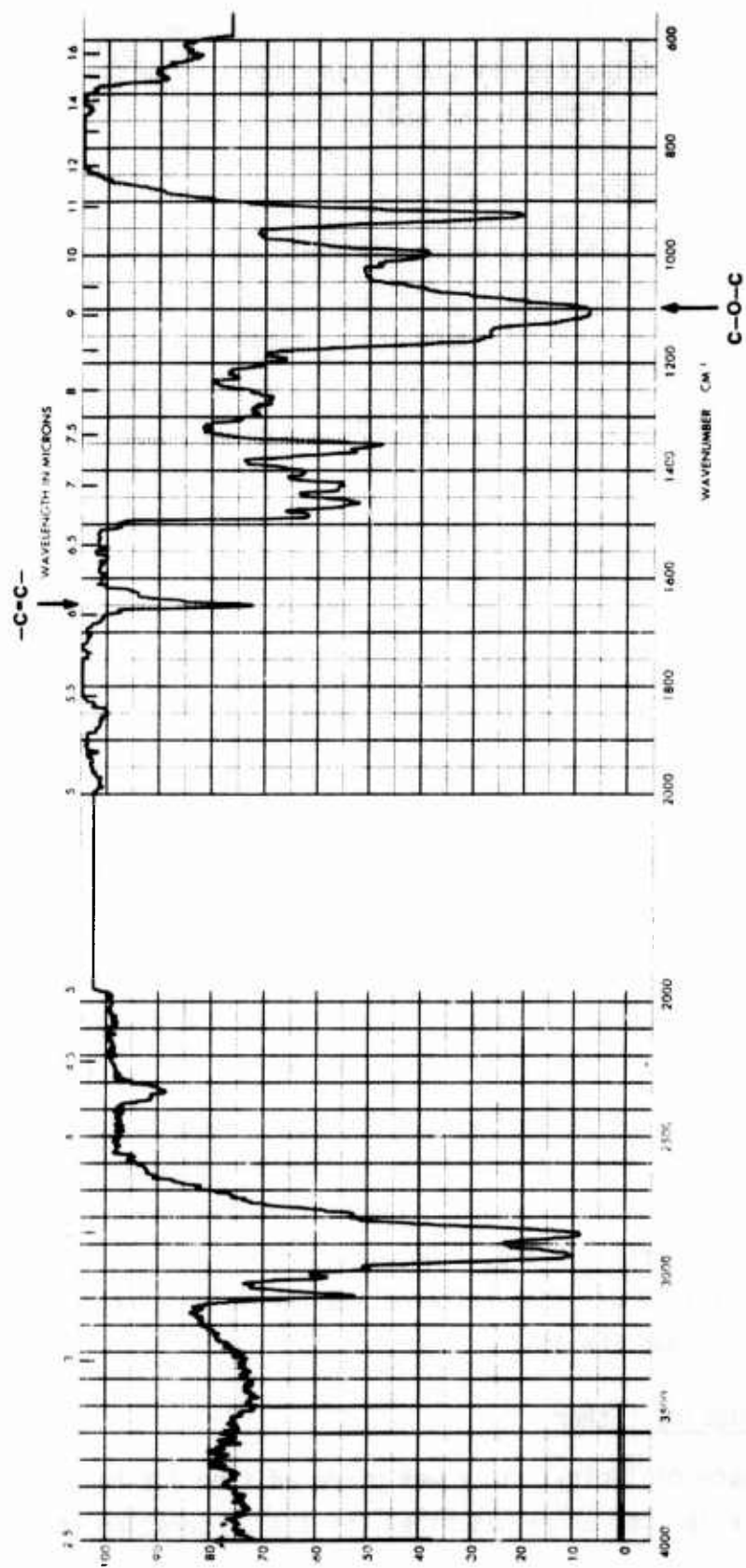


Figure 16. Infrared spectrum of 1,6-hexane diallyl ether.

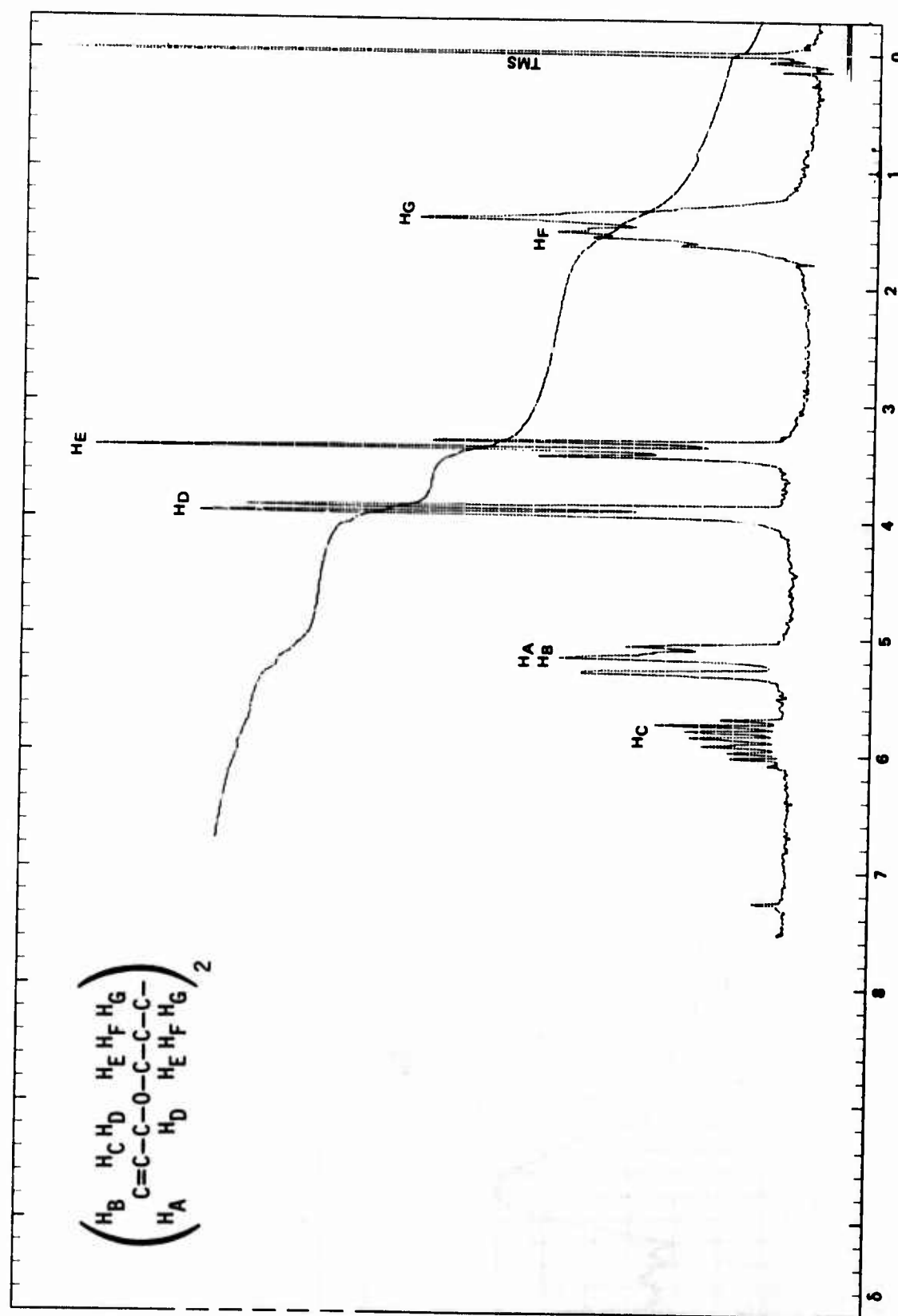


Figure 17. NMR spectrum of 1,6-hexane diallyl ether.

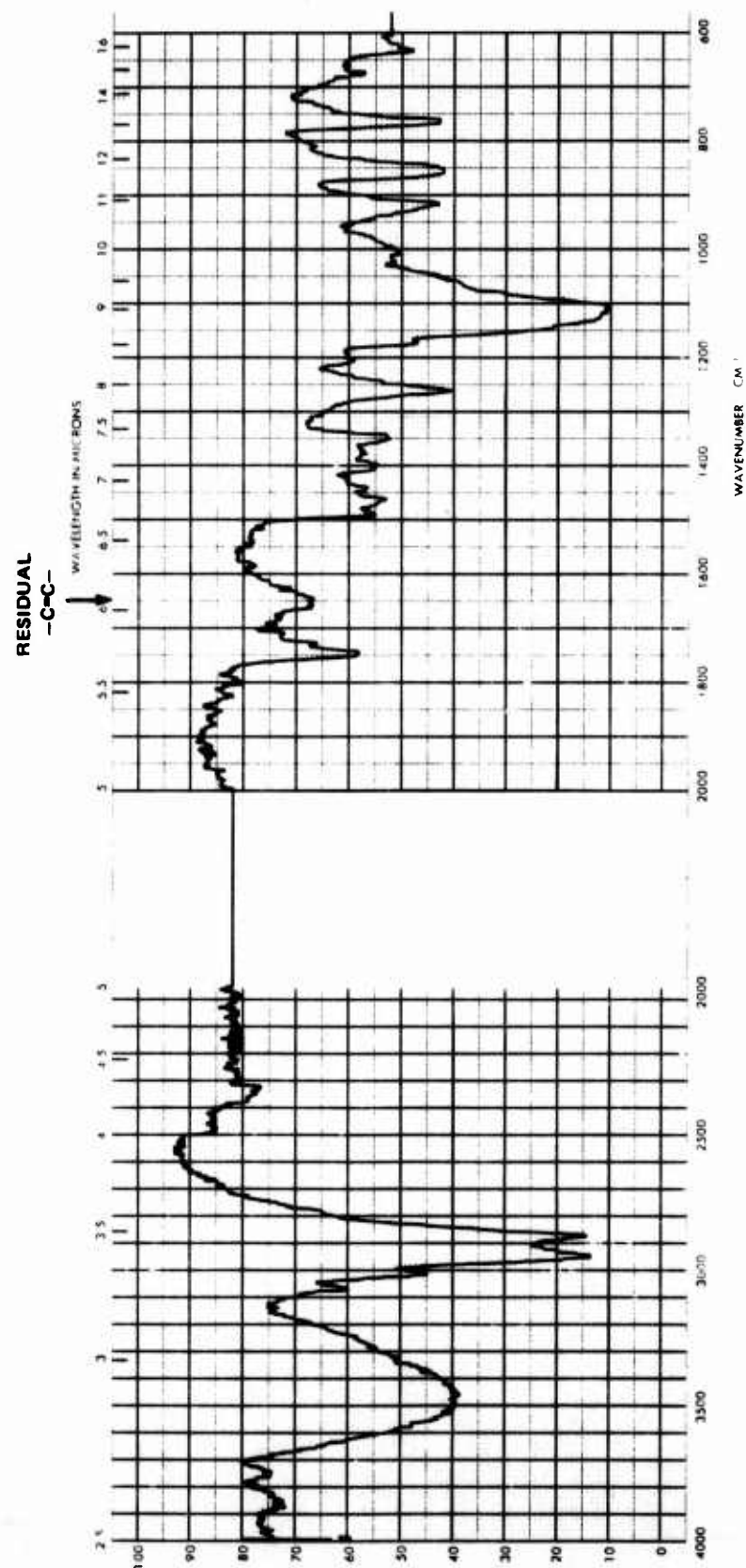


Figure 18. Infrared spectrum of 1,6-hexane diglycidyl ether from peracid oxidation EEW 200.

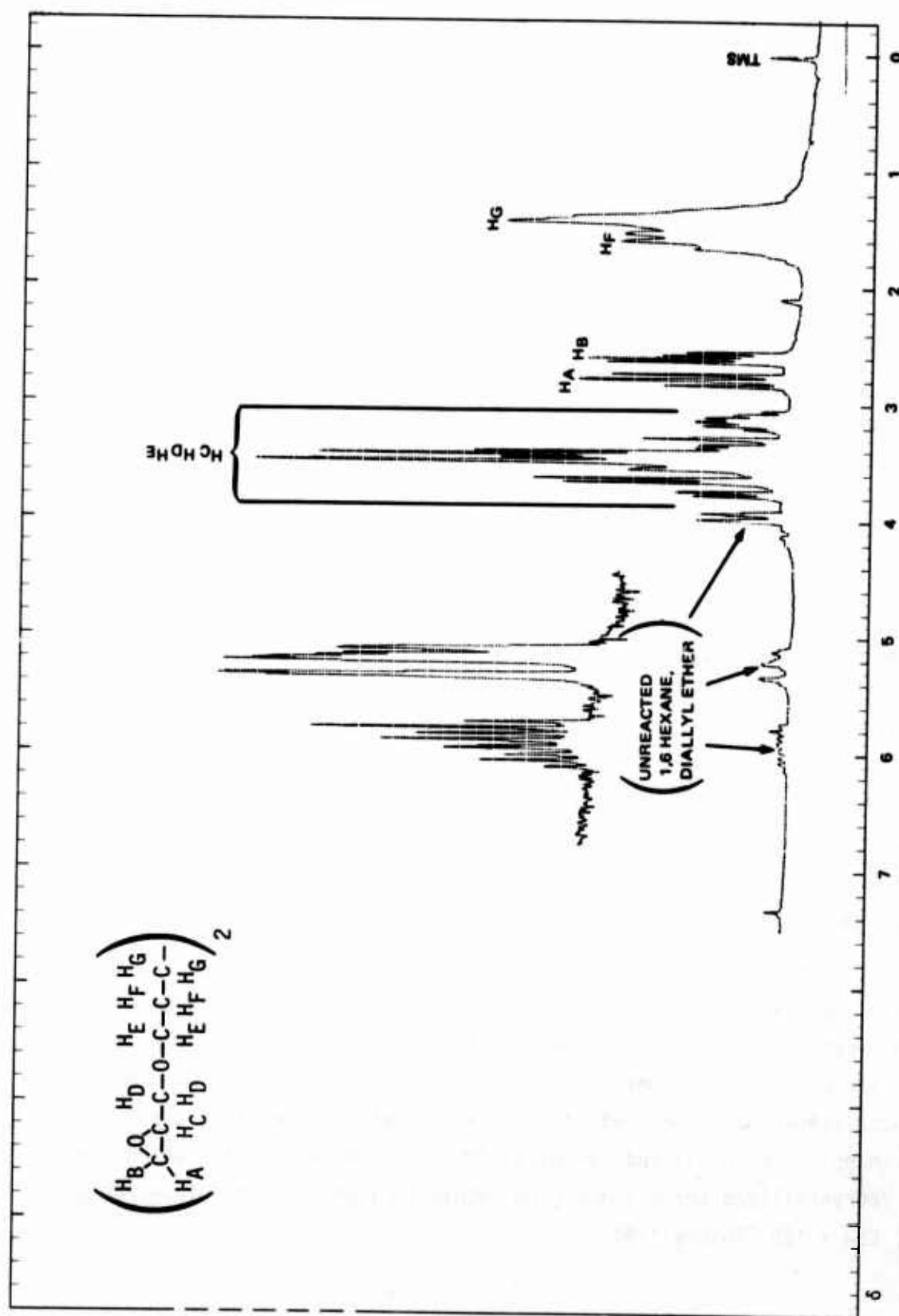


Figure 19. NMR spectrum of 1,6-hexane diglycidyl ether EEW 134. Note peaks due to unreacted diallyl ether at 4.0, 5.2 and 5.9.

diglycidyl ether. The epoxy equivalent weight was 772. Vacuum distillation (130°C, 0.05 mm) of 110 g of crude product yielded 4 g with an EEW of 144.

1,8-Octanediglycidyl Ether

1,8-octanediglycidyl ether was prepared as previously described. The epoxy equivalent weight of the crude material was 895 (Theory 129). Distillation (195°C, 0.05 mm) of 58 g crude product gave 2 g of material with EEW 615.

Neopentane Diglycidyl Ether

Neopentane diglycidyl ether was purchased from Ciba-Geigy as XU-193. The crude material had an epoxy equivalent weight of 140. Kugelrohr distillation of 250 g yielded 55 g with an epoxy equivalent weight of 114 (Theory 108).

Diglycidyl Adipate¹⁵

To a 5 liter 3 neck flask equipped with two Dean-Stark traps and a mechanical stirrer was added epichlorohydrin (2700 g, 29.2 mole). The epichlorohydrin was heated to reflux and a hot slurry containing adipic acid (87.6 g, 0.6 mole), potassium hydroxide (67.2 g, 1.2 mole), benzyltrimethyl ammonium choride (37.2 g) and water (200 ml) was added in portions over a 30 minute period. Epichlorohydrin and water were collected in the traps, the epichlorohydrin being returned to the reaction mixture and the water discarded. When addition of the hot slurry was completed, the mixture was allowed to react for 15 minutes and then cooled to room temperature.

The mixture was extracted with two 100 ml portions of water. The organic layer was dried (MgSO_4) and the epichlorohydrin removed under reduced pressure. Benzene was added and the solution stirred at room temperature for one hour. The mixture was filtered and the benzene was removed by rotoevaporation. The crude diglycidyl adipate was added to a solution of methanol-water (9:1) and cooled to 0°C. The white crystals which formed were recrystallized three times from methanol-water (9:1) to yield 248 g (88%) EEW = 125 (Theory 115).

Diglycidyl Sebacate¹⁵

Diglycidyl sebacate was prepared as described for diglycidyl adipate to yield 96 g (88%), EEW = 175 (Theory 143).

Poly(Allyl Glycidyl Ether)

Allyl glycidyl ether (Aldrich Chemical Company) 20 g was heated at reflux and small amounts of cumene hydroperoxide added periodically over three days. The starting material was distilled off under vacuum to give 10 g of yellow residue which was viscous when cooled to room temperature, EEW 101 (Theory 114).

Poly(Glycidyl Methacrylate)

Glycidyl methacrylate (92% from Aldrich) 10 g, was heated to reflux in carbon tetrachloride and a small amount of bis(2-methylpropionitrile) added. The polymer precipitated after several hours. It was filtered and air dried.

Diamines

The diamines were obtained from Aldrich Chemical Company and were used without purification unless so noted.

Polymerizations

Polymerizations were performed by mixing the epoxy resin and curing agent together using 1:1 stoichiometry and casting the mixture into a mold. Cure continued at an appropriate temperature between ambient and 220°F to avoid crystallization of one of the components or an exothermic reaction.

APPENDIX A

PROCEDURE FOR DETERMINATION OF EPOXIDE EQUIVALENT BY THE PYRIDINIUM CHLORIDE METHOD

Reagents:

1. 0.2 N pyridinium chloride in pyridine (15 ml conc. HCl per liter of pyridine)
2. Standardized 0.5 N methanolic NaOH (20 g NaOH per liter)
3. Phenolphthalein indicator (0.1 g phenolphthalein per 100 ml methyl alcohol)
4. Methyl alcohol, reagent grade

Procedure:

Place a weighed sample of epoxy compound (2 to 5 milliequiv.) into a 200-ml round-bottom flask and pipet in 25 ml pyridinium chloride-pyridine solution. Pipet 25 ml of pyridinium chloride-pyridine solution into another 200 ml flask. This will be used as a blank throughout the procedure. Swirl the solution until all the sample has been dissolved, heating gently if necessary. Use a heating mantle plus a magnetic stirrer. After the sample has dissolved, add a reflux condenser, and reflux and stir the solution for 25 minutes. After refluxing, cool the solution with the condenser in place. Add 50 ml of methyl alcohol through the reflux condenser and let drain. Remove the reflux condenser. Add 15 drops of phenolphthalein indicator. Titrate with 0.5 N methanolic NaOH from a 10-ml buret to a pink end point.

Calculations:

$$\text{Epoxide equivalent} = \frac{(16)(\text{sample weight, g})}{(\text{g of oxirane oxygen in sample})}$$

$$\text{Grams of oxirane oxygen in sample} = (A - B)(N)(0.016)$$

A = milliliters of NaOH for blank

B = milliliters of NaOH for sample

N = normality of NaOH

0.016 = milliequivalent weight of oxygen in grams

APPENDIX B
UNSATURATED COMPOUNDS DETERMINATION BY ACID
CATALYZED BROMINATION

B-1 PURPOSE AND LIMITATIONS

This procedure has been developed for the determination of unsaturation in organic compounds by the addition of bromine.

This procedure is designed to give rapid addition of bromine to the double bond as well as to minimize errors caused by substitution. Sample sizes in most cases are very small and it is recommended that a dilution of the sample in a suitable solvent be employed using 5 or 10-ml aliquots. Methanol, ethanol, acetonitrile, isopropyl ether, and acetic acid may be used as solvents. Large amounts of isopropanol, isobutanol, hexanol, acetone, tetrahydropyran, dioxane, and dimethyl cellosolve may interfere. In general, any easily oxidized compound, such as acetaldehyde or propionaldehyde, was found to interfere.

B-2 BROMINE NUMBER

This procedure may also be used to determine the bromine number of a compound. It is defined as the number of grams of bromine which will react by addition to 100 grams of the sample. For a pure compound the theoretical bromine number may be calculated from the equation:

$$\frac{2 \times \text{number of double bonds} \times 79.92 \times 100}{\text{molecular weight of the compound}} = \text{theoretical bromine number}$$

B-3 PRINCIPLE

Bromine dissolved in a methanol-water mixture which is saturated with sodium bromide forms the probable complex Br_3^- ion. In the presence of excess reagent unsaturated compounds react as follows:



In most cases, this reaction is accelerated by the presence of hydrochloric acid in the reagent. The tendency toward substitution is decreased by the presence of excess sodium bromide.

The amount of bromine consumed, which is determined by reaction of the excess reagent with an excess of potassium iodide and titrating the liberated iodine with standard sodium thiosulfate, is a measure of the unsaturated compound originally present.

B-4 REAGENTS REQUIRED

- a. Methanol reagent
- b. Bromine-bromide reagent, approximately 0.1 N; transfer 2.5 ml of c.p. bromine to a 1000-ml flask containing 300 ml of water, 300 ml of methanol, 100 g of sodium bromide and 10 ml of concentrated hydrochloric acid. Mix thoroughly and dilute to approximately 1 liter with methanol. Fit the flask with a two-hole rubber stopper and through one hole insert a 50-ml pipet so that the tip extends below the surface of the liquid; through the other hole insert a piece of glass tubing to which is attached a pressure aspirator bulb.
- c. Sodium bromide, reagent grade crystals
- d. Potassium iodide, 15 percent aqueous solution
- e. Standard 0.1 N sodium thiosulfate.

B-5 PROCEDURE

- a. To each of a sufficient number of 250-ml glass-stoppered Erlenmeyer flasks to make all sample and blank determinations in duplicate, add 5 to 10 g of sodium bromide crystals.
- b. Carefully pipet 50 ml of approximately 0.1 N bromine-bromide reagent into each of the flasks, filling the pipet by pressure from the aspirator bulb.

- c. Reserve two flasks for a blank determination. If a dilution of the sample is used, add to the blanks an amount of solvent equal to the volume of the aliquot used for the sample.
- d. Into each of the other flasks introduce an amount of sample calculated to contain approximately 3.5 milliequivalents of unsaturated compound.
- e. Allow the samples and blanks to stand together at room temperature for 2 hours.
- f. To each flask add 50 ml of methanol and 10 ml of 15 percent potassium iodide solution. Titrate immediately with standard 0.1 N sodium thiosulfate just to the disappearance of the yellow iodine color.

B-6 CALCULATIONS

Bromine number

$$\frac{(B-A)N \times 7.992}{\text{gm sample}} = \text{bromine number}$$

A = ml of N normal $\text{Na}_2\text{S}_2\text{O}_3$ required for the sample

B = average ml of N normal $\text{Na}_2\text{S}_2\text{O}_3$ required for the blank

APPENDIX C

DYNAMIC MECHANICAL TESTING*

Dynamic mechanical tests measure the response to periodic or varying forces. Tests may be made over a wide temperature range in a short time, and from the results the overall performance of the material can be predicted and many of the other mechanical properties can be estimated.

The Rheovibron is one of several instruments available for measuring dynamic mechanical properties. It is available from IMASS, Inc. (Instruments for the Materials in Structural Sciences) in Hingham, Massachusetts.

The Rheovibron is designed to measure the temperature dependence of complex modulus E^* , dynamic storage modulus E' , dynamic loss modulus E'' , and dynamic loss tangent, $\tan \delta$, of viscoelastic materials at specific selected frequencies of strain input. A small sinusoidal tensile strain is applied to the samples at one of four selectable fixed frequencies, 3.5, 11, 35, or 110 Hz. Additional frequencies from .01 to 1 Hz are available as an option. This generates a sinusoidal stress in the sample at a characteristic lagging phase angle δ . The amount of phase difference between stress and strain provides an extremely useful and convenient means of characterizing the viscoelastic properties of the material.

The instrument is equipped with unbonded strain gauge transducers which measure the absolute values of the stress and strain amplitudes. The tangent of the phase angle ($\tan \delta$) is read directly on a meter mounted on the instrument. From these data and from the specimen's geometry it is a simple matter to calculate E^* the dynamic complex modulus, E' the dynamic storage modulus, and E'' the dynamic loss modulus. From the frequency temperature dependence of the absorption maximum of E'' , the

*From L. E. Nielsen, "Mechanical Properties of Polymers," Reinhold Publishing Corp., New York, 1962.

activation energy (ΔH^*) for the viscoelastic relaxation process can be computed, providing insight into the relaxation mechanism.

The Rheovibron can be used to make measurements either by fixing the frequency and scanning temperature or by fixing temperature and changing the frequency. In most cases the former is preferred because of the much larger effect of changing temperature compared to frequency in the range for which the instrument is designed.

The dynamic mechanical properties from the various instruments may all be related through the use of complex moduli. In the case of shear, the dynamic moduli are defined by

$$G^* = G' + iG''$$

while the complex Young's moduli are defined by

$$E^* = E' + iE''$$

G^* and E^* are the complex moduli. G' and E' are the real parts of the shear and Young's moduli, respectively. The quantity i is equal to $\sqrt{-1}$, so G'' and E'' are the imaginary parts of the moduli.

If the damping is very small, $G' = G$ and $E' = E$, so the real parts of the moduli are the same as what we have been used to calling elastic moduli. In general,

$$G = |G^*| = \sqrt{(G')^2 + (G'')^2}$$

and

$$E = |E^*| = \sqrt{(E')^2 + (E'')^2}$$

The imaginary parts of the moduli are damping terms which determine the dissipation of energy into heat when a material is deformed. G'' and E'' are often called the loss moduli. A very useful damping term, called the dissipation factor or loss tangent, is defined as G''/G' or E''/E' . The dissipation factor is proportional to the ratio of energy dissipated per cycle to the maximum potential energy stored during a cycle. This quantity, also referred to as tangent delta, is seen in Figure 11.

With our resins, dynamic mechanical testing provided the very useful modulus-temperature diagrams seen in Figure 10. From this information the modulus of the rubbery plateau is determined as well as other

useful information such as the effect of cure on the modulus-temperature behavior. For example, the rubbery storage modulus, E' seen in Figure 10 is close to 2×10^8 dynes/cm² at 130°C (403°K). With the assumption that E is close to the same value as E' , the M_c is calculated to be 614 using 1.22 g/cc for ρ , 8.316×10^7 ergs/°K mole for R , 403°K for T and 2.0×10^8 dynes/cm² for E from the relationship, $E = 3\rho RT/M_c$.

In the transition region the damping is high because some of the molecular chain segments are free to move while others are not. A stiff spring (frozen-in segment) can store much more energy for a given deformation than can a weak spring (rubbery segment free to move). Thus, every time a stressed, frozen-in segment becomes free to move, its excess energy is dissipated into heat. It is characteristic of the transition region that part of the molecular segments are free to move, and the longer the time a segment is under stress the greater is the probability that it will have a chance to move so as to relieve part of this stress. This delayed response to a stress gives rise to high damping and makes the deformation lag behind the stress. The damping peak occurs in the temperature interval where many of the frozen-in segments may become mobile in a time comparable to the time required for one oscillation.

The loss modulus G'' goes through a peak at a slightly lower temperature than does the dissipation factor G''/G' . The maximum heat dissipation for a unit deformation occurs at the temperature where G'' is maximum; the temperature of this maximum at one cycle per second is very close to the value of the glass-transition temperature as determined by volume-temperature measurements. The temperature of maximum damping G''/G' generally is 5 to 15°C higher than the conventional glass transition temperature if the dynamic measurements are made at about 0.10 to 1.0 cycle per second.

The temperature at which the damping is a maximum depends upon the frequency of measurement. For most polymers, an increase of a factor of ten in frequency will raise the temperature of maximum damping approximately 7°C. More generally adopted* today is the following approximation:

*Private communication: Professor Mitchel Shen.

$$T_g = T_i - x$$

where $x \cong 3^\circ\text{C}$ for each decade of frequency and the damping peak (Inflection Temperature, T_i)* determined at 0.1 cycle per second is 10°C higher than the T_g .

Since our dynamic mechanical tests were conducted at 3.5 Hz the T_g for the 165°F cured polymer (Figure 11) using the described approximation would be estimated to be $\sim 37^\circ\text{C}$. This is reasonably close to the value obtained from volume-expansion curve (Figure 9) which provided a T_g of $\sim 34^\circ\text{C}$.

* $T_i \sim 60^\circ\text{C}$ from Figure 10 at 10^9 dynes/cm².

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