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THE EFFECT OF CHAIN STIFFNESS IN LIGHTLY CROSSLINKED EPOXIES

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ABSTRACT

Three monomer pairs were used to examine the effect of increasing backbone stiffness on material properties. Bisphenol F, resorcinol, and 2,7-dihydroxynaphthalene and their diglycidyl ether analogs of increasing stiffness were chosen for ease of processing and to avoid the complicating influences of steric hindrance, polar interactions between chains, and liquid crystallinity. Oligomeric precursors were solution polymerized to insure stoichiometric imbalance-determined crosslink density. The T_gs of the Bisphenol F, resorcinol, and 2,7-dihydroxynaphthalene LXTs are 56, 67, and 105°C, respectively, by DSC. The modulus of the Bisphenol F and resorcinol LXTs are 3.04 and 3.47 GPa, respectively.

INTRODUCTION

The variety and versatility of epoxy resins have made them a popular choice in many practical applications. Some of the more critical practical aspects of a desirable epoxy material are a final use temperature and mechanical properties suited to the intended use. Here traditional formulations encounter a point of diminishing return; to achieve higher stable use temperatures (usually T_g), the crosslink density is usually increased. This has the possibly undesirable side effect of increasing the stiffness of the material and the brittleness, leading to a compromise between use temperature and mechanical properties. Alternative approaches to improving the T_g include, for example, incorporating polar components in the backbone and stiffening the backbone of the chain. The first method will increase interactions between chains without increasing the covalent bonding. However, this will also make the material more vulnerable to solvents, another practical compromise. In the second approach, as the material properties become more backbone than crosslink driven, a higher T_g for a given crosslinking density is achieved, thus maintaining the toughness of a thermoplastic but retaining the desirable properties of a thermoset.

The concept of stiffer molecules in networks has been seen frequently in the latter half of the 1980s. Liquid crystalline polymer (LCP) molecules have become an important current topic in polymer science. Inevitably, LCPs have become incorporated into networks, both thermoset and elastomeric (e.g., Refs. 1–7). In this case, not only are the backbones stiffer but the possibility of crystallization or other long-range ordering also improves the properties of the network. Even without going to such a great degree of stiffness, however, one can envision increasing backbone stiffness: e.g., by including a larger fraction of aromatic component in the backbone, by including stiffer bonds such as sulfur, nitrogen, and oxygen, or by attaching bulky groups to hinder rotation of the main chain.

An attempt to characterize the effect of stiffening the backbone of epoxy network chains is the subject of this paper. As mentioned, incorporating polar elements in the backbone increases the vulnerability of the material, and so it was not considered. Furthermore, steric hindrance is still difficult to quantify; it is currently the province of sophisticated software developed from theories with more or less confidence, and also was avoided. A group of monomers has been chosen to avoid unusual dipoles, steric hindrances, and liquid crystallinity to isolate the effect of increasing backbone stiffness on material properties.

BACKGROUND

While some work has been done on the use of rigid (liquid crystalline) chains to enable lower crosslink densities with good material properties (e.g., Ref. 7), slightly more flexible chains might have a desirable effect as well, while yielding fewer negative processing effects. The use of stiff monomers in lightly crosslinked epoxies has been the subject of recent work by Dewhirst [8, 9]. The primary concept is that monomers of varying "stiffness," or combinations of stiff and flexible units, are reacted together. A dialcohol is reacted in nearly stoichiometric amounts with a diepoxide (Fig. 1). A slight excess of diepoxide will yield, during the initial phase of the reaction, growth of oligomeric chains terminating in epoxide. Ideally, the stoichiometric imbalance will determine the length of these oligomers statistically. In the final stages of the reaction, the residual epoxides at oligomer chain ends will undergo reaction with hydroxy functionality within the oligomers formed during chain growth, resulting in a lightly crosslinked network (LXT). By using various monomer combinations, Dewhirst has demonstrated that molecules that are expected to be "stiffer" exhibit higher T_gs and often moduli (Table 1). Similarly successful materials have been fashioned based on a rigid, sterically hindered fluorine-containing backbone [10, 11]. The latter materials show little water uptake [10] while the former show the familiar 2% epoxy moisture absorption, but without the

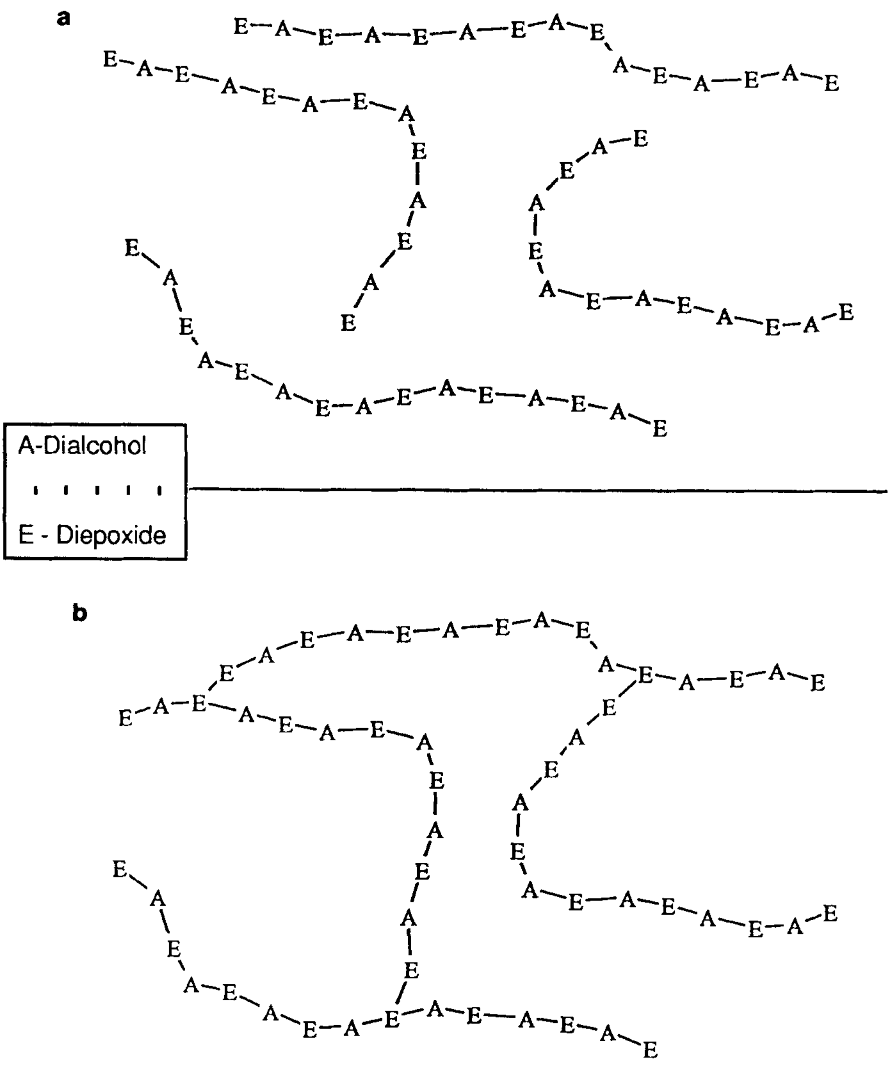


FIG. 1. Illustration of the lightly crosslinked polymer growth process. (a) In the first stage, all of the dialcohol reacts with the diepoxide to form epoxy end-capped oligomers. (b) In the second stage, the residual epoxy reacts with pendant hydroxy functionality along another oligomer backbone, forming a crosslinked polymer.

commensurate drop in T_g of standard epoxies [9]. This study was intended to extend and clarify the results of Dewhirst's work.

Curing kinetics for the urea-catalyzed light crosslinking-type reaction of Bisphenol A (BPA) with the diglycidyl ether of Bisphenol A (DGEBA) have been detailed by Ishida and Smith [12]. They used infrared spectroscopy to follow the disappearance of epoxy functionality and found the reaction to be first order in disappearance of epoxy, which is consistent with a condensation-type reaction. However, there was no indication as to the nature of the final network formed.

TABLE 1. Dewhirst Lightly Crosslinked Technology Results [2, 3][a]

	T_g, °C	Flexural modulus, ksi
BPA/DGBPA	115	369
BP/DGBPA	128	280
1,6-DN/1,6-DEDN	138	500

[a] BPA = Bisphenol A. DGEBPA = diglycidyl ether of Bisphenol A. BP = *p*-biphenol. 1,6-DN = 1,6-dihydroxynaphthalene. 1,6-DEDN = diglycidyl ether of 1,6-dihydroxynaphthalene.

The mechanisms of semiflexible biopolymers seem most likely to be of application in the predicting of LXT material behavior. Higgs and Ball [13] derived the reel-chain-rod model for helically coiled biopolymer molecules. The rod-chain portion of their analysis indicate that the rod portions must be long in comparison with the chain, 75% of the chain, before they will have any effect on the modulus.

EXPERIMENT

Chemistry

The series of monomer precursors chosen (Fig. 2) were three diphenols, each to be reacted with their respective diglycidyl ether analogs. The three diphenols chosen have a similar chemical composition, and all have a similar "bent" nature. The resorcinol and 2,7-dihydroxynaphthalene were specifically chosen over their linear analogs (hydroxyquinone and 2,6-dihydroxynaphthalene) for lower monomer melting temperatures for ease in processing, as well as to reduce the possibility of liquid crystallinity in the polymer backbone. Bisphenol F was chosen over Bisphenol A to eliminate the steric hindrances to rotation and flexure caused by the two methyl groups pendant from the carbon joining the two phenol groups; it also contains the desired "bend" in molecular form. The backbone formed from the various monomers is expected to increase in stiffness from Bisphenol F to resorcinol to 2,7-dihydroxynaphthalene (depending on method of calculation, see below). Bisphenol F and 2,7-dihydroxynaphthalene were obtained from Kennedy and Klim. Resorcinol was purchased from Aldrich Chemical. The diglycidyl ether of resorcinol was purchased from Monomer-Polymer and Dajac Laboratories, and a portion was purified. The diglycidyl ethers of Bisphenol F and 2,7-dihydroxynaphthalene were synthesized by Monomer-Polymer and Dajac Laboratories to contain <0.02% saponifiable chloride, to insure catalyst level (see below).

The diphenol of each monomer was reacted with a 4% excess of its diglycidyl ether with K_2CO_3 as a reactive catalyst (following Ref. 14) to form the oligomers. A basic catalyst is necessary: in the presence of a small amount, the reaction is nearly 100% between diglycidyl ether and diphenol; in its absence the reaction is strictly between diglycidyl ether groups [15]. The CO_3^{2-} dehydrogenates the diphenol, with CO_2 and H_2O as by-products (Fig. 3a). The phenolic ion formed then initiates chain

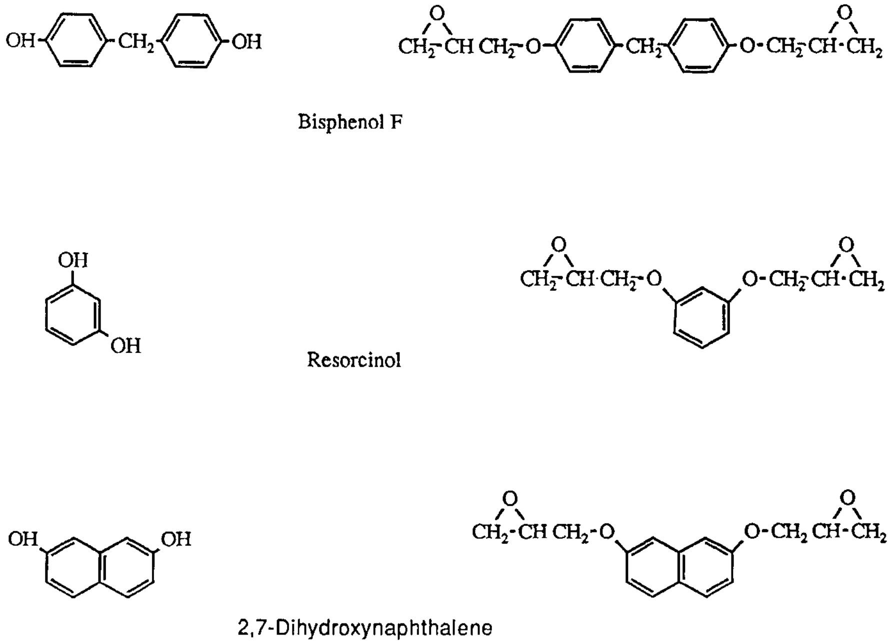


FIG. 2. The diphenol and diglycidyl ether monomer pairs chosen for this study.

growth via condensation, with the slightly basic diphenols acting as proton donors to form hydroxide when an epoxide reacts (Fig. 3b). The presence of saponifiable chloride will terminate catalysis, and so if small amounts of K_2CO_3 are used, the saponifiable chloride content must be suitably low. Under some conditions the diphenol is fully utilized in linear chain extension, after which the epoxy end-capped oligomers formed react with a hydroxy group on another chain to form crosslinks (Fig. 3c). Under other conditions the chain extension and crosslinking reactions can proceed simultaneously.

A method was designed (following Ref. 14) to insure the growth of the oligomer chains with minimal crosslinking prior to the final stages. Diphenol and a 4% excess of diglycidyl ether were dissolved in a less than 15% by weight solution with acetone. A stoichiometric amount of K_2CO_3 was added, based on diphenol. This mixture was refluxed (at 61°C) for 8 h under N_2 with stirring. Approximately one-half of the acetone was removed with a rotary evaporator. The reaction mass was then poured into about 1 L of H_2O and the organic layer was removed. The water layer was washed with three approximately 400 mL portions of diethyl ether. The organic and ether layers were combined and washed with three approximately 300 mL portions of 5% (wt) aqueous Na_2CO_3. The organic layer was dried over anhydrous Na_2SO_4. Then the ether was removed using a rotary evaporator and the remaining reaction mass was bottled. Again, the product was stored under refrigeration. The resultant oligomer was degassed under vacuum at 50°C for 5 h and then cast on RTV 11 (GE) rubber molds with Epoxy Parafilm (Price Driscol) mold release to form thin films and dogbone samples as described below. The sample was then held under vacuum for 2 h at 50°C. The mold surface was covered,

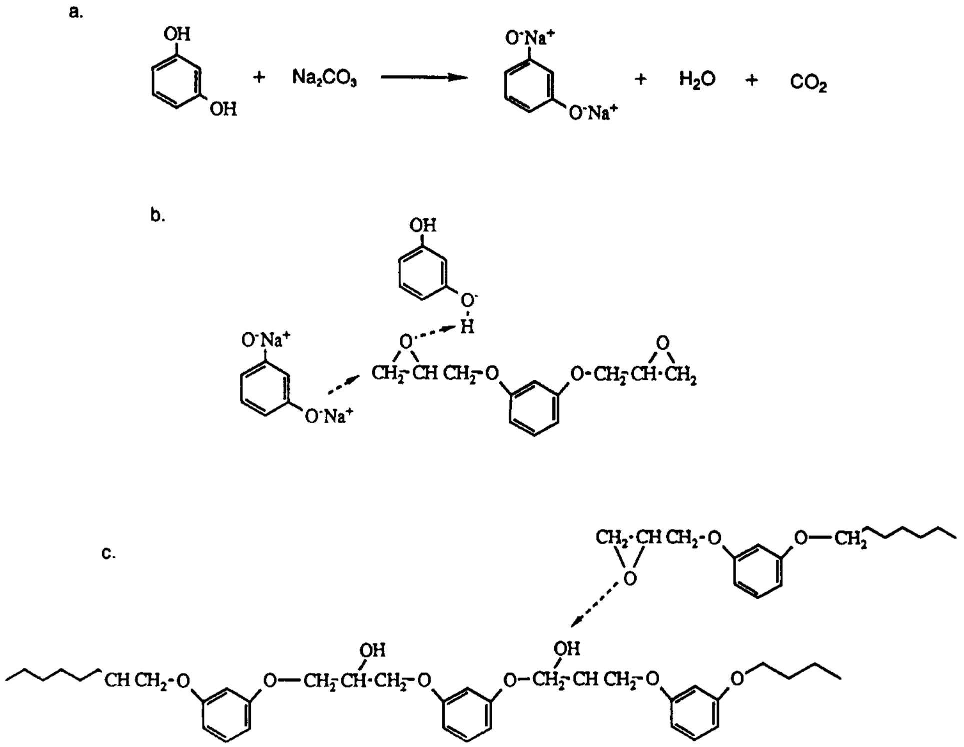


FIG. 3. Illustration of the reactions occurring during polymer growth. (a) Na_2CO_3 deprotonates the diphenol and leaves as carbon dioxide and water. (b) The deprotonated product reacts with an epoxide, with another diphenol acting as hydrogen donor. (c) The epoxy end groups react with hydroxy functionality along the oligomer backbone.

and the specimen was cured for 20 h at 180°C under an N_2 atmosphere. An additional sample of resorcinol-based oligomer was cured for 20 h at 190°C to check for full curing.

Characterization

A Perkin-Elmer Differential Scanning Calorimeter Model 4 (DSC) was used to determine the glass transition temperature of the various cured films. The heating rate was uniformly 20°C/min. A Nicolet IR 30 Fourier Transform Infrared Spectroscope (FTIR) was used in transmission to obtain spectra for cured films, uncrosslinked oligomer, and bulk grown prepolymers and diglycidyl ether materials. The 2900 wavenumber C—H stretching band was used as an internal thickness band. An Instron 8500 was used to obtain tensile moduli for dogbones of Bisphenol F and resorcinol LXTs. Dogbones had a 2.5-cm gauge length, a width of 6 mm, and a thickness greater than 2 mm. These samples were heated to 85°C immediately prior to testing to remove the effects of physical aging.

RESULTS AND DISCUSSION

For a condensation reaction, first order in both components with an excess of one or the other monomer, the average chain length as the reaction approaches completion is

$$\bar{x}_n = \frac{1 + r}{1 - r}$$

where r is the stoichiometric imbalance (modified Carothers equation). Ideally, for $r = 0.96$, as holds here, the average oligomer length is 49. Unfortunately, when polymerization occurs in the bulk, the crosslinking reaction will occur to some degree simultaneously with the chain extension reaction [16]. This will increase the crosslinking density. Thus, the T_gs reported by Dewhirst (Table 1) are likely not due solely to the stiffness in the chain backbone. The ideal picture shown in Fig. 1. is more likely to attain when the oligomers are grown in solution. A comparison can be made between the results for the oligomer-grown 2,7-dihydroxynaphthalene LXT (Table 2) and the bulk-grown 1,6-dihydroxynaphthalene LXT reported by Dewhirst which are chemically similar but have slightly different molecular bends. Here, the oligomer LXT has a glass transition 30°C lower than the melt-grown version.

The DSC results (Table 2) show other useful points. The similarity between T_gs for the two different cure temperatures for the oligomer resorcinol LXT indicates that complete reaction is achieved at the lower temperature. Furthermore, the Bisphenol F, resorcinol and 2,7-dihydroxynaphthalene LXT T_gs increase systematically.

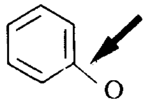
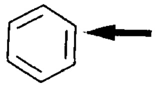
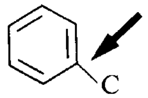
The entire premise of the lightly crosslinked resin technology was that as an increasing portion of the polymer backbone became stiff, the use temperature and properties would increase. A contour length calculation was done to evaluate the percentage of stiff chain. The calculation was done in three ways, with different assumptions about which bonds were stiff and which flexible to rotation (Table 3a). This analysis is understood to be somewhat coarse: bond type c is obviously rigid and type d flexible, but bonds a, b, and e are not so clearly defined and will be temperature-dependent. Nevertheless, method 3 gives an increase in percent of stiff bonds from Bisphenol F to resorcinol to 2,7-dihydroxynaphthalene (Table 3b), which is consistent with the DSC results reported above.

FTIR was used to analyze the chemical changes in the system and to evaluate the validity of the solution method of oligomer growth. Of primary interest are the epoxy band at 913 wavenumbers, the ether stretching between 1140 and 1085 wavenumbers, and the hydroxy stretching from 3700 to 3100 wavenumbers [12]

TABLE 2. DSC Results

Polymer	Cure temperature, °C	T_g, °C
Bisphenol F LXT	180	55
Resorcinol LXT	180	67
Resorcinol LXT	190	68
2,7-Dihydroxynaphthalene LXT	180	105

TABLE 3a. Bond Types and Stiffness

Bond	Length, Å	Stiffness: Method[a]		
		1	2	3
a. C—O	1.43	f	f	s
b. 	1.36	s	f	s
c. 	1.40	s	s	s
d. C—C	1.54	f	f	f
e. 	1.53	f	f	f

[a] s = stiff, f = flexible, i.e., rotation can occur about it.

(indicated in Fig. 4a). Also of interest is the C—H stretch at 2900 wavenumbers as an internal standard. The presence of hydroxy stretching in the diglycidyl ether monomer is indicative of hydrogen bonding, perhaps due to contamination with water. The difference between diglycidyl ether and oligomers (resorcinol, Figs. 4a and 4b; Bisphenol F, Figs. 5a and 5b; 2,7-dihydroxynaphthalene, Figs. 6a and 6b) is the epoxy peak height in Fig. 5 which drops relative to the bands at 850, 1600, and 2900 wavenumbers. This shows that the epoxy functionality was reduced during polymerization, as expected. Increases are seen in the hydroxy stretching band; however, this can be due either to the presence of residual diphenol monomer or to hydroxy functionality formed in the oligomer backbone during cure. The ether stretching region shows some activity, but the changes in ether content during cure are difficult to predict and should be small. This is reflected in the results. Based on the evidence, it seems likely that the oligomer was formed as desired. Finally, the absence of the epoxy peak in fully polymerized samples (Bisphenol F, Fig. 7; resorcinol, Fig. 8; and 2,7-dihydroxynaphthalene, Fig. 9) clearly shows complete reaction.

TABLE 3b. Contour Length Calculation Results

Polymer	% Stiffness in chain: Method		
	1	2	3
Bisphenol F LXT	55.3	41.7	69.5
Resorcinol LXT	48.2	24.4	73.2
2,7-Dihydroxynaphthalene LXT	58.3	39.3	78.4

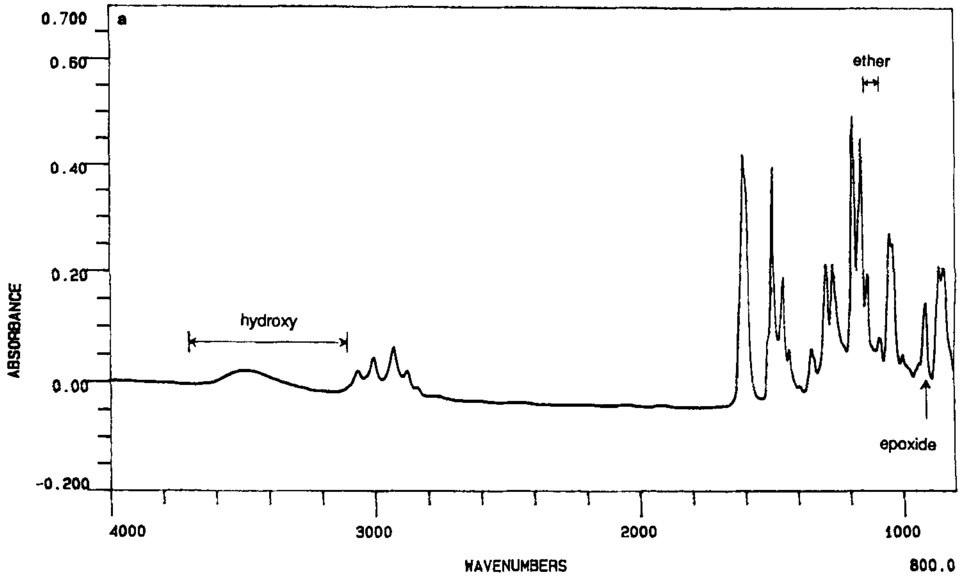


FIG. 4a. Infrared scan of the diglycidyl ether of resorcinol.

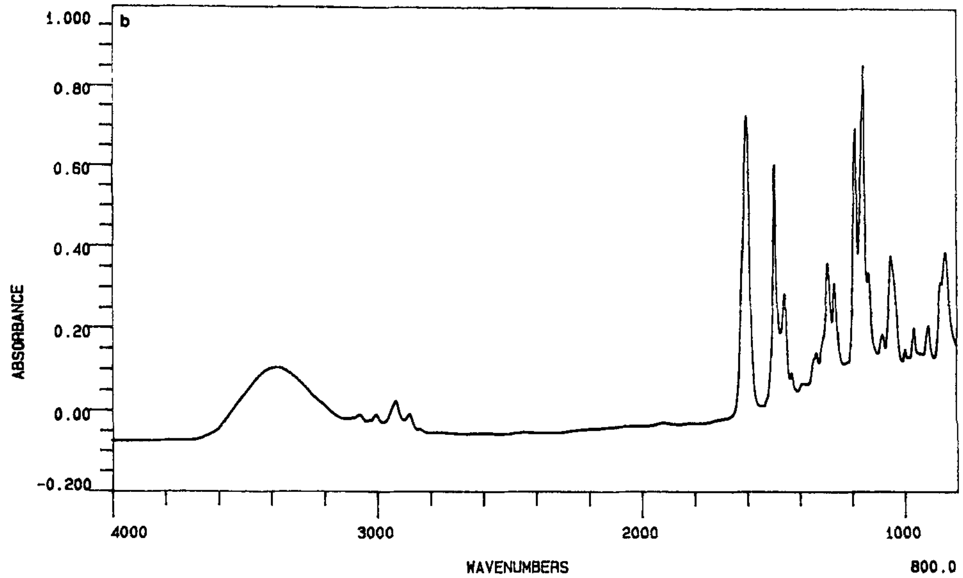


FIG. 4b. Infrared scan of the oligomeric resorcinol LXT.

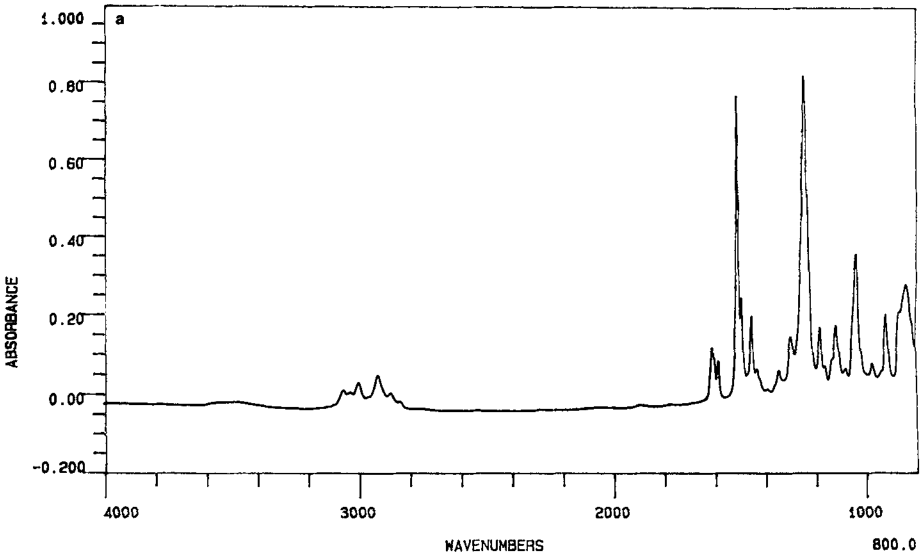


FIG. 5a. Infrared scan of the diglycidyl ether of Bisphenol F.

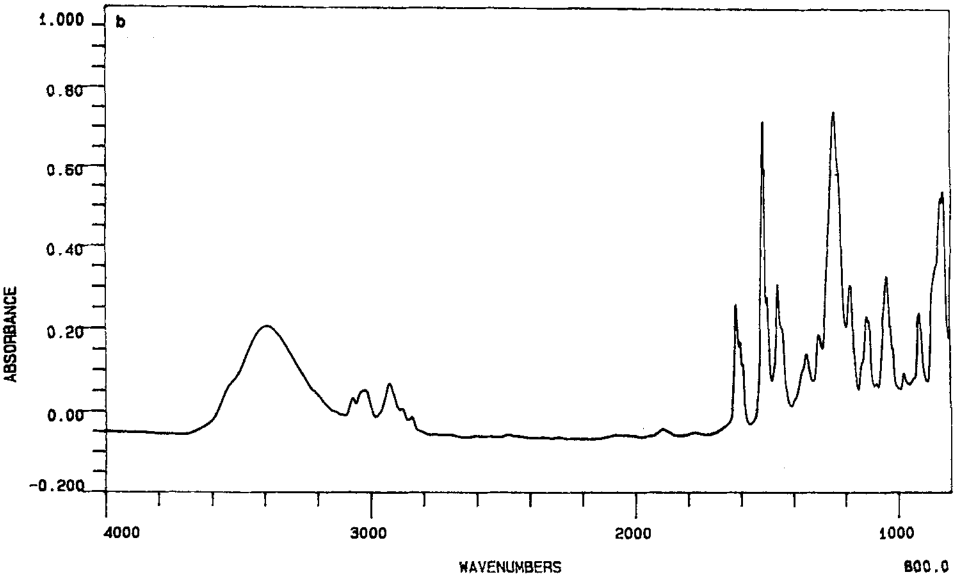


FIG. 5b. Infrared scan of the oligomeric bisphenol F LXT.

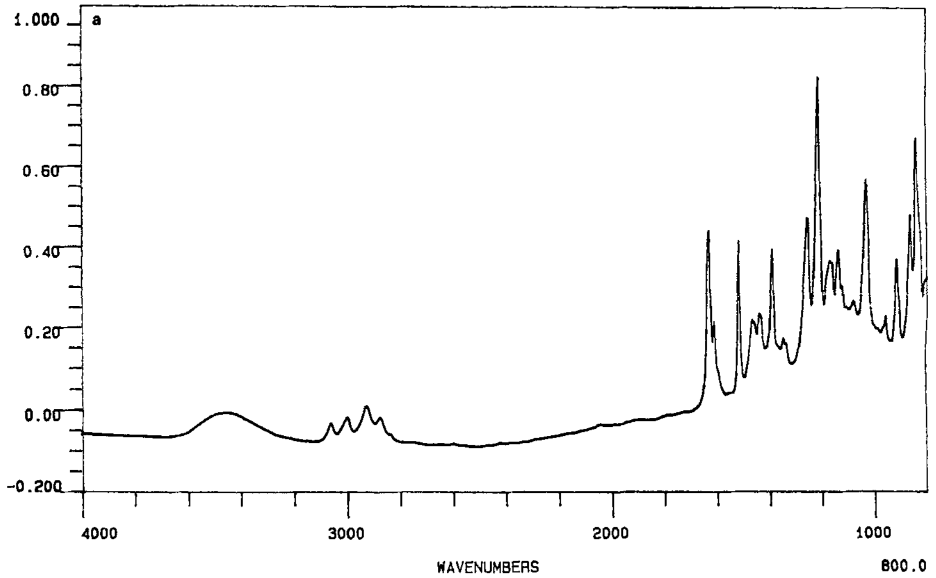


FIG. 6a. Infrared scan of the diglycidyl ether of 2,7-dihydroxynaphthalene.

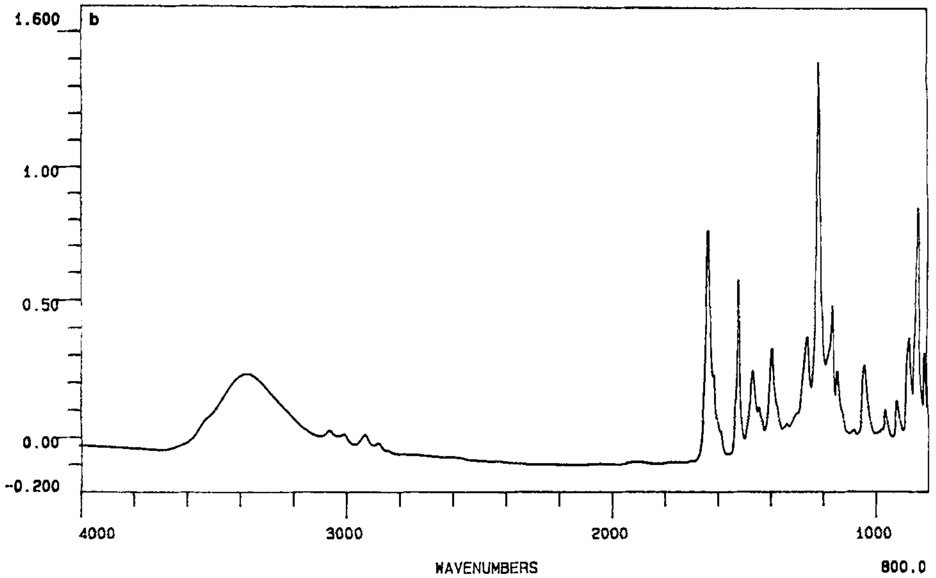


FIG. 6b. Infrared scan of the oligomeric 2,7-dihydroxynaphthalene LXT.

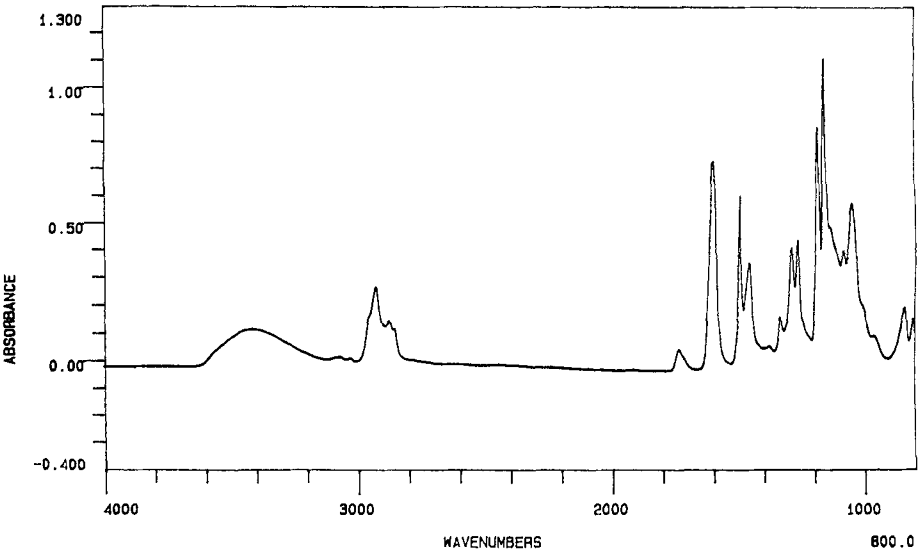


FIG. 7. Infrared scan of cured resorcinol LXT.

Mechanical tests gave tensile moduli of 3.04 GPa for the Bisphenol F and 3.47 GPa for the resorcinol LXTs, respectively, again increasing in a manner consistent with the backbone stiffness calculation. These compare very favorably with a standard, highly crosslinked epoxy resin; for instance, Epon 828 catalyst cured with EMI-24 has a modulus of 3.60 GPa. Unfortunately, voids were an unremovable problem in the dogbone samples: only incomplete mechanical data are available for

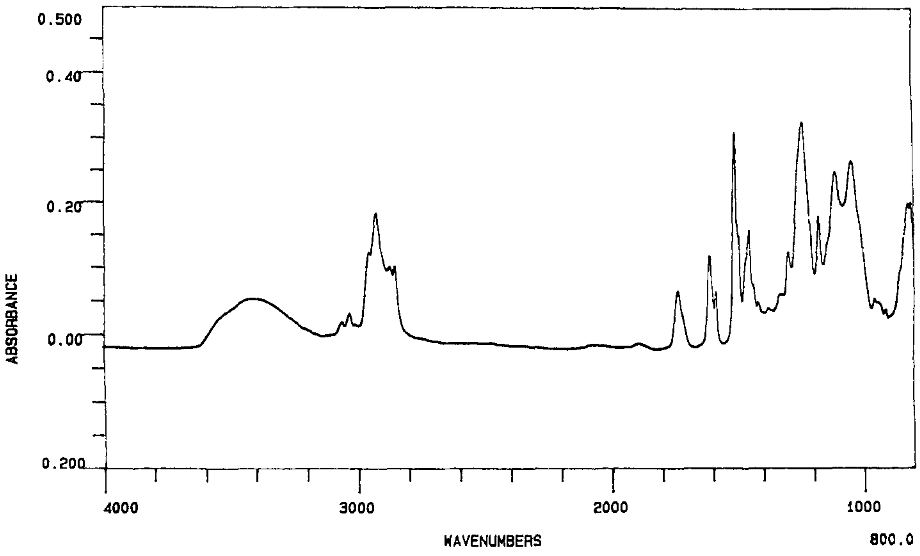


FIG. 8. Infrared scan of cured Bisphenol F LXT.

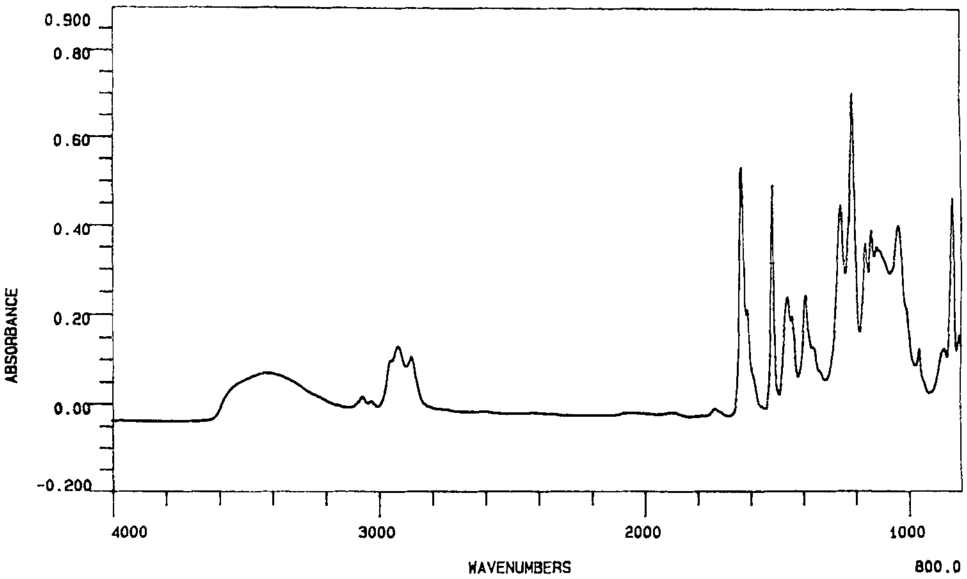


FIG. 9. Infrared scan of cured 2,7-dihydroxynaphthalene LXT.

these materials while no useable samples of 2,7-dihydroxynaphthalene LXT could be fashioned at all. The moduli are relatively high, probably due to the stiff nature of the backbones which improves the elastic effectiveness of "entanglement" effects (as discussed in Ref. 17). However, the low T_gs of both samples could lead to physical aging and changes in modulus with time.

CONCLUSIONS

A series of monomer pairs was chosen to examine the effect of increasing backbone stiffness on the material properties, especially use temperature and modulus. The monomers were chosen for low melting temperature, leading to ease of processing, and to avoid complicating influences such as steric hindrance to rotation, nonstandard polar interactions between chains, and liquid crystallinity in the polymeric products. Solution growth of oligomeric precursors was employed to insure that the crosslink density is determined by the stoichiometric imbalance. Bulk grown materials would be expected to have an increased amount of crosslinking relative to solution-grown materials, as the chain extension and chain crosslinking can occur simultaneously.

FTIR results substantiate the successful use of solution polymerization in growing oligomeric precursors. Calculations indicate that the average oligomer will be 49 monomer units in length (24 diphenols, 25 diglycidyl ethers). FTIR further shows full reaction of the epoxide groups in the fully cured LXT materials.

Contour length calculations showed great sensitivity to the choice of stiff and rotatable bonds. The method most consistent with the results gives 69.5% stiff length in the Bisphenol F LXT, 73.1% in the resorcinol LXT, and 78.4% in the

2,7-dihydroxynaphthalene LXT. The glass transition of the Bisphenol F LXT was 55.8°C, while the resorcinol LXT had a T_g of 67°C and the 2,7-dihydroxynaphthalene LXT had a T_g of 105°C based on DSC measurements. The 2,7-dihydroxynaphthalene T_g is somewhat lower than expected based on values reported by Dewhirst for his 1,6-dihydroxynaphthalene LXT. The bulk growth of the prior materials, resulting in additional crosslinking, may be the cause of this.

The modulus of the Bisphenol F-based LXT was 3.04 GPa, while that of the resorcinol LXT was 3.47 GPa. The increase is consistent with the contour length stiffness calculation. These moduli compare very favorably with the modulus of 3.60 GPa for Epon 828 cured catalytically with EMI-24, a standard, highly crosslinked epoxy formulation. The stiff backbones result in superior physical properties.

These preliminary results clearly indicate that an increase solely in backbone stiffness will indeed lead to increases in T_g and modulus. However, the T_gs of the chosen materials are all quite low, and perhaps impractical. The very rigid liquid crystals may be a way to improve this. Increasingly stiff, bent units such as diphenanthrol or 1,8-dihydroxyanthracene may also provide a satisfactory increase.

ACKNOWLEDGMENTS

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