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Synthesis and Characterization of Polymers Derived from the Copolymerization of 1,1'-Dihydroxyethyl-2,2'-Biimidazole and the Diglycidyl Ether of Bisphenol A

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SYNTHESIS AND CHARACTERIZATION OF POLYMERS DERIVED FROM THE COPOLYMERIZATION OF 1,1'-DIHYDROXYETHYL-2,2'-BIIMIDAZOLE AND THE DIGLYCIDYL ETHER OF BISPHENOL A

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ABSTRACT

1,1'-Dihydroxyethyl-2,2'-biimidazole has been used as a copolymerizing monomer with the diglycidyl ether of bisphenol A in the preparation of biimidazole-containing epoxy polymers. Polymerization reactions were studied in bulk, with and without catalyst, and in *N,N*-dimethylformamide and anisole solvents, with and without catalyst. FT-IR and NMR spectra, molecular weight, thermal and solubility characteristics were obtained. Polymers isolated as amorphous light brown solids were found to be only sparingly soluble in THF or in highly polar nitrogen-containing solvents (DMF, NMP, pyridine). These materials exhibited molecular weights up to 37 000 for SnCl₄-catalyzed polymerization carried out in DMF. A glass-transition temperature of 391°C was observed for polymers obtained under uncatalyzed solventless conditions. The glass transition temperature was 373°C for product obtained under SnCl₄-catalyzed, solventless conditions. Thermogravimetric analysis in air of polymers obtained under varying solvent and catalyst conditions showed less than 25% weight loss below 330°C and greater than 75% weight loss above 400°C.

INTRODUCTION

Many polymers of present commercial interest have relatively low melting points and are not appreciably stable above their melting points. Some undergo thermal and chemical decomposition at more elevated temperatures. Recent advances in materials application technology have created requirements for materials that will withstand prolonged exposures at temperatures in excess of 300°C and/or relatively short exposures at higher temperatures. In addition, the desire to generate polymers that have the potential to participate in dynamic processes such as organic and inorganic contaminant removal or the preparation of polymeric catalysts make studies such as this one quite significant.

2,2'-Biimidazole is a heterocyclic compound that exhibits good thermal stability as well as the ability to bind metal ions. It can also serve as a starting molecule for the formation of reactive monomers [1, 2]. Recent research on thermally stable polymers has shown that most polyaromatic heterocyclic macromolecules such as polybenzimidazoles, polybenzoxazoles, polypyrroles, and polypyridines show good thermal stability [3-5].

Investigations of the thermal stabilities of imidazole-containing polymers, other than polyimidazoles, have been reported infrequently [6, 7]. A report on the synthesis and properties of polyimidazolyl esters obtained by the polycondensation of acid chlorides of imidazolyl dicarboxylic acids with glycols demonstrates how these polyesters exhibit good thermal stability [7]. In addition, synthesized polymers often exhibit improved processability as a result of incorporating linking groups between aromatic or heterocyclic rings [8].

Epoxy resins have been established as an important macromolecular system because of the large variety of addition and polymerization reactions they can undergo. For this work, the diglycidyl ether of Bisphenol A (DGEBA) was studied in reactions with 1,1'-dihydroxyethyl-2,2'-biimidazole (HEB) to establish the effect of the incorporation of biimidazole in epoxy polymers on the thermal, molecular weight, and spectral properties of the resulting polymers.

EXPERIMENTAL

Materials and Reagents

Preparation of 1,1'-Dihydroxyethyl-2,2'-biimidazole

2,2'-Biimidazole. A 2.5:1 mol ratio of aqueous ammonia (29 wt%) and glyoxal (40 wt% in water) was put in a large beaker with stirring. The precipitate which formed immediately, was suction filtered and washed with water

several times until the filtrate was clear. Pure, light tan, needle-like biimidazole crystals were obtained upon recrystallization from hot H₂O. Infrared spectra were obtained by using a dry KBr matrix. NMR spectra were obtained with hexamethylphosphoramide as the solvent (dissolved at 100°C).

1,1'-Dihydroxyethyl-2,2'-biimidazole. Ethylene carbonate was the hydroxyethylating agent. A 0.01-mol quantity of 2,2'-biimidazole, 0.02 mol ethylene carbonate, and 0.20 mmol potassium iodide, as catalyst, were placed in a 100-mL two-neck flask equipped with a stirrer. The reactions were conducted at 100°C for about 2.5 h or until no CO₂ evolution was detected while using a bubble gas trap. Because ethylene carbonate is also used as the solvent, it was important to allow it to melt (35–37°C) at the beginning of the reaction in order to maximize blending of the reactants. The product was isolated by first washing the reaction mixture with acetone to precipitate unreacted biimidazole, which was then removed by gravity filtration. The acetone was removed from the filtrate by rotary evaporation. A dark brown, highly viscous crude hydroxyethylated 2,2'-biimidazole was collected.

In order to isolate the desired product from the reaction mixture containing monosubstituted hydroxyethylation products, the reaction mixture was eluted through a chromatography column of 28–500 mesh silica gel desiccant with dry acetone. The column was continually washed with acetone until the effluent was colorless. This was followed by a 55:45 MeOH/H₂O (degassed) solvent elution. The collected MeOH/H₂O solvent mixture was removed by rotary evaporation. The resulting product was obtained as a dark brown oil-solid product. It was stored in a desiccator over calcium chloride at room temperature. HPLC analysis was conducted to certify the purity of separation. The structure was confirmed by NMR (D₂O as solvent) and IR spectroscopy.

Characterization Methods

Fourier-Transform Infrared Spectroscopy

Infrared absorbance spectra of the oily solid on KBr pellets were obtained with a Perkin-Elmer model 1750 Fourier-transform infrared spectrophotometer under dry air purge. Twenty scans at a resolution of 2 cm⁻¹ were signal-averaged before Fourier transformation.

Nuclear Magnetic Resonance Spectroscopy

NMR spectra were obtained with a JEOL FX-100 Fourier-transform nuclear magnetic resonance spectrometer at room temperature. Tetramethylsilane (TMS) was used as an internal standard.

Differential Scanning Calorimetry

DSC measurements under N_2 atmosphere were conducted over a 50–500°C temperature range with a Perkin-Elmer DSC-4 with a data station interface. The heating rate was 10°C/min with a temperature precision of $\pm 0.2^\circ C$, and the sample weight was 5–10 mg. Temperature and enthalpy calibrations were done with indium and tin standards. A scanning auto-zero module was used to minimize instrumental nonlinearity over the temperature range of interest. Melting points were taken as the maximum in the endothermic peak, and T_g values were determined by the intersection method.

Thermogravimetry Analysis

TGA was conducted with a Perkin-Elmer TG/S/2 thermogravimetric analyzer in an air flow of 20 mL/min and at a 10°C/min heating rate.

Gel Permeation Chromatography

Molecular weights were measured with a modified-component high-pressure liquid chromatography (HPLC) system equipped with a μ -Spherogel (10^4 \AA pore size) column (Beckman). A range of standard narrow molecular weight distribution polystyrene samples was used for calibration. The eluting solvent used was DMF. Flow rates were 0.5 mL/min at room temperature. Chromatographed samples were detected with a Fresnel refractive index detector (refractive index range 1.35–1.45) at a concentration of 0.3% w/v.

High Performance Liquid Chromatograph

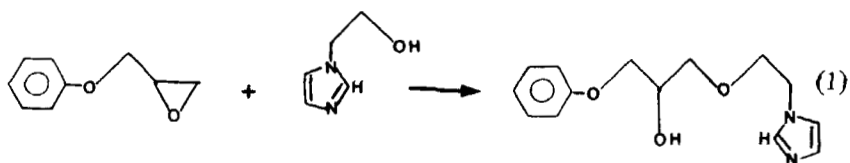
HPLC results were obtained by using a reversed-phase, chemically bonded silica gel column (LiChrosorb, RP-18 ($7 \mu m$), E. Merck) under the following conditions: methanol/ H_2O (degassed) 57.5/42.5 mixture as a solvent, UV detector (Altex Model 153) at 254 nm, flow rate 1 mL/min, and room temperature.

RESULTS AND DISCUSSION

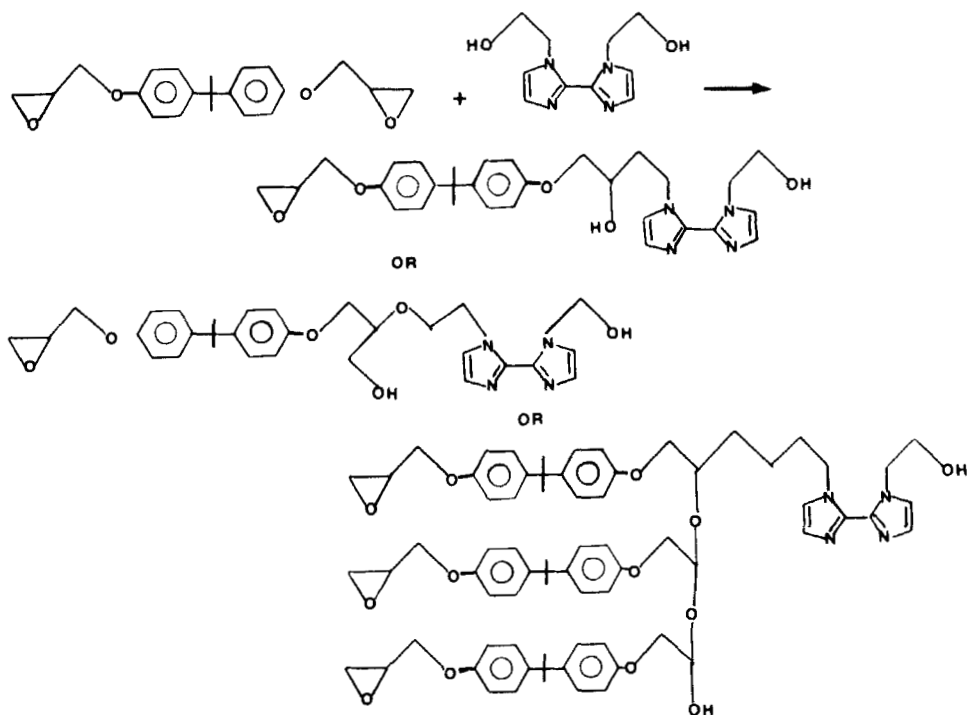
1,1'-Dihydroxyethyl-2,2'-biimidazole was synthesized as described by using a modification of a reported procedure [2]. This product was characterized by FTIR, NMR, and elemental analysis. The diepoxide of bisphenol A was analyzed and found to have an epoxy equivalent of 192–195.

A model reaction of 1-hydroxyethylimidazole with 1,2-epoxy-3-phenoxy-

propane without solvent, and with and without SnCl_4 as catalyst, was conducted in order to demonstrate reactivity between the epoxide and hydroxyethyl functional groups and to establish reaction conditions for the polymerization study.



The diol-diepoxyde polymerization reaction in this study presents some inherent complexity because of the expected mixture of products that may possibly form. Scheme 1 outlines the primary reactions for polymer formation. These reactions illustrate the formation of intermediates, the formation



SCHEME 1.

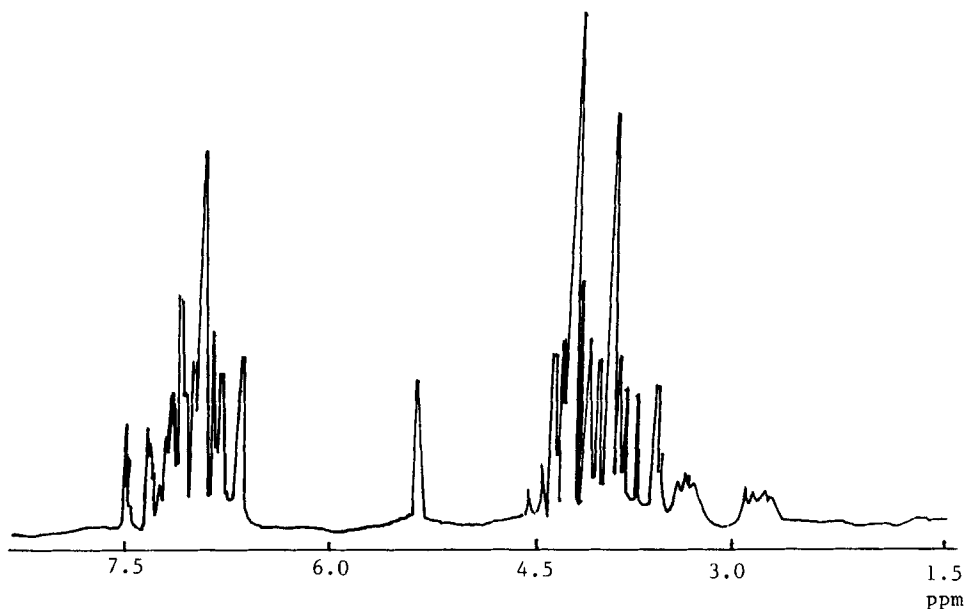


FIG. 1. 100 MHz nuclear magnetic resonance spectrum of the adduct of 1-hydroxyethylimidazole and 1,2-epoxy-3-phenoxypropane.

of linear polymer, and epoxide self-polymerization. A Lewis acid catalyst was primarily used to maximize the formation of the desired linear polymer and minimize undesired side reactions [9].

The NMR and IR spectra in Figs. 1 and 2, respectively, show the expected 8:8:1 ratio for aromatic (6.5-7.5 ppm) to aliphatic (3.4-4.5 ppm) to hydroxyl (5.5 ppm) protons and the characteristic hydroxyl ($\sim 3300\text{ cm}^{-1}$), aromatic C-H ($\sim 3000\text{ cm}^{-1}$), and the imidazole ring mode vibration ($\sim 1130\text{ cm}^{-1}$), which is consistent with the expected monoglycidyl ether-hydroxyethyl imidazole reaction product.

Table 1 summarizes the ratio of phenyl glycidyl ether and HEB used in polymerization reactions along with reaction conditions, and the thermal and molecular weight properties of products. Reactions of DGEBA with HEB using base catalyst (sodium hydroxide and tetrabutylammonium hydroxide) resulted in intractable, brittle products that were best characterized by infrared analysis. These products exhibited only small amounts of residual epoxide and hydroxyl content by infrared analysis, and suggest the occurrence of significant side reactions and crosslinking.

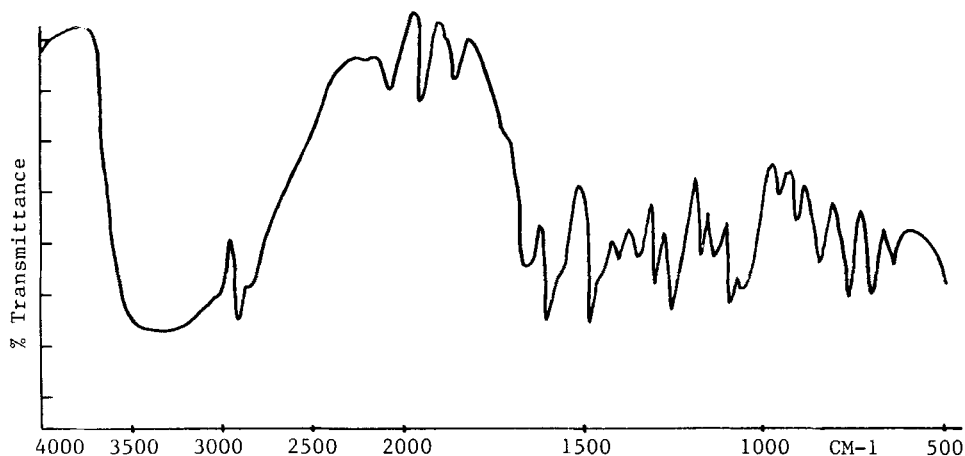


FIG. 2. Infrared spectrum of the adduct of 1-hydroxyethylimidazole and 1,2-epoxy-3-phenoxypropane.

A test self-polymerization reaction of DGEBA with 2,2'-biimidazole as a catalyst showed little polymerization at 60°C after 6 h, and this supports the noncatalytic nature of biimidazole's tertiary nitrogens.

SnCl₄ was used as a Lewis acid catalyst because of its apparent specificity for promoting the epoxide-alcohol reaction [9]. The light yellow polymer obtained after reaction for 24 h at 60°C was found to have less than 15 wt% solubility in DMF, NMP, pyridine, and THF. An apparent solvent effect is observed for reactions conducted in DMF compared with anisole or no solvent, as indicated by the higher molecular weight and higher glass transition temperature of the isolated polymer. This result is likely due to the greater solvating ability of DMF. Polymer precipitation is observed after 6-8 h of polymerization in solvents other than DMF.

Reactions in which no solvent was used resulted in products that were practically insoluble in any solvent except strong acids. When DMF was removed from completed reaction mixtures that were totally soluble, only a portion of the isolated soluble polymer could be redissolved, presumably because of continued polymerization upon heating under vacuum to remove the solvent.

The infrared spectra of DGEBA and HEB neat films on NaCl disks showed absorption bands at 3057, 1250, 916, and 830 cm⁻¹ due to the presence of epoxy groups (Fig. 3A) and absorption bands at 3227 and at 1341 and 1636 cm⁻¹ due to -OH and -C=N, respectively (Fig. 3B). Figure 3(C) shows the

TABLE 1. Summary of HEB-Epoxy Polymerizations and Product Characterization

Sample	Solvent	Catalyst	Epoxy/diol ratio	MW	TGA, % wt loss	
					(Low temperature)	(High temperature)
1	Anisole	None	1:1	9 970-9 380	(400) 15	(435) 80
2	Anisole	SnCl ₄	1:1	11 800-10 900	(400) 15	(430) 75
3	Anisole	None	1:2	14 800-13 500	(410) 20	(485) 80
4	Anisole	SnCl ₄	1:2	15 700-14 300	(410) 20	(500) 80
5	None	None	1:1	Insoluble	(330) 20	(400) 85
6	None	SnCl ₄	1:1	Insoluble	(340) 15	(430) 85
7	DMF	None	1:1	34 600-32 000	(360) 20	(460) 85
8	DMF	SnCl ₄	1:1	37 100-35 000	(360) 25	(430) 75

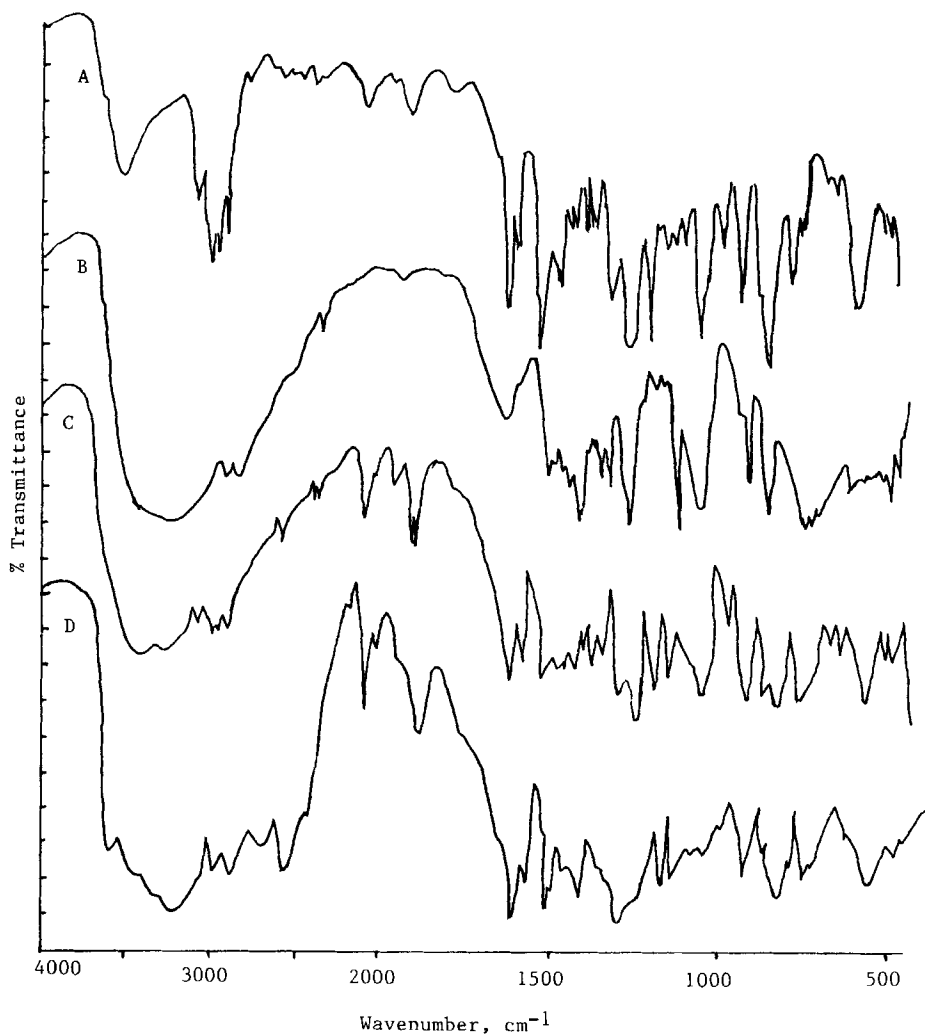


FIG. 3. (A) Infrared spectrum of uncured resin (diglycidyl ether of bisphenol A). (B) Infrared spectrum of 2,2'-dihydroxyethylimidazole (HEB). (C) Infrared spectrum of initial reaction mixture of DGEBA and HEB. (D) Infrared spectrum of cured resin.

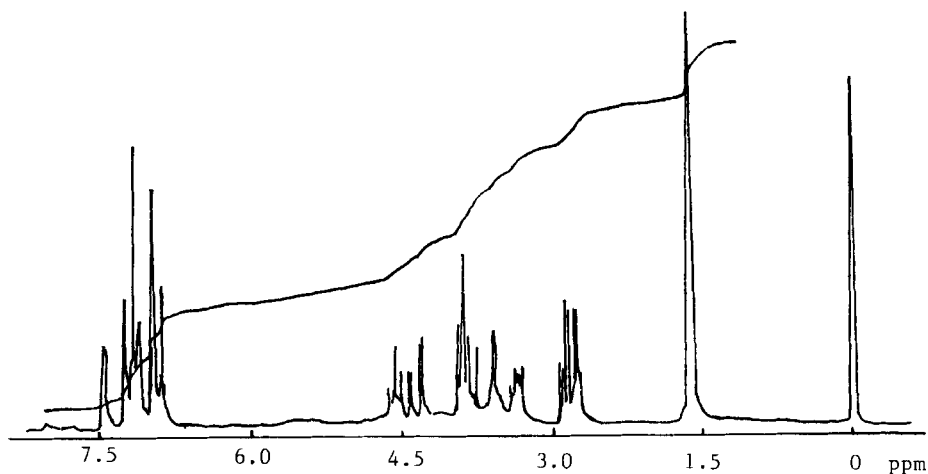


FIG. 4. 100 MHz nuclear magnetic resonance spectrum of cure resin in deuterated DMF.

infrared spectrum obtained after initial mixing of DGEBA and HEB in a 1:1 ratio. At this stage of the reaction, absorptions due to the hydroxyl (3383 cm^{-1}) and epoxy (1230 , 917 , and 830 cm^{-1}) groups are clearly evident. After 6 h at 60°C (Fig. 3D), epoxy groups are essentially absent as the original bands at 916 and 830 cm^{-1} have disappeared, while the bands assigned to $\text{C}=\text{N}$ at 1341 and 1636 cm^{-1} remain. In addition, the broad absorption appearing in the $3200\text{--}3500\text{ cm}^{-1}$ region and the general broadening of the midrange spectrum is evidence of the incorporation of biimidazole and is characteristic for polymer formation

The 100-MHz proton NMR spectrum for the polymer in DMF is shown in Fig. 4. Characteristic shifts for (a) 6-membered aromatic ring hydrogens for bisphenol A ($5.9\text{--}6.3\text{ ppm}$), (b) imidazole ring hydrogens ($6.4\text{--}6.5\text{ ppm}$), (c and d) epoxy ring hydrogens (3.7 and 3.4 ppm), (e) imidazole-linked ethyl hydrogens (3.1 ppm), (f) hydroxyl hydrogens (2.8 ppm), (g) methylene alcohol hydrogens (2.5 ppm), (h) methylene ether hydrogens (2.0 ppm), and (i) methyl group hydrogens (0.8 ppm) were found to exhibit proton ratios of $a:b:c:d:e:f:g:h:i = 4:8:1:2:8:1:1:4:6$. This suggests that SnCl_4 -catalyzed reactions in DMF result in a regular inclusion of the hydroxyethylbiimidazole during polymerization.

The DSC characterization of the solventless uncatalyzed DGEBA-HEB mixture cure reaction is shown in Fig. 5. This reaction reaches a maximum

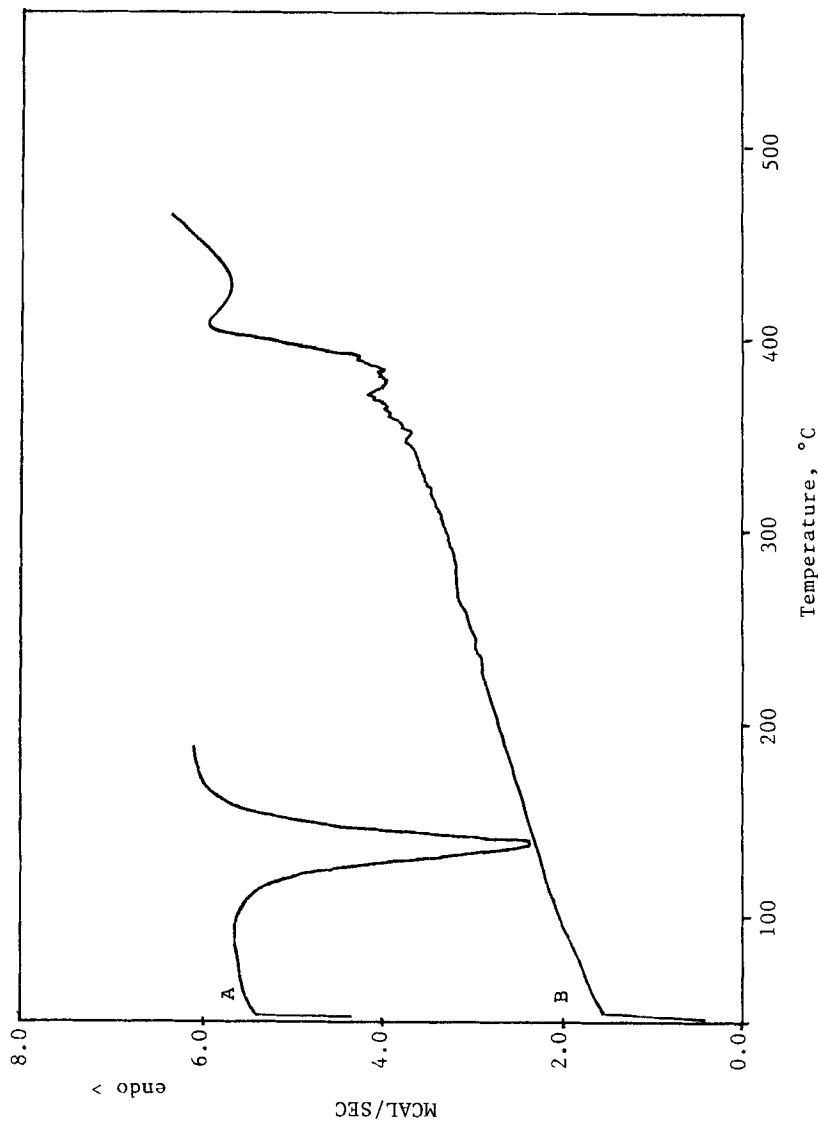


FIG. 5. (A) DSC of solventless uncatalyzed DGEBA-HEB cure reaction. (B) DSC of cured resin. DSC conducted in nitrogen at a heating rate of 20°C/min.

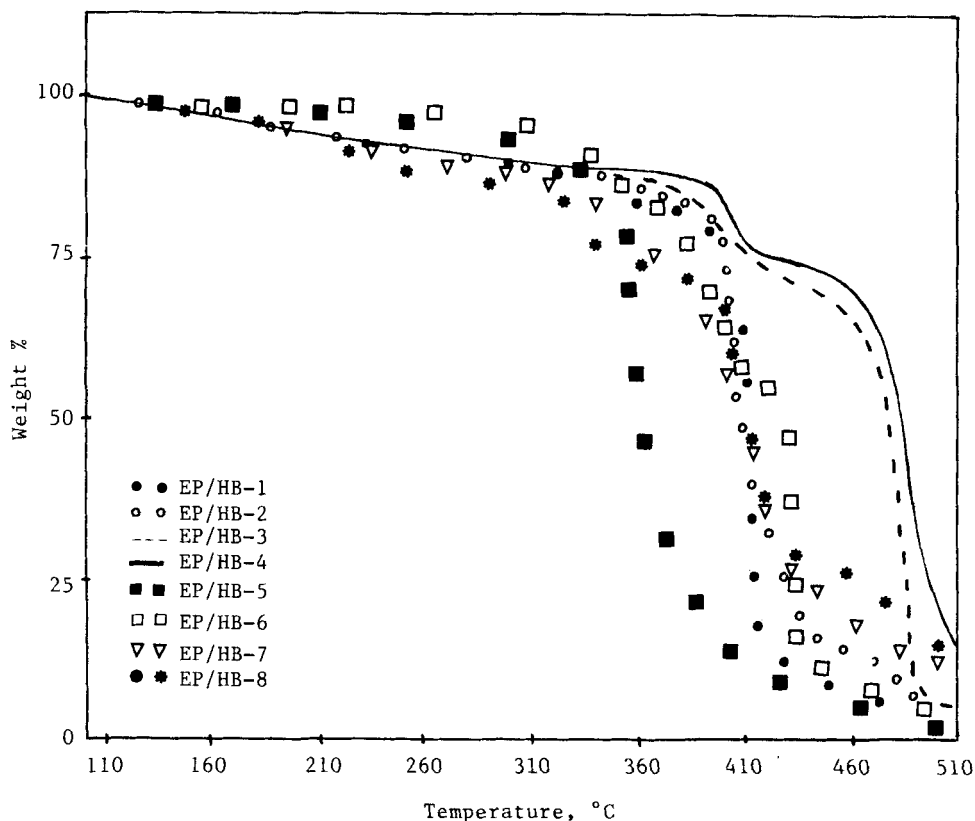


FIG. 6. TGA scans of cured resins in air. Heating rate, $10^{\circ}\text{C}/\text{min}$; air flow rate, $20\text{ mL}/\text{min}$.

at 139°C and is complete by 170°C . The reaction exhibited a ΔH_{RXN} of $-72\text{ cal}/\text{g}$. A second heating of this sample shows a glass transition at 391°C , followed by a residual exotherm. This is characteristic for thermosets when monomers are not completely converted [10]. The endotherm observed beyond 450°C is attributed to general polymer decomposition [11, 12]. Similar analysis of the solventless SnCl_4 -catalyzed cure reaction reached a maximum at 137°C and exhibited a ΔH_{RXN} of $-44\text{ cal}/\text{g}$. A second heating of this sample showed a T_g of 373°C . DSC analysis of polymers isolated from reactions in solution gave no discernable T_g , but showed gradually increasing

exotherms up to 350°C, indicative of incomplete polymerization, followed by increasing decomposition endotherms beyond 380°C.

The relative thermal stability of the polymers obtained was investigated by thermogravimetry in air and are summarized in Table 1 and in Fig. 6. The polymers were stable up to 330°C with less than 25% weight loss, followed by greater than 80% weight loss above 430°C.

CONCLUSIONS

Thermally stable polymers have been obtained by solvent and solventless curing of DGEBA with 1,1'-dihydroxyethyl-2,2'-biimidazole with and without catalyst. A two-step decomposition was observed in air for polymers in the 330-410 and 430-500°C temperature ranges. This type of polymer is expected to be useful for the preparation of laminates, composites, adhesives, metal ion chelation, and polymeric catalysts.

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