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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Fukami, Akira and Moriwaki, Toshimoto(1989) 'Preparation and Properties of Epoxy Resins Containing Quinazolone Rings', Journal of Macromolecular Science, Part A, 26: 6, 877 – 890

To link to this Article: DOI: 10.1080/00222338908052017

URL: <http://dx.doi.org/10.1080/00222338908052017>

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PREPARATION AND PROPERTIES OF EPOXY RESINS CONTAINING QUINAZOLONE RINGS

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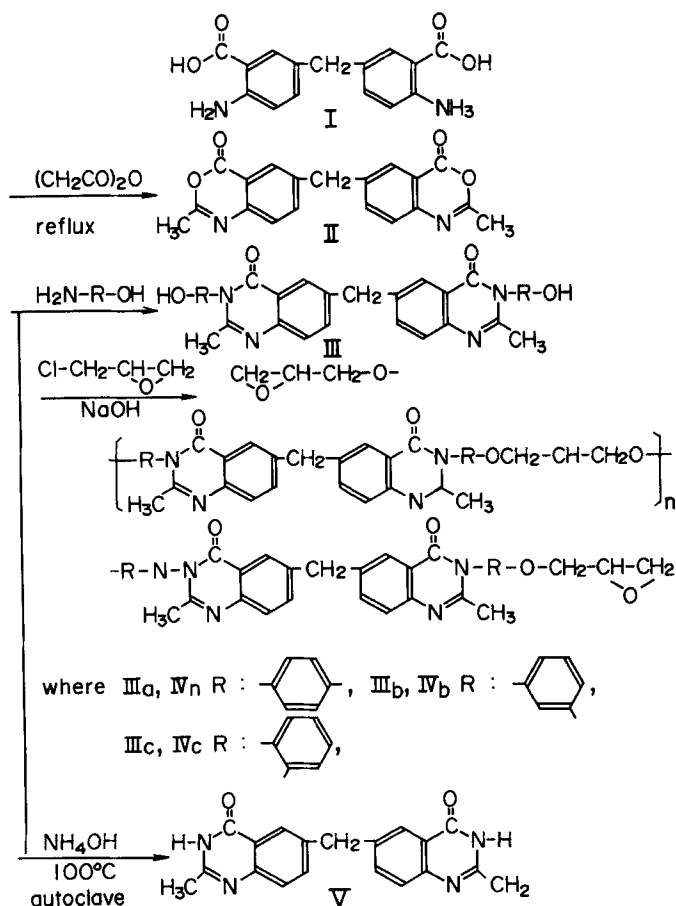
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ABSTRACT

Epoxy resins containing quinazolone rings were synthesized and characterized. Epoxy resins were made by reacting bisquinazolone phenol or bisquinazoline with epichlorohydrin or the diglycidyl ether of Bisphenol A. These resins were analyzed by DSC, GPC, IR, and NMR. The electrical and mechanical properties of the cured resins were evaluated. They have glass transition temperature above 200°C and excellent thermal stability, and T_g increases in the order of *o*-, *m*-, *p*-substituted phenol groups.

INTRODUCTION

It is well known that polymers containing aromatic heterocyclic rings in the main chain, such as polyimide, polybenzimidazole, etc., exhibit good thermal stability. Epoxy resins are widely applicable owing to their excellent workability and physical and electrical properties. However, the preparation and the properties of such resins containing heterocyclic ring has not been studied in detail. Epoxy resins containing imide rings have been synthesized,



SCHEME 1.

but they are only slightly soluble in organic solvents and have high melting points.

There have been a number of studies on the synthesis of polyquinazolones [1-4]. They were found to be relatively soluble in organic solvents and thermally stable.

In this paper the preparation and the properties of epoxy resin containing quinazolone units are reported. Bisoxazinone (II) was synthesized from

4,4-diaminodiphenylmethane-3,3-dicarboxylic acid (I) and acetic anhydride, and subsequently converted to the corresponding bisquinazolone phenols (III) and bisquinazoline (V) (Scheme 1). Bisquinazolone epoxides were prepared from these phenols and epichlorohydrin. Also, block epoxy resins containing quinazolone and Bisphenol A units were obtained from III, V, and the diglycidyl ether of Bisphenol A. The resins were cured with acid anhydrides and their electrical, mechanical, and thermal properties were studied.

EXPERIMENTAL

Materials

6,6'-Methylenebis-(2-methylbenzoxazin-4-one), II

4,4'-Diaminodiphenylmethane-3,3'-dicarboxylic acid (I) (200 g) (Ihara Chem., mp 233-235°C) was added to 1 L acetic anhydride, and the reaction mixture was refluxed for 8 h. Then the yellow precipitate was separated from the solution by filtration and washed with acetic anhydride. Repeated recrystallizations from *N,N*-dimethylacetamide gave a yellow crystalline product, mp 261-262°C.

Analysis. $C_{17}H_{14}O_4N_2$. Found: C, 67.96; H, 4.19; N, 8.51%. Calculated: C, 68.26; H, 4.22; N, 8.36%.

Bisquinazolone Phenol, III

Bisoxazinone (II) (33.4 g, 0.10 mol) and 25 g *p*-aminophenol (0.23 mol) were added to 150 mL *m*-cresol, and the reaction mixture was refluxed for 3 h. The resulting solution was poured into diethyl ether, and the precipitate was filtered and washed with methanol to remove the excess *p*-aminophenol. The product, IIIa, was dried in a vacuum oven at room temperature: mp 215°C, yield 49 g (94.9%). The infrared spectrum of IIIa (Fig. 1) showed absorption bands at 3400 cm^{-1} due to phenolic OH and 1670 cm^{-1} due to carbonyl groups ($\gamma_{C=O}$).

Analysis. $C_{29}H_{24}O_4N_4$. Found: C, 71.74; H, 4.62; N, 10.53%. Calculated: C, 72.08; H, 4.68; N, 10.84%.

IIIb and IIIc were synthesized in a similar way with *m*- and *o*-aminophenol. IIIb: yield 50.6 g (98.0%); mp 200-201°C. IIIc: yield 48.3 g (93.6%); mp 204-206°C.

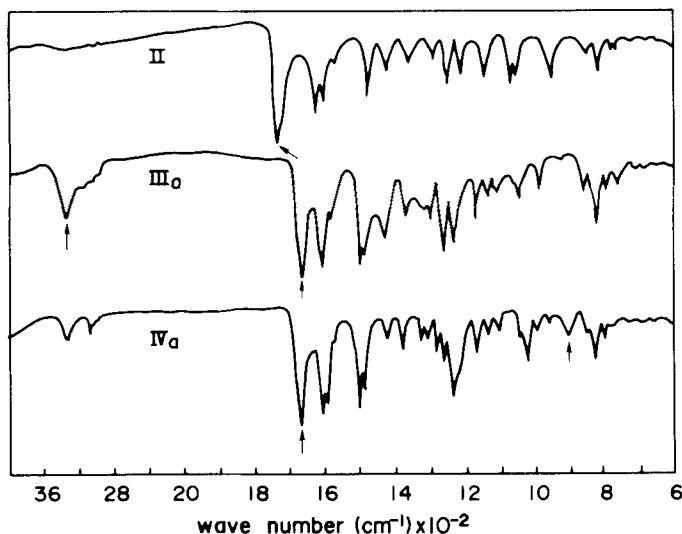


FIG. 1. IR spectra of quinazolone derivatives (KBr disk).

Bisquinazolone Epoxy Resin, IV

Bisquinazolone phenol (IIIa) (38.7 g, 0.075 mol) was added to 92.5 g (1.0 mol) epichlorohydrin, containing 2 mL water. The mixture was heated to 80°C, and 6 g (0.15 mol) of sodium hydroxide was added dropwise to the stirred solution, keeping the reaction temperature below 90°C. After the heat evolution had slowed, the solution was poured into ether, and the resulting precipitate was filtered, washed with water repeatedly, and dried in a vacuum oven at 100°C. Pale pink powder (IVa), mp 140–142°C, was obtained in 40.3 g (85.2%) yield. IR: 909 cm^{-1} due to epoxy rings ($\nu_{\text{C-O-C}}$), 1672 cm^{-1} due to carbonyl groups. Analysis: C, 69.35; H, 8.02; Cl, 0.17%; epoxide equivalent: 326. IVb and IVc were obtained by a similar method as above from IIIb and IIIc. IVb: Y, 86.7%; mp 136–138°C; epoxide equivalent: 330. IVc: Y, 82.5%; mp 129–131°C; epoxide equivalent: 333.

Bisquinazoline, V

6,6'-Methylenebis-(2-methyl-3*H*-quinazoline-4-one) was prepared from bisquinazolone (II) and aqueous NH_3 according to a literature method [5].

Other Quinazolone Epoxy Resins

Block epoxy resins were prepared by addition reaction with 10 wt% of bisquinazolone phenol (III), bisquinazoline (V), and 90 wt% of the diglycidyl ether of Bisphenol A (DGEBA, Epikote 828, epoxide equivalent 190 ± 5 , \bar{M}_n 380) by the usual procedure. The epoxy resins from III and V were obtained by heating at 140 and 180°C for 0.5 h, respectively, in the presence of triethanolamine. Epoxide equivalents of the resins from III and V were 245 and 189, respectively. These values agree with those expected from the feed composition.

Polymerization

Resins IVa, IVb, IVc, block epoxy resin, and DGEBA were cured with 80% of the stoichiometric amount of methyl nadic anhydride (MNA) in the presence of 0.5% *N,N'*-benzyl dimethylaniline (BDMA). Each mixture was dissolved in chloroform and cast onto an aluminum plate. The resulting films were cured for 2 h at 130°C, followed by 12 h at 150°C.

Characterization

The glass transition temperatures (T_g) of the films were determined by differential scanning calorimetry (DSC) under nitrogen at a heating rate of 5°C/min. Thermogravimetric analyses (TGA) were performed in a stream of nitrogen at 15 mL/min by using a Shimadzu thermal analyzer. The heating rate was 5°C/min, and the sample size was 10 mg of film. Measurements of tensile strength, elongation, and static tensile modulus were obtained with a tensile testing machine (Shimadzu IM-100). A dynamic viscoelastometer (Vibron) built by Toyo Measuring Instrument Co. was used at 110 Hz for measurements of dynamic modulus. Dielectric constants, dissipation factors, and volume resistivities were measured in the range of 20–200°C in an air-circulating oven.

RESULTS AND DISCUSSION

Preparation of Bisquinazolone Epoxy Resin

Bisquinazolone phenols IIIa, IIIb, and IIIc were obtained in good yield by reacting bisoxazinone with *o*-, *m*-, and *p*-aminophenol, respectively. The melting points of these materials increase in the order *m*-, *o*-, and *p*-substituted

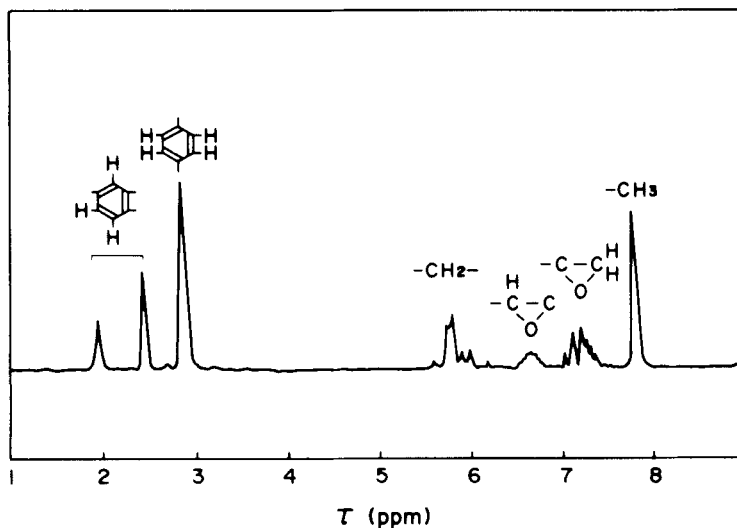


FIG. 2. NMR spectra of IVa (10% solution in CDCl_3 , 60 MHz).

compounds. The IR spectrum of III shows absorption bands at 3400 cm^{-1} due to phenolic OH and at 1670 cm^{-1} due to quinazolone ketone. The structure of III was identified as quinazolone phenol by elemental analysis.

IR spectra of reaction product IV shows an absorption band due to the epoxy ring at 909 cm^{-1} and one due to ketone at 1670 cm^{-1} . The NMR spectrum of IVa (Fig. 2) shows proton signals due to benzene at 1.94, 2.45, and 2.90 ppm; methylene at 5.79 ppm; epoxy methyne at 6.77, 7.07, and 7.23 ppm; and quinazolone ring methyl at 7.80 ppm. The structure of IVa is taken to contain the quinazolone epoxy group based on IR, NMR, and elemental analysis. Figure 3 contains the GPC plots of the addition products of bisquinazolone phenol (III) and bisquinazoline (V) to Bisphenol A type epoxy resins. New elution peaks of the block epoxy resins appeared at 45-50 mL, as expected for the increased molecular weight, while those due to III and V in the neighborhood of 52-54 mL were greatly reduced. These results indicate that the reaction products are blends, of the block epoxy resin containing quinazolone rings and DGEBA.

Bisquinazolone epoxy resins IVa, IVb, and IVc are solid and have softening points in the $129\text{-}142^\circ\text{C}$ range, which is higher than that of DGEBA. These compounds are soluble in some organic solvents (as shown in Table 1),

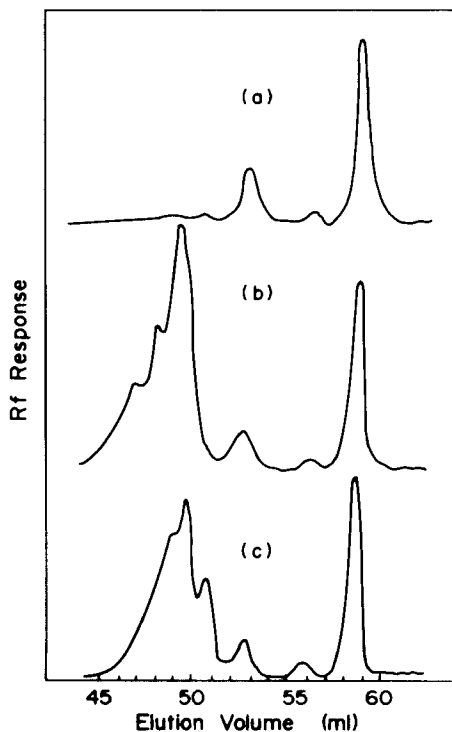


FIG. 3. GPC plots of various epoxy resins. (a) DGEBA, (b) quinazolone addition product, (c) quinazoline addition product.

and their solubilities increase in the order *o*-, *m*-, and *p*-substitution. Polar solvents are better than nonpolar ones. Heterocyclic compounds show generally poor solubility due to their rigid structure, but quinazolone epoxy resins have better solubilities due to the increased flexibility of the chain.

Properties of the Cured Resins

Dielectric constants and dissipation factors are shown in Fig. 4. The dielectric constant of IV is constant up to 200°C, while $\tan \delta$ increases slightly above 170°C. Figure 5 presents a graph of the volume resistivity.

Tensile strengths of the IV-MNA system are listed in Table 2, and the temperature dependence of the tensile modulus is shown in Fig. 6.

TABLE 1. Solubility of Bisquinazolone Epoxy Resins^a

	IVa	IVb	IVc
Methanol	-	+	++
Ether	-	-	-
Methyl acetate	-	+	+
Chloroform	++	++	++
Carbon tetrachloride	-	-	-
Pyridine	++	++	++
<i>m</i> -Cresol	++	++	++
DMAC	++	++	++
NMP	++	++	++

^a++ = soluble at room temperature, + = soluble on heating, - = insoluble.

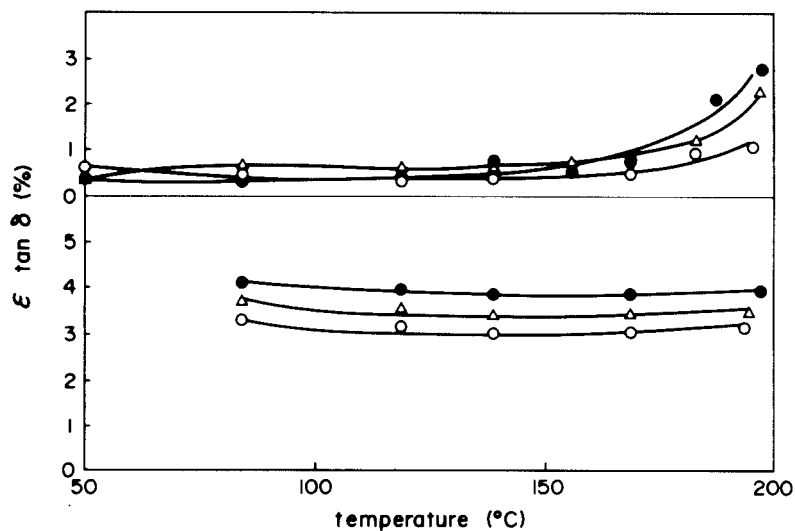


FIG. 4. Dielectric constant and dissipation factor of IV: (○) IVa-MNA, (●) IVb-MNA, (△) IVc-MNA.

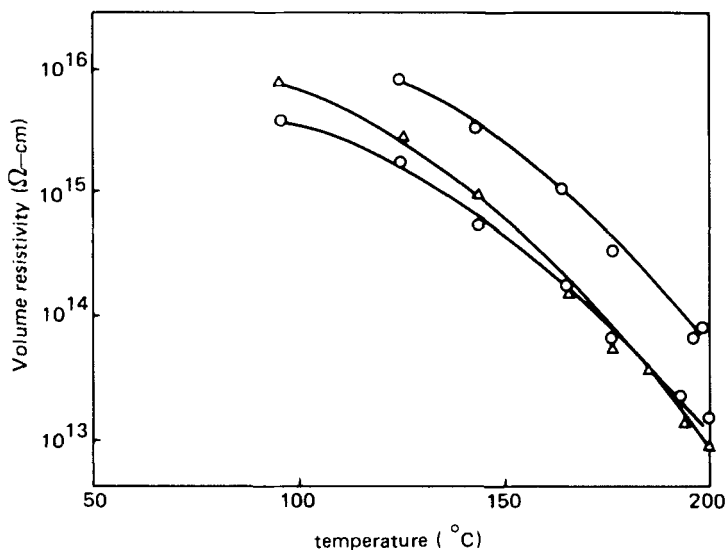


FIG. 5. Volume resistivity of IV: (○) IVa-MNA, (●) IVb-MNA, (△) IVc-MNA.

A transition, which should correspond to the T_g (Fig. 6), is found at 215°C for the resin from IVa, 207°C for IVb, and 205°C for IVc. The quinazolone epoxy resins containing *para*-substituents show a higher T_g than those containing *meta* or *ortho* substituents. This agrees with the well-known reduction of the T_g from the *para* to the *meta* configuration of aromatic polymers.

The dynamic modulus of mixtures of DGEBA and IVb cured with MNA is shown in Fig. 7. The drop in the modulus represents T_g , which is shifted to

TABLE 2. Tensile Strength of Cured Resin IV

	Tensile strength, MPa	Elongation, %	Modulus, GPa
IVa-MNA	96	4.5	2.6
IVb-MNA	110	5.0	2.3
IVc-MNA	67	4.5	2.4

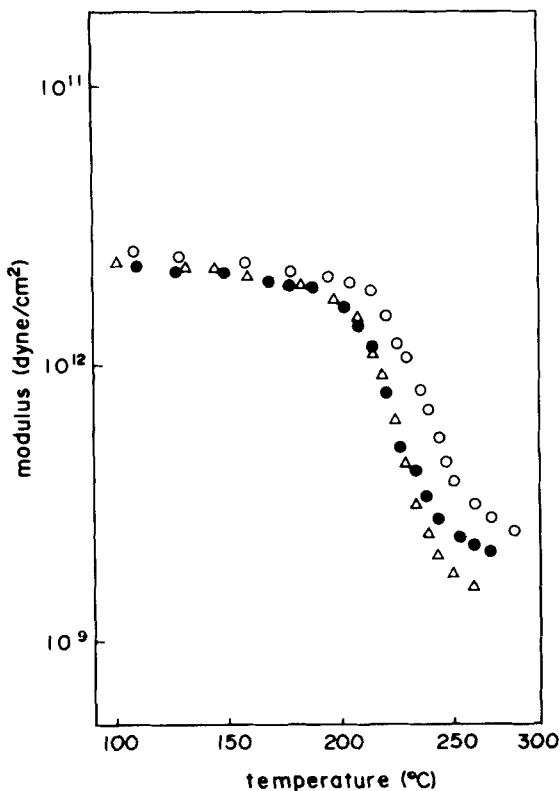


FIG. 6. Tensile modulus of cured IV: (○) IVa-MNA, (●) IVb-MNA, (△) IVb-MNA.

higher temperature with increasing IVb content (Table 3). It can be seen that the transition is due to the stiffness of the bisquinazolone phenol chain in comparison with that of Bisphenol A. The T_g values determined by DSC (Fig. 8) agree well with the above results.

Weight loss measurements were used to investigate the thermal stabilities of the epoxy resins (see Fig. 9). It increases in the order IVa, IVb, IVc, and DGEBA. The weight loss of DGEBA reaches twice that of IVa in 6 days.

The TGA curves obtained in nitrogen (Fig. 10) show a difference in the thermal degradation behavior. The decomposition temperature decreases with increasing DGEBA content from 300°C for IVa to 285°C for pure

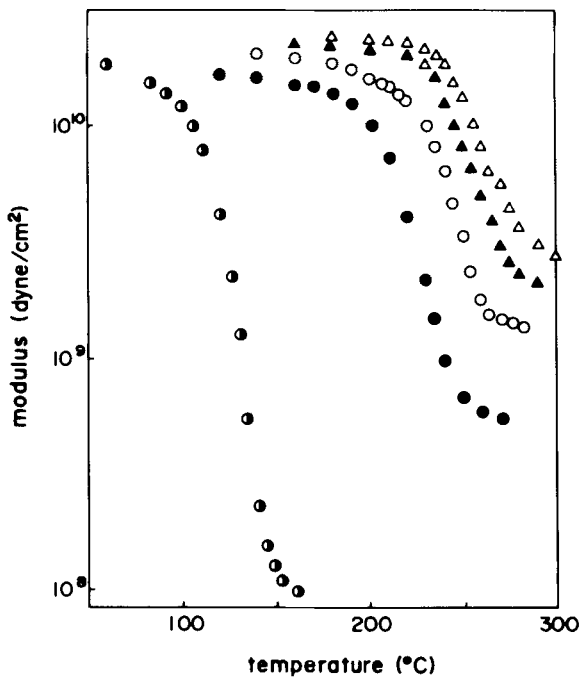


FIG. 7. Dynamic modulus of the IVb-DGEBA system: (Δ) IVb-DGEBA 90/10 w/w, (\blacktriangle) 75/25, (\circ) 50/50, (\bullet) 25/75, (\circ) 0/100.

TABLE 3. Glass-Transition Temperature of Cured Epoxy Resins

Composition, wt%					
IIIb	IVb	V	DGEBA ^a	T_g , ^b °C	T_g , ^c °C
10			90	133	
	100		0	238	220
	75		25	230	209
	50		50	218	188
	25		75	200	165
	0		100	110	91
		10	90	136	

^aDiglycidyl ether of Bisphenol A

^bDynamic viscoelastometer method.

^cDSC method.

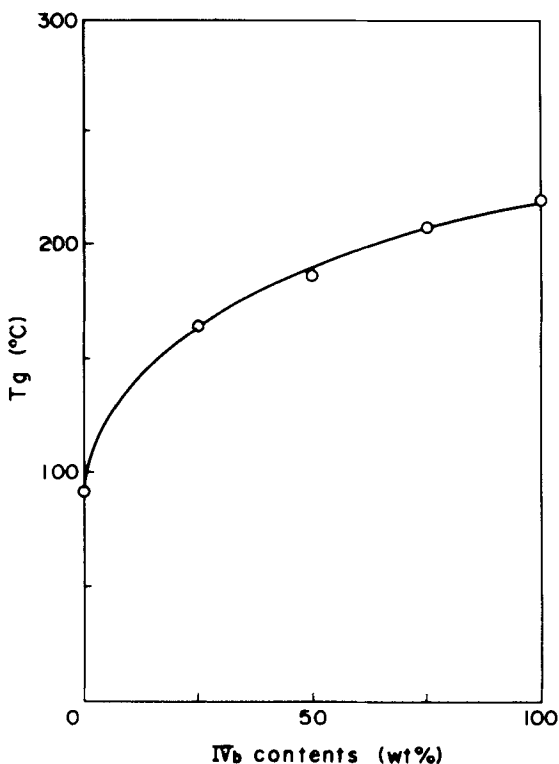


FIG. 8. Glass-transition temperature (T_g) of the IVb-DGEBA system by the DSC method.

DGEBA. At higher temperatures they seem to fall into two groups, one based on bisquinazolone epoxy resins of IV, and the other on the block epoxy resins.

Films of IVa, IVb, and IVc, 0.1 mm thick, when submerged for 14 days at room temperature in benzene, acetone, ethanol, *m*-cresol, DMAC, NMP, and 10% aqueous sulfuric acid do not change, but are discolored in 10% aqueous sodium hydroxide. Those polymers keep their initial states of flexibility, appearance, etc., that is, they have good solvent resistance.

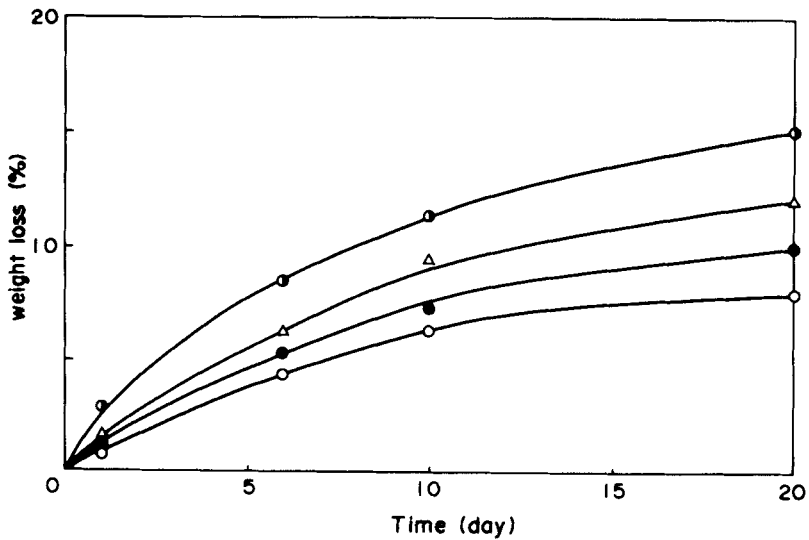


FIG. 9. Weight loss of quinazolone epoxy resin in air at 225°C (sample size $0.1 \times 10 \times 10$ mm): (○) IVa, (●) IVb, (△) IVc, (●) DGEBA.

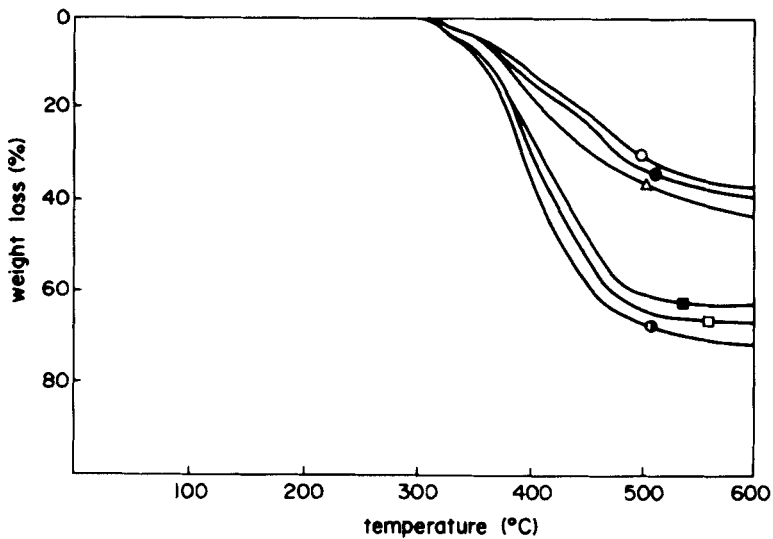


FIG. 10. Dynamic TGA of various quinazolone epoxy resins in nitrogen: (○) IVa, (●) IVb, (△) IVc, (●) DGEBA, (□) V, (■) IIIb.

CONCLUSIONS

Bisquinazolone phenol diglycidyl ethers have relatively low melting points and exhibit good solubility in organic solvents in spite of their structure based on aromatic heterocycles. The cured resins have higher T_g and thermal stability than those of the diglycidyl ether of Bisphenol A and its block epoxy resins with bisquinazolone units. These properties were found to depend on the amount of quinazolone and the location of the oxyphenylene linkage in the bisquinazolone group.

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Received March 26, 1988

Revision received June 27, 1988