

# Synthesis of Zinc-Containing Epoxy Resin

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## SYNOPSIS

Novel epoxy resins containing zinc acrylate have been synthesized by reacting zinc acrylate with bisphenol-A and an excess of epichlorohydrin. Parameters such as epoxy equivalent weight, hydroxyl content, and hydrolyzable chlorine content have been estimated. These resins, characterized by IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$ , have been evaluated by thermal analysis. Curing was carried out with polyamide at  $130^\circ\text{C}$  for 24 h. Cured resins have improved thermal and chemical resistance. The reaction follows first-order kinetics with activation energy 86 and  $34\text{ kJ mol}^{-1}$  in the presence and absence of zinc acrylate. The role of zinc, which increases epoxidation due to formation of complex with bisphenol-A, has been discussed. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Epoxy resins have been widely used as an engineering plastic because of their good mechanical, thermal, and electrical properties. A survey of the literature reveals that there are only a few communications that indicate that it is, in principle, possible to synthesize the epoxy resins containing quinazolone rings,<sup>1</sup> thiocarbonhydrazone,<sup>2</sup> ionic-containing interpenetrating polymer network,<sup>3</sup> and synthesis and rates of photocross-linking of epoxy acrylates.<sup>4</sup> Recently, we reported the synthesis and characterization of epoxy resin containing copper acrylate<sup>5</sup> and poly(copper acrylate).<sup>6</sup> There is, however, no information in the literature on the possible use, as complexing agents, of  $\text{Zn}^{2+}$  to modify such properties as chemical resistance, thermal resistance, and average molecular weight. Therefore, it is worthwhile to synthesize epoxy resin containing zinc acrylate.

In the present article, we report the synthesis and properties of epoxy resins containing  $\text{Zn}^{2+}$ .

## EXPERIMENTAL

All experiments were carried out at  $30^\circ\text{C}$ . Epichlorohydrin (Ranbaxy), bisphenol-A (Robert John-

son), toluene (Ranbaxy), pyridine (Ranbaxy), methanol (Ranbaxy), and acetylchloride (Ranbaxy) were obtained from commercial sources and used as received.

### Synthesis of Zinc Acrylate

Zinc acrylate was prepared by the reaction of acrylic acid (5–10 wt % stoichiometric excess) with zinc oxide (Ranbaxy) in toluene suspension at  $40\text{--}50^\circ\text{C}$ . The reaction was carried out for 5 h, with gradual addition of the reactants and with constant stirring. The evaporated toluene lost from the reaction vessel was constantly replaced. Water formed in the reaction was removed as an azeotropic mixture with toluene. After preliminary drying, the acrylate was washed with acetone and vacuum-dried to constant weight.<sup>7</sup>

### Synthesis of Epoxy Resins

Synthesis of epoxy resin A was carried out by reacting bisphenol-A (0.075 mol) and epichlorohydrin (0.75 mol) in three-necked flask and refluxing, followed by a gradual addition of sodium hydroxide (0.15 mol) over a period of 3.5 h. Heating was continued for an additional 15 min, after which the content was dissolved in toluene (80 mL) and the solution filtered to remove the salt. The excess of epichlorohydrin and toluene was removed by distillation under reduced pressure (400 mm). The re-

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sulting viscous product was stored in an air-tight container.<sup>8</sup>

Epoxy resin B was prepared by reacting bisphenol-A (0.075 mol) and epichlorohydrin (0.75 mol) in the presence of  $4.78 \times 10^{-3}$  molar equivalent of zinc acrylate and was prepared in a similar manner as was epoxy resin A. Epoxy resins C and D were also prepared the same way as was epoxy resin B, but the quantity of zinc acrylate was increased to  $12.53 \times 10^{-3}$  and  $20.89 \times 10^{-3}$  molar equivalent, respectively.

## CHARACTERIZATION

### Epoxide Equivalent

The epoxide equivalent of various resins was obtained using the pyridinium chloride method. A weighted sample of epoxy resin (2–4 m eq) was treated with 25 cm<sup>3</sup> of 0.2M pyridinium chloride in pyridine. The solution was warmed to dissolve the sample and then heated under reflux for 0.5 h. The solution cooled to room temperature was diluted with methyl alcohol (50 cm<sup>3</sup>) and titrated against methanolic standard NaOH (0.5M). The epoxide equivalent was calculated from the titer value.<sup>8</sup>

### Hydroxyl Equivalent

This was determined by acetylation with acetyl chloride in pyridine solution. The excess chloride was decomposed with water and the resulting acetic acid formed both in hydrolysis and in the acetylation process was titrated with a standard alkali solution. The value was calculated using following equation<sup>9</sup>:

Hydroxyl equivalent  
(eq/100 g)

$$= \frac{\text{Wt. of sample}}{\text{Normality of KOH} \times (V_1 - V_2) \times 170}$$

$V_1$  = the volume of methanolic KOH used for the blank and  $V_2$  = volume of methanolic KOH used for the sample.

### Hydrolyzable Chlorine Content

This was determined by heating the resin solution with alcoholic KOH and titrating it against standard HCl using following formula<sup>9</sup> based on the dehydrohalogenation concept:

Hydrolyzable chlorine content

$$= \frac{355 \times 10^{-4} \times \text{normality of KOH} \times \text{volume of KOH neutralized by epoxy}}{\text{Weight of sample}}$$

### Viscosity

Viscosity data of the synthesized resins were obtained using a Ubbelohde viscometer at various temperatures.

### <sup>1</sup>H-NMR Spectra

The <sup>1</sup>H-NMR spectra of the epoxy resins were recorded on a Varian EM 390 spectrophotometer using tetramethylsilane (TMS) as the internal standard.

### Infrared Spectra

The infrared spectra were recorded on a Perkin-Elmer Model 377 spectrophotometer.

### Thermal Analysis

Thermogravimetric analysis was recorded on a Stanton Redcroft thermal analyzer at a heating rate of 15°C/min under nitrogen atmosphere.

### Metal Analysis

Metal analysis was carried out by the following two methods:

1. Inductively coupled plasma emission spectrophotometry.
2. Scanning electron microscopy (SEM): Scanning electron micrographs were obtained from a JEOL JSM 840A scanning microscope on an SEM stub by silver adhesive paste.

### GPC

Average molecular weight was determined using a gel permeation chromatograph Model 440 (Water Associates, Milford, MA).

### Curing Studies

In the present study, polyamide was used as a curing agent. The resins and the curing agent were mixed in a stoichiometric amount, applied on glass and tin plates, and kept for 24 h at 30°C.

**Table I Physical Characterization of Various Epoxy Resins**

Epoxy Resin	Color	State	Refractive Index
Epoxy resin A	Light yellow	Viscous	1.5695
Epoxy resin B	Yellow	Viscous	1.5640
Epoxy resin C	Dark yellow	Highly viscous	1.5630
Epoxy resin D	Dark yellow	Highly viscous	1.5570

## RESULTS AND DISCUSSION

Physical properties of resins are listed in Table I. When the epoxidation is carried out, the reaction becomes highly exothermic and the product obtained is a highly viscous liquid. The value of the refractive index of modified epoxy resins varies from 1.5640 to 1.5570, which is less than the observed value of epoxy resin A: 1.5695.

Table II reveals that the values of the epoxide equivalent, chlorine content, and molecular weight increases as a function of the molar equivalent of zinc acrylate in epoxy resin. It is probably because of the formation of a complex between zinc and bisphenol-A that increases the values. The epoxy equivalents of various resins indicate that the value approximates one-half of the average molecular weight, showing thereby the presence of two epoxide groups per molecule, as expected. However, the values of the hydroxy content were changed from 0.12 to 0.13 eq/100 g and are the least affected. The increase of the specific gravity value is obvious due to the incorporation of metal. It is further noted that the value of ( $\eta_{sp}$ ) viscosity increases with increase in the molar equivalent of zinc acrylate, which may be attributed to the higher molecular weight of the epoxy resin as well as to the incorporation of zinc

into the epoxy resin. The percentage hydrolyzable chlorine content, which may be due to many side reactions like partial dehydrohalogenation, abnormal addition of epichlorohydrin, and formation of bound chlorine varied from 1.83 to 3.86. Figure 1 gives the variation of viscosity ( $\eta_{sp}$ ) with the temperature of various epoxy resins, which shows a fall in viscosity with increase in temperature.

## SEM

The presence of zinc in the epoxy was confirmed by scanning electron micrographs. Figure 2(a) gives the weight percentage of zinc, which is 1.72. Figure 2(b) shows zinc as a white portion present in the dark region due to the epoxy region.

## Spectral Analysis

The infrared spectra of epoxy ring compounds (Fig. 3) are reported to show absorbance in the region of 1280–1230  $\text{cm}^{-1}$  as a result of ring breathing or symmetric stretching vibration, and around 910  $\text{cm}^{-1}$ , due to symmetric stretching of the epoxy. The presence of these two bands and also the band around 2900  $\text{cm}^{-1}$  due to —CH and —CH<sub>2</sub> groups in the ring confirms the presence of the epoxy ring in these resins. The broadened band around 3400  $\text{cm}^{-1}$  indicates the presence of the —OH group, possibly due to oligomer formation. However, there is an additional band at 1750  $\text{cm}^{-1}$  due to the ester group of acrylate in epoxy resins B, C, and D.

The <sup>1</sup>H-NMR spectra of epoxy resin A shows resonance in the region  $\delta = 2.0$ –3.0 ppm, which could be attributed to the epoxide protons. The spectra show aromatic proton signals at  $\delta = 7$ –7.5 ppm and methyl proton signals at  $\delta = 1$ –2 ppm. There is an additional peak at  $\delta = 2$ –3 ppm that is due to the CH<sub>2</sub> proton (Fig. 4).

<sup>13</sup>C-NMR spectra of epoxy resin A shows a peak between  $\delta = 30$ –70 ppm due to the alkyl group. The

**Table II Analysis Report of Various Resins**

Properties	Epoxy Resin A	Epoxy Resin B	Epoxy Resin C	Epoxy Resin D
Epoxide equivalent/100 g	194	234	294	335
Specific gravity	1.173	1.1850	1.1940	1.2017
Viscosity ( $\eta_{sp}$ )	1.58	1.63	1.82	1.90
Chlorine content (%)	0.57	1.83	3.06	3.86
Hydroxyl content/100 g	0.12	0.125	0.130	0.130
Molecular weight	380	465	580	670
Epoxy content	0.51	0.503	0.506	0.50

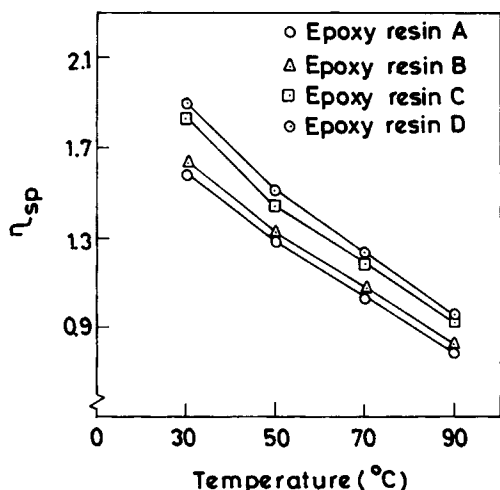
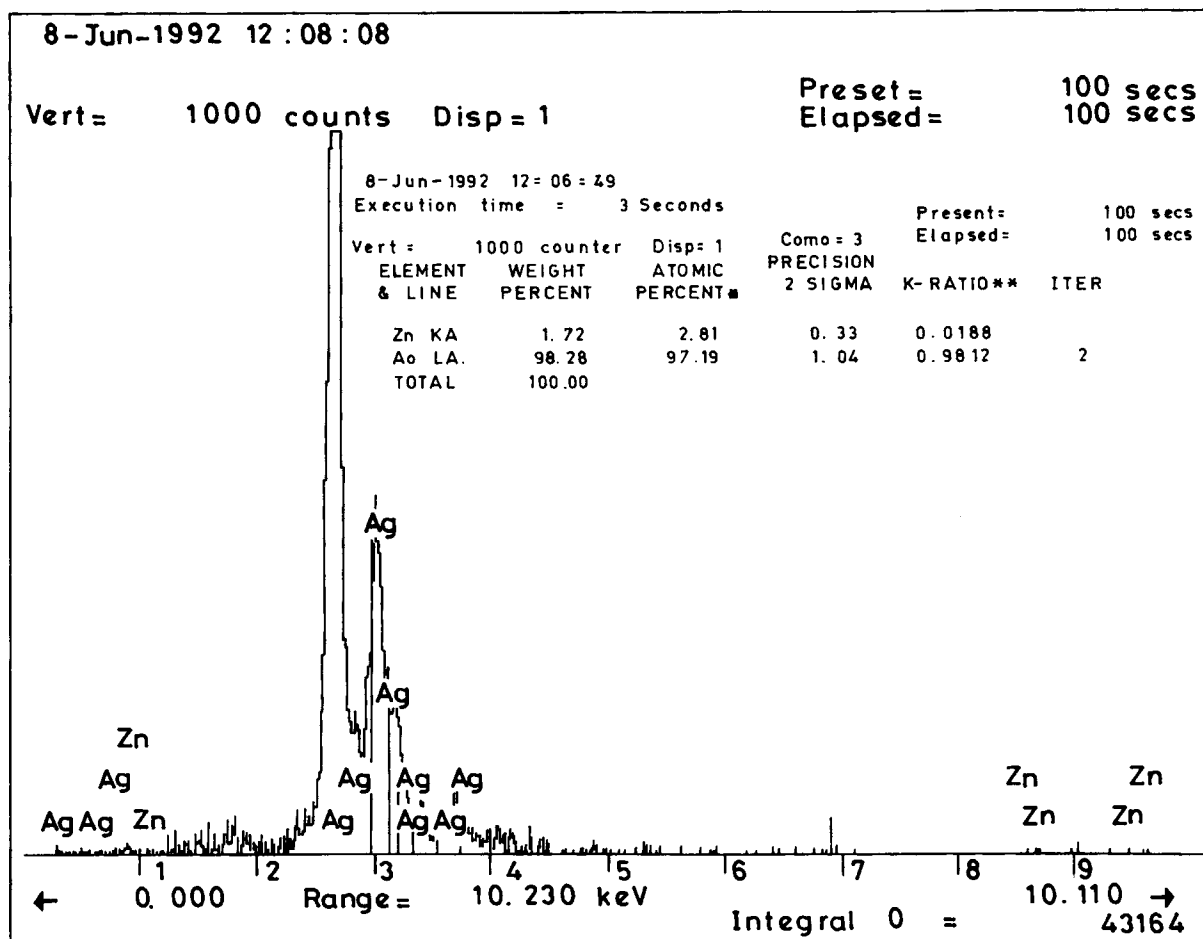


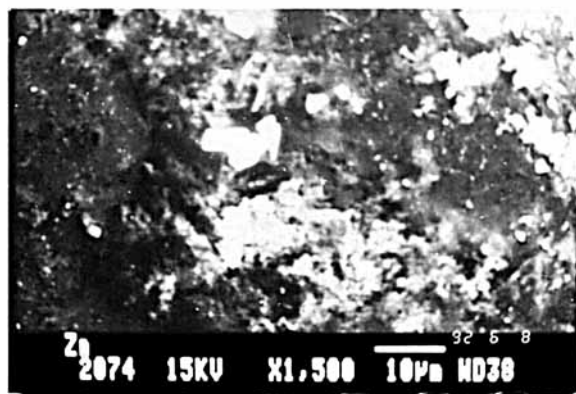
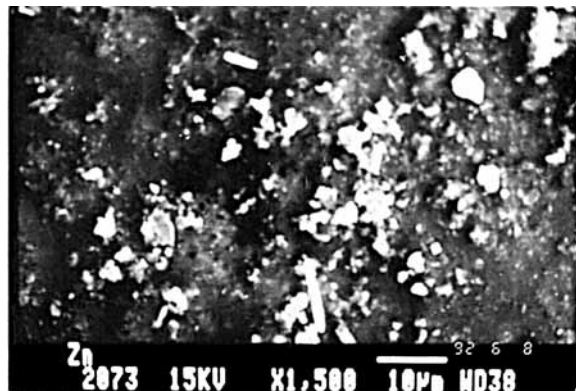
Figure 1 Relationship between  $n_{sp}$  and temperature of various epoxy resins.

peak due to aromatic carbons appears at about  $\delta = 115-128$  ppm and the peak due to carbon atom of  $C=O$  of zinc acrylate (epoxy resin B) appears at about 115 ppm. The presence of the peak at  $\delta = 155$  ppm confirms the incorporation of zinc acrylate in the epoxy resin (Fig. 5).

Table III shows the solubility and chemical resistance of the film (0.1 mm thick), of blank and modified epoxy resins, when submerged for 7 days in polar and nonpolar solvents. These polymers (epoxy resins B, C, and D) kept their initial state of flexibility and appearance, i.e., they have good solvent resistance.<sup>1</sup> However, absorption was observed when they were submerged in dioxane, toluene, and hydrochloric acid (1M), which is due to increased flexibility of the polymer chain (Table IV). This seems to be due to the presence of zinc acrylate.



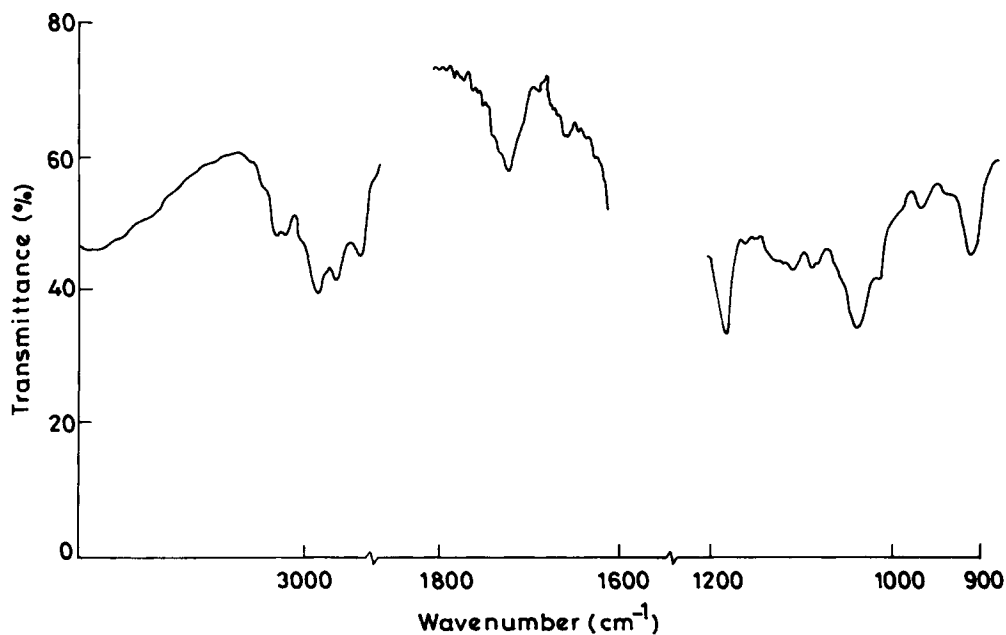
(a) Figure 2 (a) Scanning electron micrograph spectrum for modified epoxy resin (epoxy resin D). (b) Scanning electron micrographs for modified epoxy resin (epoxy resin D).

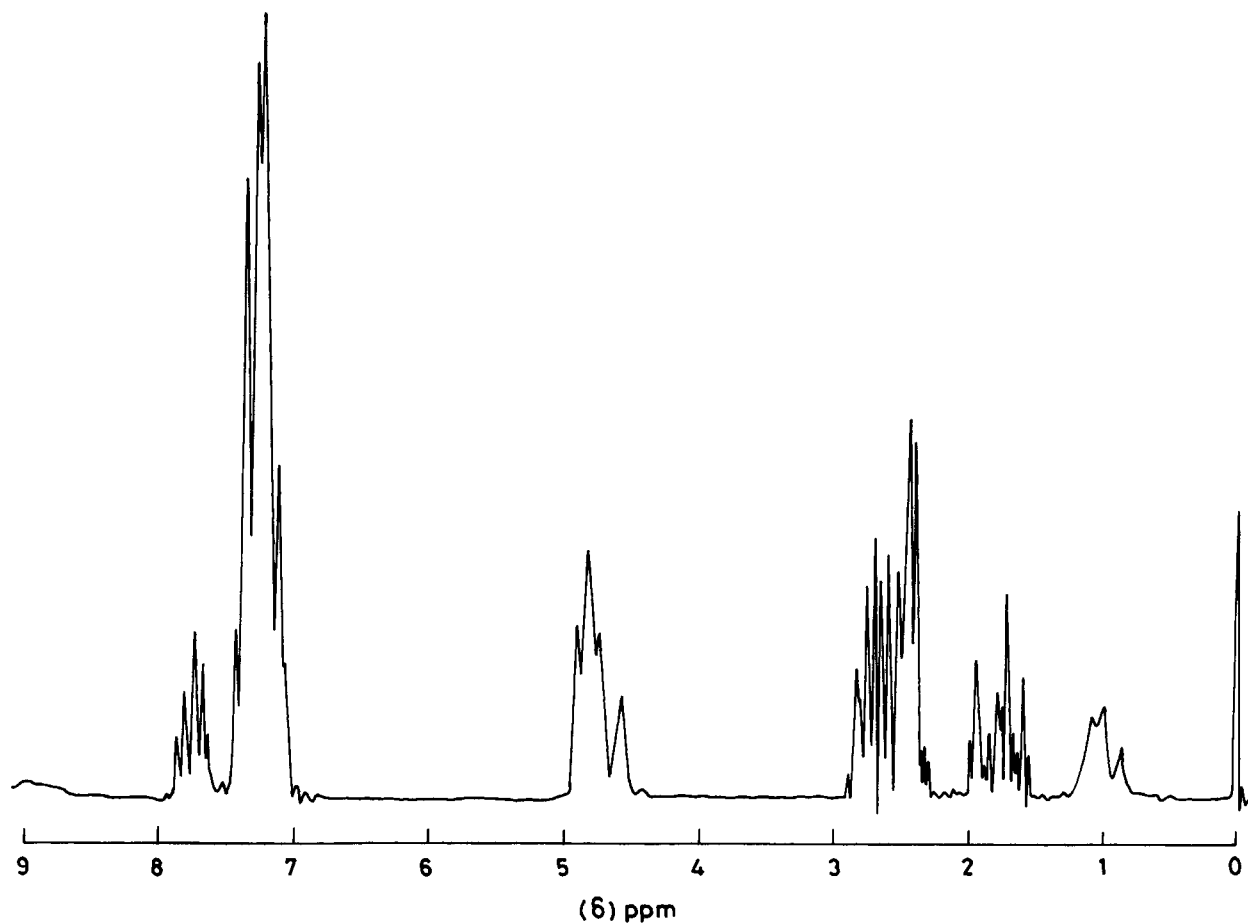
(b) **Figure 2** (Continued from previous page)**Table III Solubility and Chemical Resistance of Epoxy Resin Films**

Chemical	Epoxy Resin A	Epoxy Resin B	Epoxy Resin C	Epoxy Resin D
Methanol	-	-	-	-
Benzene	-	-	-	-
Toluene	-	-	-	-
Pyridine	-	±	±	±
Hydrochloric acid	-	-	-	-
Nitric acid	+	-	-	-
Sulphuric acid	+	+	+	+
Dioxane	-	-	-	-
NaOH	-	-	-	-
DMSO	-	-	-	-
Carbon tetrachloride	-	-	-	-

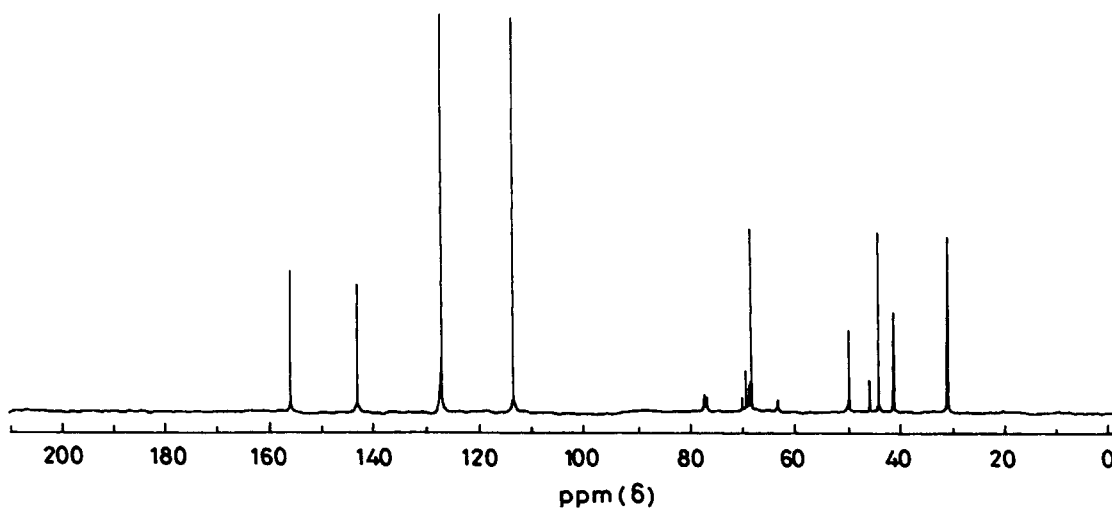
+, soluble; -, insoluble; ±, sparingly soluble.

Table V shows the properties of the cured samples. Films were found to pass the flexibility test. However, the scratch hardness increases as the molar equivalent of zinc acrylate in the epoxy resin increases. The films of modified resins (B, C, and D) were more resistant to scratch as the concentration of Zinc acrylate in the epoxy resin increased.

**Figure 3** IR spectrum of epoxy resin containing  $4.78 \times 10^{-3}$  molar equivalent of zinc acrylate (epoxy resin B).



**Figure 4** <sup>1</sup>H-NMR spectrum of epoxy resin containing  $20.89 \times 10^{-3}$  molar equivalent of zinc acrylate (epoxy resin D).



**Figure 5** <sup>13</sup>C-NMR spectrum of epoxy resin containing  $4.78 \times 10^{-3}$  molar equivalents of zinc acrylate (epoxy resin B).

**Table IV Weight Gain in Epoxy Resin Films When Submerged in Various Solvents for 7 Days**

Chemical	Epoxy Resin A	Epoxy Resin B	Epoxy Resin C	Epoxy Resin D
Toluene	—	11.76%	13.90%	21.23%
Dioxane	—	4.14%	5.43%	11.46%
Hydrochloric acid	8.77%	20.40%	24.10%	56.23%

Weight loss measurements were used to investigate the thermal stability of the epoxy resins (Fig. 6). It decreases as the concentration of zinc acrylate in the epoxy resin increases. Weight loss at temperature 200°C in epoxy resin A is much higher than that of epoxy resin D in 4 h, which indicates that Zn<sup>2+</sup> increases the thermal stability of the epoxy resin. This may be due to the pseudo-inert gas structure of zinc and its existence in only one oxidation state.

### Thermogravimetric Analysis

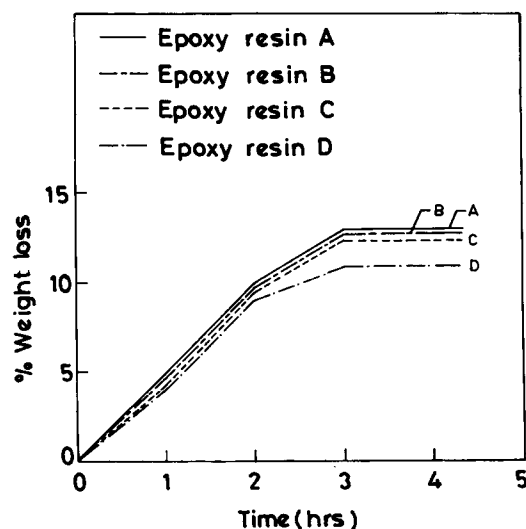
The effect of the structure of zinc acrylate on the thermal stability of epoxy resin was studied by thermogravimetric analysis (Fig. 7). A resin sample (epoxy resin D) containing zinc acrylate was stable up to 215°C and started decomposing above this temperature; however, blank epoxy resin (epoxy resin A) was stable up to 130°C. In modified epoxy resin, rapid decomposition was observed around 300–400°C and almost total volatilization occurred around 425°C. The initial weight loss (3.5%) was observed around 215 and 130°C in epoxy resin D and epoxy resin A, respectively, which confirms that incorporation of zinc increases the thermal stability of the polymer.

**Table V Properties of Epoxy Resin Films Cured with Polyamide**

Properties	Epoxy Resin A	Epoxy Resin B	Epoxy Resin C	Epoxy Resin D
Flexibility <sup>a</sup>	Passed	Passed	Passed	Passed
Scratch <sup>b</sup> (g)	1000	1100	1200	1300
( $\Delta E$ ) (kJ mol <sup>-1</sup> )	34	60.90	81.09	86.04

<sup>a</sup> One-fourth inch mandrel.

<sup>b</sup> Mechanically operated scratch hardness tester.

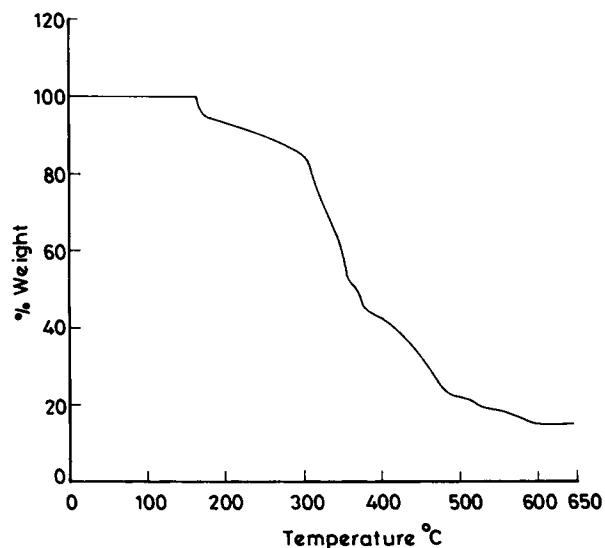
**Figure 6** Weight loss of epoxy resins A, B, C, and D at 200°C (sample size 0.1 × 10 × 10 mm).

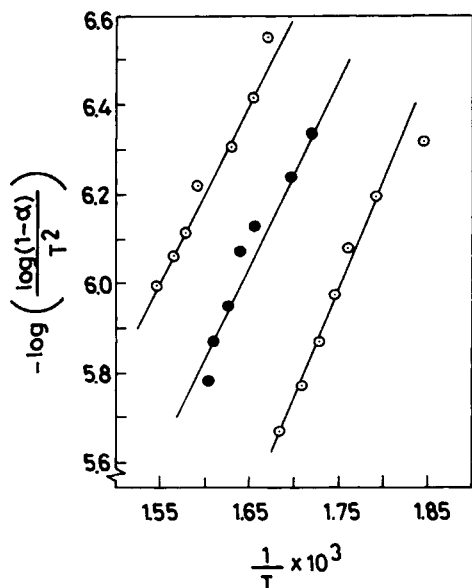
### Kinetics

The activation energy ( $\Delta E$ ) and order of reaction for the dynamic thermogram was calculated using the Coats and Redfern equation<sup>10</sup> according to which

$$\log \frac{g\alpha}{T^2} = -\frac{E}{2.3RT} + \log \frac{ZA}{BE} \left(1 - \frac{2RT}{E}\right)$$

where  $E$  = activation energy,  $B$  = linear heating rate,  $Z$  = preexponential factor, and  $T$  = temperature.

**Figure 7** TGA of epoxy resin containing  $4.78 \times 10^{-3}$  molar equivalents of zinc acrylate.



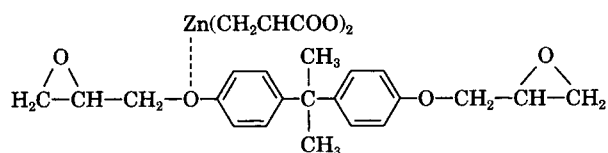
**Figure 8** A plot of  $-\log\{[-\log(1-\alpha)]/T^2\}$  vs.  $(1/T) \times 10^3$  of (—○—) epoxy resin B, (—●—) epoxy resin C, and (—○—) epoxy resin D.

The activation energy calculated from the slope of a linear graph plotted between  $\log g(\alpha)$  vs.  $(1/T) \times 10^3$  (Fig. 8) increases as the concentration of zinc acrylate in the epoxy resin increases (Table

V). The overall reaction, for blank and modified epoxy resins, follows first-order kinetics.

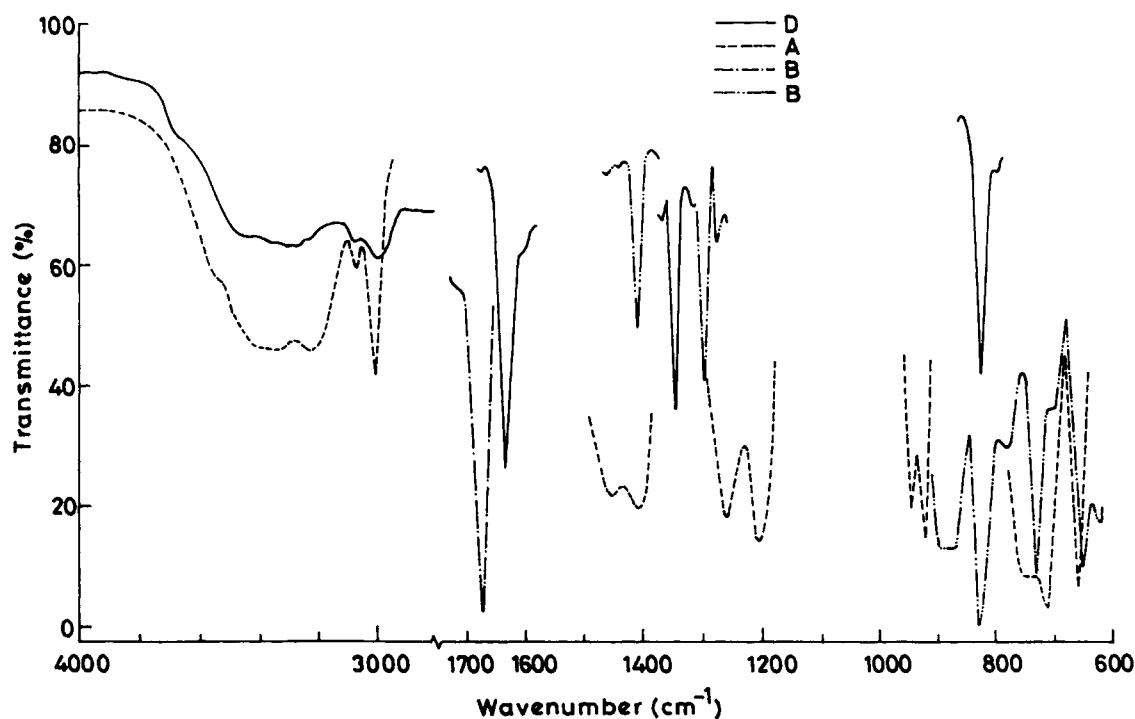
### Mechanism

We have already elucidated the mechanism of synthesis of epoxy resin in the presence of copper acrylate<sup>5</sup> and it seems that the present system also follows the same mechanism, i.e., Zn, being a transition element, forms a complex with bisphenol-A and not with epichlorohydrin, as is evident from the shifting of the OH band in the IR spectrum (Fig. 9) as well as the increase in the intensity of peak due to methylene protons in the NMR spectrum of epoxy resin D. Therefore, the following structure may be proposed for the complex:



### CONCLUSION

$Zn^{2+}$  plays the role of an activator by forming a complex with bisphenol-A, as a result of the donor-



**Figure 9** IR spectrum of (A) bisphenol-A in epichlorohydrin, (B) epichlorohydrin, (C) epichlorohydrin and zinc acrylate, and (D) bisphenol-A, epichlorohydrin, and zinc acrylate.



acceptor relation between the  $\alpha$ -orbitals of  $\text{Zn}^{2+}$  and the —OH group of bisphenol-A. This serves as an explanation for the increase of the epoxy equivalent and, hence, increase of the hydroxyl content. The modified system follows first-order kinetics with an activation energy of  $86 \text{ kJ mol}^{-1}$ .

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