

# A New Epoxy Resin/Hardener System with Variable Processing and End Properties

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## Synopsis

A combination of a standard bisphenol-A liquid epoxy resin and a zinc-pyrrolidone-carboxylate complex with a long chain poly(oxypropylene diamine) (Jeffamine D 2000) has been found to give variable processing and end properties over a very wide range, e.g., pot life < 1–70 days, Martens Heat-Distortion Temperature < 25–124°C and elongation at break 35–1%. The variation in properties is achieved simply by changing the epoxy/complex ratio. The very reactive high elongation formulation is thought to be the result of a very fast zinc catalyzed amine/epoxy polyaddition reaction and the low reactivity rigid formulation to be due to zinc-complex initiated anionic homopolymerization of the epoxy resin. The borderline concentrations are approximately 200 and 10 phr of the complex, respectively.

## INTRODUCTION

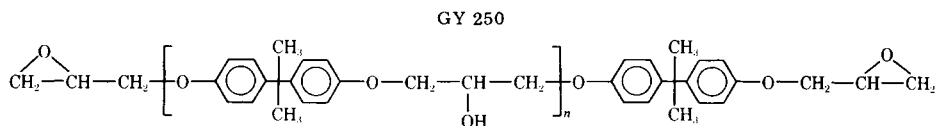
The epoxide ring is known to react with more than 50 separate chemical groups,<sup>1</sup> and it is therefore not surprising that very many substances have already been proposed as curing agents for epoxide resins. Despite this profusion, certain fundamental problems still have to be resolved.

The need for completely latent curing agents, for example, has, to our knowledge, not yet been fulfilled. The main requirement here is for rapid cure at moderately elevated temperatures (i.e., 120–150°C) coupled with an (ideally) indefinite storage life at temperatures of up to 40°C.

Among the types of compound which have already been proposed as latent accelerators and latent curing agents for epoxy resins are metal-salt amine complexes.<sup>2–6</sup> Although none of the complexes so far proposed seem to have been ultimately successful, we thought this approach to be of interest and have synthesized several new metal salt-amine complexes,<sup>7</sup> which we have found to be extremely interesting as curing agents per se. In particular we have found that the processing and end properties of certain epoxide/metal salt amine complex combinations can be varied over a very wide range simply by changing the complex concentration. In the present paper we shall present results obtained with one such system and propose possible reaction mechanisms.

## EXPERIMENTAL

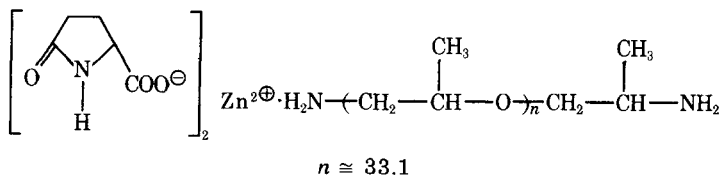
The title new epoxy resin/hardener system consisted of GY 250, a standard CIBA-GEIGY liquid bisphenol-A resin and Complex A, derived from zinc-pyrrolidone-carboxylate and Jeffamine D 2000, a poly(oxypropylene diamine):



$$n \cong 0.1$$

The GY 250 used in this study had an epoxide equivalent weight of 192:

#### COMPLEX A<sup>7</sup>



Complex A was synthesized from zinc-pyrrolidone-carboxylate (with 2 mol of water of crystallization) and Jeffamine D 2000 (Jefferson Chemical Co., U.S.A.). The final product was dried at 100°C/0.1 torr to constant weight and had an amine content of 0.825 equivalents/kg (95.5% of theory). Complex A is a clear yellow liquid with a viscosity of approximately 80,000 cP at 25°C.

ANAL. Calcd: N, 2.40%; Zn, 2.79%. Found: N, 2.66%; Zn, 2.72%.

#### C<sup>13</sup>-NMR-Data

The differences between the  $\delta_c$  values of Complex A and of Jeffamine D 2000 in the vicinity of the amine group (NCH, NCH<sub>2</sub>, N-CH-CH<sub>3</sub>) are significant and

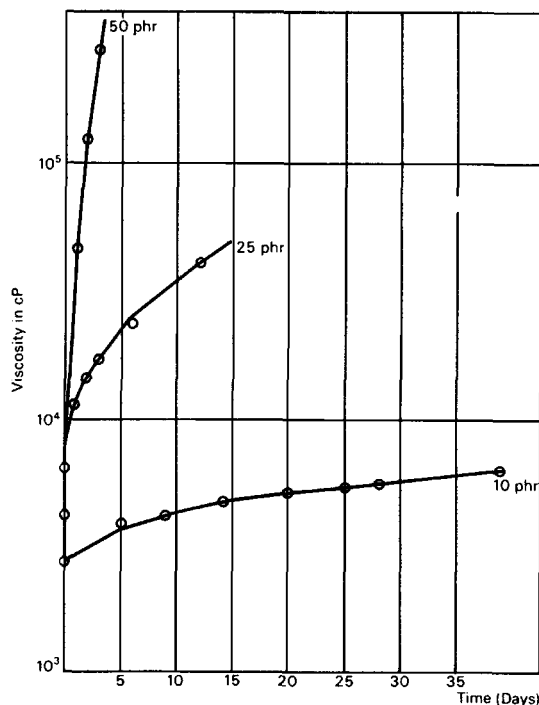


Fig. 1. GY 250/Complex A: viscosity vs. time at 40°C for various concentrations of Complex A.

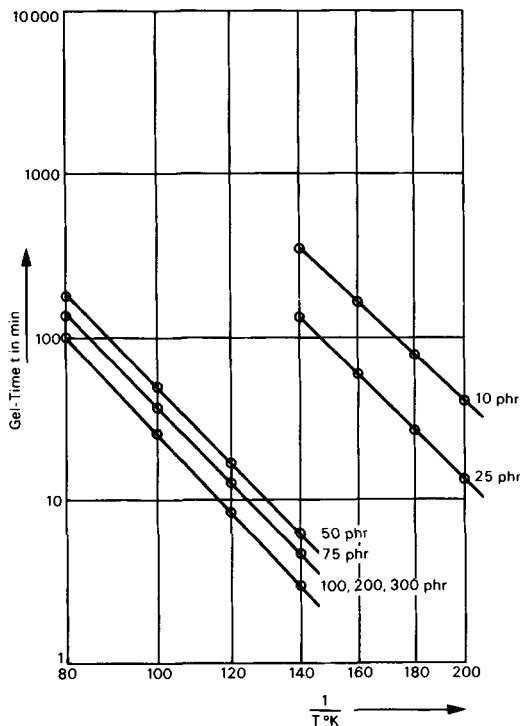


Fig. 2. GY 250/Complex A: gel time vs. temperature for various concentrations of Complex A.

indicate complex formation between the diamine and the zinc salt:

$\delta_c$	Allocation
18.6	N-CH-CH <sub>3</sub>
47.9	NCH, NCH <sub>2</sub>
47.6	

The above results agree with the formula given above. Complex A is completely soluble in GY 250 at 40°C.

### Gel Time Data

The gel times were determined on 0.5-g samples on thermostatically controlled hot plates. The temperature variance was  $\pm 0.1^\circ\text{C}$ .

### Viscosity Data

The viscosity/time data was obtained using the Hoespler falling ball method, the sample containing Hoespler tubes being stored in thermostated oil baths between and, of course, during measurements. The temperature variance was approximately  $\pm 1^\circ\text{C}$ .

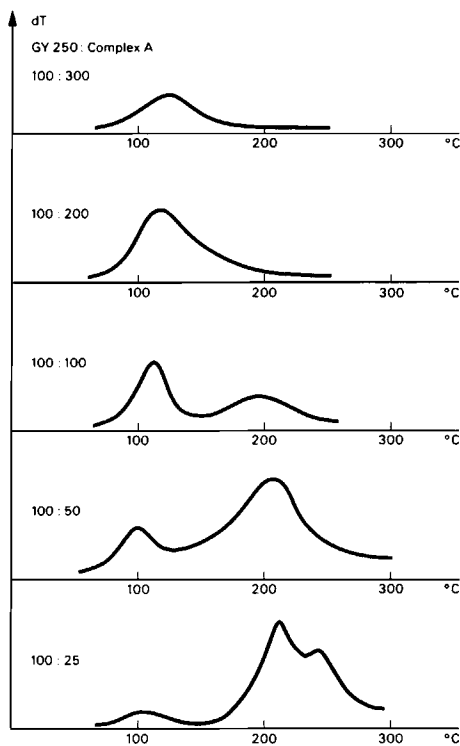


Fig. 3. DTA thermograms: GY 250/Complex A.

### Final Properties

The mechanical and electrical properties were determined according to the various Swiss (VSM) and German (DIN) norms. Other properties were determined according to CIBA-GEIGY internal standards. The norms or standards are indicated in the tables appropriately.

### Differential Thermal Analysis (DTA)

The DTA thermograms were obtained on a Mettler TA 2000 apparatus with an empty pan as reference. The conditions were: Sample quantity, ca. 20 mg; Heating rate, 4°C/min; Sensitivity, 200  $\mu$ m; Paper speed, 0.5 cm/min.

### X-ray Analysis of Zinc-Pyrrolidone-Carboxylate

The measurements were effected with a Phillips single crystal diffractometer PW 1000 with  $\lambda$   $\text{CuK}\alpha = 1.5418 \text{ \AA}$ . The intensity measurements were carried out with the same apparatus:

Reflex width: 1.6°

Measurement times: background 2  $\times$  10 s reflexes 40–56 s

Conditions:  $\theta$ -2 $\theta$ -Scan Method,  $\text{CuK}\alpha$  source, 50 kV, 30 mA, graphite monochromator

Calibration: Measurement of three reference reflexes (1,1,5), (8,2,0), and (0,12,2) after 2-h intervals

TABLE I  
 GY 250/Complex A: Processing and Final Properties as a Function of the GY 250/Complex A Ratio

Formulation	GY 250 Complex A	100 100	GY 250 Complex A	100 75	GY 250 Complex A	100 50	GY 250 Complex A	100 25	GY 250 Complex A	100 10
Initial viscosity at 40°C, cP	8850	7800	6370	4240	2640					
Usable life at 40°C to 15,000 cP	7 h 30 min	10 h	17 h 30 min	64 h	≈ 70 days					
Gel time (hot plate)										
80°C	100 min	136 min	173 min	—	—					
100°C	26 min 30 s	37 min 30 s	48 min 30 s	—	—					
120°C	8 min 30 s	13 min	17 min 30 s	—	—					
140°C	3 min 10 s	4 min 45 s	6 min 45 s	126 min	350 min					
160°C	—	—	—	54 min	161 min					
180°C	—	—	—	26 min 30 s	78 min					

Range: 706 reflexes were taken from  $2\theta = 6-134^\circ$ : 706 reflexes were calibrated and 698 were assumed to be observed [ $I > 2\sigma(I)$ ].

The monocrystal used for the measurements had the dimensions  $0.26 \times 0.13 \times 0.05$  mm. It was glued to a Lindemann glass tube with ARALDITE Rapid.

## RESULTS

### Viscosity/Time and Gel Time Data

Figure 1 gives a first indication of the variation in properties which can be achieved by varying the complex concentration. The diagram shows the viscosity of solutions of the complex in GY 250 plotted against time at  $40^\circ\text{C}$ .

As can be seen, reactivity increases within increasing Complex A concentration. It is also evident from the diagram that the complex can react catalytically as the lowest complex concentration used, 10 phr, is equivalent to only approximately 3% of the stoichiometric amount based on active (primary) amine hydrogen.

The increasing reactivity with increasing Complex A concentration can also be observed at higher temperatures, as can be seen from Figure 2 in which gel time has been plotted against temperature for complex concentrations from 10–300 phr. The seven solutions tested can be divided into two distinct groups: a low reactivity group with complex concentrations between 10 and 25 phr and a high reactivity group with concentrations of 50–300 phr.

### Physical Properties

The physical properties and some processing properties of GY 250 combinations with various concentrations of the zinc complex are given in Table I.

The cure cycles were optimized by differential thermal analysis (DTA) with respect to the transition temperature, i.e., the cure cycles given are the minimum required for maximum DTA-transition temperatures. All formulations can therefore be considered to be completely cured.

The variation in physical properties achieved by varying the concentration of the complex is considerable, as can be seen from the table. With the exception of lap shear strength all properties show very broad numerical value ranges:

Property	Numerical value range
Viscosity ( $40^\circ\text{C}$ )	8850–2640 cP
Usable life ( $40^\circ\text{C}$ ) (time to 15,000 cP)	7.5–1680 h
Gel time ( $140^\circ\text{C}$ )	3–350 min
Flexural strength	0.8–12 kg/cm <sup>2</sup>
Elongation at break	35–1%
Martens Heat Distortion Temperature	<25–124°C
Water absorption ( $23^\circ\text{C}$ )	1.7–0.2%
Power factor $\tan \delta$ , 1% value	<23–150°C
Weight loss 28 days at $180^\circ\text{C}$	7.2–3.3%

The variation of processing and end properties through variation of the curing agent concentration is, of course, well known in the epoxy technology. Epoxy resin formulations with carboxylic acid anhydrides, for example, seem to be particularly sensitive to the anhydride/epoxy ratio.<sup>8–11</sup>

Lewis acid complexes, i.e., catalytic curing agents, can also show a property/curing agent-concentration dependence as has been shown for the Boron-Tri-fluoride-Monoethylamine Complex.<sup>12</sup> The property/curing agent-concentration dependence observed by us is, therefore, per se not unique. It would appear, however, that the wide range of properties involved and the *breadth* of the actual numerical value ranges is somewhat unusual. At this stage we felt that two separate curing mechanisms might be possible and investigated the curing reaction further, as outlined below.

### DTA Thermograms

We have reproduced the GY 250/Complex E-DTA Thermograms (qualitatively) in Figure 3. The figure shows the DTA thermograms for decreasing Complex A concentrations from top to bottom, starting with 300 phr which is approximately equivalent to 100% of the stoichiometric amount based on primary amine active hydrogen. Quantitative data for the thermograms is given below.

Qualitatively, the thermograms indicate that decreasing complex concentrations lead to the superimposition of a "slow" reaction onto a preliminary "fast" reaction. The heats of reaction ratios given in Table II show that up to a complex concentration of  $\geq 100$  phr the preliminary "fast" reaction is predominant. For concentrations  $\leq 50$  phr the reverse is true. At a complex concentration of 25 phr the heat of reaction ratio is 0.07:1 and at a concentration of 10 phr, 0.02:1 (or approximately 2%), indicating that at this concentration the preliminary "fast" reaction has practically "disappeared."

The heats of reaction are, for 300, 200, 100, 50, and 25 phr of Complex A, 21.0, 18.3, 17.8, 16.3 and 17.2 kcal/mol, respectively, as compared to literature values of 25 kcal/mol for primary amine and  $\text{BF}_3\text{MEA}$  curing agents.<sup>13</sup>

The DAT thermograms seem to substantiate the belief that Complex A reacts via two separate curing mechanisms, depending on the concentration used.

TABLE II  
Quantitative DTA-Thermogram-Data for GY 250/Complex A Formulations with Variable Amounts of Complex A

Complex A concentration (phr)	$T_1^a$ (°C)	$T_2^b$ (°C)	$T_3^c$ (°C)	$\Delta H_{\text{tot}}^d$ (cal/g)	$\Delta H_1: \Delta H_2^e$
300	63	118.5	172.5	27.3	
200	63	118	207	31.7	
100	66	113.5 198.5	249.5	46.2	1.6:1
50	63	110 211	275	56.4	0.3:1
25	68.5 198	108 210 241.5	198 302	71.7	0.07:1
10	59.5 138	107 224 266.5	138 314	77.8	0.02:1

<sup>a</sup> Temperature at which an exothermic reaction starts.

<sup>b</sup> Heat of reaction maximum temperature.

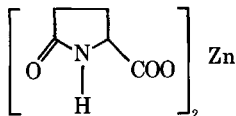
<sup>c</sup> Temperature at which the exothermic reaction ceases.

<sup>d</sup> Total heat of reaction based on the same baseline.

<sup>e</sup> Approximate ratio of heats of reaction in the case of "multireactions." Based on different baselines.

### Zinc-Pyrrolidone-Carboxylate

With the ultimate aim of discussing possible reaction mechanisms we sought some insight into the structure of Complex A. This complex is, as already mentioned, a liquid and therefore not easily amenable to structural analysis. We therefore sought indirect evidence by carrying out an X-ray structure analysis of the (crystalline) parent compound, viz. zinc-pyrrolidone-carboxylate:



We were particularly interested in finding out whether the nitrogen atom was coordinatively bonding to zinc. The results of the X-ray analysis are conclusive and show that, apart from the two carboxylate oxygens, two further oxygen atoms (from the two molecules of water of crystallization) and not nitrogen are coordinatively bonded by the central zinc atom. The configuration is strained tetrahedral. Figure 4 is a projection of the structure found whereby the two zinc-carboxylate oxygen bonds are perpendicular to the plane of the paper. It can readily be seen that the pyrrolidone nitrogen is very far away from the central zinc atom apart from the fact that the pyrrolidone ring is apparently planar so that the nitrogen lone electron pair would most probably be conjugating with the adjacent carbonyl group.

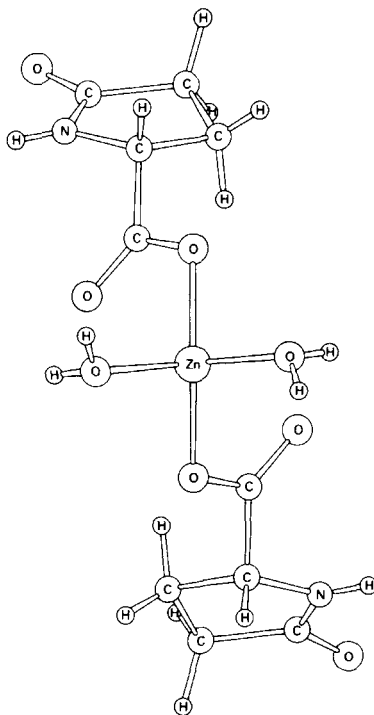


Fig. 4. Zinc-pyrrolidone-carboxylate. Projection of structure whereby the two zinc-carboxylate oxygen bonds are perpendicular to the plane of the paper.



**DISCUSSION: REACTION MECHANISM**

In discussing possible reaction mechanisms for the epoxy/Complex A reaction we have to bear in mind that we have two separate sets of experimental observations which the suggested reaction mechanism will have to account for. Taking the two borderline Complex A concentrations of 200 and 10 phr we have in the first case a very fast reaction leading to an extremely flexible product with a very low transition temperature and in the latter case a slow reaction leading to a rigid product with a high transition temperature. Considering the building blocks involved and their respective concentrations, these facts point towards an accelerated amine/epoxy polyaddition reaction in the first case and in the second to homopolymerization of the epoxy resin. In the following discussion we shall refer to these two borderline reactions as "polyaddition" and "homopolymerization."

**A. Polyaddition Reaction**

Taking the experimental observation that this reaction leads to a final structure whereby two epoxy moieties are obviously being crosslinked by a polyoxypropylene diamine as a starting point, the first question to be resolved is whether Complex A reacts per se or whether it decomposes, thereby leading to a separate reaction between the epoxy resin and the thus liberated amine.

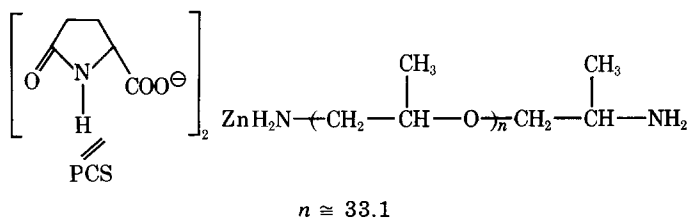
The use of metal salt-amine complexes as latent curing catalysts for epoxy resins is, as had been already mentioned, known, and the complexes are indeed supposed to decompose at temperatures between 60 and 200°C, liberating the amine.<sup>11</sup> We do not believe that this is the case with Complex A. The main reason for this belief is direct experimental evidence: The complex is thermally stable up to approximately 200°C, at which temperature some liberation of amine takes place. This fact alone would thus seem to rule out a purely thermal decomposition (the "polyaddition" reaction is completed at a temperature of 140°C); it would not, however, preclude a decomposition in the presence of the epoxy resin. We have investigated this last possibility in detail by comparing the two formulations GY 250 + 200 phr Complex A = I and GY 250 + equivalent amounts of pyrrolidonecarboxylic acid zinc salt and Jeffamine D 2000 (27.8 and 172.2 phr, respectively) = II. Formulations I and II quite clearly exhibit different reactivities and different physical properties:

	I	II
Gel time at 120°C	9 min	12 min 30 s
Cure 2 h 100°C + 4 h 140°C:		
Tensile strength (N/mm <sup>2</sup> )	2.1	1.0
95% range	1.9-2.3	0.9-1.1
Water absorption		
4 days at room temperature (%)	4.7	7.1

We shall therefore assume that Complex A reacts with the epoxy resin per se. From this point onwards the next step would be to consider the structure of Complex A with a view to integrating this structure into a possible reaction mechanism.

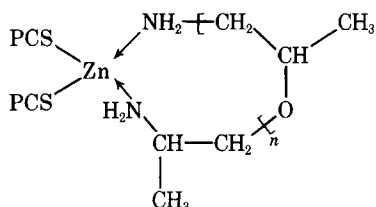
The formula of Complex A, as substantiated by elementary analysis and C<sup>13</sup>

NMR, is



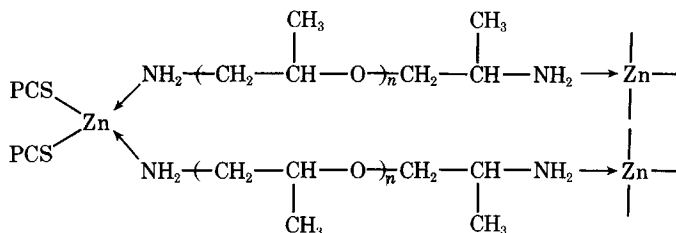
Our X-ray analysis of zinc-pyrrolidone-carboxylate (PCS) dihydrate has shown this compound to have a strained tetrahedral configuration in which the central zinc atom is directly linked to four oxygen atoms, two each belonging to the two PCS carboxylate groups and the two water molecules of crystallization. If we assume the same tetracoordinate configuration for Complex A, the following structures might be possible:

*Variant No. 1*



In this variant we would assume that zinc is simultaneously bonded to both amine nitrogens. The Zn-N bond is approximately 2 Å long and the van der Waals distances between zinc and other molecules between 3.5 and 4 Å. The total length of the diamine chain is approximately 110 Å. It seems therefore, rather improbable that the nitrogen at the end of the diamine chain would, at a given point in time, be close enough to the same zinc atom in order to bond with it.

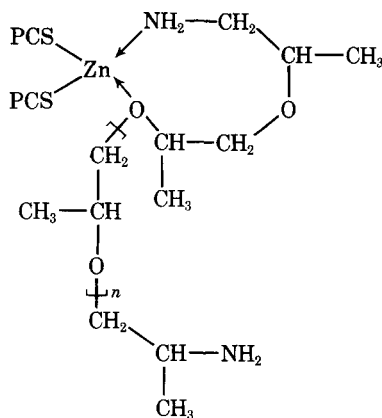
*Variant No. 2*



Here the central zinc atom would be simultaneously bonded to nitrogen atoms belonging to two separate diamine molecules.

## Variant No. 3

The diamine ligand also contains oxygen atoms so that the following structure should also be a possibility:

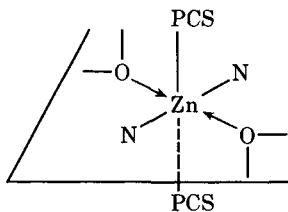


From a crystallographical point of view variant no. 2 would seem to be most probable.

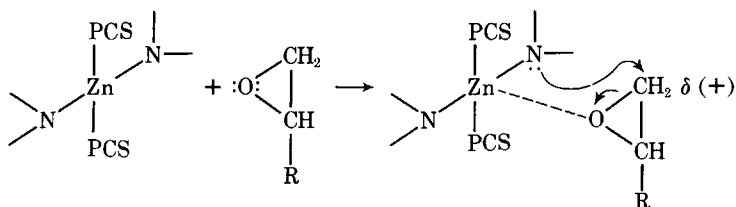
Complex A contains a residual 0,5 mol of water. The water molecules could be partly present in all three suggested variants as a fifth ligand, and indeed pentacoordination is apparently especially common for zinc.<sup>14,15</sup> Alternatively the water could take the place of an  $\text{-NH}_2$  group.

In conclusion, therefore, we feel that a tetrahedral configuration in which the central zinc atom is directly linked to two PCS radicals and to two amine nitrogens (from separate diamine molecules) is most probable for Complex A and shall continue with this structure in the following discussion. (The further consideration of all possible structures mentioned, i.e., the accommodation of residual water is not essential for the development of our suggested reaction mechanism).

In the tetracoordinate zinc complex, which we are therefore taking as a starting point for our discussion of a possible reaction mechanism, we will assume that the two primary amine nitrogen ligands occupy positions similar to those occupied by the water molecules in zinc-pyrrolidone-carboxylate, viz., in a plane approximately perpendicular to the  $\text{Zn}(\text{PCS})_2$ -axis. Epoxy oxygen should now be able to approach the complex, the point of attraction being the electropositive central zinc atom. If one epoxy group were involved, a pentacoordinate intermediate would be formed, and, if two epoxy groups were able to approach simultaneously, a hexacoordinate intermediate would be formed thus:



When the oxygen coordinates with the central zinc atom, it will be contributing a portion of its electrons to the coordinate bond. This means that the oxygen atom will acquire a partial positive charge, thereby causing a partial shift of electrons from an adjacent carbon atom of the epoxy ring. The electron deficiency thus created at the epoxy carbon atom would be a point of attack for the nearby nucleophilic nitrogen atom of the amine and an amine/epoxy reaction could now take place. The overall reaction would, therefore, be a Lewis acid accelerated amine/epoxy reaction with, possibly, a hexacoordinate  $Zn(PCS)_2$ /amine/epoxy complex as the reaction intermediate:



## B. Homopolymerization

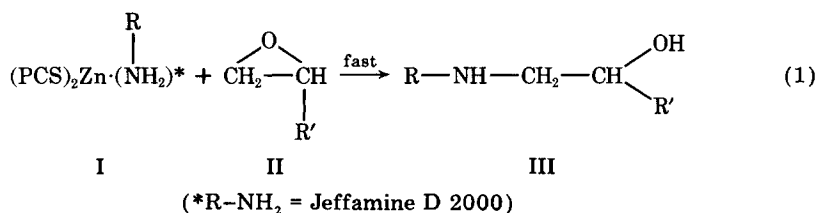
Here again the discussion may be started by considering a possible decomposition of Complex A during the reaction with the epoxy resin. The fact that Complex A is thermally stable up to approximately 200°C is less convincing here because the epoxy/Complex A reaction requires a postcure temperature of 180°C so that at least a partial decomposition of the complex would seem plausible. As in the case of the "polyaddition" reaction, we have investigated this possibility by comparing GY 250 formulations with (a) 10 phr Complex A and (b) equivalent amounts of pyrrolidincarboxylic acid zinc salt and Jeffamine D 2000 (1.38 and 8.62 phr, respectively). As before, at a Complex A level of 200 phr the complex reacted much faster than equivalent amounts of its components and led to a cured product with completely different properties:

	a	b
Cure cycle 2 h 160°C + 8 h 180°C:		
Heat distortion temperature (Martens DIN 55458)	124°C	41°C
Dielectric loss factor $\tan \delta$ :		
1% value	150°C	42°C
10% value	200°C	166°C

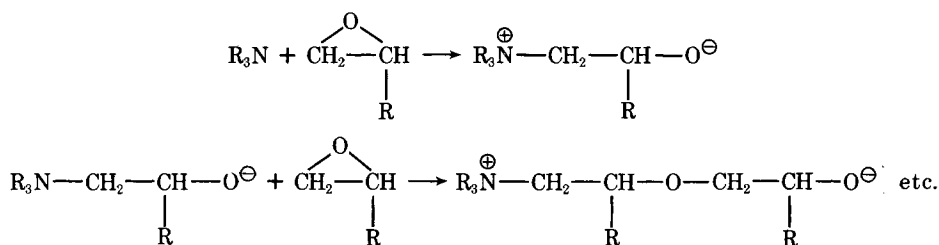
It would seem therefore that once again Complex A per se reacts with the epoxy resin. The next step would be to suggest possible ways in which Complex A might initiate the homopolymerization of the epoxy resin.

In discussing the "polyaddition" reaction at high Complex A concentrations, we proposed a Complex A/epoxy/amine reaction sequence which agreed well with the observed reactivity and end properties of the borderline formulation under discussion. We see no reason why this same reaction sequence should not take place when lower concentrations of Complex A are used. The net result is the

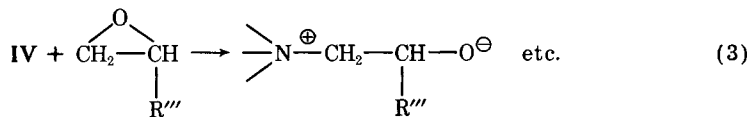
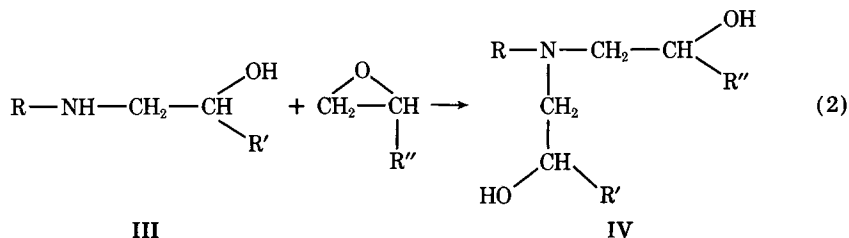
formation of a secondary amine epoxy adduct:



which is in accordance with the well-established reaction scheme for the epoxy/amine reaction.<sup>16-18</sup> The anionic homopolymerization of epoxy resins via secondary amines is well known.<sup>19</sup> The initiating effect is possibly due to the tertiary amine nitrogen which would be formed when the secondary amine has reacted again with epoxy, i.e., in effect a Lewis-base-induced anionic polymerization reaction:<sup>20</sup>



We suggest that a similar reaction sequence takes place at the borderline concentration of 10 phr Complex A, i.e.,



We would expect reaction (2) to be slower than reaction (1) and reaction (3) and the subsequent propagation reaction to proceed quite slowly.

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Received December 24, 1980

Accepted May 21, 1981