

# Synthesis of Diglycidylesters with Alicyclic Imide Structure and Their Thermal and Tertiary Amine Catalyzed Curing

M. GALIÀ, A. SERRA, A. MANTECÓN, and V. CÁDIZ\*

Universitat Rovira i Virgili, Departament de Química (Q. Orgànica), Facultat de Química, Plaça Imperial Tàrraco 1, 43005 Tarragona, Spain

## SYNOPSIS

The synthesis of new diglycidylester compounds with bicyclo[2.2.2]oct-7-ene units was carried out from the previously synthesized diimide-diacids and epichlorohydrin in excess using BTMA as catalyst. These compounds were characterized by spectroscopic techniques and have been cured either thermally or using 4-dimethylaminopyridine as tertiary amine catalyst. The study of curing reaction was carried out through thermal analysis of the reaction by differential scanning calorimetry (DSC). The concentration of the tertiary amine affects the reaction mechanism of epoxide curing, but it does not influence the thermal properties of the final product. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Epoxy resins crosslinked with several curing agents have been widely described in the literature because of their applications in different fields as castings and laminates.<sup>1</sup>

In the last years, numerous studies<sup>2,3</sup> have focused on the determination of the relationships between the chemical structure and the properties of different epoxy networks used for composite materials. However, such studies were usually carried out with commercial resins such as bisphenol A diglycidyl ether or model compounds,<sup>4-6</sup> but only few references can be found in the literature<sup>7</sup> about the curing of diglycidylesters that are important for the fabrication of electroinsulators.

Interest in the kinetics and mechanism of curing of epoxy resins largely derives from the usage of these materials. Chemical reactions that take place during cure determine the properties of the cured materials. The understanding of the mechanism and the kinetics is essential to design a model of curing process that allows us to predict the final properties of the cured material. A good model must predict too the behavior of the system during cure.

In order to improve the thermal stability, toughness, and processability of the existing thermoset resins, blending or structural modifications have been used in the past. With this aim, we have synthesized several diglycidyl compounds containing imide units (Scheme 1) that improve the thermal properties of the commercial epoxy resins and aliphatic moieties to increase the processability of the material. The imide unit introduced is a derivative of bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride and contributes also to enhance this processability. These compounds have been crosslinked either thermal or using a tertiary amine, 4-dimethylaminopyridine (DMAP), as a catalyst.

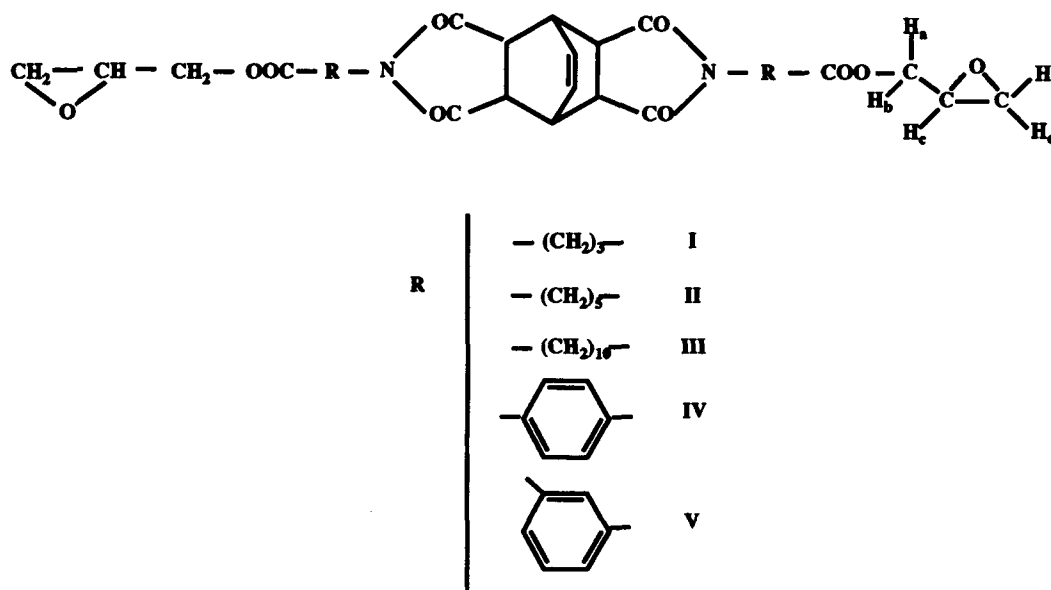
Among the techniques used to investigate the kinetics and mechanism of crosslinking, differential scanning calorimetry (DSC) has been widely developed to follow the cure reaction. In this work, we used DSC techniques, using the basic assumption that the heat evolution monitored in a DSC experiment is proportional to the extent of the reaction.

## EXPERIMENTAL

### Reagents

Bicyclo[2.2.2]oct-7-ene-tetracarboxylic dianhydride (Aldrich), 4-aminobenzoic acid (Fluka), 3-aminobenzoic acid (Merck), 11-aminoundecanoic acid

\* To whom correspondence should be addressed.



Scheme 1

(Aldrich), 6-aminohexanoic acid (Fluka), 4-aminobutanoic acid (Fluka), epichlorohydrin (Scharlau), benzyltrimethylammonium bromide (BTMA, Fluka), and 4-dimethylaminopyridine (DMAP, Fluka) were used without further purification. All solvents were purified by standard procedures.

### Synthesis of Imide Derivatives

A typical run is as follows: 0.1 mol of dianhydride, 0.2 mol of aminoacid, 100 mL of DMF, and 50 mL of benzene were introduced in a flask equipped with a thermometer, a Dean-Stark condenser, and a magnetic stirrer. The solution was heated under reflux until no water was evolved, and then the benzene was eliminated by distillation. The product was separated from the medium by filtration or precipitation in an ice-water mixture. The filtered product was washed with distilled water and dried in vacuum.

### Synthesis of Diglycidyl Compounds

The following procedure illustrates the method used to prepare glycidyl compounds: a mixture of epichlorohydrin (6 mol) and diimide-diacid (0.1 mol) was heated to 110°C and solid benzyltrimethylammonium bromide (0.01 mol) was added in one batch. The mixture was heated to reflux temperature and the reaction was controlled by TLC (toluene/acetone, proportion depending on the product) until disappearance of the initial material. After cooling at room temperature, the final product was washed

twice with water in a separating funnel. The properties of oxiranic monomers are outlined in Table I.

### Instrumentation

Infrared (IR) spectra were recorded on a Nicolet 5ZDX FT-IR spectrometer, <sup>13</sup>C-NMR spectra were obtained using Gemini 300 spectrometer with CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as solvents and TMS as internal standard. Elemental analyses were carried out in a Carlo Erba 1106 device.

Calorimetric studies were carried out on a Mettler DSC-30 thermal analyzer in covered Al pans under N<sub>2</sub>, at various heating rates (5–20°C/min). The epoxy resin was kept in vacuum at 60°C for about 24 h to remove moisture. Then the resin or the mixture of about 5 mg of known weight of the epoxy with a suitable amount of DMAP was put into an aluminum pan. Crosslinking experiments were carried out at several temperatures for 15 min. After the isothermal treatment was complete, the sample was cooled to room temperature and cured polymer *T<sub>g</sub>* and residual enthalpy of curing (if present) were tested in a dynamic experiment. Thermogravimetric analyses (TGA) were carried out with a Perkin-Elmer TGA-7 system in N<sub>2</sub>.

### RESULTS AND DISCUSSION

The first part of this work was the synthesis of the diimide-diacids from bicyclo[2.2.2]oct-7-ene-2,3,5,6-

Table I Synthesis of Diglycidyl Compounds

Compound	I	II	III	IV	V
Yield (%)	93	88	91	98	88
mp (°C)	—	—	98–99	246–247	238–239
Elemental analyses (%) <sup>a</sup>					
C	57.12 (58.87)	59.96 (61.43)	65.41 (66.12)	63.55 (64.21)	63.75 (64.21)
H	5.42 (5.66)	6.36 (6.48)	8.15 (8.24)	4.23 (4.35)	4.31 (4.35)
N	4.97 (5.28)	4.49 (4.78)	3.96 (3.86)	4.53 (4.68)	4.67 (4.68)
IR ( $\nu$ , cm <sup>-1</sup> ) KBr, NaCl	1767, 1725, 1691, 909, 732	1762, 1727, 1700, 910, 729	1767, 1721, 1703, 903, 720	1780, 1700, 1600, 1510, 910, 720	1777, 1723, 1703, 1515, 910, 753
<sup>1</sup> H NMR (DMSO-d <sub>6</sub> , TMS) $\delta$ , (ppm)	6.0(2H, t), 4.3(2H, dd), 3.8(2H, dd), 3.4(2H, m), 3.3(6H, m), 3.1(4H, m), 2.7(2H, t), 2.6(2H, dd), 2.2(4H, t), 1.6(4H, m)	6.0(2H, t), 4.3(2H, dd), 3.8(2H, dd), 3.3(4H, m), 3.2(4H, t), 3.1(4H, m), 2.7(2H, t), 2.6(2H, dd), 2.3(4H, m), 1.5(4H, m), 1.3(4H, m), 1.1(4H, m)	6.0(2H, t), 4.3(2H, dd), 3.8(2H, dd), 3.4(2H, m), 3.2(4H, t), 3.1(6H, m), 2.7(2H, t), 2.6(2H, dd), 2.3(4H, t), 1.5(4H, m), 1.3(4H, m), 1.2(24H, m)	8.1(4H, d), 7.4(4H, d), 6.3(2H, t), 4.6(2H, dd), 4.1(2H, dd), 3.6(2H, s), 3.5(4H, s), 3.3(2H, m), 2.8(2H, t), 2.7(2H, dd)	8.0(2H, d), 7.8(2H, s), 7.6(2H, t), 7.5(2H, s), 6.4(2H, t), 4.7(2H, dd), 3.6(2H, m), 3.5(4H, m), 3.4(2H, m), 2.8(2H, t), 2.7(2H, dd)
Coupling constants of glycidyl H (Hz) <sup>b</sup>					
$J_{ab}$	12.3	12.4	12.3	12.4	12.4
$J_{bc}$	6.4	6.6	6.4	6.4	6.6
$J_{ac}$	2.7	2.8	2.8	2.6	2.5
$J_{de}$	5.1	5.0	5.1	5.0	4.9
$J_{cd}$	4.5	4.5	4.5	4.3	4.6
$J_{ce}$	2.6	2.7	2.6	2.6	2.6
<sup>13</sup> C NMR (DMSO-d <sub>6</sub> , TMS) $\delta$ , (ppm)	177.3(s), 171.8(s), 130.6(d), 64.6(t), 48.8(d), 46.2(t), 42.1(d), 36.9(t), 33.3(d), 30.2(t), 22.2(t)	177.4(s), 172.6(s), 130.6(d), 64.6(t), 43.8(t), 42.2(d), 37.7(t), 33.4(d), 33.1(t), 26.7(t), 25.5(t), 23.8(t)	177.1(s), 172.4(s), 130.4(t), 64.4(t), 48.6(d), 42.1(d), 37.7(t), 33.3(d), 33.2(t), 28.6(t), 28.4(t), 28.2(t), 26.8(t), 25.9(t), 24.2(t)	176.3(s), 164.7(s), 136.3(s), 131.1(d), 129.9(d), 129.0(s), 127.0(d), 65.6(t), 49.0(d), 43.5(t), 42.5(d), 34.0(d)	176.5(s), 164.6(s), 132.5(s), 131.8(d), 131.2(d), 130.2(s), 129.3(d), 127.4(d), 65.8(t), 48.9(d), 43.4(t), 42.6(d), 34.0(d)

<sup>a</sup> Theoretical values in brackets.<sup>b</sup> See Scheme 1.

tetracarboxylic dianhydride and the corresponding amino acid. Diglycidylesters were obtained in high yields by reaction of the diimide-diacids and epi-

chlorohydrin using BTMA as catalyst, in a similar way as previously reported.<sup>8</sup> The diglycidyl compounds were characterized by elemental analyses

and IR and nuclear magnetic resonance (NMR) spectroscopy. The results are collected in Table I. As can be seen, when *R* is aromatic or a long aliphatic chain, the diglycidyl compounds (III, IV, and V) are solids with definite melting points. On the other hand, when *R* are shorter aliphatic chains, the diglycidyl compounds (I, II) are liquid at room temperature. IR and NMR data are in agreement with the proposed structures.

Preliminary DSC experiments showed that all diglycidyl compounds were capable of crosslinking without catalysts or hardeners, so the curing reaction of pure compounds was studied.

DSC thermograms of rate of heat evolution as a function of the temperature at different heating rates for compound III is shown in Figure 1. The endothermic melting peak appears at 98.7°C and the curing reaction begins after the baseline is recovered at about 300°C. In Table II the peak temperature of the curing reactions for all diglycidyl compounds are collected. This maximum seems to be independent of the structure of the *R* introduced.

It was proposed<sup>9</sup> that bicyclo[2.2.2]oct-7-ene structure may undergo a retrodegradative Diels-Alder reaction (retro D-A) that commences around

360°C in nitrogen. Keeping in mind these facts, it can be postulated that the process of Scheme 2 occurs leading to the formation of the corresponding maleimide and diene derivatives.

In all TGA curves only a slight weight loss about 360–380°C can be observed that could be related to the aforesaid retro D-A reaction. The TGA plot corresponding to III is shown in Figure 2(a). The main fragmentation products and other diene compounds do not involve weight loss because of their low volatility and/or formation of nonvolatile polymeric compounds. Thus, the above fragmentation products could be incorporated to the growing network by reaction of oxirane ring. Since this process overlaps with the crosslinking reaction monitored by DSC, measured enthalpy values are not accurate. Therefore, the variation of the maximum exotherm temperature ( $T_{\max}$ ) as a function of heating rate ( $\nu$ ) was the only method used. The shift of  $T_{\max}$  with  $\nu$  for III can be observed in Figure 1. By plotting  $\ln \nu$  vs.  $1/T_{\max}$  at different heating rates (5, 10, 15, and 20°C/min) using the following equation (Fig. 3):

$$E_a = \frac{-R\Delta \ln \nu}{1.052\Delta(1/T_{\max})}$$

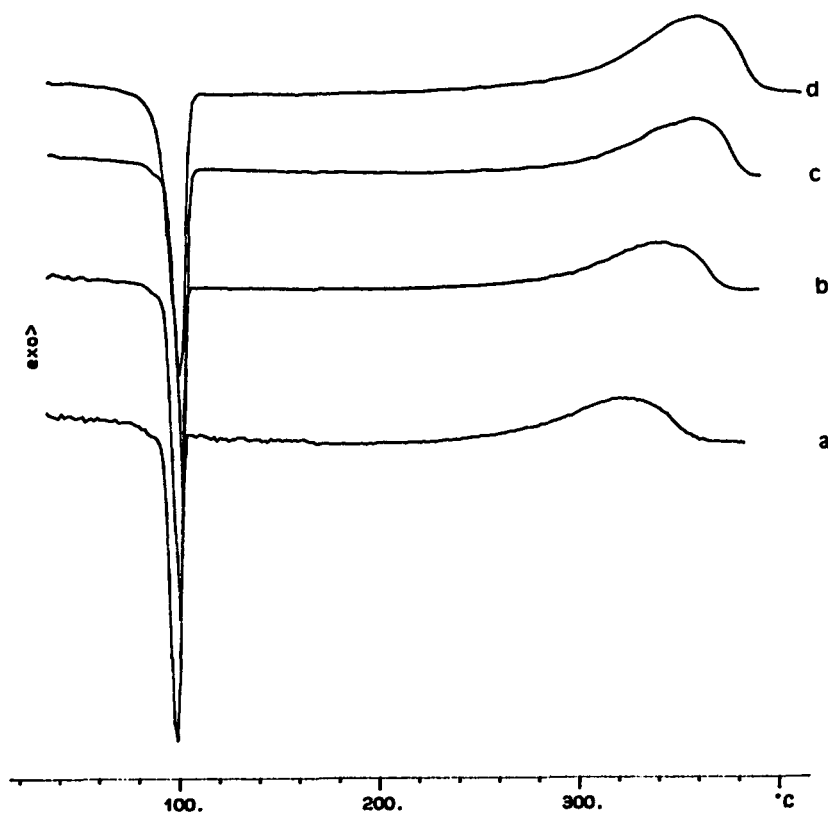


Figure 1 DSC plots of compound III: (a) 5, (b) 10, (c) 15, and (d) 20°C/min.

**Table II** Crosslinking of Diglycidyl Compounds

Compound	I	II	III	IV	V
$T_{max}$ (°C)	333	318	360	332	354
$E_a$ (kJ/mol)	104	133	104	129	111
$T_g$ (°C)	123	56	29	273	232
Crosslinking $T$ (°C)	$T_g$	$T_g$	$T_g$	$T_g$	$T_g$
280	—	35	—	190	—
290	92	43	—	243	—
300	103	48	10	276	195
310	108	53	26	—	208
320	122	—	28	—	235

the activation energy ( $E_a$ ) of the curing process can be calculated. The values obtained for all glycidyl compounds are collected in Table II. The activation energy values (104–133 kJ/mol) are comparable to the value previously reported for another diglycidyl-diimide compound.<sup>10</sup>

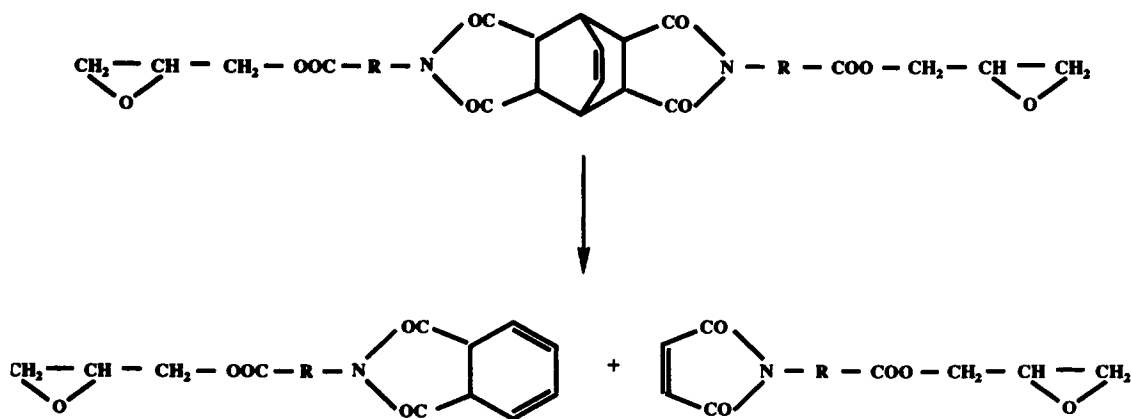
As to the curing mechanism, the reaction can begin by the opening of the oxirane ring due to attack by the imide nitrogen or, more probably due to hydroxylic or carboxylic groups, capable of behaving as catalysts.<sup>11</sup> The absence of catalysts or specific hardeners explains the high activation energies found.

In a second dynamic DSC run, the  $T_g$  values of the cured polymers could be evaluated. These values, collected in Table II, may be related to the different structures of the network if we assume that the degree of crosslinking reached is similar. An increase of about 240°C is observed due to the higher rigidity in the chains which contain aromatic rings related to the one which contains the longest aliphatic chain.

A sensitive and practical parameter to follow the

cure of reactive thermosetting systems is  $T_g$ . The most common approach is to relate the  $T_g$  of a crosslinked system to the overall conversion,<sup>12</sup> although it is accepted that the variation in  $T_g$  is attributed to various molecular parameters such as the molecular weight, the stiffness of the crosslinked chains and the free volume entrapped in the network. In the curing process of epoxide compounds, linear polymerization and crosslinking occurs, leading to an increase in the molecular weight. Also, both reactions influences the stiffness of the network. The  $T_g$  values of the polymers after isothermal treatment at several temperatures during 15 min cures are shown in Table II. These isothermal experiments make possible to reach a different degree of cure and prevent the decomposition of the polymer, ensuring that the values found for the crosslinked polymer are not affected by the degradation. In a second dynamic DSC run, the  $T_g$  values of the crosslinked polymers and the residual enthalpy of curing (if existing) were monitored. Longer times were tested but no differences of  $T_g$  were observed. The isothermal temperatures were selected from the previous dynamic experiments and increased until the maximum  $T_g$  value was reached for each polymer. As can be seen in the same table, the maximum  $T_g$  values for each polymer are reached at different crosslinking temperatures. Residual enthalpy was observed when the diglycidyl monomers contain the longer aliphatic moieties (II and III). This fact seems to suggest that the crosslinked network is flexible enough to facilitate further reactions at higher temperatures, in accordance with the above-mentioned retro D–A process.

The results obtained by TGA are shown in Table III. From the TG traces, the relative stability of the cured resins was assessed by noting the initial de-



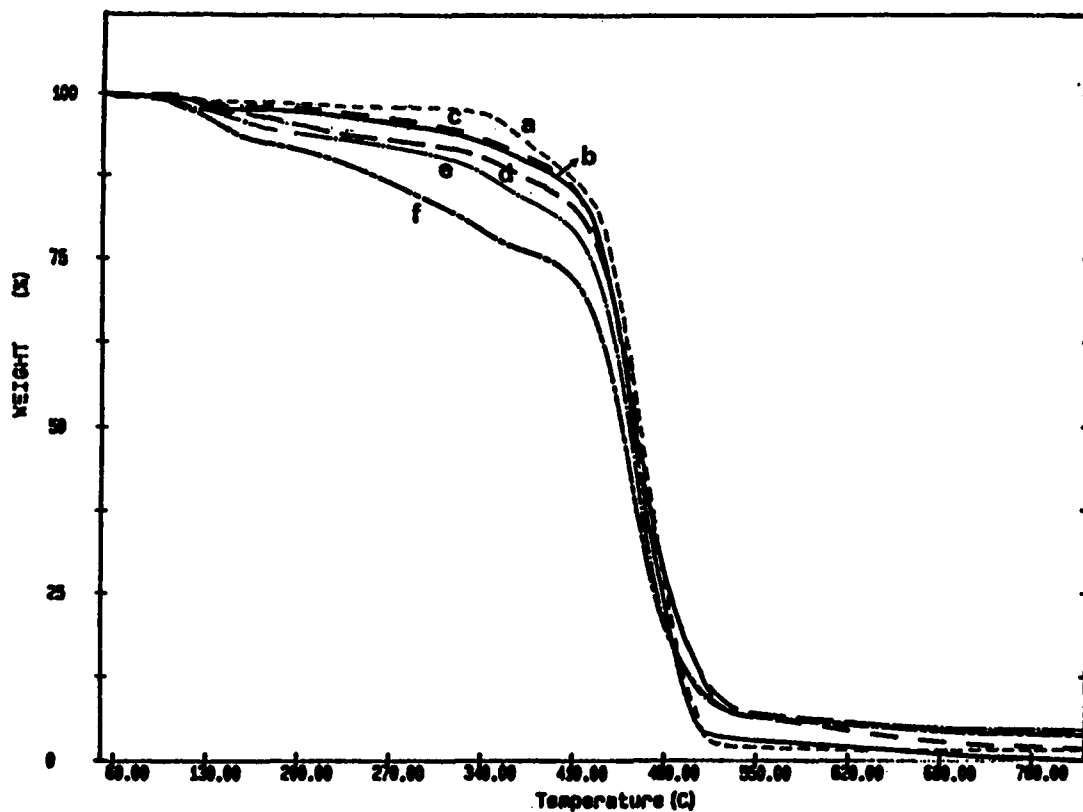


Figure 2 TGA plots of compound III: (a) without catalyst, with DMAP, (b) 0.5, (c) 1, (d) 5, (e) 10, and (f) 20 phr of catalyst ( $N_2$ ,  $10^\circ C/min$ ).

composition temperature ( $T_i$ ) and the temperature corresponding to the 10% weight loss ( $T_{10\%}$ ). From the differential thermogravimetric (DTG) traces, temperature of maximum rate of weight loss ( $T_{max}$ ) and rate of weight loss at this temperature were de-

termined ( $dW/dt$ ). As can be seen, major weight loss was observed above  $450^\circ C$ . When  $R$  was  $-(CH_2)_5-$  and  $-(CH_2)_3-$ , resins were liquid at room temperature, and weight loss was observed at slightly lower temperatures. The char yield at

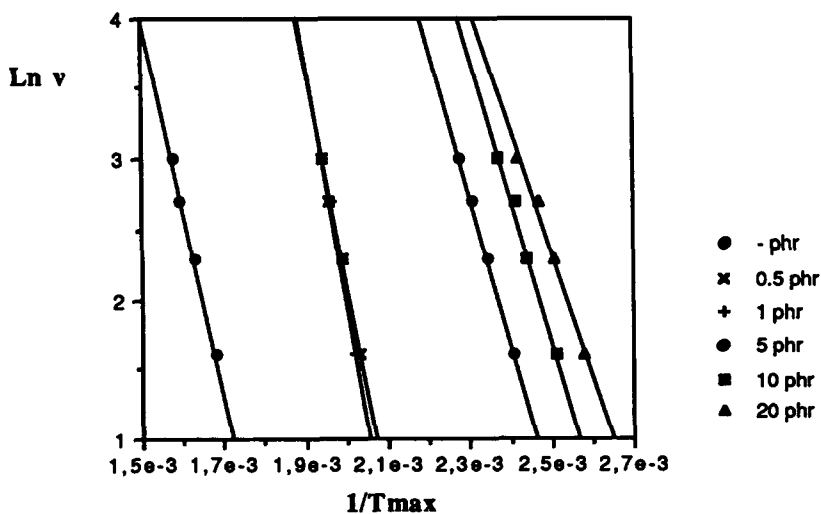


Figure 3 Ozawa plot for the crosslinking reaction of compound III.

**Table III TGA Data of the Crosslinked Diglycidylesters<sup>a</sup>**

Compound	I	II	III	IV	V
$T_i$ (°C)	343	337	358	359	347
$T_{10\%}$ (°C)	362	365	389	398	394
$T_{max}$ (°C)	451	457	472	468	469
$dW/dt$ (%/min)	11	9	23	59	26
$Y_{700^\circ\text{C}}$ (%)	11	6	1	23	19

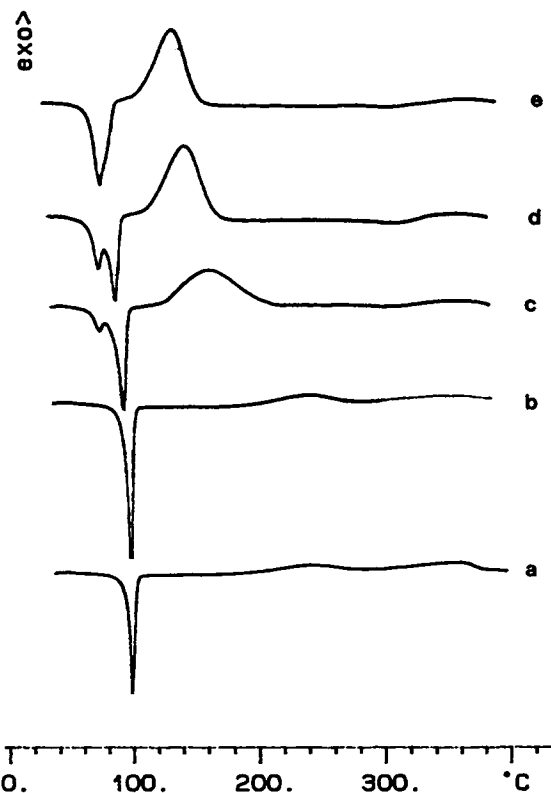
<sup>a</sup> Obtained at 20°C/min.

700°C ( $Y_{700^\circ\text{C}}$ ) in cured resins was affected by the composition. The presence of aromatic moieties in the resin formulation resulted in an increase in char yield.

Amines have been important curing agents for the curing reactions of epoxides. While primary and secondary amines play the same role in the curing reaction, tertiary amines act differently.<sup>13</sup> Recently, a reaction mechanism has been proposed for this kind of reaction,<sup>14</sup> which shows different reaction types between high and low concentrations of the tertiary amine catalyst. The first step is the opening of the oxirane ring by the amine followed by an homopolymerization reaction. On the other hand, at high concentration of tertiary amine, the epoxide group could be catalyzed by this amine for isomerization to occur and also to form allyl alcohol, which acts as a proton donor. Then, the allyl alcohol, tertiary amine, and epoxide group react together to form an active complex and to proceed to polymerization. In contrast, at a low concentration of tertiary amine, these last steps could be negligible.

We have tested how the addition of catalytic amounts of tertiary amine influences the crosslinking behavior of the above glycidyl compounds in order to improve their processability. Overall study was carried out using the diglycidyl compound III and several concentrations of 4-dimethylaminopyridine (0.5, 1, 5, 10, and 20 phr). The DSC curves are shown in Figure 4. As can be seen, two melting endotherms appear for 5 phr with peak temperatures at 76 and 96°C. The enthalpy of the former increases for 10 phr, and for 20 phr only a broad endotherm can be observed at 81°C. Moreover, exotherms attributed to crosslinking process appear at different temperatures. In Table IV, the peak temperatures of dynamic DSC curves and the measured enthalpy values are collected.

The DSC curve for 0.5 phr shows two separate exotherms after the melting process. One of them appears at the same temperature as above described



**Figure 4** DSC crosslinking plots of compound III and DMAP: (a) 0.5, (b) 1, (c) 5, (d) 10, and (e) 20 phr of catalyst (20°C/min).

when thermal curing occurs; the other one, at lower temperature, is attributed to amine-catalyzed curing. When amine catalyst concentration was increased only this latter process is observed. The higher the amine concentration, the lower is the peak temperature of the curing reactions and the higher is the curing enthalpy. In all cases, about 350°C, a slight deviation of DSC baseline may be observed which can be related to the retrodegradative Diels–Alder process mentioned above.

**Table IV Crosslinking of Diglycidyl Compound III Using DMAP as Catalyst<sup>a</sup>**

DMAP (phr)	0.5	1	5	10	20
$T_m$ (°C) <sup>b</sup>	97	97	76, 96	76, 91	81
$T_{max}$ (°C) <sup>c</sup>	242	234	167	148	140
$\Delta H$ (J/g)	52	93	191	225	248
$E_a$ (kJ/mol)	123	139	85	82	70
$T_g$ (°C)	32	17	33	37	30

<sup>a</sup> Values obtained at 20°C/min.

<sup>b</sup> Maximum temperature of the melting endotherm.

<sup>c</sup> Maximum temperature of the crosslinking exotherm.

**Table V TGA Data of the Crosslinked Diglycidyl Compound III Using DMAP as Catalyst<sup>a</sup>**

DMAP (phr)	0.5	1	5	10	20
$T_i$ (°C)	351	342	321	315	306
$T_{10\%}$ (°C)	371	379	345	334	326
$T_{max}$ (°C)	452	457	459	456	453
$dW/dt$ (%/min)	13	12	11	13	11
$Y_{700^\circ\text{C}}$ (%)	1	3	5	5	5

<sup>a</sup> Obtained at 10°C/min.

As a first approach, the Ozawa<sup>14</sup> method has been used to calculate the activation energies for the amine-catalyzed process. The values obtained are collected in Table IV. As can be seen, these values undergo a noteworthy decrease when the amine concentration increases in accordance to the above-mentioned mechanism. This variation is considerable in contrast to data reported for diglycidylether of bisphenol A and benzyldimethylamine.<sup>15</sup>

In a second dynamic DSC run, the  $T_g$  values of the crosslinked polymers were monitored. As can be seen in Table IV, similar  $T_g$  values were obtained when different amounts of amine were used and the crosslinking was carried out thermally. Finally, in Table V, TGA data of amine-catalyzed crosslinked polymers are collected. As can be seen in Figure 2, where these curves are shown, it is worth pointing out that in all cases a certain weight loss takes place in the curing process at lower temperature which reveal the formation of volatiles in this process. The main degradation temperature as well as the char yield at 700°C are comparable to the ones obtained for thermal curing.

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