

# The Boron Trifluoride Monoethyl Amine Complex Cured Epoxy Resins

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## Synopsis

The curing exotherm pattern is affected by the equivalent ratio of curing agent, boron trifluoride monoethylamine complex ( $\text{BF}_3 \cdot \text{MEA}$ ), to epoxy resin. The diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF) cures more slowly than the diglycidyl ether of bisphenol A (Epon 828). The glass transition temperatures ( $T_g$ 's) of  $\text{BF}_3 \cdot \text{MEA}$  cured Epon 828 are increased with increasing concentration of curing agent (0.0450–0.1350 eq.). Their char yields do not show a similar relationship. Char yields and  $T_g$ 's are increased by the increasing amount of curing agent for  $\text{BF}_3 \cdot \text{MEA}$  (0.0450–0.1350 eq.) cured DGEBF. The activation energies for the thermal decomposition for  $\text{BF}_3 \cdot \text{MEA}$  (0.0450 eq./epoxy eq.) cured Epon 828 and DGEBF are almost equivalent 43 and 44 kcal/mol, respectively. DGEBF when added to DGEBA improves the  $T_g$  and char yield with the  $\text{BF}_3 \cdot \text{MEA}$  curing system. The  $T_g$  of both resin systems can be increased by longer post cure, whereas the char yield does not appear to change significantly. No ester group formation is found for the  $\text{BF}_3 \cdot \text{MEA}$ -cured DGEBF, although this has been previously reported for the DGEBA system. The  $\text{BF}_3 \cdot \text{MEA}$  cure at 120°C is better than at 140°C because of vaporization and degradation of the curing agent at the higher temperature. The rapid gelation of the epoxy resin may be another reason for the lower degree of cure at high temperature.

## INTRODUCTION

Boron trifluoride monoethylamine complex ( $\text{BF}_3 \cdot \text{MEA}$ ) has been employed as an epoxy resin curing agent for coating,<sup>1</sup> varnishes,<sup>2</sup> electric insulation,<sup>3</sup> epoxy foam,<sup>4</sup> finishing of polyvinyl chloride (PVC) leather substitutes,<sup>5</sup> and glass fiber reinforcing material.<sup>6</sup> The  $\text{BF}_3 \cdot \text{MEA}$  cured epoxy resins have good strength, heat resistance, and electrical properties.  $\text{BF}_3 \cdot \text{MEA}$  can be used as a primary curing agent or a cocuring agent for epoxy resins. It reacts as a semilattent catalyst and provides long pot life for epoxy resins. It can also work as an accelerator for diaminodiphenyl sulfone (DDS)-cured epoxy resins.<sup>7</sup>

Epoxy resin, anhydride, and  $\text{BF}_3 \cdot \text{MEA}$  are combined together to yield free-flowing powders which remain stable on storage, yet fuse and cure rapidly to tough durable coatings<sup>1</sup> at moderately elevated temperatures. Varnishes<sup>2</sup> for prepregs are prepared from poly(*p*-hydroxystyrene), epoxy resin, and  $\text{BF}_3 \cdot \text{MEA}$ . Thus, glass cloths have been impregnated with this varnish. They can be further pressed between two copper foils to prepare a laminate. Electrical coils are insulated by winding with mica tape, vacuum pressure impregnated with epoxy resins containing  $\text{BF}_3 \cdot \text{MEA}$  curing agents, and then further heated for complete curing.  $\text{BF}_3 \cdot \text{MEA}$  and trimethoxyboroxine work as curing agent to react with epoxy resins for the preparation of epoxy foams.<sup>4</sup>

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$\text{BF}_3 \cdot \text{MEA}$  can be formulated with copolymer (diglycidyl ether of bisphenol A-sebacic acid) to finish PVC leather substitutes.  $\text{BF}_3 \cdot \text{MEA}$  mixes with suitable epoxy resins as binders for glass fiber reinforced plastic applications,<sup>6</sup> which show good strength, heat resistance, and electrical properties. The activation energies<sup>8</sup> of gelling epoxy with 0.03–0.093 mol of  $\text{BF}_3 \cdot \text{MEA}$  is 23 kcal/mol. The polymerization reaction is exothermic with a maximum polymerization temperature (the temperature at which the rate of polymerization is the fastest) at 130°C<sup>8</sup> (148°C,<sup>9</sup> 166°C,<sup>10</sup> or 178°C<sup>11</sup>). (These differences are probably due to different ratios of curing agent to different epoxy resins). Pfann and Kopacki<sup>11</sup> have found that 3 parts of  $\text{BF}_3 \cdot \text{MEA}$  mixed with 100 parts of Epon 828 gives an exotherm peak at 178°C, and after cure is transparent and yellow.  $\text{BF}_3 \cdot \text{MEA}$  is used extensively since it is not easily affected by moisture. Maximized mechanical and thermomechanical properties are usually obtained by using 0.05–0.07 mol of  $\text{BF}_3 \cdot \text{MEA}$  to 1 equivalent of epoxy resin.<sup>12</sup> Saeki et al.<sup>13</sup> have found that the heat deflection temperature (HDT) of the  $\text{BF}_3 \cdot \text{MEA}$ -cured resins increases with decreasing curing temperature and concentration of the curing agent, provided that the curing temperature is higher than that required to initiate the cure. The higher the postcure temperature of the  $\text{BF}_3 \cdot \text{MEA}$ -epoxy resin systems, within practical limits, the higher the heat deflection temperature. In spite of the relatively high HDTs, the thermal stability of this system is rather poor and for maximum thermal stability (measured by thermogravimetric analysis), lower concentrations of curing agent are preferred.

It is postulated that  $\text{BF}_3 \cdot \text{MEA}$  cures at its dissociation temperature,<sup>11, 14, 15</sup> but this dissociation temperature has not been defined experimentally.  $\text{BF}_3 \cdot \text{MEA}$  has not been reported to dissociate reversibly in any available literature.<sup>16, 17</sup> Harris and Temin<sup>18</sup> have studied the curing of DGEBA catalyzed by various amine boron-fluoride complexes and the corresponding salts, and have proposed that the amine boron trifluoride complexes react directly with the resin or might react first to give a salt which is then solvated by the epoxy groups of the epoxy resins. Thus weak bonds are formed between the oxygen of the epoxy group and the hydrogen atoms of the amine. This explanation is supported also by Ito and Okahashi,<sup>19, 20</sup> who have studied the epoxy resin curing with  $\text{BF}_3 \cdot \text{MEA}$  using nuclear magnetic resonance (NMR), infrared (IR), and mass spectroscopy. Dissociation of the complex into its components during curing does not occur. A shift of the N—H stretching absorption at 3280  $\text{cm}^{-1}$  by about 50  $\text{cm}^{-1}$  immediately after the mixing of the catalyst with resin indicates the formation of H bonds between the amine and the epoxy ring, and the oxonium ion and  $(\text{BF}_3 \cdot \text{NHEt})^-$  ion are apparently formed. The primary step in curing is the reaction between the  $(\text{BF}_3 \cdot \text{NHEt})^-$  ion and the epoxy group. At the same time, the oxonium ion might convert slowly into a carbonium ion and the crosslinking reaction is initiated by attack of the carbonium ion on the oxygen of the epoxy ring. Kamon et al.<sup>10</sup> have also studied epoxy resin curing with the  $\text{BF}_3 \cdot \text{amine}$  complex, using differential thermal analysis (DTA), IR, and nitron acetate method for fluoroborate<sup>21, 22</sup> determination. The DTA thermogram shows two exothermic peaks for  $\text{BF}_3 \cdot \text{MEA}$  and one peak for  $\text{BF}_4\text{NH}_3\text{C}_2\text{H}_5$ . The temperature of the peak of the higher temperature side for  $\text{BF}_3 \cdot \text{MEA}$  is almost the same as that of the peak for  $\text{BF}_4\text{NH}_3\text{C}_2\text{H}_5$ . On the basis of the analysis made by IR and

nitron acetate methods,  $\text{BF}_3 \cdot \text{MEA}$  is found to react with equimolecular amounts of the epoxy group, giving  $\text{BF}_4\text{NH}_3\text{C}_2\text{H}_5$  at the temperature of the peak on the lower temperature side. From these results, they propose that  $\text{BF}_3 \cdot \text{MEA}$  reacts with the epoxy resin in  $\text{BF}_3 \cdot \text{MEA}$ -epoxy resin system to produce  $\text{BF}_4 \cdot \text{MEA}$  before curing, and the "true catalyst" of the curing for both  $\text{BF}_3 \cdot \text{MEA}$  and  $\text{BF}_4 \cdot \text{MEA}$  systems would be the hydrogen atom located on the amine nitrogen in  $\text{BF}_4 \cdot \text{MEA}$ .

The relationship between the thermal properties, including heat resistance and thermal resistance of high polymers, and their chemical structures have been reviewed.<sup>23,24</sup> Heat resistance is defined as the highest temperature at which the polymer still retains its mechanical strength when under some given applied load.

The thermal resistance of a polymeric material is related to the decomposition temperature of the material as measured by thermogravimetric analysis. This may in turn be related to the flammability as measured by the oxygen index (OI). For polymeric materials, higher char yields are related to lower flammability. Increased char formation limits the production of combustible carbon-containing gases, decreases the exothermicity due to pyrolysis reactions, and decreases the thermal conductivity from the surface of the burning material.<sup>25-27</sup>

## EXPERIMENTAL

### Preparation of Curing Agent

$\text{BF}_3 \cdot \text{MEA}$  is obtained from ICN-K & K Laboratories, Inc., Plainview, NY. It is washed with fresh petroleum ether and then dried at reduced pressure. It is a yellowish-white crystalline solid, m.p. = 88–90°C.

### Preparation of Epoxy Resins

Epon 828 is obtained from Shell Chemical Company, Houston, TX. It is a diglycidyl ether of bisphenol A, which is used without further treatment.

DGEBF is prepared as published previously<sup>28</sup> by feeding 9,9-*bis*(4-hydroxyphenyl) fluorene and epichlorohydrin in the mole ratio of 1 : 10.

DGEBF can be recrystallized from its acetone solution by adding poor solvent (absolute alcohol) into the solution with vigorous agitation until the solution appears a little cloudy. This solution then stands until complete precipitation occurs. The white crystalline powder is collected by filtration and washed with a mixture of acetone and absolute alcohol (1 : 1). The crystalline DGEBF has a melting point of 137°C.

### Characterization of Epoxy Resin

#### *Epoxy Equivalent Weight (EEW) Determination*

The ASTM D1652-73<sup>29</sup> method is used to determine the EEW of epoxy resins. Epoxy resin, 0.2 g, is added to a 50-mL flask and then dissolved in 10 mL of 50 vol% of chlorobenzene (Aldrich analyzed grade; 99%) in chloroform. The mixture is stirred with a Teflon-coated magnetic stirring bar. Four

drops of 0.1% of crystal violet [(4,4',4''-methylidynetris-(*N,N*-dimethylaniline); Eastman)] solution in glacial acetic acid (J. T. Baker) is used as the indicator. The solution is titrated with 0.1 *N* of hydrogen bromide in acetic acid (Eastman; 30.32% in acetic acid by titration). The hydrogen bromide solution is standardized by 0.4 g of potassium hydrogen phthalate each time before using for epoxy equivalent weight determination.

### Curing Conditions for $\text{BF}_3 \cdot \text{MEA}$ -Epoxy Resins Systems

$\text{BF}_3 \cdot \text{MEA}$ , 0.045 eq., 0.090 eq., or 0.135 eq. is used individually as curing agent. Epon 828 and DGEBF are used individually or in combination as resin systems. The curing conditions are 120°C or 140°C for 3 h and addition 1 h or 3 h at 200°C and 120°C for 3 h and additional 1 or 3 h at 264°C in the nitrogen-filled and sealed glass tubes.

### Characterization of Cured Epoxy Resins

#### *Dynamic Thermal Analysis*

The thermal properties of various samples in this study were investigated on a DuPont 910 Differential Scanning Calorimeter (DSC) and a DuPont 990 Thermal Analyzer. The DuPont 951 Thermogravimetric Analyzer (TGA) was used with a DuPont 990 Thermal Analyzer for char residue determination. Samples having mesh sizes greater than 170 were used for DSC or TGA measurement. For DSC and TGA measurements, the nitrogen flow rate is 0.2 and 0.3 L/min, respectively, with a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Characterization of Epoxy Resins

The properties of the epoxy resins, in this study, are summarized in Table I.

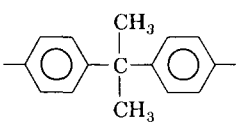
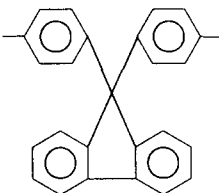
DGEBF is a white crystalline solid which has a melting temperature of 137°C (lit. mp = 132°C<sup>29</sup>). After the molten monomer is quenched, only a softening temperature at 38°C (lit = 30°C<sup>29</sup>, 70°C<sup>30</sup>) can be observed. DGEBF has a higher glass transition temperature and char yield than DGEBA.

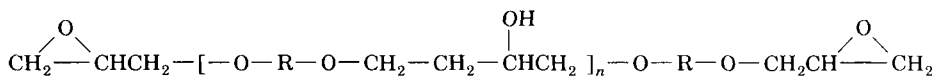
### Curing Reaction Study of $\text{BF}_3 \cdot \text{MEA}$ -Epoxy Resins

Differential scanning calorimetry (DSC) thermograms of Epon 828 or DGEBF after mixing with curing agent  $\text{BF}_3 \cdot \text{MEA}$  0.0450 eq., 0.0900 eq. and 0.1350 eq./epoxy eq. are shown in (Figs. 1 and 2). They show the curing onset temperature at about 70°C and 90°C and the maximum exotherm temperatures are about 160°C and 180°C for Epon 828 and DGEBF, respectively. This indicates that Epon 828 is more reactive than DGEBF with  $\text{BF}_3 \cdot \text{MEA}$ .

According to the study of Kamon et al.,<sup>10</sup> the above result shows that the more  $\text{BF}_3 \cdot \text{MEA}$  used, the higher the ratio of the exotherm at the lower temperature (116°C, 125°C) to that of the higher temperature (160°C, 182°C) and means that the percent conversion of  $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$  to  $\text{BF}_4 \cdot \text{NH}_3\text{C}_2\text{H}_5$  is decreased.

TABLE I  
Properties of Epoxy Resins Prepared from Epichlorohydrin and Bisphenols

Type of resin	DGEBA	DGEBF
R		
Color	pale yellow	white
Epoxy equiv wt	189.3	254
$\bar{n}$	0.13	0.11
$T_g$ (°C)	-24	38
$T_m$ (°C)	—	137
Char yield <sub>N<sub>2</sub></sub> <sup>700°C</sup>	2.4	21.4



The DSC thermograms of Epon 828 after mixing with DGEBF (0, 25, 50, 75, and 100 mol%) and  $\text{BF}_3 \cdot \text{MEA}$ , curing agent 0.0450 eq./epoxy eq. show curing onset temperatures at about 70°C and 90°C and two significant curing exotherm reactions around 160°C to 187°C and 285°C (Fig. 3). This curing delay in the DGEBF system is probably due to a viscosity effect. The exotherm at 284°C is due to further curing rather than degradation as shown by a TGA experiment indicating that degradation to volatile products occurs at over 300°C.

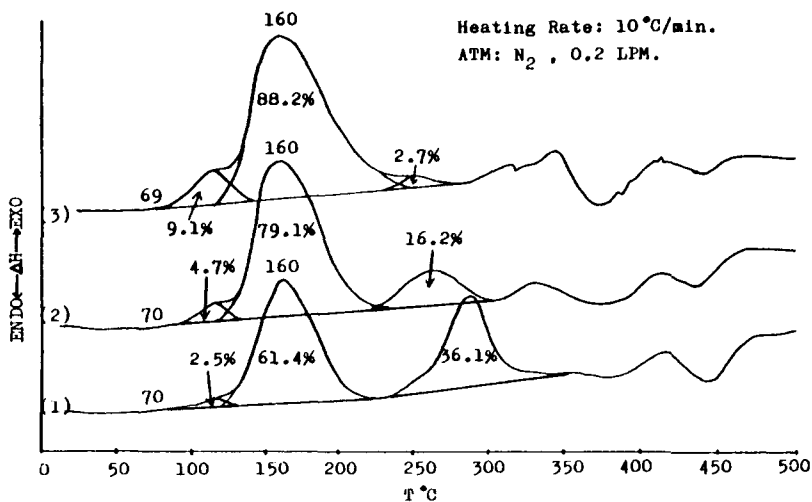


Fig. 1. DSC thermograms of Epon 828 after mixing with curing agent  $\text{BF}_3 \cdot \text{MEA}$  (1) 0.0450 eq., (2) 0.0900 eq., and (3) 0.1350 eq./epoxy eq. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.2 LPM.

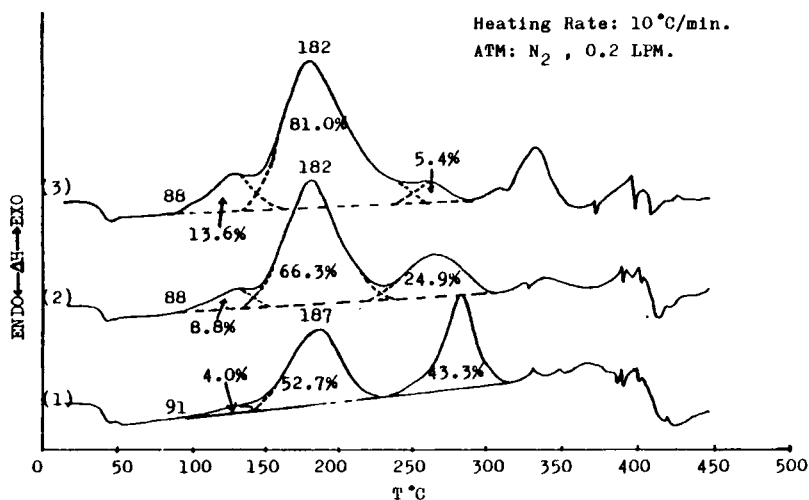


Fig. 2. DSC thermograms of DGEBF after mixing with curing agent BF<sub>3</sub> · MEA (1) 0.0450 eq. (2) 0.0900 eq., and (3) 0.1350 eq./epoxy eq. Heating rate: 10°C/min. ATM: N<sub>2</sub>, 0.2 LPM.

### BF<sub>3</sub> · MEA-Cured Epon 828 and DGEBF

The DSC thermograms for the BF<sub>3</sub> · MEA cured Epon 828 and BF<sub>3</sub> · MEA cured DGEBF which are cured at 120°C for 3 h and on additional 1 h at 200°C using equivalent ratios of curing agent to epoxy resin of 0.0450, 0.0900, and 0.1350, show *T<sub>g</sub>*'s of 61°C, 117°C, and 168°C with exotherm peaks at 260°C and 368°C; 260°C and 375°C; 375° and 414°C for Epon 828 (Fig. 4), and *T<sub>g</sub>*'s of 106°C, 119°C, and 175°C with exotherm peaks at 354°C, 385°C,

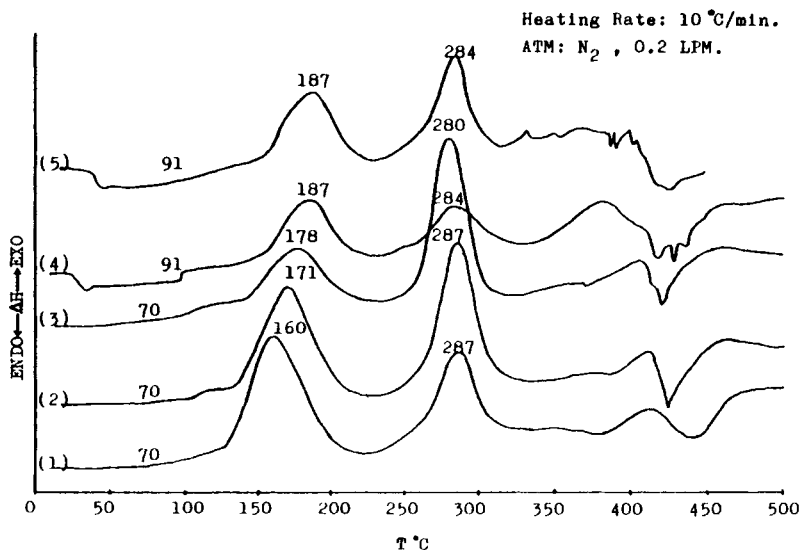


Fig. 3. DSC thermograms for Epon 828 after mixing with DGEBF (1) 0%, (2) 25%, (3) 50%, (4) 75%, and (5) 100% and BF<sub>3</sub> · MEA curing agent (0.0450 eq./epoxy eq.). Heating rate: 10°C/min. ATM: N<sub>2</sub>, 0.2 LPM.

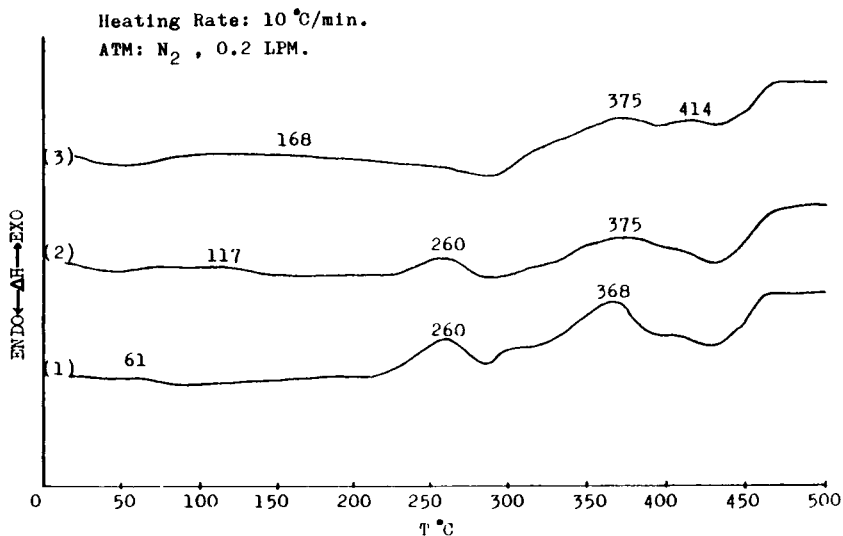


Fig. 4. DSC thermograms of  $\text{BF}_3 \cdot \text{MEA}$ -cured Epon 828. (1) 0.0450 eq., (2) 0.0900 eq., and (3) 0.1350 eq./epoxy eq. Curing conditions: 120°C 3 h and 200°C 1 h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.2 LPM.

and 410°C for DGEBF (Fig. 5). These indicate that the cured DGEBF has a higher  $T_g$  than the cured Epon 828. However, their degradation exotherms are similar. The char residues for  $\text{BF}_3 \cdot \text{MEA}$ -cured Epon 828, are 19.6%, 25.8%, and 16.5% at equivalent ratios of curing agent to epoxy resin of 0.0450, 0.0900, and 0.1350, respectively (Fig. 6). The char residues for the  $\text{BF}_3 \cdot \text{MEA}$ -cured DGEBF are 25.4%, 32.2%, and 34.8% at equivalent ratios of curing agent to epoxy resin of 0.0450, 0.0900, and 0.1350, respectively (Fig. 7).  $\text{BF}_3 \cdot \text{MEA}$ -

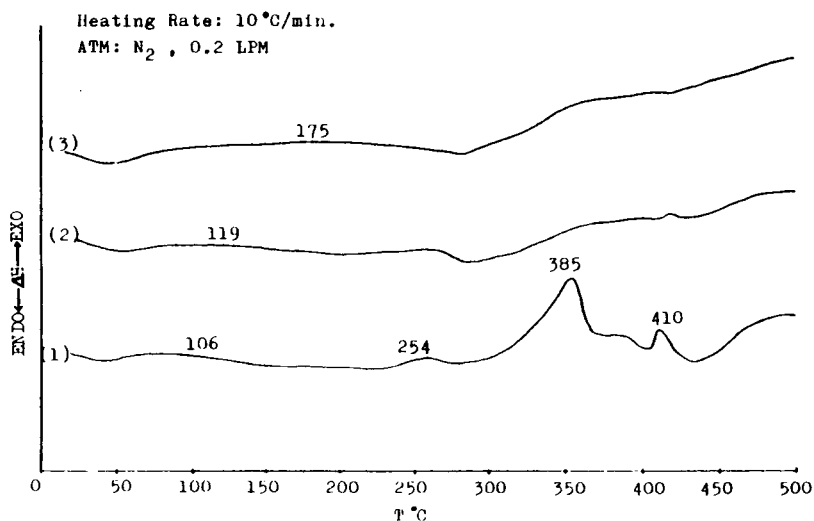


Fig. 5. DSC thermograms for  $\text{BF}_3 \cdot \text{MEA}$ -cured DGEBF. Concentrations of  $\text{BF}_3 \cdot \text{MEA}$ : (1) 0.0450 eq.; (2) 0.0900 eq.; and (3) 0.1350 eq./epoxy eq. Curing conditions: 120°C 3 h and 200°C 1 h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.2 LPM.

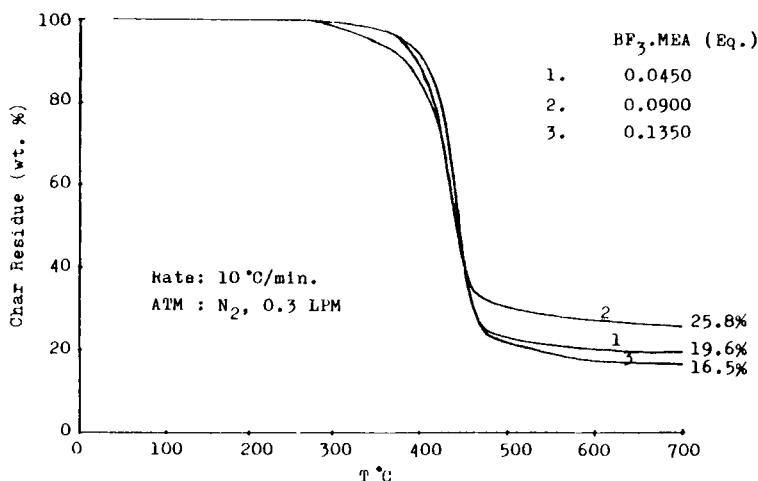


Fig. 6. TGA for cured Epon 828. Curing agent is BF<sub>3</sub> · MEA (1) 0.0450 eq., (2) 0.0900 eq., (3) 0.1350 eq./epoxy eq. Curing conditions: 120°C 3 h and 200°C 1 h. Heating rate: 10°C/min. ATM: N<sub>2</sub>, 0.3 LPM.

(0.0450 eq.) cured DGEBF at curing cycles 120°C for 3 h and 264°C for 1 h, and 120°C for 3 h and 264°C for 3 h, have char residues 28.6% and 23.8% (Fig. 8), and  $T_g$ 's of 176°C and 188°C (Fig. 9), respectively. The IR and Difference spectra of BF<sub>3</sub> · MEA-cured DGEBF do not show the formation of an ester group as previously reported by Serboli<sup>31</sup> for DGEBA (Fig. 10) and this may be due to the fact that our cures were done under nitrogen. The difference spectrum may also indicate that the longer curing cycle-cured epoxy systems may have more thermodegradation than the shorter curing cycle-cured epoxy. This is indicated by the decrease at 1526 cm<sup>-1</sup> and the increase at 1506 cm<sup>-1</sup> and may be comparable to the 1514 cm<sup>-1</sup> decrease and the 1493 cm<sup>-1</sup> increase

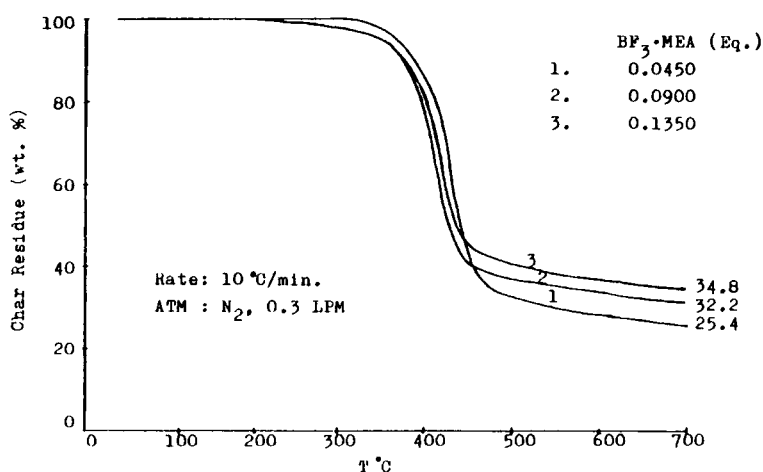


Fig. 7. TGA for cured DGEBF. Curing agent is BF<sub>3</sub> · MEA (1) 0.0450 eq., (2) 0.0900 eq., and (3) 0.1350 eq./epoxy eq. Curing conditions: 120°C 3 h and 200°C 1 h. Heating rate: 10°C/min ATM: N<sub>2</sub>, 0.3 LPM.



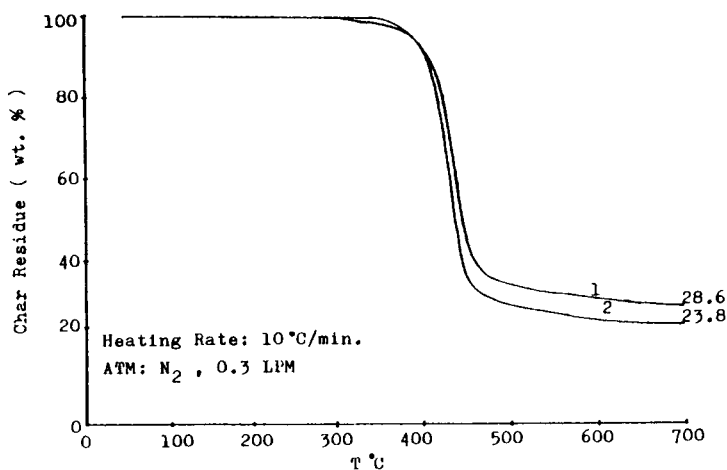


Fig. 8. TGA for  $\text{BF}_3 \cdot \text{MEA}$ -cured DGEBF. Curing agent:  $\text{BF}_3 \cdot \text{MEA}$ , 0.0450 eq./epoxy eq. Curing conditions: (1) 120°C 3 h and 264°C 1 h. (2) 120°C 3 h and 264°C 3 h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.3 LPM.

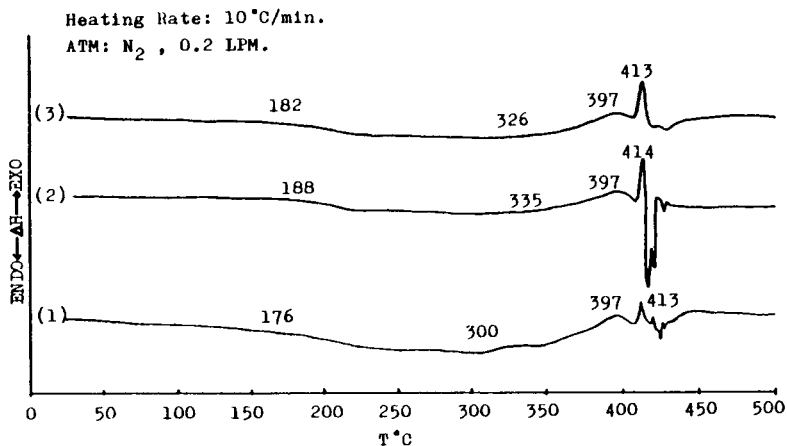


Fig. 9. DSC thermograms of  $\text{BF}_3 \cdot \text{MEA}$ -cured DGEBF. Curing agent 0.0450 eq./epoxy eq. (1) Cured at condition (a); (2) cured at condition (b), and (3) the former sample annealed at 329°C for 7 min then quenched. Curing conditions: (a) 120°C 3 h and 264°C 1 h. (b) 120°C 3 h and 264°C 3 h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.2 LPM.

for the DDS and tetraglycidyl diaminodiphenylmethane curing system. Levy et al.<sup>32</sup> have found this phenomenon and explained it as the result of decreased degradation. The absorption at  $1380 \text{ cm}^{-1}$ , assigned to aliphatic- $\text{CH}_3$  symmetric deformation,<sup>33</sup> occurs in the IR spectrum of the  $\text{BF}_3 \cdot \text{MEA}$ -cured epoxy. The shorter curing cycle-cured epoxy resin has stronger  $1380 \text{ cm}^{-1}$  absorbance than the longer curing cycle-cured epoxy resin and may indicate that the latter is more degraded than the former.

$\text{BF}_3 \cdot \text{MEA}$ -cured epoxy comixtures (Epon 828 and DGEBF 0%, 25%, 50%, 75%, and 100%), with curing conditions: 120°C for 3 h and an additional 1 h at 200°C, show  $T_g$ 's of 61°C, 68°C, 74°C, 89°C, and 106°C (Fig. 11). The relation between  $T_g$  and these compositions (Fig. 12) indicates that the  $T_g$  increases

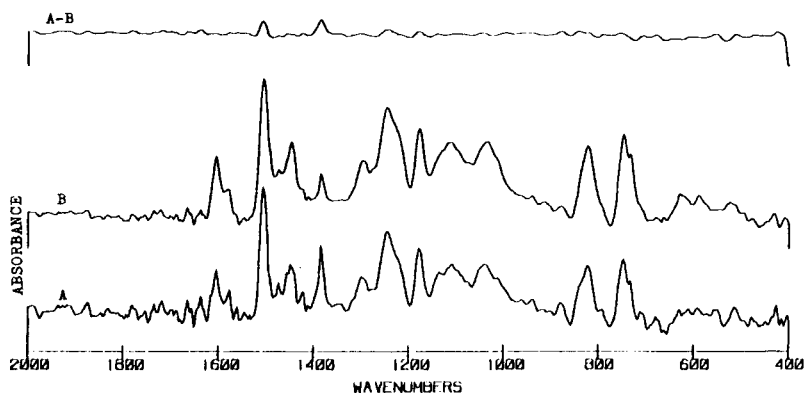


Fig. 10. IR and difference spectra of the  $\text{BF}_3 \cdot \text{MEA}$  0.0450 eq./epoxy eq. cured DGEBF. At curing conditions: (A) 120°C 3 h and 264°C 1 h, (B) 120°C 3 h and 264°C 3 h.

with increasing DGEBF concentrations. The exotherm peaks at 368°C, 370°C, 366°C, 361°C; and 419°C, 354°C, 385°C, and 410°C show they may have similar degradation exotherms. Their char residues are 19.6%, 18.6%, 19.8%, 23.6%, and 25.4%, respectively (Fig. 13). A similar study of the same compositions with a different curing cycle: 120°C for 3 h and an additional 3 h at 200°C, give  $T_g$ 's of 93°C, 96°C, 103°C, 118°C (Fig. 14), the relation between  $T_g$  and these compositions is shown in Figure 15 and char residues 19.6%, 19.1%, 20.4%, 25.6%, 25.8%, respectively (Fig. 16). Glass transition temperatures and char yields are increased by curing with a longer curing cycle. DGEBF being more aromatic and having cyclic ring units increases both the char yield and  $T_g$  of DGEBA. However, if the curing temperature increases from 120°C to 140°C for 3 h and an additional 1 h at 200°C for this system, a lower char

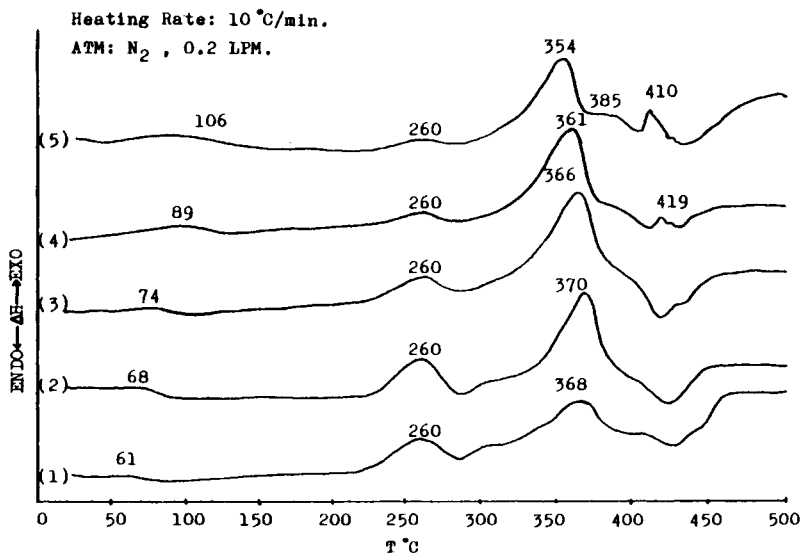


Fig. 11. DSC thermograms of  $\text{BF}_3 \cdot \text{MEA}$ -cured epoxy copolymer [Epon 828 and DGEBF (1) 0%, (2) 25%, (3) 50%, (4) 75%, and (5) 100%]; Curing agent 0.0450 eq./epoxy eq. Curing conditions: 120°C 3 h and 200°C 1h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.2 LPM.

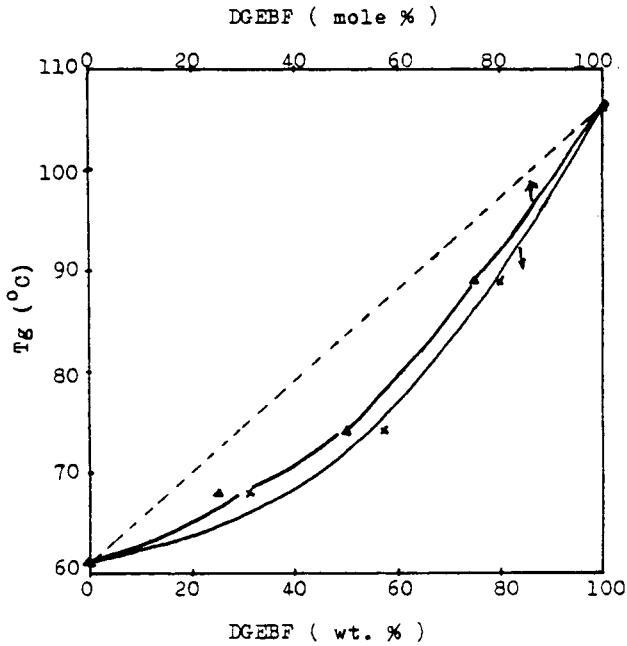


Fig. 12.  $T_g$  vs.  $\text{BF}_3 \cdot \text{MEA}$ -cured epoxy comixtures [epon 828 and DGEBF] based on weight fraction and mole fraction. (Curing agent 0.0450 eq./epoxy eq.). (Curing conditions:  $120^\circ\text{C}$  3 h  $200^\circ\text{C}$  1 h.)

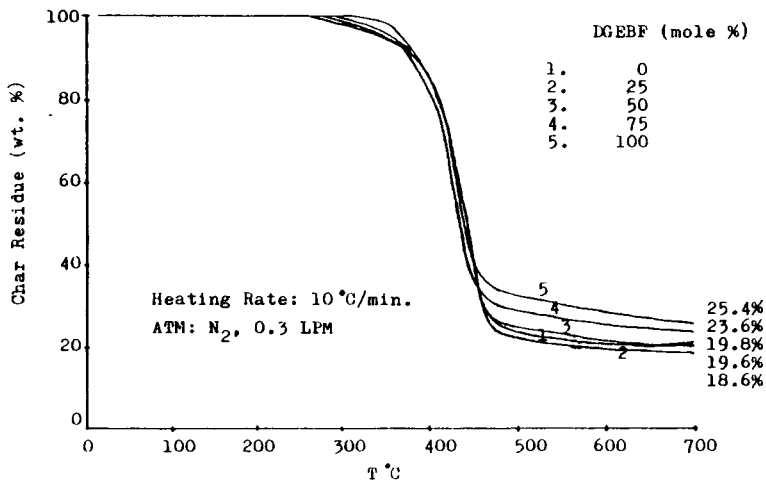


Fig. 13. TGA of various compositions of DGEBF copolymer with Epon 828. Curing agent:  $\text{BF}_3 \cdot \text{MEA}$ , 0.0450 eq./epoxy eq. Curing conditions:  $120^\circ\text{C}$  3 h and  $200^\circ\text{C}$  1 h. Heating rate:  $10^\circ\text{C}/\text{min}$ . ATM:  $\text{N}_2$ , 0.3 LPM.

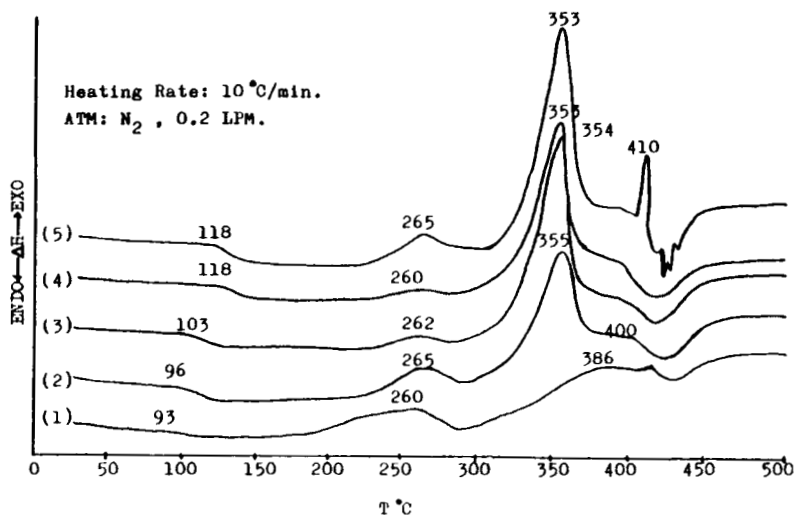


Fig. 14. DSC thermograms of  $\text{BF}_3 \cdot \text{MEA}$ -cured epoxy copolymer [Epon 828 and DGEBF (1) 0%, (2) 25%, (3) 50%, (4) 75%, and (5) 100%]; Curing agent 0.0450 eq./epoxy eq. Curing conditions: 120°C 3 h and 200°C 3 h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.2 LPM.

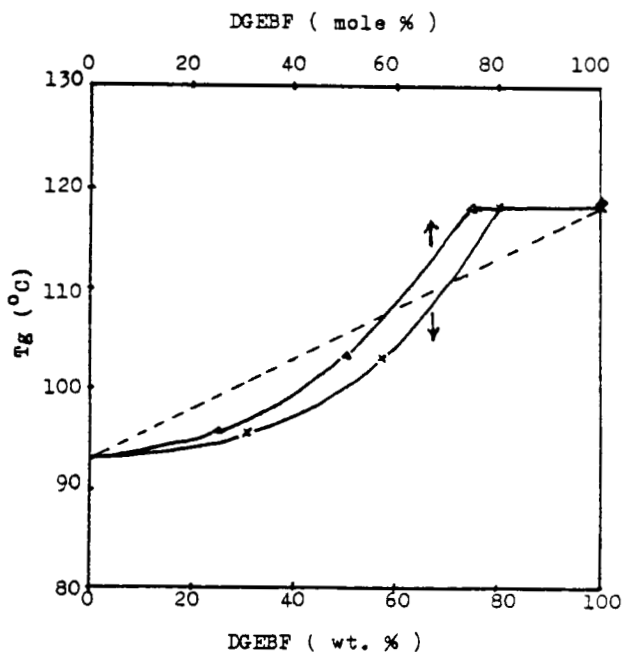


Fig. 15.  $T_g$  vs.  $\text{BF}_3 \cdot \text{MEA}$ -cured epoxy comixtures [Epon 828 and DGEBF]. Based on weight fraction and mole fraction. (Curing agent 0.0450 eq./epoxy eq.) (Curing conditions: 120°C, 3 h 200°C, 3 h.)

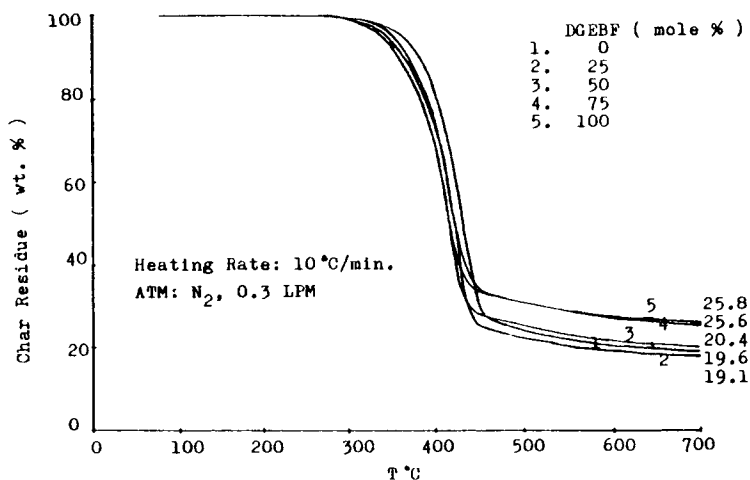


Fig. 16. TGA for various compositions of DGEFB copolymer with Epon 828. Curing agent:  $\text{BF}_3 \cdot \text{MEA}$ , 0.0450 eq./epoxy eq. Curing conditions: 120°C, 3 h and 200°C 3 h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.3 LPM.

yield is found (Fig. 17). It is due to 0.8% weight loss of  $\text{BF}_3 \cdot \text{MEA}$  at 120°C, but a 2.3% weight loss at 140°C. Either early degradation or vaporization of curing agent will lower the crosslinking density. If the gel points of these epoxy systems occur at the same conversion, then the only reason for the lower crosslinking density at higher temperature curing cycles is that the curing agent degraded or vaporized. Alternatively, early onset of the gelation may be another reason that the higher temperature curing cycle gives a lower char yield. In this case, the curing reaction of this epoxy system becomes diffusion controlled after gelation and that may cause a lower final crosslinking density for this system when compared to the lower temperature curing

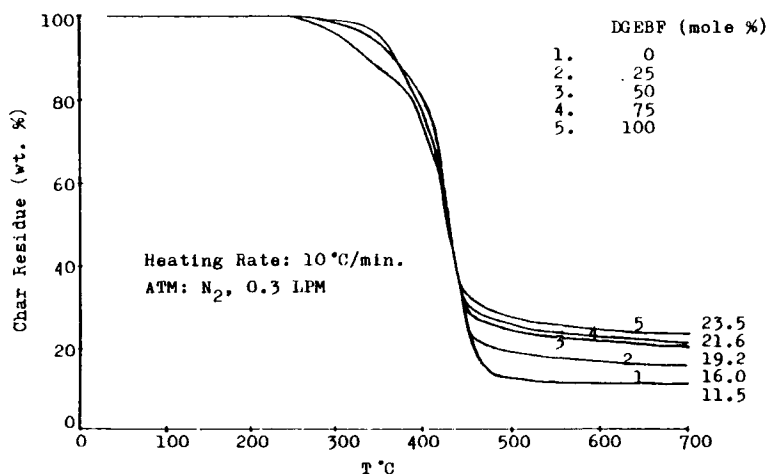


Fig. 17. TGA for various compositions of DGEFB copolymer with Epon 828. Curing agent:  $\text{BF}_3 \cdot \text{MEA}$ , 0.0450 eq./epoxy eq. Curing conditions: 140°C 3 h and 200°C 1 h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.3 LPM.

**TABLE II**  
Char Yield and  $T_g$  of  $\text{BF}_3 \cdot \text{MEA}$ -Cured Epoxy Comixtures [Epon 828 and DGEBA ((A) 0%, (B) 25%, (C) 50%, (D) 75%, and (E) 100%)]<sup>a</sup> (Curing Agent 0.0450 Eq./Epoxy Eq.)

Epoxy resin	A	B	C	D	E
$T_g^{\text{b}}$ °C	61	68	74	89	106
$T_g^{\text{c}}$ °C	93	96	103	118	118
Char yield <sup>b</sup> $\text{N}_2$ 700°C	19.6%	18.6%	19.8%	23.6%	25.4%
Char yield <sup>c</sup> $\text{N}_2$ 700°C	19.6%	19.1%	20.4%	25.6%	25.8%
Char yield <sup>d</sup> $\text{N}_2$ 700°C	11.5%	16.0%	19.2%	21.6%	23.5%

<sup>a</sup> Base on equivalent of epoxy resin.

Curing conditions:

<sup>b</sup> 120°C 3 h and 200°C 1 h.

<sup>c</sup> 120°C 3 h and 200°C 3 h.

<sup>d</sup> 140°C 3 h and 200°C 1 h.

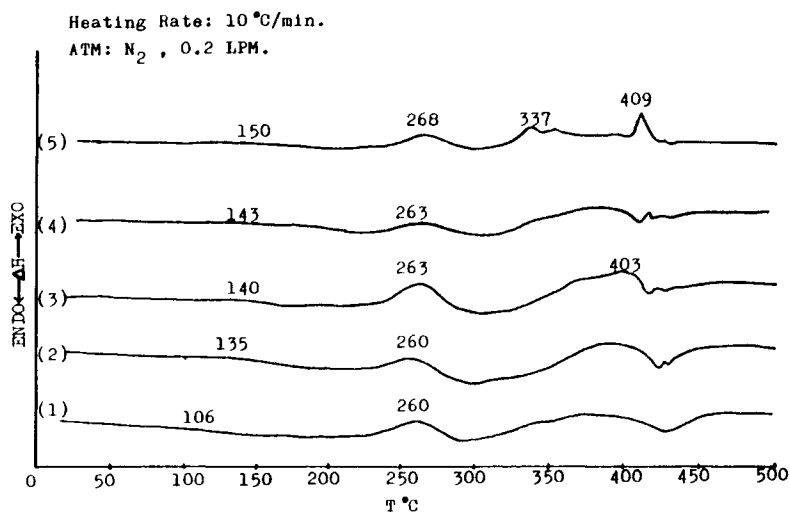


Fig. 18. DSC thermograms of  $\text{BF}_3 \cdot \text{MEA}$ -cured epoxy copolymer Epon 828 and DGEBA [(1) 0%, (2) 25%, (3) 50%, (4) 75%, and (5) 100%]; Curing agent 0.0900 eq./epoxy eq. Curing conditions: 120°C 3 h and 200°C 1 h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.2 LPM.

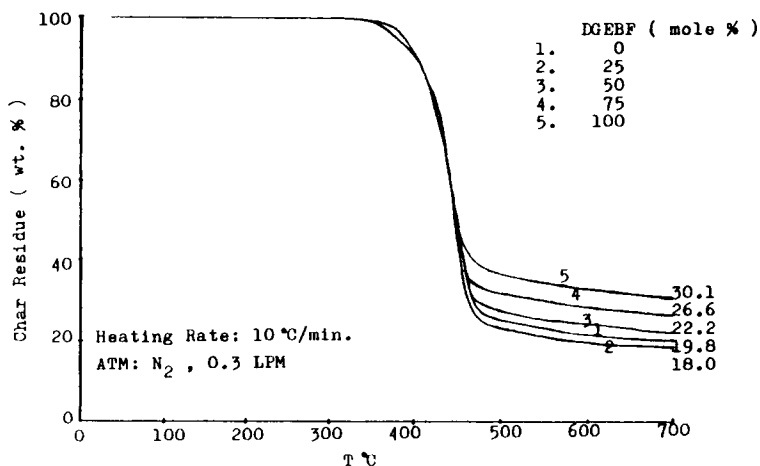


Fig. 19. TGA for various compositions of DGEBA copolymer with Epon 828. Curing agent:  $\text{BF}_3 \cdot \text{MEA}$ , 0.0900 eq./epoxy eq. Curing conditions: 120°C 3 h and 200°C 1 h. Heating rate: 10°C/min. ATM:  $\text{N}_2$ , 0.3 LPM.

TABLE III  
Char Yield and  $T_g$  of  $\text{BF}_3 \cdot \text{MEA}$ -Cured Epoxy Comixtures [Epon 828 and DGEBA ((A) 0%, (B) 25% (C) 50%, (D) 75%, and (E) 100%)]. (Curing Agent 0.0900 Eq./Epoxy Eq.)

Epoxy resin	A	B	C	D	E
$T_g$ °C	106	135	140	143	150
Char yield $_{N_2}^{700^\circ\text{C}}$	19.8%	18.0%	22.2%	26.6%	30.1%

Curing conditions: 120°C 3 h and 200°C 1 h.

cycle. Thus, the lower crosslinking density may account for the lower char yield. The above studies are summarized in Table II.

The DSC thermograms (Fig. 18) for  $\text{BF}_3 \cdot \text{MEA}$ -cured epoxy copolymers Epon 828 with DGEBA at various compositions have  $T_g$ 's which increase from 106°C to 150°C with char residues increasing from 19.8% to 30.1% (Fig. 19; Table III). The glass transition temperatures and char residues are increased with increasing DGEBA levels. The  $T_g$  and char residues obtained with 0.0900 eq.  $\text{BF}_3 \cdot \text{MEA}$  are higher than the same epoxy systems with 0.0450 eq.  $\text{BF}_3 \cdot \text{MEA}$  curing agent using the same curing cycles.

#### Determination of the Activation Energy for Thermal Decomposition

Flynn and Wall<sup>34</sup> have found that the Arrhenius activation energy can be obtained from weight loss vs. temperature at different heat rates,

$$E_a = -4.35 \frac{d(\log \beta)}{d(1/T)} \quad (1)$$

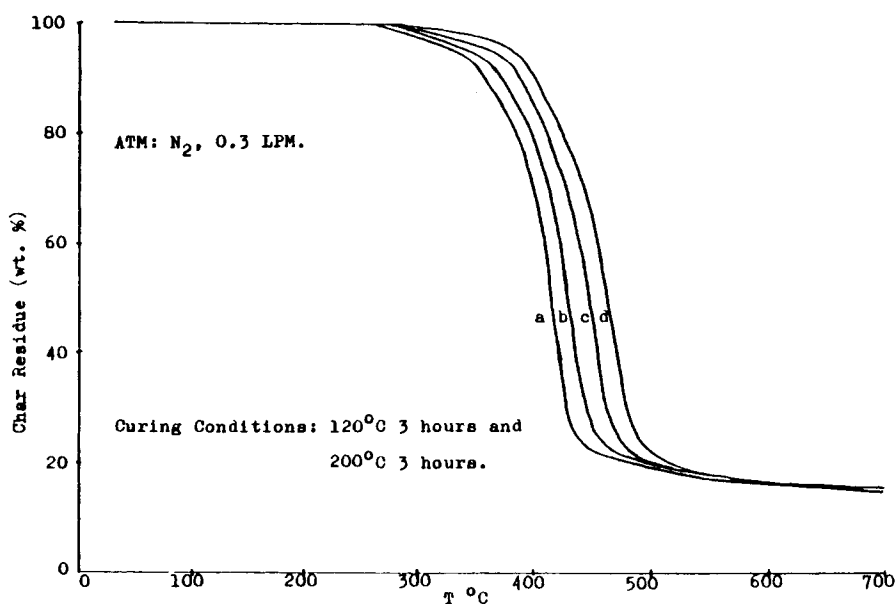


Fig. 20. TGA for  $\text{BF}_3 \cdot \text{MEA}$  (0.0450 eq./ epoxy eq.) cured Epon 828 at heating rates of (a) 0.0833, (b) 0.167, (c) 0.333, and (d) 0.833 °C/s. Curing conditions: 120°C 3 h and 200°C 3 h.

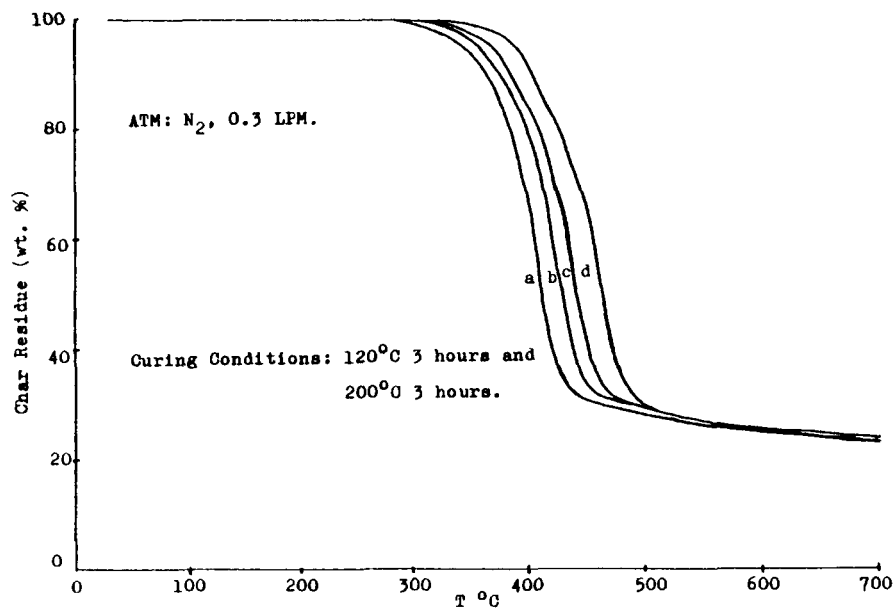


Fig. 21. TGA for  $\text{BF}_3 \cdot \text{MEA}$ -(0.0450 eq./epoxy eq.) cured epoxy comixture: Epon 828 (25 mol%) and DGEBF (75 mol%), at heating rates of (a) 0.0833, (b) 0.167, (c) 0.333, and (d) 0.833°C/s. Curing conditions: 120°C 3 h and 200°C 3 h.

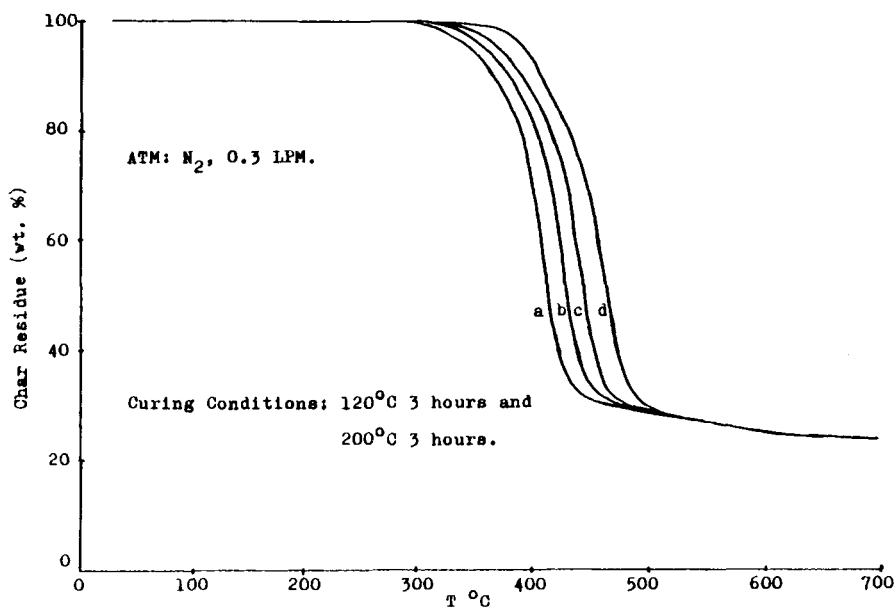


Fig. 22. TGA for  $\text{BF}_3 \cdot \text{MEA}$ -(0.0450 eq./epoxy eq.) cured DGEBF at heating rates of (a) 0.0833, (b) 0.167, (c) 0.333, and (d) 0.833°C/s. Curing conditions: 120°C 3 h and 200°C 3 h.



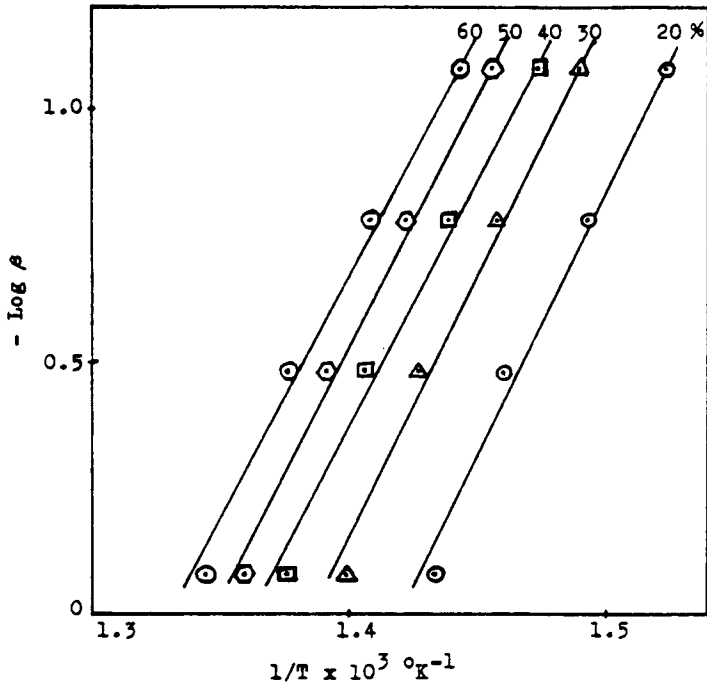


Fig. 23.  $\text{Log } \beta$  vs.  $1/T$  at 20, 30, 40, 50, and 60% weight loss from Fig. 20 for thermal degradation of  $\text{BF}_3 \cdot \text{MEA}$  (0.0450 eq./epoxy eq.) cured Epon 828.

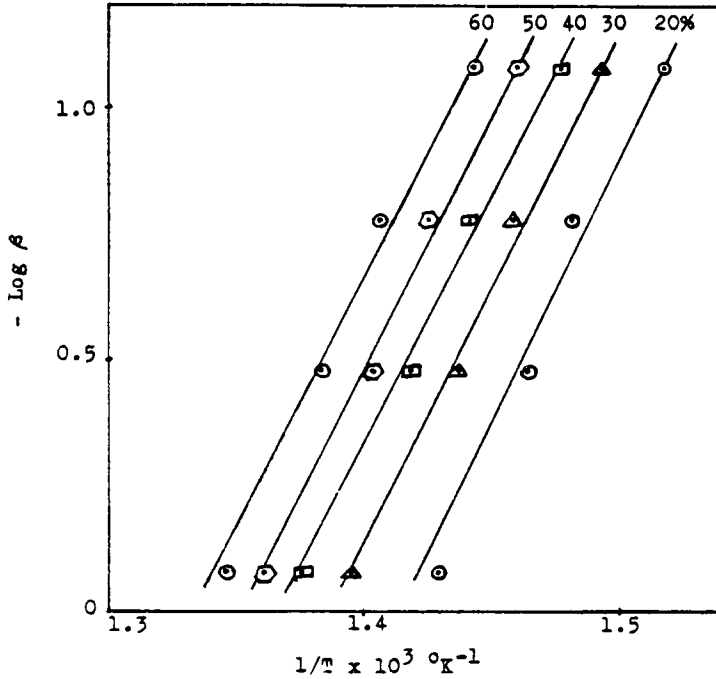


Fig. 24.  $\text{Log } \beta$  vs.  $1/T$  at 20, 30, 40, 50, and 60% weight loss from Fig. 21 for thermal degradation of  $\text{BF}_3 \cdot \text{MEA}$  (0.0450 eq./epoxy eq.) cured epoxy comixture: Epon 828 (25 mol%) and DGEBA (75 mol%).

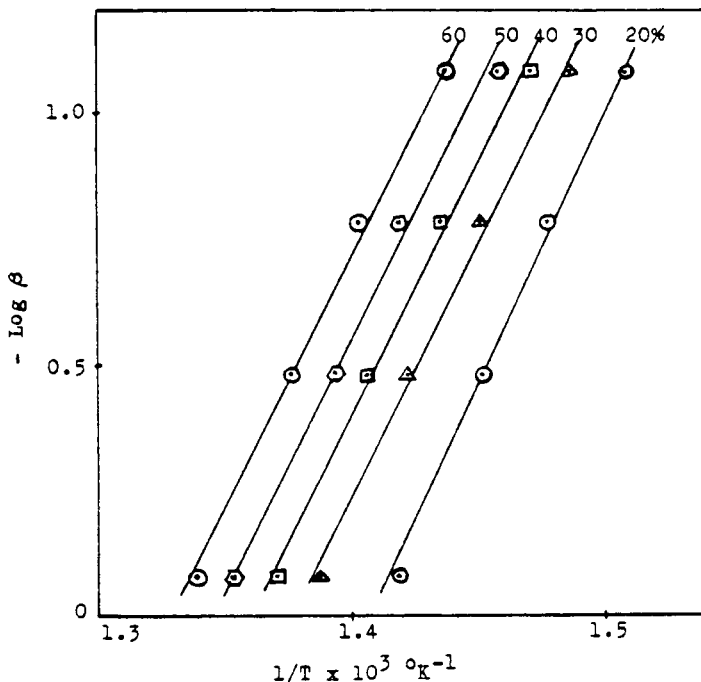


Fig. 25.  $\log \beta$  vs.  $1/T$  at 20, 30, 40, 50, and 60% weight loss form Fig. 22 for thermal degradation of  $\text{BF}_3 \cdot \text{MEA}$ -(0.0450 eq./epoxy eq.) cured DGEBF.

The TGA thermograms for the  $\text{BF}_3 \cdot \text{MEA}$ -(0.0450 eq./epoxy eq.) cured Epon 828, Epon 828 (25 mol%) and DGEBF (75 mol%), and DGEBF at 0.0833, 0.167, 0.333, and  $0.833^\circ\text{C/s}$  are obtained to determine the temperature corresponding to a constant weight loss (Figs. 20, 21, and 22). Arrhenius-like plots using heating rates as a function of temperature at different fixed weight residue percentages (Figs. 23, 24, and 25) indicate that the activation energies are 43.29, 43.65, and 44.00 kcal/mol and are approximately the same.

## CONCLUSIONS

For the epoxy curing, the curing exotherm pattern is affected by the equivalent ratio of curing agent ( $\text{BF}_3 \cdot \text{MEA}$ ) to epoxy resin. Here, DGEBF cures more slowly than Epon 828 and this is most likely related to the higher viscosity of DGEBF. The  $T_g$ 's of  $\text{BF}_3 \cdot \text{MEA}$ -cured Epon 828 are increased with increasing concentration of curing agent (0.0450–0.1350 eq.). Their char yields do not show a similar relationship. Char yields and  $T_g$ 's are increased by the increasing amount of curing agent for  $\text{BF}_3 \cdot \text{MEA}$ -(0.0450–0.1350 eq.) cured DGEBF. The activation energies of thermal decomposition for  $\text{BF}_3 \cdot \text{MEA}$ -(0.0450 eq./epoxy eq.) cured Epon 828 and DGEBF are 43.3 and 44.0 kcal/mol. They are approximately the same. DGEBF when added to DGEBA improves the  $T_g$  and char yield in the  $\text{BF}_3 \cdot \text{MEA}$  curing system. The  $T_g$  of

both resin systems can be increased by longer post cure, whereas the char yield does not appear to change significantly. No ester group formation is found for the  $\text{BF}_3 \cdot \text{MEA}$ -cured DGEBF although this has been previously reported for the DGEBA system.<sup>31</sup> The  $\text{BF}_3 \cdot \text{MEA}$  cure at  $120^\circ\text{C}$  is better than at  $140^\circ\text{C}$  because of vaporization and degradation of the curing agent at the higher temperature. The rapid gelation of the epoxy resin may be another reason for the lower degree of cure at high temperature.

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### References

1. Hysol Corp., British patent 1,043,998 (1966); *Chem. Abs.*, **65**, 18853b (1966).
2. Y. Fujwara, A. Takahashi, T. Suzuki, and N. Iwai, Japan Kokai 77 92, 280 (1977); *Chem. Abs.*, **87**, 202766m (1977).
3. J. Kumazawa, T. Takechi, H. Mitsui, R. Kumazawa, K. Umemoto, and T. Yamada, U.S. patent 3,991,232 (1976); *Chem. Abs.*, **86**, 44865r (1977).
4. J. W. Shepherd, U.S. patent 3,310,507 (1967); *Chem. Abs.*, **67**, 22590c (1967).
5. Y. S. Matveev and S. A. Pavlv, *Izv. Vyssh. Uchebn. Zaved., Tekhnol. Legk. Prom-St.*, **4**, 68 (1977); *Chem. Abs.*, **87**, 152857u (1977).
6. J. Delmonte, in *Epoxy Resins Chemistry and Technology*, C. A. May and Y. Tanaka, Eds., Marcel Dekker, New York, 1973, Chap. 9.
7. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, Chap. 22.
8. L. Kurzeja and Z. Jedlinski, *Polimery (Warsaw)*, **20** (9), 424 (1975); *Chem. Abs.*, **84**, 60403c (1976).
9. C. A. May, J. S. Fritzen, and G. R. Brown, ICCM, *Proceedings of the International Conference on Composite Materials*, **1**, 264 (1975).
10. T. Kamon, K. Saito, Y. Miwa, and K. Saeki, *Nippon Kagaku Kaishi*, **10**, 1958 (1972); *Chem. Abs.*, **78**, 73028k (1973).
11. J. R. Pfann and A. F. Kopacki, *Chem. Abs.*, **69**, 78159c (1968).
12. L. Kurzeja and Z. Jedlinski, *Polimery (Warsaw)*, **20** (10), 477 (1975); *Chem. Abs.*, **84**, 181038w (1976).
13. K. Saeki, T. Kamon, and K. Saito, *Kogyo Kagaku Zasshi*, **74** (10), 2197 (1971); *Chem. Abs.*, **76**, 60428z (1972).
14. H. Lee and K. Neville, *SPE J.*, **16**, 315 (1960).
15. V. Oakes and D. L. Voss, British Patent 885, 749 (1959).
16. C. A. Kraus and E. H. Brown, *J. Am. Chem. Soc.*, **51**, 2690 (1929).
17. C. A. Brown, E. L. Muettterties, and E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 2537 (1954).
18. J. J. Harris and S. C. Temin, *J. Appl. Polym. Sci.*, **10**, 523 (1966).
19. K. Ito and K. Okahashi, *Kogyo Kagaku Izsshi*, **71** (7) 1099 (1968); *Chem. Abs.*, **69**, 97418c (1968).
20. K. Ito and K. Okahashi, *Mitsubishi Denki Lab. Rept.*, **10** (1), 83 (1969); *Chem. Abs.*, **75**, 21609 (1971).
21. C. A. Brown, E. L. Muettterties, and E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 2537 (1954).
22. W. Lange, *Ber.*, **59**, 2107, 2432 (1926).
23. V. V. Korshak, *The Chemical Structure and Thermal Characteristics of Polymer*, translated by J. Schmorak, Keter Press, Jerusalem, 1971.
24. A. A. Askadskii and G. L. Slonimskii, *Russian Chem. Rev.*, **44** (9), 767 (1975).
25. E. M. Pearce and R. Liepins, *Environ. Health Perspec.*, **11**, 69 (1975).
26. D. A. Kourtides and J. A. Parker, 11th National SAMPE Technical Conference, 551 (1979).

27. E. M. Pearce, in *Thermal Analysis in Research and Production*, Fourth Annual Conference at the Polytechnic Institute of New York, May 14-16, 1979.
28. C. S. Chen, B. J. Bulkin, and E. M. Pearce, *J. Appl. Polym. Sci.*, **27**, 3289 (1982).
29. S. C. Lin, Ph.D., thesis, Department of Chemistry, Polytechnic Institute of New York, 1978.
30. S. C. Lin and E. M. Pearce, *J. Polym. Sci., A-1*, **17**, 3059 (1979).
31. G. Serboli, *Brown Boveri Rev.*, **52** (8), 590 (1965).
32. R. L. Levy, D. L. Fanter, and C. J. Summers, *J. Appl. Polym. Sci.*, **24**, 1643 (1979).
33. N. B. Colthup, L. H. Daly, and S. E. Wiberly, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964, Chap. 5.
34. J. H. Flynn and L. A. Wall, *J. Polym. Sci.*, **B**, **4**, 323 (1966).

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