

N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM
MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT
CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED
IN THE INTEREST OF MAKING AVAILABLE AS MUCH
INFORMATION AS POSSIBLE

The Stability of New Transparent Polymeric Materials: The Epoxy
Trimethoxyboroxine System. Part 1. The Preparation,
Characterization and Curing of Epoxy Resins and their Copolymers.

1. Introduction:

Polymers of reasonably good stability and mechanical properties useful in various materials of construction are based on the epoxy resins of the diglycidyl ether of bisphenol-A (DGEBA). The flammability of DGEBA is one of the major problems in the application of this material. Martin and Price¹ examined the effects of resin composition, curing conditions, fillers, and flame-retardant additives on the flammability as measured by the oxygen index, and observed that the oxygen index of DGEBA cured with various curing agents were between 0.198 to 0.238. They also found that fillers and flame-retardant additives can increase the oxygen index to a certain level dependent on the material and the amount used. Since these approaches involve non-compatible additives, large changes in the basic cured resin properties can be anticipated. For retention of these basic properties, a search for inherently high flame resistant epoxy resins was initiated.

In the study of various boron-containing compounds as curing agents for epoxy resins, with the purpose of increasing the thermal stability of the resultant polymers, Haworth and Pollnow² concluded that the boroxine complex showed considerable promise as a homogeneous curing agent. This latent curing agent gave cured epoxy resins with heat deflection temperatures ranging from 80° to 120°C.

The Trimethoxyboroxine (TMB) was also used in the preparation

(NASA-CR-164951) THE STABILITY OF NEW
TRANSPARENT POLYMERIC MATERIALS: THE EPOXY
TRIMETHOXYBOROXINE SYSTEM. PART 1: THE
PREPARATION, CHARACTERIZATION AND CURING OF
EPOXY RESINS (Polytechnic Inst. of New York, G3/27

N82-11208

Unclass

01977

102 NASA STI PROGRAM
DEPT. OF AERONAUTICS AND SPACE

HC A04/mF A01

of epoxy resin foams^{3,4,5} with high heat resistance. Lee and Nixon^{3,4} used a primary polyamine and trimethoxyboroxine to obtain a highly cross-linked polymer which remained rigid at temperatures up to 300°C. The addition of a mixture of boric acid and sodium borate improved the self-extinguishing properties of the epoxy-boroxine-amine system due to boron oxide formation which forms a "glass-like" coating the burning mass and hindering the access of oxygen and the egress of volatile gases.

Parker, Fohlen and Sawko first used TMB as a curing agent to prepare transparent epoxy panels which had a heat distortion temperature of 110°C. This crosslinked transparent aromatic system is thermomechanically stable to 400°C, gives a high char yield, has a high tensile strength, and shows more resistance to laser penetration than conventional transparent materials. Recently, Lopata and Riccitiello⁷ investigated this epoxy-boroxine system by differential thermal analysis (DTA) and noted the occurrence of exothermic peaks at approximately 390°, 430° and 470°C, with the major exotherm being at 430°C. They also used solvent extraction, DTA and gel permeation chromatography to study the low molecular weight part of the cured epoxy system and found that this part plays an important role in relation to the exotherm at 430°C due to the presence of unreacted epoxide rings. Furthermore, they investigated the polymerization mechanism of this particular curing agent with a model epoxide compound, phenyl glycidyl ether⁸, and found that the polymerization involves a fast-initiated, nonstationary, cationic polymerization with five elementary steps, including spontaneous and monomer transfer as well as a termination reaction as shown in Figure 1.

2181211016819542
ACCESS
67891011121314

From a flame retardancy point of view, high char yield may be related to decreased flammability as measured by the oxygen index. Increased char formation can usually limit the production of combustible carbon containing gases, decrease the exothermicity due to pyrolysis reactions, and decrease the thermal conductivity of the surface of burning material⁹. Parker, Fohlen and Sawko⁶ also reported results on the polycarbonate prepared from phenolphthalein. This material has a thermogravimetric char yield of about 54% compared to 20% for bisphenol-A polycarbonate, has high impact strength and is effective against high-energy thermal radiation. The effect of monomer structure on the thermal properties of polycarbonate has been evaluated as shown in Table 1⁶. The char yield varies from 20% for the bisphenol-A polycarbonate to 54% for the phenolphthalein polycarbonate at 800°C, while the oxygen index varies in a similar manner from 23 to 47.

Koshak, Solov'eva and Kamenskikh¹⁰ prepared a series of epoxy polymers from bisphenols including 9,9-bis(4-hydroxyphenyl)fluorene. Based upon thermal analytical studies of the cured materials, they concluded that the heat resistance and thermal stability of the polymers obtained from the diglycidyl ethers varied according to the structure of the elementary unit. They also found that the best thermal stability was possessed by polymers having a fluorene or anthrone group between the two phenyl groups. The results are shown in Table 2.

Based upon these results, the material prepared from a diglycidyl ether of phenolphthalein (DGEPP) or 9,9-bis(4-hydroxyphenyl)fluorene (DGEBF) cured with trimethoxyboroxine should show better properties

over that obtained from the DGEBA-boroxine system provided good transparency and other desired properties can be obtained.

Lo^{11,12,13,14} first used phenolphthalein and epichlorohydrin to prepare the epoxy resin in a dry or aqueous system in the presence of sodium hydroxide. The purified resin is yellow in color and has a transition temperature 30°C. Based on the reaction of phenolphthalein with sodium hydroxide, Lo proposed four possible structures present in the epoxy resin. Because of the yellow color, Lo concluded that the quinoid structure is the major product from the reaction. Furthermore, Lo assumed that the original lactoid structure of phenolphthalein changed to an ester carbonyl, because of the shift of the 1725 to 1730 cm^{-1} band of phenolphthalein to 1750 to 1760 cm^{-1} in the resin.

Salazkin, Komarova and Vinogradova¹⁵ compared the absorption infrared spectrum of DGEPP resin directly obtained from the reaction of phenolphthalein and epichlorohydrin in the presence of aqueous sodium hydroxide with some related compounds of phenolphthalein and concluded that the new formed band at 1765 cm^{-1} is due to the stretching of carbonyl group in lactoid. Based upon this fact, they confirmed that the major product in the system is the phthalide rather than the quinoid.

In order to understand the products prepared from phenolphthalein and epichlorohydrin, liquid chromatography was used to separate each component in the product and to determine the relative amount of each compound. For identifying the actual structure of each compound, IR spectroscopy, UV spectroscopy and NMR spectroscopy were applied. The epoxy equivalent weights and the softening temperatures of the components

were measured.

For the sake of understanding how the structural unit difference affects on the reactivity of epoxy resins, differential scanning calorimetry (DSC) was used to investigate the curing reactions of epoxy homopolymer systems and the copolymer systems with curing agent, TMR.

The degree of crosslinking in a network polymer has a large effect on the various properties of polymers, such as dimensional stability and resistance to solvents. One method for determining the degree of crosslinking is to extract the polymer that is not incorporated into the network structure as a sol fraction. In this study, solvent extraction by tetrahydrofuran was employed to determine the amount of gel fractions in different compositions of copolymers and to help to understand the reactivity of epoxy resins.

The useful life of a material depends on the resistance to its environmental exposure. As previously expected, DGEPP and DGEBF should have higher thermal stability than the conventional epoxy resin, DGEBA. In order to improve the heat resistance and to lower the flammability of DGEBA, it was copolymerized with DGEPP or DGEBF. For understanding how the properties change with the content of DGEPP or DGEBF, DSC and thermogravimetry (TGA) were used to investigate the various copolymer compositions of DGEBA with DGEBF system or DGEBA with DGEPP system.

Char formation has been one of the important factors that appear to relate to the flammability of a material. Martin and Price¹ concluded that the oxygen index is nearly independent of cure conditions and tends to be lowered for increasing O/C ratio in the overall composition

in their flammability study on epoxy resins. Van Drevelen¹⁶ found a correlation between oxygen index (OI) and char residue (CR) on pyrolysis for halogen-free polymers as

$$OI = \frac{17.5 + 0.4 CR}{100} \quad (1)$$

where CR is expressed as a weight percent. However, the linear relationship between the oxygen index and the char residue or the variation of the oxygen index with the change of O/C ratio has to-date been limited to the relatively few polymers investigated. In the case of the copolymer system, it may be expected that each monomer should contribute a char residue of an oxygen index proportional to its composition, if two units in the copolymer do not chemically interact in an unusual manner and the copolymer has high molecular weight. The copolymer systems, DGEBA with DGEPP and DGEBA with DGEBF, were studied to confirm the wider applicability of these correlations between the char residue or the oxygen index and the composition of copolymers, and their general use for predicting the heat resistance and the flammability of a conventional epoxy polymer system modified by copolymerization with a high performance monomer.

2. Experimental

2-1. Preparation of Bisphenols

Bisphenol A and phenolphthalein (Aldrich) were recrystallized from aqueous alcohol and alcohol, respectively.

9,9-bis(4-hydroxyphenyl)fluorene was prepared from fluorenone and phenol with a catalyst, dry hydrogen chloride and a cocatalyst, β -mercaptopropionic acid¹⁸. 1 mole of fluorenone (Aldrich) was dissolved in 8 moles of molten phenol, 4 ml of β -mercaptopropionic acid was added and then dry hydrogen chloride was bulbed in for 20 minutes. The system became very dark and finally changed to a viscous and clear liquid. The mixture was then purified by steam distillation to remove unreacted phenol, hydrogen chloride and cocatalyst. After no more phenol in the distillate could be collected, the system was treated 10 liters of cold water and 2.1 moles of sodium hydroxide to dissolve 9,9-bis(4-hydroxyphenyl)fluorene. The mixture was filtered to separate unreacted fluorenone. The filtrate was extracted with toluene to remove the impurities present in the solution, and then, acidified the aqueous layer with acetic acid to precipitate a white solid. The product contained hydrate in crystal. Dehydration product was a white powder which was recrystallized from toluene or dry ether. A transparent crystal was collected from toluene or ether solution, washed with small amount of solvent, and then, dried in a vacuum drier. Finally a white powder with a melting temperature, 224°C, was obtained.

2-2. Synthesis of Diglycidyl Ethers of bisphenols

The apparatus employed was a heated reaction kettle with a thermometer, mechanical stirrer and a water cooled condenser. The reaction kettle was charged with 1 mole of phenolphthalein (Aldrich), and a

specified amount of epichlorohydrin (15 moles, 12 moles, 9.15 moles, and 3.2 moles). Due to the low solubility of phenolphthalein in epichlorohydrin, the former was suspended in the latter. The stirrer was started and the reaction mixture was heated to 90°C. During a period of 3 to 4 hours, 2 moles of sodium hydroxide pellets were added to the reaction mixture and the reaction temperature was maintained between 90°C to 100°C. The reaction mixture changed in color from white to deep violet and then yellow. After the color of the reaction mixture had become pale yellow, the solution was filtered to separate the solid sodium chloride formed during the reaction. The salt cake was washed with additional epichlorohydrin. The unreacted epichlorohydrin. The unreacted epichlorohydrin was then distilled off under a vacuum of 30 mm-Hg from the filtrate. After no additional epichlorohydrin could be removed under this vacuum, the vacuum was decreased to 2 mm-Hg for 30 minutes at 180°C.

DGEBF and DGEBA were prepared by the same procedures as the preparation of DGEPP except the initial reactant feed ratio of the bisphenol to epichlorohydrin was 1 to 10.

2-3. Liquid Chromatography

Silica gel (Grace) with the mesh number 60 to 200 and 5 volume percent of acetone in chloroform were used as absorbent and elution solvent, respectively. The column employed had an inner diameter of 3.5 cm and a height of 40 cm. Ten to fifteen grams of the DGEPP was charged. Two different colors, red and yellow, were observed in the column at the beginning. The red color material eluted first and became colorless after elution from the column. A higher acetone

content eluent (Gradient method) was added in order to remove the slowly moving yellow material. The elution rate was 10 ml per minute and the solution was collected in 50 ml portions. The solvent was removed by simple distillation and the residue was weighed.

2-4. Product Analysis

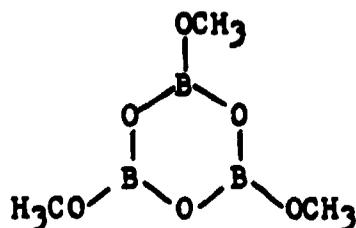
The products collected from the column were identified by UV, NMR and IR spectroscopies. The Cary-14 Spectrophotometer was used for UV studies and chloroform used as the solvent. A Varian A-6C NMR Spectrometer was used for the NMR measurements and CDCl_3 was employed as solvent. The IR spectra were obtained by reflecting the infrared beam on a sample coated on an aluminium plate using a Fourier Transform IR system with 4 cm^{-1} resolution and a double precision collection. The softening temperature of each component obtained from liquid chromatography was studied by DSC (DuPont Thermal Analyzer 900).

2-5. Epoxy Equivalent Weight Determination

ASTM-D 1652-73¹⁷ method was used to determine the epoxy content of the epoxy resins. Two tenths of a gram of the resin was added to a 50 ml flask and then dissolved in 10 ml of 50 volume percent of chlorobenzene in chloroform. The mixture was stirred with a teflon coated magnetic stirring bar. Four to six drops of 0.1 percent of crystal violet solution in glacial acetic acid was used as the indicator. The solution was titrated with 0.1 N of hydrogen bromide in acetic acid to a blue-green end point.

2-6. Curing

TMB (Aldrich) was used as the curing agent.



In order to compare the results of the cured epoxy resins, 9.5 grams of TMB was mixed with 1 equivalent of epoxy resin.^{6,7}

The DGEPP or DGEBF was powdered under room temperature and then mixed with the curing agent. The mixture of the DGEPP-TMB system was red in color.

The two component epoxy system was prepared by mixing DGEPP or DGEBF and DGEBA together at 130°C, and then, the curing agent was added to the system. The curing conditions were also investigated by DSC (DuPont Thermal Analyzer 900).

The curing was carried out at 135°C for 3 hours, 180°C for 3 hours and 220°C for another 3 hours.

DGEBA was mixed with 5 phr. of TMB and then coated on a fresh and smooth surface of aluminium plate. The DGEBA coated plate was put on a microheater which can control the constant temperature and is set up in the sample compartment of a Fourier Transform IR system (Digilab, FTS-IR Spectrometer, Model FTS-20B) right after coating. The temperature was controlled at 80°C. The heater set up is shown in Figure 2.

2-7. Thermal Analysis

The thermal properties of various samples in this study were investigated on DuPont Thermal Analyzer for DSC and a DuPont 950 Thermogravimetric Analyzer for char residue determination. All measurements were carried out under a N₂ atmosphere at a flow rate of 0.2 liter

per minute with a heating rate of 10°C/min.

2.8. Oxygen Index Measurement

The oxygen index of the various compositions of DGEBA copolymerized with DGEPP were measured using the General Electric Model CR280kf11A Fluid Flammability Test Kit which extends the oxygen index method to liquids and solid materials which can be melted or tested in powder or pellet form.

The cured epoxy resin was made into a pellet form first, and then placed in a sample cup mounted on the cup holder in the flame chamber.

The mixture of oxygen and nitrogen is passed upward through the chimney at a flow rate 3 to 5 cm/sec. The test followed the manual procedures²⁰. The oxygen index was obtained from the equation as

$$OI = \frac{O_2}{O_2 + N_2} \quad (2)$$

where the unit of gas quantity is volume.

2.9. Gel Fraction Determination

1.0 gram of cured polymer was charged into Soxhlet apparatus for 48 hours with a solvent, tetrahydrofuran. The insoluble part was collected and dried until no more weight change could be detected. The gel fraction was calculated as

$$\text{Gel Fraction} = \frac{\text{Weight of insoluble material}}{\text{Initial weight of material}} \quad (3)$$

3. Results and Discussion

3-1. Structure Study on the Phenolphthalein Epoxy Resin

The original epoxy resin of phenolphthalein produced from the reaction between phenolphthalein, epichlorohydrin, and sodium hydroxide is yellow in color. Lo^{11,12,13,14} first prepared this material and proposed that the product has four possible structures based on the equilibrium reaction between phenolphthalein and sodium hydroxide (Figure 3). Because of the yellow color and the infrared absorption band shift, Lo further assumed that the quinoid is the major product in the reaction¹¹.

Salazkin, Komarova and Vinogtadova¹⁵ compared the absorption infrared spectrum of 3,3-(bisphenyl)phthalide with those of compounds (Figure 4) which have similar or the same structures proposed by Lo, and concluded that the phthalide is the major product instead of the quinoid structure.

In order to confirm the composition and the amount of each component in the phenolphthalein epoxy resin, liquid chromatography was carried out. The pure chloroform as eluent gave a better resolution, but the mixture of chloroform and acetone have a shorter elution time. In order to get better resolution and a faster elution rate, 5% by volume of acetone in chloroform was used as solvent. Figure 5 is the dried weight of the collected material as a function of elution volume. Three peaks (defines as A, B, and C) can be observed independent of the feed ratio of epichlorohydrin to phenolphthalein in the preparation of epoxy resin. The first fraction, A, gave a colorless, transparent and very viscous material which is the major product. The second fraction, B, was solid with a very light yellow. The third fraction

C, was a yellow solid resin.

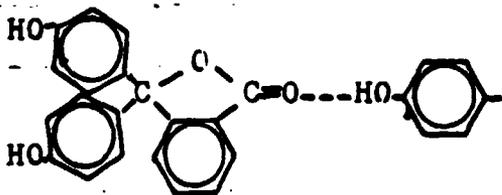
The properties of the separated components from the epoxy mixture are shown in Table 3. The softening temperature as measured by DSC and the epoxy equivalent weight both increase with increased retention volume. If the structure of the epoxy resin is the phthalide form, then, the the first peak (major peak) will be the monomer of DGEPP. No melting point was observed even when the samples were cooled and measured again, and this was indicative that the epoxy resin was in a glassy state. As the case of the DGEBA preparation²¹, the epoxy equivalent weight decreases with an increase of the initial feed ratio of epichlorohydrin to phenolphthalein as shown in Table 4. The amount of monomer formation and epoxy equivalent weight are controlled by the initial feed mole ratio of reactants. The change of weight fraction of fraction A (y) obtained from liquid chromatography with the variation of feed mole ratio (x) may be generalized and represented as

$$y = 1.0 - e^{ax} \quad (4)$$

with a boundary condition, $x = 0; y = 0$ and $x = \infty; y = 1.0$, where a is an arbitrary constant which is equal to -1.5, obtained from Figure 6, in this study.

The infrared spectra of the three components from the liquid chromatography have the same absorption patterns. They show a distinct shift of the 1725 cm^{-1} band of phenolphthalein to 1765 cm^{-1} in the resin. Lo¹¹ assumed the change of ketonic carbonyl to an ester carbonyl, but Salazkin et al¹⁵ related this to the normal phthalide carbonyl absorption by comparison with model compounds. Jones et al²²

examined the infrared spectra of 23 simple saturated and unsaturated lactones and showed that the unsaturated five member ring lactones including two phthalides gave the carbonyl absorption between 1772 cm^{-1} to 1787 cm^{-1} in CCl_4 and 1752 cm^{-1} to 1789 cm^{-1} in CHCl_3 . From these results, it can be concluded that the three components have the same structure which is the phthalide instead of the quinoid or other structures proposed by Lo. The shift of the phthalide carbonyl absorption band in the infrared spectrum may be attributed to the formation of hydrogen bonding between carbonyl group in the lactone ring and hydroxyl group which is present in phenolphthalein and absent in its epoxy resin since the proton in the hydroxyl group has been replaced by a glycidyl group. The infrared spectrum of phenolphthalein shows a very

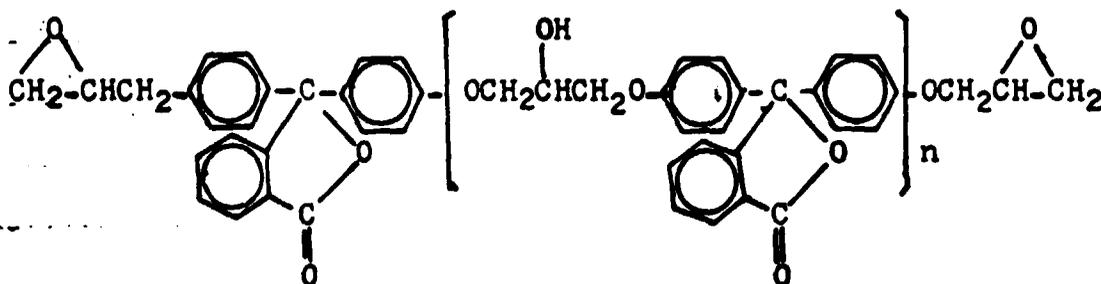


strong and broad absorption in the region from 3700 cm^{-1} to 2200 cm^{-1} which indicates the formation of hydrogen bonding. The hydrogen bonding, of course, can be formed between two hydroxyl groups, but its formation from carbonyl group and hydroxyl group appears to be important and accounts for the observed absorption band shift. The hydrogen bonding formation can decrease the charge density or bond order of the π -bond in the carbonyl group and cause the vibrational frequency shift to a lower value.

The ultraviolet spectra (Figure 7) of the three components in the epoxy resin also indicates that they have the same structure due

to the same absorption patterns. All of the three components show three absorption maximum at 238 nm, 275 nm and 282 nm which are the same as for pure phenolphthalein in the same solvent, chloroform. This is indicative that basically the epoxy resin has the same functional group - the phthalide structure - as phenolphthalein. The only difference between phenolphthalein and its epoxy resin is the extinction coefficient ratio, $E_{238 \text{ nm}}/E_{275 \text{ nm}}$. This value is 3.0 for phenolphthalein and 4.2 for each component of the epoxy resin. Furthermore, the simple compound, phthalide, also showed the same absorptions²³. If the phthalide structure is opened during resin preparation and forms an ester, then the absorptions should have some degree of shift, but, in this study, no shift was observed. It can be concluded that the assumption of the quinoid structure in the epoxy does not occur.

The extinction coefficients for each component in the DGEPP resin were calculated based on the titration result of epoxy equivalent weight determination and the structure (V) assumed below



(V)

by the equation

$$\text{Absorbance} = E \times \frac{\text{Mass of epoxy resin in 1 l. of solution}}{\text{Epoxy eq. Wt.} \times 2} \times (1+n) \quad (5)$$

and

$$\text{Epoxy equivalent weight} = (430 + 374 n)/2 \quad (6)$$

The extinction coefficients of the three peaks observed in the spectra are shown in Table 5. From this table, it may be observed that the extinction coefficients at $\lambda = 275 \text{ nm}$ and $\lambda = 282 \text{ nm}$ are about $0.45 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$ and $0.40 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$, respectively, and are independent of the component of the epoxy resin and of phenolphthalein. At $\lambda = 238 \text{ nm}$, the extinction coefficient increased from $1.42 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$ for phenolphthalein to about $1.90 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$ for its epoxy resin. From the structure (V), equation (5), equation (6) and the extinction coefficient, the epoxy equivalent weight may be calculated from ultraviolet spectral results.

Nuclear magnetic resonance spectroscopic studies of the three components in the epoxy resin show a small difference. Figure 8 is the NMR spectra of the glycidyl groups in the three components. The terminal >CH_2 group of epoxide, $-\dot{\text{C}}\text{H}$ group of epoxide and the other $-\text{CH}_2-$ group with the ether linkage have peaks at 2.8 ppm, 3.3 ppm and 4.1 ppm, respectively, which are the same as the simple model compound, phenyl glycidyl ether, with the same splitting picture and coupling constants. For component A, the integral shows the ratio of hydrogen atoms as approximately 2 to 1 to 2 which is the same as the proposed structure of monomer, the phthalide structure in Figure 3. Components B and C show a relative increase in the integral of $-\text{CH}_2-$ with ether linkage, but the ratio of proton number of terminal >CH_2 of the epoxide group and $-\dot{\text{C}}\text{H}$ group is still 2 to 1. A possible explanation for this result is that component B and component C are

not monomer and have a higher n value in the structure (V). The n values of the three component have been calculated based on this structure and from the epoxy equivalent weight determined as shown in Table 3. This structure shows that the $-CH_2-$ group with ether linkage increases relatively in intensity in the NMR spectrum as the value of n increased.

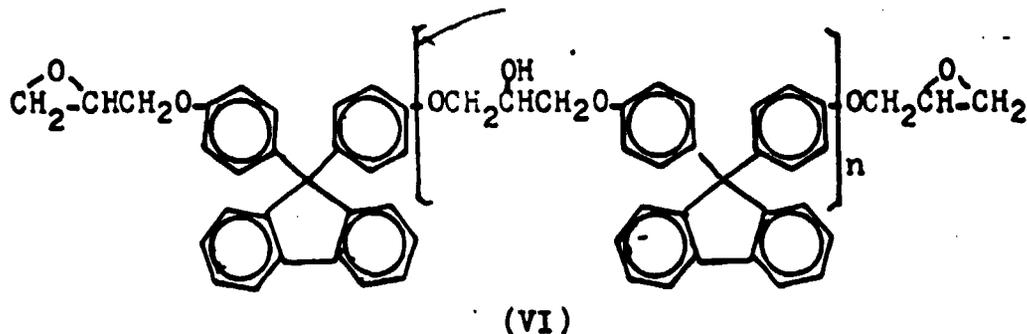
From the previous results, it may be concluded that the phthalide structure in phenolphthalein is not opened to the ester during the preparation of the epoxy resin. The only structure in the product is phthalide, even if three components were obtained from liquid chromatography. The structure of phenolphthalein in an aqueous alkaline solution is known to depend on the amount of alkali present. The formation of the epoxy resin with phthalide structure shows that a rearrangement or a shift of equilibrium between forms (II) and (I) in Figure 3, take place during the reaction and leads to the retention of the lactone ring in phenolphthalein.

The difference among the three components is the degree of polymerization and the colors they have. The reason for color formation is not clear. The softening temperature increases from A to C and is apparently due to the increase in average molecular weight.

The three components were individually cured with the same amount (9.5 g/ epoxy eq.) of curing agent, trimethoxyboroxine. After mixing the curing agent with each component, the reaction mixture gave a red color at the beginning and formed an orange transparent cured epoxy resin. Because three components with different color gave the same final result. it also seemed to confirm the same basic structure in the three fractions.

3-2. Properties of Diglycidyl Ether of 9,9-bis(4-hydroxyphenyl)fluorene (DGEBF)

Korshak et al¹⁰ first prepared this epoxy resin from epichlorohydrin, 9,9-bis(4-hydroxyphenyl)fluorene and sodium hydroxide and found that the resin cured with trimellitic anhydride or m-phenylenediamine gave very good heat resistance and high thermal stability. DGEBF is water white and has a softening temperature about 50°C obtained from DSC measurement, and an epoxy equivalent weight 305 grams per equivalent. An extremely small amount of unremovable dispersed material was present. The structure of the DGEBF is proposed as



Based on this structure and epoxy equivalent weight, the average n value can be calculated as 0.36. At the same temperature, this resin has the highest melt viscosity among the three epoxy resins, DGEBA, DGEBF and DGEPP. This may indicate the highest chain stiffness among these three resins. This property is very important in the curing process.

3-3. Curing Studies

In order to determine the best curing conditions for epoxy resins, the DSC thermal analyzer was employed to investigate the initial curing temperatures.

Figure 9 is the DSC thermograms of DGEPP, DGEBF and DGEBA after mixing with TMB. It can be observed that the mixture of DGEBA and TMB and that of DGEPP and TMB start to release heat at 70°C and 150°C, and give the maximum exotherm at 170°C and 240°C, respectively. No maximum exotherm can be detected in either the DSC thermogram of epoxy resins without curing agent or the completely cured epoxy resin in the same temperature concerned. This indicates that the peaks are attributed to the exothermic curing reactions.

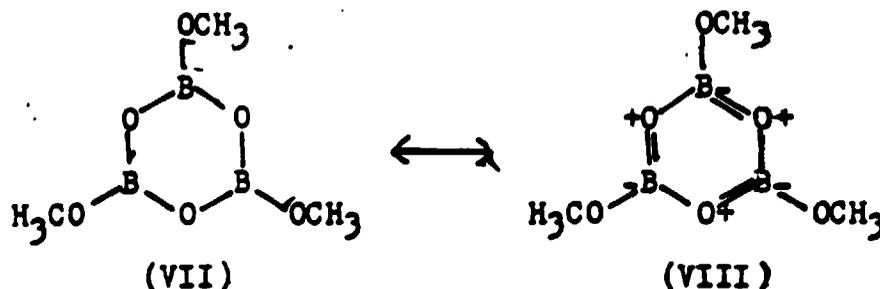
The chemical reaction rate of a closed system depends on several factors, such as the concentrations of reactants, the reactivities of the reacting functional groups and the mobilities of the molecules or the functional groups. As described above, exotherm of DGEBA in the curing is much earlier than that of DGEPP. The DGEBF-boroxine system showed a similar thermogram to that of DGEBA system except the transition temperature is 50°C compared and also exotherm has a maximum, 150°C, compared to 170°C for DGEBA.

In solvent extraction studies, gel fraction varies with the composition of the copolymers using the same curing conditions as shown in Table 6. The DGEBF copolymer with DGEBA has a almost constant gel fraction up to a 30 mole % of DGEBF content, then decreases with increased DGEBF composition, and finally reaches a 33.3 wt. % of crosslinked material. In the case of DGEPP copolymer with DGEBA, the gel formation decreases with an increase of DGEPP content, becomes lower at higher than 45 mole % of DGEPP content and has a final gel fraction of 54.3 wt. %.

Based upon these results, the lower exotherm starting temperatures of DGEBA and DGEBF curing systems and comparative gel fractions obtained

from DGEBA homopolymer and its copolymer with DGEBF extened to a 70 mole % content, it is reasonable to propose that the epoxide groups of both resins have similar chemical reactivities during curing with TMB. In the case of DGEPP, it showed a higher starting exother temperature and is incative of as epoxy-boroxine system with low reactivity. As described previously, DGEPP changed its color from yellow to red after mixing with TMB and to orange at thefinal cured stage. This may be indicative of a compoex formation between DGEPP and TMB. DGEPP, determined previously, is a derivative of phthalide and has an electron rich carbonyl group, but the TMB has three electron deficient boron atoms in a molecule. Phthalide and boroxine may form a complex and reduce the possibility of reaction between the epoxide ring and the curing agent. In the polymerization study of phenyl glycidyl ether, Lopata and Riccitiello⁸ proposed a fast initiated mechanism. The epoxide group forms a carbonium ion after rapidly reacting with TMB as shown in Figure 1. If a complex is formed between DGEPP and boroxine, then, to initiate the polymerization, one has to break this complex by heating.

From B¹¹ quadruple coupling constant in TMB study, Ring and Koski²⁴ concluded that the resonance structures of this compound are



ORIGINAL PAGE IS
OF POOR QUALITY

and 60% of the structure (VIII) is present in this material. The methoxy group also increases the acidity of the boron and thus the double-bond character. This fact indicates that TMB is present with a highly electron deficiencie and 60 % of aromaticity which is very

favorable for forming a complex with the electron rich group such as the carbonyl group in phthalide.

It is a well known trend that a molecular unit with a higher aromatic ring content has higher rigidity or stiffness and higher viscosity of its melt at a certain temperature, if all other factors are equivalent. From the structure consideration of the three epoxy resins, the measuring order of aromatic ring content is DGEBF > DGEPP > DGEBA, which also corresponds to a transition temperature and the viscosity at a certain temperature. Because of the higher viscosity of DGEBF and relatively high temperature employed in curing, DGEPP may have a higher crosslinking density at the final stage of the curing cycle, even though DGEBF is more reactive.

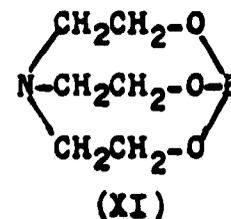
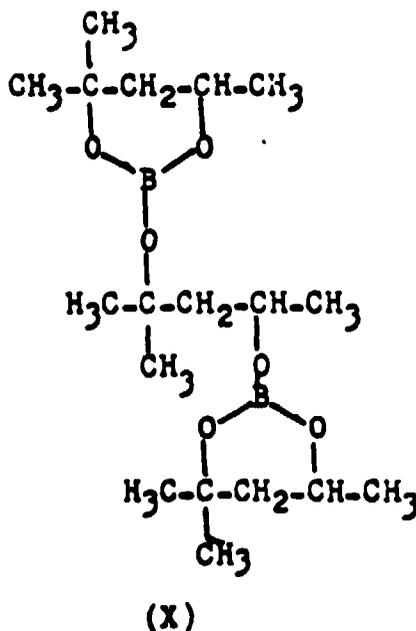
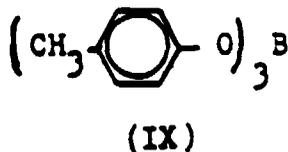
The variation of gel fraction with copolymer composition can also be explained by the same reasoning. The copolymer of DGEBF with DGEBA at a content up to about 30 mole % of DGEBF has the same or slightly increased gel fraction in weight percent. The DSC thermograms showed the same reactivity of epoxide groups in both resins, thus, the curing reaction of the copolymer with a DGEBF content lower than 30 mole % may be controlled by the reactivities of resins. If the DGEBF content is higher than 30 mole %, the viscosity of the resin will become significantly high enough to shift from a reactivity controlled curing to a diffusion controlled reaction after a certain degree of crosslinking reaction. The shifting period from a reactivity controlled reaction to a diffusion controlled one is shorter if the DGEBF content is higher, due to the higher stiffness of DGEBF unit and correspondently the higher viscosity of DGEBF. Therefore, gel fraction can be expected to

decrease with the increasing DGEBF content in the copolymerization system of DGEBA and DGEBF.

Due to the lower reactivity of DGEPP resin, its copolymer with resin should decrease the gel formation continuously with an increase of DGEPP content. Because of higher mobility of DGEPP compared to DGEBF, the high DGEPP content copolymer with DGEBA should have higher gel formation than the same content of DGEBF in the copolymer of DGEBF and DGEBA.

Furthermore, the cured DGEPP and DGEBF were very brittle and weak in strength. This may result from a relatively lower degree of crosslinking as shown in the gel fraction studies.

For improving the cured properties of DGEPP and DGEBF, three high boiling temperature boron compounds- trim,p-cresyl borate (IX), tri-hexylene glycol diborate (X) and triethanolamineborate (XI) were also investigated



but only compound (XI) which is a white solid with a melting point,

235.5°C to 238.5°C gave good cured properties for three resins under the correspondent amount of curing to TMB. Also DGEPP cured with compound (XI) appeared a pale yellow transparent tough material instead of an orange transparent weak resin cured with TMB.

For studying the curing reactions, the Fourier Transform Infrared Spectrometer was used on the DGEBA-TMB system. 8 cm⁻¹ resolution and double precision were employed. The advantages of this technique are the high sensitivity of absorption spectral detection, the same epoxy coated plate used through the whole experimental period without changing the thickness of the sample and the ability to obtain the difference spectrum from the sample spectra before and after curing.

The conventional infrared spectrometer has been used for curing studies on DGEBA curing with other curing agents^{24,25}. Due to the low sensitivity of the conventional infrared spectrometer, the results were only traced by following the change of the 910 cm⁻¹ of absorption band which was assigned as epoxide group.

Lopata and Riccitiello⁸ studied the kinetics of the bulk thermal polymerization of phenyl glycidyl ether induced by TMB using infrared absorption spectroscopy and gel permeation chromatography to follow the polymerization. Based on the results obtained, they postulated a fast-initiated, nonstationary cationic polymerization with five elementary steps, including spontaneous and monomer transfer as well as a termination reaction.

For being able to understand the reactions during the curing process of the DGEBA system, the FTIR spectrometer was used to investigate the detail chemical changes occurring during bulk polymerization. Figure 10 shows the difference spectrum of the mixture of DGEBA and TMB with

a mole ratio 7.9 to 1 before and after the sample was cured for 36.5 minutes at 80°C. From this spectrum, it can be observed that the absorption bands at 3063 cm⁻¹, 3009 cm⁻¹, 914 cm⁻¹, 860 cm⁻¹, 775 cm⁻¹ and 721 cm⁻¹ decreased after 36.5 minutes curing period. The absorption bands at 3063 cm⁻¹ and 3009 cm⁻¹ are due to the C-H stretching of the methylene and of the methin groups of the epoxide ring^{27,28}. The bands occurring at 914 cm⁻¹ and 860 cm⁻¹ are the ring deformation of epoxide group.^{29,30,31} The rocking of the epoxide ring may be assigned to be at 775 cm⁻¹ and 721 cm⁻¹ which were found to be strong absorptions at 821 cm⁻¹ and 807 cm⁻¹ in the ethylene oxide²⁷. Based on these results, the polymerization reaction has only consumed the epoxide ring.

Also increases of bands were observed at 2947 cm⁻¹, 2893 cm⁻¹, 2855 cm⁻¹ and a region between 1150 cm⁻¹ and 950 cm⁻¹. The absorption bands at 2947 cm⁻¹, 2893 cm⁻¹ and 2855 cm⁻¹ may indicate the formation of -CH₂- group without the strained epoxide ring²⁸. The absorption region between 1150 cm⁻¹ and 950 cm⁻¹ is broad and appeared that several bands overlapped together. This region may be the formation of the ether linkages and an -OH functional group³². The decreasing order of C-O vibrational frequency as a function of the group substituted on one oxygen is³²



Possibly, primary and secondary ethers, and primary and secondary hydroxyl groups can be formed directly from the terminal epoxide ring during polymerization.

Figure 11 shows the quantitative results of the variation of the bands as a function of curing time. From this figure, it may be observed that the -CH₂- and C-O-C groups form very fast initially and

then level off after an hour during the curing period. The disappearance of epoxide group has a comparable rate to the formation of $-CH_2-$ and C-O-C groups initially, but the epoxide group still decreased even after the formation of $-CH_2-$ and C-O-C groups have leveled off. This may indicate that the epoxide group reacts continuously to form some other species instead of the formation of $-CH_2-$ and C-O-C groups. This will be investigated further in the future.

3-4 Thermal Characterization

The DSC was used to study the glass transition temperature of the homopolymers, to understand the effect of copolymer composition on the glass transition temperature, and to investigate the heat change during the decomposition of the cured epoxy resins. The DSC thermograms of the cured DGEPP, DGEBF and DGEBA in an inert atmosphere of N_2 showed exothermic peaks at approximately $310^\circ C$, $390^\circ C$ and $430^\circ C$ for the first, $310^\circ C$, $380^\circ C$ and $420^\circ C$ for the second and $345^\circ C$, $390^\circ C$, $430^\circ C$ and $470^\circ C$ for the third (Figure 12). This may indicate that they have almost the same degradation paths even though different structural units are present. Therefore, it can be assumed that the degradation starts from the similar structure units - the aliphatic groups present in the three cured resins.

The glass transition as a function of composition in copolymers has been extensively studied by many investigators and the current theories were summarized by Wood³³. The glass transition of a copolymer should be equal to some type of a weight average of the individual glass transitions of the homopolymers T_{g1} and T_{g2} . For a binary copolymer, the Gordon-Taylor equation relating the glass transition to the glass transition temperatures of the homopolymers is equivalent

to

$$A_1 C_1 (T_g - T_{g1}) + A_2 C_2 (T_g - T_{g2}) = 0 \quad (7)$$

where C_1 and C_2 are the weight fractions of the constituents and A_1 and A_2 are constants. It can be rearranged to the form

$$T_g = K(T_{g2} - T_g) (C_2/C_1) + T_{g1} \quad (8)$$

and

$$T_g = -(1/K) (T_g - T_{g1}) (C_1/C_2) + T_{g2} \quad (9)$$

where $K = A_2/A_1$. Figure 13 shows the glass transition temperature as

a function of $\frac{(T_g - T_{g1}) (1 - C_2)}{C_2}$ and a function of $\frac{(T_{g2} - T_g) C_2}{(1 - C_2)}$

for DGEBA-DGEPP copolymer. From this plot, the $1/K$ value and K value can be obtained from each linear relationship. In this case, the K parameter for copolymer of DGEBA and DGEPP cured by TMB is equal to 4.0. Figure 14 is the glass transition temperatures for various compositions of DGEPP and the theoretical result obtained.

A similar treatment for the copolymer of DGEBF and DGEBA is shown in Figure 15 and Figure 16. The K parameter obtained from Figure 15 is 3.5 for this copolymer system based on the glass transition temperatures of the copolymer with the DGEBF content below 35 mole % and the homopolymer of DGEBF. From Figure 16, two glass transition temperatures for DGEBF homopolymer, 350°K and 400°K can be observed, the former is the one obtained directly from the same curing cycle as the other polymerization system. The latter was obtained by further curing at 220°C for 3 additional hours. The K parameter was calculated from 400°K to glass transition of DGEBF homopolymer. The glass transition temperature start to deviate from the Wood equation, after the DGEBF

content is higher than 35 mole %. It is lower than the predicted value and may be due to the incomplete curing indicated previously by the gel fraction study. This showed low gel formation for the high DGEBF content copolymer with DGEBA as shown in Table 6.

Char formation is important for the prediction of the flammability of a material. In this study, the char yields of homopolymers and copolymers of various compositions were investigated by thermogravimetry. Figure 17 and Figure 18 show some results of the thermogravimetric measurements of ^{homopolymers} copolymers and copolymers. From both figures, it can be observed that the decomposition temperatures are almost the same, but the char yield changes with the copolymer composition. The thermogravimetric plots also show two stage decompositions, a primary decomposition in the range 400°C to 480°C and a second pyrolysis stage above 480°C. These results are also indicative that the cured epoxy resins may have the same degradation routes as concluded from the DSC studies.

If char formation of each monomer unit in the copolymer is independent of each other chemically or there is no chemical interference between monomer units during degradation, and the polymer molecular is high, it may be assumed that the char yield of each monomer unit in the copolymer is proportional to its mole fraction and expressed as

$$Y_1 = X_1 Y_1^0 \quad (10)$$

where Y_1 and Y_1^0 are the char yields of monomer unit i in copolymer with a mole fraction X_1 and in its homopolymer, respectively. The total char yield of a copolymer, therefore, will be equal to the sum of the char yield of each monomer unit in the copolymer or

$$Y = \sum X_i Y_i^0 \quad (11)$$

Figure 19 shows the char residue at 700°C as a function of the mole fraction of DGEPP in the copolymer with DGEBA. A linear relationship between char yield and the composition of DGEPP in the copolymer can be observed. The linear relationship between char yield and copolymer composition was also observed in the copolycarbonate of bisphenol-A and phenolphthalein³⁴.

For the case of DGEBF copolymer with DGEBA, there is no linear relationship between char yield and copolymer composition observed as shown in Figure 20. It is different from the initial prediction for this copolymer system. As it can be seen, the char yield increases very fast at a low content of DGEBF and reaches a maximum value of 40 wt. % at about 20 mole % of DGEBF and then decreases. Explanations for this effect are not conclusive at this time. Possibly, it may be due to low degree of curing, if the DGEBF content is over 30 mole % in the copolymer of DGEBF and DGEBA. Another possible explanation is that the reaction between two monomer units to form more thermally stable structure under high temperature. No matter how the DGEBF changes the char yield or deviates from the predicted linear relationship, the DGEBF increases the char yield to a high value, 40 wt. % at 20 mole % of DGEBF content at 700°C. This indicates the DGEBF has a good potential to be used to modify the more flammable conventional epoxy material, DGEBA.

Similar treatment can also be applied to the flammability of the copolymer by assuming that the oxygen index of a monomer unit in its copolymer is proportional to the mole fraction in the copolymer. Then

the total oxygen index will be equal to the sum of individual value of each monomer unit.

$$OI = \sum X_i OI_i^{\circ} \quad (12)$$

where OI_i and OI_i° are the oxygen indice of monomer i in its copolymer with a mole fraction X_i and in its homopolymer, and OI is the total oxygen index. Figure 21 is the linear relationship between the oxygen index and the mole fraction of DGEPP in its copolymer with DGEBA.

Combining the Equation (11) and Equation (12), the relationship between oxygen index and char yield can be express as

$$OI = Y \frac{(OI_1^{\circ} - OI_2^{\circ})}{(Y_1^{\circ} - Y_2^{\circ})} + OI_2^{\circ} - Y_2^{\circ} \frac{(OI_1^{\circ} - OI_2^{\circ})}{(Y_1^{\circ} - Y_2^{\circ})} \quad (13)$$

or

$$OI = k_1 Y + k_2 \quad (14)$$

where $k_1 = \frac{(OI_1^{\circ} - OI_2^{\circ})}{(Y_1^{\circ} - Y_2^{\circ})}$ and $k_2 = OI_2^{\circ} - Y_2^{\circ} k_1$. Figure 22 is the oxygen

index as a function of the copolymer char yield of DGEPP with DGEBA.

The solid line in this figure is s calculated result based on $Y_1^{\circ} = 0.24$, and $Y_2^{\circ} = 0.46$ obtained from Figure 19, $OI_1^{\circ} = 0.205$ and $OI_2^{\circ} = 0.430$ taken from Figure 21 and the Equation (14)

4. References

1. F.J. Martin and K.R. Price, J. Appl. Polymer Sci., 12, 143 (1968).
2. D.T. Haworth and G.F. Pollnow, I&EC, Product and Research and Development, 1(3) 185 (1962).
3. H.H. Chen and A.C. Nixon, Am Chem. Soc., Div. Org. Coatings, Plastics Chem., Preprints, 23(1), 221 (1963)
4. H.H. Chen and A.C. Nixon, SPE Trans., 5(2), 90 (1965).
5. J. Demonte, in Handbook of Foamed Plastics, R.J. Bender Ed., Lake, New York, P. 313 (1965).
6. J.A. Parker, G.M. Fohlen and P.M. Sawko, Development of Transparent Composites and Their Thermal Responses. Paper present at conference on Transparent Aircraft Enclosures, Las Vegas, Nevada, Feb., 5-8 , (1973).
7. E.S. Lopata and S.R. Riccitiello, J. Appl. Polymer Sci., 19, 1127 (1975).
8. E.S. Lopata and S.R. Riccitiello, J. Appl. Polymer Sci., 21, 91 (1977).
9. E.M. Pearce and R. Liepins, Environmental Health Perspectives, 11, 69 (1975).
10. V.V. Korshak, L.K. Solov'eva and I.V. Kamenskh, Vysokomol. Soyed., 13, 150 (1971).
11. E.S. Lo, Ind. Eng. Chem., 52(4), 319 (1960).
12. E.S. Lo, USP 3015647 (1962); Chem. Abs., 56, 8928 (1962).
13. E.S. Lo, USP 3015648 (1962); Chem. Abs., 56, 11793 (1962).
14. E.S. Lo. USP 3008925 (1962); Chem. Abs., 56, 4974 (1962).

15. S.N. Salazkin, L.I. Komarova, and S.V. Vinogradova, *Izv. Akad. Nauk. SSSR, Ser. Kim.*, 144 (1973)
16. L.E. Nielson, *J. Macromolecular Sci.*,
17. D.W. Van Krevelen, *Polymer*, 16, 615 (1975).
18. P.W. Morgen, *Macromolecules*, 3, 536 (1970).
19. Standard Method of Test for Epoxy Content of Epoxy Resins, ASTM D 1652-73, 28, 341 (1975).
20. General Electric Model CR280KF11A Fluid Flammability Test Kit, Test Procedure Manual, 4541K 25-001C.
21. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 2-7 (1967).
22. R.N. Jones, C.L. Angell, T. Ito and R.J.D. Smith, *Can. J. Chem.*, 37, 2007 (1959).
23. W.A. Schroeder, P.E. Wilcox, K.N. Trueblood and A.O. Dekker, *Anal. Chem.*, 23, 1740 (1951).
24. M.A. Ring and W.S. Koski, *J. Chem. Phys.*, 35, 381 (1961).
25. M.A. Acitelli, R.B. Prime and E. Sacher, *Polymer*, 12, 335 (1971).
26. E. Sacher, *Polymer*, 14, 91 (1973).
27. R.C. Lord and B. Nelin, *J. Chem. Phys.*, 24, 656 (1956).
28. H.B. Henbest, G.D. Meakins, B. Nickolis and K.J. Taylor, *J. Chem. Soc.*, 1459 (1957).
29. O.D. Sheve and M.R. Heether, *Anal. Chem.*, 23(2), 277 (1951).
30. W.A. Patterson, *Anal. Chem.*, 26(5), 823 (1954).
31. J. Bomstein, *Anal. Chem.*, 30(4), 544 (1958).
32. H.A. Szymanski, *The C-O, O-O and O-H Group Frequencies of Alcohols, Ethers, Phenols, Hydroperoxides, Peroxides, Acids and Ethers*, in "Progress in Infrared Spectroscopy" H.A. Szymanski Ed., Plenum

press, New York, Vol. 3, 111 (1967).

33. L.A. Wood, J. Polymer Sci., 28, 319 (1958).

34. M.S. Lin and E.M. Pearce, Unpublished.

TABLE 1

Effect of Monomer Structure on the Thermal Properties of Polycarbonates

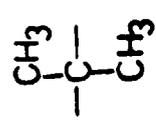
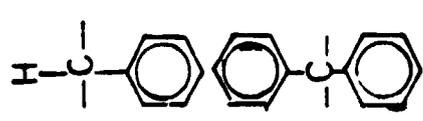
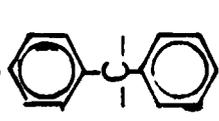
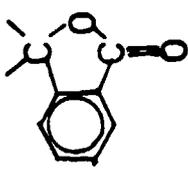
Polycarbonate Type.	-R-	Tg. °C	Tm. °C	Id. °C	Yc. %	800 °C %	O.I.
Bisphenol A		150	190	400	20	23	
Triphenyl		180	220	325	40	—	
Tetraphenyl		220	260	397	40	—	
Phenolphthalein		278	295	425	54	67	

TABLE 2

PROPERTIES OF POLYMERS OF DIGLYCIDIC ETHERS

Number of the diglycidic ether, from Table 1	Hardener	Content of polymer, %	Cocking number, %	Heat resistance under deformation, °C	T _c (temperature of the onset of deformation), °C	Thermal stability			
						temperature for 20% weight loss based on TGA, °C	weight loss (%) after heating at 300°C; time, hr		
							1	3	6
1	Trimellitic anhydride	99.2	28.9	250	90	300	44.6	77.4	90.1
	<i>m</i> -Phenylenediamine	99.0	18.0	220	80	290	48.0	82.2	93.5
2	Trimellitic anhydride	99.7	36.1	280	130	310	33.0	46.4	51.0
	<i>m</i> -Phenylenediamine	98.6	32.4	265	103	300	37.1	49.2	55.3
3	Trimellitic anhydride	99.4	39.2	270	120	310	30.3	42.8	48.9
	<i>m</i> -Phenylenediamine	96.8	35.7	250	95	305	34.5	45.3	50.8
4	Trimellitic anhydride	98.9	45.3	310	115	325	26.4	29.2	40.5
	<i>m</i> -Phenylenediamine	99.3	41.8	300	100	315	28.7	34.3	44.1
5	Trimellitic anhydride	99.7	44.4	300	160	320	14.8	22.8	29.3
	<i>m</i> -Phenylenediamine	95.0	42.1	280	120	310	16.6	27.2	37.9
6	Trimellitic anhydride	97.9	40.9	320	158	330	15.2	23.4	30.1
	<i>m</i> -Phenylenediamine	95.5	39.3	310	130	315	16.8	25.5	38.0
7	Trimellitic anhydride	95.8	53.7	300	203	320	12.1	20.6	27.3
	<i>m</i> -Phenylenediamine	95.0	52.0	285	170	310	14.8	24.4	33.8
8	Trimellitic anhydride	98.0	29.1	305	200	325	32.3	64.5	75.8
	<i>m</i> -Phenylenediamine	97.8	25.7	300	168	310	57.1	70.0	79.2
9	Trimellitic anhydride	98.5	42.6	265	160	310	18.1	24.0	32.8
	<i>m</i> -Phenylenediamine	98.7	41.3	250	145	306	23.6	27.0	40.0
10	Trimellitic anhydride	98.6	47.0	310	263	400	17.0	19.1	31.2
	<i>m</i> -Phenylenediamine	98.8	45.2	300	243	380	22.2	26.5	39.6
11	Trimellitic anhydride	99.3	56.6	330	240	370	9.3	13.2	24.4
	<i>m</i> -Phenylenediamine	98.9	51.4	305	220	350	10.8	16.1	28.6
12	Trimellitic anhydride	99.9	57.8	360	280	390	8.6	11.4	22.5
	<i>m</i> -Phenylenediamine	99.3	50.9	340	250	360	10.0	15.2	27.9
13	Trimellitic anhydride	98.5	55.0	315	220	385	8.15	12.1	25.3
	<i>m</i> -Phenylenediamine	98.0	52.1	290	240	380	9.8	14.7	30.1
14	Trimellitic anhydride	97.2	25.2	275	160	305	59.1	78.8	91.7
	<i>m</i> -Phenylenediamine	98.1	18.6	250	145	300	52.6	84.4	93.8
15	Trimellitic anhydride	98.4	19.7	260	230	309	51.5	69.1	93.2
	<i>m</i> -Phenylenediamine	98.0	15.4	240	210	280	59.5	87.5	95.1

1. Bis-(4-hydroxyphenyl)-2,2-propane. 2. Bis-(4-hydroxyphenyl)-phenylmethane. 3. 2,2-Bis-(4-hydroxyphenyl)-2-phenylethane. 4. Bis-(4-hydroxyphenyl)diphenylmethane. 5. 3,3-Bis-(4-hydroxyphenyl)-phthalide. 6. 3,6-Dihydroxyxanthene-9,9-spirophthalide. 7. 2-phenyl-3,3-bis-(4-hydroxyphenyl)phthalimidine. 8. 3,6-Dihydroxy-2,4,5,7-tetrabromoxanthene-9,9-spirophthalide. 9. Bis-(4-hydroxyphenyl)toluquinomethane. 10. Bis-(4-hydroxyphenyl)phenylacetophenone. 11. 9,9-Bis-(hydroxyphenyl)fluorene. 12. 3,6-Dihydroxy-9,9-spirofluorene. 13. 9,9-Bis-(4-hydroxyphenyl)anthrone-10. 14. Bis-(4-hydroxy-3-chlorophenyl)-2,2-propane. 15. Bis-(4-hydroxy-3,5-dichlorophenyl)-2,2-propane.

V.V. Korshak, L.K. Solov'eva and I.V. Kamenskh, Vysokomol. Soyed., 13, 150 (1971).

ORIGINAL PAGE IS
OF POOR QUALITY

ORIGINAL PAGE IS
OF POOR QUALITY

TABLE 3

Some Properties of Phenolphthalein Epoxy Resin Fractions
Obtained from Liquid Chromatography; Solvent: CHCl_3 /
Acetone (95/5 by v). Absorbent: Silica gel.

Property	Epoxy Resin		
	A	B	C
Color	White Clear	Very Light Yellow	Yellow
Softening Temp., °C	15	43	52
Epoxy Eq. Wt.	233	326	625
n_D	0.096	0.59	2.19

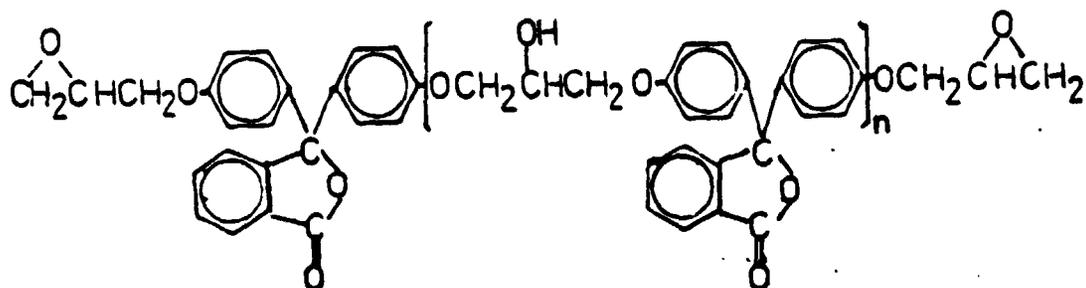


TABLE 4

The Relationships between the Initial Feed Mole Ratio of Epichlorohydrin to Phenolphthalein, Average Equivalent Weight, and Weight Fraction of Component A Obtained from Liquid Chromatography.

Initial Feed Mole Ratio. Epi./Phen.	Ave. Epoxy Eq. Wt.	Wt. Fraction of Component A
3.2	306	0.52
6.1	270	0.61
9.2	258	0.78
12.0	274	0.79
15.0	---	0.89
20.0	242	----

ORIGINAL PAGE IS
OF POOR QUALITY

TABLE 5

UV Spectral Extinction Coefficients of the Liquid Chromatographic Fractions from the Phenolphthalein Diethylidyl Ether (DCEPP)

$E = \text{Ext. Coeff.} \times 10^{-4} \text{ l mole}^{-1} \text{ cm}^{-1}$

Compound	$E_{238 \text{ nm}}$	$E_{275 \text{ nm}}$	$E_{282 \text{ nm}}$	$E_{238 \text{ nm}}/E_{275 \text{ nm}}$
Phenolphthalein	1.42	0.47	0.40	3.0
Component A	1.87	0.45	0.39	4.2
Component B	1.81	0.43	0.37	4.2
Component C	2.01	0.48	0.41	4.2

Solvent : CHCl_3

TABLE 6

The Relationship between Gel Fraction and Mole Fraction of DGEPP or DGEBF in the Copolymer with DGEBA. Curing Agent : Trimethoxyboroxine (9.5 g/epoxy eq.)

Copolymer of DGEBA and DGEPP "		Copolymer of DGEBA and DGEBF	
Mole Fraction of DGEPP (mole %)	Gel Fraction (Wt. %)	Mole Fraction of DGEBF (mole %)	Gel Fraction (Wt. %)
0.0	84.5	0.0	84.5
13.5	82.8	6.7	86.3
27.6	73.8	9.8	85.2
43.2	58.4	22.9	91.0
58.3	63.7	35.9	94.3
100.0	54.3	36.1	86.4
		62.2	63.8
		100.0	33.3

Curing Agent: Trimethoxyboroxine; 9.5 g/epoxy eq.

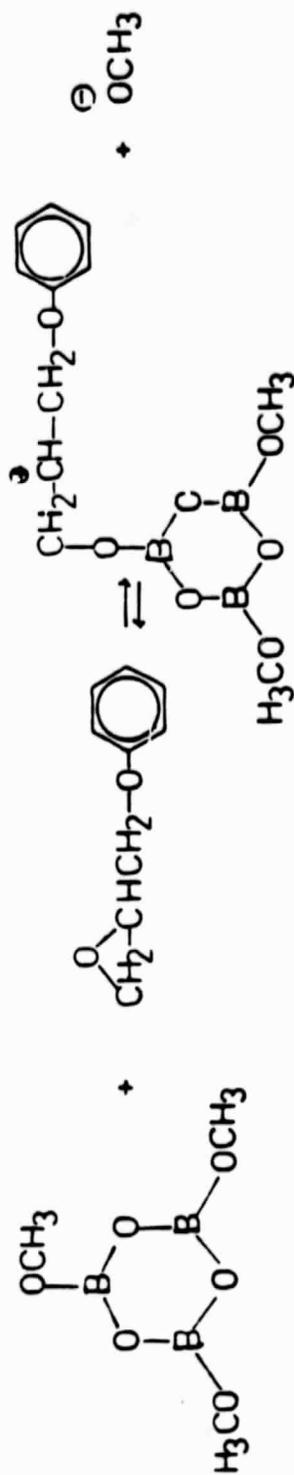
Curing Conditions: 135°C - 3 hours, 180°C - 3 hours and
218°C - Another 3 hours.

In sealed tube under N₂ gas.

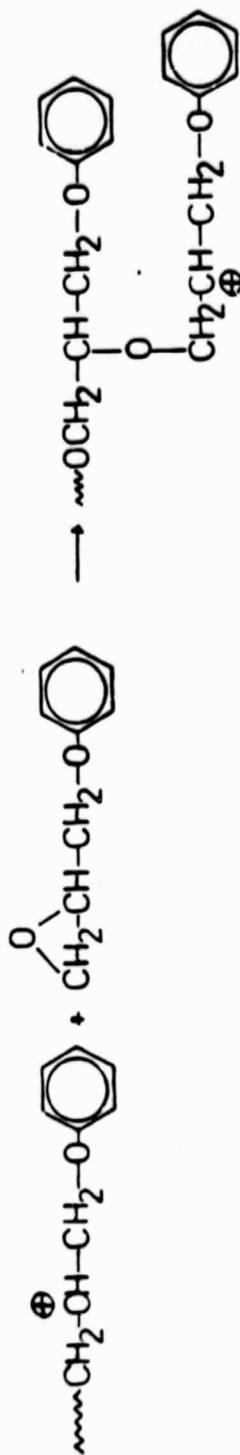
FIGURE 1

THE MECHANISM OF TRIMETHOXYBOROXINE-INDUCED THERMAL POLYMERIZATION OF PHENYL GLYCIDYL ETHER

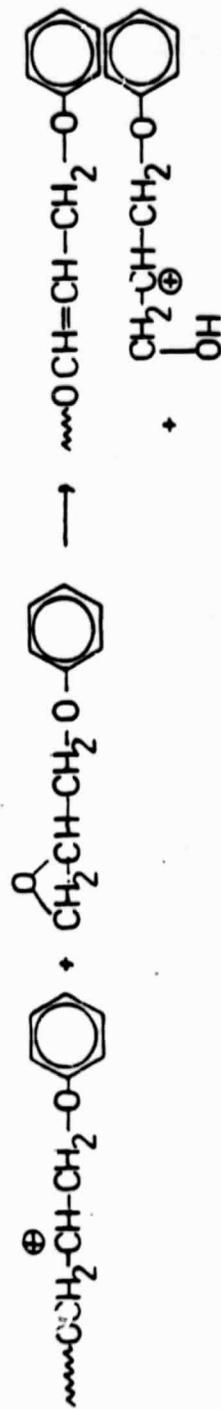
1. INITIATION



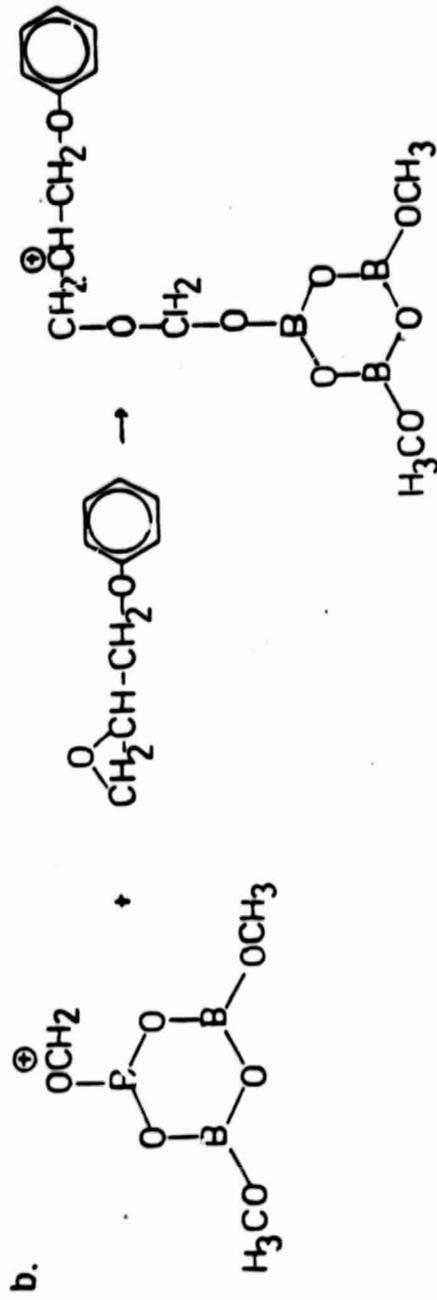
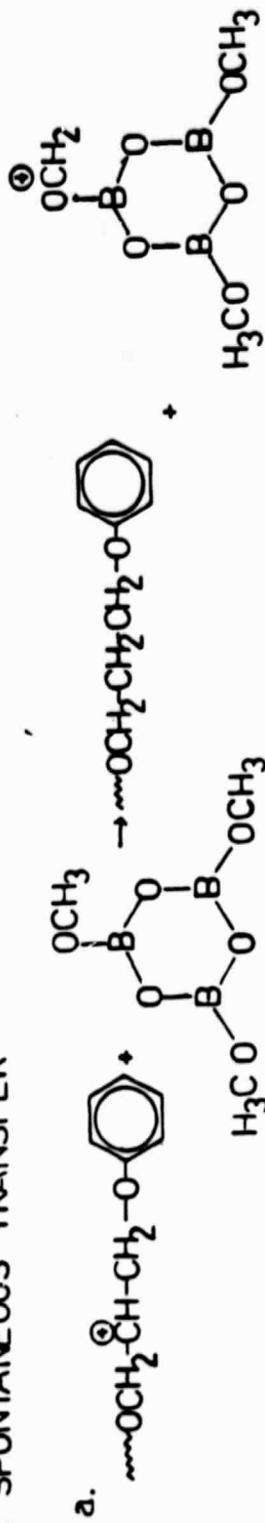
2. PROPAGATION



3 MONOMER TRANSFER



4. SPONTANEOUS TRANSFER



5. TERMINATION



FIGURE 2

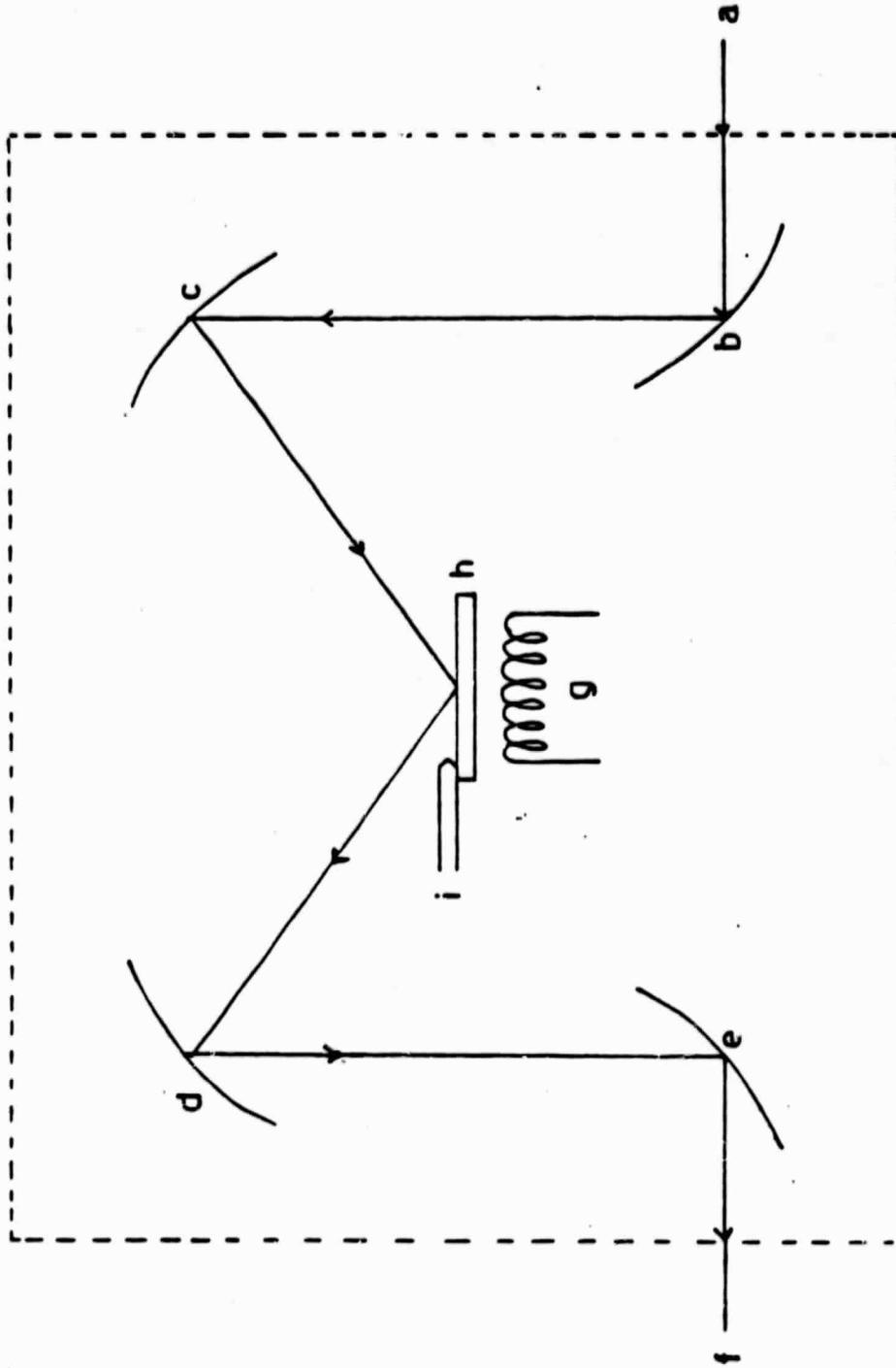


Diagram of Sample Compartment of FTIR Spectrometer

- a : Infrared source.
- b; c, d and e : Reflection mirrors.
- f : Detector.
- g : Microheater
- h : Sample plate.
- i : Thermocouple.

FIGURE 3

Possible Reactions between Phenolphthalein and Epichlorohydrin in the Presence of NaOH.

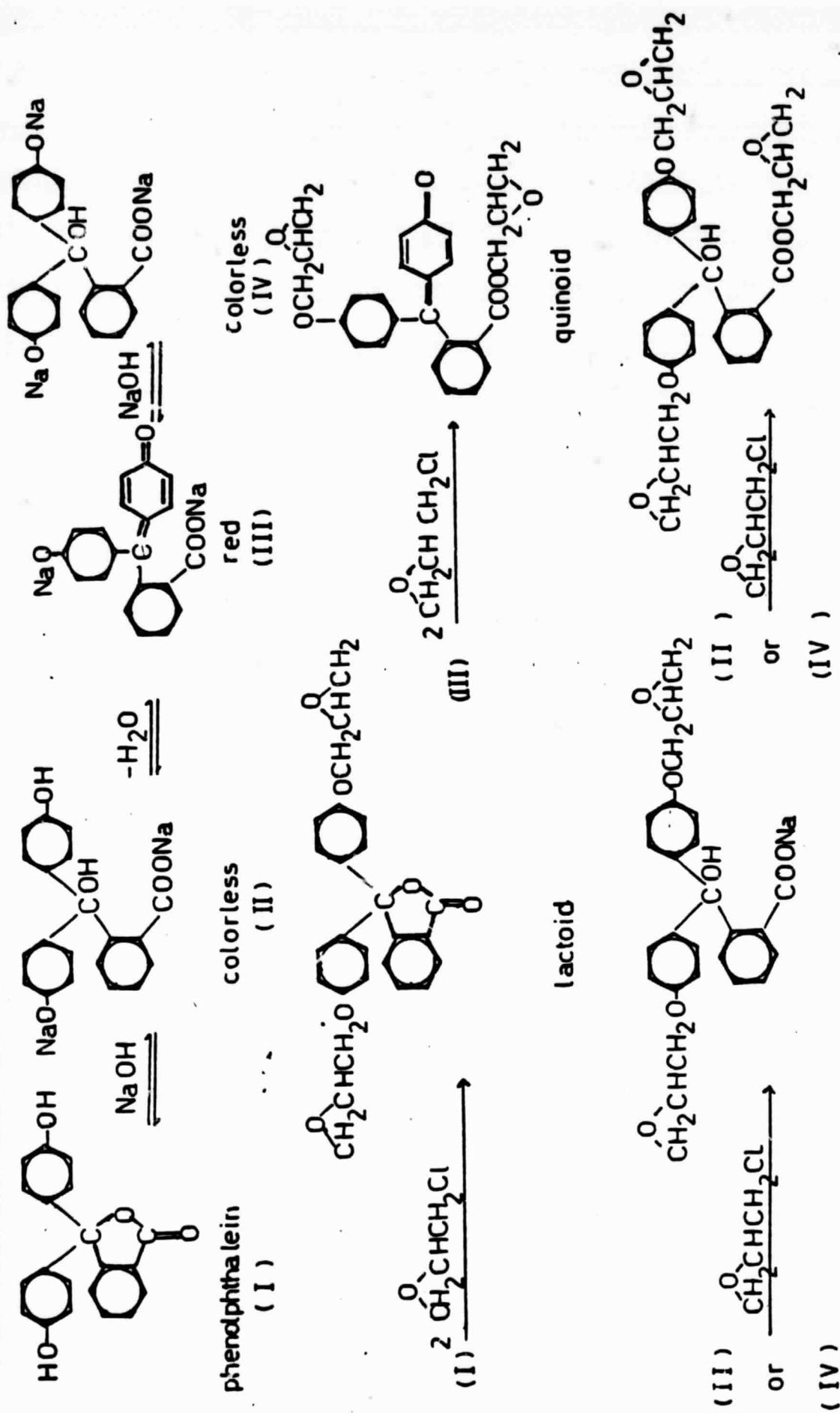
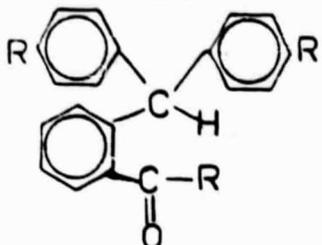
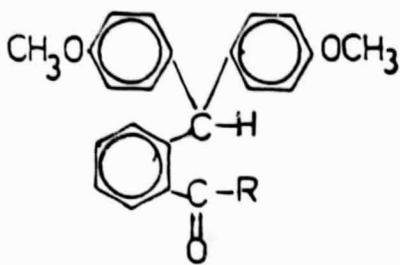
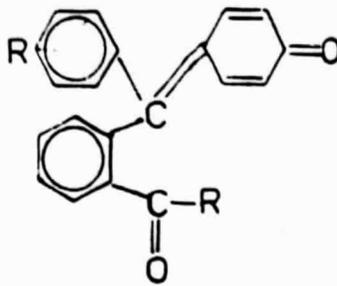
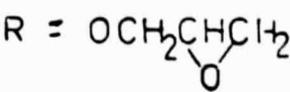
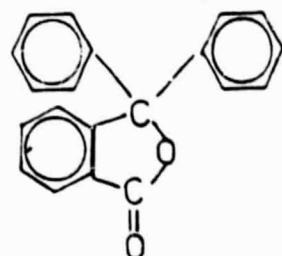


FIGURE 4

C=O Stretching Frequencies of Some Compounds

<u>COMPOUND</u>	<u>C=O STRETCHING (cm⁻¹)</u>
	1720
	1720
	1720
<p>R = </p>	
	1765

S.N. Salazkin, L.I. Komarova and S.V. Vinogradova., *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 144, (1973)

Original Wt. = 10.1854 g.

Recovered Wt. = 10.3417 g.

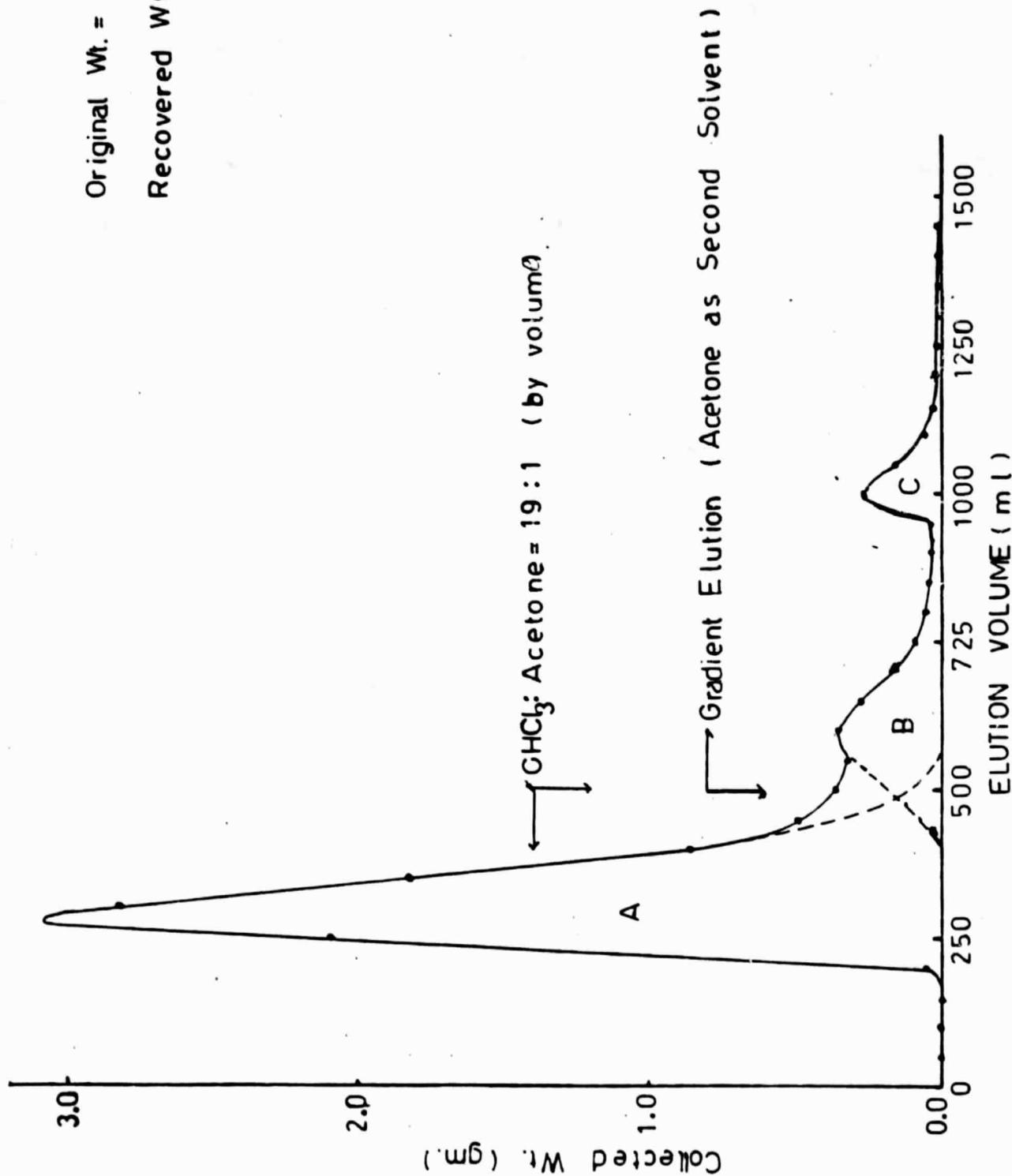


FIGURE 5. Liquid Chromatography of the Epoxy Resin of Phenolphthalein.

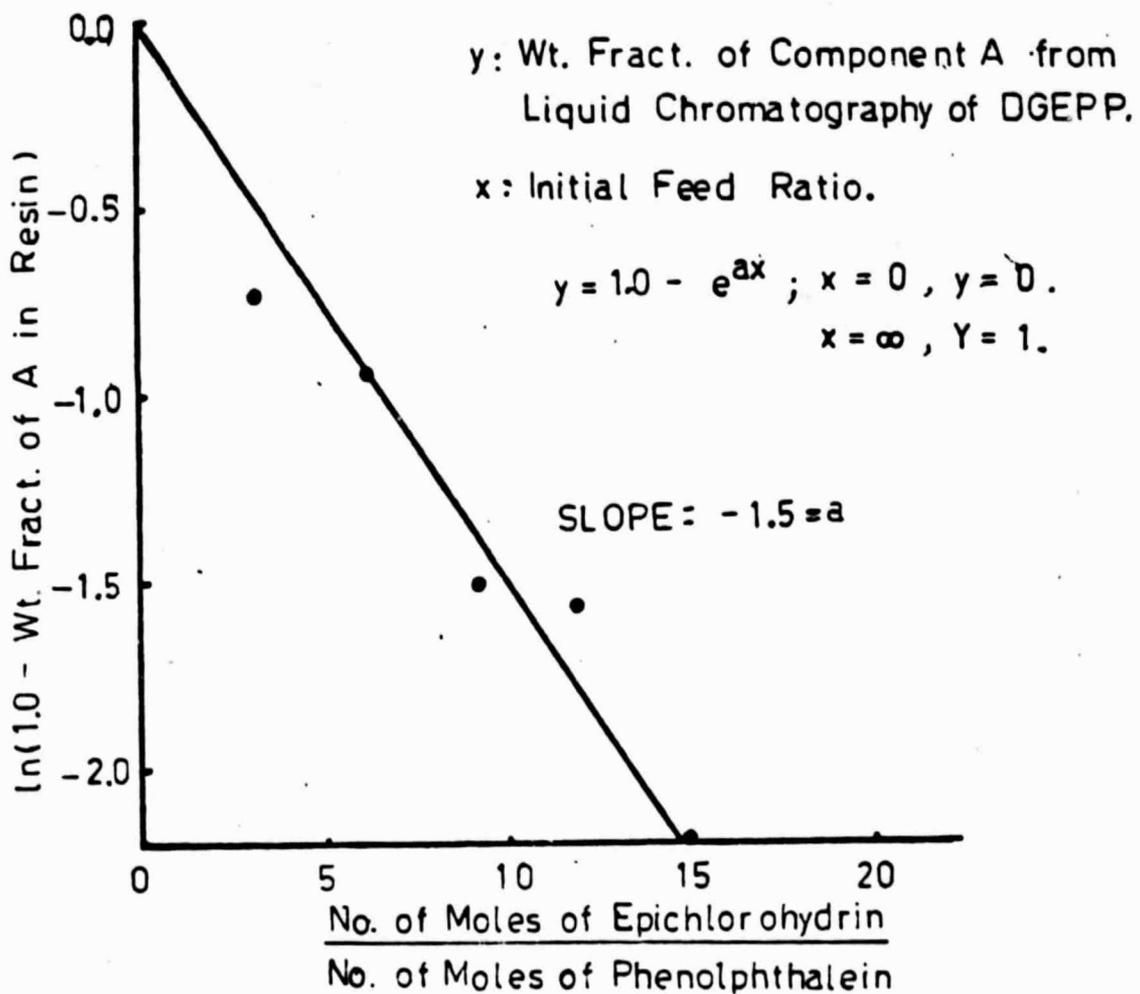


FIGURE 6.

Ln(1.0 - Weight Fraction of Component A in DGEPP)
 as a Function of Initial Feed Ratio of Epichloro-
 hydrin to Phenolphthalein.

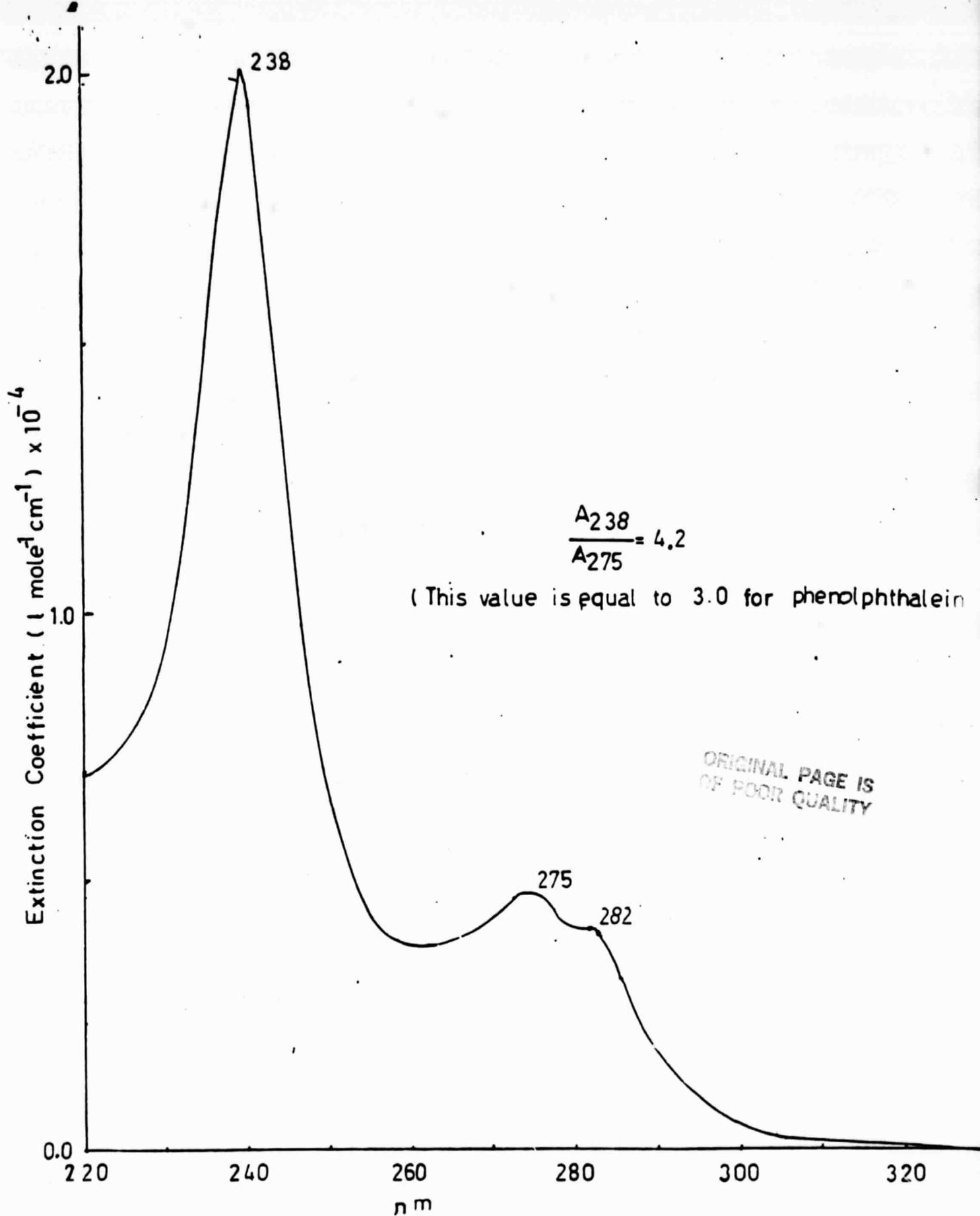


FIGURE 7.

UV Spectrum of Phenolphthalein Epoxy. Solvent - CHCl₃.

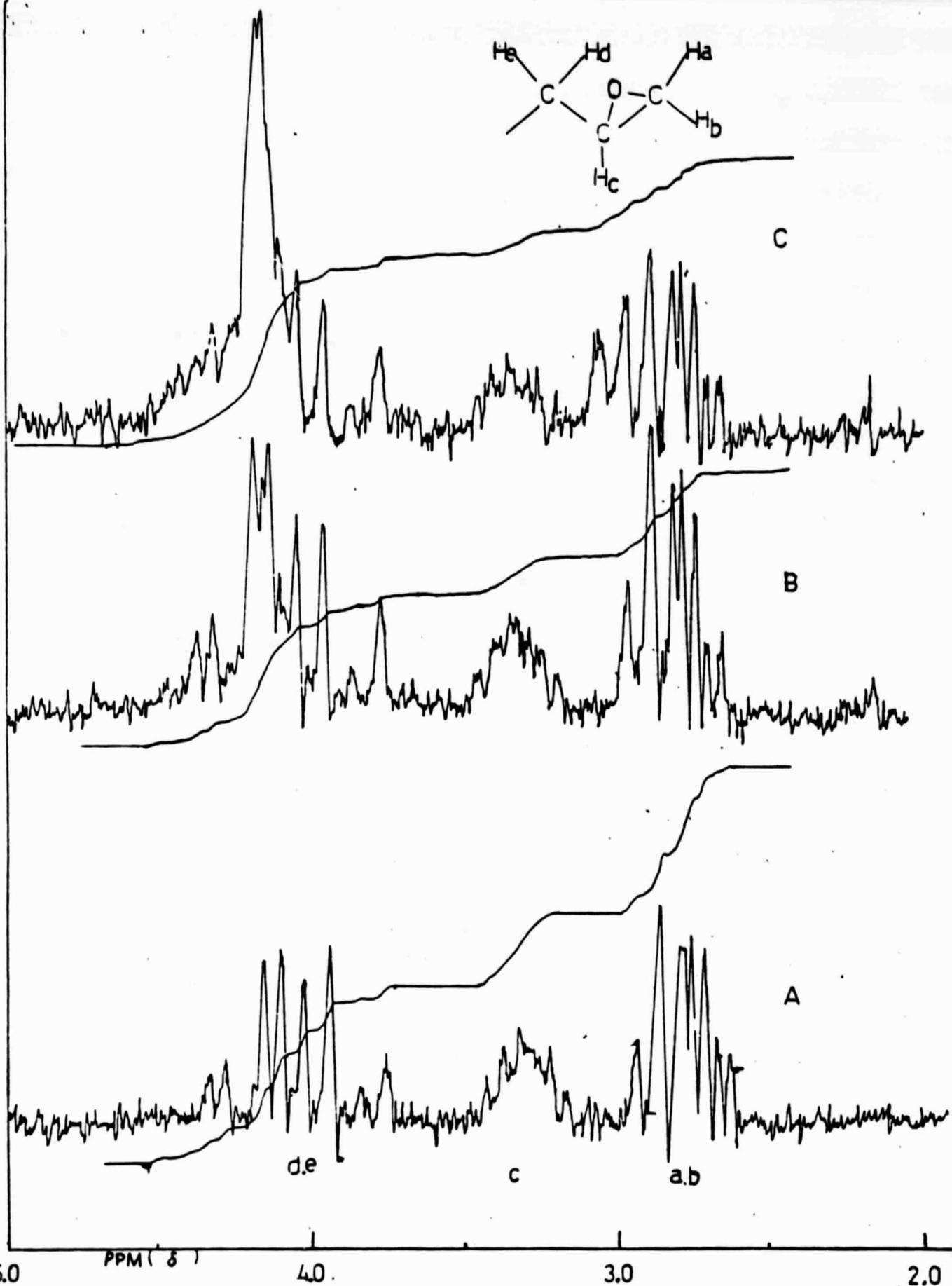


FIGURE 8

NMR Spectra of Phenolphthalein Epoxy Resins Collected from Liquid Chromatography. (Solvent - CDCl_3)

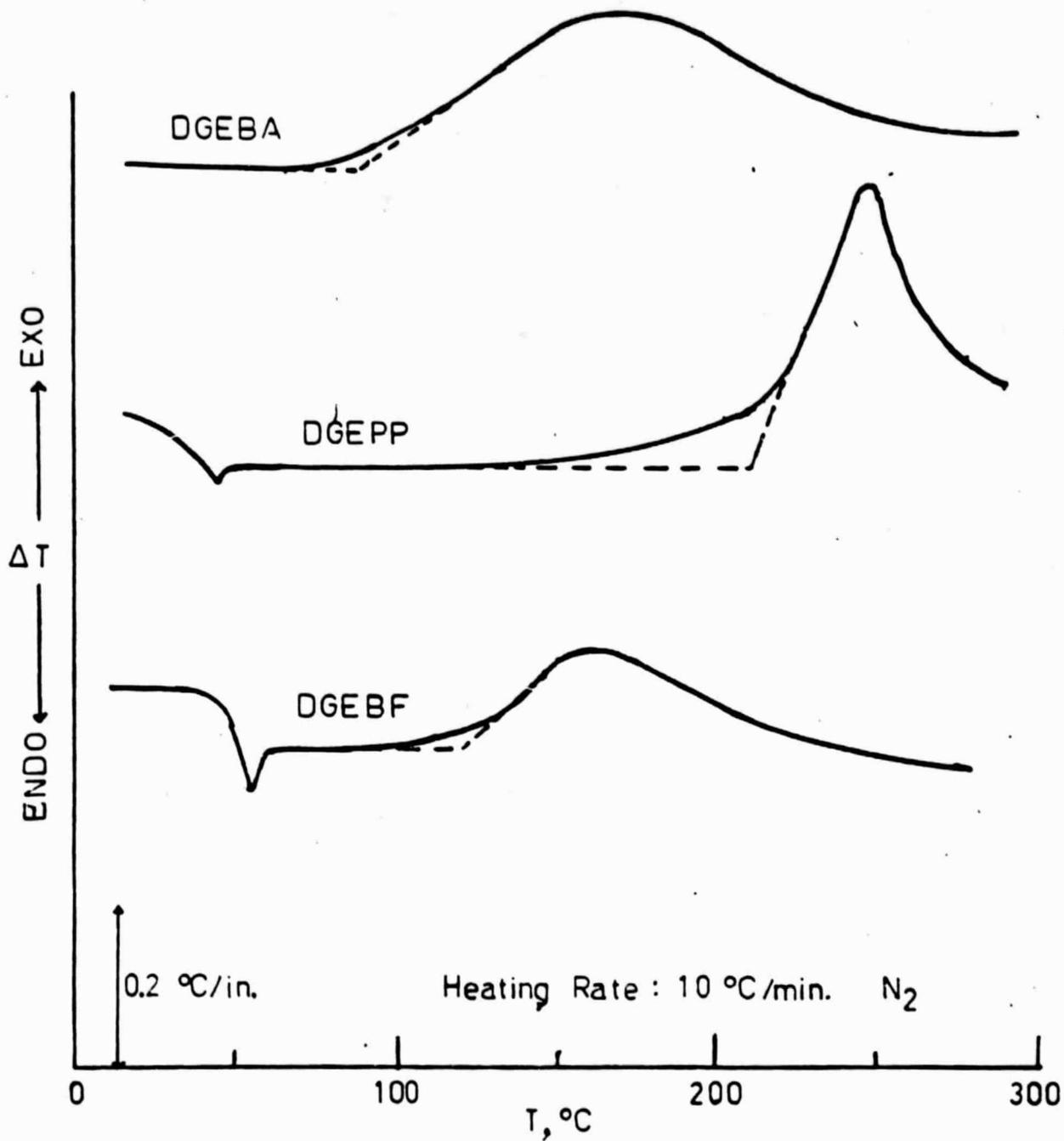


FIGURE 9. DSC Thermograms of DGEBA, DGEPP, and DGEBF after Mixing with TMB.

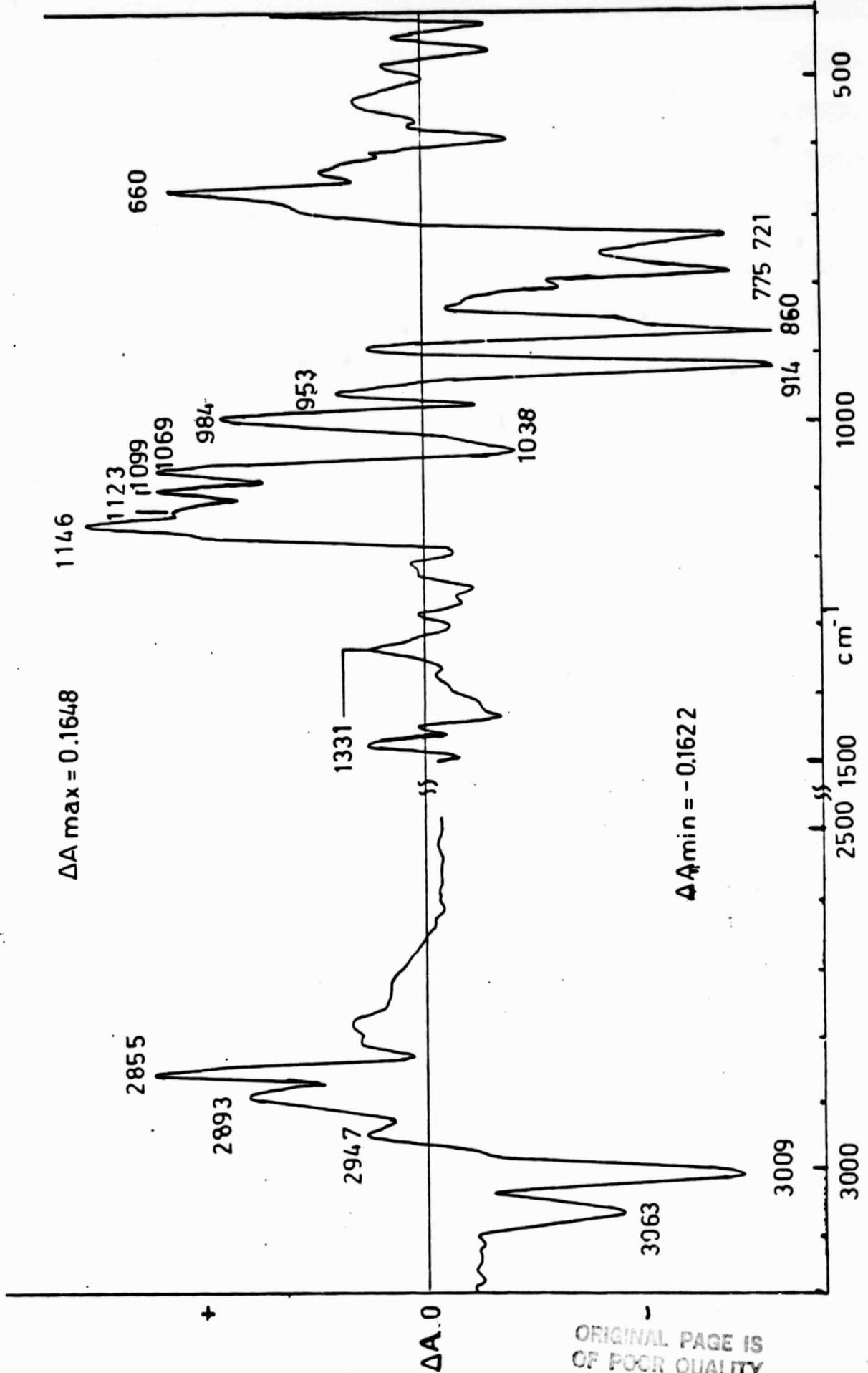


FIGURE 10. Infrared Difference Spectrum of DGEBA Before and After Curing with Trimethylborane for 36.5 Minutes at 80°C.

ORIGINAL PAGE IS OF POOR QUALITY

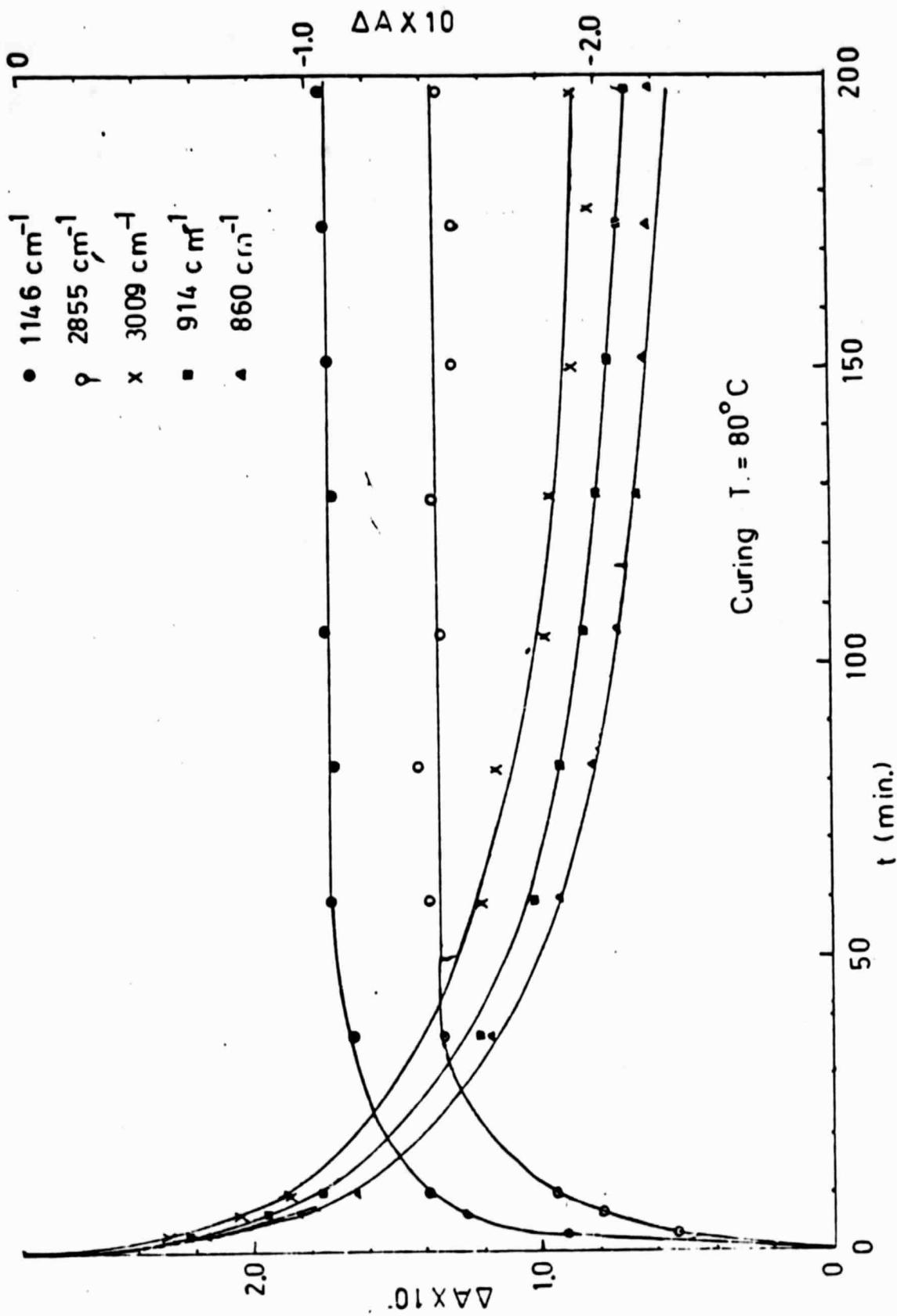


FIGURE 11. Absorbance Changes of Various Absorption Bands in the Curing Reaction of DGEBA with Trimethoxyboroxine as a Function of Curing Time.

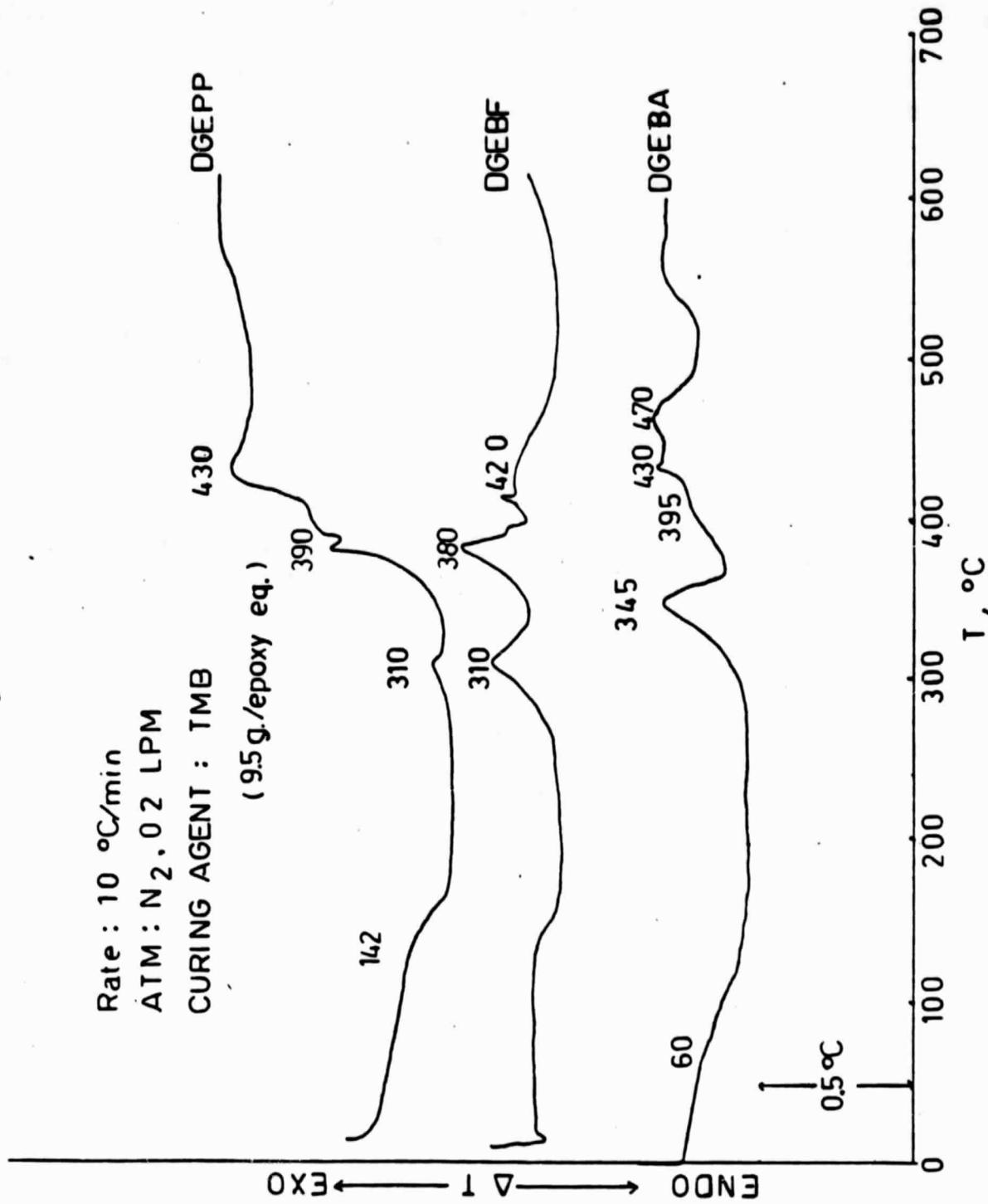


FIGURE 12. DSC Thermograms of the Cured DGEPP , the Cured DGEBA and the Cured DGEBF.

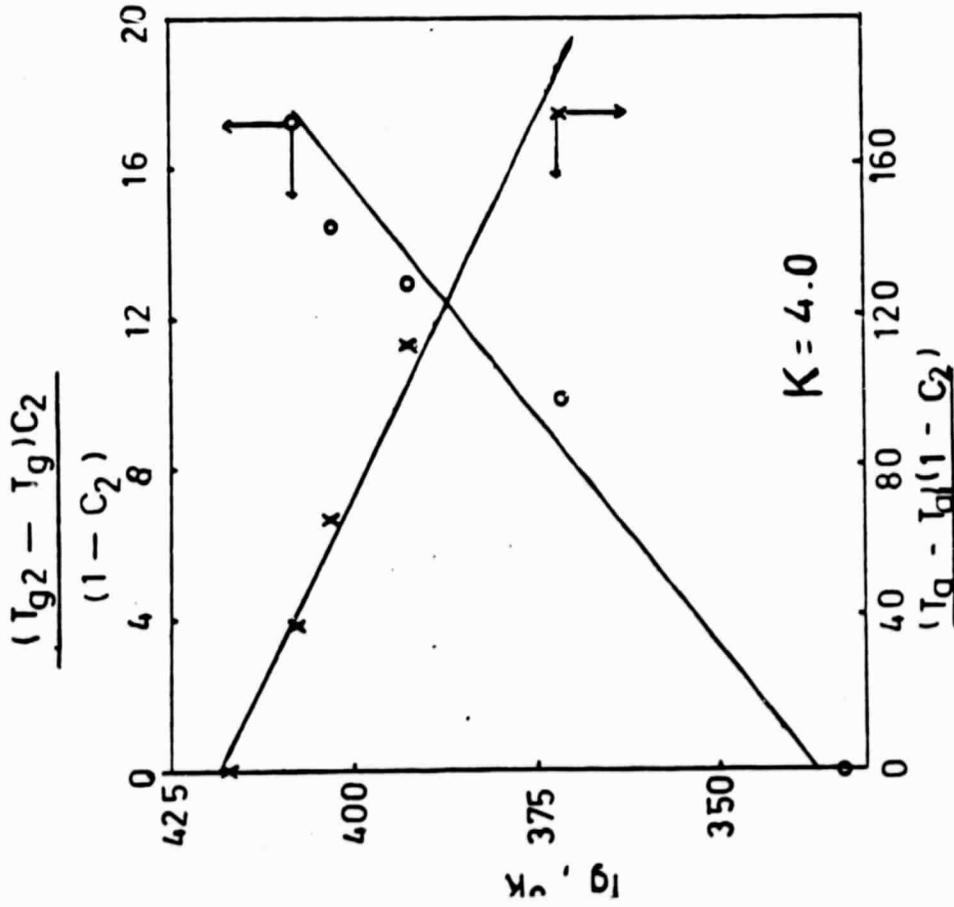


FIGURE 13. Glass Transition as a Function of

$$\frac{(T_g - T_g)(1 - C_2)}{C_2} \text{ and } \frac{(T_{g2} - T_g)C_2}{(1 - C_2)}$$

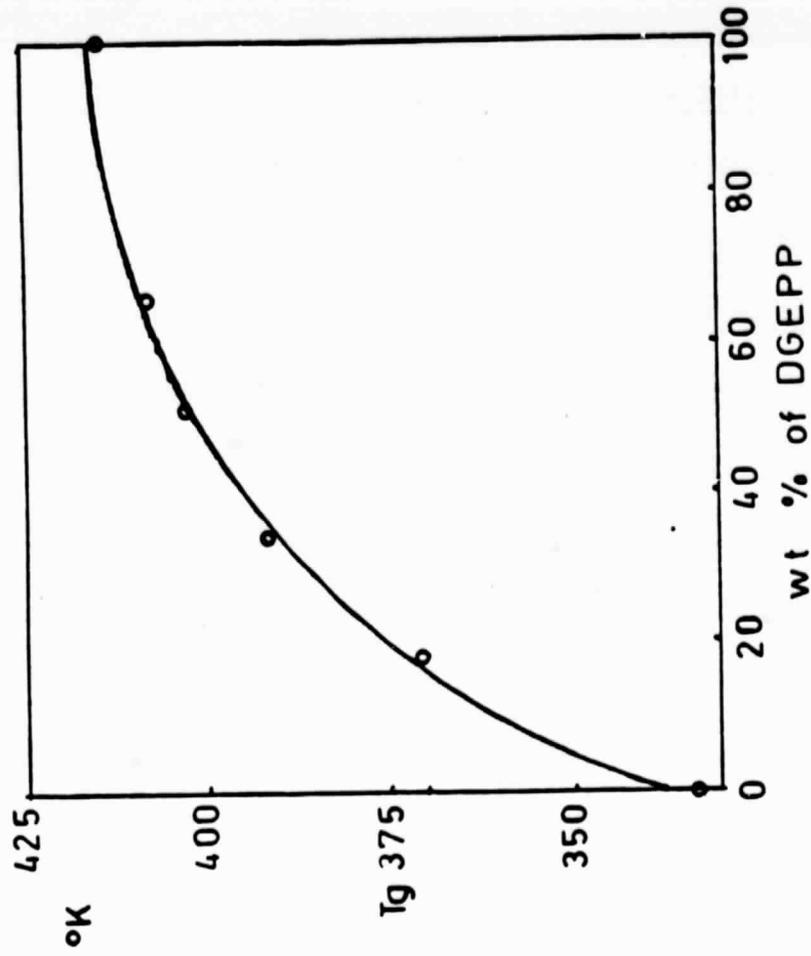


FIGURE 14. Glass Transition against the Weight Fraction of DGEPP in the Copolymer of DGEPP and DGEBA.

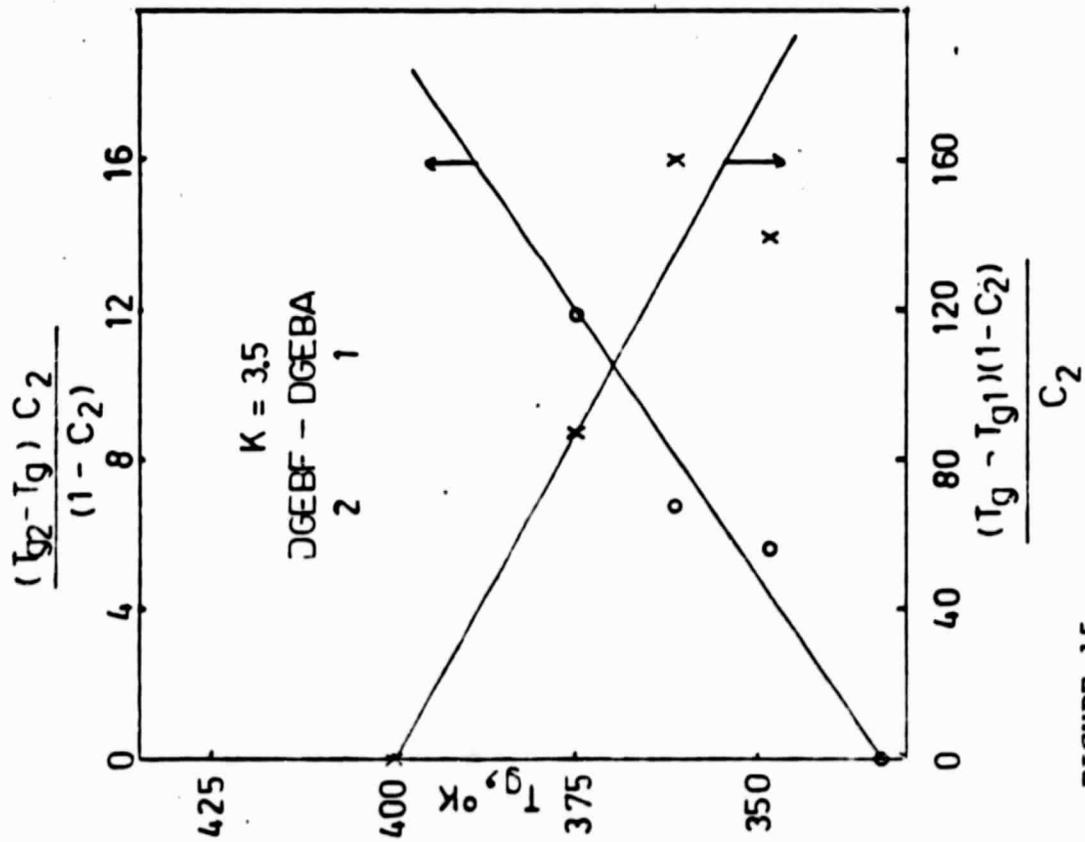


FIGURE 15.

Glass Transition as a Function of

$$\frac{(T_g - T_{g1})(1 - C_2)}{C_2} \quad \text{and} \quad \frac{(T_{g2} - T_g) C_2}{(1 - C_2)}$$

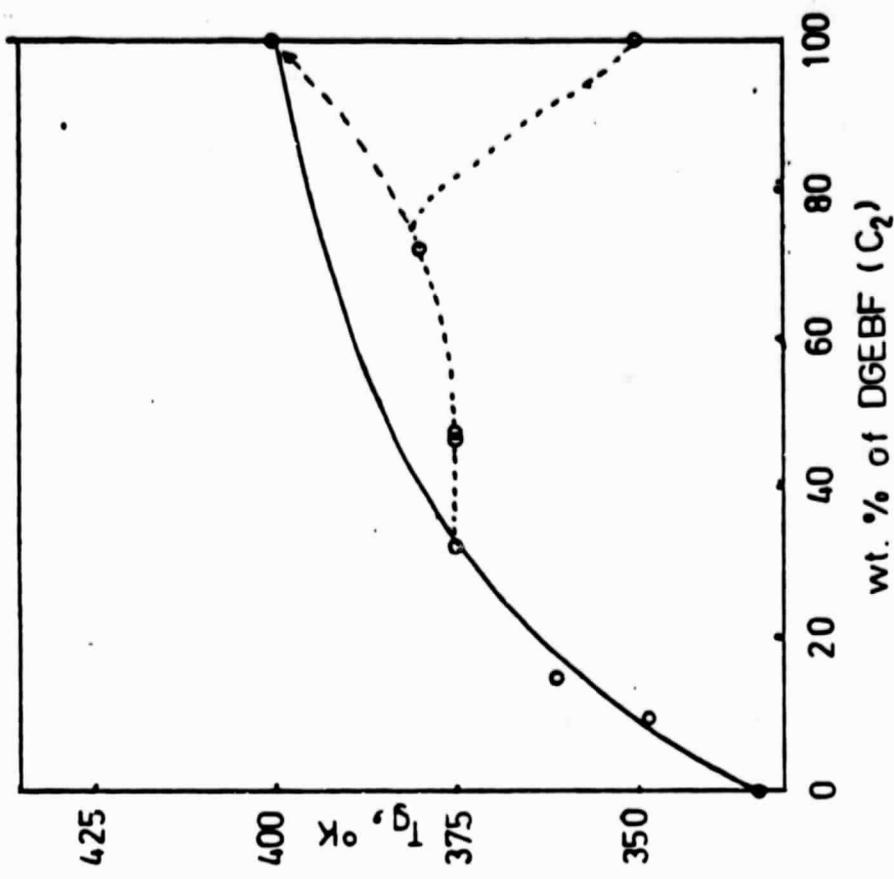


FIGURE 16.

Glass Transition vs. the Weight Fraction of DGEBF in the Copolymer with DGEBA.

DGEPP (mole %)

- 1 100
- 2 58.3
- 3 27.6
- 4 13.5
- 5 0.0

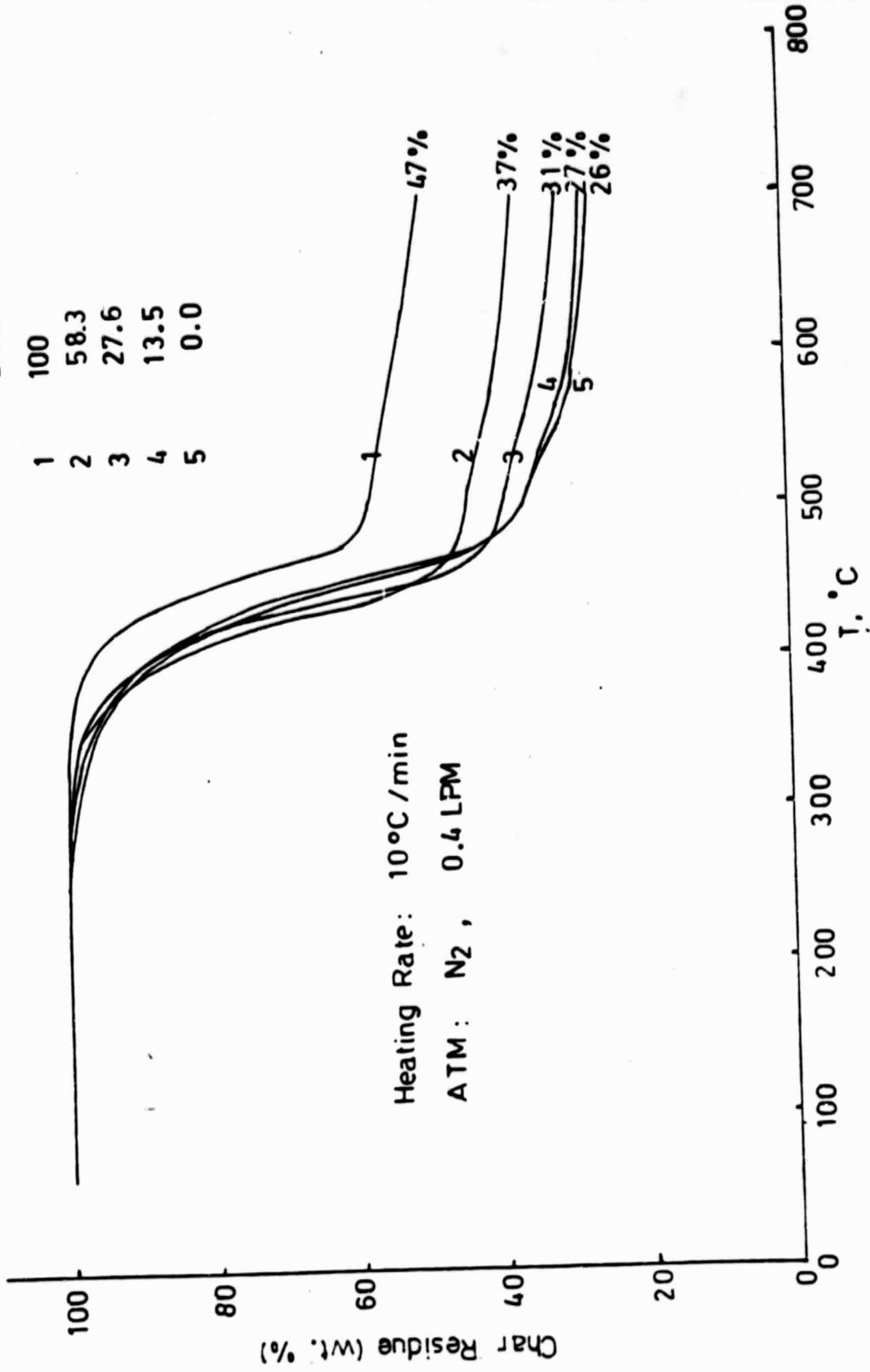


FIGURE 17. TGA of the Various Compositions of DGEPP Copolymer with DGEBA.

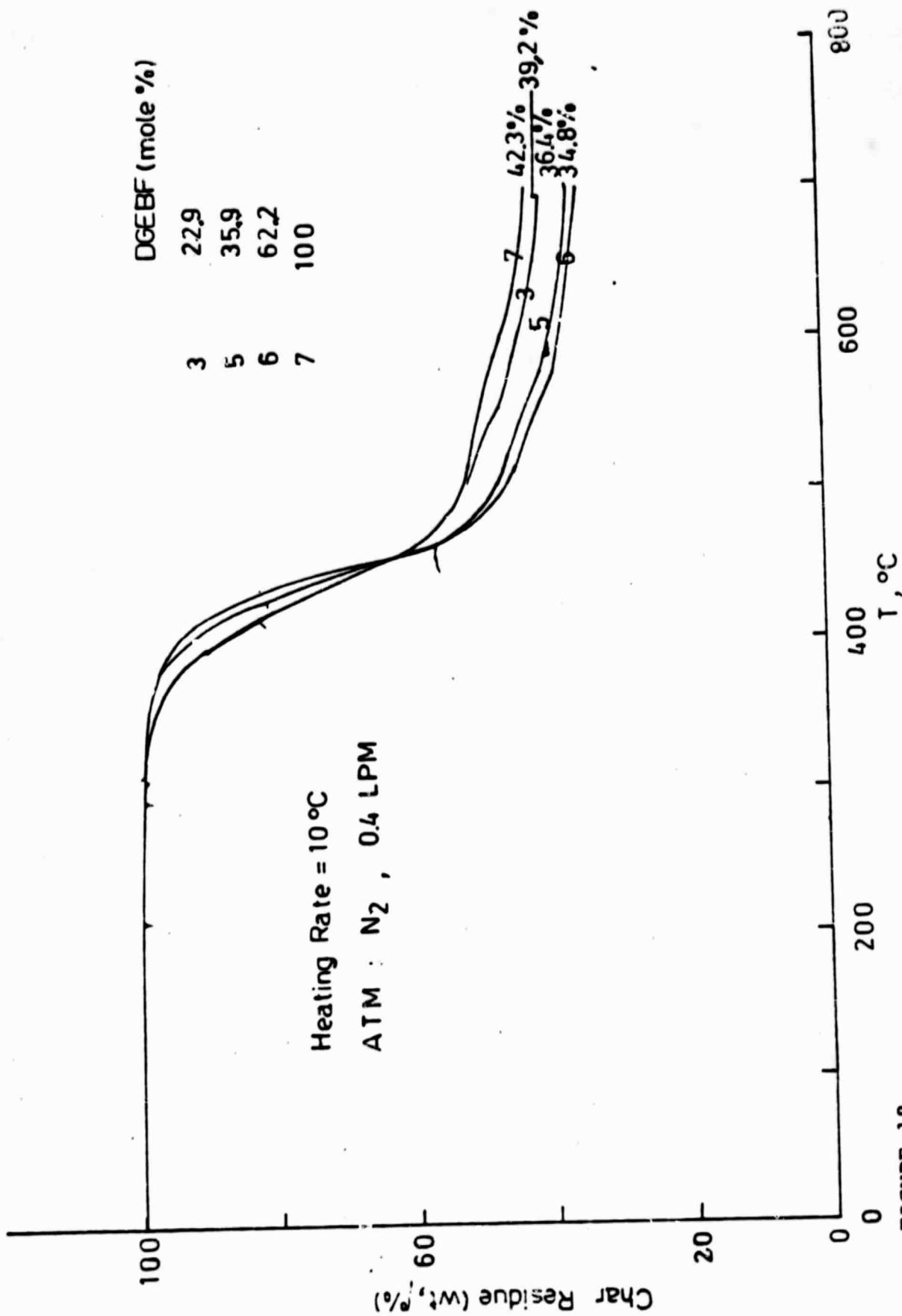


FIGURE 18.
TGA of the Various Compositions of DGEBF Copolymer with DGEBA.

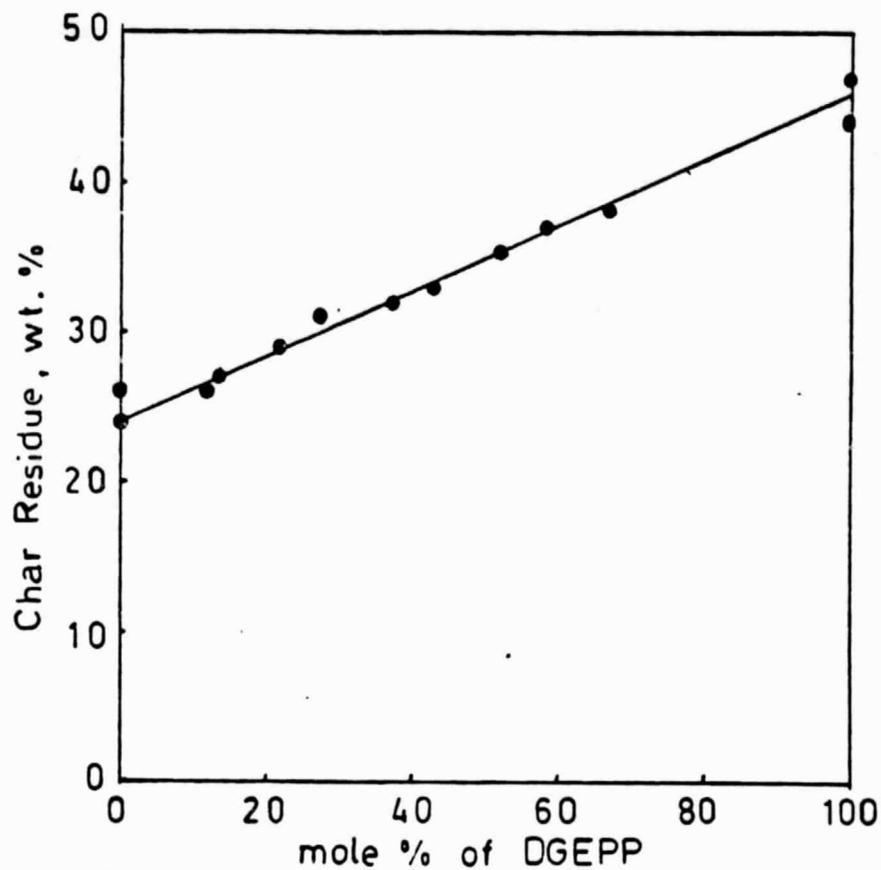


FIGURE 19.

Char Residue at 700 °C as a Function of Mole Fraction of DGEPP in the Copolymer of DGEPP and DGEBA.

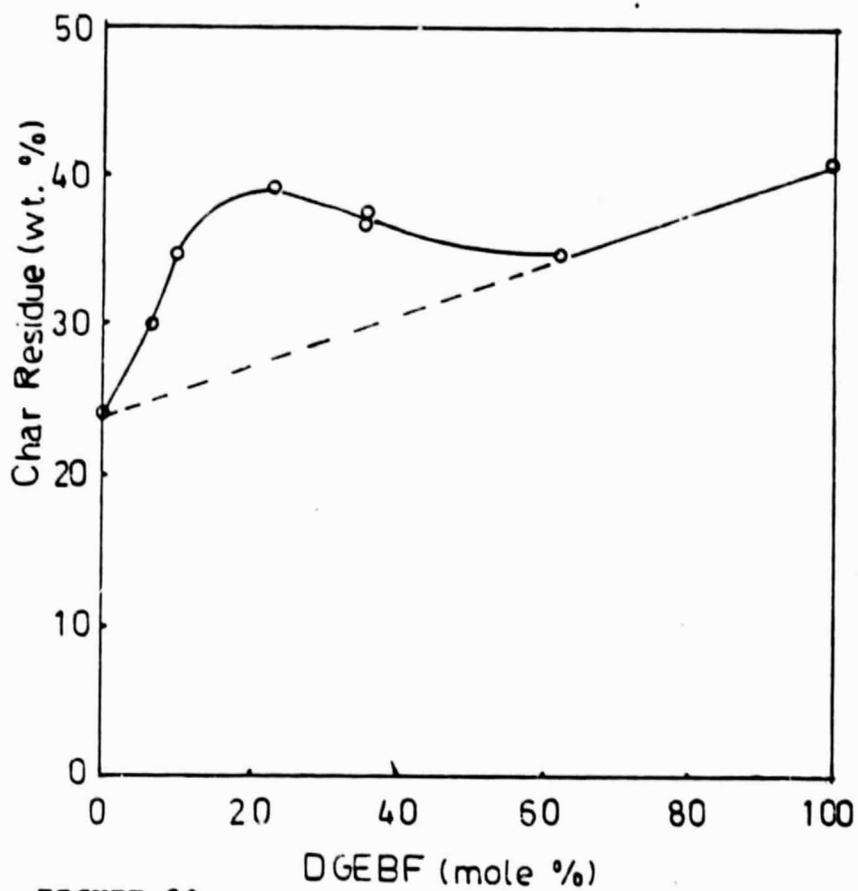


FIGURE 20.
Char Residue at 700 °C as a function of Mole Fraction of DGEBF in the Copolymer of DGEBF and DGEBA.

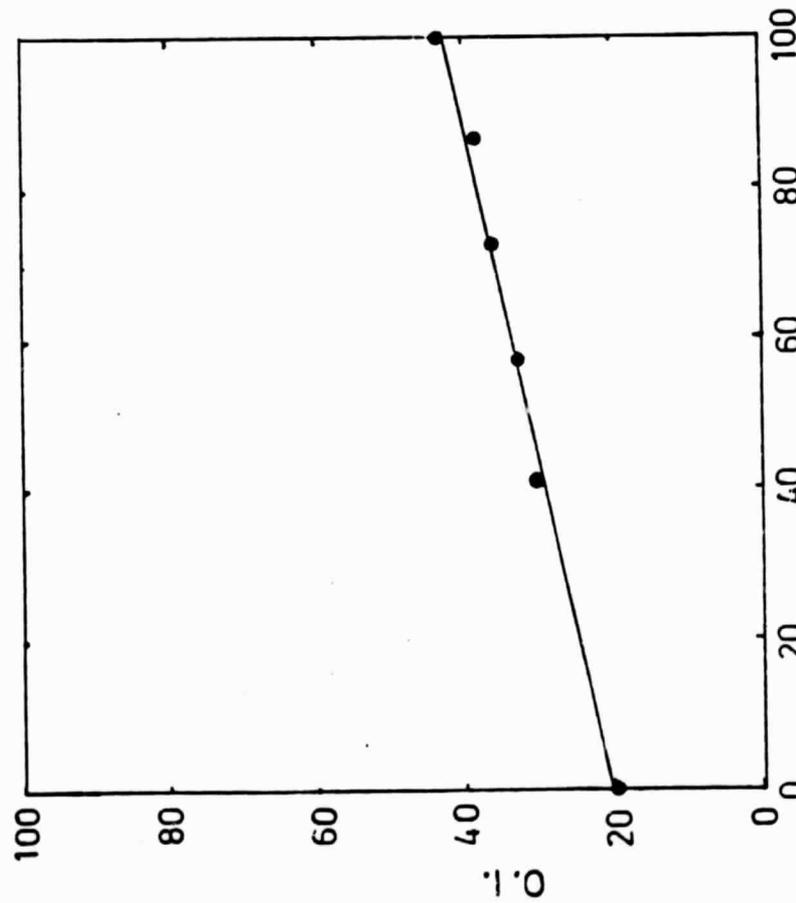


FIGURE 21. DGEPP. (mole %) Oxygen Index as a Function of the Composition of DGEPP in the Copolymer with DGEBA.

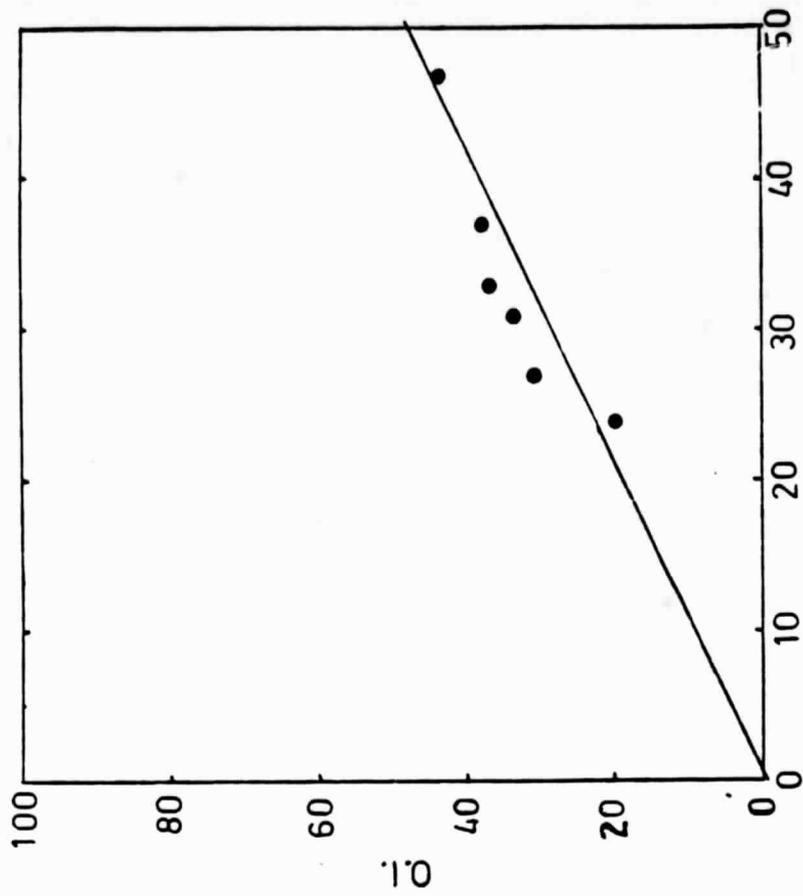


Figure 22. Char Yield, Y %. Oxygen Index against Char Yield of the Copolymer of DGEPP and DGEBA at 700 °C.