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LIQUID CHROMATOGRAPHIC ANALYSIS OF EPOXY RESINS

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SUMMARY

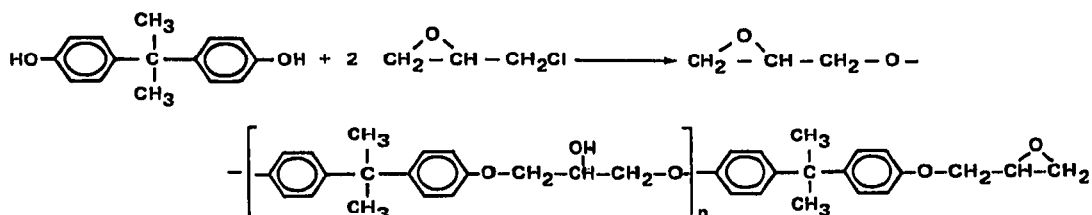
Epoxy resins are widely used adhesive materials with uses that range from home repair to binding supersonic aircraft together. Bisphenol A-epichlorohydrin comprises a major class of these adhesives. Depending on the ratio of bisphenol A to epichlorohydrin, these glycidyl resins can be formed with low, intermediate, or high molecular weights. It is possible to separate the oligomers of these glycidyl polymers from DP 0 to DP 24 by gradient elution. If unreacted *p,p'*-bisphenol A is present, it is also separated, as are various process by-products, such as 2,4-bis-(α,α -dimethyl-*p*-hydroxybenzyl)phenol. The classic approach to epoxy analysis is the determination of epoxide equivalent (ASTM D1652). This measure of the active oxirane per gram of resin gives no information on the distribution of the oxirane in the resin. Size separation allows chemists to separate oligomers with DP 0 and DP 1 and determine the average molecular weight of the epoxy.

INTRODUCTION

Epoxy resins have become widely used adhesives and structural thermosets. These resins are characterized by the oxirane ring which will react with curing agents (hardeners) or catalytically homopolymerize to form a cross-linked polymeric structure.

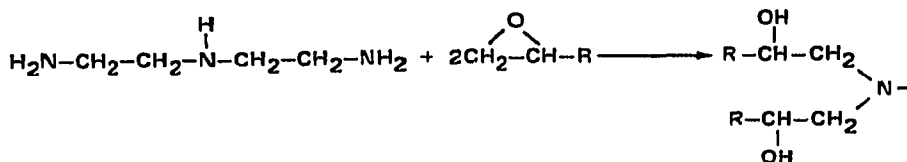
Cured epoxies are generally characterized by outstanding mechanical and electrical properties, dimensional stability, resistance to heat and chemicals, and adhesion to a wide range of materials.

The most widely used epoxy is formed by the reaction of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) with epichlorohydrin in the presence of a catalyst¹.



As the ratio of bisphenol A and epichlorohydrin is varied, epoxies of differing average molecular weights are produced. With a large excess of epichlorohydrin (15–20 moles) low-molecular-weight (n approaches zero) liquid epoxies are formed.

Epoxy resins are cross-linked (cured) by reaction at the oxirane ring. The most widely used curing agents are aliphatic and aromatic amines (for example, diethylenetriamine). However, acid anhydrides and catalysts are also used.



Hydroxyl compounds or other materials capable of hydrogen bonding accelerate the reaction of the amine hardener with the oxirane group. For optimum cross-linking with amines, it is important that, for each mole of oxirane, a mole of amine be added.

Thus, analytical procedures are required to assay the reactive groups of an epoxy resin. A variety of procedures have been developed to determine α -epoxide, hydroxyl content, and unhydrolyzed chlorohydrin content. These chemical tests only give total amounts of reactive sites, not their distribution². Liquid chromatography size separation (GPC) provides the ability to separate epoxy monomer ($n = 0$) so that epoxide and hydroxyl functionality can be determined. These values of reactive functionality compare quite favorably with the results of wet chemical tests. With GPC the separation of DP0 as well as epoxide and hydroxyl equivalents can be determined in a single run³⁻⁵.

EXPERIMENTAL

The gel permeation chromatograms were done on a Waters Associates' GPC/ALC 502/401 dual detector liquid chromatograph equipped with a C-908 siphon counter accessory. The columns were standard Waters' Poragel. The columns used have polystyrene contour chainlength exclusion limits of $1 \times 10^3 \text{ \AA}$, 500 \AA , 250 \AA , 100 \AA , and 60 \AA . The solvent, tetrahydrofuran (THF), was maintained at a flow-rate of 2.0 ml/min. A calibration curve was developed in the normal manner using monodispersed polystyrene standard (Waters) and straight-chain hydrocarbons (Humphrey, North Haven, Conn., U.S.A.).

Differential thermal analysis

Differential thermal analyses (DTA) were made on a DuPont 900 thermal analyzer with a high-temperature DTA cell (DuPont, Wilmington, Del., U.S.A.).

Liquid chromatography

Liquid chromatography (LC) separations were done on a Waters' ALC Model 202 apparatus equipped with a M/6000 solvent delivery system and gradient generator. The column used was a 2 mm \times 4 ft. Bondapak C₁₈/Corasil (Waters). The gradient

was water (distilled) to THF (uninhibited redistilled from Burdick and Jackson Labs., Muskegon, Mich., U.S.A.).

Samples

The epoxy samples were supplied by Mr. Fred Larson of Bendix (Kansas City, Mo., U.S.A.). EPON 828 lots 5KHJ12, 10JHJ2, 9NHJ10, and 12PHJ13, EPON 836, EPON 1001, and EPON 1004 were produced by Shell Chem. (Houston, Texas); DER 331 lot TB310009, DER 511, and DER 661 were produced by Dow Chem. (Midland, Mich., U.S.A.); EPI-REZ 510 lot B26808 was produced by Celanese (New York, N.Y., U.S.A.); ERL 2774 lot 1032B by Union Carbide (New York, N.Y., U.S.A.); and ARALDITE 6010 lot K275-50 by Ciba (Basle, Switzerland).

RESULTS AND DISCUSSION

Gel permeation chromatography

Using accepted techniques the size separation of liquid epoxy resins gives characteristic chromatograms (Figs. 1 and 2). The oligomer with DP 0 has a retention volume at 34 counts (1 count = 5 ml). The DP 1 retention occurs at 30.5 counts, and DP 2 at 28.5 counts. The components with retention at 32.3 and 37–39 counts (Fig. 2) are impurities. Larson has shown that the oligomer distribution determined by GPC³ can be related to epoxide equivalents and residual hydroxyl values determined chemically⁶.

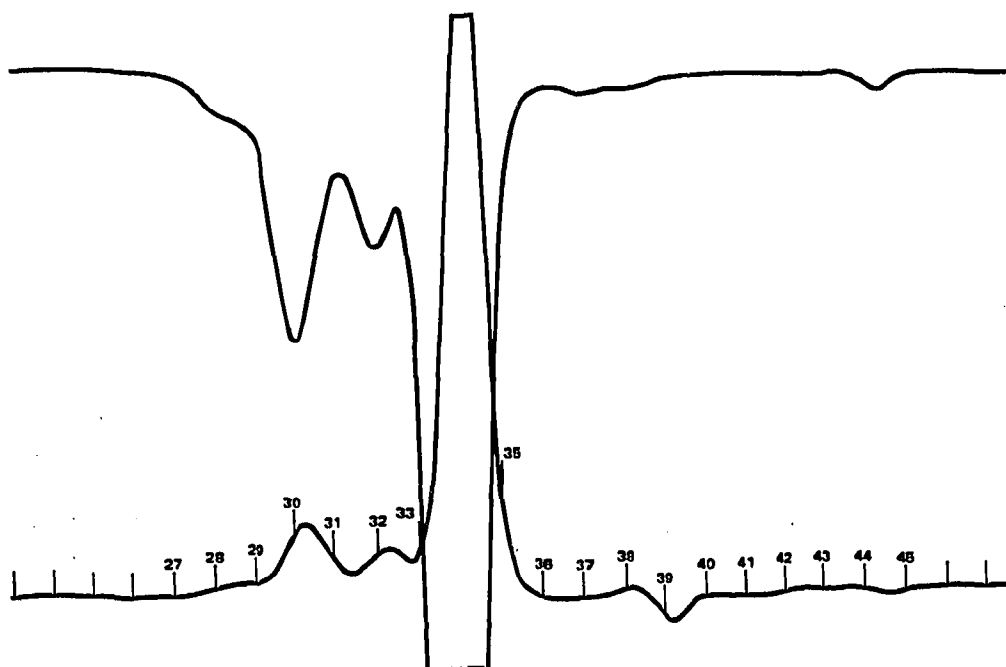


Fig. 1. GPC (size) separation of EPON 828, lot 9NHJ10. Conditions: packing, Poragel with exclusion limits of 10^3 , 500, 250, 100, and 60 Å; solvent, THF; flow-rate, 2.0 ml/min; detectors, IR, $8\times$ and UV, 0.32 a.u.f.s.

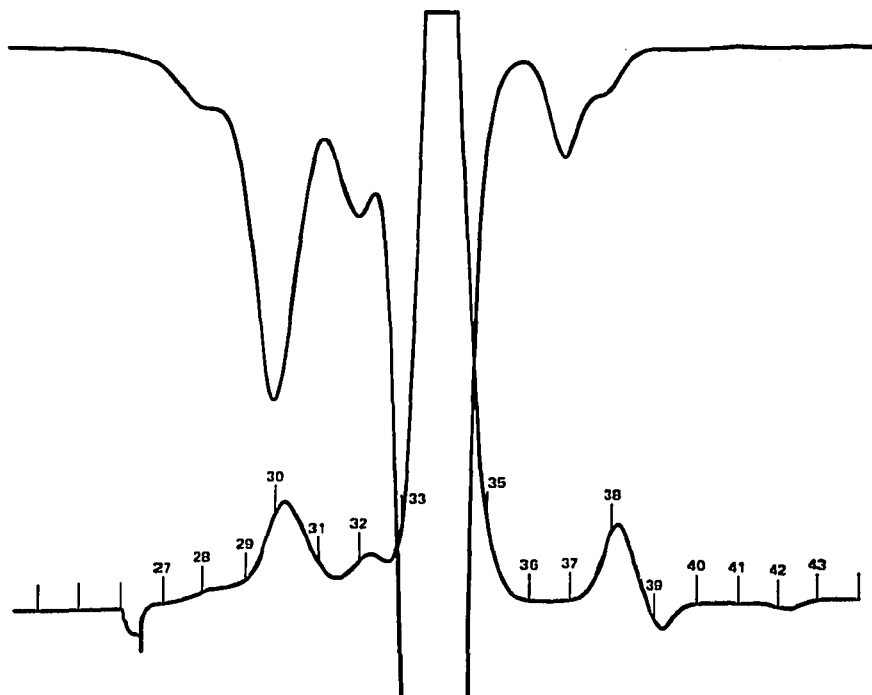


Fig. 2. GPC (size) separation of EPI-REZ 510, lot B26808. Conditions, as in Fig. 1.

Under the GPC conditions used, 2,2-bis(4-hydroxyphenyl)propane has the same retention volume as the DP 0 oligomer of the epoxy. The peak at 32.3 counts is believed to be 2,4-bis(α,α -dimethyl-*p*-hydroxybenzyl)phenol, but this has not been confirmed. The impurity peak at 37–39 counts in Fig. 2 has not been identified, but may be the diluent used to reduce the viscosity of this liquid epoxy.

Although GPC is quite useful in characterizing epoxy thermosets⁷, it does not provide a total characterization of this class of material.

Using a soft gel of high internal gel pore volume, Heitz has shown the ability to resolve epoxy oligomers from DP 0 to DP 7 (ref. 8).

Liquid chromatography

Much better resolution of epoxy has been achieved using reversed-phase partition techniques. The epoxy oligomers from DP 0 to DP 24 have been separated by this method (Figs. 3–16).

Identification of the epoxy oligomers has been made in reversed-phase separations. The retention character of *p,p'*-bisphenol A (*p,p'*-BPA) has been determined by doping techniques.

Liquid epoxy resins

In the manufacture of epoxies, bisphenol A and epichlorohydrin are allowed to react under alkaline conditions. If hydrolysis of the chlorohydrin to oxirane is incomplete, dichloride and diol impurities for each epoxy oligomer may occur. In

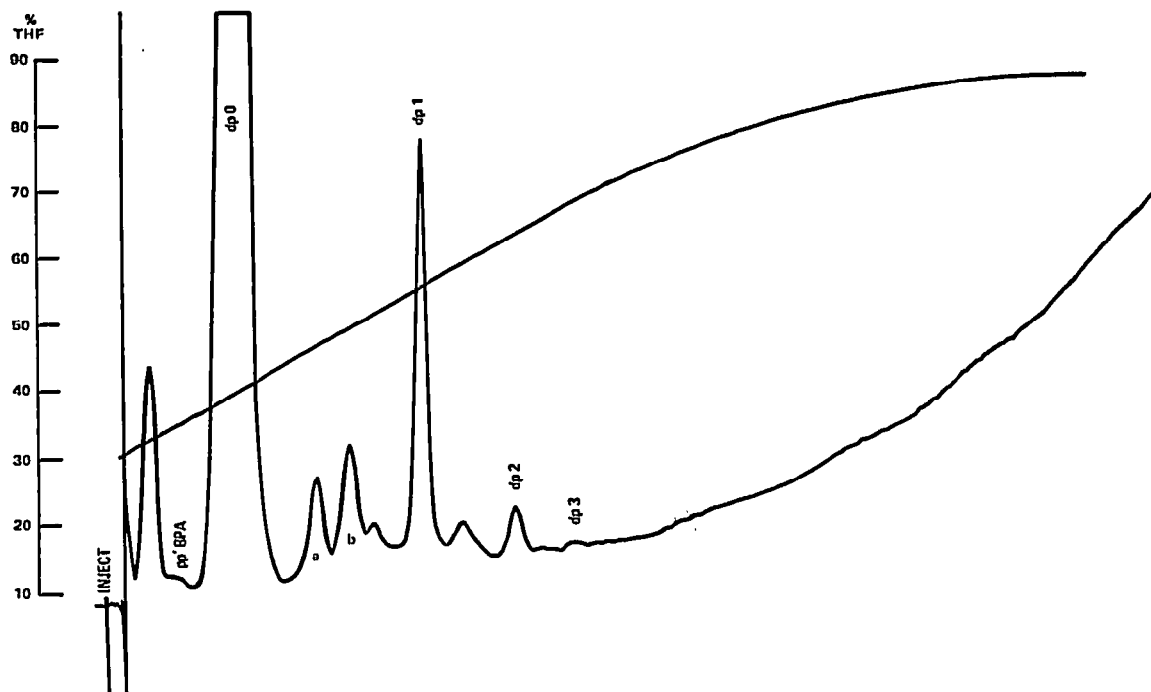


Fig. 3. Gradient separation of EPON 828, lot 5KHJ12. Conditions: packing, Bondapak C₁₈/Corasil; column 2 mm × 4 ft.; solvent, water-THF (gradient); sample size, 0.80 mg; flow-rate, 1.0 ml/min; detector, UV, 0.04 a.u.f.s.

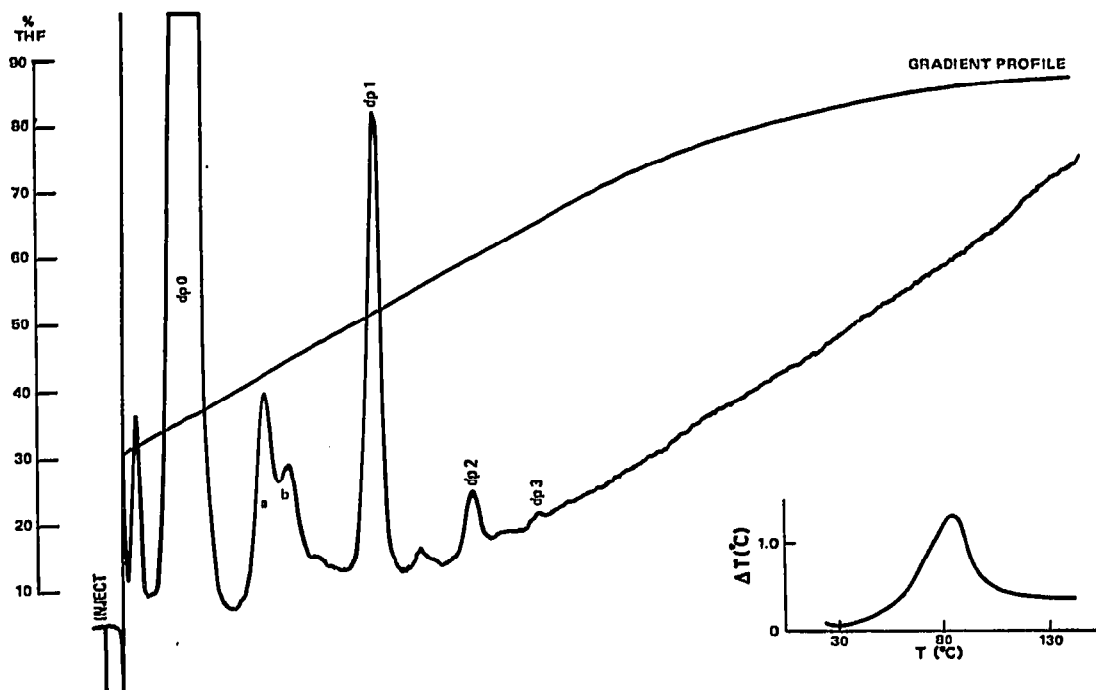


Fig. 4. Gradient separation of EPON 828, lot 10JHJ2. Conditions, as in Fig. 3.

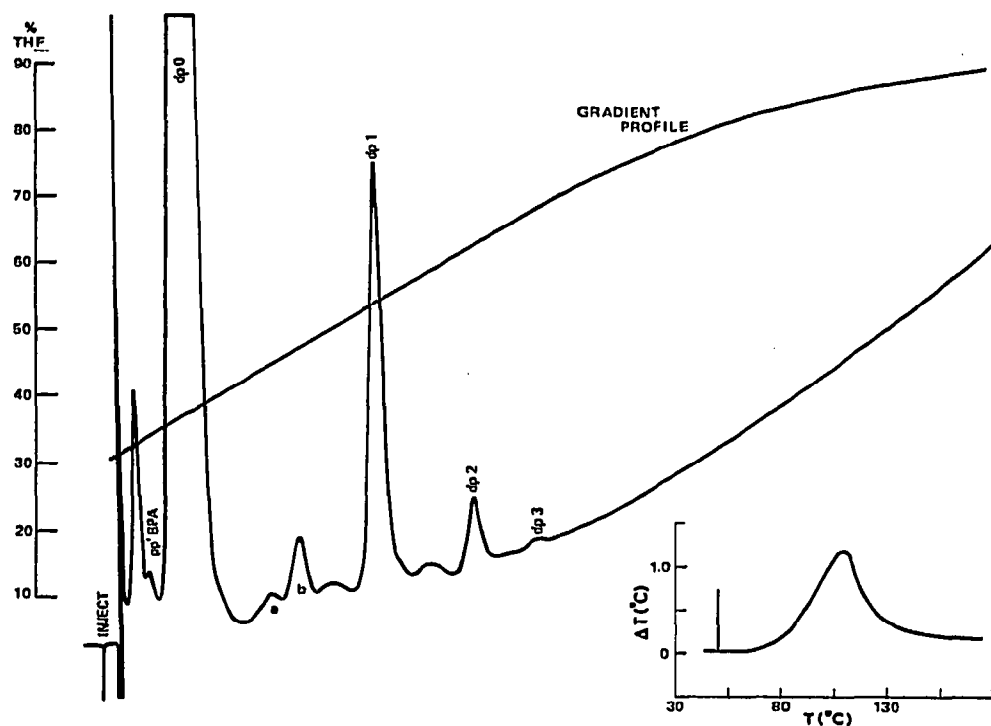


Fig. 5. Gradient separation of EPON 828, lot 9NHJ10. Conditions, as in Fig. 3.

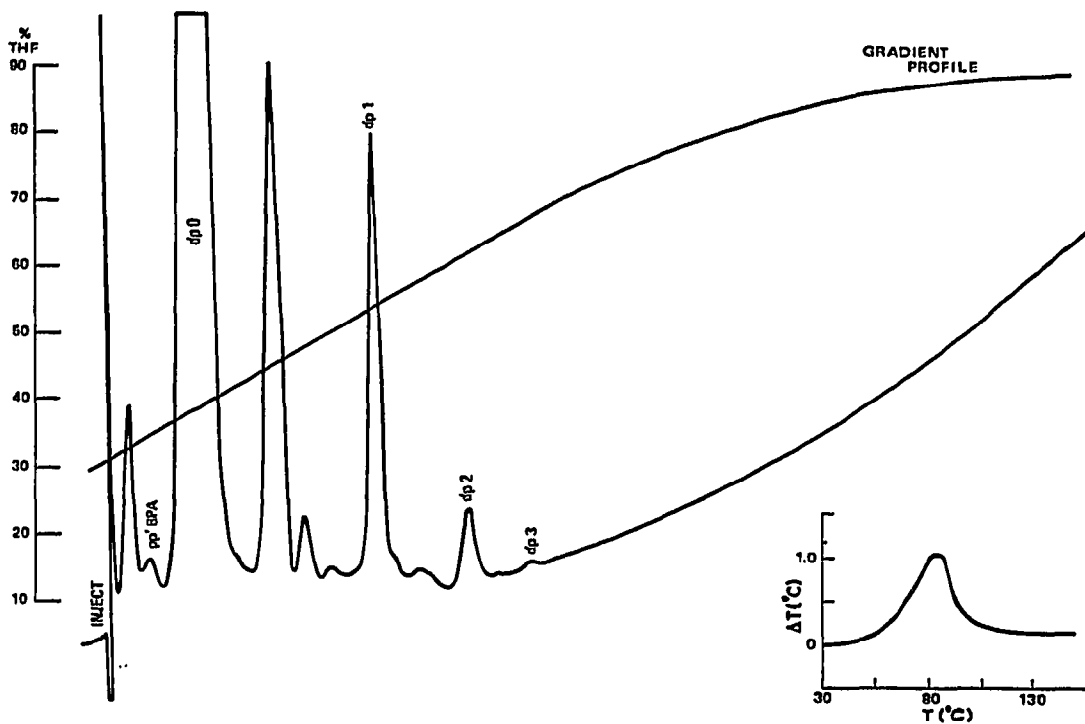


Fig. 6. Gradient separation of EPON 828, lot 12PHJ13. Conditions, as in Fig. 3.

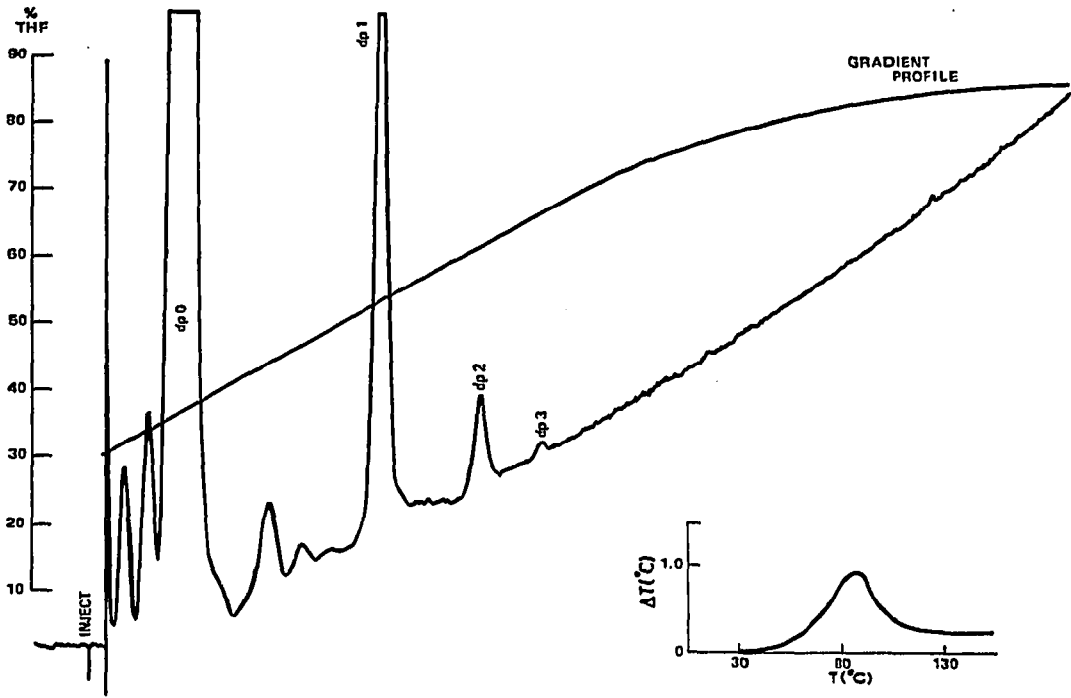


Fig. 7. Gradient separation of DER 331, lot TB310009. Conditions, as in Fig. 3.

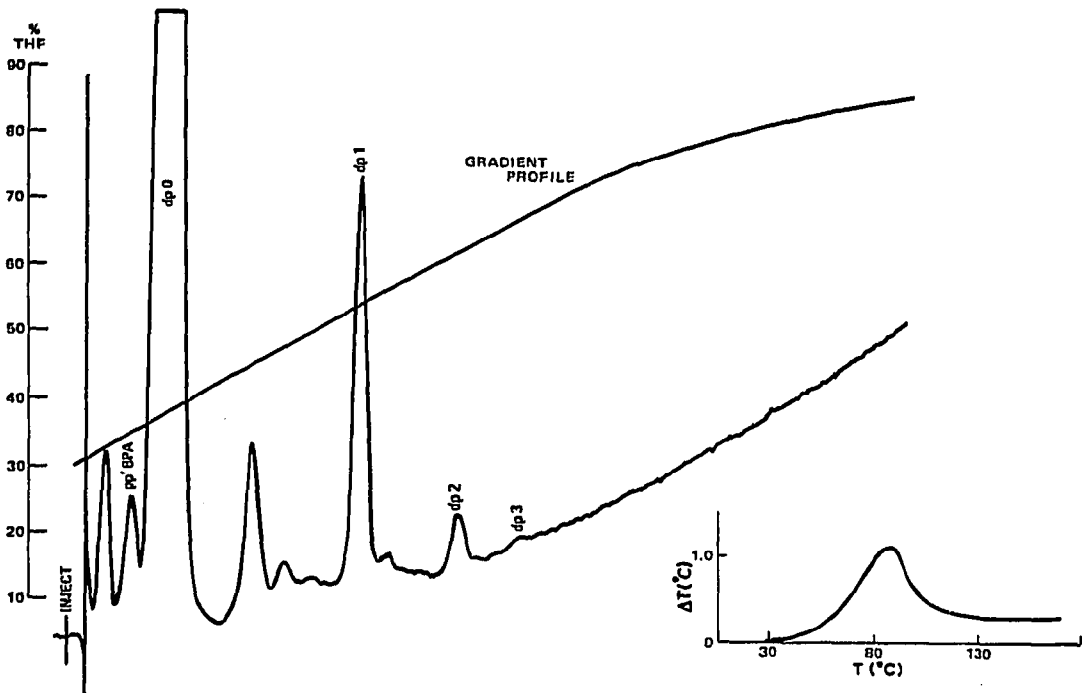


Fig. 8. Gradient separation of EPI-REZ 510, lot B26808. Conditions, as in Fig. 3.

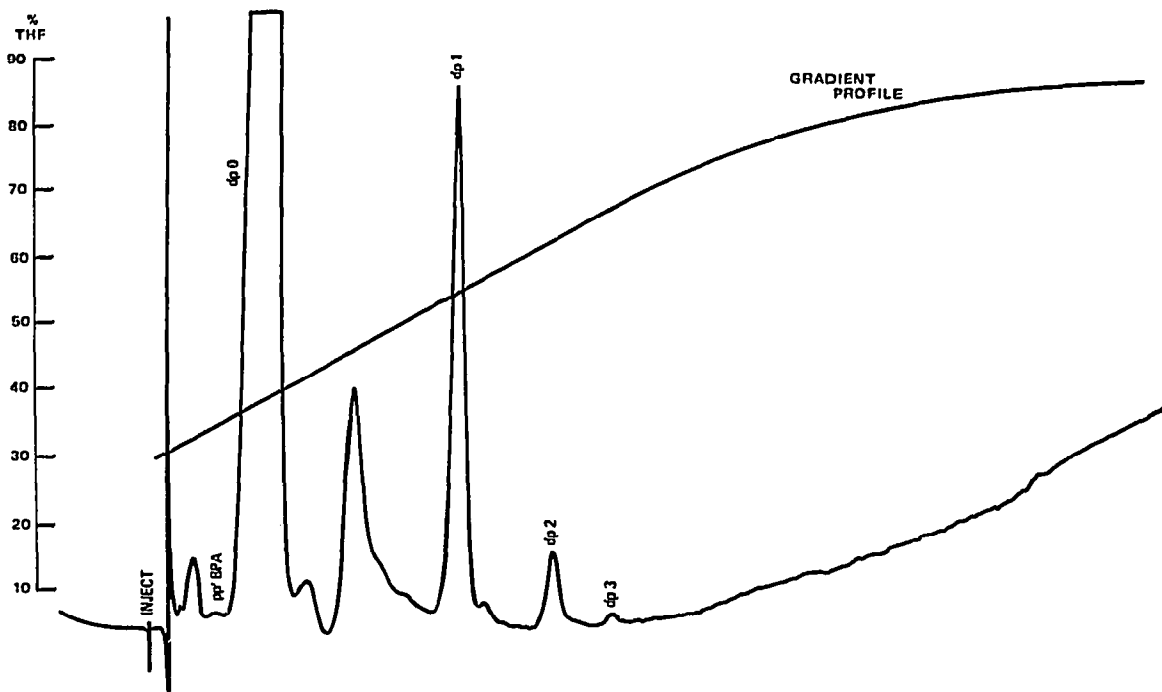


Fig. 9. Gradient separation of ERL 2774, lot 1032B. Conditions, as in Fig. 3.

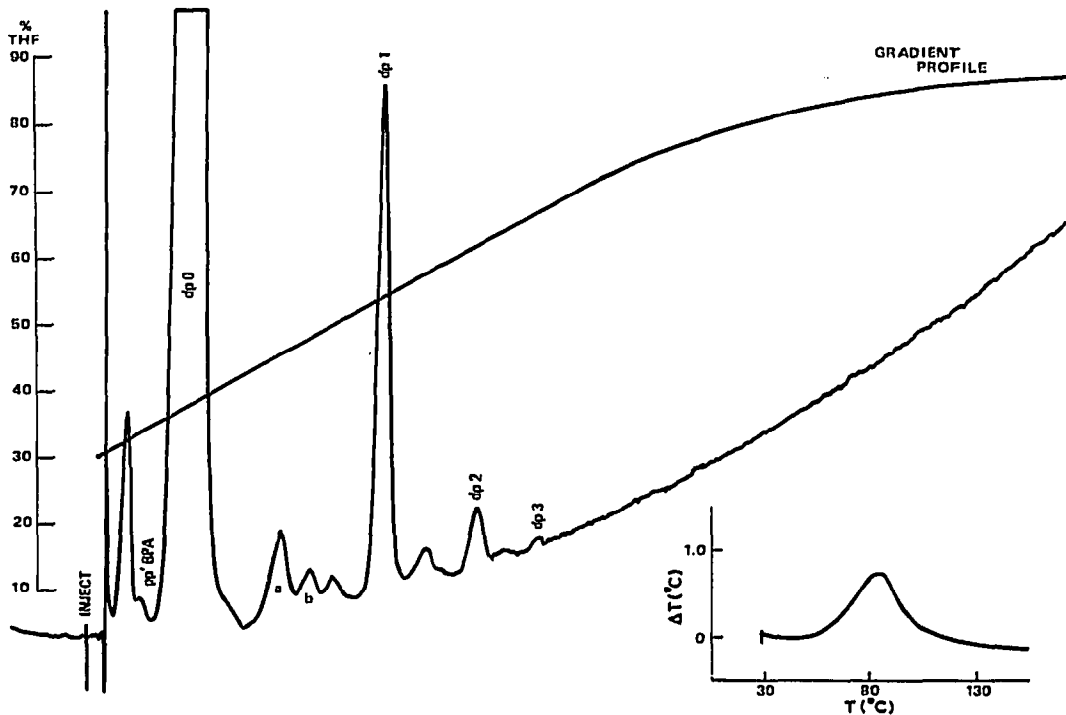


Fig. 10. Gradient separation of ARALDITE 6010, lot K275-50. Conditions, as in Fig. 3.

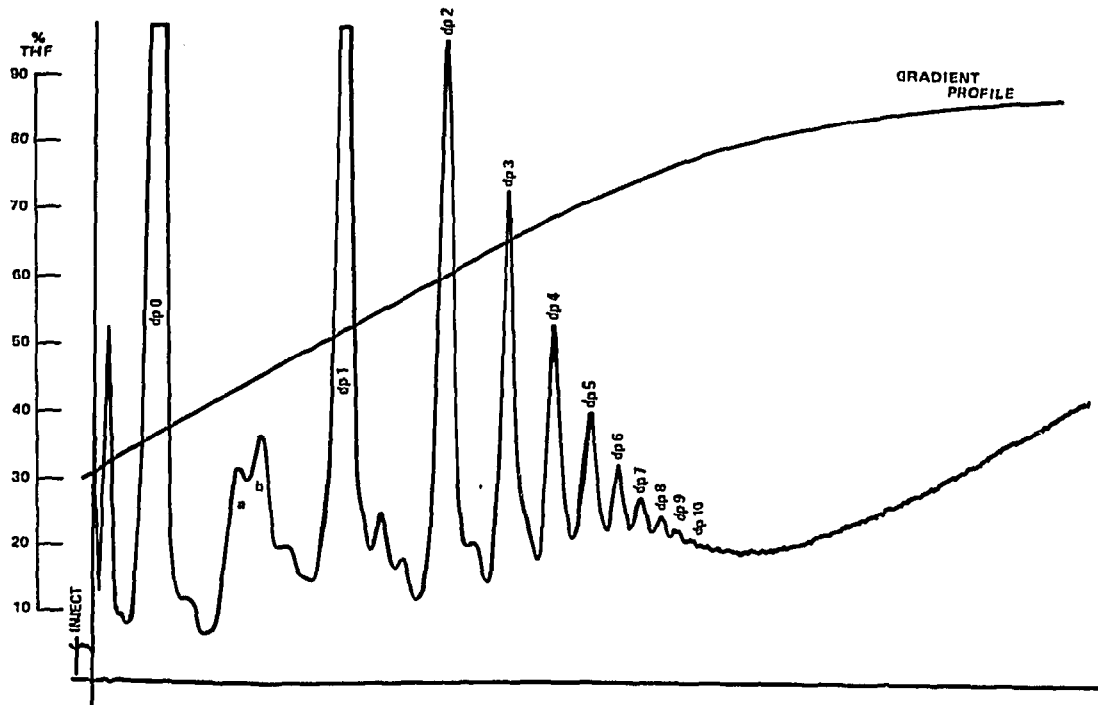


Fig. 11. Gradient separation of EPON 836. Conditions, as in Fig. 3.

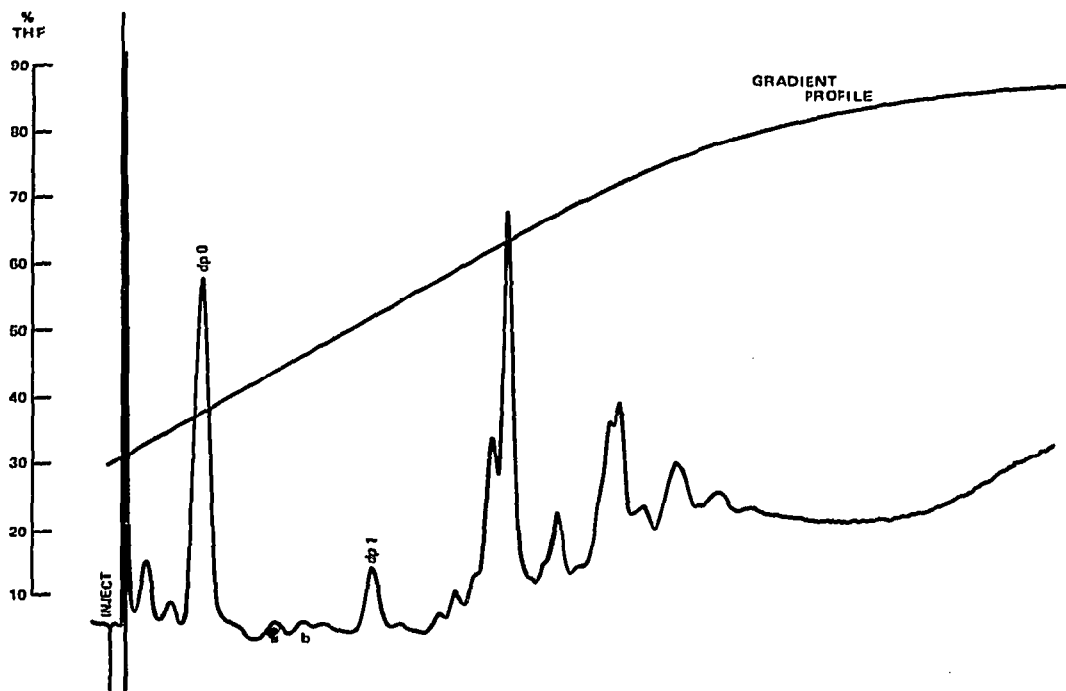


Fig. 12. Gradient separation of DER 511. Conditions, as in Fig. 3.

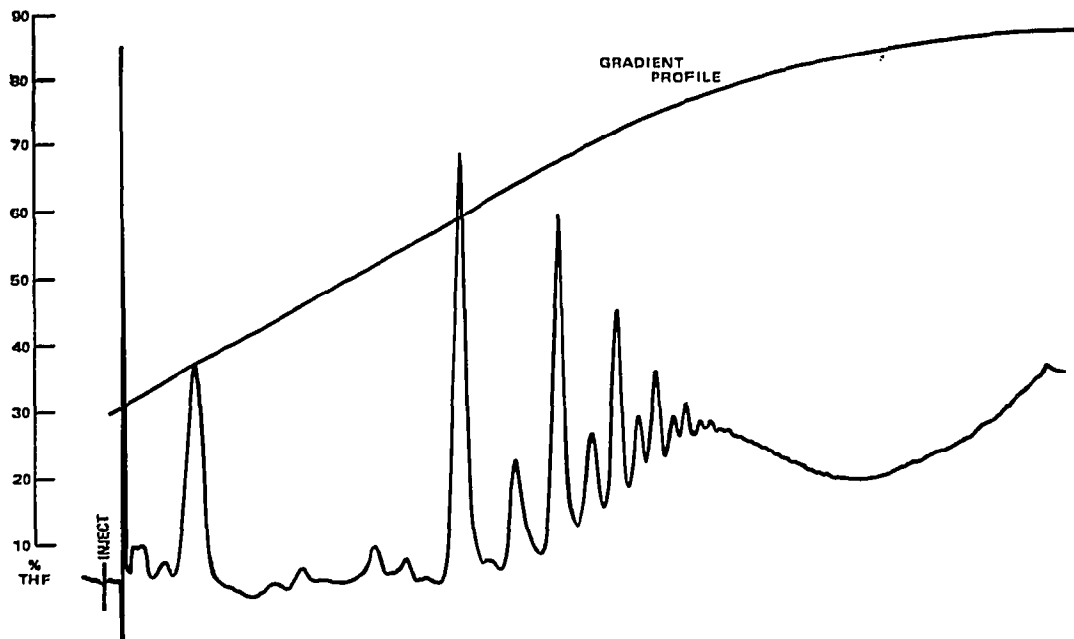


Fig. 13. Gradient separation of DER 661. Conditions, as in Fig. 3.

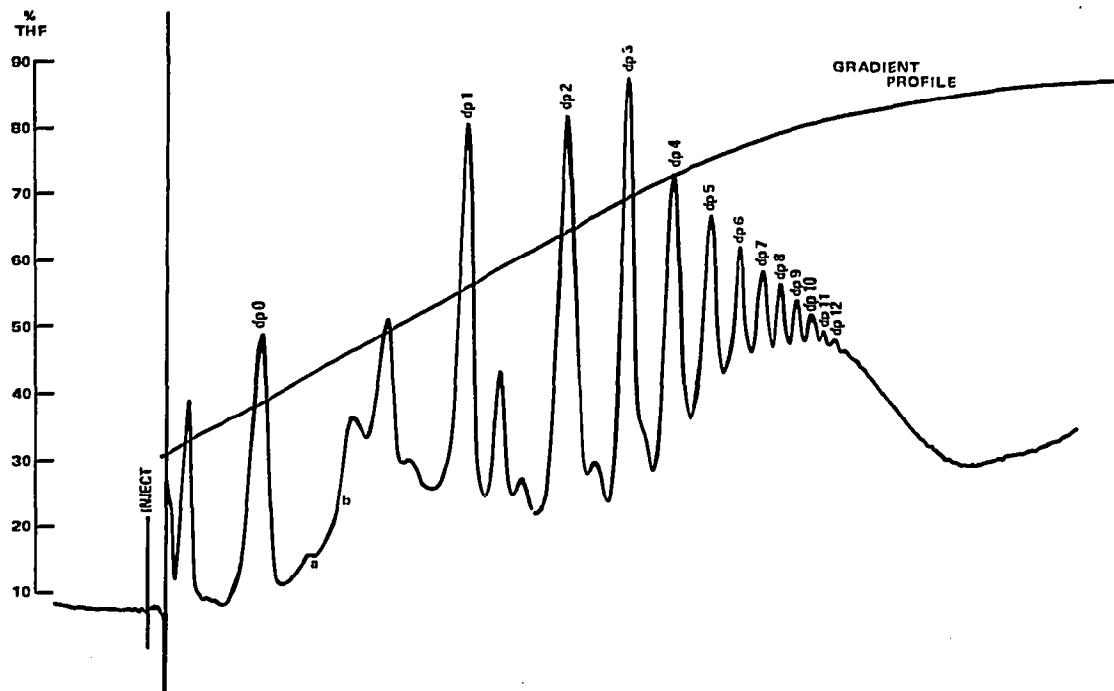


Fig. 14. Gradient separation of EPON 1001. Conditions, as in Fig. 3.

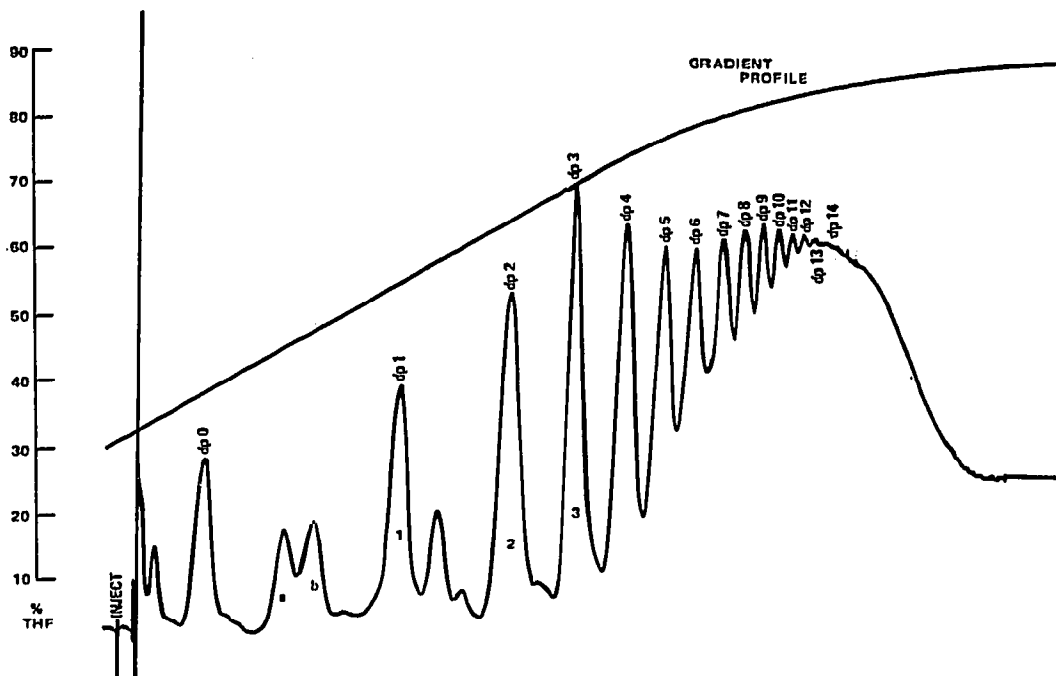


Fig. 15. Gradient separation of even-odd oligomers of EPON 1004. Conditions, as in Fig. 3.

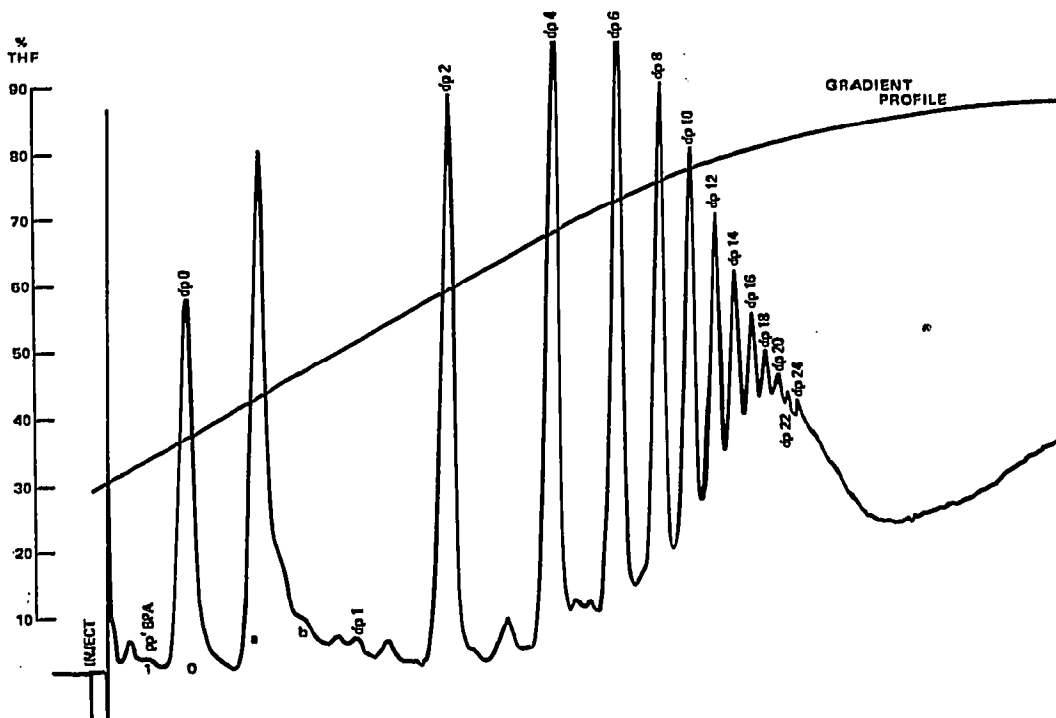


Fig. 16. Gradient separation of even oligomers of EPON 1004. Conditions, as in Fig. 3.

addition, unreacted bisphenol A may be present as well as its reaction by-products^{2,9}.

Five liquid epoxy samples (commercially claimed to be equivalent) were evaluated: Shell's EPON 828 (Fig. 3); Dow's DER 331 (Fig. 7); Celanese's EPI-REZ 510 (Fig. 8); Union Carbide's ERL 2774 (Fig. 9); and Ciba's ARALDITE 6010 (Fig. 10). The data obtained show differences in the amount of each oligomer present. The DER 331 and EPI-REZ 510 have much higher levels of *p,p'*-BPA. Variations also occur in the number and level of the "impurities".

Figs. 3-6 are four different lots of Shell EPON 828. The major difference among the four lots is the amount of each "impurity" present. Preliminary attempts have been made to identify these impurities. The impurity peak marked "a" reacted with silver nitrate, and, thus, may be unhydrolyzed chloride. Following the work of Tanaka and others, synthetics were prepared⁹. By doping techniques, it has been found that 2,4-bis(α,α -dimethyl-*p*-hydroxybenzyl)phenol also has retention at peak "a". A cyclic bis[2,2-bis(4-hydroxyphenyl)]propane has retention at peak "b". However, the isolation and identification of these two impurities from actual epoxies has not been done.

Semisolid and solid epoxy resins

This same separational approach has been extended to the semisolid and solid epoxy resins. EPON 836 (Fig. 11) is a Shell semisolid resin. The two Dow samples, DER 661 (Fig. 13) and DER 511 (Fig. 12), are widely used as printed circuit board laminates. These two are equivalent in epoxide content, but the DER 511 is a brominated material, based on tetrabromo bisphenol A. The EPON 1001 and 1004 resins (Figs. 14-16) are solid epoxies.

Differential thermal analysis

Thermal techniques have been widely used to characterize thermosets¹⁰. Thus, DTA can effectively be applied to the analysis of the degree of cure and to the selection of proper cure time, temperature, or most effective curing agent. In this work, a comparison was made of the cure temperatures of the various liquid epoxies.

TABLE I
CURE TEMPERATURE AND RANGE

| <i>Resin</i> | T_{peak} ($^{\circ}C$) | $T_{1/2}$ ($^{\circ}C$) |
|--------------|----------------------------|---------------------------|
| EPON 828 | | |
| 9NHJ10 | 85.9 | 69.7-96.7 |
| 10JHJ2 | 85.9 | 68.2-95.7 |
| 12PHJ13 | 84.9 | 68.7-93.8 |
| DER 331 | 86.9 | 70.2-98.7 |
| EPI-REZ 510 | 87.9 | 70.2-102.6 |
| ARALDITE | 84.9 | 70.4-95.7 |

Diethylenetriamine at a level of 12 parts per hundred was used. Sample loads of 25 ± 0.5 mg were scanned at $10^{\circ}/\text{min}$ from 30 to 130° .

The thermograms are inserted in the figures for each epoxy partition separation. In addition, overlays of the thermograms are shown in Figs. 17 and 18.

Under these conditions the temperature at maximum exotherm was deter-

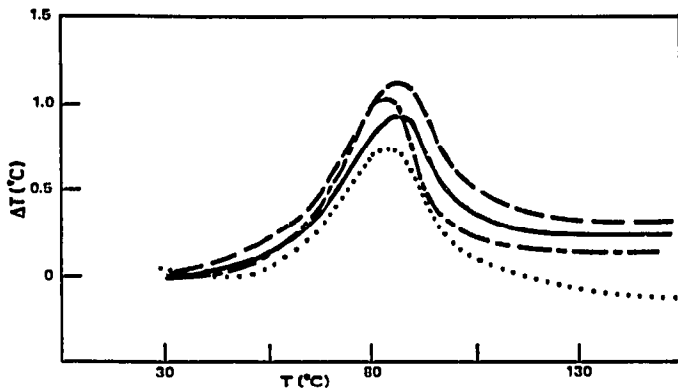


Fig. 17. DTA thermogram of comparative liquid resins. — — —, EPI-REZ; — — —, EPON 828 12PHJ-13; — — —, DER 331 TB310009; ·····, ARALDITE.

mined as were the temperatures at half-height on the exotherm (Table I). These values indicate that: (1) the more pure oligomer with DP 0 the narrower the ΔT of cure; (2) the more hydroxyl compounds, such as *p,p'*-BPA and 2,4-bis(α,α -dimethyl-*p*-hydroxybenzyl)phenol, the lower the temperature of the start of the exotherm, but the higher the temperature required for total cure.

It would appear that the hydroxyl compounds react with hardener, but do not promote cross-linking of the oxirane ring.

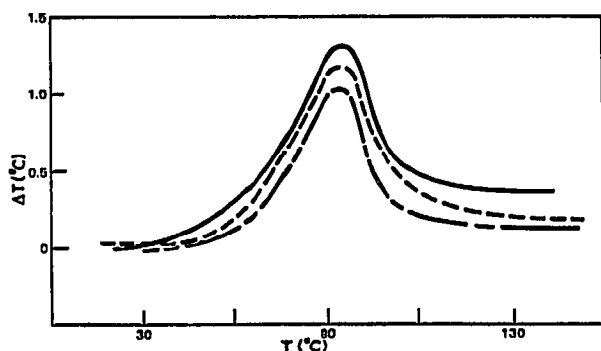


Fig. 18. DTA thermogram of three EPON 828 resins. — — —, 10JHJ2; — — —, 9NHJ10; — — —, 12PHJ13.

CONCLUSIONS

It is possible to separate the various oligomers of glycidyl bisphenol A epoxies from DP 0 to DP 24 by a reversed-phase partition gradient technique. Various impurities can also be separated, such as unreacted bisphenol A, 2,4-bis(α,α -dimethyl-*p*-hydroxybenzyl)phenol, unhydrolyzed chloride-containing compounds, and a cyclic bis[2,2-bis(4-hydroxyphenyl)]propane.

Hydroxyl equivalent can be determined by integrating the oligomer peak values for epoxide equivalent.

Accurate values of cure time, temperature, and the exotherm of cure can be predicted by determining the kinetics of reaction with any hardener.

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