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A Review of the Application of Liquid Chromatography to the Characterization of Epoxy Resins

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This review covers selected literature in the field of liquid chromatographic characterization of epoxy resins, including a number of the author's original examples of the applications of various chromatographic techniques. Several derivatization reactions are presented that can be used for the identification of components with functional groups other than epoxy. Size exclusion chromatography (SEC) coupled with a multi-angle light scattering (MALS) detector is demonstrated as the most efficient method of the determination of molar mass distribution. The number average molar masses determined by SEC-MALS are compared with those measured by vapor phase osmometry.

Keywords: Epoxy resins; HPLC; SEC; Light scattering

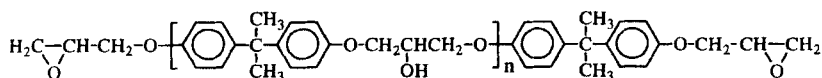
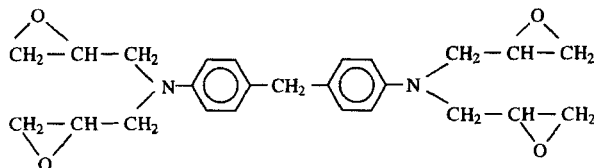
INTRODUCTION

Epoxy resins are compounds containing two or more epoxy (mostly glycidyl = 2,3-epoxy propyl) groups in the molecule. Epoxy resins are an important group of synthetic resins that have found uses in many application areas (e.g., coatings, adhesives, molding masses, fiber reinforced construction materials). Various types of epoxy resins differ in their chemical composition and molar mass. Formulas of two common epoxy resins are depicted in Figure 1 together with possible functional group irregularities.

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Bisphenol A (BA) based epoxy resin, $n = 0, 1, 2, \dots$ 

N,N,N',N'-Tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM)

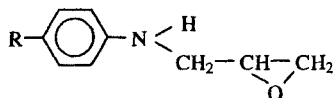
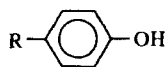
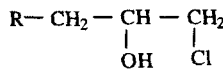
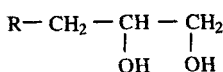


FIGURE 1 Formulas of epoxy resins discussed in this article including possible functional group irregularities.

Simple analytical characteristics (e.g., contents of epoxy groups, chlorine, α -glycol groups, viscosity or softening point) are used for routine characterization of epoxy resins. Liquid chromatographic methods can provide more information about the contents of compounds with end group other than glycidyl and about the molar mass distribution. Two methods have been used and reported in the literature: high performance liquid chromatography (HPLC) and size exclusion chromatography (SEC). The methods have been applied to the analysis of epoxy resins based on bisphenol A^[1-9], brominated bisphenol A^[10-12], bisphenol S^[13-14], aromatic glycidylamines^[15-19], epoxy novolacs^[20-21], epoxy formulations and composite matrices^[22-28], study of curing^[29-41], and determination of residual levels of bisphenols A and F in non-cured epoxy resins^[42]. Attention has been paid also to the analysis of bisphenols A^[43] and F^[44]. Separation of epoxy resins by functionality types has been achieved by means of the chromatography in the critical mode of separation^[45]. The aim of this work is to provide instructions for SEC and HPLC analysis of epoxy resins.

EXPERIMENTAL

The chromatographic system consisted of a 600 pump, a 717 auto-sampler, a 996 photodiode array detector, a 410 differential refractometer

(all Waters) and a miniDAWN multi-angle light scattering (MALS) photometer (Wyatt Technology Corporation). Data were acquired and processed by the ASTRA software in the case of SEC-MALS (Wyatt Technology Corporation) and the Millennium Chromatography Manager (Waters) in the case of SEC and HPLC.

Three PLgel 3- μ m Mixed-E 300 \times 7.5 mm columns (Polymer Laboratories) were used for the SEC separation. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.7 mL/min. The measurements were carried out at 25°C (SEC-MALS) or 40°C (SEC). The samples were injected as solutions in THF in the amount/concentration of 20 μ L/2% w/v (SEC) or 100 μ L/4–5% (SEC-MALS).

A Nova-Pak C 18 column 150 \times 3.9 mm, particle size 4 μ m (Waters) with various gradient profiles was employed for HPLC. The chromatographic conditions were flow rate: 1 mL/min, detection: 280 nm, temperature: 40°C, and sample size: 5 μ L 1% or 3% solution in THF. The following THF-water and THF-methanol-water gradients were used for the analysis of samples presented in this article: (1) 0 min—38% THF, 10 min—38% THF, 22 min—45% THF, 10% methanol, 82 min—65% THF, 20% methanol; (2) 0 min—38% THF, 10 min—38% THF, 22 min—55% THF, 82 min—85% THF; (3) 0 min—63% methanol, 7 min—63% methanol, 20 min—20% THF, 80% methanol, 23 min—20% THF, 80% methanol; (4) 0 min—38% THF, 10 min—38% THF, 22 min—55% THF, 30 min—70% THF; and (5) 0 min—10% THF, 40% methanol, 42 min—25% THF, 47% methanol, 46 min—25% THF, 75% methanol, 50 min—25% THF, 75% methanol.

RESULTS AND DISCUSSION

Two representative examples of SEC/HPLC characterization of BA-based epoxy resin are in Figures 2 and 3. The figures demonstrate the state-of-the-art separation possibilities of both techniques. The obtained data can be used for simple fingerprint batch-to-batch comparison or composition vs. property studies. Especially HPLC can detect even minor variations in chemical composition that cannot be detected by traditional analytical tests. Besides analysis of final resins, both methods can be applied to monitoring the course of the resin preparation. Two examples are depicted in Figures 4 and 5. Figure 4 presents HPLC chromatograms of samples taken from the batch during advancement reaction of low-molar-mass epoxy resin with BA. The method was used to follow the amounts of various oligomers during the resin preparation. The HPLC chromatograms in Figure 4 are completed with the number (M_n) and weight (M_w) molar mass averages determined by SEC-MALS. HPLC chromatogram of sample taken from the batch during the preparation of BA based low-molar-mass epoxy resin is

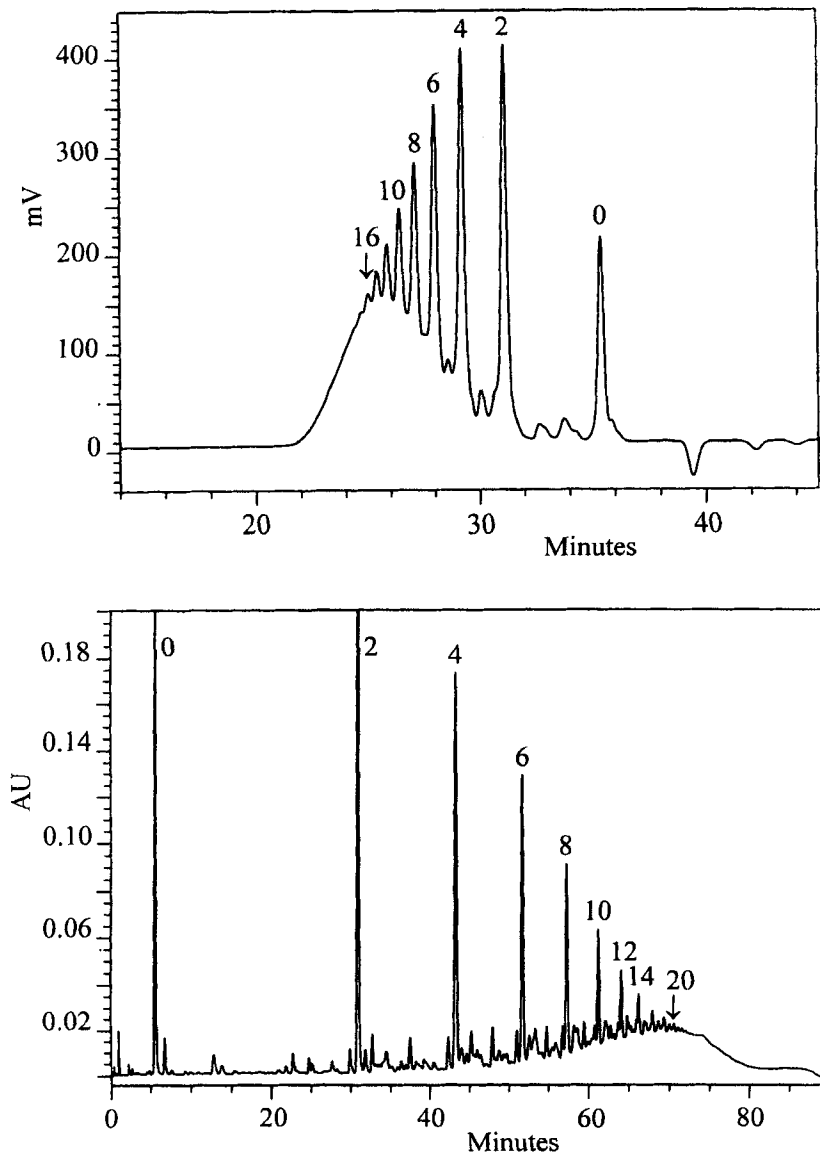


FIGURE 2 SEC (top) and HPLC (bottom) chromatograms of medium-molar-mass BA based epoxy resin. Peak identification: oligomers according to Figure 1. Gradient 1.

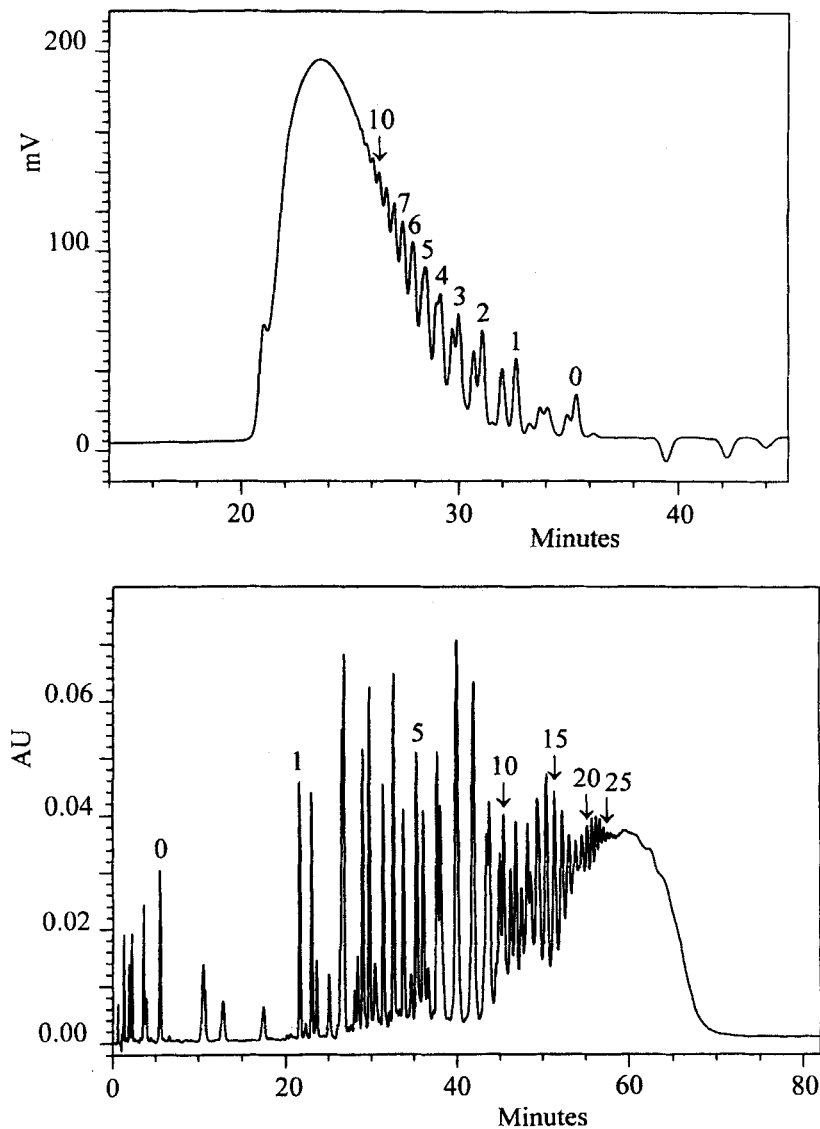


FIGURE 3 SEC (top) and HPLC (bottom) chromatograms of higher-molar-mass BA based epoxy resin. Peak identification: oligomers according to Figure 1, SEC peak at about 21 min corresponds to exclusion limit of SEC columns. Gradient 2.

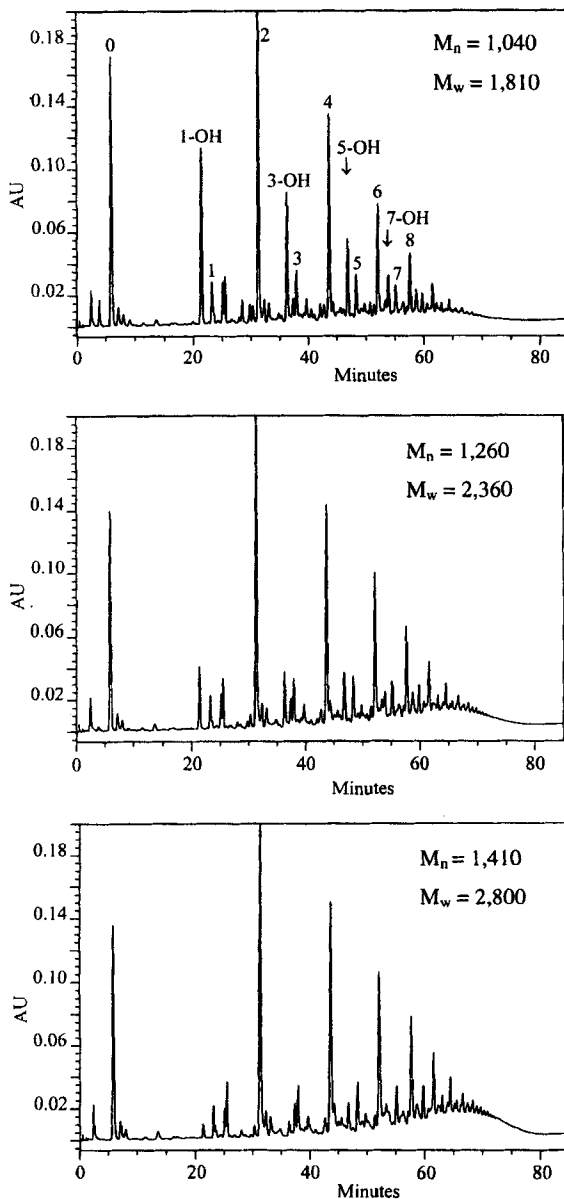


FIGURE 4 HPLC chromatograms of samples taken from the batch during the reaction of low-molar-mass epoxy resin with BA. From top to bottom: reaction time 60, 120, 300 min. Molar mass averages determined by SEC-MALS. Peak identification: epoxy oligomers and oligomers with one aromatic hydroxyl according to Figure 1. Gradient 1.

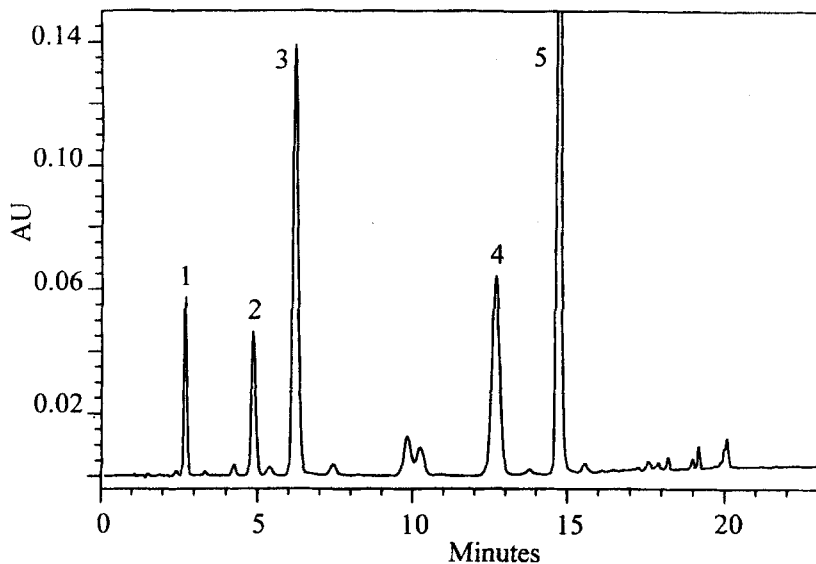
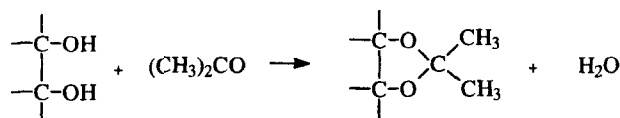


FIGURE 5 HPLC chromatogram of sample taken from the batch during the preparation of low-molar-mass BA based epoxy resin. Peak identification: 1 = BA, 2 = glycidyl ether of BA, 3 = 2-hydroxy-3-chloropropyl ether of BA, 4 = glycidyl 2-hydroxy-3-chloropropyl ether of BA, 5 = bis(2-hydroxy-3-chloropropyl) ether of BA. Gradient 3.

shown in Figure 5. The changes of relative peak areas during the reaction can provide detailed information about the reaction kinetics.

Component Identification

Components with various functional groups (Figure 1) that appear as minor peaks in the HPLC chromatograms may have a pronounced effect on resin stability and reactivity with curing agents, and on the properties of the items manufactured from the resin (e.g., tensile strength, impact resistance, chemical resistance, adhesion, appearance of paint films, glass transition temperature). Therefore, the identification of particular components in epoxy resin is important for quality control and a good understanding of the resin properties. Complete identification of all components is difficult and may require a combination of semipreparative chromatographic techniques and other instrumental analytical methods, such as infrared spectroscopy, mass spectroscopy, or nuclear magnetic resonance. Recent developments in coupling of liquid chromatography with mass spectroscopy may further facilitate complex description of



Catalysis with anhydrous copper sulphate, 50 °C



Catalysis with N-methylimidazole, 50 °C

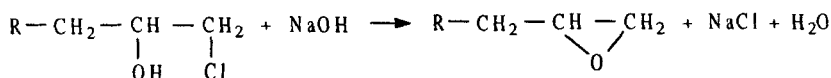
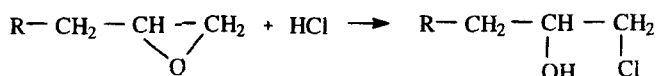


FIGURE 6 Derivatization reactions that can be used for peak identification.

epoxy resins. However, there are several simple derivatization reactions that can help in identifying some components with different functional groups. These reactions are indicated in Figure 6 and the examples of chromatograms are in Figures 7 and 8. Combination of HPLC/SEC separation, i.e., collection of particular SEC (HPLC) fractions and their subsequent HPLC (SEC) analysis^[6,17,18] as well as changes of peak intensities in chromatograms of samples taken from the batch during the sample preparation may help to interpret the chromatograms.

Component Quantification

The content of oligomer $n=0$ in epoxy resins based on bisphenol A can be estimated from the relative peak area^[9]. In the case of medium-molar-mass samples, the relative peak area of the oligomer $n=0$ is rather lower than the content determined by the detector response calibration. This fact can be explained by the slightly more intensive detector response of higher oligomers and is consistent with the work of Braun and Lee^[46] who reported moderate increase of absorption coefficient at 278 nm of BA based epoxy oligomers with increasing polymerization degree. Similarly, the relative peak area of TGDDM corresponds approximately to the real content determined by means of calibration of detector response^[18]. However, caution must be taken in the analysis of

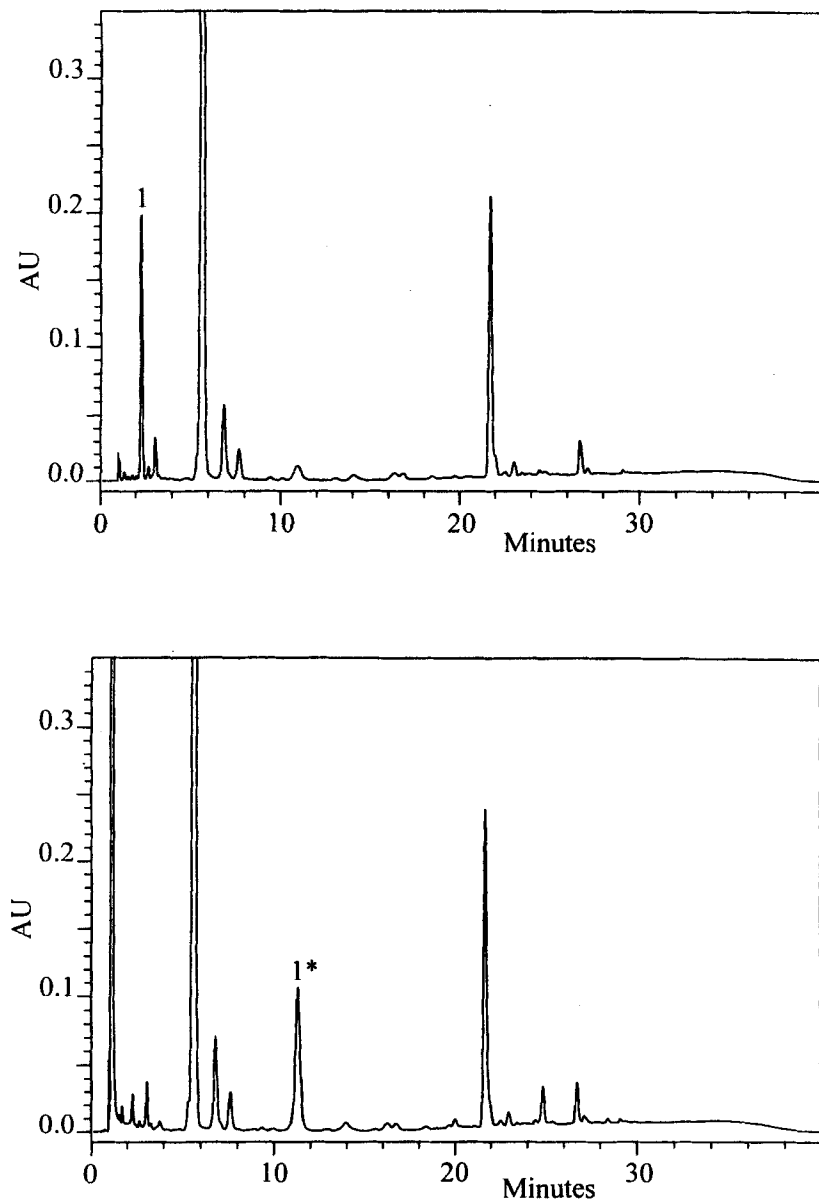


FIGURE 7 HPLC chromatograms of BA based epoxy resin before (top) and after (bottom) derivatization with acetone. Peak identification: 1 = 2,3-dihydroxypropyl glycidyl ether of BA and its isopropylidene derivative (1*). Gradient 4.

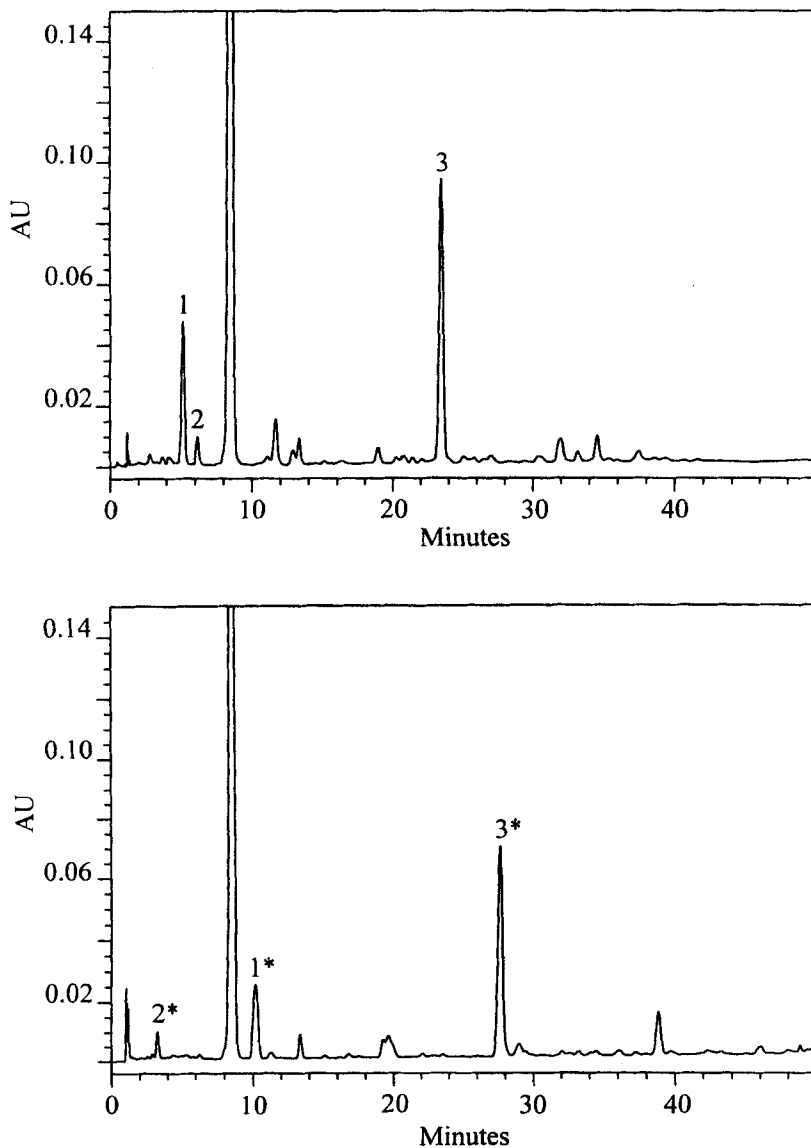


FIGURE 8 HPLC chromatograms of TGDDM based epoxy resin before (top) and after (bottom) derivatization with acetic anhydride. Peak identification: 1 = tetrahydro-3-hydroxyquinoline compound, 2 = triglycidyl-4,4'-diaminodiphenylmethane, 3 = dimer, formulas see Ref. [18], * = derivatives (1*, 3* = esters and 2* = amide). Gradient 5.

mixed epoxy resins or epoxy resin formulations, because significantly different detector responses of various compounds are highly probable.

Determination of Molar Mass Distribution

In the cases of the most common epoxies based on BA, two equations can be used for the calculation of the calibration curve of epoxy resin (EP) from that of polystyrene (PS):

$$\log M_{EP} = \frac{1}{1 + a_{EP}} \log \frac{K_{PS}}{K_{EP}} + \frac{1 + a_{PS}}{1 + a_{EP}} \log M_{PS} \quad (1)$$

$$M_{EP} = 0.84 M_{PS}^{0.987} \quad (2)$$

Equation (1) requires the constants of the Mark–Houwink relation a , K that were for BA-based-epoxy resins determined by Myers and Dagon^[47]. Equation (2) was derived by Mori^[48]. Both equations provide similar results, but careful comparison of M_n and M_w values determined by SEC, vapor phase osmometry (VPO), and SEC-MALS indicated

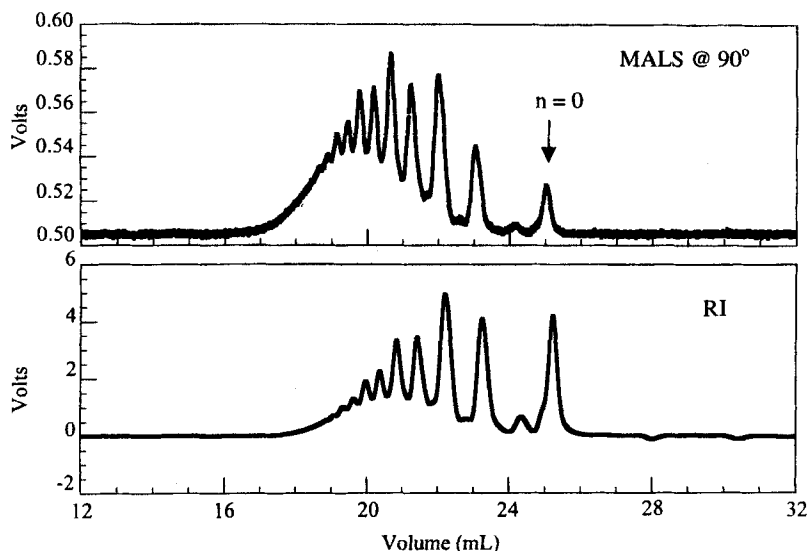


FIGURE 9 Chromatograms obtained by SEC analysis of BA-based epoxy resin with signals from MALS detector at 90° (top) and refractive index (RI) detector (bottom).

TABLE I Comparison of M_n Values of BA-Based Epoxy Resins Determined by VPO and SEC-MALS

Sample	M_n [g/mol] ^a	
	VPO	SEC-MALS
1	730	810
2	980	1,040
3	980	1,120
4	1,030	1,150
5	1,100	1,260
6	1,180	1,330
7	1,200	1,330
8	1,290	1,380
9	1,470	1,520

^a Precision $\pm 5\%$

that Equation (1) as more accurate^[9]. However, if the sample of interest contains branched molecules, the conventional SEC gives erroneous results and only connection of the SEC chromatograph to a MALS detector can provide correct molar mass characterization including identification of branching^[9]. Historically, the light scattering technique was not applicable for the characterization of oligomers. However, due to the high specific refractive index increment of BA-based epoxies and the high sensitivity of modern MALS photometers, there is no low molar mass limit for the detection of these resins. This is clearly demonstrated in Figure 9 where the refractive index and light scattering chromatograms of a BA-based epoxy resin sample are presented. The miniDAWN photometer provides good signal even for the lowest oligomer. Table I contrasts M_n values of several medium-molar-mass BA-based epoxy resin samples that were determined by VPO and SEC-MALS. The change of the specific refractive index increment with polymerization degree is a limiting factor that may influence the correctness of the M_n determination of the medium-molar-mass samples. Nevertheless, the data in Table I prove SEC-MALS to be able to provide good M_n values and to discriminate among the epoxy resin samples even in the M_n range of about 1,000.

CONCLUSIONS

SEC and HPLC are powerful analytical tools for research and development work as well as for the routine testing of various epoxy resins.

The methods provide markedly more information than traditional analytical techniques and they can be applied to the analysis of final samples, the monitoring of resin manufacture, study of the curing, and analysis of epoxy formulations. Several derivatization reactions can be used for the peak identification. Combination of SEC with MALS detector has been verified as an efficient and reliable method for the determination of molar mass distribution of epoxy resins.

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