Characterization of Bisphenol A–Based Epoxy Resins by HPLC, GPC, GPC–MALLS, VPO, Viscometry, and End Group Analysis: On the Identification of 2,3-Dihydroxypropyl-Containing Compounds, Determination of Molar Mass Distribution, and Branching

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ABSTRACT: Reversed-phase high performance liquid chromatography (HPLC), conventional gel permeation chromatography (GPC), and gel permeation chromatography coupled with a multiangle laser light scattering photometer (GPC–MALLS) were used for the analysis of epoxy resins based on bisphenol A. Compounds containing 2,3-dihydroxypropyl group were identified in HPLC chromatograms by means of the derivatization of sample by acetone. The presence of branched molecules was proved by GPC–MALLS using a molar mass versus root mean square (RMS) radius plot or molar mass versus elution volume plot. The molar mass distribution determined by HPLC was compared with that obtained by GPC–MALLS. Molar mass averages measured by means of GPC, GPC–MALLS, vapor pressure osmometry (VPO), and end group analysis (EG) were compared and the differences of results obtained by particular methods were discussed. An appropriate GPC calibration was found on the basis of literature data and the comparison of molar mass averages measured by GPC, VPO, and GPC–MALLS. The refractive index increment of epoxy resins was determined. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2432–2438, 1999

Key words: epoxy resin; liquid chromatography; gel permeation chromatography; molar mass; branching

INTRODUCTION

Epoxy resins prepared from bisphenol A (Scheme 1) are the most common epoxies of great technical importance. HPLC and GPC have become widely employed methods for the characterization of epoxy resins based on bisphenol A.[1–7] HPLC is able to separate epoxy oligomers up to the polymerization degree of about 25 and many side-reaction products or intermediates with one or two ends other than the epoxy group (e.g., 2,3-dihydroxypropyl, 2-hy-droxy-3-chloropropyl, aromatic hydroxyl). GPC can separate about 10 epoxy oligomers and the separation of compounds with different end groups is limited to the lowest oligomers ($n = 0, 1$).
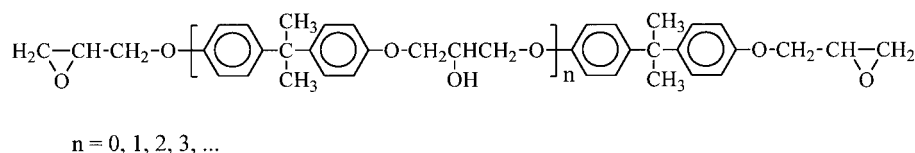
Compounds containing the 2,3-dihydroxypropyl (α-glycol) group are important side products that are formed by addition of water to an epoxy group. The comparison of several resins for powder coatings having different α-glycol content proved that α-glycol groups worsen the appearance of paint films, and decrease the impact resistance or resistance against methyl ethyl ketone of cured resins. Moreover, Sheih and Massingill reported[8] that an increased level of α-glycol in the liquid epoxy resin used for the advancement re-

$$H_2C-CH-CH_2-O-\left[\!\!\!\bigcirc\!\!\!\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\!\!\!\bigcirc\!\!\!-O-CH_2\underset{OH}{\overset{}{\underset{|}{CHCH_2}}}-O\!\!\!\right]_n\!\!\!\bigcirc\!\!\!\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\!\!\!\bigcirc\!\!\!-O-CH_2-CH-CH_2$$

n = 0, 1, 2, 3, ...

Scheme 1

action with bisphenol A greatly decreased the viscosity of the resulting advanced epoxy resin. This finding was explained by the termination effect of α-glycol in the advancement reaction. In addition, they also found that the increased level of α-glycol in the liquid epoxy resin enhanced wet adhesion (because of more hydrogen bonding), whereas the dry adhesion followed the opposite trend.

Branched molecules, which may arise by reaction of epoxy groups with aliphatic hydroxyl groups, represent another important kind of side products in epoxy resins. The branching affects the viscosity of solutions of epoxy resins and may influence the curing behavior or mechanical properties of cured resins.

The molar mass distribution is known to have a critical effect on polymer properties and applications. Since there are no commercial GPC calibration standards for epoxy resins, many plant and research laboratories apply a polystyrene calibration curve for the characterization of epoxy resins without any effort to establish a true calibration curve. This simple approach may be acceptable for a routine plant control or evaluation of reproducibility of particular production batches; nevertheless, comparisons of the polystyrene equivalent results with the data determined by absolute methods have not been reported.

The goals of this work are: (1) identification and quantification of compounds with an α-glycol group by HPLC; (2) confirmation of the ability of GPC–MALLS to determine the correct molar mass distribution of epoxy resins in the few hundred to few thousand molar mass range and application of the method to the identification of branched molecules; and (3) comparison of average molar masses determined by GPC with polystyrene calibration to those determined by absolute methods and finding a suitable GPC calibration.
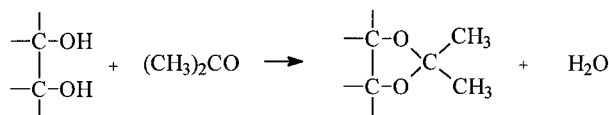
EXPERIMENTAL

The chromatographic system consisted of a 600 pump, a 717 autosampler, a 996 photodiode array detector, a 410 differential refractometer (all Waters, Milford, CT), and a DAWN-F photometer or a miniDAWN (Wyatt Technology Corp., Santa Barbara, CA). A Wyatt Optilab 903 interferometric refractometer was used for the determination of the refractive index increment of epoxy resins. Data were collected and handled by the ASTRA software for GPC–MALLS (Wyatt Technology Corp.) and the Millennium Chromatography Manager (Waters) for GPC and HPLC.

Three GPC column systems were used: (1) two Styragel HR 5E (Waters) 300×7.8 mm columns (analysis of samples M4–M12); (2) three Styragel HR 5E (Waters) 300×7.8 mm columns (analysis of samples M9, M10, and M12); and (3) two PLgel Mixed-E (Polymer Laboratories, Church Stretton, Shropshire, UK) 300×7.5 mm columns (samples M1–M4). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL/min. GPC columns were thermostated at 25°C. The columns were calibrated by polystyrene standards (Polymer Laboratories) covering the molar mass range of 1050–4,340,000 g/mol (16 standards, column system 1) or 266–34,500 g/mol (11 standards, column system 3). The samples were injected as solutions in THF in the amount/concentration of 50 μL/0.25% w/v (system 1, GPC), 100 μL/1.4% (system 1, GPC–MALLS), 150 μL/1.4% (system 2, GPC–MALLS), 20 μL/1% (system 3, GPC), or 100 μL/3 or 5% (system 3, GPC–MALLS).

A Nova-Pak C 18 column 150×3.9 mm, particle size 4 μm (Waters) with the following chromatographic conditions was employed for HPLC: solvent A: THF, solvent B: water; gradient profile (a) solid resins: 0 min, 38% A, 10 min, 38% A, 22 min, 55% A, 82 min, 85% A, (b) liquid resins: 0 min, 38% A, 10 min, 38% A, 22 min, 55% A, 30 min, 70% A; flow rate: 1 mL/min, detection: 280 nm; temperature: 40°C; sample size: 5 μL/1 or 3% solution in THF.

Derivatization with acetone was used to identify peaks of compounds containing α-glycol groups. Epoxy resin was dissolved in acetone (concentration 1 or 3%), and anhydrous copper sulfate was added (about 5%). The mixture was heated at 50°C for 2 h with occasional shaking.

$$-\overset{|}{\underset{|}{C}}\text{-OH} \quad + \quad (CH_3)_2CO \quad \longrightarrow \quad -\overset{|}{\underset{|}{C}}\overset{\text{-O}}{\underset{\text{-O}}{}}\overset{CH_3}{\underset{CH_3}{C}} \quad + \quad H_2O$$

Scheme 2

After that, the solution was filtered and directly analyzed by HPLC.

The epoxy equivalent was determined by the titration of epoxy resin solution containing tetraethyl ammonium bromide with perchloric acid according to the ISO 3001 standard. The content of α-glycol was determined using a method based on oxidation of the glycol with benzyltrimethylammonium periodate in a nonaqueous medium and subsequent titration of the liberated iodine (reduced with potassium iodine from the excess of periodate and the formed iodic acid) with sodium thiosulfate.[9]

Vapor pressure osmometer Model 233100 (Wescan Instruments, Santa Clara, CA) with THF as a solvent was used for the determination of number average molar mass.

Solution viscosities η and solvent viscosity η_s were determined at 25°C in THF using a Ubbelohde viscometer. Intrinsic viscosities $[\eta]$ were obtained by extrapolation of $(\eta - \eta_s)/\eta_s c$ to zero concentration c, according to the Huggins relation.

Diglycidyl ether of bisphenol A (DGEBA, $n = 0$) was prepared by crystallization of commercial liquid epoxy resin from a mixture of ethyl methyl ketone and methanol (1 : 4) at 5°C in the presence of activated charcoal. The purity was >99% according to HPLC. The obtained DGEBA was used for the calibration of HPLC detector response using solutions of known concentration. Epoxy resins were either commercial types (Dow Chemical, USA, or Shell, USA) or samples prepared in SYNPO's laboratories.

RESULTS AND DISCUSSION

Determination of α-Glycol–Containing Compounds

The content of α-glycol groups in a resin sample can be quantified by titration. The method provides a total content of α-glycol groups. HPLC as a separation technique can be used for the determination of several oligomers containing α-glycol. A simple way of identifying the peaks of an α-glycol group–containing compounds in an HPLC chromatogram can be derivatization of this group

and consequent change of retention times of these compounds. Any vicinal diol can react with acetone according to the reaction Scheme 2.[10]

Figure 1 presents HPLC chromatograms of epoxy resin before and after reaction with acetone. Cyclization of α-glycol groups giving isopropylidene derivatives results in a significant increase of the retention times of the α-glycol group–containing compounds. Table I presents the contents of DGEBA and α-glycol glycidyl ether of bisphenol A (GGEBA) determined by HPLC and the total content of α-glycol groups determined by titration. The data in Table I show a direct proportionality between the content of GGEBA and the total α-glycol. Since DGEBA and GGEBA have almost identical UV spectrum patterns, the content of GGEBA might be roughly estimated from the peak area similarly as in the case of DGEBA.

Determination of Molar Mass and Molar Mass Distribution

The relationship between log molar mass and elution volume must be established for a polymer
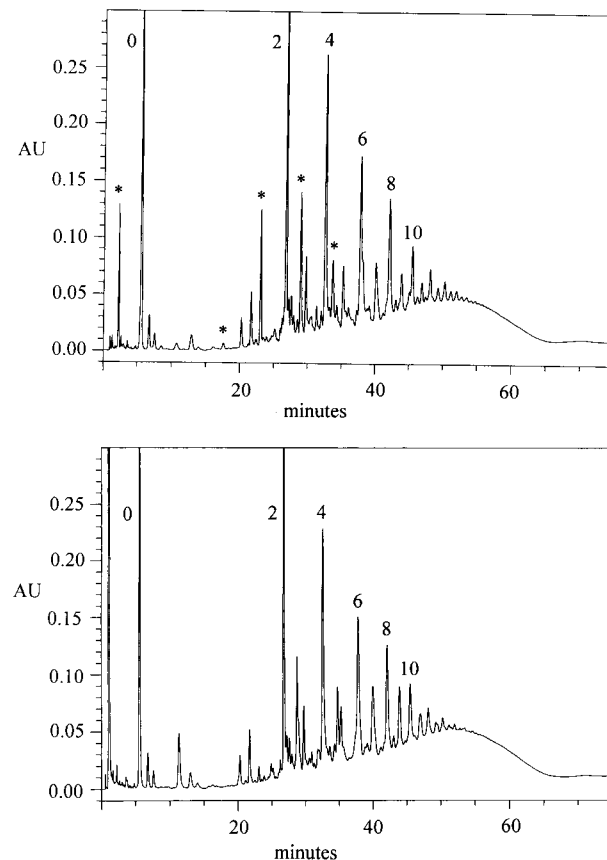
Figure 1 HPLC chromatograms of epoxy resin before (*top*) and after (*bottom*) derivatization with acetone. Peak identification: 0, 2, 4, · · · epoxy oligomers according to Scheme 1; * compounds containing α-glycol group.

Table I   Content of DGEBA, GGEBA, and Total α-Glycol Groups in Epoxy Resins

Sample[a]	DGEBA (%)[b]	DGEBA Peak Area (%)	GGEBA Peak Area (%)	α-Glycol (mmol/100 g)
G1	79.2	80.5	0.64	2.6
G2	86.0	80.3	0.93	6.2
G3	75.9	78.9	1.73	9.0
G4	82.3	78.6	2.13	10.9
G5	64.4	68.5	5.75	24.4
G6	60.8	62.4	10.59	41.8
G7	4.9	3.7	0.29	4.7
G8	4.8	3.6	0.34	7.4
G9	5.8	4.4	0.35	7.4
G10	6.8	5.2	0.58	9.3
G11	5.3	4.1	0.95	18.0

[a] Data for samples G1–G6 are averages from three measurements; precision: ±3%.
[b] Determined using the calibration curve of DGEBA.

under investigation in order to calculate molar mass distribution and molar mass averages from an experimental GPC chromatogram. In the case of epoxy resins there are no suitable standards available. Application of polymer fractionation techniques in conjunction with an absolute molar mass determination may be considered, but the experimental work is time-consuming and the quality of obtained fractions is not always good for the column calibration. In the absence of well-characterized calibration standards, a universal calibration curve based on the hydrodynamic volume calibration concept[11] can be employed. The relation between the calibration curve of a standard (mostly polystyrene, PS) and that of epoxy resin (EP) is given by eq. (1)[12]

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

where a and K are the constants of the Mark–Houwink equation.

Mark–Houwink constants of the epoxy resin were determined by Myers and Dagon ($a = 0.765$, $K = 0.0148$ mL/g, THF, 25°C, molar mass range 8600–75,000 g/mol).[13] Using the Mark–Houwink constants for polystyrene $a = 0.717$, $K = 0.0117$ mL/g (THF, 25°C, molar mass range 5000–867,000 g/mol),[14] eq. (1) demonstrates that the molar mass of the epoxy resin is lower than the molar mass of polystyrene by about 1/3.

Mori[15] found a conversion equation between the molar mass of polystyrene and molar mass of

epoxy resin using two Epikote epoxy resin samples of known number average molar masses

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

This equation is valid for THF, 25°C, and the molar mass range 900–100,000 g/mol and it demonstrates that the molar mass of the epoxy resin is lower than the molar mass of standard polystyrene by about 1/4.

Straightforward molar mass determination without column calibration can be achieved by coupling the molar mass–sensitive MALLS photometer to the GPC chromatograph. GPC–MALLS has sometimes been criticized as being unable to determine molar masses much below 10,000 g/mol, which is exactly the case for epoxy resins. Since HPLC is a suitable method for the determination of the molar mass distribution of epoxy resins up to the molar masses of about 8000, molar mass distribution curves determined by GPC–MALLS and HPLC were compared in order to show the accuracy of GPC–MALLS in the region of molar masses of the order of magnitude of several thousands (Fig. 2). Figure 2 shows very good agreement of distribution curves determined by the two different methods.

Table II compares number average (M_n) and weight average (M_w) molar masses of 12 epoxy resin samples determined by GPC with polystyrene calibration, which was converted by means of eqs. (1) and (2), GPC–MALLS, VPO, and EG.

The following conclusions can be drawn from the obtained data:
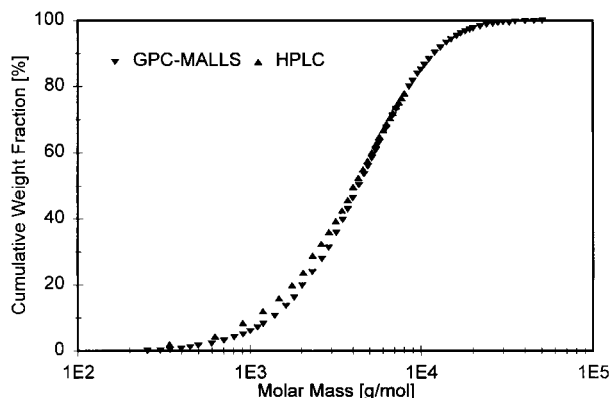
Figure 2 Comparison of cumulative distribution curves of sample M4 determined by HPLC and GPC–MALLS.

1. Both number and weight averages determined by conventional GPC using calibration established by means of polystyrene standards are substantially higher than those determined by absolute methods. The average deviations of M_n of samples M1–M12 compared with the VPO data and M_w of samples M1–M9 and M11 compared with the GPC–MALLS results are +49 and +58%, respectively. Significantly lower differences of M_w values for samples M10 and M12 may be explained by the branched structure of these samples, because elution volumes for branched molecules are always larger than those for the linear homologues of the same molar mass.

2. In contrast to the results obtained by polystyrene calibration, eqs. (1) and (2) provide molar mass averages much closer to those determined by VPO and GPC–MALLS. In spite of the failure of the universal calibration for low-molar-mass polymers,[16] eq. (1) provides good results even for samples of rather low molar mass.

3. Number average molar masses determined by VPO are lower than the values obtained by GPC–MALLS. This can be explained by a tendency of GPC–MALLS to overestimate M_n values because of limited resolution of GPC columns. Nevertheless, the agreement of both methods is quite good.

4. Number averages determined by means of EG are higher than the results gained by VPO. The values obtained by EG are influenced by two counteracting effects: (1) defects on chain ends that increase results determined by EG; (2) branching of epoxy molecules resulting in lower M_n calculated by EG. Comparison of M_w values determined by GPC and GPC–MALLS suggests a high degree of branching of sample M12. This finding is in agreement with the low M_n measured by EG. A couple of samples, M6 and M7, show very similar molar masses obtained by various methods except the values determined by EG. Higher M_n from EG for sample M6 corresponds to more chain defects in comparison with sample M7. Sample M10 has an extraordi-

Table II Comparison of Molar Masses Determined by GPC, GPC-MALLS, VPO, and EG

| Sample | M_n (g/mol)[a] | | | | | | M_w (g/mol)[a] | | | |
	GPC_{PS}	GPC-MALLS	$GPC_{eq.1}$	$GPC_{eq.2}$	VPO	EG	GPC_{PS}	GPC-MALLS	$GPC_{eq.1}$	$GPC_{eq.2}$
M1	1,590	1,430	1,150	1,220	1,180	1,420	3,800	2,600	2,600	2,800
M2	1,820	1,510	1,320	1,400	1,430	1,510	4,500	3,000	3,100	3,400
M3	1,930	1,590	1,400	1,480	1,470	1,530	5,100	3,400	3,500	3,800
M4	3,800	2,600	2,700	2,900	2,500	—	10,600	6,400	7,100	7,900
M5	4,900	4,000	3,500	3,700	2,800	5,200	14,800	9,100	9,900	10,900
M6	5,900	4,200	4,200	4,500	3,800	7,800	18,300	11,100	12,200	13,500
M7	6,100	4,400	4,300	4,600	3,500	5,500	19,800	11,800	13,100	14,500
M8	5,500	4,300	3,900	4,200	3,600	5,400	20,800	14,200	13,700	15,200
M9	7,700	6,100	5,400	5,900	5,200	8,700	27,500	16,500	18,000	20,100
M10	5,000	3,500	3,500	3,800	3,100	22,000	20,200	18,100	13,300	14,800
M11	8,200	6,900	5,800	6,200	5,700	9,200	30,400	19,300	19,900	22,200
M12	4,400	3,600	3,200	3,400	3,400	3,500	35,700	38,200	22,900	25,800

[a] Precision: $M_n \pm 5\%$, $M_w \pm 3\%$.
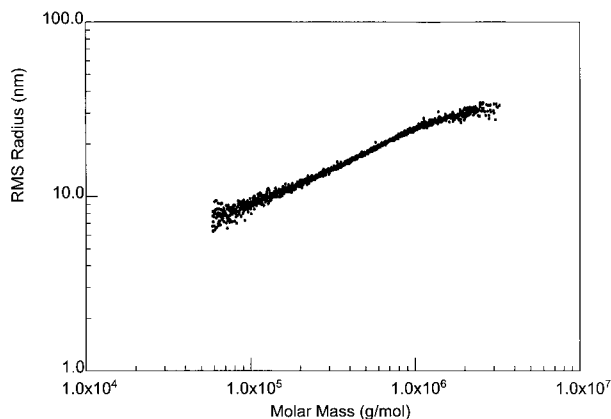
Figure 3 RMS radius versus molar mass plot for epoxy resin M12; slope = 0.43 ± 0.04.

Figure 4 Molar mass versus volume plots for samples M9, M10, and M12.

narily high M_n determined by EG, but the values from VPO or GPC–MALLS are several times lower, which corresponds to the high concentration of chain-end defects.

Determination of Branching

The fundamental description of branched polymers can be found in the study by Zimm and Stockmayer.[17] Branching can be identified by GPC–MALLS using RMS radius versus molar mass or molar mass versus volume plots.[18] The former can be used for samples with molecules large enough to measure RMS radii from the angular variation of the intensity of scattered light. Molar mass versus elution volume plot can be used even for lower-molar-mass samples, where the determination of RMS radii is inaccurate or impossible. RMS radius versus molar mass plot for sample M12 is shown in Figure 3. The slope of the plot of 0.43 is lower than the typical values for linear random coils (0.5–0.6)[18,19] and gives evidence about the presence of branched molecules. Figure 4 presents molar mass versus volume plots for samples M9, M10, and M12. The comparison of the plots proves that sample M12 is the most branched one. At a given elution volume, the molar mass increases with increased branching, because the branched molecules become more compact (i.e., tighter binding within the molecule). Intrinsic viscosity of samples M9, M10, and M12 was measured in order to gain more information about their molecular architecture. The experimental values are contrasted with those calculated from M_w using the constants of the Mark–Houwink equation for linear epoxy molecules[13] in Table III. The intrinsic viscosity is a sensitive measure of the volume occupied by a polymer

molecule in dilute solution and the data in Table III are consistent with Figure 4 and characterize sample M9 as linear and the resins M10 and M12 as branched with different degrees of branching.

Figure 5 compares GPC elution behavior of epoxy resins M9 and M12 and polystyrene. Molar mass versus volume plot of linear epoxy resin M9 approximately corresponds to eqs. (1) and (2), and explains significantly higher molar mass averages determined by conventional GPC with polystyrene calibration. The plot of branched resin M12 crosses that of polystyrene and in the higher-molar-mass region, the molar masses of highly branched molecules of resin M12 are markedly higher that those of polystyrene eluting at the same elution volume.

Determination of Refractive Index Increment

The refractive index increment *dn/dc* was estimated by ASTRA, assuming 100% mass recovery of the injected sample. ASTRA calculates the concentration of solute in each slice from the entire injected mass, the sample detector signal voltage,

Table III   Intrinsic Viscosity of Samples M9, M10, and M12[a]

Sample	$[\eta]_{experimental}$ (mL/g)	$[\eta]_{linear}$ (mL/g)	$[\eta]_{exp.}/[\eta]_{linear}$
M9	26	25	1.0
M10	20	27	0.74
M12	19	47	0.40

[a] Determined experimentally from the viscosity measurement and calculated from M_w values and constants of Mark–Houwink equation determined by Myers and Dagon for linear epoxy molecules.
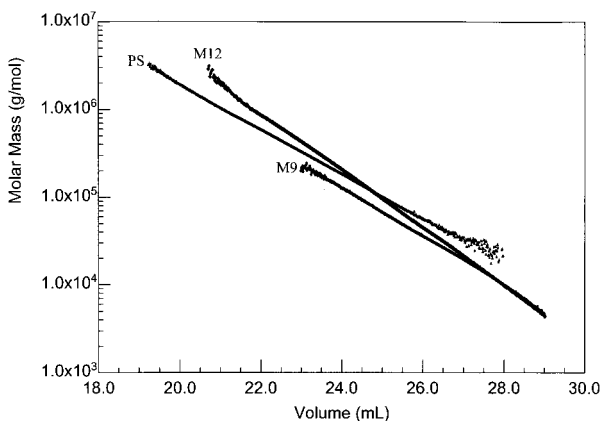
Figure 5 Comparison of molar mass versus volume plots of epoxy resins M9 and M12 with the plot of polystyrene.

and the volume of the slice. The Optilab interferometric refractometer constant (in refractive units per volt) is then used to calculate a value of *dn/dc*. The measurement of 11 samples of various epoxy resins gave the value of *dn/dc* = 0.183 ± 0.002 mL/g (THF, 25°C, M_w > 9000 g/mol). The value for samples of lower molar mass (M_w = 2600–3400 g/mol) was 0.178 ± 0.002 mL/g.

CONCLUSIONS

Compounds containing the α-glycol group can be easily identified in HPLC chromatograms after the derivatization of an epoxy resin sample by acetone under catalysis with anhydrous copper sulfate. The content of DGEBA and GGEBA can be estimated approximately from the relative peak areas.

Conventional GPC with polystyrene calibration significantly overestimates M_n and M_w values. Equations (1) and (2) can be applied for the transformation of the polystyrene calibration curve to the calibration curve of epoxy resins; the former provides results closer to the data determined by the absolute methods. Nevertheless, conventional GPC is not able to provide true molar mass distribution of branched samples that can be correctly characterized only by GPC–MALLS. This method measures accurate molar mass distribution even in the low-molar-mass

range. In addition, GPC–MALLS can prove the presence of branched molecules using the molar mass versus volume plot or the RMS radius versus molar mass plot. Additional information can be obtained by the comparison of experimental intrinsic viscosity with the value calculated from M_w determined by GPC–MALLS.

Combinations of various chromatographic, VPO, EG, and viscosimetric data can provide detailed knowledge of the molar mass distribution, chain structure, and the irregularities of the chain ends.

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