High-Performance Liquid Chromatography-Mass Spectrometry of Epoxy Resins

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ABSTRACT: The application of liquid chromatography coupled to mass spectrometry (LC-MS) for the analysis of epoxy resins is shown in two examples. Electro spray (ESI) and atmospheric pressure chemical ionization (APCI) are compared with respect to the ionization of diglycidylether of bisphenol A-based (DGEBA) epoxy resins. By-products in a typical modified solid DGEBA-based epoxy resin and in a new weatherable crosslinker for powder coating applications are characterized and discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 913–925, 1999

Key words: epoxy resin; liquid chromatography; mass spectrometry; electro spray

INTRODUCTION

Since the introduction of Araldite[®] more than 50 years ago,¹ epoxy resins enjoy an even more important role in a multitude of different application fields. A wide application range in the coatings industry, the use in fiber-reinforced organic matrix composites, in tooling applications, in the electro- and electronics industry, and as adhesives are just a few examples of the widespread use of epoxy resins today. Due to new increasingly challenging applications and closer product specification ranges, more specific methods for the characterization of epoxy resins are required in addition to application-related tests and wetchemical methods. The chromatographic methods most often used for the analysis of epoxy resins are size-exclusion chromatography (SEC) and high-performance liquid chromatography (HPLC). Although several other methods, like high-temperature gas chromatography (HTGC),² supercritical fluid chromatography (SFC),³ and matrixassisted laser desorption/ionization (MALDI) mass spectrometry⁴ have been used for the characterization of epoxy resins, they show advantages for a few selected applications. Whereas SEC is used to determine the molecular weight distribution,^{5–7} and sometimes to isolate selected fractions on a preparative scale for subsequent analytical investigations,^{8,9} it mainly lacks the chromatographic resolution of HPLC into separate individual compounds. A review on the chromatography of epoxy resins is given by Mestan and Morris.¹⁰ Recent chromatographic improvements, like the introduction of 3-µm particles for HPLC-column packings,¹¹ lead to an even better separation of individual compounds.

Another important improvement was the development of interfaces between HPLC and mass spectrometry (MS). HPLC-MS has evolved to a routine technique in many fields of modern chemistry,¹² and Gandara et al. describe the use of HPLC-thermo spray-MS for the identification of epoxy resin by-products in simulated food products.¹³ However, the use of modern ionization techniques, such as ion spray¹⁴ or atmospheric pressure chemical ionization (APCI)¹⁵ and their

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Time (min)	Acetonitrile	Water	THF
0.0	40%	60%	0%
30.0	85%	15%	0%
55.0	85%	0%	15%
65.0	85%	0%	15%

Table IGradient Used for the Separation ofDGEBA-Based Resin by HPLC

use for the characterization of epoxy resins have not yet been exploited in the literature.

EXPERIMENTAL

Chromatography

A Thermo Separation Products (TSP, San Jose, CA) HPLC system consisting of a quaternary pump (P 4000), an autosampler (AS 1000), a UV detector (UV 1000), and a PC 1000 data acquisition unit was used. Separation of epoxy resins was performed on an Ultremex $3C_{18}$ column (125 \times 4.6 mm i.d., 3- μ m particle size) from Phenomenex (Torrance, CA). The gradient profile used is shown in Table I.

Chromatography was performed at ambient temperature (ca. 21°C) at a flow rate of 1 mL/min. The injection volume was 10 μ L, and the equilibration time before injection 20 min. UV-detection was carried out at 230 nm. HPLC grade acetonitrile (Fluka, Buchs, Switzerland) and water purified with a Milli-Q reagent water system from Millipore-Waters (Milford, MA) was used. HPLC grade THF (Fluka, Buchs, Switzerland) was distilled over lithium aluminium hydride prior to use. If not stated otherwise, 0.3% (w/v) sample solutions were prepared in freshly distilled THF.

Atmospheric Pressure Chemical Ionization-Mass Spectrometry

A Perkin-Elmer Sciex API III+ triple quadrupole mass spectrometer with a heated nebulizer¹⁶ as an atmospheric pressure chemical ionization device (Perkin-Elmer Sciex, Toronto, Canada) was used. The HPLC system was connected via a steel capillary (0.1 mm i.d.) to the heated nebulizer, which was held at 490°C. Nitrogen (>99.999%) was used for both nebulization and auxiliary gas at a flow rate of 0.6 resp. 2.0 L/min to nebulize the complete HPLC flow.

For positive chemical ionization the corona discharge needle supplied a discharge current of $\sim 3 \ \mu A$ at 8000 V. The interface plate was held at 650 V, and the orifice at 35 V. The curtain gas flow (nitrogen > 99.999%) was maintained at 0.8 L/min. If not mentioned otherwise, the first quadrupole of the mass spectrometer was scanned with a step rate of 0.3 between 300 and 1200 mass-to-charge ratio (*m/z*), a dwell time of 0.61 ms, and a pause time of 0.02 ms, resulting in 0.48 scans per second.

Ion Spray with Postcolumn Buffer Addition¹⁷

An articulated ion spray probe (Perkin-Elmer Sciex, Toronto, Canada) was used for ion spray experiments. A Carlo Erba Phoenix 20 pump (Carlo Erba Instruments, Milano, Italy) supplied 100 μ L buffer solution per minute via a zero dead-volume Valco-T piece (Valco Instruments Co. Inc., Houston, TX) positioned after the UV-detector to the HPLC-flow. The complete flow was split via another Valco-T piece (split-ratio approx. 1 to 30). Approximately 32 μ L/min were fed into the ion spray source. Nebulization gas (nitrogen > 99.999%) pressure was held at 275 kPa (40 psi, resulting in a flow of 0.6 L/min). The ion spray needle was held at 5500 V. All other MS conditions were described above.

For the optimization of ionization conditions, the Phoenix 20 pump was used to supply the resin solution via a Valco-T piece into the HPLC-flow (see below). All other conditions were as mentioned above.

RESULTS AND DISCUSSION

Although pioneering work of epoxy resin separations was done on silica gel,¹⁸ recent work focuses mainly on reversed-phase (RP) material. Superior chromatographic resolution and markedly better reproducibility due to improved column technology are the main reasons for this development. One major concern in RP-HPLC of epoxy resins is

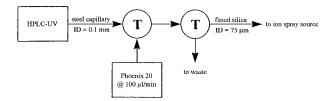


Figure 1 Schematic diagram of the postcolumn addition assembly for ion spray ionization.

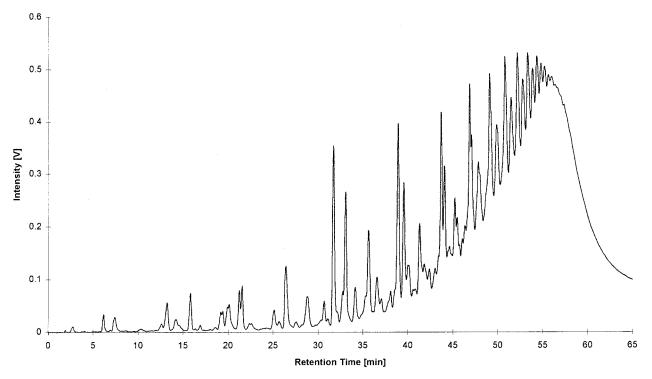


Figure 2 HPLC with UV-detection (230 nm) of Araldite GT 6609, a high molecular weight solid resin ($M_n = 2500$ g/mol, $M_w = 15,000$ g/mol).

the choice of the organic modifier.^{19,20} Although acetonitrile (ACN) shows higher selectivity for low molecular weight impurities, its solvation power is not high enough to elute higher molecular weight parts of solid epoxy resins. In contrast, tetrahydrofuran (THF) shows lower selectivity due to its high solvation power. For this reason, we chose a water-ACN gradient to separate the low molecular-weight part followed by a shallow gradient of THF up to a final amount of 15% to elute the higher molecular-weight parts of the resins (see Table I). This gradient allows the full exploitation of the capabilities of HPLC-MS, yielding good separation and sharp peaks in the low and higher molecular weight range (see Fig. 2).

Ionization Conditions

The choice of the ionization technique was still then to question. Only few publications compare electrospray ionization (ESI) and APCI on their suitability for different substance classes.^{21,22} A general assumption is that ESI is better suited for polar compounds, whereas less polar compounds may show better ionization behavior by APCI. To compare both ionization techniques with respect

to their suitability for diglycidylether of bisphenol A (DGEBA, see Fig. 2)-based epoxy resins, a defined amount of a low molecular weight solid epoxy resin has been introduced into the ion source under optimized conditions for each ionization technique. For APCI, a solution of 30 μ g/mL Araldite GT 6071 in THF was added at a flow-rate of 100 μ L/min to the HPLC-flow of 0.9 mL THF per minute via the postcolumn addition pump, resulting in the introduction of 3 μ g of Araldite GT 6071 per minute into the ion source. For comparison, the intensity of the ions of the protonated dimer (n = 1, 625 g/mol), trimer (n = 2, 909)g/mol), and tetramer (n = 3, 1193 g/mol) have been averaged over 50 scans. Previous investigations under the same conditions have shown that the ionization shows very limited temperature dependence between nebulizer temperatures of 480 to 510°C. A slight decrease in ion intensity is

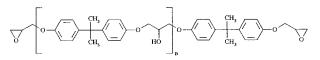


Figure 3 Structure of a diglycidylether of bisphenol A (DGEBA) epoxy resin.

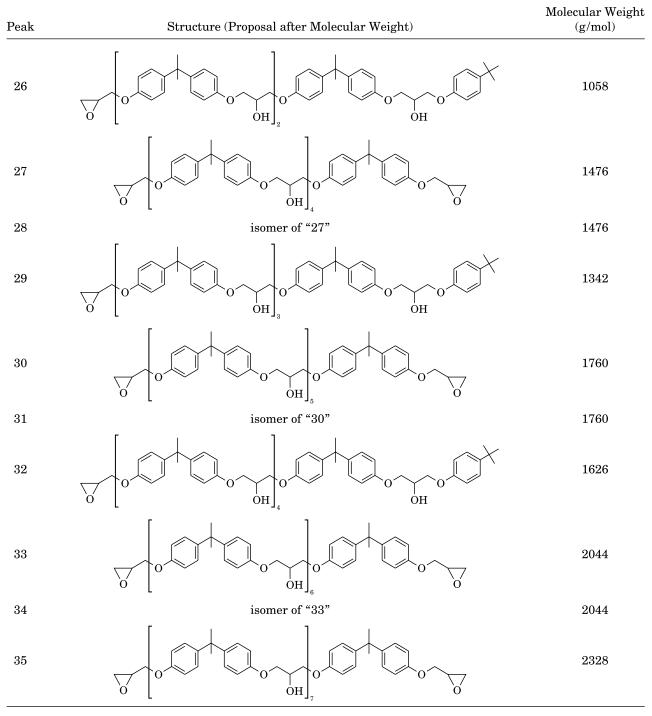
Peak	Structure (Proposal after Molecular Weight)	Molecular Weight (g/mol)
1	O OH OH	358
2		376
3		340
4	isomer of "3"	340
5		642
6		568
7		532
8		698
9		568
10		624
11		490

Table IIStructural Proposals for the Peaks Numbered in Figure 4

Peak	Structure (Proposal after Molecular Weight)	Molecular Weight (g/mol)
12		926
13		816
14	unknown	?
15		944
16	isomer of "18"	908
17	isomer of "18"	908
18		908
19		968
20	isomer of "18"	908
21		1100
22	unknown	1002
23		1136
24		1192
25	isomer of "24"	1192

Table II Continued

Table II Continued



Masses were confirmed by APCI and ESI. Structures 7 and 9 were confirmed by NMR.

visible at lower nebulization temperatures. For ESI, the same resin solution was added, but this time the HPLC flow consisted of 90% THF and 10% of an aqueous solution of 2.5% formic acid and 0.05M ammonium acetate, to simulate previ-

ously optimized postcolumn addition conditions. The whole flow of 1 mL/min is then split (split-ratio of approx. 1 to 32) to introduce approximately 32 μ L/min (corresponding to 96 ng resin per minute) into the ESI source. In this case, the

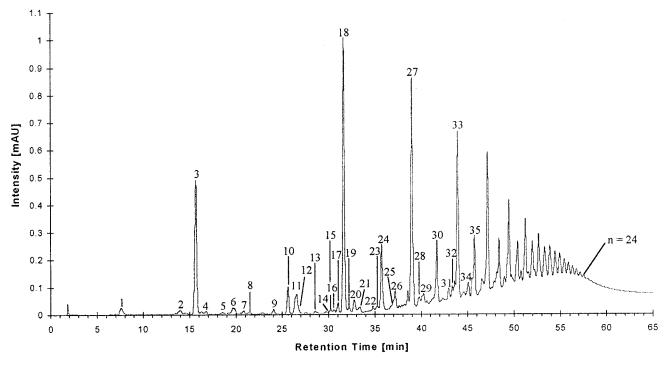


Figure 4 HPLC with UV-detection (230 nm) of *Araldite GT 6084*, a slightly modified solid epoxy resin ($M_n = 2200$ g/mol, $M_w = 5500$ g/mol).

intensity of the resulting ammonium adducts of the dimer (642 g/mol), trimer (926 g/mol) and tetramer (1210 g/mol) has been averaged over 50 scans. Although different quantities of epoxy resin are introduced into the ion sources, this comparison represents conditions normally encountered when epoxy resins are analyzed by HPLC. As advanced DGEBA molecules contain nsecondary hydroxyl groups and (2n + 2) ether functionalities that are generally easily to protonate, one would assume that ESI should yield better sensitivity over the whole mass range. The comparison shows that ESI gives better ion yield in the low molecular weight range, whereas higher homologues show almost the same intensity. Thus, the ion intensity for the dimer is eight times higher compared with APCI, whereas trimer and tetramer show the same intensity.

Table IIIGradient Used for the Separation ofAraldite PT 910 by HPLC

Time (min)	Methanol	Water
0.0	20%	80%
40.0	70%	30%
50.0	70%	30%

HPLC-MS investigations reveal even more pronounced differences at both ends of the mass range. The monomer shows much higher intensity by ESI, whereas higher homologues like the octamer (2328 g/mol) show better response by APCI. This fact is surprising, because APCI is considered as a gas-phase ionization technique, where volatilization of the analyte is necessary prior to ionization, whereas ESI is a liquid ionization technique and, thus, should preferably be advantageous for less volatile materials.

Most modifications and production related byproducts of DGEBA-based and many other epoxy resins may be detected in the mass range from 600 to 1500 g/mol. In addition to the excellent separation of components within this mass range

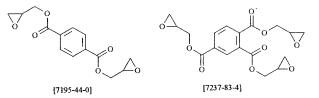


Figure 5 Structures of the main components of *Araldite PT 910*-terephthalic acid diglycidylester [7195-44-0] and trimellitic acid triglycidylester [7237-83-4].

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Peak	Structure (Proposal after Molecular Weight)	Molecular Weight (g/mol)
1		496
2	O O O O O O O O O O O H O O H O O H	296
3		378
4		278
5	O O O O O O O O O O O O O O O O O O O	314
6		470
7		700
8		370

Table IV St	ructural Proposa	als for the Pe	eaks Numbered	in Figure 6
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Peak	Structure (Proposal after Molecular Weight)	Molecular Weight (g/mol)
9		600
10	isomer of "9"	600
11	$ \begin{array}{c} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & $	1022
12		500
13		922
14		718
15		822

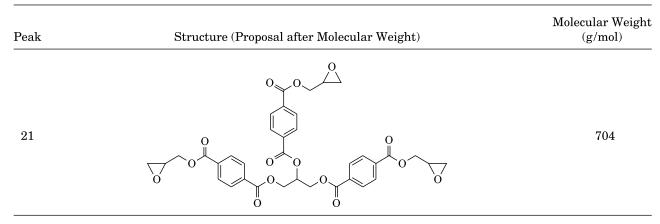
by HPLC, sensitivities of both ionization techniques are similar, allowing the use of either ionization technique or the use of both to get complementary information and mass confirmation.

Characterization of Epoxy Resins

The techniques mentioned above allow facile characterization of epoxy resins with respect to

Table IVContinued

Peak	Structure (Proposal after Molecular Weight)	Molecular Weight (g/mol)
16		1004
17	$ \bigcirc \bigcirc$	618
18		904
19		518
20		804



their individual minor constituents and by-products. For this reason detection and identification of even slight modifications, like chain terminators, process-inherent by-products, such as solvent and catalyst adducts, and products from glycidylization side-reactions, like α -glycols, chlorohydrins, and higher functional molecules,²³ is achieved in a fast and convenient way.

Figure 3 shows the HPLC chromatogram of Araldite GT 6084, a typical, slightly modified solid resin with UV detection. Excellent separation is achieved up to about n = 24. Typical for an advancement resin, homologues with an even "n" are more intense than their odd-numbered counterparts. The most interesting information, however, is contained in the smaller peaks eluting between the well-known oligomers (Table II shows the molecular weight and a corresponding structural proposal for each detected peak). Besides the existence of inherent by-products, like α -glycols (peaks 1, 5, and 12) and glycidylated α -glycols (peak 8), chlorohydrins (peaks 2 and 15) and bisphenol A-terminated homologues (peaks 6 and 23), several other peaks reveal more about the resin itself. Thus, peaks 11, 26, 29, and 32 show a molecular weight difference of 150 g/mol to their corresponding DGEBA homologues, which is derived from the molecular weight of *p*-*t*-butylphenol, a typical chain terminator. Peak 19 shows a molecular weight difference of 60 g/mol to the trimer (n = 2). Although no further homologues with this mass-difference have been detected, probably due to the small amounts present, it may be assumed that it is a (iso)propanol adduct-because isopropanol is a wellknown process solvent. Further peaks (7, 13, and 21) exhibiting a mass difference of 192 g/mol are

observed for several homologues. Preparative isolation and structural elucidation of the by-product with molecular weight 532 g/mol (monomer plus 192 g/mol) by NMR (HSQC-24 and HMBC-25 spectra) revealed a reaction product with 4-(4hydroxyphenyl)-4-methyl-2-pentanone [70205-18-4], a by-product of the bisphenol A synthesis,²⁶ yielding 4-[4-(2-hydroxy-3-{4-[1-methyl-1-(4oxiranylmethoxyphenyl)ethyl]phenoxy}-propoxy)phenyl]-4-methyl-2-pentanone (as reaction product with the monomer, peak 7). The presence of these by-products, as well as the presence of isomers of each homologue, allows assessment of the quality of the bisphenol A used for the manufacturing of a solid resin, as this phenol, as well as the o,p'-bisphenol A and the o,o'-bisphenol A is only present in lower quality bisphenol A.

As a further example for the outstanding performance of LC-MS for the characterization of epoxy resins, the corresponding analysis of a new weatherable crosslinker for polyester-based powder coatings—*Araldite PT 910* [173940-12-0]—is shown. *Araldite PT 910* (patented) is based on a mixture of glycidylesters of trimellitic and terephthalic acid (see structures) and, as a low molecular weight epoxy resin, is ideally suited for LC-MS investigations.

Due to its ester functionalities, *Araldite PT 910* has a much higher polarity than DGEBA-based epoxy resins, which makes an adaptation of HPLC conditions necessary (see Table III). The use of methanol instead of acetonitrile results in a better separation of the two main components due to the higher selectivity of methanol.

Ionization conditions are less critical than for DGEBA-based epoxy resins. ESI and APCI give excellent ion yield, which again yields comple-

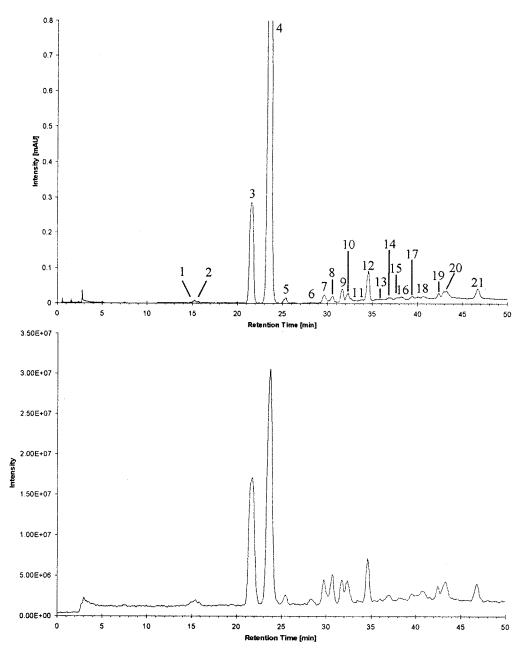


Figure 6 HPLC with UV (230 nm, above) and MS detection (ESI, below) of *Araldite PT 910*. Structural proposals for the numbered peaks are listed in Table IV.

mentary information and mass confirmation using both methods. Figure 5 shows the chromatogram with UV and MS detection of *Araldite PT 910*, and the corresponding structures are shown in Table IV.

In addition to typical glycidylization by-products, dimers, and mixed dimers (7, 9, 12) and trimers (11, 13, 15), esterification products of the secondary hydroxyl group with an aromatic acid can be detected (14 and 16 to 21). The presence of an ester of a secondary hydroxyl group has been confirmed by NMR (HSQC and HMBC) of a preparative HPLC fraction.

CONCLUSION

Both examples show the usefulness of HPLC-MS, especially the use of ESI and APCI, for the analysis of epoxy resins. Differences in the ionization behavior of epoxy resins using ESI and APCI are shown. The identification of process-inherent byproducts like chlorohydrins, α -glycols, and their glycidylated derivatives, as well as the identification of product-dependent by-products like solvent adducts, chain-terminated species, and reaction products due to impurities in the starting material allows an extensive characterization of solid epoxy resins with respect to the raw materials used for the resin, the production process, and modifications of the resin. Furthermore, it was impressively shown that in addition to bisphenol A-diglycidylether-based epoxy resins, the di- and triglycidyl esters obtained from terephthalic and trimellitic acid, respectively, also yielded a detailed structural characterization. In the latter case, ionization is facilitated compared with bisphenol A-DGE resins, due to the substantially higher polarity of the glycidyl esters.

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