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Branching in epoxy resins—analytical aspects

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Abstract

A method for the determination and quantification of higher-functional epoxides in liquid diglycidylether of bisphenol-A (DGEBA)-based epoxy resins, and for the determination and quantification of the amount of branching in solid DGEBA-based epoxy resins by ^{13}C n.m.r. is described. Model compounds were synthesised and their chemical shifts assigned. Examples for both types of resin are given, and the usefulness of the method is shown by the example of a production campaign of a solid resin. The increase of branching and the build up of molecular weight are compared and discussed. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Branching; N.m.r.

1. Introduction

The development of ever higher molecular weight diglycidylether of bisphenol-A (DGEBA)-based epoxy resins [25068-38-6] and the ongoing optimisation of process parameters for the production of such resins has led to a renewed interest in chain branching of such resins. The main disadvantage of branching is the increase of viscosity coincident with the rapid build up of molecular weight (Fig. 1).

As outlined in Ref. [1], chain branching in advanced DGEBA-based epoxy resins has at least two origins: the base-catalysed addition of epoxide to the aliphatic secondary hydroxyl group; and the presence of tri- or multifunctional impurities during the advancement reaction. Although some studies describe the theoretical background concerning the base-catalysed formation of branching points in DGEBA-based epoxy resins [2–4], only a few deal with the analytical aspects and quantitative determination of branching in such resins. The fact that the difference between the decrease in epoxy value and phenolic hydroxyls during synthesis of a resin corresponds to the amount of branching is exploited by Burchard et al. [2]. Mak and Rogers [5] describe a n.m.r. method for the quantification of branching points after derivatisation of free hydroxyl groups with trichloracetyl isocyanate with a detection limit of about 5% (branched glycerol groups *versus* hydroxyl-containing glycerol groups). Although application of this method gave some promising results [6], no detailed analytical work on the method has been reported. Markevich et al. [7] describe the use of ^{13}C n.m.r. and i.r. for the detection of branching in specially prepared 'branched' resins with the emphasis on the formation of such branched resins. Based on these results and the progress in analytical equipment, a new methodology for the identification and quantification of trifunctional species in liquid resins and branching in solid resins has been developed.

2. Experimental

2.1. Chromatography

A Thermo Separation Products (TSP, San Jose, CA, USA) h.p.l.c. system consisting of a quaternary pump (P 4000), autosampler (AS 1000), UV detector (UV 1000) and PC 1000 data acquisition unit was used. Separation of epoxy resins was performed on an Ultremex 3 C_{18} column (125 × 4.6 mm i.d., 3 μm particle size) from Phenomenex (Torrance, CA, USA). The gradient profile used is shown in Table 1.

Chromatography was performed at ambient temperature (*ca.* 21°C) at a flow rate of 1 ml/min. The injection volume was 10 μl and the equilibration time before injection 20 min. u.v. detection was carried out at 230 nm. h.p.l.c. grade acetonitrile (Fluka, Buchs, Switzerland) and water purified with a Milli-Q reagent water system from Millipore-Waters (Milford, MA, USA) was used. h.p.l.c.

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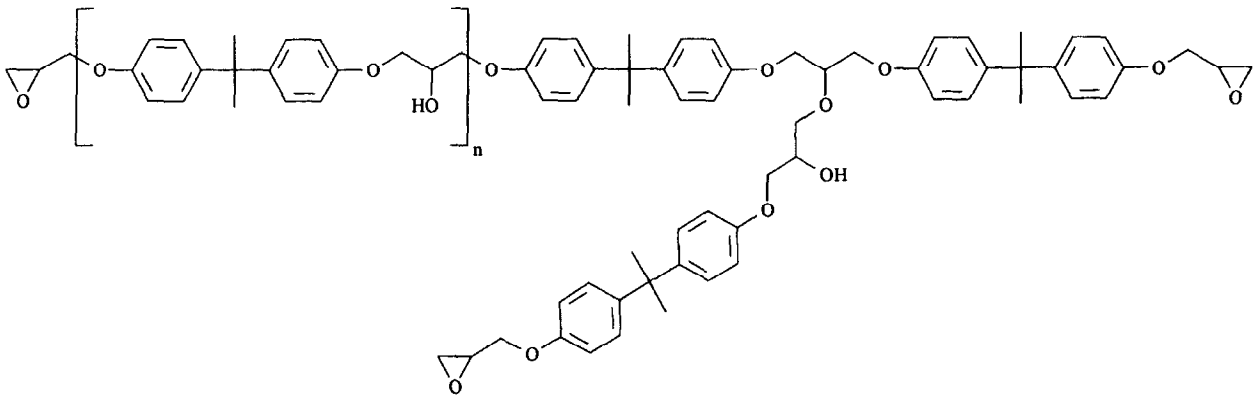


Fig. 1. Idealised structure of a branched resin.

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.

2.2. Ion spray with post-column buffer addition

A Perkin Elmer Sciex API III + triple quadrupole mass spectrometer with 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 μl buffer solution per min via a zero dead-volume Valco-T piece (Valco Instruments, Houston, TX, USA) positioned after the u.v. detector to the h.p.l.c. eluent. The combined eluent was split (split-ratio approx. 1 to 30) via another Valco-T piece using two fused silica capillaries (Composite Metal Services, The Chase, Hallow, UK) of different lengths. Approximately 32 μl/min was fed into the ion spray source (Fig. 2).

Nebulisation 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. 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. 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.

2.3. Nuclear magnetic resonance spectrometry

All carbon n.m.r. spectra were recorded on a Unity 500 spectrometer (Varian, Palo Alto, USA) equipped with a broad band switchable probe. For the determination of the amount of branching, 15 000–20 000 transitions were acquired at room temperature on saturated solutions of resins in $CDCl_3$ (5 mm n.m.r. tubes). Waltz-16 decoupling was used throughout the whole acquisition. Resonance assignments of standards were based on HSQC- [8] and HMBC- [9] spectra.

2.4. Preparation of standards

2.4.1. DGEBA-dimer

DGEBA-dimer: (1,3-bis[4-[1-methyl-1-[4-(oxiranyl-methoxy)phenyl]ethyl]phenoxy]-2-propanol, [47861-93-8]) has been isolated from Araldite GY 2600, a liquid resin with a content of approximately 18% dimer. For preparative chromatography, a 20% solution of Araldite GY 2600 in ethylacetate:cyclohexane = 3:7 was separated by m.p.l.c. using the gradient shown below on a 50 cm column with an inner diameter of 5 cm filled with silica gel (25–40 μm) (Table 2).

2.4.2. Glycidylated dimer (I)

2-{1,1-bis-{4-[1-methyl-1-(4-oxiranyl-methoxy-phenyl)-ethyl]-phenoxymethyl}-methoxymethyl}-oxirane has been prepared as follows: 14.63 g (20.16 mmol) DGEBA-dimer, 13.58 g (142.12 mmol) epichlorohydrin (technical grade) and 0.2257 g tetramethylammonium chloride were mixed in a 100 ml flask and heated under reduced pressure (approx. 85 mbar) to reflux (55°C). Sodium hydroxide (8.87 g, 22.18 mmol, as 10% solution in water) was slowly added after 20 min under reflux. After 2.5 h another 35 ml of epichlorohydrin was added. After 3 h and 20 min, the

Table 1
Gradient used for the separation of DGEBA-based epoxy resins by h.p.l.c.

Time (min)	Acetonitrile (%)	Water (%)	THF (%)
0	40	60	0
30	85	15	0
55	85	0	15
65	85	0	15

Table 2
Gradient used for the preparative separation of DGEBA-dimer by m.p.l.c.

Time (min)	Cyclohexane (%)	Ethylacetate + 1% methanol (%)
0	80	20
10	80	20
60	0	100

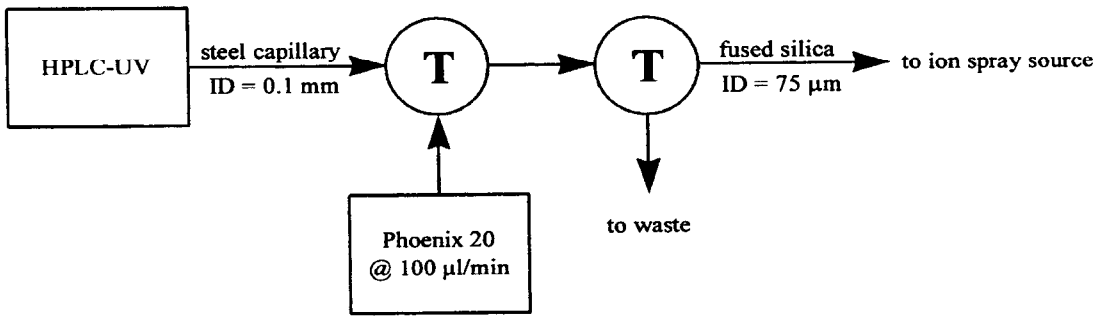
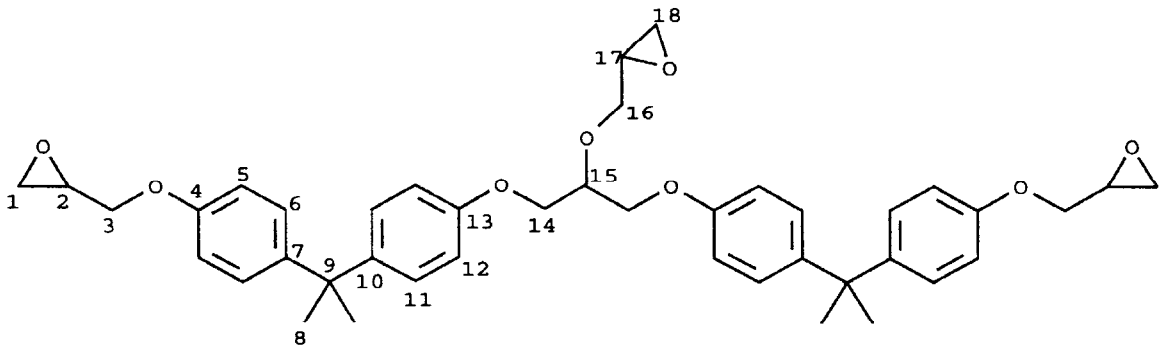


Fig. 2. Schematic diagram of the post-column-addition assembly for ion spray ionisation.

addition of sodium hydroxide was stopped. Sodium chloride precipitates out of the yellow solution. Another 10 ml of epichlorohydrin was added. After 5 h and 35 min, the reaction mixture was cooled (Fig. 3).

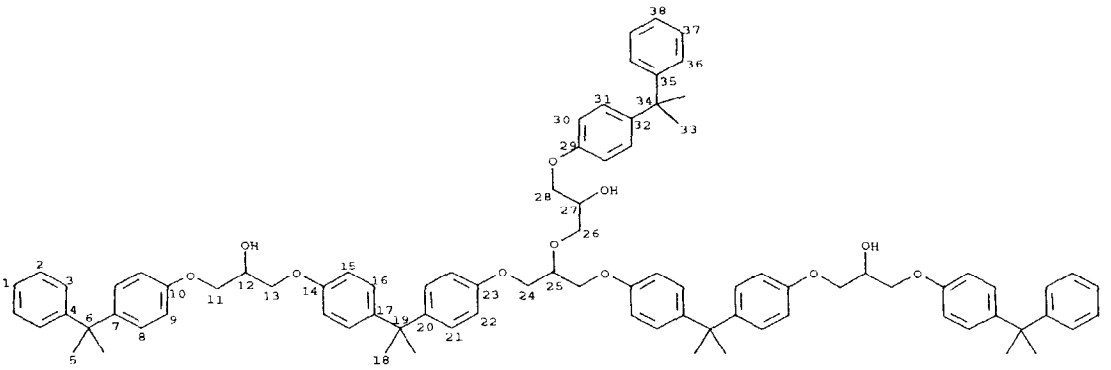
The reaction solution was diluted with 20 ml of epichlorohydrin and filtered. After extraction with 50 ml of a 10% solution of sodium dihydrogenphosphate in water (pH neutral, no emulsion), the organic phase was dried over magnesium sulfate and filtered. Epichlorohydrin was evaporated on a rotatory evaporator under reduced pressure at 80°C to yield 11.23 g of a yellowish oil with an epoxy value of 4.10 eq/kg.

Separation was carried out with a 10% solution of the oil in a 1:1 mixture of chloroform and cyclohexane using the gradient above on the silica gel column used previously.



	$\delta(^1H)$	$\delta(^{13}C)$
1	2.88 / 2.73	45.7
2	3.33	51.2
3	4.18 / 3.94	69.7
4	-	157.3
5	6.82	115.0
6	7.14	128.7
7	-	144.5
8	1.64	32.0
9	-	42.7
10	-	144.5
11	7.14	128.7
12	6.82	115.0
13	-	157.3
14	4.17 / 4.11	68.6
15	4.11	78.3
16	4.01 / 3.68	72.6
17	3.18	51.9
18	2.78 / 2.63	45.4

Fig. 3. Structure and n.m.r. shift assignment of the glycidylated dimer (I).



	δ(^{1}H)	δ(^{13}C)
1	7.20	125.6
2	7.29	128.0
3	7.27	126.7
4	-	150.8
5	1.69	30.9
6	-	42.4
7	-	143.5
8	7.18	127.9
9	6.86	114.0
10	-	156.3
11	4.15	68.7
12	4.39	68.8
13	4.15	68.7
14	-	156.3
15	6.86	114.0
16	7.18	127.8
17	-	143.7
18	1.66	31.1
19	-	41.8
20	-	143.7
21	7.18	127.8
22	6.86	114.0
23	-	156.5
24	4.16	67.8, 67.7
25	4.17	78.1
26	3.97/3.90	72.2
27	4.20	69.3
28	4.06	68.6
29	-	156.5
30	6.86	114.0
31	7.18	127.9
32	-	143.3
33	1.69	30.9
34	-	42.4
35	-	150.9
36	7.27	126.7
37	7.29	128.0
38	7.20	125.6

Fig. 4. Structure and n.m.r. shift assignment of the reaction product of (I) with 4-cumyl phenol.

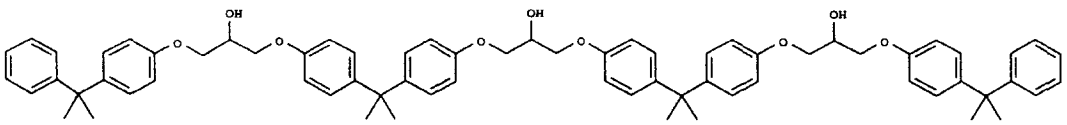


Fig. 5. Structure of the reaction product of DGEBA-dimer with 4-cumyl phenol.

2.4.3. Reaction of GDM with 4-cumylphenol

1-(1-{4-[1-(4-{2-Hydroxy-3-[4-(1-methyl-1-phenyl-ethyl)-phenoxy]-propoxy}-phenyl)-1-ethyl-ethyl]-phenoxymethyl}-2-{4-[1-(4-{2-hydroxy-3-[4-(1-methyl-1-phenyl-ethyl)-phenoxy]-propoxy}-phenyl)-1-methyl-ethyl]-phenoxy}-ethoxy)-3-[5-(1-methyl-1-phenyl-ethyl)-phenoxy]-propan-2-ol (II) has been prepared as follows: 2.9 g (4.26 mmol) GDM were mixed with 3.26 g (15.35 mmol) 4-(2-phenyl-2-propyl)phenol (4-cumylphenol, Aldrich, Buchs, Switzerland) in a 50 ml flask and heated to 120°C under nitrogen (magnetic stirring), resulting in a homogeneous solution. After the addition of 1.23 mg (approx. 200 ppm) 2-phenylimidazol (Aldrich) as catalyst, the mixture was heated to 170°C. After 90 min, another 0.5 g 4-cumylphenol and 1 mg 2-phenylimidazol was added. The reaction was followed by h.p.l.c. After 5 h, the reaction was stopped. A 10% solution (ethyl acetate:cyclohexane = 3:7) of the reaction mixture was purified via m.p.l.c. on a silica gel column with the gradient shown above to yield 3.7 g (2.81 mmol, approx. 65% of theory) of the desired white and waxy product with a purity of approximately 98% (by h.p.l.c.-u.v., 230 nm) (Fig. 4).

2.4.4. Reaction of DGEBA-dimer with 4-cumylphenol

1,3-bis-{4-[1-(4-{2-Hydroxy-3-[4-(1-methyl-1-phenyl-ethyl)-phenoxy]-propoxy}-phenyl)-1-methyl-ethyl]-phenoxy}-2-propanol (III) has been prepared as follows: the sample was prepared similar to the procedure described above. After 5 h, h.p.l.c. shows almost complete conversion and the reaction was stopped (Fig. 5).

Due to the fact that it was only prepared to facilitate n.m.r. interpretation of (II), no further purification of the white and waxy product was performed.

3. Results and discussion

Branching in solid resins may be introduced by the presence of tri- or higher functional by-products in the raw materials during the advancement reaction, and by the reaction of an epoxy group with a secondary hydroxyl group. Two types of trifunctional impurities in the raw materials have to be distinguished: that originating from the trifunctional phenol (BPX, 2,4-bis[1-(4-hydroxyphenyl)-methyl-ethyl]-1-phenol, [2300-15-4]) in the raw material (structure 18 in Table 3); and the products originating from the glycidylation of the aliphatic secondary hydroxyl group of the DGEBA-dimer and its higher homologues, with the glycidylated dimer (GDM, see Fig. 3) as the most important product. h.p.l.c. allows the separation and detection of these by-products. Fig. 6 shows the h.p.l.c. with u.v. detection of a typical commercially available liquid resin.

The molecular weight of each eluting substance was assigned using h.p.l.c.-m.s. (for details see Ref. [10]). Structural proposals for the numbered peaks are shown in Table 3.

Using high purity bisphenol-A (e.g. polycarbonate quality) for the production of liquid resins, eliminates the glycidylated BPX as trifunctional impurity, thus making those originating from the glycidylation of the secondary hydroxyl group, as process inherent by-products, the only higher functional impurities. In order to make a quantification of the amount of trifunctional by-products possible,

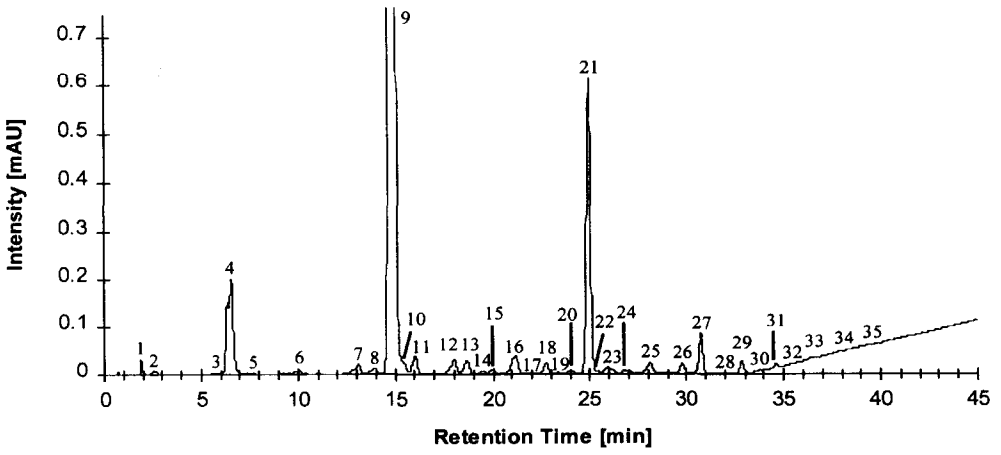
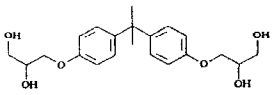
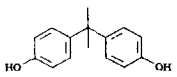
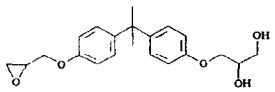
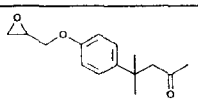
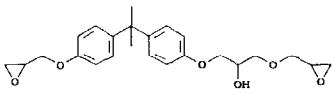
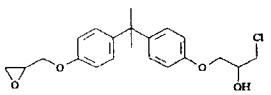
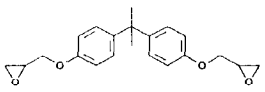
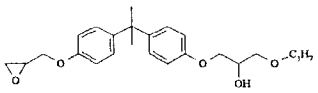
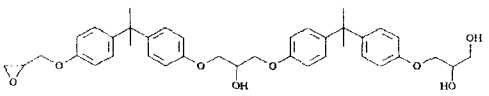
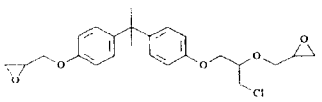
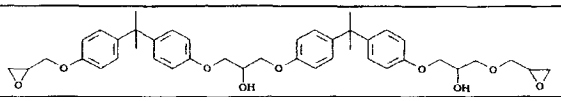
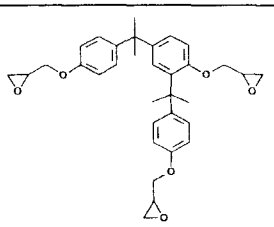
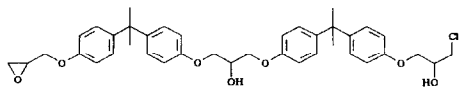
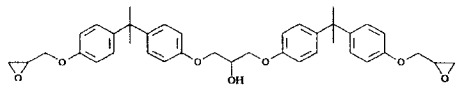
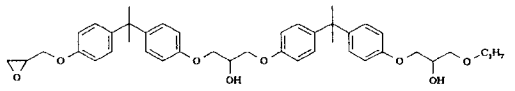
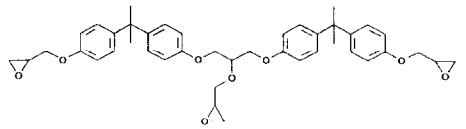
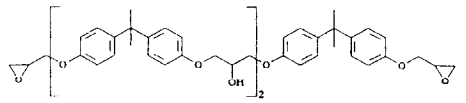
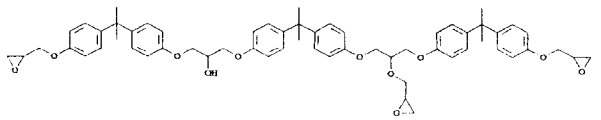
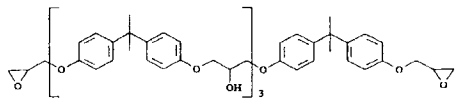
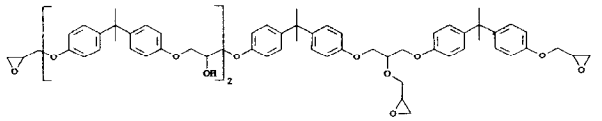
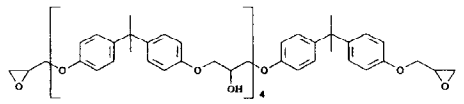
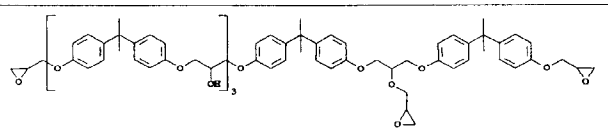


Fig. 6. h.p.l.c. with u.v. detection (230 nm) of a liquid resin (0.6% in THF). Both axes have been enlarged for more detail. Structural proposals for the numbered peaks are listed in Table 3.

Table 3
Structural proposals for the peaks numbered in Figure 6. Masses were confirmed by APCI and ESI. Structures 3, 4, 7, 9, 16 and 25 were confirmed by co-injection of the corresponding pure substances

peak	molecular weight [g/mol]	structural proposal	retention time [min]
1		solvent impurities	1.9
2	376		2.6
3	228		5.7
4	358		6.6
5	248		7.6
6	414		10.1
7	376		12.9
8	396	confirmed by ESI	13.7
9	340		14.5
10	400		15.1
11	340	isomer of "9"	15.7
12	642		17.6
13	432		18.2
14	380	confirmed by ESI	19.1
15	380	confirmed by ESI	19.5
16	698		20.7
17	698	isomer of "16"	21.6
18	530		22.3

19	660		22.9
20	624		23.7
21	624	isomer of "20"	24.5
22	684		24.9
23	624	isomer of "20"	25.5
24	716	α-glycol of peak 17 ?	26.3
25	680		27.7
26	814	confirmed by ESI	29.4
27	908		30.4
28	1000	chlorohydrin of peak 29 ?	31.4
29	964		32.4
30	1322	-	33.4
31	1098	-	33.8
32	1192		34.2
33	1248		36.0
34	1476		37.4
35	1532		38.7

the glycidylated dimer (GDM, I) was prepared and purified as analytical standard. Although this makes an exact quantification by h.p.l.c. of the amount of GDM in liquid resins possible, it does not take into account the amount of trifunctional epoxide originating from the higher homologues. Furthermore, a more interesting question is the molar ratio of trifunctional epoxides compared to linear epoxides, and not the total amount of GDM in the resin. For this

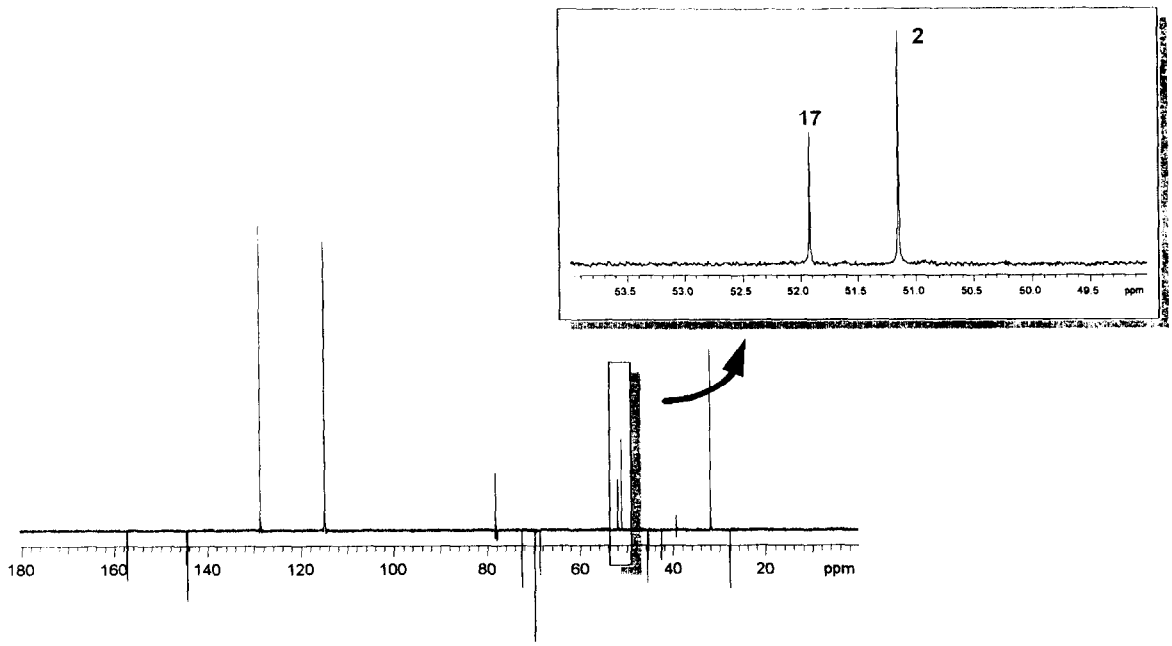


Fig. 7. ^{13}C n.m.r. (APT) of (I) in $CDCl_3$. The numbers correspond to the carbon atoms shown in the structure above. Carbon atoms 2 (50.1 ppm) and 17 (50.9 ppm) correspond to the linear and 'branched' epoxide group.

reason, a quantitative ^{13}C n.m.r. method has been developed that allows the determination of the molar ratio between linear and branched epoxide groups.

α-C atoms of the two different epoxide groups can be distinguished by ^{13}C n.m.r. (see Fig. 7). Due to the fact that the two carbon atoms have a similar chemical surrounding, it can be assumed that they show a similar relaxation behaviour and nuclear Overhauser enhancement. Thus, it is possible to use these two signals for the quantification of the amount of trifunctional epoxide groups without the use of the time-consuming inverse-gated pulse sequence. To verify this and to establish a quantitative ^{13}C n.m.r. method, a series of four standards of GDM in pure DGEBA was prepared. The results are shown in Fig. 8.

The results show that, especially in the interesting lower percentage range, excellent linearity and good accuracy is achieved with the standard ^{13}C n.m.r. pulse sequence. Dilution of the lowest standard shows that the quantification limit for this method with standard n.m.r. equipment (5 mm n.m.r. tubes) and an acquisition time of approximately 16 h (corresponding to 15 000–20 000 transitions) lies at about 0.1 mol% of trifunctional epoxide, which covers the interesting range for most liquid resins. Fig. 9 shows the region of interest of the ^{13}C n.m.r. spectrum of a typical commercial liquid resin with approximately 0.3% (mol/mol) of trifunctional epoxides.

Although this value seems rather small, the amount of trifunctionals is very important when liquid resins are advanced to solid resins, as they introduce branching, and thereby alter the final properties of the solid resin. Thus, the comparison of different liquid resins with respect to these difficult to reduce or eliminate trifunctionals is very

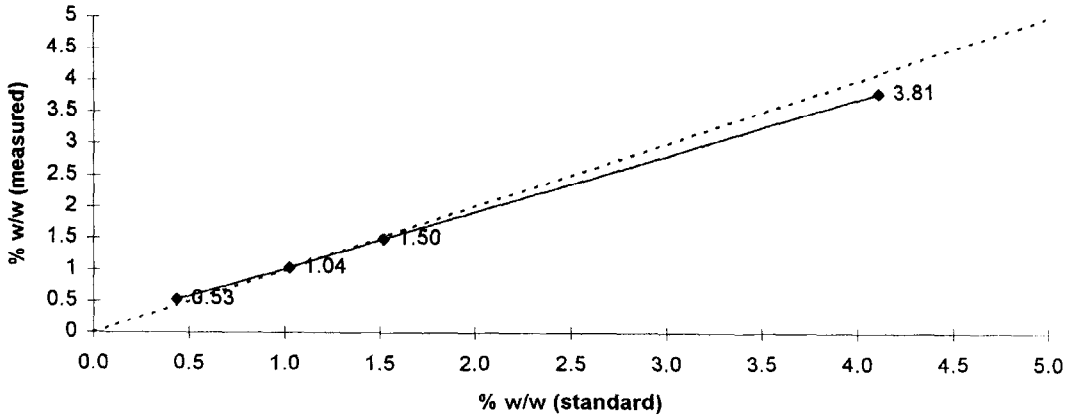


Fig. 8. Linearity of the determination of the ratio of trifunctional epoxide to linear epoxide, based on the integrals of carbon atoms 2 and 17. The dotted line shows the nominal values. Labels show the amount measured.

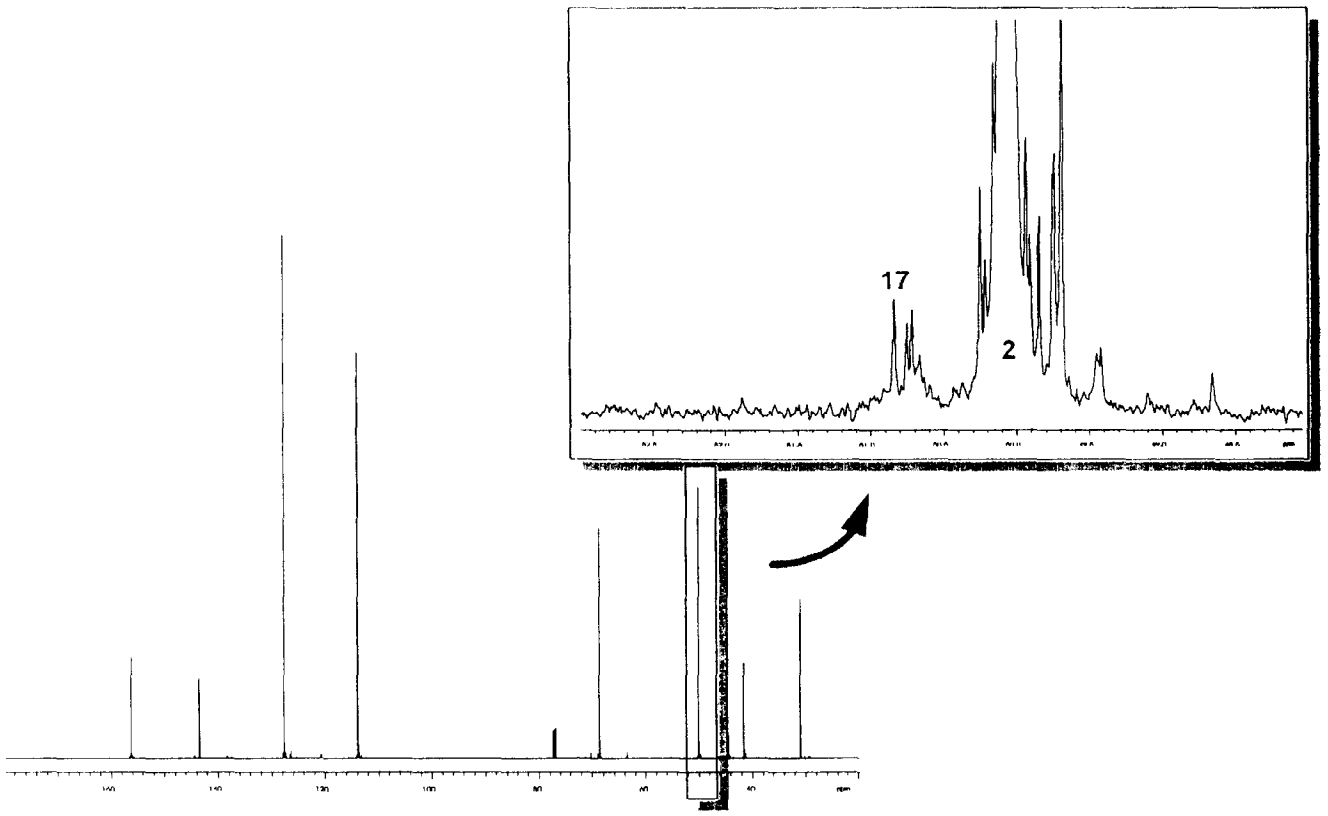


Fig. 9. ^{13}C n.m.r. spectrum of a commercially available liquid DGEBA-based epoxy resin (DER 331). The region around 50 ppm has been enhanced to show the signals of the linear (2) and trifunctional epoxide (17). Integration of these signals gives a value of approximately 0.3% (molar) of trifunctional epoxide groups.

important. It allows the selection of resins for advancement with low amounts of trifunctional materials or the optimisation of production processes to achieve this.

The amount of branching in solid resins is difficult to assess, as the high molecular weight and homologous distribution of branched molecules does not allow a chromatographic separation and determination. Direct spectroscopic measurements are the only way to identify and quantify branching points in solid resins. As for liquid resins, ^{13}C n.m.r. is the method of choice for the quantification of branched glycerol groups. As a model compound and analytical standard for branched DGEBA-based epoxy resins, compound (II) has been prepared. This compound has a branched glycerol group with a very similar chemical environment to a glycerol group in a branched epoxy resin, thus allowing it to be used as an n.m.r. standard. Fig. 10 shows the ^{13}C n.m.r. spectrum of (II).

The branched glycerol group may be distinguished at three different carbon atoms from the unbranched glycerol group (C-24, 25 and 26 *versus* 11, 12 and 13). In order to verify the linearity and accuracy of the quantification of the amount of branching, several standards of (II) in pure DGEBA-dimer were prepared. Measured values were converted into weight percent. The results (see Fig. 11) show relatively good linearity over the whole range and good accuracy in the lower percentage range.

The quantification limit using standard equipment lies at about 3% (w/w)—corresponding to a molar quantification limit of approximately 0.4%. The possibility of using any of the three signals for quantification allows compensation for interferences or overlapping signals, thus improving the accuracy of the result, which has been found to be of the order of $\pm 0.1\%$ (absolute). However, it has to be considered that carbon atoms at branching points may show different relaxation behaviour due to their different mobility. For the comparison of different solid resins, this effect has only minor importance. Fig. 12 shows the ^{13}C n.m.r. of a typical commercially available solid resin($M_n = 2000$ g/mol, $M_w = 6100$ g/mol). The integrals of all three peaks give an amount of branching of 2.0%, corresponding to approximately one branching point every 50 glycerol groups.

A survey of several different solid resins with varying molecular weights has shown that the amount of branching can not be correlated with the molecular weight of the resin. Some solid resins with lower molecular weight distribution (similar to the example shown above) show an amount of branching of up to 2.4%, whereas some high molecular weight solid resins ($M_n = 3600$ g/mol, $M_w = 22000$ g/mol)

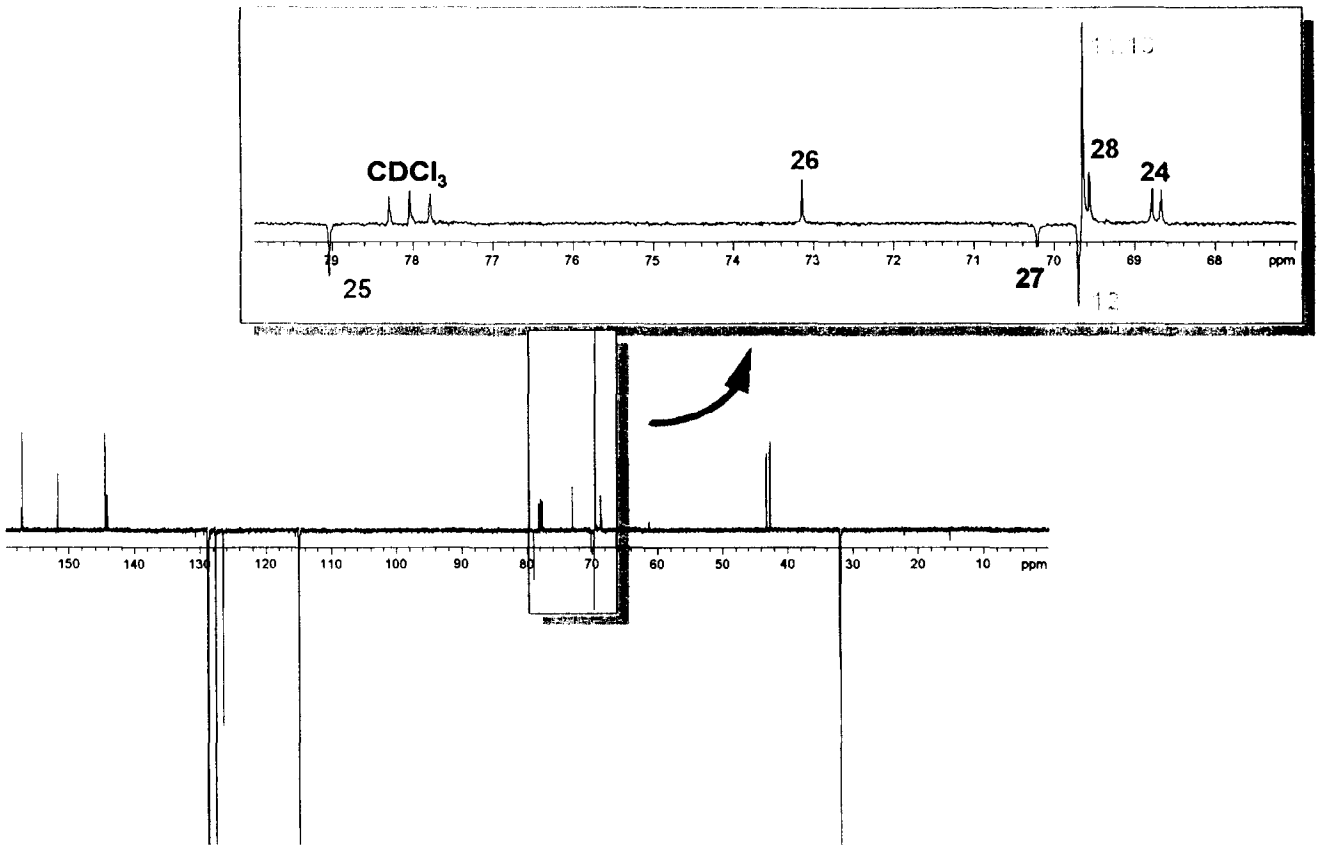


Fig. 10. ^{13}C n.m.r. (APT) of (II). The branching-relevant region has been enlarged.

show an amount of about 0.5%. Obviously, process parameters, e.g. reaction time and type of catalyst, have more influence on the amount of branching than the build up of molecular weight and the amount of trifunctionals in the liquid resin.

In order to visualise the relationship between the build up of molecular weight and the increase in the amount of branching, both values were closely followed during production of a standard solid resin. The graph below (Fig. 13) shows that during the production, most of the build up of

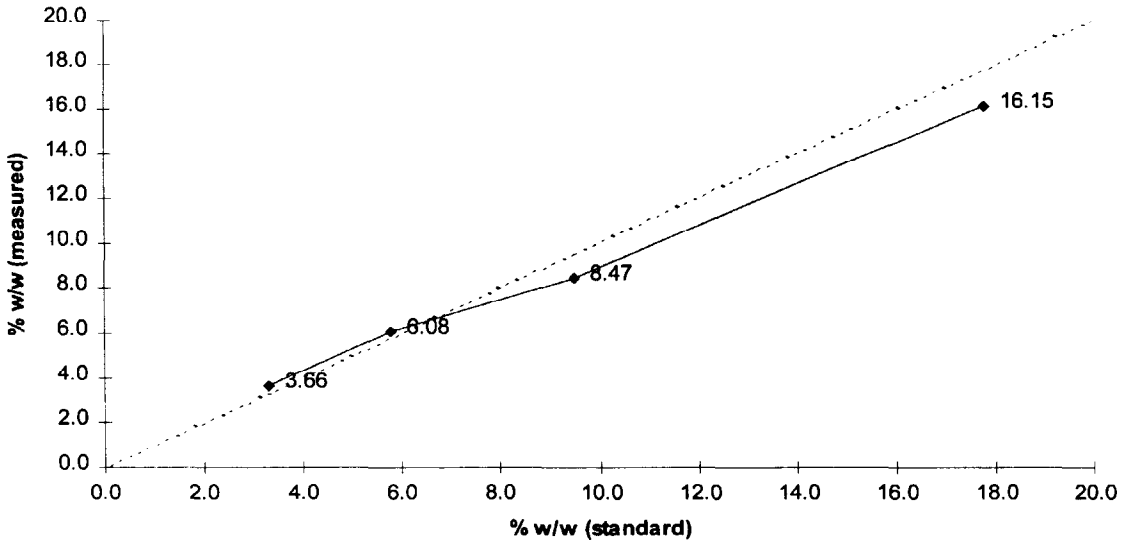


Fig. 11. Linearity of the determination of the amount of branched glycerol groups to unbranched glycerol groups, based on the average of the integrals of carbon atoms 24, 25, 26 and 28. The dotted line shows the nominal values. Labels show the amount measured.

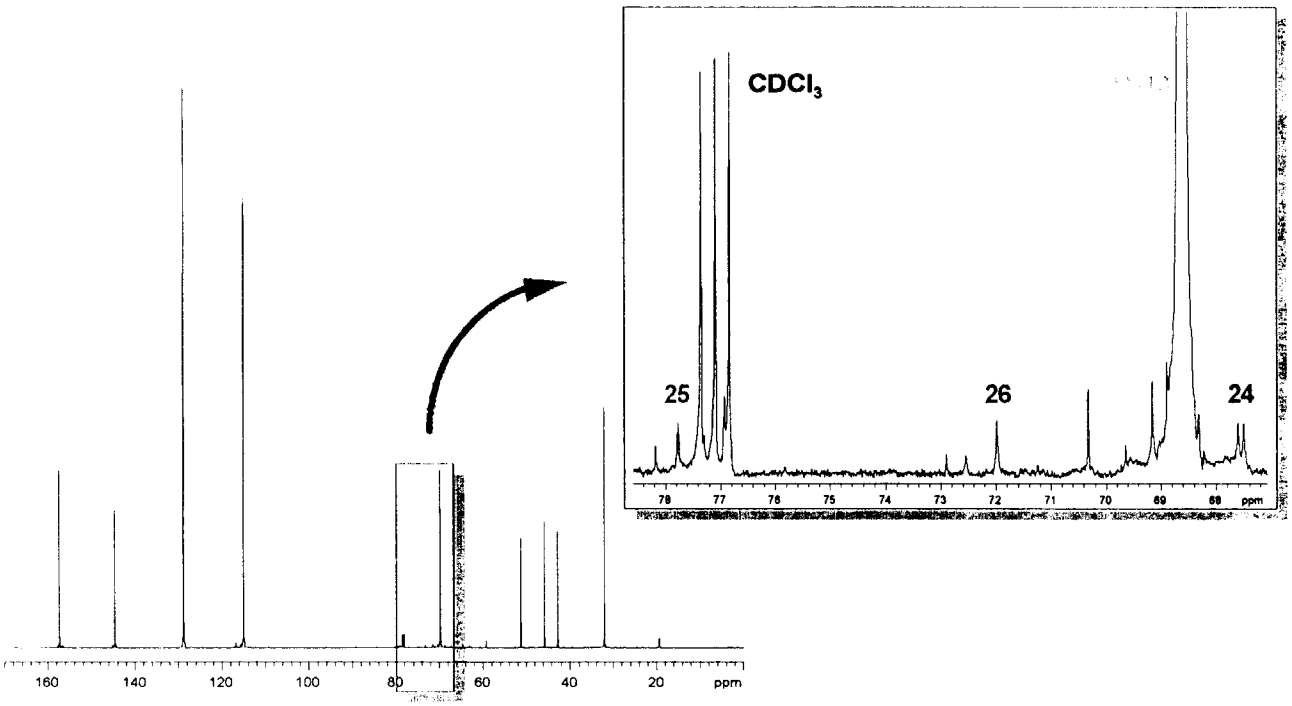


Fig. 12. ^{13}C n.m.r. spectrum of a commercially available solid DGEBA-based epoxy resin (Araldite GT 7004). The region around 70 ppm has been enhanced to show the signals of the linear (11, 12, 13) and branched glycerol groups (24, 25, 26). Integration of these signals gives a value of approximately 2.0% (molar) of branched glycerol groups.

molecular weight occurs in the first 3–4 h and rises slowly during the rest of the campaign, whereas the amount of branching rises slowly throughout the whole reaction. It seems that the branching reaction is neither dependent on the relative concentration of phenolic hydroxyl groups, as it already starts before the build up of molecular weight, nor on the concentration of secondary hydroxyl groups, as they are in great excess at the end of the reaction.

The impact of branching on the molecular weight distribution can be seen on the size exclusion chromatogram of a

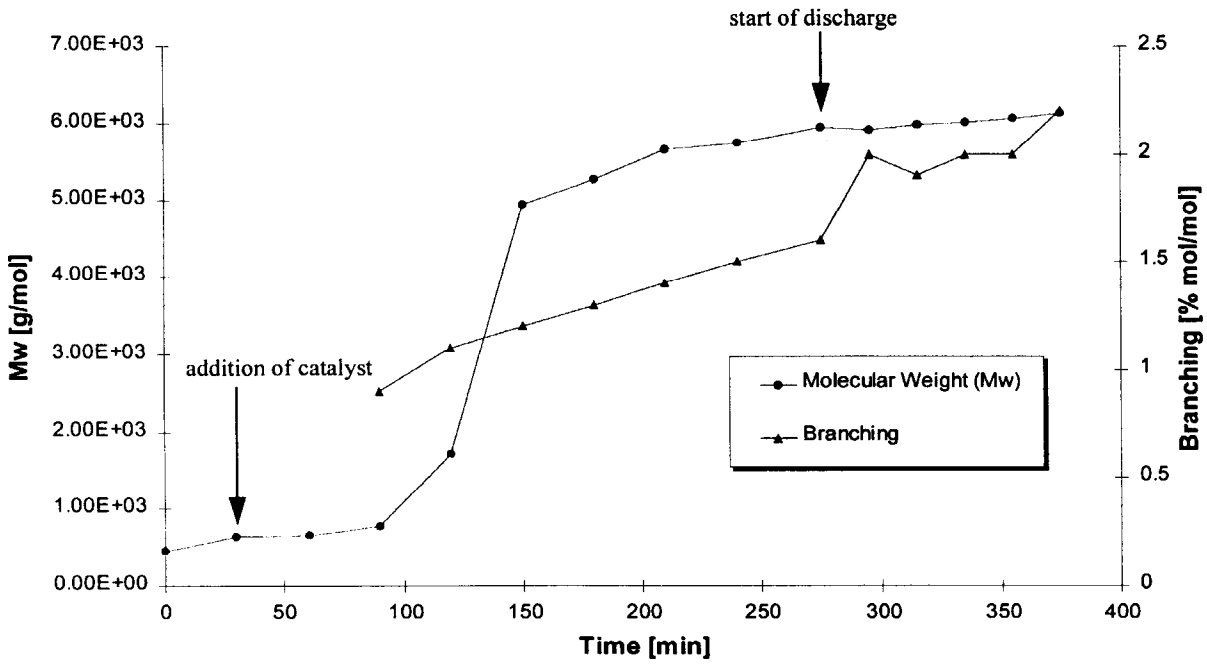


Fig. 13. Increase of molecular weight (M_w, left axis) and the amount of branching (right axis) during the production of a typical DGEBA-based solid resin. Variations from the start of discharge onwards may be due to a different sampling technique.

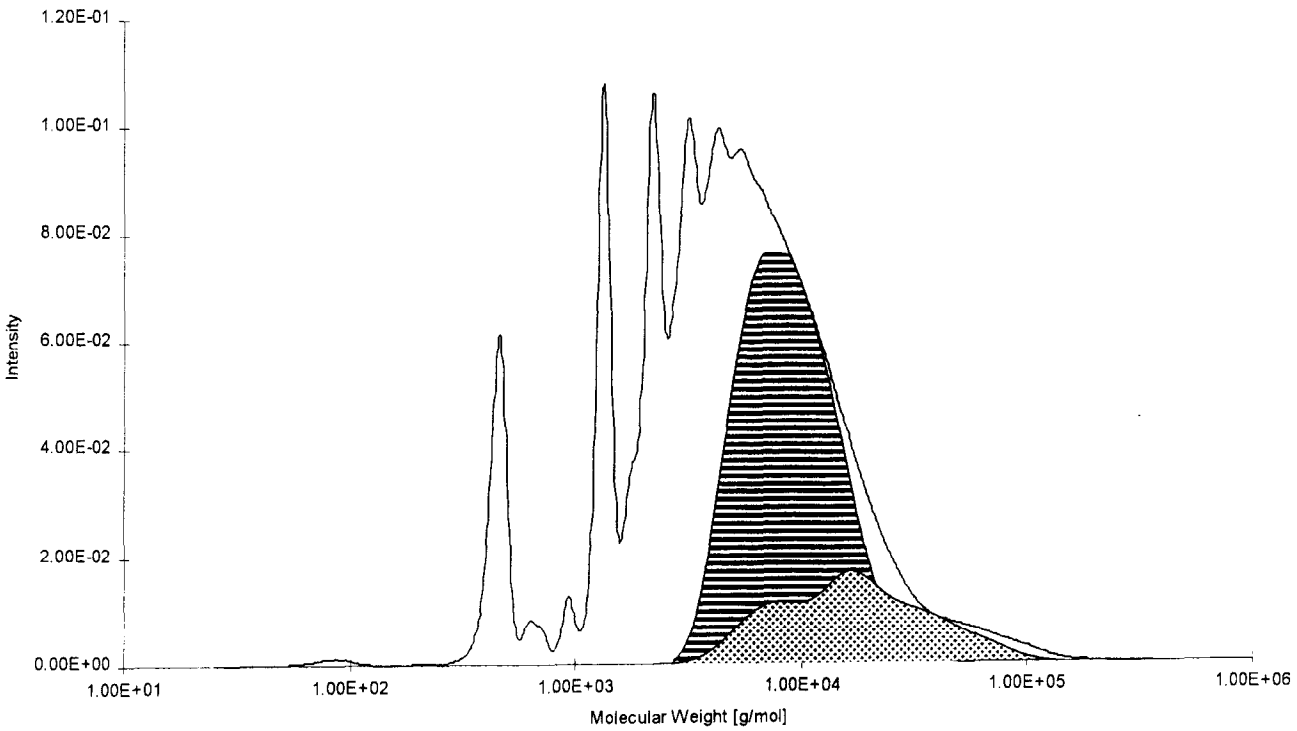


Fig. 14. Size exclusion chromatogram of a typical solid resin with an average amount of branching of 2.0%. The isolated fractions are marked by filled curves. See text for details.

solid resin. Fig. 14 shows the molecular weight distribution of a typical solid resin with relatively high M_w, caused mainly by the flat shoulder at high molecular weight.

In order to prove that this high molecular weight shoulder is in fact caused by branching, two fractions of the solid resin were isolated by preparative SEC and analysed by n.m.r. Fraction 1 shows an amount of branching of about 3.3%, the higher molecular weight fraction 2 shows an amount of 5.0%, corresponding to one branching point every 20 glycerol groups. Thus, at an approximate molecular weight of 15 000 g/mol (between fraction 1 and 2), on average every molecule has at least two branching points, leading to the excessive build up of molecular weight observed by SEC.

4. Conclusion

The methods described above allow a straightforward quantitative determination of the amount of three- or higher functional epoxides in liquid resins and the amount of branching in advanced (or solid) resins. The accuracy of the methods is confirmed by the use of especially prepared standards. The possibility to quantify the amount of branching in solid DGEBA-based epoxide resins allows the optimisation of production processes with respect to branching and allows the selectivity of advancement catalysts to be assessed. Further developments in the sensitivity of n.m.r. equipment will ultimately lead to lower detection limits, for both higher functional epoxides in liquid resins and branching points in solid resins, employing the above mentioned methods. Higher amounts of branching can be detected easily by the characteristic shoulder in the size exclusion chromatogram. This allows a quick qualitative comparison of solid resins with respect to branching via their molecular weight distribution.

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