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SEPARATION AND CHARACTERIZATION OF BY-PRODUCT OLIGOMERS IN EPOXY RESINS BY REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Three series of monoepoxide by-product oligomers in diglycidyl ethers of bisphenol A type epoxy resins were separated by reversed-phase gradient elution high-performance liquid chromatography. The by-product oligomers studied have a functional group other than a 2,3-epoxypropyloxy group as an endgroup: they have a 2,3-dihydroxypropyloxy, a 2-hydroxy-3-methoxypropyloxy or a 2-hydroxy-3-*p-tert.*-butylphenoxypropyloxy endgroup. Three oligomers of each series of by-products were isolated and characterized by infrared, mass and carbon-13 nuclear magnetic resonance spectrometry.

INTRODUCTION

Epoxy resins are widely used as thermosetting agents for various purposes, because of the excellent mechanical, electrical and chemical properties of cured epoxy resins[1,2]. These resins are characterized by the oxirane ring (epoxy group) which reacts with curing agents or catalytically homopolymerizes to form a cross-linked polymeric structure. The most widely used epoxy resins are the reaction products of epichlorohydrin with 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, BPA), the reaction giving the diglycidyl ether of BPA (I, $n = 0$) and high-molecular-weight species (DGEBA type epoxy resins):


$$(n = 0,1,2,\cdots)$$

$$(I)$$
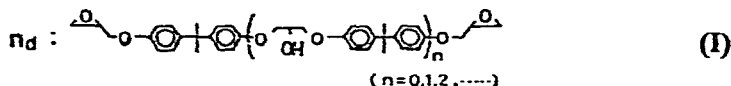
As the ratio of BPA and epichlorohydrin is varied, epoxy resins of different average molecular weights are produced.

Epoxy resins contain not only linear diepoxide oligomers (n_ds) but also small amounts of various by-product oligomers which have functional groups other than epoxide groups either as endgroups or as side chains pendant to the main

polymeric backbone[3,4]. Monoepoxide oligomers having a 2,3-dihydroxypropyloxy endgroup are well known[5-7].

$$n_h : \text{(structure II)} \qquad \text{(II)}$$
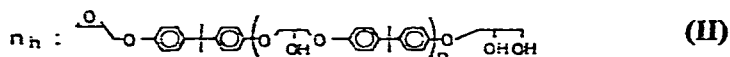
Furthermore, some manufacturing processes of epoxy resins are designed to involve the formation of by-product oligomers in addition to the main reaction of epichlorohydrin with BPA, in order to improve the properties of epoxy resins. For example, BPA is treated with epichlorohydrin in the presence of a small amount of *p-tert.*-butylphenol[8], giving a series of by-product oligomers:

$$n_b : \text{(structure III)} \qquad \text{(III)}$$
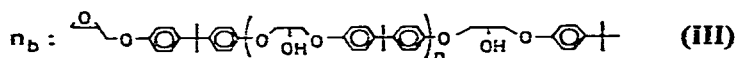
In an other process, methanol is used as a solvent[9], giving a different series of by-product oligomers:

$$n_f : \text{(structure IV)} \qquad \text{(IV)}$$
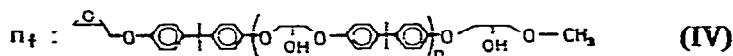
Besides these by-product oligomers, other kinds of by-products are known to be present in epoxy resins, such as a cyclic dimer[10] and several kinds of chlorine-containing by-products[5,11].

In general, by-product oligomers have a noticeable influence upon the properties of cured epoxy resins as well as on the curing reaction of epoxy resins[11,12]. Consequently, it is of practical importance to separate and characterize by-product oligomers. Chromatographic analyses using gel permeation chromatography (GPC) and high-performance liquid chromatography (HPLC) were found to be successful methods for epoxy resins. While both GPC[5-7,13-15] and HPLC methods[12,16,17] give unique and different information, the HPLC methods using gradient elution seem to give much more detailed information than the GPC methods[17]. The optimal gradient profiles were established experimentally and the good reproducibility of the quantitative analysis was demonstrated[17].

Several articles report the separation and identification of by-products or impurities in DGEBA type epoxy resins. The presence of intermediate products of the polycondensation reaction which have a 2,3-dihydroxypropyloxy (n_h) and/or 2-hydroxy-3-chloropropyloxy endgroup was shown using GPC[5-7]. Dark *et al.*[12] reported the presence of small amounts of 2,4-bis(α,α-dimethyl-*p*-hydroxybenzyl)-phenol and bis[2,2-bis(4-hydroxyphenol)]propane (a cyclic dimer), using HPLC. However, these two by-products were not isolated.

In this report we describe the results of the separation and physico-chemical characterization of the three series of the by-product oligomers n_h, n_f and n_b in DGEBA type epoxy resins by reversed-phase gradient elution HPLC.

EXPERIMENTAL

Apparatus

A Shimadzu (Kyoto, Japan)-Du Pont (Wilmington, DE, U.S.A.) 830 liquid chromatograph equipped with a Shimadzu SPD-1 variable-wavelength detector and a Shimadzu FRC-1 flow-rate controller was used at 50 °C. Columns of μBondapak C_{18} (30 cm × 3.9 mm) (Waters Assoc., Milford, MA, .US.A.) and Nucleosil 7C_{18} (25 cm × 10 mm) (Macherey, Nagel & Co., Düren, G.F.R.). The former was used as an analytical column and the latter as a preparative one. Water–acetonitrile was used as a mobile phase at a flow-rate of 1.5 ml/min. A Shimadzu SIL-1A six-port valve was used to inject samples dissolved in acetonitrile–tetrahydrofuran (9:1) onto the analytical column or in acetonitrile onto the preparative column. The column effluent was monitored at 280 nm.

A preparative GPC instrument[18] was used for rough fractionation of epoxy resins prior to the precise fractionation of certain oligomers.

Infrared spectra were taken on a Shimadzu Model 27-G infrared spectrometer and mass spectra on a Model O1SG-2 mass spectrometer (Japan Electron Optics Laboratory, Tokyo, Japan). A FX-90Q Fourier transform nuclear magnetic resonance (NMR) spectrometer (Japan Electron Optics) was used at 22.5 MHz to measure ^{13}C NMR spectra of samples dissolved in chloroform.

Reagents

Distilled water, liquid chromatography grade acetonitrile and spectroquality tetrahydrofuran were used as solvents. Analytical grade methanol, p-tert.-butylphenol, chlorobenzene and potassium hydroxide were used without further purification. All reagents were purchased from Wako (Osaka, Japan).

Epoxy resin

Two commercial epoxy resins, Epon 1001 with an epoxide equivalent of 2.1 equiv./kg and ESA 001 with an epoxide equivalent of 1.9 equiv./kg, were obtained from Shell Chem. (Houston, TX, U.S.A.) and Sumitomo Chem. (Tokyo, Japan), respectively. Epon 1001 is produced according to the taffy process* and ESA 001 is produced according to the fusion or the advancement process**[5].

In order to prepare epoxy resins containing by-product oligomers n_t or n_b, ESA 001 was allowed to react only partially either with p-tert.-butylphenol or with methanol under alkaline conditions[19]: (i) a solution of 5 g ESA 001, 4.5 g p-tert.-butylphenol and 0.28 g potassium hydroxide in 80 ml chlorobenzene was heated at 70 °C for 6 h; and (ii) a solution of 5 g ESA 001, 10 ml methanol and 0.56 g potassium hydroxide in 50 ml chlorobenzene was heated at 70 °C for 1 h. Each solution was then washed with water until the solution became neutral. The solutions were evaporated to dryness under reduced pressure.

RESULTS AND DISCUSSION

Liquid chromatography

Figs. 1 and 2 show the HPLC chromatograms of Epon 1001 and ESA 001. The convex gradient profile used is illustrated in Fig. 1. These figures indicate the

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* Taffy process: base-catalysed addition of variable amounts of epichlorohydrin to BPA.
** Fusion process: polyaddition reaction of diglycidyl ether of BPA to BPA.
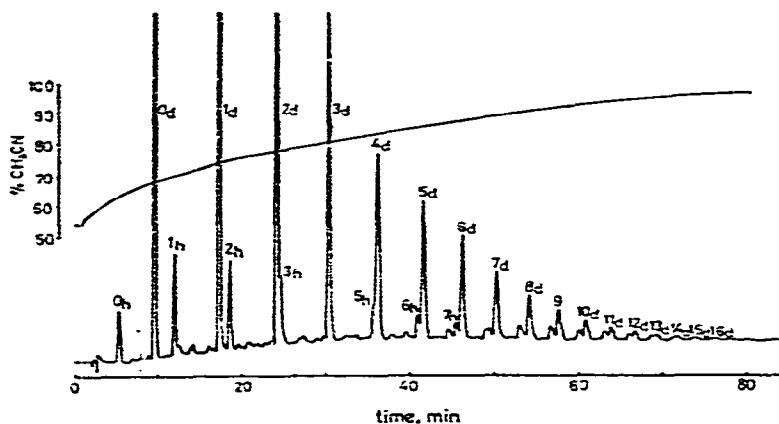
Fig. 1. HPLC chromatogram of Epon 1001. Conditions: column, μBondapak C_{18} (30 cm × 3.9 mm); mobile phase, water–acetonitrile (gradient); flow-rate, 1.5 ml/min; sample, 250 μg epoxy resin in 50 μl acetonitrile–tetrahydrofuran (9:1); detector, UV 280 nm, 0.36 a.u.f.s.
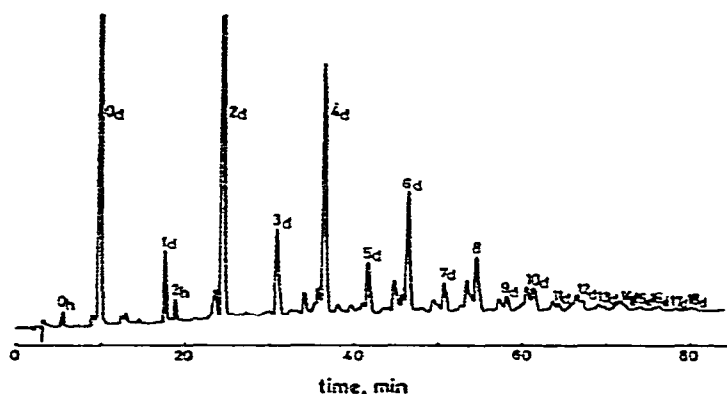

Fig. 2. HPLC chromatogram of ESA 001. Conditions as in Fig. 1.

good separation efficiency of this method: the epoxy resins are completely separated up to a diepoxide oligomer 16_d or 18_d. It was confirmed that diepoxide oligomers from 0_d to 28_d were thoroughly separated, using epoxy resins with higher molecular weights as samples. The gradient elution HPLC technique using either water–dioxane[17] or water–tetrahydrofuran[12] as a mobile phase gave poorer separation than this technique using water–acetonitrile.

Acetonitrile–tetrahydrofuran (9:1) was used as solvent rather than water–acetonitrile because of the low sample solubility in the latter. The problem of sample solubility in the application of reversed-phase gradient elution HPLC was discussed by Van der Maeden *et al.*[17]. However, the acetonitrile–tetrahydrofuran solvent gave no problems, neither extra band broadening nor sample solvent effects being found in the chromatograms of the epoxy resins analyzed in our laboratory.

As shown in Fig. 1, Epon 1001 yields a series of by-product oligomer peaks denoted by n_hs which elute faster than the corresponding diepoxide oligomer peaks

n_ds. An oligomer 4_h yields a peak at almost the same retention volume as an oligomer 3_d and does not appear explicitly in the chromatogram. Fig. 2 shows that ESA 001 also contains by-product oligomers 0_h and 2_h, although their peak heights in the chromatogram of ESA 001 are lower than those in the chromatogram of Epon 1001. These by-product oligomers n_hs were identified as II and their characterization is discussed later. In addition to the n_h oligomers, a number of other by-product oligomers appear in Figs. 1 and 2. The peak height ratio of by-product oligomers appearing around a diepoxide oligomer n_d and that diepoxide oligomer increases with increase in the molecular weight of the diepoxide oligomer n_d.

Fig. 3 shows the chromatogram of ESA 001 allowed to react partially with *p-tert.*-butylphenol. It can be seen that by-product oligomers from 0_b to 6_b have been produced by the reaction. Unreacted *p-tert.*-butylphenol yields a large peak denoted by BP between 0_b and 0_d. Fig. 4 shows the chromatogram of ESA 001 allowed to react partially with methanol. Compared with Fig. 2, a series of by-product oligomers n_fs up to 8_f now appears.
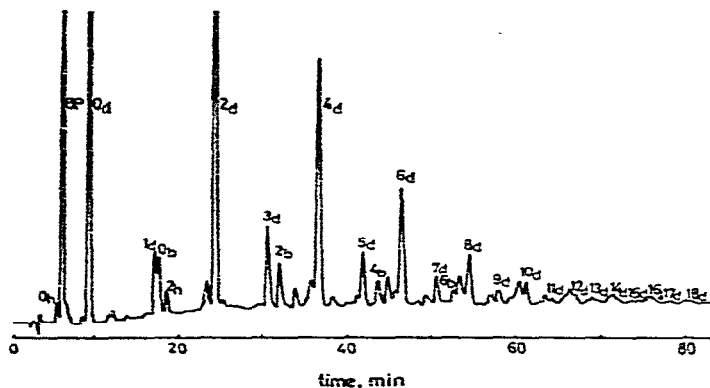

Fig. 3. HPLC chromatogram of ESA 001 allowed to react partially with *p-tert.*-butylphenol (BP). Conditions as in Fig. 1.
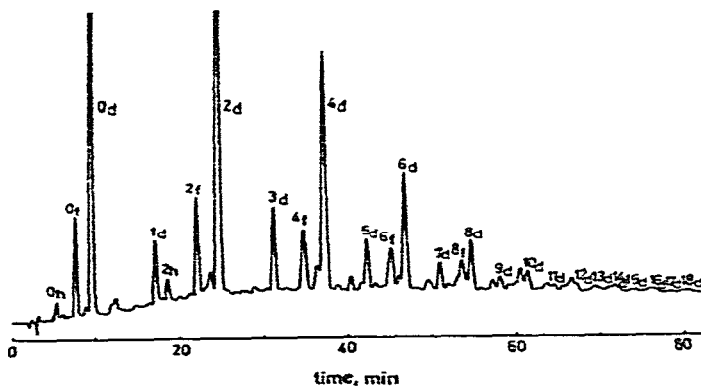

Fig. 4. HPLC chromatogram of ESA 001 allowed to react partially with methanol. Conditions as in Fig. 1.

In order to characterize the three series of the by-product oligomers n_h, n_f and n_{b}, three oligomers of each series were collected using the preparative column, preceded by rough fractionation with the preparative GPC instrument. The melting points of the by-product oligomers are listed in Table I.

TABLE I

MELTING POINTS OF BY-PRODUCT OLIGOMERS

Oligomer	M.p. (°C)	Oligomer	M.p. (°C)	Oligomer	M.p. (°C)
0_h	liquid	0_f	liquid	0_b	liquid
1_h	43.2	2_f	53.8	2_b	55.6
2_h	59.7	4_f	59.0	4_b	69.8

Infrared analysis

Fig. 5 shows the infrared spectra of 0_h, 0_f and 0_b in comparison with that of 0_d[6,7]. There are some appreciable differences among these spectra. First, compared with the spectrum of 0_d, the spectra of 0_h, 0_f and 0_b show a decrease in the intensities of two absorption bands due to an epoxy group at 912 and 860 cm^{-1} and the appearance of a O–H stretching band at 3460 cm^{-1}, as expected from the structures of 0_h, 0_f and 0_b. The by-product oligomer 0_h has the most intense O–H stretching band. Secondly, in addition to this O–H stretching band, an OH group gives two medium intensity bands at 1132 and 1106 cm^{-1} due to C–O stretching vibration, so that the absorption intensities of the by-product oligomers in the region of 1100–1140
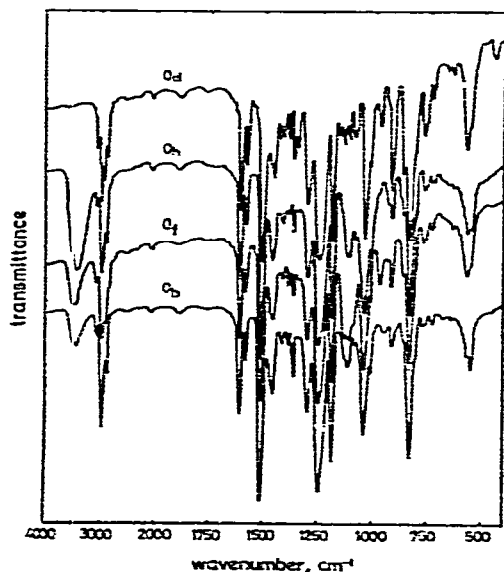

Fig. 5. Infrared spectra of by-product oligomers 0_h, 0_f and 0_b, compared with spectrum of 0_d (measured on a KRS-5 crystal).

cm^{-1} are greater than those of the diepoxide oligomer 0_d. A methoxy group of 0_f gives some bands in this region and hence the bands of 0_f in this region are the most intense of these by-product oligomers. Thirdly, the spectra of the by-product oligomers shows three weak absorption bands at 1362, 1385 and 1410 cm^{-1} in the region of 1340–1430 cm^{-1}, while the spectrum of 0_d has two other weak bands at 1346 and 1427 cm^{-1} in addition to these three bands. The two bands at 1346 and 1427 cm^{-1} are due to a 2,3-epoxypropyloxy group, because phenyl glycidyl ether and p-cresyl glycidyl ether have two bands at almost the same frequencies and because the intensities of these two bands in the spectrum of a diepoxide oligomer n_d decreased with increasing degree of polymerization, n. An isopropyl group adjacent to two benzene rings yields the three bands at 1362, 1385 and 1410 cm^{-1}. The band at 1410 cm^{-1} arises also from a tert.-butyl group and thus this band of 0_b is the most intense. The other change in C–H absorption bands appears in the region of 2830–2970 cm^{-1}. Finally, in the spectrum of 0_b a band at 555 cm^{-1} is more intense than that at 570 cm^{-1}, while in the spectra of the other oligomers the latter band is more intense than the former. These two bands are due to out-of-plane aromatic ring deformation. There are some other differences among the spectra shown in Fig. 5, but the origins of the differences are not well defined.

Mass spectroscopic analysis

The mass spectra of 0_h, 0_f and 0_b are shown in Fig. 6 together with the mass spectrum of 0_d (refs. 6 and 7). The parent ion M^+ and the ion $M^+ - 15$, formed
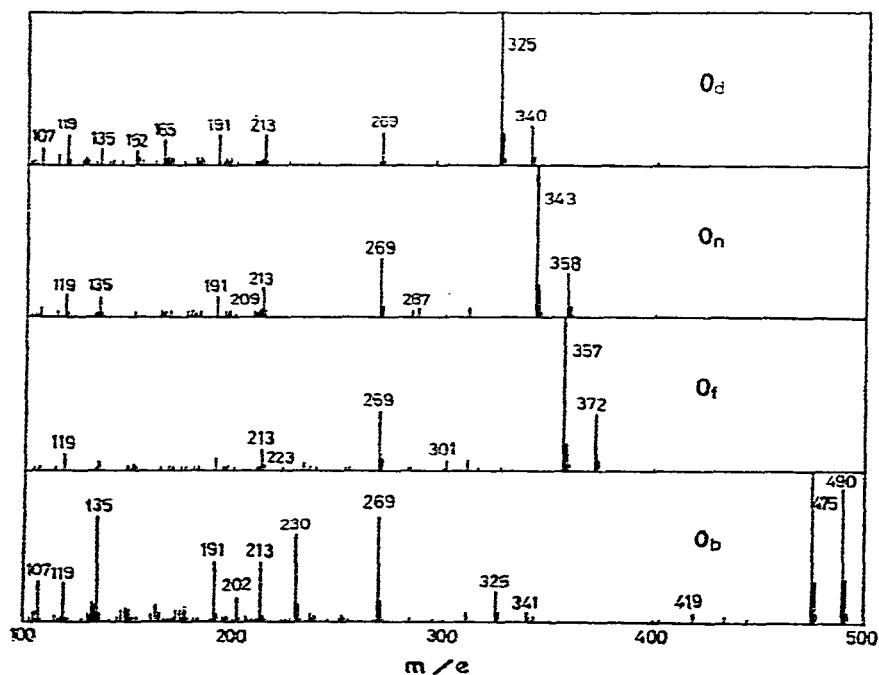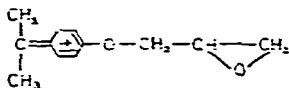

Fig. 6. Mass spectra of by-product oligomers 0_h, 0_f and 0_b, compared with spectrum of 0_d. Conditions: ionization, electron impact; ionization energy, 70 eV; ionization current, 200 μA.

through the loss of a methyl group[5,13], are always seen in the spectra. The parent ions of the three by-product oligomers 0_h, 0_f and 0_b are all in agreement with the molecular weights calculated from their structures.

In the mass spectrum of 0_d there are two major fragment ions carrying a 2,3-epoxypropyloxy group: m/e 269 and m/e 191. The ion of m/e 269 is assigned to the following structure:
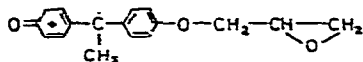
This ion results from the loss of a 2,3-epoxypropyl group by the McLafferty rearrangement and a methyl group cleavage[13]. While the by-product oligomers yield the ion of m/e 269 through the loss of a 2,3-disubstituted propyl group and a methyl group, they also yield another ion according to the same kind of fragmentation, based upon the unsymmetrical structures of the by-product molecules: 0_h, m/e 287; 0_f, m/e 301; 0_b, m/e 419. The ion of m/e 191 results from the C–C bond cleavage between an isopropyl group and an adjacent phenyl group, its structural formula being as follows:

Although very weak, another ion resulting from the same kind of fragmentation is present in the mass spectra of the by-product oligomers: 0_h, m/e 209; 0_f, m/e 223; 0_b, m/e 341. These ions are formed through the loss of a phenyl glycidyl ether group.

^{13}C *NMR analysis*[20,21]

Tables II, III and IV summarize the results of the ^{13}C NMR measurements on the three series of by-product oligomers n_h, n_f and n_b, respectively. The resonance lines in the ^{13}C NMR spectra fall in two areas, 30–75 ppm for the aliphatic carbons and 110–160 ppm for the aromatic carbons.

In the case of the by-product oligomers n_h (Table II), oligomers 0_h, 1_h and 2_h have three bands corresponding to carbons u', v' and w', which are not present in the spectra of the diepoxide oligomers n_d (ref. 21). The unsymmetrical structure of 0_h makes the chemical shifts of the carbons on one aromatic ring of a BPA residue different from those on the other aromatic ring. Carbon d yields a band at a smaller chemical shift than carbon t, while carbons e and g yield bands at larger chemical shifts than carbons s and j, respectively. These differences indicate that a 2,3-dihydroxypropyloxy group is more electronegative than a 2,3-epoxypropyloxy one. The carbon band of f is at the same chemical shift as the carbon band of k. However, the differences in the chemical shifts between the carbons on the two aromatic rings of a BPA residue disappear in the spectra of 1_h and 2_h.

As shown in Table III, two carbons w' and α of the by-product oligomers n_f yield two new peaks, compared with the spectra of the diepoxide oligomers n_d. On

TABLE II

^{13}C-NMR OF BY-PRODUCT OLIGOMERS n_h
Chemical shifts, in ppm from TMS.
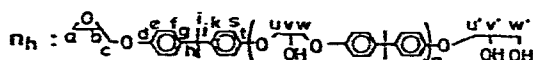
Carbon	δ (ppm)		
	0_h	1_h	2_h
a	44.74	44.76	44.76
b	50.19	50.17	50.17
c	68.76	68.82	68.82
d	156.25	156.32	156.32
e	114.04	114.01	114.01
f	127.74	127.77	127.77
g	143.77	143.69	143.69
h	41.76	41.78	41.78
i	30.99	31.04	30.99
j	143.62	143.69	143.69
k	127.74	127.77	127.77
s	113.94	114.01	114.01
t	156.34	156.32	156.32
u		68.82	68.82
v		68.82	68.82
w		68.82	68.82
u′	69.20	69.30	69.30
v′	70.42	70.43	70.43
w′	63.69	63.74	63.74

TABLE III

^{13}C-NMR OF BY-PRODUCT OLIGOMERS n_f
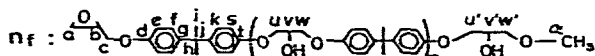
Carbon	δ (ppm)		
	0_f	2_f	4_f
a	44.77	44.71	44.76
b	50.19	50.17	50.17
c	68.79	68.82	68.86
d	156.36	156.32	156.32
e	114.06	114.01	114.06
f	127.75	127.72	127.77
g	143.68	143.70	143.69
h	41.74	41.78	41.78
i	31.03	31.04	31.04
j	143.56	143.70	143.69
k	127.75	127.72	127.72
s	113.97	114.01	114.06
t	156.41	156.32	156.32
u		68.82	68.86
v		69.01	69.06
w		68.82	68.86
u′	68.96	68.82	68.86
v′	69.07	69.01	69.06
w′	73.51	73.55	73.55
α	59.25	59.20	59.20

TABLE IV

^{13}C-NMR OF BY-PRODUCT OLIGOMERS n_b

n_b :

Carbon	δ (ppm)		
	0_b	2_b	4_b
a	44.75	44.71	44.75
b	50.17	50.12	50.17
c	68.77	68.82	68.86
d	156.34	156.27	156.33
e	114.06	114.01	114.06
f	127.75	127.72	127.77
g	143.66	143.63	143.69
h	41.74	41.73	41.78
i	31.01	30.99	31.40
j	143.66	143.63	143.69
k	127.75	127.72	127.77
s	114.06	114.01	114.06
t	156.30	156.27	156.33
u		68.82	68.86
v		68.82	68.86
w		68.82	68.86
u'	68.77	68.82	68.86
v'	68.77	68.82	68.86
w'	68.77	68.82	68.86
α	156.17	156.27	156.33
β	113.97	114.01	114.06
γ	126.28	126.21	126.26
δ	143.99	143.97	144.03
ε	34.09	34.02	34.07
ζ	31.49	31.48	31.53

the other hand the bands corresponding to carbons u′ and v′ are at the same chemical shifts as the bands corresponding to carbons u and v, respectively. As in the case of 0_h, the asymmetry in the structure of 0_f makes the carbon bands of d, e and g different from the carbon bands of t, s and k. Oligomers n_f with a higher degree of polymerization show no differences in the chemical shifts between the carbons on the two aromatic rings of a BPA residue.

In the case of the by-product oligomers n_b (Table IV) the chemical shifts for carbons u′, v′ and w′ are the same as those for carbons u, v and w. The six new bands of carbons α–ζ appear in the spectrum of 0_b in comparison with the spectrum of 0_d. The two carbon bands of α and β in the spectra of 2_b and 4_b are superimposed on the bands of the aromatic carbons of BPA residues. The unsymmetrical structure of 0_b yields the carbon band of d at a larger chemical shift than the carbon band of t. This difference disappears as the degree of polymerization of n_b increases.

The reaction of an epoxide group with an alcohol or phenol is thought to give a mixture of two isomers, a primary alcohol derivative and a secondary one. However, the by-product oligomers n_f and n_b are found to contain no detectable primary alcohol derivatives, by measuring the spin–spin coupling constants J (^{13}C–^{1}H) of the by-

product oligomers, in accordance with the experimental result that the formation of the secondary alcohol derivative in the reaction of an epoxide group with an alcohol or phenol is predominant under alkaline conditions[22].

CONCLUSION

Three series of monoepoxide by-product oligomers contained in diglycidyl ethers of bisphenol A type epoxy resins were separated by reversed-phase gradient elution HPLC. The by-product oligomers investigated have a functional endgroup other than an epoxide group: a 2,3-dihydroxypropyloxy, a 2-hydroxy-3-methoxy-propyloxy or a 2-hydroxy-3-*p-tert.*-butylphenoxypropyloxy endgroup. Three oligomers of each series of the by-products were isolated and characterized by infrared, mass and ^{13}C NMR spectrometry.

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