

# Epoxy Resins Based on Bisphenol S. II. HPLC Analysis

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## SYNOPSIS

Three types of bisphenol S (BS) based epoxy resins prepared by reaction of BS or a mixture of BS and bisphenol A (BA) with an excess of epichlorohydrin in alkaline medium or by thermal treatment of BS with diglycidyl ether of bisphenol A (DGEBA) were analyzed by reversed-phase high-performance liquid chromatography (HPLC). Some components present in the reaction products were identified by analogy with BA based epoxies, combination of semipreparative HPLC with IR and NMR spectroscopy, and derivatization of resins with HCl or NaOH. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Epoxy resins based on BS represents an important group of epoxies. In comparison with the commonest epoxies based on BA, they are more reactive with respect to amines.<sup>1</sup> The cured resins have higher glass transition temperature ( $T_g$ ),<sup>1</sup> resistance to water, acids and alkalies,<sup>2</sup> thermal resistance,<sup>3</sup> resistance to mechanical shocks,<sup>4</sup> flexural and compressive strength.<sup>5</sup> In contrast to the BA based epoxy resins,<sup>6-10</sup> little attention has been paid to the HPLC analysis of resins made from BS. This fact encouraged the development of gradient HPLC methods suitable for the characterization of various epoxy resins based on BS.

## EXPERIMENTAL

### High-Performance Liquid Chromatography

The instrument used for the analysis consisted of an SP 8100 liquid chromatograph, an SP 8440 UV/VIS detector operated at 280 nm, and an SP 4400 integrator (all Spectra-Physics). Reversed-phase HPLC was carried out using Separon SGX C 18 column (Tessek) of the dimension 250 × 4 mm (analytical HPLC) or 250 × 8 mm (semipreparative HPLC). The particle size was 5 or 7 μm. The mobile phase consisted of water, methanol, and tetrahy-

drofuran (THF) according to the gradient profiles scheduled in Table I. In analytical HPLC, the flow rate was maintained at 1 mL/min, the injection volume was 10 μL of THF solution (concentration 0.2, 0.5, or 1.2%). In semipreparative HPLC, the flow rate was 2 mL/min, the injection size was 100 μL of 50% solution in THF. To identify the HPLC peaks of compounds containing 2-hydroxy-3-chloropropyl group, the resins were derivatized with HCl or NaOH. HCl (approximately 10 molar % of epoxy groups) was added to the solution prepared for HPLC analysis. The mixture was left 4 h at room temperature and then injected. A tenfold excess of powdered NaOH was added to the solution of resin prepared for the analysis, the mixture was stored with occasional shaking for 4 h at room temperature, filtered, and injected.

### IR and NMR Spectroscopy

IR spectra were measured on the spectrometer Pye Unicam SP3-300A employing KBr disc method. NMR spectra were registered on the spectrometer Bruker AM 400 in 5 mm probes with CDCl<sub>3</sub> as a solvent and tetramethylsilane as an internal standard.

### Preparation of Resins

#### 1. Resin Based on BS

A modified procedure described by Beavers was used for the reparation of BS based resin.<sup>11</sup> Into a reactor

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**Table I** HPLC Gradient Profiles Used for the Analyses of Particular Resins

Resin Type	Time (min)	Solvent (%)		
		THF	Methanol	Water
1	0	32	0	68
	10	32	0	68
	40	65	0	35
2a	0	30	10	60
	25	40	20	40
	40	60	40	0
2b	0	30	10	60
	25	40	20	40
	70	50	30	20
	80	60	40	0

equipped with thermometer, mechanical stirrer, and reflux condenser was charged 100 g of BS and 148 g of epichlorohydrin. The stirred mixture was heated under an atmosphere of nitrogen to the temperature of 105°C. The mixture was maintained at the temperature of 100 to 110°C for 7 h while 75.2 g of 42.6% aqueous NaOH was added. The reaction mixture was kept neutral to phenolphthalein indicator. Then water and epichlorohydrin were removed at the temperature of 105°C and a pressure of 40 kPa. The reaction mixture was dissolved in boiling isobutyl methyl ketone and filtered. The final product was obtained after cooling in the form of white crystalline powder with an epoxy equivalent 0.478 mol/100 g and melting point 158–161°C. The yield was approximately 70%.

## 2. Mixed BA/BS Based Resins

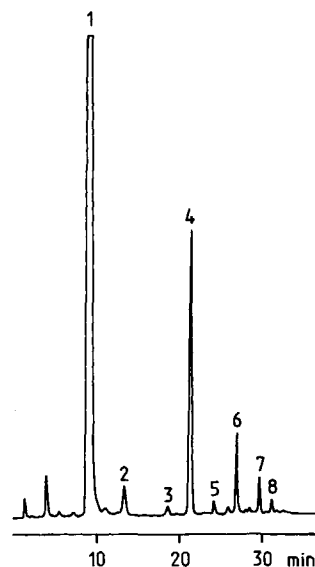
*a. Resin Prepared by Reaction of a BA/BS Mixture with Epichlorohydrin.* BA (171 g), BS (62.5 g), epichlorohydrin (930 g), and water (5 g) were heated under an nitrogen atmosphere to the temperature of 60°C, then 9.4 g of 42.4% aqueous NaOH was added and the mixture was maintained at 60°C for 30 min. NaOH (47.1 g of 42.4%) was added in equivalent portions within 3 h at regular 30-min intervals. Then nitrogen was stopped and the reaction mixture was heated to 73°C under a pressure of 35 kPa (water and epichlorohydrin distilled out). The third deal of NaOH (113.2 g of 42.4%) was dropped for 75 min at the temperature of 73°C. The rest of water was removed at the pressure of 13 kPa and temperature 150°C. The mixture was cooled to 60°C, then 340 g of isobutyl methyl ketone and 340 g of water were added. The mixture was stirred for 10 min and then transferred to a separating funnel.

After separation, the organic layer was heated to 60°C and the fourth portion of NaOH (38 g of 42.4%) was added within 20 min. After that, the mixture was maintained for 1 h at 60°C under nitrogen. The water (150 g) was added and the mixture was stirred 5 min at 50°C. The organic phase was separated and washed with 150 g of 5% aqueous NaCl solution. The mixture was heated to 65°C and stirred for 10 min and then saturated with carbon dioxide (10 min). The organic layer was separated and isobutyl methyl ketone was stripped at 150°C and 20 kPa. Hot product was filtered. Epoxide equivalent was 0.5 mol/100 g, viscosity at 25°C was 128 Pa s.

*b. Resin Prepared by Reaction of DGEBA with BS.* BS (81.2 g) and 200 g of DGEBA of 99% purity (prepared by recrystallization of commercial liquid BA-based epoxy resin from the mixture of ethyl methyl ketone and methanol 1:4) were maintained for 60 min at 160°C under nitrogen atmosphere. The melting point of the obtained product was 109°C.

## RESULTS AND DISCUSSION

A typical chromatogram of epoxy resin prepared according to the procedure (1) is in Figure 1. The chromatogram is similar to those published for low-molecular-weight BA-based epoxy resins. The com-



**Figure 1** HPLC chromatogram of BS based epoxy resin prepared by procedure (1). Product composition: DGEBS (peak 1)—82.9%, dimer (peak 4)—7.6%, trimer (peak 6)—1.5%, tetramer (peak 7)—0.7%, pentamer (8)—0.3%, glycidyl 2-hydroxy-3-chloropropyl ether of BS (peak 2)—1.2%.

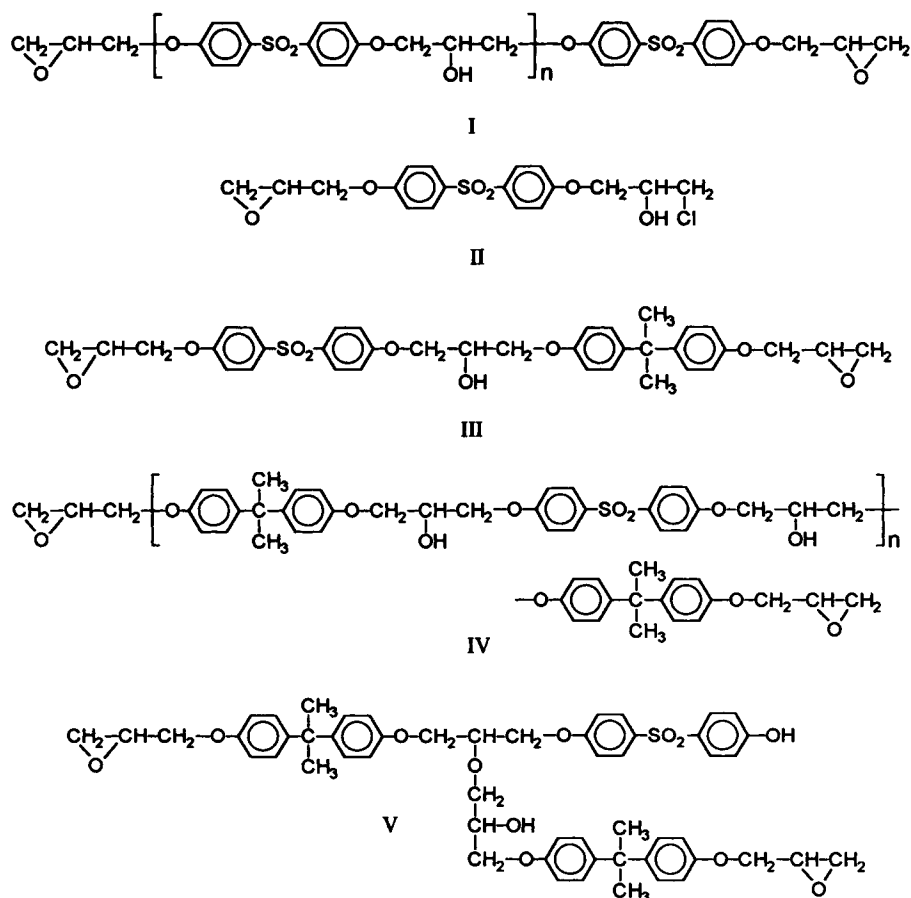


Figure 2 Formulae of some compounds discussed in the text.

pound 1 was isolated by crystallization from isobutyl methyl ketone and identified by IR and NMR as diglycidyl ether of bisphenol S (DGEBS, formula I,  $n = 0$ , Fig. 2). The IR spectrum showed characteristic  $-\text{SO}_2-$  absorption bands at  $1310\text{ cm}^{-1}$ ,  $1160\text{ cm}^{-1}$ ,  $590\text{ cm}^{-1}$ , and  $560\text{ cm}^{-1}$ .<sup>12</sup> The absorption band at  $910\text{ cm}^{-1}$  confirmed the presence of an oxirane ring. The  $^{13}\text{C}$ -NMR spectrum showed signals with chemical shifts of 70.6, 50.2, and 44.3 ppm corresponding to the glycidyl group of epoxy resin, and signals at 163.2, 130.4, 116.0, and 135.7 ppm belonging to the aromatic ring carbons. The obtained data are in very good agreement with the previously published results.<sup>13</sup> Compound 4 was isolated by means of semipreparative HPLC and identified by NMR as dimer (formula I,  $n = 1$ ). The signals in  $^{13}\text{C}$ -NMR spectrum were at 70.6, 50.3, and 44.3 ppm (glycidyl group), 163.2, 130.4, 116.0, and 135.7 ppm (aromatic ring carbons), and 68.6 ppm (carbon with a secondary  $-\text{OH}$  group on an aliphatic chain). The peaks 6, 7, and 8 can be analogically assigned to trimer, tetramer, and pentamer ( $n = 2, 3, 4$ ). The area of peaks 2, 3, and 5 markedly increased after the addition of HCl to the solution of resin. On the

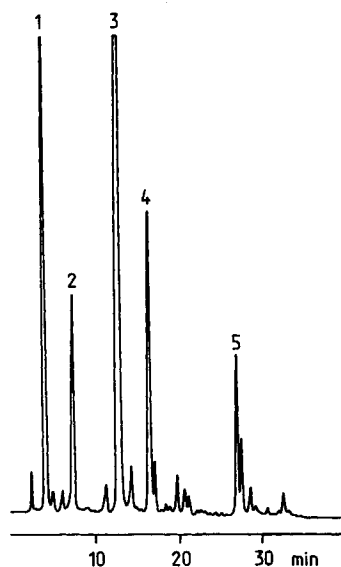
contrary, the peaks fully disappeared after the treatment with NaOH. Thus, the peaks may be assumed to correspond to glycidyl 2-hydroxy-3-chloropropyl ether of BS (formula II), bis(2-hydroxy-3-chloropropyl) ether of BS, and glycidyl 2-hydroxy-3-chloropropyl dimer, respectively.

Figure 3 presents chromatogram of the resin prepared by the procedure (2a). According to their retention times, the peaks were identified as DGEBS (peak 1), dimer of DGEBS (peak 2), DGEBA (peak 3), and dimer of DGEBA (peak 5). Compound 4 was isolated by semipreparative HPLC and identified by IR as a mixed dimer (formula III). IR spectrum showed all absorption bands typical for BA and BS based resins. The presence of a secondary hydroxyl group was proved by the absorption band at  $3500\text{ cm}^{-1}$ . The absorption line of the epoxy group showed half intensity compared with those in spectra of DGEBA and DGEBS. It was found that the detector response factor at 280 nm (expressed in area units per unit mass) of DGEBS is 2.8 times higher than that of DGEBA. An average response factor from those of DGEBA and DGEBS was used for the determination of the content of the mixed dimer.

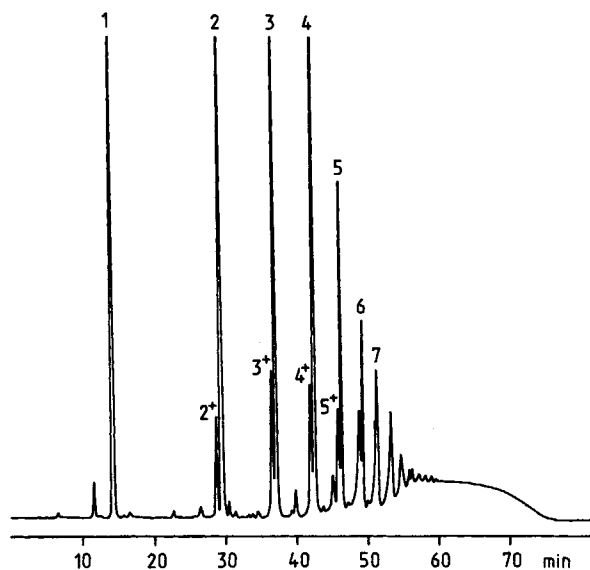
Figure 4 shows chromatogram of resin prepared by procedure (2b). HPLC can give information about two kinds of the irregularities in an oligomeric chain: (1) differences in the type of end groups, and (2) defects along the chain. Approximately constant intensity ratios of different peak series is typical for products containing several oligomeric series with the same main chain but differing in the structure of end groups. If a side reaction on the main chain occurs, then the probability of such a reaction increases with the chain length and the relative intensity of minor peak series increases with the increasing polymerization degree. This is the case of the chromatogram in Figure 4. Major peaks may be identified as oligomers containing  $n$  BS units and  $n+1$  BA units (formula IV,  $n = 0, 1, 2, \dots$ ). Satellite peaks are believed to be similar, but branched oligomers of the type V. These oligomers can arise by the reaction of epoxy group of DGEBA with a secondary hydroxyl group of the reaction product of DGEBA and BS.

## CONCLUSIONS

DGEBS, dimer to pentamer and 2-hydroxy-3-chloropropyl derivatives were found as major constituents of resin prepared by procedure (1); DGEBS, DGEBA, and their dimers, together with a mixed dimer, were identified in the resin type (2a); residual DGEBA and linear and branched mixed oligomers were found in the resin prepared according to the



**Figure 3** HPLC chromatogram of mixed BS/BA resin prepared according to procedure (2a). Resin composition: DGEBS (peak 1)—11.7%, dimer of DGEBS (peak 2)—2.5%, DGEBA (peak 3)—61.3%, dimer of DGEBA (peak 4)—4.6%, mixed dimer (peak 5)—7.7%.



**Figure 4** HPLC chromatogram of mixed BS/BA based epoxy resin prepared according to procedure (2b). Peak 1—DGEBA (formula IV,  $n = 0$ ), peaks 2, 3, 4 . . . —oligomers according to the formula IV,  $n = 1, 2, 3 \dots$ , peak/peak<sup>+</sup> intensity ratio—0.09 (peak 2), 0.18 (peak 3), 0.25 (peak 4), 0.32 (peak 5), 0.53 (peak 6).

process (2b). Reversed-phase HPLC was proved as the method capable of characterizing the composition of various BS-based epoxy resins.

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