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Liquid chromatographic analysis of cationic polymerized phenyl glycidyl ether

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ABSTRACT

Products of cationic polymerization of phenyl glycidyl ether were analysed by gel permeation chromatography and high-performance liquid chromatography. Individual oligomers were isolated by semipreparative high-performance liquid chromatography for the purposes of identification by mass spectrometry and gel permeation chromatography calibration. An equation for the conversion of the molecular weight of oligostyrene to that of oligophenyl glycidyl ether was derived. This equation was used for the determination of oligophenyl glycidyl ether molecular weight distribution by gel permeation chromatography. Molecular weight distribution curves of oligophenyl glycidyl ether samples were determined by high-performance liquid chromatography and gel permeation chromatography and compared.

INTRODUCTION

Cationic polymerization of the glycidyl (2,3-epoxypropyl) group represents an important curing reaction of epoxy resins. The term curing is used to describe the process by which one or more reactants, *i.e.*, an epoxide and a curing agent, are transformed from low-molecular-weight materials to a highly cross-linked network. The curing of the epoxy resins is based on the reaction between the epoxide molecules themselves, or the reaction between the epoxy group and other types of reactive molecules. The former is polymerization, and the latter is an addition reaction, but both result in coupling as well as cross-linking. A typical example of cationic polymerization of epoxy resins is the reaction with Lewis acids. Boron trifluoride can be used as a Lewis acid and is normally complexed with a Lewis base, *e.g.*, hydroxyl,

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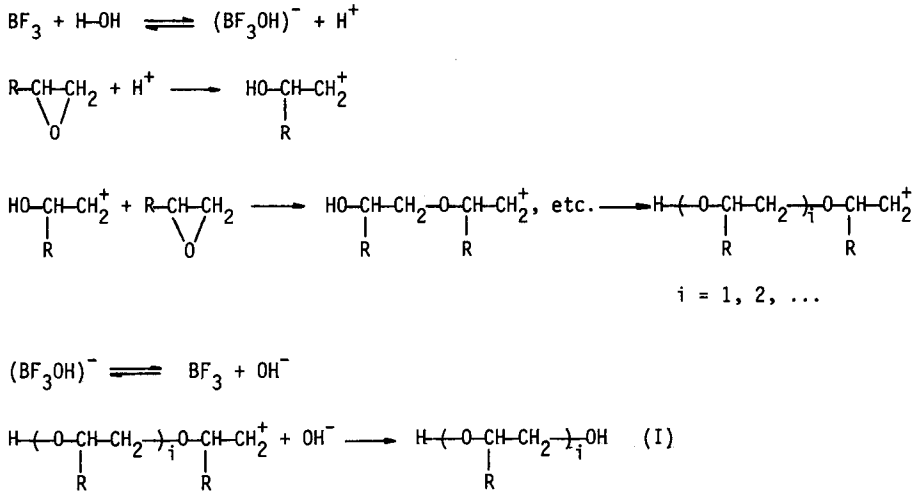
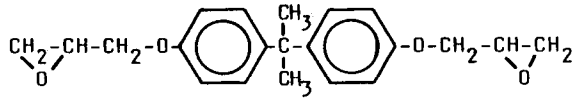
thiol or amine. The polymerization of an epoxide in the presence of boron trifluoride hydrate can be expressed in a simplified form by the following scheme:



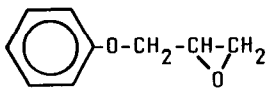
In the case of phenyl glycidyl ether (PGE), R = $-CH_2-O-C_6H_5$ and molecular weight is given by the equation:

$$M = 18 + 150i \tag{1}$$

PGE is a suitable model compound for diglycidyl ether of bisphenol A (DGEBA), as it is evident from their formulae:



DGEBA



PGE

DGEBA-based epoxy resins are the most commonly used. PGE contains only one epoxy group in its molecule, and consequently the linear soluble products arise by its polymerization. Owing to their solubility, they can easily be analysed by liquid chromatography. Gel permeation chromatography (GPC) and high-performance liquid chromatography (HPLC) have been used many times for the characterization of DGEBA-based epoxies [1–4]. The reaction of commercial epoxy resin (Epon 815) or PGE with boron trifluoride isobutanol or triol (Voranol 2070) complex has been recently investigated by GPC, differential scanning calorimetry (DSC) and gas chromatography–mass spectrometry (GC–MS) [5]. It was found that the molecular weight of polymerized PGE decreased marginally with the decreasing amount of BF_3.

GC–MS study proved the presence of the cyclic dimer with a molecular weight of 300. DSC analysis of cross-linked epoxy resin showed that the degree of cross-linking increased with increasing BF_3, which was evident from the increasing glass transition temperature.

The aims of this work are (1) the finding of separation conditions for HPLC analysis of oligophenyl glycidyl ether (OPGE), (2) the calibration of GPC columns for this material and (3) the identification of major products arising during the reaction of PGE with boron trifluoride hydrate.

EXPERIMENTAL

Gel permeation chromatography and high-performance liquid chromatography

The Spectra-Physics SP 8100 liquid chromatograph was used for GPC and HPLC analyses. The eluents were monitored with an SP 8440 UV–VIS variable-wavelength detector at 270 nm (maximum of UV spectrum of 2,3-dihydroxypropyl phenyl ether). The SP 4200 computing integrator served for data handling. This system provides for automatic reporting and plotting of background-corrected UV spectra and absorbance ratios during the course of a chromatographic run.

A set of four Microgel (Chrompack) columns, 250 × 7.7 mm (50, 100, 500, 10^3 Å), was used for GPC analyses with tetrahydrofuran (THF) as the mobile phase. Polystyrene standards purchased from Polymer Labs. (nominal molecular weights 162, 580, 1250, 1800, 3600, 7600 and 9200) were used for the calibration of GPC columns. The columns were thermostated at 40°C.

The reversed-phase HPLC with gradient elution on THF–methanol–water was carried out using Separon SGX C_{18} stainless-steel columns packed with spherical octadecylsilica gel, particle size 7 μm (Tessek, Czechoslovakia).

The simplest method of evaluation of GPC data, assuming no dispersion, was used. A chromatographic curve was divided by drawing n vertical lines from the baseline to points on the curve. The areas of these slices were used for the computation of cumulative weight distribution:

$$I_w(M_j) = \sum_{i=1}^{j} A_i \Big/ \sum_{i=1}^{n+1} A_i \qquad (2)$$

where $I_w(M_j)$ is the value of cumulative weight distribution function at the point j. The molecular weight M_j corresponding to elution time at the point j was calculated from the calibration dependence of OPGE, which was derived from the calibration dependence of oligostyrene (OS) by means of eqn. 3.

To construct the distribution curves from HPLC chromatograms, the areas of peaks of byproducts eluting between oligomers i and $i + 1$ were added to the area of oligomer i. The resulting areas were introduced into eqn. 2. Molecular weights of individual oligomers were calculated from eqn. 1.

Mass spectrometry

All mass spectra were determined using an AEI double-focusing mass spectrometer operated through an MSS electronic console. Samples were emitted into the ion source by direct inlet. The source temperature was 180°C, ionization energy 70 eV, emission 100 μA, accelerating voltage 6 kV and scan-rate 8 s/decade.

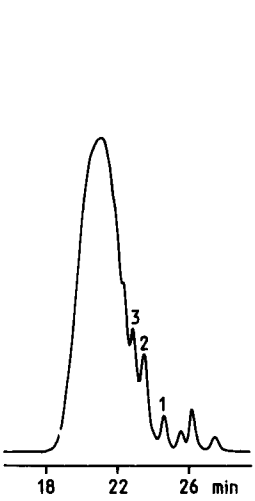
Polymerization of PGE

Polymerization of PGE was induced by 2–4% curing agent containing 10% BF_3, 21.6% water and 68.4% polyethylene glycol (PEG) 300. The polymerization was performed in bulk at the room temperature.

RESULTS AND DISCUSSION

Representative GPC and HPLC patterns of the same product of cationic polymerization of PGE are shown in Figs. 1 and 2. The gradient profile used for the analysis ensures at least partial separation of approximately twenty oligomers, which usually represents *ca.* 95% of molecules in the analyzed samples. With increasing polymerization degree, the resolution between the neighbouring oligomers decreases, as is usual in HPLC separations of oligomeric series, where restricted diffusion within the pores of the column packing and possible effects of molecular conformation contribute to band broadening of the large molecules of higher oligomers [6].

The compounds belonging to the peaks 1–13 were isolated by semipreparative HPLC (Fig. 3), and the purity of the fractions was verified by analytical HPLC (Fig. 4) under the same conditions as those used in Fig. 2. The overlap of the chromatograms in Fig. 4 with that in Fig. 2 shows that fractions obtained by semipreparative HPLC do not contain perceptible amounts of neighbouring oligomers and are suitable for GPC calibration. Compounds 1–4 were analyzed by mass spectrometry. The molecular weights of these compounds were 168, 318, 468 and 618, which correspond to the products according to formula I. Eight of the most intensive fragment ions that were



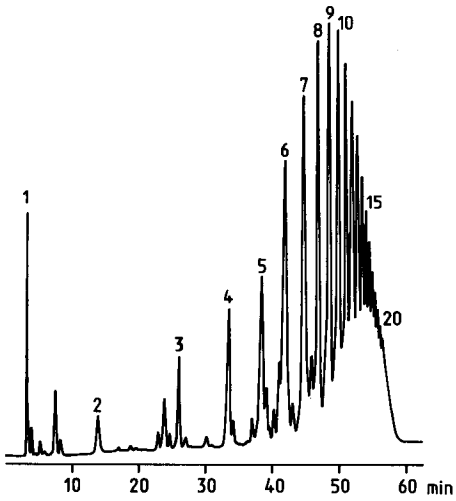


Fig. 1. GPC trace of the product of cationic polymerization of PGE. Columns, Microgel 50, 100, 500 and 10^3 Å (250 × 7.7 mm); mobile phase, THF; flow-rate, 1 ml/min; detection, UV at 270 nm; sample size, 10 µl (0.35% in THF). Peaks 1, 2, 3 = oligomers according to formula I.

Fig. 2. HPLC trace of the product of cationic polymerization of PGE. Column, Separon SGX C_{18} (250 × 4 mm); solvent gradient, THF–methanol–water (55% methanol in water from 0 to 5 min, then linear gradient to 30% THF in methanol for 50 min, 30% THF in methanol from 55 to 65 min); detection, UV at 270 nm; sample size, 10 µl (1.4% in THF). Peaks 1, 2, ... = oligomers according to formula I.

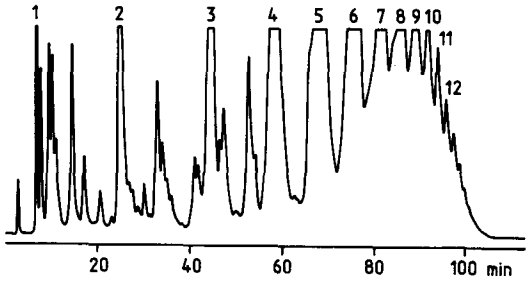


Fig. 3. Semipreparative HPLC trace of OPGE. Column, Separon SGX C_{18} (250 × 8 mm); solvent gradient, THF–methanol–water (55% methanol in water from 0 to 10 min, then linear gradient to 30% THF in methanol for 100 min); flow-rate, 2 ml/min; detection, UV at 254 nm; sample size, 100 μl (70% in THF). Peaks 1, 2, ... = oligomers according to formula I.

detected in the mass spectra of compounds 1–4 are summarized in Table I. Identity of the compound 1 was also confirmed by the same retention times and UV spectra of this substance and pure 2,3-dihydroxypropyl phenyl ether, which was prepared according to the procedure described in ref. 7. Similarly, the next major peaks (5, 6, 7, ...) may be assigned to the oligomers according to formula I.

Peaks of other substances which were not identified occur in the chromatograms, but their concentrations are small. It is possible that these peaks represent another oligomer range, *e.g.*, oligomers with PEG incorporated in the chain or cyclic oligomers formed by backbiting, etc. The identification of these products is not the aim of this work.

The GPC calibration curve of the oligomers of PGE is shown in Fig. 5 together with the calibration curve of OS. The OPGE calibration curve was obtained by relating the logarithms of molecular weight to the elution times of oligomers 1–13 which were isolated by semipreparative HPLC. A very good correlation of this dependence supports the proposed oligomer structure. The relationship

$$M_{\mathrm{OPGE}} = 0.312104 M_{\mathrm{OS}}^{1.153284} \tag{3}$$

was derived by comparing the calibration dependences of OPGE and OS. The

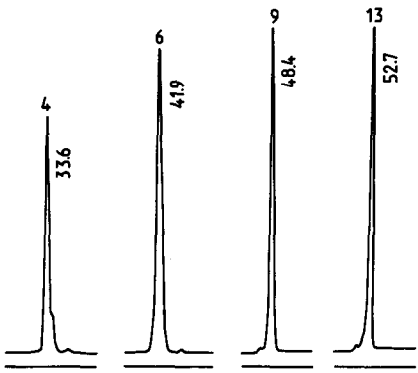


Fig. 4. HPLC traces of fractions isolated by semipreparative HPLC. Conditions as in Fig. 2.

TABLE I

EIGHT OF THE MOST INTENSIVE FRAGMENT IONS IN MASS SPECTRA OF COMPONENTS 1–4

Component	*m/z* (relative abundance)							
1	65 (6)	77 (19)	78 (6)	94 (100)	95 (13)	107 (7)	108 (8)	168 (26)
2	57 (28)	77 (65)	94 (100)	95 (23)	107 (64)	121 (26)	133 (66)	318 (39)
3	57 (14)	77 (33)	94 (32)	107 (44)	119 (29)	121 (20)	133 (100)	134 (14)
4	77 (26)	107 (38)	119 (23)	133 (100)	169 (33)	193 (40)	207 (26)	319 (37)

relationship (eqn. 3) is valid for THF, 40°C and the molecular weight range 168–1968. The extrapolation of eqn. 3 to higher molecular weights, where only OS standards are available, may be permitted to determine the molecular weight distribution of OPGE by GPC.

The cumulative weight distribution curves of the OPGE sample (the chromatograms in Figs. 1 and 2) determined by GPC and HPLC are shown in Fig. 6. The agreement of both distribution curves is evident. If the chromophoric properties of some compounds were significantly different from the others then the distribution curves would be incorrect. As the detections at other wavelengths (254, 280 nm) give practically the same relative areas of oligomer peaks in HPLC profiles as that at 270 nm, we do not suppose the presence of a significant amount of compounds with considerable different chromophoric characters, and therefore any gross errors in the obtained distribution curves are improbable.

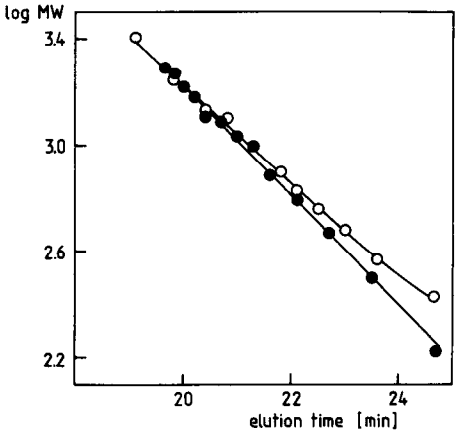


Fig. 5. GPC calibration curves of the oligomers of PGE (●) and OS (○) for Microgel columns 50, 100, 500 and 10^3 Å (250 × 7.7 mm) in THF at 40°C. Flow-rate, 1 ml/min. MW = Molecular weight.

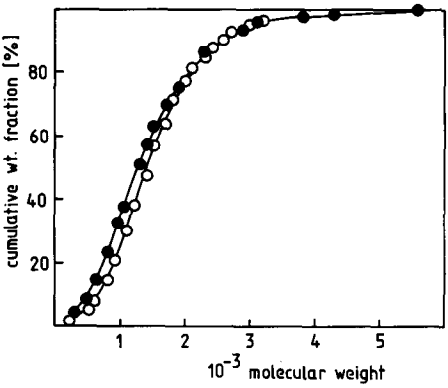


Fig. 6. Cumulative weight distribution curves of the OPGE sample determined by GPC (●) and HPLC (○).

CONCLUSIONS

GPC and HPLC enable detailed characterization of the products of cationic polymerization of PGE and can be used as suitable methods to study the influence of reaction conditions on the composition of the resulting products. OS can be used as a calibration standard for GPC and an OS calibration curve can be converted to the calibration curve of oligomers based on PGE by means of eqn. 3. The molecular weight distribution curves determined by GPC and HPLC are in very good agreement. The described calibration procedure, *i.e.*, the isolation of individual oligomers by semipreparative HPLC and finding the conversion equation based on OS, can be used as a general calibration method for oligomers.

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