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## CHARACTERIZATION OF EPOXY NOVOLAC RESINS USING PHENYL-BONDED PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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### SUMMARY

Epoxy novolac resins can be characterized using a 5- $\mu\text{m}$  phenyl-bonded phase column. Both reversed-phase (tetrahydrofuran-water) and normal phase (tetrahydrofuran-hexane and chloroform-hexane) elutions can be used to obtain a qualitative fingerprinting-type of identification and a quantitative measurement of molecular-weight distribution. The retention of epoxy novolac resins is proportional to the degree of polymerization and the mobile phase compositions.

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### INTRODUCTION

Epoxy novolac resins are one of the early developed synthetic polymers<sup>1,2</sup> that are still widely used in encapsulating microelectronic integrated circuits<sup>3</sup>. There are many methods designed to characterize the properties of these resins in order to obtain a better control of finished products performance. Analytical methods such as thermal analysis and chromatographic techniques are frequently utilized in this application.

In thermal analysis, for example, the glass transition temperature ( $T_g$ ) derived from differential scanning calorimetry (DSC) scans of epoxy-anhydride samples can be used to estimate the optimum curing temperature<sup>4</sup>, *i.e.* a maximum  $T_g$  is observed at optimum curing temperature ( $T_{oc}$ ). The glass transition temperature increases with the curing temperature and it reaches a maximum at  $T_{oc}$ . This phenomenon corresponds to the formation of a cross-linked network of epoxy resins. As samples are exposed to a curing temperature higher than  $T_{oc}$ , the network of epoxy resins start to degrade and the  $T_g$  decreases. Later, Gray<sup>5</sup> used  $T_g$  to measure the degree of cure while the epoxy resins samples were isothermally cured at different length of time. The plot of degree of cure *versus* time can be used to estimate the optimum cure time.

The glass transition temperature also correlates well with the molecular-weight distribution (MWD) and the microstructures of the polymers. Fox and Flory<sup>6,7</sup> reported that  $T_g$  increases with the molecular weight (MW) of thermoplastic polymers up to  $\text{MW} = 30,000$ . Later, Kumler *et al.*<sup>8</sup> showed that the plot of MW *versus*  $T_g$  data can be represented by three intersecting straight line regions. Their results in-

dicates that the value of  $T_g$  increases rapidly at the lower MW ranges (less than 1000) as compared to more moderate increases in the MW range of 1000 to 10,000, and it rarely changes at high MW ranges. Wrasidlo<sup>9</sup> demonstrated that any structures that reduce chain mobility will increase  $T_g$ . This can be illustrated using homochain backbone polymers. For example, polyethylene and *trans*-1,4-polybutadiene polymers are linear chain polymers without any branch groups, and have low  $T_g$  values. Substitution of methyl groups, phenyl groups and carbomethoxy groups leads to an increase in  $T_g$  as a consequence of the increase of steric hindrance about the main chain.

In chromatographic methods, size exclusion chromatography (SEC) is most frequently used to measure MWD of epoxy novolac resins<sup>10,11</sup>. The quantitative measurements of weight average molecular weight ( $M_w$ ), number average molecular weight ( $M_n$ ) and poly-dispersity ( $M_w/M_n$ ) from SEC can provide a useful vehicle to inspect the consistency of the polymer portion of epoxy molding compounds before the curing process. Any change of MWD due to the change of source of supplier or the exposure of moisture, high temperature, or any other environmental effects might offset the optimum curing conditions, *i.e.* either undercured or overcured situations might occur. Neither one of these improper curing conditions is acceptable. If the sealing ability of the encapsulant matrix is reduced; the percentage failure of finished products will increase due to the penetration of moisture and the migration of any corrosion related degradation compounds in the encapsulants.

Other chromatographic techniques are also used to characterize the epoxy novolac resins. For example, Hagnauer<sup>12</sup> demonstrated that octadecyl-bonded liquid chromatography can overcome the problem of limited peak capacity in SEC and can provide a fine resolved chromatogram for a fingerprinting type of identification. However, this method can not provide the information of MWD. Recently, Ishii and Takeuchi<sup>13</sup> used a flexible fused-silica micro-packed column (4 m  $\times$  0.33 mm, packed with TSK-GEL G3000H, 5  $\mu$ m, exclusion limits  $6 \cdot 10^4$ ) to separate Epikote oligomers in a size exclusion mode. Both the MWD and a high resolution chromatogram can be obtained from their results. The only drawback of this method is the long separation time (about 6.5 h). In this contribution, we demonstrate that a 5- $\mu$ m spherical phenyl-bonded phase column (25 cm  $\times$  4.6 mm I.D.) can be used to separate epoxy novolac resins with a much shorter separation time (less than an hour). Both the MWD information and the fingerprinting type identification can be obtained from the chromatogram. Also, upon adjusting the composition of mobile phases, not only the oligomer peaks of epoxy novolac resins can be resolved, but also a partial resolution of the isomers of these oligomers can be observed. The retention of these oligomer peaks follows both Snyder's formulation<sup>14</sup> and Martin's equation<sup>15</sup>. An equation<sup>16,17,30</sup> which combines the Snyder and Martin relations between the retention ( $\log k'$ ) is also suitable to be used to estimate the isocratic retention of epoxy novolac oligomers.

## EXPERIMENTAL

### HPLC

The chromatographic system included a Perkin-Elmer series 3B microcomputer controlled pump module, a Perkin-Elmer SIGMA 10B chromatography data

station, and a Beckman 165 variable-wavelength UV detector. The UV detector was set at a wavelength of 280 nm. The void volume of the column ( $V_0 = 3.30$  ml) used in the calculation of  $k'$  was determined by the retention of carbon tetrachloride in a hexane mobile phase. Retention data used for calculation were values averaged from three duplicate runs of the same isocratic elution.

The gradient elution follows the equation listed below<sup>18</sup>.

$$P(t) = P(i) + [P(f) - P(i)] \left( \frac{t}{T} \right)^x \quad (1)$$

where,  $P(t)$  is the percentage of solvent A as a function of time,  $P(t) = A/(A + B)\%$ ,  $P(i)$  is the initial  $A/(A + B)\%$ ,  $P(f)$  is the final  $A/(A + B)\%$ ,  $t$  is the elapsed time (min),  $T$  is the time of gradient elution and  $x$  is the gradient curvature, e.g.  $x = 1$ , linear gradient;  $x > 1$ , concave gradient; and  $x < 1$ , convex gradient.

The mobile phase conditions are described in the figure captions.

#### Column

A 25 cm  $\times$  4.6 mm I.D. Excaliber Spherisorb S5P (5  $\mu$ m) phenyl-bonded phase column (Applied Science) was used for the separation.

#### Sample

A sample of DOW D.E.N. 438 epoxy novolac resins was used for the study. The sample was dissolved in tetrahydrofuran (THF) or chloroform at a concentration of approximately 2 mg/ml.

## RESULTS AND DISCUSSION

Fig. 1 illustrates the separation of epoxy novolac resins DEN 438 on a phenyl-bonded phase column using THF-water gradient elution. About seven oligomer peaks are observed on this chromatogram. These oligomers peaks elute in the order of increasing degree of polymerization. The retention mechanism is due to the interaction between the aromatic rings in the oligomer chain and the phenyl groups of the stationary phase. Also, the solubility of oligomers decreases with increasing molecular weight (or chain length). Thus, smaller oligomers have less interaction with the stationary phase and they elute before the larger oligomers. At the mobile phase of higher concentration of stronger solvent, the solubility of resins increases, which reduces significantly the retention of resins.

Epoxy novolac resins are known to be obtained from the reaction of novolac resins with epichlorohydrin. Novolac resins can have *ortho-ortho ortho-para, para-para* linkages, thus the combination of these positional isomers increases with the degree of polymerization. Fig. 2 illustrates that the isomers of these oligomers can be further resolved in a THF-hexane gradient elution on the same phenyl-bonded phase. The chromatogram of Fig. 2 can be used for fingerprinting type of identification. However, from Fig. 2, it is difficult to sort these well resolved peaks according to the degree of polymerization. Fig. 3 illustrates a partial resolution of these isomers by using a chloroform-hexane gradient, and the number of isomer increases with increased polymerization. The larger combination of possible isomers also accounts

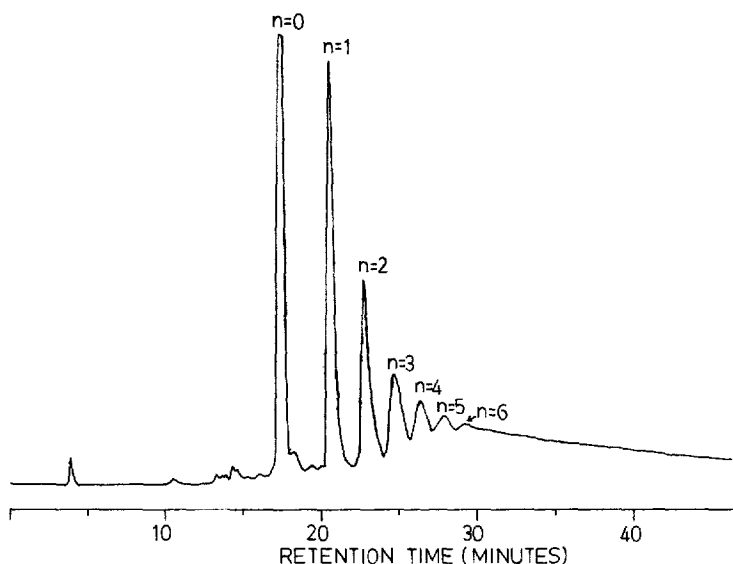


Fig. 1. Separation of DEN 438 on phenyl-bonded phase, mobile phase conditions: initially THF-water (30:70, v/v) for 5 min, then gradient elution from THF-water (30:70) to THF-water (70:30, v/v) in 40 min with a gradient curvature of  $x = 0.5$ , at a flow-rate of 1 ml/min.

for the poor resolution of larger oligomer peaks in Fig. 3.

Fig. 4 is a typical isocratic elution [THF-water (55:45, v/v)] of epoxy novolac oligomers on phenyl-bonded phase.  $\log k'$  of these oligomers is linearly proportional to the solvent composition ( $\phi$ ) of THF and the degree of polymerization ( $n$ ). This relationship can be written as

$$\log k' = (A - B\phi) + (C - D\phi)n \quad (2)$$

where  $A$ ,  $B$ ,  $C$  and  $D$  are constants. Our previous studies have already shown that

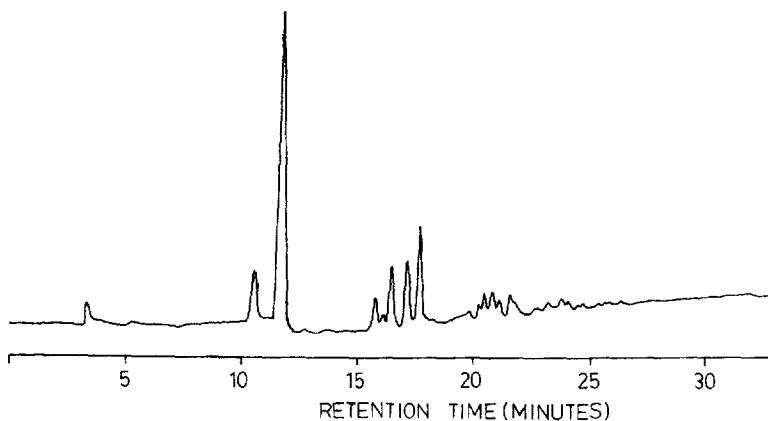


Fig. 2. Conditions the same as Fig. 1, except gradient elution started from injection, THF-hexane (10:90, v/v) to THF-hexane (60:40, v/v) in 30 min with a gradient curvature of  $x = 1$ , then mobile phase stayed at THF-hexane (60:40, v/v).

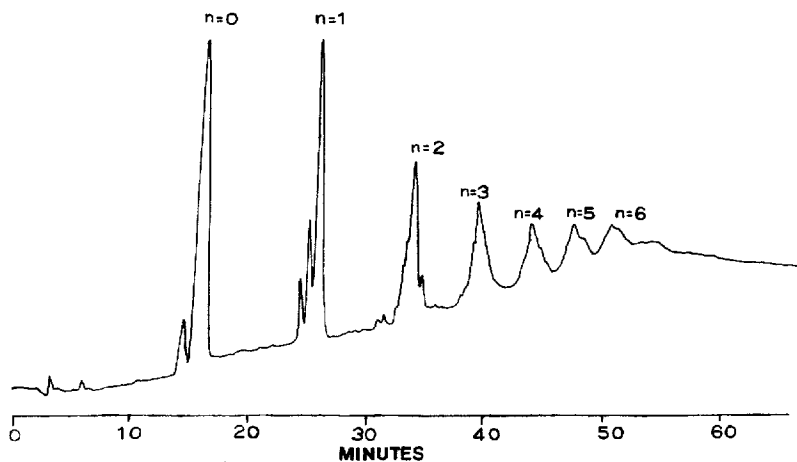


Fig. 3. Conditions the same as Fig. 1, except a linear gradient elution (curvature,  $x = 1$ ) started from injection, chloroform-hexane (20:80, v/v) to chloroform-hexane (50:50, v/v) in 25 min, then chloroform-hexane (50:50, v/v) to chloroform-hexane (80:20, v/v) in 20 min, then stayed at chloroform-hexane (80:20, v/v).

eqn. 2 can be used to estimate the isocratic retention of styrene oligomers<sup>16</sup> and water soluble polyethylene glycol oligomers<sup>17</sup> and polypropylene glycol oligomers<sup>30</sup> on chemically bonded phases. Table I lists the experimental and calculated values of  $\log k'$  of epoxy novolac oligomers in the system of THF-water binary mobile phase and phenyl-bonded stationary phase. Both the Martin equation and the Snyder formulation can be derived from eqn. 2. For example, for a specific isocratic mobile phase composition ( $\phi$  is a constant), eqn. 2 can be written as the form of the Martin equation,  $\log k' = U + Vn$ , where  $U = A - B\phi$  and  $V = C - D\phi$ . For an oligomer of fixed degree of polymerization ( $n$  is a constant), eqn. 2 can be rearranged as

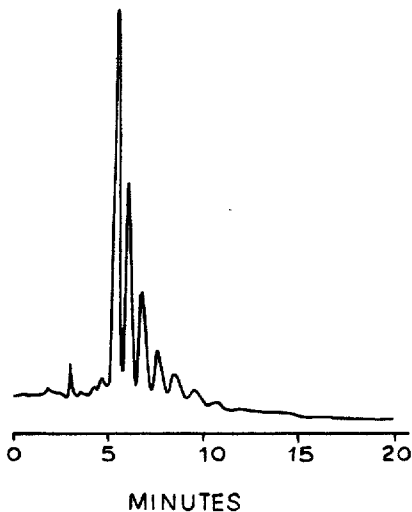


Fig. 4. Conditions the same as Fig. 1, except isocratic elution, THF-water (55:45, v/v), a flow-rate of 1 ml/min.

TABLE I

LOG  $k'$  RETENTION DATA OF EPOXY NOVOLAC RESINS DEN 438 IN THF-WATER MOBILE PHASE

$$A = 4.390, B = 8.697, C = 1.009, D = 1.450.$$

$n$	$\varphi$					
	0.45		0.50		0.55	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0	0.37	0.48	-0.08	0.04	-0.47	-0.39
1	0.84	0.83	0.30	0.32	-0.19	-0.18
2	1.22	1.19	0.59	0.61	0.05	0.03
3	1.57	1.55	0.87	0.89	0.26	0.24
4	1.90	1.90	1.12	1.18	0.46	0.45
5	2.21	2.26	1.40	1.46	0.63	0.66
6			1.68	1.74	0.80	0.87

$\log k' = (A + Cn) - (B + Dn)\varphi$ , which is exactly the same form as the Snyder formulation. The other mobile phase systems also fit into eqn. 2. Tables II and III list the experimental and calculated values of  $\log k'$  in the mobile phases system of THF-hexane and chloroform-hexane.

Phenyl-bonded phase is known to have unique selectivity in both reversed-phase and normal phase solvent systems. For example, fatty acids<sup>19</sup> and peptides<sup>20,21</sup> are separated on phenyl-bonded phase using an aqueous reversed-phase solvent system. Our recent studies<sup>16,22</sup> also showed that styrene oligomers can be separated on phenyl-bonded phase using several solvent systems such as hexane, hexane-THF, THF-water, acetonitrile-water and THF. By changing the composition of the mobile phase, the phenyl-bonded phase can behave as normal phase adsorbents, reversed-phase medium and molecular sieve. Here we also observe that epoxy novolac oligomers can be separated using either normal phase (hexane-chloroform and

TABLE II

LOG  $k'$  RETENTION DATA OF EPOXY NOVOLAC RESINS DEN 438 IN THF-HEXANE MOBILE PHASE

$$A = 1.024, B = 4.814, C = 0.829, D = 1.236.$$

$n$	$\varphi$					
	0.35		0.40		0.45	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0	-0.76	-0.66	-1.04	-0.90	-1.22	-1.14
1	-0.18	-0.26	-0.55	-0.57	-0.82	-0.87
2	0.21	0.13	-0.20	-0.23	-0.54	-0.60
3	0.55	0.53	0.16	0.10	-0.25	-0.32
4	0.96	0.92	0.41	0.44	-0.04	-0.05
5	1.32	1.32	0.73	0.77	0.24	0.22
6			0.98	1.10	0.44	0.49

TABLE III

LOG  $k'$  RETENTION DATA OF EPOXY NOVOLAC RESINS DEN 438 IN CHLOROFORM-HEXANE MOBILE PHASE $A = 1.871, B = 3.986, C = 0.957, D = 0.647.$ 

$n$	$\varphi$							
	0.75		0.80		0.85		0.90	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0	-1.20	-1.12	-1.40	-1.32	-1.61	-1.52	-1.81	-1.72
1	-0.65	-0.65	-0.80	-0.88	-1.12	-1.11	-1.33	-1.34
2	-0.08	-0.17	-0.40	-0.44	-0.69	-0.70	-0.87	-0.97
3	0.36	0.30	0.07	0.0004	-0.23	-0.29	-0.53	-0.59
4	0.80	0.77	0.48	0.44	0.11	0.11	-0.15	-0.22
5	1.23	1.24	0.87	0.88	0.48	0.52	0.16	0.16
6	1.66	1.71	1.25	1.32	0.83	0.92	0.47	0.53

hexane-THF) or reversed-phase (THF-water) solvents. This type of multimode liquid chromatographic behavior<sup>16,22,27-29</sup> blurs the distinction between reversed-phase and normal phase modes of elution. Recently, Parris<sup>23</sup> and Tallman<sup>24</sup> applied a technique called non-aqueous reversed-phase chromatography (NARP) to separate triglycerides or very long chain fatty acids. In such technique, acetonitrile or methanol are used as weak solvents and THF or dichloromethane are used as strong solvents. Usually, the solvent strength can be expressed as the relative solubility of solutes in the solvents. Thus a weak solvent for one type of solute can also be a strong solvent for the other types of solutes. For example, acetonitrile is a weak solvent for triglycerides, but is a considerable strong solvent for epoxy novolac resins (DEN 438). Experimental result showed that epoxy novolac resins can be dissolved in acetonitrile and elute as a single peak in the mobile phase of acetonitrile retention volume of 3.53 ml. In a recent review article of Majors *et al.*<sup>25</sup> was stated that in many cases the difference between mobile phase and stationary phase "polarity" is slight, and the problem in precise terminology may arise. However, it is clear that the ability of phenyl-bonded phase to separate epoxy novolac oligomers using various solvent systems further supports and extends Lock's<sup>26</sup> previous statement that in chemically-bonded phase liquid chromatography small molecules of similar type are separated on the basis of their relative solubility in the mobile phase.

The structure of epoxy novolac resins is depicted in Fig. 5. The corresponding molecular weight of the oligomers of different degree of polymerization can be cal-

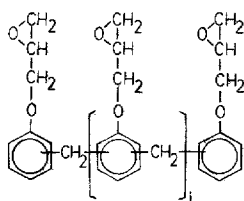


Fig. 5. Structure of DEN 438.

TABLE IV

CALCULATION OF  $M_w$  AND  $M_n$ 

$$M_n = (\sum M_i A_i) / (\sum A_i) = 447.50, M_w = (\sum M_i^2 A_i) / (\sum M_i A_i) = 529.90, M_w / M_n = 1.1841.$$

$n$	Area $M_i$	$A_i$	Corrected area $A_i' = A_i/n + 2$	$M_i A_i$	$M_i^2 A_i$
0	312	4.2825	2.1412	668.07	208,437.84
1	474	2.8252	0.9417	446.38	221,584.88
2	636	1.8367	0.4592	282.04	185,734.45
3	798	1.0852	0.2170	173.20	138,211.94
4	960	0.6553	0.1092	104.85	100,654.08
5	1122	0.3549	0.0507	56.88	63,825.42
6	1284	0.1184	0.0148	19.00	34,400.11
			$\sum A_i' = 3.9338$	$\sum M_i A_i' = 1760.42$	$\sum M_i^2 A_i' = 932848.72$

culated from

$$M_i = 312 + 162i \quad (3)$$

$$i = 0, 1, 2, 3, \dots n.$$

Table IV lists the calculated values of  $M_n$  and  $M_w$  using the corrected area of each oligomer peaks. The original area obtained from the chromatogram can not be directly used in the calculation of  $M_n$  and  $M_w$ . This is because UV absorption at 280 nm corresponds to the concentration of the aromatic rings of epoxy novolac resins instead of the number of molecules.

In summary, the retention behavior of epoxy novolac oligomers depends on the competition between the selective interaction of the phenyl-bonded phase and the solubility of oligomers in the mobile phase. This also emphasizes the importance of the mobile phase composition in the optimization of polymer separation using chemically-bonded phase liquid chromatography.

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