The Use of Liquid Chromatography for the Characterization of Novolac Resins

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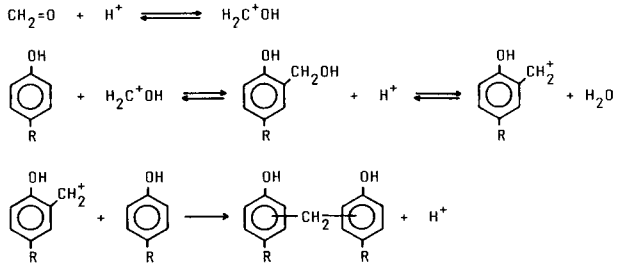
SYNOPSIS

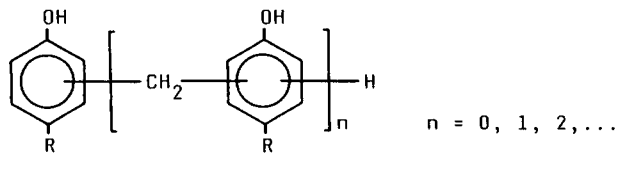
Novolac resins made by condensation of phenol or *p*-cresol with formaldehyde in various mole ratios were analyzed by reversed-phase high-performance liquid chromatography (HPLC) and gel permeation chromatography (GPC). Number-average molecular weights (M_n) of phenol novolacs were determined by GPC and vapor-phase osmometry (VPO) and compared. A relationship was found between the content of dihydroxydiphenylmethane (DHDPM) and M_n of phenol novolacs. Attention was also paid to the quantitative determination of the content of phenol and DHDPM in the analyzed samples. The molecular characters of novolacs synthesized from phenol or *p*-cresol under the same conditions were compared. A relation was found between the molecular weight of phenol novolac and the tensile strength of abrasive material based on it. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Novolac resins are the products of acid-catalyzed condensation of phenols with formaldehyde arising according to the following scheme:



The resulting products can be expressed by the following formula:



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where R = —H for phenol and molecular weight M = 94 + n · 106, and R = —CH_3 for *p*-cresol and M = 108 + n · 120. The final resins are varied mixtures of molecules differing in molecular weight and (in the case of phenol novolacs) in the content of 4,4′-, 2,4′-, and 2,2′-methylene linkages.

To characterize novolac resins, the following kinds of liquid chromatography have been used: gel permeation chromatography (GPC) on conventional columns (8 mm i.d. or more),[1-3] semimicrocolumns (1.5 mm i.d.),[2] or microcolumns (0.35 mm i.d.)[3]; and high-performance liquid chromatography (HPLC) on conventional columns (3 mm i.d. or more) under isocratic conditions by the use of reversed-phase columns[4] or using the gradient elution with reversed-phase columns together with gradient system tetrahydrofuran (THF)–water[5] or acetonitrile–water with phosphoric acid.[6] Interesting results were obtained by the use of reversed-phase microcolumns (0.7 mm i.d.) with gradient methanol–water.[7] Information regarding the molecular structure of novolac resins (number of branches, number of phenolic nuclei in the longest chain, and number of 4,4′-, 2,4′-, and 2,2′-methylene linkages) has been obtained by computer simulation of the molecular weight distribution of a hypothetical product and by comparison of this distribution with that of prepared novolac determined by GPC measurement.[8]

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The hydroxyl groups of novolac oligomers can associate with THF, which is used as the most common solvent in GPC. The solvation of hydroxyl groups is influenced by steric hindrance and deactivation of the hydroxyl groups by intramolecular hydrogen bonds.[9] The different degrees of solvation (the number of associated THF molecules) of isomers of an oligomer of a given polymerization degree result in their slightly different GPC elution volumes. This effect causes the broadening of elution bands of individual oligomers and worsens their resolution.

The aim of this work is to give a detailed survey of the possibilities of GPC and of GPC and HPLC for the characterization of novolac resins.

EXPERIMENTAL

Gel Permeation Chromatography and High-performance Liquid Chromatography

A Spectra-Physics SP 8100 liquid chromatograph was used for the GPC and HPLC measurements. The effluents were monitored with an SP 8440 UV/VIS variable-wavelength detector at 280 nm. An SP 4200 computing integrator served for handling the data.

A set of four Microgel (Chrompack) columns 250 × 7.7 mm (50, 100, 500, 1000 Å) was used for GPC analyses with THF as the mobile phase at flow 1 mL/min. Polystyrene standards purchased from Polymer Laboratories were used for the calibration of GPC columns. The samples were prepared as 0.6% solutions in THF; the injected amount was 10 μL. The columns were thermostated at 25 or 40°C.

The reversed-phase HPLC with gradient elution was carried out using a Separon SGX C 18 stainless-steel 250 × 4 mm column packed with a spherical octadecylsilica gel, particle diameter 5 μm (Tessek, Czechoslovakia). A methanol–water gradient (40% methanol at 0 min; 55% methanol from 10 to 18 min; 100% methanol from 28 to 38 min) was used for the analyses of phenol-based novolacs, and a THF–methanol–water gradient (0% THF, 50% methanol at 0 min; 50% THF, 50% methanol at 55 min) was employed in the case of *p*-cresol novolac resins. The samples were injected as 0.5–0.8% solutions in methanol or THF in the amount of 10 μL. All HPLC measurements were carried out at 50°C.

Determination of Number-Average Molecular Weight (M_n)

The determination of M_n was carried out by VPO using a molecular weight apparatus Model 233100 (Wescan Instruments).

Materials

The novolac resins to be tested were prepared by polycondensation of phenol (*p*-cresol) with formaldehyde in the mol ratio 1/0.65 to 0.9 under catalysis by oxalic acid. The reaction mixture was stirred and refluxed for 2–7 h in the case of phenol resins and 12–32 h in the case of *p*-cresol ones. The reaction was ended when the content of formaldehyde dropped under 0.3 wt %. Water and phenol (*p*-cresol) were stripped off at vacuum and temperature of 160°C.

Individual isomers of dihydroxydiphenylmethane (DHDPM) were made by the reaction of the excess of phenol with formaldehyde under catalysis by HCl or $(CH_3COO)_2Zn$. The 4,4′- and 2,4′-isomers formed in the former case, and 2,4′- and 2,2′-isomers were the major products in the latter case. The unreacted phenol was removed by vacuum-distillation and a mixture of DHDPM isomers was isolated by steam-distillation (180°C). The mixture of obtained isomers was further separated on the base of their different solubilities in benzene.

2-Methylolphenol was synthesized by reaction of 1 mol of $NaBH_4$, dissolved in 500 mL of water, with 2 mol of 2-hydroxybenzaldehyde at 45°C. A slight excess of HCl was added after cooling to the room temperature. Precipitated flakes were recrystallized from aqueous methanol with an addition of active charcoal.

2,4-Dimethylolphenol was made from 2-chlorophenol, from which 2-chlorophenol-4,6-dimethylolphenol was made by reaction with formaldehyde in alkaline medium. The substance obtained was dissolved in a threefold molar excess of 10% aqueous NaOH solution. Halogen was split off using Raney alloy. The reaction mixture was filtrated and neutralized by acetic acid to pH 8. The clear filtrate was shaken with 50 mL of diethyl ether, saturated with NaCl, and extracted by 10 portions of ether that were cumulated and dried in vacuum. The substance obtained was recrystallized from benzene.

Determination of Formaldehyde Content

The content of formaldehyde was determined by addition of excess of KCN and titration of excessive KCN using $Hg(NO_3)_2$ using diphenylcarbazon as an indicator.

RESULTS AND DISCUSSION

GPC chromatograms of phenol novolacs made by polycondensation of phenol with various amounts of formaldehyde are shown in Figure 1. Peaks of

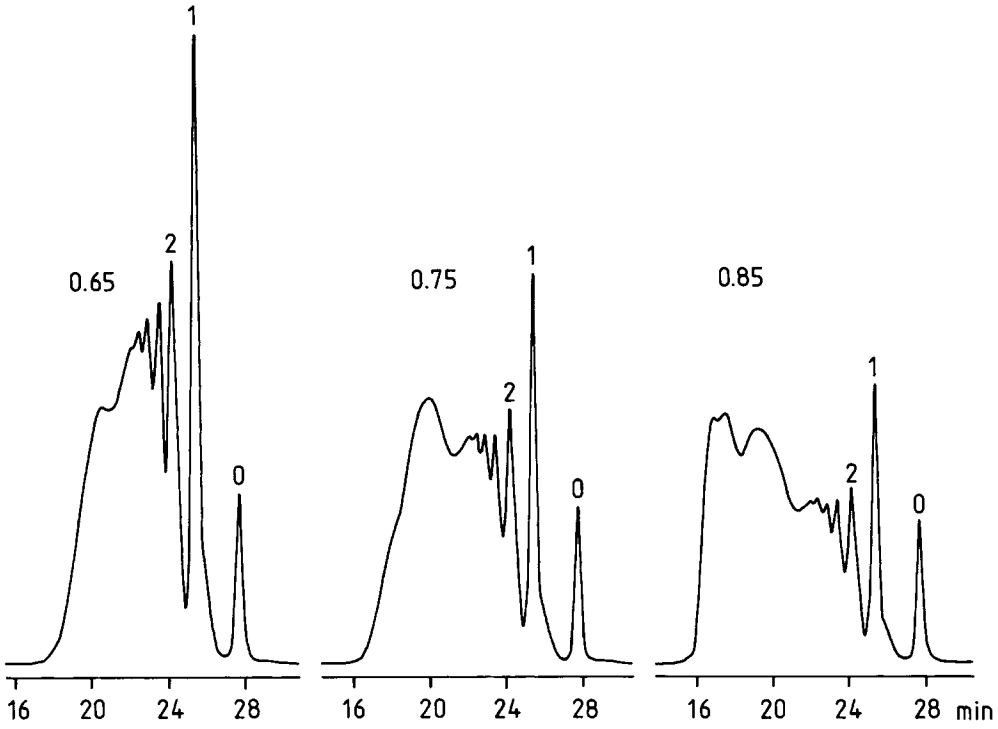

Figure 1 GPC chromatograms of phenol novolac resins (nos. express the moles of formaldehyde used per 1 mol of phenol). Peak identification: (0) phenol; (1,2, · · ·) oligomers according to formula **I.**

phenol and DHDPM (n = 1, dimer) can be easily identified in chromatograms. Other peaks with decreasing elution times can be assigned to trimer, tetramer, . . . (n = 2,3, · · ·). The GPC calibration curve of novolac oligomers was obtained by relating the logarithms of molecular weight to the elution times of individual oligomers. This calibration dependence was compared with that of styrene oligomers and the following relationships were derived:

$$M_{NL} = 0.79621 \times M_{OS}^{0.99997} \quad (1a)$$

$$M_{NL} = 0.90689 \times M_{OS}^{0.97389} \quad (1b)$$

where M_{NL} and M_{OS} are molecular weights of novolac and styrene oligomers at a given elution time. Equation (1a) is valid for the temperature of 25°C, and (1b), for 40°C. The two relationships are valid for THF and the molecular weight range is 200–624. The extrapolation of eq. (1) to higher molecular weights, where individual oligomers do not separate and only polystyrene standards are available, may be used to determine the molecular weight distribution of novolac resins by GPC.

Number-average molecular weights determined by GPC are compared with those determined by vapor-phase osmometry (VPO) in Table I. To calculate M_n from GPC chromatograms, the peak of phenol was not taken into account, and the VPO results were also corrected for the content of phenol that was determined by HPLC. The results are valid for "phenol-free" novolacs. There is a fairly good agreement between the results generated by both techniques. Nevertheless, the procedure used for calibration of GPC columns cannot give a true picture of elution behavior of novolac molecules with high

Table I M_n Values of Phenol-Based Novolacs Determined by GPC and VPO

Sample	M_n (GPC)	M_n (VPO)	$\frac{M_n \text{ (GPC)} - M_n \text{ (VPO)}}{M_n \text{ (VPO)}}$ (%)
1	420	420	0
2	440	450	−2
3	500	510	−2
4	550	620	−11
5	610	560	9
6	640	620	3
7	770	730	5
8	810	980	−17
9	850	990	−14

molecular weights, where different extents of solvation and branching of novolac chains can occur. The calibration dependence obtained by the described process is sure to be more reliable in the low molecular weight region than in the high molecular weight one, and, therefore, M_n values are certainly more accurate than weight-average molecular weights (M_w). The procedure gives results surely more correct than those that would have been calculated by means of polystyrene calibration and it is very simple and time-saving.

The calibration dependence based on eq. (1a) was compared with that obtained by well-known universal calibration:

$$\log M_p = \frac{1}{1 + a_p} \log \frac{K_s}{K_p} + \frac{1 + a_s}{1 + a_p} \log M_s \quad (2)$$

where M_p and M_s are molecular weights of a polymer to be analyzed and a standard (mostly polystyrene), and a and K are constants of the Mark–Houwink equation. Molecular weights of novolac calculated from polystyrene molecular weights using eqs. (1a) and (2) are compared in Table II. The relatively good agreement of generated values verifies the applicability of eqs. (1a) and (1b).

A hyperbolic relationship was found between the content of the dimer (DHDPM) and M_n of the phenol novolac resin (Fig. 2):

$$M_n = 119 + \frac{5088}{w} \quad (3)$$

where w is the dimer content in wt %. As the phenol content in novolac is a random quantity, dependent on the way of removal, eq. (3) was derived for "phenol-free" novolac, i.e., the content of phenol was not taken into account for the determination of M_n and

Table II Molecular Weights of Phenol Novolac Transformed from Polystyrene Molecular Weights Using Eqs. (1a) and (2)

M_{PS}	M_{NL} (1a)	M_{NL} (2)
3000	2390	1830
4000	3180	2690
5000	3980	3630
6000	4780	4630
7000	5570	5690
8000	6370	6810

Mark–Houwink parameters $a_{NL} = 0.28$, $K_{NL} = 0.73$ mL/g (Ref. 10); $a_{PS} = 0.717$, $K_{PS} = 0.0117$ mL/g (Ref. 11) were used for the transformation by eq. (2).

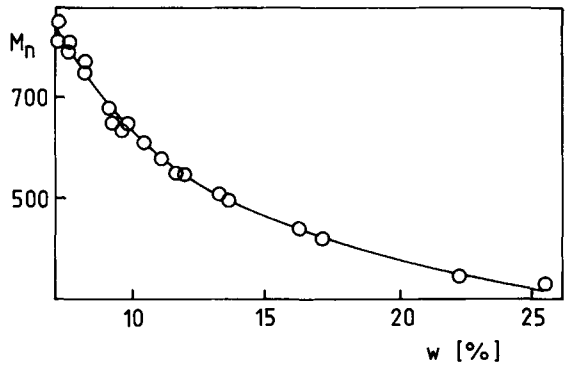

Figure 2 Relationship between the content of DHDPM and M_n value for phenol novolacs.

dimer content. For pure dimer ($w = 100\%$), eq. (3) reaches the value of 170, which corresponds approximately to the molecular weight of the dimer ($M = 200$).

The values of M_n, M_w, and M_w/M_n and the content of the dimer of the couples of novolacs prepared in the same way from phenol or *p*-cresol are compared in Table III. Phenol novolacs, in comparison with *p*-cresol ones, show in all cases significantly higher values of M_n, M_w, and the dispersion ratio M_w/M_n and lower content of the dimer. These facts can be explained as a consequence of the formation of branched molecules with high molecular weights. The dispersion ratio increases significantly with increasing extent of branching. The lower content of dimer corresponds to a possibility of the dimer to react not only with the ends of novolac chains, but also with the internal nuclei.

Table III Comparison of the Values of M_n, M_w, and M_w/M_n and the Content of the Dimer of Novolac Resins Prepared in the Same Way from Phenol or *p*-Cresol

Sample	M_n	M_w	M_w/M_n	Content of Dimer (%)
PN 0.65[a]	430	860	2.0	14.6
CN 0.65	260	350	1.3	24.9
PN 0.8	630	2410	3.8	8.9
CN 0.8	280	410	1.5	19.0
PN 0.9	870	8650	9.9	6.4
CN 0.9	350	510	1.5	12.6

[a] PN, phenol novolac; CN, *p*-cresol novolac; nos. express the mole amount of formaldehyde used per 1 mol of phenol or *p*-cresol.

Typical HPLC chromatograms of phenol and *p*-cresol novolac resins are in Figures 3 and 4. The chromatogram of *p*-cresol novolac is clear and major peaks can be identified with the oligomers according to formula **I.** The obtained chromatogram characterizes molecular weight distribution of the resin. In spite of the 99.9% purity of the starting *p*-cresol, there are many peaks of unidentified byproducts in the chromatogram. In the case of phenol novolac, the peaks of 2-methylolphenol (2-MP), 2,4-dimethylolphenol (2,4-DMP), phenol, 4,4′-dihydroxydiphenylmethane (4,4′-DHDPM), 2,4′-dihydroxydiphenylmethane (2,4′-DHDPM), and 2,2′-dihydroxydiphenylmethane (2,2′-DHDPM) were identified by the addition of standard substances to the analyzed resin. The contents of 2-MP and 2,4-DMP ranged from zero to a maximum of several tenths of a percent for all investigated resins.

Common calibration plots of phenol and isomers of DHDPM (Fig. 5) are linear within the investigated concentration range with correlation coefficients over .999. Relative detector responses expressed in area units per microgram of injected compound are the following: phenol = 1.00; 4,4′-

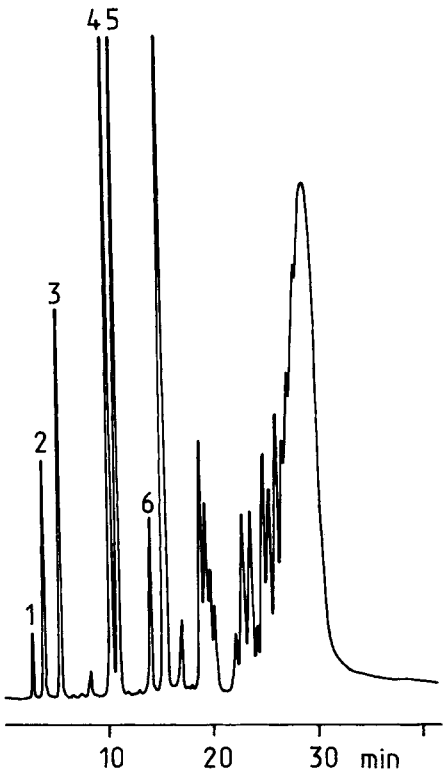

Figure 3 HPLC chromatogram of phenol novolac (phenol/formaldehyde ratio 1/0.65). Peak identification: (1) 2,4-DMP; (2) 2-MP; (3) phenol; (4) 4,4′-DHDPM; (5) 2,4′-DHDPM; (6) 2,2′-DHDPM.

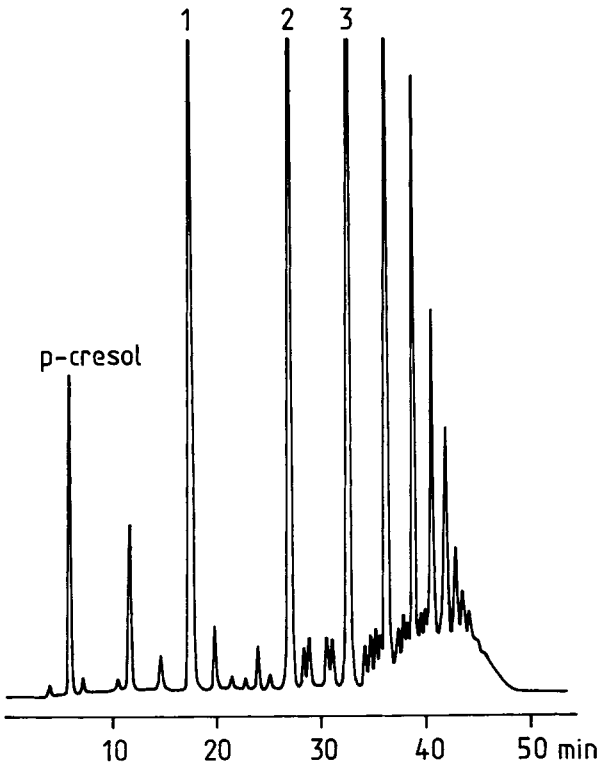

Figure 4 HPLC chromatogram of *p*-cresol novolac (*p*-cresol/formaldehyde ratio 1/0.8). Peak identification: (1,2,3, · · ·) oligomers according to formula **I.**

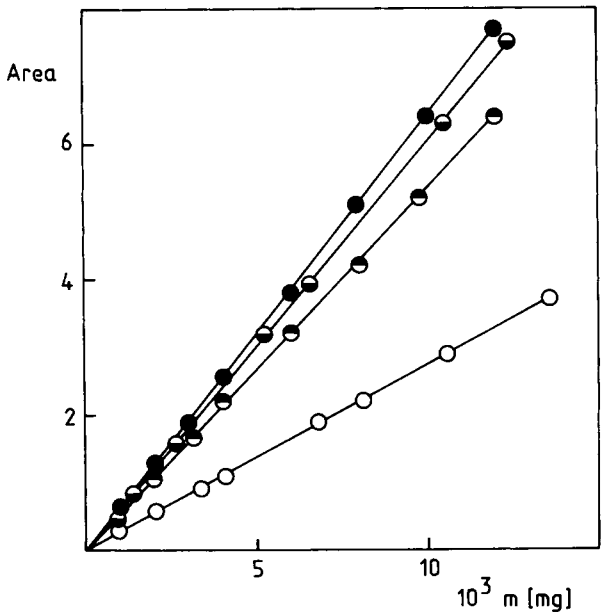

Figure 5 Detector response calibration plots for phenol and DHDPM isomers: (○) phenol; (◓) 4,4′-DHDPM; (◒) 2,4′-DHDPM; (●) 2,2′-DHDPM.

Table IV Comparison of Area Percentages of Peaks of Phenol and DHDPM in GPC and HPLC Chromatograms of Phenol Novolacs with the Actual Contents of These Compounds Determined by HPLC by Calibration of Detector Response by Pure Compounds

	HPLC Area (%)		GPC Area (%)		Content (%)	
Sample	Phenol	DHDPM	Phenol	DHDPM	Phenol	DHDPM
1	2.1	16.0	3.9	16.3	4.3	15.6
2	6.0	13.8	9.9	14.5	12.9	13.9
3	2.1	11.3	3.8	12.8	4.8	12.0
4	3.0	8.7	4.7	9.1	6.2	8.7
5	2.2	7.4	3.4	7.8	4.4	7.1
6	1.8	6.6	2.3	6.9	3.1	5.5
7	4.4	9.4	7.0	9.6	8.6	8.5
8	0.0	21.9	0.0	25.4	0.0	25.1
9	7.5	13.5	9.6	15.0	15.7	13.5
10	4.2	9.4	3.7	9.2	7.7	8.2

DHDPM = 1.97; 2,4′-DHDPM = 2.23; and 2,2′-DHDPM = 2.36. The UV response of phenol is (at 280 nm) approximately one-half of that of DHDPM, the isomers of which exhibit slightly different responses. The relative areas of the peaks of phenol and DHDPM in GPC and HPLC chromatograms are compared with the actual contents of these compounds determined by HPLC by calibration of the detector response by the pure compounds in Table IV. Higher contents of phenol in comparison with relative areas correspond to lower phenol UV response. The values of DHDPM content determined by HPLC are in good agreement with the relative areas of DHDPM peaks in chromatograms, which verifies the independence of the response factor of novolac oligomers on polymerization degree.[4]

Examples of Practical Applications

An example of detailed characterization of phenol novolac resins, differing in the phenol/formaldehyde ratio used for preparation, is given in Table V. To calculate M_n and M_w values, the GPC calibration curve was constructed by relating the logarithms of molecular weight and elution times of the first six oligomers that were separated on the column set that was employed for the analyses. In the region of lower elution times, the column set was calibrated by polystyrene standards whose molecular weights were transformed by eq. (1). The content of phenol was determined by calibration of the detector response by calibration solutions with known phenol concentration. The contents of DHDPM and higher

Table V An Example of the Arrangement of GPC Results for Phenol Novolac Resins Differing in Phenol/Formaldehyde Ratio Used for the Preparation

	Compound/Content (%)							
			Oligomer (n)					
Sample	Phenol	DHDPM	2	3	4 + Higher	M_n	M_w	M_w/M_n
0.65[a]	4.3	16.2	12.6	9.9	57.0	420	800	1.9
0.70	4.8	12.7	10.2	8.1	64.2	500	1160	2.3
0.75	3.4	11.1	9.0	7.2	69.3	550	1580	2.9
0.80	6.0	9.0	7.3	5.8	71.9	640	2380	3.7
0.85	4.4	7.7	6.0	4.8	77.1	770	4780	6.2
0.90	3.1	6.8	5.5	4.4	80.2	850	8920	10.5

[a] Numbers express the moles of formalehyde used per 1 mol of phenol.

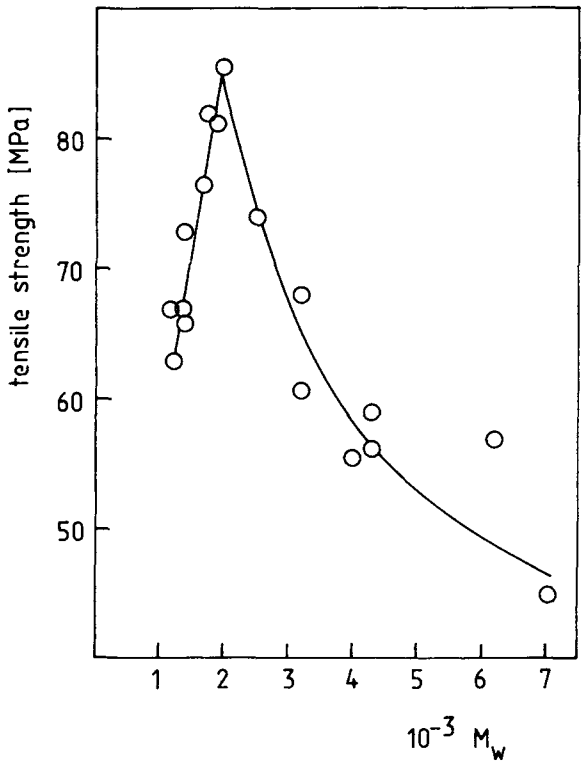

Figure 6 Dependency of the tensile strength of abrasive material on M_w of phenol novolac used for the preparation.

oligomers were equalized with corresponding area percentages. Such a schedule obtained by the GPC technique gives a good view of the molecular structure of samples and can be used for the evaluation of production reproducibility, for comparison of samples made in different ways, produced by various manufacturers, or for searching the relation between the structure of starting resins and properties of cured materials based on them.

The dependency of tensile strength of abrasive material on molecular weight of the novolac resin used for preparation is shown in Figure 6. The abrasive material tested was made from corundum grains, poly(vinyl butyral), hexamethylenetetramine, phenol novolac, and low molecular weight resol resin. The tensile strength of tested materials can be explained in the sense of the molecular structure of the starting novolac that is cured by reaction with hexamethylenetetramine and methylol groups of resol. The end nuclei of novolac molecules have two reactive sites, while the inner nuclei have only one, and in the case of branched points, they have no position capable of reaction with curing agents. The molecules with high molecular weight and a high degree of branching are less reactive and, consequently, the tensile strength increases with de-

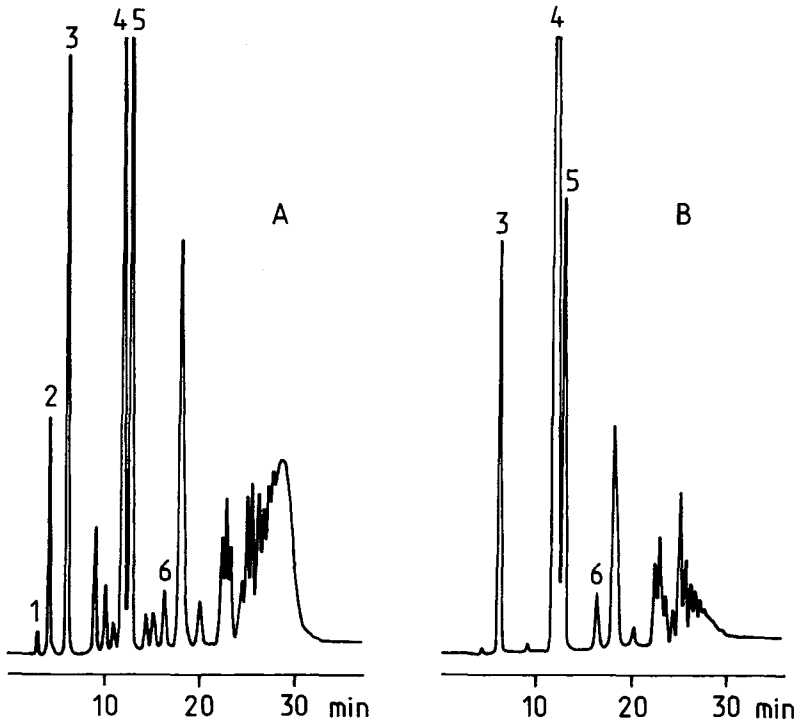

Figure 7 HPLC chromatograms of bisphenol F: (A) technical product; (B) the same product after crystallization from benzene. Peak identification as in Figure 3.

creasing molecular weight to an optimum value, where a further fall in molecular weight decreases the tensile strength as a result of too short fundamental chains of starting novolac.

Bisphenol F (4,4′-DHDPM) is an important starting material for manufacturing epoxy resins of a certain type. Technical bisphenol F may be considered as a low molecular weight novolac resin and can be analyzed in the same way. HPLC chromatograms of two bisphenol F samples (before and after crystallization from benzene) are shown in Figure 7. The method provides the content of the major component and of byproducts (2-MP, 2,4-DMP, 2,4′-DHDPM, 2,2′-DHDPM, oligomers).

CONCLUSIONS

Chromatographic comparison of novolac resins made from phenol or *p*-cresol confirms the presence of branched molecules in phenol-based resins. In case of *p*-cresol novolacs, HPLC gives a good characterization of molecular weight distribution. In the case of phenol-based novolacs, HPLC makes it possible to determine phenol, reaction intermediates (methylolphenols), and DHDPM isomers. In the region of higher polymerization degrees, the presence of high number of positional isomers of individual oligomers limits the HPLC applicability. GPC enables the description of molecular weight distribution, the determination of the content of phenol, DHDPM, and several higher oligomers. The values of M_n determined by GPC and VPO are in fairly good agreement. M_n can be estimated by eq. (3) from DHDPM content.

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