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SEPARATION OF PREPOLYMERS OF PHENOL–FORMALDEHYDE RESINS BY SUPERCRITICAL-FLUID CHROMATOGRAPHY

SADAO MORI*
Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514 (Japan)
and
TOSHINORI SAITO and MAKOTO TAKEUCHI
New Project Development Office, JEOL Ltd., Akishima, Tokyo 196 (Japan)
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SUMMARY

Prepolymers of random novolac and resol resins were separated according to the number of nuclei (phenol groups) and the number of methylol groups attached to the nuclei. Temperature programming elution at a constant column pressure and constant flow-rates of both carbon dioxide and a modifier was applied in the order of decreasing column temperature. Two pumps were installed in a supercritical chromatography system to deliver carbon dioxide and a modifier independently. Ethanol was used as the modifier. The initial column temperature was 120 or 150°C and the programming rate was 3 or 4°C/min. The back pressure at the outlet of the UV detector was between 154 and 178 kg/cm^2. Nine oligomers for novolac resins from dihydroxydiphenylmethanes (DPM) (dimer, dinuclear) to decanuclear oligomers were separated. The percentages of three isomers, 2,2′-, 2,4′- and 4,4′-DPM, of dinuclear oligomers were 6, 26 and 68%, respectively. Seven isomers of trinuclear novolac oligomers were assigned. Molecular weight averages were calculated without any calibration standards, *e.g.*, $\bar{M}_w$ = 417 and $\bar{M}_n$ = 366 for the sample examined here. Mono- to pentanuclear resol oligomers were separated. Peaks for 2- and 4-methylol phenols, 2,4- and 2,6-dimethylol phenols and 2,4,6-trimethylol phenol were assigned. Di- and trinuclear resol oligomers were separated according to the number of methylol groups attached to the phenol groups.

INTRODUCTION

Prepolymers of phenolic resins, intermediate low-molecular-weight products, are obtained by the condensation of phenol (or substituted phenols) and formaldehyde. The prepolymers (oligomers) are then cured by heating or with a suitable cross-linking agent to produce hard and solvent-insoluble products. There are three types of phenolic resin prepolymers, random novolac, high-ortho novolac and resol, depending on the catalyst. The structures and the compositions of the reaction products are complex and considerably different depending on the catalyst and the experimental conditions.

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The determination of the molecular species of these prepolymers often requires the application of several separation techniques, including high-performance liquid chromatography (HPLC), size-exclusion chromatography (SEC), and gas chromatography–mass spectroscopy (GC–MS). Resol resins were separated by SEC and the elution positions of several isomers of mono-, di- and trinuclear resol resins were estimated[1]. However, because of the limited separation capacity in SEC, only 2-methylol phenol (2-MP), 4-MP, 2,6-dimethylol phenol (2,6-DMP), 2,4-DMP and 2,4,6-trimethylol phenol (2,4,6-TMP) were separated by semi-micro HPSEC in a system which had 103 000 theoretical plates[2]. Novolac resins were also separated by the same SEC system and isomers of di-, tri-, tetra- and pentanuclear compounds were identified[2].

HPLC is the most suitable technique for the separation of such complex materials because of its high resolution. Reaction products from higher phenols and formaldehyde[3], ortho-novolac resins[4], phenol novolac and resol resins[5] and epoxy resins[6] were separated by HPLC and several isomers were characterized. However, the identification of the peaks separated is still a matter of debate. For the identification of complex structures of phenolic resins, the application of at least MS is required. GC–MS is capable of both the separation and identification of complex materials, if they can be separated by GC. Silylation of phenolic resins may enable the separation of these resins by GC[7–12]. Disadvantages of the silylation of phenolic resins followed by GC–MS are the unreliable silylation and the inability to apply this technique to higher-molecular-weight (higher nuclei) species because of their low vapour pressures.

Supercritical-fluid chromatography (SFC) has recently attracted serious attention because of its high resolution and its ease of application, similar to GC–MS. The analyses of relatively high-molecular-weight compounds have been reviewed[13]. Pressure programming to increase the pressure of the supercritical fluid (and increase its density) is usually required in the separation of oligomers which contain species with widely differing molecular weights. The addition of a polar solvent to the mobile phase is also effective in separating relatively high-molecular-weight materials[14] as well as polar oligomers[15].

This paper is concerned with a preliminary experiment on the separation of phenol–formaldehyde random novolac and resol resins by SFC. Temperature programmed elution (decreasing temperature) at a constant column pressure was applied and ethanol was added to the mobile phase as a modifier.

EXPERIMENTAL

Apparatus and elution

A JEOL supercritical-fluid chromatograph Model JSF-8800 (JEOL, Akishima, Tokyo, Japan) was used with an ultraviolet (UV) absorption detector Model CAP-UV01 operated at 210 nm. The volume of the flow cell was 1 μl and the path length was 5 mm. The pressure of the supercritical fluid was maintained constant at the detector outlet by using a constant pressure release valve actuated mechanically with a spring, screwdriver and a low-dead volume digital pressure meter. The SFC apparatus consists of two pumps, one for the delivery of liquefied carbon dioxide as the supercritical fluid (Model CAP-G03) and the other for the delivery of a modifier (Model CAP-L02). Ethanol was used as a modifier. One or two columns (25 cm × 1.7

mm I.D.) packed with silica-ODS (particle diameter 5 μm) were used and stored in a column oven to maintain the column temperature constant. A GC column oven (Hewlett-Packard Model HP 5980) was used after necessary modification for programming of descending column temperature.

The flow-rate of liquefied carbon dioxide was 300 μl/min and that of the modifier 100 or 50 μl/min. The initial column temperature was adjusted to 150 or 120°C and the column temperature was lowered at a rate of 3 or 4°C/min to 50 or 60°C. The pressure of the supercritical fluid flowing into a column was monitored at the inlet and recorded on a chart. The back pressure of the SFC system was read at the outlet of the UV detector.

Samples

Random novolac resins were prepared using 10 g of phenol, 7.4 g of a 37% formaldehyde aqueous solution (molar ratio of phenol to formaldehyde, 1:0.85) and 0.1 ml of a 3.5% hydrochloric acid solution as a catalyst. The reaction was performed at 85°C for 30 min and the reaction mixture was diluted in water, then allowed to cool. Unreacted phenol and formaldehyde were removed in vacuum together with water.

Resol resins were prepared using 10 g phenol, 15.7 g of a 37% formaldehyde aqueous solution (molar ratio of phenol to formaldehyde, 1:1.8) and 0.5 ml of a 10% sodium hydroxide solution as a catalyst. The reaction was performed at 80°C for 1 h and the reaction mixture was treated similarly to that for novolac resins.

These prepolymers were dissolved in tetrahydrofuran at about 5% concentration and the volume of these solutions injected on the column was 0.5 μl.

RESULTS AND DISCUSSION

Random novolac resins

Fig. 1 shows a typical SFC separation according to the number of nuclei. Nine oligomers from dihydroxydiphenylmethane (dimer, dinuclear) oligomers to decanuclear novolac oligomers were clearly separated and observed. The structure of novolac resins is depicted as polynuclear phenols with a methylene linkage between the aromatic nuclei[12]. The number of nuclei (the number of phenyl groups) is estimated as in Fig. 1; *i.e.*, peak c is dinuclear (dihydroxydiphenylmethanes), peak d trinuclear, peak e tetranuclear, etc.

According to the results obtained by GC–MS[12], methylol groups were not attached to each aromatic nucleus of novolac resins and the mass difference between each oligomer was 106 a.m.u. Therefore, molecular weight averages of the prepolymers can be calculated from the peak area of each oligomer and its molecular weight, if the UV response of each oligomer can be assumed to be equal. The molecular weight and relative peak intensity of each oligomer are listed in Table I. From these data, molecular weight averages can be calculated as the number average molecular weight, $\bar{M}_n = 366$ and the weight average molecular weight, $\bar{M}_w = 457$.

The content of phenol remaining in novolac resins used in this work was about 5%. The number average molecular weight calculated by including phenol was 319. The molecular weight obtained by vapour-pressure osmometry was equivalent to this value. Therefore, the method proposed here can calculate both molecular weight averages, including and excluding phenol. The calculation of molecular weight

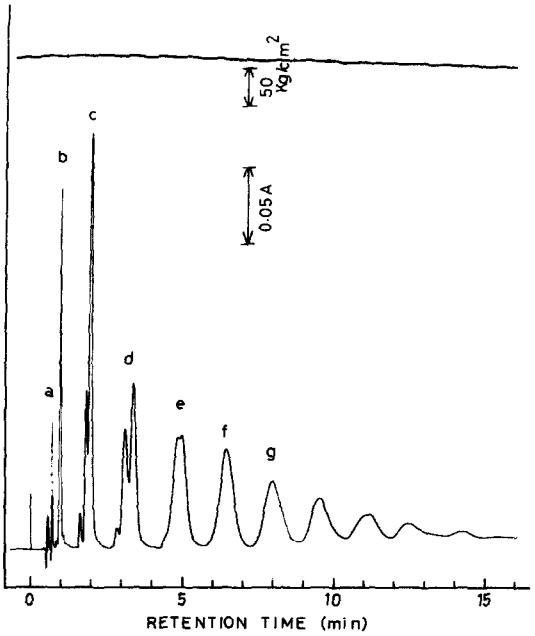

Fig. 1. SFC chromatogram of random novolac resins separated according to the number of nuclei. Flow-rates: carbon dioxide, 300 μl/min; ethanol, 100 μl/min. Column temperature: initial 120°C, final 50°C, programming rate 4°C/min. Back pressure: 162 kg/cm^2. Detector: UV at 210 nm, 0.5 a.u.f.s. Column: 250 mm × 1.7 mm. Peak identification: a = impurities; b = phenol; c = dinuclear; d = trinuclear; e = tetranuclear; f = pentanuclear; g = hexanuclear novolac resins.

averages by SEC requires the construction of a calibration graph of log molecular weight *vs.* retention volume and also the estimation of calibration parameters[16]. Our method does not require any calibration standards nor the estimation of calibration parameters. It is a direct method to obtain molecular weight averages (a self calibration method for calculating molecular weight averages) in contrast to SEC which requires calibration standards and is designated an indirect method.

TABLE I

MOLECULAR WEIGHT AND RELATIVE PEAK INTENSITY OF EACH OLIGOMER OF NOVOLAC RESINS

Number of nuclei	*Molecular weight*	*Relative peak intensity (from Fig. 1) (%)*
2	200	20.1
3	306	19.1
4	412	17.0
5	518	15.0
6	624	12.4
7	730	7.9
8	836	4.9
9	942	2.6
10	1048	1.0

The initial column temperature in Fig. 1 was 120°C and the column temperature 15 min after the injection of a sample solution was 60°C. The flow-rates of both carbon dioxide and ethanol were kept constant at 300 and 100 μl/min, respectively. The back pressure at the detector outlet was also kept constant, at 162 kg/cm^2. Therefore, the more condensed fluid flowed through the column at lower column temperature. Our (decreasing) temperature programming is a kind of density programming at constant column pressure.

Our SFC system has different features from other SFC systems for density programming and temperature programming. Density programming of other SFC systems utilizes the increase in flow-rate of a fluid or an increase in back pressure. Density programming in our SFC system arises from the result of temperature programming which is in the order of descending column temperature, though in other systems it is normally in the order of ascending column temperature. The cell block of the UV detector in this work is cooled to 20–25°C, and thus the fluid from the column becomes a liquid in an UV cell. Therefore, as far as the flow-rates at the two pumps and the back pressure at the outlet of the UV detector are constant, the liquid density at the UV cell is kept constant in spite of the change in column temperature, resulting in a stable baseline.

The column inlet pressure was monitored and recorded on a chart, and is shown at the top of Fig. 1. The initial column inlet pressure was 212 kg/cm^2 and the pressure 15 min after the sample injection was 220 kg/cm^2. The column pressure during the separation was very stable. As the back pressure in Fig. 1 was 162 kg/cm^2, the pressure drop between the column inlet and the detector outlet was 50 kg/cm^2 at the start.

The increase in column temperature results in a decrease in the density of the fluid, and therefore in an increase in retention time of a sample solute. In other words, the resolution of lower-molecular-weight solutes may be improved at the lower density of the fluid. An example is shown in Fig. 2. The initial temperature was 150°C and the back pressure was 178 kg/cm^2. Other experimental conditions were as in Fig. 1. The column temperature at the retention time of 15 min was 90°C, where hexanuclear novolac resins appeared. These oligomers appeared at a retention time of 8 min in Fig. 1, where the column temperature was 88°C. The column inlet pressure was 214 kg/cm^2 at the start and 220 kg/cm^2 20 min after the sample injection. The pressure drop between the column inlet and the detector outlet was 36 kg/cm^2 at the start.

Besides the increase in retention time of these oligomers, the resolution of di- and trinuclear oligomers was much improved. Three peaks for dinuclear oligomers and more than three peaks including shoulder peaks were observed for trinuclear oligomers. According to the GC–MS analysis[8], peak c1 can be assigned to 2,2′-dihydroxydiphenylmethane (2,2′-DPM), peak c2 to 2,4′-DPM and peak c3 to 4,4′-DPM. The percentages of these isomers were calculated from the peak areas as 6 (peak 1), 26 (peak 2), and 68% (peak 3). Trinuclear novolac oligomers should have more than three isomers and seven isomers were separated and identified by using the results of GC–MS[8].

For further improvement of the separation of trinuclear oligomers the flow-rate of the modifier (ethanol) was decreased from 100 to 50 μl/min and two columns were connected. The results are shown in Fig. 3. The column inlet pressure at the start was 218 kg/cm^2. Five peaks including one shoulder peak were observed. Trinuclear oligomers appear at retention times between 19 and 24 min. Peaks can be assigned by

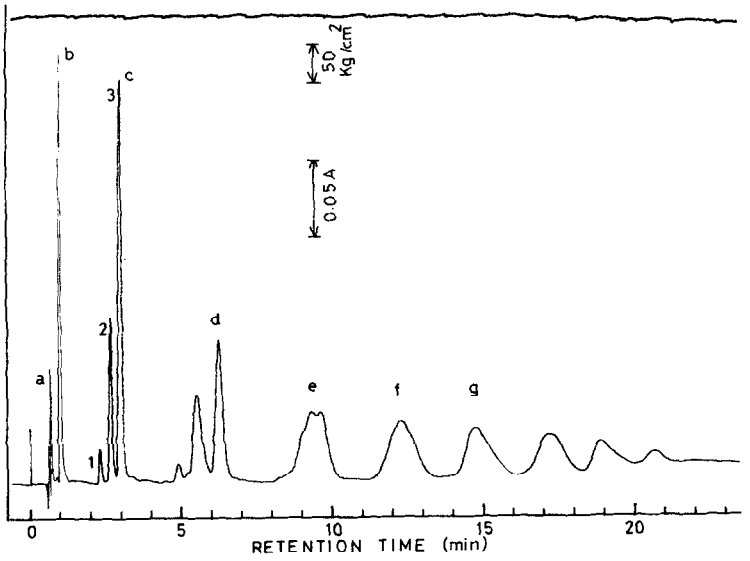

Fig. 2. SFC chromatogram of random novolac resins. Column temperature: initial 150°C, final 50°C, programming rate 4°C/min. Back pressure: 178 kg/cm^2. Other conditions and peak identification as in Fig. 1.

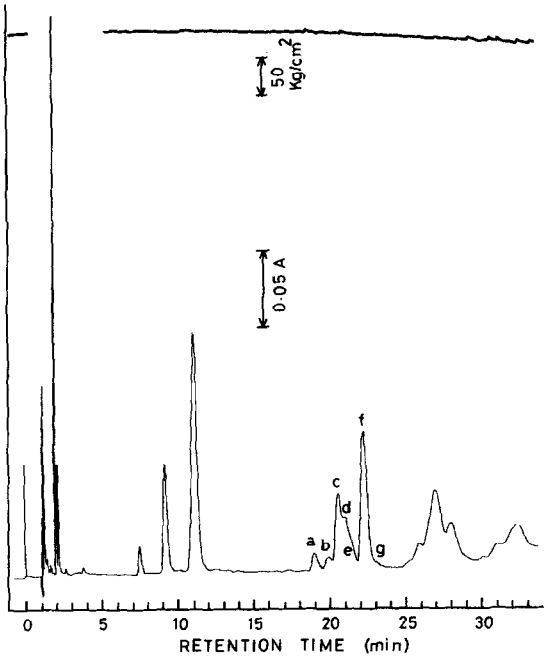

Fig. 3. SFC chromatogram of random novolac resins. Flow-rates: carbon dioxide, 300 μl/min; ethanol, 50 μl/min. Column temperature: initial 150°C, final 60°C, programming rate 3°C/min. Back pressure: 165 kg/cm^2. Detector: UV at 210 nm, 0.5 a.u.f.s. Column: 250 mm × 1.7 mm I.D. × 2. For peak identification, see text.

GC–MS[8] as follows: a is 3-(2-hydroxybenzyl)-2,2′-dihydroxydiphenylmethane (3,2-Bz-2,2′-DPM), b is 5,2-Bz-2,2′-DPM, c is 3,4-Bz-2,2′-DPM, d is 5,4-Bz-2,2′-DPM, e is 5,2-Bz-2,4′-DPM, f is 3,4-Bz-2,4′-DPM and g is 5,4-Bz-2,4′-DPM. Peaks e and g are observed by peaks d and f and are at the bottom of the right-hand side of those peaks. These assignments were based on the fact that the relative peak intensities of di- and trinuclear oligomers observed by SFC resembled those obtained by GC–MS[8] under the assumption that the elution order of novolac resin isomers by SFC was the same as that by GC.

Resol resins

The base-catalyzed condensation products of phenol with formaldehyde were resol-type resins comprised of mono- and polynuclear methylolated phenols[12] and their hemiformal isomers[10]. ^{1}H NMR spectrometric investigation of resol indicated the absence of methylene ether linkages and hemiformal groups[12].

SFC chromatograms of resol resins are shown in Fig. 4. The initial column temperature and other chromatographic conditions were as in Fig. 1. Peaks a are impurities in the sample solution and peak b is phenol. Peaks c–e are assigned to mononuclear resol oligomers, f–i to dinuclear, j–m to trinuclear and n to tetranuclear resol oligomers.

Similarly to the case of the novolac resins, the initial column temperature was increased in an attempt to improve the resolution of mono- and dinuclear resol oligomers. The results are shown in Fig. 5. The resolution of di- and trinuclear resol oligomers was not much improved as expected in contrast to novolac oligomers but

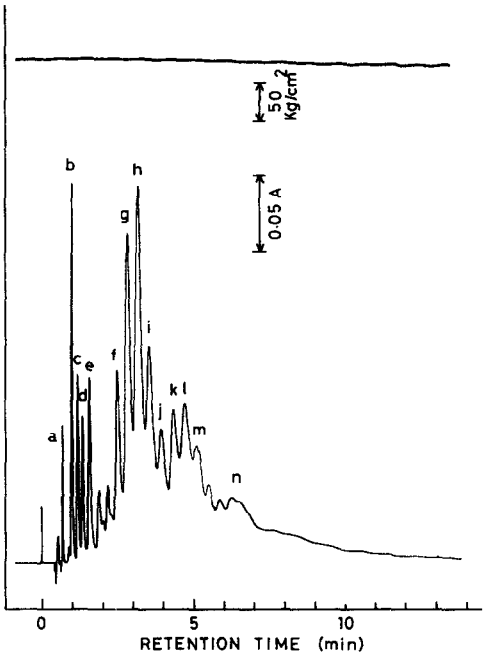

Fig. 4. SFC chromatogram of resol resins. Conditions as in Fig. 1. Column inlet pressure at the start: 200 kg/cm^2. For peak identification, see text.

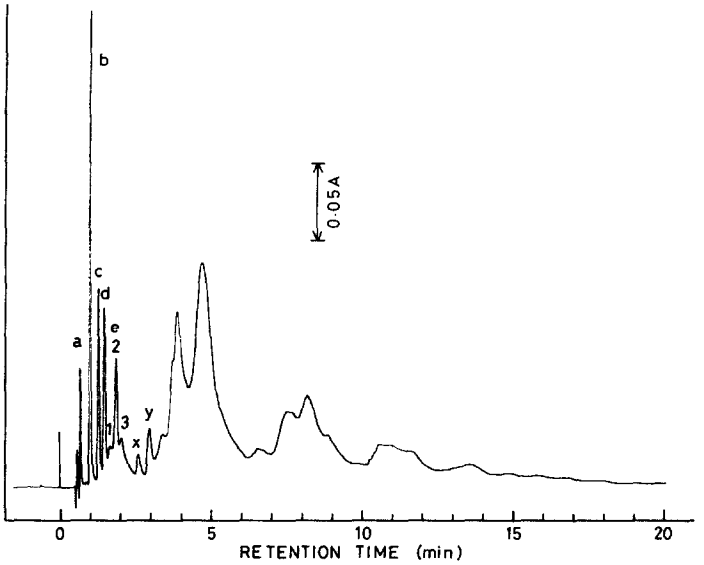

Fig. 5. SFC chromatogram of resol resins. Conditions as in Fig. 2 except the back pressure which was 173 kg/cm^2. For peak identification, see text.

peak e was split into three peaks. Peak c can be assigned to 2-MP, d to 4-MP from the results of GC–MS[9]. Similarly, peak e1 may be assumed to be 2,6-DMP, e2 to be 2,4-DMP and e3 to be 2,4,6-TMP. Oligomers from mono- to pentanuclear resols were separated under these SFC conditons.

Results obtained by decreasing the flow-rate of the modifier to 50 μl/min and connecting two columns as in Fig. 3 are shown in Fig. 6. Resol oligomers having different numbers of nuclei (aromatic groups) were clearly separated from each other. Novolac type oligomers were observed in resol resins by GC–MS[9]. Peaks x and y in Fig. 5 have the same retention times as those of 2,4′-DPM and 4,4-DPM in Fig. 2. However, the retention times of peaks x and y in Fig. 6 were not coincident with those of 2,4′-DPM and 4,4′-DPM in Fig. 3. Therefore, it was assumed that these DPMs were not included in the resol resins examined in our work. The resolution of mononuclear resol resins was not greatly improved, though the content of the modifier in the mobile phase was decreased. A peak at the front bottom of peak d and peaks x and y might be due to hemiformal isomers[10]. Peak e1 in Fig. 5. is assumed to be hidden in front of peak e in Fig. 6.

In dinuclear resol [methylolated dihydroxydiphenylmethanes (DMP)], fifteen isomers, *i.e.*, four methylol DMP, five dimethylol DMP, four trimethylol DMP and two tetramethylol DMP, were confirmed by GC MS[11]. Peak f in Fig. 6 may be provisionally assigned to methylol DMP, g to dimethyl DMP, h to trimethylol DMP and i to tetramethylol DMP. From the peak width, it can be assumed that several isomers are included in peaks f and g.

From a comparison of Fig. 4 with Fig. 6, peak j in Fig. 4 may belong to trinuclear resol oligmers as do peaks k, l and m. Trinuclear resol oligomers are composed of five different methylol groups such as mono-, di-, tri-, tetra- and pentamethylol trinuclear

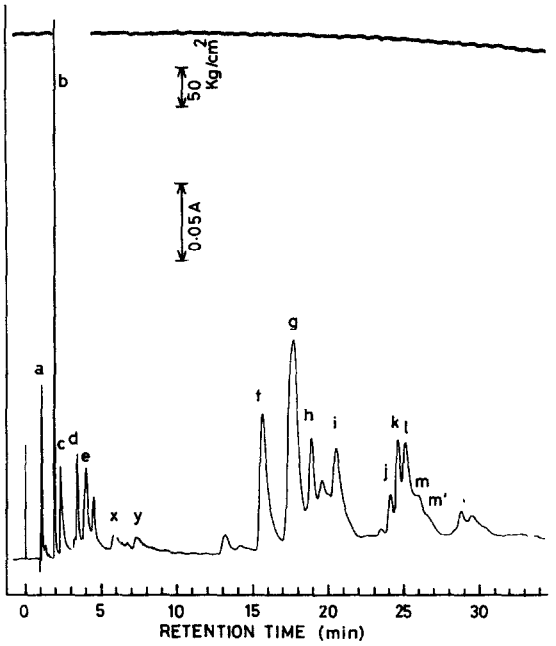

Fig. 6. SFC chromatogram of resol resins. Conditions as in Fig. 3 except the back pressure which was 154 kg/cm^2. The column inlet pressure at the start was 208 kg/cm^2. For peak identification, see text.

resol oligomers, including several isomers. Peaks j–m in Fig. 6 can be assigned to these oligomers in that order. Peaks n may be tetranuclear resol oligomers. Peaks f–n in Fig. 4 may correspond to peaks f–n in Fig. 6, though the assignment is not easy. The SFC conditions described in Fig. 4 (same as in Fig. 1) can separate resol oligomers according to the number of nuclei (phenol groups) and the number of methylol groups.

To conclude, the assignment of peaks in SFC chromatograms for both novolac and resol resins has been made by comparison with the results of GC–MS in the literature. However, these assignments are still provisional and SFC–MS is required for accurate assignments. SFC–MS is recognized to be easier than LC–MS and it is now under consideration. The technique described here is temperature programming SFC with decreasing column temperature at constant flow-rates of both carbon dioxide and a modifier and constant back pressure. This programming has the same effect as density programming SFC in increasing the fluid density, and has the advantage of a stable detector baseline because of the constant back pressure and constant temperature at the detector cell.

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