Separation and characterisation of phenol–formaldehyde (resol) prepolymers using packed-column supercritical fluid chromatography with APCI mass spectrometric detection

The Analyst

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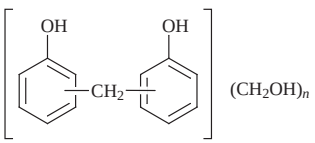
Received 2nd March 1999, Accepted 17th May 1999

Packed-column supercritical fluid chromatography (pSFC), with negative-ion atmospheric-pressure chemical-ionisation (APCI) mass spectrometric (MS) detection has been used to analyse a commercial phenol–formaldehyde (resol) prepolymer. After initial optimisation of the system using a standard dimer species [bis(2-hydroxyphenyl)methane], it was possible to identify positively 34 components in the resin sample, including the starting reagents (phenol and cresol), and a range of dimers, trimers, tetramers and pentamers, with varying phenol/cresol ratios and amounts of methylol substitution. The method requires no pre-separation derivatisation of the resin sample, and a chromatographic run time of *ca.* 10 min.

Introduction

Phenolic resins are some of the oldest synthetic polymers, and include materials such as Bakelite.[1] Their manufacture involves two stages: (i) prepolymer production by an acid or base catalysed condensation reaction between phenol (or substituted phenols) and formaldehyde; and (ii) curing of these low molecular weight intermediates by the use of heat or a cross-linking agent.

There are three basic types of prepolymer (random novolac, high-*ortho* novolac and resol), depending on the conditions used for the condensation reaction. Acid catalysed condensations produce novolac type prepolymers, whereas base catalysed conditions result in the formation of the resol prepolymer. We will concentrate in this study on resol prepolymers. A schematic representation of the compound types for the resol dimer is shown below. The formula enclosed in square brackets denotes the basic structure, and the number of methylol substituents associated with the oligomer (n = 0–4) is given in parentheses. Positional isomers for both methylol groups and the methylene linkage are associated with each of the structures, thus giving rise to a highly complex mixture.



The compositions of the prepolymers are variable and depend upon the conditions of the condensation reaction. Since the properties of the cured resin are dependent upon the prepolymer composition, characterisation of the prepolymer is desirable. Several analytical techniques have been applied to the determination of the chemical composition and structure of molecular species in these mixtures, including GC-MS,[2–5] HPLC,[6] gel permeation chromatography (GPC),[7] NMR[8] and MS.[9] Direct GC analysis of the prepolymers is impossible without derivatisation, due to the involatility and thermal instability of the compounds. GC separation of the isomers of novolac[2] and resol[3] prepolymers was achieved by formation of the trimethylsilyl derivatives. Subsequent detection by MS provided structural information for the identification of the components, and even enabled differentiation between positional isomers. However, GC-MS could not be applied to oligomers with more than three monomer units, due to the involatility of the compounds even after derivatisation. Pyrolysis GC-MS has been applied to the determination of the sequence of phenolic units and the position of the methylene linkage in the oligomers of a novolac resin.[10] GPC has been applied to resol and novolac resins, but identification was difficult due to poor separation of the components. HPLC has been the most suitable technique thus far, as it can be applied to higher molecular weight compounds than can GC and provides higher resolution than GPC. However, identification of the components still proved to be difficult. Direct MS analysis using soft ionisation techniques, including field desorption (FD), fast atom bombardment (FAB), thermospray (TSP) and desorption chemical ionisation (DCI), has been applied to the characterisation of novolac and resol prepolymers.[9] Soft ionisation methods produce simple spectra containing molecular or quasi-molecular ions, thus allowing characterisation of the resin in terms of the chemical species present, molecular weight distribution and average molecular weights. FD proved to be the most successful method for direct MS analysis of the prepolymers. However, resols still exhibited fragmentation due to thermal decomposition, which made the interpretation of the spectra difficult. Therefore, analysis of the acetylated resol derivative was performed to generate spectra without fragmentation. ^{1}H-NMR has been used for the general characterisation of the condensation products,[8] but this is unsuitable for the determination of molecular species in a complex mixture.

Packed-column supercritical fluid chromatography (pSFC) is suitable for the analysis of high molecular weight compounds, and is capable of providing faster analysis times and improved resolution compared with HPLC. Application of pSFC, using carbon dioxide with a methanol modifier, has already been demonstrated for the separation of the oligomers of novolac and resol prepolymers.[11] However, in both cases, UV detection was used and identification of individual components was difficult. Therefore coupling SFC with atmospheric-pressure chemical-ionisation mass spectrometry (APCI-MS) would allow separation and identification of the components in the prepolymer. By employing a soft ionisation technique, such as APCI, it is possible to obtain molecular weight information, which is

invaluable for the identification of components in such a complex mixture.

We have recently demonstrated the successful application of pSFC-APCI-MS to the analysis of cannabis samples,[12] polymer additives[13] and explosive substances.[14]

Experimental

All SFC analyses were performed using a Gilson packed-column SFC system (Anachem, Luton, UK) coupled to the APCI source of a Trio 2000 quadrupole mass spectrometer (VG Biotech, Altrincham, UK). The SFC mobile phase was delivered using two Gilson piston pumps. A microprocessor-controlled Gilson 308 pump, fitted with a chiller unit (Anachem) to cool the pump head to −10 °C, was used to deliver SFC-grade CO_2 (99.99%, BOC, Guildford, UK). A Gilson 306 pump was used for the programmed addition of methanol modifier to the mobile phase. The pumps were connected to a Gilson 311C dynamic mixer to ensure homogeneity of the mobile phase. UV detection was carried out at 230 nm, using a Jasco 875-CE UV detector (Jasco, Tokyo, Japan).

Separations of the resol standards and mixtures were achieved using a 25 cm × 4.6 mm id column with a C_{18} stationary phase. Samples were introduced using a 10 μl injection loop and eluted using a CO_2 mobile phase with a methanol modifier gradient. Chromatographic details are given in the appropriate Results section.

The packed-column SFC system was interfaced to APCI-MS using a tapered 75 μm id restrictor, with a heated tip, inserted into the APCI probe. The position of the restrictor and probe, the gas flow rates and probe temperature were all separately optimised.[15] Comparison with UV chromatograms showed that the interface had some effect on the chromatographic resolution. There was therefore some evidence for mass-transfer problems leading to a two-phase system and impaired resolution.[16] However, using mass-selected chromatograms, effective separations were possible, as will be discussed below. The mass spectrometer was operated in both positive- and negative-ion modes.

BP International Ltd. (Sunbury-on-Thames, UK) provided a resol sample for characterisation. The resol was produced from a condensation reaction using phenol, cresol and formaldehyde, which results in a mixture containing a range of oligomers substituted with one or more methylol groups. In addition each oligomer may contain a varying number of cresol and phenol units. A 1.5% (w/v) solution was prepared in methanol for analysis by SFC-MS.

Reference mass spectra were obtained for a resol dimer standard using a 0.04 mg ml^{-1} solution of bis(2-hydroxyphenyl) methane (M_w = 200) (Aldrich, Gillingham, Dorset, UK) in methanol. Mass spectra were recorded in both positive- and negative-ionisation modes. Tuning and optimisation of the MS parameters were also performed using replicate injections of the standard solution. Details of the optimisation processes are available as Electronic Supplementary Information.†

Results and discussion

Optimisation of chromatographic conditions

SFC-MS analysis of bis(2-hydroxyphenyl)methane was used to carry out the optimisation. It was first necessary to determine whether positive- or negative-ion APCI conditions were more suitable for the detection of such compounds. A positive-ion CI reference spectrum for bis(2-hydroxyphenyl)methane was obtained using the following conditions: elution using 5% methanol in CO_2 at a flow rate of 2 ml min^{-1}, and a back pressure of 205 bar measured at the column inlet. Ionisation was achieved using methanol reagent ions, typically [MeOH]+ and [(MeOH)2H]+, generated from the mobile phase *via* a 3.0 kV discharge at the corona pin. The source temperature was maintained at 120 °C and the probe temperature at 300 °C. Nitrogen, at 60 psi, was used as the bath and sheath gas at flow rates of 50 and 100 l h^{-1}, respectively. Ions were sampled into the mass spectrometer using a sampling cone voltage of 30 V, and full scan spectra recorded from 100 to 300 u in 1.0 s.

The mass spectrum obtained for the standard compound showed major ions in the spectrum at *m/z* 181 and 197; unfortunately, there was no molecular ion or protonated molecular ion at *m/z* 200 or 201. Therefore, identification of the components in the resol sample would be difficult due to the lack of molecular weight information in the positive ion spectra. These compounds may not be particularly amenable to protonation due to the acidity of the phenolic OH group, thus producing the spectrum observed.

A negative-ion CI spectrum for a resol dimer was obtained by eluting the standard compound with 5% methanol in CO_2 at a flow rate of 2 ml min^{-1}, and a back pressure of 195 bar measured at the column inlet. Ionisation was achieved using reagent ions generated from the mobile phase *via* a 2.5 kV discharge at the corona pin. The source temperature was maintained at 120 °C and the probe temperature at 300 °C. Compressed air, at 60 psi, was used as the bath and sheath gas, at flow rates of 50 and 100 l h^{-1}, respectively. Ions were sampled into the mass spectrometer using a sampling cone voltage of −30 V, and full scan spectra recorded from 100 to 300 u in 1.0 s. The mass spectrum of the standard compound in negative-ion mode contains a single mass peak at *m/z* 199 corresponding to the $[M - H]^-$ion. Therefore, negative-ion APCI is ideal for characterising the complex resol resin, as it is capable of providing molecular weight information without extensive fragmentation.

Optimisation of the bath and sheath gas flow rates and the source temperature was performed for negative-ion APCI. Replicate injections of the standard compound were made, and the MS response monitored using the mass chromatogram for the $[M - H]^-$ ion at *m/z* 199. The SFC and MS conditions used were identical to those stated previously in this section, except for the bath and sheath gas flow rates and the source temperature.

The optimum value for the source temperature was found to be 150 °C, for the bath gas flow rate 100 l h^{-1} and the highest sensitivity was obtained with no sheath gas. These values were then used in the analysis of the resol prepolymer, all other conditions being identical to those stated previously.

Characterisation of a resol prepolymer

In order to achieve separation of the components of the resol resin, pressure and modifier programmes were required. As a fixed restrictor was used to control the pressure, a flow programme had to be used to create the desired pressure programme. The flow and modifier programmes used and the corresponding increase in pressure are shown in Table 1.

Fig. 1 shows the UV and MS total ion current (TIC) chromatograms obtained for the resol sample. The composition of the sample is so complex that identification of components from either the TIC chromatogram or the UV trace alone is impossible as many of the components are co-eluting. This mixture can, however, be resolved and the components characterised by using the selectivity of the mass spectrometer to look at the $[M - H]^-$ ions of individual mass species.

† Available as Electronic Supplementary material; see http://www.rsc.org/supdata/an/1999/993.

The presence of starting material residues in the resol was confirmed by the mass chromatograms for $[M - H]^-$ ions at *m/z* 93 and 107 (Fig. 2), which correspond to phenol and cresol, respectively. Fig. 2(a) shows the mass chromatograms for phenol and the methylol- and dimethylol-substituted products at *m/z* 123 and *m/z* 153, respectively. Dimethylol-substituted phenol is a very minor product, as shown by comparison of the peak intensities on the mass chromatogram corresponding to *m/z* 93 + 123 + 153 in Fig. 2(a). The presence of methylol-substituted cresol is confirmed by the $[M - H]^-$ ion at *m/z* 137 in Fig. 2(b); however, in this case, the dimethylol-substituted product is not observed.

Resol oligomers, comprising phenol units only, from $n = 2$ to $n = 5$, were identified from the mass chromatograms of $[M - H]^-$ ions at *m/z* 199, 305, 411 and 517, shown in Fig. 3. All the mass chromatograms are shown with the peaks at full scale on the *y* axis; therefore, these do not show the difference in relative abundances for the components. Comparison of the relative peak areas (trimer = 100%) for each oligomer in Table 2 indicates that the dimer and trimer are the major components in the resin, whereas the pentamer is only a minor component.

Phenol and cresol were both used in the condensation reaction to produce this particular resol; therefore, each oligomer may be composed of varying numbers of phenol and cresol units. Hence, there are three possible structures for the dimer, containing zero, one or two cresol units, with molecular weights of 200, 214 and 228, respectively. For the trimer, there

Table 1 Flow and modifier programmes

Time/min	Modifier (%)	Flow/ml min^{-1}	Pressure/bar[a]
0	2	1.25	156
2	2	1.25	156
15	30	3.00	385
25	30	3.00	385

[a] Pressure at column inlet.

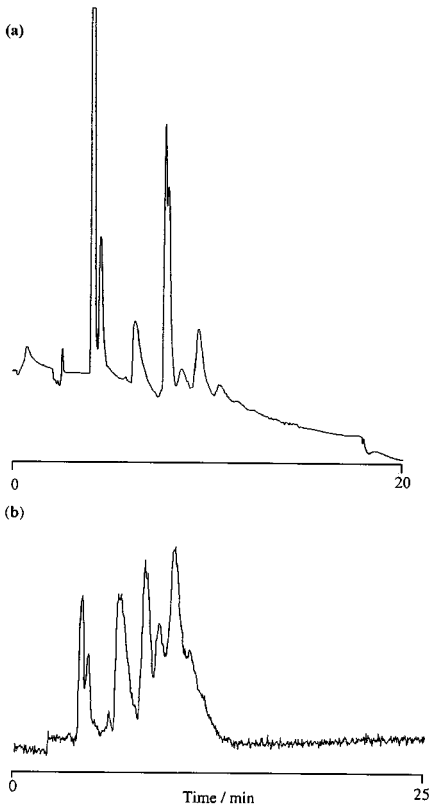


Fig. 1 SFC separation of a resol prepolymer resin with (a) UV and (b) APCI-MS detection (TIC chromatogram in the latter case).

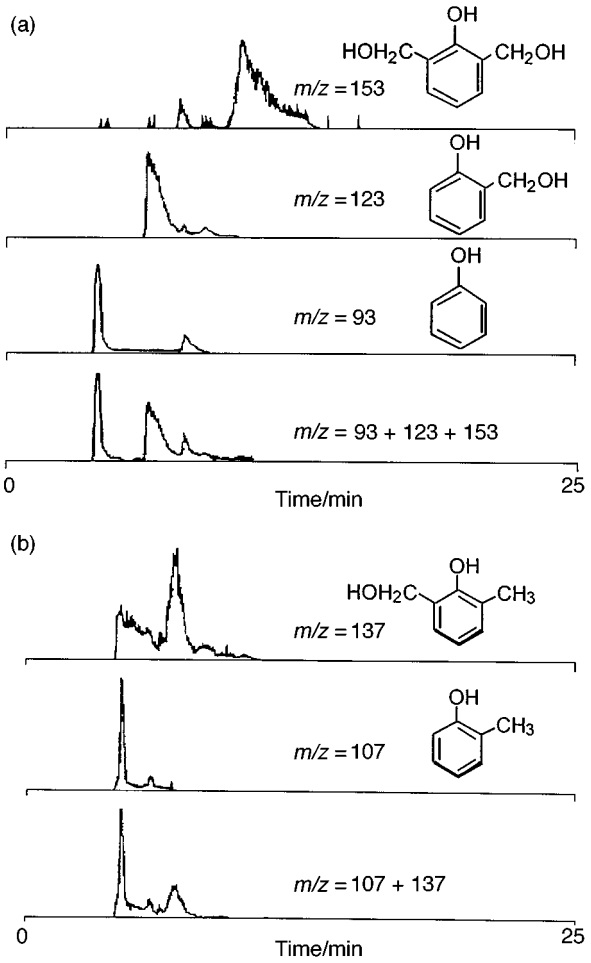


Fig. 2 Mass chromatograms for starting meterial residues in a resol prepolymer: (a) phenol and methylol-substituted products; (b) cresol and methylol-substituted products.

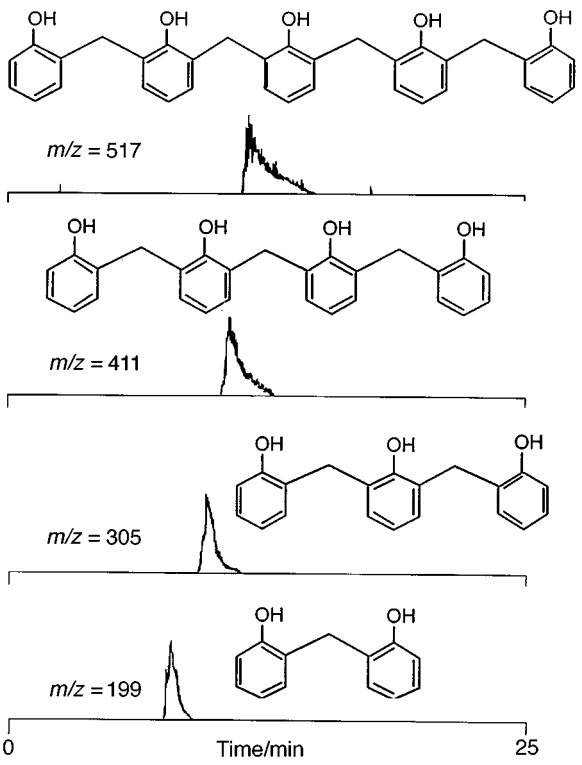


Fig. 3 Mass chromatograms for phenol oligomers of resol.

Table 2 Relative peak areas of oligomers

Phenol oligomer	*m/z*	Relative peak area
Dimer	199	51%
Trimer	305	100%
Tetramer	411	27%
Pentamer	517	5%

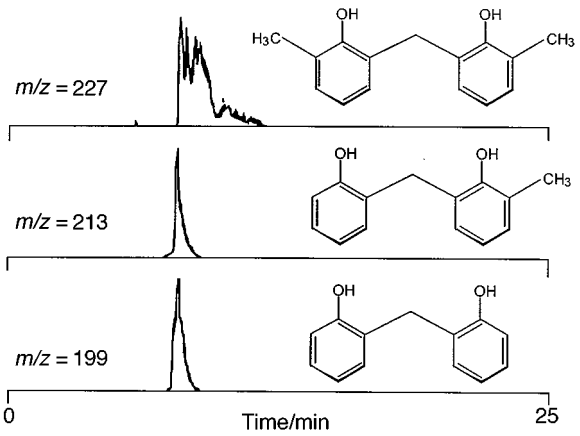


Fig. 4 Mass chromatograms for phenol and cresol dimers in resol prepolymer.

are four possible structures, five for the tetramer and six for the pentamer. The three dimers may be identified from their characteristic $[M - H]^-$ ions, and Fig. 4 shows the mass chromatograms for *m/z* 199, 213 and 227, thus confirming the presence of all three dimers in the resol prepolymer. Similarly, all four possible trimers are observed with mass chromatograms at *m/z* 305, 319, 333 and 347; however, only four structures are seen for the tetramer at *m/z* 411, 425, 439 and 453, and two structures are observed for the pentamer at *m/z* 517 and 531.

The basic conditions employed in the condensation reaction also produce oligomers with methylol substituents on the aromatic ring, similar to those shown previously for phenol and cresol monomers (Fig. 2). Fig. 5 shows the mass chromatograms for a dimer composed of one phenol and one cresol unit, containing zero, one, two and three methylol substituents:

The dimer and its methylol-substituted analogues can easily be identified from their corresponding $[M - H]^-$ ions at *m/z* 213, 243, 273, 303 and 333. However, the mass chromatogram for the tetramethylol-substituted dimer at *m/z* 333 also coincides with the mass of the following trimer:

The coincidence of masses for certain components is due to the presence of phenol and cresol analogues for each oligomer in addition to the methylol substituents. Identical masses occurred only when oligomers possessed four or more methylol substituents. The small proportion of dimethylol-substituted monomers (see above) suggests that such highly substituted oligomers are unlikely to be present in significant amounts. In addition, the trimer, tetramer and pentamer do not show such a high degree of substitution; the trimer was found to have a maximum of two methylol substituents, the tetramer only has one methylol substituent, and methylol substituted pentamer oligomers could not be detected, and no ambiguity exists.

The compounds present in the resol identified from their $[M - H]^-$ ions are listed in Table 3.

Conclusion

Packed-column SFC has been shown to be a powerful technique for the analysis of phenol-formaldehyde resin prepolymers, with negative-ion APCI-MS being capable of providing molecular weight information without extensive fragmentation.

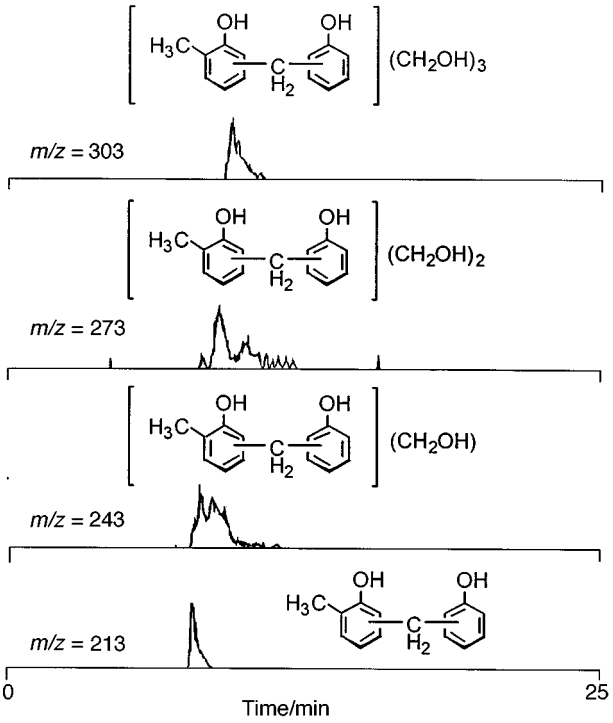


Fig. 5 Mass chromatograms of methylol-substituted dimers. (The tetramethylol-substituted dimer at *m/z* 333 coincides with the mass of the trimer).

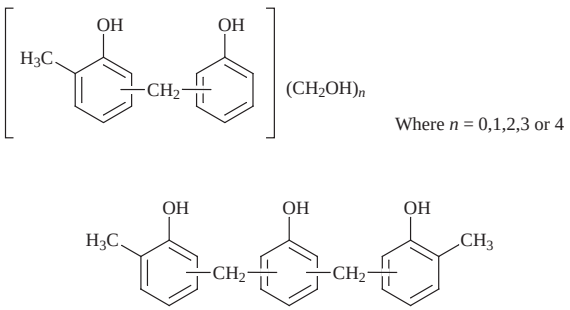


Table 3 Summary of components identified by SFC-APCI-MS in the resol prepolymer resin

Resin component	Methylol substituents	Number of cresol units 0	1	2	3	4	5
Phenol	0	93					
	1	123					
	2	153					
Cresol	0		107				
	1		137				
	2		×*				
Dimer	0	199	213	227			
	1	229	243	257			
	2	259	273	287			
	6	303	317				
Trimer	0	305	319	333	347		
	1	335	349	363	×		
	2	×	379	393	×		
	3	×	×	×	×		
Tetramer	0	411	425	439	453	×	
	1	441	455	469	×	×	
	2	×	×	×	×	×	
Pentamer	0	517	531	×	×	×	×
	1	×	×	×	×	×	×
	2	×	×	×	×	×	×

* ×, not detected.

Additionally, no sample derivatisation is required, either for the separation or detection of the components of the resol. The combination of these two techniques has enabled the identification of thirty four components, including starting material residues, from the characteristic $[M - H]^-$ ions of components in a complex resol prepolymer. The identification of chemical species and the determination of the molecular weight distribution by SFC-APCI-MS is complementary to the information obtained from other techniques such as NMR, thus enabling the analyst to produce a more complete picture of the prepolymer composition.

Acknowledgements

The authors thank their colleagues in the School of Chemistry at the University of Nottingham, especially Dr M. W. George, for stimulating discussions and helpful advice, and the technical staff for invaluable help in the maintenance of the equipment, Mr T. Lynch, now of BP Chemicals, and Dr S. Bajic of VG Biotech. They are also grateful to BP for the supply of a resin sample, to VG Biotech for financial support, and to the EPSRC for a Research Studentship (to M. J. C.).

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Paper 9/01683J