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M.A.L.D.I.-T.O.F. mass spectrometry characterization of 4-alkyl substituted phenol-formaldehyde novalac type resins

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Two methods of synthesis for 4-alkyl substituted phenol-formaldehyde resins are described. A common method for synthesis of novolac type phenol-formaldehyde resin uses sulfuric acid catalyst in the presence of xylene for azeotropic removal of water of reaction. By the use of M.A.L.D.I.-T.O.F. mass spectrometry we have demonstrated that m-xylene is incorporated into these polymers. Polymers free of impurities are best prepared using a cation exchange resin as catalyst in the presence of a less reactive solvent, e.g. chlorobenzene, or in the absence of solvents. © 1997 Elsevier Science Ltd.

(Keywords: matrix assisted laser desorption/ionization; time of flight mass spectrometry; phenol-formaldehyde resins)

INTRODUCTION

Phenol resins, considered to be the first synthetic polymers, are still a substantial business after eight decades[1–4]. These resins are prepared by the reaction of a phenol or a substituted phenol with formaldehyde under acidic or basic conditions. Acid catalyzed condensation of phenols with formaldehyde results in the formation of soluble, amorphous novolac resins.

The reaction of phenol with an aldehyde was first reported by Baeyer in 1872[5]. However, the innovative work of Baekeland in 1909[6] serves as the foundation of phenol-fornmaldehyde chemistry. 4-Alkylsubstituted phenolic resins are generally being used in applications such as coatings[7], adhesives[8,9], and as molding compounds.

Traditionally, g.c.[10], h.p.l.c.[11,12], g.p.c.[13] and n.m.r.[14–18] have been used to elucidate the structures of phenol-formaldehyde resins. They have been very useful in revealing the average molecular weights, sizes and distribution of different phenolic resins. None of these techniques, however, gives a precise description of the polymer nor do they provide an end-group analysis. Matrix assisted laser desorption/ionization time of flight mass spectrometry (M.A.L.D.I.-T.O.F.M.S.) is a soft ionization technique developed by Karas and Hillenkamp[19] and is now an established technique for the analysis of large biopolymers[20–22]. M.A.L.D.I. has also been found to be an invaluable tool for the characterization of synthetic polymers[23]. This method is very distinct from the other molecular weight determination techniques such as g.p.c., h.l.p.c., etc. since it can provide absolute molecular masses for each oligomeric species as well as furnishing information about the end-groups.

In this paper we will discuss the analysis of 4-alkylsubstituted phenol-formaldehyde oligomers and the applicability of M.A.L.D.I.-T.O.F.M.S. technique to the characterization of these oligomers with special emphasis on end-group analysis. The use of M.A.L.D.I.-T.O.F.M.S. for the analysis of phenol-formaldehyde resins has been recently reported[24].

EXPERIMENTAL

Materials

Sulfuric acid (ACP; 95–98%), hydrochloric acid (ACP; 36.5%), xylenes (Caledon; 98.5%), chlorobenzene (ACP), formaldehyde (BDH; 36.5–38%), Amberlyst-15)BDH), and 4-phenylphenol (Aldrich; 97%) were used without further purification. 4-tert-Butylphenol (Aldrich; 99%) was recrystallized from hexanes prior to use.

Matrix assisted laser desorption/ionization time of flight mass spectrometry

All samples were analysed using a Kratos Kompact MALDI-III TOF bench top model. It generates a maximum laser out of 6 mw at a wavelength of 337 nm (N_2 laser light, 3 ns pulsewidth). The average of 100 laser shots was represented in the mass spectra.

The M.A.L.D.I.-T.O.F. instrument has the capability of analysing samples in both linear and reflection modes. All samples for this paper were analysed by using the reflection mode to obtain higher mass resolution. Insulin (for low molecular weight polymers) and bovine serum albumin (for high molecular weight polymers) were used for an external mass calibration.

Sample preparation for M.A.L.D.I.-T.O.F.

All the samples (5 mg/mL) and dithranol (10 mg/mL) were prepared in chloroform solution. LiBr (5 mg/mL) was dissolved in THF. The solutions were combined in 1:2:1 volume ratio of polymer to matrix to cationization agent. 0.1 μL the mixture was applied to a spot on a sample slide and the solvent was allowed to evaporate slowly before being put into the vacuum chamber of the mass spectrometer.

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Characterization of the resins using other techniques

H.p.l.c. analyses of the 4-alkylsubstituted phenol-formaldehyde (P-F) oligomers were carried out on a Milton Roy CM4000 pump equipped with a reverse phase column (prime sphere 5 μ C8, 250 × 4.6 mm) and a u.v. detector at 300 nm. A mixture of THF and water was used as an eluent. The gradient program was as follows: Step 1, 70–95% THF over 20 min; Step 2, 95–100% THF over 5 min; and Step 3, 200–70% THF over 5 min; (recycle).

All the g.p.c. analyses were performed on a Waters 510 h.p.l.c. using four phenogel 5 μm columns (1 linear, 3 × 500 Å) arranged in series. Spectroscopic grade chloroform was used as an eluent with a flow rate of 1 mL/min. The u.v. detector was set at 254 nm and polystyrene was used as external calibrant. N.m.r. spectra were recorded on a Varian Unity 500 instrument using DMSO-d_6 or $CDCl_3$ as solvent.

Synthesis of 4-alkyl substituted phenol-formaldehyde oligomers

Method A. The synthesis of 4-alkyl substituted phenol-formaldehyde oligomers was performed following a literature procedure[25]. A 250 mL three neck round-bottom flask was equipped with a Dean–Stark trap, a condenser, a volumetric addition funnel, and a nitrogen inlet and it was charged with 4-tert-butylphenol (8 g, 53 mmol) and 105 mL xylene. The phenol went into solution at 30°C. After the addition of sulfuric acid (0.28 mL) the temperature of the reaction mixture was increased to 80°C. The formaldehyde solution was added to the reaction mixture dropwise over a period of 30 min. After the addition was complete the temperature of the mixture was raised to 120°C and the water began to be removed as an azeotrope. The mixture was stirred at this temperature for 4 h. Xylene was removed under pressure and the solid residue was dissolved in chloroform which was then washed with 0.1 M aqueous solution of potassium bicarbonate to neutralize the acid catalyst. The organic later was extracted and chloroform was removed under reduced pressure to give 85–90% yield of a white colored resin.

Method B. A 500 mL 3-neck round-bottom flask fitted with a reflux condensor and a nitrogen inlet was charged with 4-tert-butylphenol (50 g, 0.33 mol), (37%) formaldehyde solution, Amberlyst-15 (20 g, 40 wt%) and chlorobenzene (50 mL). For each mole of 4-tert-butylphenol, 0.3–0.8 mole of formaldehyde solution was added. For example, for 50 g of 4-tert-butylphenol, 20 mL solution of formaldehyde was used to obtain P/F ratio of 1/0.8. The reaction mixture was heated to 100°C and stirred continuously at this temperature for 4 h. The resin was then filtered off and chlorobenzene was removed under reduced pressure. The oligomers were then vacuum dried at room temperature to give ~90% yield of a white resin.

RESULTS AND DISCUSSION

Two synthetic methodologies were employed in the preparation of 4-alkyl substituted phenol-formaldehyde resins. In both cases a 37% solution of formaldehyde in methanol and water was used. Sulfuric acid was used as a

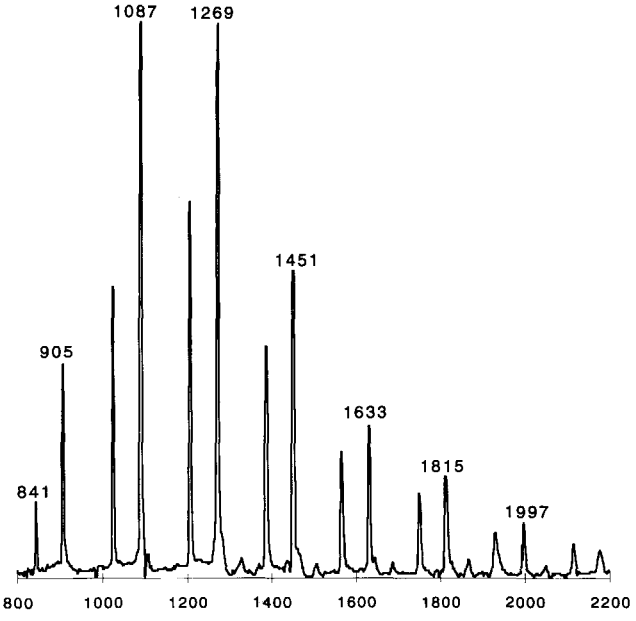


Figure 2 Proton n.m.r. spectrum of 4-tert-butylphenol-formaldehyde oligomers end-capped with xylene in dmso-d_6

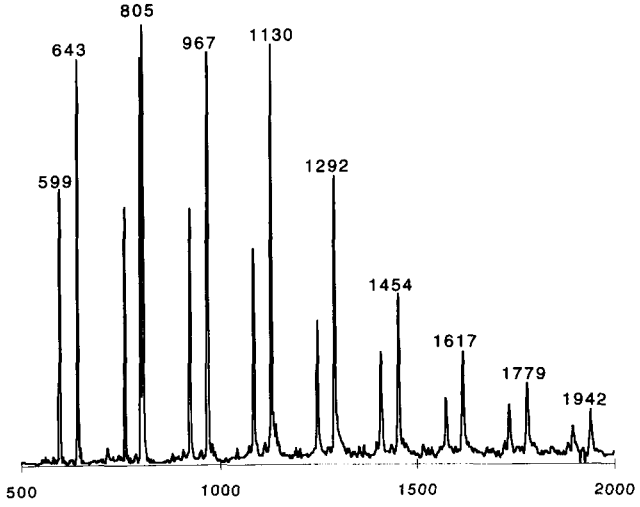


Figure 1 M.A.L.D.I.-T.O.F. spectrum of 4-tert-butylphenol-formaldehyde oligomers end-capped with xylene

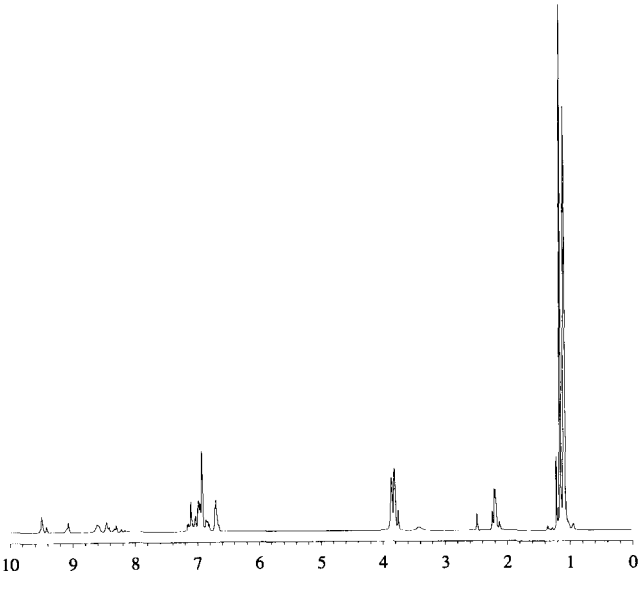


Figure 3 M.A.L.D.I.-T.O.F. spectrum of 4-phenylphenol-formaldehyde oligomers end-capped with xylene

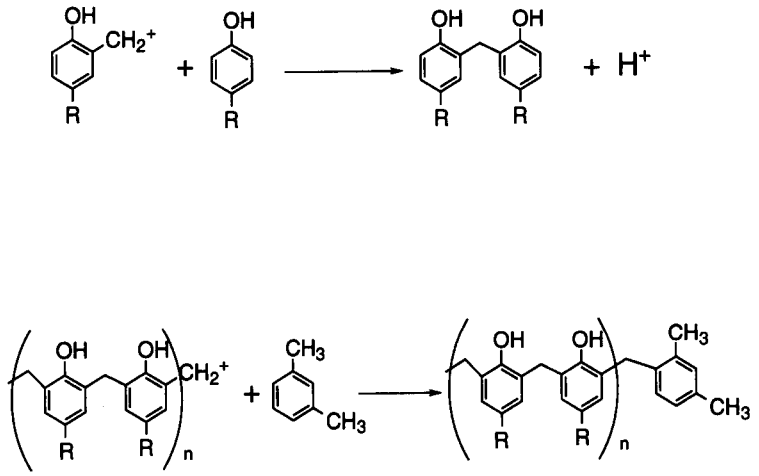
catalyst in one method while the catalyst was a cation exchange resin in the other case. Xylene, used as an azeotropic solvent in method A was replaced by chlorobenzene in Method B.

The M.A.L.D.I.-T.O.F. spectrum of the 4-tert-butylphenol-formaldehyde resin that resulted by following the literature procedure[25] is shown in *Figure 1*. It clearly demonstrates the presence of two series of oligomers when n ranges from 2 to 14. A peak with a mass difference of 44 appears between the expected oligomeric species.

For example, the peak at 642 Dalton (Da) represents a linear 4-tert-butylphenol-formaldehyde tetramer with the attachment of a lithium cation. The peak at 598 Da, however, corresponds to a phenol-formaldehyde trimer end-capped by one xylene molecule with a lithium cation attached to it. This combination of peaks repeats itself throughout the entire range of the mass spectrum for the oligomers prepared by the literature method.

The presence of xylene moieties in the polymer can be confirmed by n.m.r. The split multiplet at 2.2 ppm in the proton n.m.r. spectrum (*Figure 2*) is due to CH_3 protons of xylene end-capper present in the oligomers clusters. This multiplet disappears when xylene is not used as solvent as is shown in *Figure 8*. However, a singlet appears at around 2.2 ppm for 4-tert-butylphenol-formaldehyde oligomers that are not end-capped by xylene when the n.m.r. spectrum was taken in $CDCl_3$. This is most likely due to hydroxy protons of the strongly hydrogen bonded complexes formed by the oligomers in a non-solvating solvent like $CDCl_3$. This was observed by Yamagishi *et al.*[27] for similar kinds of molecules in $CDCl_3$. Under the same reaction conditions 4-phenylphenol was reacted with formaldehyde using xylene as a solvent. In this case if incorporation of xylene occurred we would expect a mass difference of 64 Da instead of 44 Da. The M.A.L.D.I.-T.O.F. spectrum (*Figure 3*) does in fact show the additional peaks with a mass difference of 64 Da for 4-phenylphenol-formaldehyde oligomers. By changing the catalyst from sulfuric to hydrochloric acid and changing the reaction temperature, similar M.A.L.D.I.-T.O.F. spectra were obtained, i.e. in each case xylene end-capped oligomers were observed. When oxalic acid, a mild acid, which is being widely used for production of novolac resins, was used, there was no sign of xylene end-capped oligomers in the mass spectrum. However, only very low molecular weight oligomers were obtained under these conditions.

The reaction between a phenol or a substituted phenol and formaldehyde under strongly acidic conditions, takes place by an electrophilic aromatic substitution mechanism. Benzylic carbocations that are formed under acidic



Scheme 1 Mechanism of formation of xylene end-capped phenol-formaldehyde resins

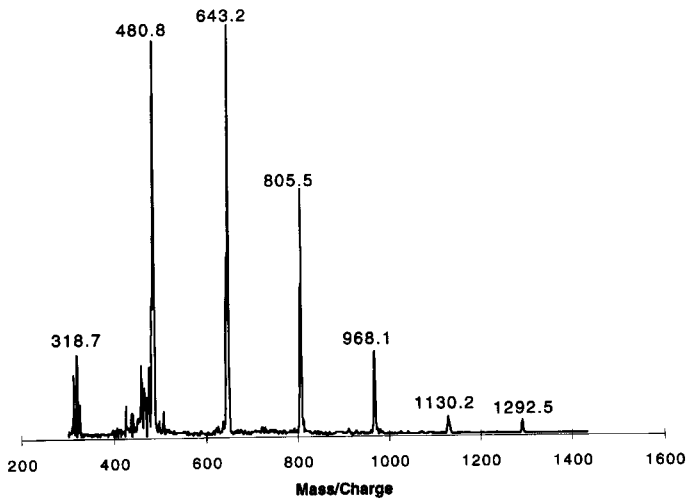
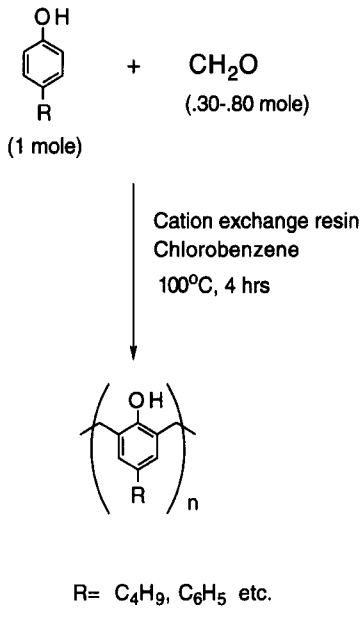


Figure 4 M.A.L.D.I.-T.O.F. spectrum of 4-tert-butylphenol-formaldehyde oligomers (P/F = 1/0.3)



Scheme 2 Synthesis of p-substituted phenol-formaldehyde oligomers by using cation exchange resin as a catalyst

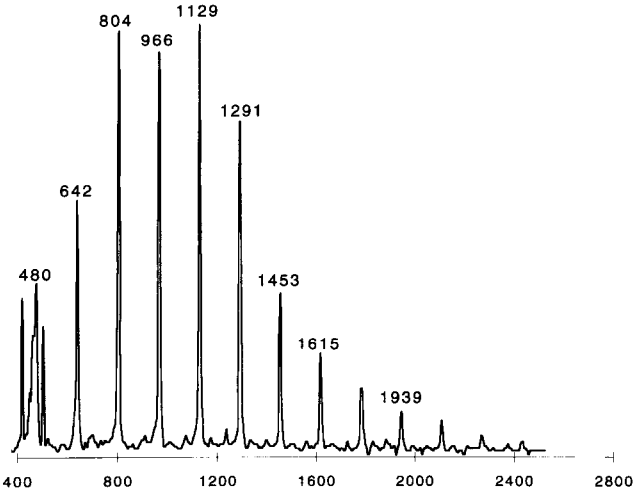


Figure 5 M.A.L.D.I.-T.O.F. spectrum of 4-tert-butylphenol-formaldehyde oligomers (P/F = 1/0.8)

conditions, react very rapidly with phenol (*Scheme 1*) to give methylene bridged dimer[26]. In the presence of xylene, however, the benzylic carbocation of the n-mer could presumably react with a xylene molecule in addition to reacting with another phenolic moiety, to yield end-capped xylene oligomers. Probably the electron donating nature of the methyl groups in xylene makes it susceptible to attack by benzylic carbocations.

To avoid the incorporation of xylene we used an alternative route for the synthesis of the phenol-formaldehyde resins (*Scheme 2*). Xylene was replaced by chlorobenzene and a cation exchange resin (Amberlyst-15) was used as catalyst.

The advantage in using a cation exchange resin is that it is reusable for long periods of time and the products are separated by a simple filtration. *Figures 4 and 5* show the M.A.L.D.I.-T.O.F. spectra of different oligometric resins with variable P/F ratios. There is no trace of any side

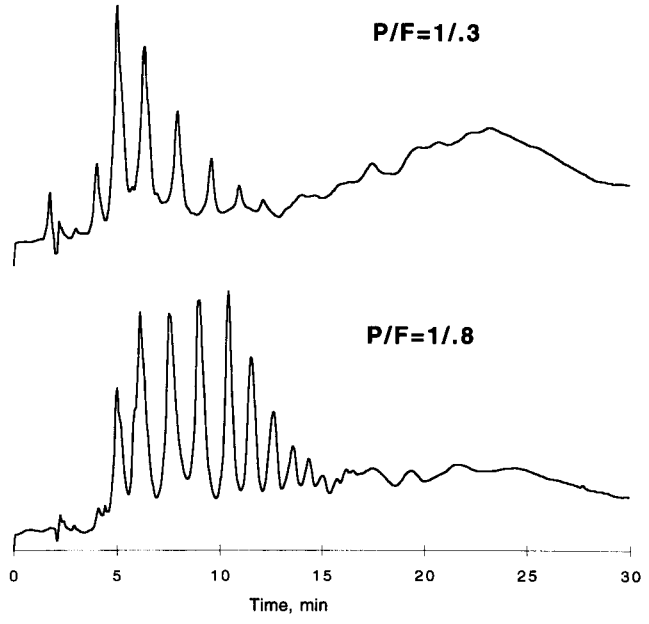


Figure 6 Gradient h.p.l.c. traces of 4-tert-butylphenol-formaldehyde oligomers

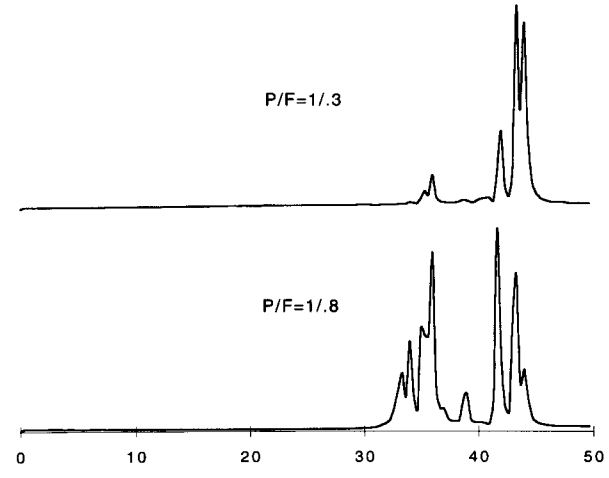


Figure 7 G.p.c. traces of 4-tert-butylphenol-formaldehyde oligomers

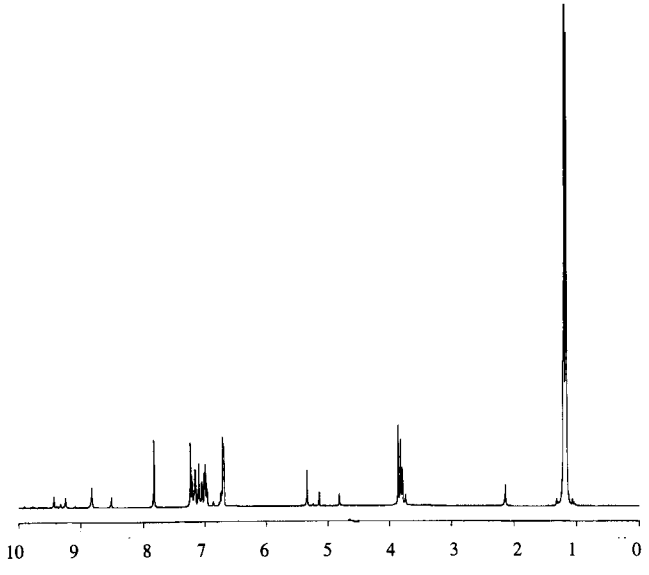


Figure 8 Proton n.m.r. spectrum of 4-tert-butylphenol-formaldehyde oligomers in $CDCL_3$

H-bonding between the OH groups of the phenolic resins. The phenomena of H-bonding in the P-F resins have been observed before[27]. When the polymer solution in $CDCl_3$ was treated with D_2O, the intensity of the peaks in the aforementioned region reduced dramatically. This provides a direct evidence of H-bonding in these resins.

CONCLUSIONS

M.A.L.D.I.-T.O.F. analysis has been found to be very valuable in characterizing the xylene end-capped 4-alkyl substituted phenol-formaldehyde oligomers. Synthesis using cation exchange resin as catalyst gave 4-alkyl substituted phenol-formaldehyde oligomers without any undesired side products.

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