Letter - spectral assignment

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A new prepolymer of resol phenol–formaldehyde resin

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Introduction

Phenol–formaldehyde resin, a synthetic polymer, has a wide range of commercial applications in products such as precoated sand, wood adhesive and fire-retardant materials.[1,2] Their manufacture involves two stages: (i) prepolymer production by an acid or base catalyzed condensation reaction between phenol (or substituted phenols) and formaldehyde; and (ii) curing of these low molecular weight prepolymers by the use of heat or a cross-linking agent.[3]

Two types of prepolymer, *i.e.* novolacs and resol, are obtained depending on pH and formaldehyde/phenol molar ratio (F/P). Novolacs are also referred to as thermoplastic phenolic resins or linear phenolic resin and can be obtained in an acidic catalysis and $F/P < 1$. Whereas resols are also referred to as thermosetting phenolic resins[1] and can be obtained in alkaline catalysis and $1 < F/P < 3$; resol prepolymer has mono-, di- and tri-methylol (CH_2OH) groups in the phenols skeleton.

NMR spectroscopy has proved to be a successful and informative tool to analyze resol resins.[4,5] However, the isolation, purification and spectroscopic studies of the individual prepolymer have been rarely reported.[6] In the present research, resol resin with $F/P = 2.0$ was synthesized, and three prepolymers from the resin were isolated, purified and structure identified by 1D and 2D NMR experiments. Among these three prepolymers, a new prepolymer was discovered. Our results will provide the additional structural information of resol resin prepolymer.

Results and discussion

The synthesized resol resin was subject to HPLC-ESI-MS analysis, and the prepolymers were monitored by their characteristic UV–Vis absorption wavelength of 283 nm(Fig. s1). The chromatographic peak at retention time of 3.07 min, 4.39 min, 7.62 min and 13.65 min showed molecular weight of 184, 320, 456 and 592 Da in the mass spectrum, with regular mass difference of 136 Da. The component at retention time of 4.39 min, 7.62 min and 13.65 min were isolated and purified by preparative HPLC, labeled as compound I, II and III, respectively.

The molecular ion peak of compound I appeared at *m/z* 319 $[M-H]^-$. Compound I was obtained as a light-yellow solid; 12.1 mg of the dry solid was fully dissolved in 0.5-ml DMSO-d_6. The ^{1}H NMR spectrum (Fig. s2), ^{13}C NMR spectrum (Fig. s3) along with HSQC data (Fig. s4) revealed the presence of:

1) aromatic protons at δ6.96, which are correlated to ^{13}C NMR resonance of δ126.46 in the HSQC spectrum;
2) oxygenated methylene protons at δ4.50, which are attributed to the methylol (CH_2OH) group in the phenol ring, such protons have correlation with ^{13}C NMR resonance of δ59.78 in the HSQC spectrum;
3) methylene protons at δ3.71, which are correlated to ^{13}C NMR resonance of δ40.98 in the HSQC spectrum, should be attributed to para/para methylene bridges according to literature.[5,7,8]
4) broad resonances of δ8.34 and δ5.22, are proved be exchangeable protons, by using experiment of the addition of H_2O into deuterated solvents.

All resonances in the ^{1}H NMR spectrum are singlets (except residual solvent signal), indicating the symmetric structure of the compound. Based on the comparison of 1D and 2D NMR data of the compound I with the published literature,[5,7,8] it was identified as dimer of tri-methylol phenol (Fig. 1 and Table 1).

The molecular ion peak of compound II appeared at *m/z* 455 $[M-H]^-$, with a mass difference of 136 Da to compound I, the molecular weight of one tri-methylol phenol unit. Compound II was obtained as a yellow solid; 13.4 mg of the dry solid was fully dissolved in 0.5-ml DMSO-d_6. The ^{1}H NMR spectrum (Fig. s6) along with ^{13}C NMR spectrum (Fig. s7), DEPT-135 (Fig. s8), gCOSY (Fig. s9), HSQC (Fig. s10) and HMBC data (Fig. s11) revealed the presence of:

1) aromatic protons at δ6.98, δ6.93, δ6.85 and δ6.80, with resonance integral of 2:2:1:1, which are correlated to ^{13}C NMR resonance of δ126.71, δ126.49, 125.93 and 129.52 in the HSQC spectrum;
2) oxygenated methylene protons at about δ4.5, which correspond to the methylene of methylol ($\underline{CH_2}OH$) group in the phenol ring, correlate to ^{13}C NMR resonance of δ60 in the HSQC spectrum; in the gCOSY spectrum, such oxygenated

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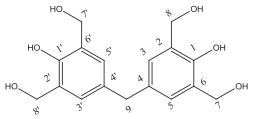

Figure 1. Structures of compound I.

Table 1. The ^{1}H and ^{13}C assignment of phenol-formaldehyde dimer

Position	δ_C	δ_H (J/Hz)
1,1′	150.20	
1,1′-OH	/	8.34 (2H,s)
2,2′,6,6′	128.39	/
3,3′,5,5′	126.46	6.96(4H,s)
4,4′	132.65	/
7,7′,8,8′	59.78	4.50 (8H,s)
7,7′,8,8′-OH	/	5.22 (4H,s)
9	40.98	3.71(2H,s)

methylene protons have correlation with exchangeable protons of δ5.21 and δ5.35, so, protons of δ5.21 and δ5.35 are attributed to OH group of methylol ($CH_2\underline{OH}$).

3) methylene protons δ3.76 and δ3.66, such protons have correlation with ^{13}C NMR resonance of δ35.09 and δ40.61 in the HSQC spectrum. According to literature data,[7,8] the resonances are attributed to para/ortho and para/para methylene bridges, respectively.
4) broad resonances of δ8.35, δ8.33, δ8.29, δ5.35 and δ5.21 are proved be exchangeable protons, by using experiment of the addition of H_2O into deuterated solvents (Fig. s12). Protons at δ8.35, δ8.33 and δ8.29 can be attributed to OH group of phenols.

The resonance assignment of compound II is shown in Table 2. From the HMBC spectrum, proton at δ35.09, which is attributed to H-10, correlates to C-1′ of δ150.65, whereas the proton at δ40.33, which is attributed to H-9, has no correlation with any OH bearing aromatic carbon. Besides, C-9 correlates to C-3′ and C-5′ of middle phenyl ring, whereas C-10 correlates to only C-3′ of the middle phenyl ring. The key HMBC correlations of compound II are shown in Fig. 2 and Table 2. The compound identified as a new prepolymer component had a linear trimer of tri-methylol phenol structure.

Compound III with HPLC retention time of 13.65 min was prepared, compound III was obtained as a yellow solid and 10.5 mg of the dry solid was prepared; however, when the compound was subjected to ^{1}H NMR experiment, because of the limited solubility in DMSO-d_6,acetone-d_6 or other deuterated solvent, it was difficult to obtain spectrum of enough signal intensity to elucidate the structure of the compound.

Experimental

Nuclear magnetic resonance spectroscopy

Compounds were dissolved in deuterated dimethylsulfoxide (DMSO-d_6, purchased from Cambridge Isotope Laboratories) and put into 5-mm NMR tubes (purchased from NORELL).

The 1D and 2D NMR spectra were recorded on an Agilent 400MR spectrometer (equipped with 5-mm ASW probe) at 298 K. Chemical shifts (δ) in parts per million are referenced to TMS at 0.00 ppm for ^{1}H and ^{13}C NMR. For ^{1}H NMR acquisition, spectrometer frequency (SF) was set at 399.79 MHz, 90° pulse of 13.2 μs for ^{1}H and spectrum was recorded with 16 scans, with a relaxation delay of 2 s between each scan. For ^{13}C NMR acquisition, spectrometer frequency (SF) was set at 100.54 MHz, 90° pulse width of 9.0 μs for ^{13}C, with a relaxation delay of 2 s between each scan. Decoupling of the ^{13}C spins during acquisition was done using the WALTZ-16. All HSQC and HMBC experiments were carried out using the recommended gradient-selected pulse sequences from the Agilent pulse sequence library, with HSQC optimized for $^{1}J_{CH} = 145$ Hz, and HMBC optimized for $^{n}J_{CH} = 8$ Hz.

Table 2. The ^{1}H and ^{13}C assignment of phenol-formaldehyde trimer

Position	δC	δH (J/Hz)	$^{1}H \rightarrow ^{13}C$ HMBC correlations
1,1″	150.22	/	
1,1″-OH	/	8.35,8.33	1,1″(150.22), 2,2″(128.14)
1′	150.65	/	
1′-OH	/	8.29	1′(150.65), 6′(128.46)
2′	128.84	/	
2,2″	128.14	/	
3,5	126.71	6.93(4H,s)	9(40.33),7,8(59.78,59.85),5,3(126.71)
3″,5″	126.49	6.98(4H,s)	10(35.09),7″,8″ (59.78,59.85),5″,3″(126.49)
3′	129.52	6.80(2H,s)	9(40.33),10(35.09),5′(125.93),1′(150.65)
5′	125.93	6.85(2H,s)	9(40.33),7′(60.53),1′(150.65),3′(129.52)
4,4′	132.77,132.59	/	
4″	131.84	/	
6, 6″	128.30	/	
6′	128.46	/	
7,7″,8,8″	59.78, 59.85	4.48(8H,s)	1,1″(150.22),6,6″(128.30),5(126.71),5″(126.49)
7′	60.53	4.48(2H,s)	
7,8,7″,8″-OH	/	5.21(4H,s)	7,7″,8,8″(59.78,59.85), 6,6″(128.30)
7′-OH	/	5.35(1H,s)	
9	40.33	3.66(2H,s)	5′(125.93),4(132.77),4′(132.59)
10	35.09	3.76(1H,s)	1′(150.65),4″(131.84),2′(128.84),3″(126.49)

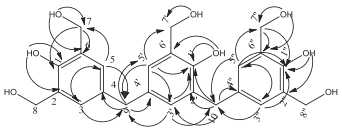

Figure 2. Structures and key HMBC (arrows) correlations of compound II.

Liquid chromatography-mass spectroscopy

HPLC-ESI-MS experiments were performed at Dionex Ultimate 3000 HPLC system connecting vial an ESI-interface with a linear ion trap mass spectrometer, LTQ-XL-MS (Thermo Finnigan, San Jose, CA, USA). Chromatographic separations were performed at 25 °C on a 250 × 4.6 mm (5 μm) Acclaim™ C_{18} column. The mobile phase contained 0.1% acetic acid solution-methanol (45:55), and the flow rate was maintained at 1.0 ml/min; the monitoring wavelength is at 283 nm. The mass spectrometer was operated in the negative mode, the spray voltage was 4.5 kV for the negative mode and the temperature of the heated capillary was set at 250 °C. Nitrogen was used as the nebulizer gas and auxiliary gas. The flow rates of the sheath gas, and sweep gas were set (in arbitrary units min^{-1}) at 20 and 2, respectively.

Preparative HPLC

Purification of prepolymer component was performed at Dionex Ultimate 3000 apparatus with Venusil® PrepG C_{18} column (10 × 100 mm), and the flow rate was maintained at 3.0 ml/min.

Synthesis of phenol–formaldehyde (PF) resin

Appropriate ratio of phenol and sodium hydroxide was heated in a three-necked flask with reflux condenser, a digital thermometer and a mechanical stirrer. Then formaldehyde aqueous solution (37%) was fed into the reactor dropwise, and the molar ration of total formaldehyde to phenol is 2.0. After the addition of formaldehyde was completed, the reaction temperature was maintained 90 °C for periods of time; when the desired content of free formaldehyde was reached, formic acid was added to stop the reaction. Then, the solution was dehydrated under vacuum. The dehydration process was stopped when reaching the desired viscosity.

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References

[1] R. A. Haupt, T. Sellers Jr. *Ind. Eng. Chem. Res.* **1994**, *33*, 693–697.
[2] G. Astarloa-Alerbe, J. M. Echeverria, J. L. Egiburu, M. Ormaetxea, I. Mondragon. *Polymer* **1998**, *39*, 3147–3153.
[3] J. Paju, T. Pehk, P. Christjanson. *P. Est. Acad. Sci.* **2009**, *58*, 45–52.
[4] J. C. Woodbrey, H. P. Higginbottom, H. M. Culbertson. *J. Polym. Sci. Pol. Chem.* **1965**, *3*, 1079–1106.
[5] R. Rego, P. J. Adriaensens, R. A. Carleer, J. M. Gelan. *Polymer* **2004**, *45*, 33–38.
[6] M. Carrott. *Analyst* **1999**, *124*, 993–997.
[7] T. H. Fisher, P. Chao, C. G. Upton, A. J. Day. *Magn. Reson. Chem.* **1995**, *33*, 717–723.
[8] T. H. Fisher, P. Chao, C. G. Upton, A. J. Day. *Magn. Reson. Chem.* **2002**, *40*, 747–751.

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