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Fractionation and characterization of phenolic resins by high-performance liquid chromatography and gel-permeation chromatography combined with ultraviolet, refractive index, mass spectrometry and light-scattering detection

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Abstract

HPLC and gel permeation chromatographic (GPC) characterization of complex phenol–formaldehyde resins is described. Reversed-phase HPLC fingerprints the phenolic monomers, dimers and some oligomers. The molecular masses of these phenolic compounds were determined using an ion trap mass spectrometer. GPC analyzes tetrahydrofuran-soluble phenolic polymers beyond HPLC capability. The molecular mass distribution and structural information of the phenolics was determined by both conventional and laser light-scattering calibration methods. GPC with both UV and refractive index detection provides weight concentration of phenolic resin and the molar concentration of the phenol unit in the oligomers or polymers.

Keywords: Phenolic resins; Detection, LC; Refractive index detection; Light-scattering detection; Phenols; Formaldehyde; Polymers

1. Introduction

The chromatographic methods most often used for the analysis of phenolic resin are high-performance liquid chromatography (HPLC) and gel permeation chromatography (GPC) [1–4]. HPLC with nuclear magnetic resonance (NMR) has been successfully used to separate and identify 42 phenolic compounds in phenolic resins by Mechin et al. [5,6]. Fourteen phenolic monomers and dimers in 12 phenol–formaldehyde resins were quantitatively analyzed by Bruze et al. [7]. The HPLC and IR spectroscopy techniques were used by Blanks to study the activation energy of phenolic resin components in phenolic resin products [8]. HPLC has had a long history in phenolic resin analysis; however, method development for HPLC of phenolic resin continues in the phenolic resin community. Brown et al. presented their HPLC analysis of SC 1008 resin work at Pittcon in 1998 [9]. Difficulties and challenges still remain in the HPLC separation and characterization of phenolic resin. Due to the substitution by the polar hydroxymethyl groups, some of the phenolic monomers show very weak retention and poor resolution in reversed-phase (RP) HPLC analysis. These phenolic monomers normally comprise 30% of the resin or 70% of the HPLC elutable phenolic compounds; therefore, incomplete analysis of these compounds can cause problems in evaluating a phenolic resin product. Due to the limitation of the polarity and solubility of the phenolic compounds in RP-HPLC

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mobile phase, only those polar and low-molecular-mass phenolics can be analyzed by RP-HPLC [7].

GPC was widely used in the phenolic resin analysis [1–3]. In most of the GPC applications, the molecular mass distribution of phenolic resin was determined by using refractive index (RI) detection and polystyrene standard calibration. As with the HPLC separation of phenolic resin, there are some challenges remaining in the GPC separation of phenolic resin as well, such as reproducibility, absolute molecular mass determination, and quantitation of the resin polymers.

In this work, the polarity, solubility and M_r distribution of phenolics in phenol–formaldehyde resin products are discussed. HPLC and GPC procedures with different detection techniques are evaluated, and potential solutions to some of the difficulties are discussed.

2. Experimental

2.1. Chemicals and standards

4-Hydroxymethylphenol (4HMP), 2-hydroxymethylphenol (2HMP), phenol, 2,2′-bisphenol F and 4,4′-bisphenol F were purchased from Aldrich. Methanol (MeOH), acetonitrile (MeCN), tetrahydrofuran (THF) and other chemicals and solvents used for HPLC, HPLC–mass spectrometry (MS), and GPC analysis were HPLC–UV grade. The nitrogen and helium gases used were 99 and 99.999%, respectively.

2.2. Apparatus

The HPLC system consists of a Hewlett-Packard 1090 equipped with a pump, an autosampler and a column compartment with photodiode array (DAD) and RI detection systems. An MS analysis was performed using a Finnigan LCQ ion trap MS system (Finnigan, San Jose, CA, USA). The HPLC columns used in this study include a LiChrospher C_{18} column and the columns listed in Table 1.

The GPC or size-exclusion chromatography system is also composed of a Hewlett-Packard 1090 equipped with a pump, an autosampler and a column compartment with DAD and RI detection systems. A multi-angle laser light-scattering detector (Wyatt Technology, Santa Barbara, CA, USA) was used on-line in the GPC system to determine the absolute molecular mass. The columns used in the GPC analysis are Styragel HR1, -2, and -3 (Waters, Milford, MA, USA).

2.3. Operating conditions

The MS detector was tuned at m/z 199 using a 0.02 mg/ml 4,4′-bisphenol F solution (MeCN) with an atmospheric pressure chemical ionization (APCI) negative mode, vaporization temperature 450°C, capillary temperature 150°C, sheath gas flow-rate 40 arb (arbitrary units for LCQ valve settings), auxiliary gas flow-rate 10 arb, 3 μl/min infusion flow and 0.3 ml/min of mobile phase (MeCN–water, 25:75). A 2-μl aliquot of 0.02 mg/ml 4,4′-bisphenol F (>98% purity) solution is then used to demonstrate the HPLC–MS sensitivity. The signal from the m/z 199 peak should be greater than $1 \cdot 10^6$ area counts or have a signal/noise ratio (S/N) of >20 with repetitive scanning from m/z 80 to 400 at 5 scans/s.

Except where otherwise specified, the columns are those listed in Table 1. The mobile phases are aqueous solutions of MeCN, MeOH, or THF. Flow-rate is 0.3 ml/min. Sample solution is 10 mg/ml

Table 1
Information on the HPLC columns used

Column	Stationary phase and size (particle size, length×I.D., mm)	Pore size (Å)	Carbon load (%)	Bonded phase coverage (μmol/m^2)	Polarity (Si–OH)
Hypersil C_{18}	C_{18} (5 μm, 100×2.0)	120	10	2.8	High
Hypersil C_8	C_8 (5 μm, 150×2.0)	120	7	3.8	High
Hypersil CN	CN (5 μm, 150×2.0)	120	4	3.5	High
Hypersil C_{18} BDS	C_{18} (5 μm, 150×2.0)	130	11	3.6	Low
Luna C_{18} (2)	C_{18} (5 μm, 180×2.0)	100	17.5	3	High

phenolic resin in MeOH–water (50:50) and the injection volume is 2 μl.

The GPC separation was accomplished with 1.0 ml/min of THF, 35°C, 15 mg/ml phenolic resin in THF and 100 μl injection. GPC fractions were collected using 100-μl injections of 100 mg/ml phenolic resin solutions with the same GPC columns as in the analytical separation.

3. Results and discussion

3.1. Evaluation of method compatibility and sample recovery

Phenolic resin is a condensation reaction product of phenol and formaldehyde. The reactivity of the phenolic compounds increases with the increase in degree of substitution and molecular mass [4]. The reactivity of the phenolics and their step-wise reaction path always produce a broad molecular mass distribution. Based on a polystyrene standard calibration, the molecular mass of phenolic polymers in a phenolic resin sample (Fig. 1a) was determined as high as 10 000, however, the concentration of the initial reactant phenol is still as high as 13%.

Three GPC fractions, labeled F9 to F11 in Fig. 1a, were collected and used in the GPC and HPLC analyses to determine the GPC separation efficiency and HPLC sample recovery. Due to the high polarity of the phenolics, aqueous mobile phase must be used in the HPLC separation to get enough retention and resolution. However, the high polarity of the HPLC mobile phase can cause solubility problems and a low sample recovery. In order to correlate the chromatographic information received from both HPLC and GPC techniques and evaluate the method compatibility and sample recovery, the three GPC fractions were re-separated using both GPC and HPLC techniques and their chromatograms are overlaid and stacked in Fig. 1a and b, respectively.

The overlaid GPC chromatograms in Fig. 1a demonstrate that the compounds in the three GPC fractions represent the phenolics in different molecular mass ranges. Based on the conventional polystyrene calibration, the average molecular mass of the phenolics are about 1000, 800 and 600 for F9, F10 and F11, respectively. The HPLC analyses of Fig. 1b show that multiple peaks can be resolved from sample F11, while F9 and F10 show mainly broad unresolved peaks.

Thus GPC and HPLC analysis indicated that HPLC has a higher separation efficiency for the phenolics of less than M_r 800. The fingerprinting information of the GPC fractions in the low-molecular-mass range can be explored by the HPLC analysis. This analysis further confirmed that due to the limited solubility of the phenolics in the HPLC mobile phase, the sample recovery for the phenolic resin can be less than 50% and the high-molecular-mass phenolics oligomers cannot be analyzed using aqueous RP-HPLC.

3.2. HPLC separation

The phenolic compounds which can be analyzed by HPLC are normally divided into two groups. The first group includes phenol and phenol–formaldehyde monomers as shown in Fig. 2a. The second group includes dimers, trimers and other oligomers as shown in Fig. 2b. These two groups can be easily resolved from each other by HPLC. However, due to the similarity of the physical and chromatographic properties of these phenolics in each group, it is difficult to completely separate and quantitatively analyze these compounds. In most cases, the six phenol–formaldehyde monomers can only be partially separated and 2,4,6-trihydroxymethylphenol (2,4,6-THMP) is eluted together with either 4-hydroxymethylphenol or 2,4-dihydroxymethylphenol (2,4-DHMP).

3.2.1. Column and mobile phase optimization

The separation of the phenolic monomers can be optimized simply by using the empirical theory regarding the linear relationship of the HPLC log retention factor (log k) and the eluent composition. The relationship can be explained as:

$$\log k = A(\%\ \text{of eluent composition}) + B \quad (1)$$

where retention factor, $k=(t_R-t_0)/t_0$, indicates the retention time of a retained sample component relative to an unretained component. A and B are the slope and intercept, respectively, of the linear equation.

In the HPLC optimization, the five formaldehyde–

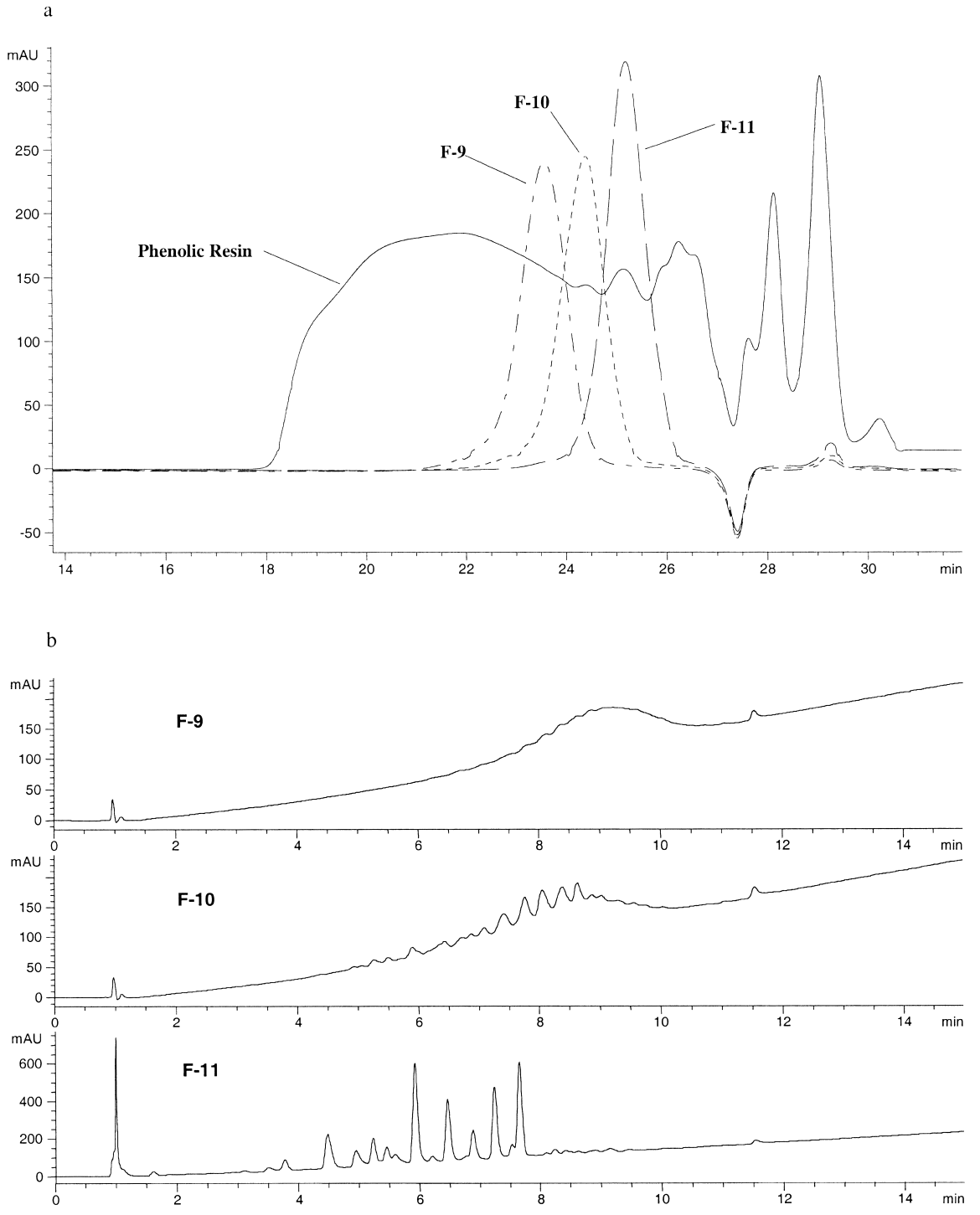

Fig. 1. (a) Overlaid GPC chromatograms of phenolic resin and three GPC fractions. (b) HPLC chromatograms of three GPC fractions. HPLC conditions: LiChrospher RP-8 (124×4.0 mm, 5 μm), water–MeOH (90:10) to (34:66) in 16 min, 1 ml/min, 218 nm.

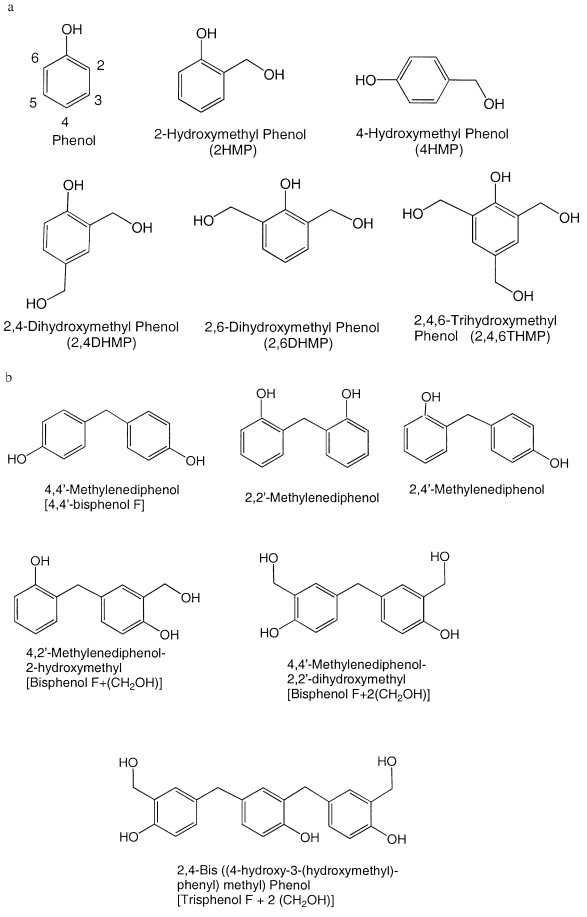

Fig. 2. (a) Structures of six phenol–formaldehyde monomers. (b) Example structures of phenol–formaldehyde dimers and trimers.

phenol monomers (excluding phenol) are selected as the target compounds for the optimization, because they are the most difficult compounds to be retained and completely separated by the RP-HPLC column. Because of the high reactivity and the purification complexity, it is difficult to obtain pure 2,4DHMP, 2,6DHMP, and 2,4,6THMP standards. Therefore, a phenolic resin sample was used in the optimization and the LC–MS selected ions, 153 for both 2,4DHMP and 2,6DHMP and 183 for 2,4,6THMP were used to identify these three target compounds. The MS selected ion chromatograms were used to obtain the retention times for the unresolved peaks. The DAD UV spectrum was used to distinguish between 2,4DHMP and 2,6DHMP because the *para*- and *ortho*-substituted phenolics show different hyperchromic effects at wavelength 225 to 230 nm.

Using a Hypersil C_{18} column with water and MeCN as mobile phase, the log *k* value was determined with different MeCN concentrations. It was found that all of the five phenolic monomers show a good linear relationship of their log *k* to the MeCN content from 2 to 6%. The optimized isocratic separation condition for the five monomers is visualized in Fig. 3. For these five compounds, 4HMP, 2,4DHMP, and 2,4,6THMP show low log *k* values, which indicates that they are the most polar and least retained phenolic compounds in the separation. From Fig. 3a, the optimized MeCN content should be between 4 and 5% on the C_{18} column. The retention time of these compounds on this column can be calculated based on the *A* and *B* values of the linear log *k* equation. Fig. 3b shows that these compounds will be retained very well when the MeCN content is less than 4% and will be eluted close to the void time when MeCN content is higher than 10%.

From the calculated retention profile we can see that the elution order will be different with different MeCN composition and the optimized separation

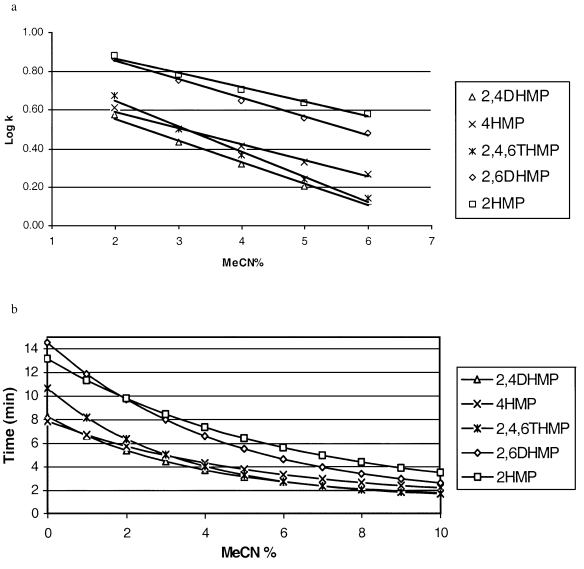

Fig. 3. Log *k* versus % MeCN of five phenolic monomers (a) and calculated retention time of five phenolic monomers (b) on a Hypersil C_{18} column (100×2.0 mm, 5 μm) with aqueous MeCN as mobile phase, 0.25 ml/min.

condition for the three most polar phenolic monomers is located in a narrow window from 4.0 to 4.5% MeCN. If MeCN content is higher than 4.5%, 2,4DHMP will elute together with 2,4,6THMP. If MeCN content is 3%, 4HMP will elute together with 2,4,6THMP.

Phenolic compounds are –OH-rich compounds, which contain phenol –OH and hydroxymethyl –OH. Like water, phenolic compounds can form hydrogen bonds in an aqueous solution. Generally, a phenolic compound with high formaldehyde substitution is more polar because of the greater number of hydroxymethyl groups. The difference between phenolic compounds and water is that when the substituted $-CH_2OH$ groups are located at positions 2 or 6 on a phenol ring, an intramolecular hydrogen bond can be formed. The formation of the hydrogen bond between phenolics and water can increase the solubility of the phenolics and reduce the HPLC retention of these compounds. In contrast, the intramolecular hydrogen bond can decrease the polarity of the compound and increase the retention factor of the compound. The change of the retention order of the phenolic monomers with different MeCN content is caused by the variation of the hydrogen bond formation.

Using the same procedure, the HPLC columns listed in Table 1 were evaluated with different mobile phase systems using these five phenolic monomers. Tables 2 and 3 list the *A* and *B* values.

Table 2
RP-HPLC retention parameters for five phenolic monomers [log $k = A(\%\ \text{acetonitrile}) + B$]

Column	Compound	*A*	*B*
Hypersil C_{18}	2,4DHMP	−0.1120	0.7688
	4HMP	−0.0824	0.7442
	2,4,6THMP	−0.1310	0.8958
	2,6DHMP	−0.0977	1.0458
	2HMP	−0.0718	0.9984
Hypersil C_8	2,4DHMP	−0.0850	0.7642
	4HMP	−0.0656	0.7871
	2,4,6THMP	−0.0981	0.8451
	2,6DHMP	−0.0765	1.0250
	2HMP	−0.0566	1.0111
Hypersil-CN	2,4DHMP	−0.0174	0.0935
	4HMP	−0.0137	0.1824
	2,4,6THMP	−0.0183	0.0745
	2,6DHMP	−0.0133	0.1932
	2HMP	−0.0095	0.2368
Hypersil-BDS C_{18}	2,4DHMP	−0.1120	0.8866
	4HMP	−0.0936	0.9087
	2,4,6THMP	−0.1337	1.0132
	2,6DHMP	−0.1025	1.1869
	2HMP	−0.0769	1.1545
Luna C_{18} (2)	2,4DHMP	−0.0913	1.0206
	4HMP	−0.0710	1.0393
	2,4,6THMP	−0.1084	1.1357
	2,6DHMP	−0.0838	1.3267
	2HMP	−0.0640	1.3220

3.2.2. Comparison of different columns

From the retention parameters listed in Tables 2 and 3, we find that the five most polar phenolic compounds can be completely separated by using all of the columns with aqueous MeCN except the CN column. Similar retention patterns to those shown in Fig. 3 were obtained. The optimized separation conditions for the three most polar phenolic monomers are still located in a very narrow window that is different for each column.

Comparing the retention behavior of the five phenolic monomers, we find that the HPLC separation is strongly related to the type of column used. All three of the C_{18} columns have given similar separation efficiency and the optimized separation on the C_{18} columns can be obtained by using 4% MeCN aqueous solution. The C_{18} columns with higher carbon loads also show higher retention ability than the C_8 and CN columns. The elution order of the six phenolic monomers on all C_{18} columns with 4% MeCN aqueous solution is: 2,4DHMP < 2,4,6THMP < 4HMP < 2,6DHMP < 2HMP < phenol.

In HPLC, the polar silanol groups on packing material can, in many cases, affect the separation efficiency. However, the similar separation behavior of these compounds on the columns with low (Hypersil C_{18} BDS) and high (Luna C_{18}) silanol distribution indicates that the column silanol polarity is not a significant factor in the phenolic separation.

For the low carbon load C_8 column, the elution order of these monomers is similar to that on a C_{18} column; however, the mobile phase for the optimized separation is slightly different, in which the MeCN content should be decreased from 4 to 3.5%.

Table 3
RP-HPLC retention parameters for five phenolic monomers [log $k = A(\%\ \text{MeOH or THF}) + B$]

Column	Compound	A	B
Log $k = A(\%\ \text{MeOH}) + B$			
Hypersil C_{18}	2,4DHMP	−0.0700	0.8922
	4HMP	−0.0553	0.8396
	2,4,6THMP	−0.0839	1.0530
	2,6DHMP	−0.0653	1.1597
	2HMP	−0.0489	1.0697
Hypersil C_8	2,4DHMP	−0.0500	0.8297
	4HMP	−0.0402	0.8273
	2,4,6THMP	−0.0601	0.9445
	2,6DHMP	−0.0454	1.0797
	2HMP	−0.0364	1.0477
Log $k = A(\%\ \text{THF}) + B$			
Luna C_{18} (2)	2,4DHMP	−0.1034	0.5996
	4HMP	−0.0848	0.6190
	2,4,6THMP	−0.0617	0.7693
	2,6DHMP	−0.0844	0.9244
	2HMP	−0.0574	1.0893

3.2.3. Comparison of different mobile phases

In HPLC phenolic resin analysis, aqueous methanol is another mobile phase commonly used. The difficulty to resolve the polar phenolic monomers by this mobile phase were also introduced in the literature [5,6,10]. As shown in Fig. 4, the optimized separation window for the three most polar phenolic monomers on C_{18} column is again narrow and the methanol content has to be as low as 1 to 2%. The elution order for the aqueous methanol mobile phase is slightly different from that of aqueous acetonitrile. The elution order on a C_{18} column with the MeOH less than 3% is: 4HMP < 2,4DHMP < 2,4,6THMP < 2HMP < 2,6DHMP < phenol. With the methanol at or above 10%, 2,4DHMP and 2,4,6THMP will elute together and the elution order will change to: 2,4DHMP + 2,4,6THMP < 4HMP < 2,6DHMP < 2HMP < phenol. This result can explain the difference of the chromatography published by Mechin et al. in two different publications [5,6]. This elution order is different from the data published by Grenier-Loustalot et al. [10] in which the 2,6DHMP was eluted earlier than 2,4DHMP. It should be mentioned that one disadvantage of using methanol as mobile phase is the dramatic increase of the retention time for complete separation.

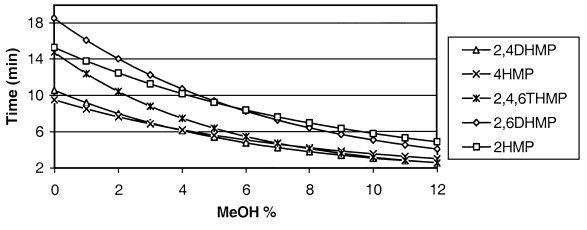

Fig. 4. Calculated retention profile of five phenolic monomers on a Luna C_{18} column (150×2.0 mm with 30×2.0 mm guard column) with aqueous THF as mobile phase.

THF is a stronger solvent in RP-HPLC and phenolic monomers can be eluted much faster. The five monomers can be baseline separated when THF content is less than 4% in the mobile phase. The A and B values using aqueous THF as mobile phase and C_{18} column are listed in Table 3. The difference in the use of THF is that the elution order of these phenolic compounds is unchanged while the retention time of phenolic compounds decreases with increasing THF concentration. This difference from the use of MeOH or MeCN as mobile phase can be explained as a lessened effect of the formation of intramolecular hydrogen bonds in the THF.

3.2.4. Sample preparation

As discussed above, only half of the phenolic compounds in phenolic resin can be eluted by HPLC. The high-molecular-mass phenolic polymer can precipitate in the aqueous mobile phase and stay in the column. Therefore, phenolic resin samples are normally prepared by use of a polar solvent to precipitate the high-molecular-mass polymers before being introduced into the HPLC system. However, this sample preparation step may affect the phenolic recovery in the HPLC analysis. In this study, the sample recoveries for phenolic monomers, dimers and trimers were evaluated.

First of all, the extraction efficiency for the phenolic compounds was evaluated by using different solvents. Tetrahydrofuran, methanol and acetonitrile were selected as the solvents to dissolve or extract phenolic compounds from phenolic resin and phenolic resin prepreg products. The extracts in these solvents were then analyzed by HPLC. The HPLC analysis shows that no difference can be detected from the HPLC elutable compounds using these

three solvents. Basically, phenolic resin is a product with a high polarity. Most of the phenolic compounds in phenolic resin contain hydroxyl groups. The polarity of the phenol–formaldehyde polymer continues to decrease as the molecular mass of the polymer increases because of the reduction of $-CH_2OH$ groups by loss of water in the condensation reaction. The less polar or higher-molecular-mass phenolic compounds can be removed simply by diluting the extract in water and filtering the resultant milky suspension. In order to evaluate the effect of the sample ''cleaning'' on the HPLC elutable compounds, the sample recoveries of phenolic monomers, dimers and trimers in a phenolic resin were studied further.

Increased formaldehyde substitution will make the phenolic compound more polar and more soluble in an aqueous solution. Therefore, the recoveries of all six phenolic monomers were evaluated using the two least polar phenolic monomers, 2HMP and phenol. The recovery of all dimers and trimers were evaluated by using two non-substituted phenolic dimers and two non-substituted phenolic trimers. Table 4 shows the recoveries of these compounds when the sample solutions were prepared in water with 10 to 40% THF, respectively. This analysis indicates that good sample recovery can be ensured by 30% THF for all monomers and dimers and 40% for all trimers. The recovery of the phenolic monomers, dimers, and trimers in 50% MeOH and MeCN solutions was also ensured by comparison with the THF sample solutions.

3.2.5. Sample overloading

In the phenolic resin analysis, the optimized HPLC separation requires using a high water content mobile phase. However, the sample preparation favors a low water content. These two opposite requirements cause a serious injection volume-overloading problem in the phenolic separation. In order to optimize the sample injection volume, the separation efficiency of four phenolic monomers was evaluated. The theoretical plate number (N) was decreased with the variation of the injection volume from 1 to 8 μl. The column efficiency decreased 11, 33, 17, and 16% for 2,4DHMP, 2,4,6THMP, 4HMP and phenol, respectively, when the injection volume increased from 1 to 2 μl. The efficiency decreased by 32, 52, 36, and 32% for the respective four compounds when 4 μl of sample solution was injected rather than 1.

When we evaluate the relative separation of 2,4DHMP and 2,4,6THMP, the resolution (R_s) between these two peaks decreased from 2 to 1.5 when the injection volume increased from 1 to 4 μl and it was even further decreased to 1.0 when 7 μl sample solution was injected. These results indicate that the injection volume should be kept below 4 μl in order to obtain a good column efficiency for the HPLC system used.

3.2.6. Phenolic resin separation and MS identification

Based on the information introduced in the sample preparation, volume overloading, and column and mobile phase optimization, methods for isocratic separation of just the phenolic monomers can be developed using C_{18} or C_8 columns with different mobile phase combination. Using C_{18} columns with 4% MeCN aqueous solution as mobile phase, a phenolic resin sample was analyzed and is shown in Fig. 5. In this separation, only the six monomers were eluted from the column. Other phenolics stayed in the column and will not interfere with the monomer analysis even with 10 injections. This chromatographic separation makes it possible to

Table 4
Relative response of phenolic compounds in sample solutions prepared in water with 10 to 40% THF

THF (%)	Relative response					
	2HMP	Phenol	4,4-Bisphenol F	2,4-Bisphenol F	Trimer 1	Trimer 2
10	13.0	20.2	0.61	0.54	–	–
20	24.0	37.6	1.17	1.09	0.02	0.01
30	25.8	40.1	2.87	3.74	0.54	0.37
40	26.0	40.1	2.74	3.63	0.55	0.41

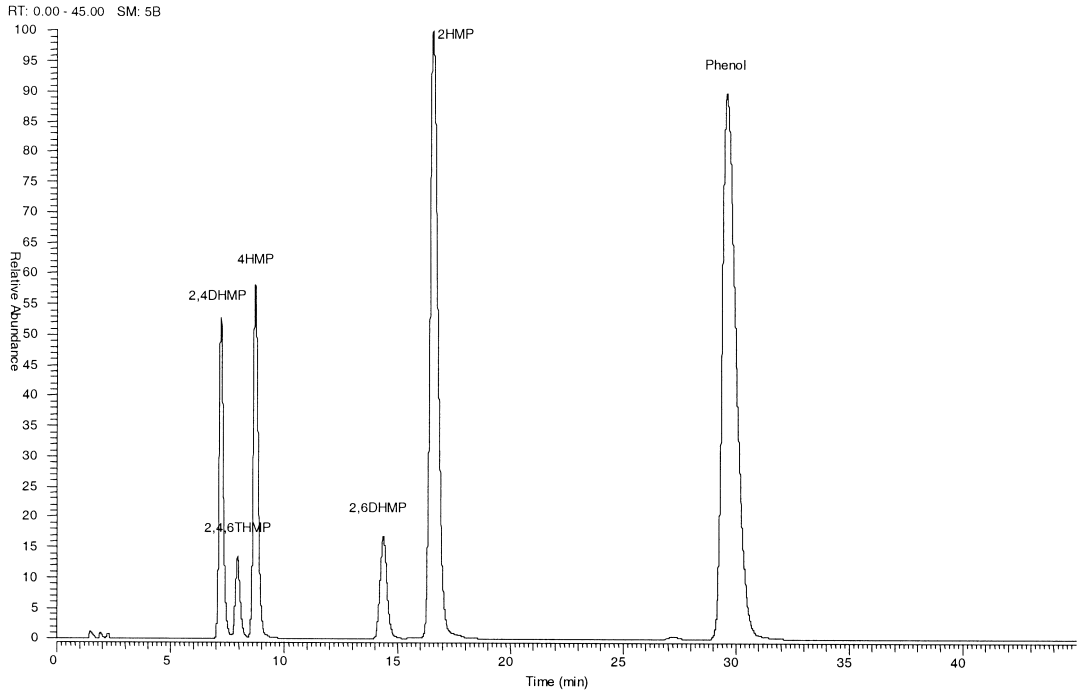

Fig. 5. HPLC separation of six phenolic monomers on a Luna C_{18} column (150×2.0 mm with 30×2.0 mm guard column) with MeCN–water (4:96), 0.3 ml/min, 273 nm.

evaluate different phenolic resin products by comparing the distribution of these compounds. Due to the high reactivity and strong correlation of the multi-substituted phenolic monomers, especially 2,4,6-THMP, to the initial ratio of phenol–formaldehyde used in the production, the content of these compounds can be used as an indicator to potentially distinguish among different phenolic resins and even the manufacturing process.

Due to the long retention of phenol by isocratic elution, a gradient separation can be performed on a C_{18} column by increasing the acetonitrile content after the three most polar phenolic monomers eluted from the column. Fig. 6 shows the gradient elution, in which not only the six phenolic resin monomers were separated, but also the high level phenolic dimers and trimers.

On-line MS detection was used in the HPLC phenolic analysis to identify the separated phenolic peaks. Based on the MS molecular mass information, the chemical composition of 27 phenolic compounds were determined and are listed in Table 5. Since negatively charged ions were monitored by the MS detector, the m/z values shown in Table 5 indicate the M−1 values (molecular ion minus one proton). Using the HPLC and MS information, the reactivity of the phenolic monomers, dimers and trimers were studied. The reactivity of the phenolic monomers in phenolic resin at 50°C was determined. The order of reactivity is: $k_{\text{phenol}} < k_{\text{2HMP}} < k_{\text{4HMP}} < k_{\text{4,6DHMP}}$ and $k_{\text{2,4DHMP}} < k_{\text{2,4,6THMP}}$. This order is different from that reported by Grenier-Loustalot et al. [11].

3.3. GPC analysis

3.3.1. Conventional GPC calibration

Due to the elution limits of the HPLC separation, the high-molecular-mass phenolic compounds and polymers were characterized by GPC. A conventional polystyrene calibration method was applied in the GPC analysis to determine the relative molecular mass distribution of number-average molecular mass (M_n), weight-average molecular mass (M_w) and polydispersity (PD). The RI response was used in the

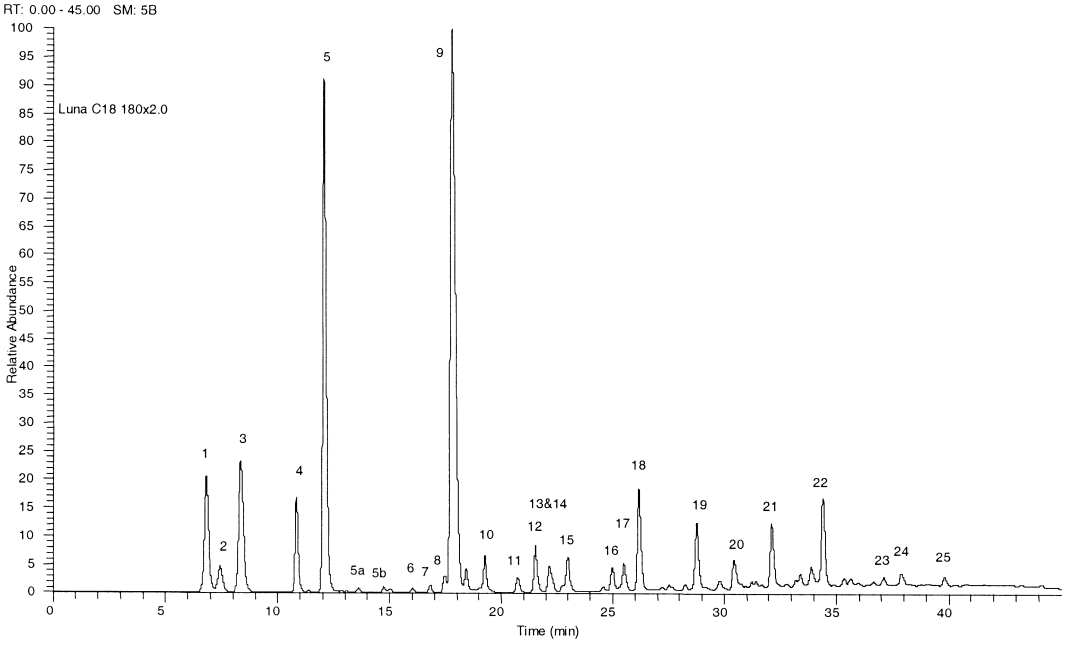

Fig. 6. Gradient elution of phenolic monomers, dimers, and trimers using a Hypersil C_{18} column (150×2.0 mm I.D. with 30×2.0 mm guard column). Mobile phase: (A) premixed MeCN–water (4:96), (B) MeCN, hold 3 min at (A–B, 100:0), then to (95:5) in 1 min, (75:25) in 22 min, (65:35) in 5 min, (60:40) in 5 min, (20:80) in 5 min, post run time 15 min, 0.3 ml/min, 273 nm.

analysis to calculate the mass percent concentration of phenolic compounds in a phenolic resin based on the refractive index response and concentration parameter (dn/dc) of phenolic compounds. The ratio of UV response versus the response of refractive index was calculated to indicate the UV response property of the phenolic resin. This parameter is a measure of the relative amount of phenol units (UV response) to the total resin mass (RI response) that has the potential to detect variation in the critical phenol–formaldehyde ratio. Table 6 shows an example of the composition of phenolic resin samples, in which mass percent concentration of isopropanol (IPA), phenol, water and calculated resin content, as well as the GPC determined resin content, molecular mass distribution (excluding phenol), and relative phenol unit are reported. The IPA and phenol content reported in Table 6 were determined by GC–flame ionization detection (FID). The moisture content was determined by Karl–Fisher titration. The calculated resin content was then determined as the difference of the sample minus these constituents. The GPC determined resin content was calculated from the RI response with the phenolic resin dn/dc value, which is 0.176 ml/g in THF at 25°C. The relative amount of chromophore (phenol unit) in the polymer per mass was calculated as the ratio of UV response at 280 nm to the RI response, which indicates the relative content of the UV absorbing phenol unit in a phenolic resin. It may thus be able to indicate the ratio of the phenol to formaldehyde used in the manufacturing process. The molecular mass and polydispersity reported in Table 6 were calculated based on the polystyrene calibration method.

3.3.2. Light-scattering molecular mass distribution

A light-scattering (LS) calibration method was applied to the GPC analysis to characterize phenolic resin as well. Due to a low light-scattering response by most phenol–formaldehyde monomers, dimers and trimers, the light-scattering-calculated molecular mass for these compounds can show high variation. Therefore, light-scattering detection is only useful to analyze the molecular mass distribution of staged or resin preimpregnated cloth (prepreg) products where high molecular mass materials are more prevalent.

Table 5
List of m/z values and chemical composition of phenolic monomers, dimers and trimers

Peak No.	m/z	Synonym[a]	Composition
1	153	2,4DHMP	2,4-Dihydroxymethylphenol
2	183	2,4,6THMP	2,4,6-Trihydroxymethylphenol
3	123	4HMP	4-Hydroxymethylphenol
4	153	2,6DHMP	2,6-Dihydroxymethylphenol
5	123	2HMP	2-Hydroxymethylphenol
5a*	197	M-1	Trihydroxymethylphenol $-CH_3$ ether[b]
5b*	167	M-2	Dihydroxymethylphenol $-CH_3$ ether[b]
6	319	D1-320	Bisphenol F+4 ($-CH_2OH$)
7	289	D2-290	Bisphenol F+3 ($-CH_2OH$)
8	319	D3-320	Bisphenol F+4 ($-CH_2OH$)
9	93	Phenol	Phenol
10	289	D4-290	Bisphenol F+3 ($-CH_2OH$)
11	259	D5-260	Bisphenol F+2 ($-CH_2OH$)
12	259	D6-260	Bisphenol F+2 ($-CH_2OH$)
13	229	D7-230	Bisphenol F+1 ($-CH_2OH$)
14	289	D8-290	Bisphenol F+3 ($-CH_2OH$)
15	259	D9-260	Bisphenol F+2 ($-CH_2OH$)
16	259	D10-260	Bisphenol F+2 ($-CH_2OH$)
17	259	D11-260	Bisphenol F+2 ($-CH_2OH$)
18	229	D12-230	Bisphenol F+1 ($-CH_2OH$)
19	229	D13-230	Bisphenol F+1 ($-CH_2OH$)
20	229	D14-230	Bisphenol F+1 ($-CH_2OH$)
21	199	4,4-Bisphenol F	4,4-Bisphenol F
22	199	2,4-Bisphenol F	2,4-Bisphenol F
23	335	T1-336	Trisphenol F+1 ($-CH_2OH$)
24	305	T2-306	Trisphenol F
25	305	T3-306	Trisphenol F

[a] For peaks 5a to 25: M=monomer, D=dimer, T=trimer.
[b] Tentatively identified compounds.

Fig. 7 shows the overlaid RI chromatograms of a prepreg phenolic resin extract with M_r 20 000 and 98 000 polystyrene standards and the LS molecular mass distribution of the phenolic polymers and the polystyrene standards. Based on light-scattering theory and using the phenolic resin dn/dc value, the molecular masses of the phenolics eluting from 17.2 to 27.0 min were calculated as $M_n=1800$, $M_w=7100$, and $M_w/M_n=4.0$. For the same elution time range, these values were calculated as 780, 4229 and 5.4, respectively, by using the polystyrene calibration.

The difference in the molecular mass distribution determined by light-scattering and conventional calibration methods can be explained by the phenolic compounds being more compact and dense than the

Table 6
GPC separation and characterization of phenolic resin

Sample	IPA (%)	Phenol (%)	Water (%)	Calculated resin (%)	RI resin (%)	UV (280 nm)/RI (unit)	M_r (RI)	Polydispersity (RI) (unit)
Resin 1	21.6	13.8	3.2	61.4	62.0	6.75	785	1.77
Resin 2	22.2	13.2	3.3	61.3	62.7	6.76	800	1.79
Resin 3	20.5	13.2	2.9	63.4	61.2	6.76	778	1.76
Resin 4	21.5	13.9	3.3	61.3	62.7	6.76	764	1.75
Resin 5	21.6	13.5	3.3	61.6	63.2	6.76	829	1.83
Resin 6	21.4	13.2	3.3	62.1	63.6	6.80	901	1.91

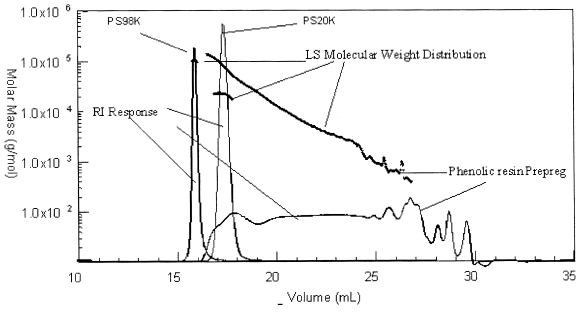

Fig. 7. Overlaid RI chromatograms of a phenolic resin prepreg extract, M_r 20 000 and 98 000 polystyrene standards and their LS molecular mass distributions.

polystyrene standard used. As shown in Fig. 7, the molecular masses of the M_r 20 000 and 98 000 polystyrene standards determined by the LS analysis are very close to their nominal values. However, the molecular masses of the phenolics that eluted in the same range as the polystyrene standards were calculated with a higher value. It is known that same retention time in a GPC separation indicates the same hydrodynamic volume. Therefore, the same hydrodynamic volume with different molecular mass indicates a different density. Using a viscometer SEC^3 (Viscotek, Houston, TX, USA) system, the phenolic resin polymer was determined to be more dense and less flexible than the polystyrene polymers as well.

4. Conclusions

Both GPC and HPLC should be used as the chromatographic techniques to separate and characterize a phenolic resin product. In HPLC analysis, phenolic compounds can form intermolecular or intramolecular hydrogen bonds in the aqueous mobile phase. The variation of the hydrogen bond formation can change the retention order of the phenolic monomers and cause difficulty in their separation. It was found that the optimized HPLC separation window is very narrow for the polar phenolic monomers, but both C_8 and C_{18} columns can give a good separation if the right mobile phase is used. Due to the incompatibility of the mobile phase polarity and phenolic solubility, it was recommended that samples be prepared with 50% MeOH or THF to remove the high-molecular-mass phenolic polymers but ensure the HPLC sample recovery. Due to the same reasons, the HPLC separation shows strong volume band-broadening, which requires that the sample injection volume be limited. Using on-line MS detection, 27 HPLC-resolved phenolic compounds were identified and reported. Based on the information received in the study, RP-HPLC methods with isocratic or gradient elution were developed and used to fingerprint phenolic monomers, dimers and trimers.

In the GPC analysis, the phenolic resin content was calculated based on the RI response and the concentration parameter (dn/dc) of phenolic compounds. The ratio of the relative amounts of phenol units (UV response) to the total resin mass (RI response) was calculated. This parameter has the potential to detect variation in the critical phenol–formaldehyde ratio. The LS analysis gives a higher molecular mass distribution than a polystyrene GPC retention calibration, which indicates that phenolic resin polymer is more dense then polystyrene polymers.

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References

[1] A. Knop, L.A. Pilato (Eds.), Phenolic Resin – Chemistry, Applications, and Performance, Springer-Verlag, New York, 1985, p. 125.
[2] M.P. Stevens (Ed.), Polymer Chemistry, Oxford University Press, New York, 1990, p. 470.
[3] K. Hibi, A. Wada, S. Mori, Chromatographia 21 (1986) 635.
[4] M.-F. Grenier-Loustalot, S. Larroque, P. Grenier, D. Bedel, Polymer 37 (1996) 939.
[5] B. Mechin, D. Hanton, J. Le Goff, J.P. Tanneur, Eur. Polym. J. 20 (1984) 333.
[6] B. Mechin, D. Hanton, J. Le Goff, J.P. Tanneur, Eur. Polym. J. 22 (1986) 115.
[7] M. Bruze, L. Persson, L. Trulsson, E. Zimerson, Contact Dermatitis 14 (1986) 146.

[8] J.W. Blanks, in Proceedings of the 1998 JANNAF RNTS Special Session, Salt Lake City, UT, 16–20 March, 1998, published by the Chemical Propulsion Information Agency of the John Hopkins University, Columbia, MD, p. 133.
[9] J.H. Brown, Y.V. Kazakevich, H.M. McNair, P.R. Young, presented at Pittcon '98, New Orleans, LA, 1–5 March 1998, Abstract 341.
[10] M.-F. Grenier-Loustalot, S. Larroque, P. Grenier, J.-P. Leca, D. Bedel, Polymer 35 (1994) 3046.
[11] M.-F. Grenier-Loustalot, S. Larroque, P. Grenier, D. Bedel, Polymer 37 (1996) 955.