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Controlled molecular weight cresol–formaldehyde oligomers

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Abstract

Controlled molecular weight, linear, *ortho*- and *para*-cresol novolac oligomers have been synthesized by using calculated amounts of a monofunctional 2,6-dimethylphenol endcapping reagent. It was found that an excess of formaldehyde was needed to achieve the targeted molecular weights, thus suggesting that a dynamic equilibrium exists in these reactions whereby formaldehyde adds and eliminates from the cresol rings. Reaction progression was monitored by both ^{13}C NMR and GPC. Number average molecular weights of these oligomers were confirmed using ^{13}C NMR spectra and were found to be comparable to the targeted molecular weights.

The glass transitions and viscosities of both the *ortho*- and *para*-cresol novolacs were compared at equivalent number average molecular weights. The T_gs increased as the molecular weights increased, but there were no observable differences between the T_gs of *ortho*- and *para*-cresol novolacs with similar molecular weights. The melt viscosities of *ortho*- and *para*-cresol novolcas with similar molecular weights were almost identical. © 2002 Published by Elsevier Science Ltd.

Keywords: Cresol; Novolac; Model phenolic oligomers

1. Introduction

Phenolic resins are among the oldest known and highest volume thermosetting materials produced in the United States [1]. Among the numerous attractive properties of phenolic resins and their networks are low cost and excellent flame retardance [2,3]. Therefore, we and others are investigating this class of materials as possible matrix resins for flame retardant structural composites. The most common phenolic pre-polymers are derived from reacting phenol with formaldehyde or with formaldehyde derivatives. This reaction occurs most rapidly under extremely acidic or basic conditions. The pH of the reactions and the stoichiometric ratio of the monomers give rise to two classes of phenolic pre-polymers known as novolacs and resoles.

Novolac oligomers are prepared in acidic media using an excess of phenol over formaldehyde. The mechanism associated with this reaction has been described in four steps (Fig. 1). First a methylene glycol is protonated by an acid from the reaction medium, which then releases water to form a hydroxymethylene carbonium ion (step 1). This ion acts as a hydroxyalkylating agent by reacting with a phenol via electrophilic aromatic substitution. A pair of electrons from the benzene ring attacks the electrophile forming a carbocation intermediate followed by deprotonation and regain of aromaticity (step 2). The methylol group of the hydroxymethylated phenol is unstable under acidic conditions and loses water readily to form a benzylic carbonium ion (step 3). This ion then reacts with another phenol to form a methylene bridge in another electrophilic aromatic substitution. This major process repeats until the formaldehyde is exhausted [4].

Typically 0.75–0.85 mol of formaldehyde are used for each mole of phenol in the synthesis of low molecular weight novolacs [1], and branched oligomers with phenol endgroups are formed since phenol is used in excess. These pre-polymers are thermally stable and can be stored effectively. Novolac crosslinking is usually achieved by introducing a source of methylene groups to form additional methylene bridges between aromatic rings. Hexamethylenetetramine (HMTA) is the most widely used curing agent (source of formaldehyde) for these reactions. Other curing agents with limited importance include *para*-formaldehyde and trioxane [1].

Resoles are obtained by reacting an excess of formaldehyde with phenol under basic conditions. This produces resins with aromatic methylol groups derived from the excess of formaldehyde. Resoles are fairly stable at ambient temperatures, but react rapidly at elevated temperatures forming methylene linkages by eliminating water and

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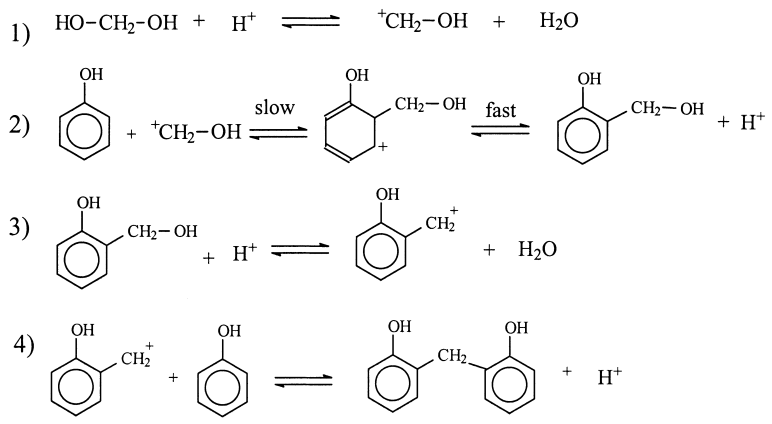

Fig. 1. Mechanism for the major process of phenolic novolac resin synthesis.

other by-products. Since these materials can be 'self'-crosslinked thermally, long-term storage is more difficult.

Regardless of the curing method, either by introducing a crosslinking agent or by thermal self-condensation, the network forming process is accompanied by the generation of volatile by-products such as ammonia, water and formaldehyde. Volatiles often cause voids in the networks [5–7]. This, along with a lack of control over crosslink density, results in brittle networks.

Void-free networks can be prepared by reacting phenolic novolacs with epoxies in reactions where the phenolic hydroxyl groups react with the epoxy groups [8–11].

Workers in our laboratories have previously demonstrated that phenolic–epoxy networks with high phenolic compositions, and with a relatively high phenol functionality per chain (~7), exhibit significantly improved toughness while retaining most of the flame retardant properties [12,13]. These improved mechanical properties were correlated with increased molecular weights between crosslinks achieved by leaving many phenolic hydroxyl groups unreacted.

Linear, cresol novolac oligomers, obtained by reacting difunctional *ortho*- or *para*-cresol with formaldehyde, are widely used as coatings, adhesives, electronic insulation materials, and for automotive applications [1]. Low molecular weight oligomers have also been reacted with epichlorohydrin to form epoxy resins [8]. A *para*-cresol novolac ($M_n = 580$ g/mol) exhibited a semi-crystalline structure with good thermal stability [14]. *Ortho*- and *para*-cresol have also been copolymerized with *meta*-cresol for use in the electronic industry as photoresists. Since *ortho*- and *para*-cresol have slower reaction rates with formaldehyde than *meta*-cresol, oligomers with *meta*-cresol blocks were obtained having primarily *ortho*- or *para*-cresol endgroups [15,16].

Ortho- or *para*-cresol novolac formation, which involves exclusively difunctional monomers, are linear condensation polymerizations. The molecular weights of these cresol novolacs, therefore, should depend on the monomer feed ratio. However, to date, cresol resin syntheses follow typical phenolic novolac synthesis procedures where reactions are terminated at a pre-determined viscosity or reaction time. The difficulty in molecular weight control arises from side reactions, which offset the stoichiometric ratio necessary to obtain target molecular weights. This paper describes the synthesis of linear controlled molecular weight cresol novolacs. The degree of molecular weight control achievable and properties such as glass transition temperatures, molecular weight distributions, and melt viscosities will be discussed. These cresol novolacs have also been crosslinked with epoxies. The network formation reactions and their properties will be addressed in a separate paper.

2. Experimental

2.1. Materials

Ortho-cresol (99 + %), *para*-cresol (99%), 2,6-dimethylphenol (99%), *para*-formaldehyde (powder, 95%), formaldehyde (37 wt% solution in water), and oxalic acid dihydrate (99%) were obtained from Aldrich. A commerical phenolic resin was kindly provided by Georgia-Pacific (Product #GP-2073). All reagents were used as received.

2.2. Molecular weight calculations

The following method was used to calculate the stoichiometric ratio of monomers required to obtain specified number average molecular weights. The molecular weight of two endcapping molecules, 2,6-dimethylphenol, and one methylene linkage, $-CH_2-$, were subtracted from the total targeted molecular weight. The remaining weight was divided by the molecular weight of each repeat unit (120 g/mol) to obtain the number of repeat units within the chain (x). The stoichiometric ratio then consisted of two moles of 2,6-dimethylphenol, x moles of cresol, and $x + 1$ moles of formaldehyde. The following example is for the stoichiometric calculation of reactants for a 2000 g/mol oligomer capped on each end with 2,6-dimethylphenol. The combined molecular weight of the

two endgroups (one methylene unit and two 2,6-dimethylphenol units) is 256. One can subtract this from the desired 2000 g/mol molecular weight of the oligomer to obtain the oligomer molecular weight satisfied by the repeat units themselves: $2000 - 256 = 1744$. The molecular weight of a repeat unit is 120 g/repeat unit. Thus, the average number of repeat units in a chain will be $1744/120 = 14.53$. The stoichiometric ratio is cresol (14.53 mol) to formaldehyde (15.53) and to 2,6-dimethylphenol (2). In the late stages of the reaction, an additional 10 mol% excess of a formaldehyde source must be added to ensure reaction completion. A typical method is given later.

2.3. Synthesis of 2,6-dimethylphenol endcapped cresol novolac resins

Ortho-cresol novolac and *para*-cresol novolac resins were prepared in the same manner. The following shows a sample reaction for preparing a 2000 g/mol *ortho*-cresol novolac resin. In a resin kettle equipped with a stainless steel mechanical stirrer and a condenser connected to an outlet, *ortho*-cresol (303.5 g, 2.81 mol), 2,6-dimethylphenol (47.2 g, 0.39 mol) and *para*-formaldehyde (94.9 g, 3.0 mol) were added. This mixture, along with oxalic acid dihydrate (2.5 wt% (2.14 mol%) based on the weight of cresol, 7.59 g) was heated for approximately 6 h at 100 °C, then an ~10 mol% excess of formaldehyde (37 wt% formaldehyde in water, 27 ml) was added to the reaction. The reaction was continued for an additional 18 h. It was washed twice with boiling deionized water, then stripped under mild vacuum while being slowly heated to 215 °C.

2.4. Sample preparation for viscosity measurement

All cresol novolac resins and the control commerical phenolic resin were vacuum stripped (30 Hg) for 2 h at 165 °C prior to any measurements.

2.5. Characterization

2.5.1. Nuclear magnetic resonance spectroscopy

^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian Unity 400 NMR spectrometer. For ^{1}H NMR, 5 mm diameter tubes containing approximately 20 mg samples dissolved in DMSO-d_6 were analyzed under ambient conditions. The experimental parameters included a 1.0 s relaxation delay, 23.6° pulse, and 6744.9 Hz spectral width. Thirty-two repetitions were used for each sample. For ^{13}C NMR, samples of approximately 0.6 g were dissolved in ~2 ml acetone or DMSO. The samples were placed in 10 mm diameter tubes for analysis under ambient conditions. An inverse gated decoupling technique with a 90° pulse, a 6 s relaxation delay, a frequency of 100.578 MHz, and 1.2 s acquisition time were used to obtain quantitative ^{13}C NMR data. Approximately 1000 repetitions were used for each sample.

2.5.2. Gel permeation chromatography

GPC was conducted on a Waters GPC/ALC 150-C chromatograph equipped with a differential refractometer detector connected in parallel to a differential viscometer detector Viscotek model 150R. The injection and column compartment, connecting line, and DV detector were individually controlled and maintained at the same temperature (60 °C). The signals from the RI and DV detectors permitted the calculation of intrinsic viscosity for universal calibration purposes by using Viscotek software Unical 4.04 assuming that the polymer concentration at the outlet of the SEC columns approached infinite dilution due to separation and column dispersion. The mobile phase was NMP (dried over phosphorus pentoxide, then vacuum distilled) with a flow rate of 1 ml/min. The columns were Styragel HT with pore sizes of 10^3 and 10^4 Å. The injection volume was 100 μl.

2.5.3. Viscosity determination

Complex viscosities were obtained from a Bohlin VOR Rheometer operating in continuous oscillation mode at a frequency of 1 Hz. Temperature control was accomplished with a Bohlin HTC. The auto-strain was set to maintain the torque at 25% of the maximum torque allowed. The maximum strain for the instrument was 0.25. Approximately 0.7 g of cresol novolac pellets were placed between the pre-heated 25 mm diameter parallel plates of the rheometer. The gap was closed to approximately 1 mm and the sides were scraped to remove excess sample before the run was started.

The glass transition temperatures of neat resins were obtained with a Perkin-Elmer DSC-7 instrument. The DSC was calibrated with indium and zinc standards, and ice water was used as the coolant. Samples in aluminum pans were heated from 20 to 180 °C. The glass transition temperatures were calculated as the midpoints of the curves.

3. Results and discussion

A series of linear, controlled molecular weight, 2,6-dimethylphenol endcapped cresol novolac resins have been synthesized via electrophilic aromatic substitution (Fig. 2). The use of *ortho*- or *para*-cresol as a monomer allows for preparing linear oligomers since the cresol ring has only two activated positions for formaldehyde substitution. By contrast, phenol has three reactive sites (i.e. both *ortho* and the *para* positions) and therefore, branching is inevitable as higher molecular weight develops. For example, branching has been shown to occur significantly once the molecular weight reached 900–1000 g/mol [1]. Addition of calculated amounts of 2,6-dimethylphenol endgroups to the linear *ortho*- or *para*-cresol–formaldehyde reactions allows for the generation of controlled molecular weight materials.

The reactivity rates for phenol versus cresol formaldehyde substitutions are different. Phenol reacts with formaldehyde

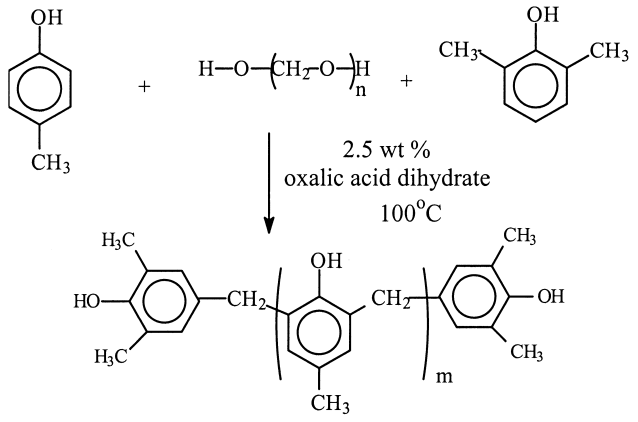

Fig. 2. Synthesis of 2,6-dimethylphenol endcapped *para*-cresol novolac resins.

approximately three times faster than *ortho*- or *para*-cresol [17]. Water reduces the rate of reaction between phenol and formaldehyde if used in large amounts [4]. In this work, cresol novolacs were prepared with *para*-formaldehyde, as opposed to aqueous formaldehyde, to achieve faster reaction rates. *Para*-formaldehyde contains only 1–9 wt% water whereas the formaldehyde typically used in phenolic syntheses contains approximately 50–63 wt% water.

Oxalic acid dihydrate was used as the catalyst since it is a relatively strong acid. It is preferred over other catalysts because resins with less color can be obtained. Moreover, there is no need to remove the catalyst after the reaction since it can be thermally decomposed to CO, CO_2, and water above approximately 180 °C [1].

In these reactions, the initial viscosities were low and the solutions were miscible. However, as the reactions proceeded and molecular weights increased, the solutions phase separated. The low molecular weight oligomers formed a water-insoluble melt, while the acid catalyst and the formaldehyde probably remained predominantly in the aqueous phase. Slow reaction rates were observed which are probably attributable to the two-phase nature. The formaldehyde added toward the end of the reactions was in an aqueous solution. Water was desirable in this stage to plasticize the reaction mixtures and lower the viscosities. This was particularly important in the syntheses of higher molecular weight cresol novolacs when the viscosities were high.

3.1. Molecular weight control and calculations

Typical phenolic novolac syntheses lack molecular weight control. The reactions are generally terminated after a certain reaction time or once a specified viscosity is reached [18]. The molecular weights of the cresol novolac resins described herein were strategically controlled by the stoichiometric ratio of *ortho*- or *para*-cresol to 2,6-dimethylphenol (Table 1). As expected, molecular weights of the oligomers increased as the amount of endcapping reagent was decreased.

The number average molecular weights in these cresol novolac syntheses were controlled by the cresol to endgroup molar ratio. However, in contrast to usual practice, it was necessary to add formaldehyde in excess to achieve full conversion of the cresol reactive ring positions. When the calculated amounts of formaldehyde were used, molecular weights of the products were always lower than the targeted molecular weights, and it was evident from ^{13}C NMR spectra that unreacted ring positions on cresols remained under such conditions. Formaldehyde was added in two positions to couple all of the reactive sites on cresol. Initially, the stoichiometric calculated amount of formaldehyde was charged to the reactions with cresol and 2,6-dimethylphenol at 100 °C. The early stages of these reactions were exothermic and the reactions refluxed. After about 6 h, more formaldehyde (10 additional mol% of the calculated amount in the form of formalin) was added to ensure that sufficient formaldehyde was available to complete the reactions.

Targeted molecular weights were consistently achieved using the approach of adding excess formaldehyde as described earlier. This suggests a reversible reaction between cresol or its derivatives and formaldehyde whereby substitution and elimination of formaldehyde occurs. This would allow for coupling regenerated ring positions and methylols to form methylene linkages and achieve the targeted molecular weights. It is also possible that some gaseous formaldehyde, formed by depolymerization of polyoxymethylene, escaped from the reactions during the initial exothermic stages.

The required stoichiometeries for controlling molecular weights were calculated using the Carother's approach. A step-growth polymerization was considered involving the reaction of monomers AWA, BYB, and AZ in which the functional groups A react with functional groups B. It was assumed that very high conversion was achieved and that

Table 1
Molecular weights of *ortho*- and *para*-cresol novolac resins calculated ^{13}C NMR. The molecular weights were controlled by adjusting the N_{AA}/N'_{ZA} ratio

Target M_n (g/mol)	N_{AA} (cresol) (mol)	N'_{ZA} (2,6-DMP[1]) (mol)	*Ortho* series M_n (g/mol)	*Para* series M_n (g/mol)
500	1	0.984	490	510
1000	1	0.323	930	1010
1500	1	0.193	1380	1460
2000	1	0.138	2250	2150

[a] 2,6-DMP—2,6-dimethylphenol.

stoichiometric amounts of A and B groups were in the reaction feed. This latter assumption can be expressed as

$$N(\mathrm{BB}) = N(\mathrm{AA}) + N(\mathrm{A})/2 \quad (1)$$

where

$N(\mathrm{BB})$ = moles of BYB

$N(\mathrm{AA})$ = moles of AWA

$N(\mathrm{A})$ = moles of AZ

The reaction of $N(\mathrm{AA})$ with $N(\mathrm{BB})$ yields a statistically determined size distribution of $N(\mathrm{A})/2$ moles of product molecules (oligomeric and polymeric) plus by-product molecules which can be represented schematically as follows:

$$N(\mathrm{AA}) + N(\mathrm{BB}) + N(\mathrm{A}) \rightarrow \sum[\mathrm{ZA–BYB–(AWA–BYB–)}_x\mathrm{–AZ}] + \text{by-products} \quad (2)$$

A 'combined endgroup' is defined as ZA–BYB–plus–AZ and an 'internal repeat unit' is defined as –AWA–BYB–. Each mole of a given product molecule therefore has one mole of combined endgroup and x moles of internal repeat units.

The number average molecular weight of the reaction product is then:

$$M_n = \frac{\text{total mass of product molecules}}{\text{moles of product molecules}}$$

$$M_n = \frac{\sum(m_e + x{\cdot}m_u)}{N(\mathrm{A})/2} \quad (3)$$

where m_e is the molar mass of the combined endgroup and m_u is the molar mass of an internal unit. The summation is over all $N(\mathrm{A})/2$ moles of product molecules and all x values. This leads to

$$M_n = m_e + X_n m_u \quad (4)$$

where X_n is the number average number of internal units in the product molecules.

By inspection of the schematic molecular structure (Fig. 2) and Eq. (4), one sees that

$$x_n = \frac{N(\mathrm{AA})}{N(\mathrm{A})/2} = 2\frac{N(\mathrm{AA})}{N(\mathrm{A})} \quad (5)$$

Arbitrarily choosing the number of moles of AWA, then substituting Eq. (5) into Eq. (4) and rearranging, one now has a complete description of the feed composition required to achieve a target M_n:

moles of monomer AWA : $N(\mathrm{AA})$

$$\text{moles of endcapper AZ} : N(\mathrm{A}) = \left[\frac{2m_u}{M_n - m_e}\right]N(\mathrm{AA}) \quad (6)$$

moles of monomer BYB : $N(\mathrm{BB}) = N(\mathrm{AA}) + N(\mathrm{A})/2$

In the present work AWA is cresol, AZ is 2,6-dimethylphenol, and BYB is formaldehyde.

3.2. Structure of reaction intermediates and products

^{13}C NMR has been used extensively to characterize phenolic resins and their synthesis and crosslinking reactions [19–23]. Carbon chemical shifts of typical phenolic resins and some related reaction intermediates are provided in Table 2. Quantitative ^{13}C NMR was used in this study to monitor reaction progress and to determine the molecular weights of the final products. Acetone was the preferred solvent for the *ortho*-cresol novolacs since its carbon peak did not overlap with the sample peaks but *para*-cresol novolacs were not soluble in acetone. DMSO, which was used to analyze the *para*-cresol novolacs, resonates at 40 ppm and overlapped with the *para–para* methylene linkages. There were no significant differences in the chemical shifts in these two solvents.

^{13}C NMR spectra provided an excellent means for structural characterization of the cresol novolac oligomers (Fig. 3). The chemical shifts for cresol novolac resins matched well with those observed for phenolic novolacs. The peaks between 150–156 ppm represent hydroxyl-substituted aromatic carbons. *Ortho*-unsubstituted aromatic carbons resonate at 118 ppm, and *para*-unsubstituted aromatic carbons are observed at 120 ppm. The rest of the aromatic carbon peaks resonate between 121 and 136 ppm. ^{13}C NMR spectra can define three distinct types of methylene linkages between aromatic rings, *para–para* (41 ppm), *ortho–para* (36 ppm), and *ortho–ortho* (31.5 ppm). The peaks between 15 and 18 ppm represent the methyl carbons on the aromatic rings.

Table 2
^{13}C NMR assignments for novolac resins and related reaction intermediates

Chemical shift region (ppm)	Assignment
150–156	Hydroxyl-substituted phenolic carbons
127–135	Other phenolic carbons
121	*Para*-unsubstituted phenolic carbons
116	*Ortho*-unsubstituted phenolic carbons
85.9	HO–CH_2–O–CH_2–OH
81.4	HO–CH_2–OH
71.1	*Para*-linked dimethylene ether
68.2	*Ortho*-linked dimethylene ether
40.8	*Para–para*methylene linkages
35.5	*Ortho–para* methylene linkages
31.5	*Ortho–ortho* methylene linkages

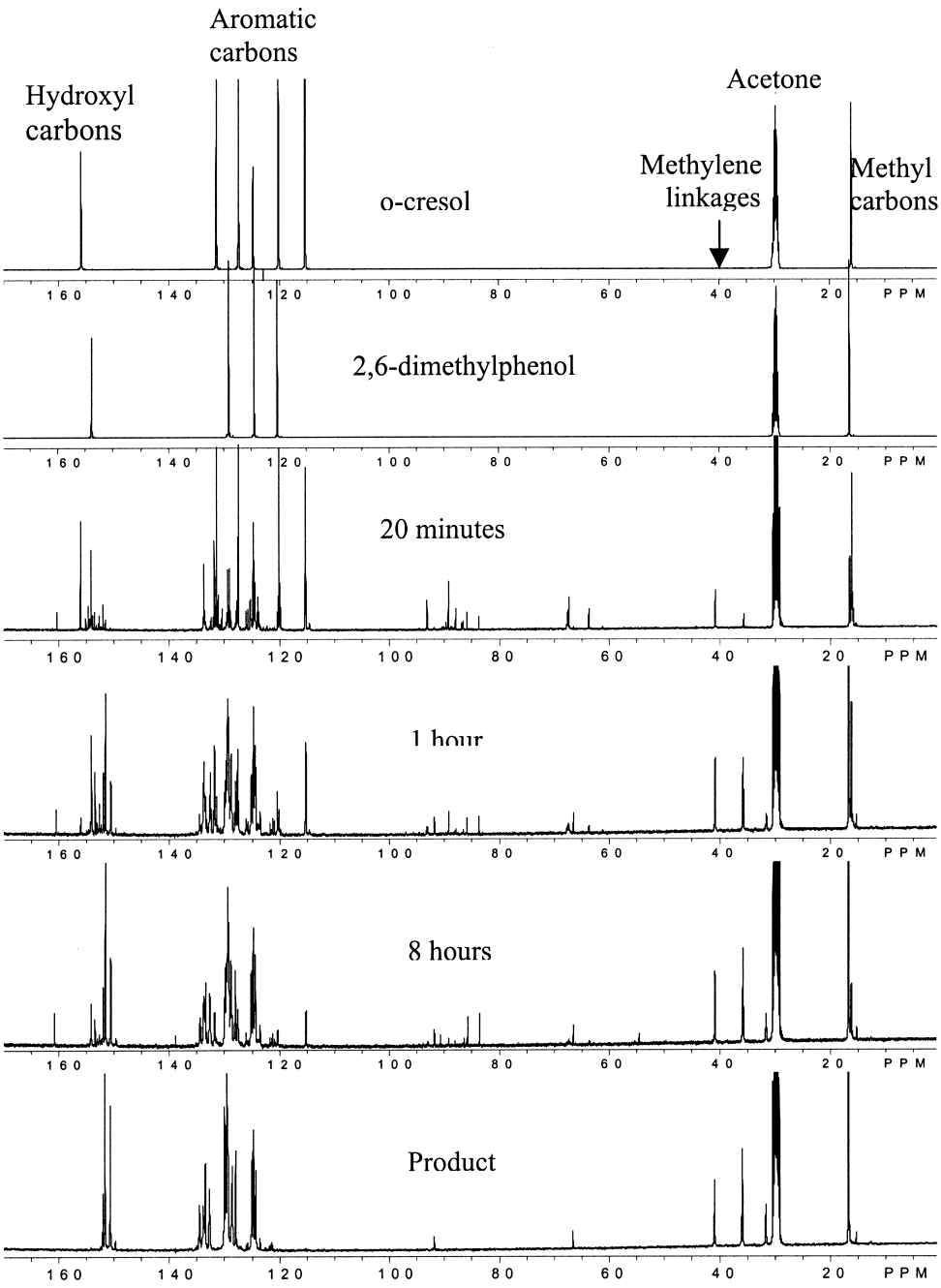

Fig. 3. ^{13}C NMR spectra monitoring a 2000 g/mol *ortho*-cresol novolac resin synthesis as a function of reaction time. The product was reacted for 24 h at 100 °C, then heated to 200 °C under mild vacuum to decompose the catalyst.

The formation of oligomers in bulk reactions at 100 °C with 2.5 wt% oxalic acid catalyst was monitored by ^{13}C NMR (Fig. 3). The first spectrum represents the reaction mixture immediately after becoming homogeneous (~20 min). The reaction had clearly begun at this stage. This was evidenced by the downfield shift of hydroxyl-substituted carbons, shifts in aromatic regions, the appearance of acetone soluble oxymethylene peaks (83–93 ppm), the formation of *para* linked dimethylene ethers (67.5 ppm) and methylols (64 ppm), and the formation of *para–para* and *ortho–para* methylene linkages. It should be noted that *para*-formaldehyde was insoluble in the acetone NMR solvent, but its derivatives were soluble. As the reactions progressed, the amount of methylol intermediates and *ortho* and *para* unsubstituted aromatic carbons decreased, and the peaks for methylene linkages increased. ^{13}C NMR spectra showed no *ortho* or *para* unsubstituted carbon peaks in products indicating full conversion of reactive ring positions.

As described in the literature [17], *para* positions on

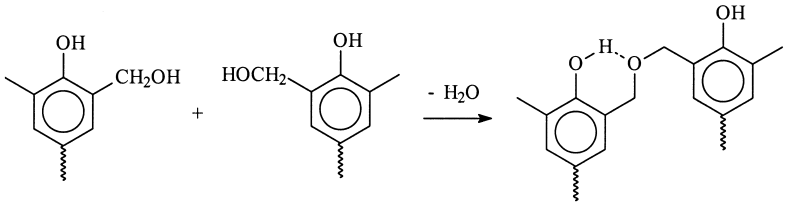

Fig. 4. Condensation of *ortho*-hydroxymethyl substitutents forming stable *ortho*-linked dimethylene ethers.

phenolic compounds react faster than *ortho* positions. ^{13}C NMR spectra revealed that *para–para* methylene linkages formed most rapidly followed by *ortho–para* methylene linkages (Fig. 3). *Ortho–ortho* methylene linkages were observed in small amounts after 1 h.

Hydroxymethyl condensation reactions, which eliminate water to form dimethylene ether linkages, are prevalent under acidic conditions. It has been suggested that dimethylene ether linkages decompose at elevated temperatures to form methylene bridges between rings [1]. ^{13}C NMR monitoring the reaction progress of these cresol novolac reactions confirmed the formation of both *ortho* (66.5 ppm) and *para* linked dimethylene ethers (67.5 ppm). *Para*-dimethylene ether linkages formed early and decomposed as the reaction proceeded (Fig. 3). *Ortho*-linked dimethylene ethers formed later and remained in the oligomer chain even after heating to 200 °C to decompose the catalyst. The high stability of *ortho*-linked dimethylene ethers was attributed to the formation of strong intramolecular hydrogen bonding (Fig. 4).

The residual dimethylene ether linkages can only account for a small fraction of the excess formaldehyde required in these reactions to achieve the targeted molecular weights (Table 3). These dimethylene ether linkages do not change molecular weights significantly.

^{13}C NMR peaks for methyl carbons were also used to monitor the cresol novolac reactions (Fig. 5). The methyl groups on *ortho*-cresol (peak E) resonate at 16.13 ppm, and the methyl groups on 2,6-dimethylphenol (peak C) resonate at 16.60 ppm. The methyl carbon on both monomers shifts downfield upon reaction of one site, then the cresol methyl shifts further downfield upon reaction of the second site. The endgroup methyls are not well resolved from the methyl groups on internal units due to the similarities in their structures. A small peak at 15.4 ppm was attributed to methyl carbons on cresol units linked with dimethylene ethers. This corresponds well with the *ortho* methyl carbon shift for 2-hydroxymethyl-4,6-dimethylphenol (15.53 ppm)

Table 3
Mole percent *ortho*-dimethylene ether linkages

M_n (g/mol)	*Ortho* series	*Para* series
500	1.3	2.8
1000	1.5	3.1
1500	1.6	3.6
2000	1.7	3.5

[24]. The ^{13}C NMR analysis showed that all the reactive positions on cresol and 2,6-dimethylphenol were reacted in the product, further confirming quantitative conversion.

The molecular weights of cresol novolac oligomers were calculated by comparing the peak intensities corresponding to methyl carbons on the endgroups versus the internal methyl carbons. Since the two peaks are not well resolved, a deconvolution technique was used to determine the peak integrations (Fig. 6). The peak area corresponding to the 2,6-dimethylphenol endgroups accounted for four methyl carbons per chain. The relative number of methyl groups within the repeat units was determined by ratioing the peak integrations of the interior methyl carbons versus the endgroup carbons, then multiplying by four.

The methyl regions of ^{13}C NMR spectra for a series of *ortho*-cresol novolac oligomers with different molecular weights were compared (Fig. 7). The peak integration ratio of internal methyl carbons to those on the endgroups (peak a to b) increased as the molecular weight increased. This was expected since more repeat units, relative to

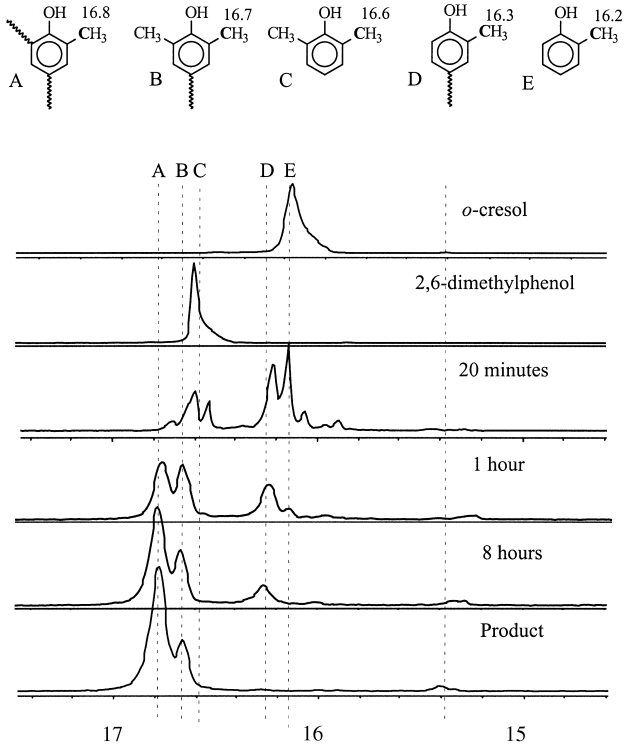

Fig. 5. Expanded ^{13}C NMR spectra monitoring a 2000 g/mol *ortho*-cresol novolac resin synthesis as a function of a reaction time.

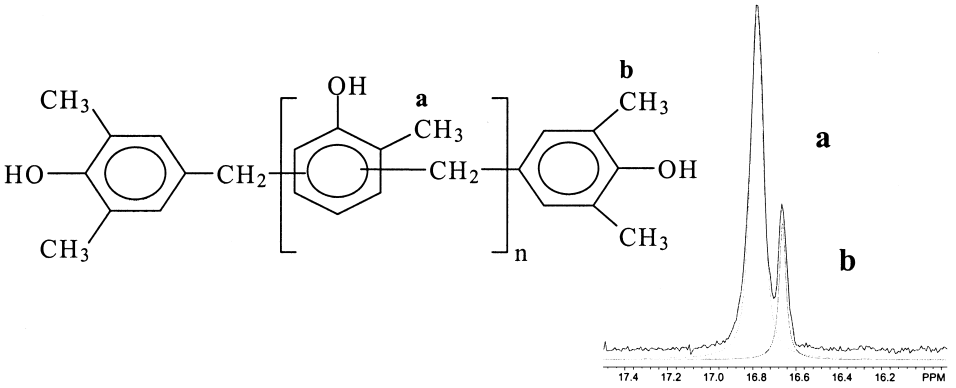

Fig. 6. Deconvolution of methyl carbon peaks.

endgroups, were incorporated as higher molecular weights developed.

The type of methylene linkages (*ortho–ortho*, *ortho–para* and *para–para*) and their relative amounts can be calculated using ^{13}C NMR. Since the endgroups formed only *para* methylene linkages, the number of *para* linked species was higher for low molecular weight oligomers (Table 4). As the molecular weight was increased, the *para–para*, *ortho–para*, and *ortho–ortho* linked methylenes approached the expected 1:2:1 statistical distribution.

Para-cresol novolac syntheses, monitored by ^{13}C NMR, showed similar reaction progress as the *ortho*-cresol novolac reactions (Fig. 8). Formation of *para*-cresol novolacs was accompanied by the downfield shift of hydroxyl-substituted aromatic carbon peaks, increases in both the *ortho–ortho* (36.5 ppm) and the *ortho–para* (40.5 ppm) methylene carbon peaks, and upfield shifts of methyl carbon peaks. The DMSO solvent peak overlapped with the *para–para* methylene carbon peak. However, this was not as important for monitoring the syntheses of *para*-cresol novolac resins since *para–para* methylene linkages only formed when two 2,6-dimethylphenol units dimerized and this was assumed to form in small amounts (especially at low 2,6-dimethylphenol concentrations).

Two types of methyl groups were observed for the *para*-cresol novolacs (Fig. 9). The *para* methyl carbons within the repeat units resonate at 26.2 ppm, and the *ortho* methyl carbons on the endcapping reagent resonate at 22.4 ppm. The formation of *ortho–para* and *ortho–ortho* methylene linkages was also monitored. Several peaks in the *ortho–ortho* methylene region were observed early in the reaction which were attributed to reaction intermediates. At the end of the reaction, only one sharp peak was present in this region.

3.3. Molecular weight and molecular distribution determined via GPC

The growth of molecular weight with time for both *ortho*- and *para*-cresol novolac syntheses was monitored using gel permeation chromatography (Fig. 10). In gel permeation chromatography, the higher molecular weight oligomers bypass the smaller pores in the packing column and elute faster, and therefore, appear at lower retention volumes. As the reactions progressed, the GPC peaks shifted to lower elution volumes and the area in the region where monomers and low molecular weight oligomers eluted (retention volume 32.6–36 ml) decreased. The final products were comprised of mostly higher molecular weight oligomers eluting between 27 and 32.6 ml.

GPC traces of *ortho*- and *para*-cresol novolacs with approximate molecular weights of 500, 1000, 1500, and

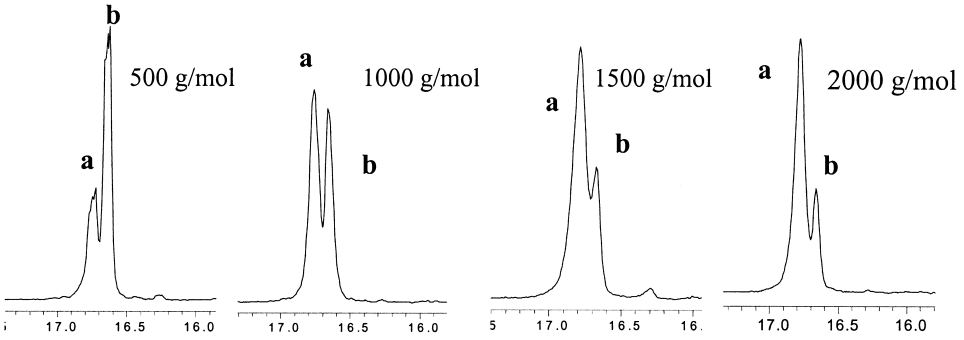

Fig. 7. Expanded ^{13}C NMR spectra of a series of *ortho*-cresol novolac resins with various molecular weights: (a) methyl carbons within the repeat units, (b) methyl carbons on the endgroups.

Table 4
Percentages of isomers formed in *ortho*-cresol novolac resins

M_n (g/mol)	*p–p* (%)	*o–p* (%)	*o–o* (%)
500	45.2	47.8	7.0
1000	31.2	49.7	19.1
1500	30.0	49.8	20.1
2000	29.2	49.3	21.5

2000 g/mol were measured (Fig. 11). For both series, the peaks shifted toward lower elution volumes as the average molecular weights increased.

GPC was used to qualitatively compare the molecular weights. Absolute molecular weights could not be derived from GPC using the viscosity detector due to their low molecular weights and correspondingly low solution viscosities. Thus, only the qualitative polydispersity of these oligomers and their intrinsic viscosities were evaluated (Table 5). Since cresol novolac resin syntheses are condensation polymerizations, the polydispersity should approach two as the molecular weight increases. Low molecular weight oligomers (500–1000 g/mol) had low polydispersity, but the polydispersity appeared to increase as the molecular weight was increased.

Table 5
Qualitative polydispersities and intrinsic viscosities of cresol novolac resins

Cresol	M_n (g/mol)	Polydispersity	Intrinsic viscosity[2] (dl/g)
Ortho	500	1.41	0.037
	1000	1.33	0.049
	1500	1.73	0.066
	2000	1.61	0.075
Para	500	1.25	0.031
	1000	1.62	0.046
	1500	1.62	0.052
	2000	2.08	0.067

[a] In NMP solvent at 60 °C.

As expected, the intrinsic viscosities increased as the molecular weight increased. However, when comparing *ortho*-cresol novolacs to *para*-cresol novolacs with similar number average molecular weights, *ortho*-cresol novolacs consistently had higher intrinsic viscosities (Table 5). This suggested that *ortho*-cresol novolacs have larger hydrodynamic volumes in the NMP chromatography solvent. It was previously reported that different novolac isomers have different elution behavior [25,26]. The difference in

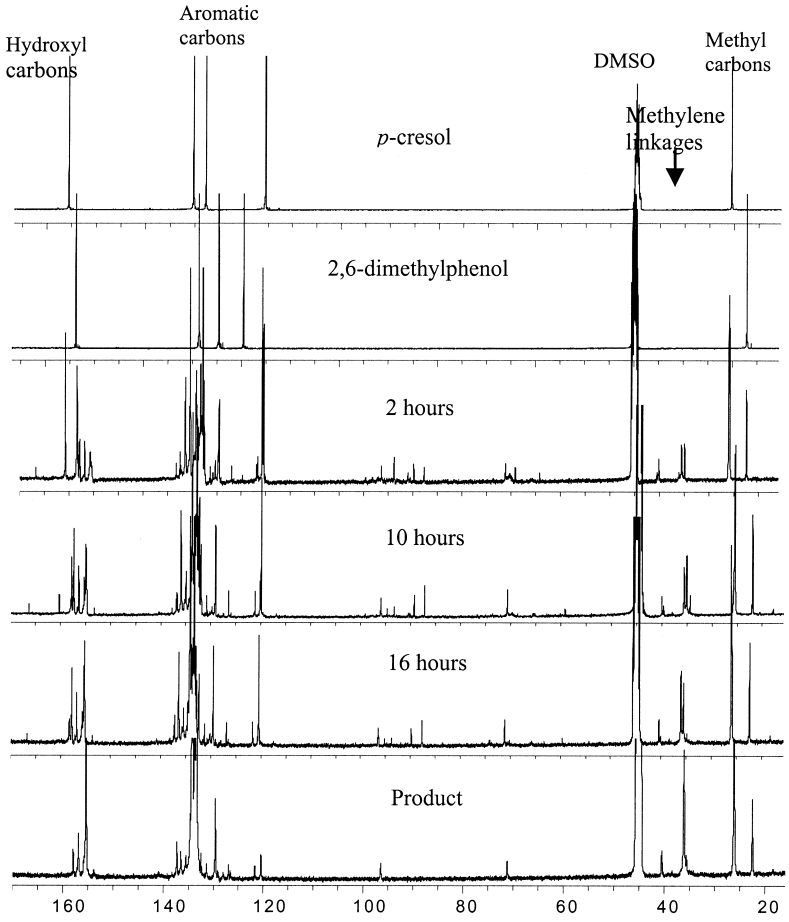

Fig. 8. ^{13}C NMR spectra of a 2000 g/mol *para*-cresol novolac resins synthesis monitored as a function of a reaction time.

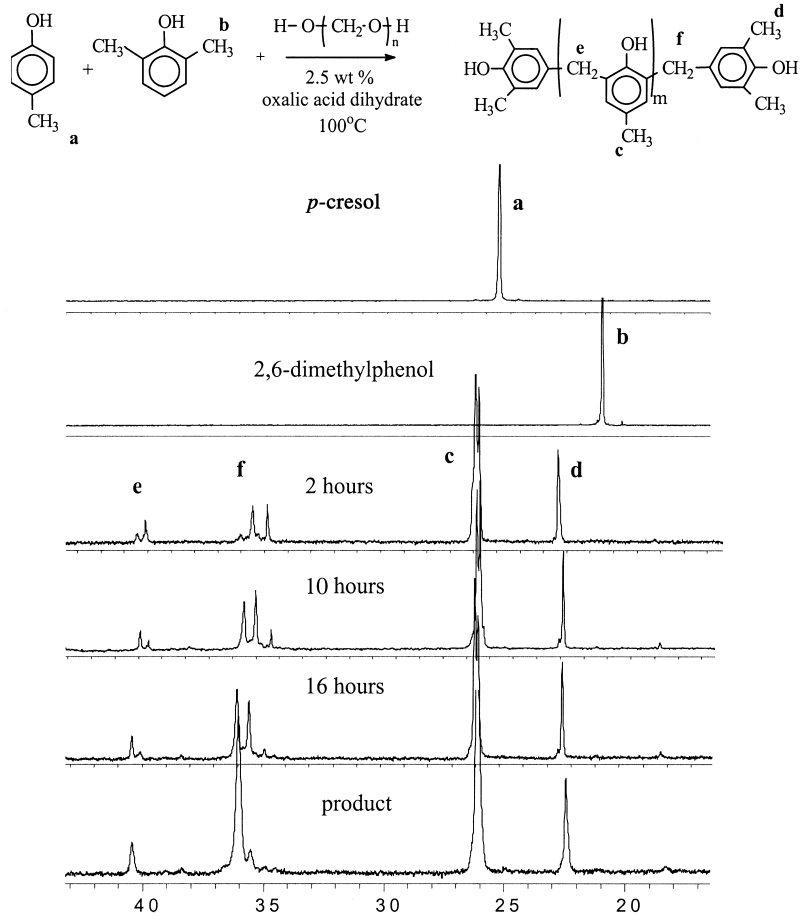

Fig. 9. Expanded ^{13}C NMR spectra monitoring the synthesis of a 2000 g/mol *para*-cresol novolac resin.

hydrodynamic volumes from oligomers with different isomer structures of *ortho–ortho*, *ortho–para*, and *para–para* was attributed to varying degrees of solvation. Oligomers with high compositions of *ortho–ortho* linkages (i.e. *para*-cresol novolac resins) may have a higher degree of intramolecular hydrogen bonding, resulting in less solvation and lower hydrodynamic volumes. The propensity for hydrogen bonding may be disrupted for *ortho*-cresol novolacs since three types of methylene linkages are available and are assumed to be distributed randomly.

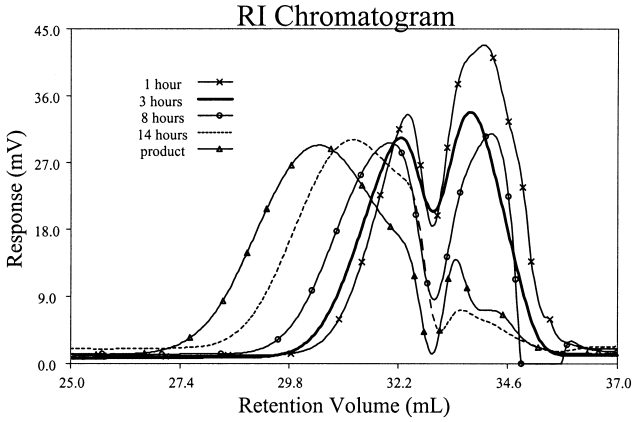

Fig. 10. GPC monitoring the synthesis of a 2000 g/mol *ortho*-cresol novolac resin as a function of reaction time.

Glass transition temperatures for both the *ortho*- and *para*-cresol novolacs increased as the molecular weight increased (Table 6). The T_gs ranged from approximately 40 °C for 500 g/mol resins to 105–110 °C for oligomers with number average molecular weights of 2000 g/mol. No significant differences were observed between the T_gs of *ortho*- and *para*-cresol novolacs with similar molecular weights.

Table 6
T_gs of cresol novolac resins as a function of molecular weight

Ortho series		*Para* series	
M_n[3] (g/mol)	T_g (°C)	M_n[3] (g/mol)	T_g (°C)
490	40	510	43
930	76	1010	76
1380	92	1460	99
2250	104	2150	110

[a] Calculated using ^{13}C NMR.

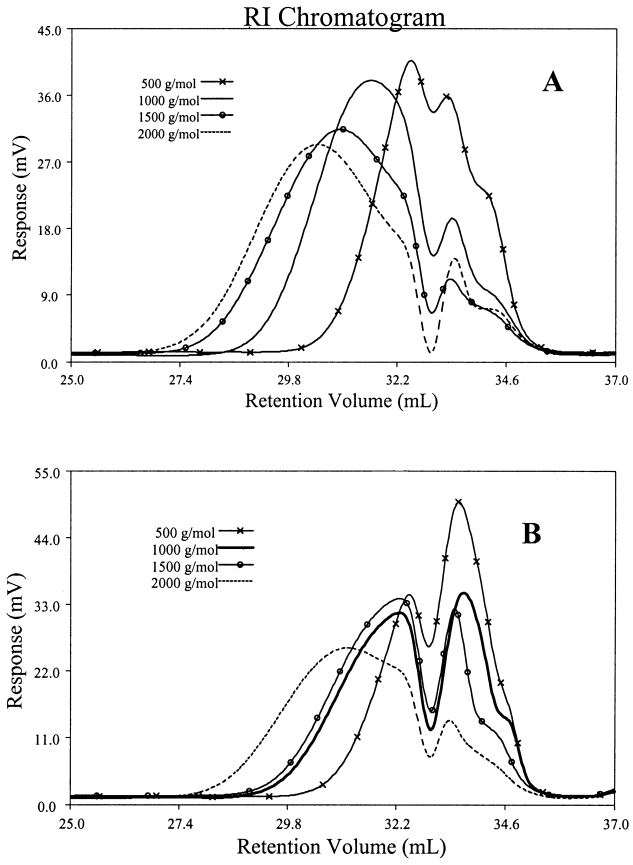

Fig. 11. GPC of cresol novolac resins with various molecular weights: (A) *ortho*-cresol novolac, (B) *para*-cresol novolac.

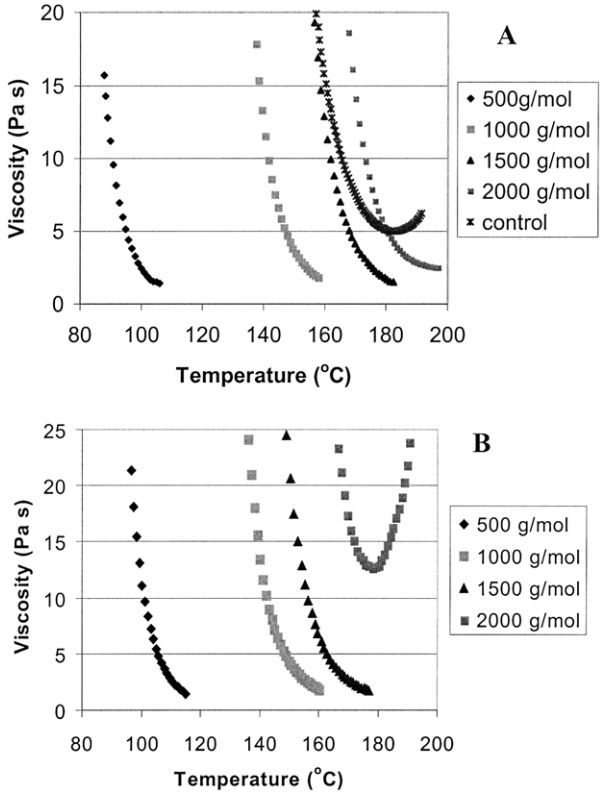

Fig. 12. Dynamic viscosity of cresol novolacs measured as a function of molecular weight (A) *ortho*-cresol novolac resins, and (B) *para*-cresol novolac resins.

3.4. Dynamic viscosities of cresol novolac resins

Efficient melt composite fabrication procedures require low viscosity resins to wet out the fibers. The viscosity profiles of a series of cresol novolacs were examined as a function of temperature at a heating rate of 2.5 °C/min (Fig. 12). All samples were vacuum stripped at 165 °C for 2 h prior to the measurements to remove residual water. As molecular weights were increased, the temperatures required for the viscosity to fall to 10 Pa s increased for both series of cresol novolac materials. *Ortho*-cresol novolacs (Fig. 12a) had similar viscosities to the *para*-cresol novolacs (Fig. 12b) with similar molecular weights at any given temperature. The viscosity of the 2000 g/mol *para*-cresol novolac oligomer decreased with increased temperature until ~180 °C, then gradually increased upon further heating. The reason for this increase in viscosity at high temperatures may be attributable to degradative crosslinking, but this is as yet unclear. It is possible that the increase in viscosity is due to o',o'-dimethylene ether oxidation to o',o'-dimethylene ether hydroperoxide formation followed by degradative crosslinking.

A branched phenolic novolac resin with a molecular weight of ~940 g/mol (M_n was determined by ^{1}H NMR) was included in the study to provide a practical comparison (Fig. 12a). However, one must be aware that this material, which was synthesized from the trifunctional phenol monomer, had a small gel fraction and its viscosity cannot be compared in terms of fundamental phenomena. The viscosity of the phenolic control reached 10 Pa s at ~165 °C, a higher temperature than that required by a 1500 g/mol cresol novolac to reach the same viscosity. This suggests that the linear cresol oligomers may be significantly more amenable to melt processing relative to phenol derived oligomers due to a wider processing window. The phenolic novolac control material behaved similarly to the 2000 g/mol *para*-cresol novolac resin where the viscosity showed a minimum at ~180 °C, then increased. In both cases, this behavior is likely attributable to crosslinking.

4. Conclusions

An important aspect of this research was to synthesize linear controlled molecular weight cresol novolac resins. In these reactions, difunctional *ortho*- or *para*-cresol was reacted with monofunctional 2,6-dimethylphenol as an endcapping reagent, *para*-formaldehyde and oxalic acid

dihydrate at 100 °C for 24 h followed by heating gradually to 200 °C under mild vacuum. The molecular weights were controlled by the cresol to endcapping reagent ratio and excess if formaldehyde was necessary to achieve the targeted molecular weights. The need for about 10 mol% excess formaldehyde was unexpected. Some of the excess formaldehyde needed could be attributed to small amounts evolving from the reaction apparatus during synthesis, and also to formaldehyde lost to dimethylene ether linkage formation. However, it was reasoned that a dynamic equilibrium reaction between formaldehyde substitution and elimination must also occur to allow for the desired molecular weights to be generated. This synthetic method consistently produced oligomer molecular weights very close to the targeted values based on endcapping reagent to cresol predicted ratios. An effective method was developed for monitoring the reaction progression and for calculating the molecular weight using ^{13}C NMR. Various chemical shifts allowed for confirmation of very high reaction conversions, which were of course necessary to achieve the targeted molecular weights.

The qualitative polydispersities obtained from GPC suggested that molecular weight distributions were reasonably narrow (<2). The glass transition temperatures increased from ~40 to 110 °C as the molecular weights were increased from 500 to 2000 g/mol, but there were no significant differences between the *ortho*- and *para*-cresol novolacs with similar molecular weights. In general, the linearity of the *ortho*-and *para*-cresol oligomers, together with their controlled molecular weights, lead to materials with controllable and predictable melt viscosities. This may be important for achieving melt processability, or for enabling melt compounding procedures, in composite fabrication. These cresol novolac resins will be crosslinked with various epoxy resins to form void-free flame retardant networks. Network properties such as toughness, flame retardance, and water uptake, as well as processability will be investigated.

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