

# Novel Two-Stage Phenol–Formaldehyde Resol Resin Synthesis

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**ABSTRACT:** The synthesis of phenol–formaldehyde resol resins was carried out in two stages to facilitate the start of a conventional batch process. In the first stage, the starting material solution was preprocessed in a continuous-flow stirred-tank reactor with a 5-min residence time. In the second stage, synthesis was continued in a batch reactor. Samples were analyzed by titrimetric methods, gas chromatography, nuclear magnetic resonance spectroscopy, and differential scanning calorimetry. Most of the starting materials were consumed in the preprocessing reactor, which allowed better control of the

reactivity of the prepolymer solution in the second stage. The methylation and condensation reactions proceeded steadily during the production process in the batch reactor. The results of the study indicated that dividing a conventional one-stage batch process into two stages could facilitate the control of the initial stages of resol production. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 371–379, 2007

**Key words:** resins; structure; synthesis; thermal properties; processing

## INTRODUCTION

Phenol–formaldehyde resol resins are produced in step-growth polymerization reactions in the presence of a basic catalyst in aqueous solution. The final product is a viscose, reddish prepolymer solution consisting of free phenol and formaldehyde, methylolphenols, and higher-molar-mass crosslinked phenolic rings. The good moisture- and weather-resistance properties of phenol–formaldehyde resol resins give them an important use as plywood adhesives.<sup>1,2</sup>

The reactions between phenol and formaldehyde under alkaline conditions are affected by various parameters, resulting in reaction kinetics that are complex. The progress of the resol synthesis depends on the concentrations of the reactive forms of the starting materials, the concentration and type of catalyst, and the process temperature. In the initial stage of the synthesis, reactions of phenol and formaldehyde produce mainly methylolphenols in highly exothermic methylation reactions. The synthesis progresses in subsequent and parallel condensation reactions between the phenolic units, resulting in the formation of oligomers with methylene bridge structures. The effects of various parameters on the methylation and condensation reactions have been widely studied and are well known.<sup>1–13</sup>

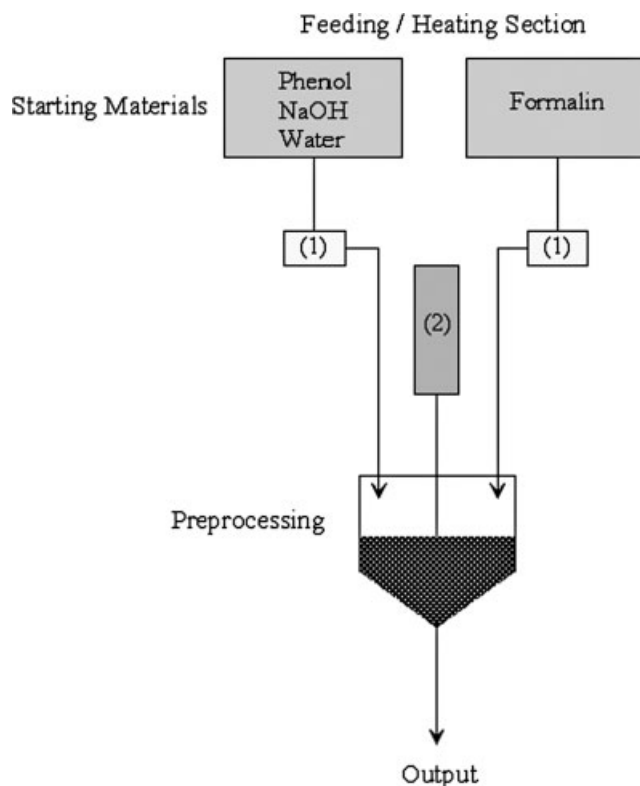
Phenol–formaldehyde resol resins are conventionally produced in batch reactors. A severe disadvantage of large batch quantities is the difficulty of controlling the process, especially during the exothermic methylation stage. Quality varies as a result. Because of their exothermic behavior, resol syntheses require close control through the entire production. Too fast evolution of reaction heat and rising solution temperature at the start of the resin production are generally controlled by charging the starting materials, typically formaldehyde as formalin solution, into the reactor gradually. However, slow charging of reagents increases the total synthesis time required for the production.

In this study, resol resin synthesis was divided into two stages to study the initial steps in the resol production process and to facilitate the start of the production in the batch reactor. In the first stage, the starting materials were preprocessed in a continuous-flow stirred-tank reactor (CSTR) with a 5-min residence time with the aim of starting the methylation reactions between phenol and formaldehyde and controlling the reactivity of the solution before the actual batch process. Preprocessing experiments were carried out in order to identify a suitable solution temperature and an initial alkalinity for the reactive mixture, so the resol process would proceed as fast as possible while still being easily controlled (steady state). In the second stage, the methylation and polycondensation reactions of the collected preprocessed solutions were continued and studied in a

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**Figure 1** Experimental setup for the preprocessing stage [pump (1), mixer (2)].

batch reactor. Temperature, behavior, and development of viscosity of the resol solutions during heating were observed, and the end products were analyzed by titrimetric methods, gas chromatography (GC), nuclear magnetic resonance spectroscopy (NMR), and differential scanning calorimetry (DSC).

## EXPERIMENTAL

### Starting materials

Phenol (>99%) was manufactured by J. T. Baker (Deventer, Holland) and formaldehyde (48 wt % formalin solution containing some methanol) by Hexion Specialty Chemicals, Inc. (Kitee, Finland). The catalyst, NaOH (Finnish Chemicals Oy, Pietarsaari, Finland), was used as a 50 wt % water solution. Two starting material solutions were prepared for the preprocessing experiments: phenol, additional water, and NaOH as a mixture and a 40 wt % formalin solution. The reagents were preheated in plastic vessels immersed in a water bath controlled by a thermostat (Lauda Ecoline E 100). The preheating temperatures (60°C–75°C) were set 4°C–5°C above the targeted preprocessing temperatures.

### Preprocessing experiments

The CSTR was used in the preprocessing stage because of its ability to yield products with a uni-

form quality in steady-state conditions. The tempered starting material solutions were fed into the preprocessing reactor with two pulsating diaphragm reagent pumps (PTFE tubes, o.d. = 3.2 mm, i.d. = 1.6 mm) manufactured by OPAM Instruments. The preprocessing reactor ( $V = 100$  mL) was a vertically stirred (Heidolph RZR 2051) and water-jacketed (controlled by Lauda Ecoline E 100) glass vessel with a bottom valve, condenser, and contact thermometer. The products were discharged continuously through the bottom valve of the reactor. The 5-min residence time was defined by pumping the starting materials into an empty vessel for 5 min before the bottom valve was opened. The height of the solution surface in the CSTR was kept constant by adjusting the bottom valve during the experiments. A schematic drawing of the preprocessing equipment is presented in Figure 1.

The preprocessing stage of the resol synthesis was studied at alkalinities of 2.4–3.0 wt % (tests P1–P5, Table I). The jacket temperature of the reactor was adjusted to achieve solution temperatures ( $T_{\text{solution}}$ ) of 56°C–70°C. The feeding pumps were calibrated to F/P molar ratios of 2.0–2.3 with a total flow rate of 6.0 mL/min (ca. 2.9 mL/min of the phenol/additional water/NaOH mixture and 3.1 mL/min of 40 wt % formalin). The first samples were taken after 10 min of preprocessing, and then at 10-min intervals for 60 min. The accuracy of the feeding procedure was limited by the capability of the pumps. The preprocessed solutions were frozen and stored for study in the batch reactor.

### Batch reactor experiments

The batch reactor was a jacketed, thermostat-controlled (Lauda E 100) glass vessel ( $V = 100$  mL) equipped with a mixer (Heidolph RZR 2051), condenser, and contact thermometer. The progress of the methylation and condensation reactions of the preprocessed solutions was studied in three experiments (B1–B3,  $V = 80$  mL) with three different preprocessed solutions (P1–P3). In experiment B1 the jacket temperature of the reactor was raised stepwise

**TABLE I**  
Reaction Conditions of Experiments in a Preprocessing Reactor with a 5-min Residence Time

Experiment	Alkalinity (wt %)	$T_{\text{solution}}$ (°C)	F/P ratio <sup>a</sup>
P1	2.4	56	2.3
P2	2.5	60	2.0
P3	3.0	60	2.0
P4	2.7	70	2.0
P5	3.0	<sup>b</sup>	2.1 <sup>c</sup>

<sup>a</sup> Set by calibrated pumps.

<sup>b</sup> Solution mixed at room temperature.

<sup>c</sup> Set by weighing.

from 60°C to 116°C over 80 min, whereas in experiments B2 and B3 the preprocessed solutions were heated at a constant jacket temperature of 105°C for 35 min. The zero time for the batch reactor experiments was the moment when the thawed and still cool preprocessed solutions were poured into the batch reactor at 105°C.

### Determinations of alkali content

The alkali content of the samples was determined by neutralizing the alkaline resin with an acid. Weighed resin samples (about 1–2 g) were dissolved in 100 mL of distilled water, and 4 drops of methyl orange + bromine cresol green (1 : 1) indicator (p.a. Merck, Darmstadt, Germany) were added. The samples were titrated with 0.1N HCl (p.a. Reagecon, Clare, Ireland) until the color of the solution changed from blue to yellowish, and alkalinity was calculated.

### Refractive index experiments

Stability of the resol solution in the preprocessing reactor was followed by measurement of the refractive indices of the resol samples during the experiments. Two small drops of tempered (20°C) samples were pipetted on the prism of an Abbe refractometer (Erma, No. 6525, Tokyo), and the refractive indices were observed. The results are shown as the average of two parallel determinations.

### Viscosity determinations

Viscosity was measured with a Brookfield DV-II+ digital viscometer with a small sample adapter and an SCN-31 spindle. Ten-milliliter resin samples were poured into the sample adapter and placed in the water-circulating jacket (25°C) of the viscometer. The samples were stabilized for about 20 min before viscosity was determined. The viscometer was calibrated with viscosity standards (Brookfield) of 100, 500, 1000, and 5000 mPa s.

### Determination of free phenol

Gas chromatography was used to measure the free phenol level of the resol resin samples. Determination was performed with an Agilent 6850 GC Series System gas chromatograph that had a 7683 series injector and with GC ChemStation software. The system consisted of an automatic syringe (10 µL), an injector (210°C), a 30 m × 0.32 mm capillary column (J&W DB-1701), and a flame ionization detector (280°C). The temperature program for the column was: starting temperature 60°C, heating to 125°C at a heating rate of 10°C/min, holding at 125°C for 2 min

heating to 200°C at a heating rate of 10°C/min, and holding at 200°C for 5 min. The burning gases were synthetic air (Oy Woikoski Ab, Voikoski, Finland) and hydrogen (Oy Woikoski Ab, Voikoski, Finland), and the carrier gas was helium (Oy Woikoski Ab, Voikoski, Finland) with a flow rate of 3.9 mL/min. The samples were prepared by dissolving 1 g of resin in 12 mL of methanol (p.a. Mallinckrodt, Deventer, Holland) and 4 mL of *m*-cresol (internal standard) solution [7.5 g *m*-cresol (p.a. Acros, Geel, Belgium)/1000 mL methanol]. Conversion of phenol was calculated from the determination of free phenol.

### Determination of free formaldehyde

The free formaldehyde content of the samples was determined by the hydroxylamine hydrochloride method using end point titration. The analysis configuration consisted of an automatic titrator (Mettler DL 77) and a Mettler DG 111-SC electrode. Resin samples (~ 2 g) were dissolved in an ethanol–water mixture [20 mL of water and 70 mL of 94 wt % ethanol (Altia, Rajamäki, Finland)], and the pH was adjusted to 3.4 with 1N HCl (p.a. Reagecon, Clare, Ireland). Under stirring, 25 mL of 5 wt % hydroxylammonium hydrochloride solution was added. The solution was allowed to stand for 30 min, and the HCl that formed was rapidly titrated with 0.1N sodium hydroxide back to pH 3.4, and the free formaldehyde content was calculated. Conversion of formaldehyde was calculated from determination of free formaldehyde.

### NMR experiments

Structural characterization of the resins was performed with a Bruker AMX-500 NMR spectrometer at 300.5 K, observing <sup>13</sup>C at an operating frequency of 125.772 MHz. Quantitative <sup>13</sup>C-NMR spectra were measured by the inverse gated proton decoupling technique. Typical acquisition parameters of the quantitative <sup>13</sup>C runs for the resins were a 90° pulse of 8 µs, a 10.0-s delay, and 1536 scans. DMSO-*d*<sub>6</sub> (99.8% deuterated dimethylsulfoxide, Euriso-top, Gif-Sur-Yvette, France) was used as a solvent, an agent to obtain a deuterium lock, and an internal chemical shift standard. The <sup>13</sup>C spectral scales were calibrated to the central resonance line of DMSO-*d*<sub>6</sub> (δ = 39.5 ppm). Cr(acac)<sub>3</sub> [tris(acetylacetonate)chromium(III), 97%; Aldrich, Milwaukee, WI] was the relaxation agent for shortening the spin-lattice relaxation time, enhancing sensitivity, and maintaining the quantitative NMR spectra.<sup>14,15</sup> The liquid NMR samples were prepared in a 5-mm NMR tube (Wilmad, royal imperial grade) by dissolving approximately 350 µL of liquid resin in about 70 µL of pure DMSO-*d*<sub>6</sub> and 280 µL of 50 mM Cr(acac)<sub>3</sub>/

**TABLE II**  
**Refractive Indices ( $n$ ,  $\pm 0.001$ ) and Viscosities of Preprocessed Solutions of Experiments P1–P4 with Initial Alkalinities (alk.) of 2.4–3.0 wt % at Preprocessing Temperatures ( $T_{\text{solution}}$ ) of 56°C–70°C**

	P1		P2		P3		P4	
	$n$	alk. (wt %)	$n$	alk. (wt %)	$n$	alk. (wt %)	$n$	alk. (wt %)
Time (min)								
10	1.436	2.4	1.436	2.6	1.445	3.0	1.441	2.7
20	1.437	2.4	1.441	2.5	1.447	3.0	1.443	2.7
30	1.437	2.4	1.440	2.5	1.447	3.0	1.443	2.7
40	1.438	2.4	1.440	2.5	1.447	2.9	1.443	2.7
50	1.438	2.4	1.441	2.5	1.446	2.9	1.443	2.7
60	1.437	2.4	1.442	2.5	1.447	2.9	1.441	2.7
$T_{\text{solution}}$	56°C		60°C		60°C		70°C	
Viscosity	6.2 mPa s		6.6 mPa s		7.2 mPa s		7.5 mPa s	

DMSO- $d_6$  mixture. The concentration of the relaxation agent in the NMR sample was optimal, 20 mM.<sup>14</sup> An integral value of 1.00 in  $^{13}\text{C}$  spectra was set to the phenoxy carbon region (150–165 ppm), and all other integrated individual signals or signal groups were scaled to that value. The  $^{13}\text{C}$ -NMR signals and the signal areas of resol resins were identified with the help of the literature.<sup>14,16–21</sup> The alkalinity of the samples affected the ppm range of the phenoxy carbon region. Higher alkalinity shifted the phenoxy area to a lower field.

### DSC experiments

The equipment used for DSC measurement was a Mettler Toledo DSC instrument with STARe thermal analysis software. The liquid resin samples (9.0–11.0 mg) to be measured were pipetted into Mettler Toledo high-pressure steel pans (30  $\mu\text{L}$ ) and sealed with gold-plated copper seals. The pans were heated from 25°C to 270°C at a rate of 10°C/min. The analysis results of DSC are presented as an average of two parallel determinations made with the same steel pan. The repeatability and reproducibility standard deviations of the reaction heat measurements for the liquid resol resins were 5% and 15%, respectively.<sup>22</sup>

## RESULTS AND DISCUSSION

### Effects of initial reaction parameters on stability and progress of resol synthesis during preprocessing

The preprocessing stage was studied at 56°C–70°C with alkalinity of 2.4–3.0 wt % and F/P molar ratio of 2.0–2.3 by determining the alkalinity, refractive indices, and end viscosity of samples collected during the preprocessing experiments (Table II). The alkalinity and refractive index of all samples, as well as the temperatures of the resin solutions, remained at a constant level during syntheses P1–P3, which indicated steady-state conditions in the preprocessing reactor. The refractive index values of the preprocessed

solutions were in the range of 1.436–1.447, which can be considered typical for resols in the early stages of synthesis.<sup>2</sup> Run P4 was exceptional because of an unstable solution temperature (70°C  $\pm$  3°C) and poor controllability during the preprocessing. Instability could be a consequence of fast, exothermic methylation reactions at a solution temperature of 70°C.

The viscosity values of preprocessed solutions determined at the end of syntheses P1–P4 differed only slightly, between 6.2 and 7.5 mPa s (Table II). Minor increases in end viscosity were observed when the temperature and alkalinity of the preprocessing solutions were increased. The highest end viscosity (7.5 mPa s) was achieved, as expected, in experiment P4, which had the highest preprocessing temperature. The accelerating effect of a high processing temperature on the progress of resol resin synthesis is well known.<sup>11,23</sup> Some of the minor differences in the end viscosity of the solutions could also be a result of the differences in the amount of catalyst used (alkalinity). In experiments P2 and P3 the temperature was 60°C, but the higher alkalinity in experiment P3 probably accelerated the methylation reactions, resulting in slightly higher end viscosity (7.2 mPa s) than with P2 (6.6 mPa s).<sup>6,9,23,24</sup>

### Effect of preprocessing on consumption of starting materials and development of structural groups

The amounts of free phenol (wt %) and formaldehyde (wt %) and the calculated conversions of the starting materials in solutions from experiments P2 and P3 confirmed that the reactions between phenol and formaldehyde started during the preprocessing stage. In P2 and P3 the conversion of phenol, 0.87 and 0.86, and of formaldehyde, 0.79 and 0.81, respectively, was high. However, the higher alkalinity in P3 seemed to cause slightly higher consumption of formaldehyde, yielding a lower free formaldehyde content (4.0 wt %) than in P2 (4.4 wt %).<sup>6,23</sup> The amounts of free phenol in P2 (4.3 wt %) and P3 (4.4 wt %) were similar. In a study by Ferrero



**TABLE III**  
<sup>13</sup>C-NMR Integration Results for Preprocessed Solutions of Experiments P2 and P3

Group	Experiment	
	P2	P3
Aromatic carbons		
Phenoxy	1.000	1.000
Free para	0.233	0.230
Free ortho	0.857	0.851
Other	3.970	3.933
Formalin hemiacetals	0.071	0.065
Oxymethylenes of formaldehyde oligomers	0.049	0.047
Phenolic hemiformals	0.467	0.426
Methylol groups		
Para	0.477	0.504
Ortho	0.840	0.900
Methylene bridges		
p-p'	0.064	0.033
o-p	—	—
o-o'	—	—
Methanol	0.101	0.106
Total formaldehyde	1.97	1.97

et al.,<sup>23</sup> the progress of the resol process was investigated in a cascade system of four CSTRs [F/P = 1.39, NaOH/P = 0.4,  $T$  (reactor) = 70°C], with a residence time of 20 min for each reactor. After the first actual reactor, the conversion of phenol was 0.57, which was much lower than that in this study, which had one CSTR with a residence time of 5 min. Despite the differences in the reaction conditions between the study of Ferrero et al.<sup>23</sup> and experiments P2 and P3 in our study (F/P = 2.0, NaOH/P = 0.2,  $T_{\text{solution}} = 60^\circ\text{C}$ ), the higher conversion of phenol in our study was mainly a result of the higher initial F/P molar ratios, which favored the substitution reactions of phenol.<sup>6</sup>

Structural characterization of the solution components was performed by comparing the results of the NMR measurements of the solution samples from P2 and P3 collected during the preprocessing stage (Table III). The accelerating effect of the higher alkalinity<sup>6</sup> in P3 on the progress of the synthesis could be seen by close analysis of the structures. The number of available free phenolic positions was nearly the same in the solutions from experiments P2 and P3, but the number of methylol groups was higher in P3 than in P2. Both samples contained far fewer free para sites than ortho sites because of the slightly higher reactivity of para positions to formaldehyde.<sup>25–27</sup> However, the greater quantity of ortho- than paramethylol groups was a result of the two reactive ortho positions of phenol available for reactions with formaldehyde.<sup>25</sup> The higher content of substituted phenolic products in the solution from experiment P3 could have caused the slightly higher end viscosity after preprocessing compared with that in P2.

The minor number of methylene bridges in the two samples at 60°C was a consequence of some condensation reactions already occurring in the preprocessing stage. Only para–para bridges were observed in the spectra because of the higher reactivity of para positions.<sup>26–28</sup> The large amount of phenolic hemiformals in the resin solutions of experiments P2 and P3 should be noted. These groups can be considered free formaldehyde reservoirs for reactions between phenolic units and formaldehyde during the next synthesis stage.<sup>19,26</sup>

### Effect of preprocessing on reactivity

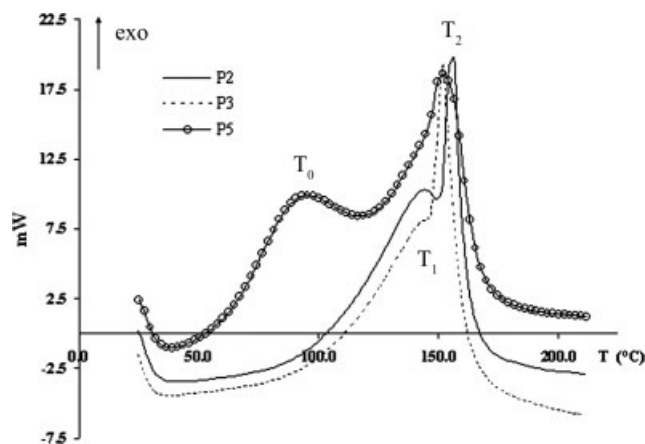
The reactivity of the preprocessed solutions from experiments P2 and P3 was compared with the reactivity of a starting material solution that did not have a preprocessing stage (experiment P5, Table I). Results of DSC analyses are shown in Table IV. The P5 solution, with an alkalinity of 3.0 wt % and an F/P molar ratio of 2.1, was prepared solely by mixing the reagents at room temperature before the DSC measurements. The released reaction heat ( $\Delta H$ ) of the P2 and P3 solutions can be considered similar, especially given the 5% repeatability of the DSC measurements. A comparison of the absolute total released heat of 578 J/g for the P5 solution, which was in agreement with that reported in the literature of 584 J/g (F/P = 2, pH = 10),<sup>29</sup> with the corresponding values for the P2 and P3 solutions showed preprocessing had a considerable effect on decreasing (ca. 200 J/g) the reactivity of the resol solutions.

Figure 2 presents the DSC thermograms of solutions from experiments P2, P3, and P5. At least two partly overlapping curing signals,  $T_1$  and  $T_2$  (condensation), can be seen. The first curing signals ( $T_1$ ) of the P3 and P5 solutions were approximated because of overlap with the second curing signals ( $T_2$ ).<sup>16,30</sup> Nevertheless, the temperatures of  $T_1$  (145°C–147°C) and  $T_2$  (151°C–156°C) and the ending temperatures of the curing (162°C–167°C) of all the samples were in the same area. The difference between the onset (start of curing) temperatures of P2 (101°C) and P3 (106°C) was 5°C. A comparison of the temperatures of the curing signals ( $T_1$  and  $T_2$ ) and the onset/ending temperatures of P2 and P3

**TABLE IV**  
DSC Analysis of the Preprocessed Solutions from Experiments P2 and P3 and the Nonprocessed Solution from Experiment P5

Experiment	$\Delta H$ (J/g)	$T_0$ (°C)	$T_1$ (°C)	$T_2$ (°C)	Onset (°C)	End (°C)
P2	–385	—	145	156	101	163
P3	–371	—	~145	151	106	162
P5	–578	94	~147	151	60 <sup>a</sup>	167

<sup>a</sup> Determined for signal  $T_0$ .



**Figure 2** DSC curves of solutions from experiments P2, P3 (with preprocessing), and P5 (without preprocessing).

showed how the higher alkalinity of P3 resulted in a slightly narrower curing profile in the thermogram.

The first signal in the DSC curve of P5 was probably mainly a result of the methylation reactions; this signal is defined as  $T_0$  in Table IV. The onset temperature of P5, which was determined for signal  $T_0$ , was very low (60°C), and, under these conditions, 60°C could be considered an upper temperature limit for the preprocessing stage. Above 60°C the preprocessing would probably be difficult to control, as was observed in the P4 preprocessing test at 70°C.

#### Effects of high-temperature heating on behavior and development of viscosity of preprocessed solutions in the batch reactor

The progress of the methylation and condensation reactions of the preprocessed solutions from experiments P1–P3 was studied in three experiments (B1–B3) in a batch reactor. The objectives were to determine the effects of high-temperature heating on the behavior and stability of the synthesis and on the development of viscosity.

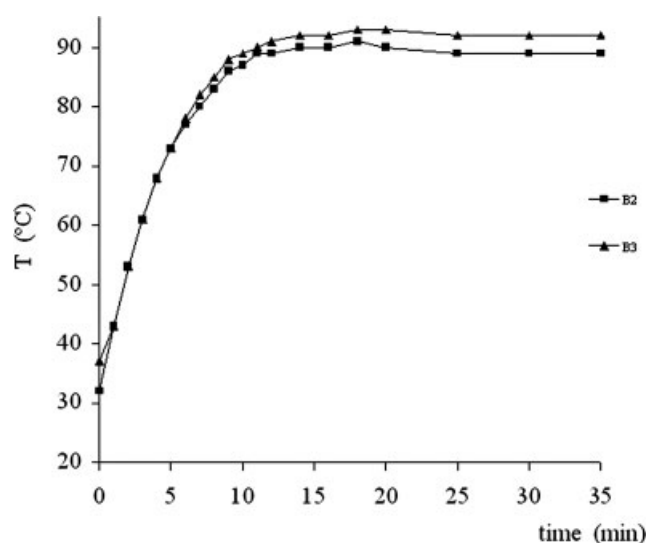
In experiment B1 the preprocessed solution was heated stepwise by raising the jacket temperature of the reactor from 60°C to 116°C in 80 min. The jacket temperature of the reactor was increased whenever the rise in the solution temperature began to slow. The end temperature of the resol solution in experiment B1 was 96°C. In the next two experiments, B2 and B3, solutions of different initial alkalinity (2.5 and 3.0 wt %) were heated at a constant jacket temperature (105°C) for 35 min, and the temperatures of the solutions were observed.  $T_{\text{solution}}$  versus batch time curves of experiments B2 and B3 (Fig. 3) showed a similar increase in solution temperatures during the first 10 min of heating, after which the temperatures stabilized to a constant of about 90°C. There were no signs that the solution temperatures in experiments

B1–B3 rose too fast, which would have created runaway conditions or gelled resin structures.

Table V shows the viscosities of the solutions at the end of the batch experiments. As expected, the end viscosities of all the solutions increased over the initial viscosities. In addition, the end viscosities increased, roughly in proportion to the batch time. The end viscosity of experiment B1, which had 80 min of synthesis time, was clearly the highest (116 mPa s vs. 24 and 34 mPa s), and its end temperature was approximately 6°C higher (96°C vs. 89°C and 92°C).<sup>31</sup> A comparison of experiments B2 and B3, which both had a 35-min batch time, suggested, in agreement with previous works,<sup>6,9</sup> that the higher alkalinity of the B3 solution accelerated the resol synthesis, leading to a higher end viscosity (34 mPa s) than that in experiment B2 (24 mPa s).

#### Consumption of starting materials and structural characterization of solutions from batch reactor experiments

The GC and titrimetric results, shown in Table V, clearly indicate that synthesis proceeded during the batch reactor experiments, as was seen in the viscosity analysis. In the solutions of experiments B2 and B3, a decrease of about 3% in the quantities of free phenol and free formaldehyde relative to the initial quantities compared was achieved after 35 min of processing. Simultaneously, the conversions of phenol and formaldehyde in experiments B2 and B3 increased by about 0.10–0.15 units. The high conversion of phenol (0.996) in experiment B1 indicated that free phenol was almost completely consumed after 80 min of batch processing. Despite experiment B1 having a longer processing time and a higher end



**Figure 3** Temperatures of solutions during batch experiments B2 and B3 as a function of batch time at constant batch reactor temperature (105°C).

TABLE V  
End Viscosities and Results of GC and Titrimetric Analyses of Solutions  
from Batch Reactor Experiments B1–B3

Experiment	End viscosity (mPa s)	Free phenol (wt %)	Conversion of phenol	Free formaldehyde (wt %)	Conversion of formaldehyde
B1	116	0.1	0.996	2.1	0.900
B2	24	1.3	0.960	1.1	0.945
B3	34	1.0	0.967	0.9	0.957

temperature, the conversion of formaldehyde was lower. This was a result of the higher F/P molar ratio (2.3) than that in experiments B2 and B3 (F/P = 2.0). A higher F/P molar ratio typically decreases the amount of free phenol in resol synthesis, whereas the amount of free formaldehyde in the resol solutions increases.<sup>6,32</sup> The consumptions and conversions of starting materials in experiments B2 and B3 were similar despite the differences in alkalinity.

The results of the NMR spectral analysis, shown in Table VI, support the above findings. Free ortho and free para sites and methylol groups were fewer, but methylene bridges were more abundant in experiment B1 than in experiments B2 and B3. This confirmed that the longer batch time and higher end temperature of B1 allowed more condensation reactions along with higher phenol conversion and higher end viscosity. The small total amount of free reactive phenolic positions (0.102) in the solution after experiment B1 was in accordance with the low content of free phenol determined by GC (Table V). After the preprocessing stage, the ratio of para methylol to ortho methylol groups in the P2 and P3 solutions was approximately 0.6, but the 35 min of batch processing decreased the corresponding ratios in

experiments B2 and B3 to approximately 0.2, indicating a higher condensation reactivity of para methylols.<sup>26–28</sup>

Experiments B2 and B3 had the same total amounts of free aromatic carbons and methylol groups, but the slightly higher total amount of methylene bridges observed in the spectrum of B3 could have been responsible for the difference between B3 and B2 in end viscosity, (34 and 24 mPa s, respectively). Analysis of the NMR results of experiments B2 and B3 showed a marked decrease in the number of phenolic hemiformal structures relative to the end of the preprocessing stage. Evidently, the hemiformal groups had cleaved and reacted with other phenolic units in the solutions.<sup>19</sup>

#### Effect of batch synthesis stage on reactivity

The reactivities of the solutions from batch reactor experiments B1–B3 were analyzed by DSC and are shown in Table VII. The least amount of reaction heat was released from the B1 solution because the condensation reactions had progressed farthest in the batch processing. The absolute reaction heat values for the B2 and B3 solutions decreased by more than 100 J/g, and the onset temperatures were shifted higher, by 9°C–13°C than the reactivities and onset temperatures of the corresponding preprocessed P2 and P3 solutions (Table IV). However, the end temperatures of the B2 and B3 solutions were nearly the same as the end temperatures of the preprocessed solutions.

The DSC thermograms recorded for the B1, B2, and B3 solutions from the batch reactor experiments are presented in Figure 4. Two curing signals appeared in each thermogram, though they partly overlapped. Park et al.<sup>32</sup> found only one exothermic peak in DSC thermograms of resol resin samples, which was inconsistent with earlier reports of two

TABLE VI  
<sup>13</sup>C-NMR Integration Results of Batch Reactor  
Experiments B1–B3

Group	Experiment		
	B1	B2	B3
Aromatic carbons			
Phenoxy	1.000	1.000	1.000
Free para	—	0.059	0.055
Free ortho	0.102	0.417	0.379
Other	5.139	4.597	4.790
Formalin hemiacetals	0.047	0.013	—
Oxymethylenes of formaldehyde oligomers	0.023	0.012	0.005
Phenolic hemiformals	0.159	0.086	0.044
Methylol groups			
Para	0.098	0.303	0.258
Ortho	1.197	1.245	1.294
Methylene bridges			
p–p'	0.351	0.258	0.258
o–p	0.383	0.133	0.169
o–o'	—	—	—
Methanol	0.136	0.105	0.098
Total formaldehyde	2.26	2.05	2.04

TABLE VII  
DSC Analysis of Solutions from Batch  
Experiments B1–B3

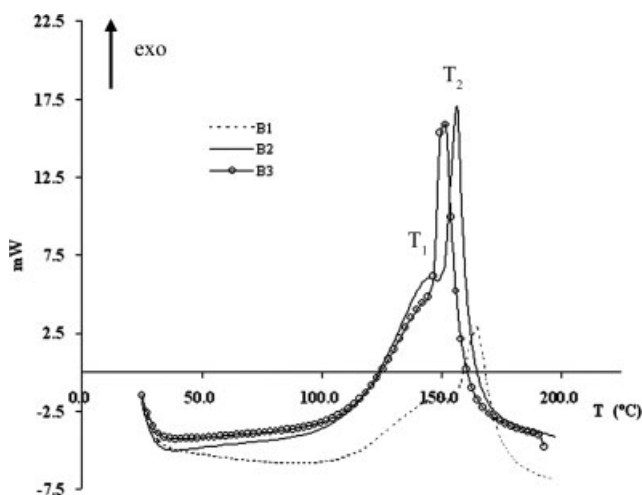
Experiment	$\Delta H$ (J/g)	$T_1$ (°C)	$T_2$ (°C)	Onset (°C)	End (°C)
B1	–177	148	165	111	175
B2	–246	145	156	114	162
B3	–260	~145	150	115	159

curing signals.<sup>16,33,34</sup> They suggested that the finding of a single signal was a result of their use of lower-molecular-weight resol samples (viscosity 24–60 mPa s). Our resol resin samples, in both the preprocessing and the batch synthesis stages, had viscosity in the range of 6.2–116 mPa s and could also be considered low-molecular-weight resols. An obvious difference between our resol samples and those of Park et al., however, is the quantity of free formaldehyde. Our samples contained 0.9–4.4 wt % free formaldehyde and those of Park et al. only 0.20–0.59 wt %. The higher free formaldehyde content could have enabled methylation reactions between the formaldehyde and phenolic units during the DSC experiments and so increased the intensity of the first curing signal ( $T_1$ ) and improved the separation of the two curing signals. Similar effects were observed in a study by Christiansen and Gollob,<sup>33</sup> who found only one curing signal at low free formaldehyde content (0.0–0.3 wt %).

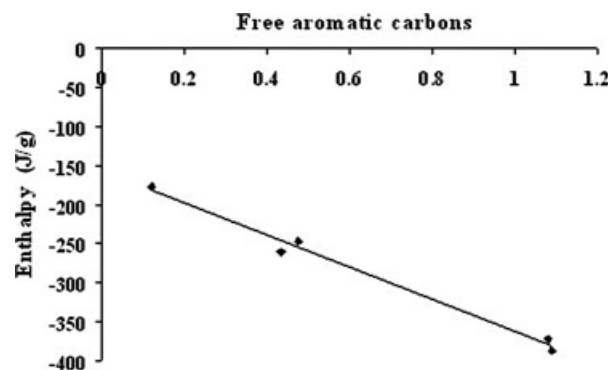
A relation between the conversion of structural groups and decreasing reaction heat during the resol synthesis could be observed by comparing the NMR and DSC results for samples taken after the preprocessing and batch synthesis stages. Under the conditions used in the study, a strong linear correlation was found between the released reaction heat (enthalpy) and the total amount of free ortho and free para carbons (Fig. 5). As the methylation and condensation reactions progressed, they decreased the total amount of available free aromatic carbons, resulting in lower reaction heat during the curing stage.

## CONCLUSIONS

The initial stage of phenol–formaldehyde resol resin synthesis was studied in a preprocessing reactor



**Figure 4** DSC curves for solutions from batch experiments B1–B3.



**Figure 5** Reaction enthalpy as a function of the total amount of free aromatic carbons.

with a 5-min residence time. The refractive index and alkalinity values of samples collected during preprocessing deviated only slightly from one another, which indicated steady-state conditions and solutions of uniform quality in the reactor. In this study the most appropriate preprocessing temperature for a typical resol solution was 60°C. The high conversion values of phenol and formaldehyde ( $\geq 0.79$ ) at the end of the preprocessing stage, which was carried out at 60°C, indicated that most starting materials were consumed in the preprocessing reactor. Despite having observed some methylene bridges in the NMR spectra of the preprocessed solutions, the preprocessing reactor (CSTR) should mainly be considered a methylation reactor. Commencement of the methylation reactions was advantageous because a part of the reaction heat was then released in the preprocessing stage. The methylation and condensation reactions and the increases in viscosity and solution temperature were steady during synthesis in the batch reactor.

Our results indicate that dividing the conventional one-stage batch process into two stages could facilitate control of the initial stages of resol production. Preprocessed solutions of uniform quality and reduced reactivity could be pumped into a temporary storage vessel and then into a batch reactor where the production of resol resin could be started without the need for the gradual addition of starting materials.

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