

## Online monitoring of synthesis and curing of phenol–formaldehyde resol resins by Raman spectroscopy

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### ABSTRACT

The synthesis and curing of phenol–formaldehyde resol resins were monitored online by Raman spectroscopy. The synthesis of the resins (F/P 2.0, alkalinity 4.5 wt%) was studied at rising temperature (40–90 °C) for 90 min and at constant temperatures (80 °C, 90 °C, 100 °C, and 110 °C) for 120 min. The progress of the curing was investigated isothermally (80 °C, 90 °C, 100 °C, and 110 °C) for 120 min for three resins with different degrees of condensation. The synthesis and curing of the resins were started in the reactor and the advancement of the methylation and condensation reactions was followed through the window of the reactor in the wave number region of 2000–400 cm<sup>-1</sup> with use of a fiber optic probe for the data collection. The Raman spectra of six model compounds (formaldehyde, phenol, 2-hydroxybenzyl alcohol, 4-hydroxybenzyl alcohol, 2-benzylphenol, and 4-benzylphenol) were analyzed to facilitate the interpretation of the spectra of the resins. The consumptions of free phenol and free formaldehyde, as well as the progress of the methylation and condensation reactions were easily monitored by following the changes in intensity of the characteristic Raman bands. The results for the cured resins obtained by Raman spectroscopy were in good agreement with the structures and residual reactivities studied by CP/MAS <sup>13</sup>C NMR spectroscopy and differential scanning calorimetry (DSC), respectively. The results of the study show Raman spectroscopy to be a promising tool for the online monitoring and control of phenol–formaldehyde resol resin synthesis and curing; in addition, Raman spectroscopy offers an effective and fast method for structural study of the solid state resins.

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### 1. Introduction

Phenol–formaldehyde resol resins are produced in a step-growth polymerization process in the presence of alkaline catalysts. The heat-curable, viscous resin solutions that are obtained are used, e.g. as plywood adhesives, impregnation resins for paper overlays, and binders for abrasive materials [1,2].

At the start of the resol synthesis, highly exothermic methylation reactions between phenol and formaldehyde yield methylolphenols. The methylation stage of the synthesis is followed by the condensation stage, in which the methylol groups react with the free sites of other phenolic species yielding methylene bridge structures between the phenolic rings [1,2]. The formation of dibenzyl ether bridges resulting from the reactions of two methylol groups is not favored in highly alkaline conditions [3–5]. The resol resin synthesis is halted when the appropriate degree of condensation in the resin (viscosity) has been achieved.

In the following heat curing stage, further condensation reactions of the resol resins are carried out typically at temperatures above 100 °C [1,2]. The curing of the resin advances in the liquid state until the resin reaches the gel point, where molar mass and viscosity of the resin tend to infinity. The result is an insoluble polymer network [1,2,6,7]. The totally crosslinked resol resins are hard, insoluble, infusible, and three-dimensional polymer networks, which provide good moisture- and heat-resistance properties [1,2].

Since understanding of the advancement of resol resin synthesis and curing processes is essential for further development of the resins, methylation and condensation reactions and structures of the resols have been followed and studied by various methods, such as FTIR spectroscopy [5,8,9], gel permeation chromatography (GPC) [10–13], <sup>13</sup>C NMR spectroscopy [14–18], and differential scanning calorimetry (DSC) [3,7,11,19]. However, none of these methods is well suited for gathering real-time information about the consumption of starting materials or structure of the resins during the resin processes, which could improve the safety and control of the synthesis and result in more uniform resin quality. The use of FTIR spectroscopy for the online process control and study of aqueous resol resins is slightly limited by the broad and overlapping signals and the disturbing effect of water [20] in the

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spectral data. Until now, liquid state  $^{13}\text{C}$  NMR spectroscopy has been the best method for detailed investigation of the structure of resin solutions, but it is far too slow for online monitoring of the resin syntheses.

Structural characterization of the cured and solid resol resins is mainly performed by solid state CP/MAS  $^{13}\text{C}$  NMR spectroscopy and FTIR spectroscopy. Solid state CP/MAS  $^{13}\text{C}$  NMR spectroscopy is an effective method to clarify the extent of the cure and structures in the cured resins; however, the technique is relatively time consuming and expensive, and careful sample preparation is required to obtain high resolution spectra.

Raman spectroscopy is a complementary method of analysis to IR spectroscopy. Interest in Raman spectroscopy as a tool for the analysis of different types of resins has increased recently, in pace with the development of Raman equipment and methods. Most of the problems (data collection, fluorescence) associated with the Raman have now been eliminated. The application of Raman spectroscopy in process control, and in the study of curing and the cured state of resins, is especially attractive because of the possibility to use fiber optic probe for the online monitoring and data collection, even through a glass window. So far, the contribution of Raman spectroscopy to the study of the synthesis of phenol–formaldehyde resol resins has been minor, probably due to the difficulties noted above. Chow and Chow [20] followed the changes in intensity of the Raman bands of resol resins during the prepolymer synthesis, and plotted the changes as a function of molar mass of the resin. In addition, Raman spectroscopy has been used in carbonization and graphitization studies of resol resins [21,22].

The objective of this work was to identify the characteristic Raman bands to be followed in Raman spectroscopic online monitoring of the advancement of the synthesis (methylation and condensation) and curing and in the study of final solid state of phenol–formaldehyde resol resins. The synthesis of the resins (F/P 2.0, alkalinity 4.5 wt%) was followed at different temperatures (40–90 °C, 80 °C, 90 °C, 100 °C, and 110 °C) for 90 min or 120 min. The effects of temperature on the advancement of the condensation reactions during the curing of three resol resin samples with different starting degrees of condensation were followed at four temperatures (80 °C, 90 °C, 100 °C, and 110 °C) for 120 min by Raman spectroscopy. Raman spectra of six model compounds (formaldehyde, phenol, 2-hydroxybenzyl alcohol, 4-hydroxybenzyl alcohol, 2-benzylphenol, and 4-benzylphenol) were measured to facilitate the interpretation of the characteristic Raman bands observed in the spectra of the resins. In addition, the structures and residual reactivities of the cured resins were studied by solid state CP/MAS  $^{13}\text{C}$  NMR spectroscopy and differential scanning calorimetry (DSC), respectively, to confirm the results of the Raman study.

## 2. Experimental section

### 2.1. Starting materials and samples for curing experiments

Solutions used in the study of resol synthesis were prepared by premixing the starting materials at room temperature. Mixing of phenol (3.24 g), 50 wt% aqueous solution of formaldehyde (formalin, 4.10 g), additional water (1.80 g), and 50 wt% NaOH solution (0.90 g) gave a formaldehyde to phenol (F/P) molar ratio of 2.0 and alkalinity of 4.5 wt%.

Three resin samples (S1, S2, and S3) synthesized for our earlier study [23] (F/P 2.0, alkalinity 4.5 wt%) were selected for investigation of the spectral changes during the curing of the resins. The experimental arrangement for our previous work, in which the resin samples were collected during a single batch process, ensured that the main difference between the samples was the degree of condensation. The properties of the resins are collected in Table 1. Samples were kept frozen before the curing experiments.

**Table 1**

Viscosities, number average molar masses ( $M_n$ ), weight average molar masses ( $M_w$ ), and polydispersity (PD) indices of resins S1, S2, and S3 used in the curing experiments

Sample	Viscosity (mPa s)	$M_n$ (g/mol)	$M_w$ (g/mol)	PD index
S1	25	469	567	1.21
S2	457	1159	2208	1.91
S3	751	1268	2630	2.08

The model compounds for the Raman studies were phenol (J.T. Baker, p.a.), formaldehyde as a 50 wt% water solution (formalin, Hexion Specialty Chemicals, Inc.), 2-hydroxybenzyl alcohol (2-methylolphenol, Aldrich, 99%), 4-hydroxybenzyl alcohol (4-methylolphenol, Fluka, >98.5%), 2-benzylphenol (Fluka, >98.5%), and 4-benzylphenol (Aldrich, 99%).

### 2.2. Raman spectrometer

The advancement of the resol resin synthesis and the curing of the resins were followed with a prototype Raman spectrometer (VTT Technical Research Centre of Finland, Optical Instrument Center, Oulu, Finland). The Raman system (Fig. 1) consisted of a semiconductor diode laser, a spectrograph, a charge-coupled device (CCD) detector, and a fiber optic probe (length ~2 m) [24] that allowed remote study of the synthesis and curing. The acquisition time of the Raman signals was 60 s and the total measurement time was 90 min or 120 min. The wavelength of the excitation laser was 830 nm, and the laser power at the sample was 100 mW. The Raman spectra were studied at the 2000–400  $\text{cm}^{-1}$  region with a spectral resolution of  $\leq 8 \text{ cm}^{-1}$ . All measurements were performed in a darkened room in the absence of daylight. The background spectrum was subtracted from the measured spectra. Raman spectral data of the resins were collected by LabVIEW-based data acquisition and analysis software. The data analysis was performed with Matlab software.

### 2.3. Raman experiments

Raman bands of six commercial model compounds were identified to facilitate the interpretation of characteristic Raman bands in the spectra of the phenol–formaldehyde resol resins. The assignments of the Raman spectra of phenol, formalin, 2-methylolphenol, and 4-methylolphenol were useful for the study of the methylation stage of the resol resin synthesis. In addition, the Raman spectra of two aromatic compounds containing methylene bridge structures, 2-benzylphenol and 4-benzylphenol, were

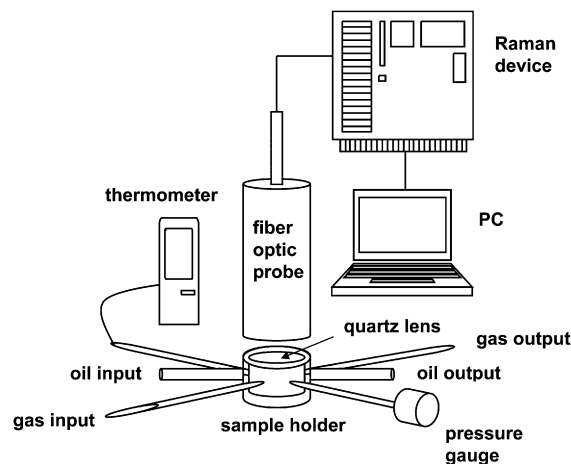


Fig. 1. Experimental arrangement for the Raman studies.

interpreted for study of the condensation stage of the synthesis. Samples were placed on the sample holder of the Raman device, and spectra were detected in a total of 50 measurements.

The synthesis and curing of the resins were performed in a reactor equipped with a heating oil jacket, gas input and output tubes, a thermometer, and a pressure gauge (Fig. 1). Samples were pipetted ( $V$  1.5 mL) into a steel sample holder (diameter  $\sim$  25 mm) surrounded by a heating oil jacket. The sample holder was sealed with a quartz-windowed steel cover through which the Raman spectra of the resins were detected. The fiber optic probe was placed above the reactor, and the height of the probe from the surface of the sample was adjusted to obtain maximum intensity in the spectra. A slow stream of nitrogen was conducted through the reactor to diminish possible oxidation reactions in the resins and to purge the steam which otherwise could condense on the quartz window and disturb the measurements. The spectral changes and advancement of synthesis of the resol resin were followed online in five Raman experiments by measuring the spectra of the premixed starting material solutions at different temperatures for 90 min or 120 min.

In the first 90-min experiment (Exp1), synthesis was started by increasing the temperature in the reactor slowly. This enabled more precise monitoring of the spectral changes occurring during the exothermic methylation stage of the synthesis. During the first 15-min, the premixed starting material solution was pipetted ( $V$  1.5 mL) into the reactor at room temperature, the reactor was sealed, and the temperature of the heating oil ( $T_{oil}$ ) was raised from room temperature to 40 °C. The experiment proceeded with  $T_{oil}$  raised by 10 °C after each 15-min period up to an end temperature of 90 °C.

The effects of temperature on the progress of the synthesis and the development of the spectra were studied by Raman spectroscopy in four experiments carried out at constant reactor temperatures. The premixed solutions were pipetted ( $V$  1.5 mL) into the heated reactor, and the spectra were detected at 80 °C (Exp2), 90 °C (Exp3), 100 °C (Exp4), and 110 °C (Exp5) for 120 min.

The progress of the curing and the Raman spectral changes were investigated by measuring the spectra of samples S1, S2, and S3 at constant temperatures for 120 min. The resins were added ( $V$  1.5 mL) to the heated reactor, and the spectra were measured at 80 °C, 90 °C, 100 °C, and 110 °C.

#### 2.4. Solid and liquid state $^{13}\text{C}$ NMR experiments

Structural characterization of the solid resin samples from the curing experiments was performed by crosspolarization/magic-angle spinning (CP/MAS)  $^{13}\text{C}$  NMR experiments. Operating frequencies of the Bruker AMX-400 NMR spectrometer were 100.625 MHz for carbon and 400.130 MHz for proton. Acquisition parameters of  $^{13}\text{C}$  NMR CP/MAS runs were a 90° pulse, a 2-ms contact time, a 4-s delay time, 15,000 scans, and 12-kHz magic angle spinning. The sample holder was a 4-mm  $\text{ZrO}_2$  rotor with a Kel-F cap. The NMR samples were prepared by milling the cured resol resins in a ball mill (Fritsch Pulverisette p-6) for 6–8 min using three large (diameter 3 cm) and six medium-sized steel balls. The finely ground resin particles were passed through a sieve with a mesh width of 63  $\mu\text{m}$  (Retsch).

The liquid state  $^{13}\text{C}$  NMR spectrum was determined with a Bruker AMX-400 NMR spectrometer at room temperature observing  $^{13}\text{C}$  at operating frequency 100.623 MHz. The method employed to obtain a quantitative  $^{13}\text{C}$  NMR spectrum was inverse gated proton decoupling. Acquisition parameters for the  $^{13}\text{C}$  measurement were a 90° pulse of 8  $\mu\text{s}$ , a 120-s delay time, and 650 scans.  $\text{DMSO-}d_6$  (99.8% deuterated dimethyl sulfoxide, Euriso-top) was used as solvent and as agent to obtain a deuterium lock. In addition, the spectral scale was calibrated to the central resonance

line of  $\text{DMSO-}d_6$  ( $\delta = 39.5$  ppm). The resin sample ( $\sim$  1 ml) was dissolved in  $\text{DMSO-}d_6$  (3 ml) and taken into a 5-mm NMR tube (VWR, 5 mm  $\times$  178 mm,  $>400$  MHz). The  $^{13}\text{C}$  NMR shifts of the solid and liquid state resins were assigned according to the literature [11,17,18,23,25,26].

#### 2.5. Differential scanning calorimetry (DSC)

The residual reactivity of the cured resol resins was determined with a Mettler Toledo DSC821 instrument with highly sensitive HSS7 sensor. The thermograms of the resin samples were analyzed by STARe thermal analysis software. The solid and powdered resin samples were weighed (9.0–11.0 mg) in the high-pressure steel pans (Mettler Toledo) and sealed with gold-plated copper seals. The closed steel pans were heated from 25 °C to 250 °C at a heating rate of 10 °C/min. The DSC results were the average of two parallel determinations made with the same steel pan. The repeatability and reproducibility standard deviations of the reaction heat measurements for the resol samples are 5% and 15%, respectively [27].

### 3. Results and discussion

#### 3.1. Assignments of Raman bands of model compounds

Raman spectra (Fig. 2) of six model compounds (formalin, phenol, 2-methylphenol, 4-methylphenol, 2-benzylphenol, and 4-benzylphenol) were measured to facilitate the interpretation of

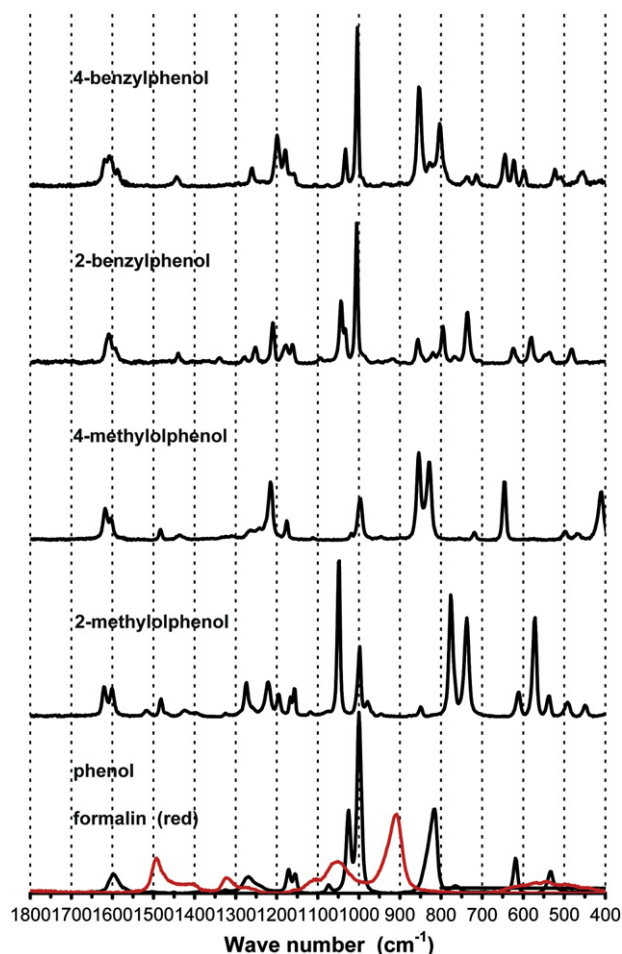


Fig. 2. Raman spectrum of phenol, formalin, 2-methylphenol, 4-methylphenol, 2-benzylphenol, and 4-benzylphenol.

characteristic Raman bands and spectral areas of the phenol–formaldehyde resins.

In aqueous solution, formaldehyde reacts with water and appears mainly in the form of methylene glycol ( $\text{HOCH}_2\text{OH}$ ). As the concentration of formaldehyde in the water solution increases, the probability of the oligomerization reactions of methylene glycols increases, and mixtures of oligomeric chain structures with variable number of  $\text{CH}_2\text{O}$  units ( $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ ) are formed [28,29]. A total of eight signals were distinguished in the Raman spectrum of formalin, shown together with that of phenol in Fig. 2. The important signals for interpretation of the Raman spectra of resol resins were the sharp medium-sized band at  $1490\text{ cm}^{-1}$  and the small band at  $1318\text{ cm}^{-1}$  assigned to vibrations of the  $\text{CH}_2$  group, and the signal at  $1074\text{ cm}^{-1}$  yielded by the  $\text{OCO}$  group of formalin [28,29]. In addition, the strongest signal of the formalin spectrum at  $912\text{ cm}^{-1}$ , interpreted as the vibration of the  $\text{OCO}$  group of  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$  oligomers [28,29], was valuable for the monitoring of formalin consumption.

The vibrational spectrum of phenol has been widely investigated both theoretically and experimentally [30–32]. In this study, the effects of water (hydrogen bonding) and  $\text{NaOH}$  on the Raman bands of phenol (Fig. 2) were taken into account by determining the Raman spectrum of phenol in alkaline water solution (1.62 g phenol, 0.9 g water, and 0.45 g 50 wt%  $\text{NaOH}$  solution). The Raman spectrum of phenol contained several useful signals for monitoring the consumption and substitution of phenol in resin synthesis. The band at app.  $1600\text{ cm}^{-1}$  assigned to the vibration of the  $\text{CC}$  bond of the ring [32] has been used in previous resin studies as an internal reference signal [33]. The main Raman bands for the evaluation of the consumption and substitution of phenol are located in the region of  $1030\text{--}530\text{ cm}^{-1}$ . Thus, the intensity changes of the strong bands at  $1026\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$  and the medium-sized signals at  $621\text{ cm}^{-1}$  and at  $536\text{ cm}^{-1}$  assigned to the vibrations of the  $\text{CC}$  bond of the ring, and the strong band at  $818\text{ cm}^{-1}$  probably produced by the combination vibration of  $\text{CC}$ - and  $\text{CO}$ -group of phenol, could be useful for the monitoring of the methylation and condensation stages as a function of time [31,32].

The model compounds used to facilitate the assignment of the bands of the methylation stage were 2-methylolphenol and 4-methylolphenol, which have a methylol group ( $-\text{CH}_2\text{OH}$ ) attached to *ortho* and *para* positions of the ring, respectively (Fig. 2). The vibrational spectra of these compounds have not yet been fully interpreted. The Raman spectra of the condensation stage of the resol resin synthesis were interpreted with the aid of model compounds 2-benzylphenol and 4-benzylphenol, which both possess the methylene bridge structure between the aromatic units (Fig. 2). The vibrational spectrum of 2-benzylphenol has been interpreted in the literature [34]. The literature assignments for diphenylmethane [35,36] and bis(2-hydroxyphenyl)methane [37], in addition to Raman group frequency tables [38,39], were used to assist the interpretation of the Raman spectra of the model compounds.

The spectral range of  $1481\text{--}1400\text{ cm}^{-1}$  was found to be important for monitoring of the synthesis and curing of the resins. In this region, the spectra of 2-methylolphenol and 4-methylolphenol showed a weak band at app.  $1481\text{ cm}^{-1}$  possibly due to vibrations of  $\text{CH}_2$  groups of the methylol group [38,39]. Similarly, in the spectrum of formalin, the signal at  $1490\text{ cm}^{-1}$  was assigned to the vibration of the  $\text{CH}_2$  group [28,29]. The spectra of 2-benzylphenol and 4-benzylphenol, in turn, showed a weak band at  $1444\text{--}1439\text{ cm}^{-1}$ , which was assigned to the vibration of the  $\text{CH}_2$  group of the methylene bridge [34]. These assignments of the bands at app.  $1481\text{ cm}^{-1}$  and  $1440\text{ cm}^{-1}$  indicate that the spectral changes in this area could be used to evaluate the advancement of the methylation and condensation stages.

An important and characteristic spectral range for methylolphenols and benzylphenols with medium to strong Raman bands was identified at app.  $1050\text{--}995\text{ cm}^{-1}$ . As for phenol, the bands of these aromatic model compounds at app.  $1000\text{ cm}^{-1}$  were most likely generated by the vibrations of the  $\text{CC}$  bonds of the ring [32]. The strongest signal in the Raman spectrum of 2-methylolphenol was at  $1046\text{ cm}^{-1}$ . Although the Raman literature for 2-benzylphenol assigns the band at  $1044\text{ cm}^{-1}$  to the ring vibration [34], it is also possible that the band of 2-methylolphenol at  $1046\text{ cm}^{-1}$  results from the  $\text{CCO}$  vibration of the methylol group [38].

The spectral region from  $900\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  containing, at least, weak ring, strong  $\text{CCO}$  group, and medium  $\text{CH}_2$ -based vibrations is sensitive to the nature, position, and number of substituents of the ring [38,39], and detailed interpretation of the bands in the region is difficult. The spectra of the model compounds nevertheless showed several characteristic Raman signals in the area, which could be useful for the monitoring of synthesis and curing of the resins. The spectra of 4-methylolphenol and the benzylphenols showed medium to strong bands in the spectral range of  $860\text{--}795\text{ cm}^{-1}$ . Two characteristic signals of 2-methylolphenol located at  $777\text{ cm}^{-1}$  and  $737\text{ cm}^{-1}$  were strong, and are important for monitoring of the resin synthesis. The Raman spectra of the benzylphenols also showed signals at app.  $737\text{ cm}^{-1}$ . Both *para*-substituted phenolic compounds, 4-methylolphenol and 4-benzylphenol, exhibited a band at app.  $645\text{ cm}^{-1}$ , which was not observed in the spectra of the other model compounds. In addition, the characteristic strong bands at  $571\text{ cm}^{-1}$  and  $409\text{ cm}^{-1}$  appearing in the Raman spectra of 2-methylolphenol and 4-methylolphenol, respectively, should be useful for following the synthesis.

### 3.2. Online monitoring of synthesis of phenol–formaldehyde resol resins at rising temperature

In Exp1, the synthesis of phenol–formaldehyde resin (F/P 2.0, alkalinity 4.5 wt%) was monitored online by Raman spectroscopy (Exp1) under conditions of rising temperature ( $40\text{--}90\text{ }^\circ\text{C}$ ). The main purpose of Exp1 was to follow the advancement of the process, especially the methylation stage, by observing the characteristic Raman spectral changes. The Raman spectra of the premixed starting material solution were measured through the quartz window of the reactor under nitrogen flow. The synthesis was started slowly by raising the temperature of the heating oil stepwise,  $10\text{ }^\circ\text{C}$  at a time, from  $40\text{ }^\circ\text{C}$  to  $90\text{ }^\circ\text{C}$ , in 15-min intervals. Total synthesis time was 90 min. This method allowed precise monitoring of the fast and exothermic methylation reactions at the initial stage of the synthesis. The Raman bands of the resin observed during the synthesis and the assignments proposed for the bands are collected in Table 2. The advancement of Exp1 from the start to the end of the synthesis is shown in Fig. 3.

As expected, the Raman spectrum of the premixed starting material solution (1 min, Fig. 3) showed the overlapping spectra of phenol and formalin. The signal at app.  $1600\text{ cm}^{-1}$  assigned to the aromatic  $\text{CC}$ -vibrations moved slightly toward higher wave numbers ( $1610\text{ cm}^{-1}$ ) as a function of synthesis time probably due to changes in the measurement environment (viscosity, concentration). The intensity of the band remained nearly unchanged, however, and it was used as an internal reference signal for the evaluation of the Raman spectral changes occurring during Exp1. Figs. 4 and 5 present the development of the intensities of selected Raman bands in the spectral regions  $916\text{--}733\text{ cm}^{-1}$  and  $1300\text{--}995\text{ cm}^{-1}$  relative to the reference band as a function of synthesis time.

The consumption of free phenol and free formaldehyde was of particular interest in Exp1. The consumption of free phenol and increase in the degree of substitution of the ring were easily observed in the spectra as decrease in the intensities of the characteristic phenol bands at  $1027\text{ cm}^{-1}$  (Fig. 5),  $1002\text{--}995\text{ cm}^{-1}$  (Fig. 5),

**Table 2**

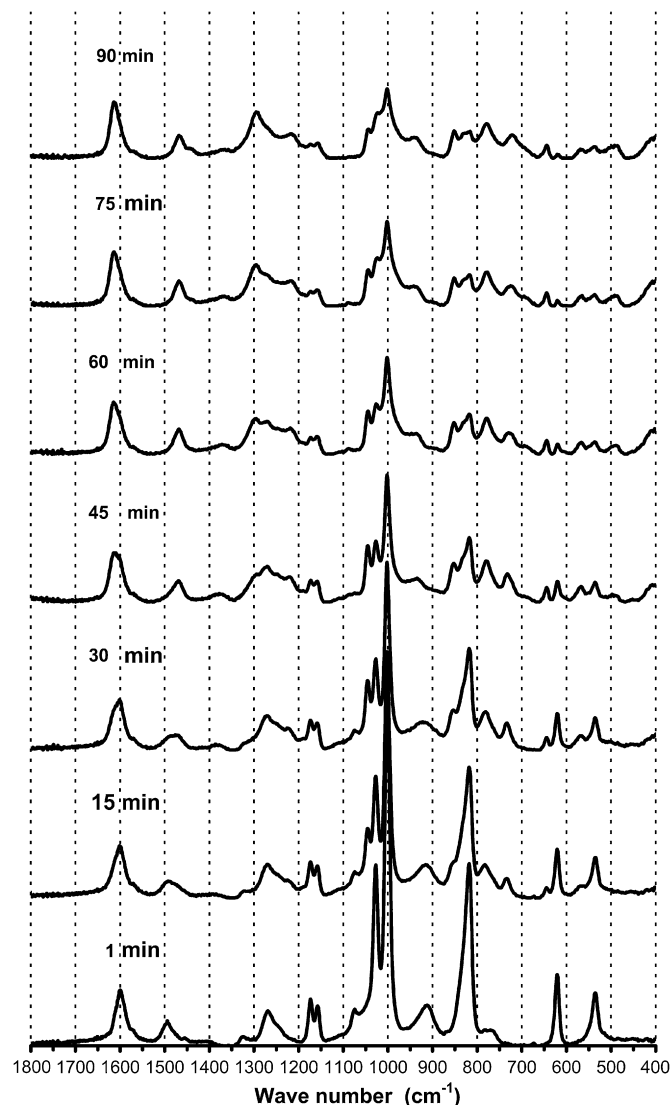
Proposed assignments of bands observed in the Raman spectra of phenol–formaldehyde resol resins

Frequency (cm <sup>-1</sup> )	Assignment	Functional group
1600–1610	$\nu$ (CC)	Ring
1494	$\beta$ (HCH)	Formalin
1469	$\beta$ (HCH)	Methylol
1438	$\beta$ (HCH)	Bridge
1370	w(HCH)/def(OH) + $\nu$ (CO)	Methylol
1324	w(HCH)	Formalin
1300–1296	t(HCH)	Bridge/methylol
1268	t(HCH)/ $\nu$ (CO)	Formalin/ring
1247	$\nu$ (ring-O)	Ring
1220–1210	$\nu$ (ring-CH <sub>2</sub> )	Ring/substituents
1174	$\beta$ (CH)	Ring
1157	$\beta$ (CH)	Ring
1074	$\nu$ (CC)/ $\nu$ (OCO)	Ring/formalin
1046	$\nu$ (CCO)/ring	Methylol/ring
1027	$\nu$ (CC)	Ring
1002–995	$\beta$ (CC)	Ring
950–920	$\gamma$ (CH)	Ring
916–912	$\nu$ (OCO)	Formalin
852	$\gamma$ (CH)	Ring
818	$\nu$ (CC), $\beta$ (CC), $\nu$ (CO)	Ring
783	$\gamma$ (CH)	Ring
770	$\gamma$ (CH)	Ring
733	$\gamma$ (CH)	Ring
645	Ring def	Ring
621	$\beta$ (CC)	Ring
567	Ring def	Ring
536	$\beta$ (CC)	Ring
492	Ring def	Ring
400	Ring def	Ring

$\nu$  = stretching vibration;  $\beta$  = bending vibration; w = wagging vibration; def = deformation vibration; t = twisting vibration; ring = ring vibration;  $\gamma$  = out-of-plane vibration.

818 cm<sup>-1</sup> (Fig. 4), 621 cm<sup>-1</sup>, and 536 cm<sup>-1</sup>. The signals of formalin at 1494 cm<sup>-1</sup> and 916–912 cm<sup>-1</sup> were clearly separated from the bands of phenol, and valuable for evaluation of the consumption in the methylation stage of the synthesis. The intensities of the bands at 1494 cm<sup>-1</sup> and 916–912 cm<sup>-1</sup> decreased during the experiment, and the bands were no longer observed as individual signals after 45 min (Fig. 3). The signal at 916–912 cm<sup>-1</sup> was instead observed as a shoulder of the band formed at 950–920 cm<sup>-1</sup>. If the intensities of this shoulder peak are taken into account when plotting the intensity as a function of time, it can be concluded that formalin was fully consumed after 75 min synthesis (Fig. 4). The weak formalin band at 1324 cm<sup>-1</sup> disappeared simultaneously with the bands at 1494 cm<sup>-1</sup> and 916–912 cm<sup>-1</sup> confirming the conclusions above. In addition, the weak shoulder at 1074 cm<sup>-1</sup>, assigned to the overlapping bands of formalin [29] and a weak ring vibration [32] (Fig. 2), disappeared in the course of the synthesis (Fig. 5), which was also in accordance with the behavior of other formalin signals.

The advancement of the methylation and succeeding condensation stages, resulting in the formation of methylol groups and methylene bridge structures, yielded several characteristic bands useful for the monitoring. A signal at 1469 cm<sup>-1</sup> appeared during the synthesis and, in addition, a weak shoulder to that band was observed at 1438 cm<sup>-1</sup> at the end of Exp1 (90 min). The peak at app. 1481 cm<sup>-1</sup> in the spectra of methylolphenols was assigned to vibration of the CH<sub>2</sub> groups of the methylol substituents [38], whereas the signal at app. 1440 cm<sup>-1</sup> in the spectra of benzylphenols was assigned to the vibrations of the CH<sub>2</sub> groups of the methylene bridges [34]. A similar distinction between these two bands has been made in Raman studies of urea–formaldehyde [40] and melamine–formaldehyde [41] resins, which contain methylol groups and methylene bridge structures between the resin units, and in a Raman investigation of phenol–formaldehyde novolac resins [33].



**Fig. 3.** Development of Raman spectra of phenol–formaldehyde resol resin in Exp 1 under conditions of rising temperature (40–90 °C).

Several changes occurred in the spectral region 1300–1150 cm<sup>-1</sup> as a function of synthesis time, and in the end the region was a broad and overlapping signal group. The spectral change at app. 1300–1296 cm<sup>-1</sup> was particularly significant for the online monitoring since the intensity of the band increased as a function of synthesis time (Fig. 5). The signal at 1300–1296 cm<sup>-1</sup> was not observed at the start of the experiment but was first seen as a shoulder peak in the 45-min spectrum. In the 60-min spectrum it was clearly distinguished from the other signals (Fig. 3). There were no significant vibrations in this region in the spectra of the model compounds. However, the band at 1300–1296 cm<sup>-1</sup> can probably be assigned to the twisting vibration of the CH<sub>2</sub> group which appears in the region [38,39]. For the aliphatic series of (CH<sub>2</sub>)<sub>n</sub>, the intensity of the band at 1305–1295 cm<sup>-1</sup> increases with *n* [38] and, in addition, the Raman spectra of polyethylenes show a strong peak in this area [42,43]. The signal at 1300–1296 cm<sup>-1</sup> may thus mainly be due to methylene bridges formed between phenolic species in the condensation reactions.

The most noticeable changes in the intensities of the Exp1 spectra were observed at the spectral region of 1080–995 cm<sup>-1</sup>. The progress of the methylation stage could easily be followed from

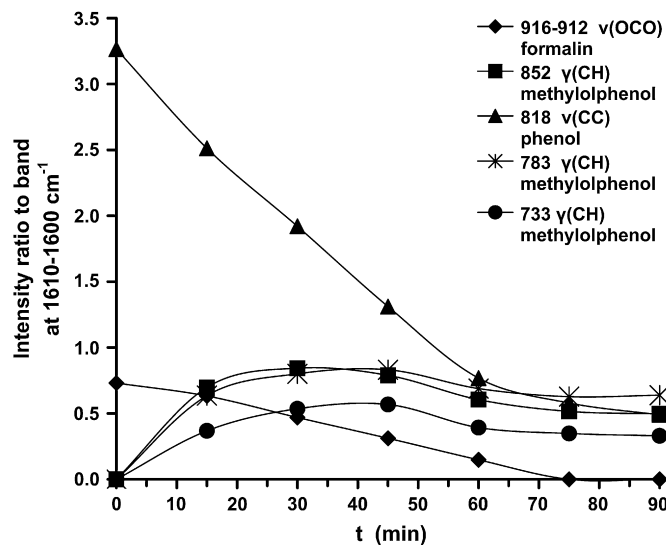


Fig. 4. Intensities of Raman bands at 916  $\text{cm}^{-1}$ , 852  $\text{cm}^{-1}$ , 818  $\text{cm}^{-1}$ , 783  $\text{cm}^{-1}$ , and 733  $\text{cm}^{-1}$  relative to the intensity of the reference band at 1600  $\text{cm}^{-1}$  as a function of synthesis time in Exp1.

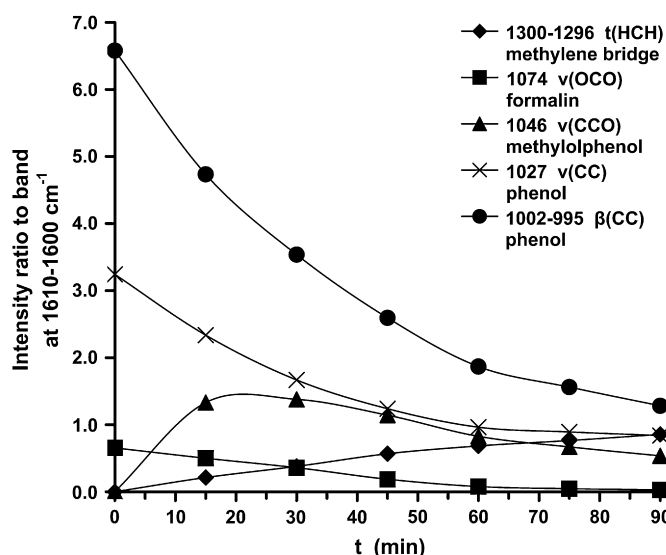


Fig. 5. Intensities of Raman bands at 1300–1296  $\text{cm}^{-1}$ , 1074  $\text{cm}^{-1}$ , 1046  $\text{cm}^{-1}$ , 1027  $\text{cm}^{-1}$ , and 1002–995  $\text{cm}^{-1}$  relative to the intensity of the reference band at 1610–1600  $\text{cm}^{-1}$  as a function of synthesis time in Exp1.

the signal at app. 1046  $\text{cm}^{-1}$  (Fig. 5), which was assigned to the CCO group of the methylol substituents ( $-\text{CH}_2\text{OH}$ ) [37] in the spectrum of 2-methylolphenol. The intensity of the band reached a maximum after approximately 20–30 min of the synthesis, and then decreased slowly. The formation and behavior of the signal gave a clear indication of the consumption of free phenol, and increasing *ortho*-substitution of the ring.

Several characteristic bands in the spectral region 950–400  $\text{cm}^{-1}$  indicated the advancement of the synthesis. An interesting signal, not observed in the spectra of the model compounds, appeared at 950–920  $\text{cm}^{-1}$ . The proposed assignment for the band is vibrations of aromatic CH groups in the substituted rings [38], which provide information about the substitution and crosslinking in the resins. The band at app. 852  $\text{cm}^{-1}$ , first seen as a shoulder in the 15-min spectrum (Fig. 3), was assigned to the vibration of the CH group of the ring. This band appeared as a strong peak in the spectra of *para*-substituted model compounds 4-methylolphenol and

4-benzylphenol. Other bands appearing for the first time in the 15-min spectrum were located at app. 783  $\text{cm}^{-1}$ , 733  $\text{cm}^{-1}$ , 645  $\text{cm}^{-1}$ , 567  $\text{cm}^{-1}$ , and 400  $\text{cm}^{-1}$ . These bands are typically assigned to the vibrations of CH groups [38], and to aromatic rings [38], which tend to be sensitive to the degree of the ring substitution. The vibrations at 783  $\text{cm}^{-1}$ , 733  $\text{cm}^{-1}$ , and 567  $\text{cm}^{-1}$  were characteristic for 2-methylolphenol, and the bands at 645  $\text{cm}^{-1}$  and 400  $\text{cm}^{-1}$  for 4-methylolphenol (Table 2), showing the changes in the *ortho* and *para* substitution of phenolic rings. The methylolphenol vibrations at 852  $\text{cm}^{-1}$ , 783  $\text{cm}^{-1}$ , and 733  $\text{cm}^{-1}$  (Fig. 4) were most intense at about 30 min, behaving consistently with the vibration at 1046  $\text{cm}^{-1}$  (Fig. 5). At 45 min, a weak signal appeared at 492  $\text{cm}^{-1}$ , which was also observed in the spectra of 2-methylolphenol and 4-methylolphenol (Fig. 2).

The results of the Raman studies of Exp1 confirmed the capability of Raman spectroscopy for the online monitoring of the methylation and condensation stages of resol resin synthesis. In addition, the Raman spectra showed several bands useful for evaluating the consumption of the starting materials, which is advantageous for the process control of the synthesis.

### 3.3. Online monitoring of synthesis of phenol–formaldehyde resol resins at constant temperatures

The effects of high synthesis temperature on the advancement of the resol resin synthesis and the development of the Raman spectra, especially during the condensation stage, were studied in four experiments. The spectral changes in the Raman spectra of the resin solutions were monitored online at constant reactor temperatures [80 °C (Exp2), 90 °C (Exp3), 100 °C (Exp4), and 110 °C (Exp5)] for 120 min. High reactor temperatures at the start of the syntheses resulted in high methylation rates, and the syntheses advanced fast to the condensation stage yielding increased molar mass and viscosity of the resin solutions. After the experiments, the Exp2 and Exp3 solutions were still in liquid state, but the resin samples of Exp4 and Exp5 were cured.

The effects of high start temperatures on the advancement of the methylation and condensation stages are clearly seen in a comparison of the Raman spectra in Figs. 6–9. Fig. 6 shows the development of the Raman spectra from the start (1 min) until the end of Exp3, which was carried out at 90 °C. Figs. 7 (Exp2), 8 (Exp4),

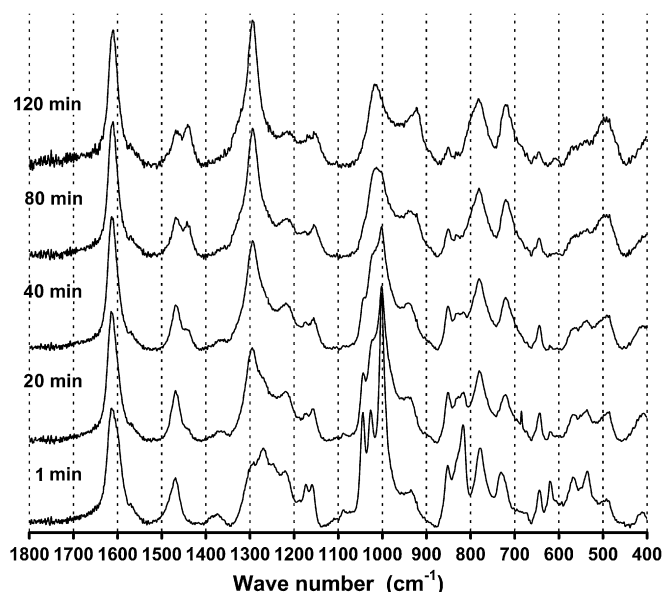


Fig. 6. Development of Raman spectra during Exp3 at 90 °C for 120 min.

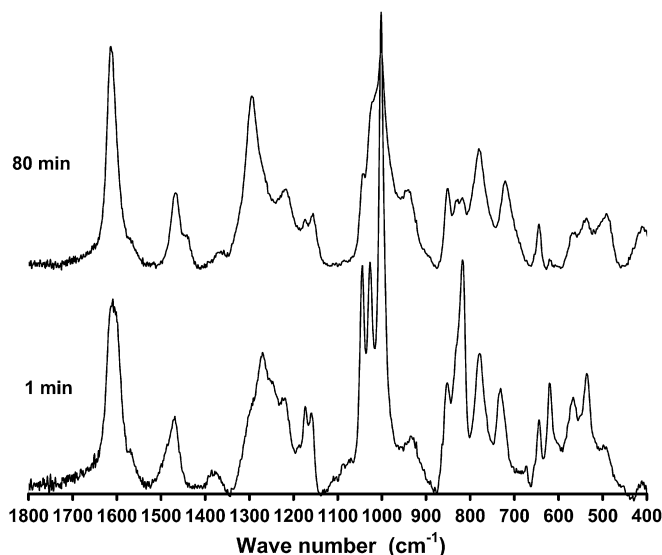


Fig. 7. Raman spectra at the start (1 min) and at 80 min in Exp2 carried out at 80 °C.

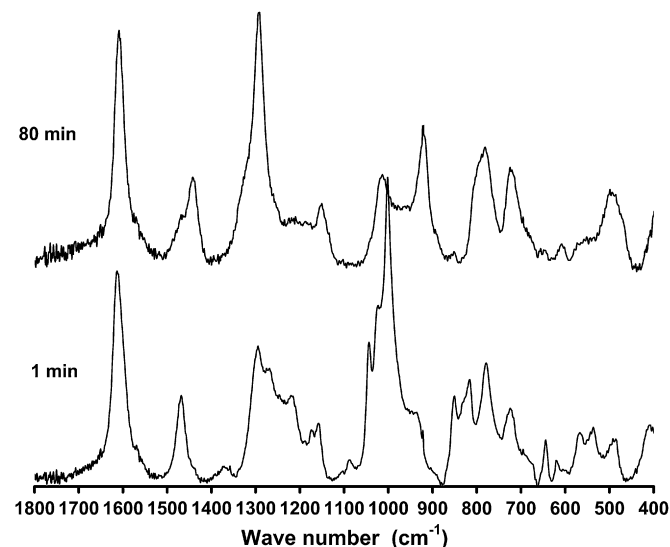


Fig. 9. Raman spectra at the start (1 min) and at 80 min in Exp5 carried out at 110 °C.

and 9 (Exp5) present the Raman spectra recorded at the start (1 min) and after 80 min of synthesis. The changes in the characteristic spectral areas of Exp2–Exp5 were similar to those of Exp1, but the syntheses progressed further than in Exp1 due to the higher start temperatures and longer reaction time.

In Exp 1, the bands at  $1469\text{ cm}^{-1}$  and at  $1438\text{ cm}^{-1}$  (shoulder peak) were assigned to the methylol and methylene bridge signals, respectively. The changes in the corresponding spectral areas in Exp2–Exp5 (Figs. 6–9) were more prominent, but in accordance with Exp1. The development of intensities of these signals is clearly seen in Fig. 6 (Exp3), in which the intensity of the band at  $1469\text{ cm}^{-1}$  decreases, while the intensity of the shoulder band at  $1438\text{ cm}^{-1}$  increases with reaction time. At the end of Exp4 (Fig. 8) and Exp5 (Fig. 9), the methylol vibration appeared only as a shoulder to the  $1438\text{ cm}^{-1}$  band indicating a high degree of condensation (crosslinking) in the resin. Higher methylolation and condensation temperatures also increased the intensity of the  $\text{CH}_2$  band at app.  $1300\text{--}1296\text{ cm}^{-1}$ . The intensity of this band was already observed to increase linearly during Exp1 (Fig. 5), and the results of experiments Exp2–Exp5 confirmed the importance of the band for the online monitoring of the condensation stage.

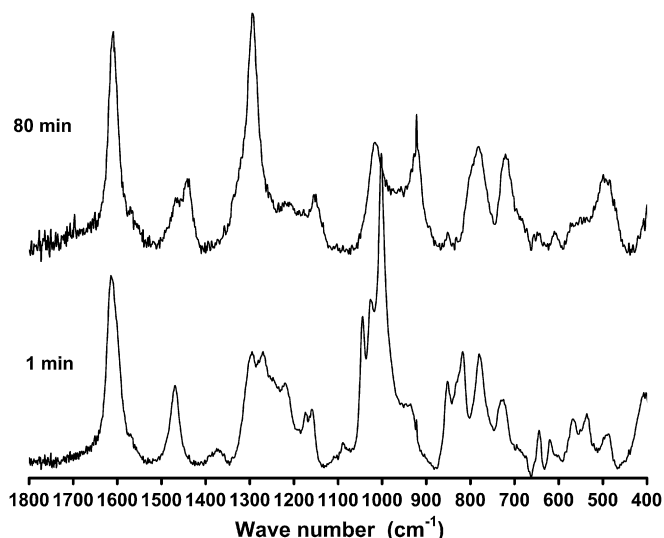


Fig. 8. Raman spectra at the start (1 min) and at 80 min in Exp4 carried out at 100 °C.

The spectral region from  $1100\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  showed dramatic changes as a function of synthesis temperature and time. The intensities of all bands at the region  $1050\text{--}1000\text{ cm}^{-1}$  decreased and the fine structure of the spectra was no longer observed. The band at app.  $950\text{--}920\text{ cm}^{-1}$  was a shoulder peak at the start of each run, but the intensity increased noticeably as a function of time and synthesis temperature. This band, which was also observed during Exp1 and assigned to vibrations of aromatic CH groups [38], could be valuable for evaluation of the degree of condensation and ring substitution of the resins.

The intensity changes at  $900\text{--}400\text{ cm}^{-1}$  were slightly less prominent than those at  $1100\text{--}900\text{ cm}^{-1}$ . However, the intensities of the bands at  $850\text{ cm}^{-1}$  and  $820\text{ cm}^{-1}$  decreased noticeably as a function of synthesis temperature and time, and the bands were not easily observed at the end of Exp4 and Exp5. As shown in Fig. 4, in Exp1 the intensity ratio of the vibrations at  $783\text{ cm}^{-1}$  and  $733\text{ cm}^{-1}$  achieved maximum value at approximately the halfway point, after which it slowly decreased, and finally stabilized at the end of the experiment. Changes in the intensities of these signals in Exp2–Exp5 were minor.

The most significant Raman spectral regions for the monitoring of the condensation stage of the resin synthesis were  $1469\text{--}1438\text{ cm}^{-1}$  indicating the ratio of methylol groups to methylene bridges,  $1300\text{--}1296\text{ cm}^{-1}$  possibly expressing the amount of methylene bridges, and  $1050\text{--}920\text{ cm}^{-1}$  showing the degree of condensation in the resin.

### 3.4. Online monitoring of curing of phenol–formaldehyde resol resins

The advancement of the curing of three phenol–formaldehyde resol resin samples (S1, S2, and S3) from the same resin synthesis but with increasing degree of condensation was followed by online Raman spectroscopic measurements at four temperatures (80 °C, 90 °C, 100 °C, and 110 °C) for 120 min. Attention was focused on changes in the intensities of the characteristic Raman bands and spectral regions as a function of curing time and temperature. In addition, the suitability of Raman spectroscopy for the study of solid state structures of the resins was clarified.

Although the structures of the phenolic species participating in the curing are complex, the primary reactions occurring during the curing are condensation reactions, which increase the degree of

substitution in the phenolic rings. Thus, the curing process was studied by monitoring the intensity changes of bands e.g. at  $1500\text{--}1400\text{ cm}^{-1}$ , at  $1300\text{--}1296\text{ cm}^{-1}$ , at  $1050\text{--}995\text{ cm}^{-1}$ , and at  $950\text{--}920\text{ cm}^{-1}$  that in Exp2–Exp5 were found to be good indicators of the degree of condensation.

In general, the changes in the spectra of the cured resins were similar to those in the experiments monitoring the synthesis (Exp1–Exp5). Owing to the low degree of condensation, the changes in the characteristic band intensities of resin S1 were clearer than those of resins S2 and S3. As expected, the most significant spectral changes occurring during the curing were in the regions of  $1470\text{--}1440\text{ cm}^{-1}$ ,  $1300\text{--}1296\text{ cm}^{-1}$ , and  $1050\text{--}920\text{ cm}^{-1}$ . All these intensity changes indicated increasing degree of cross-linking in the resin.

However, the advancement of the curing and state of the cured resin were more easily and straightforwardly studied by following the relative spectral changes at the regions  $1050\text{--}995\text{ cm}^{-1}$  and  $950\text{--}920\text{ cm}^{-1}$ . Fig. 10 shows the changes in these regions during the curing of resin S2 at  $100\text{ }^{\circ}\text{C}$  for 120 min. The intensity of the signal group at app.  $1050\text{--}995\text{ cm}^{-1}$  decreased, whereas the intensity of the signal group at  $950\text{--}920\text{ cm}^{-1}$  increased as a function of curing time.

The effect of curing temperature ( $80\text{ }^{\circ}\text{C}$ ,  $90\text{ }^{\circ}\text{C}$ ,  $100\text{ }^{\circ}\text{C}$ , and  $110\text{ }^{\circ}\text{C}$ ) on the advancement of the curing of resins S1, S2, and S3 was clearly observed by plotting the intensity ratios of the band regions  $950\text{--}920\text{ cm}^{-1}$  and  $1050\text{--}995\text{ cm}^{-1}$  as a function of curing time (Fig. 11–13). The intensity of the strongest signal in the spectral region at studied moment of curing time was used in the plotting. The strongest signal in the region  $1050\text{--}995\text{ cm}^{-1}$  shifted from  $995\text{ cm}^{-1}$  toward  $1015\text{ cm}^{-1}$  within the curing (Fig. 10). The band at app.  $950\text{--}920\text{ cm}^{-1}$  was a shoulder peak at the start of the curing, but it had shifted to app.  $920\text{ cm}^{-1}$  by the end of the experiment (Fig. 10).

The curing of resins S1, S2, and S3 advanced slowly and nearly linearly for 120 min at low curing temperatures ( $80\text{ }^{\circ}\text{C}$  and  $90\text{ }^{\circ}\text{C}$ ), and the spectral changes were minor. After the curing at  $80\text{ }^{\circ}\text{C}$ , resin S1 was not solid but a highly viscous paste, which was still

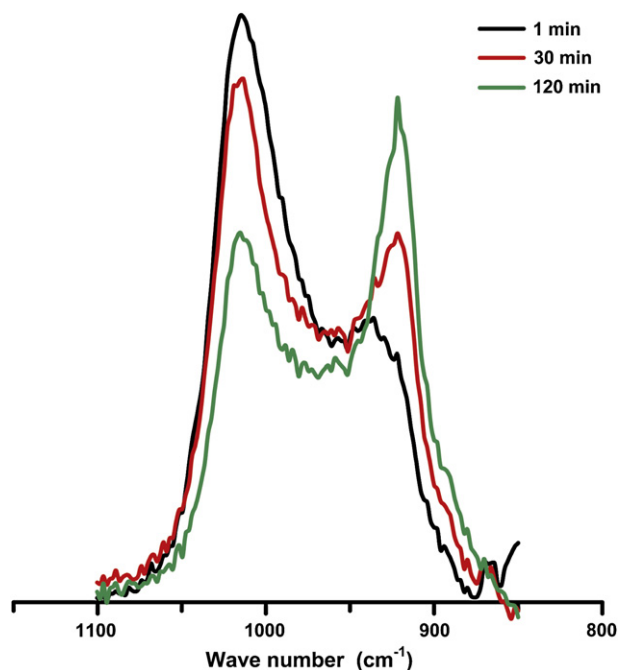


Fig. 10. Raman spectral changes at the region of  $1100\text{--}850\text{ cm}^{-1}$  during the curing of resin S2 at  $100\text{ }^{\circ}\text{C}$  for 120 min.

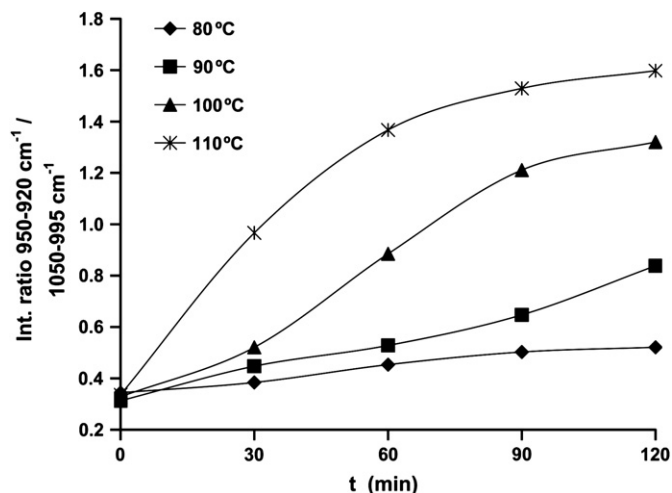


Fig. 11. Intensity ratios of Raman bands at  $950\text{--}920\text{ cm}^{-1}$  and  $1050\text{--}995\text{ cm}^{-1}$  as a function of curing time in the curing experiments of resin S1 (initial viscosity  $25\text{ mPa s}$ ) at  $80\text{ }^{\circ}\text{C}$ ,  $90\text{ }^{\circ}\text{C}$ ,  $100\text{ }^{\circ}\text{C}$ , and  $110\text{ }^{\circ}\text{C}$ .

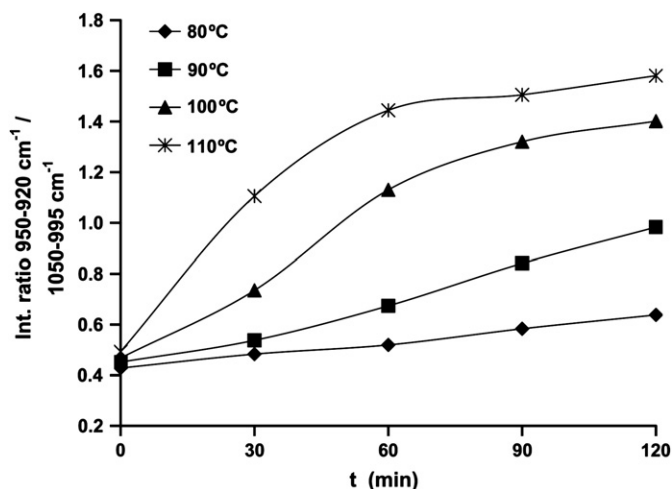


Fig. 12. Intensity ratios of Raman bands at  $950\text{--}920\text{ cm}^{-1}$  and  $1050\text{--}995\text{ cm}^{-1}$  as a function of curing time in the curing experiments of resin S2 (initial viscosity  $457\text{ mPa s}$ ) at  $80\text{ }^{\circ}\text{C}$ ,  $90\text{ }^{\circ}\text{C}$ ,  $100\text{ }^{\circ}\text{C}$ , and  $110\text{ }^{\circ}\text{C}$ .

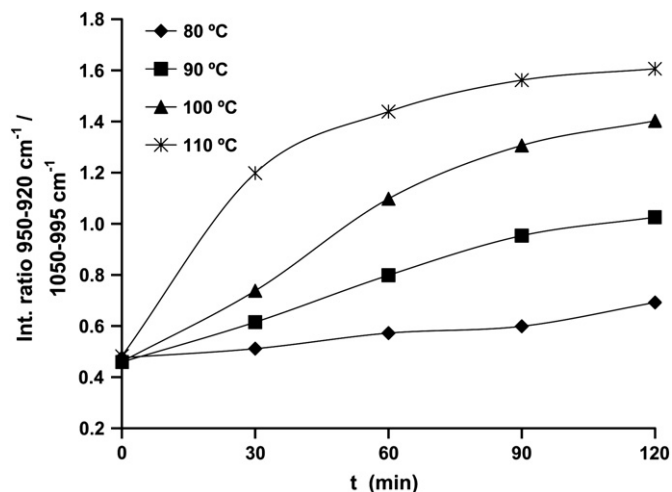


Fig. 13. Intensity ratios of Raman bands at  $950\text{--}920\text{ cm}^{-1}$  and  $1050\text{--}995\text{ cm}^{-1}$  as a function of curing time in the curing experiments of resin S3 (initial viscosity  $751\text{ mPa s}$ ) at  $80\text{ }^{\circ}\text{C}$ ,  $90\text{ }^{\circ}\text{C}$ ,  $100\text{ }^{\circ}\text{C}$ , and  $110\text{ }^{\circ}\text{C}$ .



soluble in dimethyl sulfoxide (DMSO). This indicated that the resin did not reach the gel point during the curing at 80 °C. At the end of the experiments, the intensity ratios of resins S2 and S3 were closely similar. Likewise, the intensity ratios of resins S1, S2, and S3 were closely similar after the curing at 110 °C. These results suggest that at high curing temperature the resins quickly obtained a high degree of crosslinking and a rigid network structure, which did not allow significant further structural changes at the end of the experiments.

### 3.5. Solid state CP/MAS $^{13}\text{C}$ NMR studies of cured phenol–formaldehyde resol resins

The structures of the cured phenol–formaldehyde resol resin samples from the 120-min curing experiments of resins S1, S2, and S3 at 80 °C, 90 °C, 100 °C, and 110 °C were studied by solid state CP/MAS  $^{13}\text{C}$  NMR spectroscopy, and the results were compared with the corresponding Raman measurements. The  $^{13}\text{C}$  NMR spectrum of resin S1 cured at 80 °C was measured in the liquid state because the sample was still soluble in DMSO- $d_6$ . The main focus of the  $^{13}\text{C}$  NMR studies was to determine the relative amounts of the methylene bridge and methylol group structures, which denote the extent of cure (degree of crosslinking) in the resins. The finely ground samples were spun at high magic angle spinning rates (12 kHz) to eliminate the disturbing effects of the spinning sidebands on the interpretation of the solid state spectra.

The NMR spectral areas of methylene bridges at 30–45 ppm and methylol groups at 58–65 ppm were integrated, and the ratios of these structures were used to quantify the degree of cure in the solid resin samples after the curing experiments at 80 °C, 90 °C, 100 °C, and 110 °C. Fig. 14 shows the ratios of methylene bridge structures to methylol groups in cured resin samples at different curing temperatures. The degree of cure as a function of curing temperature was similar in resins S2 and S3, which is consistent with the results of the Raman studies of the same resins. In resin S1, the increase of the crosslinking with temperature was nearly linear, and sharper than for resins S2 and S3. However, the curing of the resins at 110 °C resulted in similar methylene bridge to methylol group ratios, which was also in accordance with the Raman measurements. This indicated that the structural differences between resins S1, S2, and S3 at the start of the curing experiments were not significant for the end structure of the resins in the long-term curing (120 min) at high temperature.

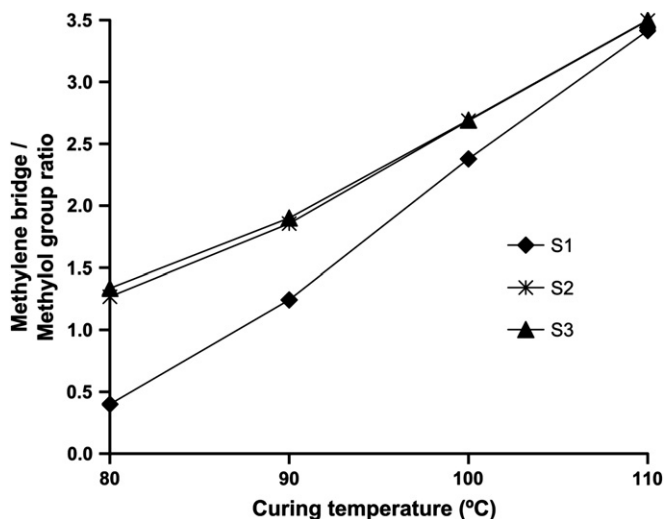


Fig. 14. Ratio of methylene bridge to methylol group structures in cured resins S1, S2, and S3 (80 °C, 90 °C, 100 °C, and 110 °C) determined by  $^{13}\text{C}$  NMR spectroscopy.

The relationship between the Raman measurements and the  $^{13}\text{C}$  NMR results for resins S1–S3 was studied by plotting the intensity ratios of the Raman band regions 950–920  $\text{cm}^{-1}$  and 1050–995  $\text{cm}^{-1}$  of each resin sample at the end of the curing experiments (120 min) as a function of the methylene bridge/methylol group ratios ( $^{13}\text{C}$  NMR) of the same samples (Fig. 15). The good ( $R^2 = 0.96$ ) and linear correlation of the intensity ratios of the Raman band regions 950–920  $\text{cm}^{-1}$  and 1050–995  $\text{cm}^{-1}$  with the  $^{13}\text{C}$  NMR results establishes Raman spectroscopy as a promising method for studying the extent of crosslinking in cured, solid-state resol resins.

### 3.6. Differential scanning calorimetric (DSC) studies of cured phenol–formaldehyde resol resins

The residual reactivities of the cured resin samples (S1, S2, and S3) were studied in post-curing experiments by DSC. As with the  $^{13}\text{C}$  NMR studies, the main purpose of the DSC measurements was to determine the extent of cure of the resins and compare the results with the Raman measurements. The reaction heat released during the DSC experiments gave comparable information to the Raman studies about the degree of crosslinking and state of the resins after the curing experiments at different temperatures. The reactivity values ( $\Delta H$ ) of the finely ground resin samples could not directly be compared with each other owing to the possible differences in the solids contents of the resin samples as a result of the curing experiments. The trends were nevertheless clear.

Fig. 16 shows the absolute values of the residual reactivities ( $\Delta H$ ) in the resins after the 120-min curing experiments at 80 °C, 90 °C, 100 °C, and 110 °C. As expected, the residual reactivities decreased as a function of curing temperature. This is consistent with the decrease in the amount of methylol groups and increase in the amount of methylene bridges seen in the Raman measurements during the curing of the resins and in the  $^{13}\text{C}$  NMR studies of the cured resins.

The Raman measurements suggested that the curing of resins S1–S3 advanced slowly at 80 °C. After 120 min, resin S1 had not reached the gel point and it was still soluble in DMSO. Thus a large amount of methylol groups were available for the condensation reactions (Fig. 14) in the DSC experiment, and residual reactivity was high ( $\sim 250$  J/g). Even though resins S2 and S3 were solid after the curing at 80 °C, the release of reaction heat was still substantial. Resins S1 and S2 also showed reactivity after curing at 90 °C, but the sensitivity of the DSC equipment was not sufficient to observe the released reaction heat from sample S3. The reactivities of resins

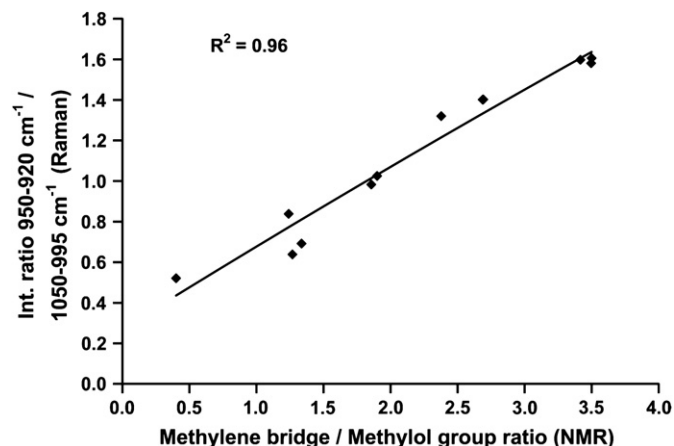


Fig. 15. Intensity ratios of the Raman band regions 950–920  $\text{cm}^{-1}$  and 1050–995  $\text{cm}^{-1}$  of resins S1, S2, and S3 at the end of the curing experiments (120 min) plotted as a function of the methylene bridge/methylol group ratio ( $^{13}\text{C}$  NMR) of the same resin samples.

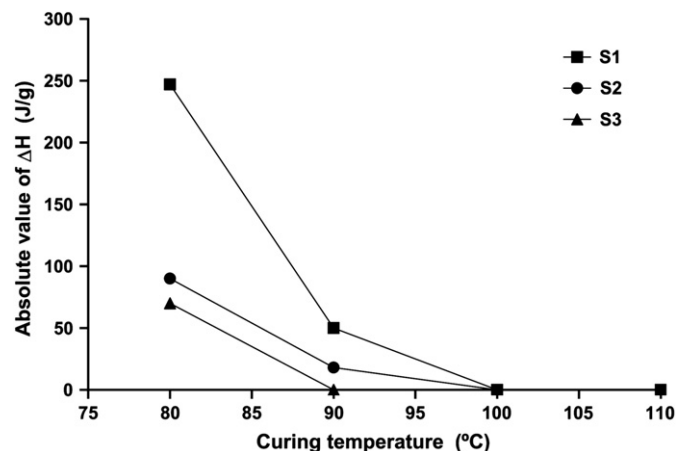


Fig. 16. DSC measurements of the residual reactivities ( $\Delta H$ ) of resins S1, S2, and S3 cured at 80 °C, 90 °C, 100 °C, and 110 °C for 120 min.

S2 and S3 were close to each other, however, in accordance with the similar structures of the resins observed in the Raman and NMR studies. The ratio of methylol groups to methylene bridges was low in resins S1–S3 cured at 100 °C and 110 °C (Fig. 14), and no residual reactivity was observed in the DSC measurements.

#### 4. Conclusions

The suitability of Raman spectroscopy for remote online monitoring of the synthesis and curing of phenol–formaldehyde resol resins was studied under different conditions. The Raman studies of model compounds gave information valuable for the assignment of the Raman bands observed in the spectra of the resol resins. The progress of both the synthesis stages and the curing of the resin was easily monitored by following the changes in intensity of the characteristic Raman bands and spectral regions as a function of time and temperature. The advancement of the methylation stage of the synthesis was seen as a decrease in the intensities of formalin bands at 1494  $\text{cm}^{-1}$ , 1324  $\text{cm}^{-1}$ , and 916–912  $\text{cm}^{-1}$ , and of phenol bands e.g. at 1030–995  $\text{cm}^{-1}$ , 818  $\text{cm}^{-1}$ , and 621  $\text{cm}^{-1}$ . The formation of methylol groups produced characteristic spectral changes at 1469  $\text{cm}^{-1}$  and 1046  $\text{cm}^{-1}$ . The progress of the condensation stage of the synthesis yielding methylene bridge structures between the phenolic units was observed as intensity changes of the Raman bands at 1438  $\text{cm}^{-1}$  and 1300–1296  $\text{cm}^{-1}$ . The advancement of the condensation was followed by observing the relative intensity changes of the spectral regions at 1050–995  $\text{cm}^{-1}$  and 950–920  $\text{cm}^{-1}$ . The intensity ratios of these regions at the end of the curing experiments, denoting the degree of crosslinking in the resins, corresponded well with the results of  $^{13}\text{C}$  NMR studies of the cured resins and investigations of residual reactivity by DSC.

In general, the results of the study indicate that Raman spectroscopy is a highly promising method for online process control of phenol–formaldehyde resol resin synthesis. The sensitivity of the method was adequate for the monitoring of the various synthesis stages. In particular, the Raman spectral changes indicating the consumptions of free formalin and free phenol and the formation of methylolphenols during the exothermic methylation stage of the resol resin synthesis could allow better process control and safety in the start stage of large-scale resol resin processes. The intensity

ratios of the Raman bands denoting the degree of condensation (crosslinking) could enable more precise stop points for the synthesis, and resin of more uniform quality. In addition, Raman spectroscopy provided an effective and fast method for structural study of the cured, solid state resins. Among others, this could be utilized in the study of fracture planes of adhesive joints and assist the development of resin composition and curing conditions in adhesive applications.

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