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Quantitative carbon-13 solid-state n.m.r. and *FT*–Raman spectroscopy in novolac resins

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A qualitative and quantitative study of the curing behaviour of a high-ortho novolac resin with paraformaldehyde under different conditions is reported. The extent of cure by means of the formaldehyde/phenol ratio, the degree of conversion, and the characterization of the final structure after curing are determined based on quantitative ^{13}C solid-state nuclear magnetic resonance with cross polarization and magic angle spinning. The T_{1H} relaxation time is measured as a probe to follow the evolution of cure. In conjunction Fourier transform–Raman spectroscopy is proposed as a qualitative tool to follow the degree of crosslinking in this high-ortho novolac. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: phenol–formaldehyde resins; crosslinking; characterization)

INTRODUCTION

Phenolic resins were the first commercial completely synthetic polymers since in 1907 their processing technique was developed by Baekeland[1]. They are thermosetting resins which have found wide industrial and commercial applications[2], and because of their excellent ablative properties and structural integrity, they are used as high-temperature polymers[1,3]. Today phenolic resins are still widely used, especially in thermal insulation materials, moulding compounds, foundry, wood products industry, coatings, and in composite materials. Low manufacturing costs, dimensional stability, age resistance and high tensile strength make them even more popular.

Under acidic conditions, reaction of an excess of phenol with formaldehyde leads to random novolacs. High-ortho novolacs are formed in the pH range 4–6 with bivalent metal acetates as catalysts. Alternatively, alkaline conditions and an excess of formaldehyde will lead to the generation of resoles. The main difference between novolac and resole resins is the presence of reactive methylol groups and occasionally dimethylene–ether linkages in resoles instead of the condensation products linked with methylene bridges as in the case of novolacs. Therefore novolac resins are thermally cured by addition of a methylene crosslinker, supplied as hexamethyltetraamine (HMTA) or paraformaldehyde, to insoluble and infusible products (*Figure 1*). Conversely resoles are transformed into three dimensional, crosslinked, insoluble and infusible polymers only by the application of heat.

The final properties of these materials depend on synthesis and operating conditions. Details of the curing process are responsible for many of the physical and mechanical characteristics. The cure time and temperature influence the resulting glass transition temperature (T_g) and the elastic modulus, being up to 7 GPa. Thus structural information and explicit knowledge relevant to the curing process is important and essential for understanding and improving the synthesis process and the use of phenolic resins.

In previous studies[1] the synthesis of phenolic prepolymers has been investigated under different sets of conditions (e.g. temperature, pH value, nature and amount of catalyst, formaldehyde/phenol-ratio (F/P),…) with differing techniques. A very good book on the chemistry of phenolic resins is available[1]. Infra-red (i.r.) and Fourier transform i.r. (*FT*i.r.)[4–8], extensive ^{1}H nuclear magnetic resonance (n.m.r.)[9–14] and ^{13}C n.m.r.[8,15–31] studies which have been carried out in the liquid state, resulted in qualitative and semi-quantitative descriptions of phenol–formaldehyde (PF) resin structures. An improved quantitative and fast liquid ^{13}C n.m.r. characterization method of novolac resins has been reported recently by our group[32].

The curing of PF resins, in general resoles and to a lesser degree novolacs, has already received a great deal of attention. Solid-state ^{13}C n.m.r. spectroscopy with cross polarization (CP)[33] and magic angle spinning (MAS)[34], is a very valuable technique to investigate curing processes[35]. This approach provides the opportunity to study these thermosetting resins under non-invasive conditions, without special sample preparation. Other conventional techniques are often inadequate in studying the curing chemistry since they require specific preparation conditions (e.g. solubility). Although i.r. and *FT*i.r. can be applied to solid polymers, it still has only limited success with phenolics confining it to qualitative work only. Most ^{13}C CP/MAS studies have reported the curing of P/F resins qualitatively[23,36–43]. They mainly confirmed the view for novolacs that crosslinking occurs with an increase in methylene bridges, while for the resoles the crosslinking happens at the expense of hydroxymethyl groups. Due to chain extension and branching it leads to a resin attaining a typically glassy structure. A semi-quantitative reliable procedure to follow the degree of cure of resoles from the ratio of methylene to aromatic carbons has been reported[44–46]. Although sorely needed for the structure property relationship, a quantitative determination

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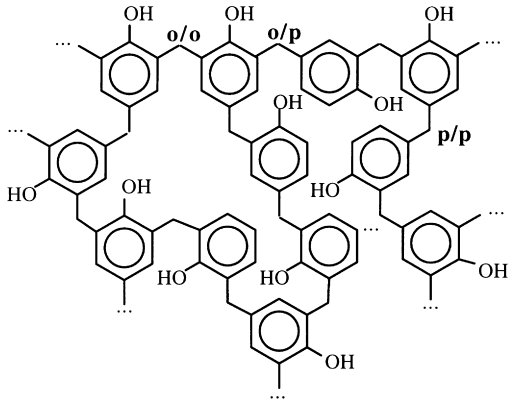

Figure 1 Structure of a novolac resin. o/o, o/p, p/p indicate the position of the methylene bridges

of the structure by n.m.r. or any other method has been difficult for various reasons.

This paper discusses the curing behaviour of novolac resins with paraformaldehyde under different conditions. A quantitative determination of the extent of cure, expressed by the F/P ratio, the degree of conversion, and the characterization of the final structure after curing is presented by carrying out quantitative ^{13}C CP/MAS solid-state n.m.r. measurements. The inversion recovery solids pulse sequence is used additionally to measure the T_{1H} relaxation time as a probe for the curing progresses. *FT*–Raman spectroscopy is used in conjunction towards a qualitative analysis of the effects on Raman signals depending on curing conditions, on the degree of cross-linking, and on the structure of the cured novolacs. Since only little information about Raman data is available in literature a somewhat more elaborated treatment is given.

EXPERIMENTAL SECTION

Samples

The reference high-ortho novolac used in the curing experiments was prepared by reaction of 1500 g of phenol (commercial grade) with 685 g of a 50% formaldehyde solution in the pH range 4–6 and in addition of bivalent metalacetate (ZnAc) catalyst. The reactor was a 5 l three-neck flask equipped with a stirrer, a cooling condenser, a thermometer, and a heating mantle. The temperature for the mixture was allowed to rise steadily to 100–102°C followed by reflux for several hours until the free formaldehyde content fell below 0.5%. After removing water under atmospheric pressure, the temperature was raised to 140°C for 90 min and the excess of phenol was distilled off under vacuum. When the viscosity reached a value between 1900 and 3000 cP and the desired softening point was obtained, the reaction was stopped. All the cured samples studied here were obtained by mixing the reference high-ortho novolac with 11 wt% of paraformaldehyde and by curing on heating at different temperatures and pressures for different times.

'Series 1' contained 10 samples, cured under atmospheric pressure at a temperature of 150°C for specific times between 0 and 180 min. Secondly, 'series 2' contained five samples, cured in a press at 150 bar and 150°C as a function of time between 0 and 20 min. Thirdly, 'series 3', consisting of seven samples, was cured at 150 bar and 180°C for times varying between 0 and 60 min. The cured samples were ground to fine powders and held at room temperature.

Phenol, diphenylmethane, bisphenol A, and paraformaldehyde used in the *FT*-Raman study were of commercial grade and used without further purification.

The six uncured random novolacs, with increasing degree of polymerization, also used in the *FT*–Raman study were prepared following the same procedure as for the high-ortho novolac. However, oxalic acid was used as catalyst instead of zinc acetate and the F/P ratios were increasing from 0.39/1 to 0.81/1[32].

Ft–Raman spectroscopy

The FT–Raman spectra are recorded on a Bruker IFS 66 *FT*i.r. spectrometer, equipped with a Raman FRA 106 module. The wavelength of the NIR ND:YAG laser is 1064 nm. All the *FT*–Raman spectra are recorded with a resolution of 4 cm^{-1} and a laser power of 100 mW.

N.m.r. measurements

The experimental procedure for a full quantitative characterization of the reference high-ortho novolac by high resolution solution ^{13}C n.m.r. has been reported previously[32].

All solid-state ^{13}C CP/MAS n.m.r. spectra of the cured, insoluble resins, were recorded at room temperature on a Varian XL-200 apparatus at 50.3 MHz. ^{13}C CP measurements are performed using mixing times ranging from 100 to 6000 μs and high power (44 kHz) ^{1}H decoupling. To permit the acquisition of quantitative spectra a delay time (6–25 s) of five times the longest relaxation time, T_{1H}, was used. The number of transients per spectrum was set to 2000, the acquisition time to 0.034 s, and the spectral width to 18 500 Hz. The filterband was set equal to the spectral width in order to obtain more quantitativeness. To minimize the effect of long term drift, the n.m.r. relaxation experiments were interleaved block averaged with 64 acquisitions per block. MAS was performed at 7 kHz using Si_3N_4 rotors. The magic angle was set with KBr, while the Hartman–Hahn conditions was adjusted using the aromatic signal of hexamethylbenzene. The chemical shift of this signal was also employed to calibrate the shift of the aromatic signal, being 132.1 ppm from tetramethylsilane, and the $\pi/2$ pulse width (8.4 μs).

T_{1H} relaxation times were measured for each sample by means of the inversion recovery method.

RESULTS AND DISCUSSION

CP/MAS quantitative reliable measurements

^{13}C solid-state n.m.r.. In order to obtain reliable quantitative results to determine the degree of curing the following procedure was used. To avoid errors coming from spinning sidebands (SSB) a high spinning speed of 7 kHz is chosen. This is required to conveniently spin out the chemical shift anisotropy and to move the residual SSB away from the desired isotropic carbon peaks of the novolac resins. In the spectrum of the reference novolac (*Figure 2b*) all peaks become resolved from the SSB. The SSB which are situated at the edges of the spectra, although rather small, were taken into account in the integration of the aromatic peaks. The use of Si_3N_4 rotors instead of Delrin spinners avoids interference from spinner signals. All ^{13}C CP/MAS spectra were measured with the same line-broadening setting of 50 Hz and the same number of transients. Peak intensities were integrated after optimized phasing and baseline correction. Experiments in duplo show that errors are smaller than 5%.

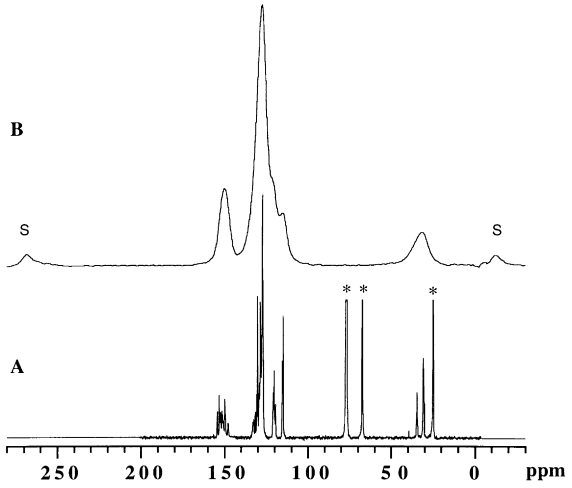

Figure 2 ^{13}C n.m.r. spectra of the reference high-ortho novolac resin: (A) liquid (solvent = THF-$CDCl_3$); (B) solid (contact time = 2 ms). The small peaks marked s denote spinning sidebands, those marked * are solvent peaks

Since in the ^{13}C CP/MAS experiments magnetization is transferred from protons to carbons, one has to respect a preparation delay of five times T_{1H} to obtain quantitative measurements. Therefore a T_{1H} relaxation study was undertaken for each sample by means of the inversion recovery method. For all samples a single T_{1H}, averaged by spin diffusion, was obtained. Short T_{2H} spin–spin relaxation time values (obtained by using the CP method), of 10–20 μs for the aromatic and aliphatic carbons, which remain approximately constant for all samples indicate also for a rigid lattice. For each measurement a preparation delay of five times T_{1H} was respected.

In the conventional CP/MAS process under Hartman–Hahn conditions the ^{1}H and the ^{13}C spin systems are spin locked in their rotating frame and are thermally in contact with each other, allowing transfer of magnetization. The simplified evolution of carbon magnetization as a function of the contact time follows the relation:

$$M = M_0[1 - \exp(-T_{CT}/T_{CH})]\exp(-T_{CT}/T_{1\rho H}) \quad (1)$$

if $T_{CH} \ll T_{1\rho H}$ and $T_{1\rho C}$. T_{CH} is the cross polarization time constant, $T_{1\rho H}$ and $T_{1\rho C}$ are the proton and carbon relaxation time constant in the rotating frame, respectively[47]. During the contact time T_{CT}, two opposite processes occur simultaneously: a build up of ^{13}C magnetization, characterized by the time constant T_{CH} and a decrease of proton magnetization in spin lock, characterized by the time constant $T_{1\rho H}$. Since protons are the basis of carbon magnetization, both T_{CH} and $T_{1\rho H}$ are dependent on the characteristic proton environment (carbon multiplicity, molecular mobility and ^{13}C–^{1}H distance)[48], making them different for most of the carbon resonances. Quantitative measurements using a single contact time are thus seldom possible. Therefore a series of spectra was taken for each sample as a function of the T_{CT} between 0.1 and 6.0 ms (a contact time study). For accurate and precise quantitative measurements, the tail of the variable contact time curve was fit to a single decaying exponential in the region where $T_{CT} > 5 \times T_{CH}$. By extrapolating this monoexponential to $T_{CT} = 0$ (monologarithmic scale) the quantitative M_0 value, proportional to the number of carbons, was obtained. The F/P ratio (r) of the cured resins, which is a measure for the degree of cure from the ratio of methylene to aromatic carbons, can now be calculated by equation (2):

$$r = M_{0Alif}/(1/6M_{0Arom}) \quad (2)$$

where M_{0Alif} and M_{0Arom} are respectively the aliphatic and total aromatic extrapolated intensities. The time constant $T_{1\rho H}$ of the single decaying exponential was also measured. Only if the $T_{1\rho H}$ values of all carbon resonances are equal, a single measurement at $T_{CT} > 5 \times T_{CH}$ yields quantitative results. For cured novolac resins, a small difference noted for $T_{1\rho H}$ between the aromatic ($\pm$7 ms) and the aliphatic signals ($\pm$6 ms), made it however inaccurate to calculate the F/P ratio at a single contact time. This explains once more why measurements at a single T_{CT} value, as at the optimum intensity (strongly T_{CH} dependent), are seldom quantitative. Further investigation on the remarkable behaviour of the relaxation parameter $T_{1\rho H}$ in cured phenolic resins has been done and will extensively be discussed and explained in a separate publication.

Characterization of the original uncured high-ortho novolac resin

The spectra obtained for the uncured reference sample are shown in *Figure 2*. *Figure 2A* shows the liquid ^{13}C n.m.r. spectrum, *Figure 2B* the normal cross polarization spectrum at a rotor spinning rate of 7 kHz. A substantial increase in linewidth is observed. Chemical shift assignments of the peaks in the ^{13}C CP/MAS spectra were based on comparison with the solution state ^{13}C n.m.r. data[32]. The aromatic region appears as two broad resonances, centred at 150 and 128 ppm. The former is due to the resonance of the hydroxyl bearing aromatic carbons, while the latter is composed of a large variety of components (ortho, para and meta aromatic carbons). The aliphatic carbon peak, due to methylene bridges, $-CH_2-$, is centred at 33 ppm. A more detailed assignment of the chemical shift of phenol formaldehyde resins is given in *Table 1*.

The structure of the high-ortho novolac used in this study has been fully characterized with the method described in an earlier report by liquid ^{13}C n.m.r.[32]. Some of the results of that characterization are presented in *Table 2*.

Characterization of the cured novolac resin

Figure 3 shows the ^{13}C CP/MAS spectra, normalized at the intensity of the aromatic peak at 150 ppm, of the three series of samples prepared from the same high ortho novolac and cured for varying times, at different temperature and pressure. For series 1 (*Figure 3A*) disappearance of paraformaldehyde is noticed at $\pm$ 90 ppm. This is seen to be complete after about 25 min of cure. There is only a little increase of the peak intensity at 33 ppm, due to the increase of aliphatic methylene carbons when crosslinking occurs. Some line-broadening occurs as curing continues. In

Table 1 ^{13}C n.m.r. liquid state assignments of Novolacs[32]

chemical shift region (ppm)	Assignment[a]
140–160	Hydroxyl-substituted phenolic carbons
131–135	Substituted para carbons
125–131	Meta carbons and substituted ortho carbons
118–122	Unsubstituted para carbons
113–117	Unsubstituted ortho carbons
40	Para–para methylene bridges (p/p)
35	Ortho–para methylene bridges (o/p)
30	Ortho–ortho methylene bridges (o/o)

[a]Ortho, meta, and para assignments are relative to the hydroxyl-substituted carbon

Table 2 Liquid ^{13}C n.m.r.-based characterization of the high-ortho novolac[a]

Free phenol extent (%)	r	n	$\overline{M_n}$	oo	op	pp	O_u	P_u
0.17	0.76	4.17	430	65.4	32.3	2.30	0.72	0.76

[a] r is the F/P ratio; n is the degree of polymerization; $\overline{M_n}$ is the number-average molecular weight; oo, op, and pp present the isomeric distribution of the different methylene group orientations; O_u and P_u are the numbers of unreacted ortho and para positions per phenolic ring as defined in equation (5). All these parameters are obtained from analysing the liquid ^{13}C n.m.r. spectrum in *Figure 2a*. This has been completely described in Ref. [32]

Table 3 Formaldehyde/phenol ratio of the cured high-ortho resins[a]

Series 1		Series 2		Series 3	
Cure-time (min)	r	Cure-time (min)	r	Cure-time (min)	r
0	0.76	0	0.76	0	0.76
5	0.77	5	0.83	2	0.80
10	0.81	10	0.87	6	0.92
15	0.84	15	0.89	8	0.95
20	0.87	20	0.95	10	0.99
25	0.88			12	1.02
40	0.91			60	1.07
50	0.92				
90	0.92				
180	0.93				

[a] r is the F/P ratio as defined in equation (2)

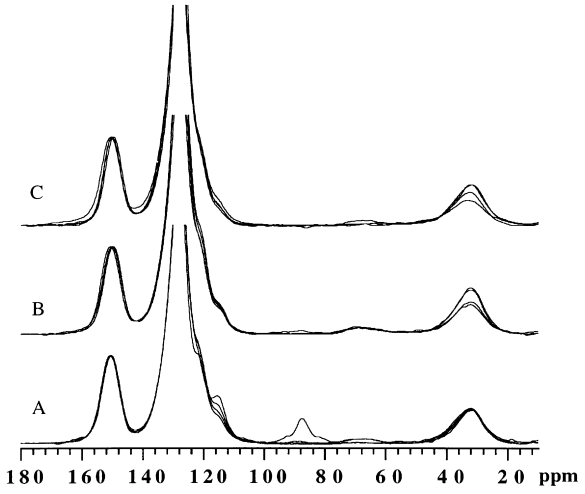

Figure 3 Effect of cure-time on the solid-state ^{13}C CP/MAS spectra of the high-ortho novolac (T_{CT} = 2 ms): (A) samples of series 1, cured under atmospheric pressure at 150°C for 5, 15, 25, and 180 min; (B) samples of series 2, cured in a press at 150 bar at 150°C for 5, 10, 15, and 20 min; (C) samples of series 3, cured at 150 bar and 180°C for 2, 6, 10, and 60 min

Figure 3B and *C* there is a more obvious increase of the methylene region as crosslinking occurs and paraformaldehyde converts to methylene bridges. The considerable structural heterogeneity including an increased number of frozen conformations may cause some line-broadening because of the chemical shift dispersion. The high field shoulder of the peak at 128 ppm, having a chemical shift of 115–120 ppm, due to the resonances of unsubstituted para and ortho aromatic carbons, decreases significantly as curing increases. Close inspection of the spectra reveals that a new region of intensity appears, at roughly 60–70 ppm, upon curing which decreases afterwards. This is due to the formation of hydroxymethyl groups and dimethylene–ether bridges in the early stage of condensation, which converts into methylene bridges when curing proceeds. The peak at 33 ppm is composed of three overlapping resonances, ortho–ortho and ortho–para methylene bridges which are dominant in high-ortho novolacs, and to a lesser degree para–para methylene bridges.

By analysing the contact time study of each sample, linear least squares fitting of the integrated aliphatic and total aromatic intensities for $T_{CT} \geq 2$ ms ($\geq 5 \times T_{CH}$) and extrapolation to $T_{CT} = 0$ allowed to calculate the F/P ratio (r) with equation (2) (as mentioned before). The results for the three series of samples are shown in *Table 3*.

Calculation of the degree of conversion. After determination of the formaldehyde/phenol ratio the degree of conversion (R, in %) can be calculated, based on the value of r and the F/P_{max}. The latter is the maximum F/P ratio that could be reached by curing with 11 wt% of paraformaldehyde.

It is possible to calculate the amount of paraformaldehyde needed for 100 g of novolac prepolymer to obtain a theoretical maximum attainable F/P ratio of 1.5, based on the information from the characterization of this resin, done by liquid ^{13}C n.m.r. (*Table 2*). This value is reached when all ortho and para positions of the phenolic rings of the resin are substituted by methylene bridges. The functionality of phenol is 3.0.

Firstly the number of phenol rings (in moles) per 100 g resin, p, is calculated. For this purpose the following equation has been used:

$$p = 100/M_m \tag{3}$$

where M_m is the mean molecular weight of one monomer unit as it is built in the resin. The latter can be obtained from the molecular weight of the novolac resin, because it consists only of phenol rings and methylene bridges, via equation (4):

$$M_m = \overline{M_n}/n \tag{4}$$

where $\overline{M_n}$ and n are the number-average molecular weight and the degree of polymerization, respectively[32]. The number of methylene bridges needed to reach the maximum F/P ratio ($r = 1.5$), is equal to 1.5 p. A number of valuable positions on the phenol rings, equal to the F/P ratio (0.76), is already substituted by methylene bridges. The total number of substituted ortho and para positions can be calculated, as reported in an earlier report[32]. Respectively, the relative amount of free unsubstituted positions (U, in %) can be derived with the next equation:

$$U = (O_u + P_u)/3 \tag{5}$$

where O_u and P_u are the contents of unreacted ortho and para positions per phenolic unit, respectively (*Table 2*). To achieve the maximum crosslinking, there must be curing agent added which supplies methylene bridges in an amount equal to $U \cdot 1.5\,p$ (in moles). The quantity of paraformaldehyde for maximum reaction extent, calculated here, amounts to 0.72 mol or 21.60 g for 100 g of resin. Industrial applications usually use only a mixture of 5–10%. Here a

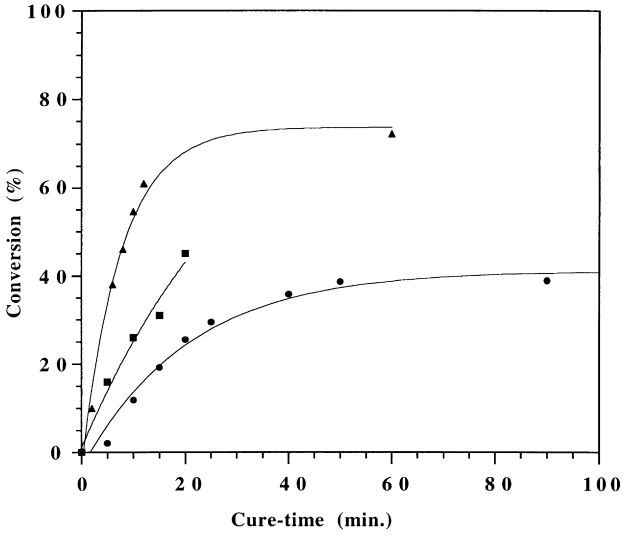

Figure 4 Extent of reaction as a function of curing time for the high-ortho novolac: ●, series 1 (the conversion value of the sample cured for 180 min is left out here); ■, series 2; ▲, series 3

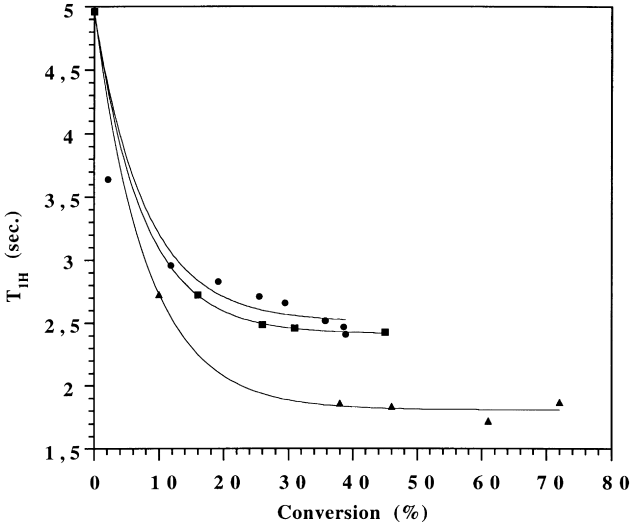

Figure 5 Spin-lattice relaxation time (T_{1H}) as a function of the extent of reaction: ●, series 1; ■, series 2; ▲, series 3

mixture of 12.43 g paraformaldehyde (11%) and 100 g of novolac resin was mixed and heated. So it is easy to calculate which F/P ratio can be reached in this case as follows:

$$12.43/21.60(1.5-0.76)+0.76=1.18 \quad (6)$$

where 0.76 is the F/P ratio of the original high-ortho novolac prepolymer, as indicated in the text (*Table 2*). Thus the maximum F/P ratio theoretically reachable is 1.18. The degree of conversion (%) for all the cured samples, as reported here, is calculated using the following equation:

$$R=100(r-0.76)/(1.18-0.76) \quad (7)$$

where $r = 1.18$ is defined as 100% conversion. The values for R determined in this way are shown in *Figure 4*. It shows the degree of conversion, R (by means of r), for the three series of samples isothermally cured *versus* the cure time. All data presented in *Table 3* and *Figure 4* indicate that the degree of advancement of the three series of samples is different due to their varying conditions of pressure and temperature during the curing. The most significant changes were observed to occur at the initial stages of curing. The degree of conversion increases with increasing cure-time, cure-temperature or cure-pressure. It appears that for each series there exists a cure limit where the degree of conversion remains approximately constant. Reaction advancement did not become total, even not at 180°C. This cure limit is elevated towards higher values of R for the series of samples cured at 180°C and 150 bar. The lowest limit value of R belongs to the series 1, cured at 150°C under atmospheric pressure. The curing reaction retarded by vitrification. It appears that the process is not only determined by the energetics of the chemical reactions involved, but also by the degree of molecular mobility in the network at a particular temperature and pressure. This is a common phenomenon for thermosettings or highly crosslinked polymers[49,50]. The crosslinking of phenolics during cure is accompanied by increases in T_g until the T_g becomes comparable to the reaction temperature. Then the resin vitrifies, which is the attendant transition of a liquid state or rubbery state to a glassy state. Further reaction is now very slow, but it should be stressed that the reaction does not stop, it continues at a lower rate[49–52].

Proton spin-lattice relaxation time (T_{1H}) measurements. As mentioned before, a T_{1H} relaxation study was undertaken for each sample by means of the solids CP/MAS inversion recovery method. For each sample a single T_{1H} for all signals was obtained, pointing to efficient spindiffusion. These T_{1H} values are presented as a function of conversion in *Figure 5*. For each series a decrease in the proton spin-lattice relaxation time corresponds with an increase of conversion up to a limit where T_{1H} remains approximately constant. Therefore the T_{1H} relaxation time can be measured as a probe to follow the curing evolution. It should be indicated that, concerning the molecular dynamics, the correlation times τ of these cured PF resins are still situated at the left side of the T_{1H} minimum in the $\log T_{1H}/\log\tau$ curve[53]. The T_{1H}-values increased as a function of measurement temperature. This probably means that the mobile end-groups are the dominant relaxation pathway for T_{1H}.

FT–Raman spectroscopy

Due to the high number of slightly different structures in the PF resins, i.r. absorption bands are often very broad and overlapping. Therefore, *FT*i.r. spectroscopy has been shown to have only limited capabilities to achieve the desired level of structural details. Raman spectroscopy, based on polarization changes during the vibrational motions, can be explored more easily for the qualitatively characterization of PF resins. Unfortunately, there is no or only little information in the literature concerning band assignments and interpretations of the changes in the Raman spectra of PF resins during cure. The band assignments are based on a combination of literature data[54] and on a short study of the Raman spectra of relevant model compounds.

Assignments of Raman bands in the spectra of some model compounds

Figure 6 presents the *FT*–Raman spectra of the model compounds studied and of the original reference high-ortho novolac. Two spectral zones can be distinguished.

Firstly the zone between 4000–2500 cm^{-1}, having as major advantage compared to *FT*i.r. that there is no interference due to hydroxyl stretching, which are not Raman active. For phenol (*Figure 6*) a strong single band at

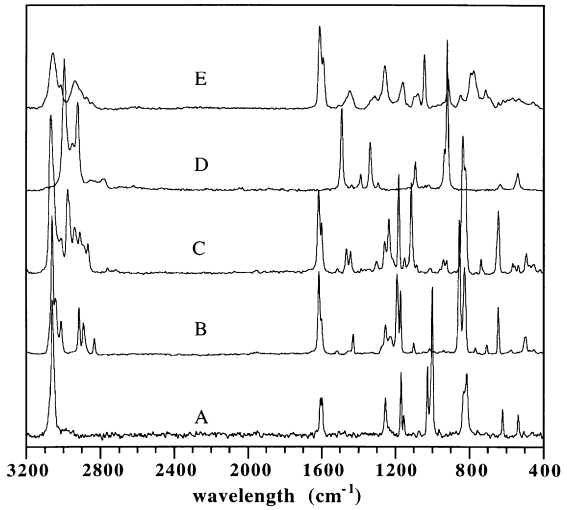

Figure 6 *FT*–Raman spectra of model compounds in the region 3200–400 cm^{-1}: (a) phenol; (b) diphenylmethane; (c) bisphenol A; (d) paraformaldehyde; (e) reference high-ortho novolac

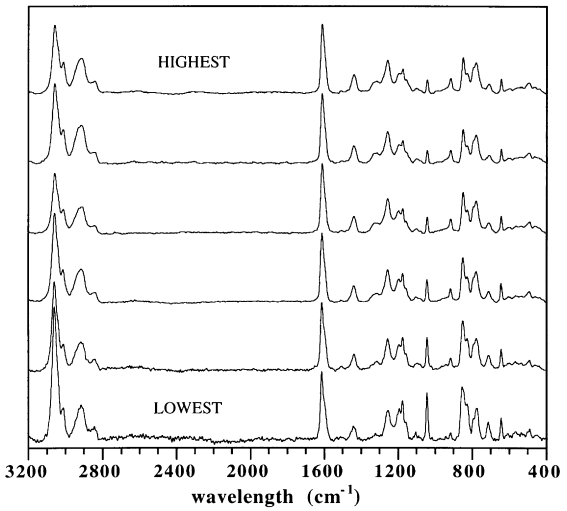

Figure 7 *FT*–Raman spectra of a series of uncured random novolacs having an increasing degree of polymerization from bottom to top

3060 cm^{-1} is observed which corresponds to the C—H stretching of the phenolic ring. In the spectrum of para–para diphenylmethane (DPM) and of bisphenol A (BPA) new aliphatic bands appear situated around at 2817–2970 cm^{-1} which are associated to the C—H stretching of methylene (—CH_2—) bridges between the two phenolic rings. In the case of BPA there is more line broadening and overlap in these bands due to the extra C—H stretching of methyl (—CH_3) groups in this region. The Raman spectrum of paraformaldehyde shows a broad band between 3025 and 2900 cm^{-1}, corresponding to the C—H stretching of the —CH_2— polyoxymethylenes. In the spectra of random (*Figure 7*) and high-ortho (*Figures 6* and *8*) novolacs always two strong bands appear at 3060 and 2940 cm^{-1} due to the C—H stretching of the phenyl ring and methylene bridges, respectively.

In the second region between 1800–400 cm^{-1} a signal at 1610 cm^{-1} is observed in all spectra, except for the paraformaldehyde, characteristic for the elongation of the aromatic ethylene bond (C=C). In the region between 1400 and 1500 cm^{-1}, assigned to —CH_2—[54], two bands can be distinguished. The band at 1485–1500 cm^{-1}, as in the spectra of paraformaldehyde, is typical for compounds containing the —O—CH_2—O— moiety. For compounds containing —CH_2— units, i.e. novolacs and resoles, a band at 1430–1470 cm^{-1} is observed. In the region of 1400–1050 cm^{-1} there is severe overlap and a definite assignment is not possible at this moment because of the complexity of this region. The signal at 1044 cm^{-1}, although present in the spectrum of phenol but absent in the spectrum of DPM and BPA, is assigned among others to substitution in the ortho position, according to *FT*i.r. literature data and by the fact that this signal is more intense for high-ortho novolacs then for random novolacs. In addition the 950–600 cm^{-1} region (characteristic of deformations of the C—H bond out of plane of the phenyl ring) enabled the different types of substitution to be characterized. The Raman wavelengths at 814 and 831 cm^{-1} are characteristic for the monosubstituted benzene ring, i.e. phenol. Similarly to the *FT*i.r. spectra, the regions of 753–794 cm^{-1}, 820–855 cm^{-1}, and 912–917 cm^{-1} can be assigned to o-substitution, p- and (o,p)-substitution, and (o,o′,p)-trisubstitution of a phenolic ring, respectively.

Study of novolacs after curing with paraformaldehyde

In *Figure 7 FT*–Raman spectra are shown of a series of uncured random novolacs with an increasing degree of polymerization and which have been fully characterized in an earlier report by liquid ^{13}C n.m.r.[32], *Figure 8* shows the FT–Raman spectra of series 3, high-ortho novolac samples cured at a temperature of 180°C and a pressure of 150 bar. All spectra in *Figures 7* and *8* are normalized on the peak at 1610 cm^{-1}, which can be used as internal reference signal since the band intensity is approximately constant in all spectra. It is obvious that some changes occur in the spectra during condensation reactions or curing.

At first view it seems unlikely that the region between 4000 and 2500 cm^{-1} will be useful for identification of the various types of methylenes, because of the strong overlap of bands expected for PF resins. However, since novolacs contain only methylene bridges between the phenolic rings this enables to calculate values which can be correlated to the real F/P ratio by simply calculating the ratio of the two band areas at 2940 and 3060 cm^{-1}. This has been done in *Figure 9* for DPM and the reference high-ortho novolac of

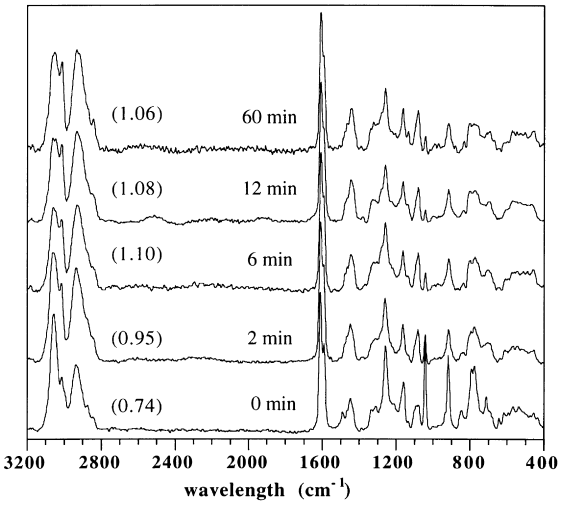

Figure 8 *FT*–Raman spectra of high-ortho samples of series 3 cured for varying times as indicated, the values between parenthesis indicate for the F/P ratio

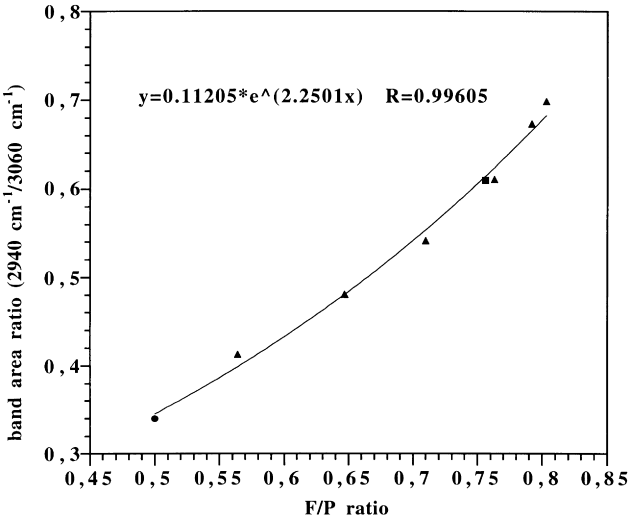

Figure 9 Correlation between the band area ratio (2940 cm^{-1}/3060 cm^{-1}) and the real F/P ratio, as determined by liquid ^{13}C n.m.r.: ●, DPM; ■, the reference high-ortho novolac; ▲, the six random novolacs

Table 4 Liquid ^{13}C n.m.r.-based data of DPM and the six random novolacs[a]

r	$\overline{M_n}$
0.50	200
0.56	231
0.65	288
0.71	353
0.76	436
0.79	497
0.80	527

[a] r is the F/P ratio; $\overline{M_n}$ is the number-average molecular weight. The first row is corresponding to DPM, the following rows present data for the six random novolacs with increasing degree of polymerization

Figure 6, and for the six random novolacs of *Figure 7*. Here the band area ratio is plotted *versus* the real F/P ratio, calculated more accurately by analysing liquid ^{13}C n.m.r. spectra and confirmed by theoretical calculations as reported in an earlier publication[32]. Some data obtained from the liquid ^{13}C n.m.r. study, characterizing the reference high-ortho novolac, DPM, and the six random novolac resins, are presented in *Tables 2* and *4*. *Figure 9* shows the empirical relation, which enables the use of FT–Raman data to make a semi-quantitative estimation of the F/P ratio and thus the number averaged molecular weight of novolac resins.

Remarkable in *Figure 8* is an obvious deviation from the expected change in the relative ratio of the two bands at 3060 and 2940 cm^{-1} for the cured high-ortho novolacs. When the curing time increases the intensity of the C—H stretching band of methylenes increases. Thus it should be possible by fitting the band area ratio (2940/3060 cm^{-1}) into *Figure 9* to calculate the corresponding F/P ratio for each cured sample. Unfortunately, this seems not to be totally true since the F/P ratios showed to be too high for the samples which were cured for short times (as indicated in *Figure 8* between parentheses). This could be explained as follows. For the uncured mixture of the native high-ortho novolac with paraformaldehyde (*Figure 8*, '0 min') the F/P ratio obtained from *Figure 9* (^{13}C liquid n.m.r.) is in good agreement with that from ^{13}C CP/MAS experiments. Notice that in this Raman spectrum there is interference at 920 and 1490 cm^{-1} due to the paraformaldehyde mixed as curing agent in the sample. However, in the spectra of the samples cured for 2, 6, and 12 min these interferences are not notable anymore but the signal at 2940 cm increases more than expected. The paraformaldehyde quickly decomposes under these circumstances into smaller units and forms the source for crosslinking. It seems as if the response factors of the Raman signals change during cure, resulting in a fast decrease of the two signals at 920 and 1490 cm^{-1} and a fast increase of the signal at 2940 cm^{-1}. This causes inaccuracies when calculating the F/P ratios or the degree of conversion according to the ^{13}C CP/MAS measurements. After a cure time of 60 min, however, there are no more 'paraformaldehyde' units left. They have reacted with free ortho and para positions on the phenolic rings or have partially evaporated. So the relative band area ratio of the two peaks at 2940 and 3060 cm^{-1} should correspond better again to the degree of curing. This results for the sample cured for 60 min in a F/P ratio of 1.06, which is in good agreement with the reported value from the ^{13}C CP/MAS experiments (*Table 3*).

CONCLUSIONS

The curing of novolacs can now be studied quantitatively by using solid-state ^{13}C CP/MAS n.m.r. This technique gives a proper view on the curing behaviour of these novolac resins and shows to what point the curing conditions are important in the study of the crosslinked networks.

The spin–lattice relaxation time T_{1H} seems to be a sensitive parameter in order to follow the curing behaviour of novolac resins. The F/P ratio which characterizes the chemical structure of the resins after final curing and the degree of conversion can be determined quantitatively from solid-state ^{13}C CP/MAS n.m.r. contact time studies, this by carefully controlling the experimental parameters and by optimizing the instrumental settings. The maximum degree of cure heavily depends on the curing conditions, i.e. cure–time, temperature, and pressure. Novolacs cured with paraformaldehyde do not reach complete conversion due to vitrification.

The Raman results are in agreement with the ^{13}C CP/MAS data and confirm that curing results in an increase of methylene bridges. *FT*–Raman spectroscopy gives additional information in combination with other spectroscopic techniques, i.e. *FT*i.r. and ^{13}C CP/MAS spectroscopy in the study of curing processes. It is also possible to extract qualitative curing data from *FT*–Raman spectra.

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