Quantitation of Microstructure of Novolac Resins: Development of Improved One- and Two-Dimensional NMR Methodologies

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ABSTRACT: The elucidation of the exact microstructure of polymers is always a challenging task. The range of molecular weights and uncontrolled polymerization leading to branching necessitates the development of better analytical methodologies. An improved methodology is presented for quantitatively estimating the microstructure of novolac resins and the percent incorporation of different monomers therein. An analysis is used that is based on the fully relaxed ^{1}H-NMR spectrum in combination with the results of two-dimensional heteronuclear single quantum correlation, double quantum filtered correlation spectroscopy, and total correlation spectroscopy. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2096–2102, 2004

Key words: microstructure; novolac; resins; NMR

INTRODUCTION

Novolac resins (acid catalyzed phenol–formaldehyde polymers) are useful in the preparation of photoresists for microlithography. Their other potential uses are coating materials, adhesives, molding compounds, abrasive materials, friction materials, foundry resins, laminates, air and oil filters, battery separators, wood and fiber bonding, carbonless copy paper, and other applications after curing.[1] Systematic studies on diazonaphthoquinone–novolac based photoresists suggested that the matrix polymer (i.e., the novolac resin) holds the key for high performance of photoresists.[2] In the currently preferred cresol–formaldehyde analogies, copolymers of *m*-cresol and *p*-cresol with an optimum percentage of 62% *m*-cresol and 38% *p*-cresol are used, which have tailor-madeìhigh orthoî alternating and semialternating structures with optimum polydispersity.[3–6] Accordingly, high ortho novolacs (Fig. 1) with more ìfreeî para positions show good lithographic performance. The proper design and tailoring of novolac resins is therefore necessary for achieving high performance photoresists.

Methodologies of quantification from NMR data

Different NMR techniques have been suggested for determining the nature and degree of substitution patterns on different ring carbons in novolac resins. Based on the IN enhancement of polarization transfer (INEPT) ^{13}C-NMR technique, a substitution index (S_n) was proposed[3] to calculate the free para positions in the resin, which in turn measures the extent of linearity of the polymers. In the case of *p*-cresol, because only two ortho positions (2 and 6, i.e., C-2 and C-4) with respect to the phenolic-OH group are free for polymerization with formaldehyde, only high ortho structures will be produced. However, in the *m*-cresol, three positions (two ortho positions, C-2 and C-6, and one para position, C-4) are free for polymerization; and if the para position also takes part in the polymerization along with the two ortho positions, then random microstructures predominate. The free para position in the *m*-cresol incorporated in the resin thus gives a quantitative measure of the degree of high ortho nature of the resin. The C-5 of *m*-cresol is always unsubstituted, because this position does not take part in the polymerization process. A comparison of the intensity of the C-4 NMR signal to that of C-5 may thus be used as an index of the linearity of the resin.

The substitution index for C-4 (S_4) may then be calculated as

$$S_4 = A_4 \times 100 / A_5 \times f_4$$

where A_4 and A_5 are the respective intensities of the C-4 and C-5 of *m*-cresol in the resin as determined from the INEPT ^{13}C spectrum and f_4 is the intensity correlation factor, which is generally considered to be 1.
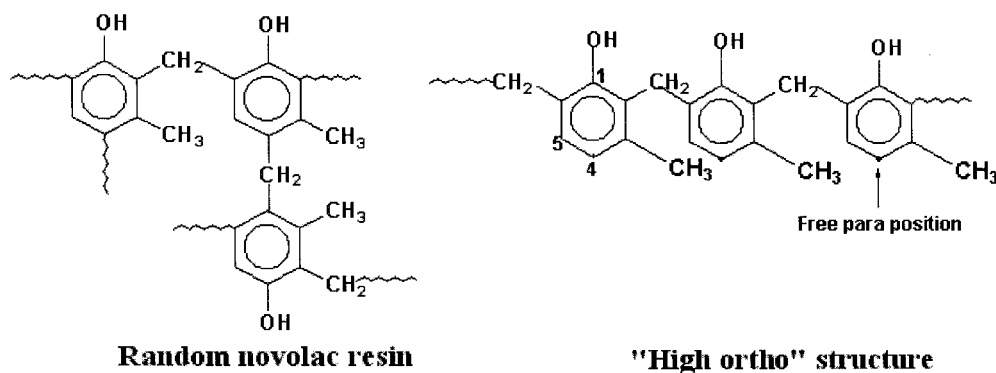
$$f_4 = a_4 / a_5$$

Figure 1 A random and high ortho novolac with *m*-cresol and formaldehyde.

where a_4 and a_5 refer to the respective C-4 and C-5 intensities of the monomeric *m*-cresol precursors.

The substitution index is later replaced by the unsubstitution index (U_n), the difference being that the latter is calculated using the more sensitive distortionless enhancement of polarization transfer (DEPT) pulse sequence rather than from INEPT.[7] The intensities in the ^{13}C-NMR spectrum of the INEPT pulse sequence are not reliable for quantitative estimation because of the nuclear Overhauser effect. The relaxation times of all the different carbon atoms in the aromatic rings were first calculated and the delay time (t_1) was set accordingly, so that the spectrum is fully relaxed. The U_4 may then be calculated directly by comparing the peak area of C-4 with that of C-5 of *m*-cresol incorporated in the polymer.
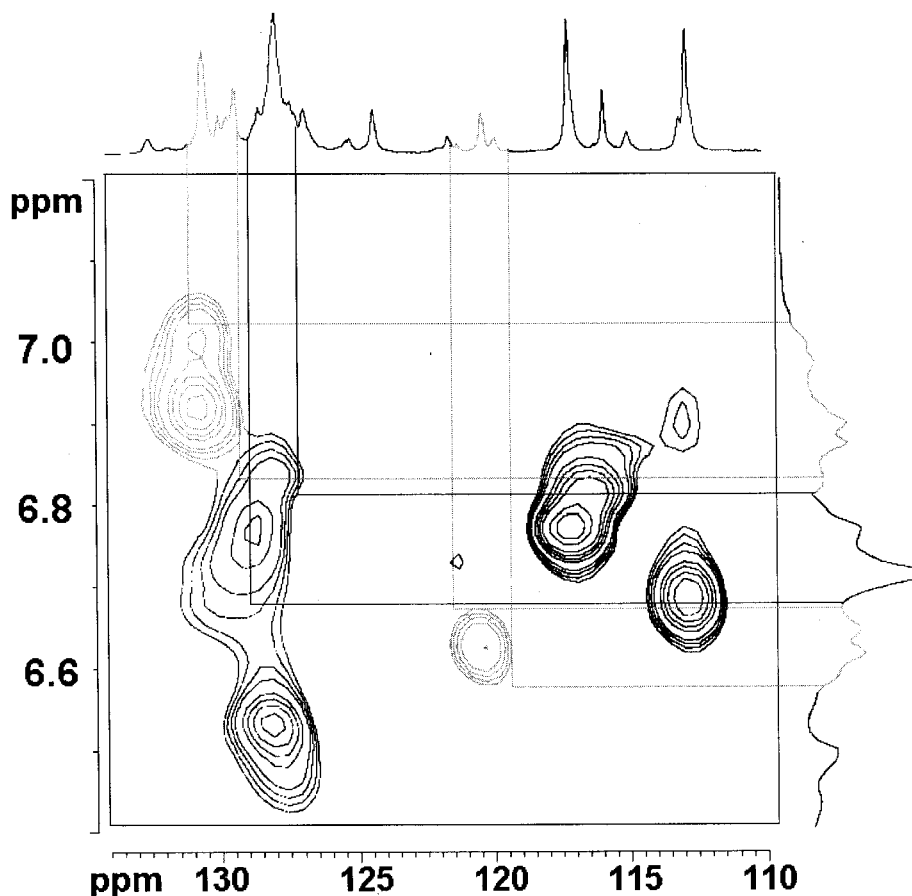

Figure 2 The ^{13}C-NMR spectrum of a novolac resin is plotted on the *x* axis and the ^{1}H-NMR spectrum is shown on the *y* axis. (gray traces) The C-5 and C-4 and hydrogens attached to the C-5 and C-4, respectively, of *m*-cresol incorporated in the polymer. (black trace) The trace around 127–129 ppm for identical C-5 and C-3 and hydrogens attached to these carbon atoms of *p*-cresol incorporated in the resin.
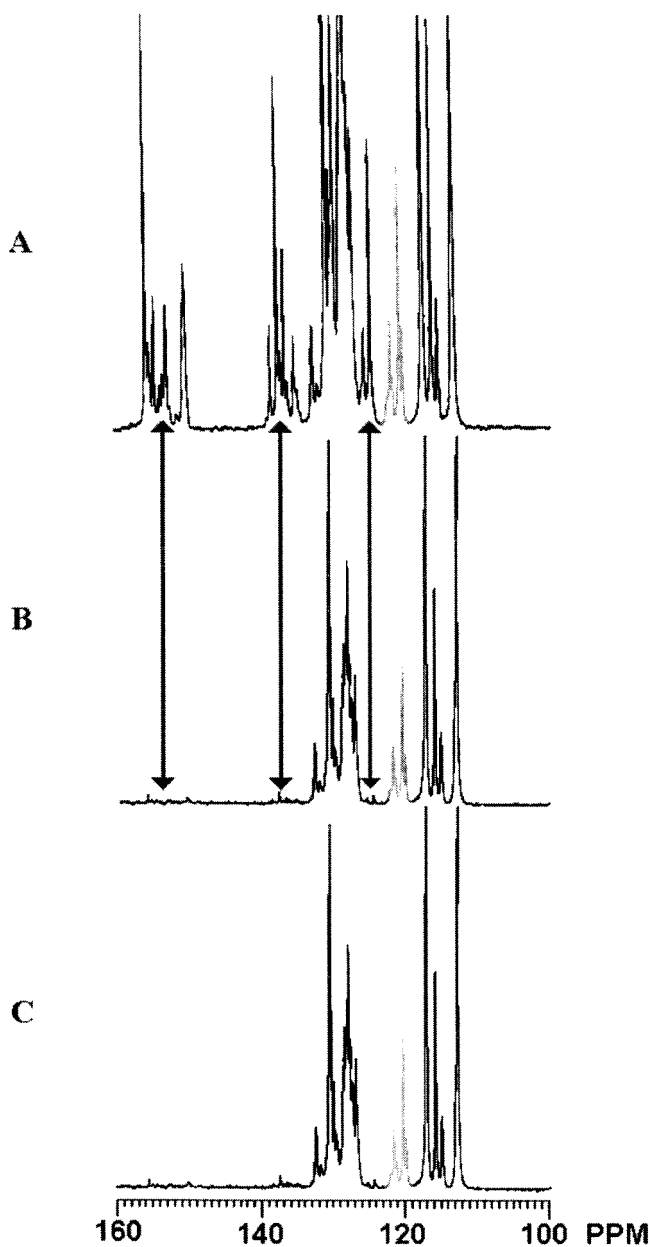
Figure 3 The ^{13}C-NMR spectrum of a novolac resin is plotted on the x axis and the ^{1}H-NMR spectrum is shown on the y axis. (gray traces) The C-5 and C-4 and hydrogens attached to the C-5 and C-4, respectively, of m-cresol incorporated in the polymer. (black trace) The trace around 127–129 ppm is for identical C-5 and C-3 and hydrogens attached to these carbon atoms of p-cresol incorporated in the resin.

$$U_4 = a_4 \times 100/a_5 \times I_4$$

where a_4 is the intensity of C-4 of m-cresol in the resin and a_5 is the intensity of C-5 in the DEPT ^{13}C-NMR spectrum of the resin. The intensity correlation factor (I_4) is

$$I_4 = a_4/a_5$$

where a_4 is the C-4 intensity in the m-cresol monomer and a_5 is the C-5 intensity in m-cresol as determined by the DEPT ^{13}C-NMR technique.

However, in the DEPT spectrum, carbon atoms in the same chemical environment (primary, secondary. or tertiary) but with a different microstructural environment (hindered or unhindered)[8,9] are not always associated with equal J values in the DEPT pulse sequence. Thus, the intensities of the carbon atoms (even of the same type: primary, secondary, or tertiary) are not totally dependable.[10]

In this article we propose an improved method of calculating the U_n value from the intensities of the fully relaxed ^{1}H-NMR spectra using two-dimensional heteronuclear single quantum correlation (HSQC), double quantum filtered correlation spectroscopy (DQF-COSY), and total correlation spectroscopy (TOCSY) experiments. The natural abundance of hydrogen nuclei is highest compared to the other NMR active nuclei, and thus for quantitative estimation from NMR spectroscopy the ^{1}H-NMR intensities would be much more dependable. The time required for hydrogen nuclei to relax back to thermal equilibrium is usually very short (T_1); hence, a ^{1}H-NMR spectrum is always fully relaxed and the intensities could be used for quantitative purposes. The degree of linearity (U_4) of this novolac copolymer was also calculated using the inverse gated broadband proton-decoupled quantitative ^{13}C-NMR spectrum.[10] The problem of the nuclear Overhauser effect and the consequent unequal polarization transfer from corresponding hydrogen to carbon atoms was obviated by using the inverse gated pulse sequence. Broadband decoupling enables us to obtain heteronuclear decoupling along with homonuclear decoupling. A pulse delay of 10 s was used to attain a fully relaxed ^{13}C-NMR spectrum for quantitative estimation of the degree of linearity. The U_4 value was found out to be 57.4 using the inverse gated broadband proton-decoupled quantitative ^{13}C-NMR spectrum, which is very well corroborated by the U_4 value (58.9) calculated based on the ^{1}H-NMR chemical shift. This shows the accuracy of the process based on the ^{1}H chemical shift intensity. This methodology is equally applicable to the calculation of the percentage of incorporation of different precursors in the polymer skeleton.

EXPERIMENTAL

The novolac resin in the study was made by a two-step procedure.[5] In the first step, p-cresol was mixed with formaldehyde and a base (NaOH) at room temperature and kept for 48 h. In the second step, the bishydroxymethylated p-cresol was allowed to react with twice the amount of m-cresol at an elevated temperature (140–150°C) for 1 h in the presence of acidic catalysts. The polymer was then subjected to steam distillation and reprecipitated from ethyl acetate and hexane. The molecular weight obtained from a GPC experiment established that a maximum of five cresol units are incorporated in the resin.
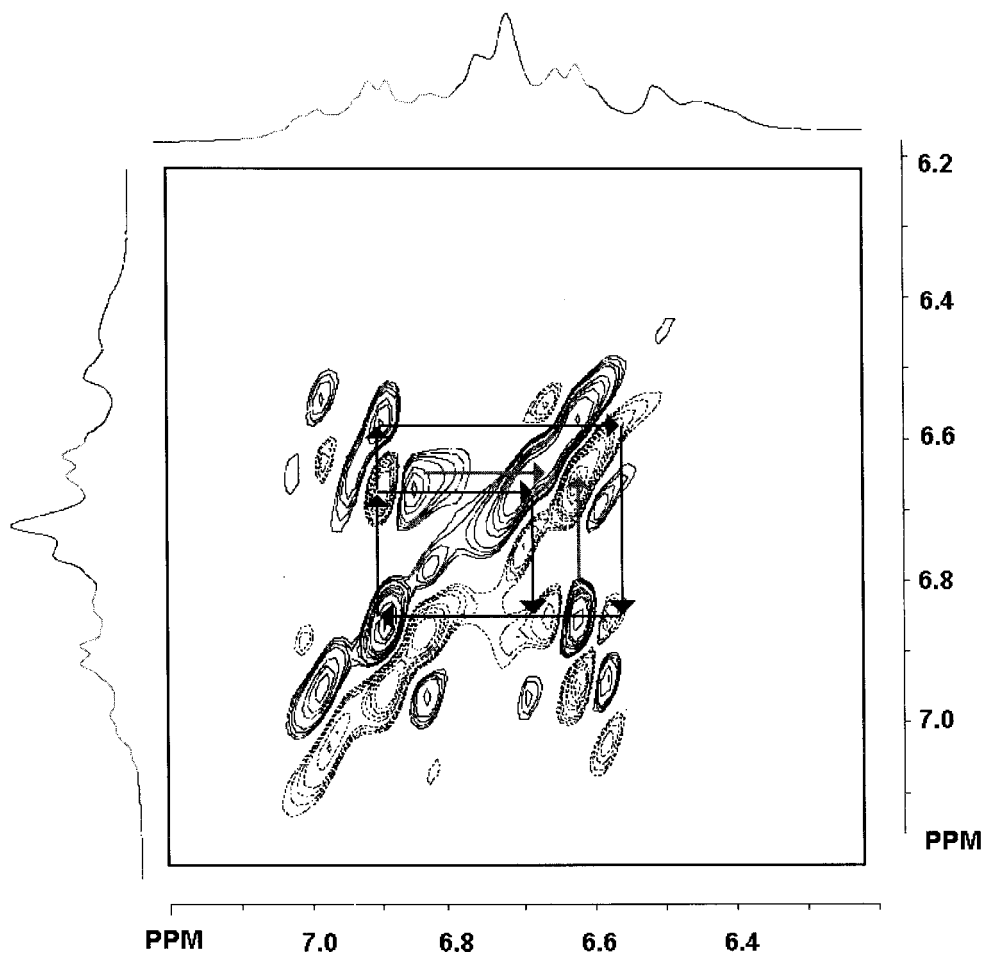
Figure 4 The expanded aromatic region of the DQF-COSY spectrum of the novolac resin. The expected cross peaks at (gray traces) δ = 6.8–7.05 with 6.65–6.7 ppm and (gray traces) δ = 6.8–7.05 ppm with δ = 6.4–6.65 ppm suggest that the ^{1}H chemical shift assignments of *m*-cresol incorporated in the polymer chain are correct. (gray arrows) The prominent cross peak of the signal at δ = 6.8 with 6.65–6.7 ppm confirms that the signal around δ = 6.8 ppm is for the hydrogen atom attached to the C-5 carbon of *m*-cresol.

The NMR spectra were recorded at room temperature on a Bruker Spectrospin DPX 300-MHz spectrometer. The sample solutions were prepared by dissolving 30 mg of sample in 0.5 mL of deuterated dimethylformamide (DMSO-d_6) for the one-dimensional (1-D) spectra and 100 mg of sample in 0.5 mL DMSO-d_6 for the 2-D NMR spectra. The ^{1}H-NMR spectra were recorded at 300.13 MHz, but the proton-decoupled ^{13}C-NMR spectra were recorded at 75.4 MHz. In the HSQC experiment the contour sizes were optimized, in which all the correlations had been seen. The mixing time was 80 ms for the TOCSY experiment. The Lorentzian curve-fitting protocol was done in Origin 6.1 software using a program written in QBasic.

RESULTS AND DISCUSSION

Polymers usually consist of a range of molecular weights because of different chain lengths in the polymer microstructure. Their ^{1}H-NMR spectra

therefore consist of quite broad and overlapping signals, making it difficult to assign the individual protons. Additional isomeric possibilities in *m*-cresol based novolac resins (linear/crosslinked and hindered/unhindered bonding) make peak assignments really difficult,[8] particularly in the aromatic region. The proton-decoupled ^{13}C-NMR signals are usually sharp and well separated compared to the ^{1}H-NMR signals. We therefore used the ^{1}H $\rightarrow$ ^{13}C $\rightarrow$ ^{1}H round trip polarization property of the HSQC experiment[11] to identify the ^{1}H-NMR signals corresponding to their ^{13}C-NMR signals, as shown in Figure 2. The gray trace at 119–121 and 129.5–132.5 ppm defines the C-4 and C-5, respectively, and protons attached to the C-5 and C-4 of *m*-cresol incorporated in the polymer skeleton. The black trace at 127–129 ppm is for the identical C-5 and C-3 of *p*-cresol incorporated in the resin. Good ^{13}C–^{1}H heteronuclear correlations were found with 119–121 ppm to δ = 6.65–6.7 ppm, 129.5–132.5 ppm to δ = 6.8–7.05 ppm, and 127–129 ppm to δ = 6.7–6.8 ppm.
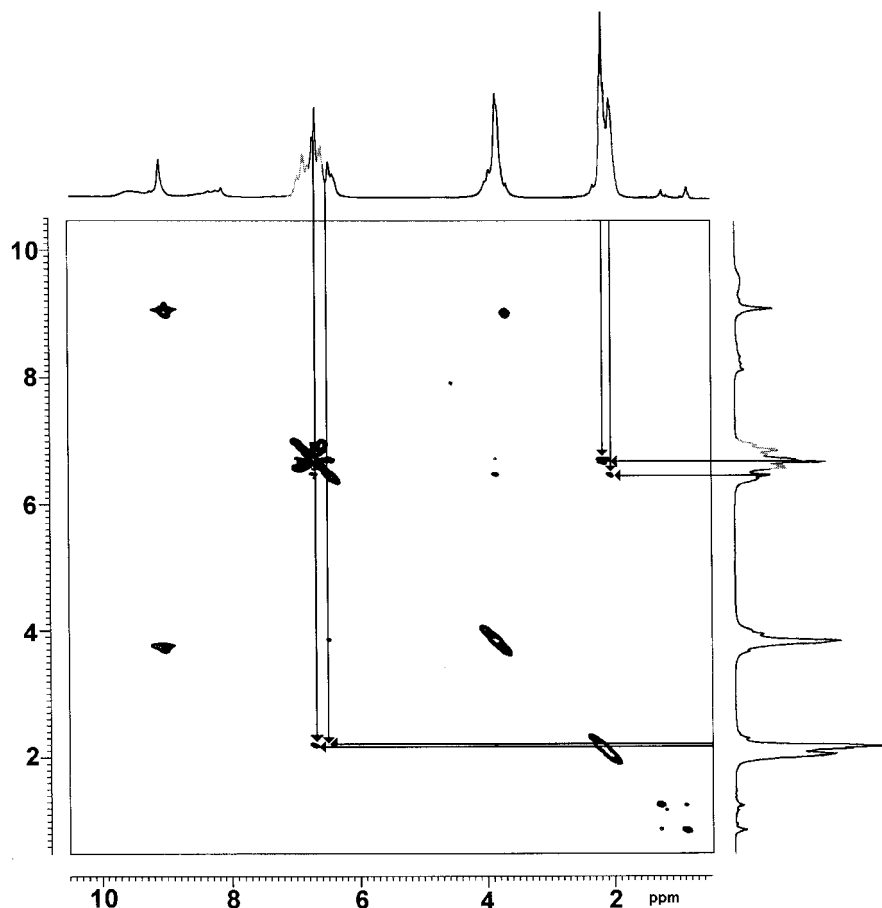
Figure 5 The TOCSY spectrum of the novolac resin. The correlations of methyl protons with the protons at around δ = 6.7–6.8 and 6.4–6.65 ppm convincingly prove that the signals the around δ = 6.7–6.8 ppm are for the meta hydrogens of *p*-cresol.

The assignment of the ^{13}C chemical shifts is made based on well-established literature values,[8,12,13] and it is crucial for the assignment of signals of the ^{1}H-NMR spectrum. These assignments are further confirmed by the fact that the ^{13}C absorption signals around 124–126 ppm in the ^{13}C-NMR spectrum of this polymer are missing in the DEPT-135° and DEPT-90° version of the spectrum, whereas the signals at around 119–121 ppm are still present in all three spectra (Fig. 3, spectra A–C). This implies that the signals at 124–126 ppm must represent a tertiary carbon (C-2 and C-6) and the latter signals in the 119–121 ppm region (gray traces) arise from the secondary carbon atom (CH, i.e., the C-4 and C-5 of *m*-cresol) incorporated in the resin (Fig. 3). Furthermore, the lack of correlation between the [13]C–[1]H chemical shifts the around 124 ppm in our HSQC experiment (Fig. 2) also establishes that these carbon atoms are tertiary in nature. The earlier finding of the ^{13}C chemical shift of C-4 incorporated in the resin microstructure at around 130 ppm,[8] taken together with the present observations regarding the involvement of C-2 and C-6 resonances, establishes the mechanism of polymerization in *m*-cresol.

These assignments of the ^{1}H chemical shifts in the aromatic region are also further confirmed from the COSY spectrum. To eliminate the perturbing singlet signals of solvent molecules and to make the 2-D map cleaner, we use the DQF-COSY experimental pulse sequence.[14] The peaks in the resin at δ = 6.8–7.05 ppm, which are assigned to the hydrogen attached in the 5-position of *m*-cresol, correlate well with the peaks at δ = 6.65–6.7 ppm for the hydrogen in the 4-position of *m*-cresol incorporated in the polymer. A small hump the around δ = 6.8 ppm showing a strong correlation (Fig. 4, gray arrows) with the signals at δ = 6.65–6.7 ppm establishes that it is from the hydrogen atom attached to the C-5 of *m*-cresol, which was not clear in the HSQC spectrum (Fig. 2). These correlations expected for hydrogen atoms adjacent to each other confirms that the ^{1}H chemical shift assignments are correct. The 6-position signal of *m*-cresol incorporated in the resin at δ = 6.4–6.65 ppm also shows the expected cross peaks with the signals of 5-position as shown in Figure 4.

To achieve the correlation from all of the protons of the same spin system, a TOCSY experiment has been carried out with longer mixing time to allow magnetization transfer to remote protons. This complements the COSY technique, and also has the important practical advantage that all the components of the cross
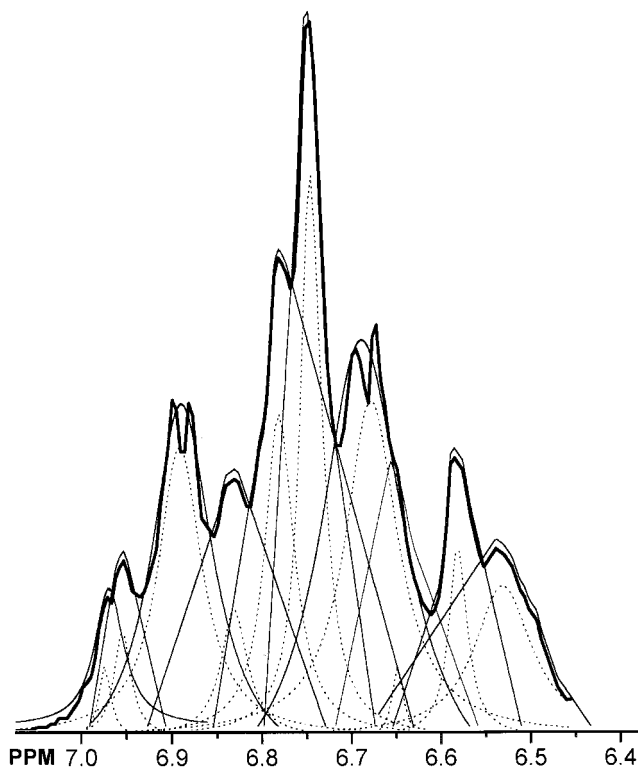
Figure 6   The expanded aromatic region of the fully relaxed ^{1}H-NMR spectrum of the novolac resin. (thick traces) The actual ^{1}H-NMR spectrum. (· · ·) The Lorentzian curve-fitting lines and (thin traces) the simulated signals of individual aromatic protons. The area under the curve is calculated using a program written in QBasic.

peaks are in phase and there is thus no peak cancellation when the *J*-couplings are poorly resolved.[15] The two identical meta hydrogens (hydrogen attached to C-3 and C-5) of *p*-cresols incorporated in the polymer chain also show the expected correlation with the methyl hydrogens attached to C-4, confirming the assignments of the chemical shift at around $\delta = 6.7$–6.8 ppm for two identical hydrogens of *p*-cresol (Fig. 5). The signals due to the two hydrogens of *p*-cresol are more intense than those due to the hydrogens of the end group of *m*-cresol observed at $\delta = 6.4$–6.65 ppm. This is corroborated by the comparatively strong correlation of the methyl protons with the protons at around $\delta = 6.7$–6.8 ppm versus that at $\delta = 6.4$–6.65 ppm.

The individual intensities of the ^{1}H-NMR spectrum were next calculated from the fully relaxed ^{1}H-NMR spectrum, and the U_4 values and percentage of incorporation of *m*-cresol were then calculated. The ^{1}H-NMR signal peak clusters were deconvoluted using a Lorentzian curve-fitting program written in Qbasic (Fig. 6), and the areas under the curves were then compared with the simulated Lorentzian peak areas.

The above analysis leads to the clear assignment that the peaks at $\delta = 6.8$–7.05 ppm are due to the meta hydrogens, the peaks at $\delta = 6.65$–6.7 ppm are due to

the para hydrogen of *m*-cresol incorporated in the polymer, and the peaks at $\delta = 6.7$–6.8 ppm are due to the two identical *m*-hydrogens of *p*-cresol incorporated in the resin. The U_4 value is calculated as

$$U_4 = (a_4 \times 100)/(a_4 + a_5)$$
$$= 1577.6 \times 100/2673.9 = 58.9\%$$

whereas a_4 is the area under the signal at $\delta = 6.65$–6.7 ppm and a_5 is the area under the signal at $\delta = 6.8$–7.05 ppm.

This high value for U_4 confirms the high ortho nature of the resin. Similarly, based on the Lorentzian curve-fitting protocol, the amount of *m*-cresol incorporated in the resin works out as

$$m\text{-cresol } (\%) = a_{5m} \times 100/(a_{5m} + [a_{5p}/2])$$
$$= 1423.9 \times 100/2249.1 = 63.3\%$$

where a_{5m} is the area under the signal for the C-5 proton of *m*-cresol at $\delta = 6.8$–7.05 ppm and a_{5p} is the area under the signals for two identical C-5 and C-3 protons of *p*-cresol at $\delta = 6.7$–6.8 ppm.

We deconvoluted our experimental absorptions using the OriginPro 6.1 library line-shape package (for Lorentzian line shapes). The deconvoluted best fit is shown as dotted traces in Figure 6. Using the above deconvoluted line shapes, the area under any particular NMR signal is calculated by the multiple Lorentzian analysis to an accuracy of ± 0.5.[16]

The area under a particular NMR absorption peak is then calculated using a program written in QBasic language. For Lorentzian line shapes appropriate to this study, the peak height is given by

$$y = y_0 + (2A/\pi) \times [\{w/(4(x - x_c)^2 + w^2)\}] \quad (1)$$

where y_o is the baseline value, A is the area, w is the width of the signal at half-height, and (x_c, y_c) correspond to the peak coordinates of the signal.

At $x = x_c$,

$$y_c = 2A/(\pi \times w) \quad (2)$$

Here y_o is considered to be zero because all peaks are extrapolated to the baseline.

The area (A) under the curve is computed by integrating eq. (1) between the lower (x_a) and upper (x_b) limit of x.

$$A = \int_{x_a}^{x_b} y \cdot dx$$

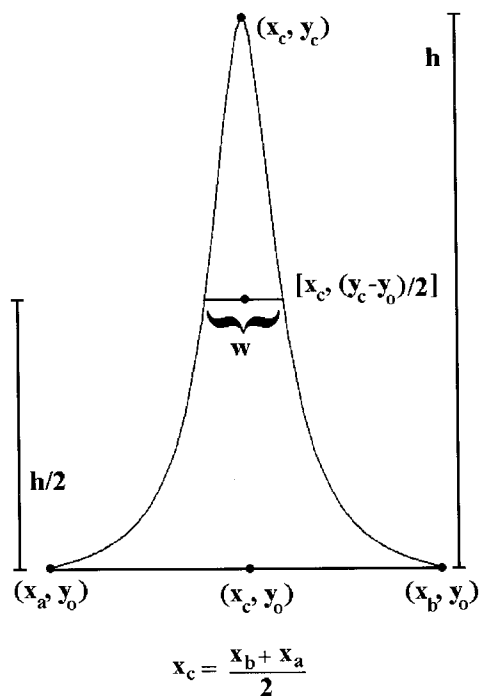Upon proper substitution, the area under the signal becomes

Figure 7 The aspects of a Lorenzian line shape: h, the height of the signal; w, the width of the signal at half-height; (x_c, y_c), the peak coordinates of the signals; y_0, the baseline value that is considered to be zero as all the signals are extrapolated to the baseline; x_a, the lower limit of the abscissa of the signal; x_b, the upper limit of the abscissa of the signal.

$$A = [\{(2Aw/\pi) \times \tan^{-1}[2(x - x_c)/w]\}/2w] \quad (3)$$

From (2) and (3)

$$A = [\{(y_c \times w)/2\} \times \tan^{-1}\{2(x - x_c)/w\}]$$

Using OriginPro 6.1 software, the values of (x_c, y_c) and w (difference between the abscissa at $y_c/2$) as shown in Figure 7 are calculated for each of the deconvoluted signals and then the areas are calculated using a program written in QBasic to an accuracy of ±0.5.

The areas calculated from the simulated Lorenzian line shapes (Fig. 6, thin trace) are then compared with the values obtained by the best-fit Lorentzian signals (Fig. 6, dotted trace) using OriginPro. Based on our simulation method, we found that 60.8% *m*-cresol ($=2673.9/4397.5$) is incorporated. Thus, there is good agreement between the percentage of incorporation values derived from the two curve-fitting techniques.

CONCLUSION

We demonstrated an improved methodology for the quantitative estimation of the linearity of polymers using the fully relaxed ^{1}H-NMR spectrum with the help of our 2-D NMR experiments. The spin-coupling topography in the polymer is better understood through these techniques. This method could also be successfully used for more precise estimation of different precursor amounts in copolymers. Our techniques substantially enhance the degree of resolution over the previously employed methods. The quantitative structural data derived by our method (U_n and percentage of incorporation) are crucial for the design of high performing photoresists and in other applications of novolac resins, as well as other polymers.

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