Determination of the Structural Configuration of Cresol–Novolak Resins by ^{13}C NMR Spectroscopy

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Synopsis

^{13}C NMR spectroscopy was used to investigate the structures of a series of pure isomeric cresylic novolak resins. Chemical shifts were measured and assigned, and end groups were distinguished from the central repeat units of the chains. Based on these measurements, the number average molecular weight of the para-cresylic oligomer was determined. A comparison of the ^{13}C decoupled and coupled spectra of the three isomeric resins indicates that the para isomer has a linear, ordered structure in which the aromatic rings are linked only by ortho–ortho′ methylene-bridging groups. The structures of the ortho and meta isomers are more complex and contain ortho–ortho′, ortho–para′, and para–para′ methylene bridges.

INTRODUCTION

Resins produced from the condensation of phenols and/or cresols with form-aldehyde are among the earliest synthetic polymers prepared and used commercially.[1,2] These resins are used on a large scale today by the electronics industry in lithographic resist formulations for fabricating microcircuits.[3–5] The condensation reaction when carried out under acidic conditions with an excess of the phenol or cresol to the formaldehyde yields a novolak resin which contains methylene bridges between the aromatic rings.[2] These resins have been shown to be complex oligomeric materials generally of low molecular weight.[6] Although much work has been carried out to elucidate their structure, most analytical techniques have had limited success in resolving their chemical complexities.[7] Recently, high resolution ^{13}C NMR spectroscopy was shown to be particularly effective for elucidating the structure of methylene-bridged polyphenols.[8,9] Other studies of solid phenolic resins by magic angle spinning techniques indicate the power and versatility of ^{13}C NMR spectroscopy for the determination of the structure of phenolic resins and related compounds.[10] This communication describes the application of high resolution ^{13}C NMR spectroscopy to the study of the structures of a series of pure isomeric cresylic novolak resins. Spectra were recorded on an IBM 200 MHz FT–NMR spectrometer. The resins were prepared from pure cresol monomers using a newly developed synthetic procedure.[6]

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EXPERIMENTAL

Materials

Ortho-, meta-, and para-cresol monomers (99+ % Gold Label, Aldrich Chemical Co.) were used without further purification. The formaldehyde source was s-trioxane (98%, Aldrich Chemical Co.).

Polymerization Procedure[6]

To a 250-mL resin kettle equipped with a mechanical stirrer, reflux condenser, addition funnel, and thermometer was added 1.0 mL (0.018 mol) concentrated sulfuric acid and 32.4 g (0.30 mol) of the cresol in a nitrogen atmosphere. The solution was heated with stirring to 90°C, and a solution of 14.9 g (0.167 mol) s-trioxane dissolved in additional cresol, 32.4 g (0.30 mol), was added dropwise at a rate which gave a pot temperature range between 105 and 115°C. As addition of the trioxane/cresol solution neared completion, the stirred mixture became viscous, and it was necessary to increase the heating rate to maintain the pot temperature. When the addition was completed, the taffylike material was heated at reflux (H_2O given off) until stirring became difficult (about 15 min). After cooling, the product was a brittle, opaque glass. The crude resin was ground into a coarse powder and dissolved in 2 L of dichloromethane. The dichloromethane mixture was partitioned first with a saturated $NaHCO_3$ solution (2×400 mL) and then with a saturated NaCl solution (1×400 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and the dichloromethane evaporated in vacuo to give a pale green foam. The foam was dried under high vacuum for 24 h, and the recovered solid was ground into a powder. Resin yields were from 80% to 90%.

Spectra

^{13}C NMR spectra of the cresylic novolaks were obtained with an IBM Instruments, Inc., WP 200 SY superconducting Fourier Transform Multinuclear NMR spectrometer with a carbon resonant frequency of 50 MHz. Approximately 400 mg of resin was dissolved in 10-mm-diameter sample tubes in $CDCl_3$ (ortho- and para-cresol novolaks) and $CDCl_3/(CD_3)_2SO$ (meta-cresol novolak).

RESULTS AND DISCUSSION

The proton decoupled spectrum obtained for the p-cresol–formaldehyde resin is shown in Figure 1(a). There are eight resonances in this spectrum which occur at 20.2 ppm, 31.7 ppm, 53.2 ppm, 115.8 ppm, 127.8 ppm, 130.9 ppm, 147.3 ppm, and 149 ppm. Carbon resonances were assigned based on the chemical shifts of various carbons that occur in definite regions of a Carbon-13 spectrum.[11] Therefore, the para-cresol spectral assignments are: para-position methyl, 20.2 ppm; methylene repeating unit, 31.7 ppm; end group C—H, 115.8 ppm; aromatics, 127.8–130.9 ppm; and C—OH, 147.3–149.9 ppm. From the coupled spectrum [Fig. 1(b)], the number of protons bonded to each carbon could be determined: i.e., carbons without hydrogens have one spectral line (singlet);
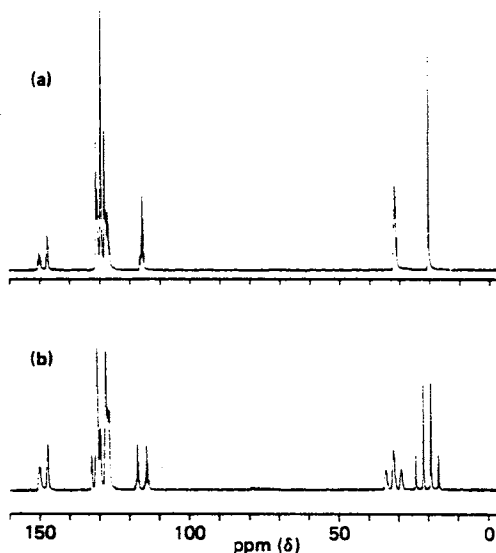
Fig. 1. The decoupled (a) and coupled (b) 50 mHz ^{13}C NMR spectrum of p-cresylic novolak resin, solvent CDCl$_3$.

carbons with one hydrogen have two spectral lines (doublet); carbons with two hydrogens have three spectral lines (triplet); and carbons with three hydrogens have four spectral lines (quartet).[12] Comparison of the decoupled spectrum with the coupled spectrum provides confirmation of the previous assignments: i.e., the resonance at 20.2 ppm is a quartet; 31.7 ppm is a triplet; 115.8 ppm, a doublet; 127.8–130.9 ppm, singlets and doublets; and 147–150 ppm, singlets.

The ring hydroxyl carbons are shifted downfield 16.2 ppm from the other ring carbons because of the electron-withdrawing effect of the OH group, which deshields the carbon nucleus. The C—OH end group is shifted 2 ppm downfield of the C—OH repeat unit because, in addition to the OH deshielding, replacement of the ortho CH$_2$ by an H results in further deshielding at the hydroxyl-bearing carbon. The C—H end group is shifted upfield from the ring carbons by 12 ppm. This shift occurs because the ring carbon in the meta position has a hydrogen bonded to it instead of a carbon, which results in some shielding of the carbon.

The decoupled spectrum with suppression of the nuclear Overhauser enhancement was used to quantitatively determine the spectral line intensities of the para-cresol resin. The average intensity of all the C—OH carbons is 23.2 (arbitrary units). This is also the approximate intensity of the methyl group which is known to be 21.7. The average intensity of C—OH and CH$_3$ (22.2) was used as the intensity number of each ring carbon, as determined by integration of the resonance lines. Therefore, the intensity of the other five ring carbons was calculated as 22.4 × 5 = 112. This is within 10% of the measured intensity of the resonances between 127 and 131 ppm, which indicates all the other ring carbons in the structure are counted.

In order to determine the average intensity of the end group carbons, the end C—OH (6.2) and end ring C—H (7.0) intensities were averaged (6.6). Subtracting the end group intensity from 22.2, the central methylene carbon intensity

was determined, i.e., 15.8. The average number of repeat units in the para-cresol oligomers was determined by calculating the central-group-to-end-group ratio and multiplying by 2 (number of end groups per chain), i.e., 15.8/6.2 = 2.3 × 2 = 4.6. From these data, the number average molecular weight was calculated by multiplying the number of repeat units by its molecular weight (120) and adding to it the molecular weight of the two end groups (218). This gave a molecular weight of the *p*-cresol oligomer of 770, a value which agreed within 6% of the vapor phase osmometer determined value of 723.

The ^{13}C decoupled spectra of the ortho, meta, and para novolak isomers are compared in Figure 2. One of the most interesting features of these spectra are the peaks in the methylene region between 31 and 40 ppm. The methylene
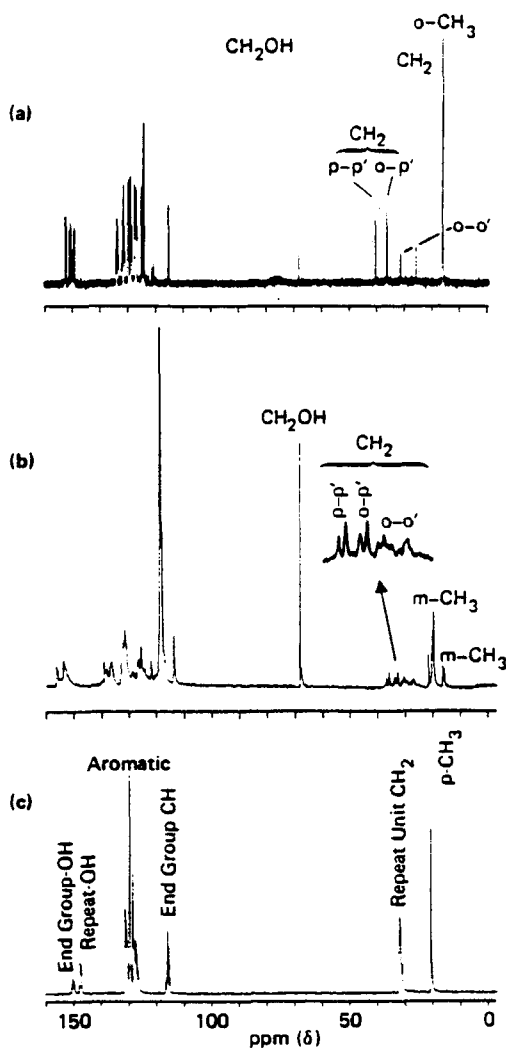

Fig. 2. The decoupled 50 MHz ^{13}C NMR spectra of the (a) ortho, (b) meta, and (c) para cresylic novolak resins. Temperature, ambient; solvent, ortho/CDCl$_3$; meta/CDCl$_3$/DMSO$_{d6}$; and para/CDCl$_3$.

carbon absorptions are the most sensitive to positional isomerism. For example, a methyl group in the para position restricts the number of possible resin structures to those linked ortho–ortho' by methylene groups. The high field absorption peak at 31 ppm is therefore assigned to the methylene CH_2's, indicative of a highly ordered ortho–ortho' chain sequence. The shielded single resonance peak at 115 ppm in the aromatic region, assigned to the CH in the ortho position at the end of the chain, is further confirmation of the ortho–ortho' bridging in this oligomer. However, a methyl group in either the ortho or meta position on the aromatic ring directs the orientation of the methylene bridging ortho–ortho', ortho–para', and para–para'. The peaks confirming these methylene bridges are those occurring at 31, 37, and 40 ppm in the spectra of the ortho and meta oligomers.

There are other structural differences observed in the spectra of these resins. The most significant of these are the methylol end groups that appear in the ortho and meta isomers at about 68 ppm. Since methylol end groups are not observed in the spectrum of the para isomer, then both methylol substitution and methylene bridge formation occur preferentially at the para position.

A comparison of the spectra of the three resins indicates that the structure of the meta isomer is the most complex. The complexity is indicated by the two methyl resonances, one at about 16 ppm, the second at 20 ppm, the multiple peaks in the methylene region between 31 and 40 ppm, and the complicated ortho and para CH end chain coupling in the aromatic region. However, it is possible to differentiate those carbons which have protons directly bonded to them, giving additional information on the number and positions of substitution on the aromatic ring.

Similar measurements to those above for a series of ortho–ortho' bridged polyphenols and phenolic model compounds indicate that it should be possible to quantitatively relate the peak areas to the relative proportions of the different functionalities present.[8,9] The use of these spectra in conjunction with proton NMR and IR analysis should prove to be a powerful technique to monitor the steric purity, the end groups and the average chain length of phenolic and cresylic resins, and other related compounds.

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