

Cashew Nut Shell Liquid Based *t*-BOC Protected Alternating "High Ortho" Copolymer as a Possible E-Beam Resist: Characterization Using Multi-Dimensional NMR Spectroscopy

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ABSTRACT: A cardanol/*m*-cresol-based copolymer was esterified using di-*tert*-butyl dicarbonate (*t*-BOC), which makes it a suitable candidate as a possible e-beam resist. This work reports a full characterization of the product using the techniques of FTIR and UV-Visible spectroscopy, one dimensional ¹H NMR, ¹³C NMR, DEPT-135. Two dimensional NMR experiments such as, COSY, HSQC, and

HMBC have been employed for exhaustive probing of the microstructural details of this derivatized copolymer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 804–810, 2008

Key words: 2D NMR; e-beam resists; CNSL; copolymer; *t*-BOC

INTRODUCTION

Cashew nut shell liquid (CNSL) is an indigenous natural product which finds many application in various fields including break-linings, surface coating, foundry core oil, lamination, and rubber compounding resins and adhesives, as composites and flame-retardants. It is also useful for insecticidal, fungicidal, antitermite, and medicinal applications.^{1,2} Cardanol is one of the major constituents and is a phenol having a long aliphatic side chain containing double bonds. Thus far, CNSL has not been used in the microelectronics industry extensively and, it is felt that CNSL based applications are "yet to find a niche" for themselves.³

E-beam resists/CA resists consist of a photo-inactive polymer and an acid labile pendant (ester group), which on exposure to light is hydrolyzed by the acid produced from the photo acid generator (PAG). On the other hand, photoresists are formulations of polymeric materials blended with photoactive compounds in a suitable solvent and are used to draw microelectronic circuits on silicon wafers. Positive and negative photoresists are the two major classes of photoresists available commercially.^{4,5} Currently, the former dom-

inate the world market and have mostly displaced the negative ones. However, the latter are still useful in micro electro mechanical systems. The random novolac resins used earlier have been now replaced by 'tailor made' alternating and semialternating "high ortho" novolacs.^{6,7}

Recent research developments in the field of nano-scale fabrication demand newer resists for high resolution geometry. The existing resists are therefore frequently modified for finer geometries. *Tert*-butoxycarbonyl (*t*-BOC) protected polymer matrix and PAGs serve as resists for image formation using e-beam exposure and "Deep UV" (DUV). Poly[*p*-((*tert*-butoxycarbonyl) oxy) styrene] has been used as a polymer matrix for this purpose.^{8–11} These form the third generation of photoresists. The application of *t*-BOC derivative of novolac resins as DUV resists has been reported.¹² Wet development image formation using e-beam exposure has also been discussed *t*-BOC has been used as an esterifying agent because it increases the glass transition temperature T_g and provides 'enhanced cleavage mechanism' of the polymer.¹³

In our earlier work,¹⁴ a *m/p*-cresol-based semialternating "high ortho" novolac copolymer was derivatized using di-*t*-butyl dicarbonate. In the present study, a cardanol/*m*-cresol-based alternating "high ortho" copolymer has been esterified using di-*t*-butyl dicarbonate, which makes it alkali insoluble. This derivative on exposure to light is hydrolyzed by the acid, produced by the PAG.

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MATERIAL AND METHODS

UV spectra were recorded on Perkin Elmer UV spectrophotometer in ethyl acetate. IR spectra were recorded on a Spectrum BX series spectrophotometer using KBr. TGA/DTA was recorded on Shimadzu DTG-60. The NMR spectra were recorded on Bruker 500 MHz instrument.

The synthesis of the resist was achieved in two stages. In the first stage, cardanol/*m*-cresol copolymer was synthesized. The second stage, which involves the derivatization of the above copolymer, is depicted in the scheme (Fig. 1).

Synthesis of CNSL-*m*-cresol based novolac resin

CNSL and cardanol-based copolymer was prepared by the two-step procedure, used by us earlier.^{15,16} In the first step, the first cresolic monomer (cardanol) was mixed with formaldehyde (37%) and sodium hydroxide in the ratio 1 : 2.2 : 1. The mixture was stirred mechanically at room temperature (25°C) for 48 h. The second cresolic precursor (*m*-cresol) was then added to the first cresolic monomer in 1 : 1 ratio. The mixture was diluted with hydrochloric acid (1 : 1) in an ice bath and the pH brought down to 4–4.5. The bis-hydroxymethylated cresol (BHMC) was separated, and the organic layer washed thoroughly with water containing 1% oxalic acid. In the second step, the third cresolic monomer (*m*-cresol) was mixed again with liquid BHMC in 1 : 1 ratio with first phenolic monomer. A 1% molar equivalent of oxalic acid (with respect to the total cresolic components) was added. Xylene was selected as the reaction medium and the water was tapped out using a Dean-Stark-trap. The mixture was refluxed at 140–150°C for

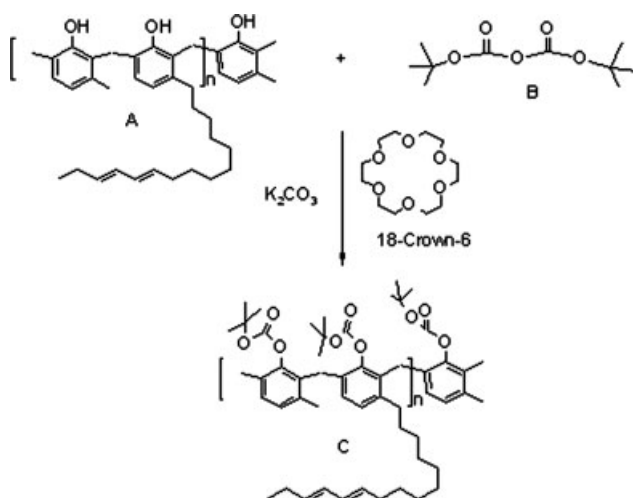


Figure 1 A: Cardanol/*m*-cresol copolymer; B: Di-*t*-butyl dicarbonate, and C: the *t*-BOC derivative of the copolymer. 18-crown-6 was used as the phase transfer catalyst.

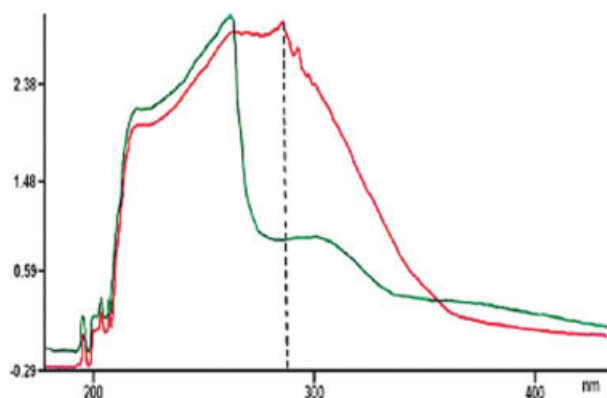


Figure 2 UV-VIS spectra of the polymer before (red curve) and after esterification (green curve). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

45 min and then steam-distilled at 180°C for another hour.

Derivatisation of the novolac resin

The esterification reaction was carried out by the standard procedure.^{11,13} Two gram (3.3 mmol) of the novolac resin was mixed with 820 mg of di-*t*-butyl dicarbonate (97%, 3.6 mmol), 500 mg of anhydrous K₂CO₃ (3.6 mmol), 10 mg of 18-crown-6 and stirred vigorously with 40 mL of THF for 3 days at room temperature. The reaction mixture was diluted with acetone (60 mL) and precipitated in water (800 mL). It was filtered off and washed several times with hot water. It was dried and reprecipitated using ethyl acetate-hexane. The final product was dried in vacuo.

RESULTS AND DISCUSSION

Spectral features the CNSL-*m*-cresol based novolac resin

As has been previously reported¹⁵ by us, the CNSL-based novolac resin has the following spectral features. The UV spectrum showed λ max at 252, 282 and a shoulder around 325 nm (Fig. 2). IR spectrum [Fig. 3(A)] showed peaks at 3390, 3010, 2924, 2852, 1654, 1610, 1585, 1500, 1458, 1273, 1100, 1003, 960, 860, 725 cm⁻¹.

In Table I, the ¹H and ¹³C chemical shift values of aliphatic region are tabulated. Since it is very difficult to identify the individual peaks arising out of *m*-cresol and cardanol, the ¹³C chemical shifts assignments were confirmed by the 2-D HSQC (Hetero nuclear Single Quantum Correlation) experiments (Fig. 4). The additional correlation, having their origin in through space coupling, brought about by the polymer microstructure were confirmed by the low 'mixing time' DQF-COSY spectrum [Fig. 5(A)] and

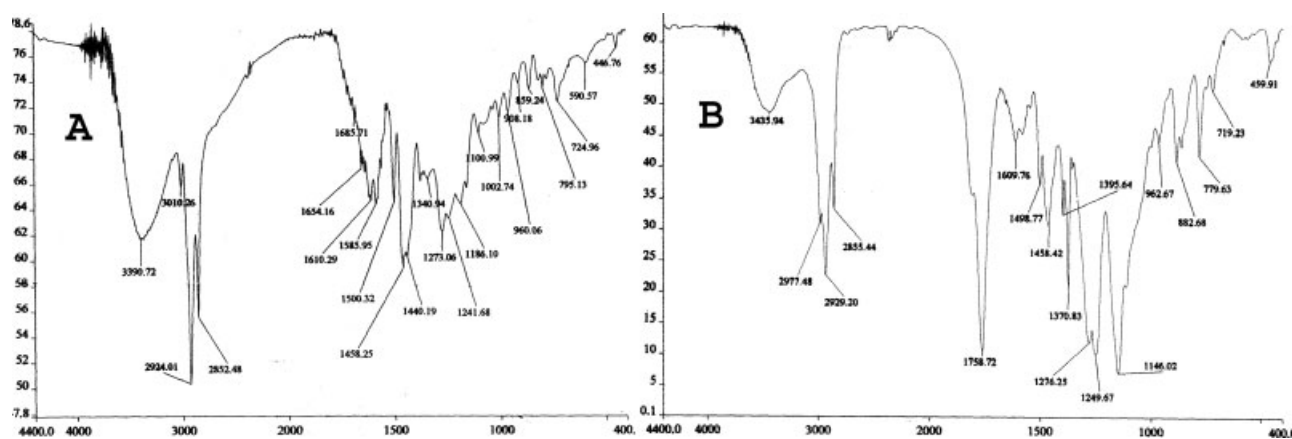


Figure 3 IR spectrum of the polymer before (A) and after, (B) derivatization.

TABLE I
NMR Spectral Data for the Cardanol/*m*-Cresol Copolymer

$^1\text{H-NMR}$ (δ)	$^{13}\text{C-NMR}$ (ppm)	DEPT-135 signal pointed	Assignments
1.2	39.8–25.3	Downward	Solvent DMSO-D6 Benzylic methylene bridge Aliphatic methylene groups
1.2	22.2	Downward	(in cardanol side chain)
2.1 and 2.3	20.8 and 19.4	Upward	Benzylic methyl group (in <i>m</i> -cresol)
0.8	13.9	Upward	Aliphatic methyl group (in cardanol side chain)

longer 'mixing time of 80 ms' TOCSY experiments [Fig. 5(B)].

Characterization of the derivatized polymer

The UV spectrum of the derivatized polymer showed λ_{max} at 252, 282 and a shoulder around 325 nm (Fig. 2). The reduced intensity of the 282 nm peak is known to be directly related to the extent of derivatization.¹³ This feature is clearly demonstrated in the present case, confirming a good degree of derivatization.

IR spectrum [Fig. 3(B)] showed the peaks at 3435, 2977, 2929, 2853, 1758, 1609, 1577, 1498, 1458, 1395, 1371, 1273, 1249, 1146, 1003, 960, 882, 860, 780 cm^{-1} . The appearance of the peak at 1758 cm^{-1} is attributed to the oxy-carbonyl moiety of the *t*-BOC group, with no shoulder at 1725 cm^{-1} which arises when derivatization is incomplete,^{13,17,18} while the doublet at 1395 and 1370 cm^{-1} is assigned to the *t*-butyl group. As expected, these peaks are absent in the polymer precursor, confirming complete derivatization of the cardanol/*m*-cresol-based copolymer. TGA/DTA of the polymer showed a clear increase in the T_g value. The T_g value for the underivatized polymer was $\approx 80^\circ\text{C}$, while it was $\approx 190^\circ\text{C}$ for the derivatized polymer.

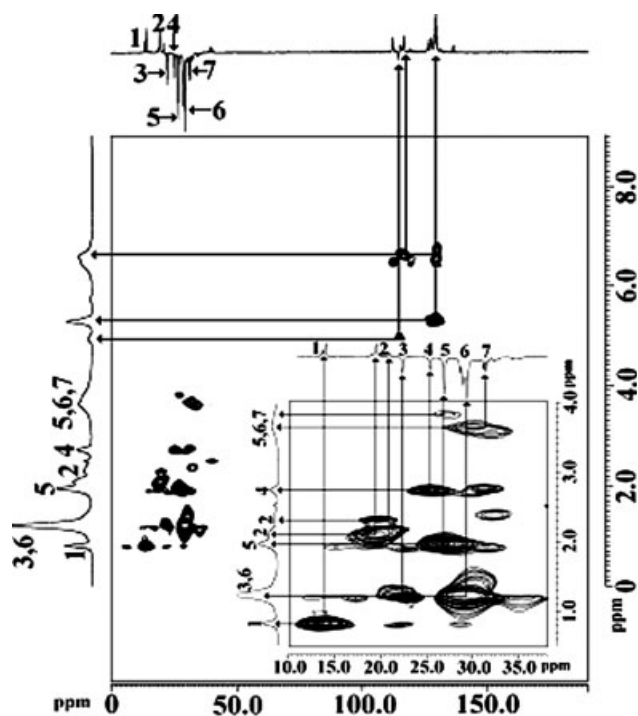


Figure 4 HSQC spectrum of *m*-cresol and cardanol-based novolac resin: The DEPT-135 spectrum is plotted along *x*-axis whereas the $^1\text{H-NMR}$ spectrum is plotted along *y*-axis. In the inset, the expanded aliphatic region correlations are shown. (Taken from Ref. 15).

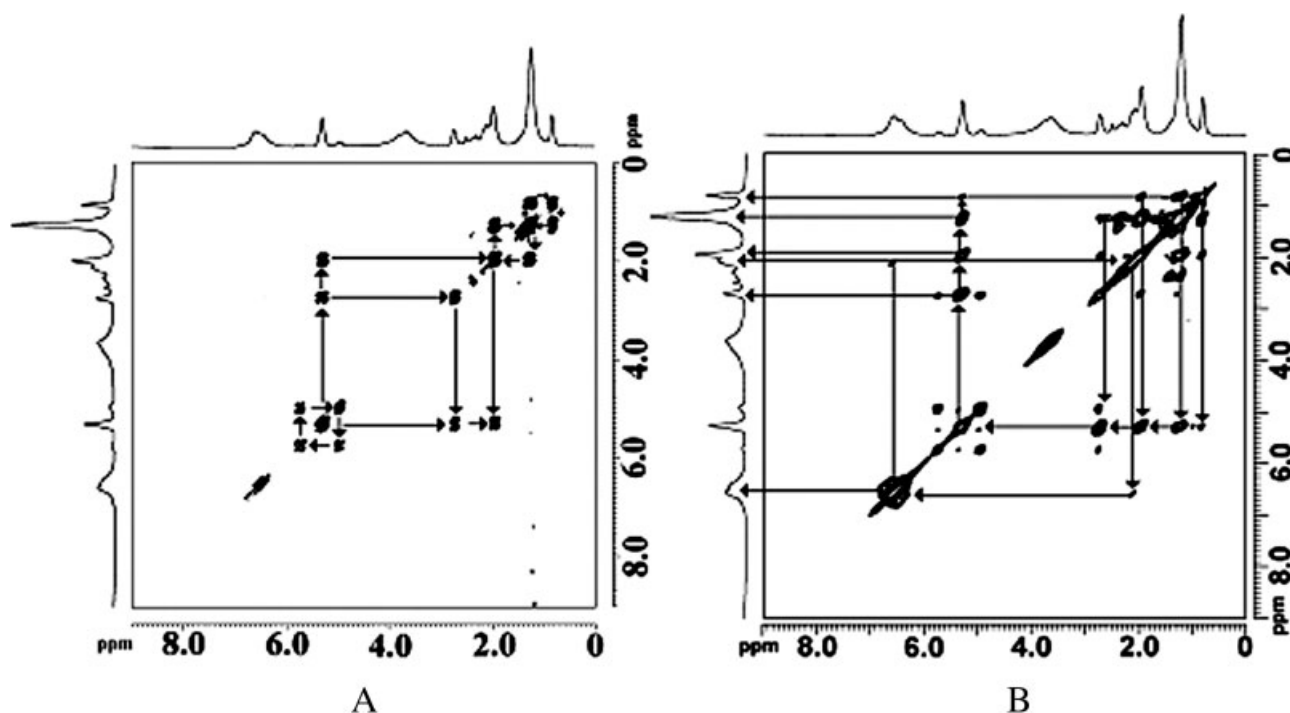


Figure 5 A: DQF-COSY and B: TOCSY spectrum of the novolac resin-based on cardanol and *m*-cresol: All the correlations, in the same spin system, are seen in the TOCSY spectrum as the mixing time is very high (80 ms) in the TOCSY experiment compared with DQF-COSY experiment. (Taken from Ref. 15).

In the preliminary 300 MHz ^1H NMR spectrum recorded in CDCl_3 , two peaks were seen, a broad one at $\delta = 1.2$ was assigned as due to the side chain of the cardanol and a new broad peak at $\delta = 1.5$ was also observed. Other peaks could not be observed due to dynamic range effect contributed by the solvent. A fresh spectrum was therefore recorded in $\text{DMSO-}d_6$, which showed all the peaks of the precursor polymer but not the one expected around $\delta = 1.5$ for methyls of the *t*-BOC group. This may be due to the fact that the peak merged with the broad peak at $\delta = 1.2$. We then recorded the CMR and DEPT. In the CMR spectrum, the *tert*-carbon of the *t*-BOC group was observed, but not the methyl groups of the *t*-BOC moiety. The oxy-carbonyl peak was also observed at 156 ppm which was seen only after the derivatization. Moreover, in the DEPT-135 all the peaks in the aliphatic region were seen pointing down, suggesting all these were CH_2 groups. Further 2D-spectroscopy experiments done at this frequency, such as HSQC and COSY, showed the expected correlations but the *t*-BOC peak could not be resolved.

To resolve this point further a fresh set of spectra were recorded in CDCl_3 at 500 MHz. The peak at $\delta = 1.55$ was clearly visible (not observed earlier) in the PMR (Fig. 6). It was assigned to the methyls of the *t*-butyl group. This peak was pointing upward in the DEPT-135 (Table II) in contrast to the benzylic

$-\text{CH}_2-$ and the $-\text{CH}_2-$ of the cardanol side chain. A new peak was observed in the aliphatic region of the CMR (Fig. 7) at 27.7 ppm assigned to be due to the methyl carbons of the *t*-BOC. The *tert*-carbon of the *t*-BOC group was observed at 83 ppm. In the HSQC experiment (Fig. 8), which is a 2D plot of ^1H - ^{13}C correlations, these peaks correlated well with the peak at $\delta = 1.55$ of the ^1H NMR spectrum, in addition to the correlation of the peak at $\delta = 1.2$ with the peak at 22 ppm for the cardanol side chain and 29–32 ppm for the benzylic methylene bridges of the polymer backbone.

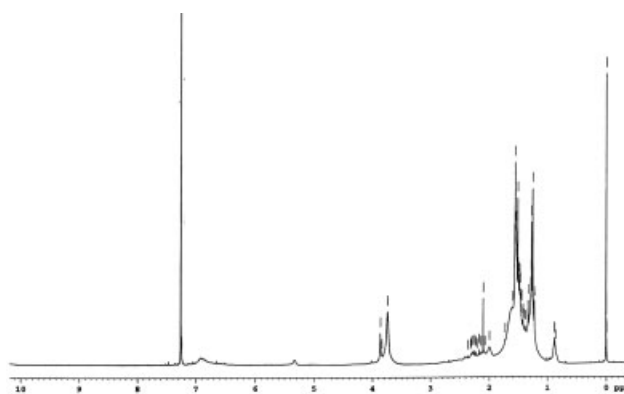


Figure 6 ^1H -NMR spectrum of *t*-BOC protected copolymer.

TABLE II
NMR Spectral Data for the *t*-BOC Protected Copolymer

$^1\text{H-NMR}$ (δ)	$^{13}\text{C-NMR}$ (ppm)	DEPT-135 signal pointed	Assignments
	170		Carbonyl of <i>t</i> -BOC
	83		<i>t</i> -carbon of <i>t</i> -BOC
7.24	77–76		Solvent (CDCl_3)
1.2	32–29	Downward	Benzylic methylene bridge
1.55 and 1.51	27	Up	Methyls of <i>t</i> -BOC
1.2	22.2	Downward	Aliphatic methylene groups (in cardanol side chain)
2.1	20.8 and 19.4		Benzylic methyl group (in <i>m</i> -cresol)
0.8	13.9		Aliphatic methyl group (in cardanol side chain)

The success of our esterification has been further established by the COSY experiment (Fig. 9). The spectrum shows a 2D plot of ^1H – ^1H correlations, where no coupling is observed in the off diagonal region of the spectrum corresponding to the *t*-BOC group. Furthermore, this experiment suggests a lack of single bond correlation between the pendant group and the molecular backbone. To get a further insight into the microstructure of the molecule in 3D space, a molecular modeling calculation was done using Hyper Chem Professional 6.03 software version. The energy minimized structure (Fig. 10) was obtained by geometrical optimization of the structures using molecular mechanics force field; Mm+ and the Steepest Descent Algorithm. The cyan colors represent carbon atoms whereas white

and red colors represent hydrogen and oxygen, respectively.

In addition to confirming the derivatization, our two-dimensional NMR experiments have collectively brought out certain novel and important features. For example, in the HSQC experiment, the correlation for the *t*-butyl group is seen to be spread over the region $\delta = 1.4$ to $\delta = 1.6$, which indicates a distinct separation of *t*-BOC groups on the phenolic –OH of the *m*-cresol and cardanol units in the polymer chain and at the end groups. In particular, the peaks at $\delta = 1.51$ and $\delta = 1.55$ arise due to *t*-BOC group at the *m*-cresol and cardanol units in the polymer chain exclusive of the end groups. This is very clearly illustrated in the heteronuclear multiple bond correlations (HMBC) experiment. The HMBC spectrum (Fig. 11) shows two

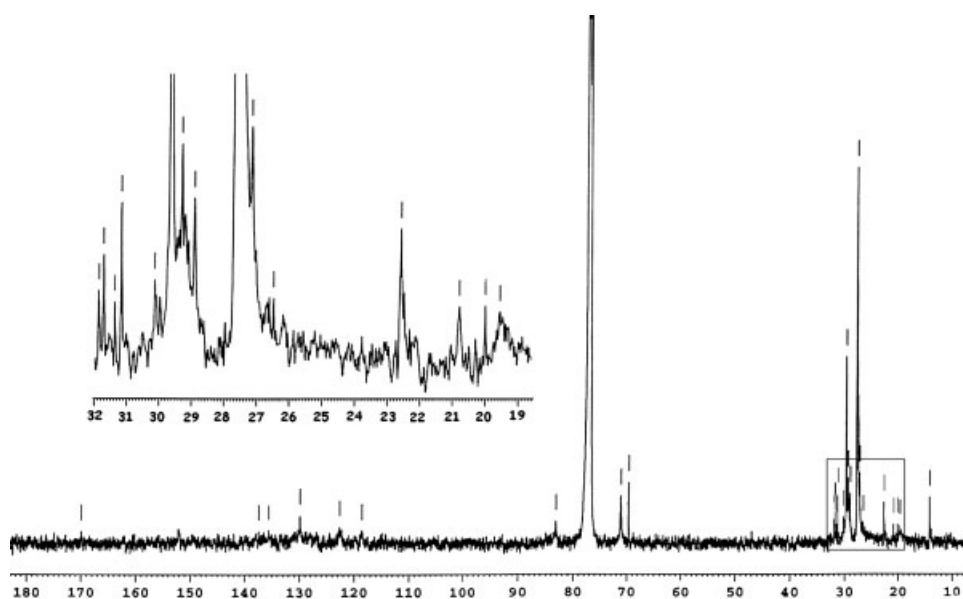


Figure 7 ^{13}C NMR spectrum of *t*-BOC protected copolymer.

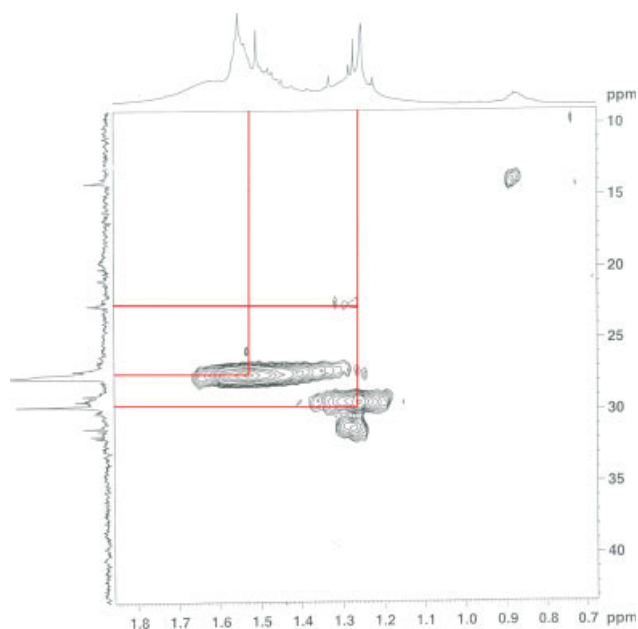


Figure 8 HSQC spectrum of *t*-BOC protected copolymer, the ^{13}C NMR spectrum is plotted along y -axis whereas the ^1H -NMR spectrum is plotted along x -axis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

distinct contours for the *t*-carbon of the *t*-BOC group, correlating with the signals at the $\delta = 1.51$ and $\delta = 1.55$.

CONCLUSIONS

This study shows that CNSL (cardanol) based alternating "high-ortho" novolac resin has been success-

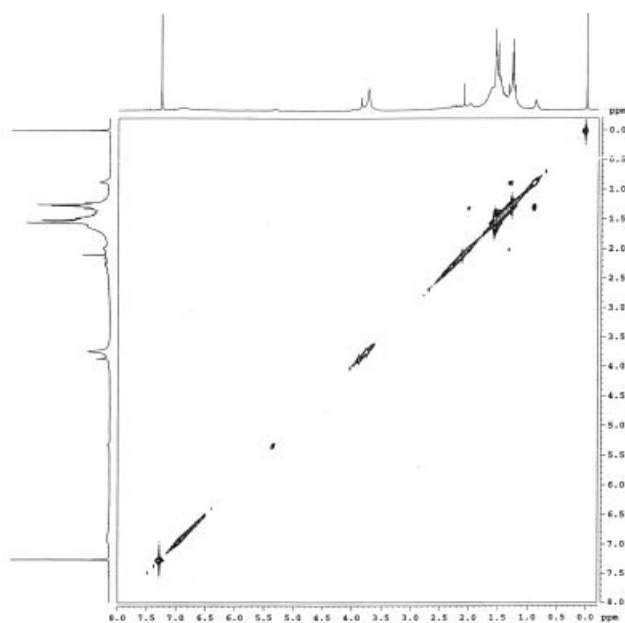


Figure 9 COSY spectrum of *t*-BOC protected copolymer, the ^1H -NMR spectrum is plotted along the x and y -axis.

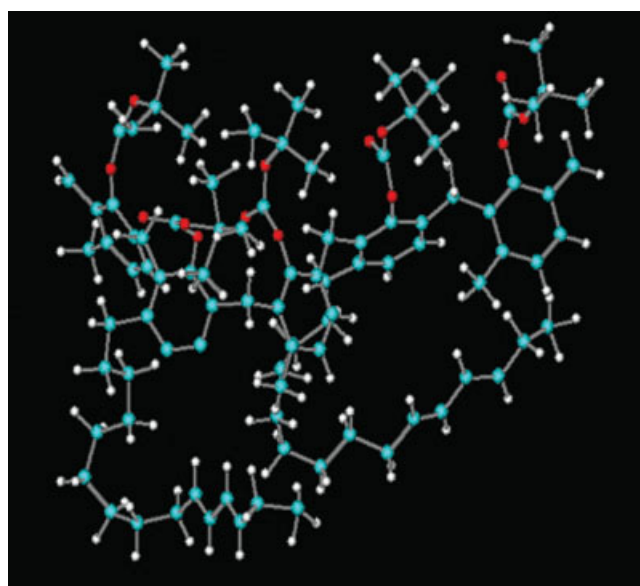


Figure 10 Energy minimized structure of the *t*-BOC protected copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fully derivatized using di-*t*-butyl dicarbonate. This was confirmed by the decrease in the intensity of the UV spectral peak at 282 nm. In its IR spectrum a peak for the carbonyl group was clearly seen along with an expected doublet. In the PMR spectrum a new large peak was seen at $\delta = 1.55$. In the CMR spectrum, the

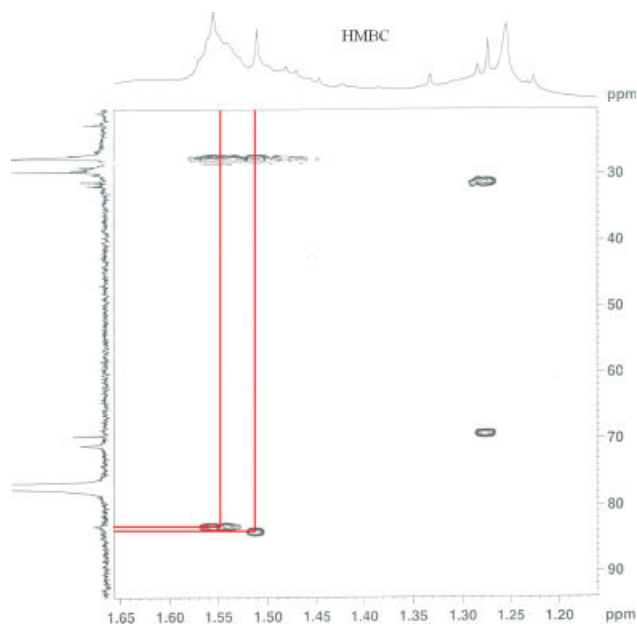


Figure 11 HMBC spectrum of *t*-BOC protected copolymer, ^{13}C NMR spectrum is plotted along x -axis whereas the ^1H -NMR spectrum is plotted along y -axis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

t-butyl group was seen at 27 ppm, while the aliphatic chain of cardanol was observed at $\delta = 1.2$. A new signal for carbonyl carbon appeared at 170 ppm.

The above 1D NMR assignments were confirmed using more detailed multidimensional NMR spectroscopic techniques to probe the microstructure of the polymer. In the HSQC spectrum, the peaks at $\delta 1.35$ – $\delta 1.6$ correlated with the peak at 27 ppm in the CMR spectrum. These arise from *m*-cresol and cardanol units in the polymer chain and the end groups. No off diagonal peaks were observed for the *t*-BOC group in the COSY spectrum, showing no one bond correlation for the *t*-butyl group with the polymer backbone. Molecular modeling also supports this conclusion. The HMBC spectrum showed that the peaks at $\delta = 1.51$ and $\delta = 1.55$ could be attributed to pendant groups of the *m*-cresol and cardanol units in the polymer chain. This new *t*-BOC protected polymer could serve as a possible e-beam resist.

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