

m/p-Cresol-Based *t*-BOC Protected Alternating “High Ortho” Copolymer as a Possible e-Beam Resist: Characterization Using Multidimensional NMR Spectroscopy

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ABSTRACT: Synthesis of a *m/p*-cresol-based novolac resin and its subsequent esterification using di-*tert*-butyl dicarbonate (*t*-BOC) is described. The product has been characterized using techniques of FTIR spectroscopy, one dimensional ¹H NMR, ¹³C NMR, and DEPT-135 spectra. Two dimensional NMR experiments like, COSY, HSQC,

and HMBC have been used for exhaustive probing of the microstructural details of the derivatized copolymer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2166–2172, 2009

Key words: 2D NMR; *t*-BOC; e-beam resists; novolac resins; copolymers

INTRODUCTION

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.^{1,2} The former currently dominate the world market and have mostly displaced the negative ones. However, the latter are, still useful in micro electro- mechanical systems (MEMS). The random novolac resins used earlier have been now replaced by “tailor made” alternating and semialternating “high ortho” novolacs.^{3,4} On the other hand, 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).

Recent research developments 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 PAG 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.^{5–8} These form the third generation of photoresists. The application of *t*-BOC derivative of novolac resins as DUV resists has been reported.⁹ 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.¹⁰

In our earlier work, a *m/p*-cresol-based semialternating “high ortho” novolac copolymer¹¹ and CNSL/*m*-cresol based alternating “high ortho” novolac copolymer¹² were derivatized using di-*tert*-butyl dicarbonate. In this study, a *m/p*-cresol-based alternating “high ortho” copolymer has been esterified using di-*tert*-butyl dicarbonate, which makes it alkali insoluble. This derivative on exposure to light is hydrolyzed by the acid, produced by the PAG.

MATERIAL AND METHODS

The NMR spectra were recorded on a Bruker 400 MHz Avance instrument operating at 400.13 MHz ¹H frequency. IR spectra were recorded on a Spectrum BX series spectrophotometer using KBr. TGA/DTA was recorded on Shimadzu DTG-60. DSC was recorded on Perkin Elmer. GPC instrument used was built by JASCO and equipped with UV and RI

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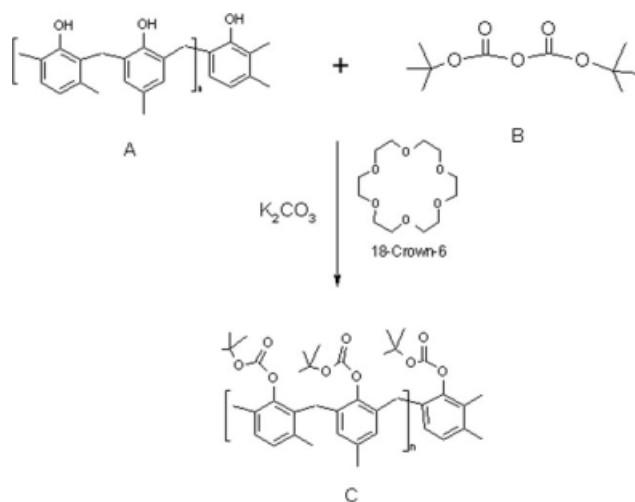


Figure 1 The *m*-cresol/*p*-cresol copolymer (A), di-*tert*-butyl dicarbonate (B), and the *t*-BOC derivative of the copolymer (C). 18-crown-6 was used as a phase transfer catalyst.

detectors. Calibration was done using polystyrene as standard. Molecular modeling calculation was done using Hyper Chem Professional 6.03 software version. The synthesis of the resist was carried out in two stages. In the first stage, *m/p*-cresol copolymer was synthesized.¹³ The second stage, which involves the derivatization of the above co-polymer, is depicted in the scheme (Fig. 1)

Synthesis

A total of 10.8 g (0.1 mol) of *m*-cresol, 16.2 g (0.2 mol) of 37% formaldehyde and 4.0 g (0.1 mol) sodium hydroxide were stirred mechanically at room temperature (25°C) for 48 h. A total of 10.8 g (0.1 mol) of *p*-cresol was then added to the mixture and it 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 was washed thoroughly twice with water containing 1% oxalic acid. In the second step, 10.8 g (0.1 mol) of *p*-cresol was mixed with liquid BHMC. A total of 2.70 g of oxalic acid was used as catalyst and xylene was selected as the reaction medium. The mixture was then refluxed at 140–150°C for 45 min and then steam distilled at 180°C for another hour. The molten resin was allowed to cool down and then the resin was leached with 30%

NaOH. The alkali solution was filtered and in the filtrate dilute HCl was added dropwise at 0°C until all the resin precipitated out. The precipitated resin was dried and then fractionated from ethyl acetate and hexane. Finally the resin was dried *in vacuo*.

Derivatization

The esterification reaction was carried out by the standard procedure.^{8,10} Novolac resin, 2.0 g was mixed with 820 mg of di-*tert*-butyl dicarbonate (97%, 3.6 mmol), 500 mg of anhydrous K_2CO_3 (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

Characterization of the novolac

The new *m/p*-cresol-based Alternating “high ortho” copolymer was synthesized¹³ using the standard procedure.^{14,15} The weight average molecular weight (M_w) was determined to be 1385 the number average molecular weight (M_n) was 522 and polydispersivity (I_p) was found to be 2.65. The IR spectra of the novolac showed peaks at 3284, 3012, 2920, 2862, 1701, 1610, 1577, 1502, 1465, 1375, 1257, 1147, 1099, 1045, 1008, 929, 860, 812, 725 cm^{-1} . The 1H -NMR and ^{13}C -NMR spectra of the novolac were recorded and the chemical shifts and coupling constants have been tabulated (Table I)

Characterization of *t*-BOC derivatized polymer

The new copolymer was then derivatized successfully as depicted in the scheme (Fig. 1). This was evident from the IR spectrum. The IR spectrum showed peaks at 2981, 2933, 2853, 1757, 1610, 1498, 1458, 1396, 1371, 1253, 1211, 1147, 1112, 1082, 1045, 1016, 889, 812, 781 cm^{-1} . Broad peak at 3284 cm^{-1} , attributed to hydrogen bonding, due to phenolic hydroxyl group, was greatly reduced. The appearance of the new peaks at 1757 cm^{-1} is attributed to the carbonyl-oxy of the *t*-BOC.^{10,16} The doublet at 1396 and 1370 cm^{-1} is assignable to the methyls of

TABLE I
Spectral Values of the Novolac Copolymer

S. no	1H -NMR (5)	^{13}C -NMR (ppm)	DEPT-135	Assignments
1	2.18–2.37	19–21	Up	Aromatic methyl(s)
2	3.92–3.94	26–33	Down	Methylene bridges
3	6.73–7.12	121–131	Up	Aromatic protons

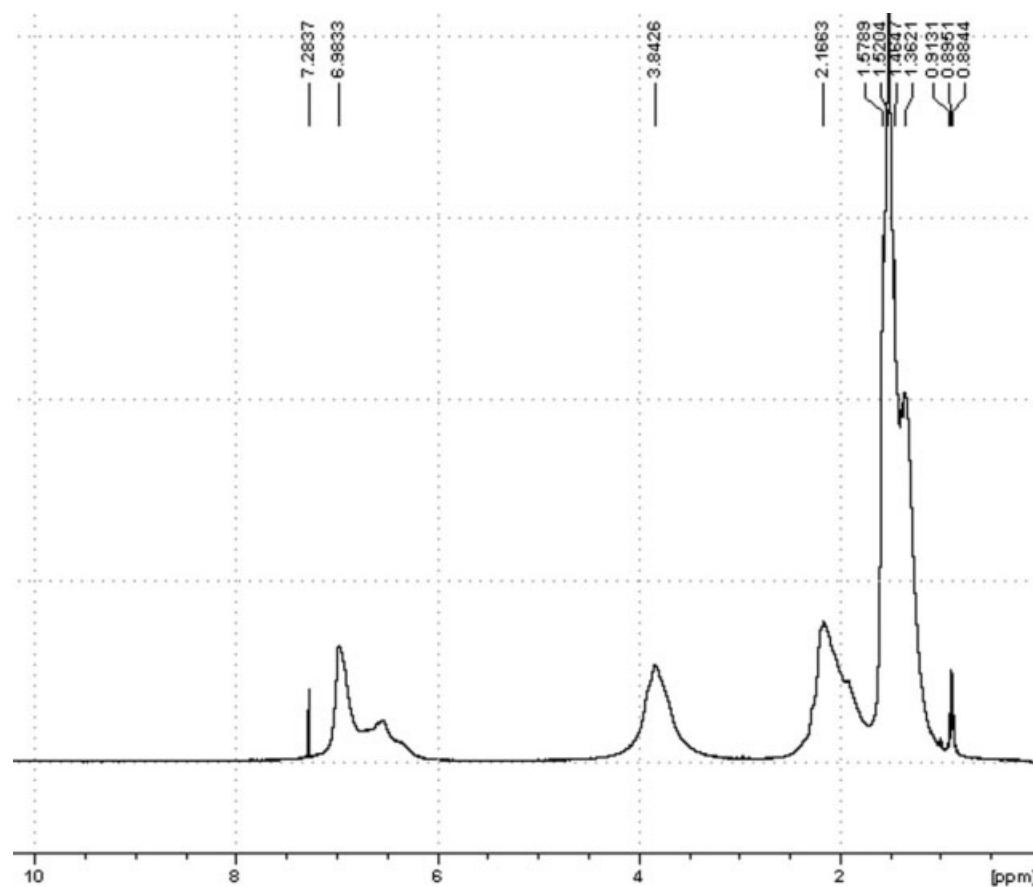


Figure 2 ^1H -NMR spectrum of the derivatized copolymer.

the *t*-BOC. These spectral features confirm the derivatization of the novolac copolymer. Moreover, the shift in the T_g value was also observed. The T_g value for the underivatized polymer was $\approx 70^\circ\text{C}$, whereas it was $\approx 165^\circ\text{C}$ after the derivatization.¹⁰

This was further confirmed by NMR spectroscopy. Taking the lead from our previous work, we chose to use the 400 MHz spectrometer for characterization. The range of molecular weights (higher I_p values) in the polymer macrostructure leads to broadening of the signals in the ^1H -NMR spectrum. This makes it difficult to assign individual signals arising from the different hydrogens. A whole battery of NMR techniques including COSY, HSQC, NOESY, and HMBC were used to characterize the polymers. The signals in the proton decoupled ^{13}C -NMR spectrum, however, are sharp and well separated. We have, thus, used the ^{13}C chemical shifts to identify the ^1H chemical shifts and then used the $^1\text{H} \rightarrow ^{13}\text{C} \rightarrow ^1\text{H}$ "round trip" polarization property of the HSQC experiment to find out the corresponding ^1H chemical shifts from ^{13}C chemical shifts.

The ^1H -NMR (Fig. 2) & ^{13}C -NMR (Fig. 3) spectra values have been tabulated (Table II). All the signals in NMR spectrum appeared to be slightly shifted up field after derivatization. The new the intense signals

at δ 1.3–1.57 were attributed to methyls of *t*-BOC in the ^1H -NMR spectrum. In the ^{13}C -NMR spectrum of *t*-BOC substituted novolac resin, the intense signal at 26.9–27.2 ppm is due to the presence of the three chemically equivalent methyl groups of *t*-BOC in the novolac microstructure (Fig. 3). This signal displayed positive intensity in the DEPT-135 spectrum indicative of a methyl carbon. The signal at 27 ppm is therefore ascribed to the three methyl groups of *t*-BOC moiety. The signals at 19.2–19.6 and 20.5–21.3 ppm in the unsubstituted novolac resin are attributed to the methyl groups attached to the aromatic rings of *p*-cresol and *m*-cresol, respectively.¹⁷ These signals appear shifted slightly upfield to 19.0 and 20.9 ppm, respectively after derivatization of the novolac resin and also display positive signal intensity in the DEPT-135. Moreover, a new peak at 83 ppm in ^{13}C -NMR was also observed which was assigned to be the *t*-carbon of the *t*-BOC group. The carbonyl of the *t*-BOC was observed at 152 ppm.

The HSQC experiment (Fig. 4), which identifies 1-bond ^1H - ^{13}C coupling shows a correlation between the methyls of the cresol at 1.95 and 2.16 with ^{13}C peaks in the DEPT-135 region at 18–21. The ^1H resonance at δ 1.36–1.57 shows a distinct correlation with the very high intensity peak at 27.3 ppm, attributed

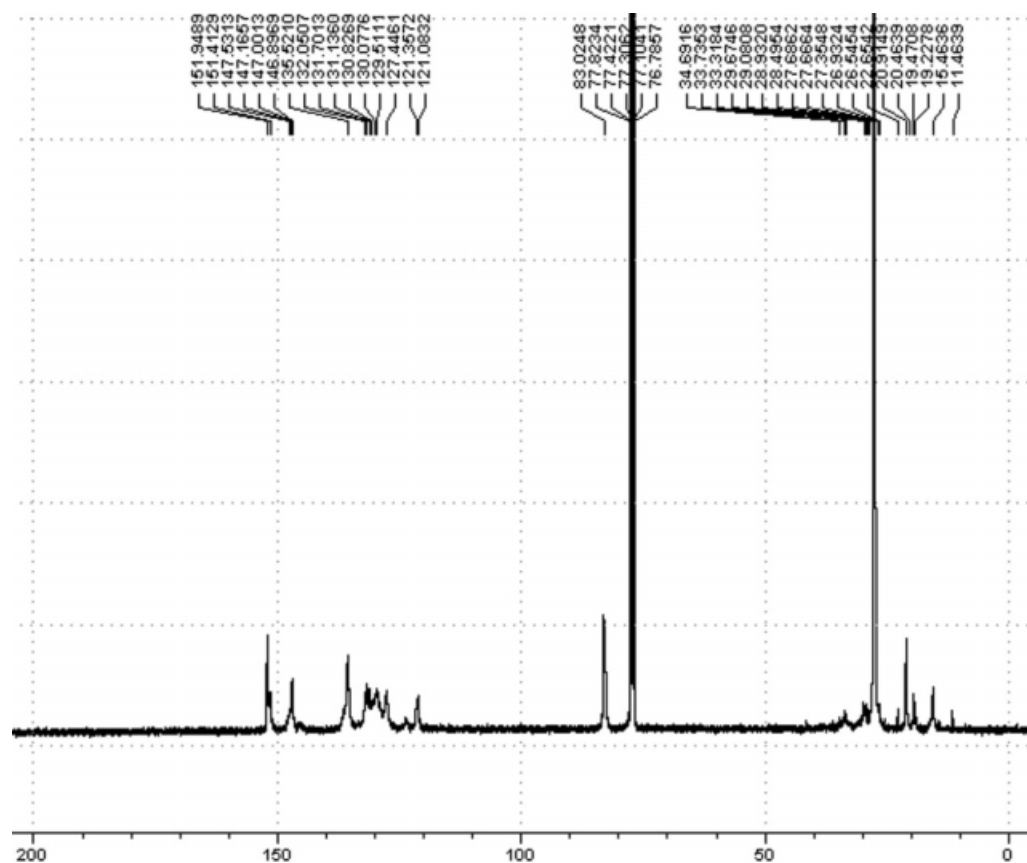


Figure 3 The ^{13}C -NMR spectrum of the derivatized copolymer.

to methyls of *t*-BOC. The benzylic methylene bridge ^{13}C resonances, with negative intensity in the DEPT-135 experiment show 3 distinct ^{13}C correlations with the ^1H resonance at δ 3.85.

As would be expected, in both low and high millisecond run of the COSY experiments (Fig. 5), no peaks were observed in the off diagonal region, suggesting no single bond coupling of the *t*-BOC group with the rest of the polymer backbone. In fact, the only cosy coupling would be from the adjacent proton of *p*-cresol. However, they cannot be made out as they are so close to the diagonal.

The HMBC experiment (Fig. 6), which indiscriminately identifies 2,3,4-bond ^1H - ^{13}C coupling provided further evidence to support the NMR assignments of the polymer. A correlation was observed between the tertiary carbon of the *t*-BOC

group at 83 ppm in the ^{13}C -NMR and the ^1H resonances between δ 1.36 and 1.57. A careful examination of this contour revealed the presence of three different types of *t*-BOC groups in the polymer chain. This is also supported by the range of ^1H resonances between δ 1.36 and 1.57 corresponding to the *t*-BOC group carbons between 27.3 and 27.7 in the ^{13}C -NMR. This can be attributed to the *t*-BOC groups on the *m/p* cresol units in the polymer chain and of the end groups which are in chemically different environments. The disparity in the HMBC cross-peak intensities between these three different *t*-BOC groups is evidenced in the inset (Fig. 6). It is clear that the $^1\text{H}/^{13}\text{C}$ cross-peak at δ 1.36/ 82.7 is of lower intensity than that of the $^1\text{H}/^{13}\text{C}$ cross-peaks at δ 1.52–1.57/83. Earlier it has been reported that, generally, the *p*-cresol group would be the end

TABLE II
Spectral Values of the Derivatized Novolac Copolymer

S. no	^1H -NMR (δ)	^{13}C -NMR (ppm)	DEPT-135	Assignments
1	1.4–1.57	27.3–27.7	Up	Methyl (s) of <i>t</i> -BOC
2	1.95–2.16	19–21	Up	Aromatic methyl(s) of cresol
3	3.85	29–33	Down	Methylene bridges
4	—	83	—	<i>tert</i> -Carbon of <i>t</i> -Boc
5	6.5–7.1	121–131	Up	Aromatic protons
6	—	152	—	Carbonyl of <i>t</i> -BOC

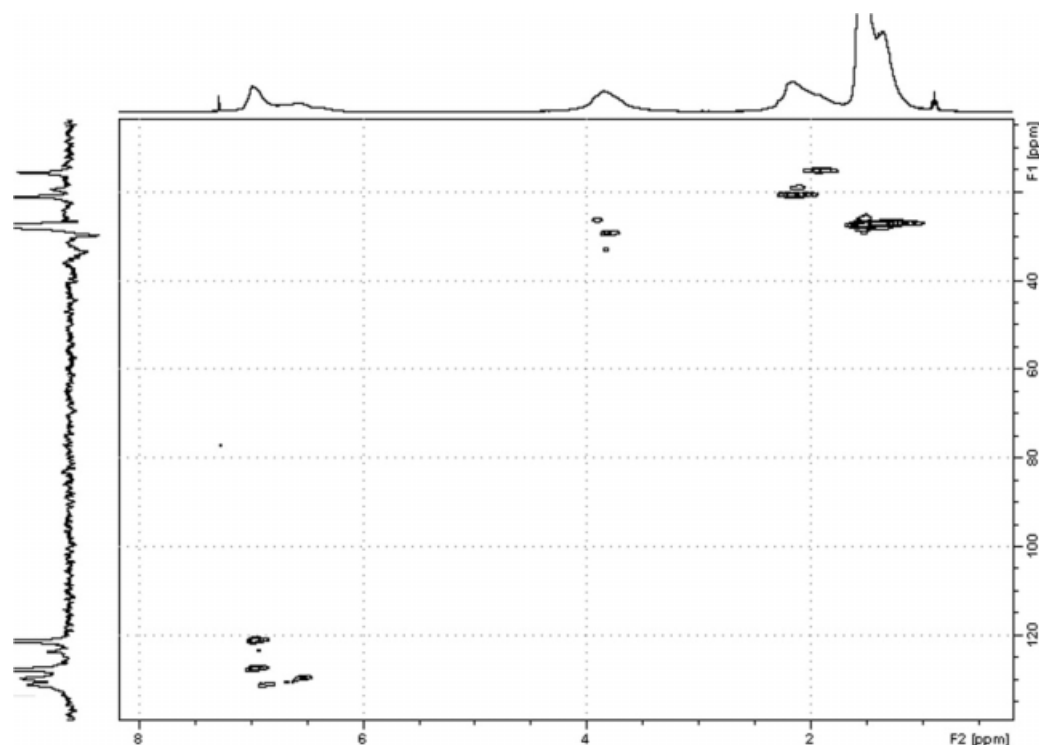


Figure 4 HSQC spectrum of the derivatized copolymer.

group in the *m/p*-cresol based novolac.¹⁸ We propose a greater degree of derivitization of *p*-cresol over *m*-cresol due to the greater acidity of the hydroxyl proton of the former as evidenced by its higher pKa value. Consequently, we assign the

lower intensity $^1\text{H}/^{13}\text{C}$ resonances at δ 1.36/ 82.7 to the terminal *p*-cresol *t*-BOC groups and the two higher intensity $^1\text{H}/^{13}\text{C}$ resonances at δ 1.52-1.57 /83 to the *p*-cresol and *m*-cresol *t*-BOC groups within the polymer chain, respectively.¹⁹

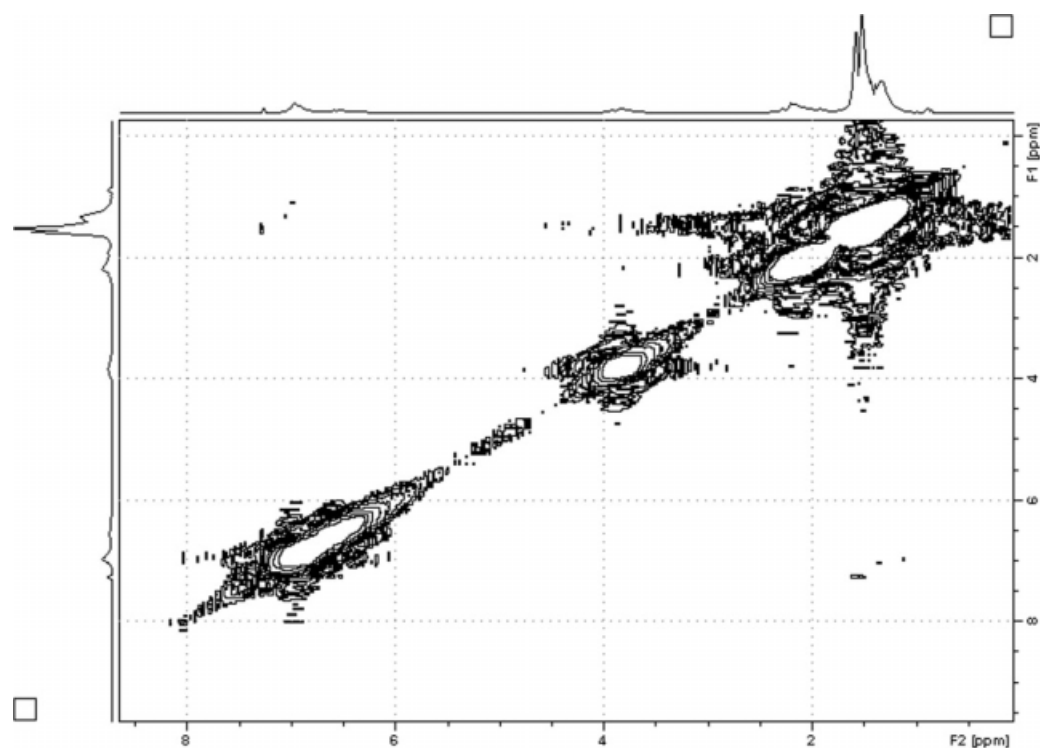


Figure 5 COSY spectrum (high intensity) of the derivatized copolymer.

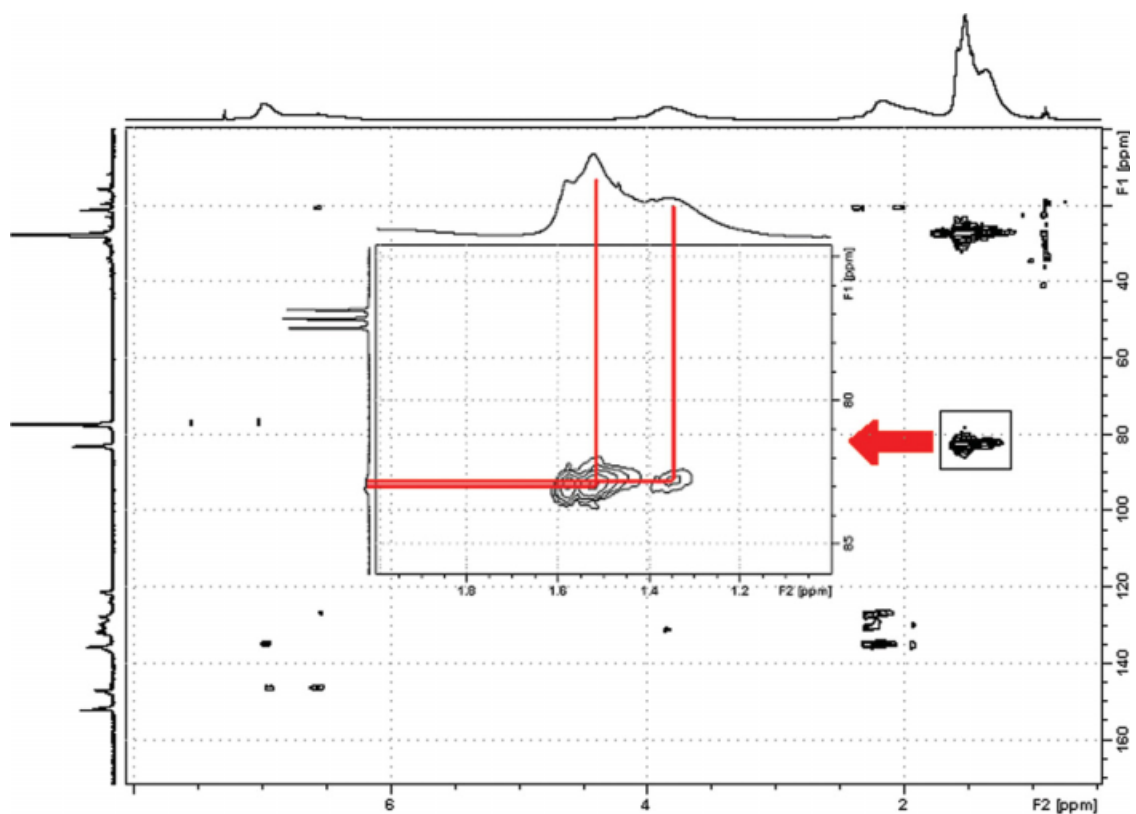


Figure 6 HMBC spectrum of the derivatized copolymer. Inset shows expanded region of cross-peak intensities between three different *t*-BOC groups. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

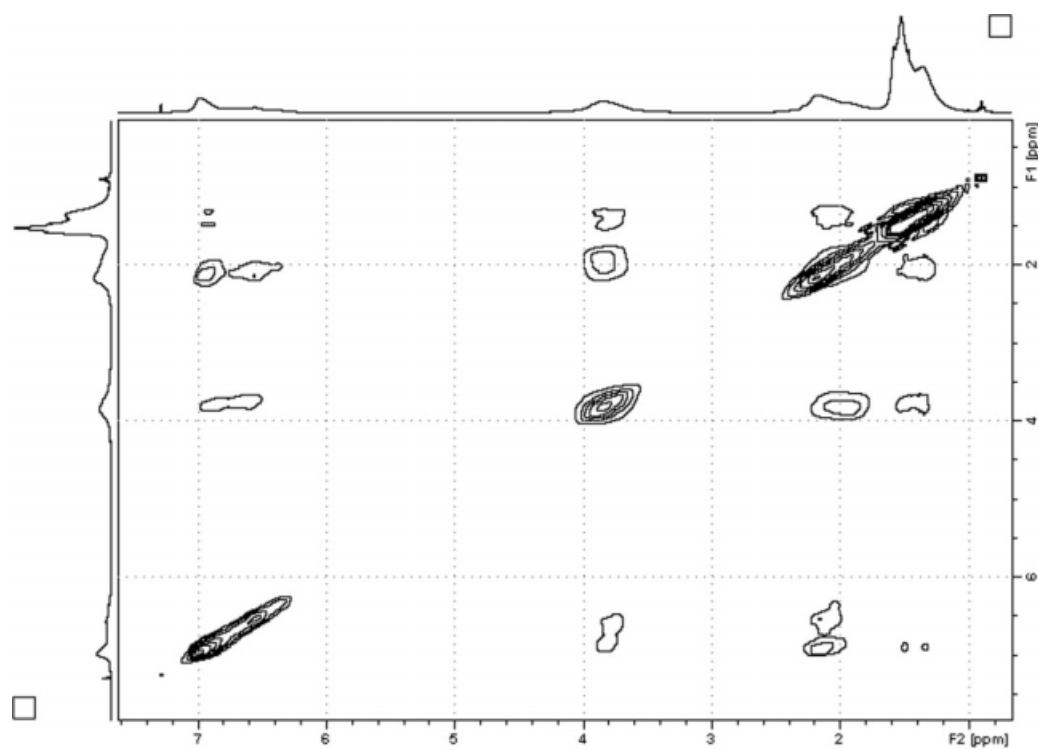


Figure 7 NOESY spectrum of the derivatized copolymer.

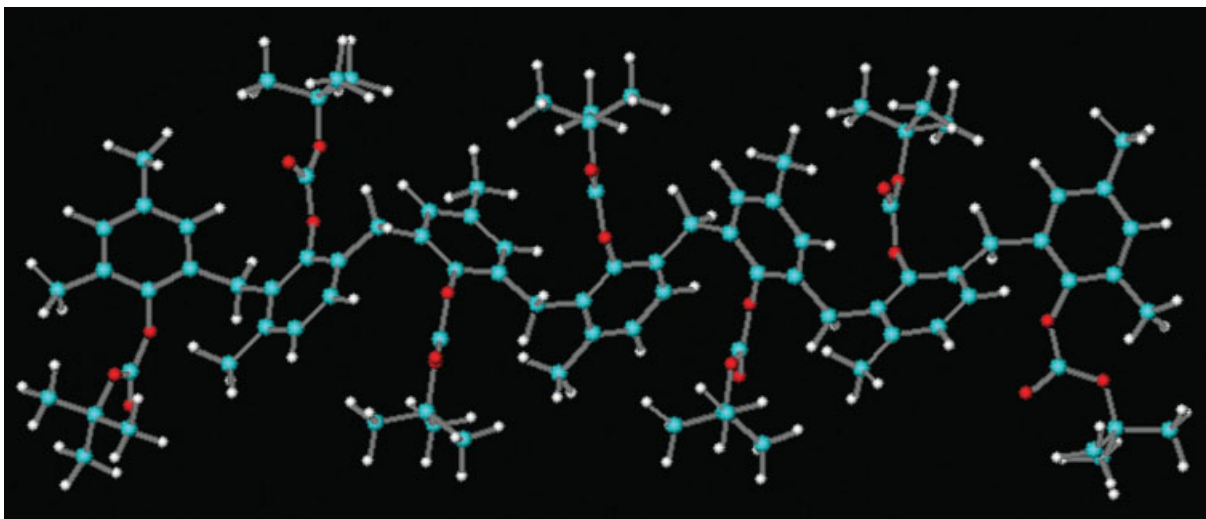


Figure 8 The minimum energy confirmation of the derivatized copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In the NOESY experiment (Fig. 7), which characterizes through space interactions, almost all peaks are seen to be correlating with each other. This can be possible only if the molecule has a “flip flop” structure, namely, the *t*-BOC group of each *p*-cresol unit is *trans* to the *t*-BOC group of a *m*-cresol unit. This is nicely supported by our molecular modeling study. Molecular modeling calculation was done using Hyper Chem Professional 6.03 software version. The minimum energy confirmation (Fig. 8) 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.

CONCLUSIONS

Our study shows that *m/p*-cresol-based *t*-BOC protected alternating “high ortho” novolac copolymer has been successfully derivatized using di-*tert*-butyl dicarbonate. In its IR spectrum, a peak for the carbonyl group was clearly seen along with an expected doublet for the *t*-butyl moiety. In the $^1\text{H-NMR}$ spectrum a new intense peak was seen at $\delta = 1.52$. In the $^{13}\text{C-NMR}$ spectrum, the *t*-butyl group was seen at 27 ppm and the tertiary carbon at 83 ppm. The carbonyl was observed at 152 ppm. These assignments were confirmed by the 2D-NMR spectroscopic techniques to probe in to the exact microstructure of the copolymer. All the microstructural detail reported in this work could make it a good candidate to serve as an e-beam photoresists.

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