

Evaluation of microlithographic performance of ‘deep UV’ resists: Synthesis, and 2D NMR studies on alternating ‘high ortho’ novolak resins

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Abstract. Lithographic evaluation of a ‘deep UV’ negative photoresist is discussed along with the synthesis of an alternating ‘high-ortho’ novolak resin. 2-D NMR studies (COSY, NOESY, HSQC, HMBC) on this resin are also discussed.

Keywords. Novolak resins; 2D-NMR; photoresist; lithography; microstructure.

1. Introduction

Micro electronic devices use microlithography for the fabrication of the ‘microchips’. Improvements in the resolution of the lithographic process lead to smaller, faster devices and hence it has been a goal of the micro-electronics related industries. Photoresists play a crucial role in ‘micro-miniaturization’ of semiconductor circuits. A photoresist mainly contains two components, a photoactive compound and a polymer matrix along with solvents and certain additives.^{1–4} Positive and negative photoresists are the two major classes of photoresists available commercially. 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).

In the case of a positive photoresist, post development, the exposed areas of the resist are washed off leading to a positive image. However, in the case of a negative photoresist following development, the exposed areas of the resist are retained, leading to a negative image.^{3,4} A major limitation of negative resists is swelling that occurs during development with organic solvents. Resist removal from the unexposed areas also degrades the sharpness of the features. For images with large spaces between features ($>10\ \mu\text{m}$) and post-baking may return the image to its original shape with slight distortions at the edges. However, images with

small separations ($<3\ \mu\text{m}$) are more challenging as resolution is lost when neighbouring images swell and coalesce with each other.⁵

Widely used polymers for these photoresists are the novolak resins which are acid catalysed phenol-formaldehyde polymers. However, this leads to random structures. The performance of a photoresist in microlithography critically depends on the nature of the novolak resin used. Recent research developments demand newer resists for high resolution geometry. A great deal of research is focused on the microstructure of novolak resins for obtaining high-resolution circuit geometry.⁵ Random novolak resins used earlier have been now replaced by ‘tailor made’ alternating and semi-alternating ‘high ortho’ novolaks. The existing resists are, therefore, frequently modified for finer geometries.^{1–4}

Aryl azide-novolak resin based negative photoresists^{6–9} obviate the problem of swelling with alkaline developers and also provide high resolution as well as high sensitivity. The use of aqueous alkaline developers also helps to overcome the environmental problems associated with earlier negative resists.

A negative photoresist consisting of 4, 4'-diazido-3, 3'-dimethoxybiphenyl and a novolak resin, called micro resist for i-line (MRI), has been evaluated. MRI has a high transmittance and a high resist contrast at i-line (365 nm). The development was done using tetra methyl ammonium hydroxide (TMAH), instead of an organic solvent.⁷ This resist combines features of both negative and positive photoresists and does not require any change in the instrumental set-up.¹⁰

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The role of novolak resins in promoting the dissolution of photoresists has not yet been fully explained.^{5,11} The novolak microstructure is, however, very crucial for the preparation of high-performance photoresists. The important governing factors include:

(i) The use of cresol-formaldehyde resins in place of phenol-formaldehyde novolak resins; (ii) the use of copolymers of *m*-cresol and *p*-cresol with an optimum percentage, and (iii) the use of 'tailor made' 'high ortho' alternating and semi alternating novolaks and 'tandem-type' novolak resins with an optimum polydispersity in place of random novolak resin.^{5,11}

A systematic study on novolak resins reveals that its composition, molecular weight and structure play a key role in lithographic performance. Low polydispersity ($PD = M_w/M_n$, where M_w = Weight average molecular weight and M_n = Number average molecular weight), 'high ortho' (this phrase is discussed) structure and cresol-formaldehyde resin in place of phenol-formaldehyde resin are preferred for positive photoresists.⁹ In recent years, 'tailor-made', 'alternating' or 'semi-alternating' and highly optimised *m*-cresol and *p*-cresol containing novolak resins have been used.¹⁰ 'Alternating' novolaks are suited for negative photoresists whereas 'semi-alternating' novolaks are good for positive photoresists.

The microlithographic technique depends critically on the differential solubility of exposed and unexposed parts of the photoresist, Photoactive components, and the matrix polymer component, hold the key to this differential solubility.¹² It is therefore important to probe the optimum structure of the novolak resins.

The preferred analytical tool for this purpose is NMR spectroscopy. Modern multinuclear NMR techniques have been increasingly deployed for determining the nature and degree of substitution patterns on different ring carbons in novolak resins. Most other spectroscopic techniques, with the possible exception of FT-IR spectroscopy, have limited success in this area of research.¹³

Since resolution of patterns is inversely related to the wavelength of exposure, emissions of high-pressure mercury lamps 436, 365 nm are giving way to systems using 248 nm, 193 nm and 157 nm excimer laser radiation. 'Deep UV' lithography involving the use of wavelength of around 254 nm is of considerable importance for fabricating solid state devices at micron resolution.^{1,2,14,15}

We report here the use of a novel photoactive component for development of 'Deep-UV' negative tone photoresist and 2-D NMR studies to evaluate its microlithographic performance.

2. Experimental

2.1 Synthesis of the Novolak Resin

m/p-cresol copolymer (MS-8) was synthesized using the standard procedure^{9,12} for two-step synthesis of novolak. 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. 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. 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 minutes 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 to the filtrate, dilute HCl was added drop-wise 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*.

2.2 Photoresist preparation

2.2a Composition A: Novolak resin (MS-8) and PAC-1 were dissolved in ethyl lactate, keeping solid content to 40% and homogenized overnight in dark and finally filtered using 2 micron pore size filters and stored in amber bottles.

2.2b Composition B: Novolak resin (MS-8) and PAC-2 were dissolved in ethyl lactate, keeping solid content to 40% and homogenized overnight in dark and finally filtered using 2 micron pore size filters and stored in amber bottles.

3. Materials 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 detectors. Calibration was done using polystyrene as standard. Molecular modelling calculation was done using Hyper Chem

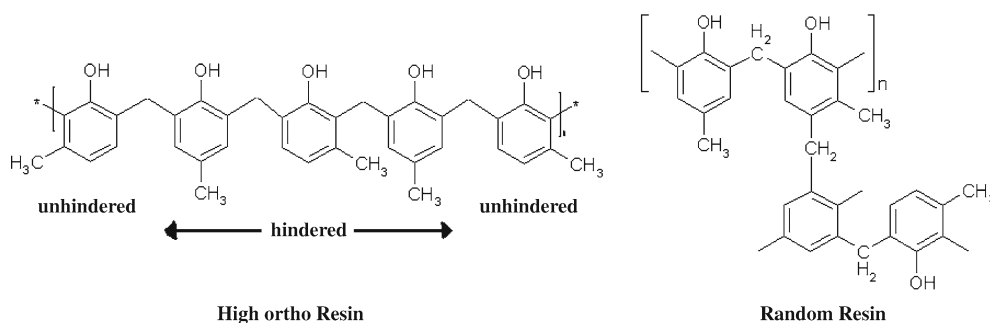


Figure 1. Random and 'high ortho' novolak with m/p-cresol and formaldehyde.

Professional 6.03 software version. The energy minimized structure was obtained by geometrical optimization of the structures using molecular mechanics force field; Mm+ and the Steepest Descent Algorithm.

4. Results and discussion

The common method for preparation of a novolak resin is condensation polymerisation between formaldehyde and phenol in presence of a catalyst.^{13,16} The prevalent method for synthesis of *random structure* novolak resins (figure 1) is the 'one-step' acid catalysed. In base catalysed reaction, resol type resins are obtained. The cresol/formaldehyde ratio plays a very important role in determining the nature of the end product.

By means of the 'two-step' procedure, one can not only get 'high ortho' linear novolaks (figure 1), but also 'tailor made' 'alternating' or 'semi-alternating' resins starting from appropriate phenolic precursors with desired percentages of p-cresol content in resin structure.^{9,17-19}

The determination of exact microstructure of a polymer is always a difficult task. In case of phenol-formaldehyde resins, a large number of possible reaction sites make structure elucidation really challenging. For example, a novolak resin of nine phenolic monomer units gives rise to 85,000 isomers of which 4401 are

linear.²⁰ Although several common analytical techniques such as FT-IR, UV, GPC, HPLC, DSC, etc. have been exploited for characterization of novolak resins, they lead only to certain bulk properties. For example, the molecular weight distribution in the resin could be calculated from the PD value obtained from GPC experiments,^{21,22} while the number of different fractions in the resin can be determined by HPLC,^{23,24} and for determining glass transition temperature (Tg) DSC is used.^{13,25} Therefore, studies using multidimensional NMR spectroscopy are necessary for obtaining several micro-structural details and are important for determining the nature and degree of substitution patterns on different ring carbons in novolak resins.

The average molecular weight (Mw) of the new novolak resin was determined to be 1385.3, the number average molecular weight (Mn) was 521.6 and PD was found to be 2.65. Thermal analysis of the copolymer showed a weight loss of 93.7% up to 600°C in three steps in its TGA/ DTA (for Supporting information see www.ias.ac.in/chemsci). In the first step, weight loss was 10% till 176°C this was followed by a plateau till 270°C, as no appreciable weight loss was observed. A sharp weight loss of 83% was observed in second step from 270°C to till 343°C, which is well-corroborated by its DSC (see supporting information) which suggest this to be an exotherm with $\Delta H = 119.3$ J/g. This is followed by an endotherm from 350°C which peaks at 367.34°C. The Tg was observed at 85.63°C.

Table 1. Spectral values of the novolak resin.

S.No.	PMR (δ)	CMR (ppm)	DEPT-135 intensity	Assignments
1	2.18–2.37	19–21	Positive	Methyls of m/p-cresol
2	3.92–3.94	29–33	Negative	Methylene bridges
3	6.73–7.12	112–138	Positive	Aromatic protons
4	-	136–138	Missing	Aromatic quat. carbons
5	-	148–153	Missing	Aromatic phenol

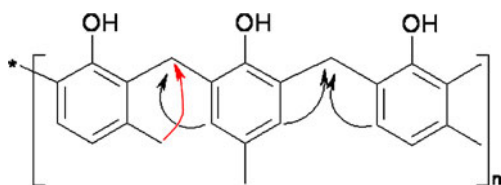


Figure 2. NOESY correlation of aromatic protons of cresol to methylene bridge of the novolak resin.

The IR spectrum showed the following peaks at 3284, 3012, 2920, 2862, 1701, 1610, 1577, 1502, 1465, 1375, 1257, 1147, 1099, 1045, 1008, 929, 860, 812, 725 cm^{-1} . Broad peak at 3284 cm^{-1} is assigned to the intramolecularly hydrogen bonded phenolic hydroxyl group and indicates the incorporation of cresolic monomers in the resin skeleton. The incorporation of *m*-cresol/*p*-cresol in the resin microstructure has been further proved by the methyl group asymmetric stretching frequency around 2920 cm^{-1} .

The absorption peaks at 1610–1465 cm^{-1} for in-plane skeletal vibration of the aromatic ring and 1257 cm^{-1} for C–O confirm the incorporation of cresolic monomer in resin microstructure. The $-\text{CH}_2-$ symmetric stretching absorption peak at 2862 cm^{-1} confirms the formaldehyde incorporation and the formation of novolak type skeleton.

The ^1H and ^{13}C NMR resonances are tabulated in table 1. ^1H NMR spectrum shows three main groupings of peaks. The group of peaks from δ 2.18–2.37 corresponds to the aromatic methyl groups while the broad resonance at δ 3.9 represents the benzylic $-\text{CH}_2-$ groups. Aromatic protons are observed in the region δ 6.7–7.1 ppm. The ^{13}C chemical shifts for the aliphatic methyl carbons are in the range of 19.6–20.7. The benzylic methylene carbons are seen to resonate in the range of 31–33 ppm. Aromatic carbons are observed at 112–155 ppm.

The resonances in the aliphatic regions are easily identified from the signs of their signal intensity in the

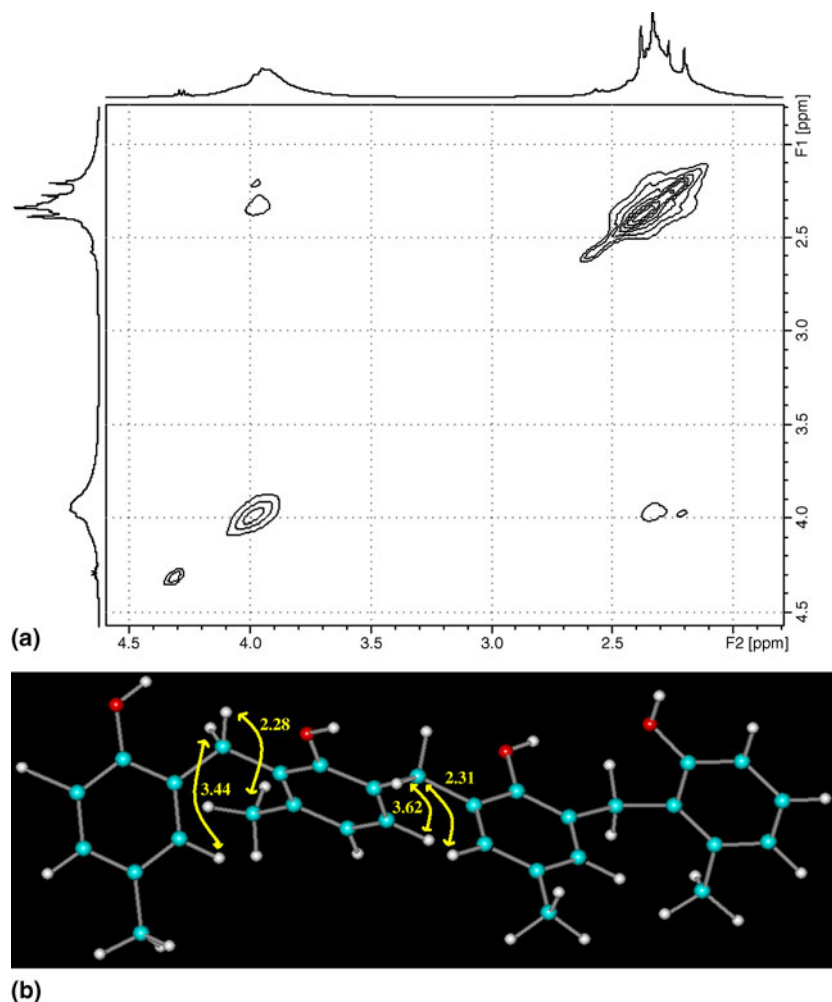


Figure 3. (a) NOESY methyl to methylene of the novolak resin. (b) Methyl to methylene bond distance of the novolak resin are observed in NOE range.

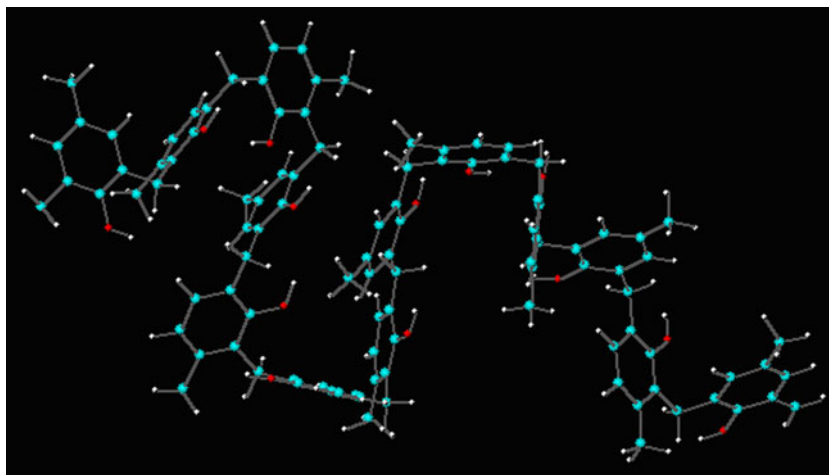


Figure 4. Energy minimized structure of the novolak resin. The cyan colours represent carbon atoms, whereas white and red colours represent hydrogen and oxygen, respectively.

DEPT-135 spectrum (see [Supporting information](#)). The four peaks at 19.6–20.7 ppm with positive intensity are attributable to the hindered and unhindered (namely, the in-chain and terminal) methyls of *m/p*-cresol (figure 1), while the two peaks with negative intensity at 31.2 and 33.1 ppm represent the methylene bridges, as would be expected from an alternating structure. The aromatic region of the DEPT-135 displays positive intensity peaks at 115 ppm and 131 ppm, clearly indicating two sets of aromatic C–H.

These assignments have been further confirmed by our HSQC experiment (see [Supporting information](#)). Using the HSQC spectrum, the ^1H NMR chemical shifts corresponding to ^{13}C NMR chemical shifts were identified. The ^{13}C NMR chemical shifts were seen to be correlated well with the ^1H NMR chemical shift at δ 2.18 to 2.37 ppm, thereby identifying the ^1H chemical shift of methyl group of *m/p*-cresol. Peaks appearing around 19.6 and 19.7 ppm and those at 20.6 and 20.7 ppm are ascribed to the 'unhindered' and 'hindered' $-\text{CH}_3$ group of *m/p*-cresol in the resin.^{26,27}

Two separate sets of peaks were observed for the aromatic carbons in their ^{13}C -NMR spectrum and are found correlating well in the HSQC with the peaks at δ 6.7–7.1. This correlation has made it possible to divide the aromatic protons into two groups δ 6.7–6.9 and δ 7.0–7.1. No separate correlations of the methyl of the cresols were observed with any subset contours. The oblong correlation contour observed showed the correlation of all the methyl protons with methyl carbon observed at 19.6–20.7. The HMBC (see supporting information), which shows multiple bond correlations also showed all the methyls correlating with both the sets of aromatic peaks in the ^1H NMR and ^{13}C NMR

spectra. Comparing the peaks at 19.6 and 19.7 ppm on one hand to the peaks at 20.6 and 20.7 ppm on the other hand, we see that the former group can be identified with the 'unhindered' methyls of terminal cresols, whereas the peaks at 20.6 and 20.7 ppm are due to 'hindered' methyls of the in-chain cresols. Furthermore, HSQC spectrum also shows that the two contours at 31.2 and 33.1 ppm correlating with δ 3.9 are due to the different types of methylene bridges arising from the arrangement of the *m*-cresols with *p*-cresol. This is seen to be further confirmed by the NOESY experiment. In the NOESY experiment (see [Supporting information](#)), two distinct cross-peaks are observed in the aromatic region from the methylene bridge resonances; however, the two contours are not of equal intensity. This is rationalized on the basis of our 'alternating' polymer structure (figure 2), according to which aromatic protons of *m/p*-cresol are correlated through space to the methylene bridges on one side (black arrows), and aromatic protons of *p*-cresol and the methyl of the *m*-cresol correlate to methylene bridge on the other side (red arrow).

Table 2. Resist preparation.

S.No.	Process steps	Conditions
1	Polymer:PAC	5: 1
2	Solvent	Ethyl lactate
3	Homogenization	36 h
4	Spin coating	3000 rpm for 25 seconds
5	Baking	80°C/40°C
6	Masks size	up to 5 μm
7	Exposure	Hg-Xe lamp 500 W for 1 min
8	Development	Tetra Methyl Ammonium Hydroxide (TMAH)

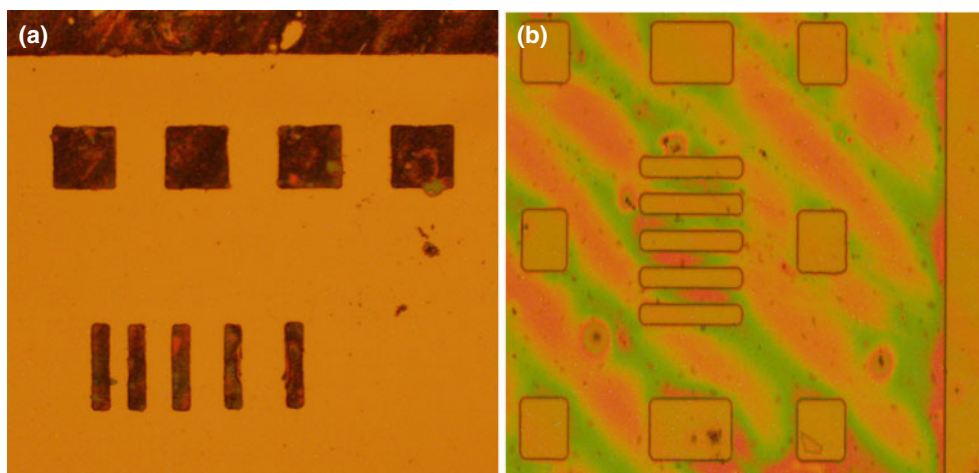


Figure 5. Optical micrograph of the resist with PAC: (a) Composition A and (b) Composition B.

This is supplemented by the contour signals for methyl to methylene in the NOESY.

This is further illustrated by an expansion of the NOESY (figure 3a), which shows the NOE of the methyl to methylene, it is clearly evident that the methyl protons of m-cresol exhibit the stronger of the two NOE cross-peaks observed from the methylene protons (figure 3b). An independent assessment of the structure implied above comes from our energy minimized structure in 3D space (figure 4) based on molecular modelling. According to these calculations, the distance between the methyl to methylene is 2.28 Å and the aromatic protons to methylene is 3.44 Å and 3.62 Å; all these values are in the observable NOE range.

The lithographic performance of the new photoresists prepared using the novolak MS-8 and aryl azides²⁸ (PAC 1 and PAC 2) was evaluated. The details of the lithographic experiments are tabulated in table 2. A typical pattern obtained on a silicon wafer using the two new photoresists, after exposure and development, is shown (figure 5). The developed wafers were observed under the optical micrograph. Both the resist compositions showed negative tone behaviour. The Square box (figure 5) is of 70 μm. The composition A (figure 5a) showed a contrast but sharp resolution was not obtained. Further development of the film led to the loss of pattern. The film thickness was less than 1 μm. However, the resist tends to wash away very fast. In the case of composition B (figure 5b), better film formation was observed. Film thickness was 1–2 μm with improved patterns and sharper resolution were obtained.

5. Conclusions

One- and two-dimensional NMR methods have been used to assign the microstructure of a new m/p-

cresol based alternating ‘high ortho’ novolak resin. This novolak resin is then evaluated for its potential in microlithography. Two compositions (A and B) were prepared using the resin (MS-8) and two different Photo Active Components (PACs). The results of our assignment could be significant for evaluating lithographic performance of the photoresists. The use of NMR techniques shows that the resin microstructure is ‘alternating’ and ‘high-ortho’ in nature. The ‘alternating’ nature of the resin ensures the optimum distribution of the cresolic component throughout the resin and molecular weight distribution of the polymer, which plays a very important role in photoresists.

Supporting Information

For supporting information, see www.ias.ac.in/chemsci.

List of figures in Supporting information:

- 1) TGA/DTA plot of the novolak resin
- 2) DSC plot of the novolak resin
- 3) DEPT-135 spectrum of the novolak resin
- 4) HSQC of the novolak resin
- 5) HMBC of the novolak resin
- 6) NOESY of the novolak resin.

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