

# Photoresists for Microlithography

## 2. The Role of Polymer Microstructure

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**Characteristics of photoresists used in microlithography are highlighted. The microstructure of the matrix polymer used in these photoresists is critical for ensuring good lithographic performance and the same can be evaluated by using modern NMR spectroscopic techniques. It is now well-known that highly ordered 'alternate' and 'semi-alternate' tailor-made novolaks lead to better performing photoresists.**

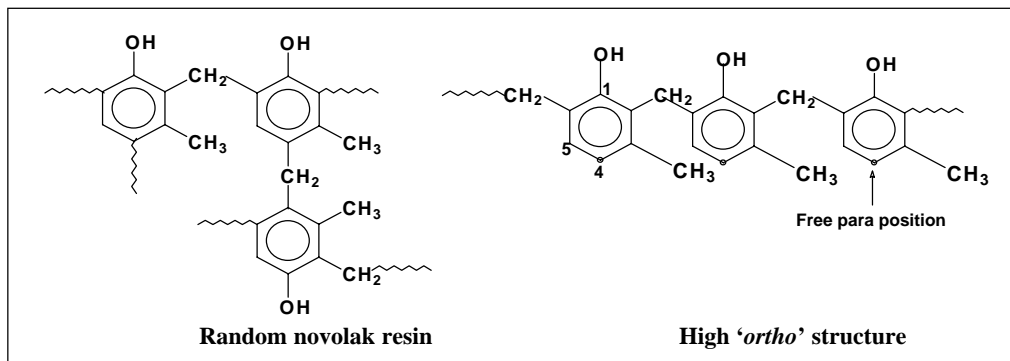
### Introduction

In the previous part of this article, we have described positive and negative photoresists and the main steps involved in the microlithography process. In this part we emphasise the importance of using structurally well-defined novolak resins for the preparation of photoresists. In his pioneering article Hanabata [1], has clearly spelt out the essential points required for the design and conception of high performance photoresists. The last decade has seen the development of modified procedures for tailor-making such well-defined novolaks, whose microstructure plays a vital role in determining their lithographic performance. Modern nuclear magnetic resonance spectroscopic techniques have been used successfully for correlating the lithographic performance of photoresists with their molecular structure.

### Novolaks

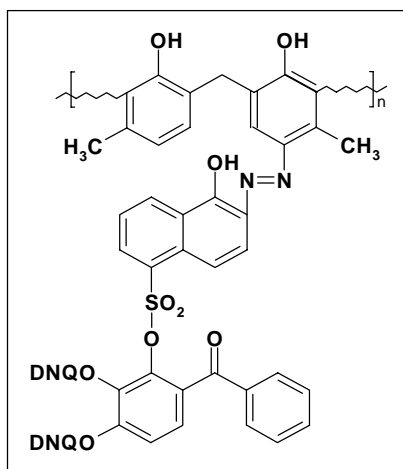
Novolaks are phenol-formaldehyde resins obtained by acid/base catalyzed polymerization of phenol and formaldehyde. Later for better lithographic performance cresol-formaldehyde resins replaced the phenol-formaldehyde resins. The novolak resins used





**Figure 1.** Random and linear 'high ortho' novolaks with *m*-cresol and formaldehyde. In 'high ortho' novolaks, the percentage of *o*-*o'* methylene bridging is very high compared to *o*-*p'* or *p*-*p'* bridging. This ensures more free/vacant *para* positions.

**Figure 2.** The azo-coupling between free *p*-position of cresol in novolak with diazo group of DNQ.



in the past were random structures but are now replaced by linear 'high ortho' novolaks (Figure 1), for improved micro-lithographic performance.

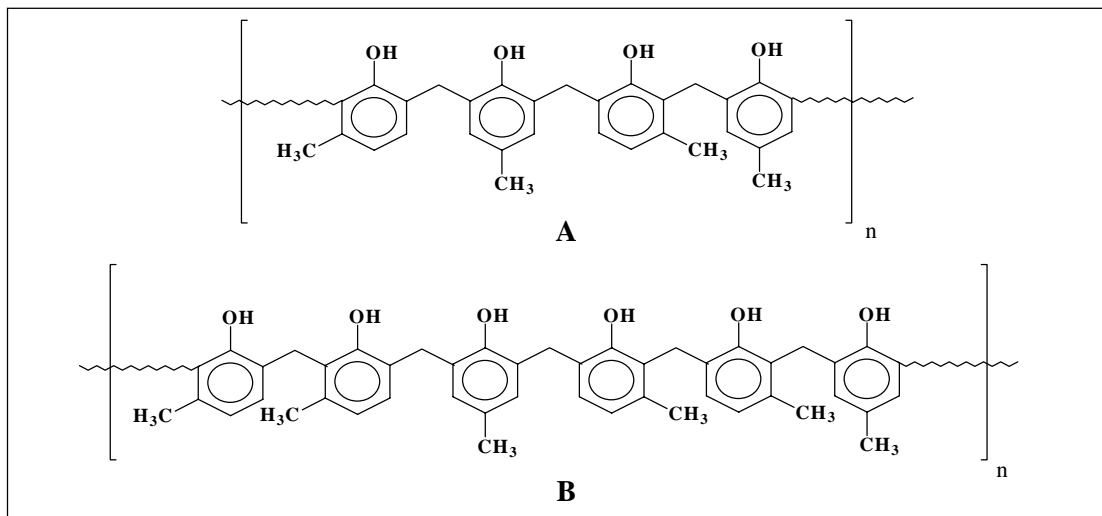
Hanabata of Sumitomo Company, Japan showed that the performance of a photoresist depends critically upon the following main factors:

### i) Methylene bridging position

Novolak resins with 'high ortho' structure have more methylene bridging in the *ortho* position and therefore more free *para* positions. These free positions can undergo azo coupling reaction in the unexposed part with the photoactive component, viz. the diazo compound. The consequent increase in molecular weight could make the unexposed part more insoluble in the alkaline developer. Thus for obtaining a higher differential solubility between the exposed and the unexposed regions, the azo-coupling reaction in the unexposed part can be quite important (Figure 2). We should remember that earlier explanations for pattern formation were based solely on the reactions occurring in the exposed regions alone.

### ii) Isomeric structure of cresol

Novolak copolymers based on two different cresols with formaldehyde are reported to be better for photoresist composition than *m*-cresol-formaldehyde resin. The sta-

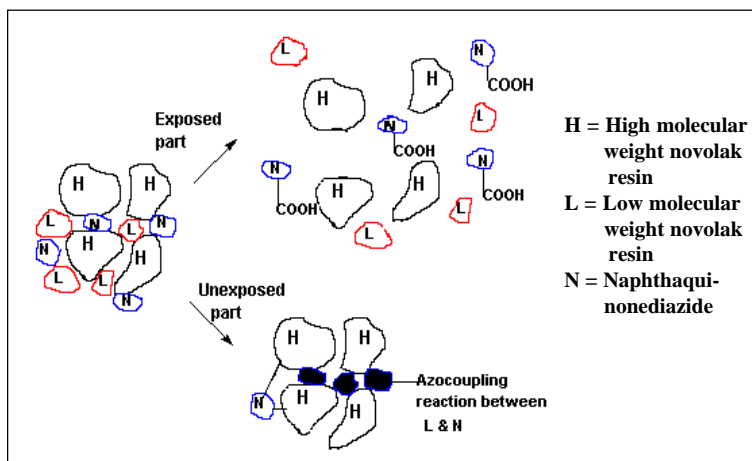


**Figure 3.** Alternating 'A' and semi-alternating 'B' novolaks based on *m*- and *p*-cresol. The former are more suited for negative photoresists whereas the latter are good for positive photoresists.

tistical alternating and semi-alternating novolaks of *m*-cresol and *p*-cresol are increasingly being used for negative and positive photoresist formulations, respectively (Figure 3).

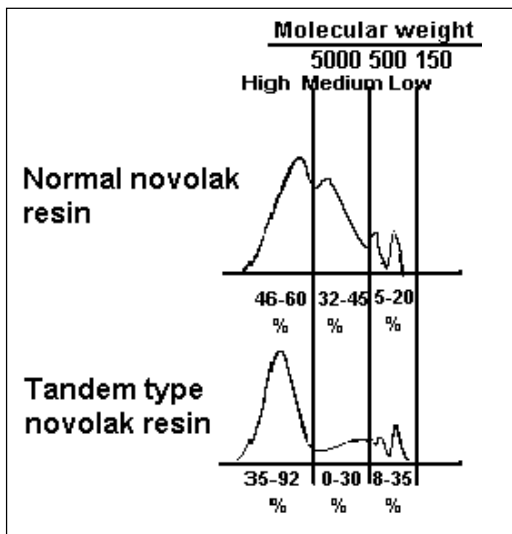
### iii) Molecular weight and molecular weight distribution

It has been found that the presence of both low and high molecular weight fraction is desirable for a good positive photoresist formulation. A *stone-wall model* (Figure 4) has been proposed by Hanabata, which emphasizes that a base catalysed azo



**Figure 4.** The 'Hanabata's stone-wall' model of mixture of low and high molecular weight novolaks with DNQ. The free para positions in cresols of low molecular weight novolaks couple well with diazo groups of DNQ in the unexposed parts and the high molecular weight novolaks make a protective layer which render solubility of the low molecular weight novolaks in the unexposed part.

**Figure 5.** The normal and 'tandem-type' novolak resins. In 'tandem-type' novolak resins the medium molecular weight fraction is much less than in normal novolak resin.



coupling reaction between diazonaphtha-quinone and the low molecular weight novolak fractions occurs during the development step, especially in the unexposed region, which retards dissolution in the unexposed parts.

#### iv) Tandem-type systems

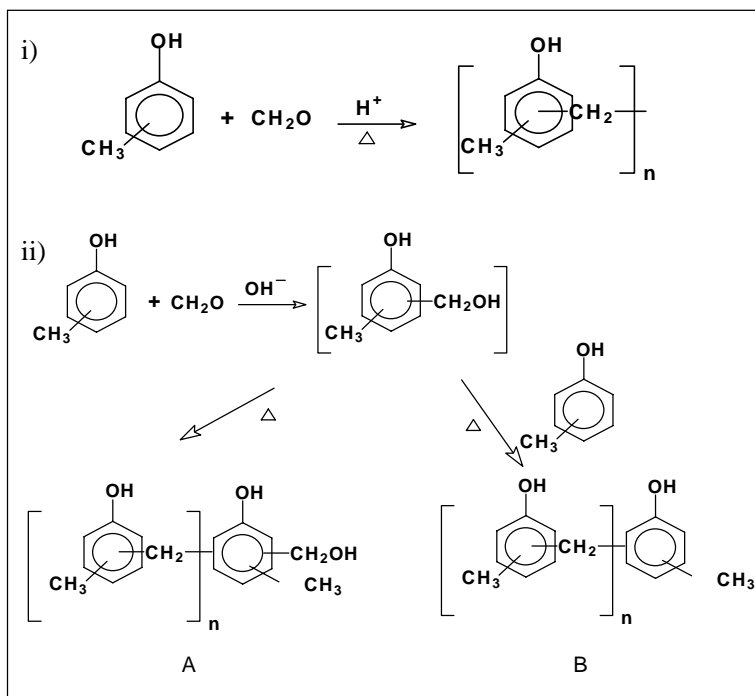
'Tandem-type' novolaks are mixtures of high and low molecular weight resins with an optimum distribution of molecular weight and are better suited for designing high performance positive photoresists. These contain less of the medium molecular weight fractions, which are believed not to participate in the dissolution promotion reactions (*Figure 5*).

#### Tailor-made Novolaks

Novolak resins are generally prepared by charging formaldehyde and phenol/cresol in different proportions in presence of acid or base at elevated temperatures. The polymer is often formed very rapidly. A heavily crosslinked network structure results, with little control over the chain formation or incorporation of different monomers in the novolak microstructure (*Figure 6*).

The one-step synthesis of novolak resins has been replaced by





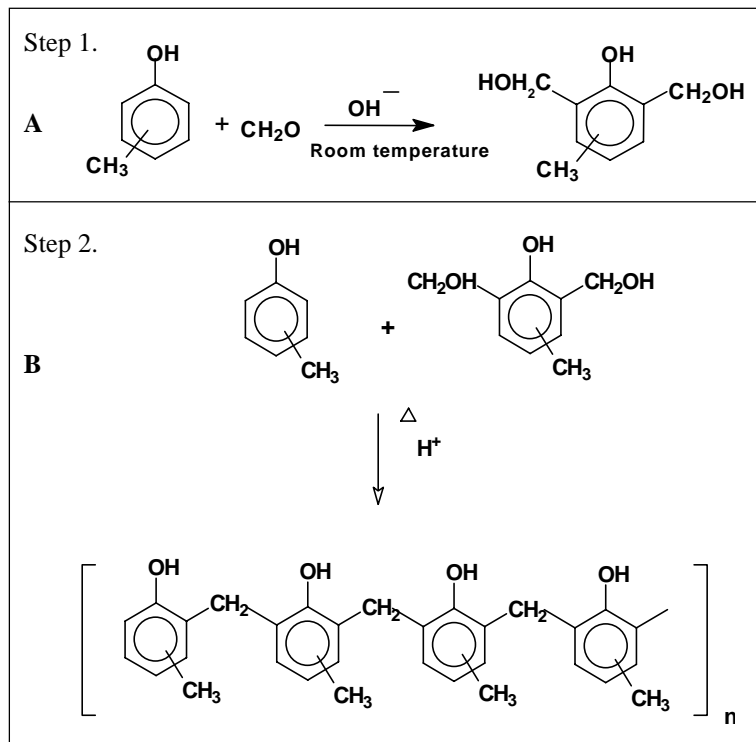
**Figure 6.** (i) The acid catalysed one pot synthesis of novolac resins and (ii) the base catalysed novolac resin formation. In case of base catalysed novolac resins, the lower molar ratio of starting monomeric phenol to formaldehyde results in resol type compounds (A), whereas the higher content of phenolic precursors gives novolac resin (B).

the two-step procedure to improve control over chain structure and formation [3]. In the first step, the formaldehyde is allowed to react with phenol/cresol at room temperature to make the bis-hydroxymethylated phenolic or cresolic compounds (*Figure 7A*). The ratio of phenol to formaldehyde is maintained at 1: 2.2 to avoid any side reaction; the temperature is also kept low to restrict oligomer formation of phenolic compound with formaldehyde in presence of base. In the next step, the desired precursor is added in the bis-hydroxymethylated compounds in the 2: 1 ratio and the mixture refluxed at 140-150°C for the polymerisation to occur (*Figure 7B*). The polymers are then subjected to steam distillation to wash out any unreacted monomers.

The polymers, particularly the synthetic polymers are always a collection of oligomers and polymers of different chain lengths. If the chain length (which is directly proportional to the molecular weight) is small, then it is called an oligomer, whereas the longer chains are the polymers. The different chain lengths or the range of molecular weight in a polymer sample is character-

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**Figure 7. (A) is base catalysed bis-hydroxymethylated cresol (BHMC) formation at room temperature and (B) is polymerisation step at elevated temperature with selected precursors and BHMC.**



ized by polydispersity (PD) value. In the ideal case, when all the polymer chains are of equal lengths, the PD value is one. The higher the value of PD, wider is the distribution of chain lengths in the polymer sample. For good lithographic performance, one needs novolak resins with an optimum PD value as explained earlier. Fractionation of novolak resins to retain only the high and low molecular weight fractions is an art by itself and there are innumerable patents describing such separations.

### Lithographic Performance of Photoresists and NMR

In the last two decades, it has become clear that most structural information that control the polymer morphology, which are very critical for good lithographic performance of photoresists, can be acquired using modern NMR techniques [4]. The 'high *ortho*' novolak resins show sharp  $^1\text{H}$ -NMR signals compared to the broad and overlapping signals of random novolak resins (Figure 8).

The quantitative estimation of linearity of a polymer is possible using 1-D and 2-D NMR techniques. Based on these percentage incorporation of different monomers in the polymer, microstructure can also be estimated, as also the different isomeric populations in the polymer. NMR spectra of model oligomers are very useful for this purpose.

### Lithographic Process and Device Making

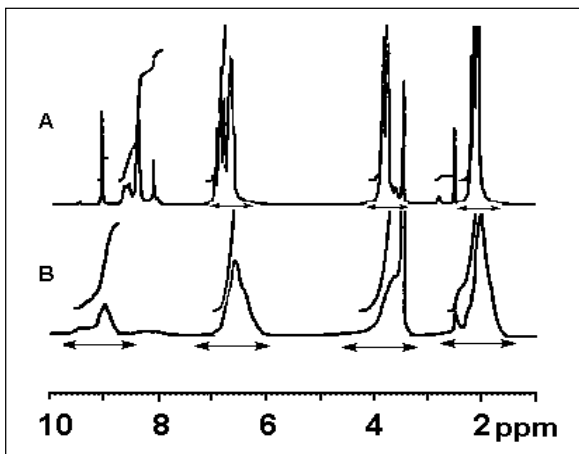
The lithographic process consists of the following important steps. The characteristic processing steps used for a typical positive photoresist are given in *Table 1*.

From this stage onwards to the making of an IC need many more steps depending upon the nature and the degree of complexity of the electronic device to be made [5].

The photograph in *Figure 9* shows a device made based on our photoresist, for the construction of a night vision camera.

### Conclusions

Tailor-made novolaks have led to the preparation high quality photoresists. The microstructure of these resins holds the key for good lithographic performance. Modern NMR spectroscopic techniques have been employed to determine the exact compo-

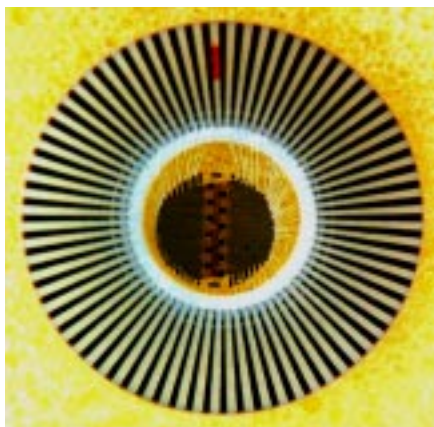


*Figure 8. 'A' is an <sup>1</sup>H-NMR spectrum of a 'high ortho' novolak, whereas 'B' is for a random novolak resin. The peaks in the former are much sharper than in the latter.*

Process steps	Typical conditions
Spin coating	2000-3000 rpm; 20sec.
Pre-bake	60-90° C; 30 mins.
Exposure	200-300 watt UV light for 10-15 sec
Developer	Tetramethyl ammonium hydroxide (TMAH)
Post-bake	60-90° C; 30 mins
Etching	With HBr-Acetic acid, Br <sub>2</sub> - HBr, etc.

*Table 1.*





**Figure 9.** The device for a night vision camera made using our photoresist.

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#### Keywords

High ortho novolak resins, NMR and lithographic performance, device fabrication.

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sition and microstructure of the polymer that in turn govern the polymer morphology. It has been estimated that about 30% of the cost of VLSI chip fabrication is due to photolithography (PLG), wherein the most crucial role is played by photoresists. Concurrent research and development is taking place in the improvement of exposure tools and in lenses and mirrors employed in these processes. Newer exposure sources, more accurate measurement tools, different techniques of mask fabrication and materials for production of masks for different wavelength ranges are being devel-

oped. Cost reduction has to keep pace with shrinkage of device geometry. For obtaining the precise line width control and higher aspect ratios of substrate topography, eventually all the steps of microlithography need to be transformed to the fully automated mode, while fine-tuning will be done through careful control and modulation of the machines used.

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#### Suggested Reading

- [1] M Hanabata, Y Uetani and A Furuta, *J. Vac. Sci. Technol.*, Vol.B7, pp.640-650, 1989.
- [2] G M Wallraff and W D Hinsberg, *Chem. Rev.*, Vol.99, pp.1801-1822, 1999.
- [3] G Baehr, U Westerwelle and G Gruetzner, *Proc. SPIE- Int. Soc. Opt. Eng.*, Vol.3049, pp.628-638, 1997.
- [4] MA Khadim, MD Rahman and D L Durham, *Proc. SPIE- Int. Soc. Opt. Eng.*, Vol.1672, pp.347-359, 1992.
- [5] *Microlithography Science and Technology*, Edited by James R Sheats, Bruce W Smith, Maecel Dekker Inc., 1998.