

## **Synthesis of Non-linear Optical Epoxy-based Polymer Used As A Negative Photoresist.**

**Dipak Kumar Mukhopadhyay**

*Institute of Science & Technology, C.K.Town, West Bengal, 721201, India*

---

### **Abstract:**

*4-nitro phenyl azo resorcinol was synthesized by the coupling reaction of 4-nitro benzene diazonium chloride with resorcinol and then it was neutralized with sodium acetate. The epoxy-based monomer was synthesized by the treatment of 4-nitro phenyl azo resorcinol with epichlorohydrin and potassium carbonate in the solvent medium of acetone and refluxed for 12h. After cooling, the reaction mixture was poured into water. Polymer was synthesized by the treatment of epoxy-based monomer with aniline at 100<sup>o</sup>c for 24h. The obtained oligomer was purified by triple reprecipitation form THF to hexane. The oligomer functionalization was carried out by treating the oligomer with 4-azido cinnamic acid in presence of DMAP and DCC in the solvent medium of THF.*

### **Keywords:**

*4-nitro phenyl azo resorcinol, epoxy-based monomer, oligomer, functionalization of oligomer.*

---

Date of Submission: 01-03-2023

Date of Acceptance: 13-03-2023

---

### **I. Introduction :**

A predominant number of researchers on polymer materials exhibiting the second order non-linear optical (NLO) activity dealt with guest-host systems or side-chain polymers where chromophore groups in side chains are covalently attached to the back bone. The benefits of the latter class of polymers are generally recognized due to a number of factors. The interest in these materials is caused by a possibility of obtaining the polymer systems with higher nonlinearity and better temporal and thermal stability of the NLO response as compared to guest-host composites with chromophore guest molecules dispersed in host polymer matrices. The determining advantage of side-chain polymer is that a high concentration of chromophore groups can be achieved without crystallization, phase separation or the formation of concentration gradients inside the polymer matrix. In addition, dye-polymer covalent attachment is shown to be highly efficient for minimizing near-IR losses.

Side-chain NLO polymers based on various classes of polymer matrices including those with low T<sub>g</sub>, relatively high T<sub>g</sub> and high T<sub>g</sub> have been synthesized and studied. Polymers with high T<sub>g</sub> are considered promising as they provide high orientational stability of chromophore groups achieved during thermo-poling of polymer films under an external electric field producing their non-centrosymmetric organization necessary to exhibit the second-order NLO activity. However, to provide chromophore orientation in such high T<sub>g</sub> matrices, the poling procedure should be performed at high temperatures above or close to the matrix T<sub>g</sub> value, that may cause chromophore destruction during poling. Further more, polymers with high T<sub>g</sub> values sometimes possess a rather high polymer chain rigidity, leading to poor film forming properties, brittleness, etc. Thus a choice of a suitable polymer backbone is a complicated task. One of the most popular classes of chromophores contain azo benzene moieties though they are characterized by rather moderate nonlinearities. The reported synthetic strategies used for chromophore binding to the polymer back bone involve either the polymerization of azobenzene-functionalized monomer, or a polymer reaction, also called post-functionalization, which allows pendent azo groups to be attached. The first method is sometimes preferable since it is rather simple and makes it possible to introduce chromophore groups into each monomer unit. However, chromophore-containing monomers are often difficult to polymerize, they produce as a rule, low-molecular weight polymer with poor film-forming properties. The second method has no these drawbacks but it involves polymer functionalization reactions proceeding often with limited yields.

Epoxy-amine matrices are intensively used for the synthesis of polymer materials with the second order NLO response due to their easy processing and poling, as well as low optical losses observed for this class of polymers. Usually, chromophore groups in such polymers are covalently attached to the main chain, so that donor end-group is embedded into the main polymer chain. Such materials are characterized by rather high values of NLO coefficients, in particular, when chromophores with acceptor nitro and tricyanovinylene groups were used.

The increasing use for high density integrated circuits has created a need for process simplification in semiconductor device fabrication in order to reduce material and labour costs and to achieve lower defect levels and improved product reliability. It is an object of this invention to provide a new negative photoresist that can be developed with aqueous base, which includes epoxy-amine matrix as a base polymer and has a photoactive moiety chemically bonded to the base polymer. According to this invention, single component epoxy-amine polymers are synthesized by covalently bonding an azide group carrying carboxylic acid to the epoxy-amine polymer. The resultant negative tone resist materials are aqueous base developable. The resist may be patterned using DUV. The negative photoresist of this invention comprise azide functionalized epoxy-amine polymers in which a photoactive element is chemically bonded to the backbone of the base polymer. Synthesis of the polymers is achieved by an esterification reaction of an aromatic azide carrying carboxylic acid group with the hydroxyl group of the epoxy-amine polymer.

## **II. Experimental**

### **2.1 Synthesis of 4-nitro phenyl azo resorcinol:**

To 20mmol of 4-nitro aniline, 5.4 ml of concentrated hydrochloric acid and 20ml of water were added. The mixture was placed in the ice-bath. To the cooled mixture, a solution of 20mmol of sodium nitrite in 3 ml of water was added dropwise and the resulting solution was stirred at a temperature between 0<sup>o</sup> and 5<sup>o</sup>c within 15 minutes. Then, the solution containing 20mmol of resorcinol in 12ml of methanol was added dropwise. The reaction was carried out for 30minutes and was neutralized with sodium acetate. After the temperature was raised to room temperature, the mixture was stirred for 1h. The product was filtered, washed with large amount of water and dried under vacuum.

### **2.2. Synthesis of epoxy based monomer:**

To a 50ml round bottom flask equipped with stirring bar, reflux condenser and nitrogen inlet, diazo resorcinol (0.0064M), epichlorohydrin (2.0ml, 0.026M) and potassium carbonate (1.8g, 0.0128M) were added. The reaction mixture was dissolved in 15ml of acetone with stirring. The reaction mixture was purged with nitrogen and heated to reflux for 12h. After cooling the reaction mixture was poured onto 200ml of water.

### **2.3. Synthesis of polyether polyol on the basis of epoxy-based diazo resorcinol and aniline:**

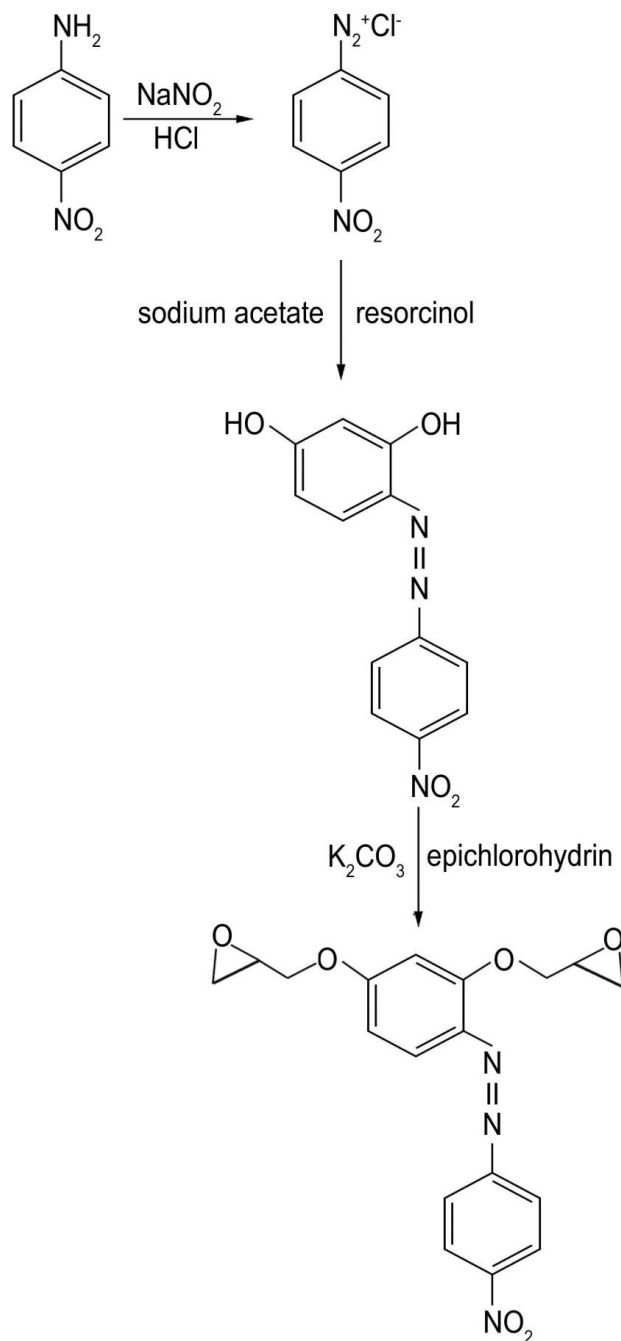
2.9 mmol of epoxy monomer and 2.9 mmol of aniline were taken into an ampoule thoroughly shaken at room temperature and purged with argon for 15 minutes. The ampoule was sealed and placed into an oven. The reaction was carried out at 100<sup>o</sup>c for 24h. Then the obtained oligomer was purified by triple reprecipitation from THF to hexane. The isolated oligomer was dried in vacuum oven till constant weight.

### **2.4. Functionalization of polymer:**

The oligomer functionalization was carried out in a flat-bottom flask at room temperature for 24h. 1.77g (2.1mmol) of oligomer was dissolved in 60ml THF, Then 0.12g (0.99mmol) DMAP, 0.56 (2.72 mmol) DCC, 0.44g (2.31 mmol) 4-azido cinnamic acid were added in this sequence to the oligomer solution agitated by a magnetic stirrer. In the end of the reaction, the formed sediment was filtered off from the mixture, and the oligomer was precipitated into hexane. For the oligomer purification, the solution-precipitation procedure was repeated twice, and the obtained oligomer was dried in the vacuum oven till constant weight.

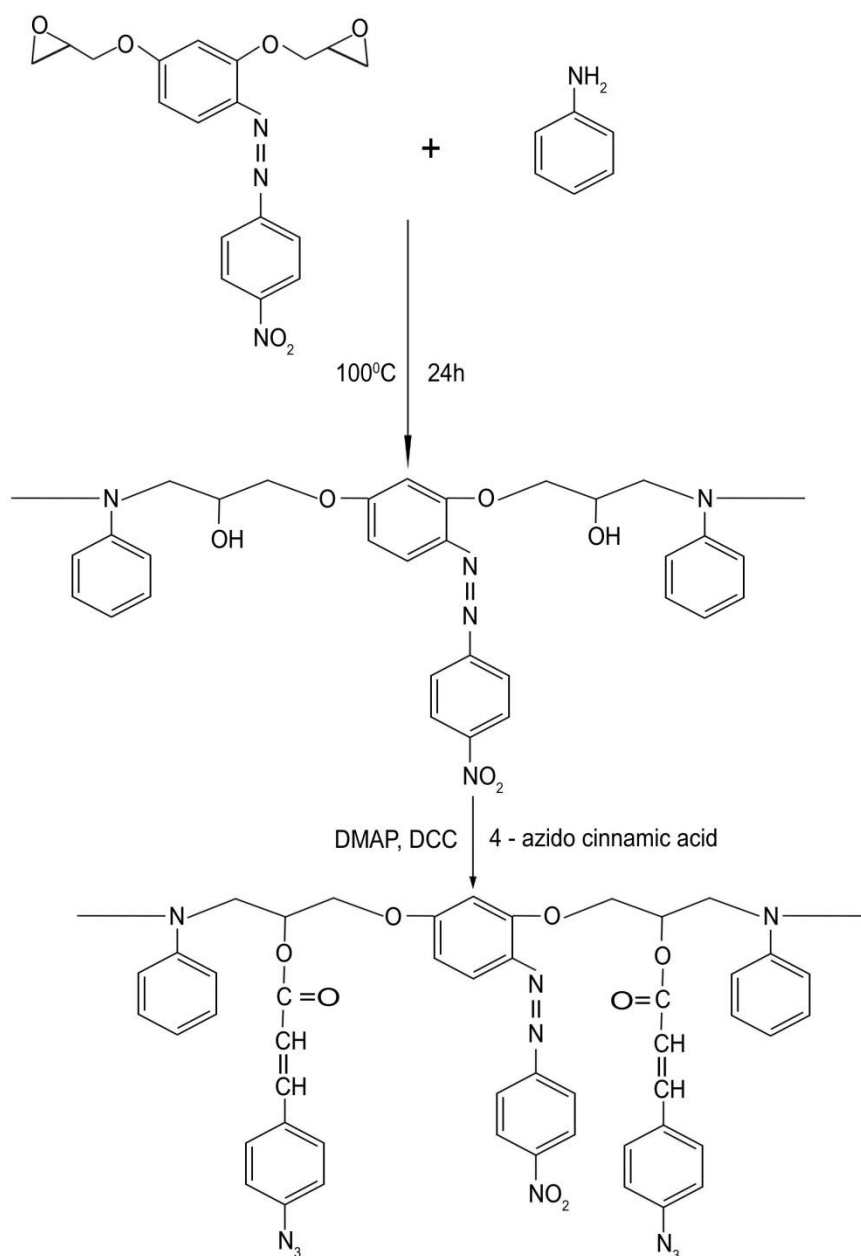
## **III. Result And Discussion:**

4-nitro phenyl azo resorcinol was synthesized by the coupling reaction of 4-nitro benzene diazonium chloride with resorcinol and then it was neutralized with sodium acetate. The epoxy-based monomer was synthesized by the treatment of 4-nitro phenyl azo resorcinol with epichlorohydrin and potassium Carbonate in the solvent medium of acetone and refluxed for 12h. After cooling, the reaction mixture was poured into water. The synthetic route of monomer was represented in scheme -I.



scheme -I.

Polymer was synthesized by the treatment of epoxy-based monomer with aniline at  $100^{\circ}\text{C}$  for 24h. The obtained oligomer was purified by triple reprecipitation from THF to hexane- The oligomer functionalization was carried out by treating the oligomer with 4-azido cinnamic acid in presence of DMAP and DCC in the solvent medium of THF. For the oligomer purification, the solution precipitation procedure was repeated twice, and the obtained oligomer was dried in vacuum oven. The synthetic route of polymer was represented in scheme-II.



Scheme -II.

#### IV. Conclusion:

IR, UV and NMR spectra revealed the successful preparation of the polymer. Reactive polyether polyol based on azo resorcinol and aniline with azo chromophore in the main chain are synthesized and characterized. The synthesized oligomer has good thermal stability and heat resistance. The synthesized oligomer is then treated with 4-azido cinnamic acid to give the functionalization of the polymer. The obtained oligomer can be used as a negative photoresist. The exposed region forms a cross-linked network and the unexposed region is soluble in aqueous base.

#### References:

- [1]. Kippelen B, Tamura K, Peyhambarian N, Padias AB, Hall Jr. HK. Phys. Rev B 1993, 48 (15): 10710.
- [2]. Yu L, Chan WK, Peng Z, Gharavi A. Acc. Chem. Res. 1996, 29:13.
- [3]. Zhang Y, Wada T, Wang L, Aoyama T, Sasabe H. Chem. Commun. 1996, 2325
- [4]. Barrett C, Chowdhury B, Natansohn A, Rochon P. Macromolecules 1998, 31, 4845
- [5]. Wright D, Diaz- Garcia MA, Casperson JD, DeClue M, Moerner WE, Twieg RJ. Appl. Phys. Lett. 1998, 73(11), 1490.
- [6]. Cox AM, Blackburn RD, West DP, King TA, Wada FA, Leigh DA. Appl. Phys. Lett. 1996,68(20),2801.

- [7]. Zhang Y, Ghosal S, Casstevens MK, Burzynski R. *J. Appl. Phys.* 1996, 79 (12), 8920.
- [8]. Silence SM, Scott JC, Stankus JJ, Moerner WE, Moylan CR, Bjorklund GC, Twieg RJ. *J. Phys. Chem.* 1995,99, 4096.
- [9]. Moon H, Hwang J, Kim N, Park SY. *Macromolecules* 2000,33(14), S116.
- [10]. Moon H, Kim N, Park sy. *Nonlinear Optics* 1999,20, 347.
- [11]. Meerholz K, Volodin BL, Sandalphon, Kippelen B, Peyghambarian N. *Nature* 1994, 371(6), 497.
- [12]. Bolink HJ, Krasnikov VV, Malliaras GG, Hadziioannou G.J. *Phys. Chem.* 1996, 100, 16 356.
- [13]. Zhang Y, Spencer CA, Ghosal S, Casstevens MK, Burzynski R, *Appl. Phys. Lett.* 1994, 64, 1908.
- [14]. Han SH, Wu JW. *J. Opt. Soc. Am B* 1997, 14, 1131.
- [15]. Sutter K, Gunter P. *J. Opt. Soc. Am B* 1990,7, 2274
- [16]. Walsh CA, Monerner We. *J. Opt. Soc. Am B* 1992, 9, 1642
- [17]. Centore R, Panunzi B, Roviello A, Sirigu A, Villano P. *J. Polym. Sci. Part A Polym. Chem.* 1996, 34, 3203.

Dipak Kumar Mukhopadhyay. "Synthesis of Non-linear Optical Epoxy-based Polymer Used As A Negative Photoresist." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 16(3), (2023): pp 28-32.