

## Synthesis of Non-linear Optical Poly (siloxane) Having Azo-benzoxazole Moiety.

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### Abstract:

4-amino benzaldehyde was diazotized with sodium nitrite and hydrochloric acid at 0<sup>o</sup>c and then it was coupled with phenol in alkaline medium giving 4'-formyl-4-hydroxy phenyl azobenzene. 4'-(6-nitro benzoxazol-2-yl)-4-hydroxy phenyl azobenzene was synthesized by treating 4'-formyl-4-hydroxy phenyl azobenzene with 2-amino-5-nitro phenol in presence of silica-Supported sodium hydrogen sulphate in the solvent medium of THF under reflux for 16h. 4'-(6-nitro benzoxazol-2-yl)-4-(allyloxy)-phenyl azobenzene was synthesized by treating 4'-(6-nitrobenzoxazol-2-yl)-4-hydroxy phenyl azobenzene with allyl bromide in presence of potassium carbonate and catalytic amount of tetrabutyl ammonium bromide in the solvent medium of acetonitrile under stirring at 80<sup>o</sup>c for 10h. Poly(siloxane) was synthesized by treating the allyl monomer with poly (methyl hydro siloxane) in presence of catalytic hydrogen hexachloro palatinate (IV) hydrate in the solvent medium of toluene under reflux at 150<sup>o</sup>c for 6h.

**Key words:** Non-linear optical, benzoxazole, Polysiloxane, hydrosilyation.

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### I. Introduction:

The design and synthesis of novel organic materials exhibiting nonlinear optical (NLO) properties is actively pursued because of the large and fast intrinsic nonlinearities, high damage threshold limits, and potential ease of processing. For these reasons, organic nonlinear optical materials have been studied extensively in various forms like crystals, organic glasses, Langmuir-Blodgett structures, vapor deposited films, clathrate complexes, polymer films, and so forth. The most promising are polymer films. The initial trend was to disperse large conjugated organic materials in glassy polymer host. These suffer from limited solubility and loss of orientation. A more advantageous strategy that evolved was to connect the active NLO species covalently to the polymer backbone. The NLO properties of these polymers originate from chromophores, which when attached via a spacer to polymer backbone, can be organized centrosymmetrically under the application of a dc electric (poling) field, resulting in a net second order susceptibility. The synthetic strategies are concentrated on maximizing chromophore polar ordering while achieving maximum persistent noncentrosymmetry. The presence of electron-donor and electron-acceptor moieties in the molecule, bounded through a pi-conjugated spacer, has been identified as the molecular feature suited to high molecular hyperpolarizability.

A variety of hyperpolarizable donor-acceptor organic molecules comprised of different acceptor units such as nitro, cyano, sulfonyl, polycyanovinyl, of diazonium salts and donor units like dialkylaminealkoxyaryl groups, ferrocene or the 1,3-dithiole ring.

The identification of more efficient donors, acceptors, and conjugating moieties for enhanced NLO effects are being increasingly pursued. The second-order polarizabilities of benzenes are well defined by a simple classical model. This model suggests that push-pull systems of type donor-pi-acceptor should have a large polarizability because these groups enhance the asymmetric distortion of the conjugated system. In a simple two-level model, polarizability is proportional to change in dipole moment between ground and first electronic state. In the electric field dependence of the NLO properties of donor-pi-acceptor molecules, the combination of amino and dicyanovinyl groups has larger value than amino and aldehyde groups, which in turn is better than methoxy and nitro groups.

In This article we have synthesized the monomer namely 4'-(6-nitro benzoxazol – 2-yl)-4-(allyloxy) phenyl azobenzene and its poly siloxane with poly (methyl hydro siloxane). In this polymer the donor-pi-acceptor moiety is retained. The donor-acceptor groups are allyloxy and nitro. Moreover, pi-conjugation bridge benzoxazole moiety is there.

## II. Experimental:

### 2.1. Synthesis of 4'-formyl-4-hydroxy phenyl azobenzene:

4-amino benzaldehyde 5.0g (0.041 mol) was dissolved in warm concentrated hydrochloric acid (13.0ml) in a 250ml beaker. The beaker was placed in an ice-salt bath and cooled to 0-5<sup>o</sup>c with vigorous stirring. To this 4.2g (0.062 mol) sodium nitrite in 8 ml cold water was added slowly with stirring. The temperature of the solution was kept below 5<sup>o</sup>c through out the addition. Phenol 3.8g (0.041 mol) was dissolved in a solution of 8.2g (0.205 mol) sodium hydroxide in 25ml of water and cooled in ice. The diazotized solution was slowly added to this alkaline phenolic solution with strring. Next, concentrated hydrochloric acid was slowly added with stirring until the reaction mixture was acidic, as checked by congored paper. The dark-red solid obtained was filtered and dried in air.

### 2.2. Synthesis of 4'-(6-nitro benzoxazol-2-yl)-4-hydroxy phenyl azobenzene:

A mixture of 4'-formyl-4-hydroxy phenyl azobenzene (1m mol), 2-amino-5-nitro phenol (1m mol) and silica-supported sodium mydrogensulphate (25 wt%) in THF (10 ml) was placed in a 50 ml round-bottom flask and stirred at reflux for 16h. The progress of the reaction was monitred by TLC. After completion of the reaction, the reaction mixture was cooled and diluted with ethyl acctate and the catalyst was removed by filtration. The filtrate was washed with diluted solution of brine and dried over sodium sulphate and evaporated under vacuum. The obtained crude product was purified by column chromatography.

### 2.3. Synthesis of 4'-(6-nitrobenzoxazol-2-yl)-4-(allyloxy) phenyl azobenzene:

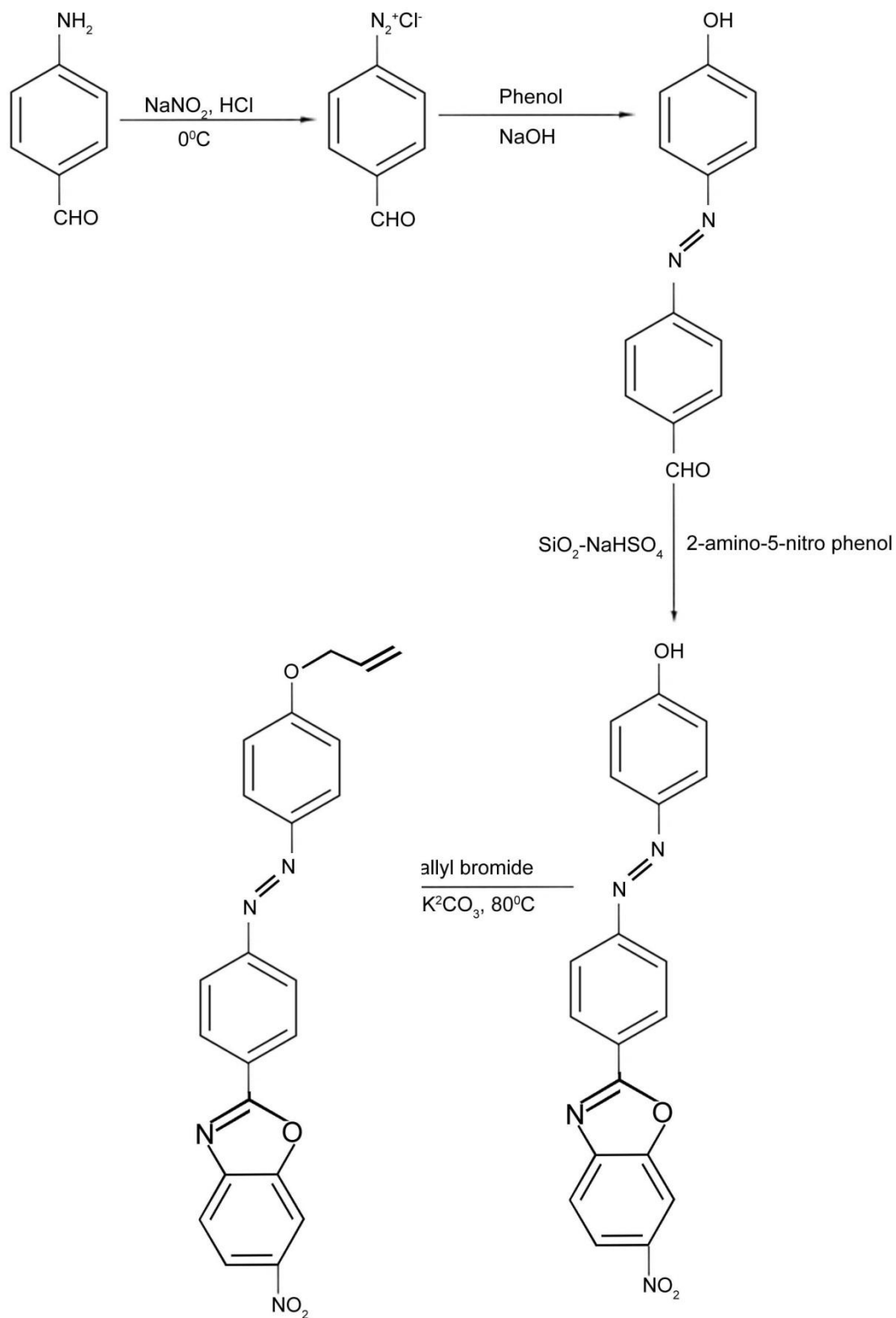
4'-(6-nitrobenzoxazol-2-yl)-4-hydroxy phenyl azobenzene 3.6g (0.01 mol) was dissolved in dry acetonitrile (50ml). To this solution, anhydrous potassium carbonate 8.7g (0.063 mol) and catalytic amount of tetra butyl ammonium bromide were added and stirred for 1h. Then allyl bromide 1.815 g (0.015mol) taken in acetonitrile was injected in over half an hour. This was stired at 80<sup>o</sup>c for 10h and reaction was monitored by TLC. After the reaction was complete, acetonitrile was distilled off, residue was mixed with chloroform and poured into cold water. This was washed several times with dilute hydrochloric acid, bicarbonate and brine solutions. The organic layer was separated and dried over anhydrous sodium sulphate and concentrated. The crude product was purified by column chromatography.

### 2.4. Synthesis of poly (siloxane):

A dried 100ml two-necked flask was equipped with a magnetic stirrer and a reflux condenser under argon. Into this flask, 4'-(6-nitro benzoxazol -2 yl)-4-(allyloxy) phenyl azobenzene (6.8g, 0.017 mol) and 50ml of toluene were added and purged with argon. The portion of poly (methyl hydro siloxane) (1.06g, 0.017mol) was dissolved with anhydrous toluene and added to the flask with several drops of hydrogen hexachloro palatinate (IV) hydrate under argon atmosphere. The solution was heated at 150<sup>o</sup>c for 6h and then poured into methanol. The precipitate was filtered, dried and purified three times by reprecipitation from mathanol.

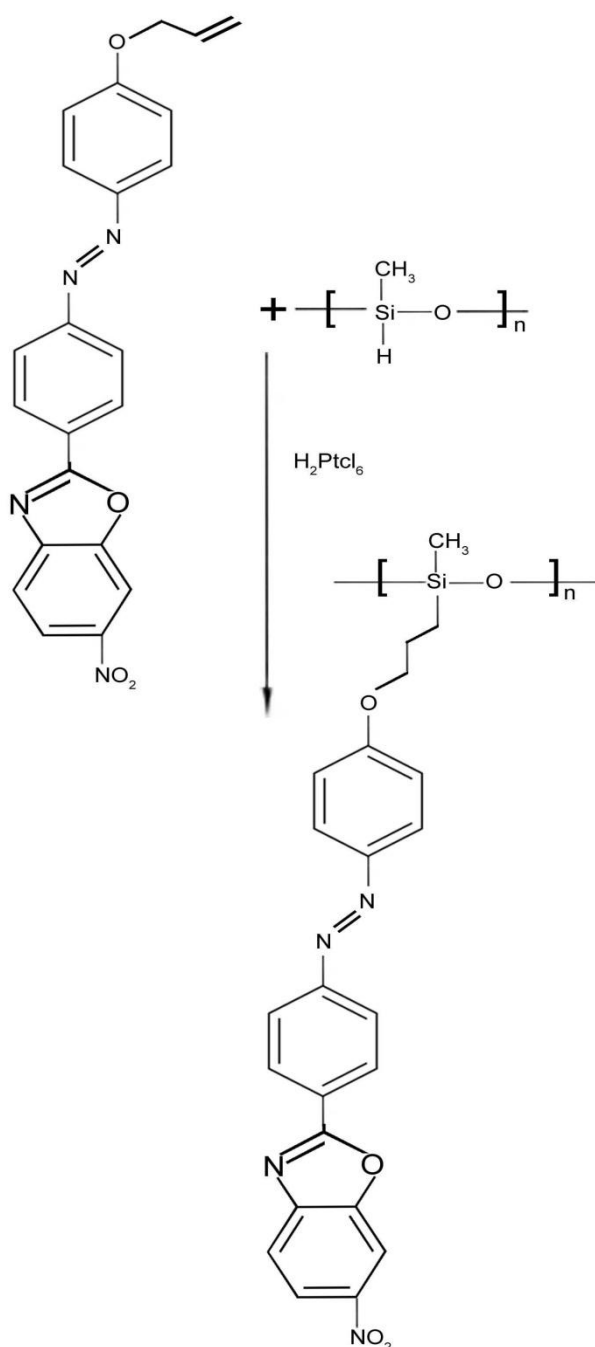
## III. Result and Discussion:

IR,UV and NMR spectra revealed the successful preparation of the polymer. 4-aminobenzaldehyde was diazotised using sodium nitrite and hydrochloric acid at 0<sup>o</sup>c and then it was coupled with phenol in alkaline medium. Next concentrated hydrochloric acid was slowly added with stirring until the reaction mixture was acidic as checked by congored paper. The dark-red solid that is azodye was filtered, washed with water and dried in air. The azodye namely 4'-formyl-4-hydroxy phenylazobenzene was treated with 2-amino-5-nitro phenol in presence of silica-supported sodium hydrogen sulphate in the solvent medium of THF under reflux for 16h. After completion of the reaction, the reaction mixture was cooled and diluted with ethylacetate and the catalyst was removed by filtration. The filtrate was washed with dilute solution of brine and dried over sodium sulphate and evaporated under vacuum. The obtained crude product namely 4'-(6-nitrobenzoxazol-2-yl)-4-hydroxy phenyl azobenzene was purified by column chromatography. After that, 4'-(6-nitroben zoxazol-2-yl)-4-hydroxyl phenyl azobenzene was dissolved in acetonitrile. To this solution anhydrous potassium carbonate and catalytic amount of tetra butyl ammonium bromide were added and stirred for 1h. Then allyl bromide in acetonitrile was injected over half an hour and this was stirred at 80<sup>o</sup>c for 10h. After the reaction was complete, acetonitrile was distilled off, residue was mixed with chloroform and poured into cold water. This was washed several times with dilute hydrochloric acid, bicarbonate and brine solution. The organic layer was separted and dried over anhydrous sodium sulphate and concentrated. The crude product was purified by column chromatography. The synthetic route of monomer was represented in scheme-I.



scheme-I.

Poly (siloxane) was synthesized by treating the allyl monomer with poly (methyl hydro siloxane) in presence of platinum catalyst in the solvent medium of toluene under reflux at 150<sup>0</sup>c for 6h. The synthetic route of polymer was represented in Scheme-II.



**Scheme-II**

#### **IV. Conclusion:**

We prepared new potentially NLO-active monomer 4'-(6-nitro benzoxazol-2-yl)-4-(allyloxy) phenyl azo benzene carrying a highly dipolar electronic system composed of phenyl groups with an electron acceptor namely nitro group. The novel chromophore 4'-(6-nitrobenzoxazol-2-yl)-4-(allyloxy) phenyl azobenzene, which could be an effective chromophore for second-order non linear optical was attached to backbone like poly (methyl hydro siloxane) by hydro silylation reaction using platinum catalyst. The new photoconducting NLO polymer has a benzoxazole moiety as a  $\pi$ -conjugation bridge.

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