

## Synthesis of Photorefractive polyester and polyurethane Of Carbazole Ring.

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**Abstract:** *N*-[2-(1,3-dihydroxy)propyl] Carbazole was synthesized by the treatment of carbazole with 2-chloro-1,3-propane diol in presence of potassium hydroxide in the solvent medium of DMF. *N*-[2-(1,3-dihydroxy)propyl]-3-(4-nitro phenyl azo) carbazole was synthesized by the reaction of *N*-[2-(1,3-dihydroxy)propyl] carbazole with 4-nitro benzene diazonium chloride in presence of sodium dodecyl benzene sulfonate in the solvent medium of DCM. Polyester was synthesized by the reaction of *N*-[2-(1,3-dihydroxy)propyl]-3-(4-nitrophenyl azo) carbazole with 6FBC in the solvent medium of DMF at 70<sup>o</sup>c for 24h. Polyurethane was synthesized by the reaction of *N*-[2-(1,3-dihydroxy)propyl]-3-(4-nitro phenyl azo) carbazole with hexamethylene diisocyanate in the solvent medium of toluene at 50<sup>o</sup>c for 3h. All the monomer and polymers were characterized by IR, UV and NMR spectroscopy.

**Key words:** *N*-[2-(1,3-dihydroxy)propyl]carbazole, *N*-[2-(1,3-dihydroxy)propyl]-3-(4-nitro phenyl azo) carbazole, polyester, polyurethane.

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### I. Introduction

In the last years the aromatic azo polymers have been widely used due to their application in different optical fields. After the photorefractive effects of organic compounds was discovered, several polymers which containing carbazole have become attractive from the point of view of their photoconductivity. The photoconductive and electro-optic functionalities in the side chain of those polymers can be considered as potential materials for photorefractive applications. Therefore the azo benzene photochemistry continue to produce unexpected phenomena because the azobenzene group is incorporated into the polymer, and in this respect the photoisomerization phenomenon can have unexpected possible consequences. It is well known that in the polymers materials with carbazole can appear the possibility of building several variable spacers between the azo group and the main chain which can increase the order degrees as well as the azo group becomes much decoupled from the main chain motion.

Photoconductive films based on poly-N-vinyl carbazole derivatives are widely used as media for recording and modulation of optical radiation. Molecules of organic additions contained in the above-indicated films serve as centres of light absorption and photogeneration of charge carriers.

The photorefractive polymers with carbazole ring and azo moieties in the side chain have all the necessary elements for photorefractivity properties (electro-optic chromophore and charge trappers). The azo containing carbazole groups provided both the photoconductivity and non-linear optical (NLO) activity and the aliphatic chain attached on the nitrogen atom of the carbazole ring acts spacer. Hence, the photorefractive polymers exhibit equally photoconductivity and optical nonlinearity. They have concerned substantial interest due to their potential applications in optical computing, optical correlation, 3D data or image storage. Large parts of the reported fully functionalized photorefractive polymers are prepared by applying of a backbone functionalized with separate charge generator, charge transporter, and non-linear optical (NLO) chromophore. The NLO chromophore and the charge transporting component compete the volume fraction in the photorefractive polymers as well.

Photorefractive materials are potentially useful for the high-density optical data storage. Image processing, dynamic holography and optical computing. Among various class of materials, photorefractive polymers are the most promising since they possess outstanding and unique advantages such as the highest figure of merit, compositional flexibility, unlimited molecular design, ease of fabrication, low dielectric constant, and low cost over the inorganic ferroelectric crystals exhibiting photorefractivity. It is well known that photorefractive is revealed as the combined activity of nonlinear optical (NLO) effect and photoconductivity. Therefore, photorefractive polymers are normally multicomponent system which comprises both NLO and photoconducting chromophore as the guest or pendant group.

The use of individual chromophores for optical non-linearity and photoconductivity, however, is usually accompanied by the phase segregation, difficulties in the synthesis, and compositional control for the optimized photorefractivity.

As a different approach to avoid these problems, multifunctional photorefractive chromophores which exhibit both the photoconductivity and NLO activity have been recently reported by many investigators. Carbazole-based push-pull type NLO molecules are typical examples of multifunctional photorefractive chromophore.

Aromatic polyesters have found a wide range of applications due to their remarkable properties such as good heat and chemical resistance, low shrinkage, low water content, and barrier properties and interesting physico-mechanical properties. However, limitations arise from their high melting temperature and limited solubility in most organic solvents. To obtain polyesters with considerably improved processing properties, several chemical modifications including (i) the introduction of bulky or non-symmetrical substituents, (ii) the use of flexible spacer, (iii) the use of non-linear or bent monomers, (iv) copolymerization of different monomers have been previously reported. A number of thermally stable aromatic polyesters have been prepared but in general the types of structures that impart thermal resistance also result in poor processing characteristics. Among the class of polymers claimed to be thermally stable only a few have achieved technological importance, some of which are polyamides, polyimides, polyquinoxalines, polyquinolines, and polybenzimidazoles. In this article we describe the synthesis of monomer namely, N-[2-(1,3-dihydroxy) propyl]-3-(4-nitro phenyl azo) carbazole and its polyesters with 6FBC and polyurethane with hexamethylene diisocyanate.

## **II. Experimental**

### **2.1. Synthesis of N-[2-(1,3-dihydroxy) propyl] carbazole:**

Powdered potassium hydroxide (14.0g) was stirred with DMF (80ml) at room temperature for 10min. The mixture was then stirred with carbazole (6.6g, 0.04mol) at room temperature for 45min. 2-chloro-1,3-propane diol (4.8g, 0.05mol) was added slowly, and the resultant mixture was allowed to stir at room temperature for 10h. The mixture was poured into water (1.2L) and the white solid was filtered, washed with water and air-dried. The solid was dissolved in 70% ethanol, and the insoluble residue was filtered out. Water was added to the filtrate until the precipitation was completed. The solid was filtered and dried under vacuum.

### **2.2. Synthesis of N-[2-(1,3-dihydroxy) propyl]-3-(4-nitro phenylazo) carbazole:**

4-nitro aniline (2.8g, 0.02mol) was dissolved in a solution of concentrated hydrochloric acid (10ml) in water (300ml). The mixture was cooled in an ice bath until the temperature was below 4°C. Then a solution containing sodium nitrite (1.6g, 0.022mol) in water (10ml) was added slowly to the 4-nitro aniline solution. The mixture was allowed to stir in the ice bath for 30 min. While the mixture was still kept in the ice bath, sodium dodecyl benzene sulfonate (1.0g) was added. A solution of N-[2-(1,3-dihydroxy)propyl] carbazole (9.64g, 0.04mol) in dichloromethane (300ml) was added to the above mixture. The resultant mixture was stirred vigorously at room temperature for 24h. Ethanol (200ml) was added and the mixture was heated to remove dichloromethane layer. The precipitate was filtered, washed with water and air-dried. The solid was recrystallized from ethanol/chloroform mixture (1:1 by volume).

### **2.3. Synthesis of polyester:**

In a 100ml flask, added 3.9g (0.01mol) of N-[2-(1,3-dihydroxy)propyl]-3-(4-nitro phenyl azo) carbazole and 40ml of 1,2-dichloro ethane. The diacid chloride monomer, 6FBC (4.09g, 0.01mol) was added into the solution at room temperature with stirring. Triethyl amine 2.02g (0.02mol) was added for acid trapper. The polymerization was carried out at 70°C for 24h. The polymer solution was poured into methanol. The precipitated solid was purified by repeated precipitation.

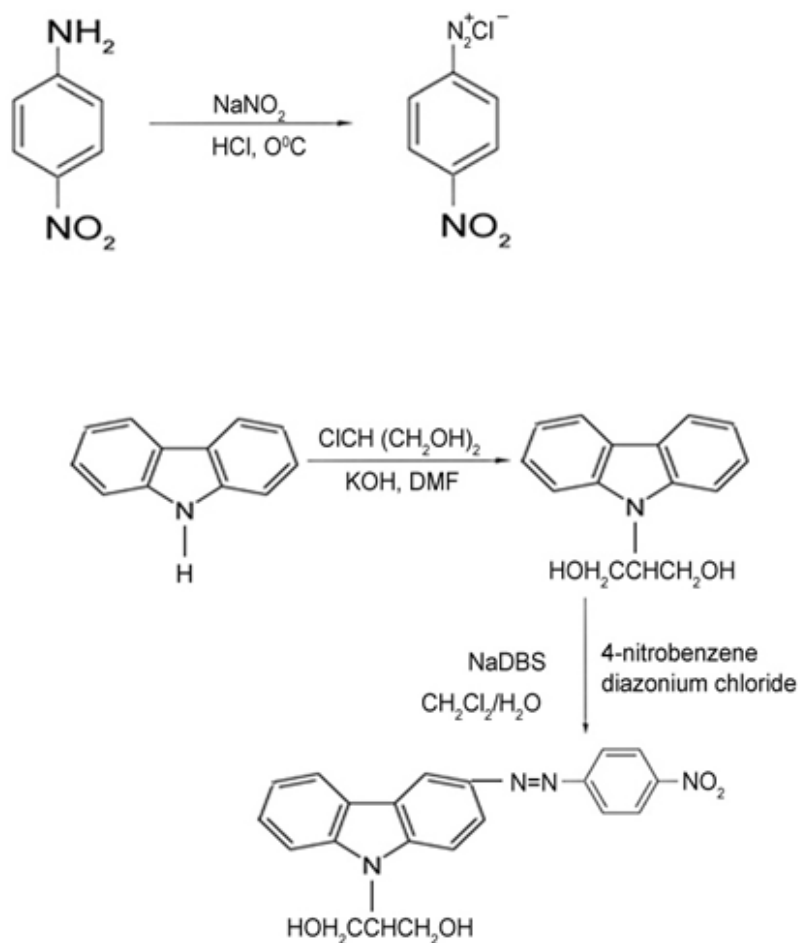
### **2.4. Synthesis of polyurethane:**

In a 100 ml flask, added 3.9g (0.01mol) of N-[2-(1,3-dihydroxy)propyl]-3-(4-nitro phenylazo) carbazole and 40ml toluene. Then hexa methylene diisocyanate 1.68g (0.01mol) was added into this solution at room temperature with stirring. The polymerization was carried out at 50°C for 4h. The polymer solution was precipitated out in hexane, filtered, washed with hexane and methanol and dried.

## **III. Result And Discussion**

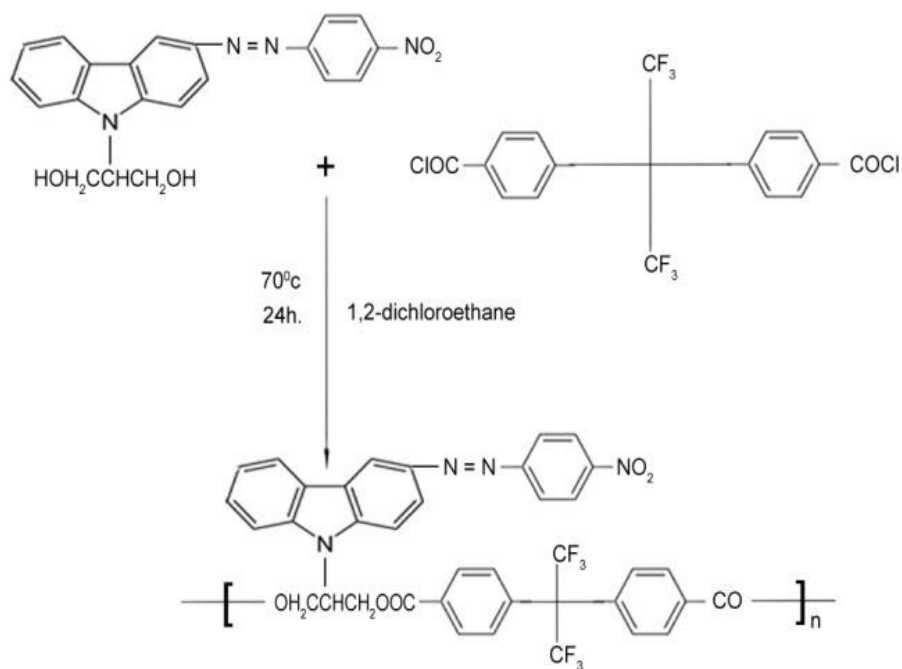
N-[2-(1,3-dihydroxy)propyl] carbazole was synthesized by the treatment of carbazole with 2-chloro-1,3-propane diol in presence of potassium hydroxide in the solvent medium of DMF. After, subsequent addition of water the product is precipitated out. Then the solid was dissolved in 70% ethanol, and the insoluble residue was filtered out. Water was added to the filtrate until the precipitation was completed. The precipitated solid was filtered and dried under vacuum. 4-nitro benzene diazonium chloride was prepared by the treatment of 4-nitro

aniline with sodium nitrite and aqueous hydrochloric acid at 0°C. N-[2-(1,3-dihydroxy) propyl] -3-(4-nitro phenylazo) carbazole was synthesized by the reaction of N-[2-(1,3-dihydroxy)propyl] carbazole with 4-nitro benzene diazonium chloride in presence of Na DBS in the solvent medium of CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O for 24h. Ethanol was added and the mixture was heated to remove dichloromethane layer. The precipitate was filtered, washed with water and air dried. The solid was recrystallized from ethanol/chloroform mixture(1:1 by volume). The monomer was characterized by IR,UV and NMR spectroscopy. The synthetic path of monomer was depicted in scheme-I.



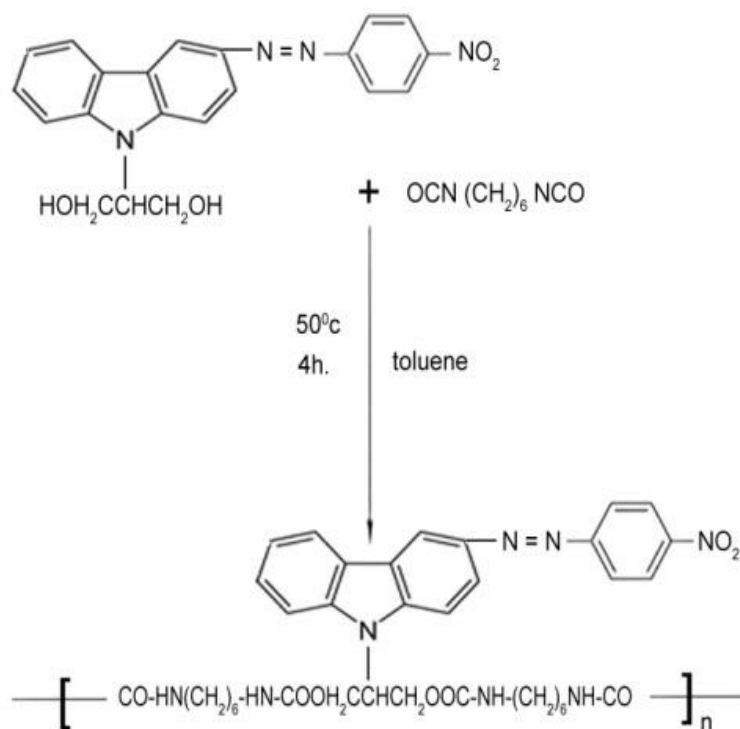
Scheme - I

Polyester was synthesized by the reaction of N-[2-(1,3-dihydroxy)propyl]-3-(4-nitro phenyl azo) carbazole with diacid chloride, 6FBC in presence of acid trapper triethyl amine in the solvent medium of 1,2-dichloro ethane at 70°C for 24h. The polymer was precipitated out in methanol and purified by repeated precipitation technique. The polyester was characterized by IR,UV and NMR spectroscopy. The synthetic path of polyester was depicted in scheme-II.



Scheme -II

Polyurethane was synthesized by the treatment of N-[2-(1,3-dihydroxy)propyl]-3-(4-nitro phenyl azo) carbazole with hexamethylene diisocyanate in the solvent medium of toluene at 50°C for 4h. The polymer was precipitated out in hexane, washed with hexane and methanol and air dried. The polyurethane was characterized by IR,UV and NMR spectroscopy. The synthetic path of polyurethane was depicted in scheme-III.



Scheme-III

Carbazole based photorefractive polyester and polyurethane have good thermal, mechanical and photochemical properties. The polymers are soluble in most common organic solvents. The electro-optic coefficient of the poled polymers can be measured at the wave length of 633nm (He-Ne laser) by using simple reflection method. The host polymer can be doped with guest molecule like TNF and dark and photoconductivity can be measured of polymer film by evaluating a current. Photo-refractivity can be studied by two-beam coupling and four-wave mixing at the electric field. The photorefractive composites can be prepared by conjugation the polymer host with sensitizer like TNF and a plasticizer like ECZ.

#### IV. Conclusion

The article summarized the novel synthesis of monomer N-[2-(1,3-dihydroxy)propyl]-3-(4-nitro phenyl azo) carbazole and its polyester and polyurethane with 6FBC and hexamethylene diisocyanate respectively. The monomer and polymers were characterized by IR,UV and NMR spectra. The synthetic polyester and polyurethane gave good thermal, mechanical and photochemical stability. Carbazole is available from coal-tar so, cheaper photorefractive polymers can be prepared. The polymers can be sensitized with TNF and good photorefractive composites can be prepared.

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