

Synthesis of Non-linear Optical Polymer of Carbazole-benzoxazole Moiety

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Abstract: *N*-(2-hydroxyethyl)carbazole was prepared by the reaction of carbazole with 2-chloroethanol in presence of powdered potassium hydroxide in the solvent medium of DMF for 10h. After subsequent addition of water the white solid was filtered. The product was recrystallized from 70% ethanol. *N*-(ethyl acetate)carbazole was prepared by refluxing *N*-(2-hydroxy ethyl) carbazole with acetic anhydride for 2h. *N*-(ethyl acetate)-3,6-diformyl carbazole was synthesized by treating *N*-(ethyl acetate)carbazole with high excess POCl₃ and DMF mixture. Pure aldehyde components were separated by flash chromatography on a silica gel column using ethyl acetate:hexane (1:10) as eluent. *N*-(ethyl acetate)-3,6-[bis(6-nitrobenzoxazol-2-yl)] carbazole was synthesized by refluxing *N*-(ethyl acetate)-3,6-diformyl carbazole with 2-amino-5-nitro phenol in the solvent medium of DMF in presence of silica supported sodium hydrogen sulphate. *N*-(2-hydroxy ethyl)-3,6-[bis(6-nitro benzoxazol-2-yl)] carbazole was prepared by the reduction of *N*-(ethyl acetate)-3,6-[bis(6-nitro benzoxazol-2-yl)] carbazole with potassium hydroxide and ethanol. The vinyl monomer was synthesized by treating *N*-(2-hydroxy ethyl)-3,6-[bis(6-nitro benzoxazol-2-yl)] carbazole with methacryloyl chloride in the solvent medium of THF. The polymerization was carried out in 1,2-dichloro benzene with 10% by weight of azobisisobutyronitrile (AIBN) as initiator.

Keywords: *N*-(2-hydroxy ethyl)carbazole, *N*-(ethyl acetate)carbazole, *N*-(ethyl acetate)-3,6-diformyl carbazole, *N*-(ethyl acetate)-3,6-[bis(6-nitro benzoxazol-2-yl)] carbazole, vinyl monomer, polymerization.

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I. Introduction:

Photorefractive polymers have attracted considerable attention owing to their potential application including high-density optical data storage, optical image processing, phase conjugation, lasing, dynamic holography, optical computing and pattern recognition. Organic materials are of particular interest because of their versatile synthetic flexibility that offers on to fine tune the optical properties at molecular level. Moreover, the optical nonlinearity in this class of materials is electronic in origin and exhibits an ultrafast response. For the least three past decades the organic systems were extensively studied for their NLO properties. The most popular system consist of a host polymer doped with physically dispersed guest dye molecules. The host polymer should be optically transparent and without NLO traits. In this way all non-linear properties arise from dispersed NLO dye molecules. NLO performance of such materials is usually attenuated by either aggregation or crystallization of dye molecules. The other approach depends on chemical binding of the dye molecules to the host polymer backbone. Some practical problems will arise when these polymers are used as photorefractive media. First the absorption maxima of these chromophores were located at wavelengths longer than 420nm with their apparent cut-off usually extended to 600nm and more. Such an insufficient transparency in the visible region is real problem. Secondly, the T_gs of polymethacrylates were too high to be poled at room temperature. Thirdly, the photoconductive sensitivity of photoconducting NLO chromophores was not high enough to ensure a fast response. In order to rectify this problems, we designed and synthesized novel photoconducting NLO chromophore *N*-(2-hydroxy ethyl)-3,6-[bis(6-nitro benzoxazol-2-yl)] carbazole in this work. The EO property is attributed to the conjugated push-pull structure of this chromophore. Carbazole, the heteroaromatic structure, was designed to work as a photoconducting moiety as well as electron donor. Benzoxazole moiety was introduced as pi-conjugation bridge instead of the conventional stilbene unit to obtain blue-shifted absorption together with the enhanced thermal and photochemical stability. The necessary characteristics for a material to be regarded as potentially photorefractive are photoconductivity and electro-optic (EO) property. Most of the photorefractive polymers reported to date are based on guest-host polymer composite, which normally consist of four components (photoconducting polymer host, NLO chromophore, plasticizer and photosensitizer). Although it is facile and versatile to prepare guest-host polymer composite, there are inherent problems, such as phase separation, which limits the concentration of dopants, and also the trade-off of photoconductivity and EO property with composition. To enhance EO property, for example, it is necessary to increase the concentration of NLO chromophore, which adversely

leads to the phase separation and decrease of photoconductivity. In this contest, the photoconducting NLO chromophore, which possesses both functionalities in a single molecule, is the right answer to overcome the above problems. The use of photoconducting NLO chromophore suppresses phase separation, and simultaneously increases EO property and photoconductivity. We have synthesized and reported various guest-host system photorefractive polymer composite based on the heteroaromatic donor moiety like carbazole and indole. It is shown that polymethacrylates containing these chromophores as a side chain exhibited excellent EO property and moderate photoconductivity. In this article the NLO monomer, N-(2-hydroxy ethyl)-3,6-bis(6-nitro benzoxazol-2-yl)carbazole was synthesized and its vinyl monomer was copolymerized with MMA. It is a fully functionalized polymer and can be used as a photorefractive material. The polymer has good thermal and photochemical properties. TNF sensitized polymer is photoconductive due to formation of a charge transfer (CT) complex.

II. Experimental:

2.1. Synthesis of N-(2-hydroxy ethyl)carbazole:

Powdered potassium hydroxide (14.0g) was stirred with DMF (80ml) at room temperature for 10 min. The mixture was then stirred with carbazole (6.6g, 0.04 mol) at room temperature for 45 min. 2-chloroethanol (4.0g, 0.05 mol) 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 white 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 cotton-like solid was filtered and dried under vacuum.

2.2. synthesis of N-(ethyl acetate)carbazole:

A stirred solution of 18.99g (90.0 μmol) of N-(2-hydroxyethyl) carbazole in 100ml of acetic anhydride was heated at reflux for 3h. After cooling, the solvent was distilled off *in vacuo*. The liquid residue was poured into water. The solid was filtered off and washed with water and methanol and dried under vacuum.

2.3. Synthesis of N-(ethyl acetate)-3,6-diformyl carbazole

N-(ethyl acetate) 3,6-diformyl carbazole was synthesized by the formylation of N-(ethyl acetate) carbazole in presence of a high excess of POCl₃ and DMF mixture. However, even at very high ratio, the formylating agent: carbazole compound is greater than 10:1 always a mixture of mono [3-formyl-N-(ethyl acetate)carbazole] and dialdehyde compound [3,6-diformyl-N-(ethyl acetate)carbazole] was obtained and pure aldehyde compound were separated by flash chromatography on silica gel column using ethyl acetate: hexane (1:10) as eluent. The monoaldehyde was the first product eluted after evaporation of the solvent. The dialdehyde was obtained as a white solid after evaporation of eluent and recrystallized from acetone. TLC, chromatography, elemental analysis and spectral data confirm the purity and structure of synthesized dialdehyde product.

2.4. Synthesis of N-(ethyl acetate)-3,6-bis(6-nitro benzoxazol-2-yl)carbazole:

A mixture of 2-amino-5-nitro phenol, (0.02mol), N-(ethyl acetate)-3,6-diformyl carbazole (0.01mol) and silica supported sodium hydrogen sulphate (50wt%) in DMF (50ml) was placed in a 250ml round-bottom flask and stirred at reflux for 16h. the progress of the reaction was monitored by TLC, hexane: ethyl acetate (4:1). After completion of the reaction, the reaction mixture was cooled and diluted with ethyl acetate 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.

2.5. Synthesis of N-(2-hydroxy ethyl)-3,6-bis(6-nitro benzoxazol-2-yl)carbazole:

A stirred solution of 8.32g (0.02mol) of N-(ethyl acetate)-3,6-bis(6-nitro benzoxazol-2-yl) carbazole and 2.24g (0.04mol) of potassium hydroxide in 50ml ethanol was heated at reflux for 3h. After cooling, the solid precipitate was filtered, washed with water. The product was recrystallized from ethanol.

2.6. Synthesis of vinyl monomer:

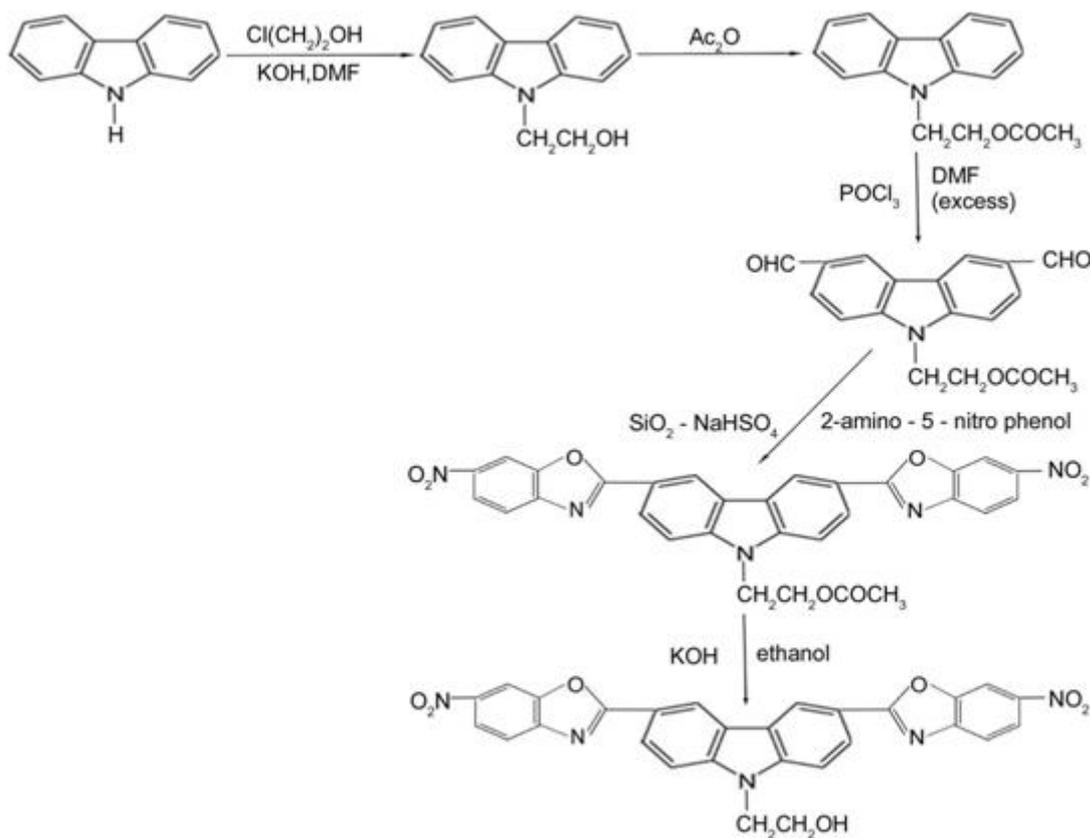
A solution of N-(2-hydroxy ethyl)-3,6-bis(6-nitro benzoxazol-2-yl)carbazole (3.74g, 0.01mol) and triethyl amine (2.02g, 0.02mmol) was dissolved in THF (100ml). A solution of methacryloyl chloride (1.4 ml, 0.01 mol) in THF (10 ml) was added slowly to the above mixture. After the addition of methacryloyl chloride, the resultant mixture was stirred at room temperature overnight. The solvent was removed by rotary evaporation, and the residue was washed with a solution of sodium carbonate (1.0g) in water (100ml). the solid was filtered, washed with water and air dried. The solid was recrystallized from ethanol/chloroform mixture (2:1 by volume).

2.7. polymerization:

The polymerization was carried out in 1,2-dichlorobenzene with 10% by weight AIBN as initiator. The monomer was allowed to polymerize under argon at 60⁰c for 2days. The polymerization was stopped by pouring the reaction mixture into ethanol. The polymer was redissolved in THF, precipitated again in ethanol and finally dried under vacuum.

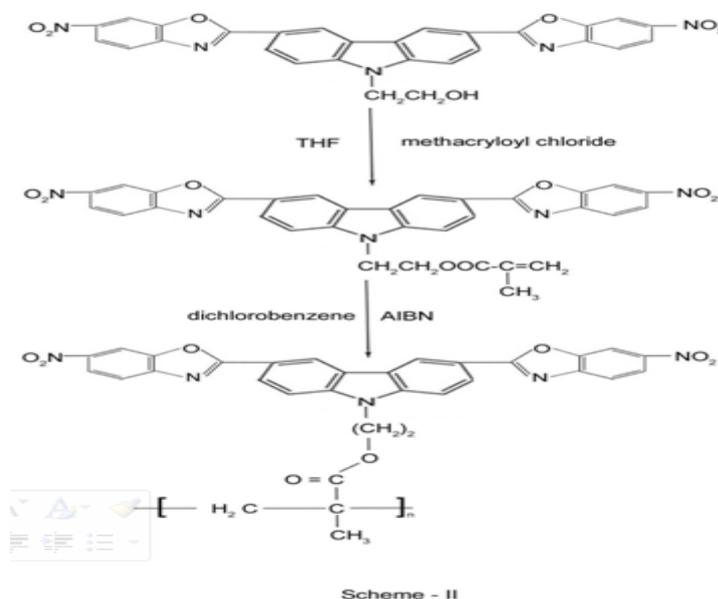
III. Result and discussion:

N-(2-hydroxy ethyl) carbazole was synthesized by treating carbazole with 2-chloro ethanol in presence of powdered potassium hydroxide in the solvent medium of DMF. After subsequent addition of water the product was precipitated out. The product was recrystallized from 70% ethanol. N-(ethyl acetate)carbazole was synthesized by reacting N-(2-hydroxy ethyl)carbazole with acetic anhydride under reflux for 3h. After cooling, the solvent was distilled off in vacuo. The liquid residue was poured into water and the solid was filtered off, washed with water and methanol and dried. N-(ethyl acetate)3,6-diformyl carbazole was synthesized by treating N-(ethyl acetate)carbazole with a high excess POCl₃ and DMF mixture. The mono and dialdehyde were separated out by flash chromatography on a silica gel column using ethyl acetate :hexane(1:10) as eluent. The dialdehyde was obtained as a white solid after evaporation of eluent and recrystallized from acetone. N-(ethyl acetate)-3,6-[bis(6-nitro benzoxazol-2-yl)] carbazole was synthesized by treating N-(ethyl acetate)-3,6-diformyl carbazole with 2-amino-5-nitro phenol in presence of silica supported sodium hydrogen sulphate catalyst in the solvent medium of DMF under reflux for 16h. After completion of the reaction, the reaction mixture was cooled and diluted with ethyl acetate 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 crude product was purified by column chromatography. N-(2-hydroxy ethyl)-3,6-[bis(6-nitro benzoxazol-2-yl)] carbazole was prepared by the reduction of N-(ethyl acetate)3,6-[bis(6-nitro benzoxazol-2-yl)]carbazole with potassium hydroxide and ethanol under reflux for 3h. After cooling, the precipitated solid was filtered off and washed with water and dried. The synthetic route of N-(2-hydroxy ethyl)3,6-[bis(6-nitro benzoxazol-2-yl)]carbazole was depicted in scheme-I.



Scheme - I

The vinyl monomer was synthesized by treating N-(2-hydroxy ethyl)-3,6[bis(6-nitro benzoxazol-2-yl)]carbazole with methacryloyl chloride in presence of triethyl amine in the solvent medium of THF stirring at room temperature overnight. The solvent was removed by rotoevaporation and the residue was washed with a solution of sodium carbonate. The solid was filtered, washed with water and dried. The polymerization was carried out in dichlorobenzene with 10% by weight of AIBN as initiator. The monomer was allowed to polymerize under argon at 60°C for 2-days. The polymer was precipitated out in ethanol. The synthetic route of monomer and polymer were depicted in scheme-2.



IV. Conclusion:

The article summarized the development of photorefractive polymer of carbazole as a pendant ring. We have synthesized the novel vinyl monomer of N-(2-hydroxy ethyl)-3,6-[bis(6-nitro benzoxazol-2-yl)]carbazole and its homopolymer with AIBN as initiator. Carbazole ring is incorporated with benzoxazole ring as pi-conjugation bridge and has good thermal and photochemical stability. The optical absorption of carbazole-benzoxazole polymer was blue-shifted compared to conventional NLO polymer. TNF sensitized polymer is photoconductive due to formation of a charge transfer (CT) complex. A good photorefractive system can be developed by composition of the polymer with sensitizer TNF and a plasticizer ECZ.

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