

Synthesis of non-linear Optical Polymer of Indole-benzothiazole moiety.

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Abstract: *N*-(1-hydroxy propyl) indole was prepared by the reaction of indole with trimethylenechlorohydrin in presence of powdered potassium hydroxide in the solvent medium of DMF stirring at first at room temperature for 4h and then at 40^oc for 12h. *N*-(propyl acetate) indole was prepared by the reaction of *N*-(1-dydroxy propyl) indole with acetic anhydride and pyridine in the water bath for 2h. *N*-(propylacetate)-3- formylindole was synthesized by the reaction of *N*-(propyl acetate) indole with POCl₃ and DMF mixture stirring at first at 0^oc for 1h and then at 100^oc for 2h. 2-[*N*-(propylacetate) indolyl]-6- nitro benzothiazole was synthesized by the treatment of *N*-(propylacetate) -3- formylindole with 2-amino-5-nitro thiophenol in presence of Baker's yeast in the solvent medum of DCM at room temperature for 30h.

2-[*N*-(1-hydroxy propyl) indolyl]-6-nitro benzothiazole was prepared by the reduction of 2-[*N*-(propylacetate) indolyl]-6-nitro benzothiazole with potassium hydroxide and ethanol. The monomer namely 2-[*N*-propyl acrylate) indolyl]-6-nitro benzothiazole was synthesized by the reaction of 2-[*N*-(1-hydroxy propyl) indolyl] – 6-nitro benzothiazole with acryloyl chloride in the medium of mixed solvent DCM and DMF and heated at reflux for 6h. Lastly the monomer was co-polymerzed with MMA in the solvent medium of NMP in a sealed ampule at 70^oc for 50h.

Key words: *N*-(1-hydroxy propyl) indole, *N*-(propyl acetate)-3-formyl indole, 2-[*N*-(1-hydroxy propyl) indolyl]-6-nitro benzothiazole, 2-[*N*-(propyl acrylate) indolyl]-6-nitro benzothiazole, co-polymerization.

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I. Introduction

Photorefractive polymers have attracted considerable attention owing to their potential applications 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 one to fine tune the optical properties at molecular level. Moreover, the optical nonlinearity in this class of materials is electronic in origin and hence exhibits an ultra fast response. For the least three past decades the organic systems were extensively studied for their NLO properties. The most popular systems 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 420 nm with their apparent cut-off usually extended to 600 nm and more. Such an insufficient transparency in the visible region is a real problem. Secondly, the *T_g*s 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 these problems, we designed and synthesized novel photoconducting NLO chromophore 2-[*N*-(hydroxyl propyl) indolyl]-6-nitro benzothiazole in this work. The EO property is attributed to the conjugated push-pull structure of this chromophore.

Indole, the heteroaromatic structure like carbazole, was designed to work as photoconducting moiety as well as electro donor. Indole was adopted over carbazole for this purpose, because indole provides better poling efficiency owing to the more compact size compared with carbazole. Benzothiazole 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 a 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 context, 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 was shown that polymethacrylates containing these chromophores as a side chain exhibited excellent EO property and moderate photoconductivity.

In this article the NLO monomer, 2-[N-(Propyl acrylate) indolyl]-6-nitro benzothiazole was synthesized and which was co-polymerized with methylmethacrylate. It is a fully functionalized polymer and can be used as a photo refractive material. The polymer has good thermal and photochemical properties. TNF sensitized polymer is photoconductive due to the formation of a charge transfer (CT) complex. A good photorefractive system can be developed by composition of the polymer with 0.2 wt% of TPY-salt.

II. Experimental

2.1. Synthesis of N-(1-hydroxy propyl) indole:

59.4g (1060 mmol) sample of powdered potassium hydroxide was stirred for 10 minutes in 200 ml dry DMF. Then, 25.0g (213 mmol) of indole was added slowly and stirred for 1h. After addition of 24.1g (255mmol) of trimethylene chlorohydrin, the solution was stirred at room temperature for 4h and then at 40°C for 12h. The resulting mixture was poured into water and extracted with ethylacetate. The extract was dried with magnesium sulphate and the solvent was removed at reduced pressure. The crude product was purified by silica gel column chromatography (ethylacetate:hexane = 1:1)

2.2. Synthesis of N-(propylacetate) indole :

A stirred solution of 15.4g (90.0 mmol) of N-(1-hydroxy propyl) indole in 100 ml of acetic anhydride was heated at reflux for 2h. After cooling, the solvent was distilled off in vacuo. The liquid residue was poured into water and the aqueous mixture was extracted with ethyl acetate. The extract was dried with magnesium sulphate, and the solvent was removed at reduced pressure. The liquid residue was chromatographed on a silica gel column (ethyl acetate : hexane = 1:4) and the solvent of the first fraction was removed at reduced pressure to yield the product.

2.3. Synthesis of N-(propyl acetate) -3- formylindole :

To a stirred solution of 13.2g (62mmol) of N-(propyl acetate) indole in 250ml dry DMF was added dropwise 14.6 ml (157mmol) of phosphorus oxychloride at 0°C. The reaction mixture was stirred at 0°C for 1h and then at 100°C for 2h. After cooling, the solution was poured into water. The resulting mixture was neutralized to PH=7 with 2(N) sodium hydroxide and extracted with DCM. The extract was dried with magnesium sulphate, and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column (ethylacetate:hexane=1:1) and the solvent of the second fraction was removed at reduced pressure to get the titled compound.

2.4. Synthesis of 2-[N-(propyl acetate) indolyl] -6-nitro benzothiazole:

8 mmol of N-(Propyl acetate)-3-formylindole, 8 mmol of 2-amino -5-nitro thiophenol and 2.0g of Baker's yeast were mixed in DCM and the mixture was stirred at room temperature for 30h. After completion of the reaction, Baker's Yeast Was filtered through a bed of celite, and the filtrate was concentrated under reduced pressure. On cooling, the solid product obtained was separated and crystallized from ethanol to afford the pure product.

2.5. Synthesis of 2-[N-(1- hydroxyl propyl) indolyl]-6-nitro benzthiazole:

A stirred solution of 8.55g (22 mmol) of 2-[N-(propyl acetate indolyl)]-6-nitro benzothiazole and 2.43g (43.2 mmol) of potassium hydroxide in 40ml of ethanol was heated at reflux for 2h. After cooling, the solvent was removed at reduced pressure. The solid residue was washed with water, filtered and dried. The product was recrystallized from ethanol.

2.6. Synthesis of 2-[N-(propylacrylate)-6nitro benzothiazole :

A 1.75 g (5m mol) of 2-[N-(1-hydroxy propyl) indolyl]-6-nitro benzothiazole and 2.02g (20 m mol) of triethylamine were dissolved in mixed solvent (DCM 50 ml and DMF 10 ml) at 0⁰c. The solution was treated under nitrogen atmosphere, with a solution of 1.81 (20 m mol) of acryloyl chloride in 15 ml DCM. The reaction mixture was heated at reflux for 6h. After cooling, the solvent was removed under reduced pressure and the residue was poured into water. The resulting solid was filtered and chromatographed on a silica gel column (ethyl acetate:hexane=1:1). The solvent of the first fraction was removed at reduced pressure to yield the solid monomer.

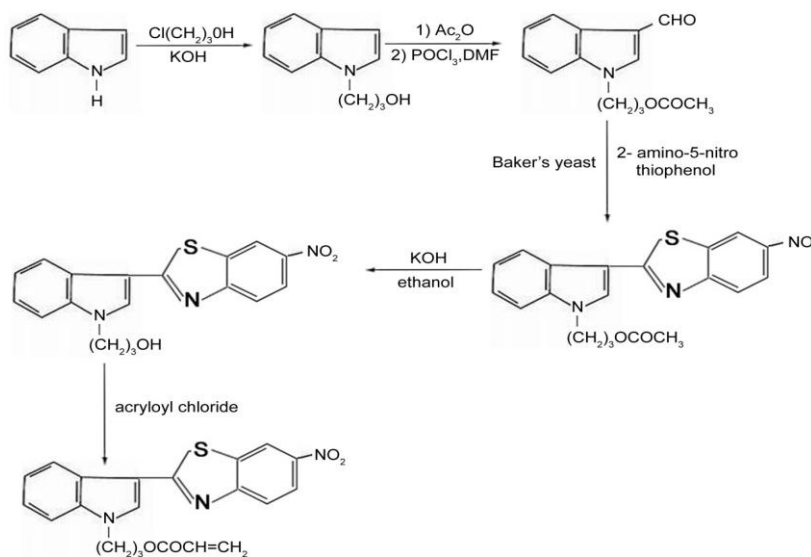
2.7. Polymerization :

A 1.01 g (2.5m mol) of monomer, 0.250g (2.5m mol) of distilled methylmethacrylate (MMA) and 0.4g (5mol%) of azobisisobutyronitrile (AIBN) were dissolved in 10ml of NMP. The solution was degassed by standard vacuumfreeze-thaw technique and heated in a sealed ampule at 70⁰c for 50h. After cooling, the resulting solution was diluted to twice its original volume with THF and poured into 200 ml of vigorously stirred methanol to precipitate the polymer. Purification was carried out by repeated reprecipitation from THF into methanol until no monomer was observed in the TLC plate. Finally pure co-polymer was obtained.

III. Result and Discussion

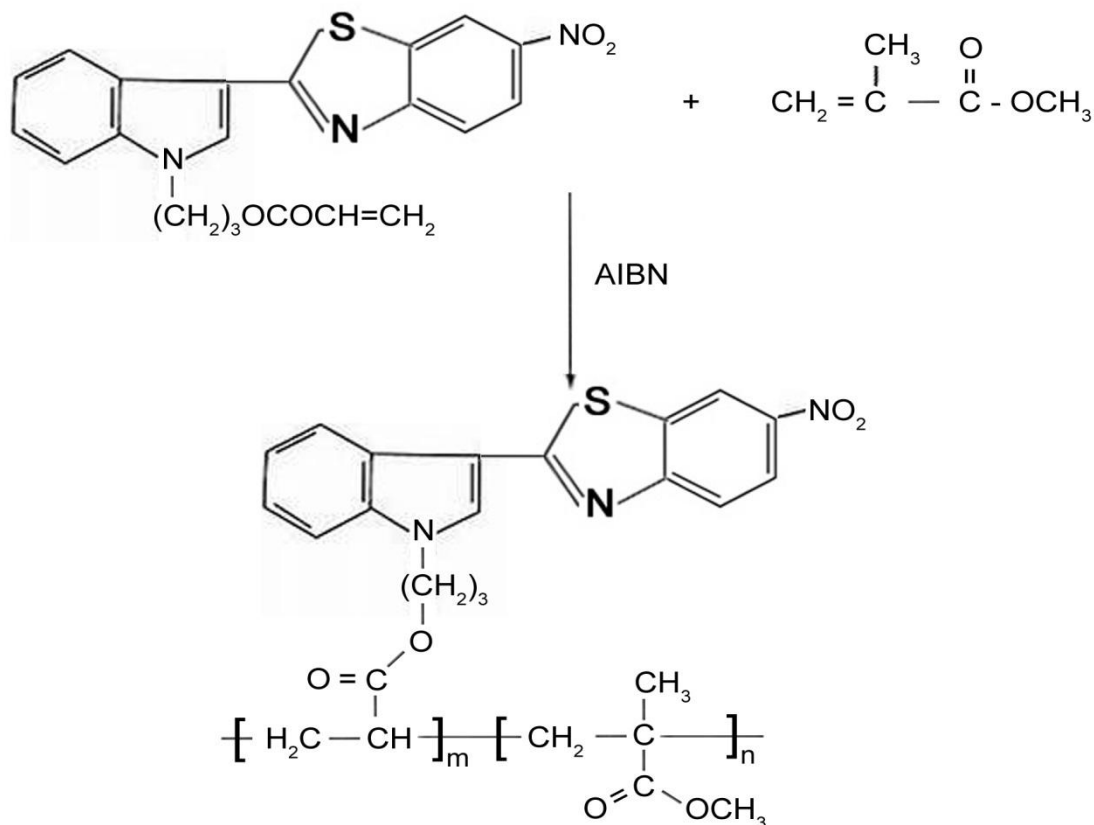
IR, UV and NMR spectra revealed the successful preparation of the polymer. The monomer namely 2-[N-(propyl acrylate)indolyl]-6-nitro benzothiazole was prepared as follows: N-(1-hydroxy propyl) indole was prepared by the treatment of indole with trimethylene chlorohydrin in presence of powdered potassium hydroxide at 40⁰c for 12h in the solvent medium of DMF. N-(propyl acetate) indole was prepared by the reaction of N-(1-hydroxy propyl) indole with acetic anhydride at 100⁰c for 2 h. N-(propyl acetate)-3-formyl indole was prepared by the reaction of N-(propyl acetate) indole with POCl₃ and DMF mixture at 100⁰c for 2h. The mixture was poured into water and neutralized to PH=7 by adding sodium hydroxide. Lastly the mixture was extracted with DCM, dried with magnesium sulphate and the solvent was removed under reduced pressure and lastly the residue was chromatographed.

2-[N-(propylacetate) indolyl]-6-nitro benzothiazole was synthesized by the reaction of N-(propyl acetate)-3-formyl indole with 2-amino-5-nitro thiophenol in presence of Baker's yeast in the solvent medium of DCM for 30h at room temperature. After completion of the reaction, Baker's yeast was filtered through a bed of celite. The filtrate was concentrated under reduced pressure and the solid product was obtained and recrystallized from ethanol. 2-[N-(1-hydroxy propyl) indolyl]-6-nitro benzothiazole was prepared by the reduction of 2-[N-(propyl acetate)indolyl]-6-nitro benzothiazole with potassium hydroxide and ethanol. After cooling, the solvent was removed under reduced pressure and the solid product was washed with water and recrystallized from ethanol. The monomer namely 2-[N-(propyl acrylate) indolyl]-6-nitro benzothiazole was synthesized by the treatment of 2-[N-(1-hydroxy propyl) indolyl]-6-nitro benzothiazole with acryloylchloride in the mixed solvent heated under reflux for 6h. After cooling, the solvent was removed under reduced pressure and the residue was poured into water. The resulting solid was filtered and chromatographed. The synthetic route of the monomer was depicted in scheme-I.



Scheme-I.

Finally, co-polymer was synthesized by the radical polymerization of 2-[N-(propylacrylate) indolyl]-6-nitro benzothiazole with methyl methacrylate in 1:1 ratio in the solvent medium of NMP using AIBN as radical initiator. The polymer was precipitated out in methanol and purified by repeated precipitation technique. The polymer was characterized by IR, UV and NMR spectroscopy. The synthetic route of polymer was depicted in scheme –II



Scheme –II

The polymer has good thermal, mechanical and photochemical properties. Indole is another hetero aromatic molecule which has a donor moiety. So, when this polymer was sensitized with TNF, a charge transfer (C.T) complex was formed. This polymer is a fully functionalized polymer and can be used as NLO polymer. A good photorefractive composite can be prepared by composition the polymer with 0.2 wt% of TPY salt.

IV. Conclusion

The article summarized the development of photorefractive polymer of indole as a pendant ring. We have synthesized the novel monomer 2-[N-(propyl acrylate) indolyl]-6-nitro benzothiazole and its co-polymer with MMA. Indole ring is incorporated with benzothiazole ring as pi-conjugation bridge and has good thermal and photochemical stability. The optical absorption of the indole-benzothiazole polymer was blue-shifted compared to conventional NLO polymer. This polymer has good photoconducting and photorefractive properties.

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