

Synthesis of Photoconducting Co-polymer of Carbazole-benzothiazole Moiety.

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Abstract: *N*-(1-hydroxy propyl) carbazole was synthesized by treating carbazole with trimethylene chlorohydrin in presence of solid sodium hydroxide in the solvent medium of acetone. *N*-(propyl acetate) carbazole was synthesized by reacting *N*-(1-hydroxy propyl) carbazole with acetic anhydride and pyridine in water bath. *N*-(propyl acetate)-3- formylcarbazole was synthesized by treating *N*-(propyl acetate) carbazole with PoCl_3 and DMF. 2-[*N*-(propylacetate) carbazolyl] benzothiazole was synthesized by treating *N*-(propyl acetate)-3- formylcarbazole with 2- amino thiophenol in presence of Baker's yeast in the solvent medium of DCM at room temperature for 30h . 2-[*N*-(1-hydroxy propyl) carbazolyl]benzothiazole was prepared by hydrolyzing 2-[*N*-(propyl acetate) carbazolyl] benzothiazole with KOH and ethanol. The monomer 2-[*N*-(propyl acrylate) carbazolyl] benzothiazole was synthesized by treating 2-[*N*-(1-hydroxy propyl) carbazolyl] benzothiazole with acryloyl chloride in presence of triethyl amine in the solvent medium of DCM. Lastly the monomer was co-polymerized with methyl methacrylate in presence of AIBN in the solvent medium of DMF.
Key words: *N*-(1-hydroxy propyl) carbazole, *N*-(propylacetate) carbazole, *N*-(propyl acetate) -3-formyl carbazole, 2-[*N*-(propyl acetate) carbazolyl] benzothiazole, 2-[*N*-(1-hydroxy propyl) carbazolyl] benzothiazole, 2-[*N*-(propyl acrylate) carbazolyl] benzothiazole, co-polymer.

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I. Introduction

Polymer with carbazole group are of considerable scientific and industrial interest because of their attractive features, such as their hole transporting, high charge carrier and electroluminescent properties. The hole transporting ability of carbazole polymers make them especially useful for applications in organic electronics. Numerous studies have been devoted to carbazole-containing polymers as a result of the success of poly(*N*-vinyl carbazole), poly(NVC), in electro photographic applications. Recent developments in this field are mostly connected to applications in polymeric light-emitting diodes, organic photorefractive materials, and photovoltaic devices. For example, conjugated poly(3,6-carbazole) and poly(2,7-carbazole) derivatives having carbazole moieties in the main chain have been employed for applications insolar cells and white-light-emitting diodes. In the past few decades, considerable attention has been given to the self-assembly of block copolymers, because of the feasibility of using them to generate nanostructured materials and their numerous potential applications in separation technology, controlled drug delivery and release, and smart catalyst separation technology.

A large number of photoconducting polymers have been synthesized using different kinds of polycyclic homo or hetero atomic aromatic compounds. In some cases aromatic groups are pendant from different kinds of polymeric backbone. But still poly vinyl carbazole is the most important one with respect to efficiency and cost of preparation. Poly(*N*-ethyl carbazolyl) methane is as efficient as poly *N*-vinyl carbazole. It is known that photon absorption by polymer can generate charge carriers under external electric field and suitable carrier injectors. Polymeric organic photoconductor mostly follow hopping mechanism of conduction. The hopping mechanism is well dependent on structural sequence and regularity of the polymer. In general, polymeric compounds are comprised of amorphous phase fully or partially. The relationship between mechanism of photoionization, photoconduction and trapping of charge carriers with respect to structure is not well established. All these studies have been made very arbitrarily.

In this article photoconducting co polymer of carbazole-benzothiazole moiety has been synthesized. It is a guest-host system main chain polymer. The co polymer can be doped with TNF and crystal violet which form a charge transfer complex. Photocurrent in the dark as well as under illumination can be measured with different voltages and different intensities.

A good photorefractive system can also be developed by conjugation the co polymer with DR-1, sensitizer TNF and plasticizer ECZ.

II. Experimental:

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

In an oven dried, one liter round-bottomed flask equipped with a magnetic stir bar and a rubber septum are placed carbazole and sodium hydroxide pellets in dry acetone, under an argon atmosphere. Stoichiometric amount of trimethylene chlorohydrin is added slowly over 15 minutes to the stirred reaction mixture at room temperature. After the addition, the reaction mixture is stirred for 8h at which time all solids are removed by filtration. The product is purified by repeated crystallization.

2.2. Synthesis of N-(propyl acetate) carbazole:

In a 100 ml round-bottomed flask 2.0g N-(1-hydroxy propyl) carbazole was mixed with 3.0 ml of pyridine. Then 3.0 ml of acetic anhydride was mixed dropwise and stirred well. The mouth of the flask was closed with the cork. After, the mixture was heated in a water bath for 2h with intermittent swirling. After the reaction was over, the mixture was cooled and precipitated out in cold water, filtered, washed with water and methanol and dried under vacuum.

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

12.0g of phosphorous oxy chloride was added dropwise to 5.8g of dimethyl formamide and stirred on ice-water bath. After that the reaction mixture was allowed to room temperature. Then 18.7g of N-(propyl acetate) carbazole was added in small portion. After overnight standing, the mixture was poured into water. The precipitate was filtered and recrystallized from ethanol.

2.4. Synthesis of 2-[N-(Propyl acetate) carbazolyl] benzothiazole:

8mmol of N-(Propyl acetate)-3-formylcarbazole, 8mmol of 2-aminothiophenol and 2.0g of baker's yeast were mixed in DCM and 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 2-[N-(Propyl acetate) carbazolyl] benzothiazole. The product was characterized by IR, UV and NMR spectroscopy.

2.5. Synthesis of 2-[N-(1-hydroxy propyl) carbazolyl] benzothiazole:

2.7mmol of 2-[N-(propyl acetate) carbazolyl] benzothiazole was dissolved in 50 ml of ethanol and 0.3g (5.4mmol) of KOH was added. The solution was mildly heated under magnetic stirring for 2h, and neutralized by HCl. After cooling, the precipitate was filtered and recrystallized from ethanol.

2.6. Synthesis of 2-[N-(propyl acrylate) carbazolyl] benzothiazole:

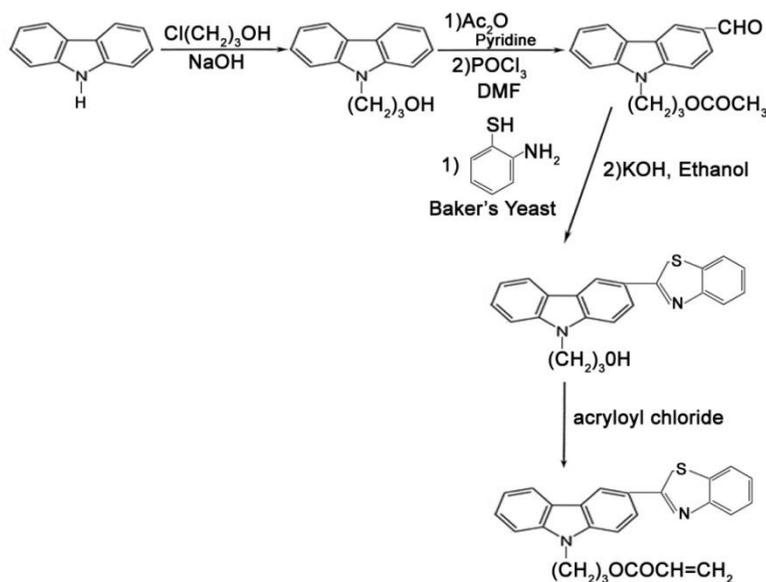
To a magnetically stirred solution of 0.55g (1.55mmol) of 2-[N-(1-hydroxyl propyl) carbazolyl] benzothiazole and 0.47g (4.64mmol) of triethylamine in 30 ml of dichloromethane, 0.28g (3.09mmol) of acryloyl chloride was added dropwise at 0°C. After stirring for 1h, the resulting solution was allowed to warm up to room temperature. After another 2h the solution was washed with brine and water, dried over magnesium sulphate, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography. The monomer was characterized by IR, UV and NMR spectroscopy.

2.7. Polymerization:

0.42g (1.02mmol) of 2-[N-(propyl acrylate) carbazolyl] benzothiazole, the monomer, 0.102g (1.02mmol) of MMA and 0.0167g (0.102mmol) of AIBN were dissolved in 5 ml of DMF. The solution was degassed by standard vacuum-freeze-thaw technique. After sealing the degassed ampoule, the reaction mixture was heated at 65°C for 48h. After cooling, the resulting solution was diluted to twice its original volume with DMF and poured in to methanol to precipitate the polymer. The polymer was characterized by FT-IR, UV and NMR spectroscopy.

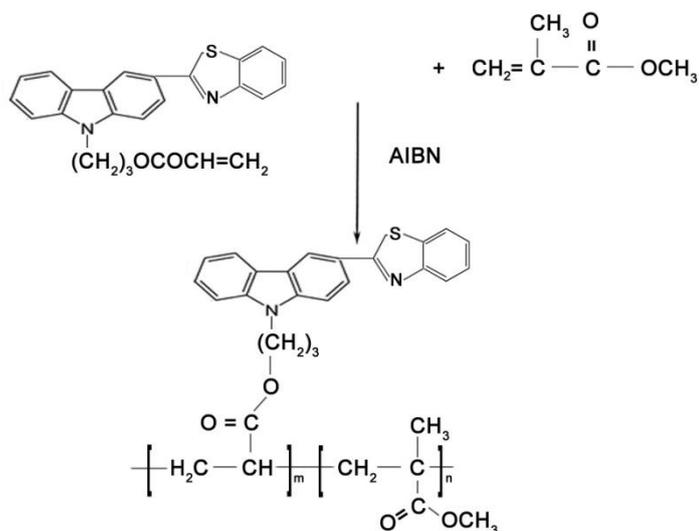
III. Result and Discussion

UV, IR and NMR spectroscopy revealed the successful preparation of the polymer. The synthetic route of the monomer was represented in scheme-I



scheme-I

Carbazole was first treated with trimethylene chlorohydrin in presence of solid NaOH in the solvent medium of acetone to prepare N-(1- hydroxyl propyl) carbazole. After that it was reacted with acetic anhydride in pyridine solution to form N-(propyl acetate) carbazole. Then N-(propyl acetate) carbazole was treated with POCl_3 and DMF to form N-(propyl acetate)-3-formylcarbazole. It was then treated with 2- aminothiophenol in presence of Baker's yeast in the solvent medium of DCM at room temperature to form 2-[N-(propyl acetate) carbazolyl] benzothiazole which was then hydrolysed with KOH and ethanol to prepare 2-[N-(1-hydroxy propyl) Carbazolyl] benzothiazole. Then 2-[N-(1-hydroxy propyl) carbazolyl] benzothiazole was treated with acryloyl chloride in presence of triethyl amine in the solvent medium of DCM to synthesize 2-[N-(propyl acrylate) Carbazolyl] benzothiazole. The synthesized monomer was characterized by FT-IR, UV and NMR spectroscopy. The monomer was then co- polymerized with MMA in presence of AIBN in the solvent medium of DMF under standard vacuum- freeze- thaw technique. The polymer was precipitated out in methanol. The synthetic route of the polymer was represented in scheme-II



scheme-II

The synthesized polymer has good mechanical property and thermal property due to carbazole-benzothiazole backbone. The incorporated benzothiazole moiety has given extra conjugation in the ring. The polymer has good

photoconducting property when it was doped with TNF or crystal violet. The photocurrent of the doped polymer can be measured in the dark or illumination at different voltages and different intensities. A good photo refractive system can be developed by conjugation of polymer with DR-1, sensitizer TNF and plasticizer ECZ. The polymer is soluble in most common organic solvents.

IV. Conclusion

The article has summarized the synthesis of novel monomer 2-[N-(propyl acrylate) carbazoly] benzothiazole and its co-polymer with methyl methacrylate. Carbazoleit self is a strong electron donating moiety which can easily form charge transfer complex with strong electron acceptor like TNF. The charge generated (hole) that will move through the polymer chain (charge transporting moiety) by hopping mechanism of conduction. The polymer can be doped with TNF or crystal violet and dark conductivity as well as photoconductivity can be measured. The photocurrent can be measured at different voltages and at different intensities. The benzothiazole moiety has given a long conjugation to the carbazole ring .The high performance photorefractive system can also be developed by doping the polymer with DR-1 and with the photosensitizer TNF and plasticizer ECZ.

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