

Synthesis of Photoconducting Co-Polymer of Carbazole-benzoxazole Moiety

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Abstract: At first 3-formyl-N-ethyl carbazole was synthesized by treating n-ethylcarbazole with $POCl_3$ and DMF. Then 3-formyl-N-ethyl carbazole was treated with 2-amino-3 hydroxy phenol in dioxane solvent medium in presence of silica supported sodium hydrogen sulphate ($NaHSO_4 \cdot SiO_2$) and refluxed for 16h to get 2-(N-ethyl carbazolyl)-4- hydroxyl benzoxazole. This monomer was then treated with methacryloyl chloride in THF solvent medium at room temperature for 50h. Lastly the second monomer namely 4-methacryloyloxy-2-(N-ethyl carbazolyl) benzoxazole was then co-polymerized with styrene in the solvent medium of DMF at $110^\circ C$ for 80h. All the monomers and co-polymer was investigated by FT-IR, UV and NMR spectroscopy. The silica supported sodium hydrogen sulphate was also prepared in the laboratory.

Key words: 3-formyl-N-ethyl carbazole, 2-(N-ethyl carbazolyl)-4-hydroxy benzoxazole, 4- ethacryloyloxy-2-(N-ethyl carbazolyl) benzoxazole, radical polymerization, Co-polymer.

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I. Introduction

Photoconductivity is the increase in electrical conductivity of a material caused by absorption of electromagnetic radiation. Photoconducting polymers are typically very good insulators in dark when the carriers of electricity free electrons and/ or holes are virtually absent. They become more conductive when exposed to light. In order to become a photoconductor, the polymer must satisfy two major requirements.

i. It must absorb light and thus allow photoexcitation of electrons from the ground state. The vacancy left behind (a hole) and the photo excited electron from a pair of charge carriers, which can be separated by the action of an electric field. ii. It must allow migration of either photoexcited electrons or holes, or both, through the polymer in the electric field towards the appropriate electrodes. Since, no ions move and matter is not displaced, the conduction process is wholly electronic with no ionic contribution.

Polymers that do not absorb light of a particular wave length can still support migration of charge carriers generated in an adjacent materials. In such a case the polymer are merely as charge transporting media. Since most known organic photoconducting polymers absorb only ultra-violet radiation, extrinsic photogeneration of charges has to be employed to make those polymers active in visible light, and in most practical organic photoconductors, the polymers are only charge-transporting media for charged photogenerated in adjacent photoconductors. Carbazole is another herocyclic compound that has been used in the synthesis of many organic photoconductors due to its photoconducting properties and high electron donating characters. Therefore these polymers possess interesting electro-optical and photo-chemical properties as well as high thermal stability due to carbazole backbone. Simple carbazole is easily available from coal-tar. Hogel first showed that poly N-vinyl carbazole has efficient photoconducting properties Which find applications in devices. A large number of photoconducting polymers have been synthesized using different kinds of polycyclic homo or hetero atomic aromatic compound, but still poly vinyl carbazole is the most important one with respect to efficiency and cost of preparation.

It is known that photon absorption by polymer can generate charge carriers under external electric field and suitable carrier injectors. Polymeric organic photoconductors mostly follow hopping mechanism of conduction. The hopping mechanism is well dependent on structural sequence and regularity of the polymer. The relationship between mechanism of photoionization, photoconduction and trapping of charge carriers with respect to structure is not well established. The photoconducting polymers are finding many important applications like xerography, photoimaging, photorefractive materials and photoelectric diodes.

In this article the first monomer namely 2-(N-ethyl carbazolyl)-4- hydroxyl benzoxazole and second monomer namely 4-methacryloyloxy-2-(N-ethyl carbazolyl) benzoxazole have been synthesized and lastly the copolymer of 4-methacryloyloxy-2-(N-ethyl carbazolyl) benzoxazole and styrene have been synthesized by radical initiated polymerization technique.

II. Experimental

2.1. Preparation of Silica supported sodium hydrogen sulphate:

To a solution of 4.14g (0.03mol) of sodiumhydrogensulphate in 20 ml of water in a 100 ml beaker containing at stir bar was added 10g of silica (230-400mesh). The mixture was stirred for 15 minutes and then gently heated on a hot plate, with intermittent swirling until a free flowing white solid was obtained. The catalyst was further dried by placing the beaker in an oven maintained at 120^oc for at least 48h prior to use. The synthesized catalyst was characterized by FT-IR spectrum.

2.2 Synthesis of N-ethyl Carbazole:

To a three-necked round bottom flask equipped with nitrogen purge and reflux condenser was added 3.34g(0.02 mol) of carbazole along with 75 ml of anhydrous DMF. To the stirred solution was added 0.72g (0.03mol) of sodium hydride. Immediately a precipitate formed with evolution of hydrogen gas. This was stirred for a further 15 minutes to dissolve the carbazole anion. Then 4.68g (0.03mol) of ethyl iodide was added in one portion. The reaction was exothermic, indicating the reaction proceed immediately. After 5h, 200 ml of water was added to give a precipitate. The product was recrystallised from chloroform.

2.3. Synthesis of 3-formyl –N-ethyl carbazole:

12 g of phosphorus oxy chloride were added dropwise to 5.8g of dimethyl formamide stirred on ice-water bath. Then the mixture was allowed to room temperature. After that 14g of N-ethyl carbazole was added in small portions. After over night standing, the mixture was poured into water. The precipitate was filtered and recrystallized from ethanol. The product was characterized by IR, UV and NMR spectroscopy.

2.4. Synthesis of 2-(N-ethyl crybazoly)-4- hydroxyl benzoxazole:

A mixture of 2-amino -3-hydroxyl phenol (1mmol), 3- formyl- N-ethyl carbazole (1.2m mol) and silica supported sodium hydrogen sulphate (25 wt%) in dioxane (10 ml) was placed in a 100 ml round bottom flask and stirred at reflux for 16h. The progress of the reaction was monitored by TLC. 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 diluted solution of brine and dried over magnesium sulphate and evaporated under vacuum. The obtained crude product was purified by column chromatography. The product was characterized by IR, UV and NMR spectroscopy.

2.5. Synthesis of 4- methacryloyloxy-2- (N-ethyl carbazoly) benzoxazole:

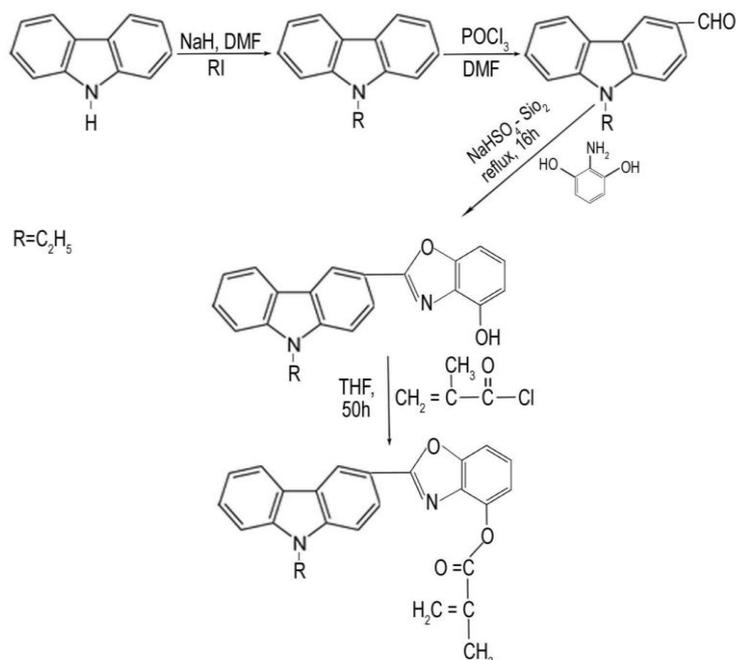
2- (N-ethyl carbazoly)-4- hydroxyl benzoxazole (3.14g, 10m mol) was dissolved in 50 ml of THF was cooled to 0^oc under nitrogen. To this solution pyridine (0.1g, 1.26m mol) and methacryloyl chloride (1.05g, 10m mol) were added dropwise simultaneously. The whole mixture was stirred for 3h. Then the reaction mixture was stirred for 50h at room temperature. The resulting mixture was washed with hydrochloric acid (0.1 M), sodium carbonate (5%) and finally with distilled water. The excess solvent was evaporated under reduced pressure. The organic layer was dried over magnesium sulphate. The reaction product obtained was purified by column chromatography using methylene dichloride. The monomer was characterized by IR,UV and NMR spectroscopy.

2.6. polymeriation:

4- methacryloyloxy -2-(N-ethyl carbaolyl) benzoxaole (1.484g,4m mol), styrene (0.416g, 4m mol) and azobisisobutyronitrile (2.14g, 13m mol) were dissolved in dry DMF (50ml). The reaction was carried out at 110^oc for 80h under nitrogen. The resulting solid was dissolved in DMF and reprecipitated from methanol. Polymer was collected by filtration, dried under vacuum and characterized by FT-IR, UV and NMR spectra.

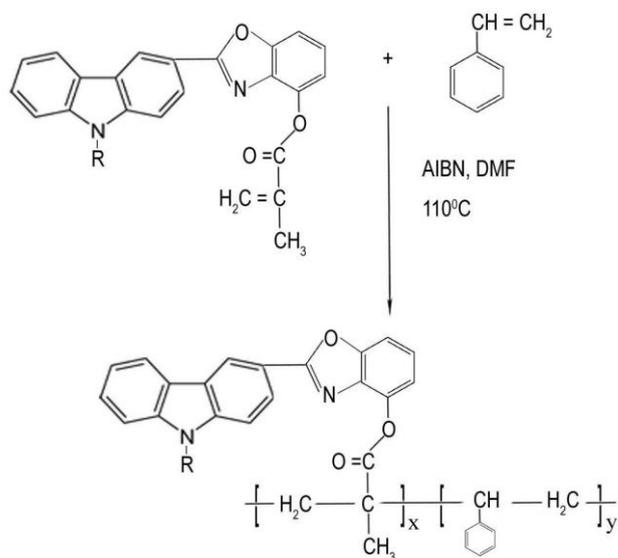
III. Result and Discussion

The study of IR, UV and NMR spectra revealed the successful preparation of the polymer. The synthetic route of the monomer starting from carbazole was presented in scheme-I.



Scheme-I

N-ethyl carbazole was synthesized by treating carbazole with sodium hydride and ethyl iodide in the solvent medium of DMF. The product was precipitated out in water. 3-formyl-N-ethyl carbazole was synthesized by reacting N-ethyl carbazole with phosphorus oxychloride and dimethyl formamide and keeping The mixture overnight. The product was precipitated out in water. After that 3-formyl-N-ethyl carbazole was treated with 2-amino-3-hydroxy phenol in the solvent medium of dioxane in silica supported sodium hydrogen sulphate and the mixture was refluxed for 16h which ultimately formed 2- (N-ethyl carbazolyl)-4- hydroxyl benzoxazole. The product was purified by chromatography. Then the monomer 4- methacryloyloxy -2- (N-ethyl carbazolyl)-benzoxazole was synthesized by treating 2-(N-ethyl carbazolyl) -4- hydroxyl benzoxazole with methacryloyl chloride in the solvent medium of THF and stirred for 50h at room temperature. The monomer was purified by column chromatography using methylene dichloride. The polymer was synthesized by treating the monomer 4-methacryloyloxy -2(N-ethyl carbazolyl) -benzoxazole with styrene in the solvent medium of DMF at 110⁰c using AIBN radical initiator. The synthetic route of the polymer was given in scheme-II



Scheme-II

The polymer was soluble in most common organic solvents. The polymer has good mechanical and thermal properties. The polymer has also good photoconducting property. The polymer can be doped with sensitizer like TNF and crystal violet to enhance the photoconductivity. The doped polymer can be used to measure photoconductivity in the dark or illumination at different voltages and different intensities.

IV. Conclusion

This article has summarized the synthesis of novel monomer 4-methacryloyloxy-2-(N-ethyl carbazolyl) benzoxazole and its co-polymer with styrene. Carbazole itself is an electron donating moiety. So, when it is doped with TNF or crystal violet a C.T. complex will be formed and corresponding charge will be generated which will move in the polymer side chain. Polymer itself is a charge transporting moiety and conduction of charge is carried by hopping mechanism. A benzoxazole moiety is incorporated to the carbazole backbone which has an extra conjugation. It is a guest-host system photoconducting polymer. The polymer can be doped with TNF or crystal violet and dark conductivity as well as photoconductivity under illumination at different intensities can be measured. Photoelectric current can also be measured at different voltages. The high performance photorefractive system can also be developed when the co-polymer will be doped with the electrooptic chromophore 2,5-dimethyl-4-(4-nitro phenylazo) anisole with the photosensitizer TNF and plasticizer ECZ.

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