

Synthesis of Photo conducting Polyurethane of Indole Moiety.

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Abstract: *N*-methyl indole was synthesized by treating indole with iodomethane in presence of sodium hydride in the solvent medium of DMF. *N*-methyl-3-formylindole was synthesized by reacting *N*-methyl indole with POCl₃ and DMF mixture in the solvent medium of orthodichlorobenzene. *N*-methyl-3-hydroxy methyl indole was synthesized by the reduction of *N*-methyl-3-formyl indole with sodium borohydride and sodium hydroxide mixture in the solvent medium of ethanol. Chloroformic ester of *N*-methyl-3-hydroxymethyl indole was prepared by reacting *N*-methyl-3-hydroxy methyl indole with phosgene and pyridine in the solvent medium of THF. 4-[*N*-methyl indolyl-3-methylene oxy carbonyl imino] styrene was prepared by reacting the chloroformic ester of *N*-methyl-3-hydroxy methyl indole with 4-amino styrene in the solvent medium of THF. Lastly the monomer namely 4-[*N*-methyl indolyl-3-methylene oxy carbonyl imino] styrene was copolymerized with methyl methacrylate with a peroxide initiator in the solvent medium of DMF. The monomer and the copolymer was characterized by IR, UV and NMR spectroscopy.

Key words: *N*-methyl-3-formyl indole, *N*-methyl-3-hydroxymethyl indole, chloroformic ester of *N*-methyl-3-hydroxymethyl indole, 4-[*N*-methyl-indolyl-3-methylene oxy carbonyl imino]styrene, copolymerization.

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I. Introduction

Carbazole derivatives are well-known to exhibit good electro and photo active properties due to their high hole transporting mobility, strong absorption in the ultraviolet spectral region and blue-light emission. Since the discovery of photoconductivity in poly (9-vinyl Carbazole) (PVK) Carbazole-Containing derivatives became the subject of numerous investigations for applications in electrophotography. The second wave of interest in Carbazole-based CTMs is connected mostly with the discovery of organic light emitting diodes and photo refractive materials. Apart from the electrophotographic photoreceptors, light-emitting diodes and photorefractive materials, Carbazole-containing transporting materials are studied as the components of photovoltaic devices and field-effect transistors. Commercial availability and relative cheapness of the starting materials, simple synthesis, number of sites available for easy functionalization, good charge drift mobility and solubility in common organic solvents make these precursors attractive building blocks for the construction of more complex materials for optoelectronic applications.

Photorefractive polymers have attracted considerable attention owing to their potential applications including high-density optical data storage, optical image processing, phase conjugation, laser dynamic holography, optical computing and pattern recognition. dynamic holography, optical computing and pattern recognition. The necessary characteristics for a material to be regarded as potentially photorefractive are photoconductivity and electro-optic property. Therefore, a candidate photorefractive polymer can be made by either incorporating these properties directly into polymer (fully functionalized polymer) or doping guest molecules into the polymer (guest-host polymer composite) to produce these properties. 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). We have synthesized and reported various photoconducting polymer based on heteroaromatic donor moiety like carbazole. It was shown that polymethacrylates containing the Carbazole ring as a side chain has excellent EO property and moderate photoconductivity.

Indole is another heteroaromatic molecule which is easily available from coal tar and has donor moiety like carbazole. Indole, the heteroaromatic structure like carbazole was designed to work as photoconducting moiety as well as electron donor. Indole was adopted over carbazole for this purpose, because indole provides better poling efficiency owing to the more compact size compared with Carbazole. Indole has also good thermal and mechanical properties. Indole has good donor moiety like Carbazole and easily formed C.T. complex with TNF or crystal violet and forming hole that will migrate to the polymer chain (charge transporting media).

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 this article photoconducting polyurethane of indole moiety has been synthesized. It is a guest-host system polymer where the host polymer matrix can be doped with the guest molecule like TNF and photoconductivity can be measured in the dark as well as under illumination at different voltages and different intensities. A good photorefractive system can be developed by conjugation the polymer with a second order NLO chromophore like DR-1, plasticizer ECZ and photosensitizer like TNF.

II. Experimental

2.1. synthesis of N-methyl indole:

To a three necked round bottom flask equipped with nitrogen purge and reflux condenser was added 2.34g(0.02mol) of indole along with 75ml 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 further 15 minutes to dissolve the indole anion. Then 4.26(0.03mol) of iodomethane was added in one portion. After 6h, 200ml of water was added to give a precipitate. The product was recrystallized from chloroform.

2.2. Synthesis of N-methyl-3-formyl indole:

Equipped a 500ml three necked flask with a sealed stirrer unit, a reflux condenser and a dropping funnel. The apparatus was assembled on a water bath in a fume cupboard. The flask was placed in a mixture of 13.1g(0.1mol) of N-methyl indole, 19g(20ml, 0.26mol) of dimethylformamide and 20ml of orthodichloro benzene and charged the dropping funnel with 27g (16ml, 0.175mol) of phosphorus oxychloride. closed the condenser and dropping funnel with Calcium chloride guard-tubes. Started the stirrer and added phosphorus oxychloride steadily. The mixture was heated on a boiling water bath for 2h. The reaction flask was then cooled in an ice - salt bath and neutralized the contents by running in aqueous sodium acetate solution. The mixture was then diluted with more water about 2 litres and allowed the mixture to stand for 2h at 0^oc. The solid was filtered off and washed with water and dried.

2.3. Synthesis of N-methyl -3-hydroxy methyl Indole

To a solution of 14.31g (0.09mol) of N-methyl -3-formyl indole in 150ml of ethanol, a mixture of 2.5 g of sodium borohydride and 20 ml of 0.4(N) sodium hydroxide in water was added dropwise. The mixture was then heated at 60^oc and stirred for 2h. Ethanol was removed under reduced pressure and the residue was poured in to water. The product was extracted with chloroform, washed with water and dried over magnesium sulphate. The solvent, chloroform was removed under reduced pressure and the crude product was isolated. The product was recrystallized from chloroform.

2.4. Synthesis of N-methyl indolyl -3- methylene oxy Carbonyl chloride:

0.04mols of phosgene mixed with toluene was taken in a three necked flask, fitted with a magnetic stirrer and a condenser. The mixture was placed in an ice-bath at 0^o-5^oc. 0.04mols of N-methyl-3-hydroxymethyl indole mixed with 50ml of THF was slowly added with vigorous stirring. 3.2 g of pyridine was added and the mixture was stirred for 3h.

2.5. Synthesis of 4- [N-methyl indolyl -3-methylene oxy carbonyl imino] styrene:

After the reaction was over, 0.04 mols of 4-amino styrene mixed with THF was quickly added to the above reaction mixture and stirred at 5^oc for 5h by the following addition of 3.2g of pyridine. The mixture was precipitated out in water. The product was filtered off, washed with water and dried. The monomer was characterized by IR, UV and NMR spectroscopy.

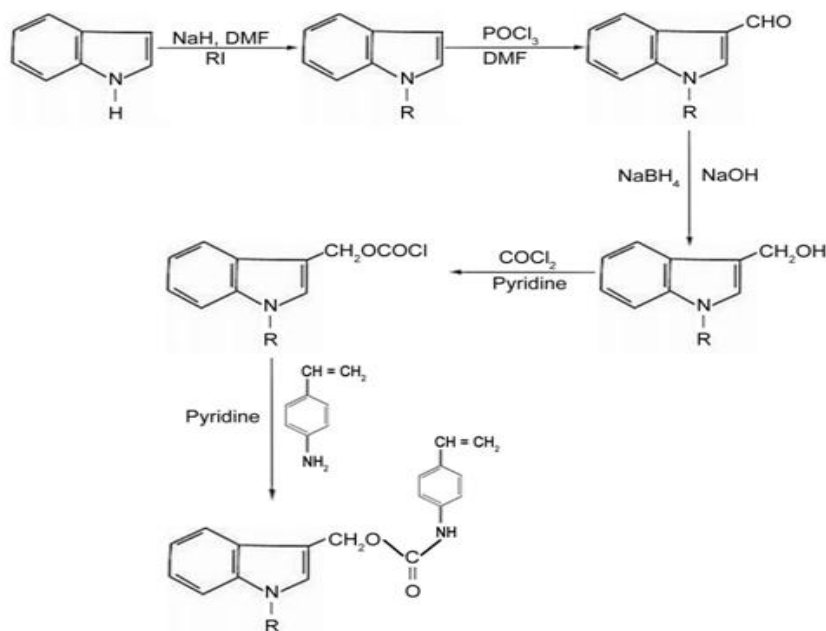
2.6. Polymerization:

4-[N-methyl indolyl-3-methyleneoxy Carbonylimino] styrene (1.15g, 3.75mmol), methylmethacrylate (0.38g, 3.75mmol) and azobisisobutyronitrile (2g, 12.19mmol) 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 stored. The polymer was characterized by IR, UV and NMR spectroscopy.

III. Result and Discussion

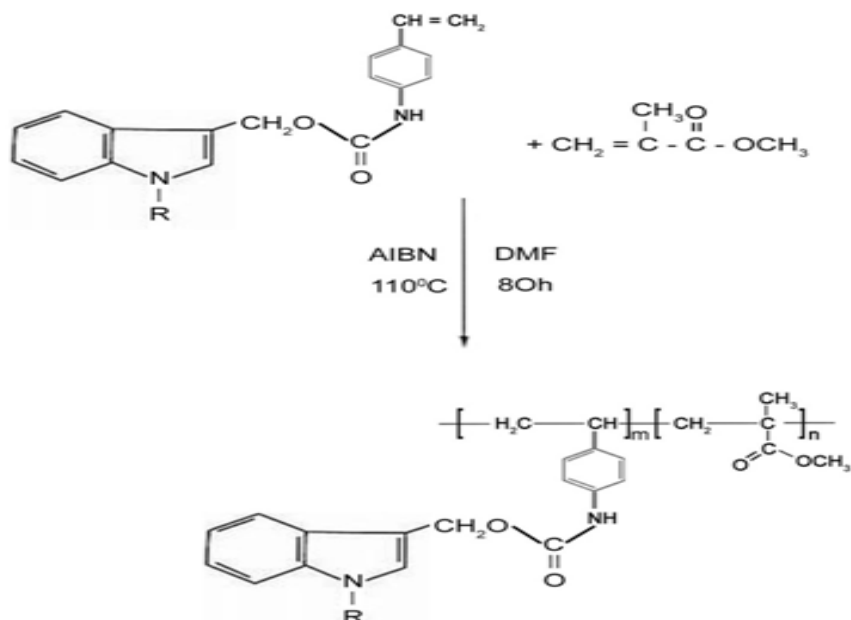
The study of IR, UV and NMR spectra revealed the successful preparation of the polymer. N-methyl indole was prepared by reacting indole with iodomethane in presence of sodium hydride in the solvent medium of DMF. After subsequent addition of water N-methyl indole was precipitated out. N-methyl-3-formyl indole was synthesized by treating N-methyl indole with POCl₃ and DMF mixture. N-methyl -3-hydroxy methyl indole was prepared by reducing N-methyl-3- formylindole with sodium borohydride in alkaline medium in ethanol

which was subsequently extracted with chloroform and recrystallized from chloroform. The chloroformic ester of N-methyl-3-hydroxymethyl indole was prepared by reacting N-methyl-3-hydroxy methyl indole with phosgene and pyridine in the solvent medium of THF. 4-[N-methyl-indolyl -3- methylene oxy Carbonyl imino]styrene was synthesized by treating the chloroformic ester of N-methyl -3-hydroxy methyl indole with 4-vinylaniline in presence of pyridine in the solvent medium of THF. The synthetic route of monomer was given in scheme-I.



Scheme-I

The co-polymer was synthesized by treating the monomer with methyl methacrylate in the presence of peroxide in the solvent medium of DMF. The polymer was precipitated out in methanol, washed with methanol and dried. The polymer was characterized by FT-IR, UV and NMR spectroscopy. The synthetic route of polymer was represented in scheme-II



Scheme- II

The polymer has good thermal and mechanical properties. The polymer was soluble in most common organic solvents. The electro-optic coefficients of the poled polymers can be measured at the wave length of 633nm (He-Ne laser) by using simple reflection method. The dark and photoconductivity of the polymer film can be measured by evaluating a current through the polymer film sandwiched between gold and ITO by using He-Ne laser as a light source. Photorefractivity 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 a second order NLO chromophore (DR-1), Sensitizer like TNF or 0.2 wt% of TPY-salt and a plasticizer like ECZ.

IV. Conclusion

The article summarizes the novel synthesis of polyurethane of electron donating heteroaromatic indole ring. The monomer and the co-polymer was characterized by FT-IR, UV and NMR spectroscopy. Indole is another heteroaromatic molecule like Carbazole which has electron donating character and forms charge transfer complex with strong electron accepting moiety like TNF. Indole is easily available from Coal-tar so a cheaper photoconducting polymer can be obtained. It is a guest-host system photoconducting polymer where the host polymer can be doped with a guest molecule like TNF and photoconductivity can be measured at different voltages and different intensities. Indole has better poling efficiency than that of Carbazole owing to its smaller size. Further a good photorefractive system can be developed by conjugation the polymer with a second order non-linear optical chromophore (DR-1) and Sensitizer like TPY-salt and a plasticizer like ECZ.

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