

Synthesis of Photoconducting Polyimide of Indole Ring.

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Abstract: *N-ethyl-3-methyl indole was synthesized by treating ethyl iodide with 3-methyl indole in presence of sodium hydride in the solvent medium of DMF. N-ethyl-3-bromomethyl indole was prepared by reacting N-ethyl-3-methyl indole with NBS and benzoyl peroxide in the solvent medium of benzene. N-ethyl-3-(N,N-diethanol amino methyl) indole was synthesized by treating N-ethyl-3-bromomethyl indole with diethanolamine in presence of potassium carbonate and trace amount of 18-crown-6 in the solvent medium of DMSO. 4,4'-(hexafluoroisopropylidene)-diphthalimide was synthesized by reacting 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride with urea by heating the mixture at 240^oC for 1h and then at 270^oC for 1h. Polyimide was synthesized by the reaction of N-ethyl-3-(N,N-diethanolamino methyl) indole with 4,4'-(hexafluoroisopropylidene) diphthalimide in presence of triphenyl phosphine and diethylazodi carboxylate in the solvent medium of super dry THF at room temperature for 4days.*

Key words: *N-ethyl-3-bromomethyl indole, N-ethyl-3-(N,N-diethanolamino methyl) indole, 4,4'-(hexafluoroisopropylidene) – diphthalimide, Polyimide.*

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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 ultra violet 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 photorefractive 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, lasing, dynamic holography, optical computing and pattern recognition. The necessary characteristics for a material to be regarded as potentially photorefractive are photoconductivity. Polymer can be made by either incorporating these properties directly into polymer (fully functionalised polymer) or doping guest molecules into the polymer (guest-host polymer composite) to produce these properties. Most of 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 photo sensitizer). We have synthesized and reported various photoconducting polymer based on heteroaromatic donor moiety like carbazole and indole. 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 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 photo conducting polyimide of indole ring has been synthesized. This is guest-host system polymer where the host polymer matrix can be doped with 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-I, plasticizer ECZ and photosensitizer like TNF.

II. Experimental:

2.1. Synthesis of N-ethyl – 3 – methyl indole::

To a three necked round bottom flask equipped with nitrogen purge and reflux condenser was added 2.62g (0.02mol) of 3-methyl indole along with 75 ml of anhydrous DMF. To the stirred solution was added 0.72 g(0.03 mol) of sodium hydride. Immediately a precipitate formed with evolution of hydrogen gas. This was stirred for further 15 mins. to dissolve the indole anion. Then 4.68g (0.03 mol) of iodoethane was added in one portion. After 10h, 200 ml of water was added to give a precipitate. The product was recrystallized from chloroform.

2.2. Synthesis of N-ethyl – 3- bromomethylindole ::

Under a nitrogen atmosphere, a mixture of N-ethyl-3-methyl indole 4.77g (0.03 mo), NBS 4.65g (0.033 mol), benzene (100ml) and benzoyl peroxide (50mg) was heated under reflux for 8h. The mixture was cooled and filtered and the filtrate was removed under reduced pressure. Water (100ml) was added and the organic layer was extracted by DCM. After removal of solvent, the crude product was recrystallized with ethanol giving N-ethyl – 3 bromomethylindole.

2.3. Synthesis of N-ethyl – 3- (N,N-diethanolamino methyl) indole ::

Into a 250ml flask added 4.76g (0.02 ml) of N-ethyl-3- bromo methyl indole and 2.76g (0.02 mol) of potassium carbonate and 50 ml of DMSO. This mixture was heated to 100^oc with stirring. Into this mixture added the solution of 4.2 g (0.04 mol) of diethanolamine in 10 ml of DMSO slowly and followed by adding 0.1g of 18-crown-6. This mixture was stirred at this temperature for 24h. Then the mixture was poured into cold water to precipitate the product. The product was purified by recrystallization from ethanol.

2.4. Synthesis of 4,4' – (hexafluoroisopropylidene)diphthalimide ::

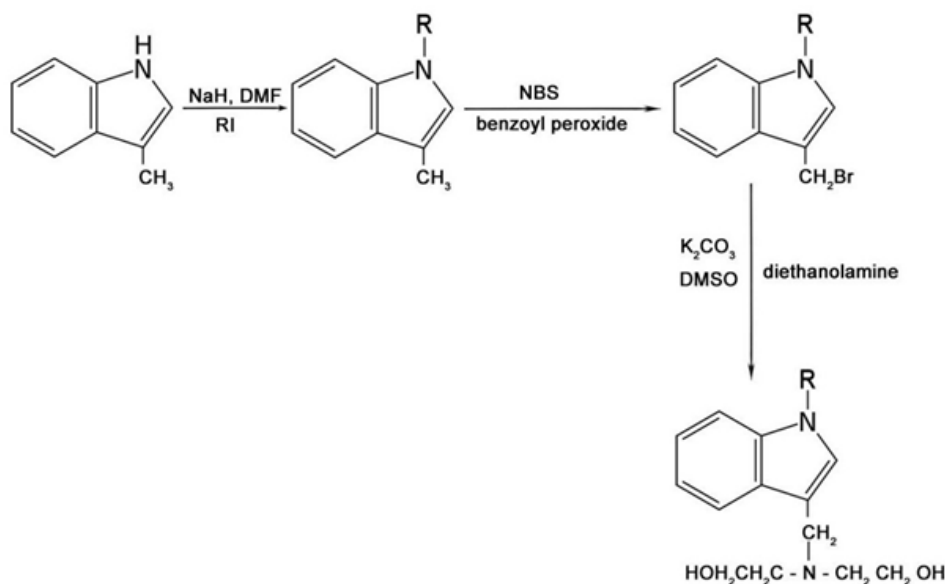
1.776g (4 m mol) of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride was mixed with 0.36g (6m mol) of urea and heated in a round bottom flask at 240^oc for 1h. After cooling the solid was pulverized and heated at 270^oc for 1h. The cooled reaction product was washed out with water, dried and recrystallized from ethanol.

2.4. Synthesis of polyimide ::

To a solution of 1m mol of 4,4'-(hexafluoroisopropylidene) diphthalimide, 1 m mol of N-ethyl-3-(N,N-diethanolaminomethyl) indole and 1.5 m mol of triphenylphosphine in super dry THF under inert atmosphere, 1.5 m mol of diethylazodi carboxylate was added dropwise under stirring and cooling. The solution stirred for 4 days at room temperature and the polymer precipitated in methanol. The isolated polymer precipitated in methanol. The isolated polymer was dried and fractionated by adding methanol to a tetrahydrofuran solution under stirring. The highest molecular weight fraction was separated and dried under Vacuum.

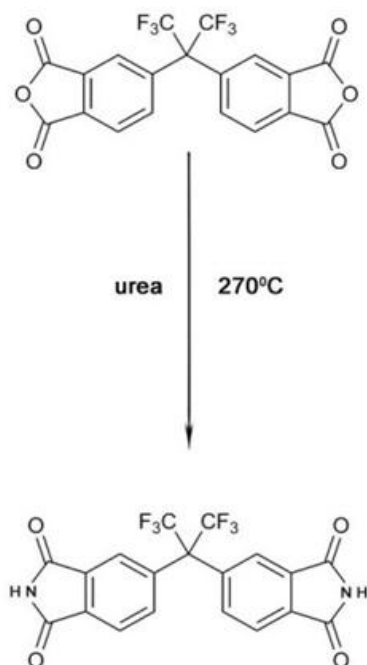
III. Result And Discussion:

The study of IR, UV and NMR spectra revealed the successful preparation of polymer. The monomer also investigated by IR, UV and NMR spectra. N-ethyl-3-methyl indole was synthesized by treating 3-methyl indole with iodoethane in presence of sodium hydride in the solvent medium of DMF under stirring for 10h. The product was precipitated in water. N-ethyl 3-bromomethyl indole was prepared by reacting N-ethyl-3-methyl indole with N-bromosuccinimide and benzoyl peroxide in the solvent medium of benzene under reflux condition for 8h. N-ethyl3-(N,N-diethanolamino methyl) indole was synthesized by treating N-ethyl-3-bromomethyl indole with diethanol amine and trace amount of 18-crown-6 in the solvent medium of DMSO under stirring at 100^oc for 24h. The synthetic route of monomer was depicted in scheme-I



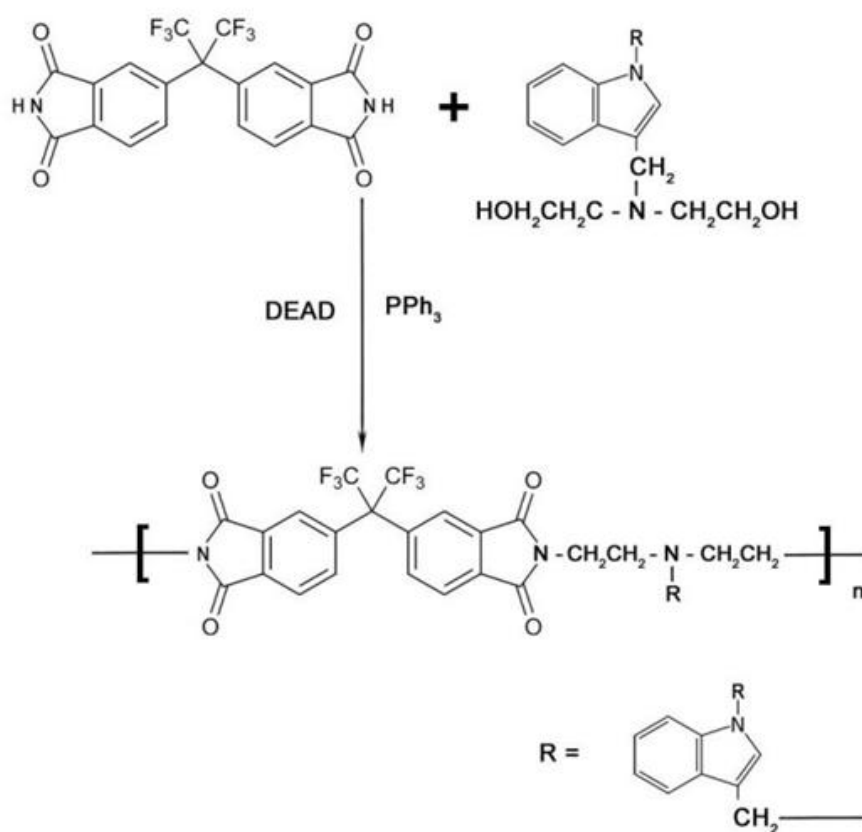
scheme-I

4,4'-(hexafluoroisopropylidene) diphthalimide was synthesized by treating 4,4'-(hexafluoroisopropylidene) diphthalic anhydride with urea heated at 240⁰c for 1h and then at 270⁰c for 1h. The synthetic route of 4,4'-(hexafluoroisopropylidene) diphthalimide is given in scheme-II.



scheme-II.

Polyimide was synthesized by treating N-ethyl-3-(N,N-diethanol amino methyl) indole with 4,4'-(hexafluoroisopropylidene) diphtalimide in presence of triphenyl phosphine and diethylazodicarboxylate in the solvent medium of THF at room temperature for 4 days. The synthesis of polyimide was a one-step process. Thereaction of di (hydroxyalkyl) indole with diimide under Mitsunobu conditions give rise to direct formation of the polyimide structure. This alternative route has several advantages compared to the classical methods. The method presented here is a fast, direct and elegant procedure to obtain the polyimide and because of the mild conditions there are no restrictions for the kind of chromophore to be incorporated into the polymer structure. The structure of the synthesized polyimide is given in scheme – III



IV. Conclusion:

We succeeded in our approach to obtain high Tg polyimide in a one step process, from di(hydroxyl alkyl) indole and diimide under Mitsunobu conditions. This method is an elegant procedure to incorporate chromophores, which may be unstable under the harsh conditions by using other approaches for chromophore synthesis. Indole-based polyimide exhibited thermal stability with high Tg and very good solubility. This polymer has inherent viscosity and exhibited attractive properties that make it suitable for a variety of applications. Indole-based PI generally possess excellent thermal, mechanical, electrical and chemical properties. Therefore, it can be used in many applications such as electronics, coatings, adhesives and composite materials.

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