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Synthesis of Photoconducting Polyester and Polyurethane 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 N-bromosuccinimide and benzoyl peroxide in the solvent medium of benzene. N-ethyl-3-(N,N-diethanolamino 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. Polyester was synthesized by treating N-ethyl-3-(N,N-diethanol amino methyl) indole with diacid chloride monomer, 6FBC at 70^0c in the solvent medium of 1,2-dichloroethane.Polyurethane was synthesized by reacting the monomer, N-ethyl-3-(N,N-diethanolaminomethyl) indole with TDI in the solvent medium of toluene. All the monomer and polymers was characterized by IR, UV and NMR spectroscopy.*

Keywords: *N-ethyl-3-methyl indole, N-ethyl -3-bromomethyl indole, N-ethyl-3-(N,N-diethanol amino methyl)indole , Polyester , Polyurethane, Polymerization.*

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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 photorefractive materials. Apart fron the electrophotographicphotoreceptors, light-emitting diodes and photorefractive materials,Carbazole-containing transporting materials are studied as the components of photo-voltaic 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, dynamicholography, optical computing and pattern recognition. The necessary characterisctics for a material to be regarded as potentially photorefractive are photoconductivity. 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 photorefractive polymers reported to date are based on guest-host polymer composite, which normally consist of four components (photoconducting polymer host, NLOchromophore, plasticizer and photosensitizer). We have synthesized and reported various photoconducting polymer based on heteroaromaticdoner 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 doner moiety like carbazole. Indole, the heteroaromatic structure like Carbazole was designed to work as photoconducting moiety as well as electron doner. 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 doner 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 photoconducting polyester and polyurethane of indole ring have been synthesized. These are 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-1, 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 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 4.68g(0.03mol) of iodoethane was added in one portion. After 10h, 200ml of water was added to give a precipitate. The product was recrystalized from chloroform.

Synthesis of N-ethyl-3-bromomethyl indole:

Under a nitrogen atmosphere, a mixture of N-ethyl-3-methyl indole 4.77g(0.03mol) N-bromosuccinimide 4.65g (0.033mol), 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 dichloromethane. After removal of solvent, the crude product was recrystalized with ethanol, giving N-ethyl-3-bromomethyl indole.

2.3. Synthesis of N-ethyl-3-(N,N-diethanolaminomethyl)indole:

Into a 250 ml flask added 4.76g(0.02mol) of N-ethyl-3-bromomethyl indole and 2.76g (0.02mol) of Potassium Carbonate and 50 ml of DMSO. This mixture was heated to 100^0c with stirring. Into this mixture added the solution of 4.2g (0.04mol) of diethanolamine in 10ml of DMSO slowly and followed by adding 0.1 g of 18-Crown-6. The mixture was stirred at this temperature for 24 h. Then the mixture was poured into cold water to precipitate the product. The product was purified by recrystallization from ethanol.

2.4. Synthesis of Polyester

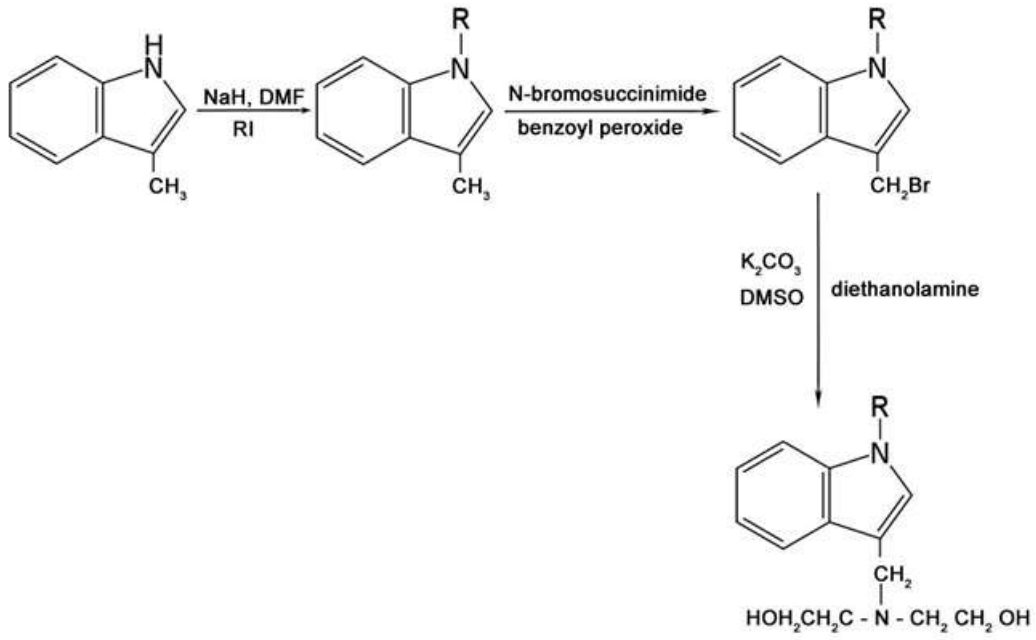
In a 100 ml flask, added 2.33g(0.01mol)of N-ethyl -3-(N,N-diethanolaminomethyl) indole and 40 ml of 1,2-dichloroethane. The diacid chloride monomer, 6FBC(4.09 g , 0.01 mol) was added into the solution at room temperature With stirring. Triethylamine2.02 g (0.02 mol) was added for acid trapper. The polymerization was Carried out at 70^0c for 24h. The polymer solution was poured into methanol. The precipitated solid was purified by repeated precipitation.

2.5. Synthesis of polyurethane:

In a 100 ml flask, added 2.33 g (0.01 mol) of N-ethyl-3-(N,N-diethanolamino methyl) indole and 40 ml of toluene. Then toluene diisocyanate (TDI) 1.74 g (0.01 mol) was added into this solution at room temperature with stirring. The polymerization was Carried out at 50^0c for 3h. The polymer solution was precipitated out in hexane filtered, washed with hexane and methanol and dried.

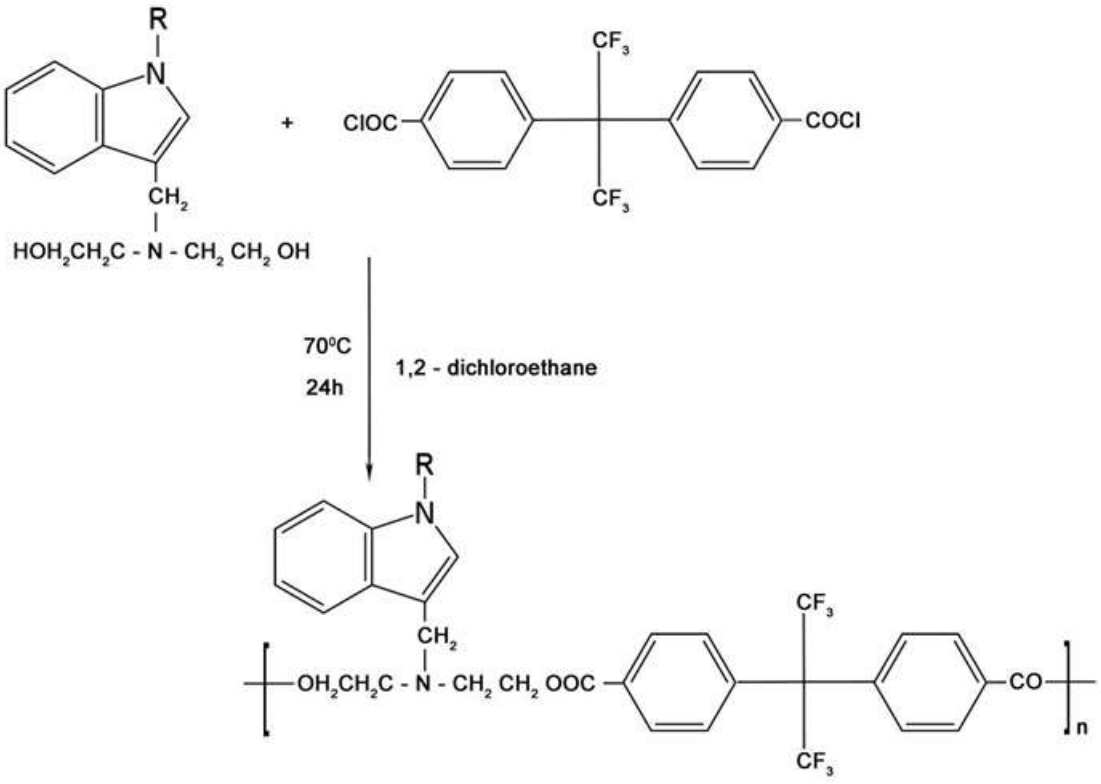
III. Result and discussion:

The study of IR, UV and NMR spectra revealed the Successful Preparation of polymers. The monomer also investigated by IR,UV and NMR spectra. N-ethyl-3-methyl indole was synthesized by treating 3-methyl indole with iodo ethane in presence of sodium hydride in the solvent medium of DMF under stirring for 10h. The product was precipitated in water. N-ethyl-3-bromo methyl indole was prepared by reacting N-ethyl-3-methyl indole with N-bromosuccinimide with benzoyl peroxide in the solvent medium of benzene under reflux condition for 8h. N-ethyl-3-(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 100^0c for 24h. The synthetic route of monomer that is N-ethyl-3-(N,N-diethanolamino methyl) indole was depicted in scheme-I



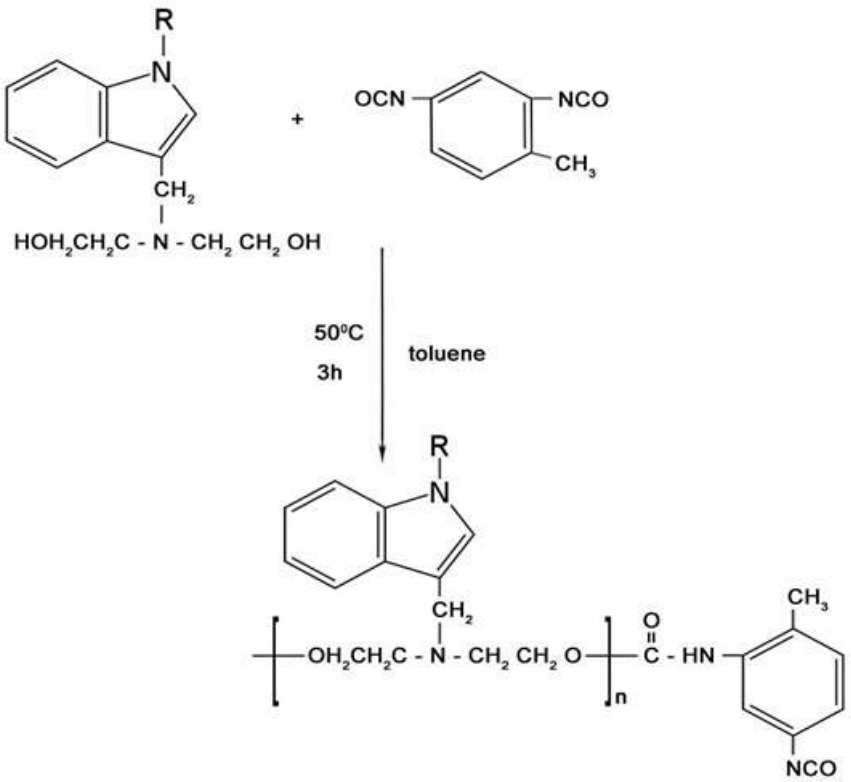
Scheme-I

The polyester was synthesized by treating N-ethyl-3-(N,N-diethanol amino methyl) indole with diacid chloride, 6FBC in the solvent medium of 1,2-dichloro ethane under stirring at 70^0 for 24h. The synthetic route of polyester was depicted in scheme-II.



Scheme-II

The polyurethane was synthesized by treating N-ethyl-3-(N,N-diethanolamino methyl) indole with TDI in the solvent medium of toluene under stirring at 50^0c for 3h. The polyurethane was precipitated out in hexane. The synthetic route of polyurethane was depicted in scheme-III.



Scheme-III

The polyester and polyurethane have good thermal and mechanical properties. The polymers are soluble in most common organic solvents. The electro-optic coefficient of the poled polymers can be measured at the wave length of 633nm (He-Ne laser) by using simple reflection method. The host polymers can be doped with guest molecule like TNF and dark and photoconductivity can be measured of polymer film by evaluating a current. Photo refractivity can be studied by two-beam coupling and four-wave mixing at the electric field. The photorefractive composites can be prepared by conjugation the polymers host with a second order NLO chromophore (DR-1), Sensitizer like TNF or 0.2wt% of TPY-salt and a plasticizer like ECZ.

IV. Conclusion:

The article summarized the novel synthesis of polyester and polyurethane of electron donating heteroaromaticindole ring. The monomer and polymers were characterized by FT-IR, UV and NMR spectroscopy. Indole is another heteroaromatic molecule like carbazole which has electron donating character and form C.T.complex with strong electron acceptor like TNF. Indole is easily available from coal-tar so, cheaper photoconducting polymers can be prepared. The polymers are guest-host system polymers where the host polymers can be doped with guest molecule like TNF and photoconductivity can be measured at different voltages and different intensities. Further, a good photorefractive composite can be developed by conjugation the polymers with a second order NLO chromophore (DR-1) and sensitized like TPY –salt and a plasticizer like ECZ.

References:

[1]. Kippelen B, Tamura K, Peyhambarian N, Padias AB, Hall Jr. HK. Phys. Rev B 1993, 48 (15): 10710.
[2]. Yu L, Chan WK, Peng Z, Gharavi A. Acc. Chem. Res. 1996, 29:13.
[3]. Z hang Y, Wada T, wang L, Aoyama T, Sasabe H. Chem. Commun. 1996, 2325
[4]. Barrett C, Chowdhury B, Natansohn A, Rochon P. Macromolecules 1998, 31, 4845
[5]. Wright D, Diaz- Garcia MA, Casperson JD, DeClue M, Moerner WE, Twieg RJ. Appl. Phys. Lett. 1998, 73(11), 1490.
[6]. Cox AM, Blackburn RD, West DP, King TA, Wada FA, Leigh DA. Appl. Phys. Lett. 1996,68(20),2801.
[7]. Zhang Y, Ghosal S, Casstevens MK, Burzynski R. J.Appl. Phys. 1996, 79 (12), 8920.
[8]. Silence SM, Scott JC, Stankus JJ, Moerner WE, Moylan CR, Bjorklund GC, Twieg RJ. J. Phys. Chem. 1995,99, 4096.
[9]. Moon H, Hwang J, Kim N, Park SY. Macromolecules 2000,33(14), S116.
[10]. Moon H, Kim N, Park sy. Nonlinear Optics 1999,20, 347.

[11]. Meerhrolz K, Volodin BL, Sandalphon, Kippelen B, Peyghambarian N. Nature 1994, 371(6), 497.
[12]. Bolink HJ, Krasnikov VV, Malliaras GG, Hadziioannou G.J. Phys. Chem. 1996, 100, 16 356.
[13]. Zhanng Y, Spencer CA, Ghosal S, Casstevens MK, Burzynski R, Appl. Phys. Lett. 1994, 64, 1908.
[14]. Han SH, Wu JW. J. Opt. Soc. Am B 1997, 14, 1131.
[15]. Sutter K, Gunter P. J. Opt. Soc. Am B 1990,7, 2274
[16]. Walsh CA, Monerner We. J. Opt. Soc. Am B 1992, 9, 1642
[17]. Centore R, Panunzi B, Roviello A, Sirigu A, Villano P. J. Polym. Sci. Part A Polym. Chem. 1996, 34, 3203.

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