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Synthesis of Photoconducting Polyester of Carbazole Ring.

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Abstract: *3,6-dibromo-9-methyl carbazole was prepared by treating 3,6- dibromocarbazole with iodomethane in presence of sodium hydride in the solvent medium of DMF and lastly the product was precipitated out by adding water.3,6-dimethyl-9-methyl carbazole was synthesized by treating 3,6-dibromo-9-methyl carbazole with methyl magnesium bromide in presence of [1,3-bis(diphenylphosphino) propane]nickel(II)chloride in the solvent medium of dry ether. 3,6-di(bromomethyl) -9-methyl carbazole was synthesized by treating 3,6-dimethyl-9-methyl carbazole with N-bromosuccinimide in presence of benzoyl peroxide in the solvent medium of benzene. 3,6-di [(hydroxy ethyl)(methyl) amino methyl]-9-methyl carbazole was synthesized by treating 3,6-di(bromo methyl) -9-methyl carbazole with 2-(methyl amino) ethanol in presence of potassium carbonate in the solvent medium of DMSO and in presence of small amount of 18- crown-6 at 100^0c for 24h. Lastly the polyester was synthesized by treating 3,6-di[(hydroxy ethyl)(methyl) amino methyl]-9-methyl carbazole with diacid chloride monomer, 6FBC in the solvent medium 1,2-dichloro ethane at 70^0c for 24h. The monomer and polyester was characterized by studying IR, UV and NMR spectroscopy.*

Keywords:*3,6-dimethyl-9-methylcarbazole,3,6-di(bromomethyl)-9-methylcarbazole,3,6-di[(hydroxy ethyl)(methyl)amino methyl] -9-methyl carbazole, 6FBC, polyester.*

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I. Introduction

Macromolecular materials with unique combination of both electronic and optical properties have attracted tremendous technological interest in the past few decades due to increasing need for low cost materials with structural flexibility. Various designing methods have been employed to achieve efficient semiconducting properties in polymers with potential applications in the field of optical storage media, dynamic holography, xerography, photorefractive composites, photovoltaic devices, light emitting diodes and many other photonic systems. The extend of pi-conjugation and the presence of aromatic amino group in the polymer structure are the common structural features of charge transporting materials. The charge transport and the semiconducting properties of these polymers depend mainly on the structure and morphology of the polymer chains.

Polymer with carbazolering 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 containing 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 clectro photographic applications. Recent developments in this field are mostly connected to applications in polymeric light emitting diodes, organic photorefractive materials and photovoltaic device. For example, conjugated poly(3,6-carbazole)and poly(2,7-carbazole) derivatives having carbazole moieties in the main chain or side chain have been employed for application in solarcells 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 application 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. 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 methanism 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 arbitrarily.

In this article novel carbazole based monomer 3,6-di[(hydroxy ethyl)(methyl)amino methyl]-9-methyl carbazole and its polyester with diacid chloride, 6FBC has been synthesized. It is a carbazole-based side chain polymer. The polymer can be doped with TNF or crystal violet to form a charge transfer complex. It is a guest-host system photoconducting polymer. Photo current in the dark as well as under illumination can be measured under different voltages and different intensities. Moreover, a good photorefractive system can be developed by conjugation the polyester with secondorder non-linear optical chromophore(DR-1), photosensitizer(TNF)and plasticizer(ECZ).

II. Experimental

2.1 Synthesis of 3,6-dibromo-9-methyl carbazole:

To a three necked round-bottom flask equipped with nitrogen purge and reflux condenser was added 6.0g(0.0185mol) of 3,6-dibromo carbazole along with 75ml of anhydrous DMF. To the stirred solution was added 0.72g(0.030mol)of sodium hydride. Immediately a yellow precipitate formed with evolution of hydrogen gas. This was stirred for a further 15min. to dissolve the carbazole anion, then 4.26g(0.030mol)of iodomethane was added in one portion. The reaction was exothermic, indicating the reaction proceeded immediately. After 5h, 200ml of water was added to give a light brown precipitate. After recrystallization from chloroform light brown needles were obtained.

2.2 Synthesis of 9-methyl-3,6-dimethyl carbazole:

In an oven-dried,1L,three necked, round-bottomed flask equipped with a magnetic stir bar, a reflux condenser and a rubber septum are placed 3,6-dibromo-9-methyl carbazole (7.0g,20.0m mol)and[1,3-bis(diphenylphosphino) propane] nickel(II)chloride(0.54g, 1.0m mol) in 500ml dry ether under an argon atmosphere. To the stirred solution at room temperature is added methyl magnesium bromide(30ml,60.0m mol) dropwise over 20min via an additional funnel. During the addition, the colour of the solution turns from orange to yellow to brown. After the addition, the reaction mixture is heated at reflux for 2h at which time the reaction is judged complete by TLC analysis. The reaction mixture is cooled to room temperature, then carefully quenched with aqueous saturated ammonium chloride(25ml) at which time a brown precipitate forms. All the contents of the reaction are transferred to a separatory funnel and successively washed with aqueous saturated sodium bicarbonate(3/50ml),brine(3/50ml) and deionized water(3X50ml). The combined aqueous layers are extracted with ethyl acetate(3X50ml). The combined organic extracts are dried over sodium sulfate, filtered and the solvent is removed under reduced pressure to give a yellow solid. recrystallization from ethanol gives 9-methyl-3,6-dimethyl carbazole as white needles.

2.3 Synthesis of 9-methyl-3,6-di(bromomethyl) carbazole:

Under a nitrogen atmosphere, a mixture of 9-methyl-3,6-di methyl carbazole 6.27g(0.03mol), N-bromosuccinimide 9.30g(0.066mol), benzene(150ml) and benzoyl peroxide(100mg) was heated under refluxfor 12h. The mixture was cooled and filtered and the filtrate was removed under reduced pressure. Water(150ml) was added and the organic layer was extracted with dichloromethane. After removal of solvent, the crude product was recrystallized with chloroform, giving 9-methyl-3,6-di(bromo methyl) carbazole.

2.4 Synthesis of 3,6-di[(hydroxyethyl)(methyl) amino methyl]-9-methyl carbazole:

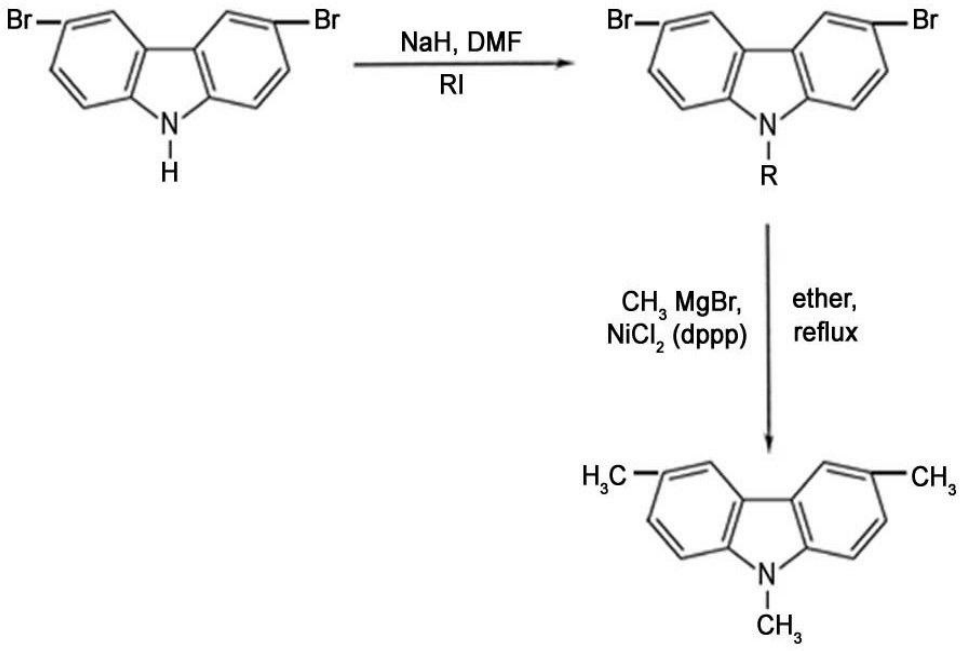
Into a 250ml flask added 7.34g(0.02mol) of 9-methyl-3,6-di(bromomethyl) carbazole and 5.52g(0.04mol) of potassium carbonate and 100ml of DMSO. This mixture was heated to 100^0c with stirring. Into this mixture added the solution of 6.0g(0.08mol) of 2-(methyl amino) ethanol in 20ml of DMSO slowly and followed by adding 0.1g of 18-crown-6. The 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 chloroform.

2.5. Synthesis of polyester:

In a 100ml flask, added 3.55g (0.01mol) of3,6-di[(hydroxy ethyl)(methyl)amino methyl] -9-methyl carbazole and 50ml of 1,2-dichloroethane. The diacid chloride monomer, 6FBC(4.09g,0.01mol) was added into the solution at room temperature with stirring. Triethylamine2.02g(0.02mol) 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.

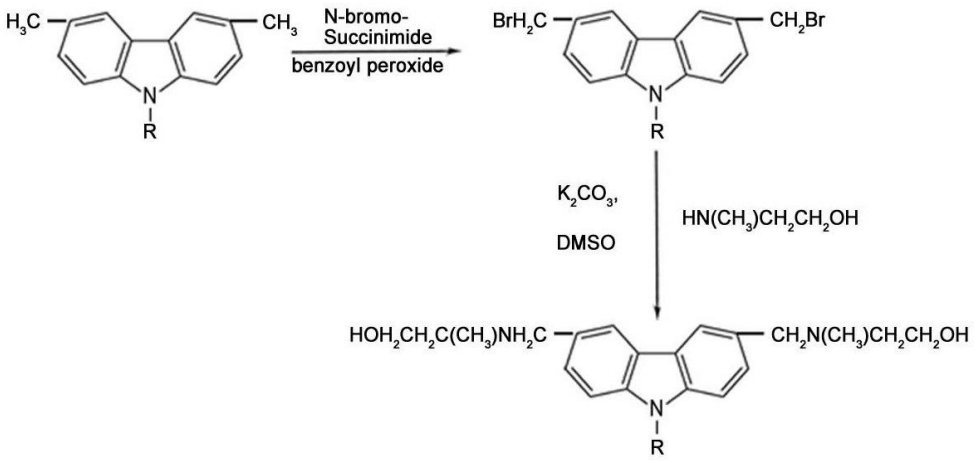
III. Result and Discussion

IR,UV and NMR spectra revealed the successful preparation of the polymer. 3,6-dibromo-9-methyl carbazole was prepared by treating 3,6-dibromo carbazole with iodomethane in presence of sodium hydride in the solvent medium of DMF. After subsequent addition of water, the product is precipitated out. The product was recrystallied from chloroform giving light brown needles of the product. 3,6-dimethyl-9-methyl carbazole was synthesized by reaction of 3,6-dibromo-9-methyl carbazole with methyl magnesium bromide in presence of[1,3-bis(diphenylphosphino) propane] nickel(II) chloride in the solvent medium of ether by refluxing 2h. The reaction mixture was quenched with aqueous saturated ammonium chloride to give a brown precipitate. By transferring the contents in a separatory funnel the product was successively washed with aqueous saturated sodium bicarbonate, brine and deionized water. The aqueous layer was extracted with ethyl acetate. The organic extracts was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure to give a yellow solid. The product was recrystallized from ethanol which gives 9-methyl-3,6-dimethyl carbazole as white needles. The product was confirmed by IR, UV and NMR spectroscopy. The synthetic route of 9-methyl-3,6-dimethyl carbazole was depicted in scheme-I.



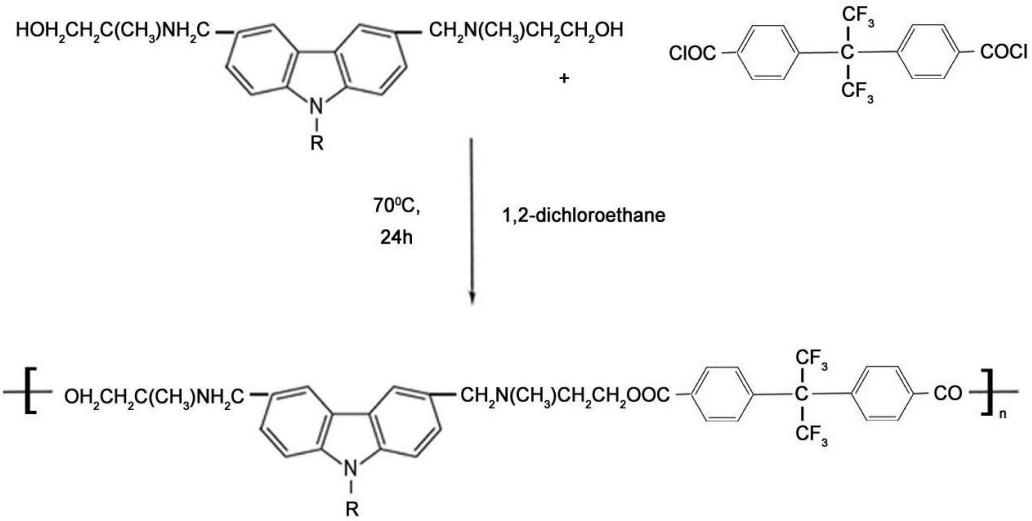
Scheme - I

9-methyl-3,6-di(bromo methyl) carbazole was synthesized by treating 9-methyl-3,6-dimethyl carbazole with N-bromosuccinimide in presence of benzoyl peroxide in the solvent medium of benzene under reflux for 12h. The mixture was cooled and filtered and the filtrate was removed under reduced pressure. Water was then added and the organic layer was extracted with dichloro methane. After removal of the solvent, the crude product was recrystallized with chloroform giving 9-methyl-3,6-di(bromo methyl) carbazole. 3,6-di[(hydroxy ethyl)(methyl) amino methyl]-9-methyl carbazole was synthesized by treating 9-methyl-3,6-di(bromo methyl) carbazole with 2-(methyl amino) ethanol in presence of small amount of 18-crown-6 in the solvent medium of DMSO at 100^0c for 24h. The mixture was poured into water and the product was precipitated out. The product was recrystallized from chloroform. The synthetic routh of the product was depicted in scheme-II.



Scheme - II

Lastly the polymer was prepared by the condensation polymerization of 3,6-di [(hydroxyethyl)(methyl) amino methyl]-9-methyl carbazole with diacid chloride,6FBC in the solvent medium of 1,2-dichloro ethane at 70^0c for 24h. The polymer solution was precipitated out in methanol. The precipitated solid was purified by repeated precipitation technique. The polymer was characterized by IR,UV and NMR spectroscopy. The synthetic route of the polymer was depicted in scheme-III.



Scheme - III

The polyester of carbazole ring has good thermal, mechanical and photochemical properties. The polymer is soluble in most common organic solvents. The host polyester can be doped with gust molecule like TNF forming a charge transfer complex, and dark and photoconductivity can be measured of the polymer film by evaluating a current. The photorefractive composites can be prepared by conjugation the polymer with a second order NLO chromophore(DR-1), sensitizer like TNF and a plasticizer like ECZ.

IV. Conclusion

The article summarized the novel synthesis of polyester of electron donating carbazole ring. The monomer and polymer were characterized by IR, UV and NMR spectroscopy. Carbazole itself a strong electron doner so it form C.T. Complex with strong electron acceptor like TNF. Carbazole is easily available from coal-tar so, cheaper photoconducting polymer can be prepared. It is a guest-host system polymer where the host polyester 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 prepared by conjugation the polyester with a second order NLO chromophore(DR-1) and sensitizer like TNF and a plasticizer like ECZ.

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