

Synthesis of Photoconducting Carbazole Based Polycarbonate.

*Dipak Kumar Mukhopadhyay

Institute of Science & Technology, C.K Town, 721201, West Bengal, India

Corresponding Author: Dipak Kumar Mukhopadhyay

Abstract: *N*-methyl carbazole was Prepared by treating Carbazole with iodomethane in presence of sodium hydride in the solvent medium of DMF. 3-formyl-*N*-methyl Carbazole was synthesized by the reaction of *N*-methyl Carbazole with POCl₃ and DMF. *N*-methyl-3-hydroxymethyl Carbazole was Synthesized by treating *N*-methyl-3-formyl Carbazole with NaBH₄ and NaOH in ethanol. *N*-methyl carbazolyl-3-methylene oxy Carbonyl chloride was prepared by treating *N*-methyl-3- hydroxymethylcarbazole with phosgene in the solvent medium of THF. 4-[*N*-methyl-carbazolyl-3-methylene oxy carbonyl-oxy] styrene was synthesized by treating *N*-methyl-carbazolyl -3-methylene oxy carbonyl chloride with 4-hydroxy styrene in the solvent medium of THF. Lastly the monomer namely 4-[*N*-methyl carbazolyl-3-methylene oxy carbonyloxy] styrene was co-polymerized with methyl methacrylate in the solvent medium of DMF.

Keywords: *N*-methyl-3- formylcarbazole, *N*-methyl-3- hydroxymethylcarbazole, 4-[*N*-methylcarbazolyl-3-methyleneoxy carbonyl oxy] styrene, radical polymerization, co-polymer.

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I. Introduction:

Polymer with carbazole group 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 makes 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 electro photographic applications. Recent developments in this field are mostly connected to applications in polymeric light-emitting diodes, organic photorefractive materials, and photovoltaic devices. For example, conjugated poly(3,6-carbazole) and poly(2,7-carbazole) derivatives having carbazole moieties in the main chain have been employed for application in solar cells 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 applications 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. poly(*N*-ethyl carbazolyl) methane is as efficient as poly *N*-vinyl carbazole. 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 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 very arbitrarily.

In this article photoconducting carbazole based polycarbonate has been synthesized. It is a side chain polymer. The polymer can be doped with TNF or crystal violet to form a C.T. complex. It is guest-host system photoconducting polymer. Photo current in the dark as well as under illumination can be measured with different voltages and different intensities. Moreover good photorefractive system can be developed by conjugation the polycarbonate with DR-1, sensitizer TNF and plasticizer ECZ.

II. Experimental:

2.1. Synthesis of *N*-methyl 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 further 15 minutes to dissolve the carbazole anion. Then 4.26g (0.03) of methyl iodide was added in one

portion. The reaction was exothermic, indicating the reaction proceeded immediately. After 5h, 200ml of water was added to give a precipitate. The product was recrystallized from chloroform.

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

12g of phosphorus oxychloride was added dropwise to 5.8g of dimethyl formamide and stirred on ice-water bath. After that the reaction mixture was allowed to room temperature. Then 13g of N-methyl carbazole was added in small portion. After over night standing, the mixture was poured into water. The precipitate was filtered and recrystallised from ethanol.

2.3. Synthesis of N-Methyl -3- Hydroxy methyl carbaole:

To a solution of 18.9 g of N-methyl -3-formyl carbazole in 400ml of ethanol, a mixture of 2.5g of sodium borohydride and 20 ml of 0.4(N) sodium hydroxide in water was added dropwise. The mixture was then heated at 60⁰c and stirred for 1h. After that the mixture was cooled to room temperature. White crystals were obtained which was filtered, washed with water, dried and recrystallized from cyclohexanone : benzene (1:1) mixture.

2.4. Synthesis of N-methyl carbazolyl -3- methylene oxy carbonyl chloride:

0.04 mols of phosgene mixed with toluene was taken in a three- necked flask, fitted with magnetic stirrer and a condenser. The mixture was placed in an ice- bath at 0⁰-5⁰c. 0.04 mols of N-methyl -3- hydroxymethylcarbazole mixed with 50 ml of THF was slowly added with vigorous stirring. The mixture was stirred for 3h.

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

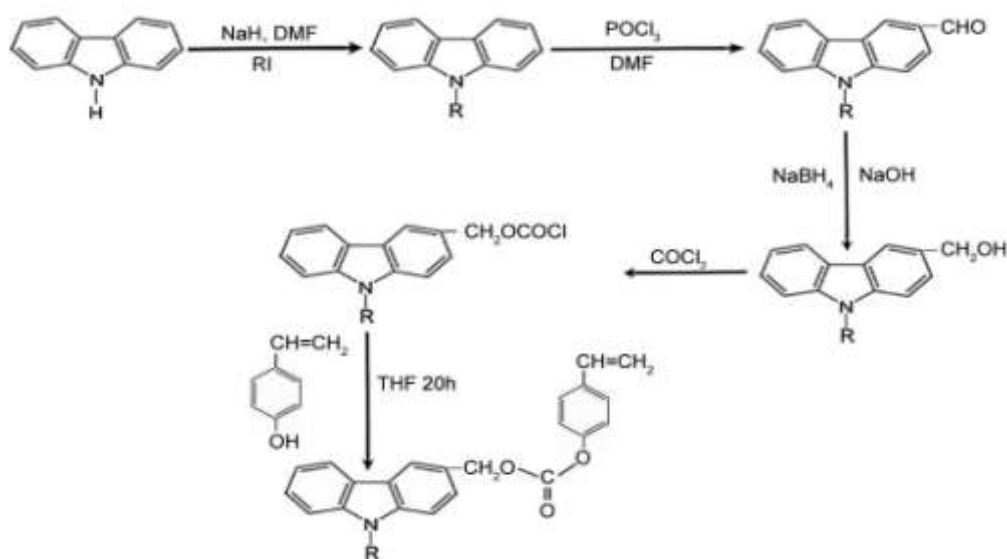
After the reaction was over, 0.04 mols of 4- hydroxyl styrene mixed with THF was quickly added to the above reaction mixture and stirred at room temperature for 20h. Then the mixture was neutralized with added triethylamine and precipitated into methanol. The precipitate was filtered and dried. The monomer was characterized by studying IR,UV and NMR spectra.

2.6. Polymerization:

4- [N- methyl carbazolyl – 3- methylene oxy carbonyl oxy] styrene (1.34 g, 3.75m mol), methyl methacrylate (0.38g, 3.75m mol) and azobisisobutyro nitrile (2g, 12.19m mol) were dissolved in dry DMF (50 ml). The reaction was carried out at 110⁰c 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.

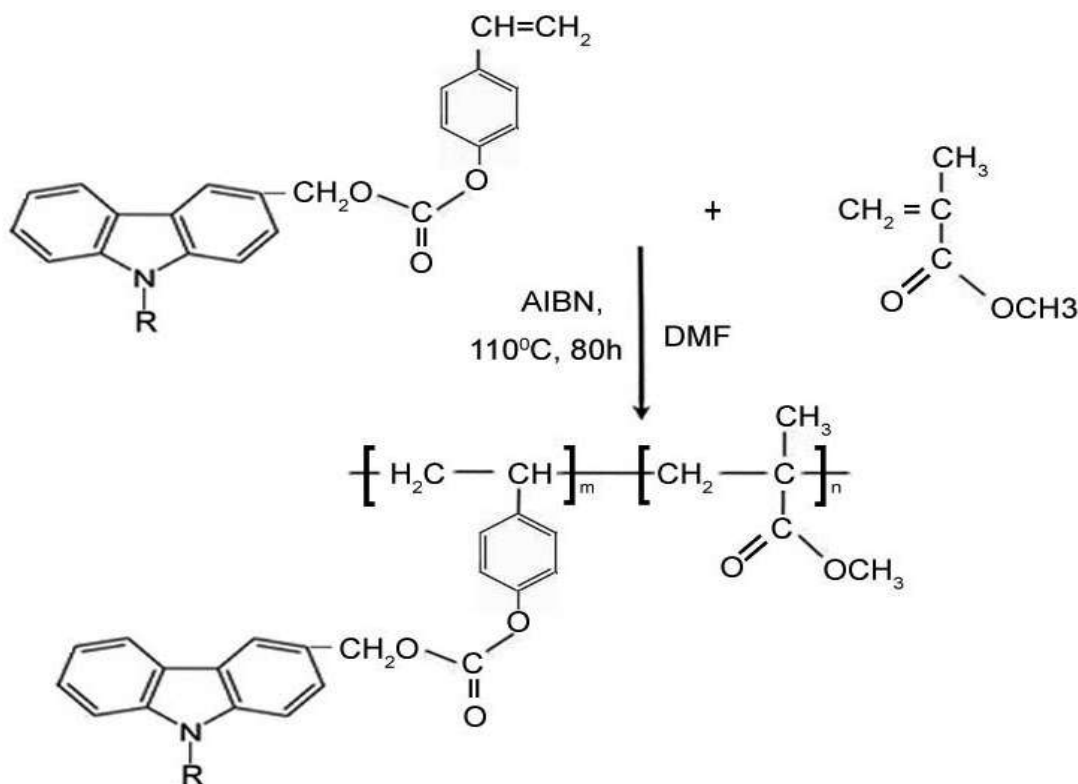
III. Result And Discussion:

IR, UV and NMR spectra revealed the successful preparation of the polymer. The synthesis of monomer starting from carbazole was represented in scheme-I.



N- methylcarbazole was synthesized by treating carbazole with iodomethane in presence of sodium hydride in the solvent medium of DMF. After subsequently adding water, N-methyl carbazole was precipitated out. Then N-methyl-3- formylcarbazole was prepared by reacting N- methyl carbazole with POCl₃ and DMF. After standing overnight the product was precipitated out in water. N- methyl -3- hydroxyl methyl carbazole was synthesized by treating N-methyl -3- formylcarbazole with sodium borohydride in presence of alkali in the

medium of ethanol. The mixture was heated at 60°C when fine crystals of N- methyl -3- hydroxyl methyl carbazole was obtained after cooling the mixture. After that N-methyl -3- hydroxyl methylcarbazole was reacted with phosgene in the solvent medium of THF for 3h. Then after the reaction was over 4- hydroxyl styrene in THF was added to the above mixture and stirred at room temperature for 20h. After that the mixture was neutralized by added triethyl amine and precipitated out in methanol. The monomer which was formed namely 4-[N-methyl carbazolyl -3- methylene oxy carbonyl oxy] styrene was characterized by studying FT-IR, UV and NMR spectroscopy. Lastly, the monomer was co-polymerized with methyl methacrylate in (1:1) ratio in presence of AIBN in the solvent medium of DMF. The polymer was precipitated out in methanol. The polymer was characterized by studying FT-IR, UV and NMR spectroscopy. The synthetic route of the co polymer was represented in Scheme-II.



Scheme-II.

The synthesized polymer was soluble in most common organic solvents. The polymer has good mechanical property and thermal property due to carbazole backbone. The polymer has good photoconducting properties. The polymer can be doped with TNF and crystal violet which will form a C.T complex between the electron donating carbazole moiety and electron acceptor like TNF. It is a non-conjugated polymer where the polymeric side chain act as a charge transporting moiety. The photocurrent of the guest- host system polymeric matrix can be measured in the dark as well as under illumination at different voltages and different intensities. Moreover, a high performance photorefractive system can be developed by mixing polymer with second order non- linear optical chromophore DR-1 and sensitizer like TNF and plasticizer like ECZ.

IV. Conclusion:

This article has summarized the synthesis of novel monomer 4- [N-methyl carbazolyl -3- methylene oxy carbonyloxy] styrene and its co-polymer with methyl methacrylate. Carbazole is a strong electron donating moiety which can easily form a charge transfer complex with strong electron accepting moiety like TNF. The charge generated (hole) that will move through the polymer chain (charge transporting medium) by hopping mechanism of conduction. It is a guest – host system photoconducting polymer. The polymer can be doped with TNF or crystal violet. The doped polymer can be used to measure dark conductivity as well as photoconductivity under illumination. The photocurrent can be measured at different voltages and at different intensities. The high performance photorefractive system can also be developed by doping the polymer with a second order non- linear optical chromophore like 2,5- dimethyl -4- (4-nitro phenyl azo) anisole with the photosensitizer TNF and plasticizer ECZ.

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