

Synthesis Of Photoconducting Polycarbonate Of Chloroformic ester of 3,6-bis-(hydroxyl methyl)-N-ethyl Carbazole With Bisphenol-A.

Dipak Kumar Mukhopadhyay

Institute of Science & Technology, C.K.Town, West Bengal, 721201, India
Corresponding Author: Dipak Kumar Mukhopadhyay

Abstract: *N*-ethyl carbazole was synthesized by treating Carbazole with ethyl iodide in presence of Sodium hydride in Solvent medium of DMF. *N*-ethyl-3, 6-diformyl Carbazole was synthesized by reacting *N*-ethyl carbazole with high excess of POCl₃ and DMF mixture. *N*-ethyl-3,6-bis(hydroxymethyl) carbazole was synthesized by treating *N*-ethyl-3,6-diformyl Carbazole with NaBH₄ and NaOH mixture. Chloroformic ester of *N*-ethyl-3,6-bis(hydroxyl methyl) carbazole was prepared by treating *N*-ethyl-3,6-bis(hydroxymethyl) carbazole with phosgene in the solvent medium of toluene. Lastly the polymer was synthesized by the polycondensation reaction of chloroformic ester of *N*-ethyl-3,6-bis(hydroxyl methyl) Carbazole with Bisphenol-A in the solvent medium of toluene and pyridine. All the monomer and polymer was characterized by IR,UV and NMR spectroscopy.

Key words: *N*-ethyl-3, 6-diformyl carbazole, *N*-ethyl-3,6-bis(hydroxymethyl) carbazole, chloroformic ester of *N*-ethyl-3,6-bis(hydroxyl methyl) carbazole, polycondensation.

Date of Submission: 26-01-2018

Date of acceptance: 15-02-2018

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 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 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 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 polycarbonate of chloroformic ester of 3,6-bis (hydroxymethyl) –*N*-ethyl carbazole with Bisphenol-A has been synthesized. The polymer has been synthesized by polycondensation reaction. It is a guest-host system of polymer. The polymer can be doped with TNF or crystal violet and photocurrent can be measured in the dark as well as under illumination at different voltages and different intensities.

II. Experimental:

2.1. Synthesis of N-ethyl 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 75ml of anhydrous DMF. To the stirred solution was added 0.72g (0.03 mol) 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 4.68g (0.03 mol) of ethyl iodide was added in one portion. After 5h, 200ml of water was added to give a precipitate. The product was recrystallized from chloroform.

2.2. Synthesis of N-ethyl-3, 6-diformyl carbazole:

N-ethyl-3, 6-diformyl carbazole was synthesized by formylation of N-ethyl carbazole in presence of a high excess of POCl_3 and DMF mixture. However, even at very high ratio, Vilsmyer formylating agent: carbazole compound is greater than 10:1 always a mixture of mono-(3-formyl-N-ethyl carbazole) and dialdehyde compound (3,6-diformyl-N-ethyl carbazole) was obtained and pure aldehyde components were separated by flash chromatography on a silica gel column using ethyl acetate: hexane (1:10) as eluent. The mono aldehyde was the first product eluted and after evaporation of the solvent, an oil product was obtained which crystallized in time. The dialdehyde was obtained as a white solid after evaporation of eluent and recrystallized from acetone. TLC chromatography, elemental analysis and spectral data confirm the purity and structure of synthesized dialdehyde product.

2.3. Synthesis of N-ethyl-3,6-bis (hydroxyl methyl) carbazole:

To a solution of 5.02g (0.02 mol) of N-ethyl-3,6-diformyl carbazole in 150 ml ethanol, a mixture of 1.5g of sodium borohydride and 20 ml of 0.4 (N) sodium hydroxide in water was added dropwise. The mixture was then heated at 60°C and stirred for 3h. 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 chloroformic ester of N-ethyl-3, 6-bis (hydroxymethyl) carbazole:

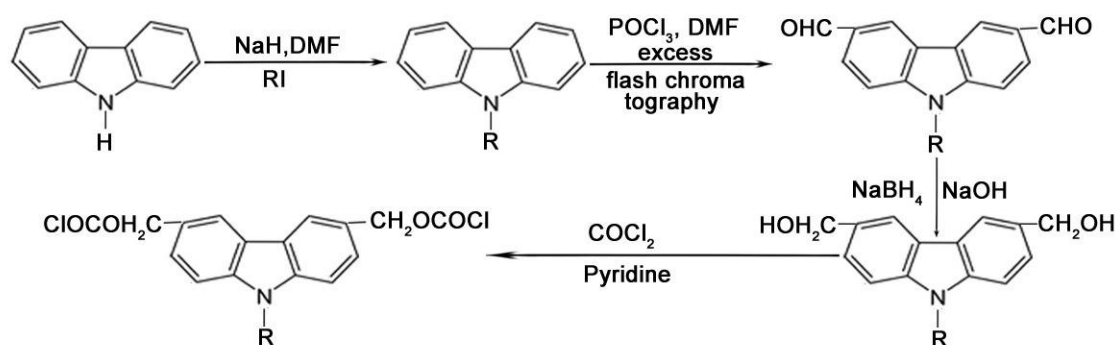
0.08 mols of phosgene mixed with toluene was taken in a three-necked flask, fitted with magnetic stirrer and a condenser. The mixture was placed in an ice-bath at 5°C . 0.04 mols of N-ethyl-3,6-bis (hydroxyl methyl) carbazole mixed with 100ml of toluene was slowly added with vigorous stirring. 6.5g of pyridine was then added and the mixture was stirred for 3h.

2.5. Polymerization:

After the reaction was over, 0.04 mols of Bisphenol-A mixed with toluene was then added to the above reaction mixture and 7.0g pyridine was added then the reaction mixture was stirred for 24h at room temperature. After that, polymer was precipitated out in methanol, washed with methanol and dried. The polymer was synthesized by polycondensation reaction. The polymer was characterized by IR, UV and NMR spectroscopy.

III. Result and Discussion

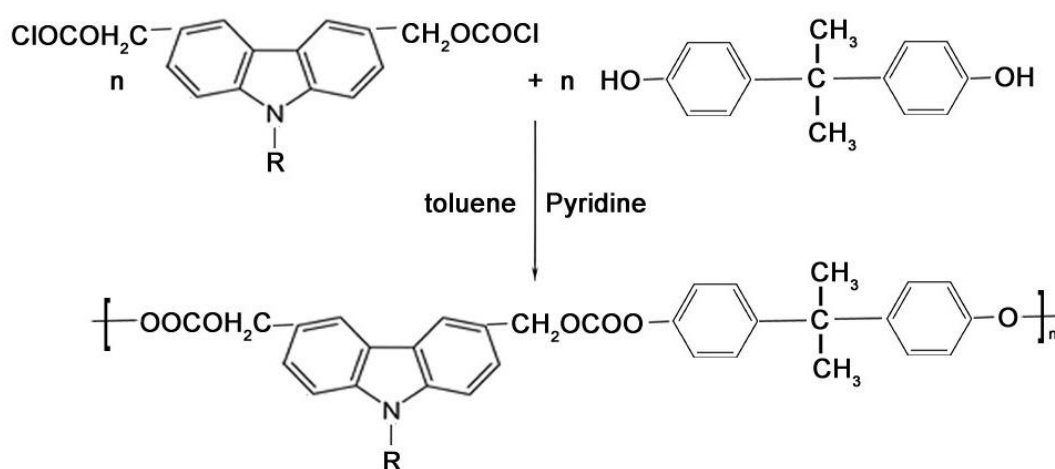
IR, UV and NMR spectra revealed the successful preparation of the polymer. The synthesis route of monomer namely chloroformic ester of N-ethyl-3,6-bis (hydroxyl methyl) carbazole, starting from carbazole was represented in scheme-I.



Scheme-I.

N-ethyl carbazole was synthesized by treating carbazole with ethyl iodide in presence of sodium hydride in the solvent medium of DMF. N-ethyl-3,6-diformyl carbazole was synthesized by reacting N-ethyl carbazole with high excess of POCl_3 and DMF mixture. Even with the treatment of carbazole: formylating agent 1:10 ratio both mono and dialdehydecarbazole was formed. After flash chromatography both mono and dialdehyde compounds were separated. The diformylcarbazole was taken for further treatment. N-ethyl-3,6-diformyl carbazole was then reduced with sodium boro hydride in presence of alkali in the solvent medium of alcohol, to synthesize N-ethyl-3,6-bis (hydroxyl methyl) carbazole. After that the monomer was synthesized by treating N-ethyl-3,6-bis (hydroxyl methyl) carbazole with phosgene in presence of pyridine in the solvent medium of toluene. The monomer namely the chloroformic ester of N-ethyl-3,6-bis (hydroxyl methyl) carbazole was then treated with Bisphenol-A in presence of pyridine in the solvent medium of toluene to synthesize the polymer. Polymerization was done simply by polycondensation reaction at room temperature for 24h.

The polymer was characterized by FT-IR, UV and NMR spectra. The synthetic route of polymer was represented in Scheme-II.



Scheme-II

The polymer has good thermal and mechanical properties due to carbazole backbone. The polymer has good photoconducting property when it was doped with TNF. The dark and photo current can be measured at different voltages and different intensities. The polymer was soluble in most common organic solvents. When the polymer was doped with TNF or crystal violet, the strong electron donating carbazole moiety formed a charge transfer complex with strong electron acceptor TNF and a hole is generated and the hole will move through the polymer chain (charge transporting moiety).

4. Conclusion:

This article has summarized the synthesis of novel monomer, chloroformic ester of N-ethyl-3, 6-bis (hydroxyl methyl) carbazole and its polymer with Bisphenol-A. 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 (a hole) that will move through the polymer chain (charge transporting media) by hopping mechanism of conduction. It is a guest-host system photoconducting polymer. The polycarbonate can be doped with TNF or crystal violet. The doped polymer can be used to measure dark current as well as photocurrent under illumination. The photocurrent can be measured at different voltages and different intensities.

References

- [1]. Kippelen B, Tamura K, Peyghambarian 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]. Zhang 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]. Meerholz 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.

IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

Dipak Kumar Mukhopadhyay "Synthesis Of Photoconducting Polycarbonate Of Chloroformic ester of 3,6-bis-(hydroxyl methyl)-N-ethyl Carbazole With Bisphenol-A.." IOSR Journal of Applied Chemistry (IOSR-JAC) , vol. 11, no. 2, 2018, pp. 43-46.