

An Approach to Synthesis of monomer 3,6 - diamino N-Substituted carbazole and its photo-conducting Polymer with Chloroformic ester of ethylene glycol, Propane-1,3- di-ol and butane- 1,4 - di-ol.

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Abstract: This review summarizes recent advances in the design and synthesis of novel monomer 3, 6-diamino N-substituted carbazole and the polymerization techniques of monomer i.e. 3, 6-diamino N-substituted carbazole with the chloroformic esters of ethylene glycol, propene glycol and 1, 4-butane di-ol. The polymers have been characterized by IR, UV-visible and NMR spectroscopy.

Key words: Monomer synthesis, urethane polymer synthesis, solution poly-condensation.

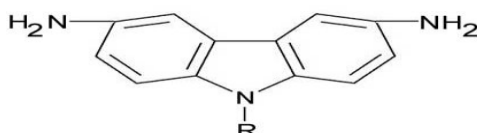
I. Introduction

Polymer with carbazole groups 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

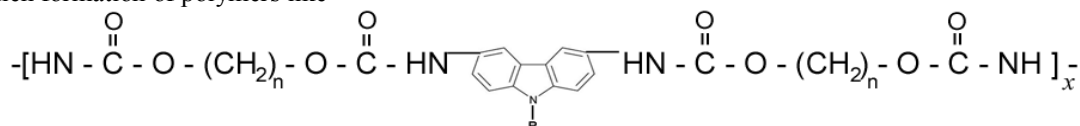
Poly (3, 6-carbazole)and poly (2,7-carbazole)derivatives having carbazole moieties in the main chain have been employed for application in solar cells and white-light-emitting diodes. In the past few decades, considerable attention has been given to the self- assembly of block copolymers, because of 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 photo conducting 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 back-bone, But still polyvinyl carbabazole 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 smostly 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 photo-ionization, photo-conduction and trapping of charge carriers with respect to structure is not well established. All these studies have been made very arbitrarily.

The aim of this review is to synthesize some polymers based on modified skeleton of N-alkyl/aryl carbazole. Carbazole is easily available from coal-tar. In this review, the monomer 3, 6-diamino N-substituted carbazole has been synthesized.



Then formation of polymers like



R= - C₂H₅, (H₃C)₃ C -
4,

n = 2, 3,

II. Experimental:

2.1. Preparation of N-substituted carbazole:

2.1.1. Preparation of N-ethyl carbazole :

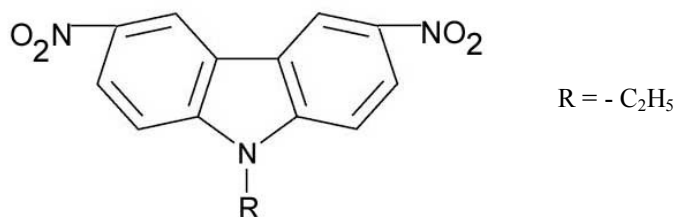
Carbazole is treated with sodium ethoxide in absolute alcoholic medium in presence of ethyl iodide. The product has been purified by repeated crystallisation. The material has been confirmed by IR, NMR, UV spectra and by observing the melting point.

2.1.2. Preparation of N-tertiary butyl Carbazole:

Carbazole is reacted with sodium ethoxide in absolute alcoholic medium in presence of tertiary butyl chloride. the product has been purified and characterised by the determination of melting point and by IR,NMR,UV spectra.

2.2. Preparation of 3, 6-dinitro N-substituted carbazole :

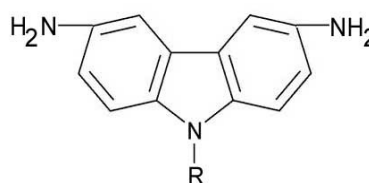
N-substituted carbazole is dissolved in glacial acetic acid and a stoichiometric amount of nitric acid mixed with glacial acetic acid is added drop wise at 20⁰c. After reaction at 40⁰c for 15h another 80cc of nitric acid together with 60cc.glacial acetic acid is added at 80⁰c for 2h, then at 100⁰c for another 30minits. After cooling, precipitated di-nitro derivative is filtered off and washed with water. Yellowish fine crystals are considered as di-nitro derivative (by cheeking the melting point).



2.3. Preparation of 3,6-diamino N-substituted carbazole :

Without further purification the crude product of dinitro derivative are reduced catalytically by using palladium catalyst in presence of cyclohexene at100⁰c.The diamino derivative is confirmed by checking the melting point and verifying the IR,NMR,UV,spectra.

C₁₄H₁₅N₃ (225.3)
Calculated N, 18.77 %
Found N, 18.42 %



2.4. Preparation of chloroformic ester of different glycols:

0.08 mols of phosgene mixed with benzene is taken in three necked flask fitted with magnetic stirrer and a condenser. The mixture is placed in an ice-bath at 0⁰-5⁰c .0.04 mols of glycol mixed with 50cc of benzene slowly added with vigorous stirring. The mixture is stirred for 3h

2.5. Preparation of the polymer:

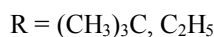
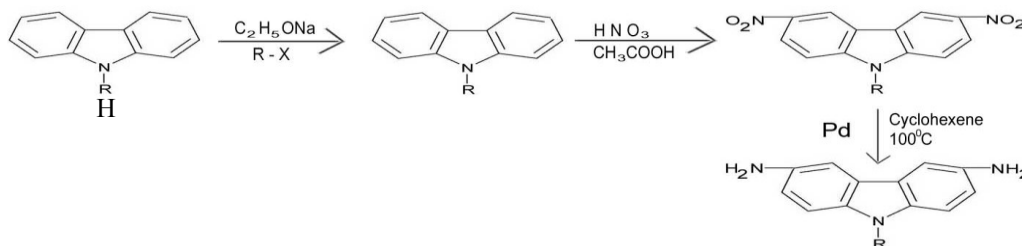
After the reaction is over 0.04 mols of 3, 6-diamino N-substituted carbazole together with 100ccof benzene is quickly added to the above mixture at 0⁰-5⁰c. The mixture is stirred vigorously. 0.08mols of triethyl amine is added to the mixture with vigorous stirring. The stirring is continued for 2h at room temperature. After completing the reaction the polymer is precipitated out in methanol, washed with water and methanol and finally with hexane and dried. The polymer is characterized by IR, NMR, UV spectra.

III. Result and Discussion :

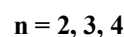
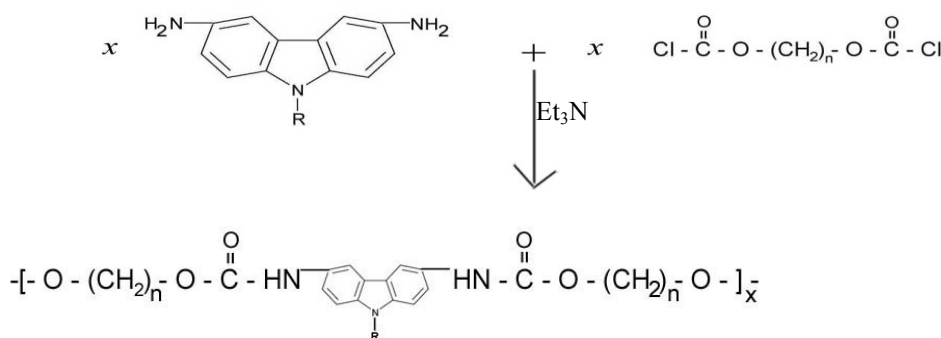
The study of IR,NMR,andUV-Visible spectra revealed the successful preparation of the polymer. The synthesis of new carbazole based diamine monomer starting from carbazole is presented in detail in scheme-I, N-ethyl carbazole is firstly dinitrated using nitric acid in presence of glacial acetic acid. In the second step the

dinitro compound is catalytically reduced using palladium catalyst in presence of cyclohexene at 100^oc. The pink-coloured compound in a reasonable yield is obtained after three precipitations of acetone solution in water, and the filtered product is dried and kept in dark and nitrogen atmosphere.

By solution polycondensation of equimolar mixture of 3, 6-diamino N-ethyl carbazole and chloroformic esters of ethylene glycol, propane – 1,3 diol and butane-1,4-diol, three urethane polymers have been synthesized (scheme-II). The reaction is carried out in benzene. The polycondensation reactions are carried out in homogeneous phase and polymers are separated in high yields by precipitation in methanol. The synthesized polymers are soluble in most common organic solvents. The polymers possess interesting electro-optical and photo- chemical properties as well as high thermal stability, mechanical strength and rigidity due to carbazole backbone.



Scheme- I, Synthesis of monomer.



Scheme-II

The formation of chloroformic esters of ethylene glycol, propane-1,3-diol and butane-1,4-diol have been prepared by treating phosgene with the corresponding glycols at 0^o-5^oc (scheme-III). The chloroformic esters are kept in the solution medium



Scheme - III

IV. Conclusion:

This review has summarized the approaches to synthesis of monomer and the corresponding polymer with the chloroformic ester of glycols. The photoconducting polymers are finding many important applications in xerography, photo imaging and other electronic devices. The most important polymer so far in commercial use is poly N-vinyl carbazole. However this polymer is quite costly and the preparation of this monomer is quite delicate. This investigation will help us to formulate a new and cheaper photo conducting polymer. Moreover, these polymer can be further studied for dark conducting in sandwich configuration at different voltages,

different temperatures with different sensitizers like TNF, crystal violet etc. same studies can be done under illumination at different wavelengths and different intensities.

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