

A Novel Route of Synthesize The Monomer 3,6-Di-Isocyanato N-Hexyl Carbazole and its photo Conducting Polymers with 1,4-Diaminobenzene and Benzidine.

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Abstract: The monomer 3, 6- Di-isocyanato N – hexyl carbzole has been synthesized and two substituted poly ureashave been synthesized by the reaction of monomer 3,6- Di –isocyanato N –hexyl Carbazole with 1, 4-Diamino benzene and benzidine.The monomer and the corresponding two poly ureas have been Characterized by UV,IR and NMR spectroscopy.

Keywords: 3, 6- Di-isocyanato N-hexyl carbazole, substituted poly ureas, Interfacial polymerization.

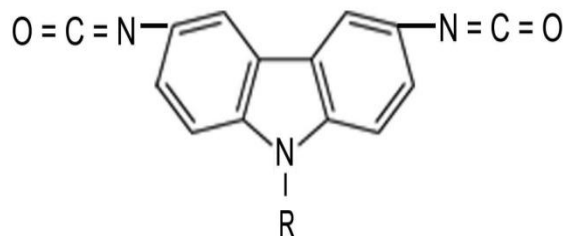
I. Introduction

Polymers containing carbazole ring have the critical importance for physical parameters of polymer,like phase transition temperatures,solubility of polymers in organic solvents, electrical conductivity, electro-luminiscentproperties,photo-refractive properties and ability to form charge transfer complexes.Carbazole decomposes at temperature higher than 260⁰c.High thermal stability of carbazole prompted us to introduce carbazole into substituted poly ureas in order to obtain products of high thermal stability. Carbazole is a monofunctional compound but 3,6- Di –isocyanato N-hexyl carbazole is a bifunctional compound and its reaction with diamine give substituted poly ureas.

Simple carbazole is easily available from coal-tar. Hogelfirst showed that poly.N- vinylcarbazole has efficientphoto-conducting properties which find applications in devices.Alarge 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 pendent from different kinds of polymeric backbone.But still poly N -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. The present art is directed toward cheaper material with excellent photo-conductivity.

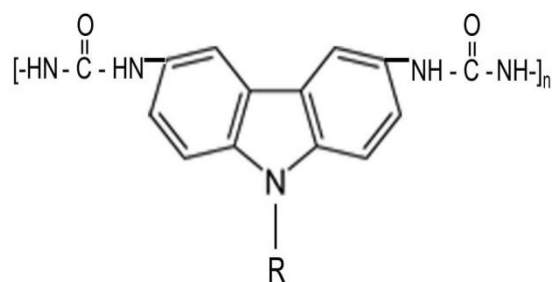
It is known that photon absorption by polymer can generate charge carriers under external electric field and suitable carrier injectors. Polymeric organic photo-conductors mostly follow hopping mechanism of conduction.The hopping mechanism is well dependent on structural sequence and regularity of the polymer.In general polymeric compounds are comprised of amorphous phase fully or partially. The relationship between mechanism of photo-ionization,photo-conduction and trapping of charge carriers with respect to structure is not well established.All the studies have been made very arbitrarily.The photo-conducting polymersare finding many important applications like xerography, photo-imaging, photo-refractive materials and photo-electric diodes.

The aim of this article is to synthesize a novel monomer, 3,6-Di-isocyanato N-hexyl carbazole.



R=C₆H₁₃

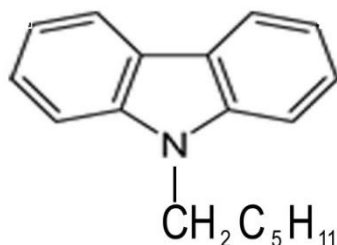
Then preparation of poly ureas of 3, 6-Di-isocyanato N-hexyl carbazole with 1, 4 -Diamino benzene and benzidine of the following structure.



II. Experimental

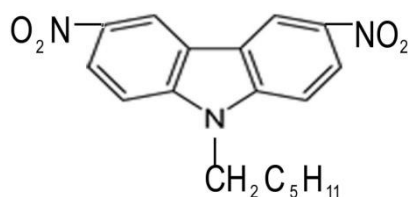
2.1 Preparation of N-hexyl carbazole:

In an oven dried, one liter round -bottomed flask equipped with a magnetic stir bar and a rubber septum are placed carbazole and sodium hydroxide pellets in dry acetone, under an argon atmosphere. Stoichiometric amount of hexyl bromide is added slowly over 15 minutes to the stirred reaction mixture at room temperature. After the addition, the reaction mixture is stirred for 8 h at which time all solids are removed by filtration. The product is purified by repeated crystallization. The product is characterized by checking the melting point and verifying IR, UV and NMR spectra.



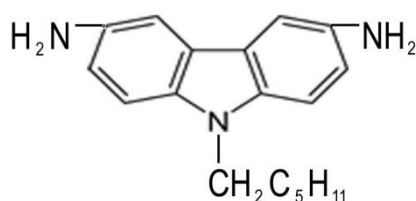
2.2 Preparation of 3, 6- dinitro N -hexyl carbazole:

To a solution of 20 g copper (II) nitrate hemi penta hydrate in a mixture of acetic acid (40 ml) and acetic anhydride (80 ml), stirred at room temperature, 20 g N -hexyl carbazole are introduced in a small portion. The reaction mixture is stirred at room temperature for an hour and then poured in ice water. The yellow precipitates filtered, washed with water until pH=7 and dried. The product is purified by repeated dissolution in THF and precipitation in water. The product is confirmed by checking the melting point and verifying IR, UV and NMR spectra.



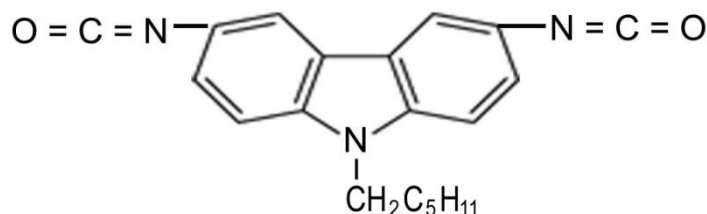
2.3 Preparation of 3, 6 -diamino N- hexyl carbazole:

A mixture formed from 10 g of dinitro compound, 56 g of stannous chloride, 180 ml of acetic acid and 30 ml of concentrated hydrochloric acid are refluxed under nitrogen atmosphere for 25 h. The initial yellow colour turns on after 1 h reflux to orange and in time becomes brown. After 8 h another portion of 10 g of stannous chloride and 5 ml of concentrated hydrochloric acid are added. After 25 h, the reaction mixture is cooled and neutralized with sodium hydroxide solution (20%) and the pink precipitate is separated by filtration, washed with water and dried. It is purified by three times precipitation in water from acetone solution. The diamino compound is kept in dark in nitrogen atmosphere. The diamino derivative is confirmed by checking the melting point and verifying IR, UV and NMR spectra.



2.4. Preparation of 3,6 -di-isocyanato N -hexyl carbazole:

0.08 mols of phosgene mixed with toluene is taken in a three necked round bottom flask, fitted with a magnetic stirrer and a condenser. Then 0.04 mols of diaminocompound with 100 cc toluene is slowly added to the reaction mixture. The mixture is stirred for 1 h at room temperature. After that 0.2 mols of triethylamine is added to the reaction mixture and stirred vigorously. Then the reaction mixture is heated at 100^oc for another 2 h. After the reaction is over the mixture is cooled and precipitated out in hexane and washed with hexane and dried. The product is confirmed by checking the melting point and verifying IR, UV and NMR spectra. The product is kept in the dark and in nitrogen atmosphere.

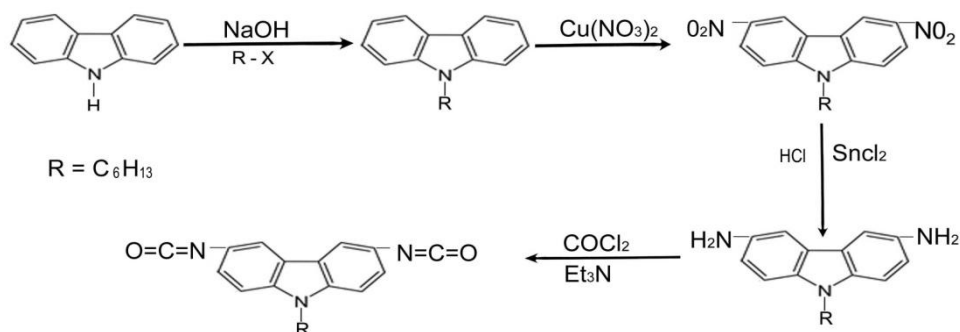


2.5 Preparation of substituted poly ureas:

Substituted poly ureas are prepared by interfacial polymerization technique. 0.04 mols of 3, 6 -di-isocyanato N- hexyl carbazole are dissolved in 100 c.c. toluene. The mixture is placed in an ice -bath at 0^o-5^oc, and then aqueous solution of 0.04 mols of diamine bishydrochloride is added slowly to the reaction mixture and vigorously stirred at low temperature. Then ice-cold 1 (N) sodium hydroxide solution is slowly added to the reaction mixture within the periods of 15 minutes to produce free diamine for reaction. The reaction mixture is stirred for another 1 h. Then poly ureas are precipitated out in methanol, washed with methanol and dried. The polymers are characterized by IR, UV and NMR spectra.

III. Result and Discussion

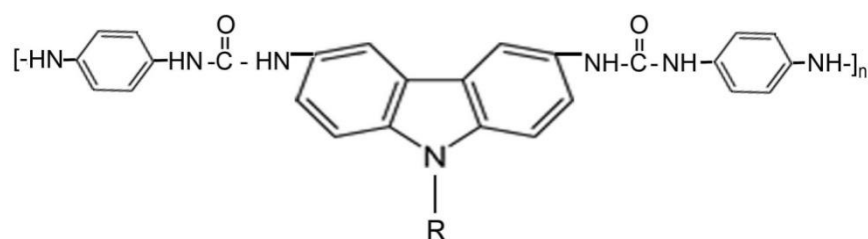
The study of IR, NMR and UV-visible spectra revealed the successful preparation of the polymers. The synthesis of new carbazole based di-isocyanato monomer starting from carbazole is presented in detail in scheme-I. N- hexylcarbazole is prepared by treating carbazole with hexyl bromide in presence of solid sodium hydroxide in the solvent medium of acetone. N-hexylcarbazole is then dinitrated using copper (II) nitrate hemipentahydrate in the mixture of acetic acid and acetic anhydride. The dinitro compound is then reduced with stannous chloride and concentrated hydrochloric acid in presence of acetic acid. A pure pink coloured product is recrystallized after three precipitations of acetone solution in water. The diamino compound is then treated with phosgene and triethylamine at first at room temperature and then heated at 100^oc for several hours. The di-isocyanate compound is precipitated out in hexane, washed with hexane and dried and kept in the dark in nitrogen atmosphere.



Scheme -I, Synthesis of monomer.

By poly addition reaction, equimolar mixture of 3, 6-di-isocyanato N-hexyl carbazole and bis hydrochloride salt of 1, 4-Diamino benzene and benzidine, two substituted poly ureas have been synthesized. The reaction is carried out in organic solvent solution of di-isocyanatocarbazole and aqueous solution of diamine bishydrochloride. The reaction mixture is treated with 1(N) sodium hydroxide solution to liberate free diamine for reaction with the isocyanato group. The polymerization process is carried out in heterogeneous phase and the polymers are separated with high yields by precipitation in methanol. The synthesized polymers are soluble in most common organic solvents. The substituted poly ureas possess interesting electro-optical and

photo-chemical properties as well as high thermal stability, mechanical strength and rigidity due to carbazole backbone. Polymer of 3, 6-di-isocyanato N -hexyl carbazole with 1, 4- diaminobenzene is depicted as a typical example in scheme-II.



Scheme - II

IV. Conclusion

This article summarizes the approaches to synthesise the monomer and the corresponding polyureas with bis hydrochloride salt of 1,4-diamino benzene and benzidine. The substituted poly ureas possess many interesting properties like electro-luminiscent property, electro-optical property. These polymers are finding many applications in xerography, photo-imaging and photo-refractive materials. The most important polymer so far in commercial use is poly N-vinyl carbazole. However this polymer is quite costly and the preparation of the monomer is quite delicate. This investigation will help us to formulate a new and cheaper photo-conducting polymer. Moreover this polymers can be studied for dark conductivity in sandwich configuration at different voltages, different temperature with different sensitizers like TNF, crystal violet etc. Same studies can be done under illumination at different wave lengths and different intensities.

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