IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 8, Issue 4 Ver. I. (Apr. 2015), PP 06-09
www.iosrjournals.org

A Novel Route of Synthesize the Monomer 3, 6- Di- isocyanato N-substituted Carbazole and its Photo conducting Polymers with Ethylene diamine, Tri methylene diamine and Tetra methylene diamine

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

Abstract: *The monomer 3, 6- Di- isocyanato N-substituted Carbazole has been synthesized and three substituted poly ureas have been synthesized by the reaction of monomer 3, 6- Di isocyanato N-substituted Carbazole with ethylene diamine, tri methylene diamine and tetra methylene diamine. The substituted poly ureas have been characterized by IR, UV and NMR spectroscopy.*

Keywords: *3, 6- Di- isocyanato N-substituted Carbazole, substituted poly ureas, Interfacial polymerization.*

I. Introduction:

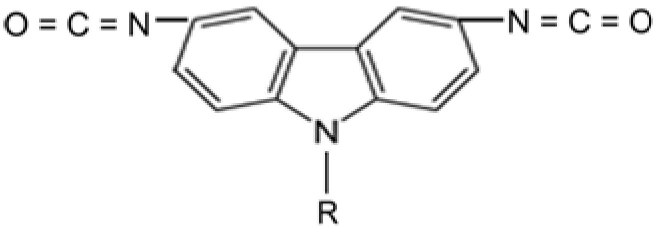
Polymers containing carbazole ring have the critical importance for physical parameters of polymer, like: phase transition temperatures, solubility of polymer in organic solvents, electrical conductivity, electro-lumescent properties, photo-refractive properties and ability to from charge transfer complexes. Carbazole decomposes at temperature higher than 260^0c. 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 mono functional compound but 3, 6- Di- isocyanato N-substituted Carbazole is a bifunctional compound and its reaction with diamines give substituted poly ureas.

Simple carbazole is easily available from coal-tar. Hogel first showed that poly N-vinyl carbazole has efficient photo-conducting properties which find applications in devices. A large number of photo-conducting polymers have been synthesized using different kinds of polycyclic homo or hetero atomic aromatic compound. In some cases aromatic groups are pendent 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. 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.

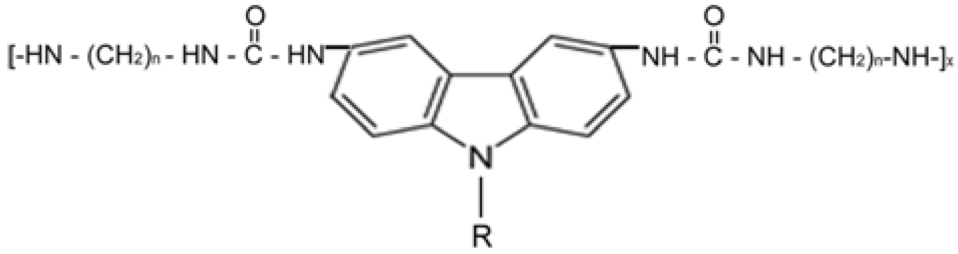
The photo-conducting polymers are finding many important applications like xerography, photo-imaging, photo-refractive materials and photo electric diodes.

The aim of this article is to synthesise a novel monomer 3, 6-di isocyanato N-substituted carbazole.



$R=C_4H_9$
$R=C_6H_{13}$

Then preparation of polymers of 3, 6- Di- isocyanato N-substituted Carbazole with ethylene diamine, tri methylene diamine and tetra methylene diamine of the following structure.



R = C_4H_9
R=C_6H_{13}

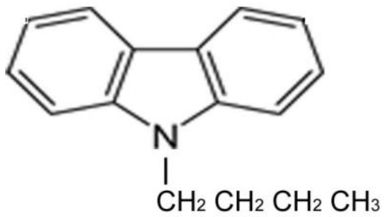
n=2,3,4

II. Experimental:

2.1 Preparation of N-substituted carbazole:

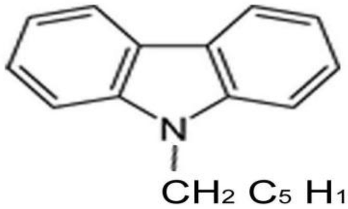
2.1.1. Preparation of N-butyl carbazole:

Carbazole is treated with sodium ethoxide and butyl bromide in absolute alcoholic medium. The product is purified by repeated crystallization. The product is verified by checking the melting point and by IR, UV and NMR spectra.



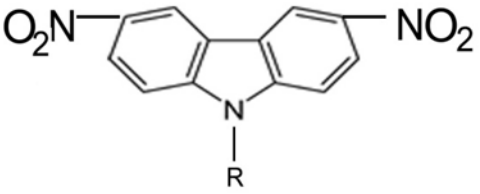
2.1.2.Preparation of N-hexyl carbazole:

Carbazole is reacted with sodium ethoxide and hexyl bromide in absolute alcoholic medium. The product is purified by repeated crystallization. The product has been confirmed by checking the melting point and verified by IR, UV and NMR spectra.



2.2 Preparation of 3, 6- Di nitro N-substituted Carbazole:

N-substituted Carbazole is dissolved in glacial acid and a stoichiometric amount of nitric acid mixed with glacial acetic acid is added drop wise at 20^0c. After reaction at 40^0c for 15h another 80cc. of nitric acid together with 60cc. glacial acetic acid is added at 80^0c for 2h, then at 100^0c for another 30 minutes. After cooling, precipitated di nitro derivative is filtered off and washed with water. Yellowish fine crystals are considered as di nitro derivated (by checking the melting point).

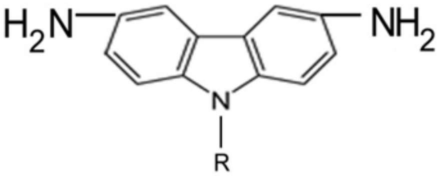


R = C_4H_9
R=C_6H_{13}

2.3 Preparation of 3, 6- Diamino N-substituted Carbazole:

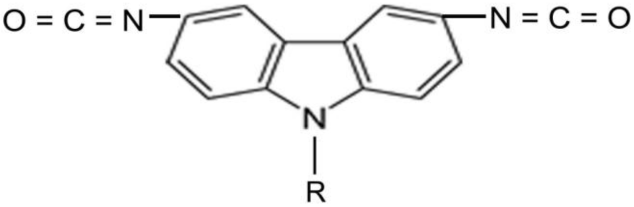
Without further purification the crude product of di nitro derivative are reduced catalytically by using palladium catalyst in presence of cyclohexene at 100^0c. The di amino derivative is confirmed by checking the melting point and verifying the IR, UV and NMR spectra.

R=C_4H_9
R=C_6H_{13}



2.4 Preparation of 3, 6- diisocyanato N-substituted Carbazole

0.08 mols of phosgene mixed with toluene is taken in a three necked round bottom flask fitted with magnetic stirrer and a condenser. Then 0.04 mols of diamino derivative together with 100cc. of toluene is slowly added to the mixture. The mixture is stirred for 1h at room temperature. After that 0.2 mols of triethylamine is added to the reaction mixture and starred vigorously. Then the reaction mixture is heated at 100^0c for another 2h. 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.



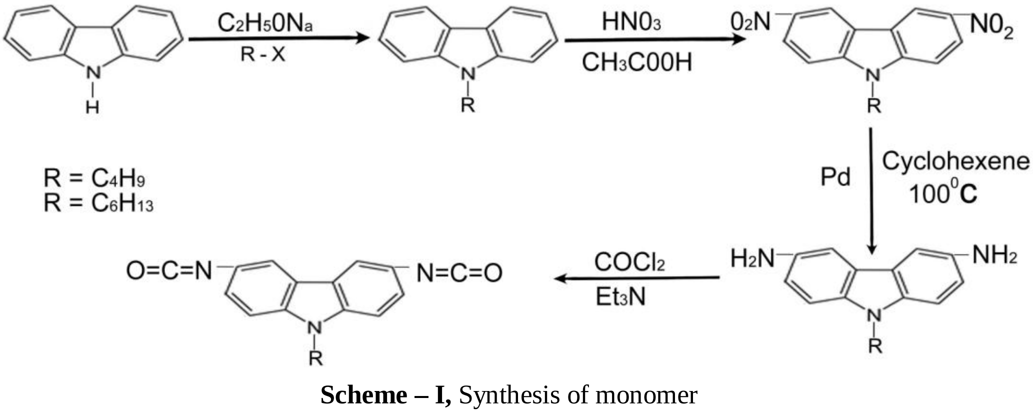
R = C_4H_9
R = C_6H_{13}

2.5 Preparation of substituted poly ureas:

Substituted poly ureas are prepared by interfacial polymerization technique. 0.04 mols of 3, 6-diisocyanato N- substituted carbazole are dissolved in 100cc.of toluene. The mixture is placed in an ice-bath at 0^0-5^0c, and then aqueous solution of 0.04 mols of diamine bis hydrochloride is added slowly to the reaction mixture and vigorously stirred at low temperature. Then ice-cold 1(N) sodium hydroxide solution slowly added to the reaction mixture within the period of 10 minutes, to produce free diamine for reaction. The mixture is stirred for another 1h then poly ureas are precipitated out in methanol, washed with methanol and water and dried. The polymers are characterized by IR, UV and NMR spectra.

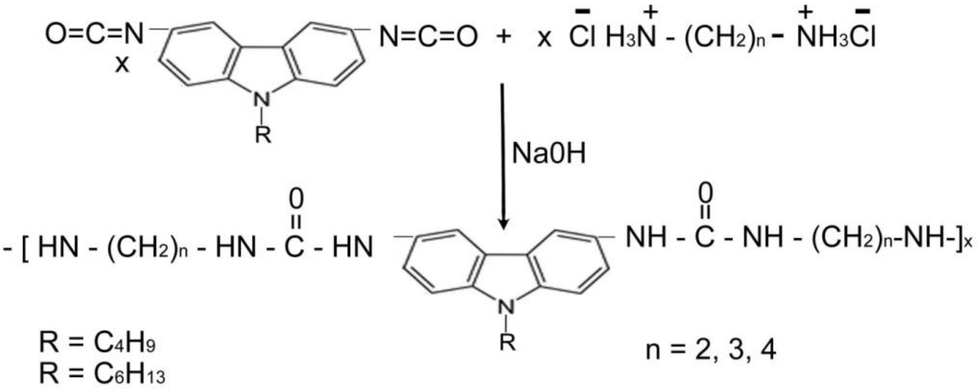
III. Result and Discussion :

The study of IR, NMR and UV-visible spectra revealed the successful preparation of the polymer. The synthesis of new carbazole based diisocyanate monomer starting from carbazole is presented in detail in scheme-I. N-substituted carbazole is prepared with corresponding alkyl halides in presence of sodium ethoxide in absolute alcoholic medium.N-substituted carbazole then 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 cyclohexenc at 100^0c. The pink colored compound is recrystallised 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 100^0c for several hours. The diisocyanate derivative is precipitated out in hexane and dried and kept in the dark in nitrogen atmosphere.



Scheme – I, Synthesis of monomer

By interfacial polymerization technique of equimolar mixture of 3, 6-diisocyanato N-substituted carbazole and bis hydrochloride salt of ethylene diamine, trimethylene diamine and tetramethylene dianine, three substituted poly ureas have been synthesized (scheme-II). The reaction is carried out in organic solvent solution of diisocyanate derivative and aqueous solution of diamine bis hydrochloride. The reaction mixture is treated with I(N) sodium hydroxide solution to liberate free diamine for reaction with isocyanate group. The polymerization process is carried out in heterogeneous phase and 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.



Scheme – II, Synthesis of Polymer

IV. Conclusion :

This article has summarized the approaches to synthesise the monomer and the corresponding polymers with the corresponding diamine bis hydrochloride. The substituted polyureas possess many interesting properties like electro-lumiscent 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 polymer can be studied for dark conductivity 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.

References

[1]. R.Lubczak,oligoe therols and polyurethanes with carbazole ring in side chain,polimery,2008,53,587-590
[2]. R, Lubczak, bifunctional oligoetherols with carbazole ring, J,Applied polymsci,2008,110,3501-3507.
[3]. R,Lubczak,linear oligoetherols and polyurethanes with carbazole ring ,J.Applied polym sci,2010,12, 201-208
[4]. R.Lubczak ,diols with carbazole ring and their aza derivatives , heterocyclic communication,2006,12, 201-208
[5]. Hoegl ,H.Om,photoelectric effect in polymers and their sensitization by doparnts ,J,phys.chem.1965,69,201-208
[6]. Grazulevicius V.J,Strohrieglp.,piclichowski J.pielichowski K.carbazole containing polymers : synthesis, properties and application. Prog polym sci2003,28,1297-1353
[7]. Burroughes J.H.,Bradly d.d.c Brown A.R., Marks R.N Macked K.Friendly R.H .,Burn P.L Holmes A.B., Light emitting diodes based on conjugated polymers ,nature 1990,347,539-541.
[8]. Li,Z.,wong L., xiong B ye c.qin li.z., novel side on pvk based nonlinear optical polymers synthesius and nlo dyes pigm 2010,84,134-139
[9]. Babine G .,Malinauskas daskeviciene D Jankauskas V ., Getauties V easily functionalizeble carbazole based building blocks with extended conjugated system for optoeleetronic applications tetrahedrom 2010,66,3199-3206
[10]. X.J.Ke, X.Z Yan .N-srisanit,M.wang ,J.W.Yang X.F Huang S.Z.Zhong, holographic storage in carbazole communications ,2003,217,69-74
[11]. Grigoras M,catanescu C.O.Imine oligomers and polymers ,J macro mol sci C-polym.Rev,2004,c44(2),1-37
[12]. Hui Z ,.GANDINI a.polymers Schiff based bearing furan moieties Eur polym J 1992,28(12)1461-9
[13]. Zhang Y.,wang L., wada T,sasab H main chain polymers with nonlinear optical chlromophores as a shipped shoulder –to-shoulder arrangement .polym J .1997,29,685-92.
[14]. Zheng Yawing L.wada T.sasabe H,. One pot synthesis of a new huperbranched polyster containing 3,6-diacceptor-substituted carbazole chlromophores for mon-linear oipties ,Macromol chem. ,phys 1996,197,667-76
[15]. Saegusa Y., koshikawa T,. Nakamura s.synthesis and characterization of 1,3,4-oxadiazole containing polyaza –methines J.polym sci part A polym chen 1992,30(7)1369-73