

## A Novel Route Of Synthesis Photo-Conducting Polymers Of 3,6-Diamino N-Substituted Carbazole With Chloroformic Ester Of Polyethylene Glycols.

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**Abstract:** Three polyurethane polymers, all containing 3,6-disubstituted carbazole ring in the main polymer chain, are synthesized by solution polycondensation of 3,6-diamino N-substituted carbazole with chloroformic ester of diethylene glycol, triethylene glycol and tetra ethylene glycol. The polymers are characterised by IR, UV, and NMR spectroscopy.

**Keywords:** Monomer synthesis, Urethane polymer synthesis, solution polycondensation.

### I. Introduction

Photoconductivity is the increase in electrical conductivity of a material caused by absorption of electromagnetic radiation. Photo-conductive polymers are typically very good insulators in dark, when the carriers of electricity free electrons and /or holes are virtually absent. They become more conductive when exposed to light. In order to become a photoconductor, the polymer must satisfy two major requirements:

i) It must absorb light and thus allow photoexcitation of electrons from the ground state. The vacancy left behind (a hole) and the photo-excited electron from a pair of charge carriers, which can be separated by the action of an electric field.

ii) It must allow migration of either photoexcited electrons or holes, or both, through the polymer in the electric field towards the appropriate electrodes. Since, no ions move and matter is not displaced, the conduction process is wholly electronic with no ionic contribution.

Polymers that do not absorb light of a particular wavelength can still support migration of charge carriers generated in an adjacent material. In such a case the polymers act merely as charge transporting media. Since most known organic photoconductive polymers absorb only ultra-violet radiation, extrinsic photogeneration of charges has to be employed to make those polymers active in visible light, and in most practical organic photoconductors the polymers are only charge -transporting media for charges photogenerated in adjacent photoconductors.

Carbazole is another heterocyclic compound that has been used in the synthesis of many organic photoconductors due to its photo-conducting properties and high electron donating character. Therefore these polymers possess interesting electr-optical and photo-chemical properties as well as high thermal stability due to carbazole backbone.

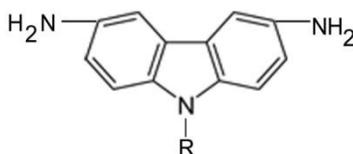
A large number of photo-conducting polymers have been synthesized but still poly N-vinyl carbazole is the most important one with respect to efficiency and cost of preparation. However only very few papers are reported about urethane polymers containing carbazole ring.

Polyurethanes exhibit interesting properties which are associated mainly with the presence of urethane sites. The polyurethanes present good thermal stability, mechanical strength, semiconducting properties and environmental stability.

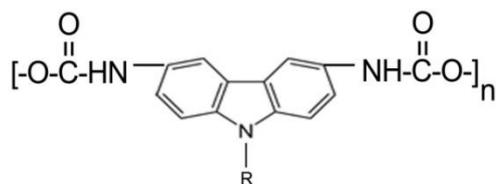
In this article the novel monomer 3,6-diamino N-substituted carbazole has been synthesized.

R=C<sub>3</sub>H<sub>7</sub>

R=CH(CH<sub>3</sub>)<sub>2</sub>



Then novel polyurethanes based on carbazole moiety in the main polymer chain have been synthesized by solution polycondensation of monomer with chloroformic ester of diethylene glycol, triethylene glycol and tetra ethylene glycol

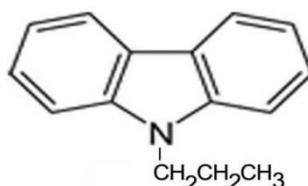


## II. Experimental

### 2.1 preparation of N-substituted carbazole :

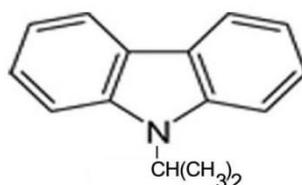
#### 2.1.1 preparation of N-propyl carbazole :

Carbazole is treated with sodium propoxide in absolute alcoholic medium in presence propyl iodide. The product has been purified by repeated crystallisation. The product has been confirmed by IR, NMR, UVspectre and observing the melting point.



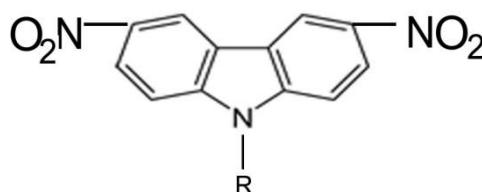
#### 2.1.2. Preparation of N-isopropyl carbazole :

Carbazole is reacted with sodium ethoxide in absolute alcoholic medium in presence of isopropyl iodide. The product has been purified by repeated crystallisation and characterized by the determination of melting point and by IR, NMR, and UV spectra.



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

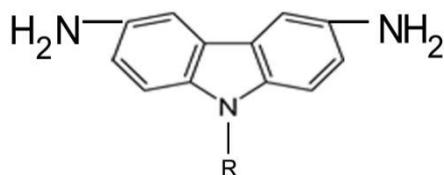
To a solution of 20g copper (II) nitrate hemi pentahydrate in a mixture of acetic acid (40ml) and acetic anhydride (80ml), stirred at room temperature, 20g N-substituted carbazole are introduced in a small portions. The reaction mixture is stirred at room temperature for an hour and then poured on ice-water. The yellow precipitate is 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 the IR, NMR, and UV spectra.



R=C<sub>3</sub>H<sub>7</sub>

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

A mixture formed from 10g of dinitro compound, 56g of stannous chloride, 180ml acetic acid and 30ml concentrated hydrochloric acid are refluxed under nitrogen atmosphere for 25h. The initial yellow colour turns on after 1h of reflux to orange and in time becomes brown. After 8h another portion of 10g stannous chloride and 5ml concentrated hydrochloric acid are added. After 25h 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 and in nitrogen atmosphere, the diamino derivative is confirmed by checking the melting point and by IR, NMR, and UV spectra.



C<sub>15</sub> H<sub>17</sub> N<sub>3</sub> (239.3)  
 Calculated N, 17.67  
 Found N, 17.32

R=C<sub>3</sub>H<sub>7</sub>

#### 2.4. preparation of chloroformic ester of different poly ethylene glycols :

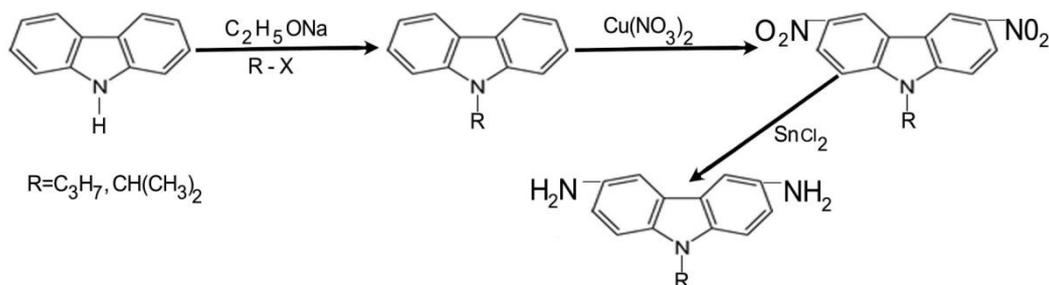
0.08mols of phosgene mixed with benzene is taken in a three necked round bottom flask equipped with a reflux condenser and a magnetic stirrer .The mixture is placed in an ice-both .Then 0.04mols of poly ethylene glycol mixed with 50ml of benzene is slowly added with vigorous stirring .After 30 minutes the ice - bath is removed and the temperature of the mixture slowly raised to 30<sup>0</sup>c.After that the reaction mixture is warmed at 50<sup>0</sup>c for 3h with vigorous stirring.

#### 2.5. Polycondensation of 3,6-diamino N-substituted carbazole and chloroformic ester of polyethylene glycols :

The above reaction mixture is cooled to room temperature and placed in an ice-bath. Another 100ml of benzene is added to the mixture.Then 0.04 mols of diamine mixed with benzene is quickly added at 0<sup>0</sup>-5<sup>0</sup>c with vigorous stirring.,Then 0.08mols of triethylamine is addedwith vigorous stirring .After 30minutes the mixture is removed from ice-bath and stirred well at room temperature for 2h .In time the polymer is precipitated out from methanol ,filtered off and washedwith methanol and finally with hexane and dried . The polymers are characterised by IR, NMR and UV spectra.

### III. Result And Discussion

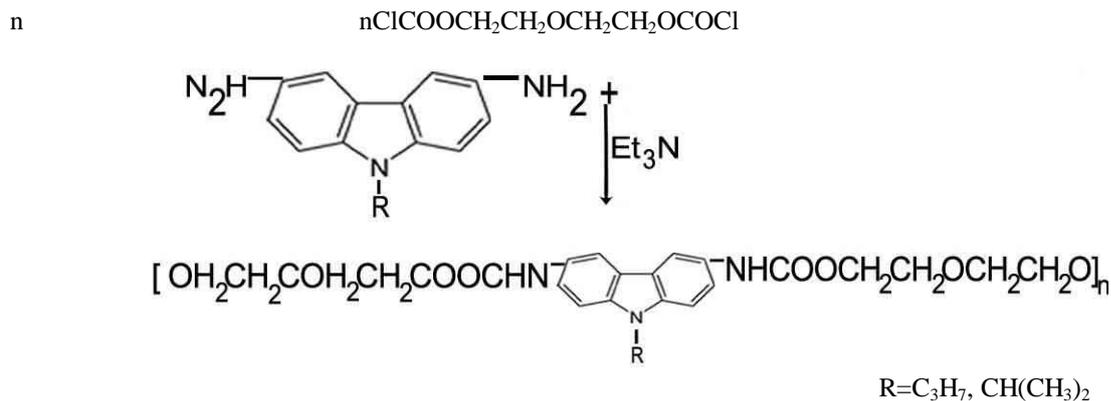
The study of IR,NMR and UV spectra revealed the successful preparation of the polymers .The synthesis of carbazole based diamine monomer starting from carbazole is presented in detail in scheme-I



Scheme – I, Synthesis of monomer

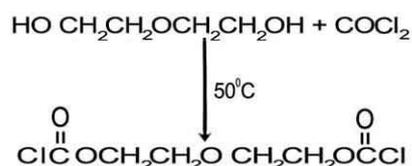
N-substituted carbazole is prepared by treating carbazole with corresponding sodium alkoxide and with corresponding alkyl halide in absolute alcoholic medium. Diamine is synthesized by a similar procedure described by chen and natansohn. N-substituted carbazole is firstly dinitrated using copper (II) nitrate hemi penta hydrate in a mixture of acetic acid and acetic anhydride In the scondstep,dinitro compound is reduced using stannous chloride in a mixture of hydrochloric acid and acetic acid at reflux temperature. .A pure, light, pink-coloured product in a reasonable yieldis obtained after three precipitations of acetone solution in water and the filtered solid product is dried and deposited in dark and nitrogen atmosphere.

By solution polycondensation of equimolar mixture of 3,6-diamino N-substituted carbazole and chloroformic esters of diethyleneglycol,triethylene glycol and tetra ethylene glycol, three urethane polymers have been synthesized .The reaction is carried out in benzene .The polycondensation reactions \are carried out in homogenous phase and the 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 regiditydue to carbazole backbone. Polymer of 3,6- diamino N-substituted carbazole with diethylene glycol is given below as a typical example in scheme-(II)



Scheme – (II), synthesis of polymer

The formation of chloro formic esters of diethylene glycol, triethylene glycol and tetra ethylene glycol have been prepared by treating phosgene with corresponding polyethylene glycol firstly at 0-5<sup>o</sup>c and then warming the mixture at 50<sup>o</sup>c. The chloroformic esters are kept in the solution medium. The chloroformic ester of diethylene glycol is given as below as a typical example in scheme-(III)



Scheme –(III) Synthesis of monomer

#### IV. Conclusion

This article has summarized the approaches to synthesis of monomer and the corresponding polymers with chloroformic ester of polyethylene glycols. The photoconducting polymers are finding many important applications in electro-luminescent and photo refractive devices. This investigation will help us to formulate a new and cheaper photo-conducting polymers. Moreover, these polymers can be further studied for dark conductivity in sandwich configuration at different voltages, different temperatures with different sensitizers like TNF and crystal violet etc. Same studies can be done under illumination at different wavelengths and different intensities. Characterization of the polymers will be the subject of further studies.

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