

Synthesis of Electro-optic Conjugated Polymer of Carbazole Ring.

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Abstract:

N-ethyl Carbazole was prepared by treating carbazole with ethyl iodide in presence of sodium hydride in the solvent medium of DMF. After subsequent addition of water *N*-ethyl carbazole was precipitated out. *N*-ethyl-3,6-diformyl carbazole was synthesized by treating *N*-ethyl carbazole with high excess of POCl_3 and DMF mixture. Then pure *N*-ethyl-3,6-diformyl carbazole was separated by flash chromatography on a silica gel column using ethylacetate /hexane (1:10) as eluent. *N*-ethyl-3,6-divinyl carbazole was synthesized by treating *N*-ethyl-3,6-diformyl carbazole with methyltriphenylphosphonium iodide and sodium hydride in the solvent medium of DMSO firstly at 0° for 1h and then at room temperature for 30h. 1,4-dioctyloxy benzene was prepared by treating hydroquinone with 1-bromo octane in presence of potassium hydroxide in the solvent medium of DMSO. 2,5-dioctyloxy-1,4-diiodobenzene was prepared by treating 1,4-dioctyloxy benzene with iodine and iodic acid in presence of sulphuric acid in the solvent medium of carbon tetrachloride and glacial acetic acid under reflux for 4h. The polymer was synthesized by Hack-coupling reaction. The two monomers namely *N*-ethyl-3,6-divinyl carbazole and 2,5-dioctyloxy-1,4-diiodo benzene were mixed with palladium (II)acetate and anhydrous DMF. Then tri-*n*-butyl amine was added to the mixture. The resulting solution was degassed by three freeze-pump-thaw cycles and stirred at 100°C for 4 days.

Keywords: *N*-ethyl-3,6-diformyl carbazole, *N*-ethyl-3,6-divinylcarbazole, 2,5-dioctyl oxy-1,4-diiodo benzene, conjugated polymer.

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I. Introduction:

The electro-optical properties of organic and polymeric materials are regarded as holding potential for developments in charge storage, analytical sensors, electroluminescent devices, optical data processing and integrated optics. For example, nowadays it is clear that sensor sensitivities and specificity can be increased by using redox polymers or that the parameters characterizing the relative strength of nonlinear optical, NLO, effects are typically 50 or 100 times greater in organic molecular systems than in inorganic dielectric insulators and semiconductors.

In addition, because of the availability of a enormous variety of organic molecules and of liquid crystalline oriented films or other ordered environments, the properties of polymeric materials may be tailored to optimize other parameters such as anisotropy, mechanical strength, processability, thermal stability, laser damage threshold, etc., while preserving intact the electronic structure responsible for the electro-optical effects. While the potential for applications is great indeed, the development of appropriate electro-optical polymeric materials is a combination of interdisciplinary tasks: (1) synthesis of macromolecules with pi-electron systems, (2) control of the molecular morphology and the detailed nature of the electronic environment of the medium, and (3) characterization of the polymer material properties.

The key structural feature of almost all the electro-optically active polymers is that they have pi-electron systems as building blocks imbedded in its structure. These unsaturated systems can be considered either as chromophores or as electrophores depending on the kind of particles, light or electrons, they interact with. While charge uptake can lead to electric conductivity, charge storage or electroluminescence (after ion recombination), the interaction with electromagnetic waves gives origin to photoconductivity, photovoltaic effects, NLO effects and so on.

Another fundamental structural feature which defines the polymer electro-optical properties is the type of unit linking the pi-electron systems. In redox polymers, the active units are linked by saturated spacers that isolate the pi-electrons. Therefore, the polymer electro-optical properties [oxidation potentials, fluorescence, band gaps etc.] are rather similar to their low molecular building blocks whereas the polymeric state is of importance by its contribution to the mechanical properties of the material. Poly(vinylcarbazole) that has been used as the photoconducting layer in photocopiers is an early example of this type of polymers. On the other hand,

conjugated polymers have unsaturated linking units. As a result, the pi-conjugation is extended over long segments of the polymer main chain until a defect, i.e. a saturated unit, interrupts the electron delocalization.

The conjugated polymer electro-optical properties are intrinsic and they often differ substantially from the redox polymers. Conjugated polymers have also received the name of conducting polymers which focuses on its ability to transport electrical charges upon oxidation or reduction, I.e. doping.

In this article, conjugated poly (arylenevinylene) based on carbazole ring has been synthesized.

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 6.68g (0.04mol) of carbazole along with 80 ml of anhydrous DMF. To the stirred solution was added 1.20g(0.05 mol) of sodium hydride. Immediately hydrogen gas was evolved. This was stirred for further 15 min to dissolve the carbazole anion. Then 7.80 g(0.05mol) of ethyl iodide was added in one portion. The reaction was exothermic, indicating the reaction proceeded immediately. After 6h, 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 /DMF mixture. However, even at very high ratio, vilsmyerformylating agent/carbazole compound (greater than 10:1) always a mixture of mono (3-formyl-N-ethyl carbazole) and dialdehyde compound (3,6-diformyl-N-ethyl carbazole) is 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 is the first product eluated and after evaporation of the solvent, an oil product is 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 mono and dialdehyde products.

2.3. Synthesis of 3,6-divinyl-N-ethyl carbazole:

A solution of 2.2 equiv of methyl triphenylphosphonium iodide in 300 ml of DMSO was treated with 2.2 equiv of sodium hydride at 0°C . After stirring for 1h (turned of yellow-red solution), 1equiv. Of 3,6-diformyl-N-ethyl carbazole slowly added the mixture was stirred at room temperature for 1h, and then at room temperature for 30h. After completion of the reaction, the mixture was poured into crushed ice (400g) and extracted with methylene chloride and dried with magnesium sulphate. The solvent was removed at reduced pressure. The residue was purified by using silica gel column chromatography.

2.4 Synthesis of 2,5-dioctyloxy-1,4-diiodo benzene:

1-bromooctane (5.018g,26mmol) was added slowly to a rapid stirring solution of hydroquinone (1.10g,10mmol) and potassium hydroxide (0.70g,12.5mmol) in DMSO (60ml). The solution turned black after stirring for 24h at room temperature and was then poured into ice-water (200ml). The dark-brown solid was collected by suction filtration, washed with cold water and cold ethanol to give a white solid of 1,4-dioctyl oxy benzene. A mixture of 1,4-dioctyloxy benzene (2.31g,7mmol),iodine (2.03g,8.0mmol), iodic acid (1.10g,6.25mmol), sulphuric acid (30%,10ml), carbon tetrachloride (15ml), and glacial acetic acid (60ml) was heated under reflux for 4h. The reaction mixture was then cooled in an ice-bath, light-brown solid was isolated by suction filtration. Recrystallization by ethanol give a yellow meedle.

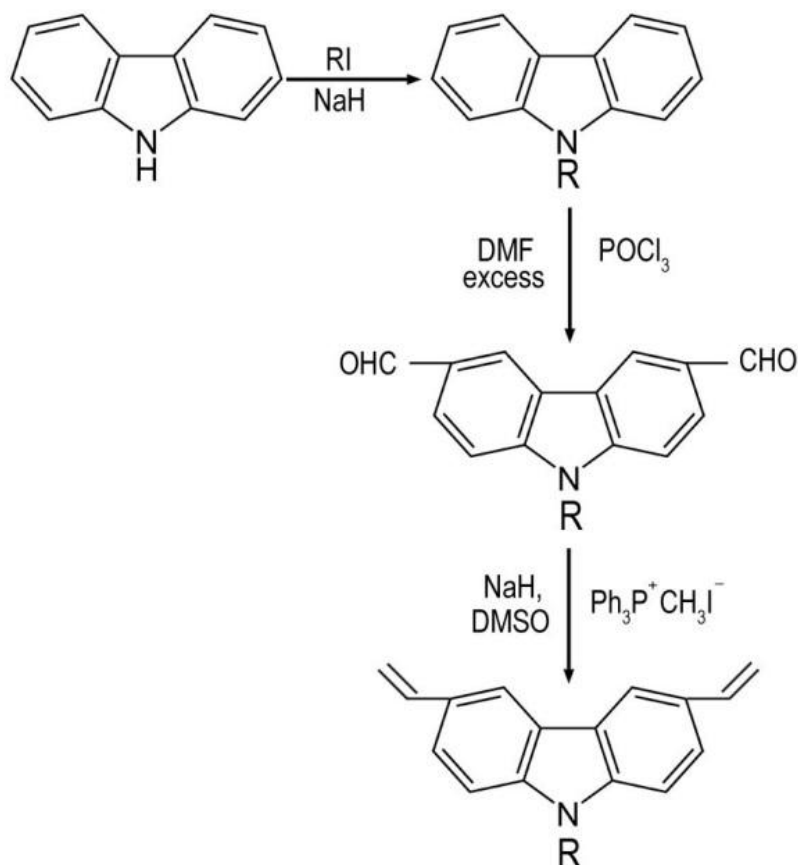
2.5. Synthesis of polymer:

Polymer was synthesized by Heck-coupling reaction. Monomer 3,6-divinyl-N-ethyl carbazole (0.0447g,0.181mmol)and monomer 2,5-di(octyloxy)-1,4-diiodo benzene (0.106,0.181mmol),and palladium (II)acetate (2mg,0.0091mmol) were added to a 50 ml close-system flask under a nitrogen atmosphere. Anhydrous DMF (5ml) was added via a syringe and tri-n-butyl amine (0.101g,0.54mmol) was added to the mixture. The resulting solution was degassed by three freeze-pump-thaw cycles. The solution was stirred at 100°C for 4 days. The reaction mixture was poured into methanol and solid was collected by filtration, and dried under vacuum for 2days.

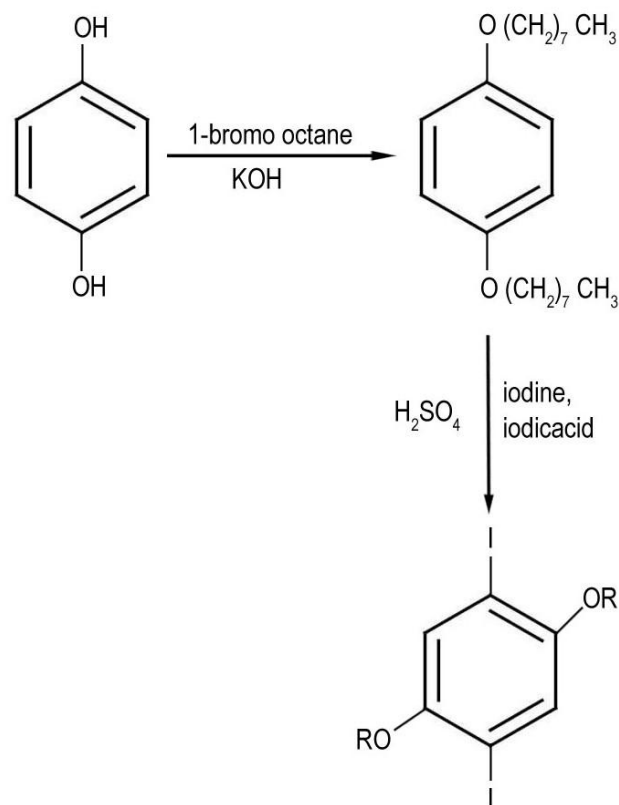
III. Result and discussion:

IR, UV and NMR spectra revealed the successful preparation of the polymer. The monomer-I was synthesized as follows: N-ethyl carbazole was synthesized by treating carbazole with ethyliodide in presence of sodium hydride in the solvent medium of DMF. After subsequent addition of water, the titled product was achieved which was recrystallized from chloroform. 3,6-diformyl-N-ethyl carbazole was synthesized by treating

N-ethyl carbazole with high excess POCl_3/DMF mixture. However, even at very high ratio, Vilsmeierformylating agent/carbazole compound (greater than 10:1) always gave mono and dialdehyde compound. The pure dialdehyde compound was obtained by making flash chromatography. The mono aldehyde is the first product eluated and the dialdehyde compound was obtained later as a white solid after evaporation of elucnt. The titled product was recrystallized from acetone. 3,6-divinyl-N-ethyl carbazole was synthesized by wittig reaction. At first triphenyl methyl phosphonium iodide and sodium hydride mixed with DMSO and stirred for for 1h at 0°C . Then, 3,6-diformyl-N-ethyl carbazole slowly added to the mixture and stirred at room temperature for 30h. After completion of the reaction, the mixture was poured into crushed ice and extracted with methylene chloride, dried with magnesium sulphate. The solvent was removed at reduced pressure. The residue was purified by using silica gel column chromatography. The synthetic route of monomer-I was represented in scheme-I.

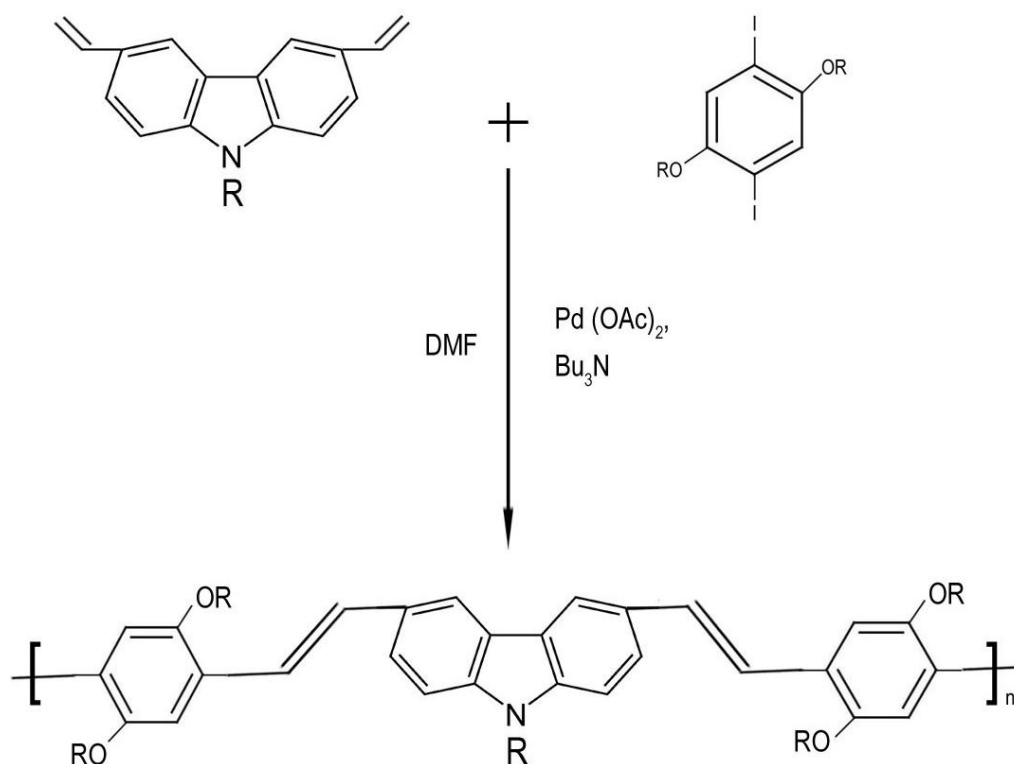


Monomer-(II) was prepared as follows: 1,4-(dioctyloxy) benzene was obtained by treating hydroquinone with 1-bromooctane in presence of potassium hydroxide in the solvent medium of DMSO, after stirring for 24h at room temperature. After that the mixture was poured into ice-water and the product was filtered which was recrystallized with cold ethanol. 2,5-di(octyloxy)-1,4-diiodo benzene was obtained by treating 1,4-di(octyloxy) benzene with iodine, iodic acid, sulphuric acid, carbontetrachloride and acetic acid by heating under reflux for 4h. The reaction mixture was cooled in ice-bath, hight-brown solid isolated by suction filtration. Recrystallization of the product by ethanol give a yellow needle. Synthetic route of monomer-II was represented in scheme-II.



Scheme-II

The polymer was synthesized by Heck-coupling reaction. 3,6-divinyl-N-ethyl carbazole, 2,5-di (octyloxy)-1,4-diiodo benzene were taken in the (1:1)ratio and with this palladium(II)acetate was mixed and taken in a 50 ml close-system flask under nitrogen atmosphere. Anhydrous DMF was added via a syringe and tri-n-butyl amine was added to the mixture. The resulting solution was degassed by three freeze-pump-thaw cycles. The solution was stirred at 100⁰c for 4 days. The reaction mixture was poured into methanol and solid was collected by filtration. The synthetic route of the polymer was represented in scheme-III.



Scheme-III

IV. Conclusion:

In conclusion, we have synthesized the two monomers namely 3,6-divinyl-N-ethyl carbazole and 2,5-di(octyloxy)-1,4-diiodo benzene and their electro-optic conjugated polymer. All monomers and polymer were characterized by IR, UV and NMR spectra. It is a PAV type conjugated polymer having carbazoling. Some of the conjugated polymers such as polyaniline, polypyrrol are electro synthesized on an electrode surface from which a film can be peeled off. This procedure arises the biggest problem in the conjugated polymer synthesis, that is, its lack of processability. Due to rigid main chain structure all this polymers are insoluble in all kind of solvents. However, for this conjugated polymer, an alternative synthetic route has been designed.

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