

Synthesis of photoconducting carbazole Based Polybenzoxazines.

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Abstract: *N*-(9-ethyl carbazolyl) benzoxazine was synthesized by the reaction of 3-amino-9-ethyl Carbazole with paraformaldehyde and 4- methyl phenol under reflux in the solvent medium of toluene. The corresponding polybenzoxazine of *N*-Carbazolylbenzoxazine monomer was synthesized by heat treatment process. The following temperature program was applied: 110^oc for 60 min., 140^oc for 30min., 160^oc for 30 min., 170^oc for 45 min, 180^oc for 45 min., 190^oc for 60 min, 200^oc for 90 min. The benzoxazine monomer and poly benzoxazine were characterized by IR, UV and NMR spectroscopy. Secondly a polymeric benzoxazine precursor was synthesized by the reaction of 3,6-diamino-*N*-ethyl Carbazole (which was Synthesized earlier) with paraformaldehyde and Bisphenol-A under reflux condition in the solvent medium of chloroform. The polymeric benzoxazine precursor was characterized by IR, UV and NMR spectroscopy.

Keywords: *N*-(9-ethylcarbazolyl) benzoxazine, polybenzoxazine polymeric benzoxazine precursor, Ring-opening polymerization.

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I. Introduction

Macromolecular materials with unique combination of both electronic and optical properties have attracted tremendous technological interest in the past few decades due to increasing need for low cost materials with structural flexibility. Various designing methods have been employed to achieve efficient semiconducting properties in polymers with potential applications in the field of optical storage media, dynamic holography, xerography, photorefractive composites, photovoltaic devices, light emitting diodes and many other photonic systems. The extend of pi-conjugation and the presence of aromatic amino group in the polymer structure are the common structural features of charge transporting materials. The charge transport and the semiconducting properties of these materials depend mainly on the structure and morphology of the polymer chains.

Lot of reports are there in the literature about the synthesis and properties of conjugated polymer systems. However, less attention was given to non-conjugated polymers. In non-conjugated polymers, the semiconducting property is based on the charge hopping from one localized site to another in the direction of electric field. In this article, Mannichphenolic type poly benzoxazines were synthesized. These polymers can be synthesized via thermally activated cationic ring opening polymerization. Firstly, one benzoxazine monomer was synthesized by the reaction of 3-amino-9-ethyl carbazole with 4-methyl phenol and paraformaldehyde and after that subsequent heat treatment process gave the polybenzoxazine. Secondly, a polymeric benzoxazine precursor was synthesized by the reaction of 3,6-diamino-9-ethyl Carbazole with Bisphenol-A and paraformaldehyde. The structure of the polymers were confirmed by FT-IR, NMR analysis.

Polybenzoxazines are non-Conjugated polymers with good thermal and mechanical and physical properties. This polymers were synthesized via heterocyclic ring opening polymerization of benzoxazine monomer at elevated temperatures. Benzoxazines are obtained by Mannich condensation of phenol, formaldehyde and an amine. The Mannich base bridge (-CH₂-NR-CH₂) characterizes the structure of the polymer, with the reaction taking place preferentially at the ortho position of the free phenolic group. The oxygen and nitrogen atom in the heterocyclic ring as well as the unobstructed ortho position in the benzene ring with respect to the phenolic group are preferred sites for ring opening. Depending upon the reaction condition, the polymerization leads to Mannichphenoxy type and Mannich phenolic type polybenzoxazines.

II. Experimental

2.1. Synthesis of *N*-(9-ethyl Carbazolyl) benzoxazine:

Paraformaldehyde (3.60g, 120mmol) was dissolved in hot toluene (200 ml). After the addition of 3-amino-9-ethyl Carbazole (12.60g, 60mmol) dissolved in toluene (60ml), the reaction was stirred under reflux for 30min. 4-methyl phenol (6.48g, 60mmol) in toluene (40ml) was added one drop at a time and the mixture was stirred

under reflux for further 18 h . The reaction was cooled down to room temperature, and the solvent was evaporated under reduced pressure. The resulting solid was dissolved in chloroform and washed with an aqueous basic solution (NaOH 1 M, 3x100ml) and water. The organic fraction was dried with anhydrous sodium sulphate and the solvent was removed under reduced pressure.

2.2. Polymerization on N-(9-ethyl carbazolyl) benzoxazine monomer:

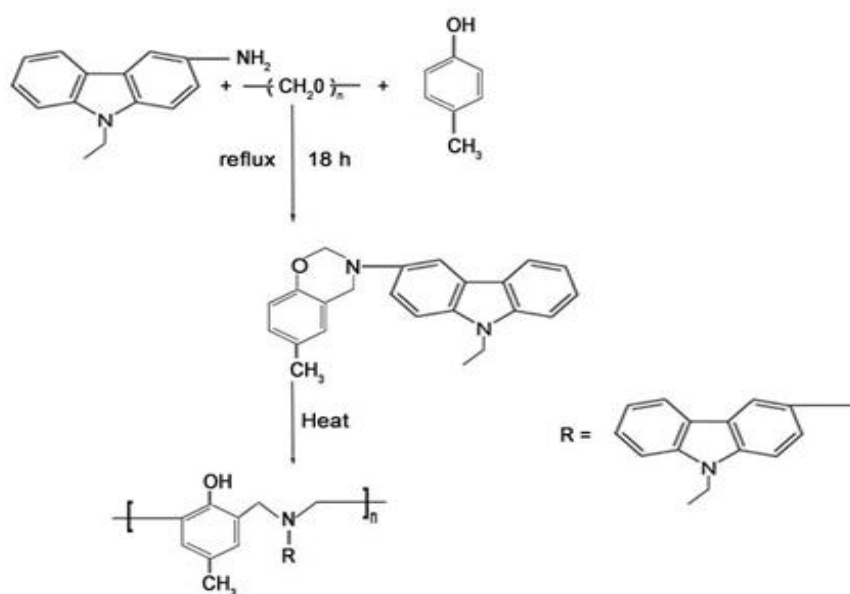
N-(9-ethyl Carbazolyl)benzoxazine monomer was placed in a silicon mold and the following temperature program was applied: 110⁰c for 60 min, 140⁰c for 30 min, 160⁰c for 30 min, 170⁰c for 45 min, 180⁰c for 45 min, 190⁰c for 60 min, and 200⁰c for 90 min.

2.3. Synthesis of polymeric benzoxazine precursor:

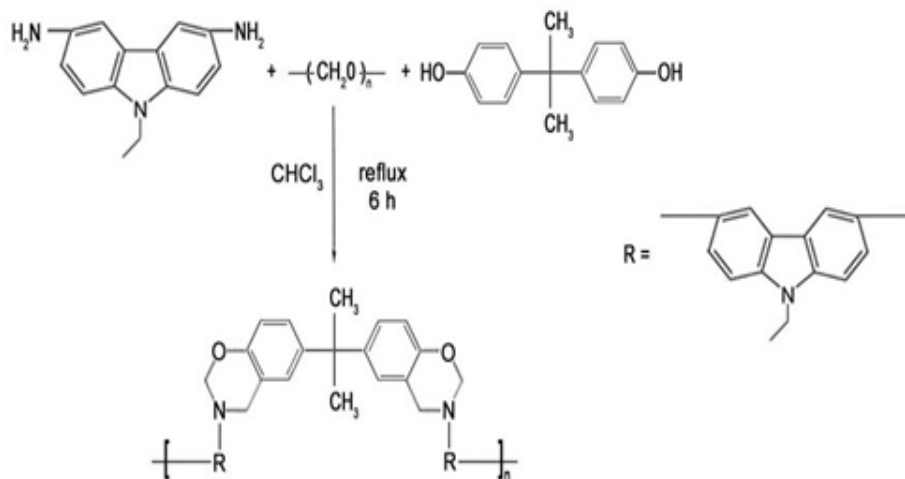
3,6-diamino-9-ethyl Carbazole (0.9 g 4mmol), Bisphenol-A (0.912 g 4mmol), paraformaldehyde (0.48 g, 16 mmol) were dissolved in 60ml of chloroform in a 250 ml three-necked round bottom flask equipped with a mechanical stirrer, a reflux Condenser and a thermometer. The reaction temperature was then raised to 110⁰c in an oil bath. The reaction time is 6h to obtain the polymer. The reaction mixture was filtered and then liquid phase was concentrated and precipitated in methanol.

III. Result and Discussion

At first, the monomer namely N-(9-ethyl Carbazolyl) benzoxazine was synthesized in a single stage by reacting stoichiometric amount of 3-amino-9-ethyl carbazole, paraformaldehyde and 4-methyl phenol under reflux in the solvent medium of toluene. Then the benzoxazine monomer was polymerized in a silicon mold by successive heat treatment process. The formation of benzoxazine monomer and its polymer were confirmed by spectral analysis. The temperature for polymerization was raised maximum up to 200c. Generally the polymerization of benzoxazine monomer can yield two types of polymer structure depending on the atom that is performing the nucleophilic attack on the electrophilic methylene group (NCH₂O). An attack by phenolic oxygen initially yields N,O-acetal linkages (phenoxy type structure), which can then rearrange into Mannich type structures exhibiting free phenolic units (phenol-type structure). In contrast, an attack by a phenolic carbon (ortho position in benzoxazine) directly results in phenolic type structure. The main driving force for ring-opening polymerization is the ring stress relief caused by the opening of the distorted 6-membered oxazine ring. Here, ring opening polymerization is achieved simply by heat treatment process without any catalyst and initiators. Monomer samples were polymerized by applying a stepwise temperature program to avoid the localized overheating of the sample upon exothermic curing. The synthetic route of benzoxazine monomer and polybenzoxazine was depicted in scheme-I



Secondly, polybenzoxazine precursor containing cyclic benzoxazine group in the backbone was synthesized by reacting 3,6-diamino-9-ethyl Carbazole (which was synthesized earlier), paraformaldehyde and Bisphenol-A under reflux in the solvent medium of chloroform. The polymeric precursor was confirmed by Spectral analysis. The synthetic route of the polymeric precursor was depicted in scheme-II



Scheme-II

The polymerization of benzoxazine monomer proceeded via the formation and propagation of oxonium ion centres. The reaction involves nucleophilic attack of benzoxazine monomer on the oxonium ion. The presence of hetero atom in the ring provides potential sites for initiation and propagation of reaction by ring opening. If the monomer contains two different types of hetero atom, the preferred site will be the one with high negative chargedistribution. The strained conformation makes the monomer to undergo cationic ring opening polymerization. Hence, the polymerization involves nucleophilic attack of monomer on either the oxygen or nitrogen sites. The attack on the oxygen and nitrogen propagation sites lead to phenolic type polybenzoxazine structure. The polymers are soluble in most of the organic solvents.

The charge transporting polybenzoxazine can be made absorptive and photoconducting in the spectral region of He-Ne laser beam (632nm) by the addition of small amount of (0.2wt%)TNF, as charge generator molecule. TNF molecule will form a C.T. complex with high electron rich carbazole ring, and therefore, a charge is generated which will move through the polymer chain. Moreover, photocurrent can be increased by doping the polymer with TNF. A photorefractive system based on charge transporting host polybenzoxazine can be developed by using a second order NLO chromophore (DR-1) and the charge generating molecule, TNF and charge transporting plasticizer(ECZ).

IV. Conclusion

This article has summarized the novel synthesis of Polybenzoxazine of Carbazole moiety. The benzoxazine monomer and its polymer were characterized by FT-IR spectra. In this article two types of polybenzoxazine were synthesized. At first, one benzoxazine monomer was synthesized by treating 3-amino-9-ethyl Carbazole, paraformaldehyde and 4-methyl phenol and subsequently the benzoxazine monomer was polymerized by heat treatment process. Secondly, a cyclic polybenzoxazine Precursor was synthesized by reacting 3,6-diamino-9-ethyl Carbazole, Paraformaldehyde and Bisphenol-A. Polybenzoxazine show good photoconducting property when it was doped with charge generator like TNF. In this case electron rich Carbazole centre form a charge transfer complex with strong electron acceptor TNF. A good photorefractive system can be developed by conjugation with a second order non-linear optical chromophore (DR-1), charge generator(TNF) and plasticizer (ECZ).

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