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# Synthesis of Photo Conducting Poly (siloxane) of Indole Ring

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***Abstract:*** *N-ethy1-3-methyl indole was synthesized by treating ethyl iodide with 3-methyl indole in presence of sodium hydride in the solvent medium of DMF. N-eyhy1-3-bromo methyl indole was prepared by reacting N-ethyl-3-methyl indole with N-bromo succinimide and benzoyl peroxide in the solvent medium of benzene. N-ethyl-3-(N-allyl-methyl amino methyl) indole was synthesized by treating N-ethyl-3-bromo methyl indole with N-methyl-allyl amine in presence of potassium carbonate in the solvent medium of DMSO at 100ºC for 24h. Poly(siloxane) was synthesized by reacting N-ethyl-3-(N-methyl-allyl amino methyl) indole with Poly (methyl hydro siloxane) in presence of several drops of hydrogen hexa chloro platinate (IV) hydrate in the solvent medium of toluene at 150ºC for 6h. The monomer and polymer were characterized by IR, UV and NMR spectra.*

***Keywords:*** *N-ethyl-3-methyl indole; N-ethyl-3-bromo methyl indole; N-ethyl-3-(N-methyl-allyl amino methyl) indole; Poly (siloxane).*

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## I. Introduction

The photorefractive effect was first reported with lithium niobate crystal more than 50 years ago[1]. A variety of potentially important applications have been proposed using inorganic crystals, including high-density optical data storage, image processing, phase conjugation, beam fanning limiter and optical correlator[2]. However, because of difficulties in crystal growth and sample preparation, inorganic crystals have been limited for mass production. For last decade, extensive studies have been carried out on organic photorefractive materials to overcome some of problems associated with inorganic materials. Photorefractive organic materials have many advantages of lower dielectric constants, lower cost, and easier processing than inorganic materials.

Among many organic photorefractive materials reported to date, polymeric host-guest system has been extensively investigated because of their excellent photorefractive properties, compositional flexibility and easy fabrication method[3,4]. The charge- transporting polymers such as poly (vinyl carbazole) or poly (siloxane carbazole), doped with nonlinear optical chromophores have been generally adopted due to their excellent photorefractive performance. The large refractive index modulations, and fast response times, have been reported with this polymeric system[5-8].

Carbazole-substituted poly siloxane (PSX-$C_Z$) is one of the most well-known photo conducting polymers for photorefractive systems [9]. The glass transition temperature (Tg) of these PSX-$C_Z$ composites could be lowered to room temperature simply by adding a NLO chromophore [10,11]. It was notable that the photorefractive properties could be improved by using a low Tg polysiloxane because this system did not contain inactive molecules such as a plasticizer [12-15].

Indole is another heterocyclic compound like carbazole which is charge transporting and have donor moiety. In this study, a new photo conducting poly (siloxane) with pendent indole ring was synthesized by hydrosilylation reaction. The indole-doped polysiloxane is a good candidate with excellent hole-mobility and photorefractivity[16-18].The photorefractive composite can be prepared by doping a nonlinear optical chromophore and photosensitizer into the new photo conducting polysiloxane.

## II. Experimental

### 2.1. *Synthesis of N-ethyl-3-methyl indole*

To a three necked round bottom flask equipped with nitrogen purge and reflux condenser was added 2.62 g(0.02mol ) of 3-methyl indole along with 75ml of anhydrous DMF. To the stirred solution was added 0.72 g(0.03 mol) of sodium hydride. Immediately a precipitate formed with evolution of hydrogen gas. This was stirred for further 15 minutes to dissolve the indole anion. Then 4.68 g(0.03mol) of iodoethane was added in one

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portion. After 10h, 200ml of water was added to give a precipitate. The product was recrystallized from chloroform.

**2.2.** ***Synthesis of N-ethyl-3-bromomethyl indole***

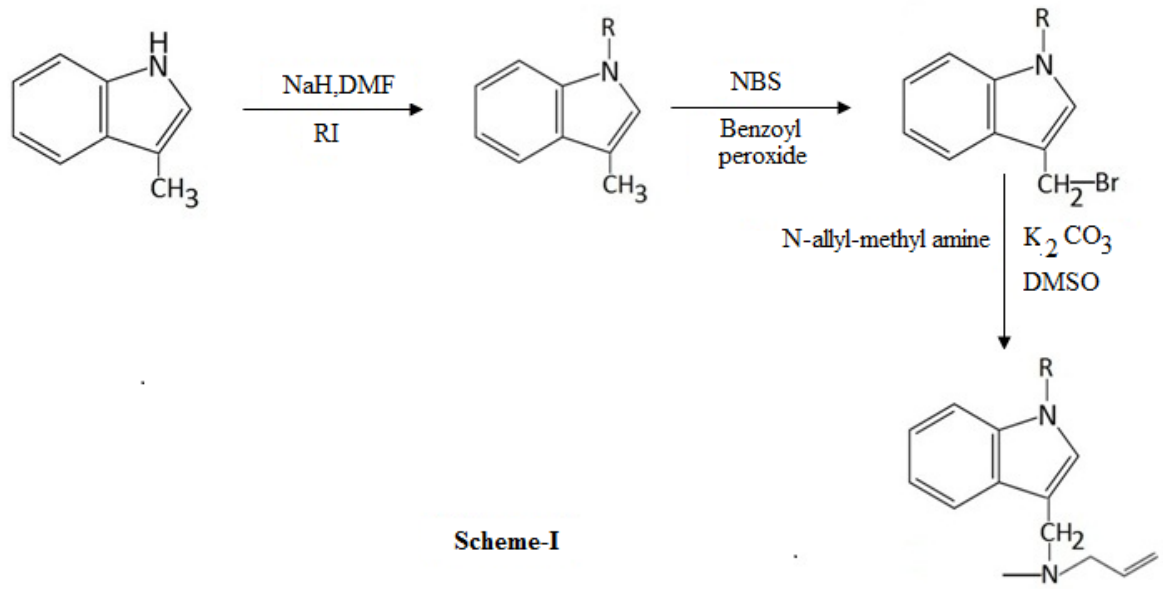
Under a nitrogen atmosphere, a mixture of N-ethyl-3-methyl indole 4.77 g (0.03mol), N-bromo succinimide 4.65g (0.033 mol), benzene (100ml) and benzoyl peroxide (50mg) was heated under reflux for 8h. The mixture was cooled and filtered and the filtrate was removed under reduced pressure. Water (100ml) was added and the organic layer was extracted by dichloromethane. After removal of solvent, the crude product was recrystallized with ethanol, giving N-ethyl-3-bromomethyl indole.

**2.3.** ***Synthesis of N-ethyl-3-(N,N-allyl methyl amino methyl) indole***

Into a 250 ml flask added 4.76g (0.02mol) of N-ethyl-3-bromomethyl indole and 2.76g (0.02mol) of Potassium carbonate and 50ml of DMSO. This mixture was heated to 100°c with stirring. Into this mixture added the solution of 2.84g (0.04mol) of N-allyl-methyl amine in 10ml of DMSO slowly and followed by adding 0.1g of 18-crown-6. The mixture was stirred at this temperature for 24h. Then the mixture was poured into cold water to precipitate the product. The product was purified by recrystallization from ethanol.

**2.4.** ***Synthesis of Poly (Siloxane)***

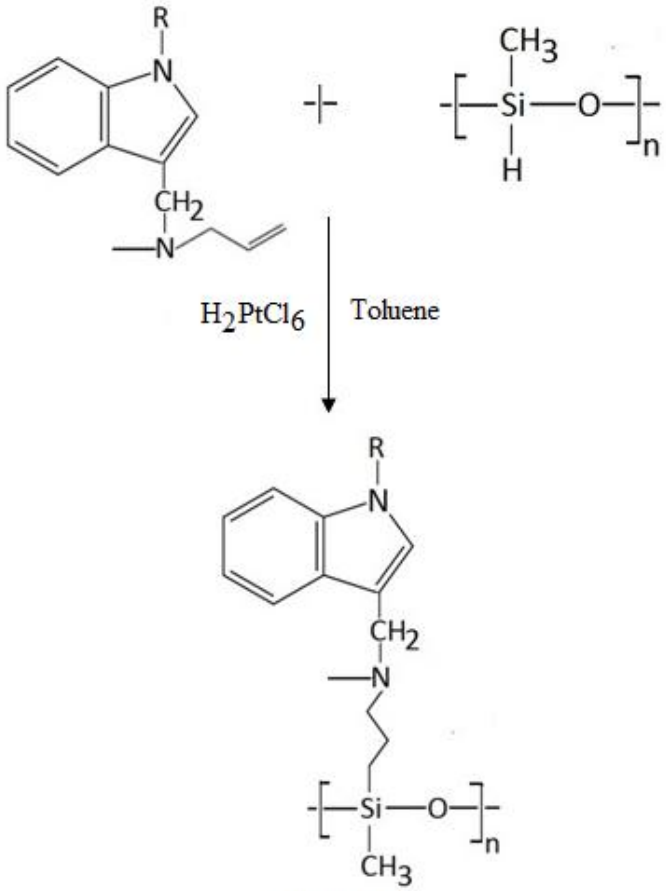
A dried 100ml of two-necked flash was equipped with a magnetic stirrer and a reflux condenser under argon. Into this flask N-ethyl-3-(N,N-allyl methyl amino methyl) indole (3.58g, 0.018mol) and 40ml of toluene were added and purged with argon. The portion of poly (methyl hydro siloxane)(1.06g,0.018 mol) was dissolved with anhydrous toluene and added to the flask with several drops of hydrogen hexachloro platinate (IV) hydrate under argon atmosphere. The solution was heated at 150ºC for 6h and then poured into methanol. The precipitate was filtered, dried and purified three times by reprecipitation from methanol [19].




**Scheme-I**

## III. RESULT AND DISCUSSION

The characterization of IR, UV and NMR speetra revealed the successful preparation of the Polymer. The monomer and the polymer were prepared as follows: N-ethyl-3-methyl indole was prepared by reacting 3-methyl indole with iodoethane in presence of sodium hydride in the solvent medium of DMF. After subsequent addition of water, the product was precipitated out and recrystallized from chloroform. N-ethyl-3-bromomethyl indole was synthesized by the treatment of N-ethyl-3-methyl indole with N-bromosuccinimide (NBS) and benzoyl peroxide in the solvent medium of benzene. The mixture was cooled and filtered and the filtrate was removed under reduced pressure. Water was subsequently added and the organic layer was extracted with dichloromethane. After removal of solvent, the product was recrystallized from ethanol. N-ethyl-3-(N,N-allyl methyl amino methyl) indole was synthesized by the treatment of N-ethyl-3-bromomethyl indole with N-allyl-methyl amine in presence of potassium carbonate in the solvent medium of DMSO at100ºC for 24h. The product was precipitated out by adding water and recrystallized from ethanol. The synthetic route of monomer was depicted in Scheme-I.




**Scheme-II**

The polysiloxane was synthesized by the treatment of N-ethyl-3-(N,N-allyl methyl amino methyl) indole with poly (methyl hydro siloxane) in presence of several drops of hydrogen hexa chloro platinate (IV) hydrate in the solvent medium of toluene under reflux for 6h. The polymer was precipitated out in methanol, filtered, dried and purified by reprecipitation from methanol. The synthetic route of the polymer was depicted in Scheme-II.

The photo conducting polymer namely indole based polysiloxane was obtained by hydrosilylation of poly (methyl hydro siloxane) with N-ethyl-3-(N,N-allyl methyl amino methyl) indole. Hydrosilylation has been known as a very convenient method for the synthesis of various silicon-containing polymer[20]. The polymer was soluble in common organic solvents. A good photorefractive system can be prepared by doping the polymer with NLO chromophore DB-IP-DC and photosensitizer TNF.

## IV. CONCLUSION

Indole-based polysiloxane as a photoconducting matrix was successfully synthesized by a hydrosilylation method with a platinum catalyst. The monomer and polymer were characterized by UV, IR and NMR spectroscopy. The photoconductivity can be measured in the dark and in presence of light after being formation of charge transfer complex with TNF. Indole itself being an electron donor it will form C.T. complex with strong electron acceptor moiety TNF. Moreover, a good photorefractive composite can be prepared of indole-based polysiloxane with a NLO chromophore DB-IP-DC and photo sensitizer like TNF.

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