

Synthesis of Photo-conducting Poly (siloxane) of Indole-phenanthrene Moiety.

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Abstract:

N-(2-hydroxyethyl)-3-vinyl indole was synthesized by the reaction of 3-vinyl indole with ethylene carbonate in presence of sodium hydride in the solvent medium of DMF at first at 0°C for 1h then at 40°C for 3h. *N*-(2-acetoxy ethyl)-3-vinyl indole was synthesized by the reaction of *N*-(hydroxyethyl)-3-vinyl indole with acetic anhydride under reflux for 3h. *N*-(2-acetoxy ethyl) indole -3-(ethenyl phenanthrene) was synthesized by the treatment of *N*-(2-acetoxyethyl) -3-vinyl indole with 9-bromo phenanthrene in presence of palladium acetate, TOP and triethyl amine in the solvent medium of DMF at 90°C for 50h. *N*-(2-hydroxy ethyl) indole-3-(ethenyl phenanthrene) was synthesized by the hydrolysis of *N*-(2-acetoxy ethyl) indole-3-(ethenyl phenanthrene) with 10% hydrochloric acid (ethanol/water=1:1) under reflux for 10h and subsequently neutralized to PH=7 by the slow and careful addition of sodium carbonate. *N*-(2-(allyloxy)ethyl) indole-3-(ethenyl phenanthrene) was synthesized by the treatment of *N*-(2-hydroxy ethyl) indole-3-(ethenyl phenanthrene) with allyl bromide in presence of potassium carbonate in the solvent medium of DMF at 80°C for 24h. Lastly, poly (siloxane) was synthesized by the treatment of monomer with poly (methyl hydro) siloxane in presence of catalyst hexachloro platinate (IV) hydrate in the solvent medium of toluene at 150°C for 8h.

Keywords:

N-(2-hydroxyethyl) -3-vinyl indole, *N*-(2-acetoxy ethyl)-3-vinyl indole, *N*-(2-hydroxy ethyl) indole -3-(ethenyl phenanthrene), *N*-(2-(allyloxy) ethyl) indole-3-(ethenyl phenanthrene), poly (siloxane).

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I. Introduction :

Recently, the development of photo-conducting polymers are gaining attention as hole-transport materials for optical information storage, photovoltaic devices, photorefractive composites, transistors, and electroluminescent devices. In the photo-conducting polymers, the current main focus is on developing polymer photorefractive materials for production of hologram recording. The basic phenomena contributing to the photorefractive effect are photoconductivity and the electro-optic effect. The specific process required for the photorefractive effect include: photogeneration of charge carriers, transport of mobile carriers, trapping of these carriers in regions of destructive interference and a change of the refractive index in response to the space-charge field. The main characteristics governing the photo-refractivity are the photoconductivity of a material. A high-speed holographic response to patterned optical illumination in photorefractive polymers depends on sufficient charge generation and charge mobility. In photorefractive effect, photoinduced charge generation is provided by a sensitizer molecule that absorbs light and then becomes reduced, injecting a hole into the material. At this step, there are an equal number of mobile holes and immobile ionized acceptors (sensitizers) created in phase with interference pattern. In photorefractive materials, the charge photogeneration process is strongly electric field dependent. To date, photoconductor was demonstrated by doping fullerenes or TNF into polymers containing electron-donating moieties in the visible region of the spectrum. The enhanced photoconductivity is attributed to the electron transfer reaction between sensitizer and polymer.

A large research effort in the development of efficient polymeric photorefractive materials has resulted in the accumulation of a wealth of information on the structure-property relationships of photo-conducting polymers. Among the photo-conducting polymers known to date, fullerene-doped poly (N-vinyl carbazole) (PVK) have been best investigated. In the design and construction of organic photo-conducting polymers, energy level differences in organic photorefractive material are of great importance. Aromatic amine compounds, such as carbazole, indole, triphenyl amine, hydrazone and other aromatic amine derivatives, are well known photo-conducting materials with high photogeneration efficiency which have already been used in xerographic applications. These molecule functional moieties possess two based properties: an easy oxidizability of the amine nitrogen atom and the ability to transport positive charges. In the design and construction of organic optoelectronic devices, energy level differences in organic photoconductors are of great importance. Two parameters that describe the highest occupied molecular orbital (HOMO) and lowest

unoccupied molecular orbital (LUMO) energy levels with respect to the vacuum level correspond to the ionization potential and the electron affinity, respectively. Therefore, it is necessary to develop charge-transport materials as well as the materials for use in organic photoconductor should meet the following requirements: the capability of forming uniform amorphous film a solution process and thermal stability, and should possess a suitable ionization potential and an electron affinity for energy level matching between the electron donor and electron acceptor, respectively. In this article we have synthesized poly siloxane of indole ring with side chain ethenyl phenanthrene. The polymer can be doped with TNF and photoconductivity can be measured.

II. Experimental:

2.1 Synthesis of N-(2-hydroxy ethyl)-3-vinyl indole:

A solution of 25.74g(0.18mol) of 3-vinyl indole in 600ml of dry DMF was vigorously stirred at 0^oc and treated with 10.8g(1.0equiv.) of sodium hydride (60%oil dispersion). After the mixture was stirred for 3h, 9.04g (0.21mol) of ethylene carbonate was slowly added. The mixture was stirred at 0^oc for 1h and then at 40^oc for 3h. To the resulting solution was added dropwise 30ml of water, followed by stirring at 40^oc for 3h. After distillation, the residue poured into water and the aqueous mixture was extracted with ethyl acetate. The extract was dried with magnesium sulphate, and the solvent was removed at reduced pressure. The liquid residue was fractionally distilled off in vacuo to yield the titled compound.

2.2 Synthesis of N-(2-acetoxy ethyl)-3-vinyl indole:

A stirred solution of 18.7g (0.1 mol) of N-(2-hydroxy ethyl)-3-vinyl indole in 100ml of acetic anhydride was heated at reflux for 3h. After cooling, The solvent was distilled off in vacuo. The residue was poured into water and the aqueous mixture was extracted with ethyl acetate. The extract was dried with magnesium sulphate, and the solvent was removed at reduced pressure. The liquid was chromatographed on a silica gel column and solvent of the first fraction was removed at reduced pressure to yield the titled compound.

2.3. Synthesis of N-(2-acetoxy ethyl)indole -3-(ethenyl phenanthrene):

9-bromo phenanthrene (1 equiv.) was dissolved in 50ml of dry DMF at 50^oc under nitrogen atmosphere. Palladium acetate (0.5 equiv.) and TOP(0.25 equiv.) were added, dissolved and stirred for 1h. N-(2-acetoxy ethyl)-3-vinyl indole (1equiv.) and TEA (1.2 equiv.) were added, dissolved, heated overnight to 90^oc and with stirred. After 50h, the reaction mixture was cooled to room temperature and poured into a large amount of water. The mixture was poured into crushed ice and extracted with chloroform and dried with magnesium sulphate. The solvent was removed under reduced pressure. The residue was purified by using silica gel column chromatography.

2.4. Synthesis of N-(2-hydroxy ethyl) indole -3-(ethenyl phenanthrene):

N-(2-acetoxy ethyl) indole-3-(ethenyl phenanthrene) was dissolved in 150ml of 10% hydrochloric acid (ethanol/water=1:2) and the solution was heated to reflux for 10h. After cooling, the solution was neutralized to P^H=7 by the slow and careful addition of sodium carbonate. The resultant solution was extracted with ethyl acetate. The extract was dried over magnesium sulphate and condensed. Recrystallization from ethyl acetate/hexane yielded the titled compound.

2.5 Synthesis of N-(2-(allyloxy)ethyl) indole -3-(ethenyl phenanthrene):

A solution of N-(hydroxy ethyl) indole-3-(ethenyl phenanthrene) (1 equiv.) in dry DMF was treated with 1.2 equiv. Of potassium carbonate at 60^oc. After stirring for 4h, 1.2 equiv. Of allyl bromide was slowly added and the mixture was stirred at room temperature, and then at 80^oc for 24h. To the resulting solution was added dropwise 5ml of ethanol and the mixture dried with magnesium sulphate, and the solvent was removed at reduced pressure. The residue was purified by using silica gel column chromatography.

2.6 Synthesis of poly (siloxane)

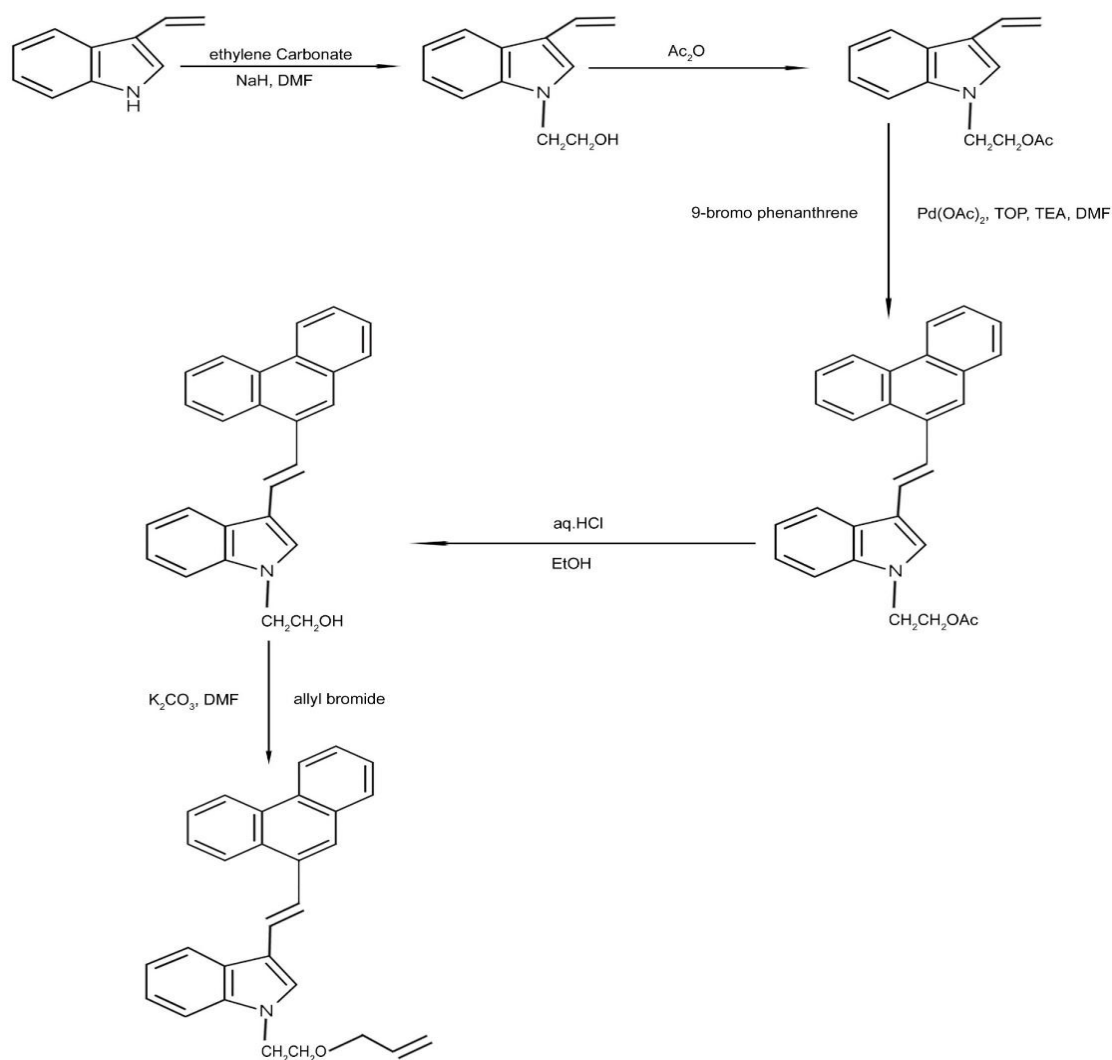
A dried 100 ml of two-necked flask equipped with a magnetic stirrer and a reflux condenser under argon. Into this flask N-(2-(allyloxy)ethyl) indole-3-(ethenyl phenanthrene) (7.254g,0.018mol) and 100ml of toluene were added and purged with argon. The portion of poly(methyl hydro) siloxane (1.06g,0.018mol) was dissolved with anhydrous toluene and added to the flask with several drops of hydrogen hexachloroplatinate (IV) hydrate under argon atmosphere. The solution was heated at 150^oc for 8h and then poured into methanol. The precipitate was filtered, dried and purified three times by reprecipitation from methanol.

III. Result and discussion:

IR,UV and NMR spectra revealed the successful preparation of the polymer. The monomer was prepared as follows:

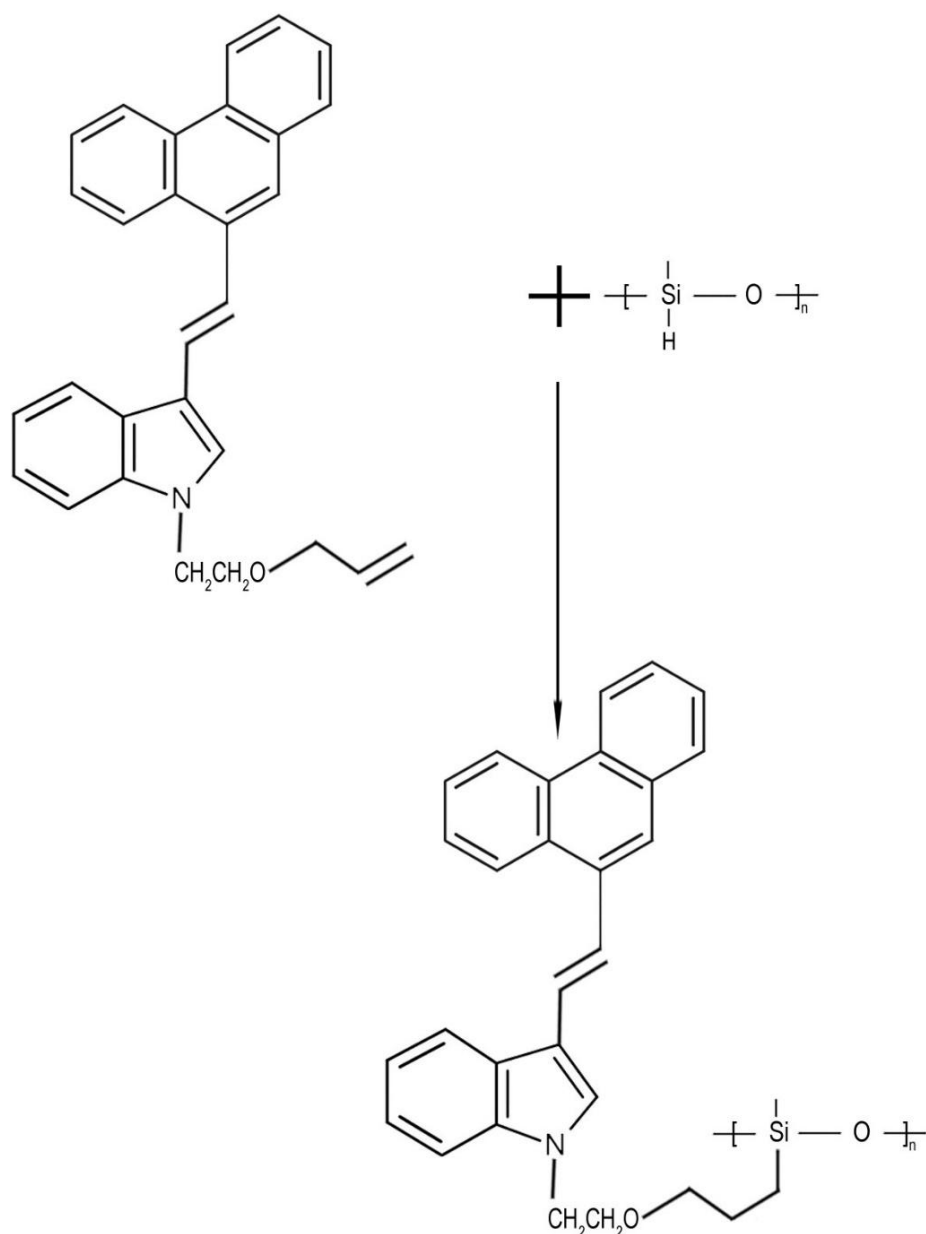
N-(2hydroxy ethyl)-3-vinyl indole was prepared by the reaction of 3-vinyl indole with ethylene carbonate in presence of sodium hydride in the solvent medium of DMF at first at 0^oc for 1h and then at 40^oc for 3h. To the resulting solution was added dropwise 30ml of water, followed by stirring at 40^oc for 3h. After distillation, the residue was poured into water and the aqueous mixture was extracted with ethyl acetate. The extract was dried with magnesium sulphate, and the solvent was removed under reduced pressure. The liquid residue was

fractionally distilled in vacuo. N-(2-acetoxy ethyl)-3-vinyl indole was prepared by the reaction of N-(2-hydroxy ethyl)-3-vinyl indole with acetic anhydride under reflux for 3h. After cooling, the solvent was distilled off in vacuo. The liquid residue was poured into water and the aqueous mixture was extracted with ethyl acetate. The extract was dried with magnesium sulphate, and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column and the solvent of the first fraction was removed at reduced pressure to yield the given compound. N-(2-acetoxy ethyl)-indole-3-(ethenyl phenanthrene) was synthesized via a Heck coupling reaction between N-(2-acetoxy ethyl)-3-vinyl indole and 9-bromo phenanthrene in presence of palladium acetate, TOP and TEA in the solvent medium of DMF heated overnight to 90°C with stirring. After 50h, the reaction mixture was cooled and poured into large amount of water. The mixture was poured into crushed ice and extracted with chloroform, dried with magnesium sulphate and the solvent was removed at reduced pressure. The residue was purified by using silica gel column chromatography. N-(2-hydroxy ethyl)-indole-3-(ethenyl phenanthrene) was prepared by hydrolysis of N-(2-acetoxy ethyl)-indole-3-(ethenyl phenanthrene) with 10% hydrochloric acid (ethanol/water=1:1) and the solution was heated to reflux for 10h. After cooling the solution was neutralized to $P^H=7$ by the slow and careful addition of sodium carbonate. The resultant solution was extracted with ethyl acetate. The extract was dried over magnesium sulphate and condensed. The monomer namely N-(2-allyloxy)ethyl)-indole-3-(ethenyl phenanthrene) was synthesized by the reaction of N-(2-hydroxy ethyl)-indole-3-(ethenyl phenanthrene) with allyl bromide in presence of potassium carbonate in the solvent medium of DMF at 80°C for 24h. To the resulting solution added dropwise 5ml of ethanol and the mixture was extracted with ethyl acetate/water. The extract was dried with magnesium sulphate and the solvent was removed at reduced pressure. The residue was purified by using silica gel column chromatography. The synthetic route to the monomer was depicted in scheme-I.



Scheme-I

Poly (siloxane) was synthesized by treating the monomer with poly(methyl hydro) siloxane in presence of catalyst hydrogen hexachloroplatinate(IV) hydrate in the solvent medium of toluene heated at 150⁰c for 8h. Then the polymer mixture was poured into methanol. The precipitate was filtered, dried and purified three times by reprecipitation from methanol. The synthetic route of polymer was depicted in scheme-II.



Scheme-II

IV. Conclusion:

In conclusion, the synthesis of novel class of hole-transporting polymer containing indole-phenanthrene moieties is reported. We have succeeded in the synthesis of indole-phenanthrene substituted poly siloxane by the hydrosilylation reaction with platinum catalyst. The polymer can be doped with TNF or TNP and photoconductivity in the dark as well as in presence of light can be measured. The polymer can be used as a hole-transporting material in various applications such as hole-transporting layer for electroluminescent devices, solar cell and photo-conducting materials. A good photorefractive composite can also be prepared by the conjugation of polymer with a second order NLO chromophore, a sensitizer and a plasticizer.

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