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Synthesis OfPhotorefractive Poly (siloxane) Of Quinoline-based Chromophore.

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Abstract: *5-formyl-8-hydroxy quinolone was synthesized by treating 8-hydroxy quinolone with chloroform in presence of 80% aqueous solution of sodium hydroxide at 80^0c for 12h. After, subsequent removal of chloroform and ethanol, the residue was diluted with water and acidified with 1% hydrochloric acid until complete precipitation. The precipitate was dried and the product was extracted with n-hexane. 5-formyl-8-allyloxy quinoline was prepared by the treatment of 5-formyl-8-hydroxy quinolone with allyl bromide in presence of anhydrous potassium carbonate in the solvent medium of acetonitrile at 80^0c for 10h. 5-(indan-1,3-dione-2-methylen)-8-allyloxy quinoline was synthesized by the treatment of 5-formyl-8-allyloxy quinoline with indan-1,3-dione in dioxane and heated under reflux for 50h. After termination of the reaction, the mixture was extracted with ethyl acetate and water. The organic layer was washed with distilled water, dried over anhydrous magnesium sulphate, ethyl acetate was removed and the residue was dissolved in acetone. The crystals formed upon standing were filtered off and washed with diethyl ether. Poly siloxane was prepared by the treatment of5 -(indan-1,3- dione-2-methylen)-8-allyloxy quinoline with poly(methyl hydro siloxane) in presence of several drops of hydrogen hexachloro palatinate(IV) hydrate in the solvent medium of toluene at 150^0c for 6h. The monomer and polymer were characterized by IR, UV and NMR spectra.*

Keywords: *5-formal-8-hydroxy quinoline, 5-formyl-8-allyloxy quinoline, 5-(Indan-1,3-dione-2-methylen)-8-allyloxy quinoline, poly siloxane.*

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I. Introduction:

The photorefractive effect was first reported with lithium niobate crystal more then 50 years ago. A variety of potentially important applications have been proposed using inorganic crystals, including high-density optical data storeage, image processing, phase conjugation, beam fanning limiter and optical correlator. 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 dielcctric constants, lower cost, and easier processing than inorganic materials.

Among many organic photorefractive meterials reported to date, polymeric host-guest system has been extensively investigated because of their excellent photorefractive properties, compositional flexibility and easy fabrication method. The charge transporting polymers such as poly(vinyl carbazole) or poly (siloxanecarbazole), 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.

Carbazole substituted polysiloxane is one of the most well-known photoconducting polymers for photorefractive system. The glass transition temperature(Tg) of these composites could be lowered to room temperature simply by adding a NLO chromophore. It was notable that the photorefractive properties could be improved by using a low Tgpolysiloxane because this system did not contain inactive molecules such as a plasticizer.

In this study a new photoconducting poly (siloxane) with pendent 5-(indan-1,3-dione-2-methylen)-8-allyloxy quinoline was synthesized by a hydrosilylation reaction. The doped polysiloxane is a good candidate with excellent hole mobility and photorefractivity.

II. Experimental:

2.1. Synthesis of 5-formyl-8-hydroxy quinoline:

A solution of 20.32g (0.14moles) of 8-hydroxy quinoline in 80ml of ethanol was mixed with 50ml of 80% aqueous solution of sodium hydroxide and refluxed at 80^0c for 1h. Then 27.46g (0.23 moles) of chloroform were added dropwise and the mixture refluxed at 80^0C for 12h. Later, the excess of chloroform and ethanol were evaporated, and the residue was diluted with 600ml of water and acidified with 1% hydrochloric acid until

complete precipitation The complex mixture on the precipitate was dried and the product was extracted with n-hexane.

2.2. Synthesis of 5-formyl-8-allyloxyquinoline:

5-formyl-8-hydroxy quinoline (3.46g, 0.02mol) was dissolved in dry acetonitrile (50ml). To this solution anhydrous potassium carbonate (2.76g, 0.02 mol) was added. Then allyl bromide (2.42g, 0.02 mol) in acetonitrile was injected. The mixture was stirred and boiled for 10h. The reaction was monitored by TLC. After the reaction was complete, acetonitrile was distilled off, residue was mixed with chloroform and poured into cold water. This was washed several times with dilute hydrochloric acid and brine solutions. The organic lager was sepatated and dried over anhydrous magnesium sulphate and concentrated. The crude product was purified by column chromatography.

2.3. synthesis of 5-(Indian-1,3-dione-2-methylen)-8-allyloxy quinoline:

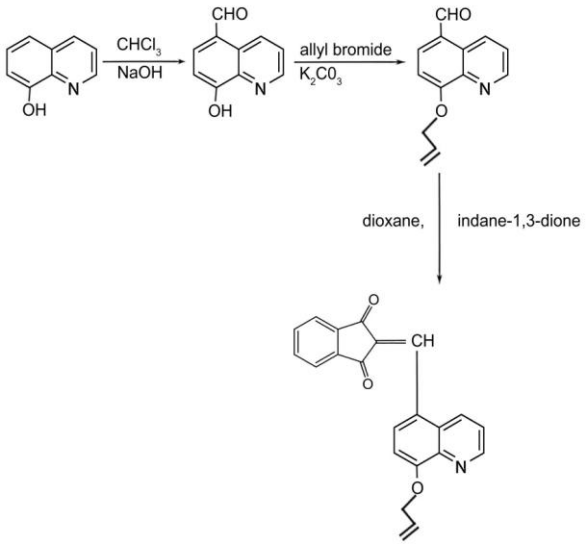
A solution of 5-formyl-8-allyloxy quinoline (2.13g,0.01mol) and Indian-1,3-dione (2.62g,0.02mol) in dioxane (50ml) was heated at reflux for 50h. After termination of the reaction (TLC control), the mixture was extracted with ethylacetate and water. The organic layer was washed with distilled water until the wash water was neutral , dried over anhydrous magnesium sulphate, ethyl acetate was removed and the residue was dissolved in acetone. The crystals formed upon standing were filtered off and washed with diethyl ether.

2.4. Synthesis of poly (siloxane):

A dried 100ml two-necked flask was equipped with a magnetic stirrer and a reflux condenser under argon. Into this flask, 5-(indan-1,3-dione-2-methylen)-8-allyloxy quinoline (5.79g, 17.57mmol) and 50ml of toluene were added and purged with argon. The portion of poly (methyl hydro siloxane) (1.06g, 0.017mol) was dissolved with anhydrous toluene and added to the flask with several drops of hydrogen hexachloro palatinate (IV) hydrate under argon atmosphere. The solution was heated at 150^0c for 6h and then poured into methanol. The precipitate was filtered, dried and purified three times by reprecipitation from methanol.

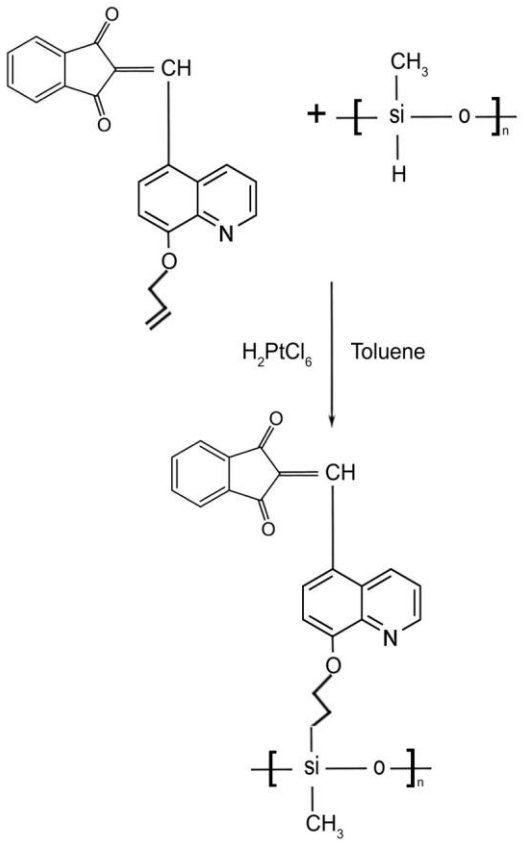
III. Result and Discussion:

IR,UV and NMR spectra revealed the successful preparation of the polymer.At first 5-formyl-8-hydroxy quinolone was prepared by treating 8-hydroxy quinoline with chloroform and sodium hydroxide in aqueous-ethanolic medium. After refluxing the mixture at 80^0c for 12h, the chloroform and ethanol was evaporated. Then the residue was diluted with water and 1% hydrochloric acid unitl complete precipitation. The precipitate was then dried and extracted with n-hexane. 5-formyl-8-allyloxy quinoline was prepared by treating 5-formyl-8-hydroxy quinoline with allyl bromide in presence of potassium carbonate in the solvent medium of acetonitrile. After the reaction was complete, acetonitrile was distilled off, residue was poured into cold water. This was washed several times with hydrochloric acid and brine solution. The organic layer was separated and dried over anhydrous magnesium sulphate and concentrated. The crude product was purified by column chromatography. 5-(indan-1,3-dione-2-methylen)-8-allyloxy quinoline was prepared by reacting 5-formyl-8-allyloxy quinoline with indane-1,3-dione under reflux for 50h in the solvent medium of dioxane. After termination of the reaction, the mixture was extracted with ethylacetate and water.The organic layer was washed with distilled water, dried over anhydrous magnesium sulphate, ethyl acetate was removed and the residue was dissolved in acetone. The crystals formed upon standing were filtered off and washed with diethyl ether. The synthetic route of monomer was depicted in scheme-I



scheme-I

Poly (siloxane) was synthesized by treating 5-(indan-1, 3-dione-2-methylen)-8-allyloxy quinoline with poly (methyl hydro siloxane) in presence of hydrogen hexachloroplatinate (IV) hydrate in the solvent medium of toluene under reflux at 150^0c for 6h. The polymer was precipitated out in methanol, filtered, dried and purified three times by reprecipitation from methanol. The photorefractive polymer namely quinoline-based polysiloxane was obtained by hydrosilylation reaction. Hydrosilyation has been known as a very convenient method of various silicon-containing polymer. The polymer was soluble in common organic solvents. The polymer has good thermal, mechanical and photochemical properties. It is a fully functionalized polymer, and has good photo refractive property. The synthetic route of the polymer was depicted in scheme – II.



Scheme-II

IV. Conclusion:

Quinoline-based polysiloxane as a photorefractive matrix was successfully synthesized by hydrosilylation method using platinum catalyst. The monomer and polymer were characterized by IR, UV and NMR spectroscopy. Quinoline-based polysiloxane is a fully functionalized photorefractive polymer. The polymer has good thermal mechanical and photorefractive properties. The polymer has good SHG prarameter.

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