

Synthesis of Non-linear Optical Polymer of Azoquinoline-based Chromophore.

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Abstract: Diazonium salt was prepared by dissolving 4-nitro aniline in acetic acid and propionic acid mixture in the hot condition and was rapidly cooled in an ice/salt bath to -5°C , then subsequent addition of nitrosylsulphuric acid, prepared from sodium nitrite and concentrated sulphuric acid. 5-(4-nitro phenyl azo)-8-hydroxy quinoline was synthesized by coupling reaction of diazo liquor with 8-hydroxy quinoline in the basic medium at 0°C for 2h. Then the p^{H} of the reaction mixture was maintained at 4-6 by the simultaneous addition of saturated sodium carbonate solution. 5-(4-nitro phenyl azo)-8-(1-hydroxy hexyl oxy) quinoline was synthesized by treating 5-(4-nitro phenyl azo)-8-hydroxy quinoline with 1-chloro-6-hydroxy hexane in the presence of potassium hydroxide and potassium iodide in the solvent medium of DMSO at 80°C for 18h. The vinyl monomer was synthesized by the treatment of 5-(4-nitro phenyl azo)-8-(1-hydroxy hexyloxy)quinoline with methacryloylchloride in the solvent medium of THF. Last, the copolymer was synthesized by the treatment of vinyl monomer with MMA in the presence of radical initiator AIBN in the solvent medium of TCE at 60°C for 2 days. The monomer and copolymer were characterized by IR, UV and NMR spectroscopy.

Key words: 5-(4-nitro phenylazo)-8-hydroxy quinoline, 5-(4-nitro phenyl azo)-8-(1-hydroxy hexyloxy)quinoline, vinyl monomer, co-polymer.

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I. Introduction

The signal propagation and switching using electron as a carrier should be changed to new system using photon in order to process enormous data faster in computing and telecommunications technology. One of important components in optical communication system would be an optical switch to digitalize all information signals. A conventional optical switching material is an inorganic crystal, for example lithiumniobate. Many organic chemists have attempted to substitute the expensive inorganic crystals with low-cost organic materials, for example, side chain non-linear optical(NLO)polymers. The advantage of NLO polymers compared to inorganic crystals include the easier fabrication of optical waveguides on device substrate, lower dielectric constants and potentially higher NLO susceptibility etc. Many researches have been focused on the enhancement of NLO activity and improvement of its temporal stability during prolonged period. For higher NLO activity, a variety of NLO chromophores have been designed and synthesized by changing the strength of electron donors and electron acceptors and the type of pi-conjugated bridge, or its length in chemical structure of chromophore, respectively. Alike to inorganic crystals, the NLO moieties(e.g. doner-bridge-acceptor) attached in a polymer backbones must be oriented one directionally by external electric field, but after removing the field the residual orientation tends to be randomized after long period or at high temperature. Therefore, it is most important to maintain the one directional alignment of NLO chromophores in polymer matrix for a long period. For this, the high glass temperature(T_g) polymers such as polyimide, polyquinoline or polyquinoxaline have been proposed for a NLO polymer backbones. Some results reveal that high T_g polymers can be good candidate materials for long-life NLO application, even if their NLO coefficients should be increased for actual application. For adopting high T_g polymers, thermally stable NLO chromophores even at high poling temperature began to be necessary. Non-linear optical(NLO) properties arise from the interaction of strong electromagnetic fields, such as the ones of laser beams, with matter. Due to the need for materials with exceptional NLO properties and fast response times in conjunction with mechanical and thermal stability and easy processing as well, intense research activity has been carried out in second-order non-linear optical materials. From the physics background it is known that the electronic structural requirement for SHG is a large value of polarizability which can be originated by a large variation of dipole moment between the ground and low lying excited states. This feature can be found either in organic or organometallic molecules providing they possess a doner and an acceptor group connected by a delocalized pi-system. In our earlier study, we have introduced an aromatic benzoxazole and benzothiazole unit as a new pi-conjugated bridge in chromophore like carbazole and indole for better thermal and photochemical stabilities.

In this study, we newly synthesized azoquinoline-based chromophore instead of benzoxazole and benzothiazole and NLO polymers(PMMA) therefrom.

II. Experimental

2.1. Synthesis of 5-(4-nitro phenyl azo)-8-hydroxy quinoline:

4-nitro aniline(0.002mol) was dissolved in hot glacial acetic acid/propionic acid mixture (2:1,6.0ml) and was rapidly cooled in an ice/salt bath to -5°C . The liquor was then added in portions during 30min. to a cold solution of nitrosylsulphuric acid(prepared from sodium nitrite(0.15g) and concentrated sulphuric acid(3ml) at 5°C). The mixture was stirred for an additional 2h at 0°C . Excess nitrous acid was destroyed by addition of urea. The resulting diazonium salt was cooled in ice/salt mixture. After diazotization was complete, the diazo liquor was slowly added to vigorously stirred solution of 8-hydroxy quinoline(0.002mol) in potassium hydroxide(0.002mol) and water(3ml). The solution was stirred at $0-5^{\circ}\text{C}$ for 2h. After 2h, the pH of the reaction mixture was maintained at 4-6 by the simultaneous addition of saturated sodium carbonate solution. The mixture was stirred for one day at room temperature. After one day, the resulting solid was filtered, washed with cold water, and dried.

2.2. Synthesis of 5-(4-nitro phenyl azo)-8-(1-hydroxy hexyloxy) quinoline:

2.94g(0.01mol) of 5-(4-nitro phenyl azo)-8-hydroxy quinoline and 1-chloro-6-hydroxy hexane(1.65g,0.012mol) were added into a two-necked 250ml round bottomed flask connected with an air condenser. Potassium hydroxide 0.7g(0.012mol), potassium iodide (3mg) and dimethyl sulphoxide(60ml) were added into the mixture. The mixture was heated at 80°C for 18h. It was then poured into water and extracted with DCM. The organic extracts were combined and washed with water three times. It was dried with magnesium sulphate and filtered. The solvent was removed under reduced pressure and the solid was recrystallized.

2.3. Synthesis of vinyl monomer:

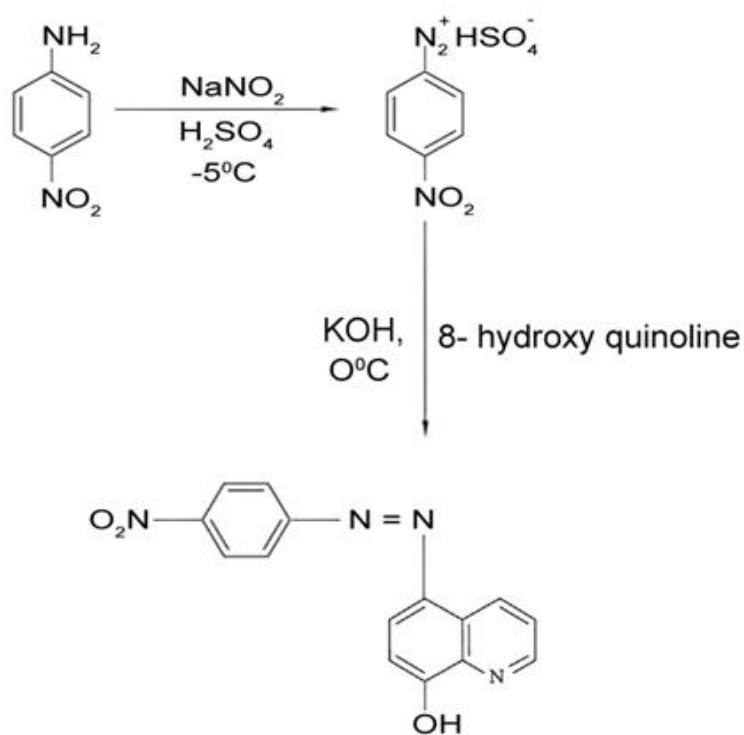
Into a 100ml flask, added 0.985g(2.5m mol) of 5-(4-nitro phenyl azo)-8-(1-hydroxy hexyloxy) quinoline, 50ml THF, and 0.523g(5.0m mol) of methacryloyl chloride. The portion of 0.76g(7.5m mol) of triethylamine was added into the solution, and stirred at 50°C under nitrogen. The mixture was poured into water, and the precipitated solid was separated by filtration and purified by column chromatography.

2.4. Polymerization:

The polymerization was carried out in 1,1,2,2-tetrachloroethane(TCE) with 10% by weight of azobisisobutyro nitrile(AIBN) as initiator. The vinyl monomer 0.693g(1.5m mol), and methyl methacrylate 0.35g(3.5m mol), and TCE and 10% by weight of AIBN were taken in 25ml polymerization ampule. The polymerization was carried out at 60°C for 2days, and poured into methanol to precipitate polymer and washed thoroughly with methanol. The polymer was dissolved in THF and reprecipitated in methanol to remove unreacted monomer or oligomers. The polymer was separated by filtration and dried in vacuum oven.

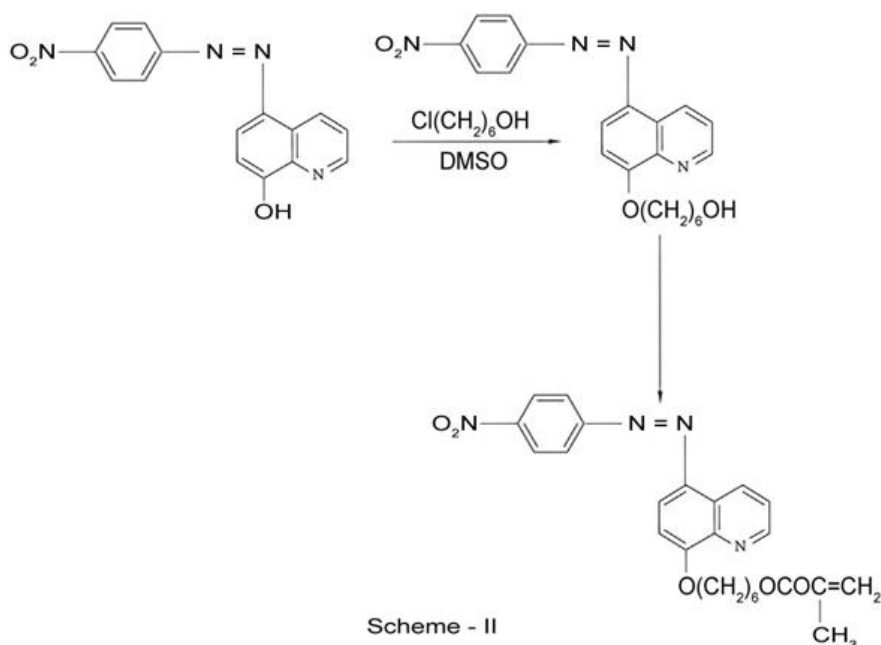
III. Result and Discussion

4-nitro benzene diazoniumsulphate was prepared by dissolving 4-nitro aniline in acetic and propionic acid mixture in hot condition and was rapidly cooled in an ice/salt bath to -5°C , then subsequent addition of nitrosylsulphuric acid(prepared from sodium nitrite and concentrated sulphuric acid. 5-(4-nitro phenyl azo)-8-hydroxy quinoline was synthesized by coupling of diazo liquor with 8-hydroxyquinoline in the basic medium at 0°C for 2h. Then the pH of the reaction mixture was maintained at 4-6 by the simultaneous addition of saturated sodium carbonate solution. The synthetic route of diazo coupling reaction was depicted in scheme-I.



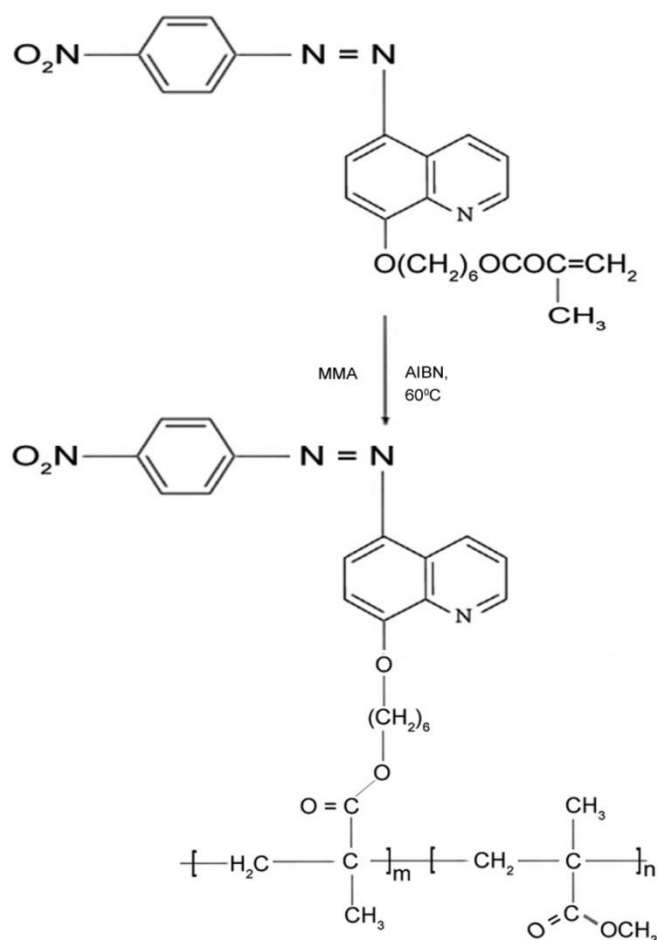
Scheme - I

5-(4-nitro phenylazo)-8-(1-hydroxy hexyl oxy) quinoline was synthesized by treating 5-(4-nitro phenyl azo)-8-hydroxy quinoline with 1-chloro-6-hydroxy hexane in the presence of potassium hydroxide and potassium iodide in the solvent medium of DMSO at 80^oc for 18h. It was then poured into water and extracted with DCM. The organic extracts were combined and washed with water. It was then dried with magnesium sulphate and filtered. The solvent was removed under reduced pressure and the solid was recrystallized. The vinyl monomer was synthesized by the treatment of 5-(4-nitro phenyl azo)-8-(1-hydroxy hexyl oxy) quinoline with methacryloyl chloride in the solvent medium of THF at 50^oc. The mixture was poured into water and the precipitated solid was separated by filtration and purified by column chromatography. The synthetic route of vinyl monomer was depicted in scheme-II.



Scheme - II

Lastly, the co-polymer was synthesized by the treatment of vinyl monomer with MMA in the presence of radical initiator AIBN in the solvent medium of TCE at 60°C for 2 days. The polymer was precipitated out in methanol. The unreacted monomer and oligomers was separated by repeated precipitation technique. The synthetic route of the polymer was depicted in scheme-III.



Scheme-III.

The monomer and polymer was characterized by IR,UV and NMR spectroscopy. The azoquinoline based chromophore has better mechanical, thermal and photochemical stability than general stilbene-based chromophores. The azoquinoline based PMMA has better SHG and EO co-efficient.

IV. Conclusion

We synthesized azoquinoline based chromophore in order to obtain more thermally stable NLO chromophore than general stilbene-based chromophores. NLO active PMMA was synthesized by using azoquinoline-based NLO chromophore. The azoquinoline-based PMMA has better thermal and photochemical stabilities. The azoquinoline-based PMMA has better SHG value and EO co-efficient.

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