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

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Abstract: *2,3-di(4-nitro phenyl)-6-hydroxy quinoxaline was synthesized by the reaction of 4,4'-dinitro benzil with 3,4-diamino phenol by warming in a water bath for 1h,in the solvent medium of rectified spirit and the product was recrystallized from ethanol.6-(1-hydroxy hexyloxy)-2,3-di(4-nitro phenyl)quinoxaline was synthesized by the reactionof 2,3-di(4-nitro phenyl)-6-hydroxy quinoxaline with 1-choro-6-hydroxy hexane in the presence of potassium hydroxide and potassium iodide in the solvent medium of DMSOat 80^0c for 18h. The vinyl monomer was synthesized by the treatment of 6-(1-hydroxy hexyloxy)-2,3-di (4-nitro phenyl) quinoxaline with methacryloyl chloride in the solvent medium of T H F. 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 60^0c for 2days. The monomer and co-polymer were characterized by IR,UV and NMR spectroscopy.*

Key words: *4,4'-di nitro benzil, 2,3-di(4-nitro phenyl)-6-hydroxyquinoxaline, 6-(1-hydroxy hexyloxy)-2,3-di(4-nitro phenyl)quinoxalinemonomer,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 the 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 lithumniobate.Many organic chemists have attempted to substitutethe expensive inorganic crystals with low-cost organic materials,forexample,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 susceptility etc. Many researches have been focused on the enhancement of NLO activity and improvementof its temporal stability during prolonged period.For higher NLO activity,a variety of NLO chromophores have been designed and synthesizedby changing the strength of electron doners and electron acceptors and the type of pi-conjugated bridge,or its length in chemical structure of chromophore,respectively. Alike to inorganic crystals,theNLO moieties(e.g.doner-bridge-acceptor)attached in 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 the most important to maintain the one directional alignment of NLO chromophores in polymer matrix for a long period. For this, the high glass temperature (Tg) polymers such aspolyimide ,polyquinoline or poly quinoxaline have been proposed for a NLO polymer back bones. Some results reveal that high Tg 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 Tgpolymers , thermally stable NLO chromophore even at high poling temperature began to be necessary.

Non-linear optical (NLO) properties arise from the interaction of strongelectromagnetic 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 molecular 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 featurecan 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 quinoxaline-based NLO chromophores instead of benzoxazole and benzothiazole and NLO polymers (PMMA) therefrom .

II. Experimental

2.1. Synthesis of 2,3-di (4-nitro phenyl) -6-hydroxy quinoxaline:

To a warm solution of 3.0 g(0.01mol) of 4,4'-dinitro benzil in 10mlrectified spirit added a solution of 1.24g(0.01mol)of 3,4-diamino phenol in 10ml rectified spirit. Thesolution was warmed in water bath for 1h, added water until a slight cloudiness persist and allowed to cool. The precipitate was filtered and recrystallised from ethanol to give the compound .

2.2. Synthesis of 6- (1-hydroxy hexyloxy) -2,3-di(4-nitro phenyl) quinoxaline :

3.88g(0.01mol)of 2,3-di(4-nitro phenyl)-6-hydroxy quinoxaline and 1-chioro -6- hydroxy hexane (1.65g , 0.012 mol) were added into atwo-necked 250 ml round bottomed flask connected with an air condenser. Potassium hydroxide 0.7g(0.012 mol) , potassium iodide(3mg)and dimethyl sulphoxide (60 ml) were added into the mixture . Themixture was heated at 80^0c for 18h . It was then poured into water and extracted with dichloromethane . The organic extracts were combined and washed with water three times . It was dired with magnesium sulphate and filtered .the solvent was removed under reduced pressure and the solid was recrystallized .

2.3. Synthesis of vinyl monomer :

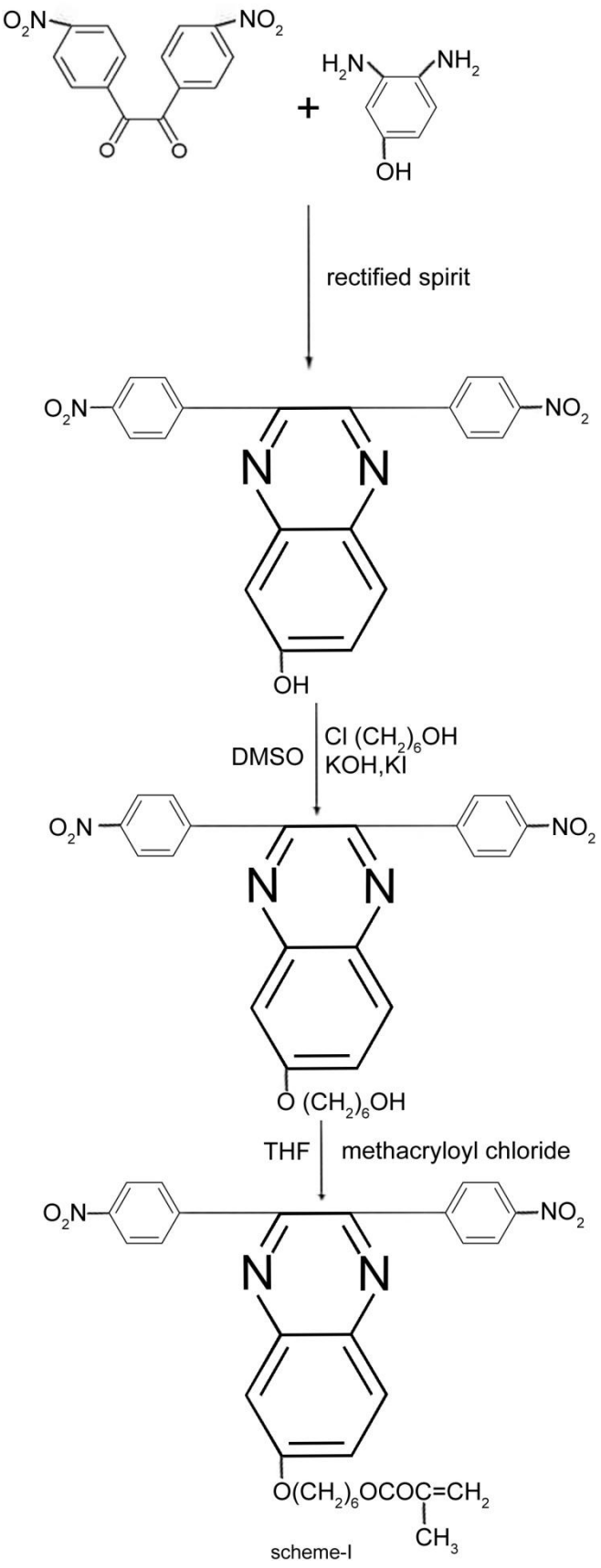
Into a 100 ml flask , added 1.22g (2.5 m mol) of 6- (1-hydroxy hexyloxy) -2,3-di(4-nitro phenyl) quinoxaline , 50 ml tetrahydrofuran , and 0.523g (5.0 m mol) of methacryloylchloride . Theportion of 0.76g(7.5 m mol) of triethyl amine was added into the solution , and stirred at 50^0c under nitrogen . The mixture was poured into water , and the precipitated solid was separated by filtration and purified by column chromatography .

2.4. Polymerization :

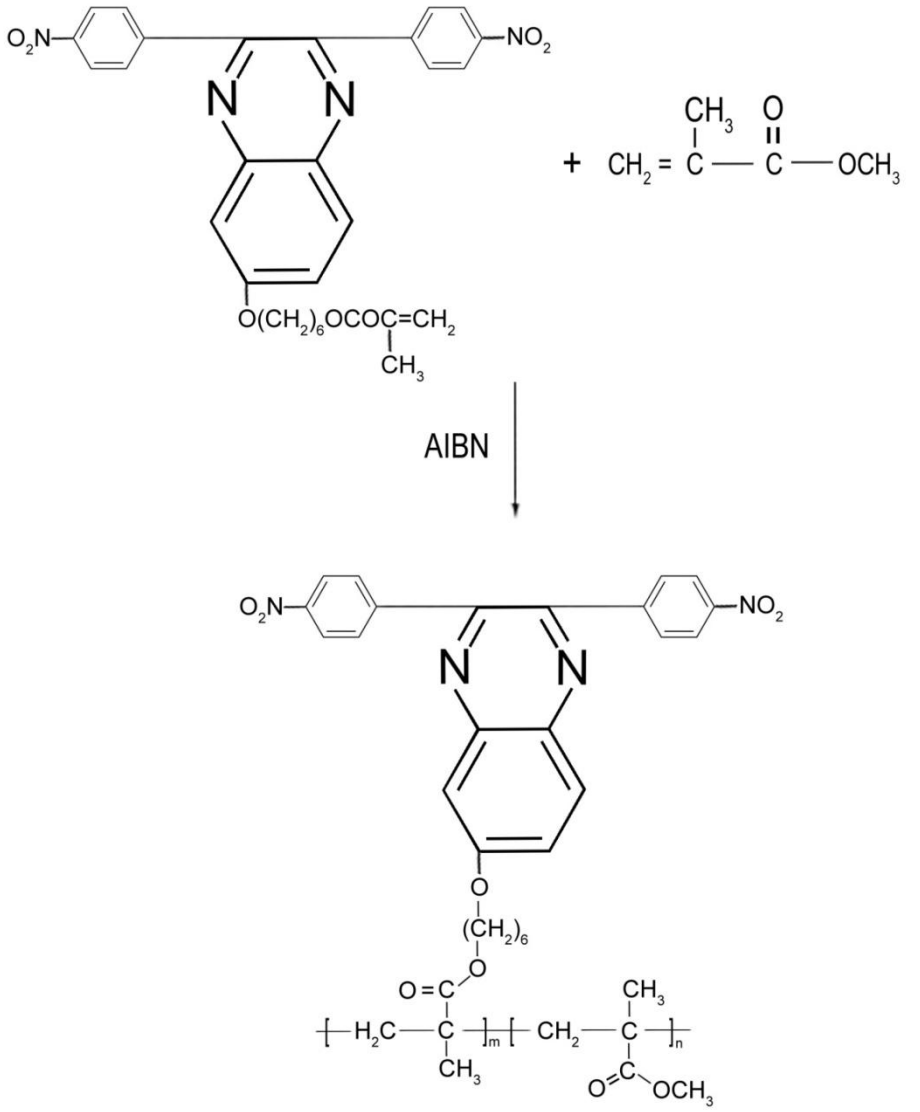
The polymerization was carried out in 1,1,2,2-tetrachloroethane(TCE) with 10% by weight of a zobisisobutyro nitrile(AIBN) as initator . The vinyl monomer 0.834g (1.5 m mol),and methyl methacrylate 0.35g (3.5 m mol),and TCE, and 10% by weight AIBN were taken in 25 ml polymerization ampoule. The polymerization was carried out at 60^0c for 2 days , 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

Both the monomer and polymer were successfully prepared which were confirmed by the investigation of IR , UV and NMR spectroscopy. 2,3-di(4-nitro phenyl)-6-hydroxy quinoxaline was synthesized by the reaction of 4,4'-di nitrobenzil with 3,4-diamino phenol by warming in water bath for an hour in the solvent medium of rectified spirit . The product was recrystallized from ethanol . 6-(hydroxyhexyloxy)-2,3-di (4-nitro phenyl) quinoxaline was synthesized by the reaction of 2,3-di(4-nitro phenyl)-6-hydroxy quinoxaline with 1-chloro -6-hydroxy hexane in the presence of potassium hydroxide and potassium iodide in the solvent medium of DMSO at 80^0c for 18h . It was then poured into water and extracted with DCM .the organic extracts washed with water, 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 6-(1-hydroxy hexyloxy)-2,3-di (4-nitro phenyl) quinoxaline with methacryloyl chloride in the solvent medium of THF at 50^0c . The mixture was poured into water and the precipitated solid was separated by filtration . The synthetic route of the monomer was depicted in scheme-I .


O2N
NO2
H2N
NH2
OH
rectified spirit
N
N
DMSO
Cl (CH2)6OH
KOH,KI
O (CH2)6OH
THF
methacryloyl chloride
O(CH2)6OCOC=CH2
CH3

scheme-I



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 60^0c for 2 days . The polymer was poured into methanol and precipitated out and washed thoroughly with methanol . The polymer was dissolved in THF and reprecipitated in methanol to remove unreacted monomer and oligomers . The polymer was separated by filtration . The synthetic route of polymer was depicted in scheme-II .

scheme-II

The quinoxalinechromophore has good non-linear activity and thermal stability .

IV. Conclusion

Quinoxalinechromophore was synthesized in order to obtain more stable NLO chromophore than general stilbene-based chromophore . NLO active polymethacrylate was synthesized by using this quinoxaline-based NLO chromophore . The polymer based on quinoxalinechromophore has enhanced thermal stability . The quinoxaline based PMMA co-polymer has good SHG and EO coefficient .

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