

Synthesis Of Non-linear Optical Polymer Of Fluorescent 1,3,5-triazine System

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Abstract:

4-(4-vinyl phenoxy)-2,6-dichloro-1,3,5-triazine was synthesized by the treatment of 2,4,6-trichloro triazine with 4-hydroxy styrene with sodium hydroxide in acetone-water medium. 4-(4-vinyl phenoxy)-2,6-bis (4-formyl phenoxy)-1,3,5-triazine was synthesized by the treatment of 4-(4-vinyl phenoxy)-2,6-dichloro-1,3,5-triazine with 4-hydroxy benzaldehyde in presence of potassium carbonate in the solvent medium of benzene under reflux for 25h. 4-(4-vinyl phenoxy)-2,6-bis (4-methanylylidene malononitrile phenoxy)-1,3,5-triazine was synthesized by the treatment of 4-(4-vinyl phenoxy)-2,6-bis (4-formyl phenoxy)-1,3,5-triazine with malononitrile in presence of piperidine in the solvent medium of ethanol stirring at room temperature for 5h. Polymerization was carried out by the treatment of monomer with methyl methacrylate in the solvent medium of DMF in presence of catalyst AIBN at 110^oc for 80h.

Keywords: 4-(4-vinyl phenoxy)-2,6-dichloro-1,3,5-triazine, 4-(4-vinyl phenoxy)-2,6-bis (4-formyl phenoxy)-1,3,5-triazine, 4-(4-vinyl phenoxy)-2,6-bis (4-methanylylidene malononitrile phenoxy)-1,3,5-triazine, polymerization.

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I. Introduction:

In the past decade, chromophore-functionalized polymer systems have been intensively studied for their nonlinear optical (NLO) properties, because of their potential applications as high speed frequency doublers and mixers, amongst others. This interest has led to the development of a large number of new chromophores with moderate to superb hyperpolarizabilities. Since polymer materials show additional advantages compared to their inorganic analogues, such as good processability, a low dielectric constant, nearly all organic NLO materials are polymeric. Nonlinear optical materials are being actively studied for such potential optoelectronics applications as second harmonic generation (SHG) and third harmonic generation (THG), holography, frequency up and down conversion, electro-optical modulation, and switching. Recently, organic poled polymer systems containing chromophores with large second-order nonlinear susceptibilities have emerged as a promising class of electro-optical materials because of their fast response time, and ease of processing for integrated assembly. These polymer materials include doping NLO dyes into amorphous polymer matrices (guest-host system), attaching NLO moieties covalently onto polymer backbone as pendant (side-chain system), incorporating NLO chromophores as part of a polymer main chain (main-chain systems), and utilization of sequential synthesis methods (cross-linked systems).

Organic fluorescent heterocyclic chromophores have a wide range of applications in molecular probes, fluorescent markers, organic light-emitting diodes (OLED), photovoltaic cells and in traditional textile and polymer fields. Electron donors like triphenylamine, diphenylamine, 1,3,5-triazines and carbazoles with high electron mobility, thermal and photochemical stability are commonly used as hole transporting materials or light-emitting materials for balanced charge injection for above mentioned application. Phenoxy substituted 1,3,5-triazine fluorescent styryl derivatives have not been exploited much in the past, but attract increasing interest as they exhibit better solubility in common organic solvents, excellent thermal and electron donating ability of phenoxy groups. The presence of electron donating phenoxy group increases the electron flow towards the electron acceptor moieties present in the molecule. From the view point of molecular design, structural features such as the long pi-conjugation style, molecular planarity and the length of the conjugated bridge play important roles in functional chromophores, which are highly promising for electronic applications like photonic materials, holographic optical data storage and organic photorefractive materials. A typical push-pull chromophore consist of a polar A-pi-D system with a planar pi-system end-capped by a strong electron donor (D) and a strong electron acceptor (A). The pi-conjugated system ensuring intermolecular charge transfer (ICT) between the donor and the acceptor is the most common of conjugated double or triple bonds in aromatic and heteroaromatic rings as well as their combinations. There has always been an effort to design and synthesized novel and well-defined organic push-pull system with prospective applications as chromophores for nonlinear optics (NLO), electronic and photonic devices, organic light emitting diodes (OLED) and functional polymers.

In this article, we have synthesized phenoxy substituted fluorescent styryl dyes and its polymers with methyl methacrylate.

II. Experimental:

2.1 Synthesis of 4-(4-vinyl phenoxy)-2,6-dichloro-1,3,5-triazine:

2,4,6-trichloro triazine (0.184g, 1mmol) in 10 ml acetone, a mixture of sodium hydroxide (0.8g, 2mmol) and 4-hydroxy styrene (0.12g, 1mmol) in 10ml acetone-water (4:1 v/v) was added slowly at 0-5^o C. The reaction mixture was stirred further for 4h. At the end of reaction, the mixture was poured into cold acidified water and filtered. Precipitate was rinsed several times with water and dried at 80^o C.

2.2. Synthesis of 4-(4-vinyl phenoxy)-2,6-bis (4-formyl phenoxy)-1,3,5-triazine:

4-hydroxy benzaldehyde (2.42g, 0.022mol) and 4-(4-vinyl phenoxy) -2,6-dichloro-1,3,5-triazine (2.95g, 0.011mol) were added to a suspension of potassium carbonate (3.04g, 0.022mol) in 50ml of benzene. The mixture was refluxed for 25h. The reaction mixture was then cooled and the solid was removed by filtration and washed with hot ethyl acetate twice. The filtrate was extracted with 10% sodium carbonate solution (20ml) twice and with water once. The organic layer was dried over anhydrous sodium sulphate and then concentrated. The powder was recrystallized from 20ml of ethanol.

2.3 Synthesis of 4-(4-vinyl phenoxy) -2,6-bis (4-methanylylidene malononitrile phenoxy) -1,3,5 triazine:

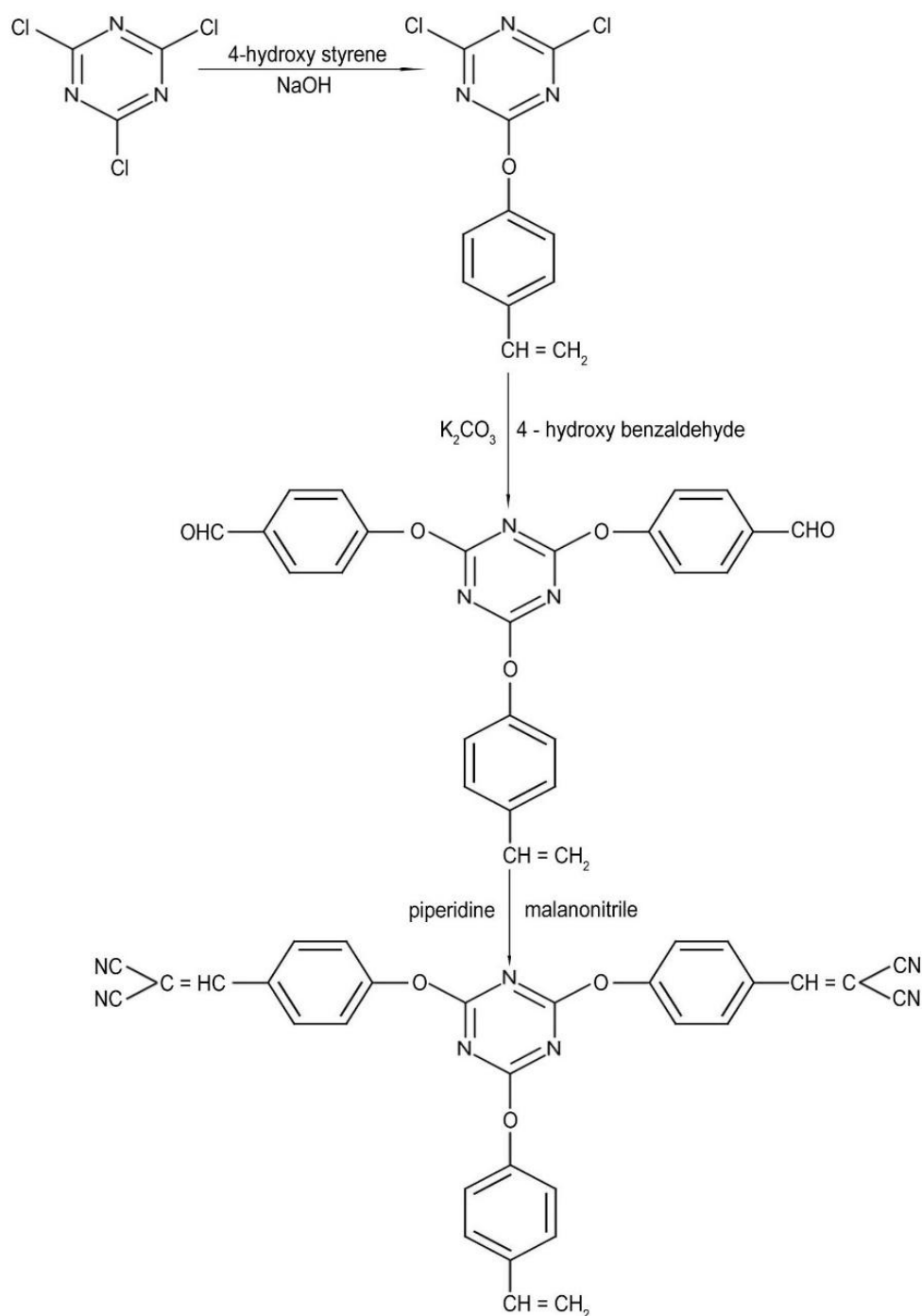
4-(4vinylphenoxy)-2,6-bis (4-formyl phenoxy)-1,3,5-triazine (1.0g, 0.0023mol) and malononitrile (0.33g, 0.0052mol) were dissolved in absolute ethanol (10ml). Piperidine (0.1ml) was added to it and the reaction mixture was stirred at room temperature for 4h, filtered the reaction mass to separate out product and recrystallized it from ethanol.

2.4 Synthesis of polymer:

Vinyl monomer (1.342g, 3.77mmol), methyl methacrylate (0.38g, 3.77mmol) and AIBN (2g, 12.19mmol) were dissolved in dry DMF (40ml). The reaction was carried out at 110^oC for 80h, under nitrogen. The polymer was precipitated out in methanol, filtered and dried under vacuum.

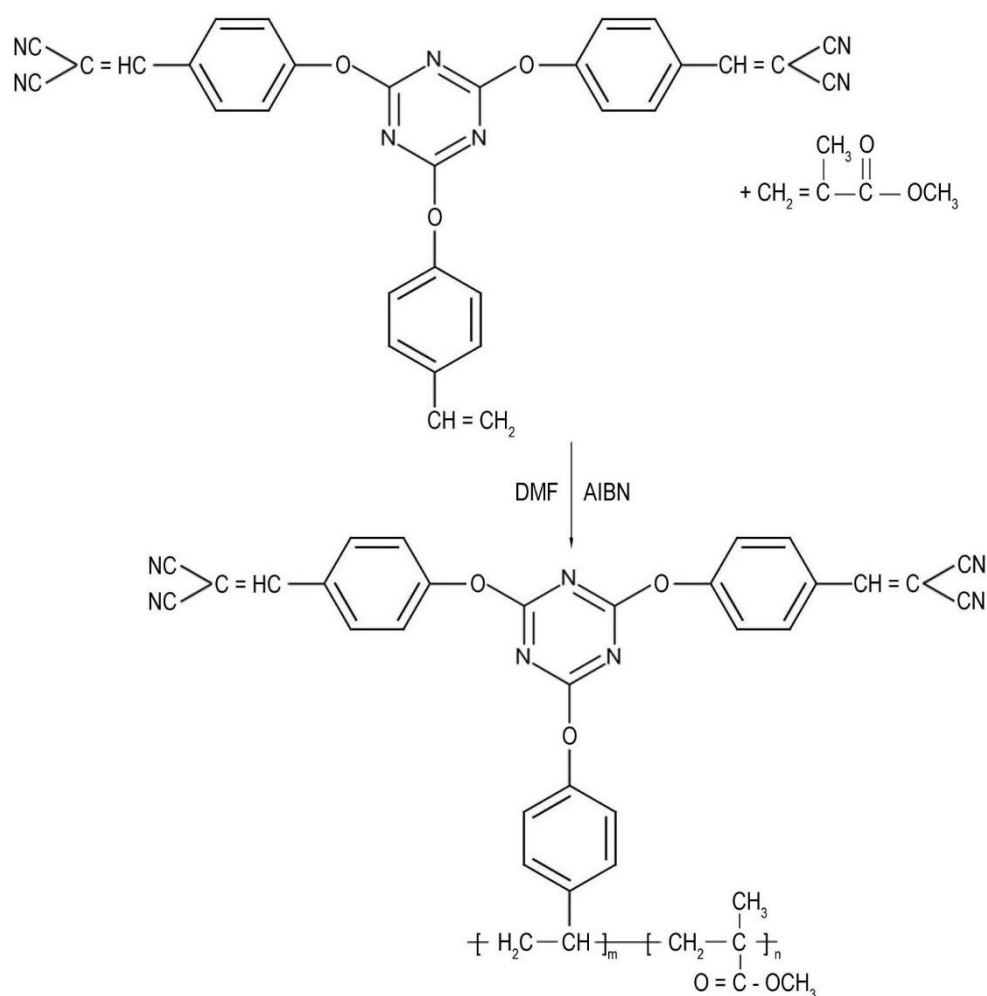
III. Result And Discussion:

UV, IR and NMR spectra revealed the successful preparation of the monomer and polymer. The monomer was prepared as follows: At first, 4-(4-vinyl phenoxy)-2,6-dichloro triazine was prepared by mixing 2,4,6 trichloro triazine with 4-hydroxy styrene in presence of sodium hydroxide in the solvent medium of acetone-water at 0^o-5^oC for 4h. At the end of the reaction, the mixture was poured into cold acidified water and filtered. 4-(4-vinyl phenoxy)-2,6-bis (4-formyl phenoxy)-1,3,5-triazine was prepared by treating 4-(4-vinyl phenoxy)-2,6-dichloro-1,3,5- triazine with 4-hydroxy benzaldehyde in presence of potassium carbonate in the solvent medium of benzene refluxed for 25h. The reaction mixture was then cooled and the solid was removed by filtration and washed with hot ethyl acetate. The filtrate was extracted with 10% sodium carbonate solution and finally with water. The organic layer was dried over anhydrous sodium sulphate and then concentrated. The powder was recrystallized from ethanol. 4-(4-vinyl phenoxy)-2,6-bis (4-methanylylidene malononitrile phenoxy)-1,3,5-triazine was synthesized by treating 4-(4-vinyl phenoxy)-2,6-bis (4-formyl phenoxy)-1,3,5-triazine with malononitrile in presence of piperidine in the solvent medium of ethanol stirred for 4h at room temperature. Filtered the product and recrystallized it from ethanol. The synthetic route of the monomer was represented in scheme-I



scheme-I

The polymer was synthesized by treating the desired monomer with MMA and AIBN as initiator in the solvent medium of DMF stirring at 110°C for 80h under nitrogen. The polymer was precipitated out in methanol, filtered and dried. Organic fluorophore contains well-defined D- Pi-A push-pull system have wide application in the field of NLO, OLED and high tech application. Electron doner diphenyl, triphenyl and carbazole conjugated with electron acceptor terminal through pi-system were reported recently for high tech application. Phenoxy substituted 1,3,5- triazine also acts as doner keeping this idea in mind we developed D-pi-A styryl derivatives. The synthetic route of the polymer is represented in scheme-II.



scheme-II

IV. Conclusion:

In summary, we have developed an efficient and simple method for the synthesis of fluorescent chromophore containing triazine core moiety and electron withdrawing cyano group. The synthesized monomer and polymer were characterized by IR, UV and NMR spectra. It was suspected that the electronic coupling between donor and receptor was sufficient to allow charge transfer in their molecule. The polymer has good thermal properties. The polymer will show positive solvatochromism with increase in solvent polarity.

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