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Synthesis of Non-linear Optical Polymer of Azo Coumarin-pyrimidine Based Chromophore.

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Abstract:
Diazonium salt was prepared by dissolving 2-amino-5-nitro pyrimidine with sodium nitrite and sulphuric acid in presenceof water. The temperature was maintained up to 5^0c. The solution was kept for 15 minutes with occasional stirring to complete the diazotization. Then diazonium salt was poured into the ice-cold solution of 8-hydroxy-4-methylcoumarin in 20ml of 10% sodium hydroxide solution and kept for 1h at 0^0-5^0c. The pH was maintained up to 5-6. 5-(5-nitro pyrimidinylazo)-8-(1-hydroxy hexyl oxy)- 4- methyl coumarin was synthesized by treating 5-(5-nitro pyrimidinylazo)-8-hydroxy-4-methyl coumarin with 1-chloro-6-hydroxy hexane in the presence of potassium hydroxide and potassium iodide in the solvent medium of DMSOat 80^0c for 20h. The vinyl monomer was synthesized by the treatment of 5-(5-nitro pyrimidinyl azo-8-(1-hydroxy hexyl oxy)-4-methyl coumarin with methacryloyl chloride in the solvent medium of THF. Lastly, the copolymer was synthesized by the treatment of vinyl monomer with MMA in presence of radical initiator AIBN in the solvent medium of DMF at 60^0c for 2 days. The monomer and copolymer were characterized by IR, UV and NMR spectra.

Keyword:
5-(5-nitro pyrimidinylazo)-8-hydroxy-4-methyl coumarin, 5-(5-nitro pyrimidinylazo)-8-(1-hydroxy hexyloxy)-4-methyl coumarin, vinyl monomer, copolymer.

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I. Introduction :

In the last years the aromatic azopolymershave been widely used due to their application in different optical fields. After the photorefractive effect of organic compounds was discovered, several polymers which containingcarbazolehave become attractive from the point of view of their photo-refractivity. The photoconductive and electro-optic functionalities in the side chain of those polymers can be considered as potential materials for photorefractive applications. Therefore, the azo benzene chemistry continue to produce unexpected phenomena because the azobenzene group is incorporated into the polymer, and in this respect the photo isomerization phenomena can have unexpected possible consequences. It is well known that in the polymer materials with carbazole can appear the possibility of building several variable spacers between the azogroup and the main chain which can increase the order degrees as well asazo group becomes much decoupled from the main chain motion.

The photorefractive polymers with carbazole ring and azomoieties in the side chain have all the necessary elements for photorefractivity properties (electro-optic chromophore and charge trappers). The azocontainingcarbazole groups provided both the photoconductivity and non-linear optical (NLO) activity, and the aliphatic chain attached on the nitrogen atom of thecarbazole ring acts as a spacer. Hence, the photorefractive polymer exhibit equally photoconductivity and optical non-linearity. They have concerned substantial interest due to their potential applications in optical computing, optical correlation, 3D data or image storage.

The ability of non-linear optical materials to transmit process and store information forms the basis of emerging optoelectronic and photonic technologies. Organic chromophore containing polymers,in which the refractive index can be controlled by light or an electric field, are expected to playa important role. NLO is an important component of photorefractive system.Organic moieties with delocalized pi-electrons distribution have been extensively investigated for their potential applications in optical switching and optical power limiting, each which require large and fast non-linearities for the purpose. The NLO response of many organic materials is extremely rapid,because the effects occur primarily throughelectron polarization, and hence there has been a focus of attention on NLO properties of the pi-conjugated system. Dye chromophores are a class of organic molecules with multiple pi-conjugated bonds, which can exhibit large optical nonlinearities and fast response time, as a result the case of polarization of their extended mobile pi-electron cloud over long distances. Strong absorption of dyes in the visible region makes them particularly suited for non-linear optical investigations. It

has also been shown that embedding dyechromophores in suitable host matrices enhance the life time stability of the dyes entrapped within it.

In present days, coumarins have vital interest due to their dominance in natural product chemistry, and have a wide range of pharmacological properties and excellent optical properties. Coumarin and its derivatives have been reported to use in optoelectronics (OLED) , solar cells,lasers, non-linear optical (NLO) and dye industries due to their favourable characteristics such as solid state emission, large stokes shift, high emission yield, significant photo-physical properties and thermal stability. Coumarin derivatives have been also reported to posses very good efficacy in anti-inflammatory,anti-tuberculosis, anti-HIV, antifungal, anti-tubulin, anti-coagulant and antioxidant activities. Azodyesare colored organic compounds and are reported to have excellent absorption, emission, molar absorption coefficient, solvatochromicbehaviour and undergo photochemical and thermal isomerization. The recent few reports evidenced that 4-hydroxy coumarins having azochromophore substitution exhibited very good optical properties, thermal stability and biological efficacy due to their increase in conjugation system between coumarin and other heterocycles through azochromophore or other functionalities.

II. Experimental:

2.1. Synthesis of 5-(5-nitro pyrimidinylazo)-8-hydroxy -4-methyl coumarin:

A cold solution of sodium nitrite (0.207g,3mmol) was added dropwise into the solution of 2-amino-5-nitro pyrimidine (3mmol) with concentrated sulphuric acid (8-9mmol) and water (5ml) were kept on an icebath. The temperature of the reaction was maintained up to 5^0c. When addition was completed the solution was kept for 15 minutes with occasional stirring to complete the diazotization. Then it was poured into an ice-cold solution of 8-hydroxy-4-methyl coumarin (3mmol) in 20ml of 10% sodium hydroxide solution. Then resultant mixture was stirred and kept on an ice bath for 1h at a temperature of 0-5^0c. The pH was maintained at about 5-6. The obtained product was filtered and washed with cold distilled water . Finally the obtained product was dried and recrystallized by ethanol.

2.2 Synthesisof 5-(5-nitro pyrimidinylazo)-8-(1-hydroxy hexyloxy)-4-methyl coumarin:

0.01 mol of 5-(5-nitro pyrimidinylazo) -8-hydroxy-4-methyl coumarin and 1-chloro-6-hydroxy hexane (1.65g,0.012mol)were added into a two-necked round bottom 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 80^0c for 20h. 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:

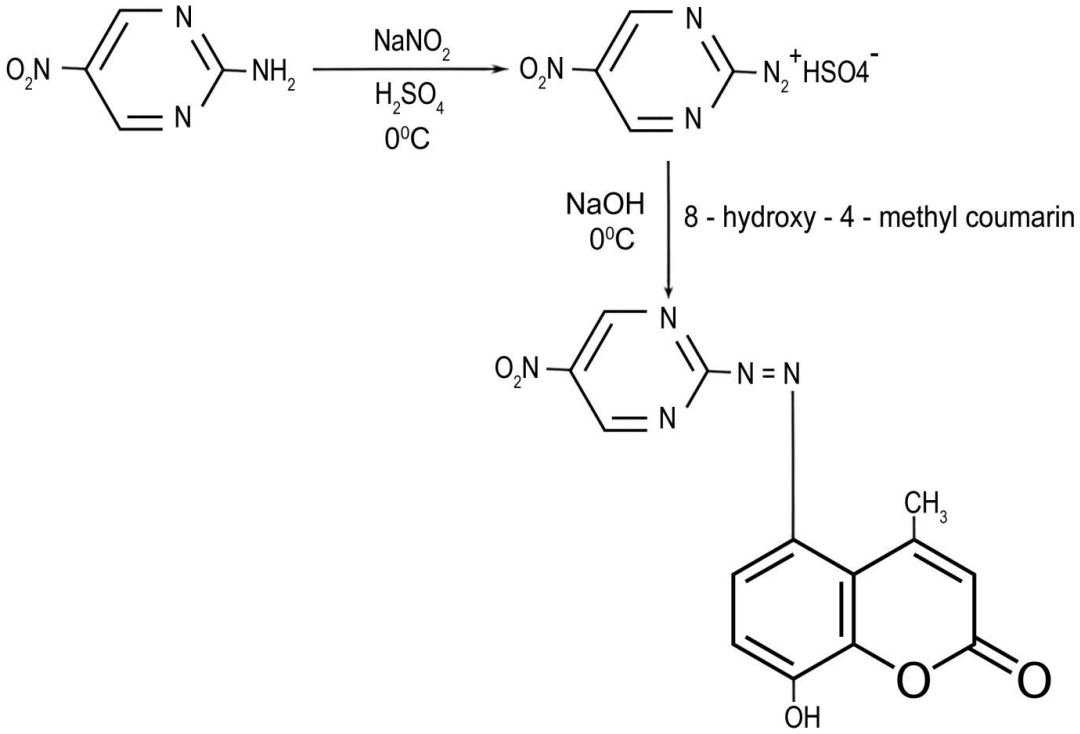
Into a 100 ml flask, added 2.5 mmol of 5-(5-nitro pyrimidinylazo) -8-(1-hydroxy hexyloxy)-4- methyl coumarin, 50ml THF, and 0.523g(5.0mmol)of methacryloyl chloride. The portion of 0.76 g (7.5mmol) of triethyl amine was added into the solution, and stirred at 50^0c under nitrogen. The mixture was poured into water, and the precipitated solid was separated by filtration and purified by column chromatography.

2.4 Polymerization:

The vinyl monomer (1.5mmol), and methyl methacrylate 0.35g(3.5mmol) and DMF and 10% by weight of AIBN were taken in 25ml of polymerization ampule. 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.

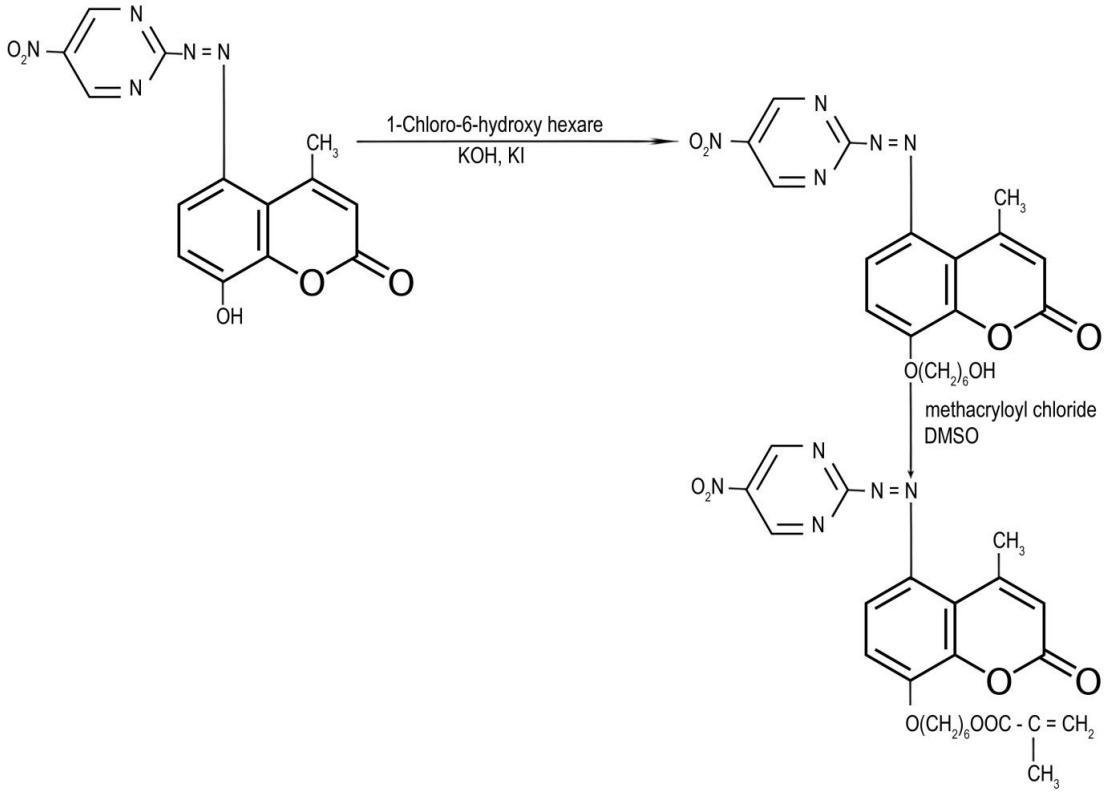
III. Result And Discussion:

5-(5-nitro pyrimidinylazo) -8- hydroxy -4- methyl coumarin was prepared as follows: Diazonium salt was prepared by dissolving 2-amino-5-nitro pyrimidine with sodium nitrite and sulphuric acid in presence of water. The temperature was maintained up to 5^0c. The solution was kept for 15 minutes with occasional stirring to complete the diazotization. Then diazonium salt was poured into the ice-cold solution of 8-hydroxy-4-methyl coumarin in 20ml of 10% sodium hydroxide solution and kept for 1h at 0^0-5^0c. The pHwas maintained up to 5-6. The synthetic route of azo dye was represented in scheme-I.



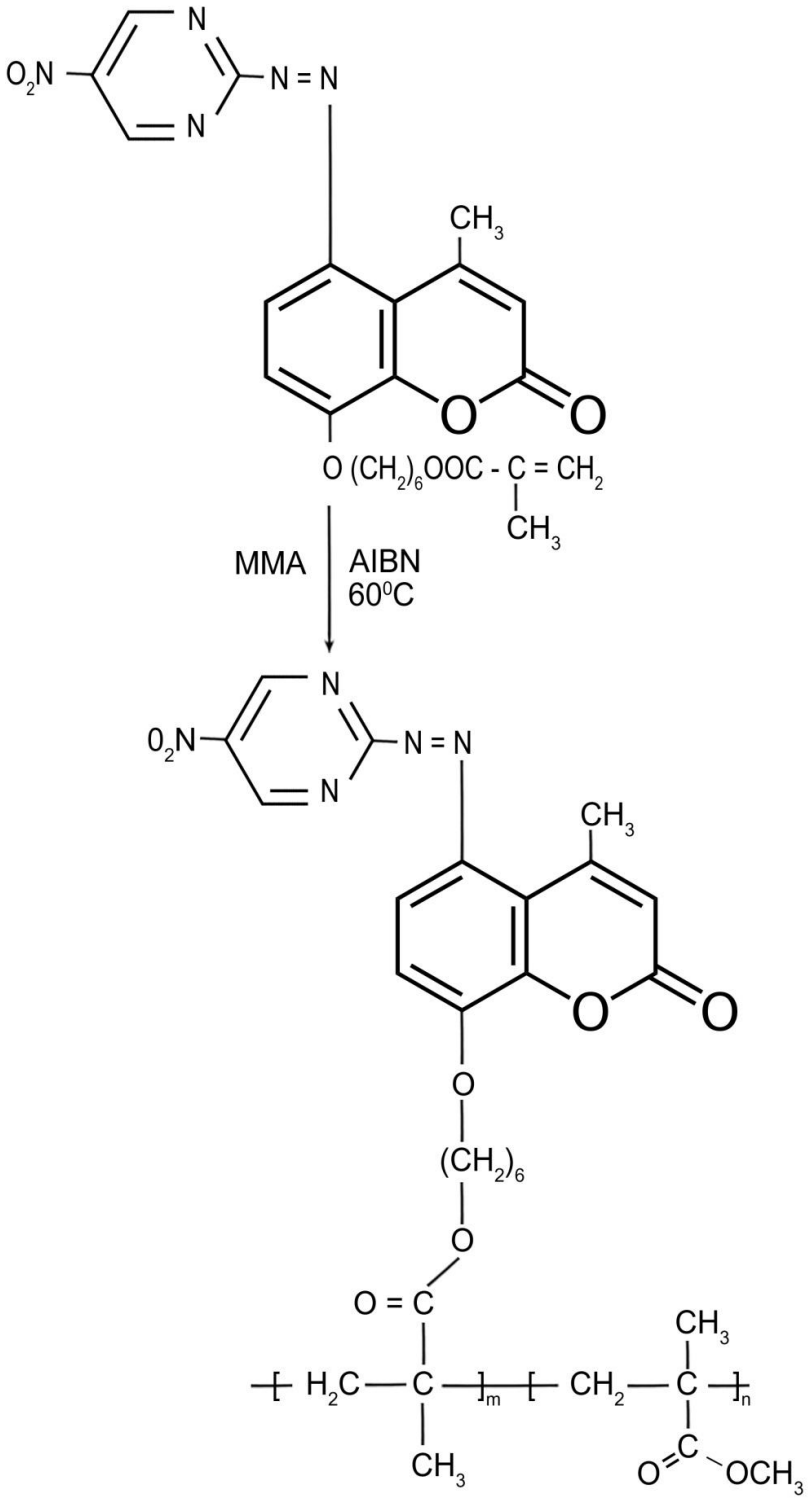
Scheme-I.

5-(5-nitro pyrimidinylazo)-8- (1-hydroxy hexyloxy)-4-methyl coumarin was prepared by reacting 5-(5-nitro pyrimidinylazo)-8-hydroxy 4-methyl coumarin with 1-cholro-6-hydroxy hexane in presence of potassium hydroxide and potassium iodide in the solvent medium of DMSO at 80^0C for 20h.It was then poured into water 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. The vinyl monomer was synthesized by the treatment of 5-(5-nitro pyrimidinylazo)-8-(1-hydroxy hexyloxy)-4- methyl coumarin with methacryloyl chloride in presence of triethyl amine and stirred at 50^0C under nitrogen. The mixture was poured into the water, and precipitated solid was separated by filtration and purified by column chromatography. The synthetic route of vinyl monomer was represented in scheme-II.



Scheme-II

Lastly, the co-polymer was synthesized by the treatment of vinyl monomer with MMA in presence of radical initiator AIBN in the solvent medium of DMF. The polymerization was carried out at 60^0C for 2 days and poured into methanol to precipitate the polymer and washed thoroughly with methanol to remove unreacted monomer or oligomers. The polymer was separated by filtration and dried in vacuum oven. The synthetic route of polymer was represented in scheme-III.



Scheme-III

IV. Conclusion:

In the present study, we have synthesized the 8-hydroxy-4- methyl coumarin-nitro pyrimidine based azo dye by thediazocoupling reaction of 2-amino-5-nitro pyrimidine with 8-hydroxy-4-methyl coumarin in ice-cold condition and have made its polymer with MMA. The synthesized dye can be characterized by various analytical and spectroscopic techniques. The synthesized polymer can exhibit a positive solvatochromicbehaviour in absorption and emission study. The azo dye and polymer can be characterized by IR,UV and NMR spectra. Various properties of the polymer can be studied by using DFT.

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