

DIAZONIUM SALT CHARACTERIZATION AND PREPARATION USING IR, UV, AND NMR SETS

¹Anisha Ganapathineedi, ²Dr.Ravi, ³Dr Ibrahim, ⁴Jyothi Srivastava

^{1,4} Assistant Professor, ^{2,3}Professor, ^{1,2,3,4}Department of Chemistry, Rishi MS Institute of Engineering and Technology for Women, Kukatpally, Hyderabad.

Abstract

By combining 2-amino-5-nitro pyrimidine with sodium nitrite and sulfuric acid in the presence of water, diazonium salt was created. Up to 50 degrees Celsius was maintained. To finish the diazotization, the solution was held for 15 minutes and occasionally stirred. After keeping the 8-hydroxy-4-methylcoumarin solution in 20ml of 10% sodium hydroxide solution at 0° to 50°C for an hour, diazonium salt was added. Up to pH 5 or 6, the pH remained maintained. five-(5-nitro pyrimidinylazo) eight- (1-hydroxy hexyl oxy) - By heating up 5-methylcoumarin, 4-methylcoumarin was created (5-nitro pyrimidinylazo) -8-hydroxy-4-methyl coumarin with 1-chloro-6-hydroxy hexane for 20 hours in the presence of potassium hydroxide and potassium iodide. The 5-(5-nitro pyrimidinyl azo) was treated to create the vinyl monomer. -8-(1-hydroxy hexyl oxy)-4-methyl coumarin in the solvent medium of THF with methacryloyl chloride. 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°c 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

Introduction

Due to their utility in several optical domains, aromatic azopolymers have seen increased utilization in recent years. Following the discovery of the photorefractive property of organic compounds, a number of polymers containing carazole have gained interest due to their photo-refractivity. These polymers' side chains, which have photoconductive and electro-optic capabilities, might be thought of as possible materials for photorefractive applications. Because the azobenzene group is integrated into the polymer, the azo benzene chemistry continues to create unanticipated phenomena, and in this regard, the photo isomerization events might have unexpected potential outcomes. It is widely known that the capability of constructing several variable spacers between the azo group and the main chain in polymer materials containing carbazole might boost the order degrees as well as azo group becomes much decoupled from the main chain motion.

The photorefractive polymers with carbazole ring and azo moieties in the side chain have all the necessary elements for photorefractivity properties (electro-optic chromophore and charge trappers). The azocontaining carbazole groups provided both the photoconductivity and non-linear optical (NLO) activity, and the aliphatic chain attached on the nitrogen atom of the carbazole 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 play an 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 through electron 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 possess very good efficacy in anti-inflammatory, anti-tuberculosis, anti-HIV, antifungal, anti-tubulin, anti-coagulant and antioxidant activities. Azodyes are colored organic compounds and are reported to have excellent absorption, emission, molar absorption coefficient, solvatochromic behaviour 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.

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 ice bath. The temperature of the reaction was maintained up to 5^oc. 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^oc. 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.

Synthesis of 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^oc 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.

Synthesis of vinyl monomer

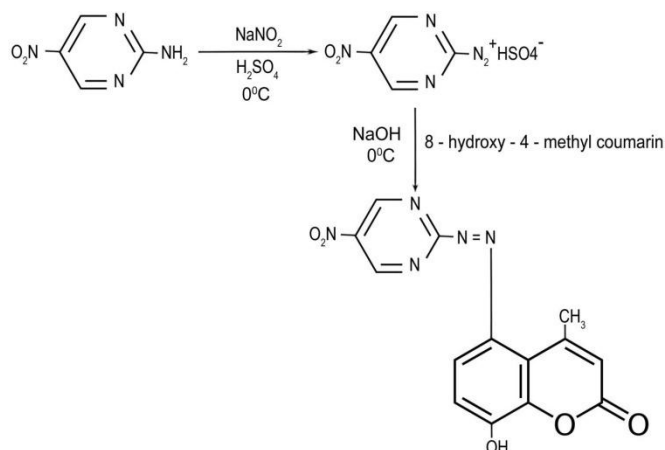
Into a 100 ml flask, added 2.5 mmol of 5-(5-nitro pyrimidinylazo)-8-(1-hydroxy hexyloxy)-4-methyl coumarin, 50ml THF, and 0.523g (5.0mmol) of methacryloyl chloride. The portion of 0.76 g (7.5mmol) of triethyl amine was added into the solution, and stirred at 50^oc under nitrogen. The mixture was poured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

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^oc 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.

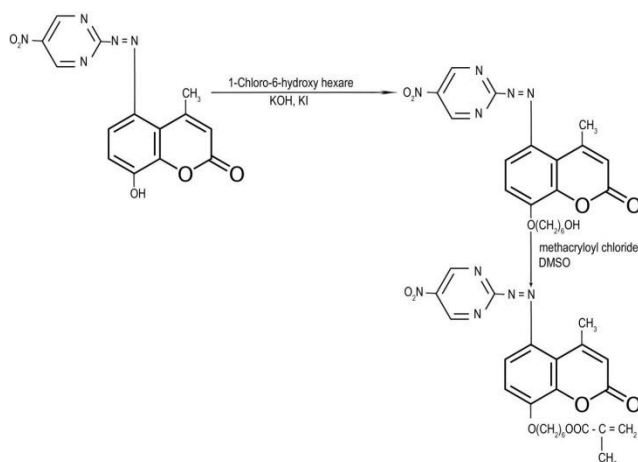
Result and Discussion

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 5⁰c. 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 0⁰-5⁰c. The pH was maintained up to 5-6. The synthetic route of azo dye was represented in scheme-I.



Scheme-I.

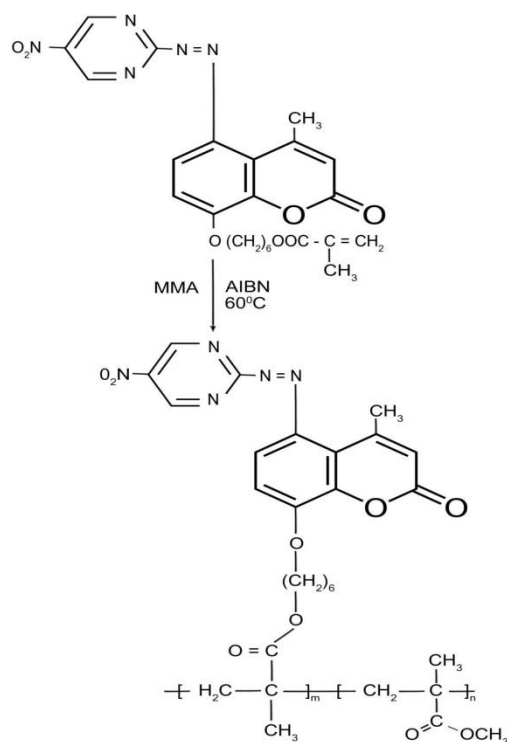
5-(5-nitro pyrimidinylazo)-8-(1-hydroxy hexyloxy)-4-methyl coumarin was prepared by reacting 5-(5-nitro pyrimidinylazo)-8-hydroxy 4-methyl coumarin with 1-chloro-6-hydroxy hexane in presence of potassium hydroxide and potassium iodide in the solvent medium of DMSO at 80⁰C for 20h. It was then poured 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 50⁰C 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 60⁰C 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

Conclusion

In the current work, we created an azo dye based on 8-hydroxy-4-methyl coumarin and nitro pyrimidine using a diazocoupling reaction between 2-amino-5-nitro pyrimidine and 8-hydroxy-4-methyl coumarin under ice-cold conditions. MMA was then used to create the dye's polymer. There are several analytical and spectroscopic methods that may be used to characterize the produced dye. Favorable solvatochromic behavior may be shown in the produced polymer in studies of emission and absorption. IR, UV, and NMR spectra can be used to identify the azo dye and polymer. DFT may be used to investigate a variety of polymer characteristics.

References

1. Kippelen B, Tamura K, Peyhambarian N, Padias AB, Hall Jr. HK. Phys. Rev B 1993, 48 (15): 10710.
2. Yu L, Chan WK, Peng Z, Gharavi A. Acc. Chem. Res. 1996, 29:13.
3. Zhang Y, Wada T, Wang L, Aoyama T, Sasabe H. Chem. Commun. 1996, 2325
4. Barrett C, Chowdhury B, Natansohn A, Rochon P. Macromolecules 1998, 31, 4845
5. Wright D, Diaz-Garcia MA, Caspersen JD, DeClue M, Moerner WE, Twieg RJ. Appl. Phys. Lett. 1998, 73(11), 1490.
6. Cox AM, Blackburn RD, West DP, King TA, Wada FA, Leigh DA. Appl. Phys. Lett. 1996, 68(20), 2801.
7. Zhang Y, Ghosal S, Casstevens MK, Burzynski R. J. Appl. Phys. 1996, 79 (12), 8920.
8. Silence SM, Scott JC, Stankus JJ, Moerner WE, Moylan CR, Bjorklund GC, Twieg RJ. J. Phys. Chem. 1995, 99, 4096.
9. Moon H, Hwang J, Kim N, Park SY. Macromolecules 2000, 33(14), S116.
10. Moon H, Kim N, Park sy. Nonlinear Optics 1999, 20, 347.
11. Meerhrolz K, Volodin BL, Sandalphon, Kippelen B, Peyghambarian N. Nature 1994, 371(6), 497.
12. Bolink HJ, Krasnikov VV, Malliaras GG, Hadziioannou G. J. Phys. Chem. 1996, 100, 16 356.

13. Zhang Y, Spencer CA, Ghosal S, Casstevens MK, Burzynski R, Appl. Phys. Lett. 1994, 64, 1908.
14. Han SH, Wu JW. J. Opt. Soc. Am B 1997, 14, 1131.
15. Sutter K, Gunter P. J. Opt. Soc. Am B 1990,7, 2274
16. Walsh CA, Monerner We. J. Opt. Soc. Am B 1992, 9, 1642
17. Centore R, Panunzi B, Roviello A, Sirigu A, Villano P. J. Polym. Sci. Part A Polym. Chem. 1996, 34, 3203