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Synthesis Of Non-linear Optical polyimide of [4-nitro phenyl -1,3-bis(azo-3-methoxy aniline)] Based Chromophore.

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Abstract:
4-nitro phenyl-1,3-bis(azo-3-methoxy aniline) was synthesized by diazotizing 4-nitro-1,3-phenylene diamine with sodium nitrite and concentrated hydrochloric acid at 0^0c and then coupling the diazonium salt with 2-methoxy aniline at 0^0c. The polyimide was synthesized by chemical imidization process. The azodye namely 4-nitro phenyl-1,3-bis(azo-3-methoxy aniline) and 6FDA in (1:1)molar ratio was stirred at 40^0C for 24h forming viscous polyamic acid solution then polyamicacid was treated with acetic anhydride and pyridine and stirred at100^0C for 24h in the solvent medium of DMF giving the corresponding polyimide.

Key words: *4-nitro phenyl-1,3-bis (azo-3-methoxy aniline),polyamic acid, polyimide.*

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I. Introduction:

The ability of nonlinear optical materials to transmit process and store information forms the basis of emerging optoelectronic and photonic technologies . Organic chromphore-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 systems. Organic moieties with delocalized pi-electrons distribution have been extensively investigated for their potential applications in optical signal processing, optical switching and optical power limiting, each which require large and fast nonlinearities for the purpose . The NLO response of many organic materials is extrermely rapid , because the effects occur primarily through electronic polarization, and hence there has been a focus of attention on NLO properties of the pi-conjugated systems.

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 each of polarization of their extended mobile pi-electron cloud over long distance. Strong absorption of dyes in the visible region makes them particularly suited for nonlinear optical investigations. It has also been shown that embedding dye chromophores in suitable host matrices enhance the life time and stability of the dyes entrapped within it.

Among the organic materials, polymeric NLO materials have been continuously drawn interest, mainly because of several advantages for photonic applications such as mechanical endurance, light weight, chemical resistance and good processability for developing optical devices. In particular very satisfactory results can be obtained by the incorporation of suitable chromophore groups to an appropriate polymer matrix either through dispersion or through anchoring by a covalent link.

Recently, polyimide containing NLO chromophores were seen to show excellent nonlinear optical properties and were used in a wide variety of practical NLO applications. Aromatic polyimides play a key role as materials for many applications ranging from dielectric films for the electronic industry and orientation layers liquid crystal industry, light weight load-bearing heat-resistant composites and adhesives for the aerospace industry, to gas-separation membranes due to their outstanding thermal, mechanical, electrical, and chemical resistance properties. Such performances have inspired many researchers to modify, study, and use polyimides in the field of optoelectronic and photonics. Polyimides, mainly with covalently bonded azobenzene derivatives, have been attracting attention in design optic (NLO) polymers, namely with respect to their second-order NLO phenomena, and their third-order NLO properties suitable for optical data storage were investigated.

In this article we have synthesized a novel azo dye namely 4-nitro phenyl-1,3-bis(azo-3-methoxy aniline) and its polyimide with 6 FDA.

II. Experimental:

2.1. Synthesis of 4-nitro phenyl-1,3 - bis (azo-3-methoxy aniline):

At first concentrated hydrochloric acid (10ml) was kept in ice cold bath for several hours. A solution of sodium nitrite (13.8g) and water (150 ml) was prepared. To this solution 4-nitro-1,3- phenylenediamine (9.18g,0.06 mol) was added under constant stirring. Then the concentrated hydrochloric acid kept in ice-cold bath was added dropwise to the above solution under stirring. To the resultant diazonium salt, 2-methoxy aniline

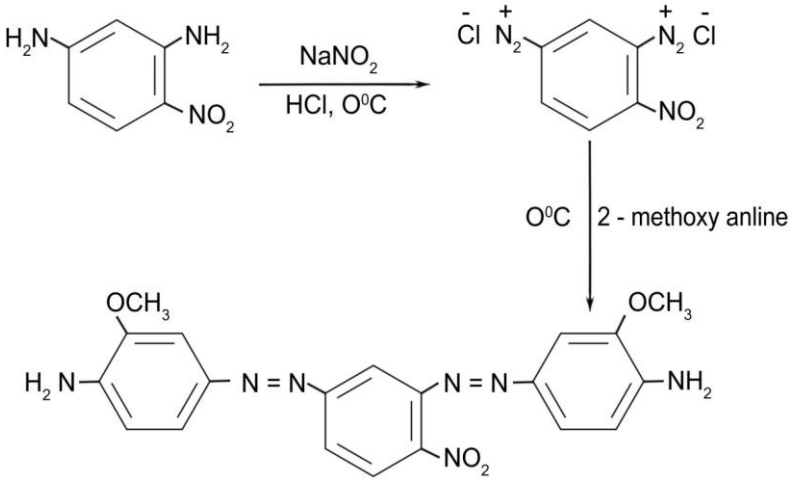
(14.76g,0.12mol) was added dropwise under constant stirring. Entire process was carried out in ice-cold bath. The resultant chromophore4-nitrophenyl-1,3-bis (azo-3-methoxyaniline) was filtered, dried and purified using ethanol.

2.2 Synthesis of polyimide:

The azodiamine (0.421g,1mmol) was dissolved in 10 ml DMF in a 50 ml round-bottom flask. Then dianhydriede, 6FDA (0.444g,1mmol) was added to the diaminesolution in one portion. The mixture was stirred at 40^0c for 24h to yield a viscous poly (amic acid) solution. Then 4 ml acetic anhydride and 3ml pyridine were added to the poly (amic acid) solution, and the mixture was heated at 100^0c for 24h to effect a complete imidization. The homogeneous polymer solution was poured slowly into an excess of methanol giving rise a precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried.

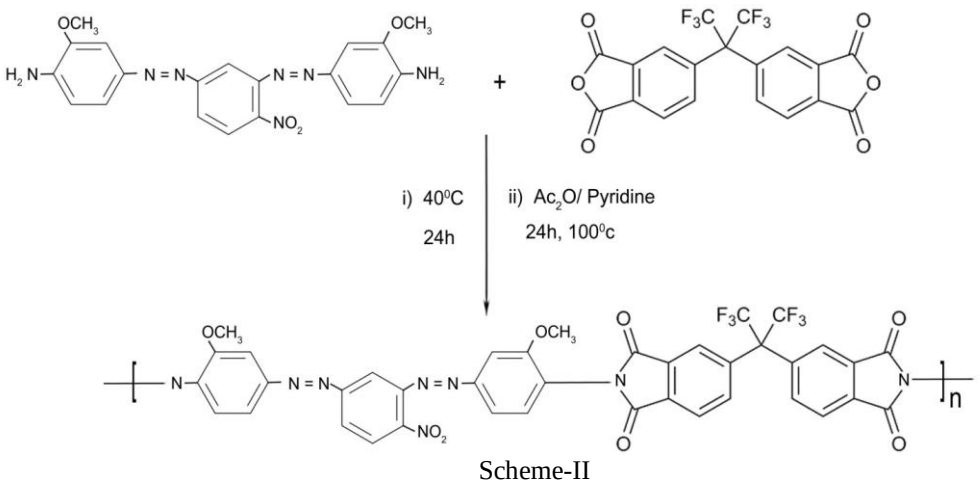
III. Result And Discussion:

IR, UV and NMR spectra revealed the successful preparation of polyimide. The monomer namely azo dye was prepared as follows: At first 4-nitro-1,3-phenylene diamine was diazotized by using sodium nitrite and hydrochloric acid at 0^0c. Then it was coupled with 2-methoxy aniline at 0^0c. The resultant chromophore namely 4-nitrophenyl-1,3-bis(azo-3-methoxy aniline) was filtered, dried and purified by using ethanol. The synthetic route of chromophore was represented in scheme-I.



Scheme-I

The polyimide was synthesized as follows: The azodiamine was dissolved in DMF. Then dianhydride, 6FDA was added to the diamine solution in one portion. The mixture was stirred at 40^0c for 24h to yield a viscous poly (amic acid) solution. Then into the mixture, acetic anhydride and pyridine was added and the mixture was heated at 100^0c for 24h to effect a complete imidization. The homogeneous mixture was poured slowly into an excess of methanol giving rise a precipitate, that was collected by filtration, washed thoroughly with hot water and methanol and dried. The synthetic route of polyimide was represented in scheme-II



Scheme-II

IV. Conclusion:

In conclusion, the new chromophore 4-nitrophenyl-1, 3-bis(azo-3-methoxy aniline) and its polyimide was synthesized. The monomer and polymer were characterized by IR, UV and NMR spectra. The new chromophore functionalized polymer has good solubility in common organic solvents. The new chromophore functionalized polyimide exhibited good thermal stability with high Tg value.

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