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Synthesis of Non-linear Optical Polyimide of Azopyrimidine - based Chromophore.

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Abstract:
4-nitro benzene diazonium chloride was prepared by the treatment of 4-nitro aniline in presence of sodium nitrite and aqueous hydrochloric acid at 0^0c. Then diazonium salt was coupled with 4,6-diamino pyrimidine in presence of 4(M) hydrochloric acid stirred for 2h at 0^0c. Then 0.001 (M) sodium hydroxide solution was added to naintian the pH=6.Polyimide of 5-(4-nitrophenylazo)-4,6-diaminopyrimidine was synthesized by chemical imidization process. At first 5-(4-nitro phenylazo)- 4, 6- diamino pyrimidine was treated with 6FDA dissolved in NMP stirring at 40^0c for 24h yielding viscous polyamic acid. To this solution acetic anhydride and Pyridine was added and stirred at 90^0c for 24h. The polyimide was characterized by IR, UV and NMR spectroscopy.

Key words: *4,6-diamino pyrimidine, 5-(4-nitro phenylazo)-4, 6-diamino pyrimidine, polyamicacid, Polyimide.*

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I. Introduction

Nonlinear optical (NLO) organic materials have been extensively investigated besauseof their broad applications in the area of optocelectronics and phtonics. The development of novel two photon absorbing(TPA) materials, which can be excited by near-infrared (NIR) light (700-1100 nm), is in area of intensive research. TPA is currently being studied for a variety of three-dimensional (3D) applications, including the micro fabrication of structures that cannot be created using standard lithographic techniques, ultrahigh-density holographic data storage, optical power limiters, upconversion lasers, two-photon fluorescence microscopy and photodynamic therapy. TPA prosess involves the simultaneous absorption of two photons in the presence of an intense laser beam, at waveleng the far from the molecule linear absorption region, whenever the material has an electronic excited level at twice the frequency of the input beam. In the linear absorption process, the absorbed light is directly proportional to the incident intensity, while in TPA the rate of energy absorbed is proportional to the square of the excitation intensity. In TPA, virtualexcited states are created with photons of half the nominal one-photon excitation energy, which provides better penetration into absorbing media and the square of intensity dependence of the absorption process allows for high 3D spatial selectivity through the use of a tightly focused laser beam and all processes are localized in the small volume. While this feature is the key to high spatial resolution. Practical applications involving TPA processes, howerer, still required materials with large absorption cross-section with large absorption coefficient. To date, various NLO molecules and molecular design rule have been investigated. Variety of doner-conjugated-doner, acceptor-doner-acceptor derivatives and the role of the pi-centre have been studied. Different compounds as conjugated bridges are employed for example fluorene, biphenyl, naphthyl groups, dithienothiophene, bis (styril) benzene derivatives and azoaromatic compounds. Nowadays, azobenzene containing meterials have been the subject of intensive research due to possibility of multiple trans-cis-trans isomerization cycles which opens a direct route to optically change molecular arrangement in nanoscaie which is attractive for various applications. The use of nonresonant excitation to alter the propertles of azo containing materials has been reported recently in the literature. Two-photon induced optical storage capability of poly(methyl methacrylate) (PMMA) doped with organometallic azoaromatic compounds, doped with DR-1, with DR13 were studied. Two-photon induced anisotropy in PMMA doped with DO13 was investigated as well. The host-guest system, even though the most convenient for preparation, has some disadvantages such as low solubility of the chromophores in the polymer matrix, phase separation of guest and host, migration or sometimes evaporation of NLO molecules from the films. To avoid those limitations NLO chromohores can be attached covalently to a polymer chain. Not so many articles report two-photon propertiesof undoped polymers. However, there is a lack of two-photon effect investigations in polymer films containing covalently bonded azobenzene derivatives into polymerbackbone. To the best of our knowledge, nonlinear absorption was measured only in solution of poly (acrylether) containing azochromphores as a side group.

Among the various azobenzene polymer systems developed, functionalized aromatic polyimides are promising optically active meterials in device applications because of their high thermal stability, high glass

transition temperature and optical transparency. Azobenzenechromophores have been incorporated into polymer structures in a variety of configurations by a number of different synthetic approaches. One of them is a direct polycondensation of the chromophore containing monomers.

In this article benzene diazonium chloride is coupled with 4,6-diamino pyrimidine giving the azo pyrimidine based chromopore which was then condensed with 6FDA gave the corresponding polyimide.

II. Experimental

2.1. Synthesis of 5 –(4-nitrophenylazo)-4,6-diamino pyrimidine:

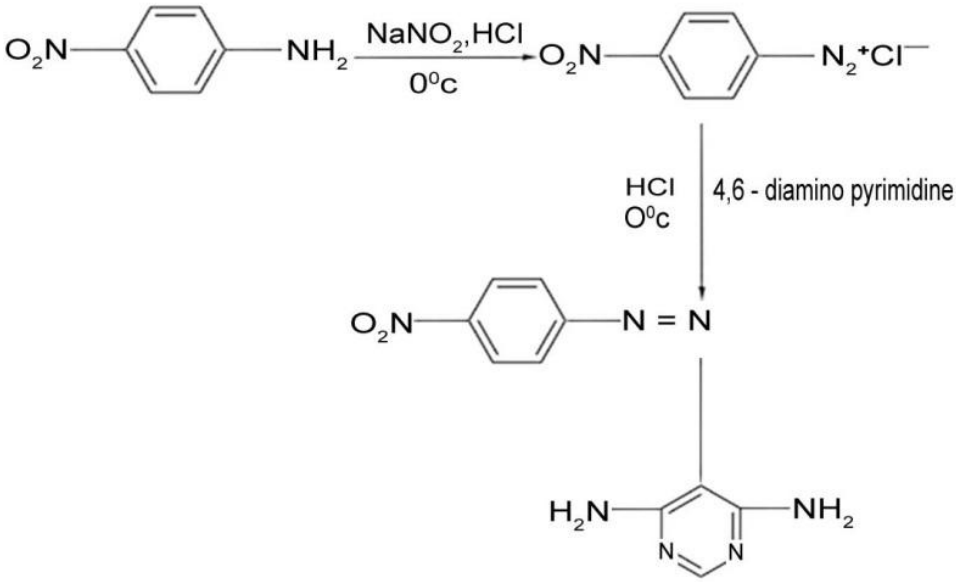
1.0 gm of 4-nitro aniline was dissolved in 16 ml of 6 (M) hydrochloric acid and cooled in an ice-bath. Sodium nitrite (0.70 g) was dissolved in small amount of water. After crushed ice was added to both solutions, the nitrite solution was slowly poured into the 4-nitro aniline solution while stiring with a glass rod under low temperature (0^0C). The solution of diazonium salt was slowly poured while stirring into a well cooled solution of 4,6-diamino pyrimidine (1.0g) in 40 ml Of 4(M) hydrochloric acid. The mixture was stirred in the ice-bath for 2h and then o.oo1(M) sodium hydroxide solution was added into the mixture until pH 6.0 was reached. The PH was determined by a universal paper. The solution was filtered and the precipitate was washed with water and air dried to give 5-(4-nitro phenyl azo)-4, 6- diamino pyrimidine. The crude product was purified by recrystallization with a mixture of ethanol-water.

2.2. Synthesis of polyimide:

Monomer, 5-(4-nitrophenylazo)-4,6-diamino pyrimidine(0.259g, 1 m mol) and 6FDA (0.44g, 1m mol) were dissolved in NMP (10ml).The solution was stirred at 40^0c under nitrogen for 24h yielding a viscous polyamic acid solution.To this solution acetic anhydride (12 ml) and pyridine (6ml)were added. The stirring was continued at 90^0c for 24 h.Then, the reaction mixture was poured into methanol, the polymer was filtered and purified by washing with methanol.

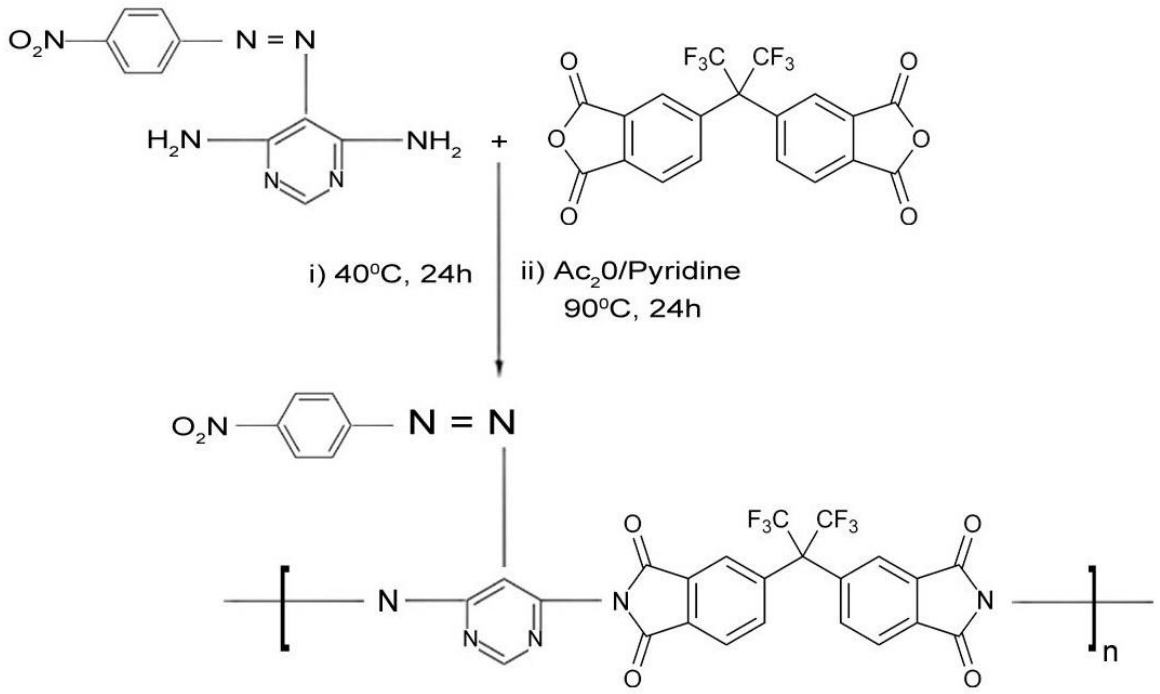
III. Result And Discussion

IR, UV and NMR spectra revealed the successful preparation of the polymer. 4-nitro benzene diazonium chloride was prepared by the treatment of 4-nitro aniline with sodium nitrite and 6 (M) hydrochloric acid. Benzene diazonium chloride was then coupled with 4,6-diamino pyrimidine in presence of 4(M) hydrochloric acid. Then 0.001(M) sodium hydroxide solution was added to the mixture until pH6 was reached. The mixture was then filtered washed with water and air dried. The dye was recrystallized from ethanol-water mixture. The Synthetic route of the monomer was represented in scheme-I



scheme-I

Polyimide was synthesized as follows:The monomer namely5-(4-nitrophenyl azo) – 4,6 diamino pyrimidine and 6FDA was dissolved in NMP and the mixture was allowed to heat at 40^0c for 24h which result the formation of viscous polyamicacid solution. Then this mixture was mixed with acetic anhydride and pyridine and heated at 90^0c for 24h. After that, The mixture was poured into methanol and the polymer was purified by washing with methanol. The synthetic route of polyimide was represented in scheme-II.



scheme-II.

The polyimide has good thermal and mechanical properties with high Tg value. The polymer was soluble in common organic solvents.

IV. Conclusion

In conclusion, The new polyimide containing azo pyrimidine based chromophore was synthesized. The monomer and polymer were characterized by IR, UV and NNR spectroscopy. The new chromohore functionalized polyimide exhibited good thermal stablilty with high Tg value. The polymer has very good solubility in common organic solvents.

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