SYNTHESIS AND CHARACTERISATION OF DIAMINE CONTAINING ANISIDINE BASED NLO CHROMOPHORE

S.Devarajan[1] ,

V.Sindhu[2]

Physics,
Central Institute of Plastics Engineering and Technology,
Chennai,India

Abstract: We have synthesised a diamine containing anisidine based nonlinear optical chromophore via π-conjugated bridge in order to prepare more thermally stable chromophores. The chromophore is synthesised by using m-Phenylene diamine consisting of amine group as a electron donor and p-nitroaniline consisting of nitro group as electron acceptor through π-conjugated system. After performing FTIR, NMR,UV-vis,Fluorescence emission and TGA it is confirmed that the chromophore is thermally stable and the diamine group in it enables it to be used as one of the monomer in the synthesis of nonlinear optical(NLO) polyimide.

Introduction: The ability of nonlinear 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 systems. Organic moieties with delocalised 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 extremely 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 [1].

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 ease of polarisation of their extended mobile pi-electron cloud over long distances [2]. Strong absorption of dyes in the visible region makes them particularly suited for nonlinear optical investigations[3].It has also been shown that embedding dye chromophores in suitable host matrices enhances the lifetime and stability of the dyes entrapped within it[2].

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[4-7].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[8]. A chromophore containing thiadiazole was synthesised and reported [9].Here we have replaced thiadiazole group by anisidine in order to improve thermal and optical properties. m-Phenylenediamine an electron donor ,p-Nitroaniline, an electron acceptor group are synthesised in order to get NLO chromophore.

Experimental Section:

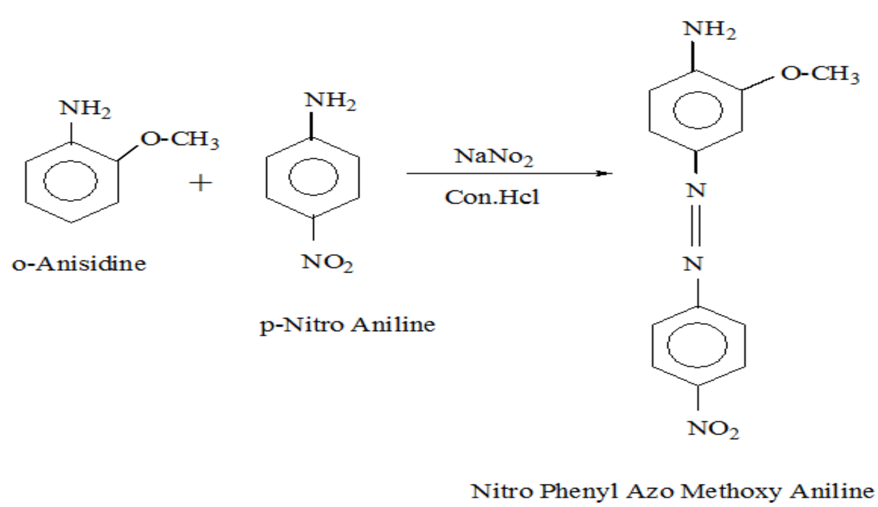
Materials : 4,4'-(hexafluoroisopropylidene)diphathalic anhydride (6FDA),p-Nitro aniline,o-Anisidine ,m-Phenylene diamine,Sodium nitrite,Conc. Hydrochloric acid,Sodium hydroxide,Methanol ,Hexane,Dimethyl formamide (DMF),Pyridine,Poropionic Anhydride and Solvents.

m-phenylenediamine is produced by hydrogenation of 1,3-dinitrobenzene. Dintrobenzene is prepared by dinitration of benzene.

Synthesis of p-nitroaniline : It is produced by amination of 4-nitrochlorobenzene . 4-nitroaniline is obtained from aniline where an electrophilic aromatic substitution takes to install nitro group para to amino group. After this reaction, a separation must be performed to remove 2-nitroaniline, which is also formed in a small amount during the reaction.

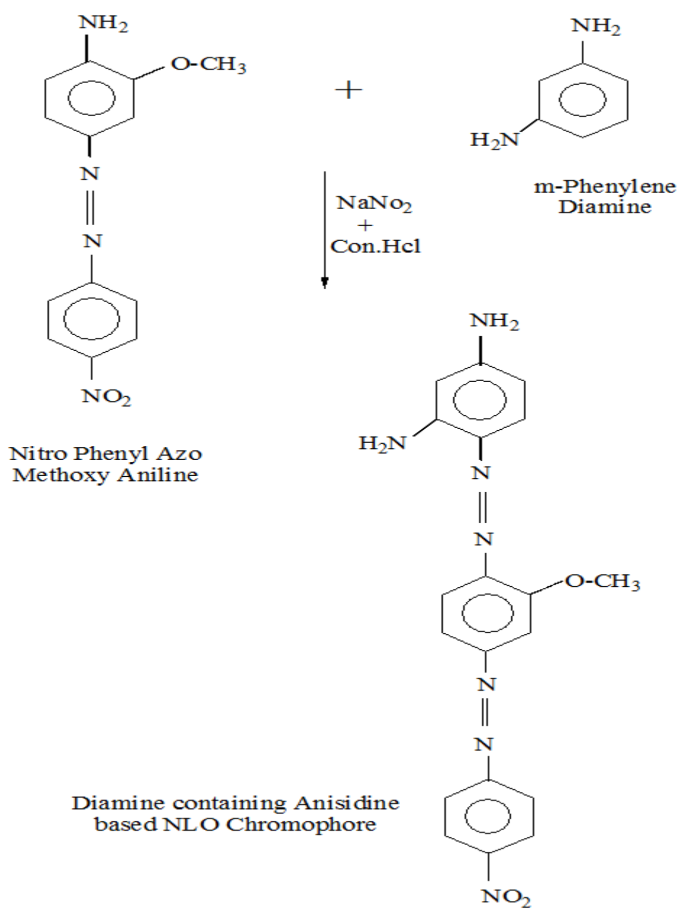
Synthesis of NLO chromophore: It is a two step process: The first step is the recation of p-niroaniline and o-anisidine with various agents to form a primary chromophore.;The second step is the addition of m-phenylene diamine to the primary chromophore to yield the final diamine containing chromophore.

Synthesis of stage -1 chromophore: The entire process was carried out under equimolar concentration of 0.0625 mole. At first concentrated Hcl (5ml) was kept in ice cold bath for several hours. A solution of sodium nitrite (6.9g) and water (120mL) was prepared. To this solution, p-nitroaniline (8.63g,0.0626 mole)was added under constant stirring. Then the concentrated kept in cold bath was added drop wise to the above solution under stirring. To the resultant diazonium salt, o-anisidine (7.6g,0.0625 mole) was added drop wise under constant stirring. Entire process was carried out in ice cold bath , since the diazonium ion formed during the reaction is very reactive above 5^{0}C and releases nitrogen gases and causes thermal degradation. The resultant chromophore (nitro phenyl azo methoxy aniline chromophore) was filtered, dried and purified using methanol.



Scheme 1. Stage -1 chromophore Nitro phenyl azo methoxy aniline chromophore

Synthesis of stage-2 chromophore:This process was carried out under equimolar concentration of 0.025 mole. First a solution of sodium nitrite (7g) and water (120 mL) was prepared. To which, nitro phenyl azo methoxy aniline chromophore (stage1)(6.807 g, 0.025 mole) was added under constant stirring.The concentrated Hcl was added dropwise under constant stirring. To the resultant diazonium salt, o-anisidine (2.704 g, 0.025 mole) was added. Entire process is carried out in ice cold bath, since the diazonium ion formed during the reaction is highly reactive and releases nitrogen gases and causes for thermal degradation. In this process, sodium carnate (2.269 g) was added as a buffer to maintain the Ph throughout the reaction process. This reaction is shown in scheme 2. The resultant chromophore (diamine containing anisidine based chromophore) was filtered, dried and purified using acetone.



Scheme 2 Diamine containing anisidine based chromophore

Results and Discussions:

FTIR analysis: Figure.1 shows FTIR of stage 1 chromophore. This analysis confirms the functional groups present in it. It reveals the presence of the following functional groups as in Table.1.

FTIR of stage 2 chromophore is shown in Figure.2, which indicates the presence of following functional groups as shown in Table.2.

NMR Analysis: NMR spectra of stage 2 (Final) chromophore is shown in Figure.3. It reveals that chemical shifts at 6-8 ppm confirms the presence of aromatic C-H group protons, 3.3 ppm confirms the presence of amine group protons and 3.6-3.85 ppm confirms the presence of methoxy group protons. Hence, it's concluded that the above mentioned groups are present in the chromophore.

UV-vis spectrum: Figure.4 shows the UV-vis spectrum of final chromophore . Azobenzene monomers contain intramolecular charge transfer chromophores and their UV-visible absorption bands depend upon the combination of electron donating and withdrawing moieties in the molecules (chromophoric groups).

The absorption spectroscopy of the final chromophore was analysed and it reveals maximum absorbance at 493nm in the visible region and this is because of the azo group n-π* transition.

TGA analysis: Thermal degradation of stage 1 chromophore is shown in Figure.5 .It is observed that there is no thermal transition below 200^0C, so the synthesised NLO chromophore will improve the thermal stability of final NLO polyimide during the polymerisation.

Thermal degradation of final chromophore shown in Figure.6 reveals that there are twothermal transitions below 278^0C and below 490^0C which indicates that the chromophore is thermally stable.

Conclusion: A new thermally stable NLO chromophore was synthesised. Its structure was confirmed using FTIR and NMR analysis. This chromophore is soluble in many organic solvents and hence it can be attached to a polyimide chain for applications in fibre optic communication, optical switching devices.

Acknowledgement: We thank DAE-BRNS for the grant offered by them to carry out this work.

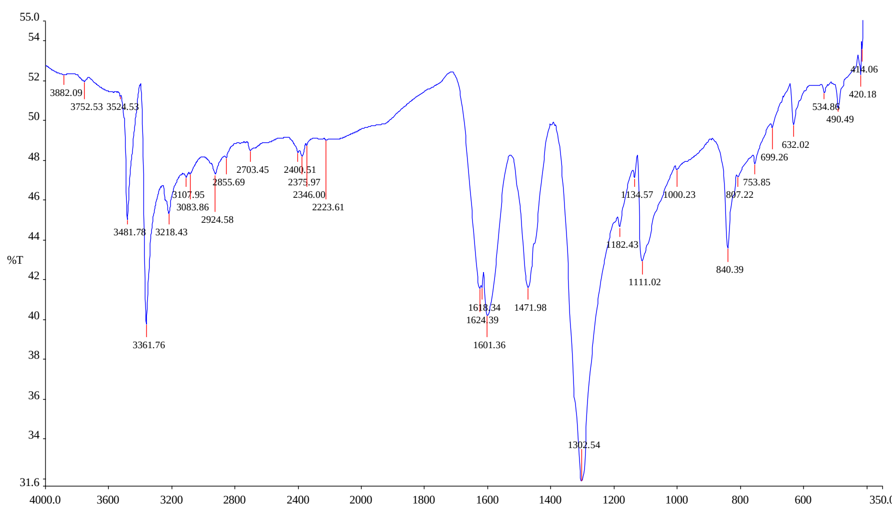


Figure.1

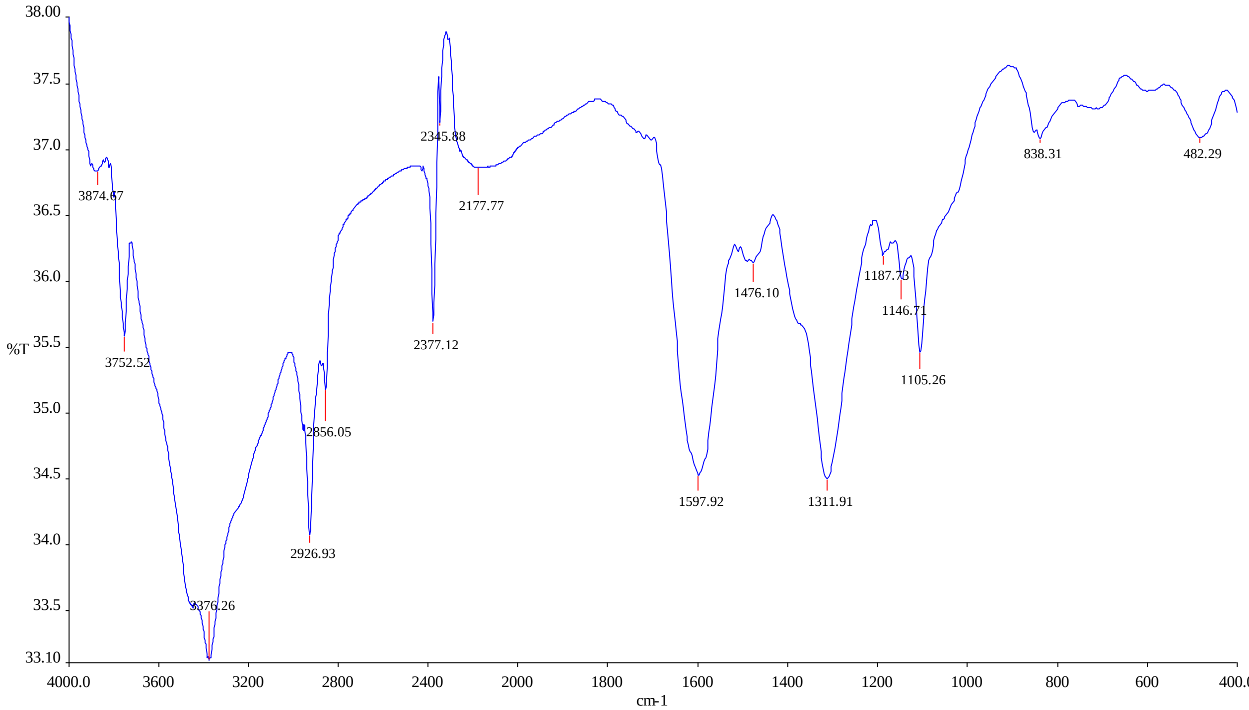


Figure .2

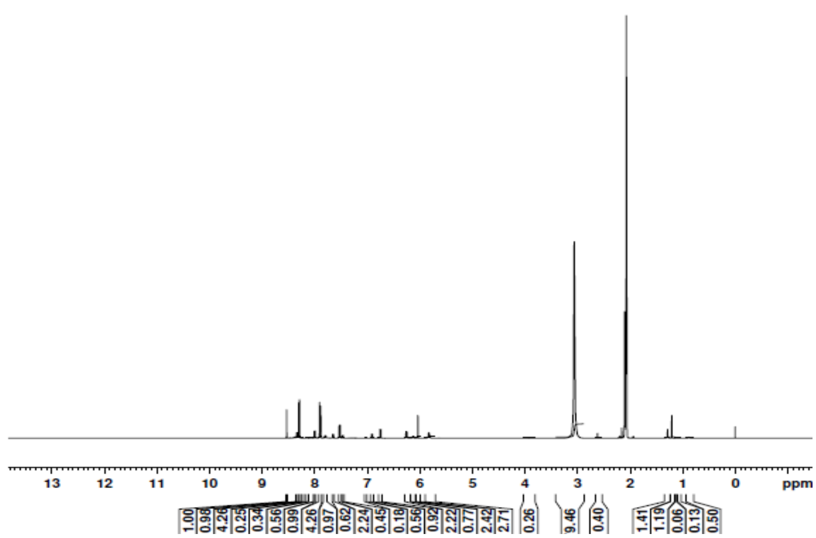


Figure .3

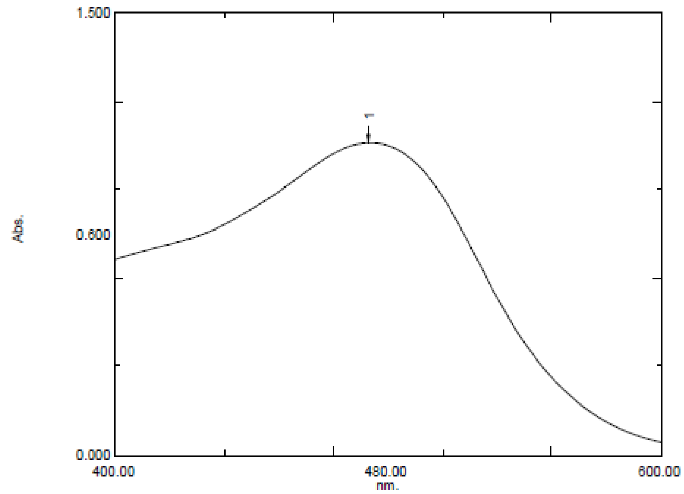


Figure.4

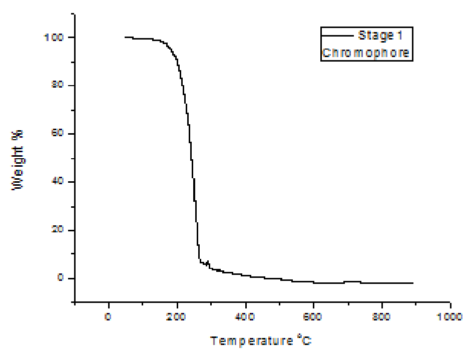


Figure.5

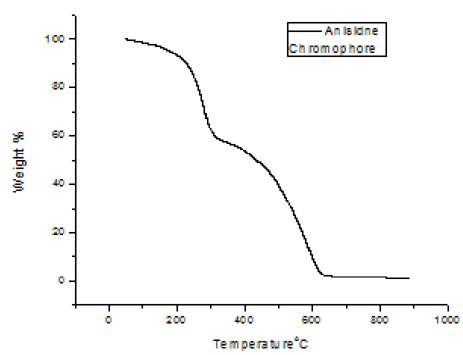


Figure.6

Group	Wave number (cm^{-1})
-N-O (stretch)	1302
-O- (stretch)	1111
C=C (stretch)	1601
N-H (stretch)	3361
Aromatic C-H (stretch)	3083
C-N (stretch)	2223
Alkane C-H (stretch)	2855

Table.1

References:

1. Min Ho Kim, Jung –II Jin, Chul Joo Lee, Nakjoong Kim, Ki Hong.Park ,"Synthesis and Characterisation of Nonlinear Optical Polymers Having Quinoline-based Chromophores", (2002), Bull.Kor.Chem.Soc. .,Vol.23,pp.964.

2. Schafer, F. (1997), 'Dye Lasers'.;Second revised edition , Springer Verlag, Vol.1

3. S. M. Tambe, A. A. Kittur, S. R. Inamdar, G. R. Mitchell, and M. Y. Kariduraganavar, "Synthesis and characterization of thermally stable second-order nonlinear optical side-chain polyimides containing thiazole and benzothiazole push-pull chromophores," Optical Materials, vol. 31, no. 6, pp. 817–825, 2009.

4. Burland,D.M.; Miller, R.D.; Walsh, C. "Second-order nonlinearity in poled-polymer systems", (1994), Chem. Rev.,Vol.94.pp.31

5. Dalton, L.R.; Harper, A.W.; Ghosn, R.; Steier, W.H,;Ziari, M,; Fetterman, H.; Shi, Y,; Mustacich,R.V,;Jen,A.K,; Shea K."Synthesis and Processing of Improved Organic Second-Order Nonlinear Optical Materials for Applications in Photonics", (1995) J Chem Mater, Vol.7, pp.1060

6. Marks, T. J. and Ratner, M. A. "Design, synthesis, and properties of molecule-based assemblies with large second order optical nonlinearities", Angew. Chem. Int. Ed. Engl., Vol. 34, pp. 155-173, 1995.

7. Tambe,S.M,; Kittur,A.A,;Inamdar,S.R., Mitchell, G.R.; Kariduraganavar, M.Y., "Synthesis and

characterization of thermally stable second-order nonlinear optical side-chain polyimides c containing thiazole and benzothiazole push-pull chromophores", (2009), Opt.Mat.Vol.31,pp.817

8. Subashchandra.M,; Timbe, Ragavendrda,G,; Sanjeev,R,;Mahadevappa,Y,; "Synthesis and characterization of nonlinear optical side-chain polyimides containing the thiadiazole chromophores ", (2011), J.Appl. Poly.Sci, Vol.125,pp.1049-1058.