Synthesis and Characterization of Fluoropolyimide Containing NLO Chromophore obtained from Azo Dye based NLO Chromophore Sources

Sindhu V1*, Devarajan2
1Department of Physics, Velammal Institute of Technology, Chennai, India
2Department of Physics, Central Institute of Plastics Engineering and Technology, Chennai, India
sindhusririni@gmail.com

Abstract-Nonlinear optical polyimide was synthesized by using NLO chromophore obtained from natural renewable resource i.e., Castor oil. The use of natural renewable resource materials eliminate the usage of nonrenewable material and are used in optical applications. Thermally stable Nonlinear Optical Polyimide was synthesized using condensation polymerization technique. The polyimide was prepared using 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 2,2-Bis(3-amino-4-hydroxyphenyl) hexafluoropropane and for Nonlinear Optical Chromophore, Nitrophenylazo phenylamino alkyl group was used. The resulting polyimide and its monomer were characterized by Fourier Transform Infrared spectroscopy, UV-vis spectroscopy and Fluorescence spectroscopy. This chromophore was attached to polyimide having good solubility in organic solvents and has easy process ability to make a thin film. The chromophore contains long alkyl chain group, it has double bond imparting self plasticizing effect to enhance the flexible property of the polymer. This synthesized chromophore has electron donor and acceptor group connected by pi conjugated system and are covalently linked to main polymer backbone.

Key Words: Aromatic diamine, Polycondensation, N methyl aniline, Ricinoleic acid, Diethyl azodicarboxylate, Triphenylphosphine, Castor Oil.

1. INTRODUCTION
Nonlinear optical (NLO) polymers are the most popular of all high performance/ high temperature polymers of which polyimides (PIs) which are useful as adhesives, coatings, composite matrices, films, fibers, foams and membranes in a variety of applications [1,2]. In recent years, interest in (PIs), having a favorable combination of properties such as high optical transparency, low refractive index, low dielectric constant, high glass transition temperature (Tg), easy fabrication and good mechanical properties have been increased in the fields of optical devices [3,4,5]. In this work, we synthesized a novel chromophore [6-10] and a hydroxyl polyimides based on the fluorine – containing monomers 4,4′ – (hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 2,2′ – bis (3 amino-4- hydroxy-phenyl) hexafluoro propane, followed by the covalent bonding of a chromophore onto the backbone of the polyimide via the Mitsunobu reaction[11, 12-19].

2. EXPERIMENT
(i) Materials
High purity chemicals [4,4′ – (hexafluoroisopropylidene)diphthalic anhydride (6FDA) 99 %, Alfa Aesar; 2,2 – Bis (3 –amino – 4- hydroxyphenyl) hexafluoropropane, TCI; Diethyl azodicarboxylate (DEAD) ; Triphenylphosphine, dimethylacetamide (DMAc), Merck; Tetrahydrafuran, Merck; Xylene, Across Organics; ethanol AR 99.9%, Changshu Yangyuan; N-methyl aniline, Spectrochem; 4 –Nitroaniline, Loba Chemie, Sodium hydroxide, Thomas Baker; Thionyl chloride, Ranchem; Hydrochloric acid, Merck, Glacial acetic acid, Merck; Sodium acetate, Merck; commercial castor oil were used as received.

(ii) Synthesis of Ricinoleic acid
A 720 ml of 1N NaOH and 80 ml of fatty acid (Castor Oil) were taken in a round-bottomed flask and refluxed for one hour. Porcelain pieces are put inside the round-bottomed flask to avoid spitting out of solution. Condenser and continuous supply of water was provided during the reflux. Cotton plug was kept on the neck of the condenser to avoid evaporation. The refluxed mixture was taken in a separating funnel in a small amount and to that more amount of 1N Hydrochloric acid is added and allowed to stand for some time. Then the aqueous layer was discarded and the organic layer containing fatty acid was collected in a flask. Ricinoleic acid ( 2.0 gram) was transferred to a 500 ml round bottom flask. Thionylchloride (Socl2,5ml) was added and refluxed for 2 hours. It was then distilled to remove the excess thionylchloride from the mixture and the remaining trace of thionylchloride is removed in vacuum at 40°C. This is shown in Scheme.1.

(iii) Synthesis of an NLO Chromophore
To a stirred solution of p-nitroaniline ( 13.81g, 0.10 mol)in methanol/Hcl ( 1:1 60 ml), sodium nitrite (7.59 g,0.11 mol) was added in ice water ( 15%, m/m) at 0°C. The mixture was stirred at room temperature for 1h, and then the mixture was added drop by drop into a solution of N-methyl -N-Ricinoleyl aniline (35.09 g, .099 mol) with abundance of HAc-Nac. The mixture was stirred for 0.5 h, followed by stirring at 40-50°C for 20 min. The solution was cooled down and further recrystalized from toluene/methanol (4:1) to give a yield. Synthesis route is shown in Scheme.2.
(iv) Hydroxyl polyimide synthesis

The polymerization was conducted in a nitrogen flushed three-neck flask with a magnetic stirrer, reverse Dean-Stark trap, and reflux condenser filled with dry xylene. A stoichiometric amount of 6FDA (3.332 G, 7.50mmol) was added to solution of 2,2’-bis (3-amino-4-hydroxyphenyl) hexafluoropropane (2.747g, 7.5mmol) in 30ml DMAC at 0°C. The solution was then heated to room temperature and magnetically stirred over night under nitrogen to form the poly(amic acid) solution. The poly(amic acid) was thermally cyclized in an oil bath/programmable oven by programmed heating rate.

(v) Synthesis of side-chain polyimide based on 6FDA

In the past decade, several synthetic routes for side chain NLO polyimides have been developed through chromophore containing diamine synthesis by Yu et al., [20-24] and Miller co-workers and through Mitsunobuo reaction. Hydroxyl polyimide (0.387 g, 0.50 mmol), PPh3 (0.393 g, 1.50 mmol) and NLO chromophore (0.532g, 1.00 mmol) were dissolved in dry THF (15 ml) successively. Diethyl azodicarboxylate (DEAD) (0.260 g, 1.5 mmol) was added drop by drop into the solution under nitrogen atmosphere. The reaction mixture was stirred for 2 days at room temperature, then the resulting reaction solution was added drop by drop into a solution of methanol/water (300ml 1:1) and 2N HCl (5ml) [24]. The collected solid was further dissolved in THF (10 ml) and casted on a glass plate and then dried at 60°C under vacuum oven for 12 hours to form the thin film[25].The synthesis route is shown in Scheme.3.

---

Copyright © IJPOT, All Rights Reserved
(vi) Measurement

The FTIR spectra were recorded on a Thermo Scientific NICOLET 6700 model spectrometer. The UV visible spectra were collected on a Perkin-Elmer lambda 35 model spectrometer and Fluorescence Emission spectra were recorded using Fluoromax -2, ISA, Jobin-Yvon-SPEX Edison spectrometer.

3. RESULT AND DISCUSSION

Polyimide was synthesized using a traditional two-step synthetic method that included a polycondensation between a diamine and dianhydride to form poly(amic acid) and a chemical, thermal imidization to form a polyimide FTIR spectrum of polyimide is shown in Fig. 1, and the characteristic absorption bands of polyimide is Table.1. NLO polyimide shows the clear appearance of 1781 cm\(^{-1}\) and 1713 cm\(^{-1}\) bands characteristic of C=O stretching in imide rings and a 1357 cm\(^{-1}\) band characteristic of C-N stretching in imide rings which indicates the existence of the imide groups. The characteristic absorption peaks of the nitro groups at 1512 cm\(^{-1}\) and 1296 cm\(^{-1}\) also indicate the existence of the NLO chromophore.

<table>
<thead>
<tr>
<th>Group</th>
<th>Wave number (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O (stretching)</td>
<td>1781</td>
</tr>
<tr>
<td>C-N (stretching)</td>
<td>1357</td>
</tr>
<tr>
<td>NO(_2) group</td>
<td>1512 and 1296</td>
</tr>
</tbody>
</table>

The UV-vis spectra of polyimide is shown in Fig. 2. Polyimide with NLO chromophore exhibit an absorption peak of 300 nm, which is indicates the presence of absorption groups.

The emission spectrum of polyimide with NLO chromophore is shown in Fig. 3, which indicates an emission from 310-400 nm.

Thermal characterization is shown Fig. 4 which indicates hydroxyl polyimide has decomposition temperature of the range 300-400°C. While NLO polyimide shows the temperature range of 210-280°C, which is lesser than the hydroxyl polyimide. This might be due to increase in flexibility of NLO polyimide, which is attached with NLO chromophore in hydroxyl polyimide back bone.
The TGA interpretation are shown in Table 2. These result support the following argument: as the NLO chromophore loading level increases, the weight loss increases accordingly [17].

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl polyimide</td>
<td>300-400°C</td>
</tr>
<tr>
<td>NLO Polyimide</td>
<td>210-280°C</td>
</tr>
</tbody>
</table>

4. CONCLUSION

We have prepared the fluorine containing hydroxyl polyimide and then a novel NLO chromophore. By covalent bonding NLO chromophore was introduced to the hydroxyl polyimide via a mild Mitsunobu reaction. In this fluoropolyimide chain, fluorine containing NLO polyimide has easy processing characteristics, and high thermal stability due to their ricinoleic acid long alkyl chain group. This ricinoleic acid alkyl chain group has more electron donating behavior which improves the chromophore’s polarizability.

ACKNOWLEDGMENT

The authors would like to thank the DAE for their financial support (Grant No. 2012/34/75/BRNS).

REFERENCES


