Synthesis and Characterization of Carbazole Based Donor-Acceptor-Donor Type Polymer for NLO Applications

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Abstract: Carbazole based NLO polymer was synthesized by using Knoevenagel condensation. The polymer is found to be fully soluble in high polar solvents like dimethyl formamide and dimethylsulfoxide. By using GPC and tetrahydrofuran as a solvent, the molecular weight is found to be 5000 g/mol. Thermal analysis exhibited thermal stability of the polymer up to 400 °C and glass transition temperature (Tg) at 214 °C. The polymer film has good optical transparency. The non-centrosymmetry in the film was induced by corona poling for second order NLO property, whereas z-scan technique is used to understand third order NLO property. The effective TPA coefficient (β) found to be 5.1 X 10⁻¹² m/W. Computational study indicated that the total charge is located at the center of the molecule in HUMO case whereas in the case of LUMO the charge is spreads out from the center of the molecule.

1. Introduction

Nonlinear optical (NLO) materials are known to be used for good number of photonic applications[1-3]. Polymers are attractive medium for application in optical electronic devices due to superiority in chemical resistivity, processability, lighter in weight and mechanical endurance[4-5]. A good NLO polymer needs to have better optically transparency, high optical thresholds to laser power, and large NLO coefficient[6-7]. Organic polymers having large nonlinear optical response (χ(2) & χ(3)), low optical losses, fast response, have potential applications in optical switches, telecommunications, optical data storage, optical information processing, modulators, and other all-optical devices[8-9]. A large number of highly conjugated polymers have been studied for their second and third-order optical nonlinearities[10-11]. Among non-conjugated polymers, the third-order NLO susceptibility of 6-(9H-carbazol-9-yl) hexyl acetate (CHA) i.e. χ(3) and two photon absorption Figures of Merit (FOMs) were found to be 1.58 × 10⁻⁸ (esu) and 4.55, respectively[12].

Poly(N-vinylcarbazole) (PVK) is a non-conjugated polymer and a well-known hole-transporting material and has strong absorption in the ultraviolet and emission in the blue region[13]. The third-order NLO susceptibility was also studied with substituted carbazole, which has exhibited three times larger value than the unsubstituted PVK[14]. Symmetric-type D-π-D carbazole derivatives, 3, 6 - disubstituted carbazole chromophores with two styryl bridges of the two-dimensional conjugated D-π-D
system were studied for third-order nonlinear optical properties using single-beam Z-scan technique with femtosecond laser pulses at 800 nm. Hyperbranched donor–acceptor polyfluorenes based on 1,3,6,8-tetrasubstituted carbazole core were synthesized and characterized for third order NLO properties using Z-scan technique and their third order nonlinear susceptibility was around $1.4 \times 10^{-15}$ esu. Non-conjugated conductive polymers have been shown to have quantum dot characteristics because of the confinement of charges within sub-nanometer domains. Such confinement has affected a large increase in third order optical nonlinearities for these systems. Study of quadratic electro-optic effect in non-conjugated conductive polymers including cis-1,4-polyisoprene, 1,4-trans polyisoprene,poly(β-pinene),poly(ethylenepyrolyediyi) derivative and polynorbornene have shown very large Kerr-coefficients (about 30 times that of conjugated polymers).

Considering the potential of non-conjugated polymer for large third order non-linearity, attempt has been made to modify carbazole derivatives to design conjugated structure having donor-acceptor centres. Further, the conjugated structures are isolated by alkyl chain to make the whole system non-conjugated in nature. Further, electron accepting group is attached via conjugated backbone. Individual conjugated segment is connected via alkyl spacer in the polymer chain.

2. Corona poling and Z-scan measurement
For second order NLO property, the polymer was coated on ITO glass slide by spin coating and was poled by applying electric field of 4.8 kV through the tungsten needle by keeping it at 0.8 cm from the surface of the film which is mounted on heating stage. From the absorption data we calculated the order parameter ($\phi$) by using the equation $\phi = 1 - A_1/A_0$ where $A_0$ and $A_1$ are the absorbances of the polymer film before and after the poling. For third order NLO activity open aperture z-scan technique was used where Nd: YAG laser at 532 nm of 5 ns pulses were focussed on to polymer solution in chloroform.

3. Synthesis of monomers

1,6-di(9H-carbazol-9-yl)hexane (2)

Carbazole (3 g, 0.0179 mol), potassium hydroxide (2 g, 0.035 mol) were taken in 100 ml round bottom flask and stirred for 30 min in 10 ml of DMSO. Then 1.4 ml (0.0089 mol) of dibromohexane was added drop wise and maintained at 80°C. Finally the polymer was precipitated in excess of methanol and filtered to collect light yellow coloured solid.

Yield: 58%; mp: 120 °C; FT-IR (KBr): ν (cm$^{-1}$) 3049, 2926, 2853, 1594, 1320, 1218, 760, 722; $^1$H NMR (CDCl$_3$, 500 MHz, δ): 8.1 (d, J = 8, 4H), 7.4 (m, 4H, Ar H), 7.3 (d, 4H, Ar H), 7.2 (m, 4H, Ar H), 4.2 (t, 4H, N-CH$_2$), 1.8 (m, 4H), 1.4 (m, 2H, aliphatic); $^{13}$C NMR (CDCl$_3$, 125 MHz, δ):140, 125, 122, 120, 118, 108, 42, 28, 27.

9,9’-(hexane-1,6-diyl)bis(9H-carbazole-3-carbaldehyde) (3)

Compound 2 (1 g, 2.403 mmol) was taken in 100 ml round bottom flask containing 40 ml of dichloroethane. Then 1 ml of DMF added to it and the reaction bath was cooled below 10°C for 20 min. 1 ml of POCl$_3$ was slowly added to it and reaction mixture was refluxed for 4 hrs. Finally the reaction mixture was poured in to aqueous sodium acetate solution and extracted with chloroform, thrice. Finally the crude product was purified by column chromatography.

Yield: 73%; mp: 153 °C; FT-IR (KBr): ν (cm$^{-1}$) 3052, 2932, 2856, 2742, 1677, 1592, 1330, 1177, 749; $^1$H NMR (CDCl$_3$, 300 MHz, δ): 10.04 (s,2H), 8.54 (s, 2H), 8.11 (d, 2H), 7.93 (d, 2H), 7.49 (d, 2H), 7.33 (m, 6H), 4.21 (s, 4H), 1.79 (m, 4H), 1.33 (m, 4H); $^{13}$C NMR (CDCl$_3$, 75 MHz, δ): 191, 141, 128, 127, 126, 123.9, 123.0, 122, 120.7, 120.3, 109, 108, 43, 28, 26.

4. Synthesis of Polymer (P1)

2-(2,6-dimethyl-4H-pyran-4-ylidene)malononitrile (1) (0.1 g, 0.58 mmol) and compound 3 (0.58 mmol) were charged in a well dried 25 ml RBF connected to Schlenk tube with purging of nitrogen continuously. Then, 3 ml of dry pyridine with 0.1 ml of piperidine (1.16 mmol) were also charged and refluxed for 60 hrs. Finally the polymer was precipitated in excess of methanol and filtered to collect
solid polymer as residue. It was purified by soxhlation in methanol to remove oligomers. Further the light red coloured polymer was dried under vacuum for 24 hrs at room temperature. Yield: 88 %; FT-IR (KBr): ν (cm\(^{-1}\)): 3049, 2932, 2855, 2204, 1644, 1594, 1422, 1231; \(^1\)H NMR (CDCl\(_3\), 500 MHz, δ): 8.21-7.96 (br,14H), 7.36-7.22 (br,4H), 4.33-4.24 (br,4H), 1.82-1.67 (br,4H), 1.48-1.11 (br,2H).

5. Results and discussions

Synthesis and Characterization

Synthetic route of monomers to polymer were shown in Scheme 1& 2.

2-(2, 6-dimethyl-4H-pyran-4-ylidene) malononitrile (1) was synthesized as per literature procedure\(^{[19]}\). Carbazole was treated with dibromohexane in presence of potassium hydroxide to get compound 2. Then compound 2 is subjected to standard Vilsmeier-Haack reaction by using phosphorous oxychloride and DMF to get compound 3. All the monomers show characteristic peaks in \(^1\)H-NMR for confirming their structures. 9,9'-(hexane-1,6-diyl)bis(9H-carbazole-3-carbaldehyde) (3) shows strong peak at 10.04 ppm which confirms the presence of aldehydic proton. This is also confirmed by FT-IR spectra which show characteristic peak at 1677 cm\(^{-1}\) for carbonyl stretching and 2856 and 2742 cm\(^{-1}\) for aldehydic proton. Finally compound 3 was reacted with equivalent amount of compound 1 in pyridine by using strong base, piperidine, by Knoevenagal condensation to afford the polymer (P1) with good yield. FT-IR (Figure 1) shows a peak near 2200 cm\(^{-1}\) which confirms the presence of cyano group in polymer which is due to the presence of dicyanomethylene moiety incorporated during polymerization. \(^1\)H-NMR of the formed polymer also shows characteristic peak around 7.3-7.2, which confirm the presence of stilbene double bond protons and the broadening of peak also assured the success of polymerization. \(^1\)H-NMR spectra also shows a small peak for aldehydic proton, indicating presence of some percentage of aldehyde at the end of the polymer chain.

![Scheme 1. Synthetic route for preparation of monomers](image1)

![Scheme 2. Synthetic route for preparation of polymer (P1)](image2)
The formed polymer is partially soluble in solvents like tetrahydrofuran and chloroform whereas, it is completely soluble in dimethyl formamide (DMF) and dimethylsulphoxide (DMSO). Gel permeation chromatography (GPC) study indicates that the molecular weight of the polymer is around 5000 g/mol with polydispersity index of 3.2. The low molecular weight is due to partial solubility of polymer in mobile solvent, THF, used in GPC. Thermogravimetric analysis (TGA) indicates 10 % wt loss up to 400 °C. The higher thermal stability may be due to the two dimensional structure of the donor-acceptor-donor in the polymer which is also observed in the case of phenothiazine based polymer in our earlier study[10]. The differential scanning calorimeter (DSC) study indicates that the Tg of the polymer is 214 °C. Thus, the polymer having Y-type moieties shows better thermal stability due to their two dimensional architecture (2D). Their optical characteristics together with high glass transition temperature and thermal stability make this polymer very interesting and useful as NLO polymer.

6. Corona poling and optical properties
For studying second order NLO characteristics, thin film of the polymer was cast from their chloroform solution (few drops of DMF added for complete miscibility) over ITO glass slide. Figure 2 shows the electronic spectra of the polymer. From this it is evident that there is a decrease in absorption in UV-vis spectrum of the polymer film after poling. This change in spectra confirms alignment of NLO active moiety in non-centrosymmetric fashion. From the change in absorption, the order parameter ($\phi$) was calculated and found to be 0.26.

It is well known that third harmonic generation and Z-scan techniques can detect different nonlinear optical contributions[20]. Precisely, the former technique detects only the electronic contribution to the nonlinear response, while the latter can detect the electronic contribution together with others, such as the molecular orientation, redistribution, etc. The duration of the laser pulses is known to plays very important role for the ongoing physical processes during laser excitation. Practically, the laser pulse duration influences the contributions from different physical
mechanisms, which, in turn, can contribute to the observed nonlinearities, each one exhibiting a characteristic response time (e.g. electronic response, molecular orientation, vibrational contributions, population re-distribution, thermal effects, transient nonlinearity)\(^2\). Thus, the use of picosecond and nanosecond excitation allow the determination of the electronic and the transient nonlinear response of NLO polymers.

7. Z-scan measurement
In z-scan measurement a graph is drawn between z position and transmission of input beam energy (532 nm, 5 ns laser excitation) (Figure 3).

![Figure 3. Open aperture z-scan of polymer P1](image)

Here beam energy is measured by two pyroelectric probes out of which one monitors input energy and other the transmitted energy. From this figure it is noticed that the material exhibits optical limiting property because transmittance decreases with increase in pump fluency\(^2\). Further it is also observed that transmission response is symmetric about the focus and intensity dependant absorption effect is noticed. It can be observed that the system exhibits a pre-focal peak followed by a post-focal valley, indicative of self-defocusing behavior corresponding to negative sign nonlinear refraction, when excited with either picosecond or nanosecond laser pulses in the visible region\(^2\). The self defocusing effect is due to local variation of refractive index with temperature. The localized absorption of tightly focused beam propagating through the absorbing dye medium produces a spatial distribution of temperature in the dye solution and a phase distortion of the propagating beam occurs due to spatial variation of refractive index that act as a thermal lens\(^2\). The experimental data points are in well agreement with the numerical data points which were observed from the Figure 3 and also by curve fitting procedure. From this the effective TPA coefficient (\(\beta\)) found to be 5.1 \(\times 10^{-12}\) m/W.

8. Computational Study
The minimum energy based geometry optimization of polymer (P1) was performed at different levels of theory, namely at Hartree-Fock (HF), DFT-B3LYP and MP2 with one of the basis sets 6-311G* using Gaussian 09 software. The optimized energy and electrical dipole moment of P1 is shown in Table 1 whereas HOMO and LUMO molecular orbitals are shown in Figure 4. It is observed that the total charge is located at the center of the molecule in the HUMO case whereas in the case of LUMO, the charge is spreads out from the center of the molecule.
Figure 4. HOMO and LUMO configuration of the carbazole which is obtained from the DFT (B3LYP) 6-311G** basis sets

Table 1. Energy and dipole moment of P1 which is calculated from the theoretical quantum mechanical calculations using HF, DFT and MP2 methods

| Polymer /basis set | Theoretical calculations (gaseous state) |   |   |   |
|-------------------|---------------------------------------|---|---|---|
|                   | HF 6-311G**  | DFT 6-311G** | MP2 6-311G** |
| Energy (in a.u)   | -1745.18 | -1756.75 | -1749.21 |
| Dipole moment (Debye) | 5.906  | 7.466  | 5.905  |
| HOMO value        | -0.19830 | -0.19581 | -0.27533 |
| LUMO value        | -0.00348 | -0.06929 | 0.05719 |

9. Conclusions
Carbazole based NLO polymer was synthesized by using Knoevenagel condensation reaction to yield polymer soluble in highly polar solvents like dimethyl formamide and dimethylsulphoxide. The GPC study of polymer indicated the molecular weight was around 5000 g/mol. Thermal analysis showed that the polymer, having Tg at 214°C, was stable up to 400°C. The polymer film has good optical transparency. The non-centrosymmetry was checked by poling for second order NLO property, and the SHG measured was found to be negligible. The z-scan technique was used to find out the polymer’s third order NLO property. The effective TPA coefficient (β) found to be 5.1 X 10^{-12} m/W. As observed in computational study, the total charge is located at the center of the molecule in HUMO case whereas in the case of LUMO charge is spreads out from the center of the molecule.

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