Chapter 5

PHOTOVOLTAIC AND NLO APPLICATIONS OF THE CONJUGATED POLYMERS

5.1 Introduction
5.2 Results and discussion
5.3 Conclusion

Conducting polymers have found a wide range of applications in the field of electronics and photonics, exploiting the unique physical, chemical and electrical properties of the polymers. Inherent electrical conductivity is the most notable property of conducting polymers, which is closely connected to the charge transfer rate and electrochemical redox efficiency. Most conducting polymers act as semiconductors, eventhough, several studies on metallic conducting polymers have been reported. In this chapter, the photovoltaic and nonlinear optical applications of conducting polymers are discussed. We have explored the photoactivity of the polymers by fabricating a heterojunction with a device structure of ITO/In$_2$S$_3$/polymer/ Ag. Further improvement in the power conversion efficiency can be achieved by optimizing the device parameters. The nonlinear absorption coefficient ($\beta$), nonlinear refractive index ($n_2$), the real and imaginary parts of $\chi^{(3)}$ (Re $\chi^{(3)}$ and Im $\chi^{(3)}$) and the third order nonlinear susceptibility $\chi^{(3)}$ of the polymers were also evaluated.
5.1 Introduction

In this 'polymer age', tremendous advancement has been made in the field of optoelectronics by new designs and new concepts in materials science. The replacement of traditional inorganic semiconductors by organic molecules, polymeric or even biological materials has been termed as 'molecular electronics'. Molecular electronic materials can offer viable alternatives to the traditional inorganic materials in many applications because of their abundance, diversity, ease of production, fabrication and potential high performance/low cost.\textsuperscript{1-10} Now-a-days, various polymeric materials have replaced the conventional materials such as metals and alloys in number of applications, like, aerospace, light engineering machinery, household goods, electronics etc, thus bringing about cost-effectiveness, reduction in size and weight. This has been possible because of the various mechanical and electrical properties which can be tailored into the polymers by a number of synthetic and processing techniques. Molecular engineering helps to control the electronic/optical properties of a resulting device by altering/modifying the polymer structure before fabricating the actual device. However, there still remains some fields where polymers have to enter in which metals still have an upper hand. Nevertheless, this situation may not last long since rapid advances are taking place in the field of conducting polymers. Literature suggests that they are promising in chemical and bio-sensors, field-effect transistors, light emitting devices, solar cells, super capacitors, actuators and separation membranes etc.\textsuperscript{11-20}

The present chapter is concerned with the photovoltaic and third order nonlinear optical properties of the synthesised conjugated polymers.
5.1.1 Photovoltaics

As a solution to present-day energy crisis, solar energy has received much attention as an alternative source of energy due to its natural abundance and non-polluting nature. Amongst the various methods, photovoltaics has gained much popularity owing to its potential ability to provide cheap electricity. So far, only the traditional inorganic semiconductors (viz. CdS, Cu2S, Si, GaAs etc.) have been mainly used in fabricating photovoltaic solar cells. After the emergence of conducting polymers, as a new class of semiconducting materials, it has generated considerable interest in the fabrication of polymer based solar cells.20-26

In the present chapter, we have explored the photovoltaic property of a bilayer heterojunction. In a bilayer OPV cell, sunlight is absorbed in the photoactive layers composed of donor and acceptor semiconducting polymeric materials to generate photocurrent. The donor material (D) donates electrons and mainly transports holes and the acceptor material (A) withdraws electrons and mainly transports electrons. Due to the concentration gradient, the excitons diffuse to the donor/acceptor interface (Exciton Diffusion) and separate into free holes (positive charge carriers) and electrons (negative charge carriers) (Charge Separation). A photovoltaic device is generated when the holes and electrons move to the corresponding electrodes by following either donor or acceptor phase (Charge Extraction). Fig 5.1 represents the fundamental architecture of bilayer heterojunction.
In this thesis, the photovoltaic property of a bilayer heterojunction ITO/In$_2$S$_3$/polymer/Ag has been evaluated. In polymer solar cells, the front electrode is a transparent conducting oxide, such as indium-tin oxide (ITO), for hole collection. For the efficient operation of the device, the back electrode must be a low work function metal, which facilitates the collection of electrons. However, these metals are reactive and get easily oxidized in air. The corrosion is normally addressed by capping the reactive metal with a less reactive metal and by encapsulating the device to protect it from environmental effects during operation. On the other hand, the devices can be made more stable by inverting the device geometry such that the holes and electrons generated in the active layer in the direction opposite to that in a normal device. In this reversed geometry, a hole blocking layer, usually, an inorganic n-type semiconductor is inserted between the ITO and the active layer so that only electrons are collected by the ITO, where as the
back electrode becomes the hole collecting positive electrode, which can be made from a high work function metal that is more stable in air. Here, we have used indium sulfide (In$_2$S$_3$) as the electron selective layer. In$_2$S$_3$, an n type compound semiconductor with high electron affinity, wide band gap and excellent photosensitivity, should function as efficient electron acceptor/hole blocking layer in polymer photovoltaics. Its potential as buffer layer material in inorganic solar cells has already been demonstrated.  

### 5.1.2 Nonlinear optics

The unusual optical properties of conducting polymers like large nonlinear optical response, low switching energy, rapid switching times make them useful in the field of optoelectronics, which is aimed at replacing metal compounds that operate using electricity. Many approaches have been exploited to engineer the nonlinear optical response in conjugated polymers including the extension of conjugation length and the increase in planarity of the conjugated backbone. It was found that the magnitude of the third-order nonlinearity increases as the conjugation length increases and also incorporation of donors and acceptors into conjugated molecules could induce a charge redistribution upon photoexcitation resulting in exceptionally large third-order nonlinearities.

Third order nonlinear optical properties provide the means to control light with light, to alter the frequency of the colour of light and to amplify one source of light with another. Because of their large optical nonlinearities and good mechanical, chemical, thermal and optical stability, polymer materials are among the leading practical materials for device applications. A number of techniques have been proposed to obtain information about the
dispersion, the sign and the contributions of both the real and imaginary parts of the nonlinear optical response. Five experimental techniques are currently widely used to characterize the third order nonlinear optical coefficient $\chi^{(3)}$ of materials: a) The degenerate four wave mixing technique (DFWM), which gives the magnitude and response of $\chi^{(3)}$ b) Optical Kerr effect (OKE), which is normally sensitive to the real part of $\chi^{(3)}$, but can be modified to determine the imaginary part c) the Z-scan technique, which gives the size and sign of the nonlinearity and also allows time resolution d) third harmonic generation, which probes the electronic component of the nonlinearity and e) the electric field induced second harmonic generation technique (EFISH) which is used to measure the nonlinear response in liquids.

5.1.2.1 Z-scan technique

The third order NLO properties of the polymers were investigated using z-scan technique. The Z-scan technique was developed to simultaneously measure the magnitude of both the nonlinear refraction (NLR) and nonlinear absorption (NLA). The sign of the nonlinear refractive index ($n_2$) can also be obtained at the same time.

In nonlinear optics, z-scan measurement is used to measure the nonlinear refractive index $n_2$ and the nonlinear absorption coefficient via the "closed" and "open" methods respectively. In closed z-scan setup, an aperture is placed to prevent some of the light from reaching the detector. A lens focuses the laser to a certain point, and after this point, the beam naturally defocuses. After a further distance, an aperture is placed with a detector behind it. The aperture causes only the central region of the cone of
light to reach the detector. In open z-scan, the aperture is removed or enlarged to allow all the light to reach the detector. This is used in order to measure the nonlinear absorption coefficient. For materials with negative $n_2$, the profile of the z scan transmittance curve consists of a peak followed by a valley. For positive $n_2$ materials, the profile is reversed with a valley-peak sequence. The preceding description assumes that the sample is purely refractive and nonlinear absorption is not present. In cases in which the material has a significant nonlinear absorptive coefficient, the z scan profile is distorted, multiphoton absorption suppresses the peak and accentuates the valley, and saturation produces the opposite response.40

5.1.2.2 Optical limiting

An optical limiter is a device designed to keep the power, irradiance, energy or fluence transmitted by an optical system below some specified maximum value regardless of the magnitude of the input, i.e., maintaining a high transmittance at low input powers. The most important application of this device is the protection of sensitive optical sensors and components from laser damage. There are many other potential applications for these devices, including laser power regulation, stabilization or restoration of signal levels in optical data transmission or logic systems.41-43

Optical limiting effect results from intensity dependent optical nonlinear processes viz (a) nonlinear absorption (NLA) (b) nonlinear refraction (NLR) (c) nonlinear scattering (NLS), (d) photorefraction (PR) and (e) optically induced phase transitions. The minimum criteria identified for a material to act as an effective optical limiter are a) having a high linear transmittance b) a low limiting threshold c) a fast response time (e.g.
picoseconds or faster) c) a broad band response (e.g. the entire visible spectrum). d) low optical scattering.

Various approaches have been developed towards better optical limiting based on, e.g., electro-optical, magneto-optical, and all-optical mechanisms. The all-optical limiters rely on materials that exhibit one or more of the nonlinear optical mechanisms: two-photon absorption (TPA), excited state absorption (ESA), free carrier absorption, thermal defocusing and scattering, photorefraction, nonlinear refraction, induced scattering. Coupling two or more of these mechanisms has also achieved enhancement in optical limiting, like self-defocusing in conjunction with TPA, TPA in one molecule with ESA in another molecule.44

5.2 Results and discussion

5.2.1 Photovoltaic device fabrication

Photovoltaic activity of all the synthesised conjugated polymers were evaluated, in which one polymer was found to be promising. Heterojunction photovoltaic device was fabricated using the polymer (P(FMT) (poly-dimethoxythiophene–alt-dioctyl fluorene) as the active layer and the compound semiconductor In$_2$S$_3$ as the electron collecting layer. In$_2$S$_3$ is an n-type semiconductor having high electron affinity and is a potentially good acceptor material like CdS and TiO$_2$ for polymer solar cells. Indium sulfide (In$_2$S$_3$) thin films were deposited on ITO coated glass substrates by spraying aqueous solutions of indium chloride (InCl$_3$), and thiourea (CS(NH$_2$)$_2$), keeping the substrate at 350ºC with a spray rate of 4 ml/min. The thickness of the film was 200 nm. Heterojunctions were prepared by spin coating a solution of polymer in chlorobenzene, on top of the In$_2$S$_3$ layer. The layer
thickness was approximately 100 nm as obtained from Stylus profilometer measurements. Silver electrodes were vacuum deposited (at a pressure of \( \sim 6 \times 10^{-6} \) Torr) on top of the polymer layer and served as the end contact. The schematic diagram is shown in figure 5.2. Dark and illuminated J-V characteristics of the cell were measured using a Keithley Source Measure Unit (SMU, K236) and Metric’s Interactive Characterization Software (ICS). The cell was illuminated using a tungsten halogen lamp, with an intensity of 50mW/cm\(^2\), on the substrate surface. An infrared filter, along with a water jacket, was used to ensure that there was no heating of the cell during the measurement.

**Fig. 5.2: Schematic diagram of In\(_2\)S\(_3\)/Polymer heterojunction**

Figure 5.3 shows the current density-voltage (J-V) characteristics of the heterojunction of the polymer P(FMT) under illumination and in the dark. As could be seen, the device clearly exhibits rectifying behaviour in the dark which may be due to the barrier formed at the In\(_2\)S\(_3\)/ polymer
interface. Under white light illumination, the device of P(FMT) exhibits a short circuit current density (Jsc) of 0.69 mA/cm² and open circuit voltage (Voc) of 463 mV. The fill factor (FF) and efficiency for P(FMT) were calculated to be 30 and 0.09% respectively.

![J-V characteristics of ITO/In₂S₃/polymer/Ag heterojunction of P(FMT)](image)

**Fig. 5.3: J-V characteristics of ITO/In₂S₃/polymer/Ag heterojunction of P(FMT)**

### 5.2.2 Open and Closed Scan Measurements

By employing the z-scan technique developed by Sheik Bahae et al, the third-order nonlinear susceptibility χ (3) of synthesized copolymers in chloroform was evaluated. NLO measurements were performed by single by single beam z scan technique with nanosecond laser performed with a Q-switched Nd: YAG laser system (Spectra Physics LAB – 1760) with pulse width of 7 ns at 10 Hz repetition rate and 532 nm wavelength. In the
experiment, a Gaussian laser beam was focused to a narrow waist (42.56 μm). The sample was mounted on the translation stage and the transmitted intensity through the sample was measured, with and without the presence of an aperture at far field in front of the photodetector. As the sample moves through the beam focus (z = 0), self-focusing or self-defocusing modifies the wavefront phase, thereby modifying the detected beam intensity. The Rayleigh length, \( Z_0 = \pi \omega_0^2 / \lambda \), was calculated to be a higher value greater than the thickness of the sample cuvette (1mm), an essential requirement for z-scan experiments. The system was calibrated using CS\(_2\) as the standard. The transmitted beam energy, reference beam energy and their ratios were measured simultaneously by an energy ratiometer having two identical pyroelectric detector heads. The effects of fluctuations of laser beam was eliminated by dividing the transmitted power by the power obtained at the reference detector. Optical power limiting measurements were also carried out to investigate the power limiting behaviour of the samples.\(^{46}\)

To investigate the optical limiting property of the polymers, the nonlinear transmission was measured as a function of input fluence. Optical limiting property of a material is mainly due to absorptive nonlinearity, which corresponds to the imaginary part of third-order susceptibility, i.e., it could be due to TPA, free carrier absorption, RSA, self-focusing, self-defocusing or induced scattering. In conjugated polymeric materials, electrons can move in the molecular orbitals, which results from the linear superposition of the carbon p\(_z\) atomic orbitals. This leads to high optical nonlinearity, which increases with conjugation length. On the other hand, nonlinearity is the result of an optimum combination of various factors such as
\( \pi \)-delocalization length, donor–acceptor groups, dimensionality, conformation, and orientation for a given molecular structure. The results indicate that these polymers can be used for optical power limiting at high laser fluences.\(^{47-50}\)

Here, the third order NLO properties of all the polymers were investigated using z-scan technique.\(^{51}\) The open aperture (OA) z-scan trace of all the synthesized polymers were carried out. The nonlinear absorption coefficient, \( \beta \) was obtained by fitting the experimental scan plot of the OA measurement to equation (1):\(^{51}\)

\[
T(z) = \frac{c}{q_0 \sqrt{\pi}} \int_{-\infty}^{\infty} \ln (1 + q_0 e^{-t^2}) dt \quad \text{...........................(5.1)}
\]

where, \( q_{0(x,t)} = \beta I_0(t) L_{eff} \) and \( L_{eff} = \frac{1 - e^{-\alpha t}}{\alpha} \) the effective thickness with linear absorption coefficient, \( \alpha \) and \( 'I_0' \) is the irradiance at focus. The imaginary part of the third order susceptibility is given by the equation (2):\(^{51}\)

\[
I_m = \frac{n_0^2 c^2 \beta}{24 \pi^2 \omega} \quad \text{..................................................(5.2)}
\]

where, \( n_0 \) is the linear refractive index of the polymer solution, \( 'c' \) is the velocity of light in vacuum, \( '\omega' \) is the angular frequency of radiation used. Closed aperture z-scan technique was carried out to determine the sign and magnitude of nonlinear refraction (NLR) property of the polymers. The NLR z-scan curve after excluding nonlinear absorption effects was obtained from the ratio of closed aperture normalized z-scan data to the
corresponding normalized open aperture data. The normalized transmittance, \( T(z) \) for NLR is given by the equation, \(^{51}\)

\[
T_z = 1 - \frac{4x\Delta\phi_0}{(x^2 + 9)(x^2 + 1)}
\] .............................................. (5.3)

where \( T(z) \) is the normalized transmittance for the pure refractive nonlinearity at different \( z \), \( \phi_0 \), is on- axis nonlinear phase shift and \( x \) is given by \( z/z_0 \). The nonlinear refractive index (\( n_2 \)), the real parts of \( \chi^{(3)} \) (\( \text{Re} \chi^{(3)} \)) and third order nonlinear susceptibility (\( \chi^{(3)} \)) are calculated by the following equations. \(^{51}\)

\[
n_2(\text{esu}) = \frac{en_0}{40\pi} \gamma
\] ............................................... (5.4)

\[
\text{Re} \chi^{3} = \frac{n_0n_2}{3\pi}(\text{esu})
\] ................................................ (5.5)

\[
\chi^{(3)} = \text{Re} \chi^{(3)} + i\mu X^{(3)}
\] ........................................... (5.6)

where, ‘\( \gamma \)’ is the molecular cubic hyperpolarizability of the polymer which can be estimated through the equations \( \gamma = \frac{\Delta n_0}{I_0} \) and \( \Phi \Delta n_0 = \frac{\Delta \phi_0}{k_{eff}} \) where, ‘\( k \)’ is the wave vector.

a) Fluorene-Quinoxaline polymers

The open –aperture (OA) z-scan trace of the three polymers P(FQ-A), P(FQ-B) and P(FQ-P) in CHCl\(_3\) is shown in figure 5.4.
Fig. 5.4: Open aperture z-scan traces of the polymers: a) P(FQ-A), (b) P(FQ-B) and (c) P(FQ-P). (Energy of the laser is 100 μJ)

Here, the three polymers show a normalized transmittance valley, indicating that the polymers behave as reverse saturation absorber (RSA) with a positive NLO absorption coefficient. The nonlinear absorption of the three copolymers were fitting well with two photon absorption (TPA). The calculated values of nonlinear absorption coefficient ($\beta$, m/W) and imaginary value of third order nonlinear susceptibility ($\chi^{(3)}$ esu) are given in the
The polymers show large optical nonlinearity due to strong delocalisation of \( \pi \) electrons.

**Table 5.1:** Nonlinear absorption coefficient \( (\beta, \text{m/W}) \), imaginary value of third order nonlinear susceptibility \( (\text{Im } \chi^{(3)} \text{ esu}) \) and optical limiting threshold \((\text{GW/cm}^2)\) of copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \beta \times 10^{10} ) (m/W)</th>
<th>( \text{Im } \chi^{(3)} \times 10^9 ) (esu)</th>
<th>Optical limiting threshold ((\text{GW/cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(FQ-A)</td>
<td>8.32</td>
<td>0.79</td>
<td>0.47</td>
</tr>
<tr>
<td>P(FQ-B)</td>
<td>5.32</td>
<td>0.69</td>
<td>0.48</td>
</tr>
<tr>
<td>P(FQ-P)</td>
<td>7.86</td>
<td>1.04</td>
<td>0.47</td>
</tr>
</tbody>
</table>

**Optical limiting**

Recently, Conducting polymers have drawn significant attention as optical limiters for eyes or for sensor protection from laser or laser threats on the battle-field. Optical limiters are devices that transmit light at low input fluences or intensities, but become opaque at high inputs. The optical limiting property occurs mostly due to absorptive nonlinearity, which corresponds to the imaginary part of third-order susceptibility. An important term in the optical limiting measurement is the limiting threshold. It is obvious that the lower the optical limiting threshold, the better the optical limiting material. The nonlinear optical properties of conducting polymers are of great interest for optical switching, pulse power shaping of an OPO (optical parametric oscillator)/OPG (optical parametric generator), and other nonlinear optical applications. However, the great potentials of conducting polymers as optical power limiters have just begun to be recognized. Optical limiting experiment was carried out
at 532 nm using OA z-scan technique. Fig 5.6 shows the transmitted energy of the polymers P(FQ-A), P(FQ-B) and (c) P(FQ-P). Here the three polymers show comparable optical limiting threshold values (Table 5.1).

Fig. 5.6: Optical limiting curves of the polymers a) P(FQ-A), (b) P(FQ-B) and (c) P(FQ-P).
b) Fluorene-thiophene copolymer

The open –aperture (OA) and closed aperture z-scan trace of the two polymers P(FMT), and P(EF) in CHCl₃ were taken. Fig 5.7 presents the open aperture z-scan traces of the copolymers. The solid curves in the figure are the theoretical fit to the experimental data.

![Diagram of z-scan traces]

*Fig. 5.7: Open aperture z-scan traces of the polymers P(FMT) and (c) P(EF). (Energy of the laser is 100 μJ).*

Here the open aperture z-scan traces of the polymers show normalized valley, indicating the presence of reverse saturation absorption (RSA) with a positive coefficient. It is seen that the experimental curve is fitted well with two photon absorption theory. The calculated values of nonlinear absorption coefficient (β, m/W) and the imaginary part of third order nonlinear susceptibility (χ(3) esu ) are given in the table 5.2. From the table it is clear that two polymers show comparable third order nonlinear response. In donor-acceptor polymers nonlinearity is mainly due to strong delocalisation of π electrons.
Table 5.2: Nonlinear absorption coefficient ($\beta$, m/W), imaginary value of third order nonlinear susceptibility ($\text{Im } \chi^{(3)}$, esu) and optical limiting threshold (GW/cm$^2$) of copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\beta \times 10^{10}$ (m/W)</th>
<th>$\text{Im } \chi^{(3)} \times 10^9$ (esu)</th>
<th>Optical limiting threshold (GW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(FMT)</td>
<td>12.93</td>
<td>1.72</td>
<td>0.32</td>
</tr>
<tr>
<td>P(EF)</td>
<td>12.98</td>
<td>1.86</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The nonlinear refractive (NLR) property of the copolymers were also investigated using closed aperture method. After excluding the nonlinear absorption effects, the pure NLR z-scan curves can be obtained by dividing the closed aperture z-scan data by corresponding open aperture data.

The polymers P(FMT) and P(EF) show the transmittance maximum followed by valley pattern. The copolymers show strong self defocussing behaviour and negative nonlinear refraction coefficient, $n_2$. Here nonlinear refractive index $n_2$, the real part of $\chi^{(3)}$ and the third order nonlinear susceptibility were also calculated by using the equations 4-6.

![Closed aperture z-scan traces of the polymers P(FMT) and (c) P(EF).](image)

(Energy of the laser is 100 μJ)
Optical limiting

Optical limiting experiment was carried out at 532 nm for the polymers P(FMT) and P(EF) using OA z-scan technique. The deviation from linearity is taken as the optical limiting threshold. Here the optical limiting threshold values of the polymers P(FMT) and P(EF) are 0.48 GW/cm² and 0.35 GW/cm² respectively as shown in figure 5.9 and Table 5.2.

![Optical limiting curves of the polymers P(FMT) and P(EF).](image)

**P(FMT)**  
**P(EF)**

**Fig. 5.9: Optical limiting curves of the polymers P(FMT) and (c) P(EF).**

c) EDOT based polymers

The open –aperture (OA) z-scan trace of P(EHT) and P(EC) in CHCl₃ is shown in figure 5.10. Here the copolymers show a normalized transmittance valley, showing reverse saturation type of absorption with positive NLO absorption coefficient. The normalised transmittance for open aperture z-scan was calculated. The theoretical curves obtained with the equation 3 (Section 5.2.2) were fitted with the experimental data for RSA. The nonlinear absorption coefficient ($\beta$, m/W) and the imaginary part of third order nonlinear susceptibility ($\chi^{(3)}$, esu) were calculated. The results are given in Table 5.3.
Fig. 5.10: Open aperture z-scan traces of the polymers P(EHT) and (c) P(EC). (Energy of the laser is 100 μJ).

Table 5.3: Nonlinear absorption coefficient ($\beta$, m/W), imaginary value of third order nonlinear susceptibility ($\text{Im}\chi^{(3)}$, esu) and optical limiting threshold (GW/cm$^2$) of copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\beta \times 10^{10}$ (m/W)</th>
<th>$\text{Im}\chi^{(3)} \times 10^9$ (esu)</th>
<th>Optical limiting threshold (GW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EHT)</td>
<td>13.15</td>
<td>2.73</td>
<td>0.38</td>
</tr>
<tr>
<td>P(EC)</td>
<td>12.35</td>
<td>1.62</td>
<td>0.28</td>
</tr>
</tbody>
</table>

In the closed aperture z-scan technique, P(EC) shows the transmittance maximum followed by valley pattern. It exhibits strong self defocussing behaviour and negative nonlinear refraction coefficient, $n_2$. Here nonlinearity is mainly due to charge transfer from donor to acceptor i.e., due to strong delocalisation of $\pi$-electrons. The nonlinear refractive index $n_2$, the real part of $\chi^{(3)}$ and the third order nonlinear susceptibility values were also calculated and is shown in Table 5.6. For the closed aperture z-scan of polymer P(EHT), the signal obtained did not fit well in the theoretical curve.
Optical limiting

Figure 5.12 shows the transmitted energy of copolymers as a function of input fluence. The optical limiting process occurs mostly due to nonlinear absorption. When the energy reaches optical limiting threshold, the transmitted energy starts to deviate and exhibits an optical limiting effect. Here the optical limiting threshold values of the polymers P(EHT) and P(EC) are 0.47 GW/cm² and 0.48 GW/cm² respectively (Table 5.3).
d) Cyanovinyline based polymers

Here, the three polymers (P(CN1), P(CN2) and P(CN3) show normalized valley in the open aperture z-scan technique, indicating that the polymers are behaving as reverse saturation absorber (RSA) with a positive NLO absorption coefficient (Figure 5.13). The nonlinear absorption of the three copolymers was fitting well with the two photon absorption (TPA). The calculated values of nonlinear absorption coefficient (β, m/W) and imaginary value of third order nonlinear susceptibility (χ(3), esu) are given in the table 5.4.

![Open aperture z-scan traces of the polymers P(CN1), P(CN2) and P(CN3). (Energy of the laser is 100 μJ).](image)
Table 5.4: Nonlinear absorption coefficient ($\beta$, m/W), imaginary value of third order nonlinear susceptibility ($\text{Im } \chi^{(3)}$, esu) and optical limiting threshold (GW/cm$^2$) of copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\beta \times 10^{10}$ (m/W)</th>
<th>$\text{Im } \chi^{(3)} \times 10^9$ (esu)</th>
<th>Optical limiting threshold (GW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(CN1)</td>
<td>9.47</td>
<td>1.25</td>
<td>0.47</td>
</tr>
<tr>
<td>P(CN2)</td>
<td>10.36</td>
<td>1.38</td>
<td>0.37</td>
</tr>
<tr>
<td>P(CN3)</td>
<td>2.53</td>
<td>0.34</td>
<td>0.45</td>
</tr>
</tbody>
</table>

The nonlinear refractive (NLR) property of the copolymers were also investigated using closed aperture method. After excluding the nonlinear absorption effects, the pure NLR z-scan curves can be obtained by dividing the closed aperture z-scan data by corresponding open aperture data.

The polymer P(CN1) and P(CN2) show the transmittance maximum followed by valley pattern. The copolymers show strong self-focussing behaviour and negative nonlinear refraction coefficient, $n_2$. Here nonlinear refractive index $n_2$, the real part of $\chi^{(3)}$ and the third order nonlinear susceptibility were also calculated using the equations. The results show that the polymers show good nonlinear optical response and can be ideal candidates for nonlinear optical devices.
Figure 5.14: Closed aperture z-scan traces of the polymers P(CN1) and P(CN2) (Energy of the laser is 100 μJ).

Optical limiting

To investigate the optical limiting threshold of the polymers P(CN1), P(CN2) and P(CN3) open aperture z-scan technique was used. Optical limiting property of a material is mainly due to absorptive nonlinearity, is the result of a combination of factors such as extent of conjugation, donor-acceptor groups, dimensionality, conformation and orientation. As shown in figure 5.15, the optical limiting threshold values for the polymers P(CN1), P(CN2) and P(CN3) are 0.47 GW/cm², 0.37 GW/cm² and 0.45 GW/cm² respectively (Table 5.4). The results show that the polymers can be used for optical power limiting at high laser fluences.
e) Phenylene based polymers

The third order NLO properties of phenylene based polymers were also investigated using z-scan technique. The open aperture z-scan traces of the three polymers in chloroform is given in the fig 5.16. From the plot it is clear that the three polymers show reverse saturable absorption. The nonlinear absorption coefficient ($\beta$, m/W) is obtained by fitting the experimental data using the equation 1 and imaginary value of third order nonlinear susceptibility ($\chi^{(3)}$ esu) is also calculated and is shown in Table 5.5.
Fig. 5.16: Open aperture z-scan traces of the polymers P(PDO), P(POF) and P(PF). (Energy of the laser is 100 μJ).

Table 5.5: Nonlinear absorption coefficient (β, m/W), imaginary value of third order nonlinear susceptibility (Im $\chi^{(3)}$ esu) and optical limiting threshold (GW/cm$^2$) of copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\beta \times 10^{10}$ (m/W)</th>
<th>$\text{Im } \chi^{(3)} \times 10^9$ (esu)</th>
<th>Optical limiting threshold (GW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PDO)</td>
<td>3.0</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td>P(POF)</td>
<td>6.93</td>
<td>9.24</td>
<td>0.43</td>
</tr>
<tr>
<td>P(PF)</td>
<td>8.02</td>
<td>1.06</td>
<td>0.43</td>
</tr>
</tbody>
</table>
Optical limiting

Optical limiters are devices designed to have high transmittance for low level inputs, while blocking the transmittance for high intensity laser beams.

Molecules that exhibit reverse saturable absorption (RSA) show strong limiting behavior. Here the optical limiting property of the polymers P(PDO), P(POF) and P(PF) were studied and is shown in figure 5.17 and Table 5.5. All the polymers show comparable optical limiting property and are promising candidates for future optical limiters.

Fig. 5.17: Optical limiting curves of the polymers P(PDO), P(POF) and P(PF)
In closed aperture z-scan, only five polymers exhibited peak-valley characteristics, indicating the negative NLR index due to self defocussing. The nonlinear refraction coefficient ($n_2$) and the real value of third order nonlinear susceptibility ($\chi^{(3)}$) of these polymers were calculated and are given in table 5.6.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Nonlinear refractive index $n_2 \times 10^9$ (esu)</th>
<th>Imaginary part of nonlinear Susceptibility $\text{Im}\chi^{(3)} \times 10^9$ (esu)</th>
<th>Real part of nonlinear susceptibility $\text{Re}\chi^{(3)} \times 10^9$ (esu)</th>
<th>Nonlinear susceptibility $\chi^{(3)} \times 10^9$ (esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(CN1)</td>
<td>-0.11</td>
<td>1.25</td>
<td>-0.02</td>
<td>1.56</td>
</tr>
<tr>
<td>P(CN2)</td>
<td>-0.12</td>
<td>1.38</td>
<td>-0.02</td>
<td>1.37</td>
</tr>
<tr>
<td>P(EC)</td>
<td>-0.27</td>
<td>1.62</td>
<td>-0.04</td>
<td>1.62</td>
</tr>
<tr>
<td>P(EF)</td>
<td>-0.14</td>
<td>1.86</td>
<td>-0.02</td>
<td>1.86</td>
</tr>
<tr>
<td>P(FMT)</td>
<td>-0.25</td>
<td>1.72</td>
<td>-0.04</td>
<td>1.72</td>
</tr>
</tbody>
</table>

5.3 Conclusion

Photovoltaic and NLO properties of all the synthesized copolymers were evaluated. Of these polymers, P(FMT) showed good photovoltaic activity with device structure of ITO/In$_2$S$_3$/P(FMT)/Ag. Third order nonlinear optical studies were also conducted for all the thirteen polymers. It was found that all the synthesised donor-acceptor conjugated polymers showed good third order nonlinear optical properties because of the strong intramolecular charge transfer between the donor and the acceptor units. All
the copolymers showed optical power limiting behaviour at 532 nm. Thus all the synthesised polymers can be used as ideal candidates in nonlinear optical applications.

References


