3.1 Introduction

Molecularly doped photoconductors are liable to phase separation when more components are added for additional functionality.\textsuperscript{1,2} This is a potential drawback for their application to photorefractivity where components will be present for inducing electro-optic functionality and for reducing the glass transition temperature of the photorefractive composite. Although the approach to molecularly doped photoconducting system is rather simple, for practical applications more stable systems are required. If the polymer backbone as such is photoconducting, the stability can be improved. Also, this has an added advantage that the polymer itself takes part in the grating formation whereas in molecularly doped systems, the host polymer has the role of an inert matrix and it does not actively participate in charge transport or generation.\textsuperscript{3}

In this chapter, three polybenzoxazines are studied for possible use in photorefractive polymers. Though non-conjugated, these polymers possess electronically isolated electron rich units in its main chain. There are reports on methods for tailoring chemical\textsuperscript{4,5} and physical properties\textsuperscript{6} of this class, but polybenzoxazines have not been studied for optoelectronic applications so far. The polymers were doped with electron acceptor molecules
mentioned in Section 1.4.6 to study the possibility of getting an enhancement in photocurrent. It is to be noted that the systems presented in this chapter are only photoconducting, no dipolar molecules were added with an intention to induce photorefractivity. The aim was to identify molecules with good photoconductivity and spectral response. $C_{60}$ and two more electron acceptor molecules, 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,4,6-trinitrophenol (TNP) were tried as photosensitizers.

3.2 Preparation of sandwich cell Structure

Sandwich cells of the polymer for electrical measurements were prepared as follows. 8 wt% solution of the polymer was prepared in chloroform which also contained 1 wt% dioctyl phthalate (DOP), which was found to increase the stability of the polymer on ITO substrates. The solution was filtered through a $0.2 \mu m$ teflon filter and casted onto clean ITO plates. The casted samples were allowed to dry overnight at room temperature ($28 \pm 1^0 C$) and then transferred to a vacuum desiccator and kept at $\sim 10^{-2}$ Torr. A drying period of 48 h was given for maximum solvent removal. Film thickness was determined using a stylus profiler (Dektak 6M) and those with nearly 15-20 $\mu m$ were selected for the deposition of top electrode.

To sensitize the polymer with electron acceptors, the molecules given in Section 1.4.6 were used. TCNQ, TNP and $C_{60}$ were used as dopants. The concentration of these molecules was kept to $\sim 10^{-5}$ mol/l.

Top electrode was given by vapor deposition of silver in a vacuum chamber. To avoid damage to the film surface, the rate of deposition of silver was kept low. The active area of the device, defined by the silver contact was in the range 36-42 mm$^2$. As silver could form unreacted contacts with organic molecules, complications due to chemically induced interfacial states could be discarded. The general structure of the sandwich cell was ITO/Polymer:DOP:Dopant/Ag. Synthesis of these molecules are given elsewhere. Following sections gives the details of the polymers and the results obtained.
3.3 Poly(6-tert-butyl-3,4-dihydro-2H-1,3-benzoxazine)

Poly(6-tert-butyl-3,4-dihydro-2H-1,3-benzoxazine), labeled as P1, is a non-conjugated polymer with an electron rich phenyl ring. The structure of the molecule is shown in Fig. 3.1. The t-butyl substituent on this ring is expected to increase the density of electrons in the ring. Non-bonding electrons are available on the nitrogen and oxygen. As such, the polymer could be regarded as comprising electronically isolated electron rich groups. The glass transition temperature of the polymer was 46°C, determined using DSC. The molecule is soluble in organic solvents such as toluene, chloroform and chlorobenzene. It has good film forming properties and the films are transparent.

![Figure 3.1: Poly(6-tert-butyl-3,4-dihydro-2H-1,3-benzoxazine), (P1).](image)

The number average molecular weight (\(M_n\)) of P1 was 403 and weight average molecular weight (\(M_w\)) was 1080, which were estimated using size exclusion chromatography. The polydispersity index (\(M_w/M_n\)) was 2.7.

3.3.1 Optical absorption spectrum

The optical absorption spectrum of P1 in solution and in film form on quartz substrate are shown in Fig. 3.2. The onset of absorption in the visible was near 490 nm. The absorption coefficient (\(\alpha\)) was evaluated using the relation \(\alpha = (A/L) \ln(10)\) with \(A\) as the measured absorbance and \(L\) as the film thickness in cm.
The first absorption band in the visible (375-475nm) region correspond most probably to a weak $n - \pi^*$ transition\(^9\) which also give rise to strong fluorescence. It involve the excitation of the non-bonding orbital electrons on the hetero atom to the $\pi^*$ molecular orbital extending over the conjugated part in the polymer. The nature of the transition ($n - \pi^*$ or $\pi - \pi^*$) was clarified by studying the effect of polarity of solvent on this transition. It was based on the hydrogen bonding effect, which induce a blue shift in the absorption band corresponding to an $n - \pi^*$ transition.\(^{10-12}\)

The solvent effect on the band was studied using solvents Acetic acid, Dimethylformamide (DMF) and Toluene. Fig. 3.3 shows the blue shift
of this absorption band when the solvent was changed from least polar (toluene) to highly polar (acetic acid) thereby confirming the transition to be $n - \pi^*$. 

### 3.3.2 Fluorescence quenching

The polymer showed fluorescence when excited with light of energy greater than the optical gap. The fluorescence spectrum of the polymer was studied with and without electron acceptors. Emission from the molecule was quenched when electron acceptor molecules (TCNQ, TNP and C$_{60}$) were present. The quenching of fluorescence intensity when P1 was doped with the same concentration of electron acceptors is shown in Fig. 3.4.

![Fluorescence quenching effect of TCNQ, TNP and C$_{60}$.](image)

Figure 3.4: Fluorescence quenching effect of TCNQ, TNP and C$_{60}$. Excitation was at 400nm.

The fluorescence quenching could be either due to electron transfer or due to energy transfer. The strength of energy transfer depends on the Förster radius which in turn depends on the relative overlap between emission band of polymer and the absorption band of the acceptor. If the emission band of the polymer and the absorption band of the dopant are not overlapping, the possibility of quenching through an energy transfer can be ruled out. The absorption spectra of the electron acceptor molecules in chloroform were given in section 1.4.6. The absorption spectra of TNP and TCNQ were not overlapping with the emission spectrum of P1. Thus the possibility of energy transfer appeared to be low. Absorption spectrum
of \(C_{60}\) overlaps with the emission spectrum of P1. There are literature reports about the ultra-fast electron transfer reaction in \(C_{60}\) doped polymers and resulting fluorescence quenching.\(^\text{16}\) Transient fluorescence experiments may be required for conclusive statements about electron transfer.

### 3.3.3 Cyclic voltammetry

Cyclic Voltammetry was used to estimate the reduction potential of the polymer as explained in Section 1.6.5. The cyclic voltammogram of P1 is shown in Fig. 3.5.

![Cyclic voltammogram of P1.](image)

The onset of reduction was at -540 mV. The corresponding LUMO position was estimated to be 3.86 eV. Assuming the optical gap as the separation between the HOMO and LUMO levels, the HOMO was estimated to be 6.27 eV. The optical gap was estimated to be 2.41 eV. It is to be noted that the single particle LUMO position would be higher by the exciton binding energy,\(^\text{17}\) hence there exists an uncertainty up to the value of the exciton binding energy in the above values. Moreover, the solid state values of HOMO and LUMO energy levels usually depend on other factors such as the polarizability of the matrix.\(^\text{18}\)

### 3.3.4 Temperature dependence of conductivity

Measurement of the current-voltage characteristics with temperature permitted the study of the temperature dependence of conductivity (\(\sigma\)) of
the samples. Figure 3.6 shows the dependence of the dc conductivity on temperature.

The temperature dependence of \( \sigma \) showed the semiconducting behavior with two activation energy regions. The near room temperature region showed an activation energy of 0.26 eV while the lower temperature region showed an activation energy of 0.20 eV. Both these values were calculated from the slope of the graph in the regions of interest.

### 3.3.5 Modulated photocurrent measurement

The spectral dependence of the photocurrent was studied using the modulated photocurrent technique explained in section 1.6.4. The photocurrent action spectrum was measured for different electric fields. The spectra are given in Fig. 3.7 for both polarities of ITO.
Figure 3.7: Photocurrent action spectra of sandwich cells of P1 (ITO/P1:DOP/Ag) for ITO_+ (left) and ITO_- (right).

The spectra were similar with respect to the biasing given to the electrodes. When light is absorbed by an organic semiconductor, the primary product is an exciton. It is the dissociation of this exciton which initiate charge generation. If the exciton density created by light was dissimilar at the top and bottom contacts, the spectra would depend on the polarity of the electrodes and the efficiency with which the electrode dissociates the exciton. Such a behavior was absent, which was primarily due to the low absorption in the film. Due to weak absorption, illumination could be considered uniform throughout the bulk and thus a uniform density of excitons was expected.¹⁹

Figure 3.8: Optical absorption spectra of the electron acceptor molecules C_{60}, TNP and TCNQ in chloroform.

The photocurrent action spectra were recorded for the films doped with electron accepting molecules TNP, TCNQ and C_{60} also. Optical absorp-
tion spectra of these sensitizer molecules were given in section 1.4.6. It is reproduced here as Fig. 3.8.

3.3.5.1 Effect of TNP

Absorption of TNP was strong in the 400nm region (Fig. 3.8). The spectrum of P1 doped with TNP showed an increase in absorption in the 425nm region of the absorption spectrum of P1.

Figure 3.9: Absorption spectrum of P1 doped with TNP.

Fig. 3.10 shows the photocurrent action spectra of the sandwich cell ITO/P1:TNP:DOP/Ag for both polarities of ITO.

Figure 3.10: Photocurrent action spectra of sandwich cells of P1 doped with TNP for ITO+ (left) and ITO− (right).

TNP was not a good photosensitizer for P1 as the spectral response of
films of P1 doped with TNP did not show an appreciable increase in photocurrent.

### 3.3.5.2 Effect of TCNQ

Optical absorption of TCNQ is at its maximum near 400nm region (Fig.3.8). This molecule is considered to be a strong electron acceptor. The charge transfer complexes of TCNQ were subjected to numerous studies.\textsuperscript{20,21} The absorption spectrum of P1 doped with TCNQ is shown in Fig. 3.11. The spectrum was similar to the undoped film except an increase in absorbance. Also, the absorption in the near infra red region was increased with the characteristic bands of TCNQ. But the photocurrent in this region remained unchanged.

![Absorption spectrum of P1 doped with TCNQ.](image)

Figure 3.11: Absorption spectrum of P1 doped with TCNQ.

The figure (Fig. 3.12) shows the action spectra of sandwich cells with TCNQ as the dopant. But there was no significant increase in the photocurrent when doped with TCNQ.
TCNQ was also not able to act as a good sensitizer for P1. The order of photocurrent remained the same.

### Effect of C$_{60}$

C$_{60}$ has the ability to increase the hole mobility in hole transport layers.\textsuperscript{22} It can also serve as a good photosensitizer for photorefractive polymers.\textsuperscript{23} Optical absorption of this molecule span the entire visible spectrum. Absorption spectrum of P1 doped with C$_{60}$ is shown in Fig. 3.13.

Absorption spectrum of the C$_{60}$ doped state of P1 did not show the formation of any new bands. The spectrum was only a simple overlap of
the spectra of both molecules thereby indicating weak mixing of ground state electronic wave functions. The photocurrent action spectrum of P1 doped with C$_{60}$ is shown in Fig. 3.14. Doping the polymer with C$_{60}$ yielded higher photocurrents along with an increase in photocurrent near the red region of the spectrum.

![Figure 3.14: Photocurrent action spectra of sandwich cells of P1 doped with C$_{60}$ for ITO$^+$ (left) and ITO$^-$ (right).](image)

C$_{60}$ doped P1 showed photoconductivity in the entire visible region of the spectrum. Fig. 3.15 shows a comparison between the photocurrent values for positive and negative biasing to ITO.

![Figure 3.15: Comparison of the action spectra showing the bias dependence of photocurrent for 30V/$\mu$m.](image)
Biasing given to ITO had a small effect on the magnitude of the measured photocurrent. Photocurrent was more when ITO was negatively biased with respect to the other electrode. This behavior and its possible reason are discussed in section 3.4.5.1.

### 3.3.6 Photoconductive sensitivity

Photoconductive sensitivity (S) of the doped polymer is the material parameter of interest. It was estimated using equation 1.16. The photoconductive sensitivity for selected wavelengths are shown in Table 3.1.

#### Table 3.1: Photoconductive sensitivity of the sandwich cells of P1 for different wavelengths (@30V/µm, ITO−).

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Photoconductive Sensitivity $10^{-14}$ (S cm W$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{60}$</td>
</tr>
<tr>
<td>440</td>
<td>1336</td>
</tr>
<tr>
<td>490</td>
<td>1487</td>
</tr>
<tr>
<td>530</td>
<td>1488</td>
</tr>
<tr>
<td>630</td>
<td>2034</td>
</tr>
</tbody>
</table>

Photoconductive sensitivity of the order of $10^{-12}$ S cm W$^{-1}$ was reported for $C_{60}$ sensitized photorefractive polymers. Photoconductive sensitivity observed in P1 doped with $C_{60}$ at 30V/µm was of the order of sensitivity values required for observing photorefractive effect in polymers. A value of $1.07 \times 10^{-11}$ (S cm W$^{-1}$) was reported for a PVK:$C_{60}$ based photorefractive polymer. Thus P1:$C_{60}$ may be used as a photoconducting host provided the photoconductive sensitivity is not reduced when electro-optic functionality is incorporated by other molecules.
3.4 Poly(6-tert-butyl-3-methyl-3,4-dihydro-2H-1,3-benzoxazine)

Structure of Poly(6-tert-butyl-3-methyl-3,4-dihydro-2H-1,3-benzoxazine), labeled as P2, is shown in Fig. 3.16. The polymer P2 was a slightly modified form of P1. A methyl group was linked to the nitrogen in the monomer unit of P1 to get P2. The electron donating nature of this unit is expected to shift the HOMO level towards higher energy.\(^{28}\) Higher HOMO level favor hole injection from the ITO electrode,\(^ {29}\) which further result in a higher exciton dissociation rate.

![Structure of Poly(6-tert-butyl-3-methyl-3,4-dihydro-2H-1,3-benzoxazine), P2.](image)

The glass transition temperature of this polymer was 49\(^0\) C. The number average molecular weight (\(M_n\)) was 239 and weight average molecular weight (\(M_w\)) was 971, as estimated using size exclusion chromatography. The polydispersity index (\(M_w/M_n\)) was 4.

3.4.1 Optical absorption spectrum

The optical absorption spectrum of the polymer is shown in Fig. 3.17 for both film and solution. Film thickness was 1.2 \(\mu\)m, solution concentration was 0.001g/ml in chloroform and path length was 1 cm.
3.4.2 Fluorescence quenching

Fluorescence from the polymer was quenched in the presence of electron accepting molecules. TNP, TCNQ and \( \text{C}_60 \) were tried as photo-sensitizers.
for P2 also. Thus the effect of these molecules on the fluorescence intensity was studied. Fig. 3.19 shows the reduction in intensity observed when the film of P2 was doped with electron acceptor molecules.

![Figure 3.19: Fluorescence quenching effect of TNP, TCNQ and C\textsubscript{60} on P2.](image)

As earlier, observation of fluorescence quenching alone could not be considered as a solid evidence for an electron transfer. But there was an increase in photocurrent yield as will be seen in Section 3.4.5.1. This hints at the possibility of an electron transfer process.

### 3.4.3 Cyclic voltammetry

The cyclic voltammogram of P2 is shown in Fig. 3.20. The onset of reduction was at -620 mV. The corresponding LUMO position was estimated to be 3.78 eV and HOMO was 6.41 eV. The optical gap was 2.63 eV.

![Figure 3.20: Cyclic voltammogram of P2.](image)
Above values do not include the correction for the exciton binding energy. The exciton binding energy in polymers is of the order of 0.5 eV.\textsuperscript{30}

### 3.4.4 Temperature dependence of conductivity

The temperature dependence of electrical conductivity of P2 is shown in Fig. 3.21. Two activation energies were extracted from the slopes of the graph.

![Temperature dependence of conductivity](image)

Figure 3.21: Temperature dependence of the dark conductivity of P2. The line is a linear fit to the data.

The below room temperature region gave an activation energy of $121(\pm5)$ meV and the lower temperature region gave an activation energy of $52(\pm4)$ meV.

### 3.4.5 Modulated photocurrent measurement

The photocurrent action spectrum of P2 is shown in Fig. 3.22 for different electric fields. The photocurrent was more for ITO biased positive showing that the ITO could inject more holes into the polymer than silver. The work function of the electrodes were almost the same (-4.8eV for ITO and -4.7eV for silver). The barrier for hole injection from ITO to the polymer might be smaller by 0.1eV, resulting in slightly higher current when ITO
was biased positive. The value of 0.1 eV was so small that this much asymmetry in injection barrier could not cause a significant change in the shape of the photocurrent action spectrum as revealed by the similarity in action spectra for both polarities. As the reversal of biasing resulted in only a small decrease in the photocurrent, the photocurrent was not only due to electrode sensitized dissociation of excitons, but also from the dissociation in the bulk, the latter being the higher.31

Figure 3.22: Photocurrent action spectra of sandwich cells of P2 for ITO\(^+\) (left) and ITO\(^-\) (right).

Generally, in organic semiconductors, photoconductivity is not through a direct generation of carriers, but through the formation and subsequent dissociation of an exciton. The exciton can dissociate at impurity sites, interfaces with asymmetric ionization potentials or it can be dissociated by a strong electric field.30,32

A close examination of the photocurrent action spectra revealed a small shift of the action spectra onset to lower energies at higher electric fields. This could be due to the enhanced dissociation of the less hot excitons (vibrationally relaxed)\(^{33}\) as the additional energy required for dissociation could also be supplied in the form of electric field.
3.4.5.1 Effect of TNP

The absorption spectrum of P2 doped with TNP is shown in Fig. 3.23. Significant increase in absorption was observed in the spectrum when doped with TNP.

![Absorption Spectra](image)

Figure 3.23: Absorption spectra of the films of P2 and its doped form with TNP.

Exciton dissociation can also happen at an interface where there is an ionization potential mismatch. This effect is very important in the case of organic photovoltaic devices and has been the idea behind bulk heterojunction solar cells. The effect of TNP on the action spectrum was studied for both polarities of ITO. The electron acceptor (TNP) doped samples showed an increased photocurrent yield along with a shift in the onset of photoaction spectrum. The spectra are shown in Fig. 3.24.
TNP increased the photocurrent to the values obtained by doubling the field in undoped case. This time the photocurrent was more for the case with ITO biased negative. The reason might be related to the increased absorbance in the film on doping with TNP. After doping there was a significant increase in the absorption coefficient of the host polymer. The excitations were more near the ITO and low near the silver electrode due to the self absorption in the film. Thus the number of excitons near the ITO will be very much higher than near silver. Such a higher density of excitons increases the possibility of exciton-exciton annihilation effect resulting in reduced number of free carriers.

Figure 3.24: Photocurrent action spectra of sandwich cells of P2 doped with TNP for ITO_+ (left) and ITO_- (right).

Figure 3.25: Plot of the difference in photocurrents for ITO_{neg} and ITO_{pos} for two electric fields.
The possibility of the existence of this effect in this case was evident from
the field dependence of action spectra in the high absorbing region. In Fig
3.25, the difference between the photocurrents for ITO\textsubscript{neg} and ITO\textsubscript{pos} is
plotted for 20 and 30V/\textmu m. It was seen that the difference decreased when
the electric field was increased. It is well understood that bimolecular
recombination rate is inversely related to electric field as field induced
dissociation start to compete with the former.\textsuperscript{36} Koch et. al.,\textsuperscript{37} reported
that the hole injection properties of virtually any organic-metal interface
can be optimized by using strong electron acceptors. They also reported
that the extent of increase in hole injection depend on the number of
acceptor molecules in direct contact with the metal surface. Thus the low
current in the ITO negative case might be due to the increase in hole
injection from silver electrode along with bimolecular recombination near
ITO.

\subsection{3.4.5.2 Effect of TCNQ}

The absorption spectrum showed a slight hyperchromic shift on doping
with TCNQ as shown in Fig. 3.26.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{absorption_spectra.png}
  \caption{Absorption spectra of the films of P2 and its doped from with
  TCNQ.}
\end{figure}

The photocurrent action spectra of the TCNQ doped sandwich cells of P2
are shown in Fig. 3.27 for both polarities of ITO. TCNQ did not give an
increase in photocurrent yield similar to the case with P1.
3.4.5.3 Effect of C\textsubscript{60}

The absorption spectrum of P2 doped C\textsubscript{60} film is shown in Fig.3.28. Absorbance in the entire visible region was increased.

Figure 3.28: Absorption spectra of the films of P2 doped with C\textsubscript{60}.

Action spectrum of P2:C\textsubscript{60} is shown in Fig.3.29. Photocurrent was considerably higher when P2 was doped with the molecule C\textsubscript{60}. Also, the sensitivity in the red region of the spectrum was enhanced, which make P2:C\textsubscript{60} a photoconductive system sensitive for red lasers.
Figure 3.29: Photocurrent action spectra of sandwich cells of P2 doped with C$_{60}$ for ITO$^+$ (left) and ITO$^-$ (right).

Similar to electron acceptor doped P1, the photocurrent was more when ITO was negatively biased. It could be due to the effects discussed previously, that is, dopant (electron acceptor) assisted increase in hole injection rate and bimolecular recombination. Figure 3.30 shows the bias effect for an applied field of 30V/$\mu$m.

Figure 3.30: Comparison of the action spectra showing the bias dependence of photocurrent for 30V/$\mu$m.
3.4.6 Photoconductive sensitivity

The sensitivity of the polymer to light, expressed as the photoconductive sensitivity ($S$) was estimated based on the modulated photocurrent measurement. Table 3.2 shows the values of $S$ obtained for P2 along with the values obtained when doped with electron acceptors. Here also C$_{60}$ was the best photosensitizer but the values of photoconductive sensitivity were slightly less than the values obtained in the case of P1:C$_{60}$.

Table 3.2: Photoconductive sensitivity of the sandwich cells of P2 for different wavelengths (@30V/µm, ITO$_-$).

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>C$_{60}$</th>
<th>TNP</th>
<th>TCNQ</th>
<th>Undoped</th>
</tr>
</thead>
<tbody>
<tr>
<td>440</td>
<td>816</td>
<td>36</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>490</td>
<td>825</td>
<td>17</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>530</td>
<td>726</td>
<td>12</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>630</td>
<td>1445</td>
<td>12</td>
<td>12</td>
<td>1</td>
</tr>
</tbody>
</table>

3.5 Poly(6-tert-butyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine)

Structure of the polymer is shown in Fig. 3.31. In this polymer, which was labeled as P3, a phenyl group was attached to the nitrogen.

Figure 3.31: Poly(6-tert-butyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine), (P3).
The glass transition temperature of this polymer was 52°C. The number average molecular weight (M_n) was 268 and weight average molecular weight (M_w) was 900, as estimated using size exclusion chromatography. The polydispersity index (M_w/M_n) was 3.3.

### 3.5.1 Optical absorption spectrum

Absorption spectra of the polymer is shown in Fig. 3.32. Compared to P1 and P2, the absorption coefficient of P3 was considerably increased. This may be due to the increase in the conjugation in the monomer of the polymer.

![Optical absorption spectrum](image)

Figure 3.32: Absorption spectra of the polymer P3 in solid (film on quartz). Inset shows the absorption spectrum of a chloroform solution of P3.

The low intensity absorption band in the visible region was studied using the blue shift method described earlier. The observed blue shift is shown in Fig. 3.33.

![Blue shift in absorption band](image)

Figure 3.33: Blue shift in the absorption band with increasing polarity of solvent.
The blue shift band was of very low intensity, it was clearly seen in solution form or thick film form.

3.5.2 Fluorescence quenching

In the case of P3, the molecule C_{60} showed the highest degree of fluorescence quenching. Fig. 3.34 shows the quenching of fluorescence in P3 films by the electron acceptor molecules.

Figure 3.34: Fluorescence quenching effect of TNP, TCNQ and C_{60} on P3.

3.5.3 Cyclic voltammetry

Cyclic Voltammetry was done to estimate the reduction potential of the polymer as explained in Section 1.6.5. The cyclic voltammogram of P3 is shown in Fig. 3.35.

Figure 3.35: Cyclic voltammogram of P3.
The onset of reduction was at -640 mV. The corresponding LUMO position was estimated to be 3.76 eV. The actual LUMO position may be higher by the exciton binding energy ($\approx$ 0.45eV).\textsuperscript{17} HOMO was estimated to be 6.09 eV. The optical gap was taken to be 2.33 eV. The HOMO and LUMO energy levels of P3 are very near to the reported energy levels of C$_{60}$, which are 6.2eV and 3.6eV respectively.\textsuperscript{22}

### 3.5.4 Temperature dependence of conductivity

The temperature dependence of electrical conductivity is shown in Fig. 3.36. The variation was Arrhenius type with more than one activation energy. Two activation energies were determined assuming the form $\sigma = \sigma_0 e^{-E_a/kT}$ for the variation of electrical conductivity. Here $\sigma_0$ is a prefactor value of the conductivity, $E_a$, the activation energy, $T$, the absolute temperature and $k$, the Boltzmann constant.

<table>
<thead>
<tr>
<th>$\log_{10}(\text{S.m}^{-1})$</th>
<th>$1000/T$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-27.2</td>
<td>3.2</td>
</tr>
<tr>
<td>-26.8</td>
<td>3.4</td>
</tr>
<tr>
<td>-26.4</td>
<td>3.6</td>
</tr>
<tr>
<td>-26.0</td>
<td>3.8</td>
</tr>
<tr>
<td>-25.6</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Figure 3.36: Temperature dependence of the dark conductivity of P3. Dotted lines are linear fits.

The below room temperature activation energy was 430 meV and the lower temperature activation energy was 64 meV. This indicated that the conduction mechanism near room temperature and at lower temperatures were different.
3.5.5 Modulated photocurrent measurement

The photocurrent action spectra of P3 are shown in Fig. 3.37 for different electric fields.

Figure 3.37: Photocurrent action spectra of sandwich cells of P3 for ITO$^+$ (left) and ITO$^-$ (right).

The photocurrent was higher when the ITO electrode was positively biased. This increase in the photocurrent might be due to the difference in charge injection efficiencies of both the electrodes when appropriately biased.

3.5.5.1 Effect of TNP

Doping P3 with TNP increased its absorption coefficient slightly in the ultra-violet region. Photocurrent spectra with TNP as the sensitizer are shown in Fig. 3.38.

Figure 3.38: Absorption spectra of the films of P3 with and without TNP.
Figure 3.39: Photocurrent action spectra of sandwich cells of P3 doped with TNP for ITO\textsuperscript{+} (left) and ITO\textsuperscript{−} (right).

No significant increase in photocurrent was observed for TNP doped P3. Also, the polarity dependence of photocurrent remained the same.

### 3.5.5.2 Effect of TCNQ

Absorption spectrum of P3 doped with TCNQ is shown in Fig. 3.40. Possibly due to the low concentration of the dopant, the spectrum of P3 showed no significant modifications, except an increase in absorbance.

Figure 3.40: Absorption spectra of the films of P3 and its doped form with TCNQ.

Photocurrent action spectra of P3 with TCNQ as dopant are shown in
Fig. 3.41. TCNQ was not a good photosensitizer for P3, the order of photocurrent remained the same.

Figure 3.41: Photocurrent action spectra of sandwich cells of P3 doped with TCNQ for ITO⁺ (left) and ITO⁻ (right).

3.5.5.3 Effect of C₆₀

Photocurrent measurements were also performed with C₆₀ as the sensitizer. The optical absorption spectrum of the doped film is shown in Fig. 3.42.

Figure 3.42: Absorption spectra of the films of P3 with and without C₆₀.

There was an increase in the absorption coefficient of the doped film in the entire visible region. The absorption spectrum of the film of P3:C₆₀ could be considered as a superposition of the optical absorption spectra of
P3 and C\textsubscript{60}. Corresponding photocurrent action spectra are given in Fig. 3.43.

![Photocurrent action spectra](image)

Figure 3.43: Photocurrent action spectra of sandwich cells of P3 doped with C\textsubscript{60} for ITO\textsuperscript{+} (left) and ITO\textsuperscript{−} (right).

The photocurrent detected in the C\textsubscript{60} doped case was three orders of magnitude higher than the undoped case. The spectral yield of photocurrent with C\textsubscript{60} was entirely different, but resembled the optical absorption of C\textsubscript{60} and the fluorescence spectrum of P3.

The fluorescence from the polymer was efficiently quenched by C\textsubscript{60} as shown in Fig. 3.34. As the photocurrent was very high, the quenching might be due to the ultra fast electron transfer which is reported to occur from an excited polymer chain to C\textsubscript{60}.\textsuperscript{24} When light is absorbed by an organic semiconductor, the primary product is an exciton. It is the dissociation of this exciton which initiates charge generation. Excitons created by light absorption, which normally radiatively recombine, were getting dissociated by C\textsubscript{60}. The closeness of the energy levels of the host and the dopant might be the reason for the efficient photocurrent generation. It has already been shown that energetically relaxed excitons (those created with no excess energy from the photons) can only be dissociated at charge transfer centers during the diffusion of excitons.\textsuperscript{33}

The magnitude of photocurrent action spectrum was highly dependent on the biasing given to the electrodes. Higher values were obtained when ITO was negatively biased. This could be due to the increase in injection
from silver mediated by the acceptor molecules. Bimolecular recombination effect could also be a reason for the polarity dependent increase in current as discussed in Section 3.4.5.1.

### 3.5.6 Photoconductive sensitivity

Photocurrent was dependent on the electric field applied across the polymer. The photoconductive sensitivity of P3 doped with C$_{60}$ was very high. Values of $S$ for the sandwich cells are given in Table 3.3.

Table 3.3: Photoconductive sensitivity of the sandwich cells of P3 for different wavelengths (@10V/µm, ITO$_-$).

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Photoconductive Sensitivity $10^{-14}$ (S cm W$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C$_{60}$</td>
</tr>
<tr>
<td>440</td>
<td>28280</td>
</tr>
<tr>
<td>490</td>
<td>28610</td>
</tr>
<tr>
<td>530</td>
<td>27433</td>
</tr>
<tr>
<td>630</td>
<td>34100</td>
</tr>
</tbody>
</table>

From the above table, it can be seen that P3 with C$_{60}$ as sensitizer is sensitive to most of the common laser wavelengths. The photoconductive sensitivity is sufficiently high for photorefractive effect.$^{25-27}$ Other electron acceptor molecule did not give increased photosensitivity.

### 3.5.7 Time of flight experiment

Carrier mobility could be estimated using the time of flight (TOF) method explained in Section 1.6.1. The photocurrent transient for the undoped P3 film is shown in Fig. 3.44. The transit time of the carriers (electrons, as the ITO was negatively biased) was estimated from the knee in the photocurrent transient.
Figure 3.44: Current transient in a TOF experiment done on the sandwich cell of P3. White line is a 100 point adjacent average of the data.

Carrier mobility estimated was $2.77 \times 10^{-5}$ cm$^2$ V$^{-1}$ S$^{-1}$ at an electric field of 20 V/µm. Transport of carriers was not completely dispersive as a well defined knee was observed in the TOF signal.\textsuperscript{22}

### 3.6 Summary and conclusions

Three polybenzoxazines were studied using different electron acceptors for possible use as sensitive photoconductors for photorefractive polymer systems. The HOMO and LUMO energy levels of the polymers were estimated using cyclic voltammetry. Values of these energy levels are important when considering the applicability of these polymers to other fields such as LEDs or other organic semiconductor based devices. Absorption spectra of all three polymers showed low absorption in the red and green regions of the visible spectrum.

Fluorescence emission from the polymers were found to reduce in the presence of dopants. The photocurrent is expected to increase if this fluorescence quenching is related to an efficient dissociation of the initially created excitons, which normally under go radiative recombination, in to free carriers. Three different electron acceptors were used as dopants, but a quenching associated with an increase in photocurrent was observed only in the case of C$_{60}$ doping.
Photocurrent measurements were done in the sandwich cell configuration on the three polymers. Measurements were done with and without a sensitizer. While the molecule C$_{60}$ acted as a very good sensitizer for all three polybenzoxazines, the electron acceptors 2,4,6-trinitrophenol (TNP) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) were not able to enhance the photocurrent. The increase in photocurrent when the polymers were doped with C$_{60}$ could be due to an electron transfer reaction. The electron transfer from an excited polymer to C$_{60}$ occurs in the picosecond time scales.\textsuperscript{16,24} This is shorter than the lifetime of excited states ($10^{-8}$S) which cause fluorescence. The quenching and the corresponding increase in photocurrent might be due to this ultra-fast electron transfer.

The photoconductive sensitivity was estimated and was found to be sufficient to observe photorefractive effect, based on literature reports.\textsuperscript{25–27} The molecule Poly(6-tert-butyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine) showed the highest sensitivity when doped with C$_{60}$.

References

References


