Synthesis and Characterization of Photoconductive Poly(2-methacryloyl-1-(4-azo-1’-phenyl)aniline-co-styrene)

2.1 Introduction

Photoconducting polymers are the subject of intense study owing to their potential applications in photorefractive devices,\(^1\) light emitting diodes,\(^2\) photovoltaic\(^3\) and many other optoelectronic devices. The possibility of adjusting the properties by modifying the structure is the attractive feature of polymeric systems. Photoconductivity in polymeric systems is a complex process involving absorption of radiation, generation of charge carriers, injection, transport, recombination and trapping.\(^4\)\(^-\)\(^6\)

One of the necessary requirements for photorefractivity is photoconductivity.\(^7\)\(^-\)\(^10\) The polymeric photoconductor used in practise are based on two type of systems. In the first, the charge transporting unit is a part of the polymer chain\(^11\)\(^,\)\(^12\) and in the second, low molecular weight charge generating and charge transporting molecules are embedded in a polymeric matrix. These are called molecularly doped polymers.\(^13\)\(^,\)\(^14\) A large number of polymers with charge-transporting units in the side chain and main chain, polymers with π-conjugated and σ-conjugated main chain were extensively studied.\(^6\)\(^,\)\(^15\)\(^-\)\(^17\) Different classes of photoconducting poly-
mers were discussed in Chapter 1.

In this Chapter, two different types of polymeric photoconductors are described. The first one is a molecularly doped polymer. For the present study, 2,4,6-trinitrophenol (TNP) was selected as electron acceptor, aniline as electron donor and PMMA as inert polymer matrix. The second photoconducting polymer system is a copolymer of 2-methacryloyl-1-(4-azo-1'-phenyl)aniline and styrene. The synthesis and characterization of this copolymer are also described in this chapter.

2.2 Molecularly Doped Polymers

Systems with charge generating and charge transporting molecules dispersed in an inert polymer matrix, known as molecularly doped polymers, have been the subject of numerous investigations\(^{14}\). The charge generating units are usually electron acceptors or charge transfer complexes of acceptors with donor type molecules\(^{13,18-21}\). In molecularly doped polymers, charge transport is a hopping process among the donor–acceptor molecules\(^{22,23}\). The energetic disorder between the donor and acceptor plays an important role in hopping charge transport\(^{24,25}\). The inert polymer matrix affects the energetic disorder of hopping sites during charge transport\(^{24}\).

2.3 Experimental Section

2.3.1 Materials

Aniline (Merck, AR Grade) and methanol (Sd fine, AR Grade) were purified, dried and distilled by the standard procedures\(^{26}\). Chloroform (98%, Merck, Spectroscopic Grade) was used as received. 2,4,6-trinitrophenol (Sd Fine Chemicals, AR grade) was purified by two fold recrystallization using ethanol and dried under vacuum over P\(_2\)O\(_5\) for three days. Poly(methyl methacrylate) (Mw-75,000) was reprecipitated thrice from chloroform-methanol and dried under reduced pressure.
2.3.2 Instrumentation

Absorption spectra of the samples were recorded using a Jasco V-570 UV/VIS/NIR spectrophotometer. The thickness of the film samples were measured using a Stylus (Dektak 6M) profiler.

2.3.3 Sample Preparation

The samples for photocurrent measurements were prepared by drop casting a solution of PMMA (7 wt%) containing TNP and aniline in chloroform. Three types of samples were prepared with TNP:aniline mole ratio as 1:0, 1:1 and 1:100. The concentration of TNP (0.0873 mmol) was kept low to reduce chances of phase separation. The solution was passed through a 0.2 µm PTFE filter and deposited on indium tin oxide (ITO) coated glass substrates. Overnight evaporation of the solvent at room temperature (28°C) and subsequent drying of the films for 12 h in vacuum chamber (at 10^{-2} Torr), resulted in good optical quality films of about 16 µm thickness, measured using a Stylus profiler. Silver top contacts of 25 mm^2 active area were vacuum deposited on the slightly yellow polymer films.

Modulated photocurrent detection method using a lock-in-amplifier (Stanford SR830) coupled with a chopper (Stanford SR540) was used for the measurement of the photogenerated voltage across a load resistance connected in series with the sample and a high voltage DC power supply (Stanford PS350). The spectral dependence of photocurrent was measured using the dispersed output of a Fluoromax-3 fluorimeter. The samples were irradiated from the ITO side.

2.4 Results and Discussion

Aromatic amines with unshared pair of electrons generally act as electron donors. Electron acceptors on the other hand are electron deficient species. The molecularly doped polymer (MDP) system chosen for the present study contains aniline as electron donor and TNP as electron acceptor. Aniline and TNP were dispersed in PMMA. The molecular structures
of PMMA, aniline and TNP are shown in Figure 2.1. A charge transfer complex formation was evident from the optical absorption spectra of the MDP compared to individual molecules.

![Chemical Structures of Poly(methyl methacrylate), Aniline and 2,4,6-trinitrophenol.](image)

Figure 2.1: Chemical Structures of Poly(methyl methacrylate), Aniline and 2,4,6-trinitrophenol.

### 2.4.1 Optical Absorption

The absorption spectra of aniline, TNP, TNP: aniline (1:1) and TNP:aniline (1:100) dispersed in PMMA are shown in Figure 2.2.

![UV-Vis Absorption Spectra of Aniline (A), 2,4,6-trinitrophenol (B), 2,4,6-trinitrophenol:Aniline (1:1), (C) and 2,4,6-trinitrophenol:Aniline (1:100), (D) in Poly(methyl methacrylate) Matrix.](image)

Figure 2.2: UV-Vis Absorption Spectra of Aniline (A), 2,4,6-trinitrophenol (B), 2,4,6-trinitrophenol:Aniline (1:1), (C) and 2,4,6-trinitrophenol:Aniline (1:100), (D) in Poly(methyl methacrylate) Matrix.

The absorption spectrum of TNP:aniline in 1:1 mole ratio showed bathochromic and hyperchromic shifts compared to neat samples indicating formation of a charge-transfer complex between aniline and TNP. The spectrum of TNP:aniline in 1:100 mole ratio showed an increase in absorbance,
implying a strong dependence on the concentration of the donor molecules.

### 2.4.2 Photocurrent Action Spectrum

The photocurrent action spectra of TNP:aniline in 1:1 mole ratio and 1:100 mole ratio in PMMA at an electric field of 20 V/µm are shown in Figure 2.3.

![Photocurrent Action Spectra of 2,4,6-trinitrophenol: Aniline (1:1), (A) and 2,4,6-trinitrophenol: Aniline (1:100), (B) in Poly(methyl methacrylate) Matrix.](image)

The sample with 1:1 mole ratio of TNP and aniline showed a maximum photocurrent of 0.23 pA (at 3.35 eV). Further addition of aniline molecules as a 1:100 resulted in considerable increase of photocurrent. The maximum photocurrent observed for TNP and aniline in 1:100 sample was 0.6 pA (at 3.35 eV). In the visible region (at 2.9 eV), the maximum photocurrent observed was 0.10 pA (1:1) and 0.55 pA (1:100) respectively. The decrease of photocurrent in TNP:aniline complex with 1:1 ratio may be due to the release of lesser number of free charge carriers. Photocurrent as function of applied electric field and intensity are studied and reported in detail elsewhere. An increase was observed in photocurrent upon increasing the electric field. The intensity dependence of photocurrent showed linear behavior indicating absence of bimolecular recombination and heating effects. The system showed a photoconductive sensitivity of the order
of $10^{-13}$ S cm/W. The main drawback with this system was the phase separation upon addition of excess dopants. Also, the photoconductive sensitivity of this system was very low.

### 2.5 Photoconducting Poly(2-methacryloyl-1-(4-azo-1’-phenyl)aniline-co-styrene)

Molecularly doped systems have attracted great attention because of their importance in the construction of transport theories in amorphous photoconductors.\(^{22}\) The main drawback with these systems is phase separation due to the presence of large number of low molecular dopants in the inert polymer host matrix.\(^{28}\) Hence the application of molecular doping towards stable photorefractive polymer systems is limited. In order to decrease the chances of phase separation, polymers were synthesized with charge transporting units chemically attached to the main chain or as side chain.\(^{29-31}\) Most of the photorefractive systems studied to date consist of charge transporting polymers as host for a wide variety of electro-optic chromophores.\(^{5,32,33}\)

In this section, the synthesis and characterization of a non-conjugated photoconducting copolymer, poly(2-methacryloyl-1-(4-azo-1’-phenyl)aniline-co-styrene) is described in detail. The LUMO and the HOMO levels of the polymer were evaluated using cyclic voltammetry. The lock-in technique described earlier was used to study the spectral dependence of photocurrent. The effect of C\(_{60}\) as electron acceptor on the optical absorption and photocurrent behavior of the polymer was also studied.

### 2.6 Experimental Section

#### 2.6.1 Materials

Styrene (Alfa Aesar, 97 %) was shaken with a 10 % sodium hydroxide solution to remove the inhibitor, washed with distilled water, dried over anhydrous calcium chloride and distilled under reduced pressure. Tetrahy-
drofuran (THF) (Rankem, AR Grade), methanol (S.d. Fine, AR Grade) and toluene (Rankem, AR Grade) were purified, dried and distilled by the standard procedures.\(^{26}\) Fullerene (Alfa Aesar, 97 %) was dried under vacuum over P\(_2\)O\(_5\) for three days. The following were used as received: Concentrated hydrochloric acid (Merck, AR Grade), sodium nitrite (Merck, AR Grade), crystallized sodium acetate (Merck, AR Grade), petroleum ether (Merck, AR Grade), diethylether (Rankem, AR Grade), glacial acetic acid (Merck, AR Grade), carbontetrachloride (Merck, AR Grade), pyridine (Alfa Aesar, 97 %), methacryloyl chloride (Alfa Aesar, 97 %), sodium carbonate (S.d. Fine, AR Grade), anhydrous sodium sulfate (Alfa Aesar, 97 %), methylene chloride (Alfa Aesar, 97 %), azobisisobutyronitrile (Spectrochem, 97 %), dimethyl formamide (DMF) (Spectrochem, Spectroscopic Grade, 98 %) and chloroform (Merck, Spectroscopic Grade, 98 %).

### 2.6.2 Instrumentation

NMR spectra were recorded with Bruker Advance II NMR spectrometer operating at 400 MHz for \(^1\)H and at 100 MHz for \(^{13}\)C. FT-IR spectra of the samples were taken on a Bruker 550 spectrometer. Absorption spectra of the samples were recorded using a Jasco V-570 UV/VIS/NIR spectrophotometer. A Fluoromax-3 fluorimeter was used to record the fluorescence spectra of the samples. CHN estimations were taken from Elementar Vario EL III CHNSO elemental analyzer. The molecular weight of the synthesized polymers was determined by SEC, (Waters 2414) using a column packed with polystyrene gel beads. Toluene was used as the eluent and the molecular weight was calibrated using polystyrene standards. The molecular weight was further estimated with Jeol SX 102 mass spectrometer. Glass transition temperature was determined from DSC, (Q-100, TA Instruments) under nitrogen at heating rate of 10 °C/min. Thermal stability was determined from TGA, (Q-50, TA Instruments) under nitrogen at a heating rate of 20 °C/min. Electrochemical measurements were performed in a three electrode BASi Epsilon electrochemical workstation.
2.6.3 Synthesis

2.6.3.1 Synthesis of Diazoaminobenzene

Aniline (14 g, 150 mmol) dissolved in hydrochloric acid (4 M) was cooled to 0\(^{\circ}\)C. The solution was kept in an ice-bath under magnetic stirring. A solution of sodium nitrite (5.2 g, 75.36 mmol) in distilled water (12 mL) was cooled to 0\(^{\circ}\)C. This cold solution was added drop wise to aniline solution with constant stirring. Crushed ice (50 g) was introduced into the system to keep the temperature at 0\(^{\circ}\)C. Crystallized sodium acetate (21 g, 256 mmol) dissolved in distilled water (40 mL) was added to the above mixture, upon which a yellow solid precipitated. The solid was collected via filtration and washed with cold distilled water (250 mL). The compound was recrystallized from light petroleum.

Yield: 89 %; mp: 95-96 \(^{\circ}\)C. FTIR (KBr) \(\nu \text{ cm}^{-1}\): 3332 (aromatic NH st), 1454 (-N=N st), 3201 (aromatic CH st), 1600-1545 (aromatic C=C st). \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta\): 4.77 (s, 1H), 9.71 (m, 1H), 7.24-7.49 (m, 2H), 7.14-7.53 (m, 2H), 7.99 (m, 1H). \(^13\)C NMR (100 MHz CDCl\(_3\)) \(\delta\): 117.93, 130.72, 121.11, 129.59, 117.93, 125.24, 122.78. Mass (m/e): 197 (molecular ion peak). Anal. Calcd for: C\(_{12}\)H\(_{11}\)N\(_3\) - C, 73.07; H, 5.62; N, 21.30. Found: C, 73.15; H, 5.60; N, 21.25.

2.6.3.2 Synthesis of p-Aminoazobenzene

At first, aniline hydrochloride was prepared by treating aniline (2 g, 21.50 mmol) with HCl (3 mL, 12 M) and this mixture was cooled to 0\(^{\circ}\)C. Upon cooling, the off white solid precipitated out was filtered and washed with diethylether.

Finely crushed diazoaminobenzene (5 g, 25.38 mmol) was dissolved in aniline (15 g, 161.29 mmol). Aniline hydrochloride (2.5 g, 19.37 mmol) was added to it. The reaction mixture was heated at 40-45 \(^{\circ}\)C for 1 h and the reaction was allowed to stand for further 30 min. The aniline present in excess was removed as a soluble acetate by treating with glacial acetic acid (15 mL) diluted with distilled water (15 mL). The mixture was stirred for 15 min, during which, precipitation of p-aminoazobenzene
was observed. The precipitate was filtered and washed several times with distilled water. The orange-yellow solid obtained was recrystallized from carbontetrachloride.

Yield: 68 %; mp: 125 °C. FTIR (KBr) ν cm⁻¹: 3323, 3315 (aromatic NH₂ st), 1452 (-N=N st), 3207 (aromatic CH st), 1600-1540 (aromatic C=C st). ¹H NMR (400 MHz CDCl₃) δ: 2.21 (s, 2H), 9.71 (m, 1H), 7.24-7.49 (m, 2H) 7.14-7.53 (m, 2H), 7.99 (m, 1H). ¹³C NMR (100 MHz CDCl₃) δ: 114.54, 130.72, 121.11, 129.59, 117.93, 125.24, 122.78, 145.17, 149.74. Mass (m/e): 197 (molecular ion peak). Anal. Calcd for: C₁₂H₁₁N₃ - C, 73.07; H, 5.62; N, 21.30. Found: C, 73.10; H, 5.62; N, 21.28.

2.6.3.3 Synthesis of 2-Methacryloyl-1-(4-azo-1'-phenyl)aniline

p-Aminoazobenzene (2.0 g, 10.16 mmol) was dissolved in 25 mL dry THF under N₂. To the solution, pyridine (0.1 g, 1.26 mmol) and methacryloyl chloride (1 mL, 10.26 mmol) were added drop wise simultaneously. The reaction was carried out at 0°C with magnetic stirring for 3 h and then at room temperature for 48 h. The resulting mixture was washed with HCl (0.1 M), Na₂CO₃ (5 %) and finally with distilled water. The excess solvent was evaporated under reduced pressure. The organic layer was dried over anhydrous Na₂SO₄. The reaction product obtained was purified by column chromatography using methylene dichloride.

Yield: 72 %; mp: 128 °C. FTIR (KBr) ν cm⁻¹: 1454 (-N=N st), 3332 (aromatic NH st), 3207 (aromatic CH st), 1600-1545 (aromatic C=C st), 1715 (C=O st), 1674 (H₂C=C), 2958, 2849 (sy & ay C-H st). ¹H NMR (400 MHz CDCl₃) δ: 1.72 (s, 1H), 9.71 (m, 1H), 7.24-7.49 (m, 2H), 7.14-7.53 (m, 2H), 7.99 (m, 1H), 1.59 (s, 3H), 4.15 (s, 2H). ¹³C NMR (100 MHz CDCl₃) δ: 160.73, 130.72, 121.11, 129.59, 117.93, 125.24, 122.78, 145.17, 149.74, 24.36, 114.54. Mass (m/e): 265 (molecular ion peak). Anal. Calcd for: C₁₆H₁₅N₃O - C, 72.43; H, 5.70; N, 15.84. Found: C, 72.45; H, 5.73; N, 15.82.
2.6.3.4 Polymerization

2-methacryloyl-1-(4-azo-1’-phenyl)aniline (1 g, 3.77 mmol), styrene (0.39 g, 3.75 mmol) and azobisisobutyronitrile (2 g, 12.19 mmol) were dissolved in dry DMF (35 mL). The reaction was carried out at 110 °C for 72 h, under N₂. The resulting solid was dissolved in DMF and reprecipitated from methanol. Polymer was collected by filtration, dried under vacuum, and obtained as a dark brown powder.

Yield: 68 %. FTIR (KBr) ν cm⁻¹: 1460 (-N=N st), 3332 (aromatic NH st), 3207 (aromatic CH st), 1600-1545 (aromatic C=C st), 1715 (C=O st), 2924 (H₂C), 2958, 2849 (sy & ay C-H st, -CH₃).

¹H NMR (400 MHz CDCl₃) δ: 2.21 (s, 1H), 9.71 (m, 1H), 7.24-7.49 (m, 2H), 7.14-7.53 (m, 2H), 7.99 (m, 1H), 0.40 (s, 3H), 2.21, 2.17 (s, 4H).

¹³C NMR (100 MHz CDCl₃) δ: 160.73, 130.72, 121.11, 129.59, 117.93, 125.24, 122.78, 145.17, 149.74, 21.54, 44.21, 40.43.

2.6.4 Sample Preparation

The samples for photocurrent measurements were prepared by drop casting an 8 wt% solution (7 mL) of the polymer and DOP (1 wt%) in chloroform. The polymer:C₆₀ composite was prepared by dissolving of C₆₀ (6.55 x 10⁻⁶ moles) and dioctylphthalate (1 wt%) in 8 wt% solution (7 mL) of the polymer in chloroform. The concentration of C₆₀ molecules were kept at 10⁻⁵ moles/litre. The solution was passed through a 0.45 μ Nylon filter and deposited on ITO coated glass substrates. Overnight evaporation of the solvent at room temperature (28 °C) and subsequent drying of the films for 12 h in vacuum chamber (at 10⁻² Torr), resulted in good optical quality films of about 15 μm thickness, measured using a Stylus profiler. Silver top contacts of 36 mm² active area were deposited on the polymer films. Photoconductivity measurements were done using the modulated photocurrent technique.¹³
2.7 Results and Discussion

2.7.1 Synthesis and Characterization

Poly(2-methacryloyl-1-(4-azo-1'-phenyl)aniline-co-styrene), comes under the class of polymers with side chain electronically isolated photoconducting groups discussed in Section 1.2.2. It is a copolymer of 2-methacryloyl-1-(4-azo-1'-phenyl)aniline and styrene. The polymer was synthesized via radical initiated polymerization of 2-methacryloyl-1-(4-azo-1'-phenyl)aniline and styrene, using solution polymerization technique.

![Figure 2.4: Synthesis Route of Diazoaminobenzene.](image)

![Figure 2.5: Synthesis Route of p-Aminoazobenzene.](image)

![Figure 2.6: Synthesis Route of 2-Methacryloyl-1-(4-azo-1'-phenyl)aniline.](image)

The synthesis route of monomers diazoaminobenzene, p-aminoazobenzene and 2-methacryloyl-1-(4-azo-1'-phenyl)aniline are shown in Figure 2.4, Figure 2.5 and Figure 2.6. Diazoaminobenzene and p-aminoazobenzene were
obtained by the standard diazotization of benzenamine. The synthesis of 2-methacryloyl-1-(4-azo-1’-phenyl)aniline was carried out by reacting p-aminooazobenzene and methacryloyl chloride. The monomers were obtained in acceptable yields. The monomers have good solubility in common organic solvents such as THF, DMF, chloroform, acetone and acetonitrile. The structure of monomers were confirmed using elemental analysis, FT-IR, ($^1$H & $^{13}$C) NMR and mass (FAB-MS) spectral analysis.

The synthesis route of poly(2-methacryloyl-1-(4-azo-1’-phenyl)aniline-co-styrene) is shown in Figure 2.7. Copolymerization of 2-methacryloyl-1-(4-azo-1’-phenyl)aniline was carried out in dry DMF using azobisisobutyronitrile (AIBN) as a radical initiator. The polymer was obtained in moderate yield (68 %) with good solubility in common organic solvents such as chloroform, acetone, THF, DMF, toluene and acetonitrile. The structure of the polymer was confirmed using FT-IR and ($^1$H & $^{13}$C) NMR spectroscopy. The average molecular weight and polydispersity index of the polymer were determined using SEC. The polymer can be processed into thin transparent films. The polymer has a deep brown color.

The $^1$H NMR spectrum of the polymer is shown in Figure 2.8. The detailed spectral values of monomers and polymer are given in the section 2.6.3. The resonance peak at 2.21 ppm correspond to proton of the
NH group. The peaks at 7.82, 7.10, 7.91, 7.92, 7.48 and 7.50 ppm are assigned to the aromatic protons. The resonance at 4.40 ppm correspond to vinyl proton (H\textsubscript{2}C=C-) and the peak at 1.59 ppm to methyl proton of the monomer 2-methacryloyl-1-(4-azo-1'-phenyl)aniline.

Figure 2.8: $^1$H NMR Spectrum of the Polymer.

The absence of peak at 4.40 ppm and the shift of resonance peak of the methyl proton from 1.59 ppm to higher field (0.40 ppm) in the NMR spectrum of poly(2-methacryloyl-1-(4-azo-1'-phenyl)aniline-co-styrene) indicated polymerization. In addition, the NMR spectrum of the polymer displayed peaks corresponding to methylene protons in the main chain (2.17 and 2.21 ppm).

Figure 2.9: $^{13}$C NMR Spectrum of the Polymer.

The structure of the polymer was further confirmed with $^{13}$C NMR. The $^{13}$C NMR spectrum of the polymer is shown in Figure 2.9. The resonance peaks at 149.71, 145.33, 136.86, 132.13, 121.22, 117.66 and 117.92 ppm are assigned to aromatic carbon. The resonance signal at 152.95 and 145.40 ppm correspond to the aromatic carbon (C-N=N-C). The peak at 114.54 ppm due to vinyl carbon is absent in the NMR spectrum of the polymer.
The resonance peak at 24.36 ppm of methyl carbon is shifted to 21.54 ppm in the spectrum of poly(2-methacryloyl-1-(4-azo-1’-phenyl)aniline-co-styrene). Two new peaks found at 44.21 and 40.43 ppm in the spectrum were attributed to methylene carbons of 2-methacryloyl-1-(4-azo-1’-phenyl)aniline and styrene, which confirmed copolymerization.

![FT-IR Spectrum of the Polymer](image)

Figure 2.10: FT-IR Spectrum of the Polymer.

FT-IR spectrum of the polymer is shown in Figure 2.10. The band at 3424 cm\(^{-1}\) is associated with the NH group. The band at 1454 cm\(^{-1}\) is the symmetric stretching of N=N group. The disappearance of band around 1647 cm\(^{-1}\), stretching vibration of aliphatic double bond of the monomer, and the presence of new band at 2857 and 3019 cm\(^{-1}\) are attributed to methylene aliphatic single bond asymmetric and symmetric C-H stretching vibration.

![Size Exclusion Chromatogram of the Polymer](image)

Figure 2.11: Size Exclusion Chromatogram of the Polymer.
Figure 2.11 shows SEC of the polymer. The number average molecular mass ($M_n$) was 4987 and weight average molecular mass ($M_w$) was 12326. The polydispersity index ($M_w/M_n$) obtained was 2.47. The polymer exhibited a broad molecular weight distribution.

![Figure 2.11: SEC of the polymer.](image)

Figure 2.12: Differential Scanning Calorimetric Curve of the Polymer.

The DSC curve of the polymer is shown in Figure 2.12. The glass transition temperature of the polymer was 46.85 °C. The polymer showed well defined melting point at 72.98 °C.

![Figure 2.12: DSC curve of the polymer.](image)

Figure 2.13: Thermogram of the Polymer.

The thermogram of the polymer is shown in Figure 2.13. The degradation process started at around 273.72 °C and reached maximum degradation...
at 426.12 °C. The polymer showed good thermal stability indicating occurrence of strong inter- and intramolecular dipolar interactions originated by the presence of high charge delocalization in the macromolecular side chain.\textsuperscript{34}

**2.7.2 Electrochemical Properties**

The conducting and semiconducting properties of polymers generally depend on the extent of separation between the HOMO and LUMO energy levels.\textsuperscript{35,36} The lower the energy gap, better the semiconducting properties. Polymers with increased conjugation have lower energy gap between the HOMO-LUMO levels.\textsuperscript{37,38}

The electrochemical behavior of the polymer was studied using cyclic voltammetry. The measurement was carried out at 25°C in dimethylformamide solution containing 0.1 M tetrabutylammonium chloride as supporting electrolyte with a glassy carbon working electrode. Ag/AgCl was used as the reference electrode. The experiment was calibrated with the standard ferrocene/ferrocenium redox system. The potential was cycled between 0 to 2 V at a constant sweep rate of 25 mVs\textsuperscript{-1}. The cyclic voltammogram is shown in Figure 2.14.

![Cyclic Voltammogram of the Polymer](image)

**Figure 2.14: Cyclic Voltammogram of the Polymer.**

The polymer showed the onset of reduction at -0.626 eV. The onset potential was used to calculate the LUMO level, according to the equation,
\[ E_{LUMO} = [E_{\text{red (onset)}}] + 4.4 \text{ eV}. \] The LUMO energy level was estimated as 3.77 eV. The actual single particle LUMO position is higher by the exciton binding energy (\(~ 0.5 \text{ eV}). The HOMO level for the polymer was obtained from the optical gap calculated from the absorption edge. The HOMO energy level of the polymer was 5.75 eV. The optical gap of the polymer was 1.98 eV. The values are calculated based on 4.4 eV for ferrocenium redox system with respect to zero vacuum level.\(^{40}\)

### 2.7.3 Optical Absorption

The optical absorption spectra of the polymer films with and without C\(_{60}\), are shown in Figure 2.15. The spectrum of C\(_{60}\) in chloroform is also given, which showed all characteristic bands in the range 4.5-1.9 eV. The polymer showed two absorption bands centered in the 3.62-1.63 eV and 4.39-3.66 eV spectral regions. The intense band appeared in the low energy region is related to the combined contributions of the n-\(\pi^*\), first \(\pi-\pi^*\) and internal charge transfer electronic transitions of azobenzene chromophores.\(^{41}\) The band in the high energy corresponds to the \(\pi-\pi^*\) electronic transition of the aromatic ring. Upon addition of C\(_{60}\) to the polymer, no additional absorption bands appeared in the spectrum, which could be due to weak mixing of the ground state electronic wave functions.\(^{42}\)

![Figure 2.15: Optical Absorption Spectra of the Polymer, C\(_{60}\) and C\(_{60}\) Doped Copolymer.](image)
The photoluminescence studies were carried out on undoped and C\textsubscript{60} doped polymer samples.\textsuperscript{43} Fluorescence quenching was observed upon doping with C\textsubscript{60}. The addition of 0.00487 mmol of C\textsubscript{60} quenches the photoluminescence (PL) intensity of polymer by 66\%. Enhanced photoconductivity was observed in C\textsubscript{60} doped polymer samples. The efficient quenching of PL intensity and enhanced photocurrent on addition of C\textsubscript{60} may possibly be due to photoinduced charge transfer of electrons from the polymer to the acceptor molecule.\textsuperscript{44}

### 2.7.4 Photocurrent Action Spectrum

Photocurrent action spectrum of undoped and C\textsubscript{60} doped samples at an electric field of 10 V/\textmu m with ITO biased positive is shown in Figure 2.16.

![Photocurrent Action Spectra of the Polymer and C\textsubscript{60} Doped Copolymer.](image)

The polymer showed maximum photocurrent of 2.25 \mu A/m\textsuperscript{2} at 2.5 eV and 3.84 \mu A/m\textsuperscript{2} at 3.6 eV. The photocurrent of the polymer was significantly enhanced upon addition of small amount of C\textsubscript{60}. The polymer doped with C\textsubscript{60} showed a maximum photocurrent of 15.79 \mu A/m\textsuperscript{2} (1.99 eV), 15.14 \mu A/m\textsuperscript{2} (2.5 eV) and 27.31 \mu A/m\textsuperscript{2} (3.6 eV) respectively. The enhanced photoconductivity could be due to the electron transfer reaction between C\textsubscript{60} and the polymer.
The photoconductive sensitivity of the polymer was found to be $10^{-12}$ S cm/W. The C$_{60}$ doped polymer showed enhanced photoconductive sensitivity. The photoconductive sensitivity observed was $22.9 \times 10^{-12}$ S cm/W at 630 nm.

2.8 Conclusions

Photoconductivity studies were done on molecularly doped PMMA with aniline as electron donor and TNP as electron acceptor. Bathochromic shift was observed in the absorption spectrum in dispersed state indicating formation of charge transfer complex between aniline and TNP, similar to TNF-PVK system. A maximum photocurrent of 0.6 pA (3.35 eV) was observed at an electric field of 20 V/µm. The photoconductive sensitivity of the molecularly doped system was found to be $10^{-13}$ S cm/W.

Non-conjugated photoconducting copolymer, poly(2-methacryloyl-1-(4-azo-1'-phenyl)aniline-co-styrene) was synthesized via radical initiated polymerization of 2-methacryloyl-1-(4-azo-1'-phenyl)aniline and styrene, using solution polymerization technique. The structure of the polymer was confirmed using ($^1$H and $^{13}$C) NMR and FT-IR spectroscopy. The polymer showed broad distribution of molecular weights. Quenching of photoluminescence and enhancement of photoconductivity upon addition of C$_{60}$ were observed. The polymer showed maximum photocurrent of $2.25 \mu$A/m$^2$ (at 2.5 eV) at an electric field of 10 V/µm. The photoconductive sensitivity of the polymer was found to be $10^{-12}$ S cm/W. The C$_{60}$ doped polymer showed a maximum photocurrent of 15.14 µA/m$^2$ (at 2.5 eV) at 10 V/µm. The photoconductive sensitivity of the C$_{60}$ doped polymer was $22.9 \times 10^{-12}$ S cm/W.
References


