Synthesis and Characterization of Electro-Optic Poly(3-methacryloyl-1-(4’-nitro-4-azo- 1’-phenyl) phenylalanine-co-methyl methacrylate

5.1 Introduction

Non-linear optical chromophore functionalized polymers have greater advantages over the guest-host systems. In guest-host systems, the NLO chromophore possessing high first hyperpolarizability are dispersed in an inert amorphous polymer matrix of high optical transparency. However, guest-host systems are found to be of low NLO activity. Orientational relaxation, poor solubility, thermal and environmental instability of chromophores in the host polymer matrix are major reasons behind low NLO activity. In order to improve the above mentioned drawbacks, various designing methods were adopted to attach NLO chromophores into the polymer backbone. The designing method involves NLO chromophore functionalized side-chain and main-chain polymers, chromophoric main-chain polymers with NLO-active side chains, crosslinked NLO polymers and ferroelectric polymers.

In this chapter, the synthesis, characterization and electro-optic studies on a NLO-chromophore functionalized polymer are discussed. In NLO-chromophore functionalized polymers, the NLO chromophores are cova-
lently bonded to the polymer backbone via chemical modifications.\textsuperscript{12} The advantages of NLO-chromophore functionalized polymers over guest-host systems are: high concentration of NLO chromophores can be introduced to the polymer backbone, absence of phase separation, greater stability towards orientational relaxation and they can be processed into thin films.\textsuperscript{13–15} This class of polymers usually have polystyrene, poly(methyl methacrylate) and polyethylene type backbone.

The electro-optic polymer, poly(3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl)phenylalanine-co-methyl methacrylate) was synthesized via radical polymerization. It is a copolymer of methyl methacrylate and azo dye-substituted methacrylate. Azo-substituted polymers are receiving greater attention because of their potential applications in the field of non-linear optics, optical storage media, etc.\textsuperscript{16,17} Azo polymers have good transparency and high non-linear optical susceptibility.\textsuperscript{18–20} The presence of azo group in the chromophore results in extended conjugation.\textsuperscript{21} The extended conjugation between donor and acceptor groups is responsible for enhanced NLO properties.

The synthesized polymer was characterized by NMR ($^1$H, $^{13}$C) and FT-IR spectroscopy. The copolymer system showed an increased stability compared to the guest-host system studied in the previous chapter. The molecular weight was determined by SEC. The glass transition temperature, thermal stability and the degradation behavior was studied using DSC and TG analysis. The optical absorption spectrum of the copolymer was also studied. The electro-optic coefficient of the copolymer was measured using a transmission technique.

### 5.2 Experimental section

#### 5.2.1 Materials

4-nitroaniline (98 %, Merck) was purified by recrystallization from ethanol. The following chemicals were used as received without further purification: concentrated hydrochloric acid (Merck, AR Grade), sodium nitrite (Merck, AR Grade), sodium hydroxide (Merck, AR Grade), L-phenyl alanine (Alfa
Aesar, 98 %), methacryloyl chloride (Alfa Aesar, 97 %), pyridine (Alfa Aesar, 97 %), benzoyl peroxide (Alfa Aesar, 97 %), chloroform (Merck, Spectroscopic Grade, 98 %), toluene (Merck, Spectroscopic Grade, 98 %) and methyl methacrylate (Alfa Aesar, 97 %). Methanol (Spectrochem, AR Grade) and THF (Rankem, AR Grade) were purified, dried and distilled by the standard procedures.\textsuperscript{22}

\section*{5.2.2 Instrumentation}

The instrumentation techniques employed for the study of molecules are described in detail in section 2.6.2.

\subsection*{5.2.3 Synthesis}

\subsubsection*{5.2.3.1 Synthesis of p-Nitroazobenzene hydrochloride}

p-Nitroaniline (30.2 g, 219.0 mmol) dissolved in hydrochloric acid (6 N) was cooled to 0 °C. The solution was kept in an ice-bath under magnetic stirring. The solution of sodium nitrite (16 g, 230.0 mmol) in water (75 mL) was cooled to 0 °C. This cold solution was added drop wise to p-nitroaniline hydrochloride solution. The temperature of the reaction was kept at 0 °C, upon which a yellow colored diazonium salt was obtained. Yield: 92 %; mp: 98 °C. FTIR (KBr) $\nu$ cm$^{-1}$: 1341 (C-NO$_2$, sy st), 1516 (C-NO$_2$, ay st), 1448 (-N=N st), 3095 (aromatic C-H st), 1594, 1635 (aromatic C=C st). $^1$H NMR (400 MHz CDCl$_3$) $\delta$: 7.20- 7.59 (m, 4H). $^{13}$C NMR (100 MHz CDCl$_3$) $\delta$: 125, 126, 130, 115. Mass (m/e): 185 (molecular ion peak). Anal. Calcd for: C$_6$H$_4$N$_3$O$_2$Cl - C, 38.83; H, 2.17; N, 22.64. Found: C, 38.86; H, 2.17; N, 22.61.

\subsubsection*{5.2.3.2 Synthesis of 1-(4'-nitro-4-azo-1'-phenyl)phenylalanine}

L-phenyl alanine (7.8 g, 54.0 mmol) dissolved in 10 % sodium hydroxide solution (45 mL) was cooled to 0 °C. The solution was kept in an ice-bath under magnetic stirring. To this, cold p-nitroazobenzene hydrochloride (0 °C) solution was added drop wise with stirring. The reddish brown
precipitate obtained was filtered, washed with cold distilled water and dried. The compound was recrystallized from glacial acetic acid.

Yield: 64%; mp: 128 °C. FTIR (KBr) $\nu$ cm$^{-1}$: 1516 (C-NO$_2$, ay st), 1341 (C-NO$_2$, sy st), 1448 (-N=N sy st), 3095 (aromatic C-H st), 1594, 1635 (aromatic C=C st), 2915 (aliphatic CH$_2$, ay st), 2843 (aliphatic CH$_2$, sy st), 2962 (aliphatic C-H, sy st), 3269, 3372 (NH$_2$ st), 1247 (aliphatic C-N st), 3428 (aliphatic O-H st), 1716 (aliphatic C=O st), 1742 (aliphatic C-O st). $^1$H NMR (400 MHz CDCl$_3$) $\delta$: 8.05-8.09 (m, 4H), 6.60-6.64 (m, 4H), 2.17 (d, 2H), 2.24 (t, 1H), 1.57 (s, 2H), 9.36 (s, 1H). $^{13}$C NMR (100 MHz CDCl$_3$) $\delta$: 135, 125, 126, 141, 142, 113, 25, 77, 175. Mass (m/e): 314 (molecular ion peak). Anal. Calcd for: C$_{15}$H$_{14}$N$_4$O$_4$ - C, 57.32; H, 4.49; N, 17.85. Found: C, 57.30; H, 4.51; N, 17.85.

5.2.3.3 Synthesis of 3-methacryloyl-1-(4'-nitro-4-azo-1'-phenyl)-phenylalanine

1-(4'-nitro-4-azo-1'-phenyl)phenylalanine (3.0 g, 9.50 mmol) and methacryloyl chloride (1 mL, 10.26 mmol) dissolved in dry THF (25 mL) was cooled to 0 °C under N$_2$. To this mixture pyridine (0.1 g, 1.26 mmol) was added drop wise. The reaction was carried out for 36 h at reflux temperature. The reaction mixture was cooled and filtered. The brown solid obtained was purified by recrystallization from ethanol.

Yield: 58%; mp: 135 °C. FTIR (KBr) $\nu$ cm$^{-1}$: 1516 (C-NO$_2$, ay st), 1341 (C-NO$_2$, sy st), 1448 (-N=N sy st), 3095 (aromatic C-H str.), 1594, 1635 (aromatic C=C str.), 2926 (aliphatic CH$_2$, ay st), 2962 (aliphatic C-H, sy st), 3369 (aliphatic N-H st), 1247 (aliphatic C-N st), 3428 (aliphatic O-H st), 1716 (aliphatic C=O st), 1742 (aliphatic C-O st), 1677 (C=C st), 3107, 3073 (aliphatic =C-H st), 2959 (aliphatic CH$_3$, sy C-H st), 2852 (aliphatic CH$_3$, ay C-H st). $^1$H NMR (400 MHz CDCl$_3$) $\delta$: 8.05-8.54 (m, 4H), 6.92-7.92 (m, 4H), 2.12 (d, 2H), 2.36 (t, 1H), 9.36 (s, 1H), 1.72 (s, 1H), 9.81 (s, 1H), 0.79 (s, 3H), 4.15 (s, 2H). $^{13}$C NMR (100 MHz CDCl$_3$) $\delta$: 145, 121, 123, 128, 129, 110, 23, 29.18, 172, 29.73, 10, 125. Mass (m/e): 382 (molecular ion peak). Anal. Calcd for: C$_{19}$H$_{18}$N$_4$O$_5$ - C, 59.68; H, 4.74; N, 14.65. Found: C, 59.64; H, 4.76; N, 14.65.
5.2.3.4 Polymerization

3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl)phenylalanine (1 g, 3.77 mmol), methyl methacrylate (0.39 g, 3.75 mmol) and benzoyl peroxide (2 g, 12.19 mmol) were dissolved in dry DMF (40 mL). The reaction was carried out at 110 °C for 78 h, under N₂. The resulting solid was dissolved in DMF and reprecipitated from methanol. The polymer was collected by filtration, dried under vacuum, and obtained as a dark brown powder.

Yield: 54%; mp: 122 °C. FTIR (KBr) ν cm⁻¹: 1516 (aromatic C-NO₂, ay st), 1341 (aromatic C-NO₂, sy st), 1448 (-N=N sy st), 3095 (aromatic C-H st), 1594, 1635 (aromatic C=C st), 2944 (aliphatic CH₂, ay st), 2962 (aliphatic C-H, sy st), 3369 (aliphatic N-H st), 1247 (aliphatic C-N st), 3433 (aliphatic O-H st), 1721 (aliphatic C=O st), 1742 (aliphatic C-O st), 2959 (aliphatic CH₃, sy C-H st), 2852 (aliphatic CH₃, ay C-H st). ¹H NMR (400 MHz CDCl₃) δ: 7.07-7.51 (m, 4H), 6.91-6.99 (m, 4H), 2.12 (d, 2H), 2.36 (t, 1H), 9.38 (s, 1H), 1.74 (s, 1H), 9.81 (s, 1H), 3.53 (s, 3H), 1.87, 1.90 (s, 4H), 0.77, 0.95 (s, 6H). ¹³C NMR (100 MHz CDCl₃) δ: 145, 121, 123, 129, 110, 23, 51.06, 177, 178, 52.75, 16.47, 18.74, 54.46, 44.56, 44.90.

5.2.4 Sample Preparation

The samples for electro-optic studies were prepared as follows: 8 wt% solution eletro-optic polymer in chloroform was prepared. The solution was filtered through a 0.45 μm Nylon filter and deposited on patterned ITO coated glass substrates. The films were dried at room temperature (28 °C) for 12 h and then in vacuum chamber (at 10⁻² Torr) for 24 h. The sample was heated to 100°C and the second patterned ITO substrate was placed on top of the first. The film thickness was controlled by using a 48 μm Teflon spacer between the substrates. The sandwiched sample was cooled and the ITO’s were glued together using a thermally stable adhesive. Refractive indices of the doped matrix were measured using an Atago DRM2 refractometer. A value of 1.673 was obtained at 590 nm.
5.3 Results and Discussion

5.3.1 Synthesis and Characterization

Azo polymers are of two types: Side chain and main chain azo polymers, based on the position of the -N=N- (azo) group. The presence of azo group in the main chain and side chain polymers provides long conjugation between donor and acceptor groups. Azo polymers generally have polystyrene, poly methacrylates, polyesters, polysiloxanes, polycarbonates, polysilanes etc. as polymer backbones. They are usually synthesized by polymerization and copolymerization of styrene, methacrylates, esters, silanes, siloxanes etc. with azo substituted monomers. The NLO properties of azo polymers have been investigated in detail.

Copolymerization of 3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl)phenylalanine with methyl methacrylate is a two-step synthesis. Figure 5.1, Figure 5.2, Figure 5.3 and Figure 5.4 illustrate the multi-step synthesis of NLO molecule with methyl methacrylate. The first step involves preparation of NLO molecule. The synthesis of NLO molecule, 1-(4’-nitro-4-azo-1’-phenyl)phenylalanine, was carried out from L-phenyl alanine through coupling with p-nitroazobenzene hydrochloride. 1-(4’-nitro-4-azo-1’-phenyl)phenylalanine was reacted with methacryloyl chloride in appropriate ratio to give 3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl) phenylalanine in 48 % yield. The structure of the monomers were confirmed by elemental analysis, NMR ($^1$H and $^{13}$C) and mass spectral analysis.

![Figure 5.1: Synthesis Route of p-Nitroazobenzene hydrochloride.](image-url)
Figure 5.2: Synthesis Route of 1-(4’-nitro-4-azo-1’-phenyl)phenylalanine.

Figure 5.3: Synthesis Route of 3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl)phenylalanine.

The second step is the radical polymerization of 3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl)phenylalanine with methyl methacrylate by using benzoyl peroxide as a thermal initiator. The reaction was carried out in dry DMF. The initiator was added to a prewarmed solution containing a mixture of \( x \) moles of NLO molecule and \((100 - x)\) moles of methyl methacrylate monomer. The polymerization was carried out at 110 °C in DMF for 8 h. The crude polymeric product was dissolved in DMF and precipitated by the addition of methanol. The polymer was obtained in acceptable (54%) yields. NMR (\(^1H\) and \(^13C\)) and FT-IR spectral analysis confirms copolymerization. The glass transition temperature and the thermal stability of the copolymer was determined by DSC and TG analysis. The average molecular weight and polydispersity index of the copolymer was determined using SEC. The polymer can be processed into thin transparent
films. The copolymer has a reddish brown color.

Figure 5.4: Synthesis Route of the Polymer.

The $^1$H NMR spectrum of the copolymer is shown in Figure 5.5. The detailed spectral values of monomers and polymer are given in the experimental section. The resonance peak at 1.72 ppm corresponds to proton of the amino group. The peaks at 8.05-8.54 ppm and 6.92-7.92 ppm are assigned to the aromatic protons. The resonance at 4.15 ppm corresponds to vinyl proton (CH$_2$=C-) and the peak at 0.79 ppm to methyl proton of 3-methacryloyl-1-(4'-nitro-4-azo-1'-phenyl)phenylalanine. The absence of peak at 4.40 ppm and the appearance of two resonance peaks at 0.77 and 0.95 ppm (methyl proton) in the NMR spectrum of poly(3-methacryloyl-1-(4'-nitro-4-azo-1'-phenyl)phenylalanine-co-methyl methacrylate) indicated polymerization. In addition, the NMR spectrum of copolymer displayed peaks corresponding to methylene protons in the main chain (1.87 and 1.90 ppm).
The structure of the copolymer was further confirmed by $^{13}$C NMR. The $^{13}$C NMR spectrum of the copolymer is shown in Figure 5.6. The resonance peaks at 145, 121, 123, 128 and 129 ppm are assigned to aromatic carbons. The resonance signal at 110 ppm corresponds to the aromatic carbon (C-N=N-C). The peak at 125 ppm due to vinyl carbon is absent in the NMR spectrum of the copolymer. The resonance peak at 16.47 and 18.74 ppm are of methyl carbon in the spectrum of poly(3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl) phenylalanine-co-methyl methacrylate). Two new peaks were found at 44.56 and 44.90 ppm in the spectrum, attributed to methylene carbon of 3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl)-phenylalanine and methyl methacrylate which confirmed copolymerization.
FT-IR spectrum of the copolymer is shown in Figure 5.7. The band at 3369 cm\(^{-1}\) was associated with N-H stretching vibration. The band at 1448 cm\(^{-1}\) was the symmetric stretching of N=N group.

The disappearance of band around 3107, 3073 cm\(^{-1}\) (stretching vibration of aliphatic =C-H group) and 1677 cm\(^{-1}\) (stretching vibration of aliphatic double bond of the monomer) and the presence of new bands at 2857 and 3019 cm\(^{-1}\) indicate polymerization. The bands at 2857 and 3019 cm\(^{-1}\) are attributed to methylene aliphatic single bond asymmetric and symmetric C-H stretching vibration. The intense peak at 1721 cm\(^{-1}\) corresponds to aliphatic C=O stretching vibration.

Figure 5.7: FT-IR Spectrum of the Polymer.

Figure 5.8: SEC Chromatogram of the Polymer.
Figure 5.8 shows SEC chromatogram of the copolymer. The number average molecular mass ($M_n$) was 3175 and weight average molecular mass ($M_w$) was 6408. The polydispersity index ($M_w/M_n$) obtained was 2.01.

![Figure 5.8: SEC chromatogram of the copolymer.](image)

Figure 5.9: DSC curve of the Polymer.

The DSC thermogram of the copolymer is shown in Figure 5.9. The glass transition temperature ($T_g$) of the polymer is 96.75 $^\circ$C. The polymer showed well defined melting point at 121.83 $^\circ$C. The $T_g$ of the side-chain polymer depends on the mole ratio of NLO molecules and methyl methacrylate molecules. $T_g$ also depends on the structure of the NLO molecules and the spacer which links the NLO molecule to the polymer main chain.\(^{29}\)

![Figure 5.9: DSC curve of the Polymer.](image)

Figure 5.10: Thermogram of the Polymer.

The thermogram of the copolymer is shown in Figure 5.10. The degrada-
tion process started at around 298 °C and reached its maximum rate of 0.81 %/°C at 401 °C was assigned as the degradation of C-C, C-O and C-N bonds. 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{30}

### 5.3.2 Optical Properties

The UV-Vis spectra of copolymer is shown in Figure 5.11. Azo aromatic type molecules are characterized spectroscopically by a low-intensity n-π* band in the visible region of the spectrum and a high intensity π-π* band in the UV region of the electronic spectrum.\textsuperscript{23}

![Figure 5.11: UV-Vis Spectrum of the Polymer.](image)

The absorption spectrum of the polymer could be considered as a superposition of a low intensity band centered in the 3.45-1.72 eV region and a high intensity band in the 4.34-3.45 eV region. The intense band appeared in the low energy region is related to the combined contributions of the n-π*, first π-π* and internal charge transfer electronic transitions of azobenzene chromophores. The band in the high energy region corresponds to the π-π* electronic transition of the aromatic ring.\textsuperscript{31}
5.3.3 Electro-optic Properties

The electro-optic polymer, poly(3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl)-phenylalanine-co-methyl methacrylate), comes in the class of side-chain polymers. The transmission technique was employed for the measurement of electro-optic coefficient. The method and experimental technique was described in detail in chapter 4. The side-chain polymer exhibited a maximum electro-optic coefficient of 4.75 pm/V.

5.4 Conclusions

Poly (3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl) phenylalanine-co-methylmethacrylate) was synthesized via radical initiated polymerization. It was a copolymer of 3-methacryloyl-1-(4’-nitro-4-azo-1’-phenyl)phenylalanine and methyl methacrylate. The structure of the polymer was confirmed by FT-IR and NMR (1H and 13C) analysis. The polymer showed good thermal stability. The polymer system exhibited a maximum electro-optic coefficient of 4.75 pm/V.

References