JOURNAL OF **Applied Polymer** SCIENCE   **WILEY**

Synthesis, characterization, photophysical and surface properties of poly(amino naphthalene) and its poly(azomethine) compound

İsmet Kaya[1] [ORCID] | Burçin Akyüz[1] | Şahin Özel[1,2]

[1]Department of Chemistry, Polymer Synthesis and Analysis Laboratory, Çanakkale Onsekiz Mart University, Çanakkale, Turkey

[2]Department of Chemistry, Uludağ University, Faculty of Science and Arts, Bursa, Turkey

Correspondence

İsmet Kaya, Department of Chemistry, Polymer Synthesis and Analysis Laboratory, Çanakkale Onsekiz Mart University, 17020, Çanakkale, Turkey.
Email: ikaya@comu.edu.tr and kayaismet@hotmail.com

Abstract

In this study, 8-((4-hydroxybenzylidene)amino)naphthalene-2-ol (ANAPSB) compound was synthesized from condensation reaction of 8-amino-2-naphthol (ANAP) with 4-hydroxybenzaldehyde and then ANAPSB and 8-amino-2-naphthol were polymerized via oxidative polycondensation alkaline medium by H_2O_2 (35% aqueous solution) as oxidant at 70°C 14 h. The structures of compounds were confirmed by UV–Vis, ^1H-^{13}C-NMR and FT-IR measurements. The surface morphologies of PANAP and PANAPSB were examined with SEM analyses. The electrochemical properties of 8-amino-2-naphthol, poly(8-amino-2-naphthol) (PANAP), ANAPSB and poly(8-((4-hydroxybenzylidene)amino) naphthalene-2-ol) (PANAPSB) were determined by cyclic voltammetry technique. The thermal properties of compounds were found by TG-DTA analysis. The glass transition temperatures (Tg) of PANAP and PANAPSB were determined from DSC measurements. The Tg values of PANAP and PANAPSB were found to be 159 and 150°C, respectively. The Mn, Mw, Mp, Mz and PDI values of the PANAP and PANAPSB were calculated from gel permeation chromatography measurements. The optical and fluorescence properties of the compounds were determined by UV–Vis and fluorescence measurements, respectively. The optical band gap values of ANAP, PANAP, ANAPSB and PANAPSB were calculated as 3.12, 1.61, 2.79 and 1.57 eV, respectively.

KEYWORDS

fluorescence property, oxidative polymerization, poly(azomethine), Schiff base

1 | INTRODUCTION

Poly(imine)s structures known as Schiff bases or poly(azomethine)s have received intense interest in recent years due to their potential applications and other important properties.[1–3] Oligo(phenol) derivatives containing imine groups (—HC═N—) have used in a few area such as effective catalysts, heat-resistant, semiconductors[4] compounds, the formation of new polymer metal complexes,[5] for analytical purposes and to prevent environmental pollution.[6]

Conjugated poly(azomethine)s have used in the production of polymeric light emitting diodes (PLED)[7,8] and solar cells.[9,10] Also, they have showed fluorescence

properties because of conjuge π-bonding.[11–13] Furthermore, poly (azomethine)s have the ability to form a good film[14,15] for high-quantum efficiency, light emitting, sensitivity to photonic and electronic stimuli, macromolecular interaction and multi-color emission properties when excited at certain wavelengths.[16–18] Kaya et al. have long studied the thermal, electrochemical, optical, and electrical properties of poly(azomethine)s.[19,20] However, the application areas of aromatic poly(imine)s have limited due to their high-melting points and low-solubilities properties.[21] To overcome these difficulties, they tried different alternatives such as adding ether, ester, alkoxy, alkyl and methylene groups between aromatic rings.[22,23] High quality conjugated polymer containing naphthalene group was synthesized by Doğan et al. and they were observed that DMSO emits yellow light at 300 nm. It has also been determined that the polymers show high-electrical conductivity.[24]

In this study, it was aimed to obtain macromolecular products of a functional aromatic compound containing naphthalene unit in its structure via oxidative polycondensation in alkaline medium. Some properties of obtained products such as thermal, optical and fluorescence were investigated. The macromolecular compounds which the naphthalene unit containing both amine and hydroxyl groups in structure were obtained by H_2O_2, which is a moderate oxidant. Before, Schiff base compound was obtained from condensation reaction of 4-hydroxybenzaldehyde with 8-amino-2-naphthol. The structures and characterizations of 8-((4-hydroxybenzylidene)amino)naphthalene-2-ol, poly (8-amino-2-naphthol) and poly(8-((4-hydroxybenzylidene) amino)naphthalene-2-ol) were determined from FT-IR, ^{1}H NMR, ^{13}C NMR, UV–Vis, CV, TG-DTA and fluorescence measurements. After, the 8-amino-2-naphthol and 8-((4-hydroxybenzylidene)amino)naphthalene-2-ol compounds were converted to macromolecular products in alkaline medium by H_2O_2 (35% aqueous solution) oxidant. The average molar mass distributions and glass transition temperatures (T_g) of the obtained PANAP and PANAPSB polymers were determined from GPC and DSC measurements, respectively. The surface properties of the PANAP and PANAPSB were determined from SEM measurements.

2 | EXPERIMENTAL

2.1 | Materials

8-amino-2-naphthol and 4-hydroxybenzaldehyde were obtained from Sigma-Aldrich Chemical Co. (Germany) DMF, DMSO, DMAC, tetrahydrofuran, chloroform, acetone, ethanol, methanol, dichloroethane, acetonitrile, NaOH and hydrogen peroxide (H_2O_2, 35% aqueous

solution) were obtained from Merck Chemical Co. (Germany) and used as received without purification. Hydrogen peroxide (H_2O_2, 35% aqueous solution) was used as oxidant at the oxidative polycondensation reactions.

2.2 | Synthesis of Schiff base.

8-amino-2-naphthol (2 mmol, 0.318 g) was dissolved in a 100 mL round-bottom flask by adding 10 mL of methanol. Then, 4-hydroxybenzaldehyde (2 mmol, 0.244 g) was dissolved in 10 mL methanol and was added to the ANAP solution in the flask. The reaction medium was carried out under reflux at 60°C for 10 h. The reaction mixture was transferred to a petri dish to remove the methanol at room temperature.[25] Then, Schiff base compound was crystallized in hot EtOH. The yield of ANAPSB was found to be 70%. The reaction procedure of Schiff base (ANAPSB) was shown in Scheme 1.

UV–Vis spectra, λ_{max} (nm): 298, 356. ^{1}H NMR (DMSO-$_{d6}$, δ, ppm): 10.12 (s, 1H, —OH$_1$), 9.68 (s, 1H, —OH$_2$), 8.49 (s, 1H, —CH=N—), 7.01 (d, 1H, Ha), 7.60 (d, 1H, Hb), 7.74 (d, 1H, Hc), 7.22 (t, 1H, Hd), 7.07 (d, 1H, He), 7.52 (s, 1H, Hf), 7.86 (d, 1H, Hg), 6.92 (d, 1H, Hh). ^{13}C NMR (DMSO-$_{d6}$, δ, ppm): 155.40 (C1-ipso, —OH), 130.56 (C2), 119.22 (C3), 128.66 (C4-ipso), 113.39 (C5), 123.25 (C6), 105.38 (C7), 147.82 (C8-ipso), 129.70 (C9-ipso), 128.24 (C10), 161.08 (C11, —CH=N), 125.33 (C12-ipso), 116.13 (C13), 131.16 (C14), 159.92 (C15-ipso—OH).

2.3 | Synthesis procedure of PANAPSB

The 2 mmol (0.526 g) of the synthesized Schiff base (ANAPSB) was dissolved in a two necked round bottom flask (100 mL) attached with a reflux condenser and magnetic stirrer containing in 30 mL of aqueous NaOH solution (0.1 M). The temperature was fixed at 70°C and stirring was continued by adding H_2O_2 (35% aqueous solution) to the reaction mixture at regular intervals for thirty minutes. The 1.5 mL of H_2O_2 (35% aqueous solution) was included into the flask within reaction time. When oxidant was added to reaction mixture, the color of reaction medium was turned black. The reaction was carried out at reflux for 14 h and then reaction mixture was neutralized with an equivalent amount of 0.1 M HCl solution.[26,27] The reaction product was filtered and the poly(8-((4-hydroxybenzylidene)amino)naphthalene-2-ol) (PANAPSB) was dried in a vacuum oven at 50°C for 24 h. The yield of PANAPSB was found to be 60%. The synthesis procedure of PANAPSB is given in Scheme 1.

SCHEME 1 Synthesis procedures of ANAPSB and PANAPSB [Color figure can be viewed at wileyonlinelibrary.com]
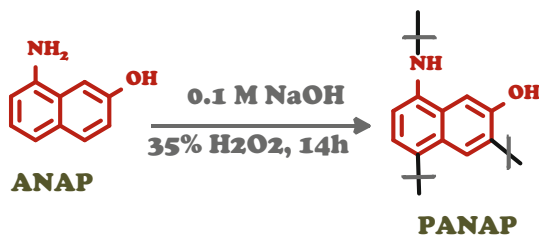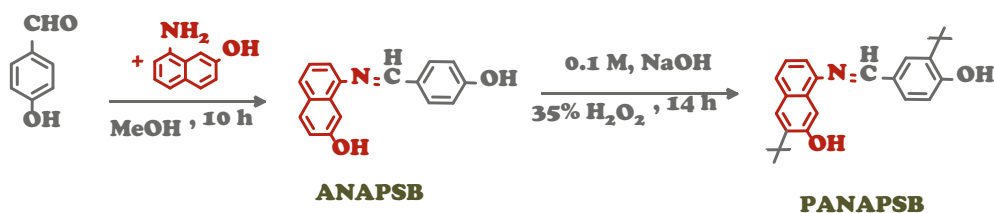
SCHEME 2 Synthesis procedure of PANAP [Color figure can be viewed at wileyonlinelibrary.com]

UV–Vis spectra, λ_{max} (nm): 315, 438, 712. ^{1}H NMR (DMSO-$_{d6}$, δ, ppm): 9.46 (s, 1H, —OH1), 9.09 (s, 1H, —OH2), 8.52 (s, 1H, —CH=N—), 6.47 (s, 1H, terminal-Ha), 7.62 (d, 1H, Hb), 7.74 (d, 1H, Hc), 7.39 (t, 1H, Hd), 6.83 (d, 1H, He), 7.48 (s, 1H, Hf), 7.97 (d, 1H, Hg), 7.80 (d, 1H, Hh), 6.67 (d, 1H, Hi). ^{13}C NMR (DMSO-$_{d6}$, δ, ppm): 166.45 (C1-ipso, —OH), 130.64 (C2-ipso), 121.90 (C3), 134.52 (C4-ipso), 117.78 (C5), 132.99 (C6), 107.97 (C7), 149.27 (C8-ipso), 134.99 (C9-ipso), 131.71 (C10), 175.46 (C11, —CH=N), 138.60 (C12-ipso), 119.76 (C13), 134.59 (C14-ipso), 167.04 (C15-ipso—OH), New peak observed 120.55 ppm for C—C coupling.

2.4 | Oxidative polycondensation procedure of ANAP

The poly(8-amino-2-naphthol) was synthesized from oxidative polycondensation reaction of 8-amino-2-naphthol (ANAP) in alkaline medium by H$_2$O$_2$ (35% aqueous solution) to be oxidant. 2 mmol (0.318 g) of 8-amino-2-naphthol (ANAP) was dissolved in a two necked round bottom flask (100 mL) attached with a reflux condenser and magnetic stirrer containing in 30 mL of aqueous NaOH solution (0.1 M). The H$_2$O$_2$ (35% aqueous solution) oxidant was added to reaction medium by a dropping funnel at 70°C. The reaction medium was turned to black as a result of polymerization. The reaction mixture was refluxed for 14 h at 70°C and then was neutralized with an equivalent amount of 0.1 M HCl solution.[27] The product was filtered and it was washed with ethanol to remove unreacted monomer.[28–32] The poly (8-amino-2-naphthol) (PANAP) was dried in a vacuum oven at

50°C for 24 h. The yield of PANAP was found to be 70%. The synthesis procedure of PANAP was given in Scheme 2.

The UV–Vis spectra λ_{max} (nm) for ANAP: 315, 347. ^{1}H NMR (DMSO-$_{d6}$, δ, ppm) for ANAP: 9.39 (s, 1H, —OH), 5.26 (s, 2H, -NH$_2$), 6.94 (d, 1H, Ha), 7.56 (d, 1H, Hb), 6.99 (d, 1H, Hc), 6.97 (t, 1H, Hd), 6.57 (d, 1H, He), 7.21 (s, 1H, Hf). ^{13}C NMR (DMSO-$_{d6}$, δ, ppm) for ANAP: 154.31 (C1-ipso, —OH), 129.71 (C2), 118.29 (C3), 124.92 (C4-ipso), 108.24 (C5), 123.63 (C6), 104.71 (C7), 143.43 (C8-ipso), 129.10 (C9-ipso), 116.33 (C10).

The UV–Vis spectra λ_{max} (nm) for PANAP: 329, 440, 612. ^{1}H NMR (DMSO-$_{d6}$, δ, ppm) for PANAP: 8.49 (s, 1H, —OH), 9.12, 5.64 (s, 1H, -NH), 5.24 (s, 2H, terminal-NH$_2$), 6.14 (d, 1H, terminal-Ha), 7.53 (s, 1H, Hb), 6.44 (s, 1H, Terminal-Hc), 6.93 (t, 1H, Hd), 6.56 (d, 1H, He), 7.22 (s, 1H, Hf). ^{13}C NMR (DMSO-$_{d6}$, δ, ppm) for PANAP: 166.68 (C1-ipso, —OH), 135.35 (C2), 116.30 (C3), 124.91 (C4-ipso), 107.99 (C5), 118.27 (C6), 104.57 (C7), 147.84 (C8-ipso), 129.50 (C9-ipso), 123.40 (C10). New peak observed 149.19 ppm for C—N coupling.

3 | CHARACTERIZATION

The Fourier Transform Infrared (FT-IR) spectra were obtained using Perkin Elmer Frontier FT-IR/FIR Spectrometer Frontier (USA) with Attenuated Gladi ATR PIKE technologies accessory between 4000 and 400 cm^{-1}. ^{1}H-NMR and ^{13}C-NMR measurements of the synthesized compounds were carried out by Agilent (USA) brand 600 MHz ^{1}H-NMR150 MHz ^{13}C-NMR using DMSO-d$_6$ as solvent at 25°C. Thermal properties were measured with the Perkin Elmer Diamond Thermal Analysis device between 20 and 1000°C in N$_2$ atmosphere (200 mL min^{-1}) with a heating rate of 10°C per minute. DSC measurements were carried out with Perkin Elmer Sapphire DSC device in aluminum capsules between 30 and 400°C with an increase of 10°C per minute in N$_2$ atmosphere (200 mL min^{-1}). The optical properties of compounds were determined by a dual-beam UV–Vis spectrophotometer (AnalytikJena 210 Plus, UK) and a quartz cuvette. DMSO was used as solvent at UV–Vis spectrophotometer measurements of compounds. Fluorescence
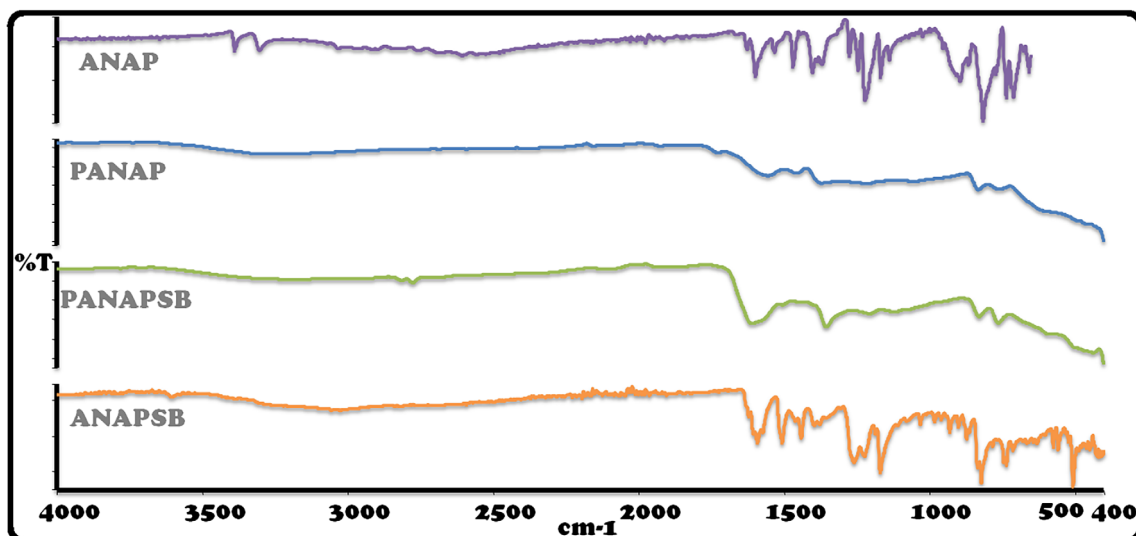
FIGURE 1   FT-IR spectra of ANAP, PANAP, PANAPSB and ANAPSB [Color figure can be viewed at wileyonlinelibrary.com]

measurements of compounds were made using RF-5301 PC spectrometer device (Japan). For the fluorescence measurements of compounds were used DMF as solvent. The analysis was performed by setting the excitation and irradiation slit interval to 5 nm. Electrochemical measurements of the samples were performed with a CHI 660C Electrochemical Analyzer (Texas, USA). In the electrochemical system, glassy carbon is used as the working electrode, platinum wire is used as the counter electrode, and silver wire is used as the reference electrode. 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in acetonitrile was used to be the electrolyte solution. The electrochemical cell was passed through an argon atmosphere for 10 min before measurements at room conditions. Detailed surface images of the PANAP and PANAPSB surface were obtained with the JSM-7100F Field Emission SEM (JEOL, Japan) device. Spray coating process was used to make a thin gold/palladium film over the polymer samples.

The gel permeation chromatography-Light Scattering (GPC-LS) instrument of the Malvern Viscotek GPC Dual 270 max (UK) was used to determine the polydispersity index (PDI) and average molecular weight of polymers. The weight average molecular weight (Mw), The number-average molecular weight (Mn), Z-average molecular weight (Mz), and peak molecular weight (Mp) values of PANAP and PANAPSB were determined by 8.00 mm i.d × 300 mm double column and a refractive index detector (RID) and Light Scattering Detector (LSD). DMF was used as the eluent containing 40 mM LiBr at a flow rate of 1.0 mL min^{-1} and the oven temperature was 55°C.

4 | RESULTS AND DISCUSSION

4.1 | Characterization of PANAP, ANAPSB and PANAPSB.

FT-IR spectra of PANAP, ANAPSB and PANAPSB are shown in Figure 1. In the FT-IR spectrum of PANAP, the stretching vibration band belonging to —OH group was seen at 3150 cm^{-1}. The stretching vibration band of the C=C group was seen at 1555 cm^{-1} and 1456 cm^{-1}, while the stretching vibration band belonging to the C—O group was seen at 1213 cm^{-1}. The stretching vibration band of N—H group was observed at 3263 cm^{-1}. The stretching vibration band of aromatic C—H bonding was observed at 3068 cm^{-1}. In the FT-IR spectrum of ANAPSB, the stretching vibration band of —OH group was seen at 3240 cm^{-1}. The stretching vibration band of —C=N group was seen at 1621 cm^{-1}. The stretching vibration band of C=C bonding was seen at 1591 cm^{-1} and 1506 cm^{-1}, while the stretching vibration band of C—O bonding was seen at 1169 cm^{-1}. The stretching vibration band of aromatic C—H bonding was seen at 3059 cm^{-1}.

In the FT-IR spectrum of ANAPSB, it was observed that the signals in the aldehyde carbonyl (—C=O) group and the amine (—NH$_2$) group disappeared and were replaced by the stretching vibration band of the imine (—CH=N) group. As a result of the reaction of the amine group in ANAP and the aldehyde group in 4-hydroxybenzaldehyde, the imine bond in ANAPSB was realized. The appearance of the imine bond in the FT-IR spectrum is an indication that the Schiff base has been formed. In the FT-IR spectrum of PANAPSB, the
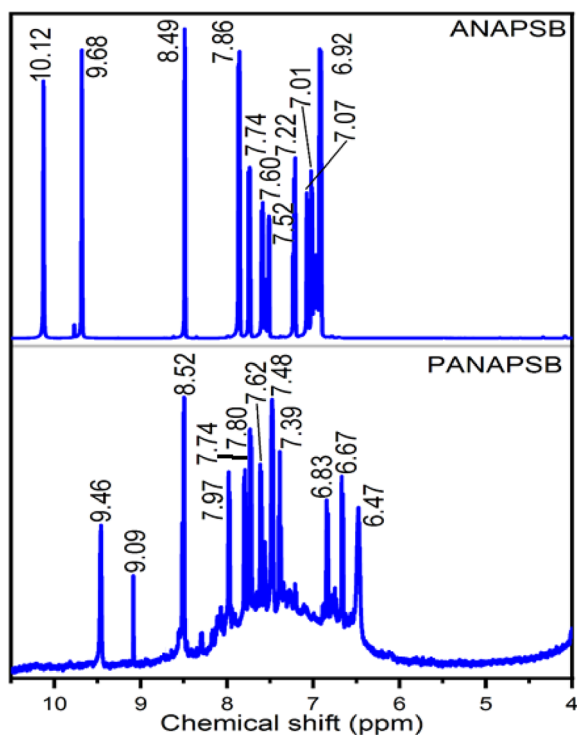
FIGURE 2 ^{1}H NMR spectra of ANAPSB and PANAPSB. [Color figure can be viewed at wileyonlinelibrary.com]
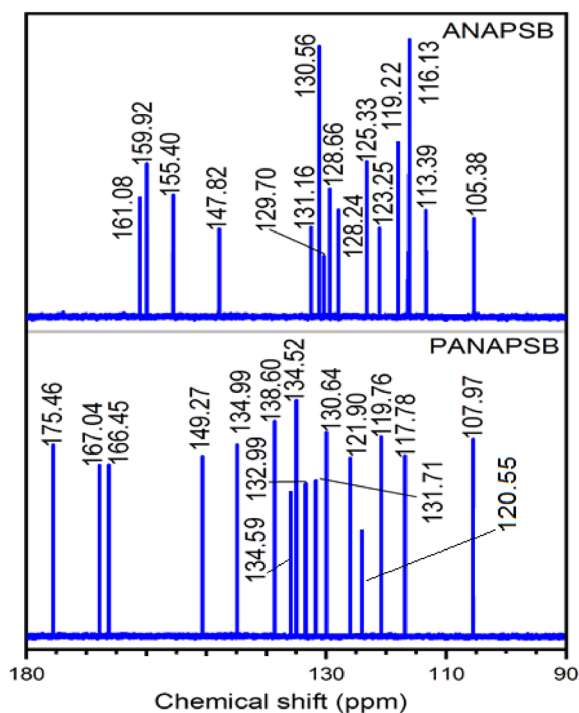
FIGURE 3 ^{13}C NMR spectra of ANAPSB and PANAPSB. [Color figure can be viewed at wileyonlinelibrary.com]

stretching vibration band of —OH group was observed at 3187 cm^{-1}. The stretching vibration band belonging to the -C=N bonding was observed at 1610 cm^{-1}. The
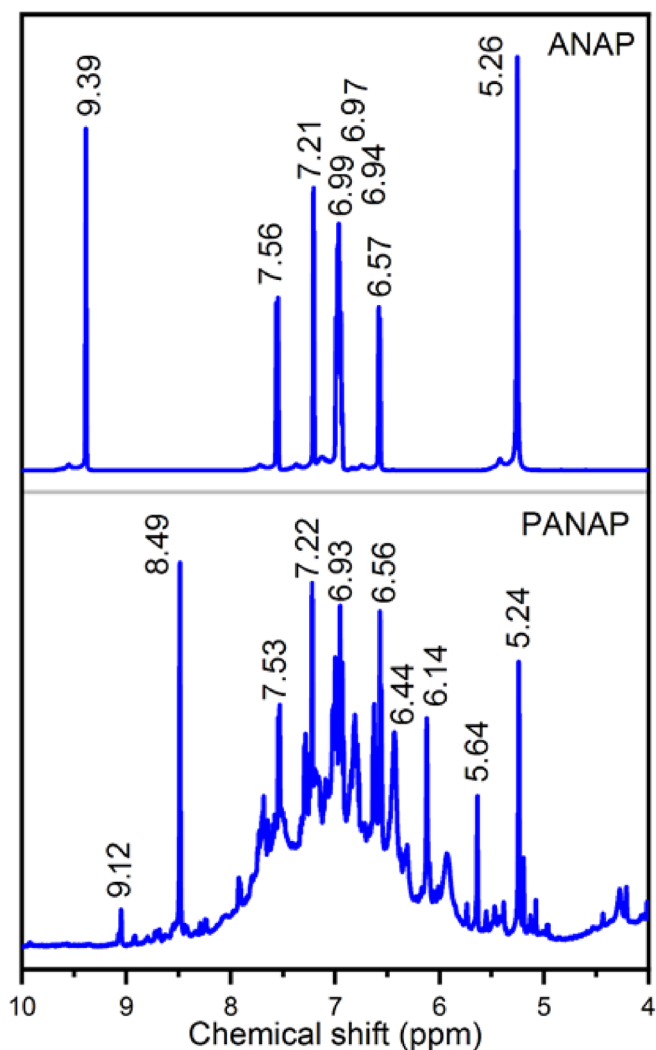

FIGURE 4 ^{1}H NMR spectra of ANAP and PANAP. [Color figure can be viewed at wileyonlinelibrary.com]

stretching vibration band of the C=C bonding was observed at 1572 cm^{-1}and 1549 cm^{-1}, while the stretching vibration band of the C—O bonding was observed at 1213 cm^{-1}. The bending vibration band of S-O bonding was observed at 761 cm^{-1}, while the stretching vibration band belonging to the aromatic C—H bonding was observed at 3057 cm^{-1}. In the FT-IR spectrum of ANAPSB and PANAPSB, the stretching vibration bands of the imine (—CH = N) groups were observed at 1621 cm^{-1} and 1610 cm^{-1}, respectively. This value indicates that the poly(imine) compound was formed.

^{1}H NMR and ^{13}C NMR spectra of ANAPSB Schiff base and PANAPSB polymer are shown in Figures 2 and 3, respectively. When 1H-NMR spectrum of ANAPSB is examined, the proton signals of the hydroxyl—OH group were observed at 10.12 and 9.68 ppm. The signal of the proton in the —CH=N group was seen at 8.49 ppm. The signals of aromatic protons were seen between 6.92 and
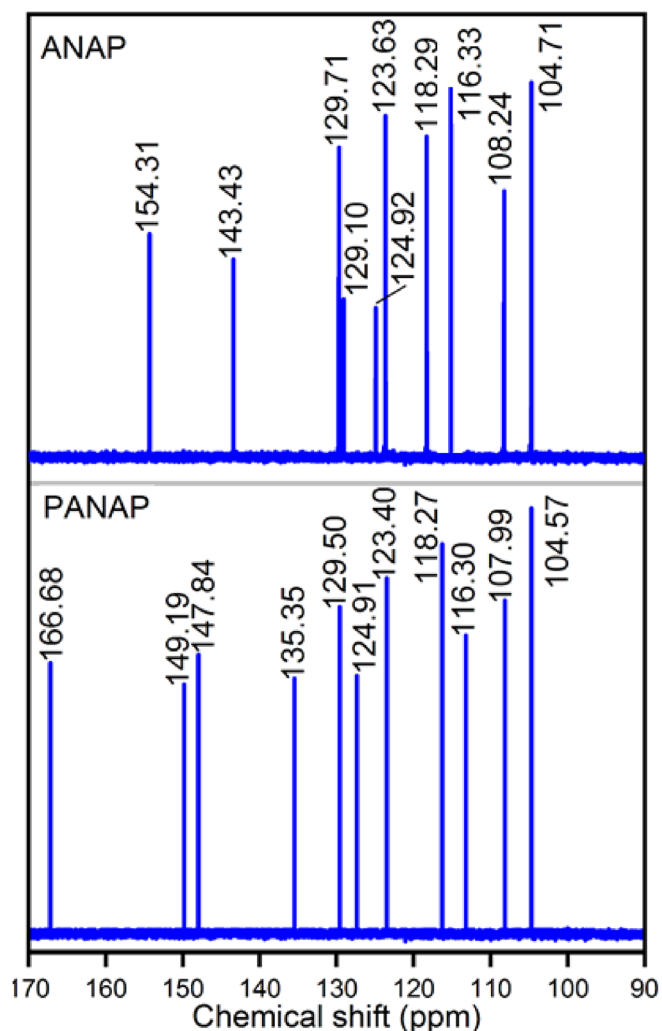
FIGURE 5 ^{13}C NMR spectra of ANAP and PANAP. [Color figure can be viewed at wileyonlinelibrary.com]

7.86 ppm. When the ^{13}C-NMR spectrum was examined, the carbon atom attached to the —CH═N group was seen at 161.08 ppm. The carbon atom signals of ANAPSB were observed at 155.40 (C1-ipso, —OH), 130.56 (C2), 119.22 (C3), 128.66 (C4-ipso), 113.39 (C5), 123.25 (C6), 105.38 (C7), 147.82 (C8-ipso), 129.70 (C9-ipso), 128.24 (C10), 161.08 (C11, —CH═N), 125.33 (C12-ipso), 116.13 (C13), 131.16 (C14), 159.92 (C15-ipso—OH). When ^{1}H-NMR spectrum of PANAPSB is examined, the proton signals of the hydroxyl—OH group were observed at 9.46 and 9.09 ppm. The signal of the proton in the —CH═N group was seen at 8.52 ppm. The signals of aromatic protons were seen between 6.47–7.97 ppm. When the ^{13}C-NMR spectrum was examined, the carbon atom attached to the —CH═N group was seen at 175.46 ppm. The signals (ppm) of carbon atoms of PANAPSB were observed at 166.45 (C1-ipso, —OH), 130.64 (C2-ipso), 121.90 (C3), 134.52 (C4-ipso), 117.78 (C5), 132.99 (C6), 107.97 (C7), 149.27 (C8-ipso), 134.99 (C9-ipso), 131.71 (C10), 138.60

(C12-ipso), 119.76 (C13), 134.59 (C14-ipso), 167.04 (C15-ipso—OH). A new peak was observed at 120.55 ppm due to C—C coupling.

^{1}H NMR and ^{13}C NMR spectra of ANAP and PANAP are shown in Figures 4 and 5, respectively. The proton signal of the hydroxyl—OH group of ANAP was observed at 9.39 ppm. The signal of the proton in the –NH$_2$ group was seen at 5.26 ppm. The signals of Ha, Hb, Hc, Hd, He and Hf aromatic protons were seen at 6.94, 7.56, 6.99, 6.97, 6.57 and 7.21 ppm, respectively. According to ^{13}C NMR, the signals of C1-ipso, C2, C3, C4-ipso, C5, C6, C7, C8-ipso, C9-ipso and C10 aromatic carbon atoms of ANAP were observed at 154.31, 129.71, 118.29, 124.92, 108.24, 123.63, 104.71, 143.43, 129.10 and 116.33 ppm, respectively.

It is seen that Figure 4, the proton signal of the hydroxyl—OH group of PANAP was observed at 8.49 ppm. The signals of the protons in the –NH and terminal -NH$_2$ groups were seen at 9.12, 5.64 ppm and 5.24 ppm, respectively. The signals of Ha, Hb, Hc, Hd, He and Hf aromatic protons were seen at 6.14, 7.53, 6.44, 6.93, 6.56 and 7.22 ppm, respectively. According to ^{13}C NMR in Figure 5, the signals of C1-ipso, C2, C3, C4-ipso, C5, C6, C7, C8-ipso, C9-ipso and C10 aromatic carbon atoms of PANAP were observed at 166.68, 135.35, 116.30, 124.91, 107.99, 118.27, 104.57, 147.84, 129.50 and 123.40 ppm, respectively. Because of C—N coupling, new peak was observed 149.19 ppm.

UV–Vis spectra of ANAP, PANAP, ANAPSB Schiff base and PANAPSB polymer are given in Figure 6. The λ_{max}, λ_{onset} and E_g results of the UV–Vis Spectra of the compounds obtained are shown in Table 1. The optical band gap (E_g) values of ANAP, PANAP, ANAPSB and PANAPSB were calculated from λ_{onset} values of UV–Vis spectra of compounds. These values of ANAP, PANAP, ANAPSB and PANAPSB were found to be 3.12, 1.61, 2.79 and 1.57 eV, respectively. When the UV–Vis spectra were examined, it was found that the bands in polymer compounds were wider and their wavelengths were larger than Schiff bases. When the UV–Vis spectra of polymers are examined, the bands observed are very close to each other, this shows that the molecular structure of the polymers is similar and functional groups (—OH or —CH═N) have similar inductive and resonance effects.[33] Wider absorption bands represent polymerization. In the literature, polymers with E_g value less than 3.0 eV are known as semiconductors, while polymers with E_g value greater than 3.0 eV are known as insulators.[34] PANAP, ANAPSB, PANAPSB are semiconductors and ANAP is insulating.

The cyclic voltammograms were taken to examine the electrochemical properties of the compounds obtained and the graphics were given in Figure 7. Optical and electrochemical values of the synthesized substances are
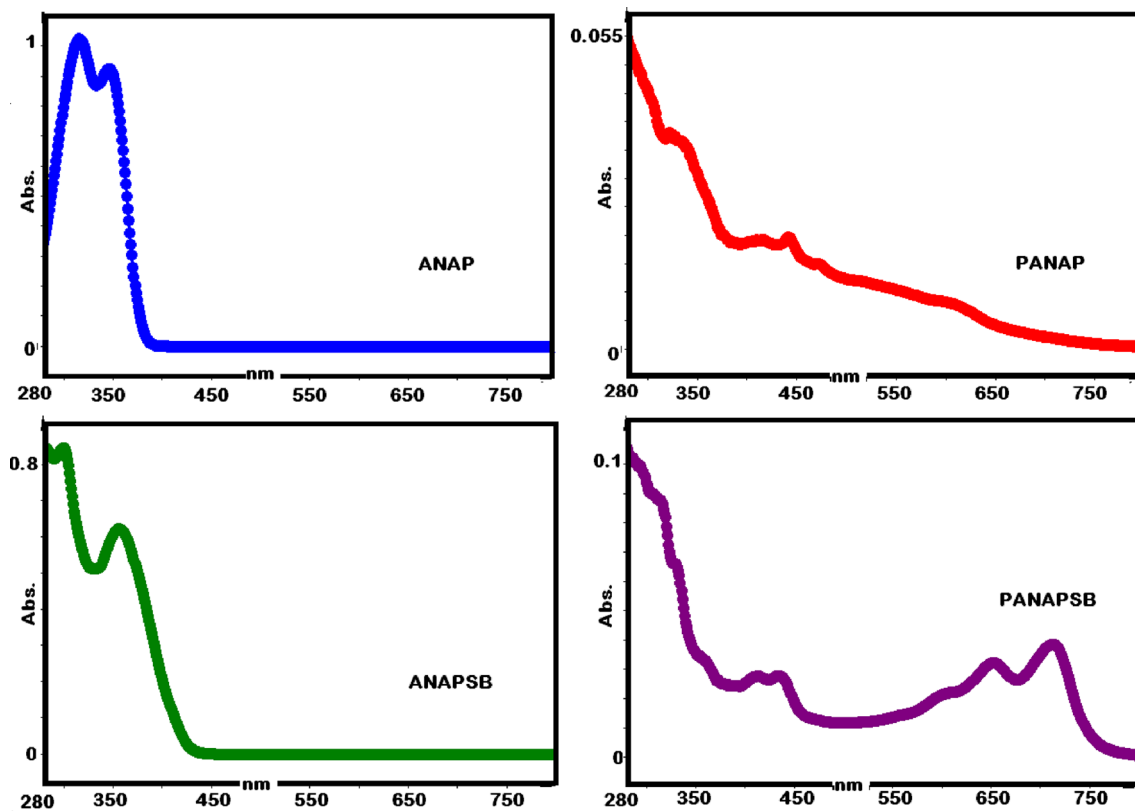
FIGURE 6 UV-Vis spectra of ANAP, PANAP, ANAPSB and PANAPSB. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 The optical and electrochemical values of synthesized monomers and polymers

Compounds	$E_{ox.}$ (V)	HOMO (eV)[a]	$E_{red.}$ (V)	LUMO (eV)[b]	E'_g (eV)[c]	λ_{onset} (nm)	E_g (eV)[d]
ANAP	1.5630	5.953	−1.7157	−2.6743	3.28	397	3.12
	1.2535	−5.6435			2.97		
	0.6823	−5.0723			2.4		
PANAP	1.4560	−5.846	−0.6747	−3.7153	2.13	768	1.61
	1.0512	−5.4412	−0.9424	−3.4476	1.99		
			−1.3675	−3.0225	2.42		
ANAPSB	1.5952	−5.9852	−1.2939	−3.0961	2.89	444	2.79
		−5.4775	−1.7472	−2.6428	2.84		
		−5.0247			2.38		
PANAPSB	1.3776	−5.7676	−1.216	−3.174	2.59	788	1.57
			−1.3019	−3.0881	2.68		

[a]Highest occupied molecular orbital.
[b]Lowest unoccupied molecular orbital.
[c]Electrochemical band gap.
[d]Optical band gap.

shown in Table 1. $E_{HOMO} = − (4.39 + E_{ox})$ and $E_{LUMO} = − (4.39 + E_{red})$ equations were used for the calculations electrochemical values of compounds. Also, the electrochemical band gap (E'_g) values of ANAP, PANAP, ANAPSB and PANAPSB were calculated from the formula $E'_g = E_{LUMO} − E_{HOMO}$.[35] These E'_g values of ANAP,

PANAP, ANAPSB and PANAPSB were found to be 3.28, 2.13, 2.89 and 2.59 eV, respectively.

When the electrochemical band gap (E'_g) values were calculated from cyclic voltammetric measurement and optical band gap (E_g) values calculated from UV–Vis analysis. When these values were compared, it is observed to
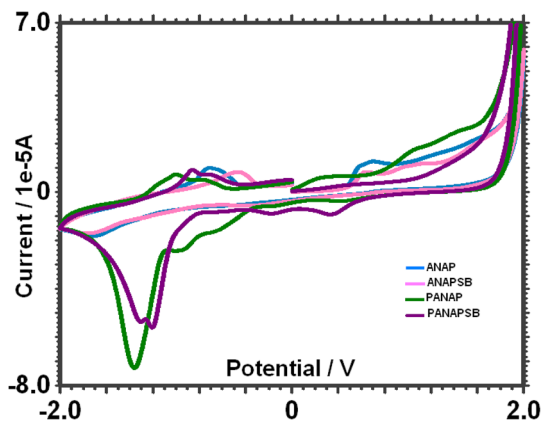
FIGURE 7 CV graphics of ANAP, ANAPSB, PANAP and PANAPSB [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 8 Fluorescence spectra of PANAP due to excitation at different wavelengths (a) (conc.: 0.05 mg mL^{-1}) and different concentration (b) (Slit width: 5 nm in all measurement) in DMF solution. [Color figure can be viewed at wileyonlinelibrary.com]

be compatible with each other. These results showed that the polymers had slightly lower Eg values than their monomers due to their polyconjugated structure.[36]

4.2 | Fluorescence spectra of synthesized compounds.

Fluorescence spectra of the synthesized PANAP and PANAPSB are shown in Figures 8 and 9, respectively.
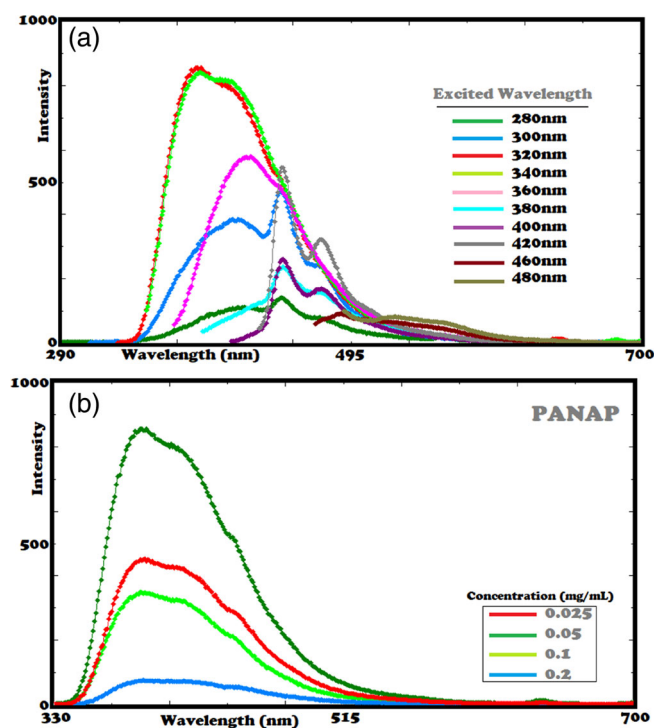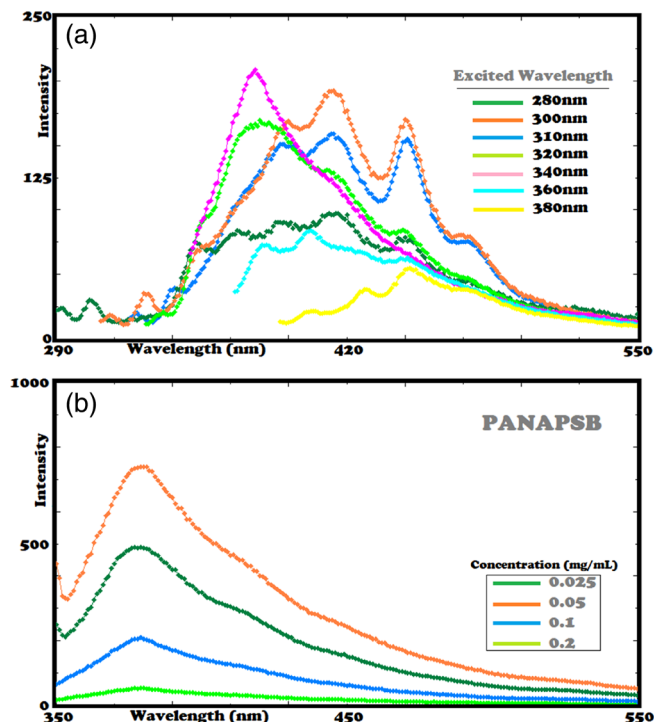

FIGURE 9 Fluorescence spectra of PANAPSB due to excitation at different wavelengths (a) (conc.: 0.05 mg mL^{-1}) and different concentrations (b) (Slit width: 5 nm in all measurements) in DMF solution. [Color figure can be viewed at wileyonlinelibrary.com]

Fluorescence measurements were made by preparing solutions of different concentrations in DMF solvent, and fluorescence quantum yields (QYs) were determined using the comparative method as described in the literature.[37] It has been previously observed that various polymeric systems, including polyvinyl pyridine gels, poly(amidoamine) nanoparticles, poly(amidoamine)s, exhibit multicolor emission behavior.[38–40]

In the analyses performed, the slit interval was determined as 5 nm. For PANAPSB, the maximum emission wavelength was observed at 380 nm at a concentration of 0.05 g L^{-1}.

It is seen that Figure 8a, blue emissions were observed at 280, 300, 320, 340, 360, 380, 400, 420, 440 and 480 nm in DMF solution (0.05 mg mL^{-1}) of PANAP. The highest intensity value for PANAP was observed in 0.05 mg mL^{-1} DMF solution (Figure 8b). It is seen that Figure 9a, blue emissions were observed at 280, 300, 320, 340, 360 and 380 nm in DMF solution (0.05 mg mL^{-1}) of PANAPSB. It is seen that Figure 9b, the highest intensity value for PANAPSB was observed in 0.05 mg mL^{-1} DMF solution. As seen hat in Figures 8b and 9b, with decreasing concentrations of PANAP and PANAPSB fluorescence intensity increases and reaches to optimum value at 0.05 mg mL^{-1}, then its emission is quenched with reducing concentration.

It is seen that in Figures 8a and 9a, when excitation took place at 355 nm and 340 nm for PANAP and PANAPSB, respectively, both PANAP and PANAPSB the highest intensity values were observed at fluorescence measurements.

4.3 | GPC analysis of PANAP and PANAPSB.

Gel permeation chromatograms (GPC) of PANAP and PANAPSB polymers obtained by oxidative polycondensation are given in Figure 10. The determined weight average molecular weight (Mw) of PANAP was 9800 Da and the number average molecular weight (Mn) was 9250 Da. The molecular weight distributions determining the polydispersity index (PDI) were found as (Mw/Mn): 1.059. The Mw and the Mn and PDI values of PANAPSB were calculated to be 10,350 Da and 9900 Da and 1.046, respectively. The z-average molecular weight (Mz) and peak average molecular weight (Mp) values of PANAP and PANAPSB were calculated to be 10,300, 7800 Da and
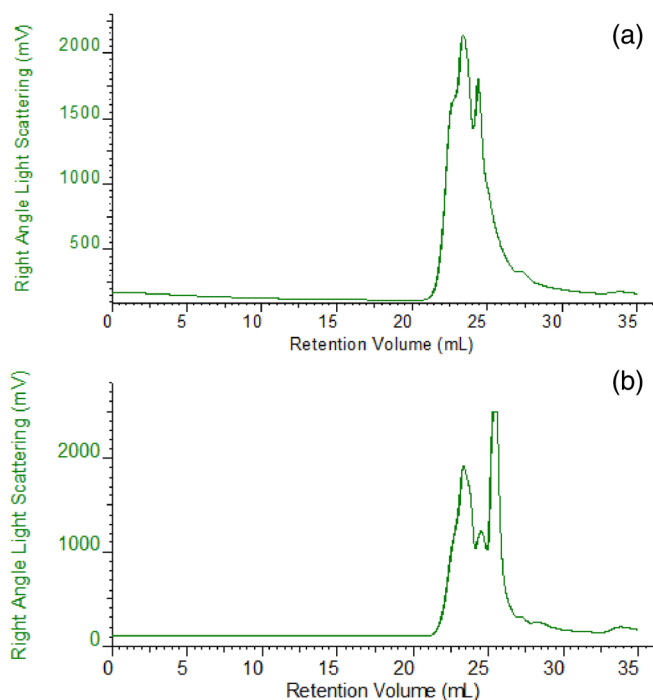
10,900 and 8350 Da, respectively. PDI values of PANAP and PANAPSB were calculated according to both Mw/Mn and Mz/Mn ratios. PDI (Mz/Mn) values of PANAP and PANAPSB were calculated to be 1.114 and 1.101, respectively. As seen in Figure 10, the chromatograms of both polymers was observed to be two fractions. However, the retention times of the chromatograms of the fractions were very close to each other. Also, it indicates that the chain lengths
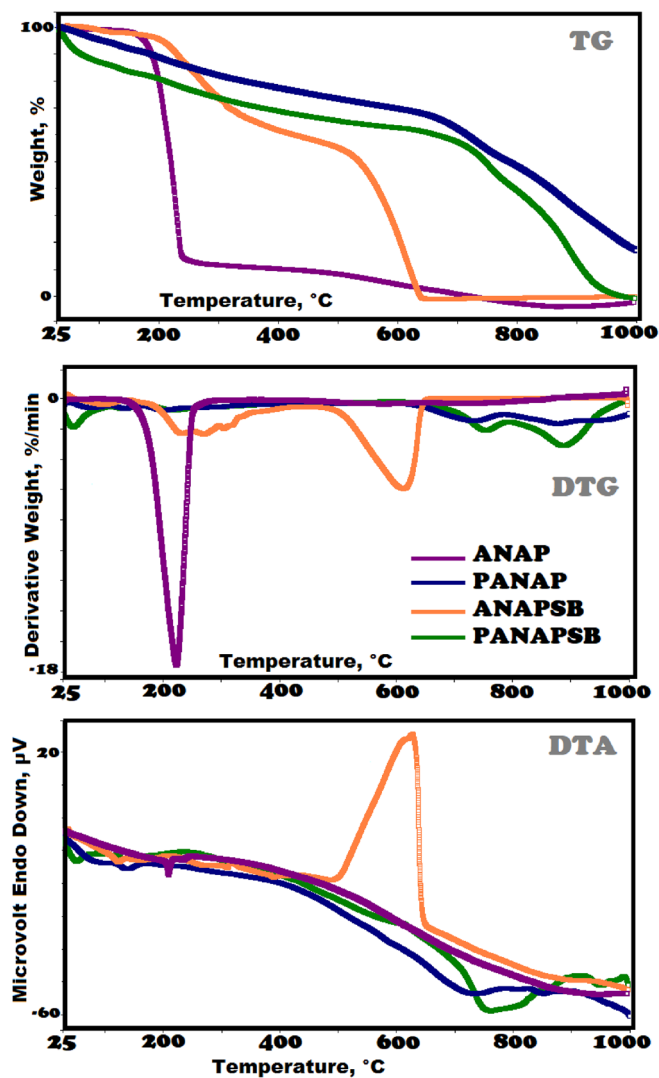
FIGURE 11 Thermal analysis curves of ANAP, PANAP, ANAPSB and PANAPSB. [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 10 GPC chromatogram of PANAP (a) and PANAPSB (b). [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 The molecular weight and PDI data of PANAP and PANAPSB

Polymer	Mn (Da)	Mw (Da)	PDI (mw/Mn)	Mz (Da)	PDI (Mz/Mn)	Mp (Da)
PANAP	9250	9800	1.059	10,300	1.114	7800
PANAPSB	9900	10,350	1.046	10,900	1.101	8350

TABLE 3 TG-DTA and DSC analysis results of monomer and polymers

Compounds	T_{ID} [a]	T_{DM} [b]	TG (°C)			DTA (°C)		DSC	
			T_{20} [c]	T_{50} [d]	% char at (1000°C)	Exo	Endo	T_g (°C) [e]	ΔCp J/g °C [f]
ANAP	186	223	200	220	0.0	—	210, 235	—	—
PANAP	179	201,734,878	536	822	25.00	—	—	159	0.008
ANAPSB	203	250,612	276	536	0.0	627	—	—	—
PANAPSB	183	217,753,886	562	830	0.0		—	150	0.102

[a]The initial decomposition temperature.

[b]Decomposition temperature at maximum weight loss rate.

[c]Temperature corresponding to 20% weight loss.

[d]Temperature corresponding to 50% weight loss.

[e]Glass transition temperature.

[f]Change of specific heat during glass transition.

of the PANAP and PANAPSB are close to each other. The Mn value of the polymerization product of 8-amino-2-naphthol which was carried out using NaOCl (30% aqueous) as the oxidant at 25 °C 1.0 M HCl solution was found to be 2200 Da.[24] While a polymer product of 8-amino-2-naphthol was formed in alkaline medium, a product at the level of oligomer was obtained in acidic medium. The molecular weight and PDI data of PANAP and PANAPSB are given in Table 2.

4.4 | Thermal analyses of ANAP, PANAP, ANAPSB and PANAPSB.

Thermal analyses curves of ANAP, PANAP, ANAPSB and PANAPSB are given in Figure 11. While the temperature at which ANAP begins to degrade is 186°C, its T_{max} value is 223°C. The temperatures at which 20% and 50% mass losses occurred were found to be 200 and 220°C. While the temperature at which PANAP begins to decompose is 179°C, its T_{max} values are 201°C, 734°C and 878°C. The temperatures at which 20% and 50% mass losses occurred were found to be 536°C and 822°C. While the degradation of ANAP was completed at 720°C, the residual amount of its polymer at 1000°C was 25%. Thermal degradation of PANAP occurred in three steps. The mass loss of the first step between 150 and 580°C was calculated as 21.53%. The mass loss of the first step between 580 and 790°C was calculated as 20.79%. The mass loss of the third step between 790 and 1000°C was calculated as 32.58%. The loss due to the absorbed water between the polymer chains was calculated as 8% up to 150°C. The temperature at which ANAPSB begins to decompose is 203°C, while T_{max} values are 250 and 612°C. Thermal degradation of ANAPSB occurred in two steps. The mass loss of the first step between 120 and 450°C was
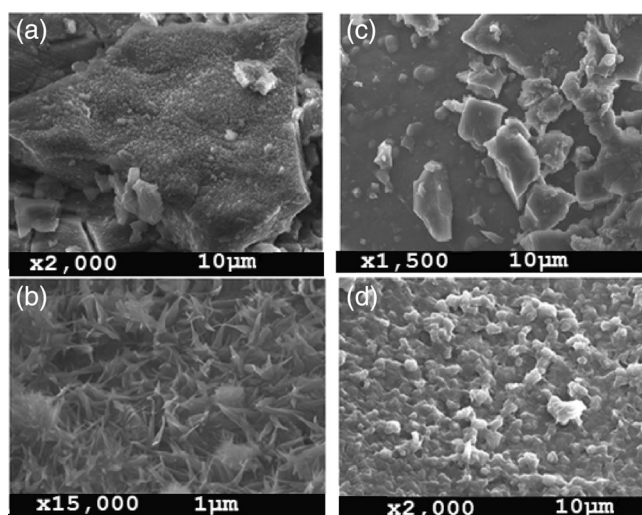

FIGURE 12 SEM images of PANAP (a, b) and PANAPSB (c, d).

calculated as 39.49%. The mass loss of the second step between 450 and 640°C was calculated as 58.49%. The loss due to the absorbed water between the polymer chains was calculated as 1.28% up to 120°C. The temperature at which PANAPSB begins to decompose is 183°C, while T_{max} values are 217, 753 and 886°C. Thermal degradation of PANAPSB occurred in three steps. The mass loss of the first step between 150 and 600°C was calculated as 20.88%. The mass loss of the second step between 600 and 795°C was calculated as 22.30%. The mass loss of the third step between 795 and 975°C was calculated as 40.16%. The loss due to the absorbed water between the polymer chains was calculated as 16.65% up to 150°C. The temperatures at which 20% and 50% mass losses occurred of PANAPSB were found to be 562 and 830°C. The temperatures at which 20% and 50% mass losses occurred of ANAPSB were found as 276 and 536°C. The ANAPSB lost

TABLE 4 Solubility determination values of the obtained compounds at room temperature

Solvent	Compounds			
	ANAP	PANAP	ANAPSB	PANAPSB
Acetone	+	−	+	−
Methanol	+	+	+	±
Ethanol	+	−	+	±
DMF	+	+	+	+
DMSO	+	+	+	+
DMAC	+	−	+	+
THF	+	−	+	−
Chloroform	−	−	−	−
Acetonitrile	+	+	+	+
Dichloroethane	−	−	−	−

Note: +, soluble; ±, partially soluble; −, insoluble.

all of its mass at 640 °C, while PANAPSB lost all of its mass at 975°C.

Table 3 shows the thermal data of the ANAP, PANAP, ANAPSB and PANAPSB. These results obtained from the graphs show that the initial decomposition temperatures of monomers (T_{on}) are lower than the polymers. It can be said that these results are directly proportional to the molecular weights of the polymers obtained.[24,41,42]

4.5 | Surface morphology of polymers

SEM photographs of PANAP and PANAPSB compounds are given in Figure 12. When the SEM image of the synthesized PANAP compound was examined at 15000×, it was observed that it had a crystalline structure. When the SEM image of the synthesized PANAPSB compound was examined, it was observed that the compound had a spongy structure.

4.6 | Solubility

The solubility determinations of the obtained compounds were measured in test tubes at room temperature as 1 mg 1 mL^{-1} concentrations in various organic solvents. The solubility of the samples is usually obtained by the use of alkyl substituents and provides a great advantage in terms of characterization, preparation and practical use of the products.[43]

The solubility values of the synthesized compounds are shown in Table 4. The ANAP and ANAPSB were soluble in strongly polar solvents such as methanol, ethanol, acetone, DMF, DMSO, THF, acetonitrile and DMAC, while they were not dissolved in chloroform and dichloroethane. Similarly, PANAP and PANAPSB were soluble very good in polar solvents such as DMF, DMSO, acetonitrile and DMAC.

5 | CONCLUSIONS

In this study carried out, polymers of 8-amino-2-naphthol and its Schiff base compound was achieved in aqueous alkaline medium by H_2O_2 (35%) oxidant. The structures of monomer, Schiff base and polymers were confirmed by FT-IR, ^{1}H-NMR, UV–Vis and ^{13}C-NMR measurements. According to the thermal analyses, value of residue at 1000 °C of PANAP was higher than other ANAP, ANAPSB and PANAPSB compounds. Due to these properties, PANAP can be used as an additive to increase the oxidation induction time of aliphatic polymers such as poly(propylene) and poly(ethylene). The Mn values of PANAP and PANAPSB were between 9250 Da and 9900 Da, and PDI values were between 1.059 and 1.046. According to the results obtained from the characterization, PANAP and PANAPSB were determined to have narrow molecular distribution. Low-PDI values have shown that PANAP and PANAPSB have a monodisperse population of polymer chains. The T_g of PANAP and PANAPSB were found to be 159 and 150°C, respectively, from DSC measurements. The electrochemical HOMO-LUMO energy levels and electrochemical band gaps (E'_g) were calculated from cyclic voltammetry (CV) measurements and E'_g values of ANAP, PANAP, ANAPSB and PANAPSB were calculated to be 3.28, 2.13, 2.89 eV and 2.59 eV, respectively. The low electrochemical band gap values of polymers show that they can be used at photovoltaic devices. The fluorescence intensity value of PANAP was observed to be higher than PANAPSB.

AUTHOR CONTRIBUTIONS

Ismet Kaya: Conceptualization (equal); formal analysis (equal); investigation (equal); methodology (equal); resources (equal); software (equal); supervision (lead); validation (equal); writing – original draft (equal); writing – review and editing (equal). **Burçin Akyüz:** Conceptualization (equal); data curation (equal); formal analysis (equal); methodology (equal); resources (equal); software (equal); validation (equal); writing – original draft (equal); writing – review and editing (equal). **Şahin Özel:** Conceptualization (equal); data curation (equal); investigation (equal); methodology (equal); software (equal); validation (equal); writing – original draft (equal); writing – review and editing (equal).

CONFLICT OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY STATEMENT

Research data are not shared.

ORCID

İsmet Kaya https://orcid.org/0000-0002-9813-2962

REFERENCES

[1] M. Grigoras, N. C. Antonoaia, *Eur. Polym. J.* **2005**, *41*, 1079.
[2] K. Suematsu, K. Nakamura, J. Takeda, *Colloid Polym. Sci.* **1983**, *261*, 493.
[3] S. Banerjee, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3565.
[4] C. Mallet, M. Le Borgne, M. Starck, W. Skene, *Polym. Chem.* **2013**, *4*, 250.
[5] M.-F. Zaltariov, M. Cazacu, A. Vlad, L. Sacarescu, S. Shova, *High Perform. Polym.* **2015**, *27*, 607.
[6] G. D'alelio, J. Crivello, R. Schoenig, T. Huemmer, *J. Macromol. Sci. Chem.* **1967**, *1*, 1161.
[7] M. Palewicz, A. Iwan, A. Sikora, J. Doskocz, W. Strek, D. Sek, B. Mazurek, *Act. Phys. Polonica* **2012**, *121*, 16.
[8] S. Dineshkumar, A. Muthusamy, P. Chitra, S. Anand, *J. Adhes. Sci. Technol.* **2015**, *29*, 2605.
[9] A. Iwan, B. Boharewicz, I. Tazbir, M. Malinowski, M. Filapek, T. Kłąb, B. Luszczynska, I. Glowacki, K. P. Korona, M. Kaminska, *Sol. Energy* **2015**, *117*, 246.
[10] K. Gawlinska, A. Iwan, Z. Starowicz, G. Kulesza-Matlak, K. Stan-Glowinska, M. Janusz, M. Lipinski, B. Boharewicz, I. Tazbir, A. Sikora, *Opt. Electron. Rev.* **2017**, *25*, 274.
[11] İ. Kaya, M. Yıldırım, A. Aydın, *Org. Electron.* **2011**, *12*, 210.
[12] N. Khalid, A. Bibi, K. Akhtar, K. Mustafa, M. Khan, N. Saeed, *Polym. Plastics Technol. Mater.* **2019**, *58*, 419.
[13] E. Hamciuc, M. Homocianu, C. Hamciuc, I.-D. Carja, *High Perform. Polym.* **2018**, *30*, 339.
[14] M. Palewicz, A. Iwan, J. Doskocz, W. Strek, D. Sek, B. Kaczmarczyk, B. Mazurek, *Polym. Bull.* **2011**, *66*, 65.
[15] M. Rusu, A. Airinei, G. G. Rusu, L. Marin, V. Cozan, P. RÂmbu, I. Caplanus, G. I. Rusu, *J. Macromol. Sci. Part B* **2011**, *50*, 1285.
[16] K. Temizkan, İ. Kaya, *Mater. Sci. Eng., B* **2020**, *282*, 115782.
[17] C. Mallet, A. Bolduc, S. Bishop, Y. Gautier, W. Skene, *Phys. Chem. Chem. Phys.* **2014**, *16*, 24382.
[18] M.-H. Tremblay, T. Skalski, Y. Gautier, G. Pianezzola, W. G. Skene, *J. Phys. Chem. C* **2016**, *120*, 9081.
[19] İ. Kaya, M. Kamacı, *Prog. Org. Coat.* **2012**, *74*, 204.
[20] İ. Kaya, F. Kolcu, G. Demiral, H. Ergül, E. Kiliç, *Des. Monomers Polym.* **2015**, *18*, 89.
[21] Z. Youming, D. Xinrong, W. Liangcheng, W. Taibao, *J. Inclusion Phenom. Macrocyclic Chem.* **2008**, *60*, 313.
[22] D. Nepal, S. Samal, K. E. Geckeler, *Macromolecules* **2003**, *36*, 3800.
[23] S. B. Park, H. Kim, W. C. Zin, J. C. Jung, *Macromolecules* **1993**, *26*, 1627.
[24] F. Doğan, İ. Kaya, A. Bilici, M. Yıldırım, *J. Polym. Res.* **2015**, *22*, 104.
[25] S. Dineshkumar, A. Muthusamy, *Polym.-Plast. Technol. Eng.* **2016**, *55*, 368.
[26] I. Kaya, A. Vilayetoglu, H. Mart, *Polymer* **2001**, *42*, 4859.
[27] I. Kaya, B. Akyüz, F. Kolcu, H. Söyüt, *React. Funct. Polym.* **2022**, *175*, 1381.
[28] I. Kaya, S. Koça, *Polymer* **2004**, *45*, 1743.
[29] A. Özbülbül, H. Mart, M. Tunçel, S. Serin, *Des. Monomers Polym.* **2006**, *9*, 169.
[30] M. Mostefai, M. C. Pham, J. P. Marsault, J. Aubard, P. C. Lacaze, *J. Electrochem. Soc.* **1996**, *143*, 2116.
[31] M.-C. Pham, M. Mostefai, P.-C. Lacaze, L. H. Dao, *Syn. Mater.* **1994**, *68*, 39.
[32] X. G. Li, M.-R. Huang, Y. Yang, *Polym. J.* **2000**, *32*, 348.
[33] J. Longun, B. Buschle, N. Nguyen, M. Lo, J. Iroh, *J. Appl. Polym. Sci.* **2010**, *118*, 3123.
[34] İ. Kaya, B. S. Sandal, H. Karaer, *J. King Saud Univ. Sci.* **2019**, *31*, 75.
[35] M. Cazacu, M. Marcu, A. Vlad, G. I. Rusu, M. Avadanei, Chelate polymers. VI., *J. Organomet. Chem.* **2004**, *689*, 3005.
[36] R. J. Turton, *Physics of Solids*, Oxford University Press, Oxford **2005**.
[37] R. Cernini, X. Li, G. Spencer, A. Holmes, S. Moratti, R. Friend, *Synth. Met.* **1997**, *84*, 359.
[38] İ. Kaya, T. Yılmaz, *J. Fluoresc.* **2017**, *27*, 379.
[39] J. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, NY **1999**.
[40] E. Vaganova, M. Rozenberg, S. Yitzchaik, *Chem. Mater.* **2000**, *12*, 261.
[41] B. Lu, J. Xu, C. Fan, F. Jiang, H. Miao, *Electrochim. Acta* **2008**, *54*, 334.
[42] A. Bilici, F. Dogan, M. Yıldırım, İ. Kaya, *J. Phys. Chem. C* **2012**, *116*, 19934.
[43] N. Kuramoto, A. Tomita, *Synth. Met.* **1997**, *88*, 147.