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Synthesis of Poly(azomethine) Containing Sulfonic Acid Unit Oxygen and Sulphur Bridged: Investigation of Its Thermal, Optical and Electrochemical Properties

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Abstract

In this study, a poly(azomethine) compound (SBP) containing sulfur and oxygen bridge was obtained from 4,4'-[thiobis(4,1-phenyleneoxy)]dibenzaldehyde (DBA) and 4,4'diamino-2,2'-biphenyl sulfonic acid from condensation reaction. Structural, optical, electrochemical and morphological analyzes of the obtained polymeric material were performed. Structural characterizations were performed from 1H-NMR and FT-IR spectra. Optical properties were determined in the UV-Vis spectrum and the optical band gap was calculated as 3.63 eV. Electrochemical properties were investigated by cyclic voltammetry (CV) and HOMO-LUMO and electrochemical band gap values were calculated. In addition, with the help of Gel Permeation Chromatography (GPC), the average molecular mass was found 5050 Da. Thermogravimetric analysis (TGA) results showed that the thermal degradation of SBP occurred in four steps and the maximum mass loss was at 391 °C. The surface analysis of the obtained polymeric material was investigated with scanning electron microscope (SEM) and it was determined that the surface was rough.

Keywords: Schiff base, poly(azomethine), sulphanilic acid, electrochemical band gap, thermal analysis.

1. Introduction

The imine compound form the reaction of a carbonyl and an amine compound under suitable conditions is called Schiff base [1]. These compounds, first synthesized by Hugo Schiff, are highly researched substances due to their relatively easy synthesis, obtained compounds having wide range of colors and high thermal and mechanical features [2–4]. With the polycondensation of two reagents with diamine and dicarbonyl groups, long-chain poly(imine), also known as poly(azomethine) compounds, are obtained [5,6]. Due to their high conjugation, poly (azomethine) compounds generally have improved optical, electrochemical, thermal and mechanical properties. In this way, they have a wide application network [7–9]. In addition, these compounds allow the design of materials that can tune their properties in the desired direction, due to the diversity of monomers [10]. Poly(azomethine) features could be improved by changing the colors, conductivity or solubility with various organic and inorganic dopants such as m-cresol, methane sulfonic acid, $SnCl_2$ [11–13]. 10-Camforsulfonic acid was doped into a poly(azomethine) compound obtained in a study by Iwan et al., and its solubility was improved with photovoltaic parameters for solar cell application [14].

Among the dopant materials used, especially sulfonic acid derivatives have an important place due to the increase in solubility, high conductivity and thermal stability and flexibility they bring to the material [15,16]. In fact, it has been reported that a fluorene-based poly(azomethine) acquires photoluminescence and electroluminescence properties when only sulfonated polystyrene is added to the compound and its protonation is increased [17]. In addition, sulfonic acid groups are also used in active catalyst systems, dyes, detergents and surfactants [18–21].

In this study, it was aimed to obtain a poly(azomethine) compound with especially high thermal resistance. In the light of this information, a dialdehyde compound (DBA) was obtained by bromine elimination from 4-

Bromobenzaldehyde and 4,4'-thiodiphenol; and a Schiff base polymer (SBP) was synthesized from 4,4'-diamino-2,2'-biphenyl sulfonic acid and DBA by Schiff base reaction. After the synthesized DBA and SBP were characterized, their optical, electrochemical, thermal and surface properties were investigated.

2. Materials and Methods

2.1. Materials

4-Bromobenzaldehyde, 4,4'-thiodiphenol, 4,4'-diamino-2,2'-biphenyl sulfonic acid, K_2CO_3, para-toluensulfonic acid (PTSA) used as reagents and catalyst in the study and solvents dimethyl sulfoxide (DMSO), methanol and dimethylacetamide (DMA) were obtained from Merck Co (Germany). All chemicals and solvents were used without further purification.

2.2. Synthesis of DBA

DBA was obtained by bromine elimination reaction by using 4-bromobenzaldehyde instead of 4-iodobenzaldehyde using the method given in the literature [22]. 1.091 g (0.005 mol) of 4,4'-thiodiphenol was dissolved in 15 mL of DMA in a 100 mL three-necked flask. 1.382 g (0.01 mol) of K_2CO_3 was weighed and added to the flask. It was stirred for 1 hour at 150°C under reflux in Ar atmosphere. Then, 2 g (0.01 mol) of 4-bromobenzaldehyde was weighed into a beaker and 6.5 mL of DMA was dissolved. The mixture was added dropwise to the flask. After 12 hours of reaction at 150°C, the product was precipitated in ice water and filtered. It was dried in a vacuum oven at 50°C for 12 hours. The reaction scheme is shown in Figure 1A.

2.3. Synthesis of SBP

Weighed 0.670 g (0.0015 mol) of synthesized DBA and 0.516 g (0.0015 mol) of 4,4'-diamino-2,2'-biphenylsulfanic acid. The weighed substances were added into a 100 mL three-necked round bottom flask and it was dissolved in 20 mL of DMA. As a catalyst, PTSA 0.285g (0.0015 mol) was weighed and 2 mL of toluene was added by dissolving and mixed. After stirring under an argon atmosphere at 150 °C for 4 hours, it was cooled under an argon atmosphere at room temperature for 9 hours. The product was precipitated with methanol and washed with methanol to remove unreacted materials, dried in a vacuum oven at 50°C for 3 hours. The reaction scheme is given in Figure 1B.

^{1}H NMR (DMSO-d6, δ, ppm): 9.76 (s, terminal -CHO), 8.10 (s, -SO_3H), 7.81 (s, -C=N), 7.49 (d, Hd), 7.41 (d, Hb), 7.16 (s, Hf), 7.11 (d, He), 7.05 (d, Hc), 6.90 (s, terminal –NH_2), 6.67 (d, Ha).

^{13}C NMR (DMSO-d6, δ ppm): 191.51 (terminal –CHO), 166.36 (-C=N-) and 116.74, 119.17, 122.10, 126.28, 127.91, 128.62, 138.11, 146.43, 147.12, 157.14, 162.97 (Ar-C).

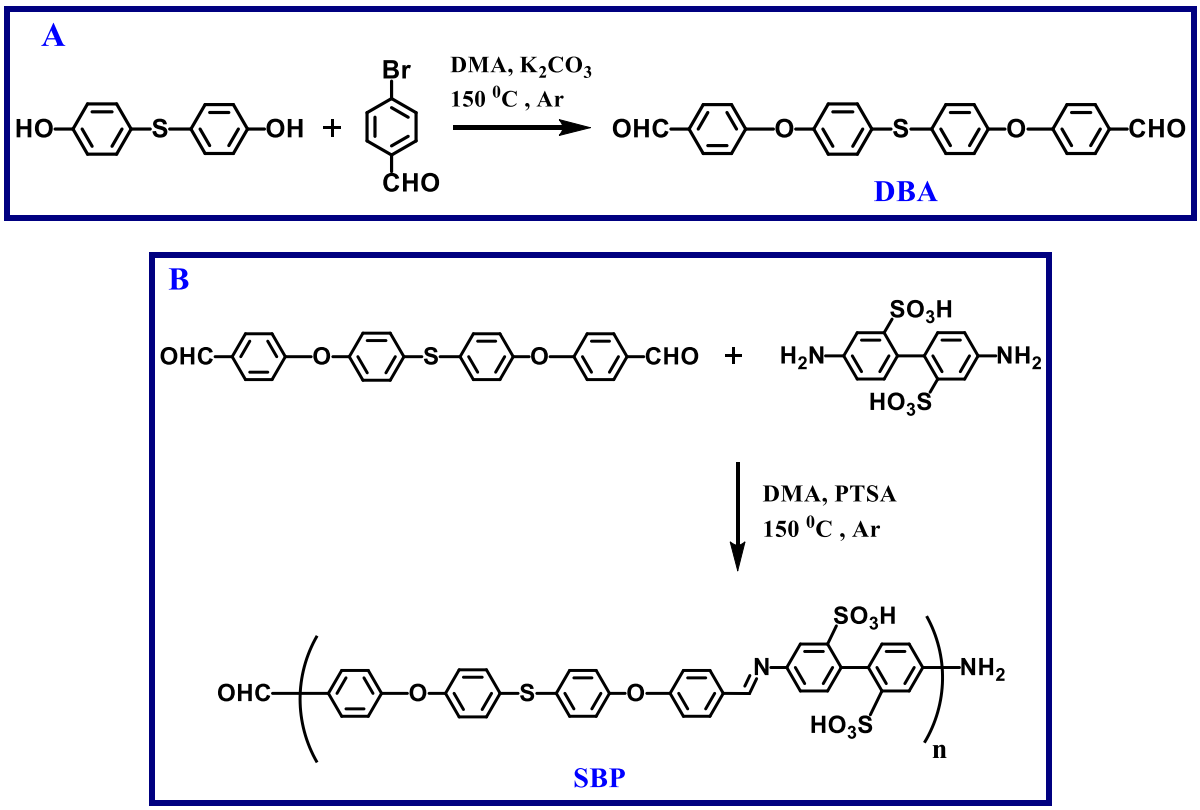

Figure 1. Reaction scheme of a) DBA and b) SBP synthesis.

2.4. Characterization techniques

The FT-IR spectrophotometer used for the structural analysis of the obtained DBA and SBP is a Perkin Elmer Spectrum-One instrument with ATR sampling accessory. Spectra were obtained in the range of 4000-400 cm^{-1} at room temperature. ^{1}H-NMR and ^{13}C-NMR techniques were used in nuclear magnetic resonance spectrophotometer analysis, which is another structural characterization. ^{1}H-NMR (400 MHz, DMSO, $SiMe_4$ internal standard) and ^{13}C-NMR (100.6 MHz, DMSO, $SiMe_4$ internal standard) spectra were obtained using the solutions of the samples in DMSO using Bruker AC FT-NMR instrument.

Optical properties of the obtained materials were examined with Analytikjena Specord 210 Plus UV-Vis spectrophotometer device. Spectra were obtained from solutions of DBA and SBP prepared in DMA at room temperature in the range of 280-800 nm.

The electrochemical character of DBA and SBP was analyzed by cyclic voltammetry (CV). Voltamograms were obtained with a CH instruments 660 C electrochemical Analyzer (CH Instruments, Texas, USA) at room temperature and using 0.1 M tetrabutylammonium hexafluorophosphate (TBA) as the electrolyte solution. A triple electrode system (Ag reference electrode, Pt counter electrode and glassy carbon working electrode) was used. After the film of SBP dissolved in DMF was prepared by casting solution on a glass slide surface, the measurement of solid state conductivity was made with a two-probe Keithley 2400 Electrometer.

The thermal stability of the samples was examined with the Perkin Elmer Spphire Differential Scanning Calorimetry device, which measures the mass loss with an increase of 10 °C per minute in a nitrogen atmosphere. The molecular weight of the polymer (SBP) was determined by gel transmission chromatography-light scattering (GPC-LS) analysis with the Malvern Viscotek GPC Dual 270 max system with a refractive index detector (RID) and 8.00 mm x 300 mm dual column. The column temperature was 55 °C. DMF at a flow rate of 1.0 mL min-1 was used as eluent including 40 mM LiBr. In order to examine the surface properties of the polymeric material, after the samples were subjected to gold and carbon coating, JEOL SEM-7100-EDX scanning electron microscope was used.

3. Results and Discussion

3.1. Structural Analysis

DBA, a dibenzaldehyde compound obtained from the bromine elimination reaction from 4,4'-thiodiphenol and bromo-benzaldehyde, was examined by FTIR spectroscopy. In a study by Culhaoğlu and Kaya [22], the FT-IR spectra of this synthesized substance were compared and it was observed that the spectra were compatible with each other. FT-IR spectra of synthesized DBA and SBP are shown in Figure 2. The characteristic -C=O vibration of the aldehyde group in the structure of DBA was observed at 1685 cm^{-1} and the -C-O-C- vibration arising from the oxygen bridge in the structure was observed at 1227 cm^{-1}. In the spectrum of SBP obtained as a result of polymerization of DBA with 4,4'-diamino-2,2'-biphenylsulfanic acid, a derivative of sulfanilic acid, the characteristic imine (-C=N-) vibration, originating from the Schiff base, was observed at 1601 cm^{-1}. In addition, aromatic -C-H vibrations in the structure of SBP appeared at 3116 cm^{-1} and 3045 cm^{-1}, aromatic C=C vibrations at 1593 cm^{-1} and 1573 cm^{-1}, and -C-O-C- vibration at 1221 cm^{-1}. The disappearance of the carbonyl vibration of the aldehyde and the amine vibration of the 4,4'-diamino-2,2'-biphenylsulfanic acid observed in DBA in the SBP formed as a result of the polymerization reaction, and the emergence of the vibration peak of the imine is an indication of the formation of the Schiff base polymer.

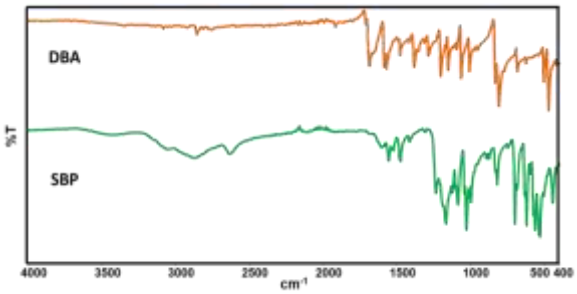

Figure 2. FT-IR spectra of DBA and SBP.

A poly(azomethine) compound, SBP, was obtained after the reaction of the carbonyl group of the dibenzaldehyde compound DBA and the amine group of 4,4'-diamino-2,2'-biphenylsulfanic acid, which is a sulfanilic acid derivative, with the presence of PTSA catalyst. ^{1}H-NMR spectra were taken and shown in Figure 3. The signal seen at 7.81 ppm in the ^{1}H-NMR spectrum belongs to the characteristic imine proton formed as a result of the reaction of the amine and carbonyl. The proton signals of the terminal aldehyde and terminal amine at the ends of the polymer chain formed as a result of polymerization were observed in the spectrum at 9.76 ppm and 6.90 ppm, respectively. The acid protons from the sulfanilic acid in the SBP chain corresponded to the singlet signal seen at 8.10 ppm. Also, the signals seen in the spectrum at 7.49 ppm, 7.41 ppm, 7.16 ppm, 7.11 ppm, 7.05 ppm and 6.67 ppm belonged to Hd, Hb, Hf, He, Hc and Ha on the aromatic ring, respectively.

Celal Bayar University Journal of Science
Volume 18, Issue 2, 2022, p 185-191
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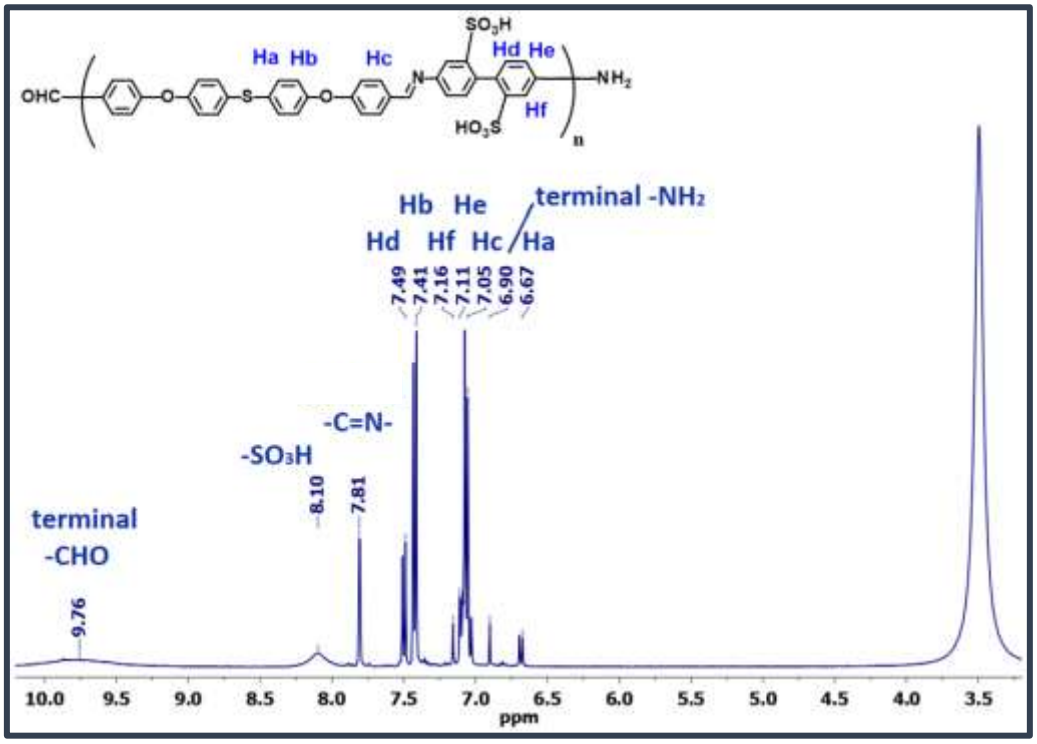

Figure 3. ^{1}H-NMR spectrum of SBP.

3.2. Optical Analysis

The optical properties of the synthesized DBA and SBP were investigated by UV-Vis Spectroscopy and the spectra obtained from the solutions prepared in DMA are shown in Figure 4. In the spectrum of DBA, a shoulder shape observed at 289 nm was observed, which is caused by the electronic transitions of π→π* phenyl groups in the structure. When the spectrum of SBP, a Schiff base polymer, is examined, a peak belonging to the characteristic imine group n → π* electronic transition is observed at 312 nm. The optical properties of the synthesized DBA and SBP were investigated by UV-Vis Spectroscopy and the spectra obtained from the solutions prepared in DMA are shown in Figure 4. In the spectrum of DBA, a shoulder shape observed at 289 nm was observed, which is caused by the electronic transitions of π→π* phenyl groups in the structure. When the spectrum of SBP, a Schiff base polymer, is examined, a peak belonging to the characteristic imine group n → π* electronic transition is observed at 312 nm. The most important reason for the expansion of this signal is the increased conjugation in the polymeric structure.

3.3. Electrochemical analysis

Electrochemical properties of DBA and SBP were investigated by cyclic voltammetry. The voltammograms obtained in the electrolyte solution at room temperature and in an argon atmosphere between +1600 mV and -1600 mV are given in Figure 6. Reduction potential (E_{red}) and oxidation potential (E_{ox}) of DBA and SBP were obtained from voltammograms. From these obtained E_{ox} and E_{red} values, HOMO - LUMO energy levels and

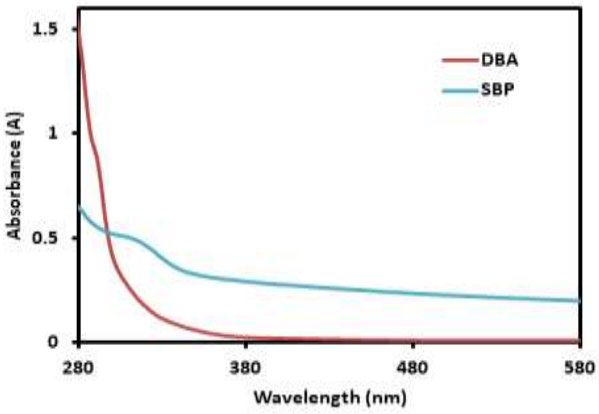

Figure 4. UV-Vis Spectra of DBA and SBP.

electrochemical band gap (E'_g) were calculated with the help of the formulas given in the literature[24,25]:

$$E_{HOMO} = -(4.39 + E_{ox}) \quad (1)$$

$$E_{LUMO} = -(4.39 + E_{red}) \quad (2)$$

$$E'_g = E_{LUMO} - E_{HOMO} \quad (3)$$

Celal Bayar University Journal of Science
Volume 18, Issue 2, 2022, p 185-191
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From voltammograms, E_{ox} and E_{red} values were found to be +0.86 V and -0.94 V for DBA, and +1.27 V and -1.09 V for SBP, respectively. E_{HOMO}, E_{LUMO} and E'_g values were calculated in the light of the formulas given above and -5.25 eV, -3.45 eV and 1.80 eV for DBA; for SBP, it was calculated as 5.66 eV, -3.30 eV and 2.36 eV, respectively. As a result of the polymerization, it was observed that the E'_g value increased due to the increased conjugation.

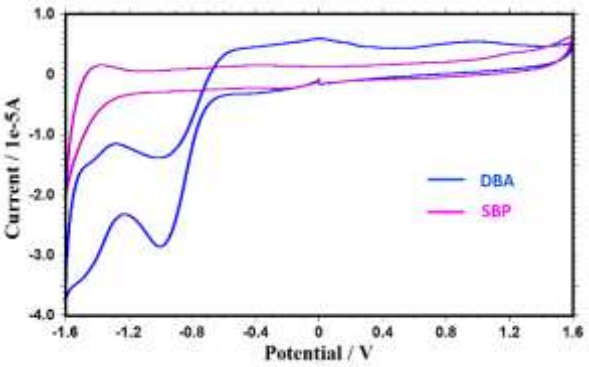

Figure 5. Voltammograms of DBA and SBP.

3.4. Conductivity of SBP

The conductivity measurement of SBP was made with the aid of a film formed on the glass surface using the casting method. After the analysis using the two-probe technique, the conductivity value of SBP was calculated as 2.35 x 10^{-10} S/cm. Since it was stated in the studies that the conductivity values of undoped poly(azomethine) compounds were generally observed in the range of 1 x 10^{-9} – 1 x 10^{-11} S/cm, the result was found to be compatible with previous studies[22]. Therefore, it turned out that the conductivity of the obtained SBP was low.

3.5. Thermal stability analysis

The thermal properties of the obtained polymer SBP were investigated by TGA and TGA-DTG-DTA curves are given in Figure 6. Accordingly, it was observed that the mass loss was 9.92% when heated up to 105°C, and this loss was due to the organic solvent and moisture in the sample. It was found that decomposition took place in four steps, except for moisture loss, and the total mass loss was 98.74%. The temperatures at which maximum mass loss occurred in each step were found as 303 °C, 391 °C, 436 °C and 513 °C. As a result of heating at 1000 °C, the amount of residue was calculated as 1.26%. According to DTA analysis, exothermic peak was observed at 442°C due to mass loss.

The thermal stability of some of the poly(azomethine) studies, which were similar to the SBP obtained within the scope of the study, were given in Table 1. Accordingly, the thermal stability of the SBP obtained especially thanks to the sulfonic acid and thioether groups was found to be higher when compared to the reference studies [2,6,8].

3.6. Molecular weight and morphology of SBP

The molecular weight of the obtained polymer SBP was determined by gel permeation chromatography (Figure 7). Four types of molecular weight values were calculated from the GPC analysis results: Number average molecular weight (Mn), weight average molecular weight (Mw), peak average molecular weight (Mp) and Z average molecular weight (Mz). Accordingly, Mn, Mw, Mp and Mz values of SBP were calculated as 5050, 5150, 5000 and 5200 Da, respectively. Accordingly, it was revealed that the new material obtained was at the level of oligomers. In addition, the polydispersity index (PDI) calculated from the ratio of Mw to Mn and expressed as the width of the molecular weight distribution was found to be 1.020.

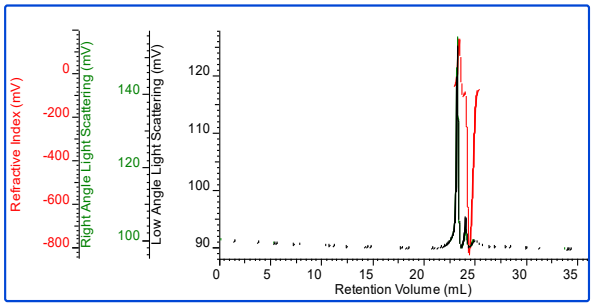

Figure 7. GPC analysis of SBP synthesis.

The structural properties of the obtained polymer were investigated by scanning electron microscopy (SEM). The SEM images given in Figure 8 showed that the obtained polymer SBP had an agglomerated structure. When the magnification was increased, the particles were found to have an irregular shape.

Table 1. Comparison of SBP with similar studies in references.

Polymers	Properties of polymer	Degradation temperature	Ref
Thiosemicarbazide base polymer	Thermally stable polymers	270 °C	2
Poly(phenoxy-imine)s	Photovoltaic properties	155 – 185 °C	6
Poly(azomethine)	Antimicrobial properties	230 – 335 °C	8
SBP	Thermally stable polymers	303 – 513 °C	in the study

Celal Bayar University Journal of Science
Volume 18, Issue 2, 2022, p 185-191
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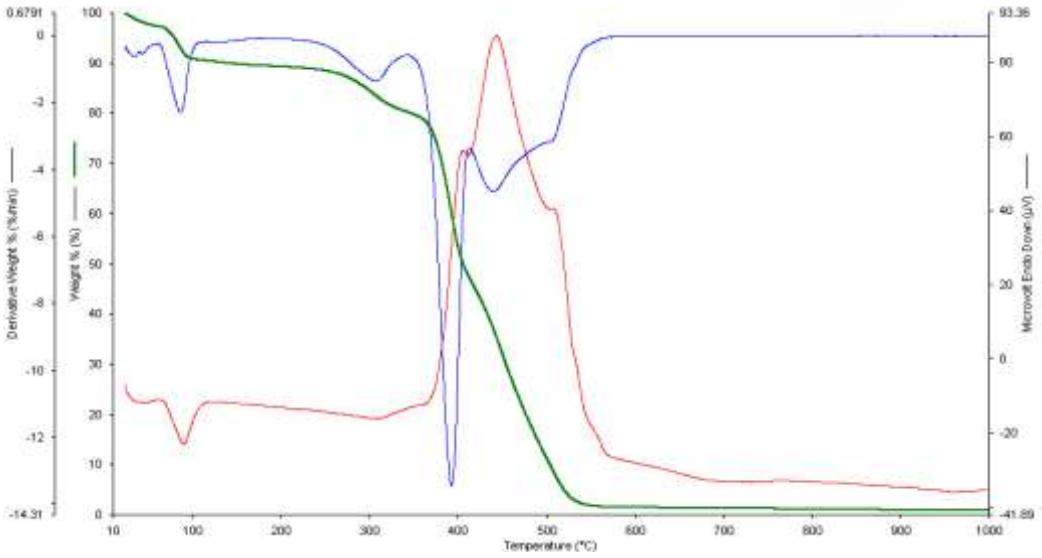

Figure 6. TGA-DTA-DTG curves of SBP.

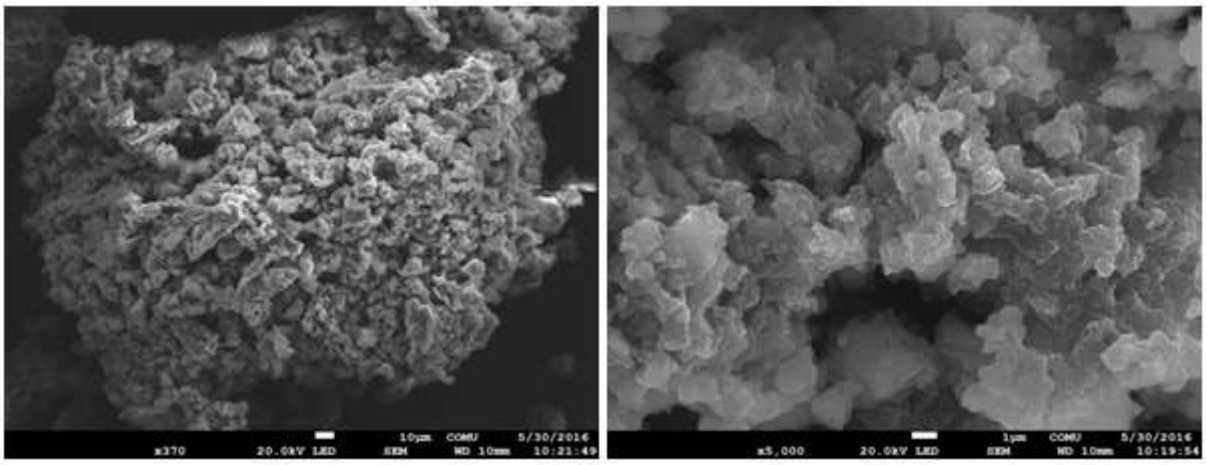

Figure 8. SEM images of SBP.

4. Conclusion

A dialdehyde compound (DBA) was synthesized by bromine elimination reaction using 4-bromobenzaldehyde from 4,4'-thiophenol, and characterized by FT-IR. SBP in poly(azomethine) structure was obtained by reaction of Schiff base from sulfonic acid derivative 4,4'-diamino-2,2'-biphenyl sulfonic acid and obtained DBA, and the structure of this unique polymer was elucidated by ^{1}H-NMR, ^{13}C-NMR and FT-IR. Optical properties of both synthesized materials were examined by UV-Vis spectroscopy and E_g values were calculated. Depending on the imine group in the structure of SBP, the n→π* transition was observed at 312 nm and the E_g value was calculated as 3.62 eV. E'_g values were calculated from the electrochemical properties of DBA and SBP examined by CV, and were calculated as 1.80 eV and 2.36 eV, respectively, and it was revealed that this difference was due to the conjugate structure of the polymer. Also the conductivity of the SBP was measured and it was found that the 2.35 x 10^{-10} S/cm value and the electrical conductivity were very low.

The molecular weight of the obtained SBP was determined by GPC and it was found that the number average molecular mass was 5050 Da. It was found that SBP, which was found to be thermally stable, decomposed in four steps and the residual amount was 1.26% after heating at 1000 °C. In addition, it was determined by SEM images that the polymeric material had a rough surface.

Author's Contributions

Elif Karacan Yeldir: Made whole experiments and analyzed of results for the article. Drafted and wrote the manuscript.

Ethics

There are no ethical issues after the publication of this manuscript.

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