황과 산소를 함유하는 새로운 Schiff Base 고분자의 합성, 특성분석, 열적 안정성과 전도성

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Synthesis, Characterization, Thermal Stability and Conductivity of New Schiff Base Polymer Containing Sulfur and Oxygen Bridges

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Abstract: In this study, we proposed to synthesize thermally stable, soluble and conjugated Schiff base polymer (SbP). For this reason, a specific molecule namely 4,4'-thiodiphenol which has sulfur and oxygen bridge in its structure was used to synthesize bi-functional monomers. Bi-functional amino and carbonyl monomers namely 4,4'-[thio-bis(4,1-phenyleneoxy)]dianiline (DIA) and 4,4'-[thiobis(4,1-phenyleneoxy)]dibenzaldehyde (DIB) were prepared from the elimination reaction of 4,4'-thiodiphenol with 4-iodonitrobenzene and 4-iodobenzaldehyde, respectively. The structures of products were confirmed by elemental analysis, FTIR, ^{1}H NMR and ^{13}C NMR techniques. The molecular weight distribution parameters of SbP were determined by size exclusion chromatography (SEC). The synthesized SbP was characterized by solubility tests, TG-DTA and DSC. Also, conductivity values of SbP and SbP-iodine complex were determined from their solid conductivity measurements. The conductivity measurements of doped and undoped SbP were carried out by Keithley 2400 electrometer at room temperature and atmospheric pressure, which were calculated via four-point probe technique. When iodine was used as a doping agent, the conductivity of SbP was observed to be increased. Optical band gap (E_g) of SbP was also calculated by using UV-Vis spectroscopy. It should be stressed that SbP was a semiconductor which had a potential in electronic and optoelectronic applications, with fairly low band gap. SbP was found to be thermally stable up to 300 °C. The char of SbP was observed 29.86% at 1000 °C.

Keywords: conjugated schiff base polymer, polyazomethine, polyimine, thermal analysis, conductivity.

Introduction

Polyazomethines were prepared by Adams and co-workers from condensation reaction of terephthalaldehyde with benzidine in 1923.[1] Polymers with a system of -HC=N- bonds in their main chain have been drawing attention of researches due to their importance in many aspects such as high thermal stability, excellent mechanical strength, good optoelectronic, non-linear optical, conducting, liquid crystal, fiber-forming and electroluminescence properties.[2-12] They are also studied in fundamental studies.[13] Unfortunately, polyazomethines have generally poor solubility and high melting temperature, which minimize their practical applications. Many kinds of polyazomethines such as polyazomethine ethers,[14] polyazomethine acrylates,[15] polyazomethine carbonates,[16] polyazomethine amide esters[17] and polyazomethine sulfones[18] have been synthesized to solve this problem and improve their applications. Additionally, polyazomethines containing methoxy substituents had been presented with fine solubility and high thermal stability.[19] Polyazomethines derived from alkoxy-substituted benzidine had been previously presented as good soluble poly-

mers.[20] The attempts to increase of solubilities of poly-azomethines by side-group functionalization were clearly reviewed by Iwan and Sek.[21] Copolymers with phenyl-substituted quinoxaline rings proved to be beneficial.[22,23] Dendritic phenylazomethines supply a good solution, because of their frameworks around various functional cores.[24,25] Some articles which describe catalytic properties explained the protonation of polyimines with heteropolyanion.[26,27]
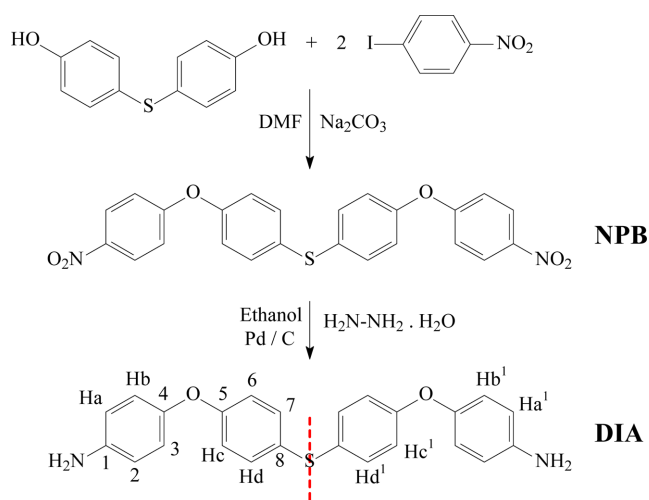
The syntheses of soluble conjugated and thermally stable azomethine polymers are very important topic in literature. The synthesized SbP was soluble in polar solvents and thermally stable up to 300 °C because of proper choice of diamine and dicarbonyl monomers. In our previous study we reported that oligo- azomethine ethers containing chlorine atoms, had higher thermal stability than oligoazomethine ethers containing no chlorine atoms.[28]

Experimental

Materials. 4-Iodonitrobenzene, 4-iodobenzaldehyde, 4,4'-thiodiphenol, p-toluene sulfonic acid (PTSA) dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-methylpyrolidonone (NMP), m-cresol, ethanol (EtOH), methanol (MeOH), ethyl acetate, chloroform ($CHCl_3$), acetone, benzene, CCl_4, CH_2Cl_2, heptane, hexane, toluene, acetonitrile (CH_3CN), and anhydrous sodium carbonate (Na_2CO_3) were supplied from Merck Chemical Co. (Germany) and used as received.

Synthesis of 1,1'-Thiobis[4-(4-nitrophenoxy)benzene] (NPB) and 4,4'-[thiobis(4,1-phenyleneoxy)]dianiline (DIA). The synthesis of NPB and DIA was done according to the reaction presented in Scheme 1. 4,4'-Thiodiphenol 10.90 g (0.05 mol) dissolved in 50 mL of DMF was added into 250 mL three-necked flask equipped with a condenser and magnetic stir bar. Anhydrous sodium carbonate 13.25 g (0.125 mol) was added to reaction flask. The mixture was heated for 1 h at 150 °C. 4-Iodonitrobenzene 24.90 g (0.1 mol) dissolved in 50 mL of DMF was added into the reaction mixture under argon atmosphere. The mixture was heated for another 8 h at 150 °C with continuous stirring. The mixture was cooled and poured into 250 mL of ice water. The crude product was washed three times with 250 mL of water for separation of mineral salts, filtered and dried in vacuum desiccators 24 h at 30 °C in yield 68%. The IR spectrum exhibited absorptions at 1594 and 1338 cm^{-1} (-NO_2) and 1243 cm^{-1} (C-O-C), respectively.

Calcd. for $C_{24}H_{16}N_2O_6S$; C, 62.60%; H, 3.50%; N, 6.08%;
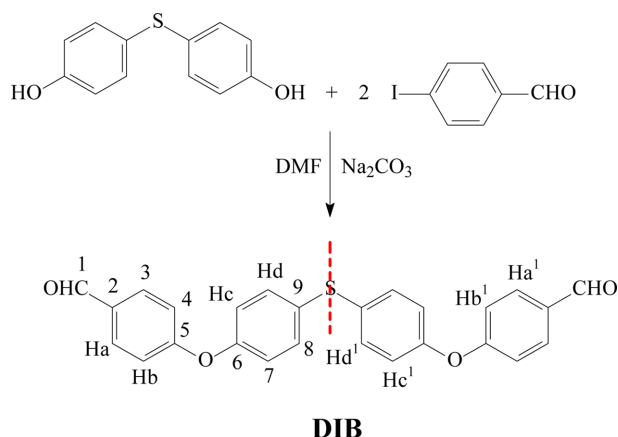

Scheme 1. Synthesis of NPB and DIA compounds.

O, 20.85%. Found; C, 62.03%; H, 3.57%; N, 6.18%; O, 20.99%.

The obtained dinitro compound (NPB) 4.60 g (0.01 mol), 0.04 g of 10% Pd-C, and 100 mL ethanol were introduced into three-necked flask to which hydrazine monohydrate (30 mL) was added drop wise over a period of 1 h at 85 °C. After addition of hydrazine monohydrate, the reaction was continued at reflux temperature for another 24 h. The mixture was then filtered to remove Pd-C. After cooling, the precipitated DIA crystals were isolated by filtration in yield 26% (mp: 107-111 °C). The infrared spectrum showed absorptions at 3386 and 3317 cm^{-1} (N-H) and 1229 cm^{-1} (C-O-C), respectively.

Calcd. for $C_{24}H_{20}N_2O_2S$; C, 71.98%; H, 5.03%; N, 6.99%; O, 7.99%. Found; C, 72.16%; H, 4.92%; N, 7.11%; O, 7.62%. DIA; ^{1}H NMR (DMSO-d_6): δ ppm, 5.02 (s, 4H, -NH_2); 6.61 (d, 4H, Ar-H$_{aa'}$); 6.76 (d, 4H, Ar-H$_{cc'}$); 6.82 (d, 4H, Ar-H$_{bb'}$); 7.27 (d, 4H, Ar-H$_{dd'}$). ^{13}C NMR (DMSO-d_6): δ ppm, 145.46 (C1), 114.34 (C2), 117.80 (C3), 146.24 (C4), 159.11 (C5), 121.51 (C6), 127.96 (C7), 133.16 (C8).

Synthesis of 4,4'-[thiobis(4,1-phenyleneoxy)]dibenzaldehyde (DIB). DIB was synthesized according to the reaction presented in Scheme 2. 4,4'-Thiodiphenol 10.90 g (0.05 mol) dissolved in 50 mL of DMF was added into 250 mL three-necked flask equipped with a condenser and magnetic stir bar. Anhydrous sodium carbonate 13.25 g (0.125 mol) was added to flask. 4-Iodobenzaldehyde 23.20 g (0.1 mol) dissolved in 50 mL of DMF was added into the reaction mixture under argon atmosphere. The reaction mixture was heated for 12 h at 150 °C with continuous stirring. The mixture was cooled and poured into 250 mL mixture of methanol/water

Scheme 2. Synthesis of DIB.

(1:1 by volume). The precipitate was washed in 250 mL water for three times to separate mineral salts in yield 65% (mp: 132-134 °C). DIB was filtered, dried in vacuum desiccator 24 h at 30 °C and recrystallized from methanol. The IR spectrum exhibited absorptions at 1691 cm^{-1} (CHO) and 1232 cm^{-1} (C-O-C). Calcd. for $C_{26}H_{18}O_4S$; C, 73.22%; H, 4.25%; O, 15.01%. Found; C, 73.09%; H, 4.13%; O, 14.88%. DIB; ^1H NMR (DMSO-d_6): δ ppm, 9.84 (s, 2H, -CHO); 7.89 (d, 4H, Ar-H$_{aa'}$); 7.34 (d, 4H, Ar-H$_{bb'}$); 6.84 (d, 4H, Ar-H$_{cc'}$); 7.44 (d, 4H, Ar-H$_{dd'}$). ^{13}C NMR (DMSO-d_6): δ ppm, 191.98 (C1), 132.71 (C2), 133.52 (C3), 117.28 (C4), 162.41 (C5), 155.02 (C6), 118.58 (C7), 121.72 (C8), 129.85 (C9).
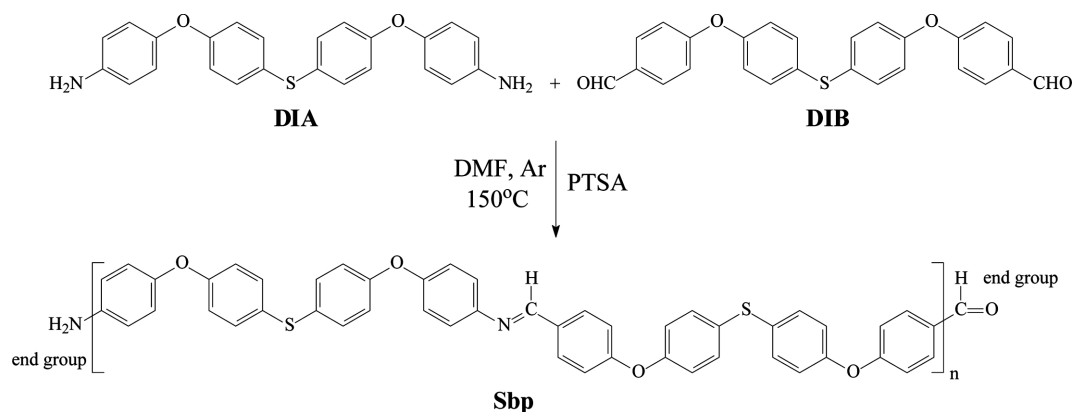
Synthesis of Conjugated Schiff Base Polymer (SbP). DIA 2.0 g (0.005 mol) and DIB 2.13 g (0.005 mol) were dissolved in 30 mL DMF in 250 mL three-necked round bottom-flask equipped with a reflux condenser, a gas inlet-outlet, a Dean-Stark trap and a magnetic stirrer. Then 2 mL of toluene (in order to remove water as an azeotropic mixture) and p-tol-

uene sulfonic acid as catalyst were added and purged with a stream of argon. Reaction mixture was stirred for 3 h at room temperature and 9 h at reflux temperature under argon atmosphere. After cooling at room temperature, SbP was precipitated into methanol, washed with methanol to remove unreacted monomers and dried at 50 °C for 3 h in a vacuum oven. The general reaction and the structure of SbP were given in Scheme 3 (Yield: 96%).

SbP: FTIR (cm^{-1}); 3116, 3045 (Ar-CH); 1623 (-C=N-); 1599, 1580 (C=C phenyl); 1227 (-O-CH$_2$ ether); 1679 (carbonyl in group end); 3435, 3350 (amino in group end). ^1H NMR (DMSO-d_6): δ ppm, 9.91 (s, 1H, CHO end group); 8.12 (s, 1H, HC=N-); 7.98 (d, 2H, H$_{16}$); 7.92 (d, 2H, H$_9$); 7.10 (d, 2H, H$_8$); 7.08 (d, 2H, H$_{10}$); 7.03 (m, 8H, H$_4$, H$_5$, H$_{12}$, H$_{13}$); 6.99 (d, 2H, H$_{15}$); 6.93 (m, 4H, H$_2$, H$_7$); 6.86 (m, 8H, H$_3$, H$_6$, H$_{11}$, H$_{14}$); 6.80 (d, 2H, H$_1$); 5.13 (s, 2H, NH$_2$). ^{13}C NMR (DMSO-d_6): δ ppm, 190.95, 162.94, 160.19, 159.11, 158.42, 156.89, 153.44, 153.06, 151.82, 150.63, 146.00, 141.13, 133.75, 133.38, 131.68, 131.18, 128.98, 125.88, 122.18, 120.81, 120.13, 118.75, 118.44, 118.25, 116.50. $(C_{49}H_{35}NO_4S_2)_n$ Calcd. for; C, 76.84; H, 4.61; N, 1.83; O, 8.36. Found; C, 76.33; H, 4.92; N, 2.02; O, 8.17.

Electrical Property of SbP. Conductivity measurement was measured on a Keithley 2400 Electrometer. The pellet was pressed on hydraulic press developing up to 1687.2 kg/cm^2. Iodine doping was carried out by exposure of the pellet to iodine vapor at atmospheric pressure and room temperature in a desiccators.[29]

Measurements. The infrared spectra were measured by Perkin Elmer Spectrum One FTIR system. The FTIR spectra were recorded by using universal ATR attachment sampling (powder form directly usable) accessory within the wave-

Scheme 3. Synthesis of Schiff base polymer.

lengths of 4000-650 cm^{-1}. Synthesized compounds were characterized by elemental analysis (LECO-CHNS-932) and ^{1}H NMR (Bruker Avance DPX-400) recorded at 25 °C using DMSO-d_6 as solvent. Thermal data were obtained using Perkin Elmer Diamond Thermal Analysis instrument. The DTA-TGA measurements were performed between 20-1000 °C (in N$_2$, rate 10 °C/min). DSC analysis was carried out using PerkinElmer Pyris Sapphire DSC. DSC measurement was performed between 25 and 450 °C in an aluminum pan (in N$_2$, 10 °C min^{-1}). The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) values of SbP were determined by size exclusion chromatography, SEC (Shimadzu Co., Japan). For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm inside diameter ×300 mm columns was used with DMF (0.4 mL/min) as the eluent applied at polystyrene standards. A refractive index detector was used to analyze the product at 25 °C.
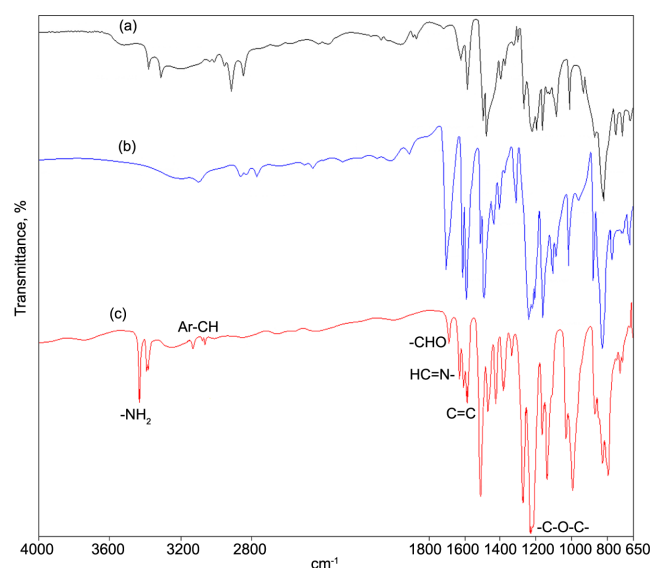
Results and Discussion

Solubility. DIA and DIB were prepared from the reaction of 4,4'-thiodiphenol with 4-iodonitrobenzene and 4-iodobenzaldehyde as shown in Schemes 1 and 2, respectively. DIA and DIB had needle shaped crystal structure with white and yellowish colors respectively. The solubility of DIA and DIB were high in organic solvents because of sulfur, ether, amino and carbonyl groups. DIA and DIB were soluble in lots of organic solvents such as DMF, DMSO, NMP, m-cresol, ethanol, methanol, ethyl acetate, chloroform and acetone. They were not soluble in benzene, CCl$_4$, CH$_2$Cl$_2$, heptane, hexane, toluene and acetonitrile. The presence of oxygen and sulfur atoms on polymer chain increased the solubility. Because of this reason, SbP was also highly soluble in aprotic solvents such as DMF, NMP, DMSO and m-cresol. It was not soluble in ethanol, methanol, ethyl acetate, chloroform, benzene, CCl$_4$, CH$_2$Cl$_2$, n-heptane, n-hexane and acetonitrile. Condensation reaction was conducted in dry DMF under argon atmosphere to protect the polymerization of initial diamine monomer. SbP powder was washed a few times with methanol/water (v/v, 1:1), to remove monomers from the product. The solution color changed from yellow to violet during polymerization. Solubility test results of monomers and SbP were shown in Table 1.

FTIR and NMR Spectrums. After completion of the synthetic studies, all compounds were characterized by FTIR, ^{1}H NMR and elemental analysis. FTIR spectra of DIA, DIB and

Table 1. Solubility Test Results of Synthesized Monomers and SbP (0.05 g in 10 mL)

Solvents	Compounds		
	DIA	DIB	SbP
DMF	+	+	*
DMSO	+	+	*
NMP	+	+	*
m-Cresol	+	+	*
C$_2$H$_5$OH	+	+	-
CH$_3$OH	+	+	-
Ethyl acetate	+	+	-
CHCl$_3$	+	+	-
Benzene	-	-	-
CCl$_4$	-	-	-
CH$_2$Cl$_2$	-	-	-
Heptane	-	-	-
Hexane	-	-	-
Toluene	-	-	-
CH$_3$CN	-	-	-

+Soluble at room temperature. *Soluble by heating. -Insoluble.

Figure 1. FTIR spectra of DIA (a); DIB (b); SbP (c).

SbP were given in Figure 1. There were significant changes between initial compounds and product. A new and sharp azomethine peak appeared. In FTIR spectra of diamine and dicarbonyl monomers, aromatic C-H vibration was observed between 3042-3017 cm^{-1} and 3068-3028 cm^{-1}, respectively. Furthermore, characteristic amine (-NH$_2$) stretching vibrations
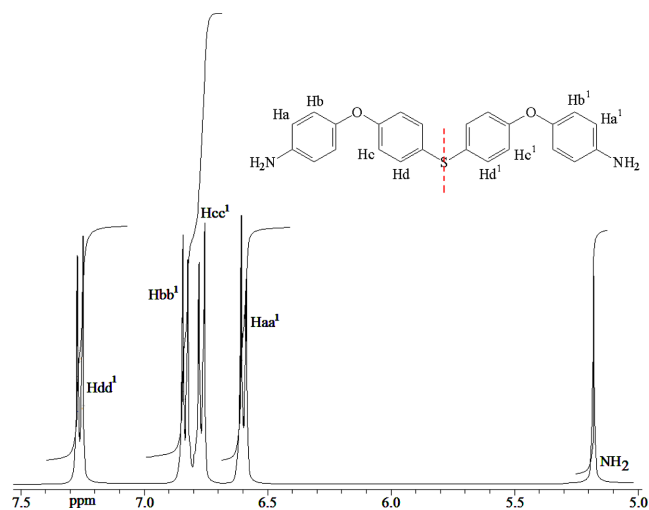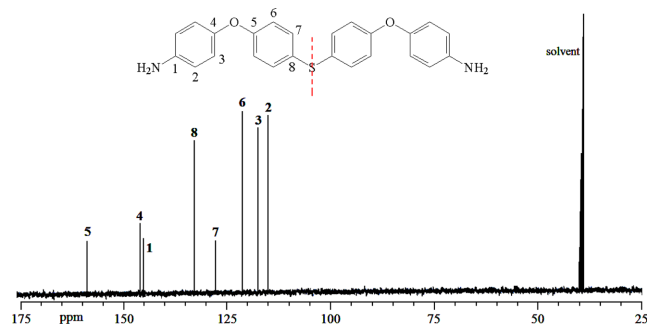
Figure 2. ^{1}H NMR spectrum of DIA.

Figure 3. ^{13}C NMR spectrum of DIA.

of diamine compound observed at 3386 and 3317 cm^{-1}. Carbonyl (-CHO) vibration was observed at 1691 cm^{-1}. Finally, in FTIR spectra of SbP, which was synthesized from the condensation reaction of DIA with DIB azomethine stretching vibration was observed at 1623 cm^{-1}. This value has demonstrated to be formation of imine bonding at the structure of

polymer.

Molecular structures of all compounds were identified from their ^{1}H NMR and ^{13}C NMR spectra recorded in DMSO-d_6. ^{1}H NMR and ^{13}C NMR spectra of DIA, DIB and SbP were given in Figures 2-7 and these results indicate that all reactions were completed successfully. In the ^{1}H NMR spectrum of SbP, the signals of imine proton and aromatic protons were observe at 8.12 and 6.80-7.98 ppm, respectively.

Molecular Weights. SEC analysis of SbP was performed at 55 ℃ using DMF/MeOH (v/v, 4/1) as eluent at a flow rate of 0.4 mL/min. According to the SEC chromatogram, number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) values of SbP were calculated according to a polystyrene standard calibration curves. It was observed that SbP contains approximately 40 repeating units with these results. According to SEC analyses M_n, M_w and PDI values of SbP were found to be 28940, 34060 and 1.177 g mol^{-1}.

Optical and Conductivity Properties. According to CV measurements, the calculated HOMO-LUMO energy levels and electro optical band gap (E'_g) for SbP are as follows: -5.59, -3.03 and 2.56 eV. These data were estimated by using the oxidation onset ($E_{ox.}$) and reduction onset ($E_{red.}$) values, as shown in Figure 8 for SbP. The calculations were made by using the following equations:[30]

$$E_{HOMO} = -(4.39 + E_{ox.}) \qquad (1)$$
$$E_{LUMO} = -(4.39 + E_{red.}) \qquad (2)$$
$$E'_g = E_{LUMO} - E_{HOMO} \qquad (3)$$

The HOMO-LUMO energy levels and the electrochemical band gaps were also shown schematically in Figure 8. The results indicate that after polycondensation reaction, HOMO
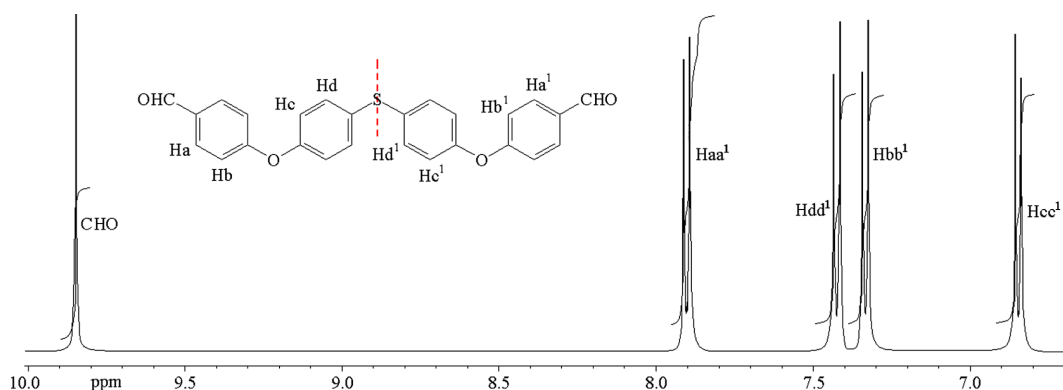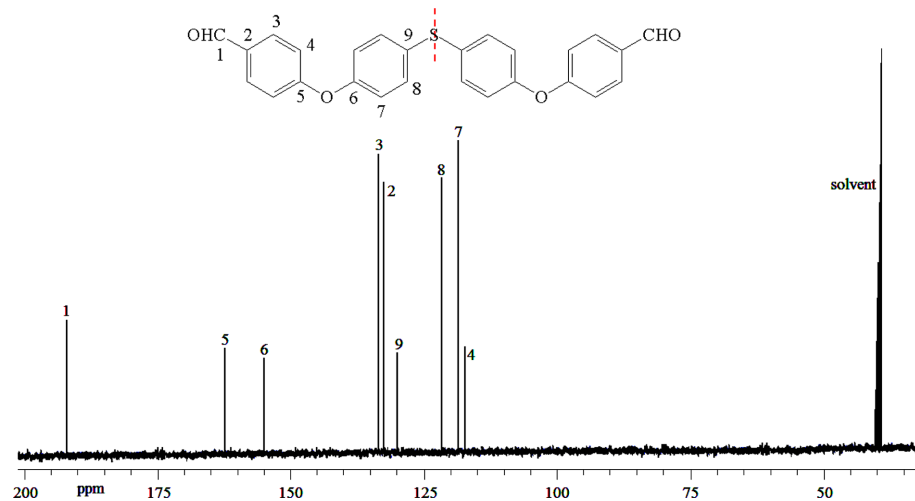

Figure 4. ^{1}H NMR spectraum of DIB.
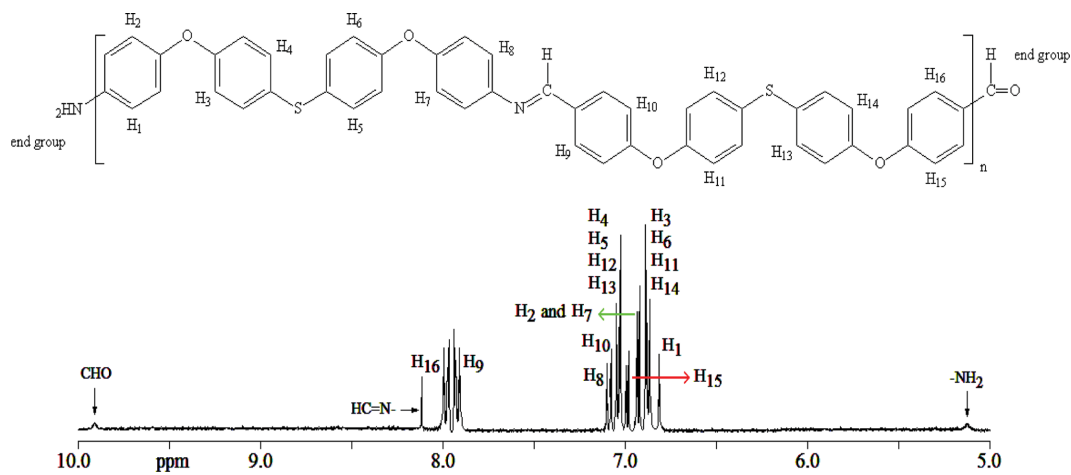
Figure 5. ^{13}C NMR spectrum of DIB.

Figure 6. ^{1}H NMR spectrum of SbP.

Figure 7. ^{13}C NMR spectrum of SbP.

Figure 8. Cyclic voltammogram of SbP.

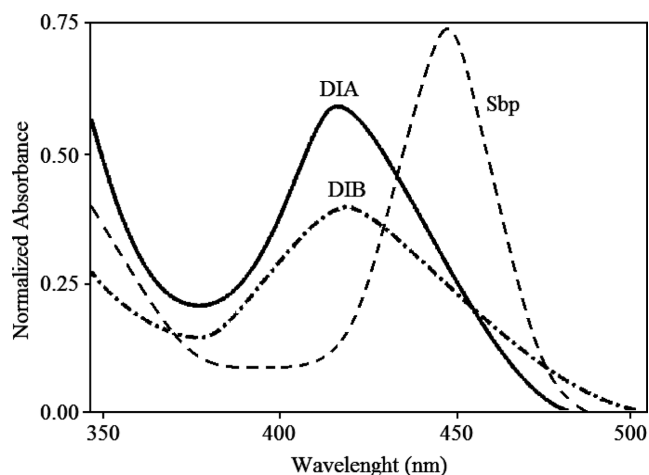**Figure 9.** UV-Vis absorption spectra of monomers and SbP in DMSO solution.

energy level increased while LUMO energy level decreased and electrochemical band gap (E'_g) of SbP was lower than those of the monomers. The low band gaps facilitated the electronic transitions between HOMO and LUMO energy levels and made the polymers more electro-conductive than the monomers.

UV-Vis spectra were measured by Perkin Elmer Lambda 25 and the absorption spectra of SbP were recorded in DMSO solvent(Figure 9). According to these spectra; the absorption edges of SbP shifted to higher wavelength values. This is because of fully conjugated structure of synthesized SbP which increase HOMO and decrease LUMO energy levels thus resulting in fairly lower band gaps. The optical band gap (E_g) of SbP was calculated from its absorption edge.[30,31] These results indicate that synthesized SbP has lower optical band gaps when compared with the monomers, as expected. Optical band gap value (E_g) of polymer is calculated as in the literature using the following equation (eq. (4)). According to UV-Vis measurement, optical band gap value (E_g) and λ_{max} values of SbP were found to be 2.62 eV and 474 nm, respectively. These values can be calculated from the absorption edge given in Figure 9.
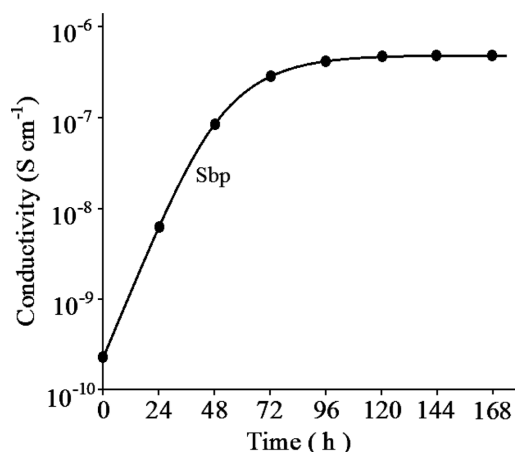
$$E_g = 1242/\lambda_{onset} \qquad (4)$$

Optical band gap values (E_g) of poly(2-(4-bromobenzylideneamino)phenol) and poly(2-(4-bromobenzylideneamino)-5-methylphenol)[32] had been found as 2.57 and 2.99 eV. Similar result was observed in this polymer.

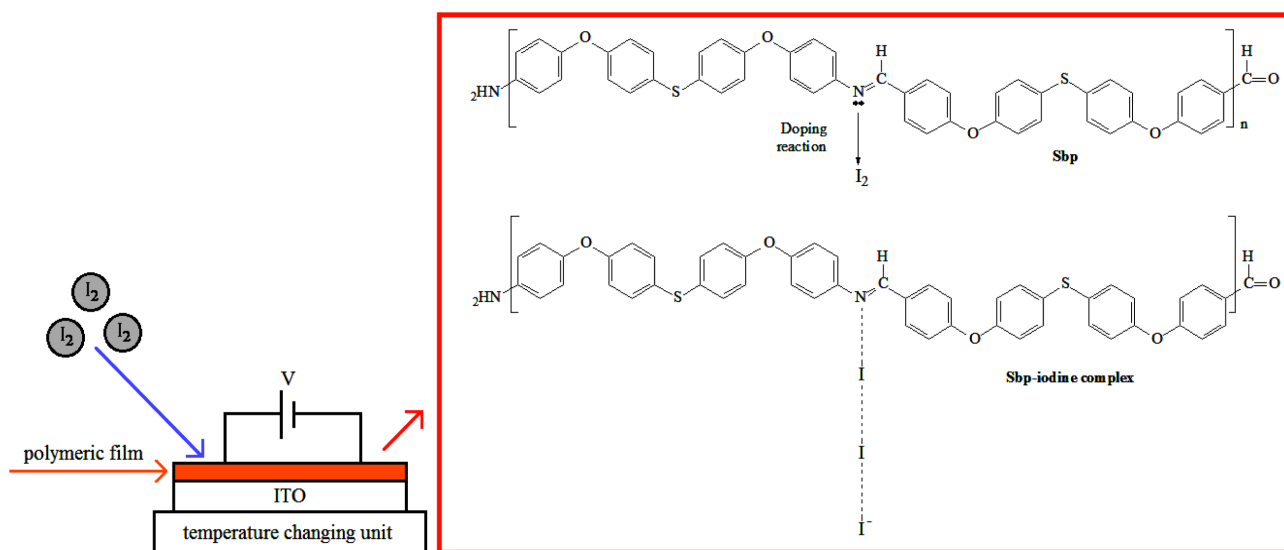The conductivity measurement of SbP was carried out with

Figure 10. Change in the electrical conductivities of SbP during the process of iodine doping at 25 °C.

an electrometer using a four-point probe technique. The color of polymer changed from brown to black and its conductivity increased by a thousand orders of magnitude during doping period. The result in Figure 10 shows that electrical conductivity of SbP during coordination of iodine at 25 °C. Since nitrogen is an electronegative element and capable of coordinating with iodine molecule, Diaz *et al.* suggested a conductivity mechanism of imine (HC=N-) polymers when doped with iodine.[29] Undoped polyazomethines and their derivatives have similar conductivity values from 10^{-11} to 10^{-9} S/cm and while doped with iodine ranges from 10^{-7} to 10^{-6} S/cm. The low conductivity values were attributed to the low degree of conjugation in the polymers caused by non-planarity of the polymer chains. On rising the temperature, the conductivity of polymer also increased slightly and polymers showed a semi-
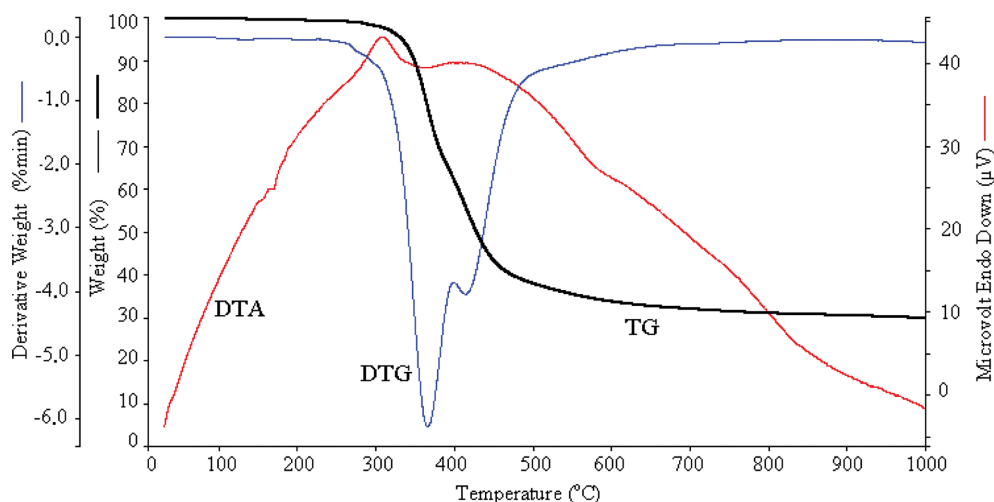
Scheme 4. Proposed conductivity mechanism of SbP with iodine molecule.

conductor behavior at higher temperatures.[33-35] The conductivity mechanism on polymer backbone can be proposed as shown in Scheme 4. Electrical conductivity values of imine structure polymers such as poly(2-(4-bromobenzylideneamino)phenol) and poly(2-(4-bromobenzylideneamino)-5-methylphenol) had been found as 11.33×10^{-10} and 6.40×10^{-10} S/cm at 25 °C.[32] As a result, the conductivity of SbP increased when doped with iodine and this polymer could be used as a semiconductive polymer in electronic, opto-electronic, electroactive and photovoltaic applications. Schiff bases, Schiff bases-metal complex compounds and Schiff base polymers could be used as photovoltaic materials.[36]

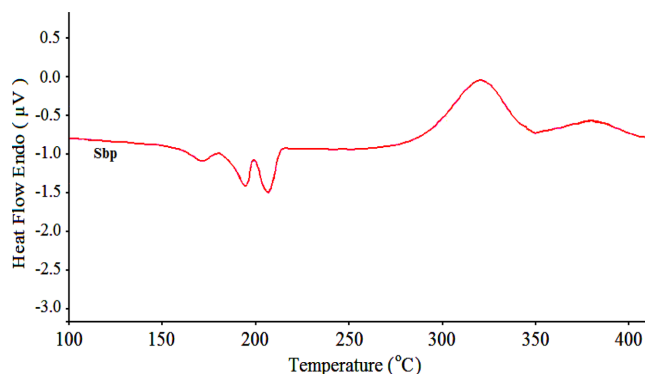**Thermal Analysis.** The TGA-DTG and DTA curves of SbP were given in Figure 11. The 20% and 50% weight losses of SbP were observed at 358 and 431 °C, respectively. SbP has onset temperature at 337 °C. The char of SbP was found to be 29.86% at 1000 °C. TGA data indicated that the SbP exhibited high thermal stability. According to TG-DTG curves, thermal degradation of SbP occurred in one steps. T_{max} values of SbP were observed at 364 and 414 °C. The weight loss of the step was found 49.20% between 337-435 °C. According to DTA analysis, endothermic and exothermic peaks were observed at 206 and 308 °C, respectively.

DSC analysis investigated transition temperature and phase duration for SbP. The phase transition temperature and DSC thermogram of SbP was displayed in Figure 12. The ther-

Figure 11. TGA, DTA and DTG curves of SbP.

Figure 12. DSC curve of SbP.

mogram shows endothermic peaks. According to Figure 12, the first peak at lower temperature indicates T_g and others are due to melting (T_m) and isotropic phase transition (T_i) and (ΔT) is different temperature between T_m and T_i, respectively. T_g, T_m, T_i and ΔT values of SbP were found as 163, 195, 207 and 12 ℃, respectively.

Conclusions

Novel soluble SbP based on 4,4'-[thiobis(4,1-phenylene-oxy)]dianiline (DIA) and 4,4'-[thiobis(4,1-phenyleneoxy)] dibenzaldehyde (DIB) incorporated into the polymer chain was synthesized. It was indicated that sulfur and oxygen bridges made SbP soluble. According to the results, fine solubility of synthesized polymer maximized its practical applications. The introduction of rigid units such as benzene rings into the poly-mer backbone would increase the polymer-polymer interaction and significantly diminished the solubility. In contrast, the introduction of sulfur or ether linkage units into the polymer backbone would decrease the polymer-polymer interaction and increase the solubility. Although lots of the conjugated poly-azomethines and their derivatives had poor solubility, the syn-thesized SbP showed good solubility because of the existence of sulfur and ether linkages. The molecular structure of the synthesized SbP was identified by FTIR, ^{1}H NMR, ^{13}C NMR and elemental analyses.

Optical property of synthesized SbP was also investigated. It was found that SbP has 2.62 eV band gap due to their fully conjugated structure. Electrical conductivity measurement showed that SbP can be used as a semiconductor which has a potential for electronic, optoelectronic applications. The con-ductivity increased approximately by one thousand orders of magnitude during doping period. The results of TGA-DTA analyses showed that SbP has enough resistance against ther-

mal decomposition. The carbine residue of this polymer was observed 29.86% at 1000 ℃. DSC curve of SbP showed three endothermic peaks at 163, 195 and 207 ℃. These temperatures indicate T_g, T_m and T_i, respectively.

References

1. R. Adams, R. E. Bullock, and W. C. Wilson, *J. Am. Chem. Soc.*, **45**, 521 (1923).
2. S. K. Menon, S. K. Jogani, and Y. K. Agrawal, *Rev. Anal. Chem.*, **19**, 361 (2000).
3. M. Grigoras, O. Catanescu, and C. I. Simionescu, *Revue Roumaine de Chimie*, **46**, 927 (2001).
4. C. Simionescu and D. Filip, *Materiale Plastice*, **37**, 42 (2000).
5. P. K. Dutta, P. Jain, P. Sen, R. Trivedi, P. K. Sen, and J. Dutta, *Eur. Polym. J.*, **39**, 1007 (2003).
6. İ. Kaya and M. Gül, *Polymer(Korea)*, **32**, 295 (2008).
7. P. Kannan, S. Raja, and P. Sakthivel, *Polymer*, **45**, 7895 (2004).
8. J. M. Adell, M. P. Alonso, J. Barbera, L. Oriol, M. Pinol, and J. L. Serrano, *Polymer*, **44**, 7829 (2003).
9. M. Grigoras and N. C. Antonoaia, *Eur. Polym. J.*, **41**, 1079 (2005).
10. D. Nepal, S. Samal, and K. E. Geckeler, *Macromolecules*, **36**, 3800 (2003).
11. D. Ribera, A. Mantecon, and J. Serra, *J. Polymer Sci., Part A: Polym. Chem.*, **40**, 4344 (2002).
12. S. H. Jung, T. W. Lee, Y. C. Kim, D. H. Suh, and H. N. Cho, *Opt. Mater.*, **21**, 169 (2002).
13. E. J. Choi, J. C. Ahn, L. C. Chien, C. K. Lee, W. C. Zin, D. C. Kim, and S. T. Shin, *Macromolecules*, **37**, 71 (2004).
14. L. Marin, V. Cozan, M. Bruma, and V. C. Grigoras, *Eur. Polym. J.*, **42**, 1173 (2006).
15. H. Tanaka, Y. Shibahara, T. Sato, and T. Ota, *Eur. Polym. J.*, **29**, 1525 (1993).
16. S. J. Sun, T. C. Chang, and C. H. Li, *Eur. Polym. J.*, **29**, 951 (1993).
17. C. H. Li and T. C. Chang, *J. Polym. Sci., Part A: Polym. Chem.*, **29**, 361 (1991).
18. L. Marin, V. Cozan, and M. Bruma, *Polym. Adv. Technol.*, **17**, 654 (2006).
19. U. Shukla, K. V. Rao, and A. K. Rakshit, *J. Appl. Polym. Sci.*, **88**, 153 (2003).
20. H. C. Kim, J. S. Kim, K. S. Kim, H. K. Park, S. Baek, and M. Ree, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 825 (2004).
21. A. Iwan and D. Sek, *Prog. Polym. Sci.*, **33**, 289 (2008).
22. C. Hamcium, E. Hamcium, I. A. Ronova, and M. Bruma, *High Perform. Polym.*, **9**, 177 (1997).
23. M. Bruma, B. Schulz, T. Töpnick, R. Dietel, B. Stiller, F. Mercer, and V. N. Reddy, *High Perform. Polym.*, **10**, 207 (1998).
24. M. Higuchi, S. Shiki, K. Ariga, and K. Yamamoto, *J. Am. Chem. Soc.*, **123**, 4414 (2001).
25. K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta, and H. Chiba,

Nature, **415**, 509 (2002).

26. E. Stochmal-Pomarzanska, S. Quillard, M. Hasik, W. Turek, A. Pron, M. Lapkowski, and S. Lefrant, *Synth. Met.*, **84**, 427 (1997).

27. W. Luzny, E. Stochmal-Pomarzanska, and A. Pron, *Synth. Met.*, **101**, 69 (1999).

28. İ. Kaya and S. Çulhaoðlu, *Polimery-W*, **54**, 266 (2009).

29. F. R. Diaz, J. Moreno, L. H. Tagle, G. A. East, and D. Radic, *Synth. Met.*, **100**, 187 (1999).

30. R. Cervini, X. C. Li, G. W. C. Spencer, A. B. Holmes, S. C. Moratti, and R. H. Friend, *Synth. Met.*, **84**, 359 (1997).

31. K. Colladet, M. Nicolas, L. Goris, L. Lutsen, and D. Vanderzande, *Thin Solid Films*, **451**, 7 (2004).

32. İ. Kaya, A. Avcı, and Ö. Gültekin, *Chinese J. Polym. Sci.*, **30**, 796 (2012).

33. S. C. Ng, H. S. O. Chan, P. M. L. Wong, K. L. Tan, and B. T. G. Tan, *Polymer*, **39**, 4963 (1998).

34. A. G. El-Shekeil, H. A. Al-Saady, and F. A. Al-Yusufy, *New Polym. Mater.*, **5**, 131 (1998).

35. A. G. El-Shekeil, M. A. Khalid, and F. A. Al-Yusufy, *Macromol. Chem. Phys.*, **202**, 2971 (2001).

36. A. W. Jeevadason, K. K. Murugavel, and M. A. Neelakantan, *Renew. Sust. Energ. Rev.*, **36**, 220 (2014).