

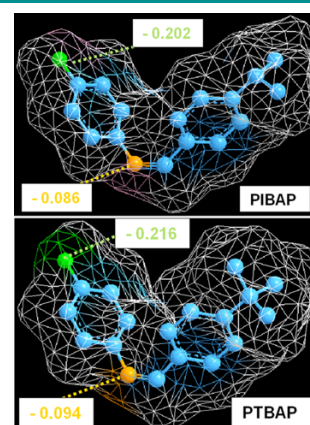
# Reaction Conditions, Photophysical, Electrochemical, Conductivity, and Thermal Properties of Polyazomethines

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**Abstract:** In this paper, a series of Schiff bases and their polyazomethine derivatives were synthesized *via* condensation and oxidative polycondensation reactions of 4-aminophenol with 4-isopropylbenzaldehyde or 4-*t*-butylbenzaldehyde. Polymerization reaction conditions for polymerization yield of polyazomethines were investigated by changing some experimental parameters such as time and temperature using different oxidants like alkaline NaOCl (30%) and air. The structural characterizations of Schiff bases and polymers were performed using FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and SEC techniques. Photophysical properties were studied UV-vis and photoluminescence spectroscopies. Electrochemical properties were also investigated cyclic voltammetry (CV) and electrochemical band gaps determined in the range 1.73 to 2.63 eV. Thermal properties of the compounds were investigated using TG-DTA and DSC techniques and char residue at 1000 °C determined between 3-6% and 39-34% for Schiff bases and polyazomethines, respectively. Moreover, conductivity measurements were done using four-point probe technique at both doped with iodine vapor and un-doped state.



**Keywords:** polyazomethine, schiff base, reaction conditions, conductivity, thermal properties.

## 1. Introduction

Conjugated polyazomethines (PAMs) are an interesting class of conjugated polymers<sup>1</sup> and they are also known as polymeric Schiff bases or polyimines. These polymers have gained much attention due to isoelectronic character of azomethine (-N=CH) bonding<sup>2</sup> and superior properties such as semi-conductivity, optical, electrochemical, nonlinear optical, good thermal stability and ability to form coordination complexes with different metal ions.<sup>3-6</sup> These polymers contain nitrogen atoms (-N=CH) in polymer backbone<sup>7</sup> and they have promising applications in electronics, optoelectronics and photonics such as electrochromic devices (ECD), organic field effect transistors (OFET), organic light emitting diodes (OLED), organic photovoltaic devices (OPVD) and fluorescence sensors.<sup>8-12</sup> Additionally, these polymers have further advantageous such as simple and easy preparation without use stringent reaction conditions and metal catalysts, little or no-purification and using water as solvent.<sup>13,14</sup>

Polyimines have been synthesized using both electrochemical and oxidation polymerization techniques.<sup>15,16</sup> Oxidative polymerization was carried out using different oxidants such as aqueous NaOCl, H<sub>2</sub>O<sub>2</sub>, or air.<sup>17,18</sup> The advantages of this polymerization technique are cheapness and environmentally friendly of the used oxidants, mild reaction condition and high solubility of the

obtained polymers.<sup>15,19</sup> Over the past years, polyimines have been a widespread interest due to superior properties such as metal ion complexing agent,<sup>20</sup> high thermal stability,<sup>21</sup> corrosion inhibitors,<sup>22</sup> mechanical strength,<sup>23</sup> catalyst carriers,<sup>24</sup> electrochromic and electrochemical sensor,<sup>25</sup> organic solar cell,<sup>26</sup> liquid crystal,<sup>27</sup> fiber forming,<sup>28</sup> and biological.<sup>22</sup>

Therefore, in this paper Schiff bases and their polyazomethine derivatives were prepared using different benzaldehydes and 4-aminophenol. The structural characterization of these compounds was done by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and SEC analysis techniques. Polymerization reaction conditions were also studied in the 40 to 90 °C temperature ranges and different polymerization time using aqueous NaOCl solution (30%) and air oxygen as oxidants. Also, photophysical properties were determined using UV-vis and photoluminescence (PL) spectroscopies, and fluorescence behaviors of compounds were investigated in DMF solution. Electrochemical properties were studied using cyclic voltammetry (CV), and HOMO-LUMO values and electrochemical band gap of the compounds were calculated. Thermal degradation properties of the polyazomethines were determined using TG-DTA and DSC techniques.

## 2. Experimental

### 2.1. Material

4-isopropylbenzaldehyde (IBA) and 4-*t*-butylbenzaldehyde (TBA)

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were supplied from Alfa Aesar and Fluka, respectively. 4-aminophenol (AP), acetonitrile (MeCN), acetone, chloroform (CHCl<sub>3</sub>), dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol (EtOH), ethyl acetate, hydrochloric acid (HCl), potassium hydroxide (KOH), sodium hypochlorite (NaOCl) and toluene were also supplied from Merck and they used as received.

## 2.2. Preparation of schiff bases

Schiff bases were abbreviated as IBAP and TBAP, and they synthesized *via* condensation reactions of IBA (1.48 g, 10 mmol) or TBA (1.62 g, 10 mmol) with AP (1.09 g, 10 mmol) for 4 h at 60 °C (Scheme 1) as in the literature.<sup>29</sup> The yield of IBAP and TBAP were found as 86 and 84%, respectively.

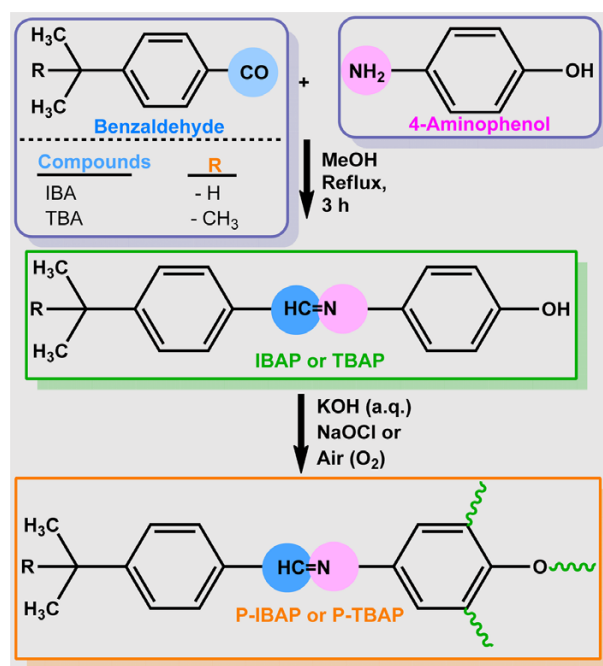
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ , ppm; 9.51 (hydroxyl, -OH, s, 1H), 8.58 (imine, -N=CH, s, 1H), 7.83 (Ar-CH, d, 2H), 7.36 (Ar-CH, d, 2H), 7.20 (Ar-CH, d, 2H), 6.83 (Ar-CH, d, 2H), 2.94 (-CH<sub>3</sub>, m, 1H) and 1.23 (-CH<sub>3</sub>, d, 6H) for IBAP; 9.53 (hydroxyl, -OH, s, 1H), 8.56 (imine, -N=CH, s, 1H), 7.84 (Ar-CH, d, 2H), 7.50 (Ar-CH, d, 2H), 7.21 (Ar-CH, d, 2H), 6.85 (Ar-CH, d, 2H), and 1.23 (-CH<sub>3</sub>, d, 9H) for TBAP.

<sup>13</sup>C NMR (100.6 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ , ppm; 156.94 (imine, -N=CH, C<sub>5</sub>), 156.16 (-C-OH, C<sub>3</sub>), 151.51 (Ar-CH, C<sub>9</sub>-ipso), 142.76 (Ar-CH, C<sub>4</sub>-ipso), 134.32 (Ar-CH, C<sub>6</sub>-ipso), 128.38 (Ar-CH, C<sub>7</sub>), 126.68 (Ar-CH, C<sub>8</sub>), 122.39 (Ar-CH, C<sub>1</sub>), 115.69 (Ar-CH, C<sub>2</sub>), 33.47 (-CH, C<sub>10</sub>) and 23.66 (Ar-CH, C<sub>11</sub>) for IBAP; 156.80 (imine, -N=CH), 156.20 (-C-OH), 153.67 (Ar-CH, C-ipso), 142.78 (Ar-CH, C-ipso), 133.91 (Ar-CH, C-ipso), 128.12 (Ar-CH), 125.49 (Ar-CH), 122.40 (Ar-CH), 115.71 (Ar-CH), 34.63 (-C-CH<sub>3</sub>) and 30.94 (-CH<sub>3</sub>) for TBAP.

## 2.3. Preparation of polyazomethines (PAMs)

PAMs were abbreviated as PIBAP and PTBAP, and they prepared *via* oxidative polycondensation reactions of the preformed Schiff bases in the presence of aqueous solution of NaOCl (30%) or air O<sub>2</sub> as the oxidative reagent at different temperature range (40 to 90 °C) as in the literature.<sup>30,31</sup> Synthesis procedure of polymers was as follows: IBAP (0.239 g, 1×10<sup>-3</sup> mol) or TBAP (0.253 g, 1×10<sup>-3</sup> mol) were placed in 100 mL three-necked round bottom flasks, which fitted with a condenser, a thermometer and a magnetic stirrer. IBAP or TBAP was dissolved in an aqueous KOH solution (2×10<sup>-3</sup> mol). After heating the reaction mixture to 30 °C, an aqueous NaOCl or air was added to mixture drop by drop during 20 min. Reactions were maintained at different temperatures (40-90 °C) and times (1, 3, and 5 h), and cooled at room temperature. The reaction mixture was neutralized using 2×10<sup>-3</sup> mol aqueous HCl solution at room temperature and the obtained polyazomethines were washed by MeOH (2×25 mL) and hot water (3×50 mL) to remove the unreacted components. The products were dried in a vacuum oven at 110 °C for 24 h (Scheme 1). % Polymerization yield was also calculated by dividing the dried polymer weight to the sum of monomer and KOH weights.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ , ppm; 9.96 (hydroxyl, -OH, s, 1H), 9.18 (imine, -N=CH, s, 1H), 7.90 (Ar-CH, d, 2H), 7.16 (Ar-CH, d, 2H), 6.85 (Ar-CH, d, 2H), 2.95 (-CH<sub>3</sub>, m, 1H) and 1.22 (-CH<sub>3</sub>, d, 6H) for PIBAP; 9.98 (hydroxyl, -OH, s, 1H), 9.19 (imine, -N=CH,



**Scheme 1.** Synthesis scheme of Schiff bases and their polyazomethine derivatives.

s, 1H), 7.88 (Ar-CH, d, 2H), 7.55 (Ar-CH, d, 2H), 6.83 (Ar-CH, d, 2H), and 1.30 (-CH<sub>3</sub>, d, 9H) for PTBAP.

<sup>13</sup>C NMR (100.6 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ , ppm; 167.33 (imine, -N=CH, C<sub>5</sub>-ipso), 157.85 (-C-OH, C<sub>3</sub>-ipso), 155.46 (Ar-CH, C<sub>9</sub>-ipso), 148.49 (Ar-CH, C<sub>4</sub>-ipso), 134.51 (Ar-CH, C<sub>6</sub>-ipso), 129.47 (-C-C coupling), 128.74 (Ar-CH, C<sub>7</sub>), 126.52 (Ar-CH, C<sub>8</sub>), 125.52 (Ar-CH, C<sub>1</sub>), 115.76 (Ar-CH, C<sub>2</sub>), 30.85 (-CH, C<sub>10</sub>) and 23.54 (Al-CH<sub>3</sub>, C<sub>11</sub>) for PIBAP; 167.27 (imine, -N=CH), 160.14 (-C-OH), 155.81 (Ar-CH, C-ipso), 147.53 (Ar-CH, C-ipso), 134.42 (Ar-CH, C-ipso), 129.19 (-C-C coupling), 128.02 (Ar-CH), 126.51 (Ar-CH), 126.36 (Ar-CH), 115.73 (Ar-CH), 34.77 (*ter*-C) and 30.86 (Al-CH<sub>3</sub>) for PTBAP.

## 2.4. Characterization

The infrared spectra were obtained by Perkin Elmer FT-IR Spectrum one using the universal ATR sampling accessory (4000-550 cm<sup>-1</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were recorded in deuterated DMSO-*d*<sub>6</sub> at 25 °C. Tetramethylsilane (TMS) was used as internal standard. The number-average molecular weight (*M<sub>n</sub>*), the weight-average molecular weight (*M<sub>w</sub>*) and *M<sub>w</sub>*/*M<sub>n</sub>* value were determined using Shimadzu VP-10A size exclusion chromatography (SEC). A refractive index detector (RID) was used to analyze the polymer at 45 °C.

## 2.5. Photophysical properties

Ultraviolet-visible (UV-vis) spectra were recorded by Analytikjena Specord 210 Plus at 25 °C. The measurements were carried out in DMSO solution. The optical band gaps (*E<sub>g</sub>*) were calculated from the absorption edges as in the literature.<sup>31</sup> Photoluminescence (PL) measurements were performed in DMF solution using a Shimadzu RF-5301PC spectrofluorometer. Concentration of

PIBAP or PTBAP solutions and slit width of the spectrofluorometer were adjusted to  $12.5 \text{ mg L}^{-1}$  and  $3 \text{ nm}$  for all measurements, respectively.

## 2.6. Electrochemical properties

Cyclic voltammetry (CV) measurements were carried out with a CHI 660C Electrochemical Analyzer (CH Instruments, Texas, USA) at a potential scan rate of  $20 \text{ mV/s}$ . All the experiments were performed in a dry box filled with argon at  $25 \text{ }^\circ\text{C}$ . The system consisted of a CV cell containing glassy carbon (GCE) as the working electrode, Ag wire as the reference electrode and platinum wire as the counter electrode. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple. The half-wave potential ( $E^{1/2}$ ) of ( $\text{Fc}/\text{Fc}^+$ ) measured in  $0.1 \text{ M}$  tetrabutylammoniumhexafluorophosphate ( $\text{TBAPF}_6$ ) MeCN solution is  $0.39 \text{ V}$  with respect to Ag wire. The voltammetric measurements were carried out in MeCN/DMSO mixtures (v/v: 4/1). The electrochemical band gaps ( $E'_g$ ) were calculated from the oxidation and reduction onset values as in the literature.<sup>32</sup>

## 2.7. Electrical conductivity

Conductivities of PIBAP and PTBAP were measured on a Keithley 2400 Electrometer. The powder polymer samples were converted to pellets using a hydraulic press developing up to  $1687.2 \text{ kg/cm}^2$ . Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator.<sup>30</sup>

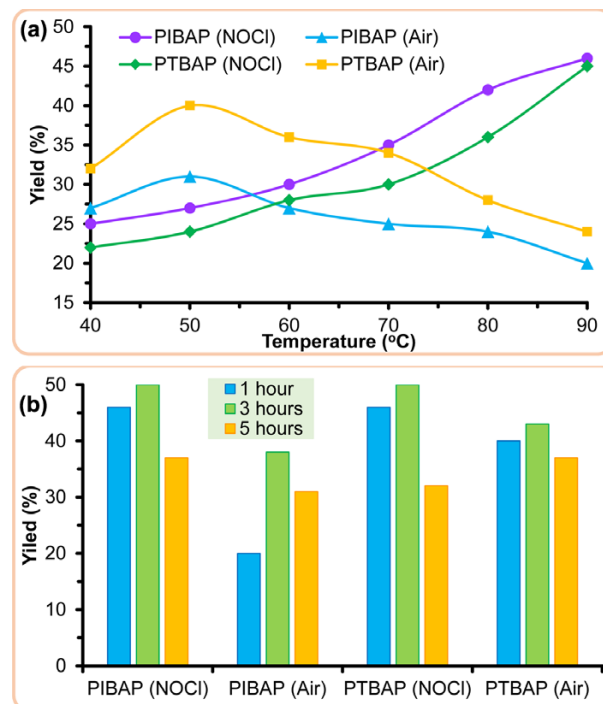
## 2.8. Thermal characterization

TG-DTA measurements were performed using Perkin Elmer Pyris Sapphire TG-DTA. In these measurements were carried out in the range of  $20$  to  $1000 \text{ }^\circ\text{C}$  with heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere. Similarly, DSC analyses were carried out in the range  $25$  to  $420 \text{ }^\circ\text{C}$  with heating rate  $10 \text{ }^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere using a Perkin Elmer Pyris Sapphire DSC.

## 3. Results and discussion

### 3.1. Detection of the optimum reaction conditions, solubility and characterization

As known, oxidative polymerization of monomers could be affected to different reaction parameters such as polymerization temperature and time, concentration of monomer and type of oxidants. Therefore, to determine the optimum polymerization conditions, oxidative polymerization reaction of IBAP and TBAP were performed using the different oxidants such as NaOCl and air in aqueous KOH solution between  $40$  and  $90 \text{ }^\circ\text{C}$  temperature ranges at constant monomer concentration (Figure 1(a)). Monomer, KOH and NaOCl concentrations were adjusted as  $0.02$ ,  $0.04$ , and  $0.02 \text{ mol L}^{-1}$ , respectively, and air volume was also adjusted as  $8.5 \text{ L h}^{-1}$  in the mentioned polymerization reactions. In addition, polymerization reactions were carried out at differ-



**Figure 1.** Reaction yields of PIBAP and PTBAP at the different temperature (a) and different time (b) (Conditions:  $[\text{IBAP}] = 0.02$ ,  $[\text{TBAP}] = 0.02$ ,  $[\text{KOH}] = 0.04$ ,  $[\text{NaOCl}] = 0.02 \text{ mol L}^{-1}$  and air =  $8.5 \text{ L h}^{-1}$ ).

ent reaction time such as 1, 3, and 5 h (Figure 1(b)) to determine the optimum reaction time. As can be seen in Tables 1, 2, and Figure 1, % polymerization yield of PIBAP was determined in the range 25 to 46% for NaOCl and 20 to 31% for air between  $40$  and  $90 \text{ }^\circ\text{C}$  temperature ranges and the maximum reaction yield was found as 46% for NaOCl and 31% for air at  $90 \text{ }^\circ\text{C}$  and  $50 \text{ }^\circ\text{C}$  after one hour polymerization reaction, respectively. In addition, % reaction yield of PTBAP was determined in the range 22 to 45% for NaOCl and 24 to 40% for air at the mentioned temperature range and the maximum % polymerization yield was calculated as 45% for NaOCl and 40% for air at  $90 \text{ }^\circ\text{C}$  and  $50 \text{ }^\circ\text{C}$  after one hour polymerization reaction, respectively. These results indicated that the optimum polymerization temperature was  $90 \text{ }^\circ\text{C}$  and  $50 \text{ }^\circ\text{C}$  for NaOCl and air, respectively, due to the hydrolysis and over-oxidative reaction of side reaction were stimulated at higher temperature.<sup>33</sup> To determine the optimum reaction time, polymerization reaction was performed during 3 and 5 h polymerization times and % polymerization yield of PIBAP was calculated as 50 and 37 for NaOCl at  $90 \text{ }^\circ\text{C}$ , 38 and 31 for air at  $50 \text{ }^\circ\text{C}$  after 3 and 5 h polymerization, respectively. Similarly, % polymerization yield of PTBAP was found as 50 and 32 for NaOCl at  $90 \text{ }^\circ\text{C}$ , 43 and 37 for air at  $50 \text{ }^\circ\text{C}$  after 3 and 5 h polymerization, respectively. According to these results, when the polymerization time was increased in the range 3 to 5 h, % reaction yield of polymers were increased during three hours polymerization reaction while % polymerization yield decreased during 5 h. Due to this tendency, the optimum reaction time was found as 3 h. As a result, the highest polymerization yields were obtained as 50% (both of polymers) for 3 h at  $90 \text{ }^\circ\text{C}$  using  $0.02 \text{ mol L}^{-1}$  NaOCl as oxidant and 38 and 43% for 3 h at  $50 \text{ }^\circ\text{C}$  using air as oxidant for PIBAP and PTBAP, respectively.

**Table 1.** The optimum oxidative polycondensation reaction conditions of IBAP in the aqueous alkaline medium for NaOCl and air oxidant

Run	Temp. (°C)	Time (h)	[IBAP] <sub>0</sub> (mol/L)	[KOH] <sub>0</sub> (mol/L)	[NaOCl] <sub>0</sub> (mol/L)	Yield of PIBAP (%)
1	40	1	0.02	0.04	0.02	25
2	50	1	0.02	0.04	0.02	27
3	60	1	0.02	0.04	0.02	30
4	70	1	0.02	0.04	0.02	35
5	80	1	0.02	0.04	0.02	42
6	90	1	0.02	0.04	0.02	46
7	90	3	0.02	0.04	0.02	50
8	90	5	0.02	0.04	0.02	37
9	90	3	0.02	0.04	0.04	41
Run	Temp. (°C)	Time (h)	[IBAP] <sub>0</sub> (mol/L)	[KOH] <sub>0</sub> (mol/L)	Air (L/h)	Yield of PIBAP (%)
1	40	1	0.02	0.04	8.5	27
2	50	1	0.02	0.04	8.5	31
3	60	1	0.02	0.04	8.5	27
4	70	1	0.02	0.04	8.5	25
5	80	1	0.02	0.04	8.5	24
6	90	1	0.02	0.04	8.5	20
7	50	3	0.02	0.04	8.5	38
8	50	5	0.02	0.04	8.5	31

**Table 2.** The optimum oxidative polycondensation reaction conditions of TBAP in the aqueous alkaline medium for NaOCl and air oxidant

Run	Temp. (°C)	Time (h)	[TBAP] <sub>0</sub> (mol/L)	[KOH] <sub>0</sub> (mol/L)	[NaOCl] <sub>0</sub> (mol/L)	Yield of PIBAP (%)
1	40	1	0.02	0.04	0.02	22
2	50	1	0.02	0.04	0.02	24
3	60	1	0.02	0.04	0.02	28
4	70	1	0.02	0.04	0.02	30
5	80	1	0.02	0.04	0.02	36
6	90	1	0.02	0.04	0.02	45
7	90	3	0.02	0.04	0.02	50
8	90	5	0.02	0.04	0.02	32
9	90	3	0.02	0.04	0.04	39
Run	Temp. (°C)	Time (h)	[TBAP] <sub>0</sub> (mol/L)	[KOH] <sub>0</sub> (mol/L)	Air (L/h)	Yield of PIBAP (%)
1	40	1	0.02	0.04	8.5	32
2	50	1	0.02	0.04	8.5	40
3	60	1	0.02	0.04	8.5	36
4	70	1	0.02	0.04	8.5	34
5	80	1	0.02	0.04	8.5	28
6	90	1	0.02	0.04	8.5	24
7	50	3	0.02	0.04	8.5	43
8	50	5	0.02	0.04	8.5	37

Solubility tests of the compounds were done using 1 mg compound and 1 mL different solvents such as acetone, MeCN, CHCl<sub>3</sub>, EtOH, ethyl acetate, toluene, THF, DMSO, and DMF. According to the solubility tests of the compounds, the synthesized compounds were completely soluble in polar aprotic solvents such as DMSO and DMF, partly soluble in non-polar solvents such as toluene and chloroform while the polymers were insoluble acetone, EtOH and ethyl acetate. These solubility results could be the higher Dimroth-Reichardt ( $E_T$ ) polarity of DMSO ( $E_T=46.47$ ) and DMF ( $E_T=45.74$ ) than the other solvents.<sup>34</sup>

IBAP, TBAP, P-IBAP, and P-TBAP were characterized using FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and SEC techniques. FT-IR spectra of

these compounds were comparatively given in Figure 2. Characteristic carbonyl (-C=O) stretch vibration of 4-isopropylbenzaldehyde and 4-*t*-butylbenzaldehyde was observed at 1698 and 1697 cm<sup>-1</sup>, respectively, and amine (-NH<sub>2</sub>) stretch vibration of 4-aminophenol observed at 3341 cm<sup>-1</sup>. In the FT-IR spectra of IBAP and TBAP, these stretch vibrations of aldehyde and amine were disappeared, and new imine (-N=CH) stretch vibration was observed at 1620 and 1618 cm<sup>-1</sup> instead of these stretch vibrations, respectively. Also, hydroxyl (-OH) stretch vibration of Schiff bases was observed at 3210 cm<sup>-1</sup>. Some additional stretch vibrations such as aliphatic -CH and aromatic -C=C were observed in the range 2867 to 2969 and 1502 to 1607 cm<sup>-1</sup>, respectively. As

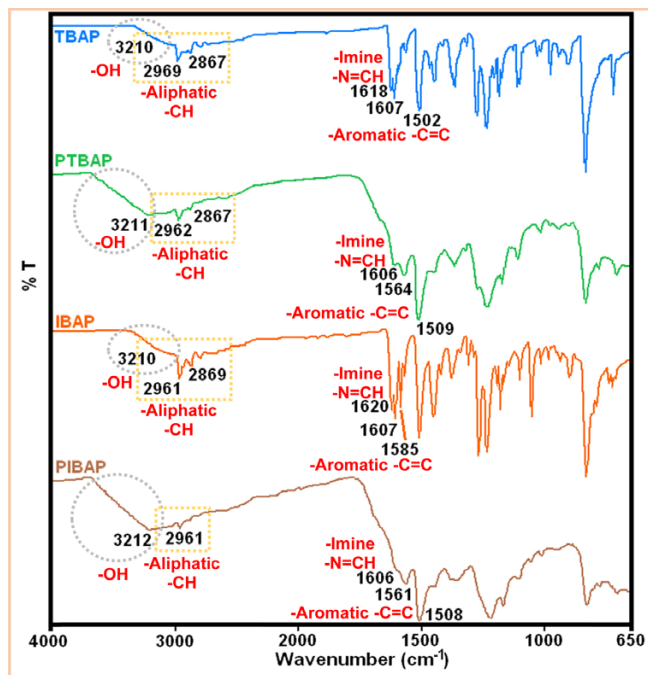


Figure 2. FT-IR spectra of TBAP, PTBAP, IBAP, and PIBAP.

can be seen in FT-IR spectra of PIBAP and PTBAP, imine stretch vibrations were shifted by approximately 14 and 12  $\text{cm}^{-1}$  relative to those of IBAP and TBAP (1620 and 1618  $\text{cm}^{-1}$ ). This shift is attributed to formation of the poly-conjugated polyazomethine structure *via* polycondensation reaction of IBAP and TBAP. Hydroxyl (-OH), aliphatic -CH and aromatic -C=C stretch vibrations of these polymers were observed in the range 3211 to 3212, 2867 to 2962, and 1508 to 1564  $\text{cm}^{-1}$ , respectively. When compared to the FT-IR spectra of Schiff bases and their oxidative polymerization products, the FT-IR peaks of polyazomethines have broader than Schiff bases because of their poly-conjugated structures.

To identify of the structures of monomers and polymers,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of these compounds were also measured in  $\text{DMSO}-d_6$ .  $^1\text{H}$  NMR spectra of IBAP and PIBAP were given in Figure 3. Also, NMR data all of the compounds were summarized in experimental section. As can be seen in  $^1\text{H}$  NMR spectra of IBAP and TBAP, hydroxyl (-C-OH) and imine (-N=CH) protons of these compounds were observed at 9.51-9.53 and 8.58-8.56 ppm, respectively. -C-OH and -N=CH protons of PIBAP and PTBAP were observed at 9.96-9.98 and 9.18-9.19 ppm, respectively. These results indicated that these proton peak values of PIBAP and PTBAP were shifted to higher chemical shifts when compared to IBAP and TBAP values. Also, aromatic protons (Ar-CH) were observed in the range 6.25 to 7.90 ppm and aliphatic protons (Al-CH) observed at 1.22 to 2.95 ppm.

$^{13}\text{C}$  NMR spectra of IBAP and PTBAP were given in Figure 4. As can be seen in Figure 4, hydroxyl (-C-OH) and imine (-N=CH) carbon peaks of IBAP and TBAP were observed at 156.94-156.80 and 156.16-153.67 ppm, respectively. These peaks of PIBAP and PTBAP were observed at 167.33-167.27 and 157.85-160.14 ppm, respectively. According to these results, -C-OH carbon peak values of PIBAP and PTBAP were approximately shifted 11 ppm to higher chemical shifts while a significant change was not observed to the imine carbon peak values. -C-C coupling carbon peak val-

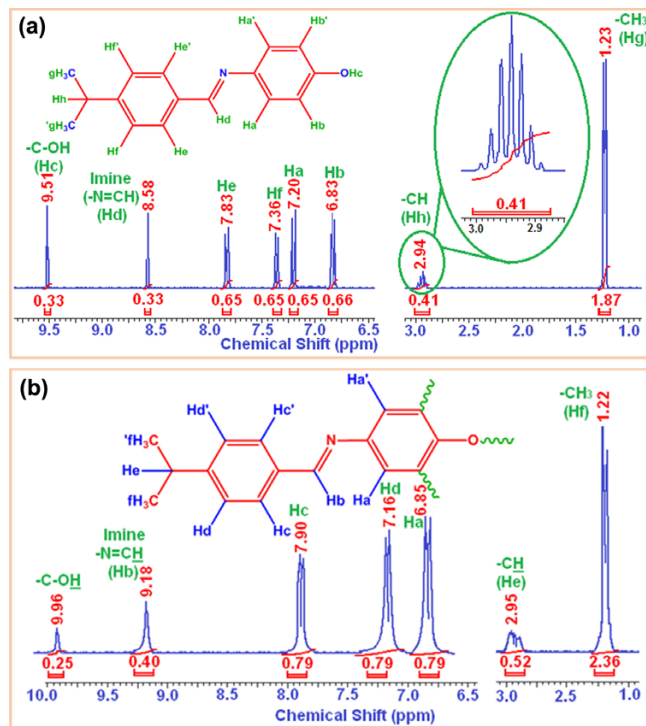


Figure 3.  $^1\text{H}$  NMR spectra of IBAP (a) and PIBAP (b).

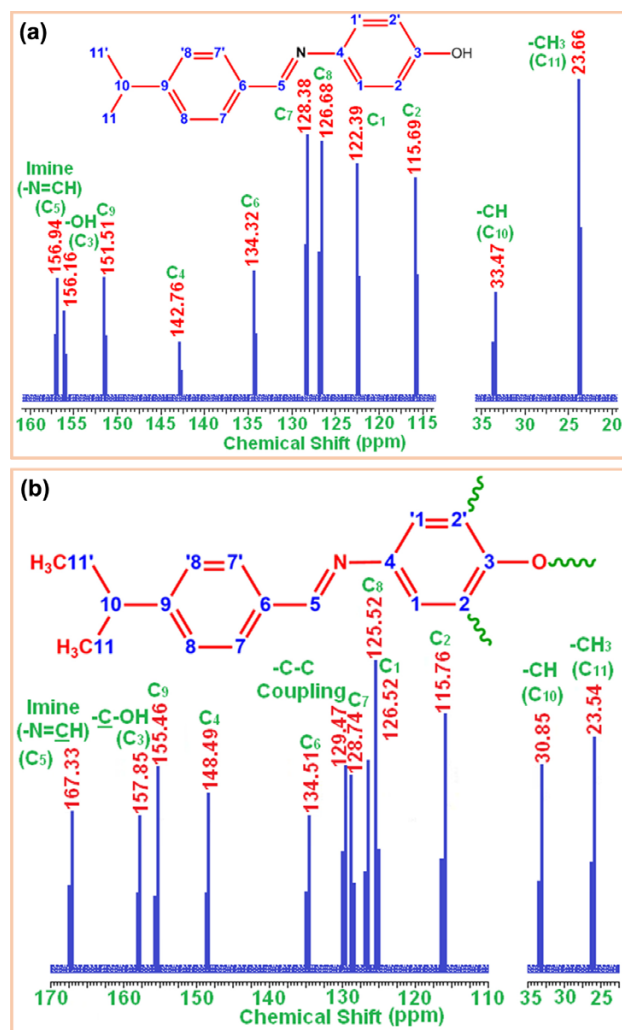
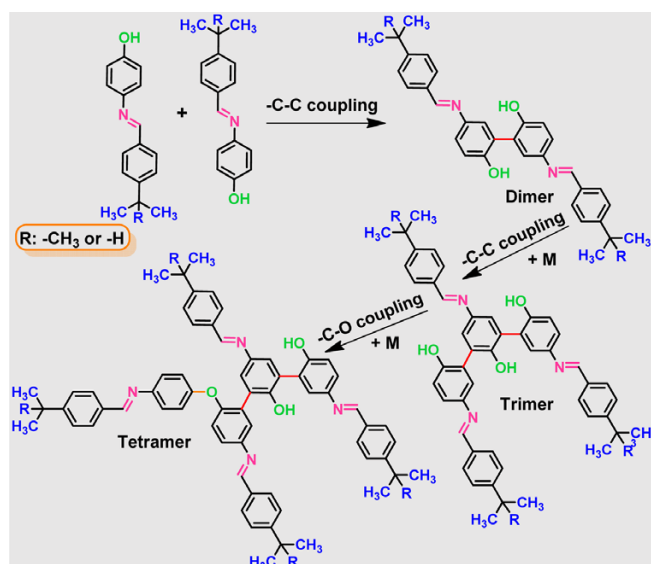


Figure 4.  $^{13}\text{C}$  NMR spectra of IBAP (a) and PIBAP (b).



**Scheme 2.** Presentation of oxidative polymerization of polymers by alternative -C-C and -C-O coupling.

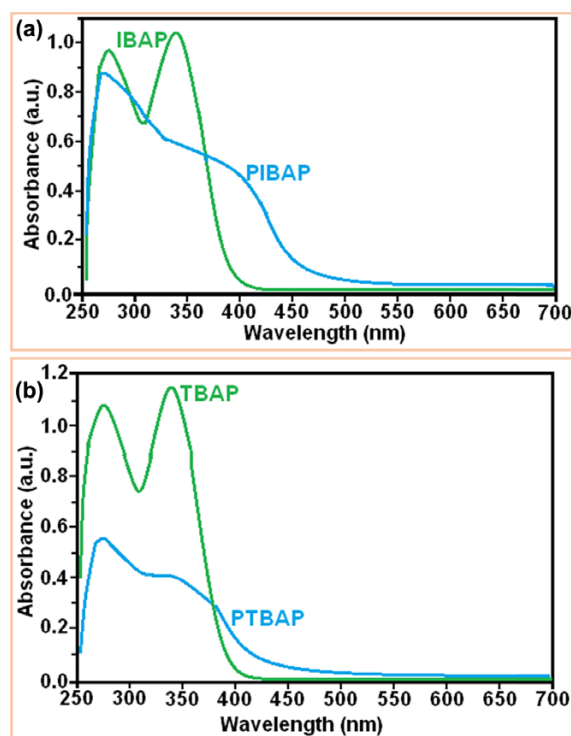
ues of PIBAP and PTBAP were observed at 129.47 and 129.19 ppm, respectively. Moreover, aromatic and aliphatic carbon peaks were observed in the range 115.69 to 155.81 ppm and 23.54 to 34.77 ppm, respectively.

In a previous paper, we showed that phenol-based Schiff bases could be polymerized -C-C and -C-O coupling of monomer units as shown in Scheme 2. -C-C/-C-O coupling ratio was calculated using the integration of -OH/-N=CH and -C-C/-C-O ratio found as 37/63 and 40/60 for PIBAP and PTBAP, respectively.<sup>30</sup>

SEC results of polymers were summarized in Table 3.  $M_n$  value of PIBAP and PTBAP was calculated as 13,400 and 11,900, respectively. PDI value of these compounds was determined as 1.22 and 1.30. These results showed that PIBAP and PTBAP have nearly repeat units between 56-67 and 48-61. The  $M_n$  and  $M_w$  results indicated that PIBAP has higher  $M_n$  and  $M_w$  value than PTBAP. As can be seen in the structure of polymers, PTBAP has higher methyl as steric hindrance. As known, as this steric effect was increased in polymer yield often resulted in low product polymer.<sup>35</sup>

### 3.2. Photophysical properties of schiff bases and polymers

Photophysical properties of Schiff bases and their polymers were investigated using ultraviolet-visible (UV-vis) and photoluminescence (PL) spectroscopy techniques. UV-vis spectra of these compounds were comparatively given in Figure 5. As can be seen in Figure 5, Schiff bases and their polymer derivatives exhibited two maximum UV-vis absorption wavelengths in the range 272 to 276 nm and 340 to 398 nm due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of azomethine group, respectively. According



**Figure 5.** UV-vis spectra of IBAP, PIBAP (a) and TBAP, PTBAP (b).

to  $n \rightarrow \pi^*$  transition results, these transitions of polymers were shifted to higher wavelengths due to poly-conjugated structures.

Optical band gaps of IBAP, TBAP, PIBAP, and PTBAP were calculated using the following equation as in the literature<sup>31</sup> and the obtained results given in Table 4.

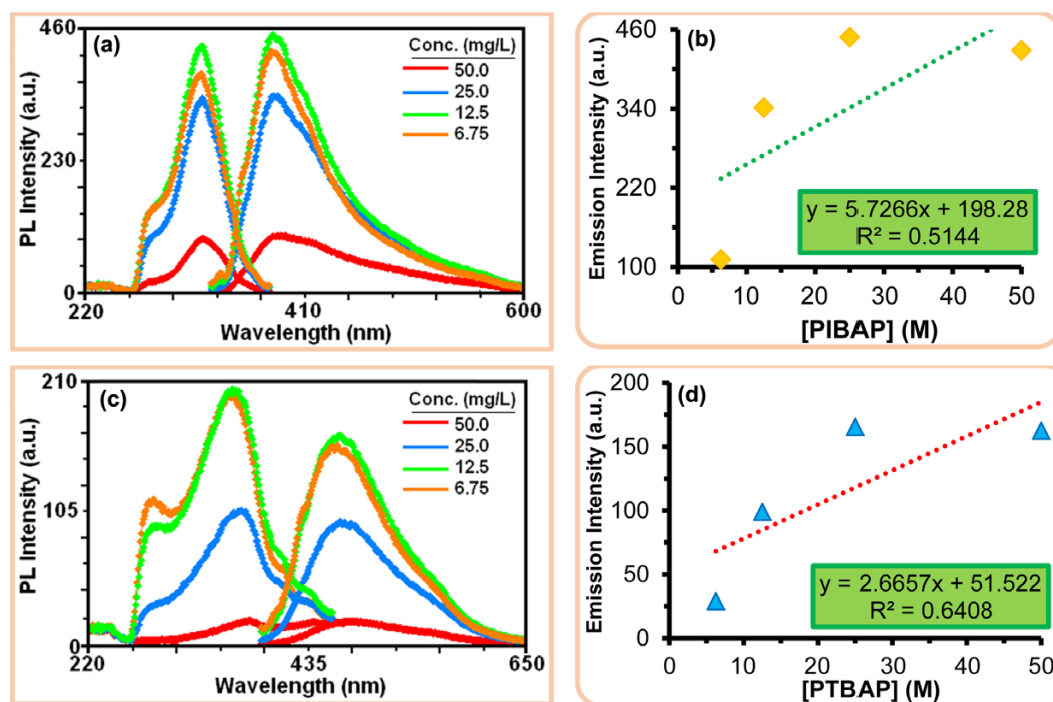
$$E_g = \frac{1240.8}{\lambda_{onset}} \quad (1)$$

$\lambda_{onset}$  value of IBAP, TBAP, PIBAP, and PTBAP was determined as 408, 404, 480, and 465 nm, respectively. Optical band gap ( $E_g$ ) of IBAP, TBAP, PIBAP, and PTBAP compounds was calculated as 3.04, 3.07, 2.59, and 2.67 eV, respectively. These results showed that polymers have lower optical band gap than Schiff bases due to their poly-conjugated structure. Moreover, when compared to the optical band gap of Schiff bases and their polyazomethine derivatives, Schiff base and its polymer derived from IBA have higher optical band than the derived from TBA due to further methyl substitute group number of PTBAP than PIBAP.

PL spectra of PIBAP and PTBAP were given in Figure 6. The obtained results were also summarized in Table 4. According to Figure 6, while concentration of polymers was decreased in the range 50 to 12.5 mg L<sup>-1</sup>, emission intensity increased at this concentration range. When polymer concentration was adjusted as 6.25 mg L<sup>-1</sup>, emission intensity of polymers decreased. PL

**Table 3.** SEC analysis results of PIBAP and PTBAP

Compounds	Total			Fraction I				Fraction II				Fraction III			
	$M_n$	$M_w$	PDI	$M_n$	$M_w$	PDI	%	$M_n$	$M_w$	PDI	%	$M_n$	$M_w$	PDI	%
PIBAP	13,400	16,400	1.22	16,400	18,200	1.11	65	11,100	11,500	1.13	14	5,100	6,200	1.24	21
PTBAP	11,900	15,500	1.30	14,600	16,800	1.15	70	9,300	11,400	1.22	10	3,700	4,900	1.32	20



**Figure 6.** Photoluminescence spectroscopy and the correlation between polymer concentration and emission intensity of PIBAP (a, b) and PTBAP (c, d).

**Table 4.** UV-vis and PL data of the Schiff bases and polyazomethines

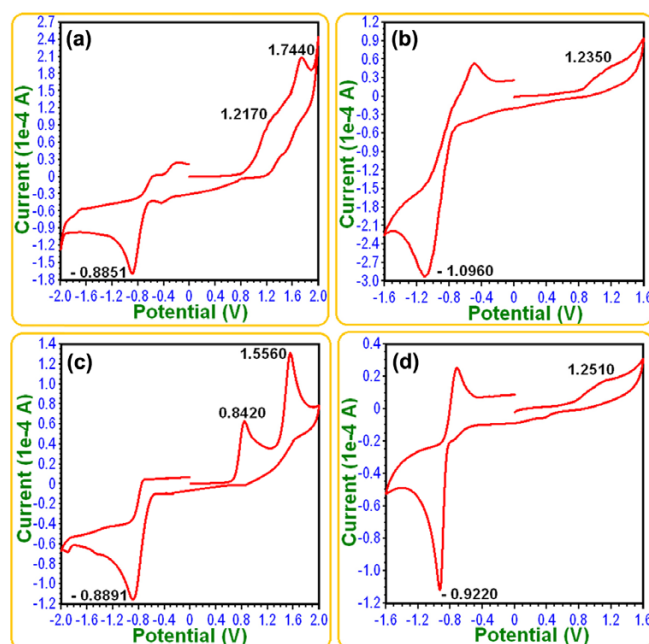
Compounds	UV-vis			Conc. (mg/L)	PL						
	$\lambda_{max}$ (nm)	$\lambda_{onset}$ (nm)	$E_g^a$ (eV)		$\lambda_{Ex}^b$ (nm)	$\lambda_{Em}^c$ (nm)	$\lambda_{max(Ex)}^d$ (nm)	$\lambda_{max(Em)}^e$ (nm)	$I_{Ex}^f$	$I_{Em}^g$	$\Delta\lambda_{ST}^h$
IBAP	276, 342	408	3.04	-	-	-	-	-	-	-	-
TBAP	277, 340	404	3.07	-	-	-	-	-	-	-	-
PIBAP	272, 398	480	2.59	12.5	320	383	321	383	430	450	70
PTBAP	275, 353	465	2.67	12.5	380	467	363	467	201	165	90

<sup>a</sup>Optical band gap. <sup>b</sup>Excitation wavelength for emission. <sup>c</sup>Emission wavelength for excitation. <sup>d</sup>Maximum excitation wavelength. <sup>e</sup>Maximum emission wavelength. <sup>f</sup>Maximum excitation intensity. <sup>g</sup>Maximum emission intensity. <sup>h</sup>Stokes shift.

results indicated that PIBAP has higher excitation and emission intensity than PTBAP. This could be probably the structure of the polyazomethines. As can be seen in Scheme 1, PTBAP has further methyl substitute group number than PIBAP. Also, this substitute group is electron-donating group.<sup>36</sup> On the other hands, PTBAP (90 nm) has the higher Stokes shift value than PIBAP (70 nm) due to the polarity and dielectric constants of DMF and the structure of PAMs.<sup>36</sup> Moreover, the correlation between polymer concentration and emission intensity of PIBAP and PTBAP was given in Figure 6(b) and (d). As can be seen in these figures a linear relationship between the polymer concentration and emission intensity was obtained with regression coefficients  $R_1=0.5144$  and  $R_2=0.6408$  for PIBAP and PTBAP, respectively.

### 3.3. Electrochemical properties

Electrochemical properties of the compounds were investigated using CV technique (Figure 7) and the obtained results given in Table 5. The ionization potential ( $E_{IP}$ ), electron affinity ( $E_{EA}$ ) and electrochemical band gap ( $E'_g$ ) of IBAP, TBAP, PIBAP, and PTBAP were calculated using the following equations as in the literature.<sup>7</sup>



**Figure 7.** Cyclic voltammograms of IBAP (a), PIBAP (b), TBAP (c), and PTBAP (d).

**Table 5.** Electrochemical results of IBAP, TBAP, PIBAP, and PTBAP

Compounds	$E_{red,onset}$ (eV)	$E_{EA}^a$ (eV)	$E_{ox,onset}$ (eV)	$E_{IP1}^b$ (eV)	$E_{ox,onset}$ (eV)	$E_{IP2}$ (eV)	$E'_{g1}^c$ (eV)	$E'_{g2}^c$ (eV)
IBAP	-0.8851	-3.50	1.2170	-5.61	1.7740	-6.13	2.11	2.63
TBAP	-0.8891	-3.50	0.8420	-5.23	1.5560	-5.95	1.73	2.45
PIBAP	-1.0960	-3.29	1.2350	-5.63	-	-	2.34	-
PTBAP	-0.9220	-3.47	1.2510	-5.64	-	-	2.17	-

<sup>a</sup>Electron affinity. <sup>b</sup>Ionization potential. <sup>c</sup>Electrochemical energy band gaps.

$$E_{IP} = -(E_{ox,onset} - 0.39) - 4.80 \quad (2)$$

$$E_{EA} = -(E_{red,onset} - 0.39) - 4.80 \quad (3)$$

$$E'_g = E_{IP} - E_{EA} \quad (4)$$

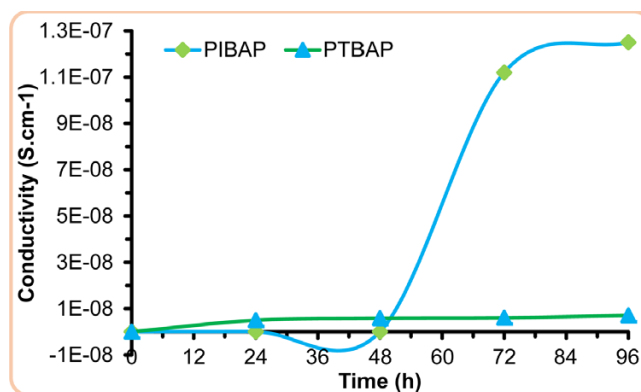
As can be seen in Figure 7, polymers have only one oxidation onset ( $E_{ox,onset}$ ) whereas Schiff bases have two oxidation peak. This could be probably disappear of the phenolic hydroxyl group as results of -C-O coupling during the polymerization reaction. Additionally, Schiff bases and polyazomethines have one reduction onset ( $E_{red,onset}$ ). The reduction onset peak was attributed to the reduction of imine group (-N=CH) in the structure *via* protonation of imine nitrogen and oxidation peak attributed to the oxidation of free hydroxyl (-OH) group of the compounds to form phenoxy polaron structure (PhO<sup>•</sup>).<sup>37,38</sup>

Ionization potential ( $E_{IP}$ ) and electron affinity ( $E_{EA}$ ) of IBAP, TBAP, PIBAP and PTBAP were determined in the range -6.13 to -5.23 and -3.50 to -3.29 eV, respectively. Additionally, electrochemical band gap of these compounds was calculated between 1.73 and 2.63 eV. When compared to the second electrochemical band gap ( $E'_{g2}$ ) of IBAP and TBAP with electrochemical band gap of polymers, as a results of poly-conjugated structures of PIBAP and PTBAP have lower electrochemical band gap than Schiff bases. Additionally, PTBAP has lower electrochemical band gap than PIBAP. According to the literature, four structural factors was affected the energy level of HOMO-LUMO.<sup>36</sup> One of these factors is electron-withdrawing or electron-donating substituents. According to Scheme 1, has further methyl substitute group number than PIBAP.

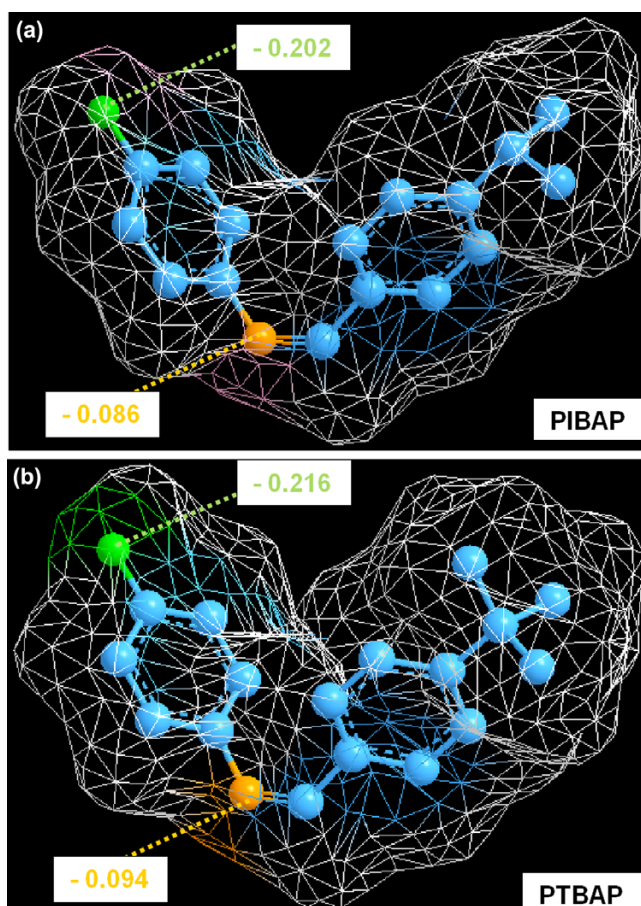
### 3.4. Electrical conductivities

Electrical conductivity behavior of PIBAP and PTBAP was studied using a Keithley 2400 Electrometer and the obtained data were given in Figure 8. Electrical conductivity value of PIBAP and PTBAP was  $3.1 \times 10^{-11}$  and  $4.3 \times 10^{-11}$  S cm<sup>-1</sup> at un-doped state, respectively. When PIBAP and PTBAP were doped with iodine, their electrical conductivity values increased about 2-116, 3-137, 3871-141, and 4032-165 times for 24, 48, 72, and 96 h doping time, respectively. As can be seen in these results, electrical conductivity of PTBAP was showed a significant increase after 24 h doping time whereas electrical conductivity of PTBAP showed a similar tendency after 72 h.

Electrical conductivity data showed that PTBAP has higher electrical conductivity than PIBAP at un-doped state whereas PIBAP has higher conductivity than PTBAP at doped state. Figure 9 shows Huckel charge of these compounds. As can be seen in Scheme 1, PIBAP and PTBAP have imine (-N=CH) and hydroxyl (-OH) groups as chromophore group in the structure. Huckel



**Figure 8.** Electrical conductivity of PIBAP and PTBAP.



**Figure 9.** The calculated Huckel charge of atoms in PIBAP (a) and PTBAP (b) (Blue: Carbon, orange: Nitrogen, green: oxygen and hydrogen atoms were not shown).

charges of these polyazomethines were determined as -0.216/-0.202 and -0.094/-0.086 for -OH and -N=CH group, respectively.<sup>39,40</sup>



These charges showed that chromophore groups of PIBAP has a bit higher electron density than PTBAP. According to the doping mechanism between iodine and poly(azomethine)s, imine nitrogen of polymers was coordinated iodine molecules *via* electrostatic interaction.<sup>3,30</sup> The calculated imine charges of PIBAP and PTBAP were supported the electrical conductivity values of these compounds due to the higher electron density of PIBAP than PTBAP. As known, when polyazomethines were doped

with iodine they formed polaron structure between iodine and imine nitrogen ( $-N=CH$ ) of polyazomethines as a results of high electron density.<sup>41,42</sup>

### 3.5. Thermal characterization

Thermal degradation behaviors of Schiff bases and their polyazomethine derivatives were studied using TG-DTA and DSC techniques. TG-DTA thermograms of these compounds were given in Figure 10 and the results also summarized in Table 6. Onset temperature ( $T_{on}$ ) of IBAP and TBAP was determined as 241 and 252 °C, respectively. This temperature of PIBAP and PTBAP was also determined as 154 and 148 °C, respectively. Char residue at 1000 °C of IBAP, TBAP, PIBAP, and PTBAP was calculated as 6, 3, 39, and 34%, respectively. These results showed that polyazomethines have higher char than Schiff bases due to polyconjugated structures. Additionally, PAMs were showed a linear decrease on weight losses as the temperature increased. A similar tendency was not observed for Schiff bases because of their thermally unstable properties. When compared to the thermal properties of polyazomethines, PIBAP has higher onset temperature and char than PTBAP. Additionally, the glass transition temperature ( $T_g$ ) values of PIBAP and PTBAP were found as 142 and 136 °C, respectively.

### 4. Conclusions

Schiff bases and polyazomethines were successfully synthesized using different aldehydes and aminophenol. The optimum polymerization reaction conditions as a function of polymerization yields were studied by changing some experimental parameters such as time and temperature using different oxidants like alkaline NaOCl (30%) and air. The obtained results showed that maximum yield was obtained at 90 and 50 °C during three hours polymerization time for NaOCl and air as oxidant, respectively. The structural characterization of the compounds was performed using FT-IR, NMR and SEC analysis techniques. Electrical conductivity of the polyazomethines was studied as dependent the time. Molecular weight and electrical conductivity of PIBAP has higher than PTBAP. Moreover, optical and electrochemical properties of the compounds were investigated using UV-vis, PL and CV techniques. Optical and electrochemical band gaps of the compounds were calculated in the range 2.59 to 3.07 and 1.73 to 2.63 eV, respectively. Thermal properties of the compounds were studied using TG-DTA and DSC techniques. Thermal degradation data of the compounds showed that polyazomethines have higher thermal stability than Schiff bases.

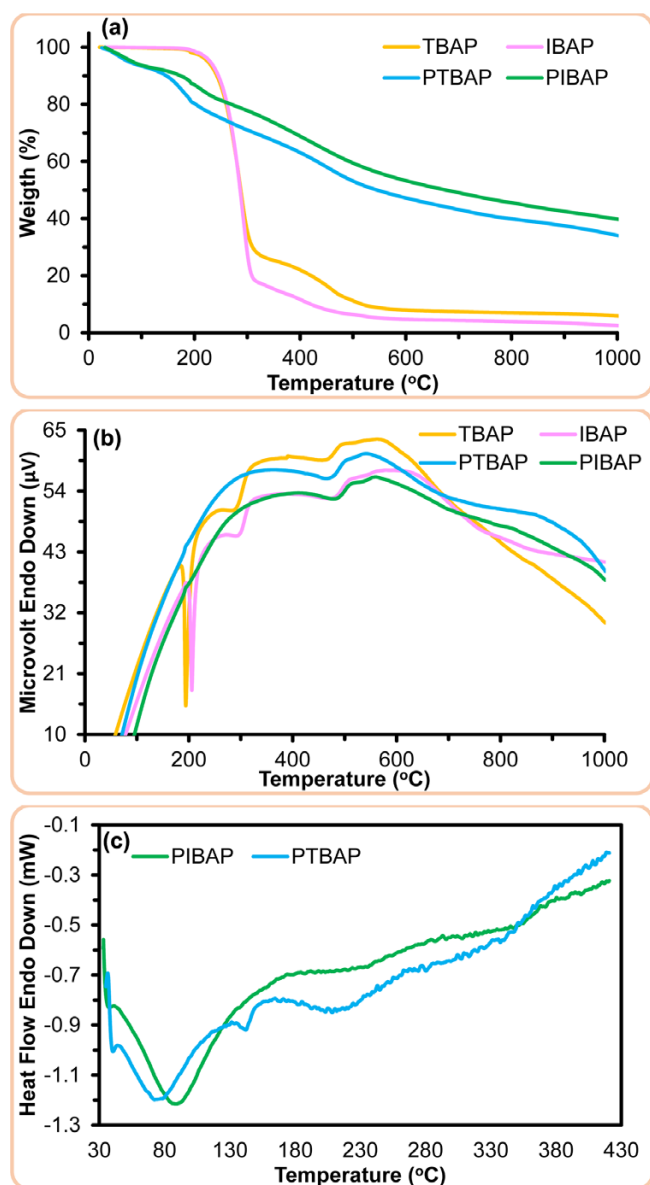


Figure 10. TG (a), DTG (b), and DSC (c) curves of PIBAP and PTBAP.

Table 6. TG-DTA and DSC data of the compounds

Compounds	TGA				Char (%)	DTA		DSC	
	$T_{on}^a$ (°C)	$T_{max}^b$ (°C)	$T_{20}^c$ (°C)	$T_{50}^d$ (°C)		$T_{endo}$ (°C)	$T_g^e$ (°C)	$\Delta C_p^f$ (J/g °C)	
IBAP	241	270, 390	246	272	3	190, 281, 456	-	-	
TBAP	252	283, 453	256	287	6	195, 289, 463	-	-	
PIBAP	154	190, 406	250	661	39	465	142	0.066	
PTBAP	148	176, 453	201	541	34	467	136	0.047	

<sup>a</sup>The onset temperature. <sup>b</sup>Maximum weight loss temperature. <sup>c</sup>20% weight loss temperature. <sup>d</sup>50% weight loss temperature. <sup>e</sup>The glass transition temperature. <sup>f</sup>Change of specific heat.

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