

## SYNTHESIS AND CHARACTERIZATION OF A NEW DYESTUFF POLYMER SOLUBLE IN ALKALINE AQUEOUS MEDIA

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**Abstract** Novel dyestuff polymers were successfully obtained through oxidative polymerization technique. The synthesized Schiff base and its polymer were soluble in alkaline aqueous medium and they have various colors in different solutions. Also, it can be said that the synthesized compounds are suitable as coloring agent (dyestuff) for textile applications. Fluorescence properties of the compounds were determined in DMF with different concentrations (mg/L). Poly-tris(4-aminophenyl)methanol (P-TAPM) has quite high emission and excitation intensity values. Optical and electrochemical band gaps of the polymers were lower than those of the monomers indicating the more conjugated structure of the polymers. The oxidized states of the novel dyestuff compounds were examined by cyclic voltammetry (CV) technique. The solid state conductivity measurements showed that the synthesized polymers were semiconductors when exposed to the iodine vapour their conductivities could be increased. P-TAPM had the highest undoped conductivity. Thermal characterizations of the synthesized compounds were carried out by TG-DTA and DSC methods.

**Keywords:** Dyestuff polymers; Thermal properties; Fluorescence; Oxidative polymerization.

### INTRODUCTION

The topic of intrinsically colored polymers has received attention recently; polymeric pigments can be regarded as insoluble polymers which have a chromophoric centre within their structure. Four classes arise: (a) Polymers, which as a result of secondary reaction become intrinsically colored; (b) Polymeric pigments derived from the formation of color sites within a substrate where hitherto they were absent such as the action of reactive dyes on natural polymers; (c) Macromolecules which are formed as a result of addition polymerization reactions in which one of the monomers is colored; (d) Intrinsically colored polymers resulting from stepwise polymerization reactions, such as the product of the reactions of multifunctional colored compounds. Within this category are the anthraquinones, azo compounds and phthalocyanines, *etc*<sup>[1]</sup>. Thus, the design and synthesis of bi-functional colorants has received considerable attention because such colorants can be utilized as monomers for functional polymers *via* polyaddition and polycondensation reactions<sup>[2]</sup>. Owing to the inherent non-leaching behavior and good light fastness combined with the special properties of polymers<sup>[3, 4]</sup>, there has been much emphasis given to the synthesis of polymers containing chromophoric groups<sup>[5–9]</sup>, for example, the aromatic azo and imine groups which can form the part of the main chain. In addition, there are several reports regarding bisazomethine (bisani) dye in which imine group formed by Schiff reaction of aromatic aldehyde with aromatic amine<sup>[10]</sup>.

Recently, Schiff bases containing imine bond and various properties of their oxidative polymers have been studied by Kaya's working group. Kaya *et al.* reported the combination of the advantages of the fluorene moiety

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Received December 24, 2012; Revised February 14, 2013; Accepted February 21, 2013

doi: 10.1007/s10118-013-1361-1

and oligophenol based polyazomethines. They grafted 9,9'-bis(4-aminophenyl)fluorene (FDA) units onto aromatic oligosalicylaldehyde (OSA), oligo-4-hydroxybenzaldehyde (O-4-HBA) and oligo-3,4-dihydroxybenzaldehyde (O-3, 4-HBA) by azomethine linkages which resulted in the polyconjugated fluorene polymers. The Schiff base models of FDA were also prepared by condensation reaction with salicylaldehyde, 4-hydroxybenzaldehyde and 3, 4-dihydroxybenzaldehyde<sup>[11]</sup>. In another work they investigated the electrochromic application of newly synthesized imine-bounded phenol and oligophenol (2,3-TMAP and P-2,3-TMAP) containing electropolymerisable thiophene moiety as the side group<sup>[12]</sup>. Additionally, this report is another product than their working field. Dihydroxyazo and imine structural dyes and their some metal complexes compounds have been most widely used in fields such as dyeing textile fibre, biomedical workings and electrooptical apparatus<sup>[13]</sup>. Herein, at this work, TAPMDHBA was obtained through condensation reaction, polymers were synthesized using oxidative polymerization technique and these compounds were characterized by various techniques and methods. Polymeric materials have more properties as well known. Principally, we synthesized a monomeric and polymeric dyestuff and reported their conductivity, thermal and fluorescent properties *etc.* Consequently, the observations and experiments showed that the synthesized compounds have quite important performance for various application fields. Moreover, the synthesized polymers could be also used in electronic, optoelectronic, electro-active and photovoltaic applications due to having semi-conductive structures, and the compounds could be suitable as coloring agent for textile applications. Also, with the fine thermal stabilities they can be promising candidates for aerospace applications and obtaining excellent dyeing properties for use in electrophotography, and also for preparing dyes and pigments that have different groups in their molecules. Moreover, there are many reactive groups such as amino and hydroxyl groups. These type polymeric compounds can be used as coloring agent<sup>[14]</sup>. It has high dye fixation and good wet fastness on wool. Therefore, polymeric dye agents were brought in the dye sector.

## EXPERIMENTAL

### Materials

Tris(4-aminophenyl)methanol (pararos aniline base) (Across) and 3,4-dihydroxybenzaldehyde (Aldrich) were used as received. Acetonitrile, acetone, methanol, toluene, chloroform, hexane, dichloromethane, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO) and ethyl acetate were supplied from Merck Chemical Co. (Germany) and they were used as received. Sodium hypochlorite (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey).

### Equipments

The infrared and ultraviolet-visible spectra were measured by Perkin Elmer FTIR Spectrum one and Perkin Elmer Lambda 25, respectively. The FTIR spectra were recorded using universal ATR sampling accessory (4000–550  $\text{cm}^{-1}$ ).  $^1\text{H}$ -NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were also recorded by using deuterated DMSO- $\text{d}_6$  as a solvent at 25 °C. The tetramethylsilane was used as internal standard. The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI) of poly-4,4',4''-[4,4',4''-(hydroxymethanetriyl)tris(benzene-4,1-diyl)tris(azan-1-yl-1-ylidene)]tris(methan-1-yl-1-ylidene)tribenzene-1,2-diol (P-TAPMDHBA) and poly-tris(4-aminophenyl)methanol (P-TAPM) were determined by using gel permeation chromatography/multi-angle light scattering technique (GPC/MALS) with Macherey-Nagel GmbH & Co. (Germany) (10 nm and 7 nm diameter loading material) 7.7 mm *i.d.*  $\times$  300 mm columns, DMF/MeOH eluent (0.4  $\text{mL}\cdot\text{min}^{-1}$ , *V/V*, 4/1) and a refractive index detector at 30 °C (Shimadzu Co. Japan). The fluorescent properties of the compounds were investigated using a Shimadzu RF-5301PC spectrofluorophotometer. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis systems. The TG-DTA measurements were made between 20–1000 °C (in  $\text{N}_2$ , rate 10 K/min). DSC analysis of the oxidative polymers was carried out by using Perkin Elmer Pyris Sapphire DSC, and the measurements were made between 25–420 °C (in  $\text{N}_2$ , rate 20 K/min). Conductivities of the synthesized materials were measured on a Keithley 2400 Electrometer, using four point probe technique. Iodine doping was carried out by exposure of the materials to iodine vapor at atmospheric pressure in a desiccator at 25 °C.

### Syntheses of TAPMDHBA, P-TAPMDHBA and P-TAPM

4,4',4''-[4,4',4''-(hydroxymethanetriyl)tris(benzene-4,1-diyl)tris(azan-1-yl-1-ylidene)]tris(methan-1-yl-1-ylidene)tribenzene-1,2-diol (TAPMDHBA) was prepared by the condensation reaction of tris(4-aminophenyl)methanol (TAPM) (0.350 g, 0.001 mol) with 3,4-dihydroxybenzaldehyde (0.414 g, 0.003 mol) in 50 mL THF, achieved by boiling the mixture under reflux for 2 days. After evaporation of THF, Schiff base was obtained as black powder and recrystallized from methanol/THF (1:1, *V/V*) and dried in a vacuum oven at 60 °C<sup>[15]</sup>.

TAPMDHBA: <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 9.72 (s, 4H, Ar—OH), 6.66 (s, 1H, Al. —OH), 8.38 and 8.46 (s, 2H, CH=N), 5.90 (s, 2H, —NH<sub>2</sub>), 6.86 and 6.81 (d, 2H, Ar—Ha), 7.15 (d, 2H, Ar—Hb), 7.48 (m, 4H, Ar—Hc), 7.30 (m, 4H, Ar—Hd), 7.40 (d, 2H, Ar—He), 6.95 (d, 2H, Ar—Hf), 7.28 (s, 2H, Ar—Hg). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 145.21 (C1), 115.52 (C2), 128.84 (C3, C7, C18), 136.42 (C4), 73.02 (C5), 141.61 (C6, C17), 124.50 (C8, C19), 145.88 (C9, C20), 152.14 (C10, C21), 131.80 (C11, C22), 123.04 (C12, C23), 117.02 (C13, C24), 149.51 (C14, C25), 146.09 (C15, C26), 114.36 (C16, C27).

P-TAPMDHBA was synthesized through oxidative polycondensation of TAPMDHBA by using 30% aqueous solution of NaOCl as oxidant. TAPMDHBA (0.666 g, 0.001 mol) was dissolved in THF and placed into a 250 mL three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and an addition funnel containing NaOCl. Reaction was maintained under reflux for 5 h and the reaction mixture was cooled at the room temperature followed by evaporating in a vacuum evaporator. For the separation of unreacted monomers, the obtained product was washed with methanol (3 × 10 mL) and then dried in a vacuum oven at 60 °C<sup>[16]</sup>.

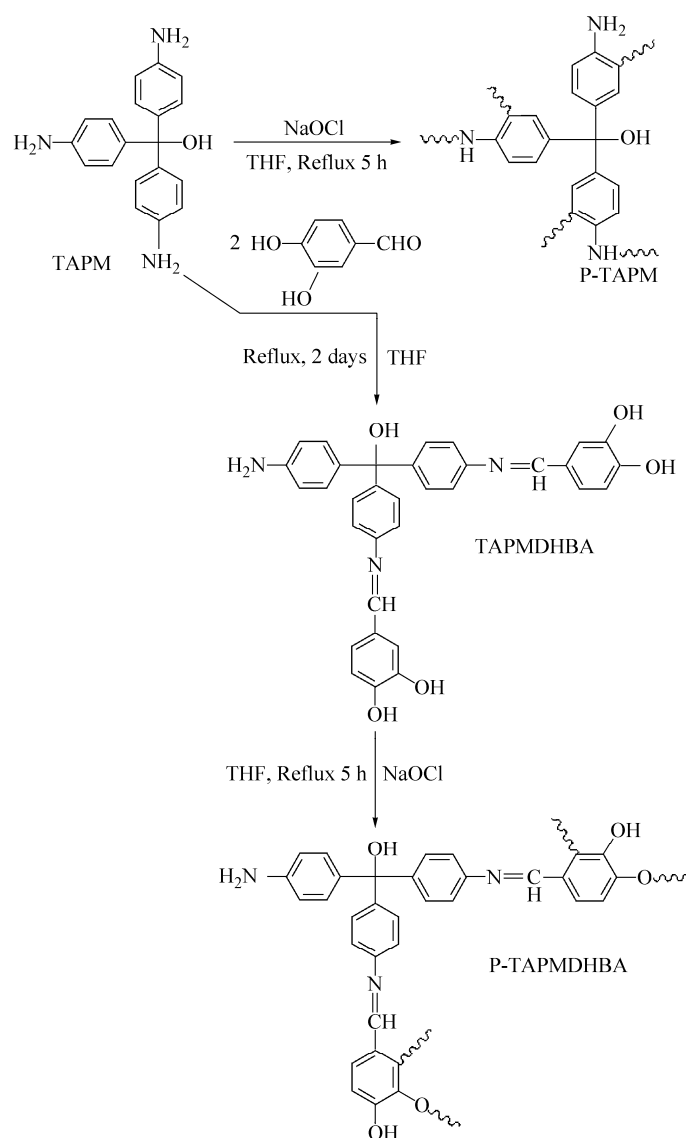
P-TAPMDHBA: <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 9.69 (s, 2H, Ar—OH<sub>1</sub>, Ar—OH<sub>2</sub>), 9.52 (s, 2H, Ar—OH (terminal)), 5.93 (s, 2H, —NH<sub>2</sub>), 6.19 (s, 1H, Al. —OH), 8.42 and 8.36 (s, 2H, CH=N), 6.61 and 6.59 (d, 2H, Ar—Ha), 7.12 and 7.10 (d, 2H, Ar—Hb), 7.46 and 7.43 (m, 4H, Ar—Hc, Ar—Hg), 7.27 and 7.25 (m, 4H, Ar—Hd, Ar—Hh), 7.17 (d, 1H, Ar—He), 6.82 and 6.80 (d, 1H, Ar—Hf), 6.95 and 6.93 (d, 2H, Ar—Hi), 6.88 (d, 1H, Ar—Hj). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 145.67 (C1, C15), 115.52 (C2), 128.51 (C3), 136.75 (C4), 67.02 (C5), 141.20 (C6, C17), 131.78 (C7, C18), 122.06 (C8, C19), 146.03 (C9, C20), 160.43 (C10), 119.63 (C11, C22), 124.19 (C12, C27), 112.37 (C13), 152.64 (C14), 125.79 (C16), 156.64 (C21), 124.91 (C23), 144.33 (C24), 139.24 (C25), 114.33 (C26), 133.16 and 129.32 (new peaks).

Poly-tris(4-aminophenyl) methanol was synthesized by oxidative polymerization reaction of tris(4-aminophenyl) methanol by using NaOCl as oxidant in THF. Reaction was maintained under reflux for 5 h, the reaction mixture was cooled at the room temperature followed by evaporating in a vacuum evaporator. For the separation of unreacted monomers, the obtained product was washed with methanol (3 × 10 mL) and then dried in a vacuum oven at 60 °C. The synthetic routes of the synthesized materials are shown in Scheme 1.

P-TAPM: <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 6.36 (s, 1H, Al. —OH), 5.97 (s, 2H, —NH<sub>2</sub>), 5.39 (s, 2H, —NH), 6.65 (d, 3H, Ar—Ha), 7.50 (d, 3H, Ar—Hb), 7.54 (d, 3H, Ar—Hc), 6.69–6.74 (m, 4H, Ar—Hd, Ar—He). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 144.52 (C1), 115.90 (C2), 126.03 (C3), 133.86 (C4), 130.11 (C5), 121.41 (C6), 82.41 (C7), 133.19 (C8), 129.75 (C9–C13, C15–C19), 126.90 (C10–C12, C16–C18), 143.97 (C11), 136.28 and 134.35 (new peaks)

### Optical and Electrochemical Properties

Ultraviolet-Visible (UV-Vis) spectra were measured by Perkin Elmer Lambda 25. The absorption spectra were recorded by using DMSO and methanol at 25 °C. The optical band gaps ( $E_g$ ) were calculated from their absorption edges. Cyclic voltammetry (CV) measurements were carried out with a CHI 660 C Electrochemical Analyzer (CH Instruments, Texas, USA) at a potential scan rate of 0.3 V/s. All the experiments were performed in a dry box filled with argon at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple. The half-wave potential ( $E^{1/2}$ ) of (Fc/Fc<sup>+</sup>) measured in acetonitrile solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was found to be 0.39 V with respect to Ag wire. The voltammetric measurements were carried out in acetonitrile for TAPM and TAPMDHBA and acetonitrile/DMSO mixture (*V/V*: 10/1) for the polymers. The HOMO-LUMO energy levels and electrochemical band gaps ( $E_g'$ ) were calculated from the oxidation and reduction onset values<sup>[16]</sup>.



**Scheme 1** The synthetic routes of P-TAPM, TAPMDHBA and P-TAPMDHBA

### Electrical Conductivity Properties

Conductivities of the synthesized compounds were measured on a Keithley 2400 Electrometer, using four point probe technique. Instrument was calibrated with ITO glass plate. The pellets were pressed on hydraulic press developing up to 1687.2 kg/cm<sup>2</sup>. Iodine doping was carried out by exposure of the material pellets to iodine vapor at atmospheric pressure in a desiccator at 25 °C.

### Fluorescence Measurements

A Shimadzu RF-5301PC spectrofluorophotometer was used in fluorescence measurements. Emission and excitation spectra of the synthesized compounds were obtained in different concentrations with DMF. The optimum emission and excitation wavelengths for each compound were determined. Also, optimizations of the concentrations to obtain maximal emission intensity values were investigated in DMF.

## RESULTS AND DISCUSSION

### Solubilities of the Compounds

The solubility test is achieved as 1 mg/1 mL. According to the solubility test results, P-TAPMDHBA was partly soluble in methanol, ethanol, acetone and ethyl acetate and also, it was completely soluble in DMF and alkaline distillation water, TAPMDHBA was completely soluble in DMF and THF. Also, it was partly soluble in methanol, ethanol, acetone and ethyl acetate. P-TAPM was DMF and THF soluble but it was partly soluble in ethyl acetate, methanol, ethanol and acetone. While TAPMDHBA and P-TAPMDHBA were soluble in alkaline distillation water, this could be explained with free  $\text{—OH}$  groups into their structures<sup>[17]</sup>. Consequently, this property is very important in textile applications. Tris(4-aminophenyl)methanol was a macromolecular dye. Additionally, the synthesized polymer and monomer are derivative of tris(4-aminophenyl)methanol. These compounds could be used as coloring agent (dyestuff) for textile applications.

### Structures of the Compounds

The FTIR spectra of the synthesized compounds are obtained and shown in Fig. 1. FTIR spectra of TAPM and P-TAPM had quite important differences.  $\text{NH}_2$  and  $\text{O—H}$  stretch vibrations of TAPM and P-TAPM are observed in the range of  $3362\text{--}3347\text{ cm}^{-1}$  and  $3220\text{--}3202\text{ cm}^{-1}$  as a widespread peak, respectively. Additionally, the peaks at  $1605$  and  $1618\text{ cm}^{-1}$  show the  $\text{—NH}$  bending vibrations. Aromatic  $\text{C—H}$  and  $\text{C=C}$  vibrations are also observed between  $3220\text{--}3027$  and  $1586\text{--}1582\text{ cm}^{-1}$ , respectively. The widespread peak at  $3362\text{ cm}^{-1}$  monitoring within FTIR spectrum of the synthesized polymer (P-TAPM) is related to  $\text{NH}_2$  groups because of the polymer chains growing during the oxidative polymerization. Figure 1 shows FTIR spectra of TAPMDHBA and P-TAPMDHBA. As seen in Fig. 1, the imine bond formation ( $\text{HC=N}$  stretch vibration) is indicated as a widespread edge in the range of  $1620\text{ cm}^{-1}$ <sup>[18]</sup>. The characteristic peaks related with  $\text{—NH}_2$  and  $\text{—OH}$  stretching vibrations are found at  $3453\text{--}3336$  and  $3212\text{ cm}^{-1}$  in FTIR spectrum of TAPMDHBA. Aromatic  $\text{C—H}$  peak was observed at  $3027\text{ cm}^{-1}$ . As seen in FTIR spectrum of P-TAPMDHBA,  $3200\text{ cm}^{-1}$  stretching peak area is almost related to  $\text{—OH}$  groups in the polymer chains during the oxidative polymerization. The other characteristic peaks are given in Fig. 1 which clearly shows that polymerization is successfully achieved.

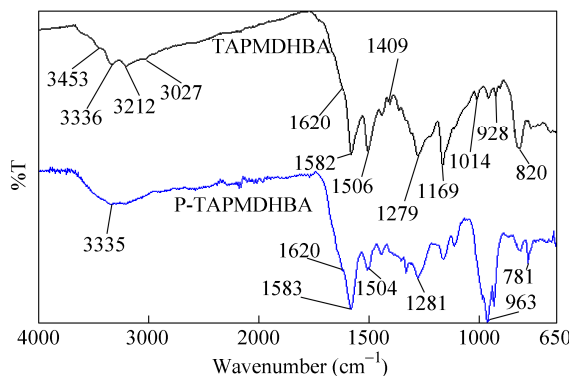
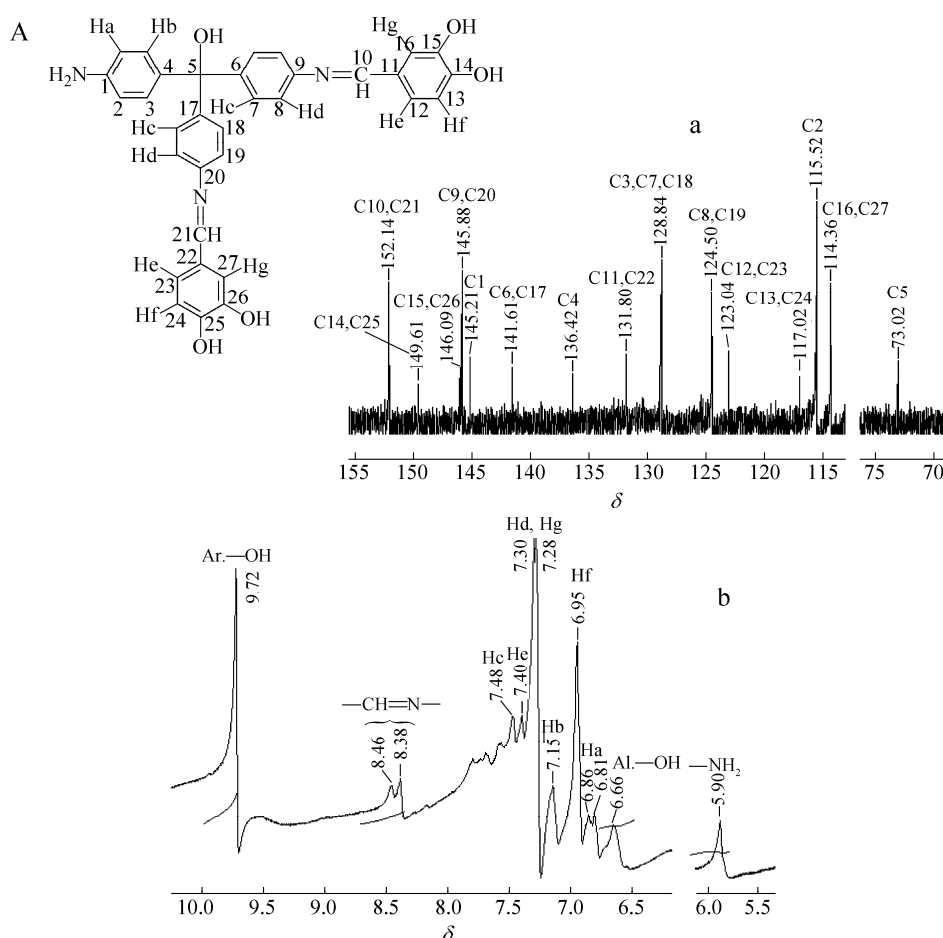


**Fig. 1** The FTIR spectra of TAPMDHBA and P-TAPMDHBA

In the  $^1\text{H-NMR}$  spectrum of P-TAPM the proton values related to benzene rings are between  $\delta = 7.50$  and  $6.63$ , and the peaks at  $\delta = 6.36$ ,  $5.97$  and  $5.39$  point out the aliphatic  $\text{—OH}$ ,  $\text{—NH}_2$  and  $\text{—NH}$  protons which confirm the proposed structure, respectively, as reported in the literature<sup>[19–21]</sup>. The one proton integration value was equal to  $0.005$ . This explains that there is one  $\text{—NH}_2$  group in the structure of the polymer (P-TAPM). Therefore, the integration region value of one  $\text{—NH}_2$  group is  $0.01$ . Moreover, it can be said that oxidative polymerization proceeds on the other  $\text{—NH}_2$  groups. Additionally, new peaks at  $\delta = 136.26$  and  $134.35$  appear in  $^{13}\text{C-NMR}$  spectrum of P-TAPM. These peaks confirm the polymeric structure and demonstrate the  $\text{C—C}$  or  $\text{C—NH—C}$  couplings. Aliphatic  $\text{—OH}$  group is curtailed by other aromatic groups and also, it shifts to lower

regions at around  $\delta = 6.0$  and  $5.0$ . Figure 2A gives the  $^{13}\text{C}$ -NMR (Fig. 2A-a) and  $^1\text{H}$ -NMR (Fig. 2A-b) spectra of TAPMDHBA, respectively and explains completely the structure of the monomer because of integration region of  $-\text{OH}$ ,  $\text{CH}=\text{N}$ , aliphatic  $-\text{OH}$  and  $-\text{NH}_2$  groups. One proton integration value was approximately 0.05. Also,  $\text{CH}=\text{N}$  had two different peak values because of the asymmetric structure of Schiff base, as expected. Fig. 2A-a shows  $^{13}\text{C}$ -NMR peak values of TAPMDHBA. There is only one free amino ( $-\text{NH}_2$ ) group in the structure of the monomer and combine with two aldehyde compounds. Fig. 2B shows  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectra of P-TAPMDHBA, respectively. As seen in Fig. 2B-a, new peaks were appeared at  $\delta = 133.16$  and  $129.32$ . Additionally, NMR spectra show that the polymerization proceeds on  $-\text{OH}$  groups and *-ortho* positions of  $-\text{OH}$  groups by  $\text{C}-\text{C}/\text{C}-\text{O}-\text{C}$  coupling. This explains with  $^1\text{H}$ -NMR spectrum of the polymer (P-TAPMDHBA). For example, the peaks related to  $-\text{OH}$  groups at  $\delta = 9.69$  and  $9.52$  have integration value with 0.01. This means that the polymerization proceed on  $\text{C}-\text{O}-\text{C}$  coupling because of the peak intensity at  $\delta = 9.52$  decreases and the peak at  $\delta = 9.52$  is named as terminal  $-\text{OH}$ . Also, as seen in its  $^{13}\text{C}$ -NMR spectrum, this state is a result of chemical shifts. The mentioned chemical shifts are also evidence of the polymer structures. Oxidative polycondensation reaction of the phenolic compounds proceeds *via* combination of the monomers by coupling of the phenylene (*-ortho* and *-para* positions of phenol) and oxyphenylene radicals. These combinations result in  $\text{C}-\text{C}$  and  $\text{C}-\text{O}-\text{C}$  couplings and the increasing conjugation. As a result, the coupling carbons in the polymer structures have lower electron densities and resultantly higher chemical shifts than those in their monomer compounds<sup>[16]</sup>. But aliphatic structured units like aliphatic  $-\text{OH}$  group in the structure shift to lower regions in  $^1\text{H}$ -NMR spectrum because of being curtailed<sup>[22]</sup>. As seen in Fig. 2B-b, it can



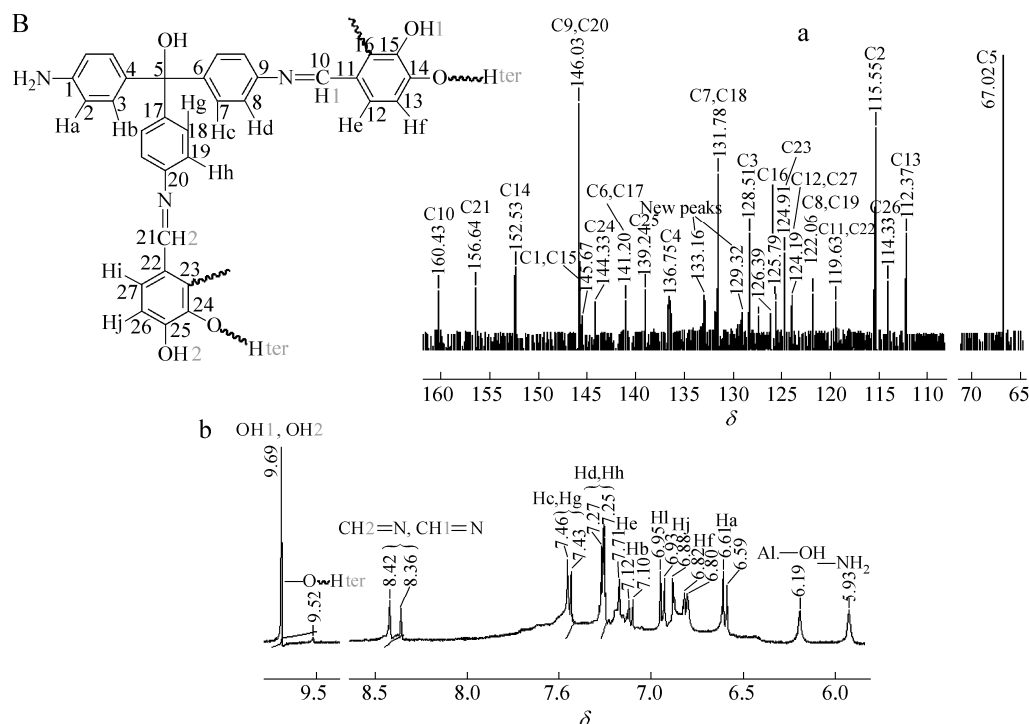


**Fig. 2** (A) (a)  $^{13}\text{C}$ -NMR and (b)  $^1\text{H}$ -NMR spectra of TAPMDHBA and (B) (a)  $^{13}\text{C}$ -NMR and (b)  $^1\text{H}$ -NMR spectra of P-TAPMDHBA

be said that the polymerization process does not progress on  $-\text{NH}_2$  groups. This is demonstrated by the integration region and the peak at  $\delta = 5.93$  in  $^1\text{H}$ -NMR spectrum of P-TAPMDHBA and also, a bit change as chemical shifts is available in spectrum of its monomer. Also, as seen in FTIR spectrum of P-TAPMDHBA the  $3200\text{ cm}^{-1}$  peak area shows the oxidative polymerization event. Moreover, widespread peak at around  $3336\text{ cm}^{-1}$  is related to  $-\text{NH}_2$  groups. This peak evidences that polymerization proceeds only on  $-\text{OH}$  groups.

### Optical and Electrochemical Behaviors

The UV-Vis spectroscopic studies were carried out with DMSO solutions of the polymers and methanol solutions of TAPM and TAPMDHBA, respectively. The UV-Vis spectra of the synthesized compounds are shown in Fig. 3. According to these spectra, a red shift occurs at the absorption edges of the synthesized polymers compared with the monomers. This is because of the polyconjugated structures of the polymers which increase HOMO and decrease LUMO energy levels thus, result in lower band gaps. The optical band gaps ( $E_g$ ) of the monomers and polymers are calculated as in the literature<sup>[23]</sup> and given in Table 1. These results show that the synthesized polymers have lower optical band gaps compared with their monomers, as expected. It is seen in Fig. 3, the shifting of the  $-\text{CH}=\text{N}-$  group band of the polymers has demonstrated the formation of the polymeric conjugate  $\pi$  system.

**Table 1.** Electronic structure parameters of the synthesized compounds

| Compounds  | HOMO <sup>a</sup> (eV) | LUMO <sup>b</sup> (eV) | $E_g^c$ (eV) | $E_g'^d$ (eV) | $\lambda_{\text{max}}^e$ (nm) |
|------------|------------------------|------------------------|--------------|---------------|-------------------------------|
| TAPM       | -5.49                  | -2.37                  | 2.02         | 3.12          | 336                           |
| P-TAPM     | -5.25                  | -2.42                  | 1.95         | 2.83          | 332                           |
| TAPMDHBA   | -5.60                  | -2.26                  | 1.96         | 3.34          | 321                           |
| P-TAPMDHBA | -5.50                  | -2.47                  | 1.89         | 3.03          | 336                           |

<sup>a</sup> Highest occupied molecular orbital, <sup>b</sup> Lowest unoccupied molecular orbital, <sup>c</sup> Optical band gap, <sup>d</sup> Electrochemical band gap, <sup>e</sup> Maximum absorbance wavelength

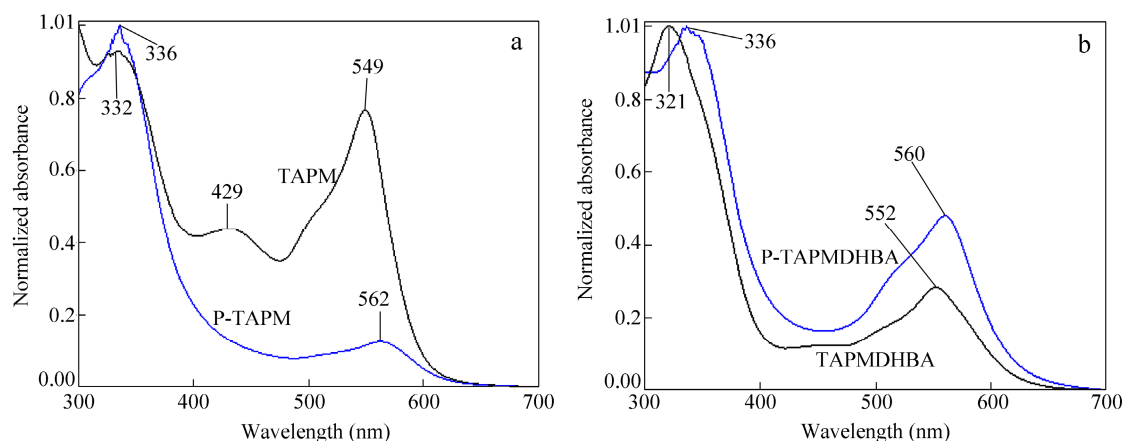


**Fig. 3** UV-Vis spectra of (a) TAPM and P-TAPM, and (b) TAPMDHBA and P-TAPMDHBA

Cyclic voltammograms of the synthesized compounds are given in Fig. 4. As seen in Fig. 4(a) these voltammograms have oxidation steps. The peak at 1.08 V at the voltammograms of TAPM indicates the oxidation of  $-\text{NH}_2$  groups. Also, at the voltammograms of P-TAPM the peak at 0.85 V indicates the oxidation of  $-\text{NH}$  group, and the peak at 1.37 V indicates the oxidation of  $-\text{NH}_2$  groups, agreed with the literature data<sup>[24]</sup>. In reduction area at the voltammograms of P-TAPM the peaks at  $-1.22$  V and  $-1.98$  V appear. Also, the reduction peak at  $-2.018$  V for TAPM is observed. The cyclic voltammograms of TAPMDHBA and P-TAPMDHBA are given in Fig. 4(b). As seen in voltammograms of TAPMDHBA the widespread peak at 1.213 V is related to oxidation process of  $-\text{NH}_2$  and  $-\text{OH}$  groups. Additionally, two oxidation steps are obtained at cyclic voltammograms of P-TAPMDHBA. These oxidation peaks are 1.12 V and 1.37 V, respectively. The peak at 1.12 V is related to  $-\text{OH}$  groups in the structure of the polymer and the oxidation peak at 1.37 V shows oxidation of free  $-\text{NH}_2$  groups, as expected<sup>[11]</sup>.

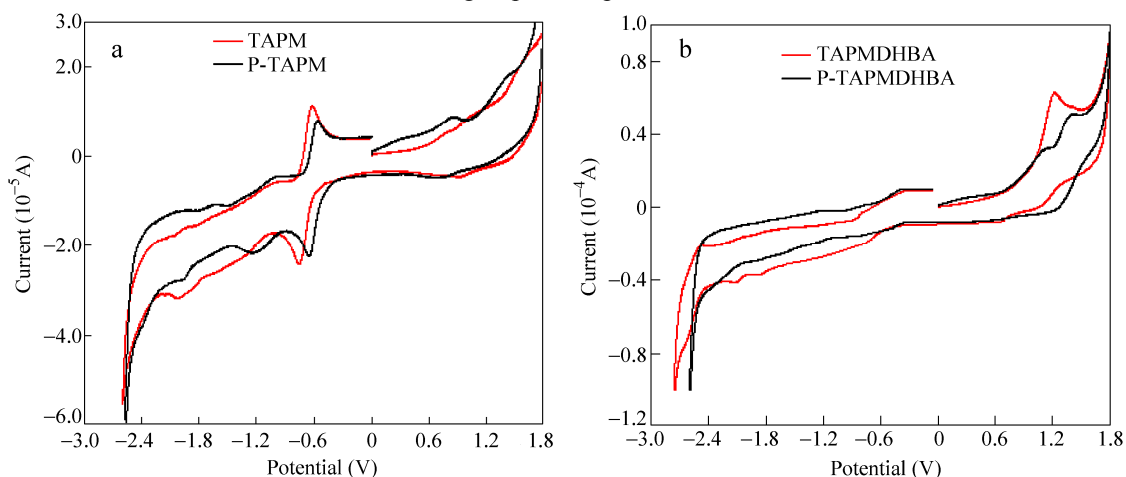


**Fig. 4** Cyclic voltammograms of (a) TAPM and P-TAPM, and (b) TAPMDHBA and P-TAPMDHBA

According to the cyclic voltammetry (CV) measurements, the HOMO-LUMO energy levels and the electrochemical band gaps ( $E_g'$ ) are calculated as in the literature<sup>[25]</sup> and shown in Table 1. As seen in Table 1 the electrochemical band gaps are a bit higher than the optical band gaps and also, the electrochemical band gaps of the monomers are higher than those of their polymers, as expected. This could be explained by their polyconjugated structures. Additionally, lower band gaps facilitate the electronic transitions between HOMO-LUMO energy levels and make the polymers more electro-conductive than the monomers.

### Fluorescence Measurements

Fluorescence measurements of the synthesized materials are carried out using DMF. The fluorescence spectra of TAPMDHBA, TAPM and P-TAPM in DMF with different concentrations (mg/L) are given in Fig. 5. The optimization of the concentrations to obtain maximal emission and excitation intensity is also investigated in DMF because all of the compounds are completely soluble in DMF. The solutions are prepared as 10 mg/10 mL.

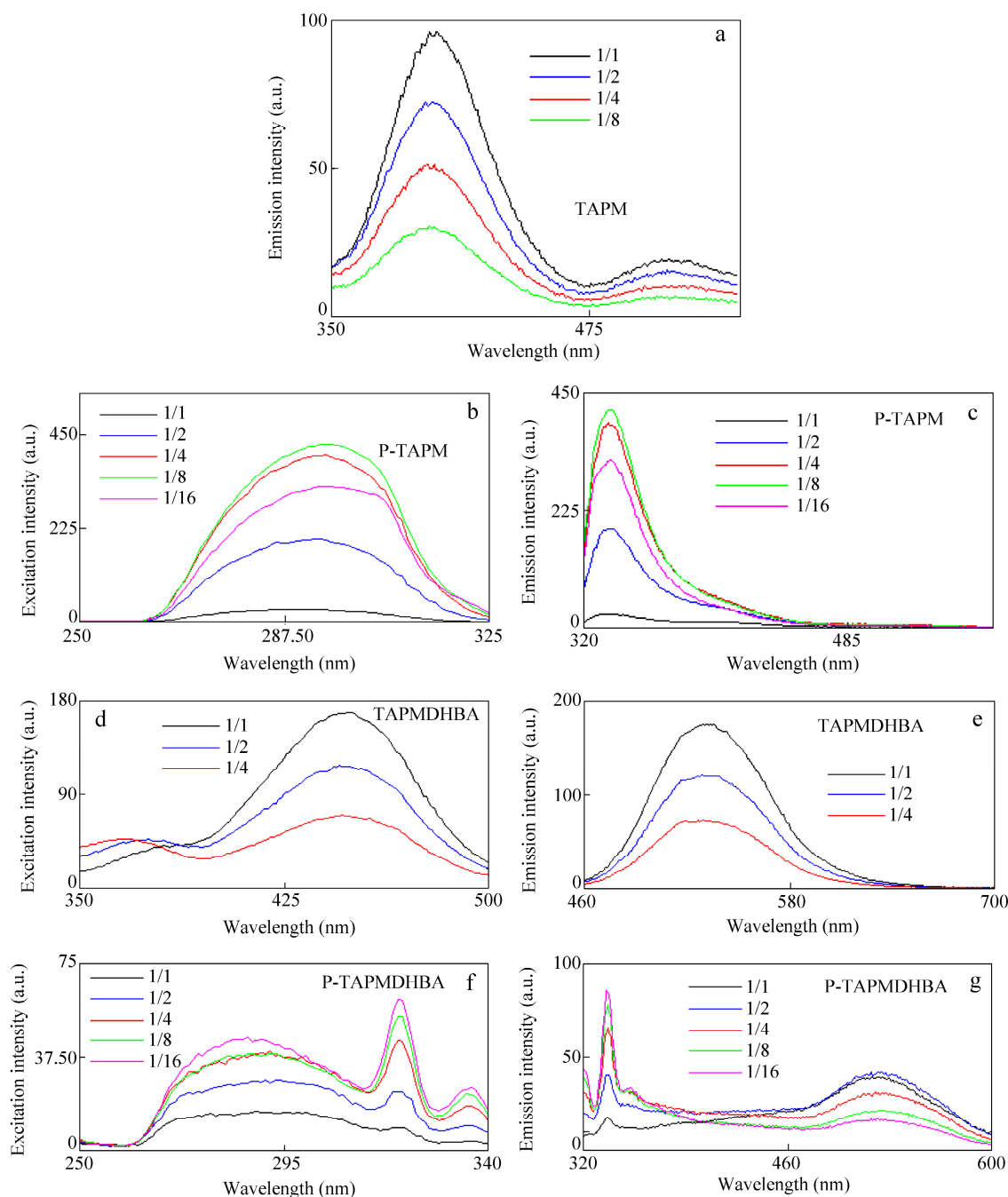


**Fig. 5** The changes of the emission and excitation intensities of the synthesized compounds related to different concentrations (Slit:  $\lambda_{\text{Ex}}$  5 nm,  $\lambda_{\text{Em}}$  5 nm)

Then, solutions are diluted to the stated concentrations. The obtained results show that the synthesized compounds have the maximum fluorescence intensity in different concentrations. Also, P-TAPM has more fluorescence intensity than the other compounds. Additionally, the fluorescence intensity values at 10 mg/10 mL concentration of the compounds are given in Table 2.

**Table 2.** Fluorescence spectral data of the synthesized compounds in DMF

| Compounds  | $\lambda_{\text{Ex}}^{\text{a}}$ | $\lambda_{\text{Em}}^{\text{b}}$ | $\lambda_{\text{max (Ex)}}^{\text{c}}$ | $\lambda_{\text{max (Em)}}^{\text{d}}$ | $I_{\text{Ex}}^{\text{e}}$ | $I_{\text{Em}}^{\text{f}}$ |
|------------|----------------------------------|----------------------------------|----------------------------------------|----------------------------------------|----------------------------|----------------------------|
| TAPM       | 278                              | 521                              | —                                      | 400                                    | —                          | 96                         |
| P-TAPM     | 296                              | 337                              | 295                                    | 336                                    | 30                         | 29                         |
| TAPMDHBA   | 447                              | 541                              | 448                                    | 532                                    | 170                        | 176                        |
| P-TAPMDHBA | 305                              | 355                              | 288                                    | 522                                    | 16                         | 42                         |

<sup>a</sup> Excitation wavelength for emission, <sup>b</sup> Emission wavelength for excitation, <sup>c</sup> Maximum excitation wavelength, <sup>d</sup> Maximum emission wavelength, <sup>e</sup> Maximum excitation intensity, <sup>f</sup> Maximum emission intensity. Concentration: 10 mg/10 mL

### Electrical Conductivities

Electrical conductivities of the synthesized compounds and the changes of electrical conductivity related to doping time with iodine are shown in Fig. 6. As well known, there is an opposite tendency between the HOMO-LUMO band gap and the conductivity. As stressed before lower band gap facilitates the electronic transition from bulk to vacuum energy level. This results in higher conductivity. P-TAPM with the lowest band gap has also the highest undoped conductivity. An important increase of the conductivity is attained when iodine is employed as doping agent. According to the electrochemical band gaps the values of TAPMDHBA and P-TAPMDHBA are a bit higher than those of P-TAPM. Therefore, their conductivities are lower than P-TAPM. Maximum conductivity increasing is obtained for P-TAPM *via* iodine doping from between  $10^{-9}$  and  $10^{-8}$  S/cm to  $10^{-7}$  S/cm by increasing time. It is seen that the conductivity values of TAPMDHBA increase from between  $10^{-10}$  and  $10^{-9}$  S/cm to between  $10^{-8}$  and  $10^{-7}$  S/cm by increasing time<sup>[11]</sup>. As a result, P-TAPM has the highest saturated conductivity. This is possibly because of iodine molecules coordination with free  $-\text{NH}_2$  groups into the polymer chain of P-TAPM. According to doping mechanism, nitrogen, being a very electronegative element, is capable of coordinating with an iodine molecule. As a result, a charge-transfer complex between  $-\text{NH}_2$  groups and dopant iodine is formed and a considerable increase in conductivity can be observed<sup>[26]</sup>. The compounds with  $-\text{NH}_2$  groups could also be useful materials in electronic or opto-electronic studies after a long time iodine doping. TAPMDHBA and P-TAPMDHBA have imine bonds in their structures and due to the high conductivity properties TAPMDHBA and P-TAPMDHBA are semi-conductive compounds. Conductivity measurements of imine polymers were previously studied and considerable increases were reported when they were doped with iodine<sup>[26, 27]</sup>. Doping procedure of conducting polymers has attracted much attention of researchers into this field so far<sup>[28, 29]</sup>. This procedure produces a lot of application fields for conducting polymers. With these properties conducting polymers are used in gas sensing materials against several kinds of electro-donor (such as  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  *etc.*) and electro-acceptor (such as  $\text{I}_2$  and  $\text{NO}_2$ ) gases<sup>[30–33]</sup>. These studies show that the doping level and electrical conductivities of a conducting polymer can be changed considerable by doping with chemical vapors. The sensing process of the conductive/semi-conductive polymers generally depends on the electron transferring mechanism from and to the analytes<sup>[34]</sup>. Electron transferring causes changes in resistance and work function ( $W_{\text{f}}$ ) of a conducting polymer as well as shifting of absorption edge. These kinds of polymers can be used to develop a gas sensor by measuring of the mentioned physical changes. The proposed fluorene co-polyphenols, thus, could also be used as an active layer in gas sensors for detection of electro-acceptor gases like iodine vapour by measuring of the conductivity change.

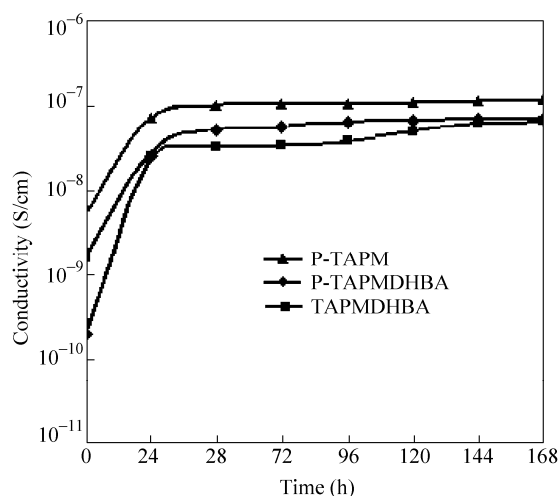


**Fig. 6** Electrical conductivity changes of the I<sub>2</sub>-doped and undoped compounds versus doping time at 25 °C

### Thermal Analysis

Thermal degradation data of the compounds (TGA, DTG, DTA and DSC) are summarized in Table 3. TGA curves of the synthesized compounds are shown in Fig. 7. According to the TGA results, the initial degradation temperature ( $T_{on}$ ) of TAPM is lower than that of P-TAPM. This may be explained as the formation of the polymeric structure during the oxidative polymerization reaction. Also, P-TAPMDHBA has higher initial degradation temperature ( $T_{on}$ ) than its monomer and this can be attributed to its thermal stability<sup>[11, 27]</sup>. Additionally, temperatures corresponding to 20% and 50% weight losses of the polymers are higher than those of their monomers. For example, these values for P-TAPM and P-TAPMDHBA are 422, 816 °C and 660, 875 °C, respectively. According to DTG curves,  $T_{max}$  values of P-TAPMDHBA are found as 260, 866 and 950 °C, respectively and these values are clearly higher than those of its monomer. According to DTA analysis, the endothermic peaks have observed for the compounds. For example, endothermic peak values are 497 °C for TAPM; 557 °C for P-TAPM; 536 °C for TAPMDHBA; 497, 792 and 875 °C for P-TAPMDHBA, respectively. P-TAPMDHBA has an exothermic peak at 267 °C. The initial degradation temperature values of poly[2-(4-bromobenzylideneamino)phenol] and poly[2-(4-bromobenzylideneamino)-5-methylphenol] were 170 °C and 174 °C, respectively<sup>[35]</sup>. The glass transition temperatures ( $T_g$ ) of the polymers were determined from DSC measurements and  $T_g$  values of P-TAPMDHBA and P-TAPM were found as 105 °C and 125 °C, respectively. Also, during the glass transitions, the specific heat ( $\Delta C_p$ ) changes were calculated from software program of DSC. For P-TAPMDHBA it was found as 0.230 J/g.K. It has an exothermic peak at 274 °C. Additionally,  $\Delta C_p$  value for P-TAPM is found to be 0.535 J/g.K. According to the DMA (dynamic mechanical analyzer) analysis, phase transition temperature of P-TAPMDHBA was recorded as two steps until 200 °C and calculated as 85 °C and 181 °C across  $\tan\delta$  value.

**Table 3.** Thermal degradation values of the synthesized compounds

| Compounds  | TGA             |                    |                 |                 |                     | DTA           |
|------------|-----------------|--------------------|-----------------|-----------------|---------------------|---------------|
|            | $T_{on}^a$ (°C) | $T_{max}^b$ (°C)   | $T_{20}^c$ (°C) | $T_{50}^d$ (°C) | Char at 1000 °C (%) | Endo (°C)     |
| TAPM       | 118             | 124, 302, 481, 872 | 305             | 589             | 9                   | 497           |
| P-TAPM     | 170             | 227, 388, 520, 836 | 422             | 816             | 31                  | 557           |
| TAPMDHBA   | 127             | 172, 398           | 387             | —               | 53                  | 536           |
| P-TAPMDHBA | 227             | 260, 866, 950      | 660             | 875             | 12                  | 497, 792, 875 |

<sup>a</sup> The onset temperature, <sup>b</sup> Temperatures of the maxima of the peak, <sup>c</sup> Temperature corresponding to 20% weight loss, <sup>d</sup> Temperature corresponding to 50% weight loss

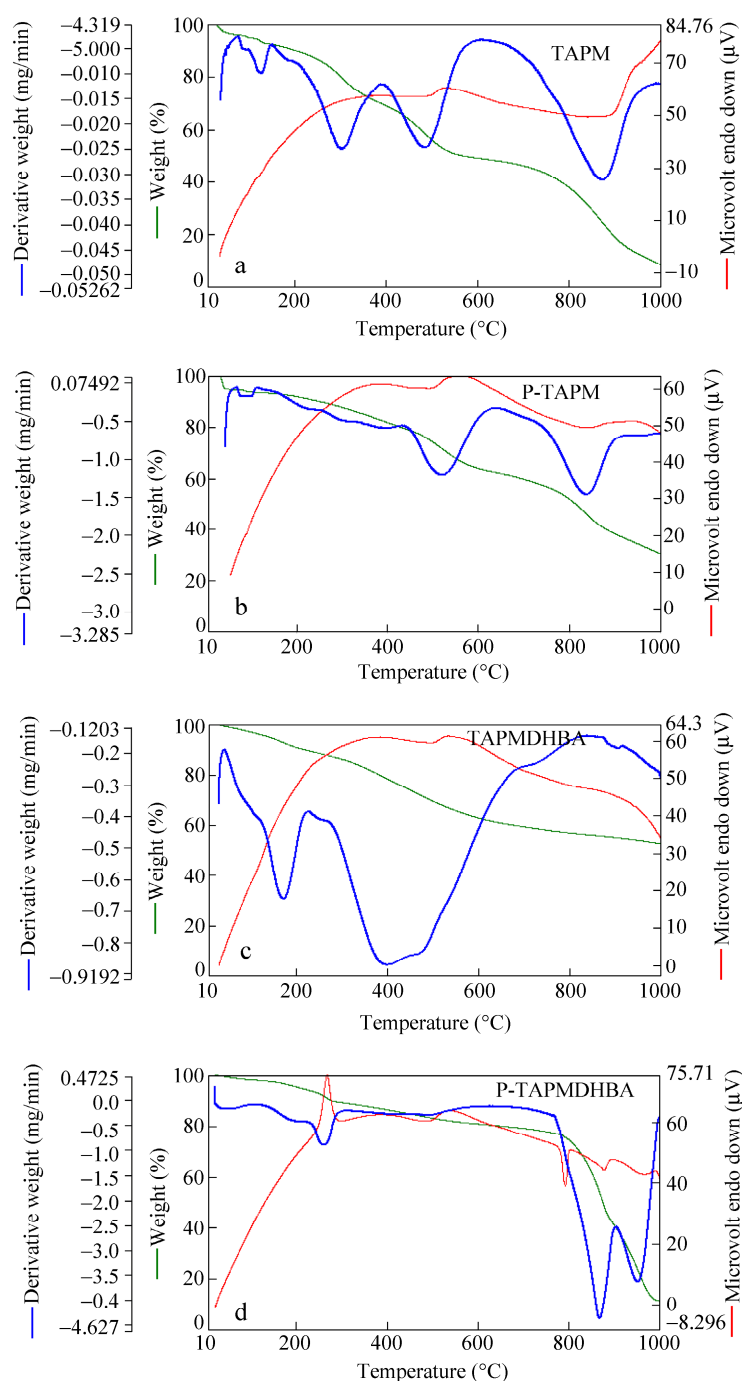


**Fig. 7** Thermal curves of the (a) TAPM, (b) P-TAPM, (c) TAPMDHBA and (d) P-TAPMDHBA compounds

### **Dyeing Process and Colors Properties**

TAPM, P-TAPM, TAPMDHBA and P-TAPMDHBA are solved in THF because of easily evaporating of THF. After, wools are placed in dye solutions 24 h. Dyed wools are displaced from solution medium and dried. Then the wools are put into water in order to investigate that the solubility are dried again. Dyed wools do not color in aqua medium, as expected. Figure 8 shows their photographs after dye process. As seen in Fig. 8, the compounds have originally different and stable colors. This may be attributed to the good penetration and

affinity of the dye for the wool structure. Therefore, these dyestuffs are suitable for textile applications because of these properties. These dyes give a narrow range of color ranging from yellow to red with good levelness, brightness and depth on the wool. The variation in the shade of the dyed wool results from both the nature and position of the substituent present on the groups of  $-\text{NH}_2$ ,  $-\text{NH}$ ,  $-\text{OH}$  and imine<sup>[13, 14, 36]</sup>. The dyed wools have fairly good to good light fastness; very good to excellent washing, perspiration and sublimation fastness and good to very good rubbing fastness properties<sup>[37]</sup>. Figure 9 shows color changes of P-TAPM, TAPM, TAPMDHBA and P-TAPMDHBA (A) in room media and for (B) UV light-long wave in different solvents. However, according to different solvents color changes the compounds are very important for various applications as pH, solvatochromic *etc.*<sup>[38]</sup>. As seen in Fig. 9, the compounds have clearly color changes in different solvents. But, color change of P-TAPMDHBA is the same for each two media. This can be explained with the polymerization. It has long polymer chains and also, its solubility is quite low in organic solvents (see Fig. 9 (4)). At the same time, color change is related to the structure of compounds. This is due to the polymer series having a side chain of OH groups which reacts with the reactive dye<sup>[39]</sup>.



**Fig. 8** The colors of wools dyed with the compounds

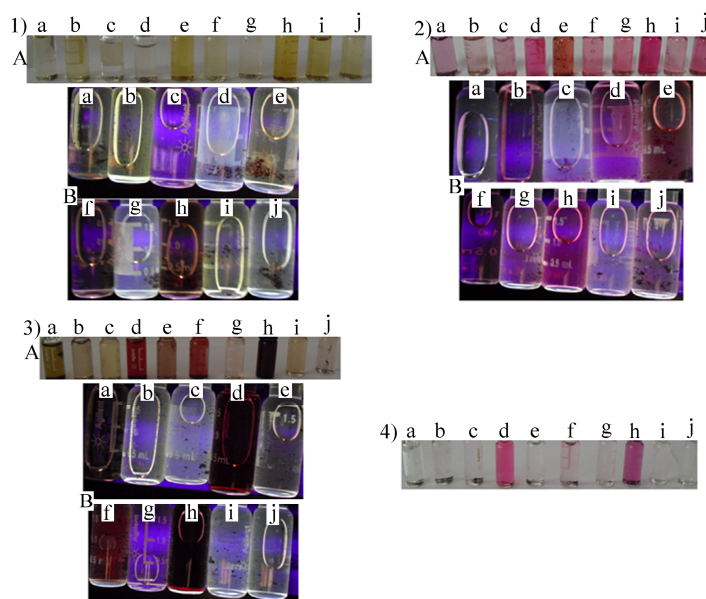


**Fig. 9** Colors changes of (1) P-TAPM, (2) TAPM, (3) TAPMDHBA and (4) P-TAPMDHBA (A) in room media and (B) for UV light-long wave in different solvents (a: toluene, b: chloroform, c: hexane, d: methanol, e: THF, f: acetone, g: acetonitrile, h: DMF, i: dichloromethane, j: ethyl acetate)

### SEC Analysis

According to the SEC measurements, the calculated number-average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity index (PDI) values of P-TAPMDHBA and P-TAPM are given in Table 4. As seen in Table 4, P-TAPMDHBA and P-TAPM had three main fractions. According to the SEC results, P-TAPM has higher average molecular weight than P-TAPMDHBA. This can be explained as polymerization of free  $\text{NH}_2$  groups. Although the polymers have high average molecular weights they can be

soluble in alkaline aqueous. This is a result of free  $\text{NH}_2$  groups in the polymer chains. In addition, according to the total values the molecular weights of P-TAPM and P-TAPMDHBA is approximately 5400 and 5700  $\text{g}\cdot\text{mol}^{-1}$ , respectively. Also, their PDI values are 1.065 for P-TAPM and 1.044 for P-TAPMDHBA, respectively. This can be explained that polymer chain lengths are roughly close to each other. For example, PDI values for all the polymers are close to 1 in all the fractions, as expected. In first and second fractions, P-TAPM and P-TAPMDHBA consist of the polymeric chains. However, in third fractions they have oligomeric chains. Also, oligomeric units are of quite high percentages like 65% for P-TAPM and 58% for P-TAPMDHBA. Moreover, according to SEC analysis it can be seen that P-TAPMDHBA contains approximately 11 repeat units for its first fraction and P-TAPM contains approximately 18 repeated units for its first fraction.

**Table 4.** SEC analyses results of the synthesized polymers

| Table 4. SEC analyses results of the synthesized polymers |                                          |       |       |            |       |       |    |             |       |       |    |              |       |       |    |
|-----------------------------------------------------------|------------------------------------------|-------|-------|------------|-------|-------|----|-------------|-------|-------|----|--------------|-------|-------|----|
| Compounds                                                 | Molecular weight distribution parameters |       |       |            |       |       |    |             |       |       |    |              |       |       |    |
|                                                           | 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   | %  |
| P-TAPM                                                    | 5400                                     | 5750  | 1.065 | 49450      | 52400 | 1.060 | 20 | 24580       | 25600 | 1.042 | 15 | 4150         | 4400  | 1.060 | 65 |
| P-TAPMDHBA                                                | 5700                                     | 5950  | 1.044 | 41400      | 42850 | 1.035 | 33 | 18700       | 19300 | 1.032 | 9  | 3100         | 3300  | 1.065 | 58 |

## CONCLUSIONS

Novel dyestuffs, Schiff base and Schiff base substituted polyphenol derivatives were synthesized by condensation reaction of TAPM with 3,4-dihydroxybenzaldehyde. Solubility tests showed that P-TAPMDHBA and TAPMDHBA were soluble in alkaline aqueous media. These compounds could be used as coloring agent (dyestuff) for textile applications. Observations showed that the dyed wools with these materials have fairly well to good light fastness, very good to excellent washing, perspiration and sublimation fastness and good to very good rubbing fastness properties. According to the electrochemical analysis, the synthesized polymers had quite low band gaps as expected. P-TAPM had the lowest band gap and resultantly the highest undoped conductivity. Increasing conductivity with iodine doping makes the synthesized polymers highly promising for using in gas sensing devices. Thermal degradation characteristics were determined. Also, the polymer models were found to be more stable compounds than their monomers. The initial degradation temperatures of the polymers were quite high in the range of 170–227 °C. With the fine thermal stabilities they can be promising candidates for aerospace applications. Moreover, the synthesized polymers could be also used in electronic, optoelectronic, electro-active and photovoltaic applications due to having semi-conductive structures.

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