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Heat resisting and water-soluble chocolate polyesters containing azomethine group

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In this study, soluble in water poly(azomethine-ester)s (PAEs) were synthesized via elimination reactions of aromatic dihydroxy compounds containing imine bonding with terephthaloyl chloride. The structures of Schiff bases (SBs) and PAEs containing different aliphatic chains were confirmed by FT-IR, ^{1}H-NMR, ^{13}C-NMR and UV-Vis analyses. Physicochemical properties of the new polymers were characterized. Thermal properties of the compounds were investigated by TGA-DTA, DMA and DSC. According to TGA measurements, the starting degradation temperatures (T_{on}) of P-1, P-2, P-3, and P-4 poly(azomethine-ester)s were found as 255 °C, 232 °C, 222 °C, and 221 °C, respectively. The starting degradation temperatures of the poly(azomethine-ester)s were higher than their Schiff base compounds. According to dynamical mechanical analysis (DMA) measurements, glass transition temperature (T_g) of P-1, P-2, P-3, and P-4 poly(azomethine-ester)s were found as 95 °C, 138 °C, 140 °C, and 145 °C, respectively. The morphological and topographic properties of the PAEs containing azomethine linkage in the main chain were investigated by FE-SEM and AFM, respectively. The molecular mass distributions of PAEs were determined by gel permeation chromatography (GPC). Electrochemical (E'_g) and optical band gap (E_g^{opt}) values of the prepared SBs and PAEs were calculated from cyclic voltammetry (CV) and UV-Vis analyses. The electrochemical band gap (E'_g) values of P-1, P-2, P-3 and P-4 were found as 2.44 eV, 2.41 eV, 2.39 eV and 2.39 eV, respectively, from the cyclic voltammetry.

Keywords: *poly(azomethine-ester); Schiff base, water-soluble; electrochemical properties; thermal degradation; elimination reactions*

1. Introduction

Water-soluble polymers are used in many fields including food, textiles, construction and pharmaceutical industries, coating technologies, dye industry, adhesives, and water cleaning [1–3]. Developments of nanotechnology, environmental engineering, biomedical engineering, information technologies and smart devices with biocompatible and environment-friendly properties resulted from extensive studies of these compounds [4–6]. Information technology created new applications for these materials such as electrically-sensitive or optical films. Synthetic water-soluble polymers have been designed with properties never realized before in natural polymers to meet the requirements of these novel applications. Architectural freedom places water-soluble polymers in a center of the fields of nanotechnology and smart materials [7].

Polyazomethines are π conjugated polymeric materials that possess good mechanical properties and high thermal stability, and exhibit the properties of liquid crystals. They have already been used in optoelectronic and nonlinear optical materials [8].

Polymers that contain imine and ester groups in main-chain demonstrate double-degradation properties both chemical and biological. Generally, the degradation rate of these polymers decreases when the number of imine groups in the polymeric chain increases. They are thermodynamically stable and maintain their molecular weight and mechanical strength in air. Still, the imine bonds easily hydrolyze, when they are exposed to water, breaking up the polymer chains into oligomers. After such water cracking, these oligomers are biodegraded into CO_2 and water. Additionally, the imine bonds are restored by evaporation of water, leading to improvement of the molecular weight and the mechanical properties of the PAEs.

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The PAEs are considered to be a class of double-degradable polymers, combining chemical and biological degradability features [9].

The main aim of the present study was to synthesize novel poly(azomethine-ester)s soluble in water via elimination reactions of aromatic dihydroxy and terephthaloyl chloride compounds. The structures of P-1, P-2, P-3 and P-4 poly(azomethine-ester) compounds were confirmed by FT-IR, UV-Vis, ^{1}H- and ^{13}C-NMR. The characterizations of this poly(azomethine-ester)s were performed by TG-DTA, DSC, DMA, FE-SEM, AFM, CV and GPC. Thermal stabilities of SB-1, SB-2, SB-3 and SB-4 and P-1, P-2, P-3 and P-4 poly(azomethine-ester)s were studied by TG-DTA. Electrochemical properties such as the HOMO, LUMO energy levels and electrochemical band gaps (E'_g) of all monomers and poly(azomethine-ester)s were calculated from oxidation and reduction onset values by cyclic voltammetry measurements. The optical band gaps (E_g^{opt}) of SB-1, SB-2, SB-3 and SB-4 and P-1, P-2, P-3 and P-4 poly(azmethine-ester)s were calculated from absorption edges of UV-Vis spectra.

2. Experimental

2.1. Chemicals

Ethylene diamine, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane were supplied by Fluka. 2-hydroxybenzaldehyde, terephthaloyl chloride, sodium carbonate (Na_2CO_3), dimethylformamide (DMF), methanol (MeOH), ethyl acetate, hexane, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), acetonitrile were purchased from Merck Chem., Co. (Germany).

2.2. Synthesis of Schiff bases and their polyesters

Schiff bases abbreviated as SBs were prepared by the condensation reaction of 2-hydroxybenzaldehyde (0.02 mol) with ethylenediamine (0.01 mol) (1,4-butanediamine, hexamethylenediamine, octamethylenediamine (0.01 mol)) in 60 mL of methanol, by boiling the mixture under reflux for 6 h (Fig. 1). The obtained SBs were filtered, recrystallized from acetonitrile and dried in vacuum desiccators [9, 10]. The yields of SB-1, SB-2, SB-3 and SB-4 compounds were found as 73 %, 74 %, 74 % and 76 %, respectively.

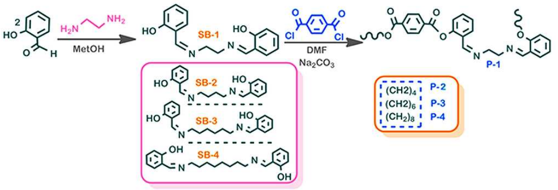

Fig. 1. Synthesis of Schiff base and poly(azomethine-ester)s.

Poly(azomethine-ester)s were synthesized by the condensation reaction of the obtained Schiff bases with terephthaloyl chloride. The polymers were abbreviated as P-1, P-2, P-3 and P-4. Synthesis procedures of the PAEs were as follows: SB-1 (0.04 mol) and dry DMF (25 mL) were charged into a 250 mL round-bottom flask. An amount of 0.02 mol of Na_2CO_3, dissolved in DMF (5 mL), was added to this mixture and heated (60 °C, 1 h) with stirring under argon atmosphere. An amount of 0.02 mol of terephthaloyl chloride, dissolved in DMF (30 mL), was added to this mixture. The temperature increased to 150 °C and the reaction mixture was stirred under argon atmosphere for 5 h and left overnight for completion of the reaction. The reaction solution was poured into 200 mL of chloroform and the precipitated crude product was collected [11]. The obtained PAEs were washed with methanol (25 mL). The polymers were dried in a vacuum oven at 70 °C for 36 h [12]. The yields of P-1, P-2, P-3 and P-4 poly(azomethine-ester)s were found as 68 %, 69 %, 69 % and 67 %, respectively.

2.3. Characterization techniques

Infrared spectra were measured by PerkinElmer Spectrum One FT-IR system and recorded for a solid sample in a powder form at room conditions using universal ATR sampling accessory within the wavelengths of 4000 cm^{-1} to 650 cm^{-1}.

UV-Vis spectra of Schiff bases and poly(azomethine-ester)s were measured in Analytik Jena Specord 210 Plus at 25 °C using DMF as a solvent. ^{1}H NMR and ^{13}C NMR spectra (JEOL ECX-400 II and 100.6 MHz) were obtained by DMSO-$_{d6}$ as a solvent at room temperature. The GPC analyses were performed using a Shimadzu 10AVp series HPLC-GPC system, calibrated with a mixture of polystyrene standards. The analyses were carried out by DMF/MeOH (v/v, 4/1) as eluent at a flow rate of 0.4 mL/min at room temperature. Polystyrene standards were used because they are similar in terms of aromaticity with bifunctional organic polymeric particles. Electrochemical properties of nanoparticles were explored with a CHI 660C Electrochemical Analyzer (CH Instruments, Texas, USA) in 0.1 mol·L^{-1} tetrabutylamonium hexafluorophosphate as supporting electrolyte. The voltammetric measurements were performed in a dry box under argon gas atmosphere at room temperature. A glassy carbon working electrode (GCE) and an Ag wire were used as reference electrodes. Platinum wire was used as a counter electrode. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated from oxidation and reduction onset values [13]. The surface morphologies of the polyesters were determined by a JEOL JSM-7100F Schottky field emission scanning electron microscope. The TG/DTG-DTA thermograms were recorded using a PerkinElmer diamond thermal analysis in dynamic nitrogen atmosphere at a flow rate of 200 mL·min^{-1} from 293 K to 1273 K. The heating rates were chosen as 10 °C·min^{-1} and the sample mass ranged from 8 mg to 10 mg. A platinum crucible was used as a sample container. DSC measurements were performed between 25 °C and 450 °C (in N$_2$, heating rate 10 °C·min^{-1}) using a PerkinElmer Pyris Sapphire DSC instrument. Topography and 3D images of the polymeric films were recorded by atomic force microscopy (AFM) Alpha 300 A (WITec, Ulm, Germany). Specified surface areas of the polymers were scanned angularly by a cantilever in non-contact mode (AC, 42 N/m, 285 kHz). DMA tests were carried out by PerkinElmer Pyris Diamond DMA 115 V using a single cantilever in a bending mode at a frequency of 1 Hz, a heating rate of 3 °C·min^{-1} and in the range of 20 °C to 350 °C. The samples were prepared as follows: 0.5 g of polymer was placed into the titanium clamps (supplied from Triton Technology, Ltd., United Kingdom) and closed by bending the clamps at both sides.

3. Results and discussion

3.1. Solubility

All of the synthesized poly(azomethine-ester)s and their Schiff bases were found to be soluble in water, but insoluble in some non-polar solvents like benzene, hexane and toluene. PAEs were also insoluble in various organic solvents such as chloroform, tetrahydrofuran, dimethyl sulfoxide and dichloromethane. They only were partially soluble in DMF. The poly(azomethine-ester)s were insoluble in most of the organic solvents maybe due to the induction of flexibility via the spacer chain in the polymer backbone in addition to the inclusion of bent shaped aliphatic groups that are typical of poly(azomethine-ester)s and Schiff bases, which then make them more processable and feasible for various potential applications. Images of poly(azomethine-ester)s granules and their solubilities in waters are given in Fig. 2 and Fig. 3, respectively.

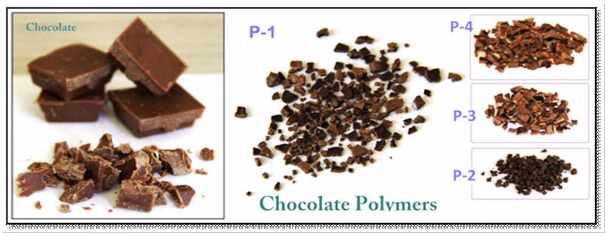

Fig. 2. Image of poly(azomethine-ester) granules.

Fig. 3. Solubility process of P-1 in water.

3.2. Spectral characterization of the compounds

The structures of the poly(azomethine-ester)s and Schiff bases were confirmed via FT-IR, ^{1}H and ^{13}C NMR spectroscopy. A new large band between 3280 cm^{-1} and 3200 cm^{-1} was found which proves and verifies the structure of SBs. Aliphatic stretch vibrations were observed in the range of 2912 cm^{-1} to 2900 cm^{-1}. FT-IR spectra of all the SBs are quite similar to each other on account of structural similarities. Last four spectra of PAEs presented a strong band at around 1730 cm^{-1} after the polymerization, representing the functional group of C=O ester, which confirmed the success of polymerization [14, 15] to form P-1, P-2, P-3 and P-4, as illustrated in Fig. 4. In the first four spectra of SBs (Fig. 4), a strong peak was observed between 1665 cm^{-1} and 1636 cm^{-1} azomethine (C=N) stretching [15, 16]. All homologous series of the polymers were found to give similar results.

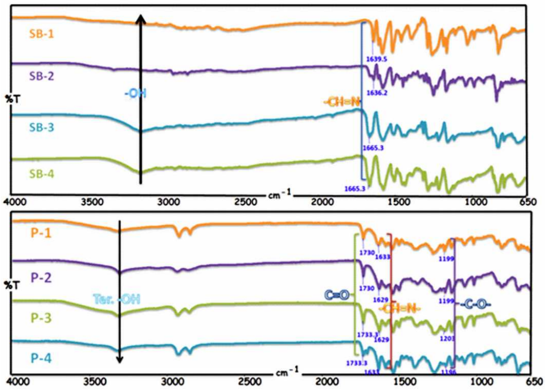

Fig. 4. FT-IR spectra of the SBs and PAEs.

The ^{1}H NMR spectra of SB-3 (Fig. 5) showed the occurrence of signals broadening and imine peak of this monomer were observed at 8.47 ppm. The proton decoupled ^{13}C NMR spectrum of SB-3 (Fig. 5) exhibited the expected peaks for each of the carbon atoms of the Schiff base in which the chemical shift of C=N (imine) appeared at 165.64 ppm and the chemical shift of C–OH was found at 160.88 ppm [17].

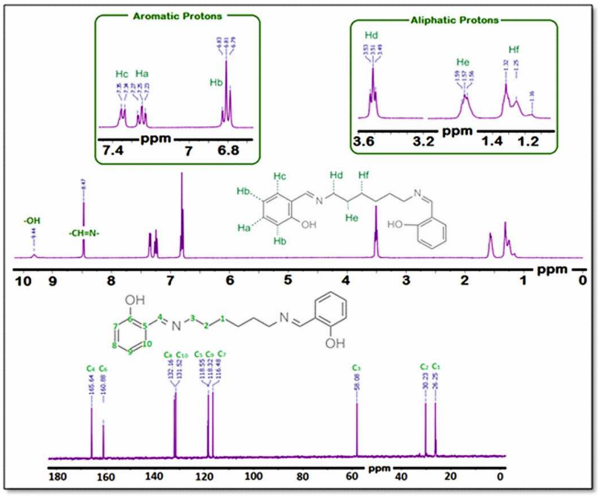

Fig. 5. ^{1}H and ^{13}C NMR spectra of SB-3.

The aromatic and aliphatic proton signals in the ^{1}H NMR spectra of P-3 were observed at about 8.20 ppm to 6.69 ppm and 1.21 ppm to 3.43 ppm. Imine peak was observed at 8.56 ppm, while a small peak of terminal –OH at 10.06 ppm (Fig. 6). According to, the ^{13}C NMR data of P-3, ester carbonyl and imine carbons were observed at 167.16 ppm to 166.09 ppm and 165.64 ppm, respectively [18]. Aliphatic –CH$_3$ signal of P-3 was seen between 28.88 ppm and 58.84 ppm, while the other peaks of ipso aromatic carbons of the P-3: C6 and C16, in the range of 159.96 ppm to 162.23 ppm, respectively. Aromatic carbons were also observed between 165.64 ppm and 116.13 ppm (Fig. 6). NMR analysis results confirmed the formation of poly(azomethine-ester)s and Schiff bases.

The molecular weights distributions of the resulting poly(azomethine-ester)s were determined by gel permeation chromatography (GPC). The number-average molecular weight (M$_\text{n}$), the weight-average molecular weight (M$_\text{w}$) and the polydispersity index (PDI) values of PAEs were calculated in DMF solution by polystyrene standards. The values of M$_\text{n}$, M$_\text{w}$ and PDI values of P-1 were determined as 11550 Da, 15600 Da and 1.35, respectively.

To examine the electronic states of the polyesters, UV-Vis absorption and photoluminescence measurements were performed. Fig. 7 shows UV-Vis spectra of PAEs and SBs, and the obtained results are also summarized in Table 1. According to UV-Vis spectra of SBs, they show three

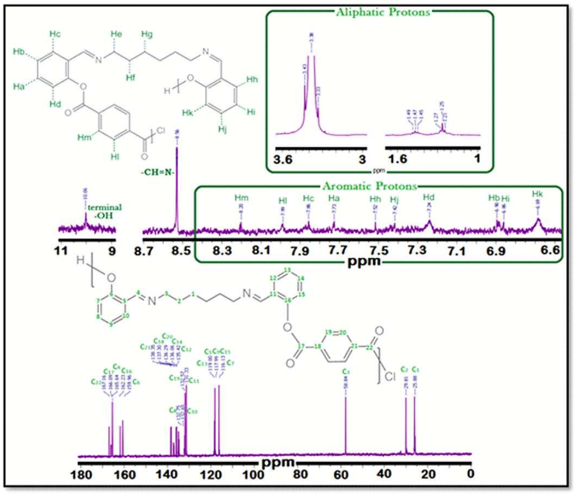

Fig. 6. ^{1}H and ^{13}C NMR spectra of P-3.

absorption bands. The first absorption band is observed between 280 nm and 290 nm due to $\pi \rightarrow \pi^*$ transition of benzene linkage. The second and third absorption bands are observed in the range 290 nm to 350 nm and 351 nm to 455 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of azomethine linkage, respectively [18]. According to UV-Vis spectra of the PAEs, they show four absorption band. The first absorption band is observed between 280 nm and 320 nm due to $\pi \rightarrow \pi^*$ transition of benzene linkage. The second absorption bands are observed between 320 nm and 380 nm to $\pi \rightarrow \pi^*$ transition of ester linkage. The third and fourth absorption bands are observed in the range 380 nm to 500 nm and 500 nm to 710 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of azomethine linkage, respectively [17, 19].

Table 1. Optical band gaps, λ_{max}, λ_{onset} values of the Schiff bases and their poly(azomethine-ester)s.

Compounds	λ_{max} [nm]	λ_{onset} [nm]	$^a(E_g^{opt})$ [eV]
SB-1	257, 315, 412	444	2.80
SB-2	255, 314, 402	448	2.77
SB-3	253, 317, 400	451	2.75
SB-4	254, 313, 404	455	2.73
P-1	320, 405, 548, 687	702	1.76
P-2	301, 347, 415, 599	702	1.76
P-3	280, 342, 480, 680	703	1.77
P-4	280, 347, 487, 682	705	1.76

^{a}Optical band gap

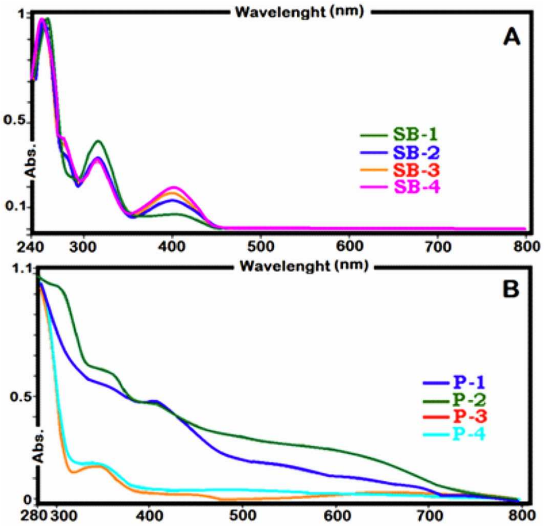

Fig. 7. Absorption spectra of SBs and PAEs.

3.3. Electrochemical properties

The electrochemical behavior of SBs and PAEs was investigated by cyclic voltammetry (CV) with a three-electrode electrochemical cell. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and electrochemical band gap (E'_g) values of PAEs were calculated in order to understand electronic structures of the synthesized materials. The cyclic voltammograms of the Schiff bases and poly(azomethine-ester)s are given in Fig. 8. HOMO, LUMO and E'_g values of the Schiff bases and poly(azomethine-ester)s were calculated by using equation 1, equation 2 and equation 3, respectively, as in literature [17, 19] and the obtained results are summarized in Table 2.

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

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

$$E'_g = E_{LUMO} - E_{HOMO} \tag{3}$$

The onset oxidation potential ($E_{ox.}$) values of the Schiff bases and poly(azomethine-ester)s were

Table 2. Electrochemical data of the Schiff bases and their poly(azomethine-ester)s.

Compounds	$E_{ox.}$ [V]	[a]HOMO [eV]	$E_{red.}$ [V]	[b]LUMO [eV]	[c]E'_g [eV]
SB-1	1.3261	−5.7161	−1.2610	−3.1290	2.59
SB-2	1.3636	−5.7536	−1.2727	−3.1173	2.64
SB-3	1.3513	−5.7413	−1.2604	−3.1296	2.61
SB-4	1.2949	−5.6849	−1.2604	−3.1296	2.56
P-1	1.2698	−5.6598	−1.1729	−3.2171	2.44
P-2	1.0449	−5.4349	−1.3726	−3.0174	2.41
P-3	1.2450	−5.6350	−1.1477	−3.2423	2.39
P-4	1.2821	−5.6721	−1.1102	−3.2798	2.39

[a] Highest occupied molecular orbital

[b] Lowest unoccupied molecular orbital

[c] Electrochemical band gap.

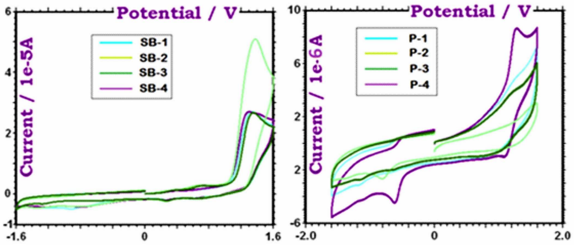

Fig. 8. Cyclic voltammograms of SBs and PAEs (scan rate: −0.2 V/s to 0.2 V/s).

in the range 1.2949 V to 1.3636 V and 1.0449 V to 1.2821 V, respectively. The HOMO energy levels of the Schiff bases and poly(azomethine-ester)s were determined between −5.69 eV to −5.75 eV and −5.44 eV to −5.67 eV, respectively. Similarly, the onset reduction potential ($E_{red.}$) values of the Schiff bases and poly(azomethine-ester)s were between −1.2604 V and −1.2727 V and −1.1102 V and −1.3726 V, respectively. The LUMO energy level of the Schiff bases and poly(azomethine-ester)s were calculated between −3.12 eV and −3.13 eV and −3.02 eV to −3.28 eV, respectively. The electrochemical band gaps (E'_g) of SB-1, SB-2, SB-3 and SB-4 were calculated as 2.59 eV, 2.64 eV, 2.61 eV, and 2.56 eV, respectively. The electrochemical band gap (E'_g) of poly(azomethine-ester)s were calculated according to the literature [20] and equation 3. The values of P-1, P-2, P-3 and P-4 were determined as 2.44 eV, 2.41 eV, 2.39 eV and 2.39 eV, respectively. According to these results, the poly(azomethine-ester)s had quite low-electrochemical band gap values.

3.4. Thermal properties

The thermal properties of PAEs were investigated by using TGA-DTA and DSC techniques to determine the thermal degradation pattern and glass transition temperature. TGA-DTA curves of the poly(azomethine-ester)s are shown in Fig. 9 and thermal analysis results for monomers and poly(azomethine-ester)s are summarized in Table 3.

As can be seen in Fig. 9, P-1, P-2 and P-3 decomposed in three steps whereas P-4 decomposed in two steps. According to TGA-DTA thermograms, the onset temperatures of SB-1, SB-2, SB-3 and SB-4 were found as 150 °C, 138 °C, 112 °C, and 126 °C, respectively. According to TGA curves of the poly(azomethine-ester)s, the onset temperatures of P-1, P-2, P-3 and P-4 were found as 255 °C, 232 °C, 222 °C, and 221 °C, respectively. The onset temperatures (T_{on}) of the poly(azomethine-ester)s were found higher than for Schiff base compounds. The T_{on} values of SB-1 and P-1 were found higher than other Schiff bases and polymers. Thermal stabilities of these compounds are very good, because the aliphatic bridge is the shortest between imine bonding in SB-1 and P-1 compounds. The % chars of P-1, P-2, P-3, and P-4 were found as 13 %, 12 %, 7 %, and 4 %, respectively, at 1000 °C. Both onset

Table 3. Thermal degradation data of water-soluble SBs and PAEs.

Compounds		SB-1	SB-2	SB-3	SB-4	P-1	P-2	P-3	P-4
The first step	$^{a}T_{on}$	150	138	112	126	255	232	222	221
	$^{b}T_{max}$	160	150	138	179	433	263	418	438
	$^{c}T_{end}$	208	218	227	253	495	350	477	540
	$^{d}\%$	47	47	53	45	31	15	35	30
The second step	$^{e}T_{str.}$	208	218	227	253	495	350	477	540
	T_{max}	301	313	318	318	575	552	850	855
	T_{end}	1000	1000	1000	377	725	800	913	1000
	%	35	45	43	32	21	47	48	63
The third step	$T_{str.}$	–	–	–	377	725	800	913	–
	T_{max}	–	–	–	439	949	977	972	–
	T_{end}	–	–	–	1000	1000	1000	1000	–
	%	–	–	–	17	35	26	13	–
$^{f}T_{20}$		145	150	131	162	350	457	460	411
$^{g}T_{50}$		244	247	196	279	714	620	817	858
^{h}Char [%]		15	8	4	6	13	12	4	7

[a] The onset temperature
[b] Maximum weight loss temperature
[c] Thermal degradation finishing temperature
[d] Weight loss at the steps
[e] Thermal degradation starting temperature
[f] 20 % weight loss
[g] 50 % weight loss
[h] Char at 1000 °C

temperature and % char values at 1000 °C of P-1 were higher than for other poly(azomethine-ester)s because P-1 poly(azomethine-ester) had the shortest chain. T_{max} values of SB-1, SB-2, SB-3 and SB-4 and P-1, P-2, P-3 and P-4 were found as 160 °C, 150 °C, 138 °C and 179 °C and 433 °C, 263 °C, 418 °C and 438 °C, respectively. Also, the high values of T_{max} of the poly(azomethine-ester)s are probably related to their molecular weights.

DSC and DMA curves of the poly(azomethine-ester)s are shown in Fig. 10 and Fig. 11, respectively. According to DSC measurements, the glass transition temperatures (T_g) of P-1, P-2, P-3, and P-4 were found as 140 °C, 145 °C, 149 °C, and 155 °C, respectively. According to these results, the highest $T_g$value was found for P-4 poly(azomethine-ester). Also, the ΔCp values of P-1, P-2, P-3, and P-4 were calculated from DSC curves as 0.124 J/g·K, 0.140 J/g·K, 0.148 J/g·K, and 0.150 J/g·K, respectively.

Dynamic mechanical analysis (DMA) of the polymers was carried out using single cantilever bending mode. Storage modulus (E'), loss modulus (E''), and tangent delta (tanδ) were measured as the functions of the sample temperature [21]. DMA analyses of PAEs were carried out as a function of temperature in the range 20 °C to 350 °C. Tanδ curves of the crosslinked PAEs are shown in Fig. 11. The glass transition temperature (T_g) of the poly(azomethine-ester)s were calculated from the maximum value in the tanδ curve. The glass transition temperature (T_g) values of P-1, P-2, P-3, and P-4 were determined as 95 °C, 138 °C, 140 °C, and 145 °C, respectively. The T_g values of the PAEs raised with increasing the chain length of poly(azomethine-ester)s. When compared

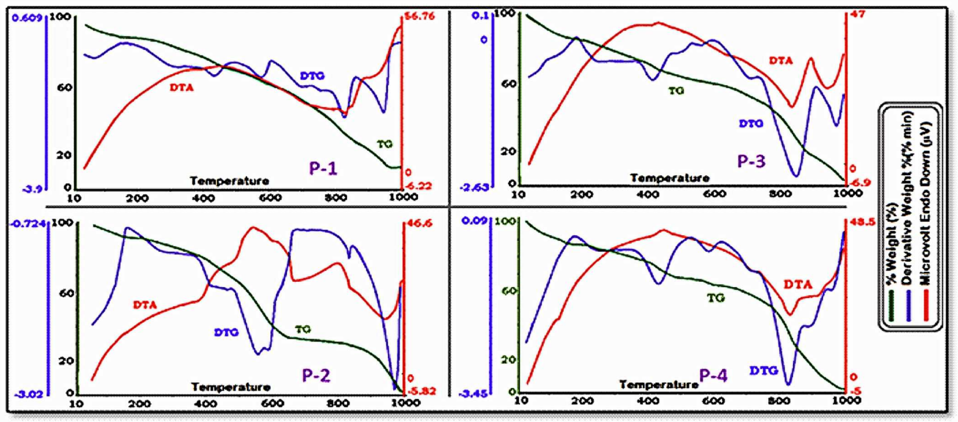

Fig. 9. TG, DTG and DTA curves of the synthesized PAEs.

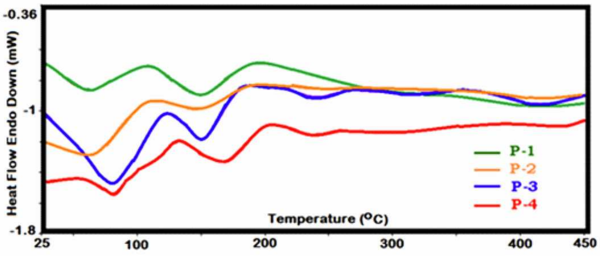

Fig. 10. DSC curves of the synthesized PAEs.

to glass-transition temperature obtained from DMA and DSC, T_g values of poly(azomethine-ester)s are almost the same and the slight differences result from the different nature of these two methods. As it is known, DMA measures the change in the mechanical response of the poly(azomethine-ester) chains.

3.5. Morphological properties

AFM was used in order to evaluate the evolution of topography and the surface roughness of the poly(azomethine-ester)s (Fig. 12). Fig. 13 shows the 3D, topography and phase images of P-1 sample. Root mean square roughness values (Sq) for the polymers P1, P2, P3 and P4 are 6.8 nm, 7.5 nm, 7.3 nm and 6.5 nm, respectively. According to AFM images of the poly(azomethine-ester)s, the surfaces of these poly(azomethine-ester)s seem to be dispersed and inhomogeneous, having partly spherical shapes [22, 23].

FE-SEM technique was used to investigate surface morphology of the polyesters. Fig. 14 shows FE-SEM photographs of P-1, P-2, P-3 and P-4 with different particle sizes. According to FE-SEM images, the polyesters have a highly notched, indented and roughened surface [21, 24]. From the AFM and FE-SEM images it is seen that all the polymers have similar surfaces.

4. Conclusions

Poly(azomethine-ester)s soluble in water were successfully synthesized from Schiff bases synthesis process. The chemical structures of monomers and polymers were confirmed by ^{1}H NMR, ^{13}C NMR and FT-IR, UV-Vis spectroscopy. According to the thermal analysis results, the onset temperature of P-1 was higher than of the other poly(azomethine-ester)s because the chain length of P-1 was shorter than of the other poly(azomethine-ester)s. The results from thermogravimetric analysis revealed that thermal stability of P-1, P-2, P-3 and P-4 species gradually decreased. The inventions described in this article seem to be particularly important from a commercial point of view to meet the strict requirements for several potential applications of such poly(azomethine-ester) species in structural materials. The HOMO, LUMO energy levels and electrochemical band gaps (E'_g) of the monomers and poly(azomethine-ester)s were calculated from

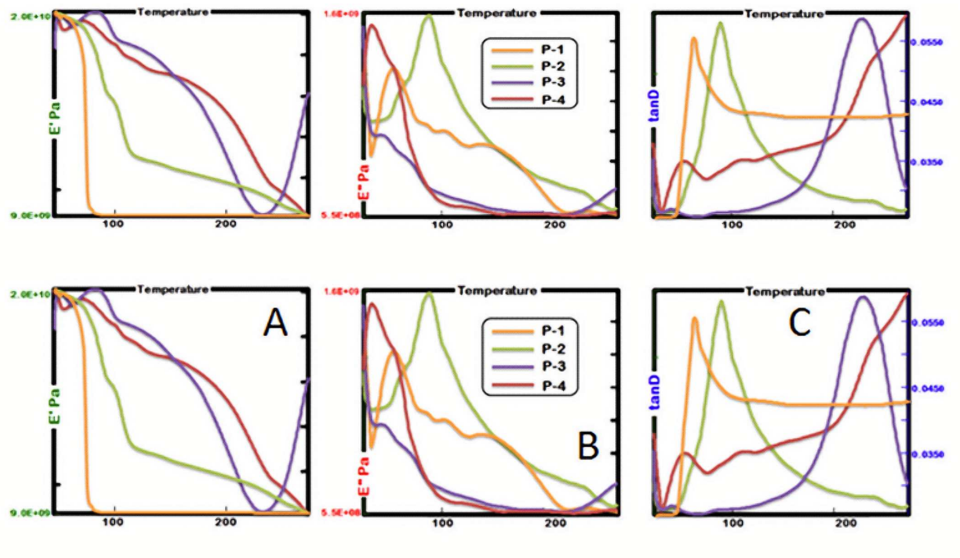

Fig. 11. Graphs of E′ (A), E″ (B) and tanδ (C) moduli versus temperature for PAEs.

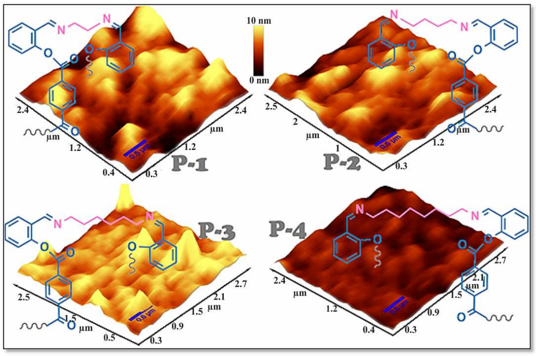

Fig. 12. AFM images of P-1, P-2, P-3 and P-4, respectively.

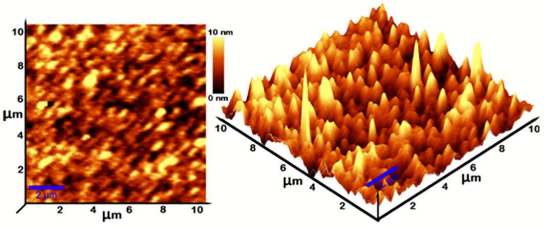

Fig. 13. Surface topography and 3D image of P-1 sample.

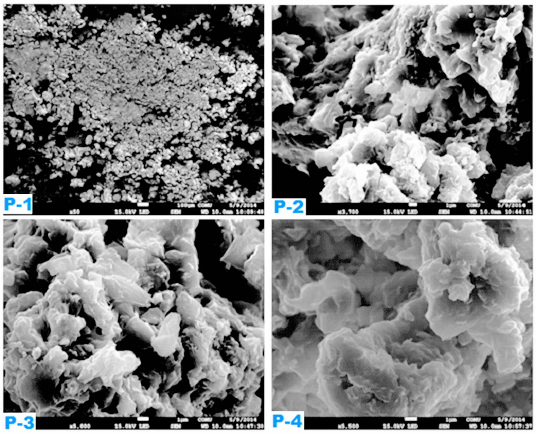

Fig. 14. FE-SEM images of poly(azomethine-ester)s.

oxidation and reduction onset values by cyclic voltammetry measurements. Both electrochemical band gaps (E'_g) and optical band gap (E_g^{opt}) values of poly(azomethine-ester)s were found less than those of their Schiff bases compounds. Therefore, the poly(azomethine-ester)s can be used for optical and photovoltaic applications.

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