

Fluorescence, thermal and electrochemical properties of poly(azomethine-urethane)s containing sulfone group

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Abstract In this study, the new sulfone group-containing poly(azomethine-urethane)s (PAZUs) were synthesized to investigate the effects various diisocyanates on the thermal, fluorescence, electrochemical and morphological properties. The structures of PAZUs have been confirmed by FT-IR, NMR, and SEC analyses. The electrochemical behaviors of the PAZUs were examined by cyclic voltammetry. Optical properties were investigated by UV–Vis and fluorescence measurements. The PAZUs were further characterized by TGA, DSC, SEM, and AFM techniques. TGA analyses results showed considerable increase in the thermal stability of polyurethanes due to the introduction of azomethine bond in the main chain. Consequently, because of the fine thermal properties the obtained materials can be used to produce thermally stable materials.

Keywords Poly(azomethine-urethane)s · Sulfone · Thermal analysis · Cyclic voltammetry · Band gap

Introduction

Among the huge group of organic compounds, Schiff base polymers or polyazomethines (PAZs) attracted considerable interest from researchers due to their good properties such as thermal stability, fiber-forming, paramagnetism, semiconductivity, and resistance to high energy [1–5]. Despite the favorable properties of PAZs, generally they suffer from low solubility. The most employed

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strategy to overcome the limited solubility is the modification of the chain itself, like the incorporation of new functionalities such as flexible segments [e.g., $-\text{O}-$, $-\text{SO}_2-$, $-\text{CH}_2-$, $\text{C}(\text{CF}_3)_2$, and $-\text{NHCO}-$] into the polymer chain. For this aim, various derivatives of PAZs have been reported [6–15].

Polyurethanes (PUs) are an important class of polymer materials with many appealing properties. They have many industrial applications due to the possibility of tailoring their properties through their chemistry. They can be used in several products such as furniture, coatings, adhesives, constructional materials, textiles, paints, elastomers, and synthetic leathers [16–18]. Azomethine derivatives of polyurethanes were reported in literature, and their thermal, semi-crystalline, and optical properties were investigated [19–22]. According to our knowledge, no study has been reported PAZUs containing sulfone unit by now. This class of PAZUs, thus, still needs to be researched with new contributions.

In this study, the Schiff base including sulfone group was synthesized and then converted to its poly(azomethine-urethane) derivatives using different diisocyanates (2,4-toluenediisocyanate, methylene-di-*p*-phenyldiisocyanate, hexamethylenediisocyanate). The synthesized compounds were characterized by using FT-IR, NMR and SEC analyses. Thermal data of polymers were obtained by TGA and DSC techniques, respectively. The electrochemical properties of the PAZUs were examined by means of cyclic voltammetry (CV). Also, fluorescence properties of the PAZUs were investigated in solution forms. The effect of concentration on fluorescence intensity was examined.

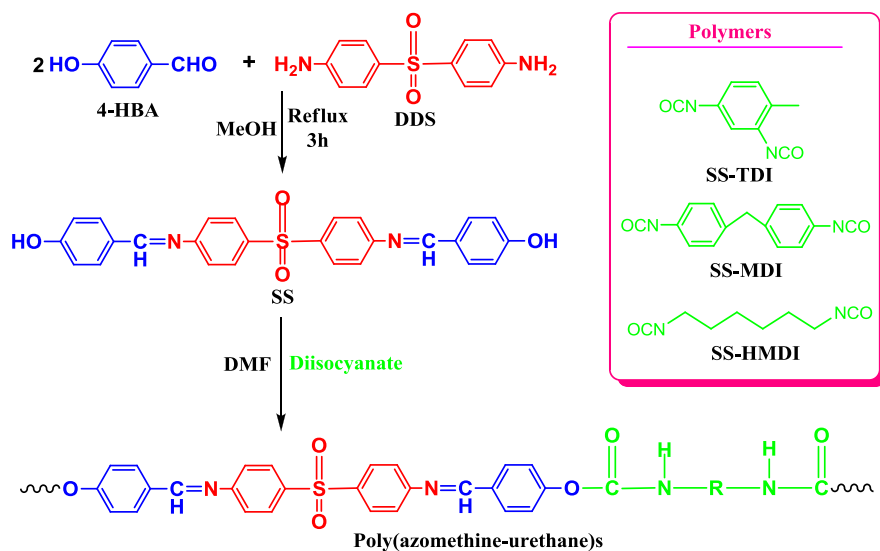
Experimental

Materials

2,4-Toluenediisocyanate (TDI), methylene-di-*p*-phenyl-diisocyanate (MDI), hexamethylene diisocyanate (HDI) were supplied from Aldrich Chemical Co (USA). 4,4'-Diaminodiphenyl sulfone (DDS), 4-hydroxybenzaldehyde (4-HBA), dimethylformamide (DMF), dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), methanol (MeOH), acetonitrile, acetone, and n-hexane were supplied from Merck Chemical Co. (Germany). All chemicals were used as received.

Preparation of the SS

Sulfone group-containing Schiff base abbreviated as SS was prepared by the condensation reaction of DDS (0.005 mol) with 4-HBA (0.010 mol) in 50 mL of methanol, by boiling the mixture under reflux for 3 h (Scheme 1). The obtained SS was filtered, recrystallized from acetonitrile and dried in vacuum desiccators [23]. The yield of SS was found as 85 %.



Scheme 1 Synthesis of Schiff base and poly(azomethine-urethane)s

Syntheses of the PAZUs

Poly(azomethine-urethane)s were synthesized by the condensation reaction of the preformed Schiff bases with diisocyanates (TDI, MDI, and HMDI). Polymers were also abbreviated as SS-TDI, SS-MDI, and SS-HMDI. Synthesis procedure of the PAZUs is as follows: SS (0.01 mol) and dry DMF (30 mL) were charged into a 250-mL round-bottom flask and heated (60 °C) with stirring under argon. An amount of 0.01 mol of diisocyanates (TDI, MDI, or HMDI), dissolved in DMF (30 mL), was added to this mixture. The temperature increased at 110 °C and the reaction mixture was stirred under nitrogen for 5 h and left overnight for the completion of the reaction. The obtained PAZUs were washed with methanol (25 mL) and THF (25 mL) to remove the unreacted components [24, 25]. The polymers were dried in a vacuum oven at 70 °C for 36 h. The yields of SS-TDI, SS-MDI, and SS-HMDI were found as 87, 83, 88, and 88 %, respectively. All the synthesis procedures are summarized in Scheme 1.

Characterization techniques

The IR and UV–Vis spectra were recorded by PerkinElmer FT-IR Spectrum one and Analytikjena Specord 210 Plus, respectively. FT-IR spectra of the prepared thin films were obtained on a KBr pellet PerkinElmer FT-IR Spectrum one. ^1H and ^{13}C -NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were also obtained using deuterated DMSO- d_6 as a solvent at room temperature. Tetramethylsilane (TMS) was used as an internal standard. Thermal characterization was performed by PerkinElmer Diamond Thermal Analysis system.

Thermogravimetric analysis (TGA) was carried out between 10 and 1000 °C (in N₂, rate 10 °C/min). DSC measurements were performed using PerkinElmer Pyris Sapphire within the temperatures of 20–450 °C (in N₂, rate 10 °C/min). The molecular weights of the PAZUs were determined by size-exclusion chromatography (SEC) techniques of Shimadzu Co. For SEC investigations, DMF (0.4 mL/min) as solvent and polystyrene standards were used. A refractive index detector (RID) was used to analyze the PAZUs at room temperature. Scanning electron microscopy (SEM) photographs of the PAZUs were recorded by means of a Philips XL-305 FEG SEM instrument. Before the measurements, PAZUs were dried in a vacuum oven at 75 °C for 24 h to remove the residual moisture. Gold–palladium-coated thin films of the PAZUs were used for SEM analyses. Topography and 3D images of the polymeric films were determined using atomic force microscopy (AFM) Alpha 300 A (WITec, Ulm, Germany). Specified surface areas of polymers are scanned angularly by non-contact mod cantilever (AC, 42 N/m, 285 kHz).

Optical and electrochemical analyses

Ultraviolet–visible (UV–Vis) analyses of PAZUs were made by Analytikjena Specord 210 Plus. The absorption measurements were carried out using DMSO as a solvent at room temperature. All electrochemical analyses were performed using a CHI 660 C Electrochemical Analyzer (CH Instruments, Texas, USA) at a potential scan rate of 20 mV/s. The measurements were carried out in a dry box filled with N₂ at 25 °C. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc⁺) couple. The half-wave potential ($E^{1/2}$) of (Fc/Fc⁺) measured in acetonitrile solution of 0.1 M tetrabutylammoniumhexafluorophosphate and was 0.39 V with respect to Ag wire. The voltammetric analyses were performed in DMSO/acetonitrile mixture (v/v: 2/3) for and the PAZUs. The HOMO/LUMO energy levels and electrochemical band gaps (E'_g) were calculated from oxidation and reduction onset values [23].

Fluorescence measurements

Fluorescence measurements were performed using A Shimadzu RF-5301PC spectrophotometer. Emission and excitation measurements of the PAZUs were made in DMF solutions. The effect of concentration on fluorescence intensity was examined. The slit width was set at 5 nm.

Results and discussion

Solubilities and structures of the compounds

The solubilities of the compounds at different solvents are listed in Table 1, indicating that all the synthesized compounds are soluble in highly polar solvents such as DMSO, DMF, and NMP, while they are insoluble in methanol, acetone, and n-hexane. Additionally, the synthesized diol monomer is soluble in THF. PAZUs

Table 1 Solubility test results of the synthesized compounds

Compounds	DMSO	DMF	NMP	THF	Acetone	MeOH	Hexane
SS	+	+	+	+	–	–	–
SS-TDI	+	+	+	–	–	–	–
SS-MDI	+	+	+	–	–	–	–
SS-HMDI	+	+	+	–	–	–	–

+ soluble, ± partially soluble, – insoluble

have higher molecular weights than the synthesized monomer (SS). The molecular weights of polymers are important parameters for solubility in organic solvents. As molecular weight increases, the solubility of a polymer decreases. This same behavior is also observed as hydrogen-bonding degree increases. The strong hydrogen in the polymer chains inhibits the interactions between polymer chains and solvent molecules. As a result, because polymer chains could not be transported into solution, their solubilities are limited in this medium [18, 19].

FT-IR spectra of the all synthesized compounds are listed in Table 2. As seen in Table 2, characteristic aldehyde ($-\text{CH}=\text{O}$) and hydroxyl ($-\text{OH}$) peaks of 4-dihydroxy benzaldehyde (4-HBA) are observed at 1688 and 3024 cm^{-1} , respectively. At the FT-IR spectral data of DDS, $-\text{NH}_2$ peaks is observed at between 3393 and 3371 cm^{-1} . The structure of the synthesized SS is confirmed by growing imine ($-\text{CH}=\text{N}$) peak with disappearing of the $-\text{NH}_2$ peak at PDA and the carbonyl ($-\text{C}=\text{O}$) peak of 4-HBA used in the condensation reaction. At the FT-IR spectral data of SS, azomethine ($-\text{CH}=\text{N}$) and hydroxyl ($-\text{OH}$) peaks are observed at 1653 and 3371 cm^{-1} , respectively. According to FT-IR spectral data of TDI, MDI, and HMDI, characteristic diisocyanate $-\text{N}=\text{C}=\text{O}$ peaks are observed at 2230, 2265, and 2250 cm^{-1} , respectively, which agrees with the literature [24, 26]. According to Table 2, hydroxyl ($-\text{OH}$) group at SS, $-\text{N}=\text{C}=\text{O}$ stretch vibrations of the diisocyanates (TDI, MDI, and HMDI) disappear due to urethane formation. Moreover, in the FT-IR spectral data of SS-TDI, SS-MDI, and SS-HMDI, the new peaks appear at 3305–3349 and 1706–1715 cm^{-1} , respectively, which could be attributed to urethane $-\text{NH}$ and carbonyl ($-\text{C}=\text{O}$) stretch vibrations, respectively. Azomethine linkages ($-\text{CH}=\text{N}-$) in the structures of the PAZUs are observed between 1655 and 1660 cm^{-1} . Some additional peaks including aromatic $-\text{CH}$ (3010–3063 cm^{-1}) stretch and aliphatic $-\text{CH}$ (2857–2952 cm^{-1}) vibration are also shown in Table 2. The analysis results clearly verify the formation of PAZUs [19, 27, 28].

^{13}C -NMR spectrum of SS is shown in Fig. 1. According to the spectrum, imine ($\text{CH}=\text{N}$) carbon (C5) is observed at 163.38 ppm. Also, aromatic carbons of SS are observed in the range of 113.3–162.8 ppm. ^1H -NMR spectra of SS and PAZUs are also shown in Figs. 2 and 3. According to the ^1H -NMR spectra of SS, hydroxyl ($-\text{OH}$) and imine ($-\text{CH}=\text{N}$) protons are observed at 9.24 ppm and 8.42 ppm, respectively. Aromatic protons of SS are observed between 6.57 and 7.776 ppm. According to Figs. 2 and 3, urethane ($-\text{NHCO}$) protons of SS-TDI, SS-MDI and SS-HMDI are observed at 10.08, 10.08, and 10.58 ppm, respectively. Also, imine

Table 2 FT-IR spectral data of synthesized compounds

Compounds	Urethane-NH	Urethane-C=O	Imine-CH=N	Aromatic-CH	Aliphatic-CH	Aldehyde-C=O	Isocyanate-N=C=O	-OH	-NH ₂
DDS	-	-	-	3063, 3041	-	-	-	-	3393, 3371
4-HBA	-	-	-	3010	-	1688	-	3024	-
TDI	-	-	-	3039	2952	-	2230	-	-
MDI	-	-	-	3031	2924	-	2265	-	-
HMDI	-	-	-	-	2940, 2861	-	2250	-	-
SS	-	-	1653	3059, 3024	-	-	-	3371	-
SS-TDI	3349	1715	1660	3037	2923	-	-	-	-
SS-MDI	3305	1706	1658	3028	2901	-	-	-	-
SS-HMDI	3305	1708	1655	3028	2923, 2857	-	-	-	-

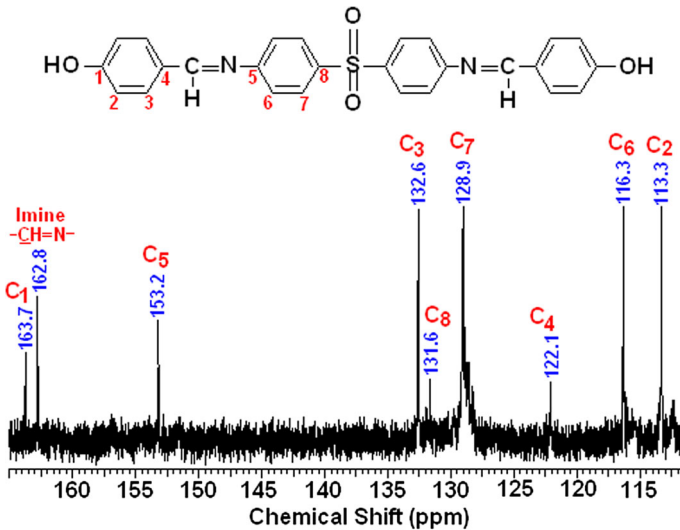


Fig. 1 ^{13}C -NMR spectra of SS

protons of SS-TDI, SS-MDI and SS-HMDI are observed at 8.42, 8.51, and 9.77 ppm. Aromatic ring protons are observed between 6.55 and 7.93 ppm for all synthesized polymers. Methyl ($-\text{CH}_3$) protons of SS-TDI and aliphatic $-\text{CH}_2-$ protons of SS-MDI are observed 2.17 and 3.78 ppm, respectively. Also, aliphatic protons of SS-HMDI are observed between 1.22 and 3.04 ppm. NMR analyses results indicate the formation of polymers [24, 28].

Size-exclusion chromatography

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) values of SS-TDI, SS-MDI, and SS-HMDI were determined by SEC technique using RI detector. According to the SEC results, the M_n values of SS-TDI, SS-MDI, and SS-HMDI were calculated as 7140, 7200, and 6600 g mol^{-1} , respectively. The M_w values of SS-TDI, SS-MDI, and SS-HMDI were calculated as 8500, 8600 and 7000 g mol^{-1} , respectively. Also, PDI values of SS-TDI, SS-MDI, and SS-HMDI were determined as 1.191, 1.194 and 1.061, respectively. According to the total values of average molecular weight, SS-TDI, SS-MDI, and SS-HMDI have nearly 10–12, 9–11 and 9–10 repeated units.

Fluorescence properties

Fluorescence measurements of the PAZUs are carried out using DMF solutions at different concentrations [5]. The effects of concentration on the fluorescence intensity were determined. The obtained spectral data of the PAZUs are seen in Figs. 4, 5 and 6. The fluorescence analysis results are also summarized in Table 3. Figures also show the concentration–fluorescence intensity relationships of the

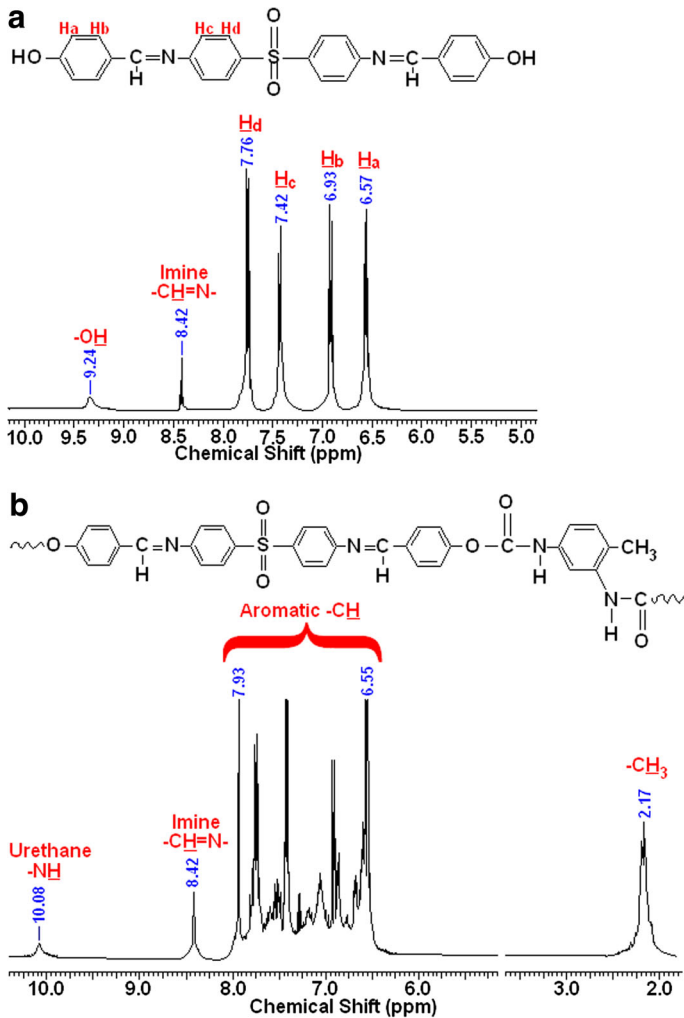


Fig. 2 ¹H-NMR spectra of SS (a) and SS-TDI (b)

polymers. As seen in Figs. 4, 5, 6 and Table 3, the optimum concentration to obtain maximum emission–excitation intensities change between 10 and 0.3 mg/mL. The results show that the order of the fluorescence intensities of the PAZUs is different and is as follows: SS-MDI > SS-TDI > SS-HMDI. According to Table 3, SS-MDI has highest fluorescence intensity. These results clearly point out that the emission intensity of aliphatic and aromatic PAZUs was not the same, which confirms that the fluorescence intensity is influenced by insertion of phenyl and alkyl groups in the polymer backbone [29].

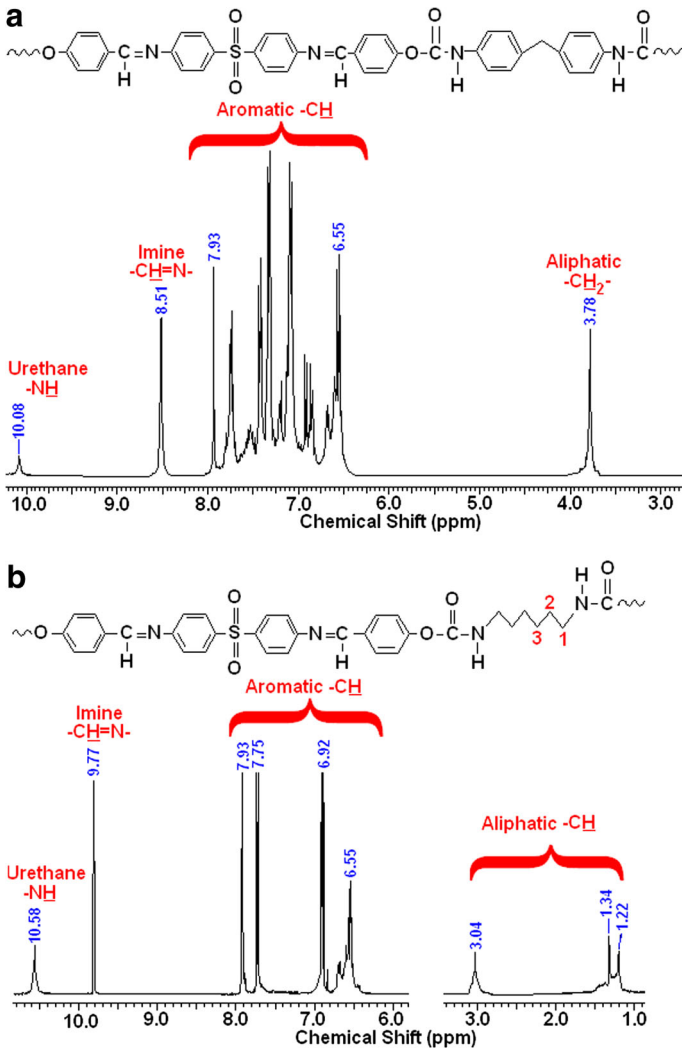


Fig. 3 ¹H-NMR spectra of SS-MDI (a) and SS-HMDI (b)

Optical and electrochemical properties

UV–Vis spectra of the synthesized compounds are comparatively given in Fig. 7. According to Fig. 7, the absorption peaks of poly(azomethine-urethane)s appear between 280 and 290 nm, due to the urethane group in the structure. Also, π – π^* transition peaks of the compounds were observed between 320 and 334 nm, respectively, due to azomethine linkage in the structure [26].

The cyclic voltammograms of the PAZUs are seen in Fig. 8 and the results are listed in Table 4. From the cyclic voltammetric studies, the onset potentials for oxidation of PAZUs were observed to be 1.560, 1.539, and 0.834 V, while reduction

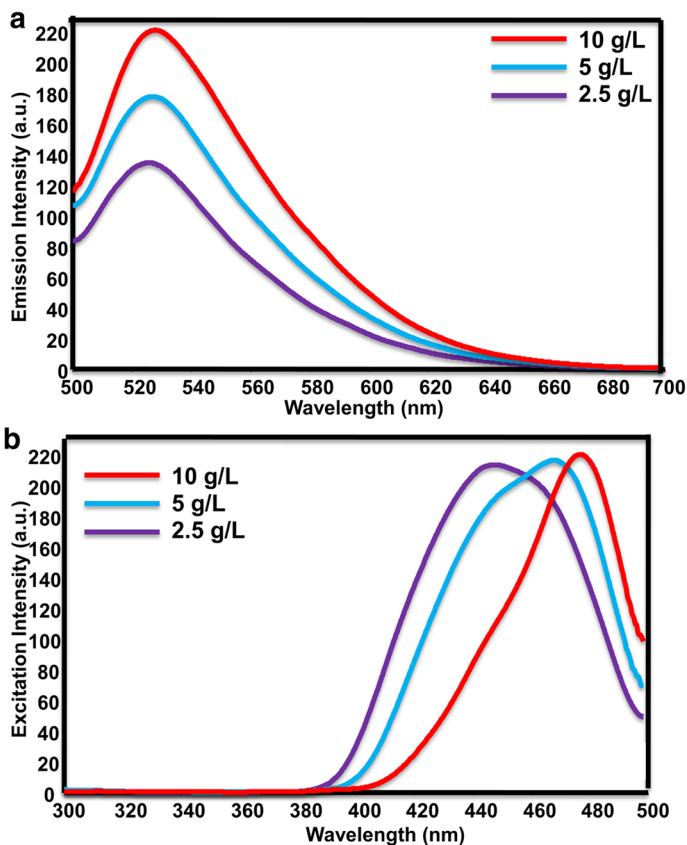


Fig. 4 Emission (a) and excitation (b) spectra of SS-TDI in DMF

potentials were -0.986 , -0.144 , and -0.896 V for SS-TDI, SS-MDI, and SS-HMDI, respectively. The HOMO–LUMO energy levels and electrochemical energy gaps (E'_g) were calculated from oxidation and reduction onset values as in the literature [23]. According to Table 4, the HOMO energy levels (E_{HOMO}) of SS-TDI, SS-MDI, and SS-HMDI were calculated as -5.95 , -5.93 , and -5.22 , respectively. Also, the LUMO energy levels (E_{LUMO}) of SS-TDI, SS-MDI, and SS-HMDI were calculated as -3.40 , -4.25 , and -3.49 eV, respectively. Additionally, the electrochemical band gap (E'_g) values of SS-TDI, SS-MDI, and SS-HMDI were calculated 2.55, 1.68, and 1.73 eV, respectively. According to these calculated values, SS-MDI, and SS-HMDI can be promising candidate for use in polymer-based solar cells [26, 30].

Thermal properties

Thermal properties of the sulfone group-containing PAZUs are evaluated by TGA technique. TG–DTG curves of the PAZUs are shown in Fig. 9, and the obtained

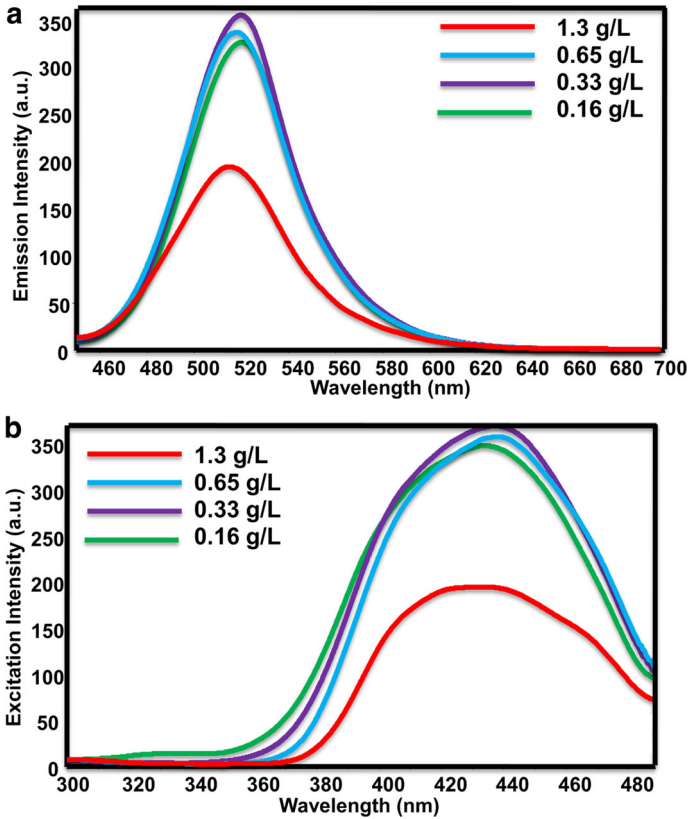


Fig. 5 Emission (a) and excitation (b) spectra of SS-MDI in DMF

results are also listed in Table 5. According to the DTG curves, the PAZUs thermally degrade in three steps. Nearly, 3 % weight losses between 20 and 120 °C are attributed to losses of moisture, adsorbed solvent [31]. Table 5 indicates that SS-HMDI has the highest onset temperature (T_{on}). All the synthesized polymers have quite high T_{on} above 160 °C. T_{on} and carbene residue are 164 °C and 36 % for SS-TDI; 168 °C and 39 % for SS-MDI; 183 °C and 28 % for SS-HMDI, respectively. The results showed that at lower temperature during the TGA experiments, the SS-HMDI prepared from the aliphatic diisocyanate was more stable than the aromatic diisocyanate (TDI and MDI) containing PAZUs, whereas at higher temperature the stability order followed the reverse trend. The aromatic rings, with 2,4-toluenediisocyanate and methylene-di-*p*-phenyldiisocyanate groups formed rigid chains, which makes intermolecular interactions difficult and thereby reduces thermal resistance at the beginning of the process, but at high temperatures aromatic diisocyanate-based PAZUs showed improved stability [32, 33]. These results are consistent with those reported previously [34, 35]. In comparison to typical polyurethanes, the PAZUs showed very good thermal stability.

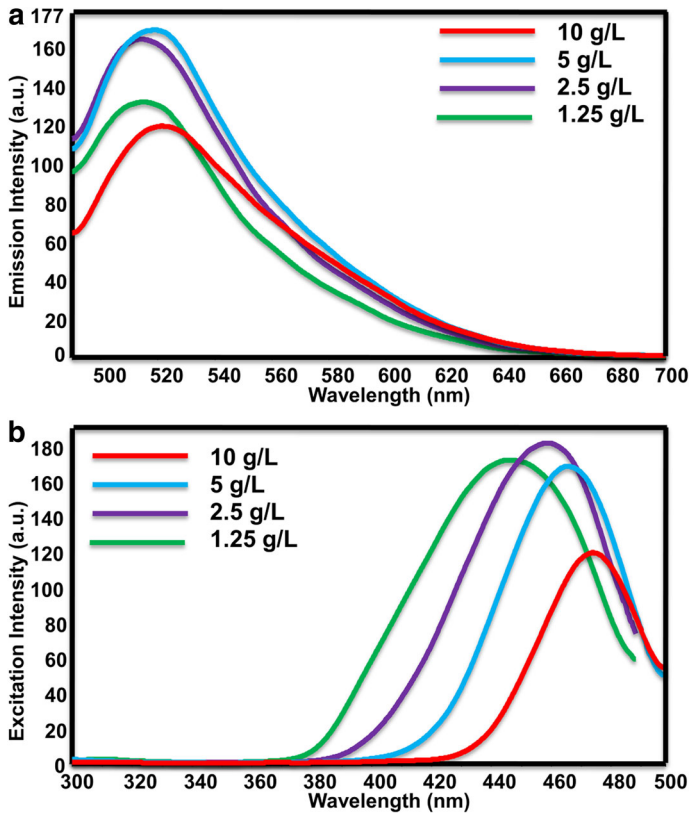


Fig. 6 Emission (a) and excitation (b) spectra of SS-HMDI in DMF

Table 3 Fluorescence spectral data of the PAZUs

Compounds	Conc. (mg/mL)	$\lambda_{\text{Ex}}^{\text{a}}$	$\lambda_{\text{Em}}^{\text{b}}$	$\lambda_{\text{max(Ex)}}^{\text{c}}$	$\lambda_{\text{max(Em)}}^{\text{d}}$	I_{Ex}^{e}	I_{Em}^{f}	$\Delta\lambda_{\text{ST}}^{\text{g}}$
SS-TDI	10	480	530	477	528	220	221	51
SS-MDI	0.3	430	520	437	520	369	353	83
SS-HMDI	5	470	500	465	519	168	168	54

^a Excitation wavelength for emission

^b Emission wavelength for excitation

^c Maximum excitation wavelength

^d Maximum emission wavelength

^e Maximum excitation intensity

^f Maximum emission intensity

^g Stoke's shift

DSC curves of the PAZUs are shown in Fig. 10 and analysis results are also listed in Table 5. According to the DSC curves, the glass transition temperatures (T_g) are determined as 127, 133, and 148 °C for SS-TDI, SS-MDI, and SS-HMDI,

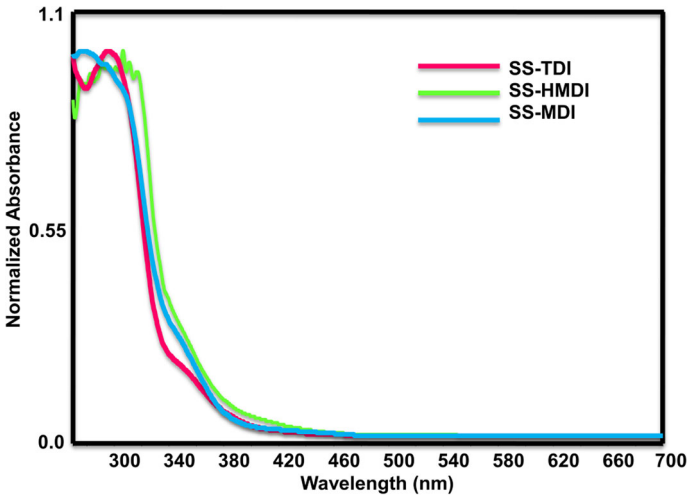


Fig. 7 Absorption spectra of the PAZUs

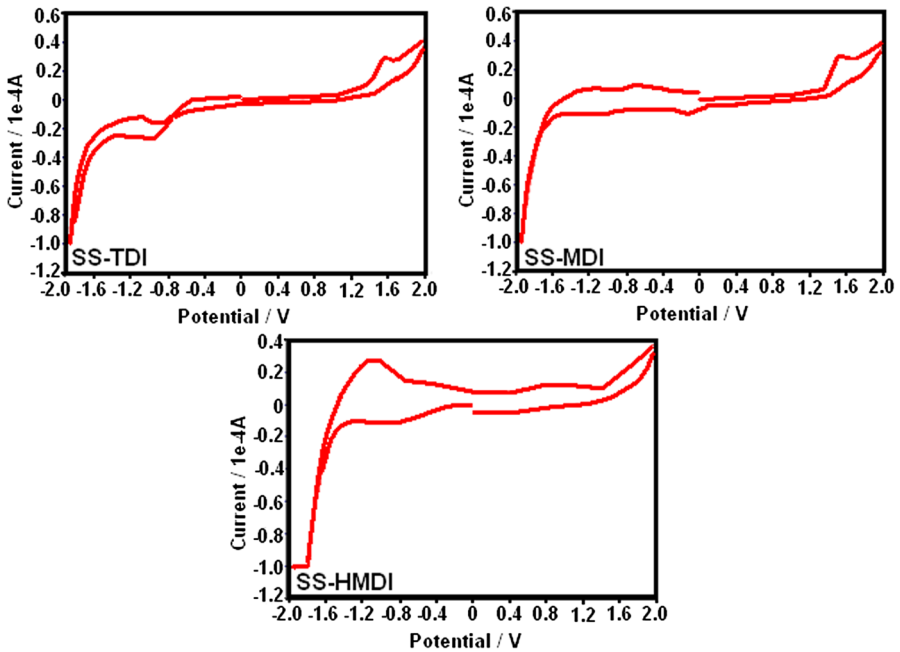


Fig. 8 CVs of the synthesized PAZUs

respectively. The results showed that SS-HMDI has the highest glass transition temperatures (T_g). This is a result of the rigidity of the aromatic diisocyanates (TDI and MDI), which limits the possibility of achieving physical cross-linking points

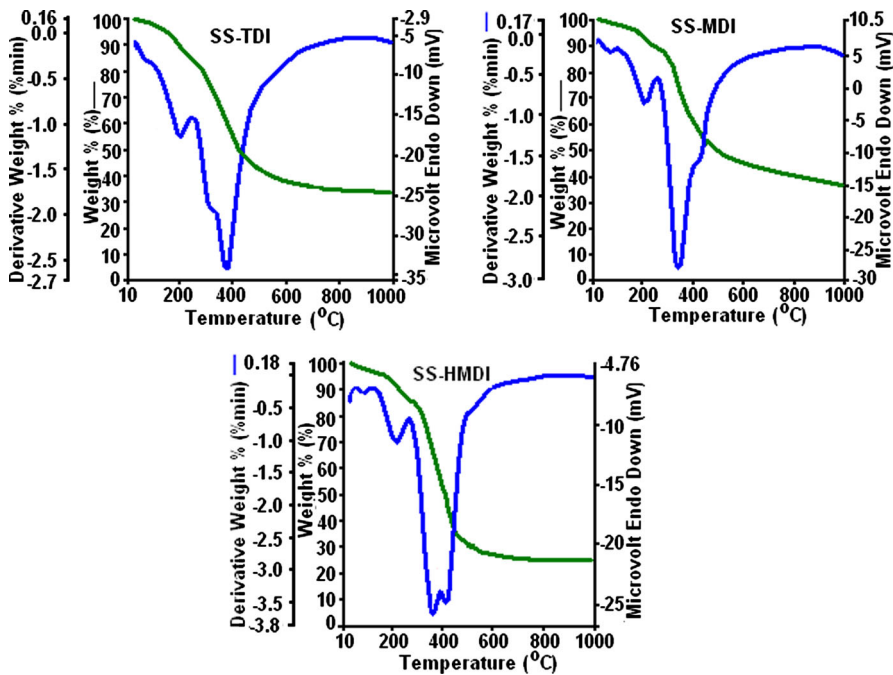
Table 4 Electronic structure parameters of the PAZUs

Compounds	HOMO (eV) ^a	LUMO (eV) ^b	E_g^c (eV)
SS-TDI	5.95	3.40	2.55
SS-MDI	-5.93	-4.25	1.68
SS-HMDI	-5.22	-3.49	1.73

^a Highest occupied molecular orbital

^b Lowest unoccupied molecular orbital

^c Electrochemical band gap

**Fig. 9** TG and DTG curves of the PAZUs

and decreases the cohesion between molecular chains [36]. Also, the changes of the specific heats (ΔC_p) during the glass transitions are calculated from DSC measurements. The ΔC_p values of SS-TDI, SS-MDI, and SS-HMDI are calculated as 0.256, 0.351, and 0.122 J/g °C, respectively. The peaks until 110 °C could be attributed to losses of moisture or absorbed solvent [37].

Scanning electron microscopy

The morphological properties of powder forms of the PAZUs are investigated by SEM technique. SEM images of SS-TDI, SS-MDI, and SS-HMDI are given in

Table 5 Thermal analysis results of the PAZUs

Compounds	T_{on} (°C) ^a	W_{max} T (°C) ^b	20 % weight losses	50 % weight losses	% char at 1000 °C	DSC	
						T_g (°C) ^c	ΔC_p (J/g °C) ^d
SS-TDI	164	204, 320, 376	303	449	36	127	0.256
SS-MDI	168	212, 343, 413	337	534	39	133	0.351
SS-HMDI	183	221, 365, 417	334	418	28	148	0.122

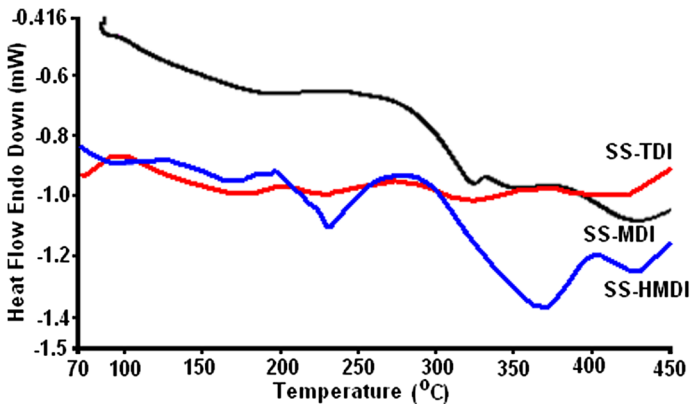
^a The onset temperature^b Maximum weight temperature^c Glass transition temperature^d Change of specific heat during glass transition**Fig. 10** DSC curves of the PAZUs

Fig. 11. As seen in Fig. 11a, b, SS-TDI has porous structure. Figure 11c, d has smooth structure. As seen in Fig. 11e, f, SS-HMDI has sharp particle structure.

Atomic force microscopy

The AFM topography and 3D images of SS-TDI and SS-HMDI are given in Fig. 12. The films were prepared by spin-coating technique onto glasses THF solutions of polymers. After the deposition of the polymeric layer on glass plates, the samples were thermally annealed for 2 h at 60 °C under vacuum. The images were obtained using an AFM in a non-contact (tapping) mode. Here, the compact particle structures of SS-TDI and SS-HMDI are seen to be partly spherical shapes, dispersed and nonhomogeneous. The base particles look like ellipsoid shape, as shown in Fig. 12b.

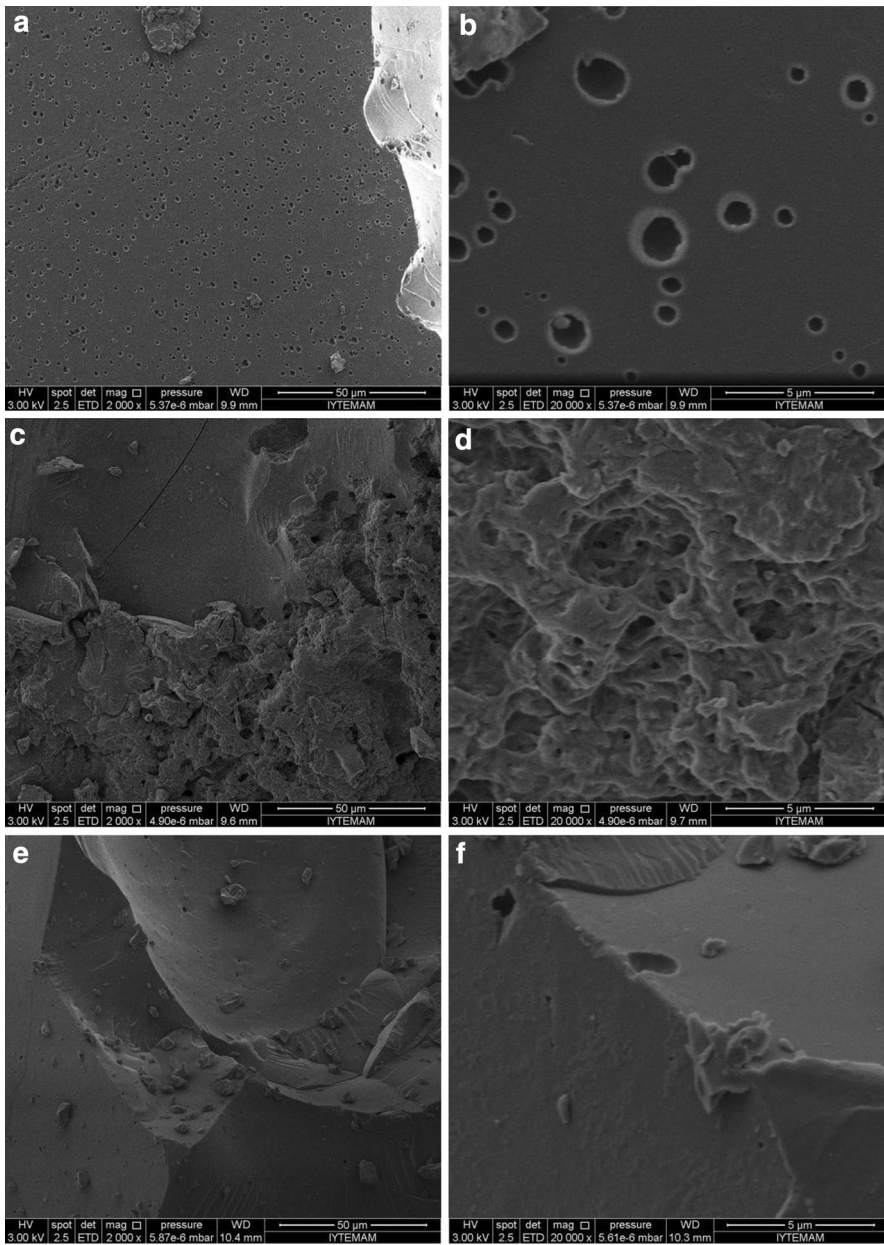


Fig. 11 SEM photographs of SS-HMDI (a, b), SS-MDI (c, d) and SS-TDI (e, f)

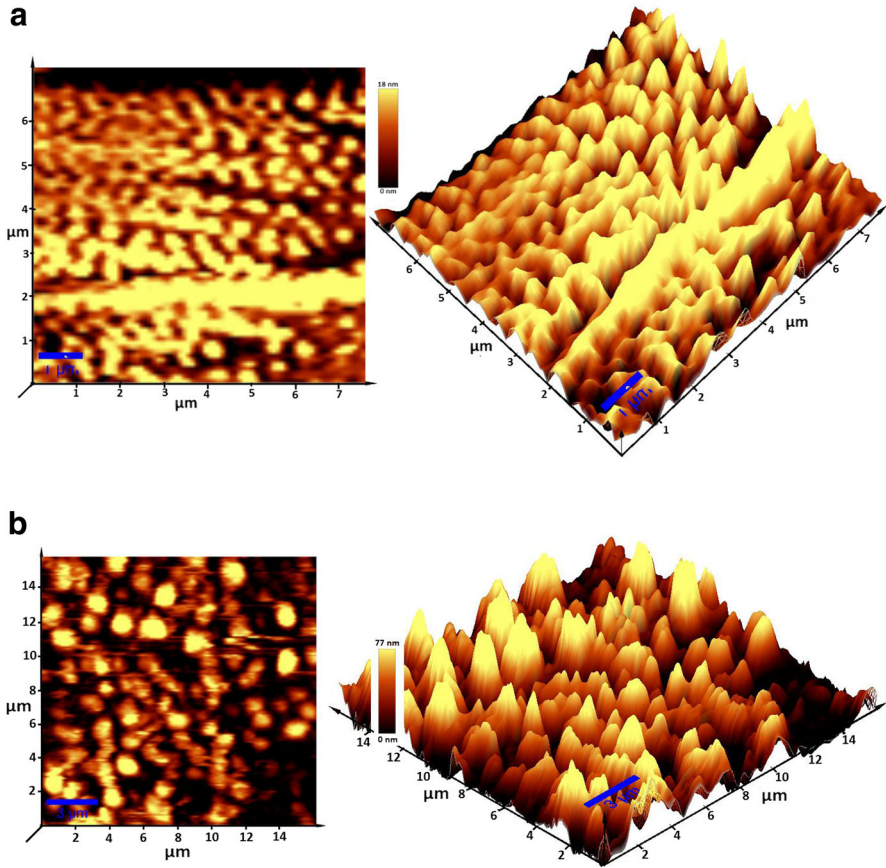


Fig. 12 AFM image of the SS-TDI (a) and SS-HMDI (b)

Conclusion

A novel sulfone group-containing low band gap poly(azomethine-urethane)s were synthesized by polycondensation reaction. The synthesized polymers were characterized by solubility tests, FT-IR, NMR, and SEC techniques. Solubility tests demonstrated that the synthesized polymers are soluble in DMSO, DMF, and NMP. Fluorescence properties of the synthesized PAZUs were examined in DMF solution. Fluorescence analysis results indicated that SS-MDI has higher excitation and emission intensity than the other polymers. According to the electrochemical band gap values, PAZUs have between 1.73 and 2.55 electrochemical band gap values. The calculated band gaps are suitable to make the synthesized PAZUs highly promising for photovoltaic applications. Thermal degradation behaviors of the PAZUs were also examined. They have onset temperature between 164 and 183 °C. TGA results showed that the incorporation of azomethine segments into the polyurethane chain improved its thermal stability. The fine fluorescence and thermal

characteristics of the obtained PAZUs could make these polymers appropriate for thermally stable light-emitting materials.

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References

1. Adams R, Bullock JE, Wilson WC (1923) Contribution to the structure of benzidine. *J Am Chem Soc* 45:521–527
2. Kaya İ, Bora E, Aydın A (2014) Synthesis and characterization of Schiff base derivative with pyrrole ring and electrochromic applications of its oligomer. *Prog Org Coat* 77:463–472
3. Grigoras M, Catanescu CO, Simionescu CI (2001) Poly(azomethine)s. *Rev Roum Chim* 46:927–939
4. Grigoras M, Catanescu CO (2004) Imine oligomers and polymers. *J Macromol Sci Part C Polym Rev* 44:131–173
5. Kaya İ, Avcı A, Gültekin Ö (2012) Syntheses and characterization of poly(iminophenol)s derived from 4-bromobenzaldehyde: thermal, optical, electrochemical, and fluorescent properties. *Chin J Polym Sci* 30:796–807
6. Kaya İ, Temizkan K, Aydın A (2013) Synthesis and characterization of ether bridged polymers and their fluorescent, thermal, conductivity, optical and electrochemical properties. *J Electroanal Chem* 708:54–61
7. Aly KI, Abbady MA, Mahgoub SA, Hussein MA (2007) Liquid crystalline polymers IX Main chain thermotropic poly(azomethine-ether)s containing thiazole moiety linked with polymethylene spacers. *Express Polym Lett* 1:197–207
8. Marin L, Cozan V, Bruma M, Grigoras VC (2006) Synthesis and thermal behaviour of new poly(azomethine-ether). *Eur Polym J* 42:1173–1182
9. Zhang Q, Li S, Li W, Zhang S (2007) Synthesis and properties of novel organosoluble polyimides derived from 1,4-bis[4-(3,4-dicarboxylphenoxy)]tritypcenedianhydride and various aromatic diamines. *Polymer* 48:6246–6253
10. Mehdipour-Atei S, Sarrafi Y, Hatami M (2004) Novel thermally stable polyimides based on flexible diamine: synthesis, characterization, and properties. *Eur Polym J* 40:2009–2015
11. Kaya İ, Avcı A, Kolcu F, Çulhaoğlu S (2014) Synthesis, characterization, optical, and electrochemical properties of thermal stable novel poly(azomethine-ether)s. *Des Monomers Polym* 17:481–490
12. Tanaka H, Shibahara Y, Sato T, Ota T (1993) Preparation and thermal behavior of spin polymers and their precursors based on azomethine mesogens. *Eur Polym J* 29:1525–1530
13. Sun SJ, Chang TC, Li CH (1993) Preparation and thermal behavior of spin polymers and their precursors based on azomethine mesogens. *Eur Polym J* 29:951–955
14. Li CH, Chang TC (1991) Thermotropic liquid crystalline polymer. III. Synthesis and properties of poly(amide-azomethine-ester). *J Polym Sci Polym Chem* 29:361–367
15. Marin L, Cozan V, Bruma M (2006) Comparative study of new thermotropic polyazomethines. *Polym Adv Technol* 17:664–672
16. Arukula R, Thota AR, Rao CRK, Narayan R, Sreedhar B (2014) Novel electrically conducting polyurethanes with oligoanilines: synthesis, conductivity, and electrochemical properties. *J Appl Polym Sci* 131(40794):1–13
17. Jaruchattada J, Fuongfuchat A, Pattamaprom C (2012) Rheological investigation of cure kinetics and adhesive strength of polyurethane acrylate adhesive. *J Appl Polym Sci* 123:2344–2350
18. Suhas DP, Jeong HM, Aminabhavi TM, Raghu AV (2014) Preparation and characterization of novel polyurethanes containing 4,4'-(oxy-1,4-diphenyl bis(nitromethylidene))diphenol Schiff base diol. *Polym Eng Sci* 54:24–32
19. Kaya İ, Avcı A (2012) Synthesis, characterization, and thermal stability of novel poly(azomethine-urethane)s and polyphenol derivatives derived from 2,4-dihydroxy benzaldehyde and toluene-2,4-diisocyanate. *Mater Chem Phys* 133:269–277
20. Stoica G, Stanciu A, Cozan V, Stoleriu A, Timpu D (1998) New aromatic poly(azomethine-urethane)s. *J Macromol Sci A* 35:539–546

21. Buruiana EC, Olaru M, Simionescu BC (2002) Synthesis and properties of some new polyazomethine-urethanes. *Eur Polym J* 38:1079–1086
22. Reddy KR, Raghu AV, Jeong HM (2008) Synthesis and characterization of novel polyurethanes based on 4,4'-(1,4-phenylenebis[methylidenedinitrilo]) diphenol. *Polym Bull* 60:609–616
23. Kaya İ, Bilici A, Saçak M (2009) Study on synthesis, characterization, thermal stability and conductivity properties of a new conjugated oligoazomethine and some of its metal complexes. *J Inorg Organomet Polym* 19:443–453
24. Kaya İ, Avcı A (2012) Synthesis, characterization, and thermal degradation of new aromatic poly(azomethine-urethane)s and their polyphenol derivatives. *J Polym Res* 19(9780):1–14
25. Kaya İ, Yıldırım M, Avcı A, Kamacı M (2011) Synthesis and thermal characterization of novel poly(azomethine-urethane)s derived from azomethine containing phenol and polyphenol species. *Macromol Res* 19:286–293
26. Kaya İ, Kamacı M (2012) Synthesis, optical, electrochemical, and thermal stability properties of poly(azomethine-urethane)s. *Prog Org Coat* 74:204–214
27. Kaya İ, Yıldırım M, Kamacı M, Avcı A (2011) New poly(azomethine-urethane)s including melamine derivatives in the main chain: synthesis and thermal characterization. *J Appl Polym Sci* 120:3027–3035
28. Kaya İ, Kamacı M (2012) Novel poly(azomethine-urethane)s and their polyphenol derivatives derived from aliphatic diisocyanate compound: synthesis and thermal characterization. *J Appl Polym Sci* 125:876–887
29. Ghaemya M, Aghakhani B, Taghavi M, Nasab SMA, Mohseni M (2013) Synthesis and characterization of new imidazole and fluorine-bisphenol based polyamides: thermal, photophysical and antibacterial properties. *React Funct Polym* 73:555–563
30. Tamilavan V, Song M, Jin SH, Hyun MH (2011) Synthesis and photovoltaic properties of heteroaromatic low-band gap oligomers for bulk heterojunction solar cells. *Synth Met* 161:1199–1206
31. Kaya İ, Bilici A, Saçak M (2006) Synthesis, characterization and antimicrobial properties of oligo-4-[pyridine-3-yl-methylene] amino]phenol. *J Appl Polym Sci* 102:3327–3333
32. Chattopadhyay DK, Webster DC (2009) Thermal stability and flame retardancy of polyurethanes. *Prog Polym Sci* 34:1068–1133
33. Liu J, Ma D (2002) Study on synthesis and thermal properties of polyurethane-imide copolymers with multiple hard segments. *J Appl Polym Sci* 84:2206–2215
34. Kamacı M, Kaya İ (2014) photophysical, electrochemical, thermal and morphological properties of polyurethanes containing azomethine bonding. *J Macromol Sci A* 51:805–819
35. Kamacı M, Kaya İ (2014) Synthesis, thermal and morphological properties of polyurethanes containing azomethine linkage. *J Inorg Organomet Polym* 24:803–818
36. Potolinca VO, Buruiana E, Oprea S (2013) Dielectric behavior of polyurethane and polyurethane-urea elastomers with pyridine moieties in the main chain. *J Polym Res* 20(237):1–9
37. Kaya İ, Yıldırım M, Avcı A (2010) Synthesis and characterization of fluorescent polyphenol species derived from methyl substituted aminopyridine based Schiff bases: the effect of substituent position on optical, electrical, electrochemical, and fluorescence properties. *Synth Met* 160:911–920