

Novel Poly(azomethine-urethane)s and Their Polyphenol Derivatives Derived from Aliphatic Diisocyanate Compound: Synthesis and Thermal Characterization

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ABSTRACT: Until now, only a few kinds of poly(azomethine-urethane)s (PAMUs) including aromatic hydroxy benzaldehyde and aminophenol compounds were obtained and studied with thermal degradation steps. However, oligo/polyphenol-based PAMUs have not been synthesized yet. In this study, some kinds of this class of PAMUs were synthesized in three steps. At the first step polyurethane (PU) was synthesized by the copolymerization reaction of 2,4-dihydroxybenzaldehyde with hexamethylene diisocyanate (HDI) under argon atmosphere. At the second step, the poly(azomethine-urethane)s (PAMUs) were obtained by graft copolymerization of the preformed PU with aminophenols (2-aminophenol, 3-aminophenol, and 4-aminophenol). At the last step the obtained PAMUs were converted to the polyphenol derivatives via oxidative

polycondensation reaction (OP). The structures of the obtained compounds were confirmed by FTIR, UV-vis, ¹H-NMR, and ¹³C-NMR techniques. The number-average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) values of the synthesized compounds were determined by the size exclusion chromatography (SEC). The synthesized compounds were also characterized by solubility tests, TG-DTA, and DSC. Fluorescence measurements were carried out in various concentrated DMF solutions to determine the optimum concentrations to obtain the maximal PL intensities. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 876–887, 2012

Key words: poly(azomethine-urethane)s; thermal degradation; fluorescence; aminophenols

INTRODUCTION

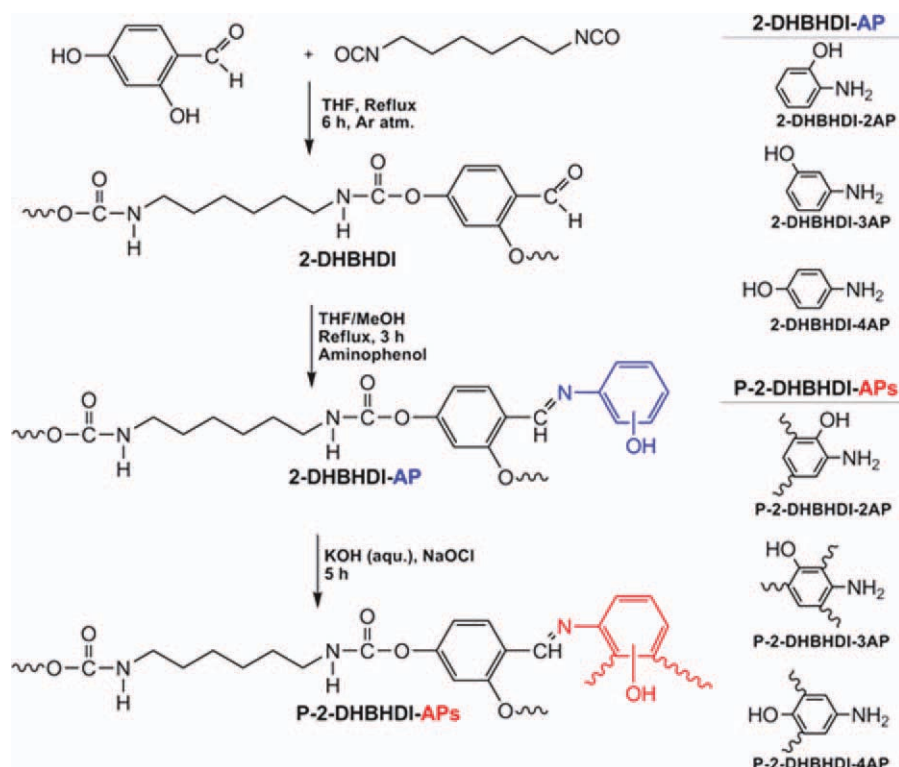
Polyurethanes (PUs) represent a class of polymers that have found a lot of application.¹ A number of studies have been carried out because of their singular properties and to understand their both chemical and physical properties and structures.² Several researches exist in the development of thermally stable polymers due to they use in very applications. A typical example of this polymers is polyurethanes, which are widely used in the aerospace, foam, elastomers and construction industries. Consequently, their thermal stability has been studied extensively in the literature for many years.^{3–5} Also, PUs have a lot of applications in furniture, automotive seat cushions and carpet cushion, in automobile seats, water vessels electronic components, and wheels.⁶

On the other hand, one attractive class of polymers is poly(azomethine)s (PAMs), which contain azomethine (–CH=N–) linkages in the main chain and are known to exhibit good thermal stability and

have many desirable properties such as electrical conductivity, thermal stability, solubility, optical, and electrochemical band gaps.^{7,8} However, PAMs especially aromatic derivatives have low solubility. To solve this problem, a number of PAMs like poly(-azomethine ether)s,⁹ poly(azomethine carbonate)s,¹⁰ poly(amide-azomethine-ester)s,¹¹ poly(azomethine-ester)s,¹² poly(amide-azomethine-ether)s,¹³ poly(azomethine sulfone)s,¹⁴ and poly(azomethine-amide)s¹⁵ have been synthesized so far. But poly(azomethine-urethane)s^{16–18} have not been synthesized except a few studies. Especially, their polyphenol derivatives have not been synthesized yet. A few of these studies investigated the effect of the azomethine linkages on thermal stability.¹⁹ Also, Simionescu et al. were synthesized urethane compounds with Schiff base structure and characterized their thermal properties²⁰, Tang and Chang were synthesized novel poly(azomethine-urethane)s and investigated thermotropic liquid-crystalline properties²¹ and, Kaya et al. were synthesized new poly(azomethine-urethane)s including melamine and studied with thermal degradation step.²²

Oligophenols and their azomethine derivatives had been previously synthesized by oxidative polycondensation method and presented in the literature

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Scheme 1 Syntheses of 2-DHBHDI, PAMUs, and polyphenol derivatives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with their several useful properties. Such as the use of water as a medium, to be easy to apply and environmentally harmless.^{23–25} Also using cheap oxidants such as NaOCl, H₂O₂ and air is another advantage of this method.

At the first part of this study, we synthesized novel PAMUs including functional phenolic groups in main chain and then converted to their polyphenol derivatives using the oxidative polycondensation method in an aqueous alkaline media. At the second part, we characterized the synthesized compounds using FTIR, UV-vis spectra, ¹H- and ¹³C-NMR and SEC analyses. TG-DTA technique was used to deter-

mine the stabilities to degradation of thermal degradation. DSC analyses of the obtained compounds were carried out to determine the glass transition temperatures (*T_g*). The fluorescence spectra of synthesized compounds were also carried out to determine maximal emission–excitation intensities. The obtained PAMUs and their polyphenol derivatives have different aminophenols. The effects of various substituents on the properties of PAMUs and their polyphenol derivatives containing azomethine linkage were investigated. Different effects of this property were discussed affecting the thermal stability, solubility, and optical properties.

TABLE I
Solubility Tests of the Synthesized Compounds

Solvents/ Compounds	2- DHBHDI	2-DHBHDI- 2AP	2-DHBHDI- 3AP	2-DHBHDI- 4AP	P-2-DHBHDI- 2AP	P-2-DHBHDI- 3AP	P-2-DHBHDI- 4AP
MeOH	–	⊥	–	⊥	⊥	⊥	⊥
THF	–	+	–	⊥	⊥	–	⊥
Acetonitrile	–	⊥	–	⊥	⊥	⊥	⊥
Ethyl Acetate	–	⊥	–	⊥	–	–	–
CHCl ₃	⊥	⊥	–	–	⊥	⊥	⊥
Acetone	–	+	–	⊥	+	–	⊥
DMF	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+
Toluene	–	–	–	–	–	–	–

+, Soluble; –, Insoluble; ⊥, partly soluble.

Syntheses of the poly(azomethine-urethane)s

Preformed 2-DHBHDI was used in synthesizing of the PAMUs (2-DHBHDI-2AP, 2-DHBHDI-3AP, and 2-DHBHDI-4AP). Reactions were carried out by grafting of the aminophenols onto 2-DHBHDI. Synthesis procedure of the PAMUs is as follows: 2-DHBHDI (1.23 g, 4×10^{-3} mol) was dissolved in 60 mL DMF/MeOH (1/3) mixture and added into a 250 mL three-necked round-bottom flask which was fitted with condenser, and magnetic stirrer. Reaction mixture was heated up to 60°C and equivalent amount of aminophenols (APs) (2-aminophenol, 3-aminophenol and 4-aminophenol) (0.437 g, 4×10^{-3} mol) was added into the flask. Reactions were maintained for 3 h, cooled at the room temperature. The obtained PAMUs were washed by methanol (2×50 mL), acetonitrile (2×50 mL), and distilled water (2×100 mL) to remove the unreacted components. The products were dried in a vacuum oven at 75°C for 24 h. (yields 85, 65, and 96% for 2-DHBHDI-2AP, 2-DHBHDI-3AP, and 2-DHBHDI-4AP, respectively).²⁶

Syntheses of the polyphenols derivatives of the PAMUs

The polyphenol derivatives of the P-PAMUs (P-2-DHBHDI-2AP, P-2-DHBHDI-3AP, and P-2-DHBHDI-4AP) were synthesized via oxidative polycondensation of 2-DHBHDI-2AP, 2-DHBHDI-3AP, and 2-DHBHDI-4AP with aqueous solution of NaOCl (30%), respectively. Synthesis procedure of the P-PAMUs is as follows: P-2-DHBHDI-2AP, P-2-DHBHDI-3AP, and P-2-DHBHDI-4AP (0.8 g, 2×10^{-3} mol) were dissolved in an aqueous solution of KOH (30%, 0.03 mol) and placed into a 50 mL three-necked round-bottom flask. They were fitted with a condenser, thermometer, and stirrer and an addition to funnel containing NaOCl (0.122 mol). NaOCl was added drop by drop over about 20 min. The reaction mixtures were heated to 80 °C. The reaction mixtures were cooled to room temperature, and then 0.03 mol HCl (37%) was added. For the separation of mineral salts, the mixture was filtered and washed in 25 mL of hot water for three times. Then, unreacted PAMUs were separated from the reaction products by washing with ethanol and dried in a vacuum oven at 60°C (yields 49, 36, and 66% for P-2-DHBHDI-2AP, P-2-DHBHDI-3AP, and P-2-DHBHDI-4AP, respectively).²⁷ All the synthesized procedures were summarized in Scheme 1.

Characterization techniques

The solubility tests were carried out in different solvents by using 1 mg sample and 1 mL solvent at 25°C. The infrared and ultraviolet-visible spectra

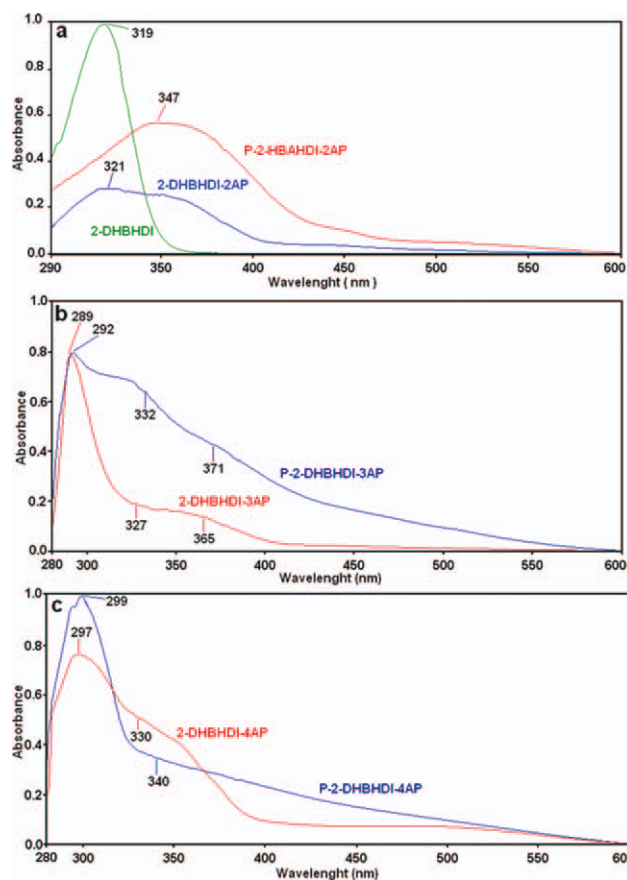


Figure 3 UV-vis spectra of 2-DHBHDI, 2-DHBHDI-2AP, P-2-DHBHDI-2AP (a), 2-DHBHDI-3AP, P-2-DHBHDI-3AP (b), and 2-DHBHDI-4AP, P-2-DHBHDI-4AP (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were measured by Perkin Elmer FT-IR Spectrum one and Perkin Elmer Lambda 25, respectively. The FTIR spectra were recorded using universal ATR sampling accessory ($4000\text{--}550\text{ cm}^{-1}$). UV-vis spectra of the synthesized compounds were determined by using DMSO as the solvent. ^1H - and ^{13}C -NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were also recorded by using deuterated DMSO- d_6 as a solvent at 25°C. Tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20 and 1000°C (in N_2 , 10°C/min). DSC analyses were carried out between 25 and 420°C using Perkin Elmer Pyris Sapphire DSC. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC) techniques of Shimadzu For SEC investigations, an SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. \times 300 mm columns was used; eluent: DMF (0.4 mL/min), polystyrene standards were used. Moreover, a UV detector

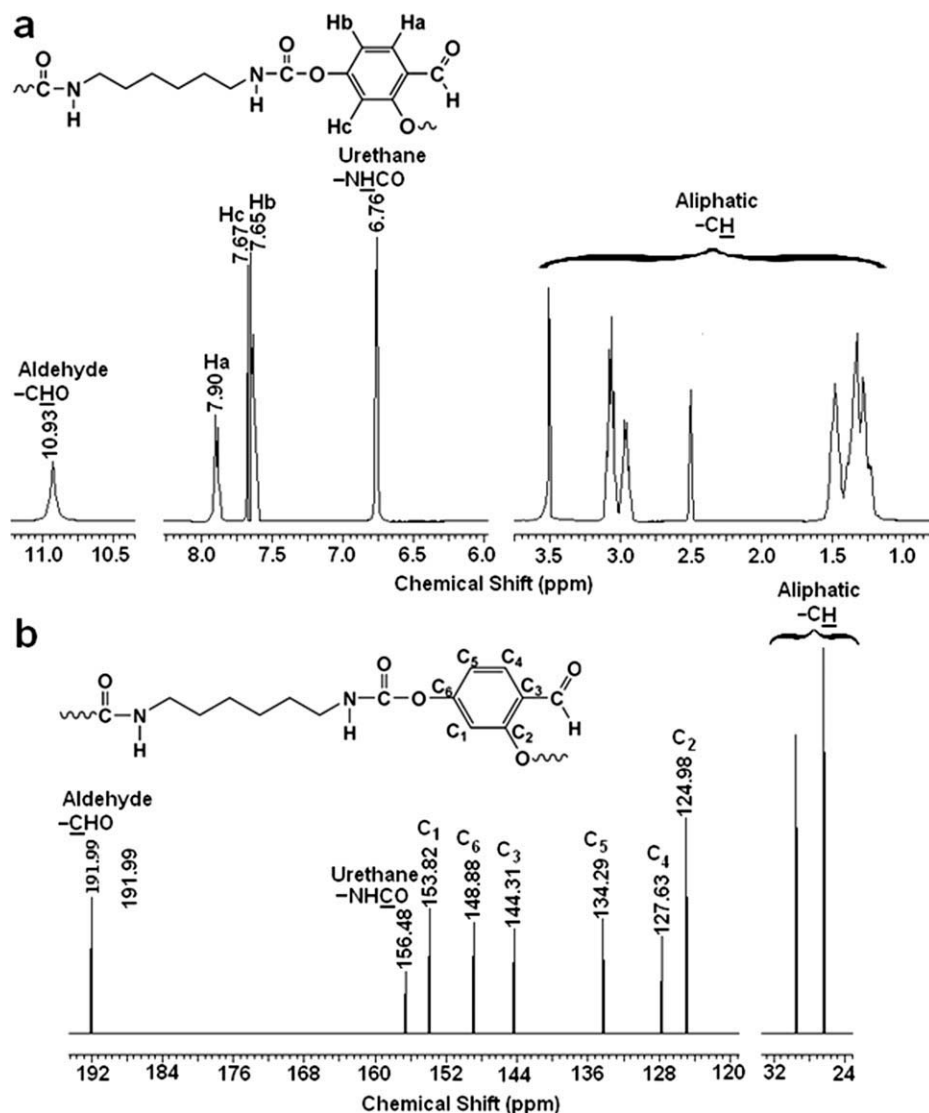


Figure 4 ^1H -NMR (a) and ^{13}C -NMR (b) spectra of 2-DHBHDI.

was used to analyze the products at 25°C. The fluorescence spectra were recorded by using a Shimadzu RF-5301PC spectrofluorophotometer.

RESULTS AND DISCUSSION

Solubilities and structures of the PU, PAMUs, and polyphenol derivatives

2-DHBHDI is light yellow colored while 2-DHBHDI-2AP and 2-DHBHDI-3AP are dark red colored, 2-DHBHDI-4AP and P-2-DHBHDI-4AP are black colored, P-2-DHBHDI-2AP and P-2-DHBHDI-3AP are dark brown colored. The solubility test results are shown in Table I. According to the obtained results all of the synthesized compounds completely soluble in only strong polar solvent like DMSO and DMF while they are all insoluble toluene. 2-DHBHDI is partly soluble in CHCl_3 while insoluble in THF,

MeOH, acetonitrile, ethyl acetate, and acetone. 2-DHBHDI-2AP is completely soluble in THF and acetone whereas partly soluble in MeOH, acetonitrile, ethyl acetate, CHCl_3 . 2-DHBHDI-3AP is insoluble all of used solvents expect for DMSO and DMF. 2-DHBHDI-4AP is partly soluble MeOH, THF, acetonitrile, ethyl acetate and acetone while insoluble in CHCl_3 . P-2-DHBHDI-2AP is completely soluble in acetone, partly soluble in MeOH, THF, acetonitrile, and CHCl_3 but insoluble ethyl acetate. P-2-DHBHDI-3AP and P-2-DHBHDI-4AP are partly soluble in MeOH, acetonitrile, and CHCl_3 while insoluble in ethyl acetate and acetone.

FTIR spectra of HDI, 2,4-dihydroxy benzaldehyde, 2-DHBHDI, 2-DHBHDI-2AP, and P-2-DHBHDI-2AP are given in Figure 1. Similarly, FTIR spectra of 2-DHBHDI-3AP, 2-DHBHDI-4AP, P-2-DHBHDI-3AP, and P-2-DHBHDI-4AP are given in Figure 2. According to Figure 1, at the spectrum of HDI

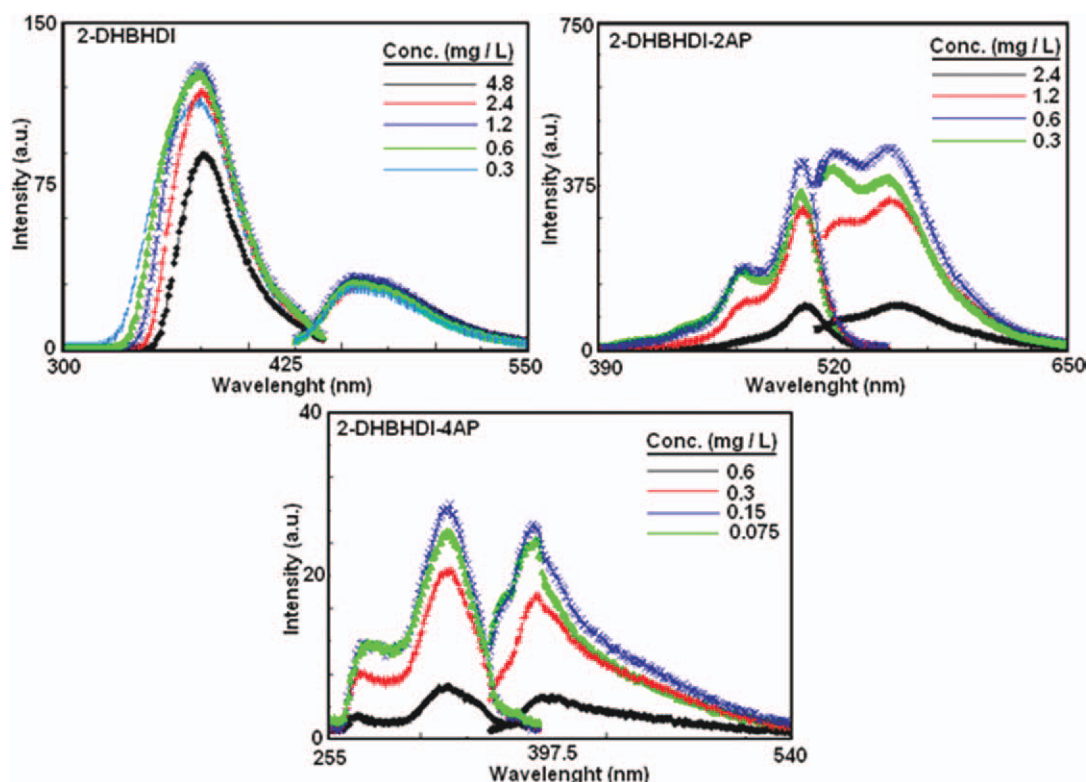


Figure 7 Emission and excitation spectra of various concentrated solution of 2-DHBHDI, 2-DHBHDI-2AP, and 2-DHBHDI-4AP in DMF. Slit width: λ_{EX} : 3 nm, λ_{EM} : 3 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

also given in Figures 5 and 6. According to Figure 5 $-\text{OH}$, imine ($-\text{CH}=\text{N}$) and urethane ($-\text{NHCO}$) protons are observed at 9.71–9.71, 8.44–8.36, and 6.77–6.61 ppm for 2-DHBHDI-2AP and 2-DHBHDI-4AP, respectively. At the spectra of P-2-DHBHDI-2AP and P-2-DHBHDI-4AP the same peaks are observed at 9.83–8.01, 7.86–8.92, and 6.68–6.61 ppm, respectively. Also aliphatic $-\text{CH}$ protons are observed between 1.0 and 3.5 ppm for 2-DHBHDI-2AP and 2-DHBHDI-4AP. At the spectra of P-2-DHBHDI-2AP and P-2-DHBHDI-4AP these peaks are observed between 1.0 and 3.0 ppm.

Size exclusion chromatography

According to the SEC chromatograms, the calculated number-average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) values of the synthesized PU, PAMUs and their polyphenol derivatives measured using UV detector are given in Table II. According to Table II, the synthesized PAMUs (2-DHBHDI-2AP, 2-DHBHDI-3AP, and 2-DHBHDI-4AP) have higher molecular weights than the starting polyurethane (2-DHBHDI). Similarly, polyphenol derivatives of the P-PAMUs (P-2-DHBHDI-2AP, P-2-DHBHDI-3AP and P-2-DHBHDI-4AP) have also higher molecular weight than the PAMUs as expected. This is the evi-

dence of the increasing molecular weights during the polymerization steps. According to the total values 2-DHBHDI-2AP, 2-DHBHDI-3AP, and 2-DHBHDI-4AP have 54–55, 12–13, and 16–17 repeated units, respectively. Similarly, P-2-DHBHDI-2AP, P-2-DHBHDI-3AP, and P-2-DHBHDI-4AP have 51–52, 77–78, and 77–78 repeated units, respectively.

Fluorescence characteristics

Fluorescence measurements of the synthesized compounds are carried out using DMF for the PU, PAMUs, and their polyphenol derivatives. Measurements were made for various concentrations to determine the optimal conditions. Figures 7 and 8 show the excitation and emission spectra of 2-DHBHDI, 2-DHBHDI-2AP, 2-DHBHDI-4AP, P-2-DHBHDI-2AP, P-2-DHBHDI-3AP, and P-2-DHBHDI-4AP in DMF. These figures also indicate the concentration-fluorescence intensity relationships of the compounds. As seen in these figures, the optimum concentration to obtain maximal emission–excitation intensities changes between 1.2 and 0.075 mg/L. The obtained results are also summarized in Table III. These results clearly indicate that the PU and PAMUs derived from 2-aminophenol, 2-DHBHDI-2AP and P-2-DHBHDI-2AP, have quite higher fluorescence wavelengths and intensities than the others.

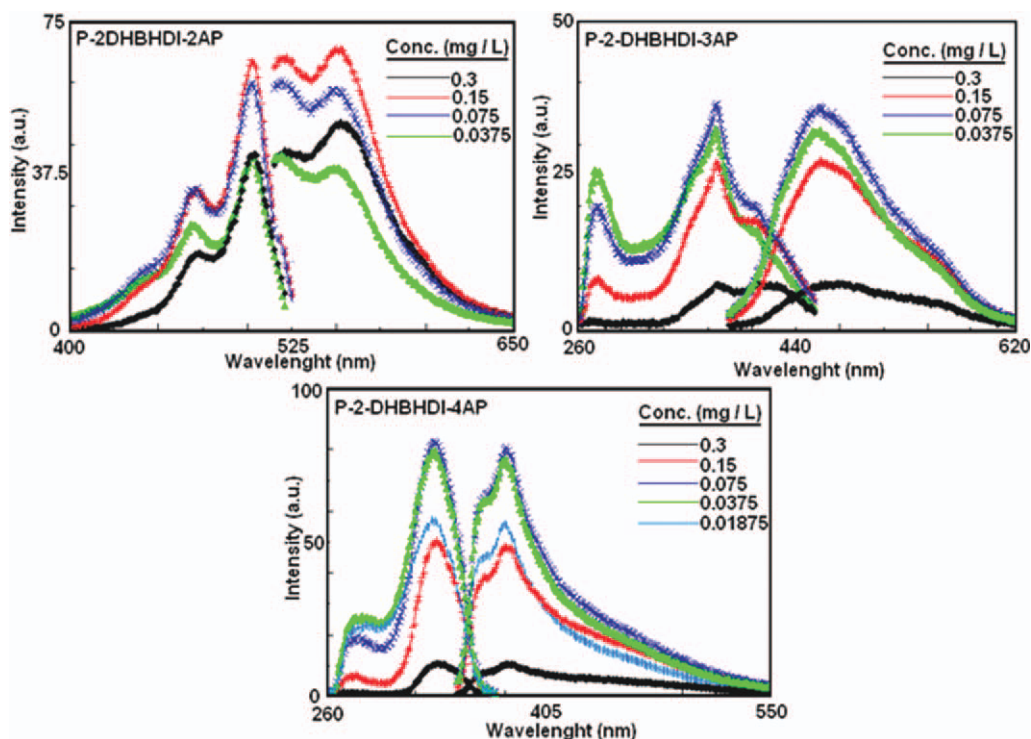


Figure 8 Emission and excitation spectra of various concentrated solution of P-2-DHBHDI-2AP, P-2-DHBHDI-3AP, and P-2-DHBHDI-4AP in DMF. Slit width: λ_{Ex} : 3 nm, λ_{Em} : 3 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Both 2-DHBHDI-2AP and P-2-DHBHDI-2AP give the emission peaks at 550 nm with the intensities of 460 and 67 nm, respectively, while the others show relatively lower peak wavelengths in the range of 375–460 nm and the intensities between 25 and 80 nm. Fluorescence characteristics of 2-DHBHDI-2-AP resembles those of “Acridine yellow” presented in the literature.²⁸ Acridine yellow has the excitation and emission peaks at 470 and 550 nm, respectively. Similarly, the new presented PAMU, 2-DHBHDI-2-AP, has the 503 nm excitation and 550 nm emission peaks. As a result, 2-DHBHDI-2-AP and P-2-DHBHDI-2-AP could be used as the alternative yel-

lowish light emitting diodes with their high quantum yields as well as the suitable fluorescence wavelengths.

Thermal characterization

The result of TGA are summarized in Table IV. According to the obtained TG curves 2-DHBHDI-2AP decomposes in two steps while the others decompose in three steps between 20 and 1000°C. Table IV indicates that the PAMU derived from 3-aminophenol, 2-DHBHDI-3AP, has the highest onset temperatures (T_{on}). Also when compared the first

TABLE III
Fluorescence Spectral Data of the Synthesized Compounds

Compound	Conc.(mg/L)	^a λ_{Ex}	^b λ_{Em}	^c $\lambda_{\text{max}}(\text{Ex})$	^d $\lambda_{\text{max}}(\text{Em})$	^e I_{Ex}	^f I_{Em}
2-DHBHDI	1.200	415	448	373	458	129	33
2-DHBHDI-2AP	0.600	504	558	503	550	428	460
2-DHBHDI-4AP	0.150	343	396	328	381	28	26
P-2-DHBHDI-AP	0.150	503	521	502	550	65	67
P-2-DHBHDI-AP	0.075	377	466	374	460	36	35
P-2-DHBHDI-AP	0.075	336	381	330	376	82	80

^a Excitation wavelength for emission.

^b Emission wavelength for excitation.

^c Maximum emission wavelength.

^d Maximum excitation wavelength.

^e Maximum excitation intensity.

^f Maximum emission intensity.

TABLE IV
TGA Data of the Synthesized Compounds

Compounds	First degradation step (°C)			Second degradation step (°C)			Third degradation step (°C)			Char at 1000°C (%)	Losses of solvent/absorbed water(%)
	aT_{on}	bT_{max}	cT_{end}	dT_{start}	T_{max}	T_{end}	T_{start}	T_{max}	T_{end}		
	Weight loss (%)	Weight loss (%)	Weight loss (%)	Weight loss (%)	Weight loss (%)	Weight loss (%)	Weight loss (%)	Weight loss (%)	Weight loss (%)		
2-DHBHDI	163	190	250	250	288	390	390	445	1000	25.40	2.00
2-DHBHDI-2AP	161	234	345	345	449	1000	1000	-	-	19.50	2.00
2-DHBHDI-3AP	185	213	230	230	267	300	300	438	1000	28.40	3.90
2-DHBHDI-4AP	158	158	189	189	269	309	309	440	1000	26.75	6.60
P-2-DHBHDI-2AP	188	231	300	300	365	410	410	449	1000	22.70	11.40
P-2-DHBHDI-3AP	195	357	400	400	448	1000	1000	-	-	30.05	11.00
P-2-DHBHDI-4AP	148	159	185	185	304	410	410	451	1000	15.00	7.00

^a Thermal degradation onset temperature.

^b Maximum weight loss temperature.

^c Thermal degradation finished temperature.

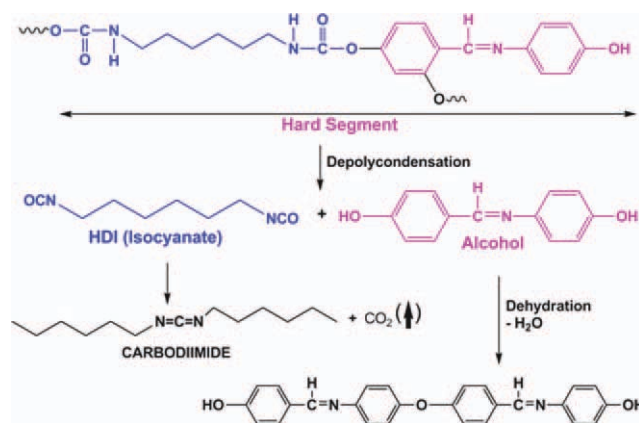
^d Thermal degradation started temperature.

TABLE V
DTA and DSC Data of the Synthesized Compounds

Compounds	DTA		DSC	
	Endo peak (°C)	Exo peak (°C)	T_g (°C)	ΔC_p (J/g K)
2-DHBHDI	128, 448	178,272	160	0.144
2-DHBHDI-2AP	173, 250, 450	303	158	0.143
2-DHBHDI-3AP	207, 272	-	135	0.328
2-DHBHDI-4AP	172, 261, 311	231	155	1.585
P-2-DHBHDI-2AP	245	390	184	0.258
P-2-DHBHDI-3AP	-	-	158	0.028
P-2-DHBHDI-4AP	201, 312	495	144	0.407

degradation steps the peak degradation temperatures of the PAMU derived from 2-aminophenol, 2-DHBHDI-2AP, is higher than the others PAMUs. On the other hand, polyphenol derivatives of PAMU derived from 3-aminophenol, P-2-DHBHDI-3AP, is higher than the others of polyphenol derivatives of PAMUs. These differences probably depend on the steric effect of the substituted -OH groups. P-2-DHBHDI-3AP has *m*-aminophenol while P-DHBHDI-2AP and P-2-DHBHDI-4AP have *o*-aminophenol and *p*-aminophenol, respectively. The char residues of 2-DHBHDI, 2-DHBHDI-2AP, 2-DHBHDI-3AP, P-2-DHBHDI-2AP, P-2-DHBHDI-3AP, and P-DHBHDI-4AP are 25.60, 20.80, 28.85, 27.00, 22.30, 30.00, and 15.10, respectively. According to these results P-2-DHBHDI-3AP has the highest resistance against thermal degradation.

Also, the obtained results from DSC traces are summarized in Table V. According to DSC traces, the glass transition temperatures (T_g) of 2-DHBHDI, 2-DHBHDI-2AP, 2-DHBHDI-3AP, 2-DHBHDI-4AP, P-2-DHBHDI-2AP, P-2-DHBHDI-3AP, and P-2-DHBHDI-4AP were found as 160, 158, 135, 155, 184, 158, and 144°C, respectively. The obtained results clearly indicate that the PAMU derived from 2-



Scheme 2 Thermal degradation step of the synthesized poly(azomethine-urethane)s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

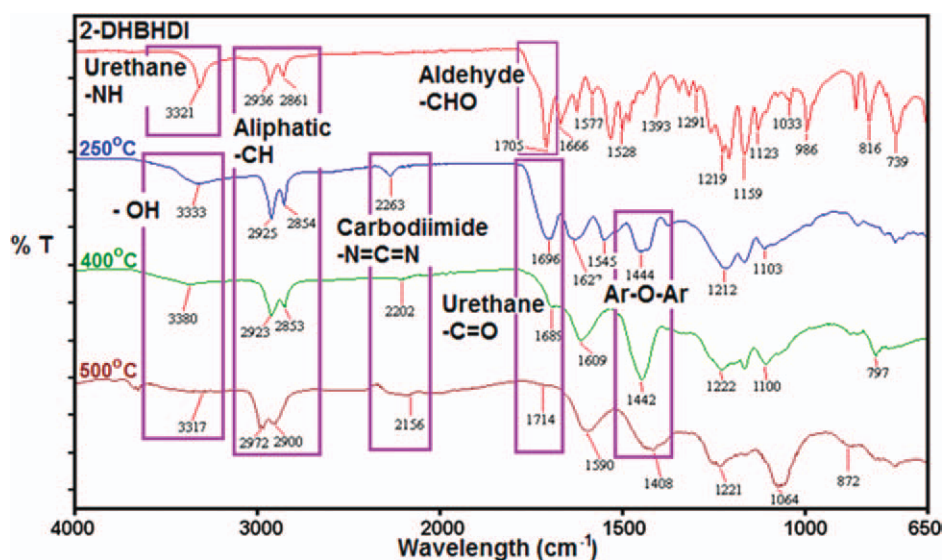


Figure 9 FT-IR spectra of 2-DHBHDI after heating until various temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aminophenol, P-2-DHBHDI-2AP, has the highest T_g temperature. In addition a broad peak ranging from 25 to 135°C is clearly observed. This peak probably arises from removal of THF as adsorbed solvent.²⁹

Thermal degradation

As known, the thermal degradation of PUs occurs in two to three-step process.^{30–34} The first step is related to degradation of the hard segment, which results in the formation of isocyanate and alcohol, primary or secondary amine and olefin and carbon dioxide. The second and third steps of degradation include the decomposition of the soft segment by

dehydration process. The thermal stability of PUs depends primarily on the polymerization ↔ depolymerization equilibria of the functional groups in the polymer molecule.^{35,36} The isocyanate formed during thermal decomposition may be dimerized to carbodiimide. Carbodiimide can then react with urethane groups to form a crosslinked structure. Obtained results have been also confirmed by FTIR spectra of the thermodegradation products (Scheme 2).

To explain the thermodegradation steps of the synthesized 2-DHBHDI and 2-DHBHDI-4AP FTIR spectra of the products after heating until various temperatures are obtained and given in Figures 9

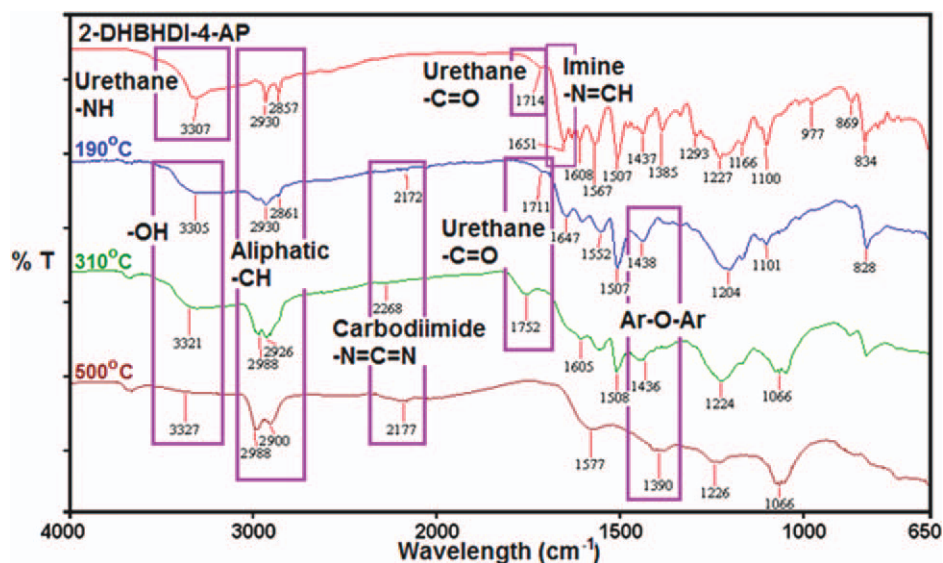


Figure 10 FT-IR spectra of 2-DHBHDI-4AP after heating until various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 10, respectively. In the spectra of 2-DHBHDI characteristic carbodiimide (—N=C=N—) peak is observed at 2263 cm^{-1} for 250°C , 2202 cm^{-1} for 400°C , and 2156 cm^{-1} for 500°C which agree with the literature values.³⁰ In the spectra of 2-DHBHDI-4AP the same peak is observed at 2172 , 2268 , and 2177 cm^{-1} for 190 , 310 , and 500°C , respectively. Additionally, after the depolymerization step with heating up to higher temperatures —OH functionalized 2-DHBHDI and 2-DHBHDI-4AP are expected to form new ether-bridged structures with dehydration.³⁰ As seen in Figure 9 when 2-DHBHDI is heated up to 250 and 500°C , respectively, new broad absorption bands appear at 1444 , 1442 , and 1408 cm^{-1} for 250 , 400 , and 500°C , respectively, indicating the Ar—O—Ar ether bond formation. Also, the intensities of O—H stretch vibrations at 3333 , 3380 , and 3317 cm^{-1} for 250 , 400 , and 500°C , respectively, decrease due to the dehydration. According to the these results, urethane —C=O peak was disappeared with increasing temperature both 2-DHBHDI and 2-DHBHDI-4AP. Also, the intensity of carbodiimide (—N=C=N—) vibration was increased with increasing temperature. These results clearly show that thermodegradation steps of the synthesized 2-DHBHDI and 2-DHBHDI-4AP are obtained with the proposed structures shown in Scheme 2.

Similarly, according to Figure 10, Ar—O—Ar ether bond and the intensity of O—H stretch vibrations of the 2-DHBHDI-4AP is observed at 3305 , 3321 , and 3337 cm^{-1} and 1438 , 1436 , and 1390 cm^{-1} for 190 , 310 , and 500°C , respectively.

CONCLUSIONS

Novel PU, PAMU, and their polyphenol derivatives were synthesized by copolymerization, graft copolymerization, and oxidative polycondensation reactions, respectively. The obtained compounds were characterized by UV-vis, FTIR, NMR, and SEC analyses. Photo luminescence (PL) spectra of the synthesized compounds were obtained in DMF solutions showing that the novel PAMUs derived by grafting of 2-aminophenol onto the PU are highly fluorescent and can be used in preparation of the alternative yellowish emitting diodes. SEC result showed that obtained polyphenol derivatives of PAMUs and 2-DHBHDI-2AP have quite high molecular weight between $18,300$ and $42,600$. The effects of different positions hydroxyl groups in aminophenol groups on thermal stability, solubility, and optical properties were also clarified. Thermal characterizations were carried out by TGA, DTA and DSC techniques. Also, thermal degradation steps of the new PU, PAMUs, and their polyphenol derivative were clarified using the FTIR spectra of the degraded forms at various temperatures. Physical changes of the PAMUs were displayed at various

temperatures showing that the colors of the PAMUs change from light to dark forms as a result of the thermal degradation. According to thermal characterizations results, T_g values OF synthesized compounds have change from 135 to 184°C . Because of good thermal properties they can be promising candidates for aerospace application and they can be used to produce temperature-stable materials.

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