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Synthesis and characterization of new poly(azomethine-urethane) and polyphenol derivatives obtained from 3,4-dihydroxy benzaldehyde and hexamethylene diisocyanate

Summary — Oligophenol based poly(azomethine-urethane)s (PAMUs) including azomethine linkages were synthesized in three steps. At the first step, polyurethane (PUR) was synthesized in the copolymerization reaction of 3,4-dihydroxy benzaldehyde with hexamethylene diisocyanate (HDI) under the argon atmosphere. At the second step, the PAMUs were obtained by graft copolymerization of the preformed PUR with aminophenol (2-aminophenol, 3-aminophenol, or 4-aminophenol). At the last step, the obtained PAMUs were converted to their polyphenol derivatives *via* oxidative polycondensation reaction. The structures of the obtained compounds were confirmed by FT-IR, UV-vis, ^{1}H NMR, and ^{13}C NMR techniques. The molecular weight distribution parameters of the synthesized compounds were determined with the size exclusion chromatography (SEC). The synthesized compounds were also characterized by solubility tests, TGA, DTA, and DSC. Fluorescence measurements were carried out in various concentrated dimethylformamide solutions to determine the optimum concentrations to obtain the maximal fluorescence intensities.

Keywords: poly(azomethine-urethane), oxidative polycondensation, thermal degradation, thermal analysis, hexamethylene diisocyanate.

SYNTEZA I CHARAKTERYSTYKA NOWYCH POCHODNYCH POLI(AZOMETINO-URETANU) I POLIFENOLI OTRZYMANYCH Z 3,4-DIHYDROKSYBENZALDEHYDU I DIIZOCYJANIANU HEKSAMETYLENU

Streszczenie — Poli(azometino-uretany) (PAMU) zawierające ugrupowania azometinowe syntezowano w trzech etapach. Pierwszy etap to reakcja kopolimeryzacji 3,4-dihydroksybenzaldehydu z diizocyjanianem heksametylenu (HDI) w atmosferze argonu, w której otrzymuje się poliuretan (PUR). W reakcji kopolimeryzacji szczepionej PUR z aminofenolem (2-aminofenolem, 3-aminofenolem lub 4-aminofenolem) stanowiącej drugi etap powstają PAMU, które następnie są przekształcane do odpowiednich pochodnych polifenolu w procesie polikondensacji utleniającej (schemat A). Strukturę otrzymanych związków potwierdzono metodami FT-IR, UV-vis, ^{1}H NMR i ^{13}C NMR (rys. 1—6). Za pomocą chromatografii żelowej (SEC) określano również parametry rozkładu ciężaru cząsteczkowego (tabela 3). Scharakteryzowano także rozpuszczalność zsyntetyzowanych związków w szeregu wybranych rozpuszczalników oraz zbadano ich stabilność termiczną metodami TGA, DTA i DSC (rys. 9, tabele 5 i 6). Przeprowadzono badania fluorescencji roztworów otrzymanych polimerów w dimetyloformamidzie, co umożliwiło wyznaczenie optymalnego stężenia tych roztworów pozwalające na uzyskanie maksymalnej intensywności fluorescencji (tabela 4).

Słowa kluczowe: poli(azometino-uretan), polikondensacja utleniająca, degradacja termiczna, analiza termiczna, diizocyjanian heksametylenu.

Polyurethanes (PURs) have a large number of applications in many fields of modern life. They represent a class of polymers that have found a widespread use in the medical, automotive, and industrial fields [1]. PURs have a poor heat resistance that largely limits their usage as engineering materials [2]. Their thermal stability is dependent to a great extent on the chemical structure of their backbones which consist of various hard and soft segments [3, 4]. Generally, PURs consist of hard and soft segments derived from isocyanate and polyol, respectively. The ratio of the hard to soft segment has an influence on dispersion stability, thermal and mechanical properties

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[5—7]. In addition, Janik and Balas [8] synthesized segmental polyurethanes (PUR) *via* two-stage synthesis method and found that composition of the PUR affects the equilibrium swelling in dimethylformamide as well as mechanical properties.

Oligophenols and their derivatives have been used in various fields because of their electron structure properties. They have useful properties such as paramagnetism, semi-conductivity, electrochemical potential and resistance to high energy. Because of these properties, they were used to prepare composites with resistance to high temperature, thermostabilizers and graphite materials, epoxy oligomer and block copolymers, adhesives, photoresistant and antistatic materials [9]. Oligophenols have been prepared by polycondensation reaction of the corresponding monomer using several methods including enzymatic polymerization [10], catalytic polymerization [11], electropolymerization [12], and oxidative polycondensation in an aqueous medium in the presence of an oxidant like NaClO, H_2O_2, *etc*. [13]. Each mentioned method has some advantages and disadvantages in comparison to the others. However, the last method has been widely used due to being cheap and environmentally harmless.

Additionally, one attractive class of macromolecules are poly(azomethine)s (PAMs). PAMs with their functional azomethine linkages (-CH=N-) in the main chain are known to exhibit good thermal stability as well as many desirable properties such as paramagnetism, semi-conductivity, electrochemical potential, and resistance to high energy due to the resonance stabilization of poly Schiff base unit [14, 15]. On the other hand, PAMs, especially their aromatic derivatives suffer from low solubility. To solve this problem, many kinds of PAMs have been synthesized so far [14—17]. However, only a few kinds of PAM urethane derivatives have been reported [18—21] and there is still a need to synthesize new functional kinds in this area and develop their properties. In addition, oligophenol PAM derivatives including urethane linkages have not yet been reported in literature and need to be investigated.

Oligophenols including azomethine linkages have been also successfully synthesized by oxidative polycondensation method in aqueous media using cheap oxidants like NaOCl, H_2O_2, and air and presented with their optical, electrochemical, electrical, and thermal properties [22, 23].

The aim of this study, was to synthesize new kinds of poly(azomethine-urethane)s (PAMUs) including functional phenolic groups and then conversion to their polyphenol derivatives using the oxidative polycondensation method in an aqueous alkaline media. The obtained materials were characterized using FT-IR, UV-vis spectra, ^{1}H and ^{13}C NMR and SEC analyses. TGA and DTA technique was used to investigate the thermal stability of polymers. Thermal degradation steps of the novel PUR, PAMUs, and polyphenol derivatives were clarified *via* FT-IR analyses of products degraded at various temperatures. DSC analyses of the obtained compounds were applied to determine the glass transition temperatures (T_g). Also the fluorescence spectra of synthesized compounds were carried out to determine the maximal emission-excitation intensities.

EXPERIMENTAL

Materials

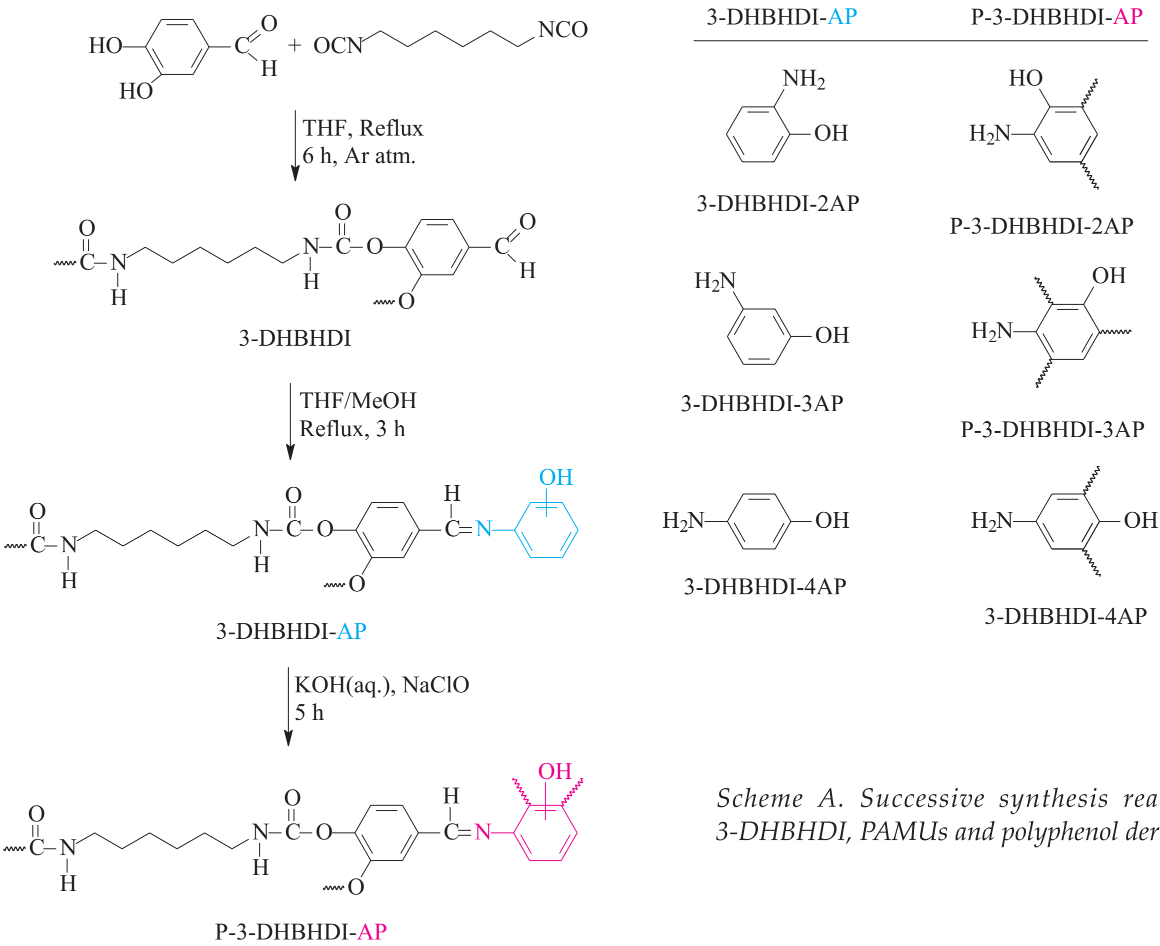
3,4-dihydroxybenzaldehyde, hexamethylene diisocyanate (HDI), 2-aminophenol (2-AP), 3-aminophenol (3-AP), 4-aminophenol (4-AP), dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), methanol, acetonitrile, acetone, toluene, ethyl acetate, $CHCl_3$, H_2SO_4, KOH, and HCl were supplied by Merck Chemical Co. (Germany) and they were used as received. 30 % aqueous solution of sodium chlorate(I) (NaClO) was supplied by Paksoy Chemical Co. (Turkey).

Synthesis of 3-DHBHDI

4-formyl-2-hydroxyphenyl-6-formamidohexylcarbamate (3-DHBHDI) was synthesized by copolymerization reaction of 3,4-dihydroxybenzaldehyde with hexamethylene diisocyanate (HDI) under the argon atmosphere according to Scheme A. The synthesis procedure of 3-DHBHDI is as follows: 3.0 g of HDI ($1.8 \cdot 10^{-2}$ mol) was dissolved in 50 cm^3 of THF and added into a 250 cm^3 three-necked round-bottom flask fitted with condenser, magnetic stirrer and inert argon gas supplier. The solution was heated up to 60 °C and equivalent amount 2.5 g of 3,4-dihydroxybenzaldehyde ($1.8 \cdot 10^{-2}$ mol) was added into the flask. The reaction mixture was maintained for 6 h, cooled at the room temperature, and kept for 24 h. THF was removed in evaporator. Obtained 3-DHBHDI was washed with methanol (twice, each time using 50 cm^3), acetonitrile (twice, each time using 50 cm^3), and water (twice, each time using 100 cm^3) to remove the unreacted components. The product was dried in a vacuum oven at 75 °C for 24 h. The final yield was 97 % [24].

Syntheses of the PAMUs

Preformed 3-DHBHDI was used in synthesizing of the PAMUs [2-hydroxy-4-(2-hydroxybenzoyl)phenyl-6-formamidohexylcarbamate, (3-DHBHDI-2AP), 2-hydroxy-4-(3-hydroxybenzoyl)phenyl-6-formamidohexylcarbamate (3-DHBHDI-3AP) or 2-hydroxy-4-(4-hydroxybenzoyl)phenyl-6-formamidohexylcarbamate (3-HBHDI-4AP)]. Reactions (Scheme A) were carried out by grafting aminophenol onto 3-DHBHDI. Synthesis procedure of PAMU is as follows: 0.93 g of 3-DHBHDI ($3 \cdot 10^{-3}$ mol) was dissolved in 60 cm^3 of DMF/CH_3OH (1/3) mixture and added into a 250 cm^3 three-necked round-bottom flask fitted with condenser and magnetic stirrer. The solution was heated up to 60 °C



Scheme A. Successive synthesis reactions of 3-DHBHDI, PAMUs and polyphenol derivatives

and equivalent amount 0.327 g ($3 \cdot 10^{-3}$ mol) of aminophenol (2-AP, 3-AP or 4-AP) was added into the flask. The reactions mixture were maintained for 3 h, cooled at the room temperature. The obtained PAMU was washed with methanol (twice, each time using 50 cm^3), acetonitrile (twice, each time using 50 cm^3), and distilled water (twice, each time using 100 cm^3) to remove the unreacted components. The product was dried in a vacuum oven at 75 °C for 24 h. Yields of these reactions for 3-DHBHDI-2AP, 3-DHBHDI-3AP, and 3-DHBHDI-4AP, reached 91, 59, and 83 %, respectively [25].

Syntheses of the polyphenol derivatives of PAMUs

The polyphenol derivatives of PAMUs (P-3-DHBHDI-2AP, P-3-DHBHDI-3AP and P-3-DHBHDI-4AP) were synthesized *via* oxidative polycondensation of 3-DHBHDI-2AP, 3-DHBHDI-3AP or 3-DHBHDI-4AP with 30 % aqueous solution of NaClO. 0.8 g of 3-DHBHDI-2AP, 3-DHBHDI-3AP or 3-DHBHDI-4AP ($2 \cdot 10^{-3}$ mol) was dissolved in 30 % aqueous solution of KOH (0.03 mol) and placed into a 50 cm^3 three-necked round-bottom flask. It was fitted with a condenser, thermometer, stirrer and additionally with funnel containing NaClO (0.122 mol). NaClO was added dropwise for about 20 min. The reaction mixtures were then heated to 80 °C. The reaction mixtures were cooled to room temperature, and then 37 % aqueous solution of HCl (0.03 mol) was added. For the separation of mineral salts, the mixture was filtered and three times washed in 25 cm^3 of hot water. Then, unreacted PAMUs were separated from the reaction products by washing with ethanol and dried in a vacuum oven at 60 °C. P-3-DHBHDI-2AP, P-3-DHBHDI-3AP and P-3-DHBHDI-4AP was obtained with yields 37, 44 and 57 %, respectively [26]. All the synthesis procedures were summarized in Scheme A.

Methods of testing

The solubility tests were carried out in different solvents, using 1 mg sample and 1 cm^3 of solvent at 25 °C.

The infrared and ultraviolet-visible spectra were determined by Perkin Elmer FT-IR Spectrum and Perkin Elmer Lambda 25, respectively. The FT-IR spectra were recorded using universal ATR sampling accessory (4000—550 cm^{-1}). UV-vis spectra of the synthesized compounds were determined using dimethyl sulfoxide (DMSO) as a solvent. ^1H NMR and ^{13}C NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were also recorded using deuterated DMSO-d_6 as a solvent at 25 °C. Tetramethylsilane (TMS) was used as internal standard.

Thermal data were obtained using Perkin Elmer Diamond Thermal Analysis. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were made between 20 and 1000 °C (in N$_2$, at 10 °C/min). Differential scanning calorimetry (DSC) analyses were carried out between 25 and 420 °C (in N$_2$, at 20 °C/min) using Perkin Elmer Pyris Sapphire DSC.

Physical changes of the synthesized polyurethane (3-DHBHDI) with exposing to the thermal degradation steps are displayed as photographs obtained using a "Mettler Toledo MP70".

The number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$) and dispersity ($Đ$) were determined with size exclusion chromatography (SEC) techniques of Shimadzu Co. For SEC investigations, an SGX (100 Ĺ and 7 nm diameter loading material) 3.3 mm i.d. x 300 mm columns was used. As an eluent DMF (0.4 cm^3/min) were used with polystyrene as a standard. Moreover, a UV detector was used to analyze the products at 25 °C.

The fluorescence spectra were recorded using a Shimadzu RF-5301PC spectrofluorofotometer.

RESULTS AND DISCUSSION

Solubility and structures of the PUR, PAMUs, and polyphenol derivatives

3-DHBHDI is a light brown colored solid while 3-DHBHDI-2AP is dark brown, 3-DHBHDI-3AP is dark red, 3-DHBHDI-4AP, P-3-DHBHDI-2AP, P-3-DHBHDI-3AP, and P-3-DHBHDI-4AP are black colored. The solubility test results are shown in Table 1. According to the obtained results all of the synthesized compounds are completely soluble only in strongly polar solvents like DMSO and DMF while they are completely insoluble in toluene. 3-DHBHDI is partly soluble in acetonitrile and insoluble in methanol, THF, ethyl acetate, CHCl$_3$, and acetone. 3-DHBHDI-2AP is completely soluble in THF and partly soluble in methanol, acetonitrile, ethyl acetate, CHCl$_3$, and acetone. 3-DHBHDI-3AP is insoluble while 3-DHBHDI-4AP and P-3-DHBHDI-2AP are partly soluble in all solvents used except DMSO and DMF. P-3-DHBHDI-3AP is partly soluble in THF and insoluble in methanol, acetonitrile, ethyl acetate, CHCl$_3$, and acetone. P-3-DHBHDI-4AP is partly soluble in methanol but insoluble in THF, acetonitrile, and acetone.

FT-IR spectra of the starting materials and the synthesized compounds are given in Figures 1 and 2. Their FT-IR spectral data are also given in Table 2. According to Figure 1 at the spectrum of HDI characteristic isocyanate -C=O and -C=N peaks are observed at 2250 and 1584 cm^{-1}, respectively, which agrees with the literature values [27]. At the spectrum of 3,4-dihydroxy benzaldehyde characteristic aldehyde and -OH peaks are observed at 1751 and 3206 cm^{-1}, respectively. As can be seen in Table 2, an -OH

T a b l e 1. Solubility tests of the synthesized compounds (meaning of symbols: + soluble, — insoluble, ⊥ partly soluble)

Solvent	3-DHBHDI	3-DHBHDI-2AP	3-DHBHDI-3AP	3-DHBHDI-4AP	P-3-DHBHDI-2AP	P-3-DHBHDI-3AP	P-3-DHBHDI-4AP
Methanol	—	⊥	—	⊥	⊥	—	⊥
THF	—	+	—	⊥	⊥	⊥	—
Acetonitrile	⊥	⊥	—	⊥	⊥	—	—
Ethyl acetate	—	⊥	—	⊥	⊥	—	—
CHCl$_3$	—	⊥	—	⊥	⊥	—	—
Acetone	—	⊥	—	⊥	⊥	—	—
DMF	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+
Toluene	—	—	—	—	—	—	—

T a b l e 2. FT-IR spectrum data of synthesized compounds and starting materials

Compound	Vave number of characteristic bands, cm^{-1}							
	urethane -NH	urethane -C=O	imine -N=CH	aliphatic -CH	aldehyde -CHO	isocyanate -C=O	isocyanate -C=N	-OH
HDI	—	—	—	2938, 2862	—	2250	1584	—
3,4-dihydroxybenzaldehyde	—	—	—	—	1751	—	—	3206
3-DHBHDI	3323	1690	—	2930, 2850	1717	—	—	—
3-DHBHDI-2AP	3305	1696	1647	2933, 2857	—	—	—	—
3-DHBHDI-3AP	3309	1692	1649	2933, 2856	—	—	—	—
3-DHBHDI-4AP	3285	1698	1653	2931, 2856	—	—	—	—
P-3-DHBHDI-2AP	3333	1694	1639	2933, 2857	—	—	—	—
P-3-DHBHDI-3AP	3325	1680	1649	2933, 2856	—	—	—	—
P-3-DHBHDI-4AP	3290	1698	1629	2932, 2857	—	—	—	—

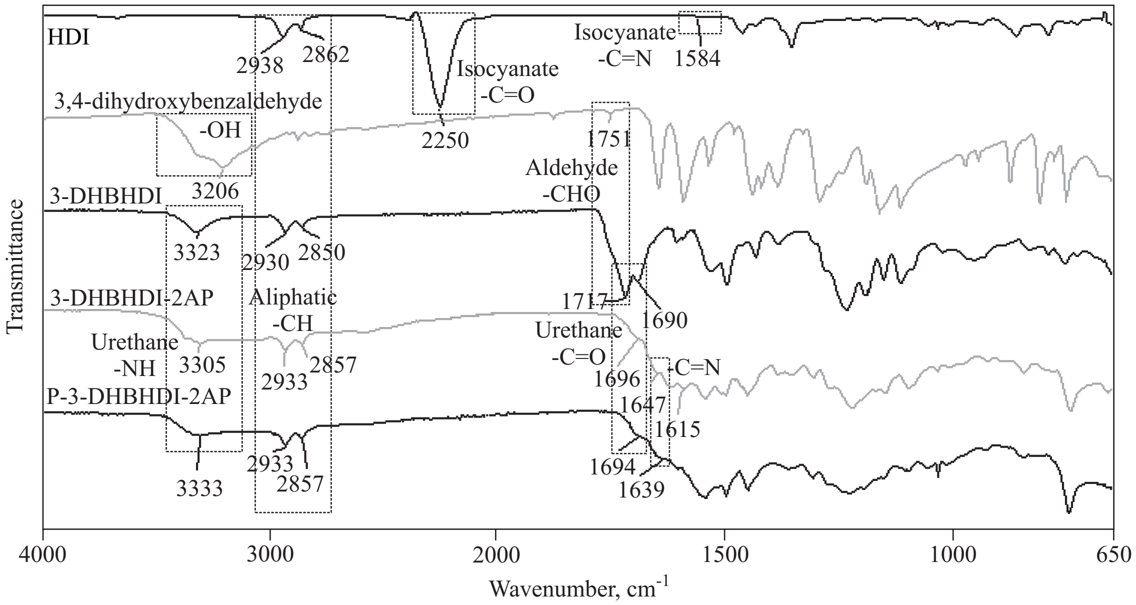


Fig. 1. FT-IR spectra of HDI, 3,4-dihydroxy benzaldehyde, 3-DHBHDI, 3-DHBHDI-2AP and P-3-DHBHDI-2AP

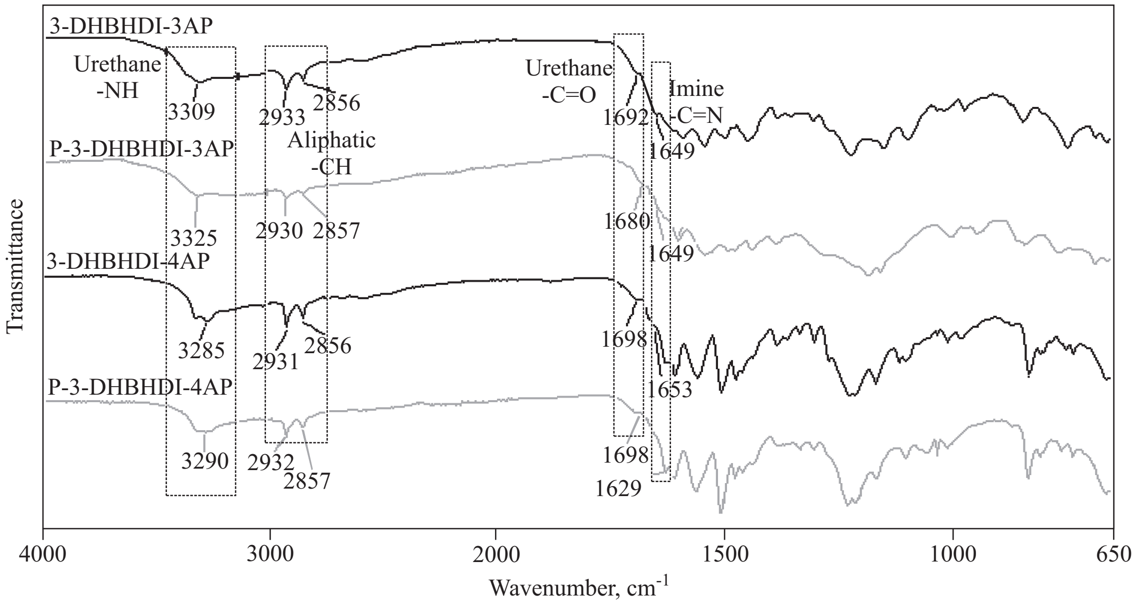


Fig. 2. FT-IR spectra of 3-DHBHDI-3AP, P-3-DHBHDI-3AP, 3-DHBHDI-4AP and P-3-DHBHDI-4AP

group at 3,4-dihydroxy benzaldehyde and -C=O and -C=N stretch vibrations of HDI disappear due to the urethane formation. Moreover, at the FT-IR spectrum of 3-DHBHDI new peaks appear at 3323 and 1690 cm^{-1}, respectively, which could be attributed to urethane -N-H and carbonyl (-C=O) stretch vibrations, respectively. Similarly, at the FT-IR spectra of 3-DHBHDI-2AP and P-3-DHBHDI-2AP these peaks are observed at 3305, 3333 and 1696, 1694 cm^{-1}, respectively. At the spectra of 3-DHBHDI-3AP, 3-DHBHDI-4AP, P-3-DHBHDI-3AP, and P-3-DHBHDI-4AP the same peaks are observed at 3309, 3285, 3325, and 3290, respectively for -N-H and 1692, 1698, 1680, and 1698 cm^{-1}, respectively for -C=O. Also, at the spectra of the PAMUs and polyphenol derivatives the aldehyde peak disappears because of the azomethine formation which is placed at 1717 cm^{-1} at the spectrum of 3-DHBHDI. According to Figs. 1 and 2 azomethine bonds (-C=N) in the structures of the synthesized compounds are observed between 1629 and 1653 cm^{-1}. The values of the azomethine peaks of the polyphenol derivatives are a bit lower than those of PAMUs. This is probably due to the electron withdrawing effect of the urethane groups in the polymer structures which decreases the electron density of imine carbon and consequently imine vibration, as observed in the previous studies [27]. Observed results clearly confirm the polyurethane formation.

UV-vis spectra of the synthesized compounds are comparatively given in Figure 3. According to the figure, the absorption peak of 3-DHBHDI appeared at 299 nm

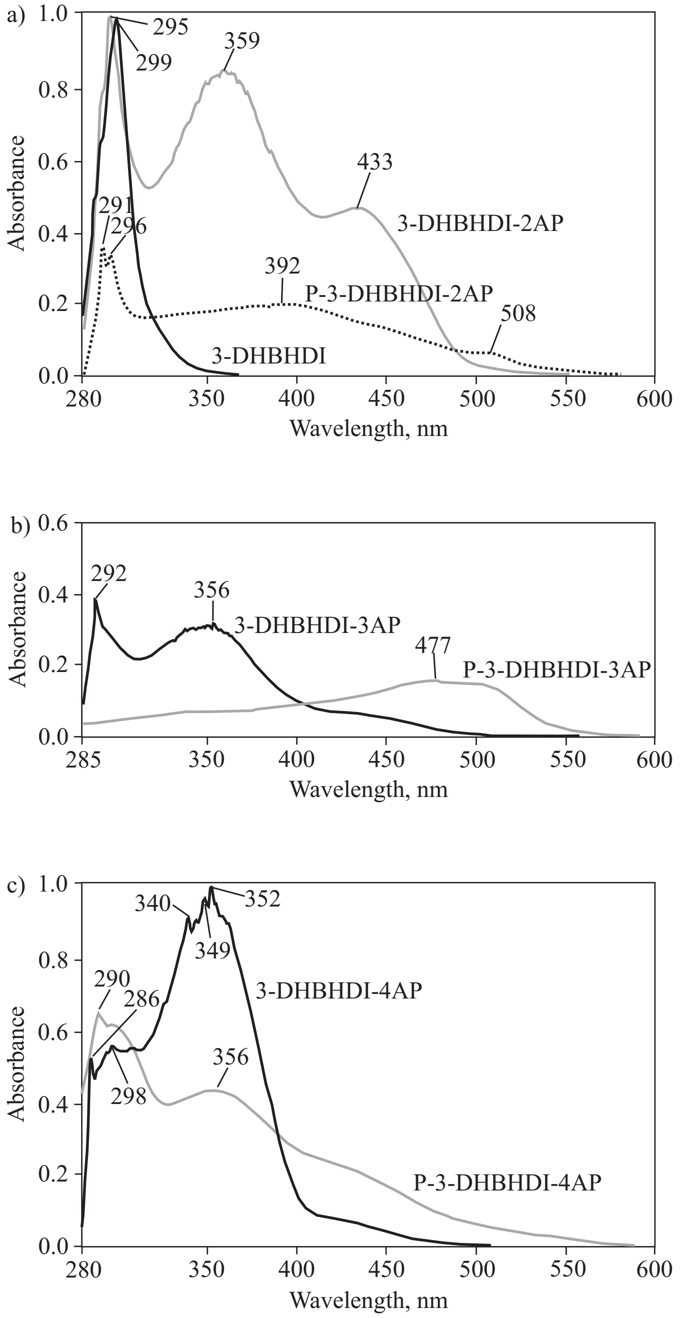


Fig. 3. UV-vis spectra of: a) 3-DHBHDI, 3-DHBHDI-2AP, P-3-DHBHDI-2AP; b) 3-DHBHDI-3AP, P-3-DHBHDI-3AP; c) 3-DHBHDI-4AP, P-3-DHBHDI-4AP

due to the urethane group in the structure. It is clearly observed that after the graft copolymerization onto 3-DHBHDI new peaks at around 350—360 nm and 430 nm appear indicating the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the formed azomethine linkage. Similar peaks are also observed at the polyphenols' spectra. However, the polyphenol derivatives have red shifted spectra as compared to the PAMUs, indicating the higher conjugation. Observed results show that the conjugation of the synthesized compounds increases stepwise during the graft copolymerization and the oxidative polycondensation reaction which results in lower band gaps.

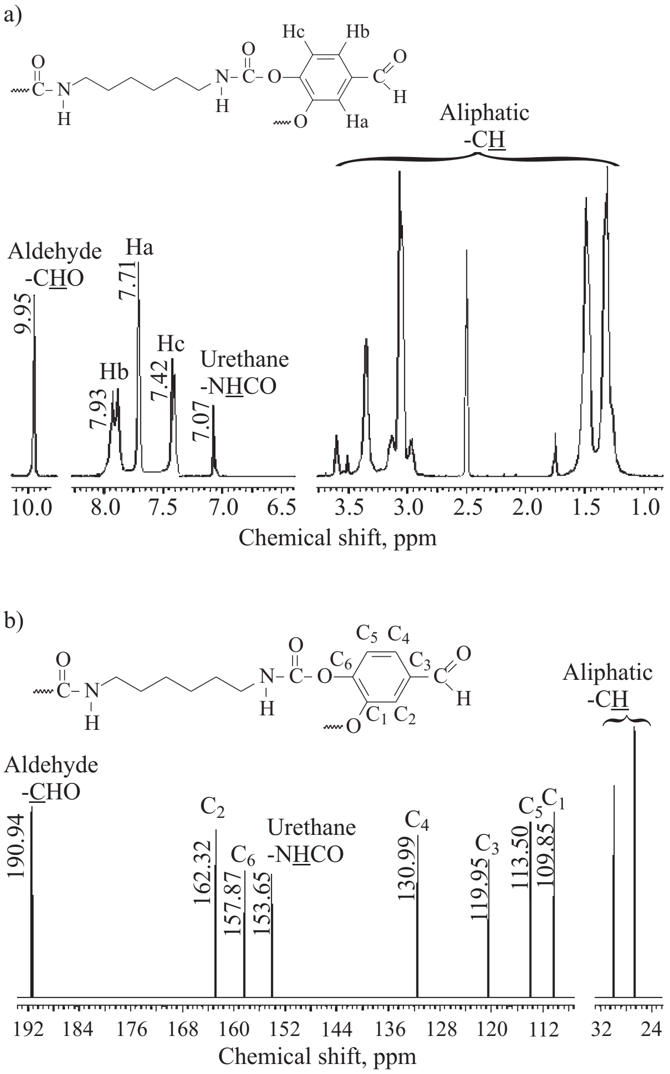


Fig. 4. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of 3-DHBHDI

^{1}H NMR and ^{13}C NMR spectra of 3-DHBHDI are also given in Figure 4. According to Fig. 4a urethane and aldehyde protons (-NHCO and -CHO) are observed at 7.07 and 9.95 ppm, respectively. Also aliphatic protons are observed between 1.0 and 4.0 ppm. ^{13}C NMR spectrum of 3-DHBHDI at Fig. 4b also confirms the structure by the peaks observed at 153.65 and 190.94 ppm, which could be attributed to the urethane and aldehyde carbons, respectively. Additionally, aliphatic -CH peaks are observed between 24 and 32 ppm. These results clearly show that the synthesized polyurethane is obtained with the proposed structures shown in Scheme A.

^{1}H NMR spectra of 3-DHBHDI-2AP, 3-DHBHDI-3AP, 3-DHBHDI-4AP and their polyphenol derivatives are also given in Figures 5 and 6, respectively. According to Fig.5 -OH protons are observed at 9.83, 9.19 and 8.73 ppm for 3-DHBHDI-2AP, 3-DHBHDI-3AP, and 3-DHBHDI-4AP, respectively. At the spectra of P-3-DHBHDI-2AP, P-3-DHBHDI-3AP, and P-3-DHBHDI-4AP the same peaks are observed at 9.83, 9.19, and 8.91 ppm, respectively. Imine (-CH=N) protons of 3-DHBHDI-2AP, 3-DHBHDI-3AP, 3-DHBHDI-4AP,

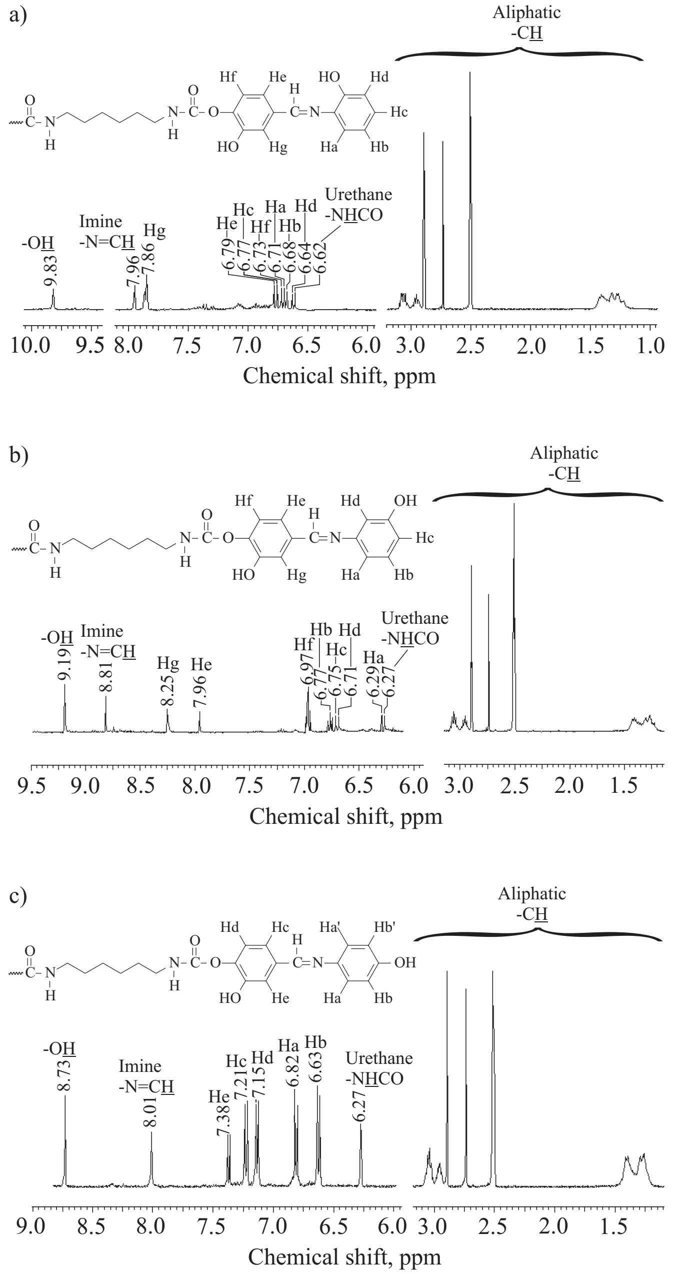


Fig. 5. ^1H NMR spectra of: a) 3-DHBHDI-2AP, b) 3-DHBHDI-3AP, c) 3-DHBHDI-4AP

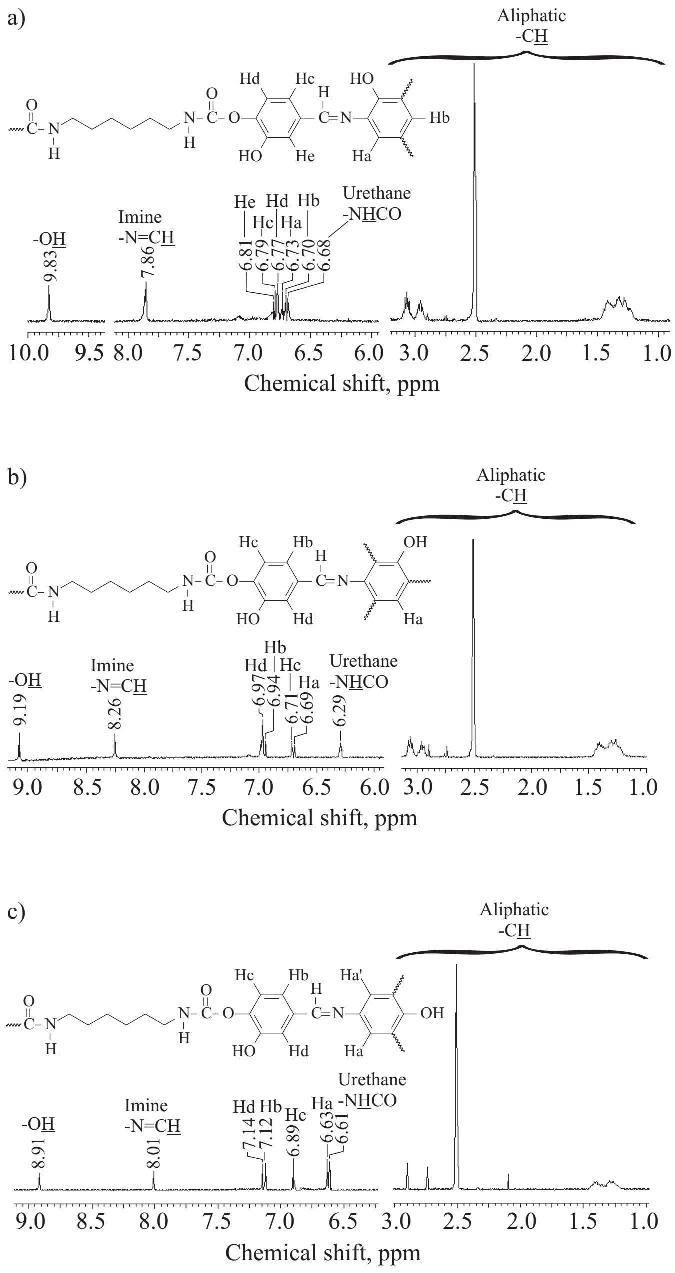


Fig. 6. ^1H NMR spectra of: a) P-3-DHBHDI-2AP, b) P-3-DHBHDI-3AP, c) P-3-DHBHDI-4AP

P-3-DHBHDI-2AP, P-3-DHBHDI-3AP, and P-3-DHBHDI-4AP are also observed at 7.96, 8.81, 8.01, 7.86, 8.26, and 8.01 ppm, respectively. Urethane (-N$\underline{H}$CO) protons of 3-DHBHDI-2AP, 3-DHBHDI-3AP, 3-DHBHDI-4AP, P-3-DHBHDI-2AP, P-3-DHBHDI-3AP, and P-3-DHBHDI-4AP are observed at 6.62, 6.27, 6.27, 6.68, 6.29, and 6.61 ppm, respectively. Also aliphatic -C$\underline{H}$ protons are observed between 1.0 and 3.0 ppm for both the PAMUs and their polyphenol derivatives.

SEC and fluorescence measurements

According to the SEC chromatograms, the calculated number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$), and dispersity ($Đ$) values of the synthesized PAMUs measured using UV detector are given in Table 3. According to Table 3 the synthesized PAMUs (3-DHBHDI-2AP, 3-DHBHDI-3AP and 3-DHBHDI-4AP) have higher molecular weights than the starting polyurethane (3-DHBHD). Similarly, polyphenol derivatives of the PAMUs (P-3-DHBHDI-2AP, P-3-DHBHDI-3AP and P-3-DHBHDI-4AP) have also higher molecular weights than the PAMUs as expected. This is the evidence of the increasing molecular weights during the polymerization steps. According to the total values the synthesized PAMUs have nearly 10—12 repeated units. Similarly, the polyphenol derivatives, P-3-DHBHDI-2AP, P-3-DHBHDI-3AP, and P-3-DHBHDI-4AP, have about 60—61, 20—21, and 56—57 repeated units, respectively.

T a b l e 3. SEC analyses results of the synthesized compounds

Compound	Total			Molecular weight distribution							
				fraction I				fraction II			
	$\overline{M}_n$	$\overline{M}_w$	Đ	$\overline{M}_n$	$\overline{M}_w$	Đ	%	$\overline{M}_n$	$\overline{M}_w$	Đ	%
3-DHBHDI	3350	3560	1.063	5380	6100	1.133	33	2350	2360	1.004	67
3-DHBHDI-2AP	4800	5000	1.042	4800	5000	1.042	100	—	—	—	—
3-DHBHDI-3AP	4200	5200	1.238	4200	5200	1.238	100	—	—	—	—
3-DHBHDI-4AP	4600	4900	1.065	4600	4900	1.065	100	—	—	—	—
P-3-DHBHDI-2AP	24 900	36 000	1.445	24 900	36 000	1.445	100	—	—	—	—
P-3-DHBHDI-3AP	8300	9100	1.096	8300	9100	1.096	100	—	—	—	—
P-3-DHBHDI-4AP	23 400	29 150	1.245	23 400	29 150	1.245	100	—	—	—	—

T a b l e 4. Fluorescence spectral data of the synthesized compounds (λ_{Ex} — excitation wavelength for emission, λ_{Em} — emission wavelength for excitation, $\lambda_{max(Ex)}$ — maximum emission wavelength, $\lambda_{max(Em)}$ — maximum excitation wavelength, I_{Ex} — maximum excitation intensity, I_{Em} — maximum emission intensity

Compound	Concentration, mg/dm^3	λ_{Ex}	λ_{Em}	$\lambda_{max(Ex)}$	$\lambda_{max(Em)}$	I_{Ex}	I_{Em}
3-DHBHDI-2AP	2.400	503	524	500	536	551	504
3-DHBHDI-3AP	0.018	279	320	283	314	67	62
P-3-DHBHDI-2AP	0.018	504	560	503	550	762	679
P-3-DHBHDI-3AP	0.009	289	320	284	311	40	36
P-3-DHBHDI-4AP	0.009	305	340	300	337	19	20

Fluorescence measurements of the synthesized compounds are carried out using DMF for PUR, PAMUs, and their polyphenol derivatives. Measurements are made for various concentrations to determine the optimal conditions. Figures 7 and 8 show the excitation and emission spectra of 3-DHBHDI-2AP, 3-DHBHDI-3AP, P-3-DHBHDI-2AP, P-3-DHBHDI-3AP, and P-3-DHBHDI-4AP in DMF. These figures also indicate the concentration-fluorescence intensity relationships of the compounds. As can be seen in these figures the optimum concentration to obtain maximal emission-excitation intensities vary between 2.4 and 0.01875 mg/dm^3. The obtained results are also summarized in Table 4. These results clearly indicate that the PAMUs derived from 2-aminophenol, 3-DHBHDI-2AP and P-3-DHBHDI-2AP, have significantly higher fluorescence wavelengths and intensities than the others. 3-DHBHDI-2AP and P-3-DHBHDI-2AP give the emission peaks at 536 and 550 nm with the intensities of 504 and 679 a.u., respectively, while the others show relatively lower peak wavelengths in the range of 310—340 nm and the intensities between 20 and 70 a.u. Fluorescence characteristics of 3-DHBHDI-2AP resembles those of “Acridine orange” presented in the literature [28]. Acridine orange has the excitation and emission peaks at 500 and 530 nm, respectively. Similarly, the new presented PAMU, 3-DHBHDI-2AP, has the 500 nm excitation and 536 nm emission peaks. As a result, 3-DHBHDI-2AP and P-3-DHBHDI-2AP could be used as the alternative

T a b l e 5. TGA data of the synthesized compounds (T_{on} — thermal degradation onset temperature, T_{max} — maximum weight loss temperature, T_{end} — final thermal degradation temperature)

Compound	First degradation temperature, °C				Second degradation temperature, °C				Third degradation temperature, °C				Char at 1000 °C %	Loss of absorbed solvent %
	T_{on}	T_{max}	T_{end}	Percentage of weight loss	T_{on}	T_{max}	T_{end}	Percentage of weight loss	T_{on}	T_{max}	T_{end}	Percentage of weight loss		
3-DHBHDI	169	192	253	28	253	365	405	22	405	445	1000	24	25	1
3-DHBHDI-2AP	172	231	320	47	320	339	397	8	397	445	1000	25	18	3
3-DHBHDI-3AP	214	250	393	46	393	446	1000	26	—	—	—	—	26	3
3-DHBHDI-4AP	249	262	398	42	398	447	1000	22	—	—	—	—	31	6
P-3-DHBHDI-2AP	189	219	387	43	387	444	1000	30	—	—	—	—	25	2
P-3-DHBHDI-3AP	212	256	377	31	377	445	1000	30	—	—	—	—	36	4
P-3-DHBHDI-4AP	228	267	291	18	291	329	393	22	393	444	1000	26	28	6

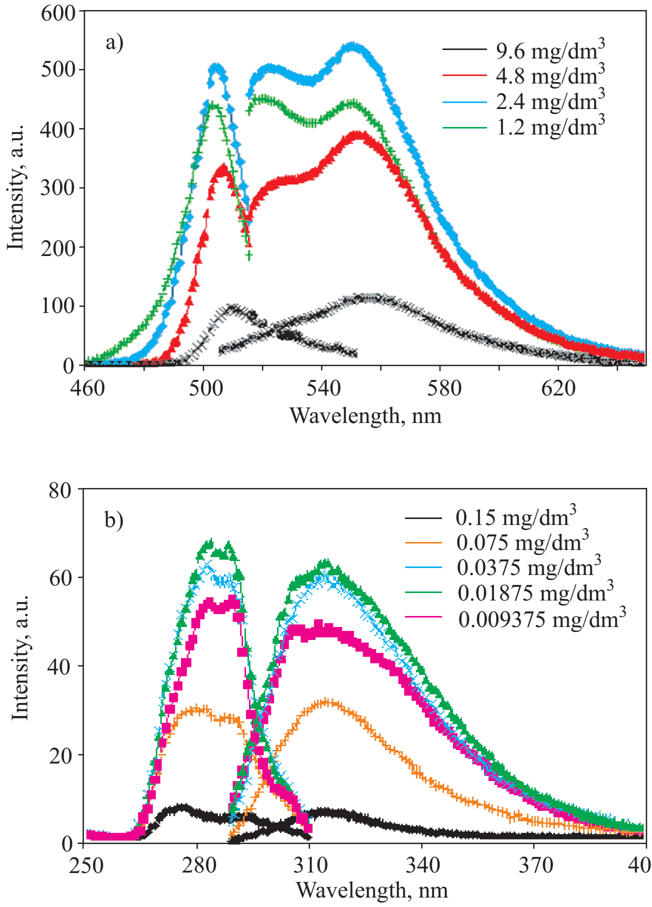


Fig. 7. Emission and excitation spectra of solutions at various concentrations of 3-DHBHDI-2AP (a) and 3-DHBHDI-3AP (b) in DMF; slit width: λ_{Ex} — 3 nm, λ_{Em} — 3 nm

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

Thermal characterization

Thermograms of the synthesized compounds are given in Figure 9. The results of TGA are also summarized in Table 5. According to the obtained TG curves 3-DHBHDI, 3-DHBHDI-2AP, and P-3-DHBHDI-4AP decompose in three steps while the others decompose in two steps between 20 and 1000 °C. Table 5 indicates that 3-DHBHDI-4AP has the highest onset temperature (T_{on}). Many of the synthesized PAMUs have quite high T_{on} values, above 210 °C. However, the initial polyurethane (3-DHBHDI), PAMU and its polyphenol derivative synthesized using 2-aminophenol as the grafting agent (3-DHBHDI-2AP and P-3-DHBHDI-2AP) have relatively

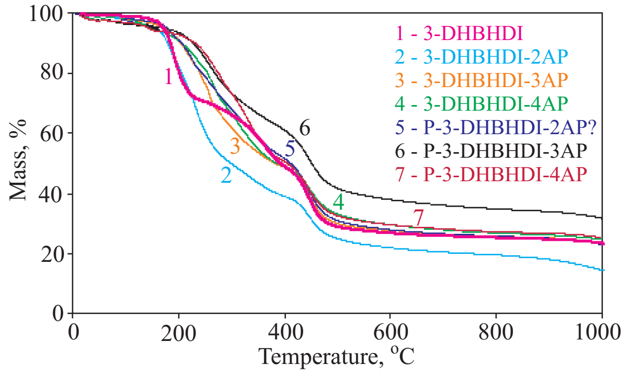


Fig. 9. Thermograms of the synthesized compounds

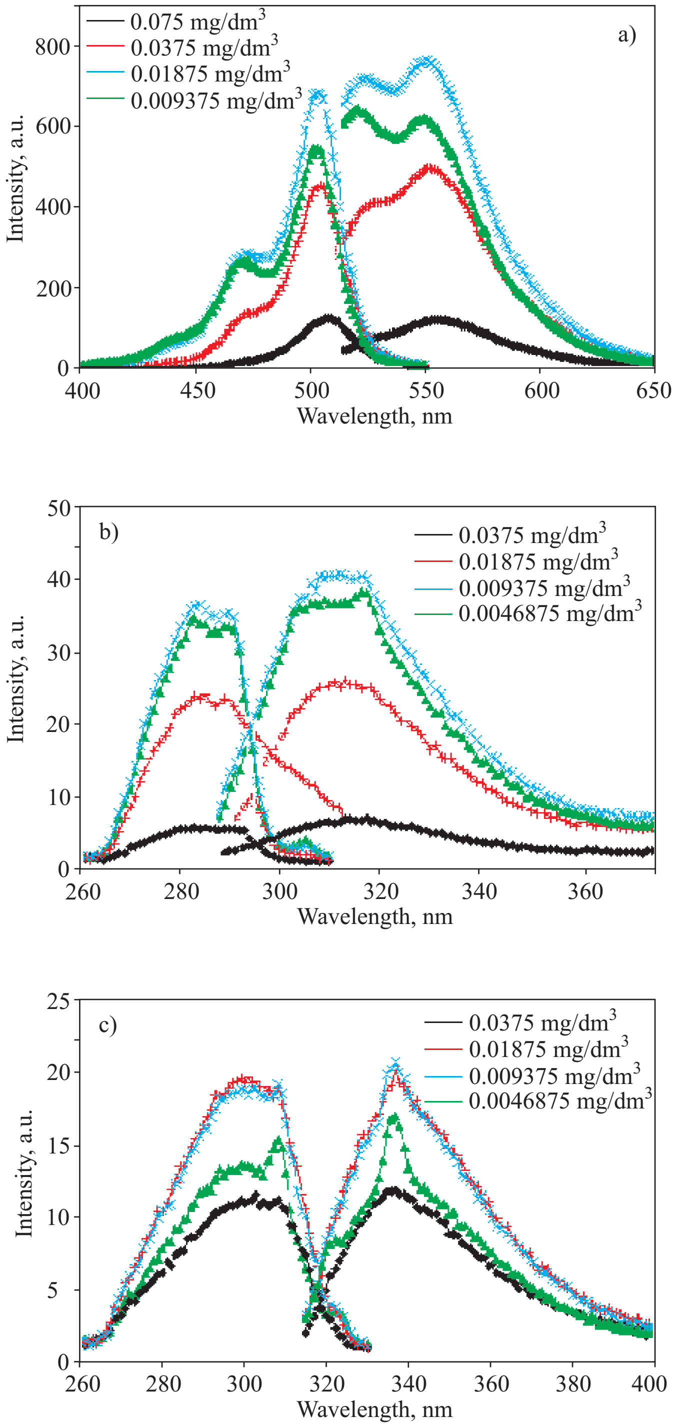


Fig. 8. Emission and excitation spectra of solutions at various concentrations of P-3-DHBHDI-2AP (a), P-3-DHBHDI-3AP (b) and P-3-DHBHDI-4AP (c) in DMF; slit width: λ_{Ex} — 3 nm, λ_{Em} — 3 nm

low T_{on} values between 170 and 190 °C indicating the lower thermal stability. Values of the char at 1000 °C for all investigated PAMUs are in the range 18—36 %.

Table 6. DTA and DSC data of the synthesized compounds (T_g — glass transition temperature, ΔC_p — change of the heat capacity at constant pressure)

Compound	DTA		DSC	
	Endothermic peak temperature, °C	Exothermic peak temperature, °C	T_g °C	ΔC_p J(mol·K)
3-DHBHDI	158, 386	234	138	0.475
3-DHBHDI-2AP	187	—	162	0.057
3-DHBHDI-3AP	233, 274	313	153	0.050
3-DHBHDI-4AP	260	—	181	0.048
P-3-DHBHDI-2AP	—	—	178	0.115
P-3-DHBHDI-3AP	258	—	171	0.020
P-3-DHBHDI-4AP	150, 280	—	214	0.116

The obtained results of DTA and DSC investigation are summarized in Table 6. According to DSC curves the determined glass transition temperatures (T_g) are between 138 and 214 °C. The broad peaks until 138 °C could be attributed to the absorbed solvent removal [29].

Thermal degradation photographs obtained for 3-DHBHDI at various temperatures, presented in Figure 10 indicate an apparent color change from light to dark with increasing temperature. At 140 °C the color is light yellow, while above 145 °C the color becomes gradually darker due to the first degradation step of 3-DHBHDI, as given in Fig. 10 and Table 5.

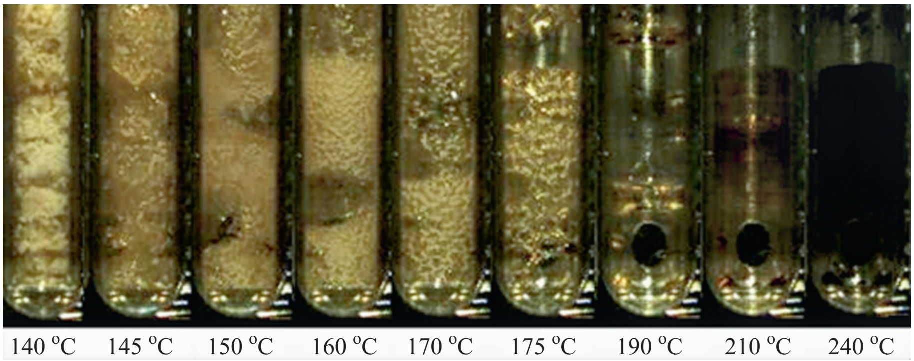
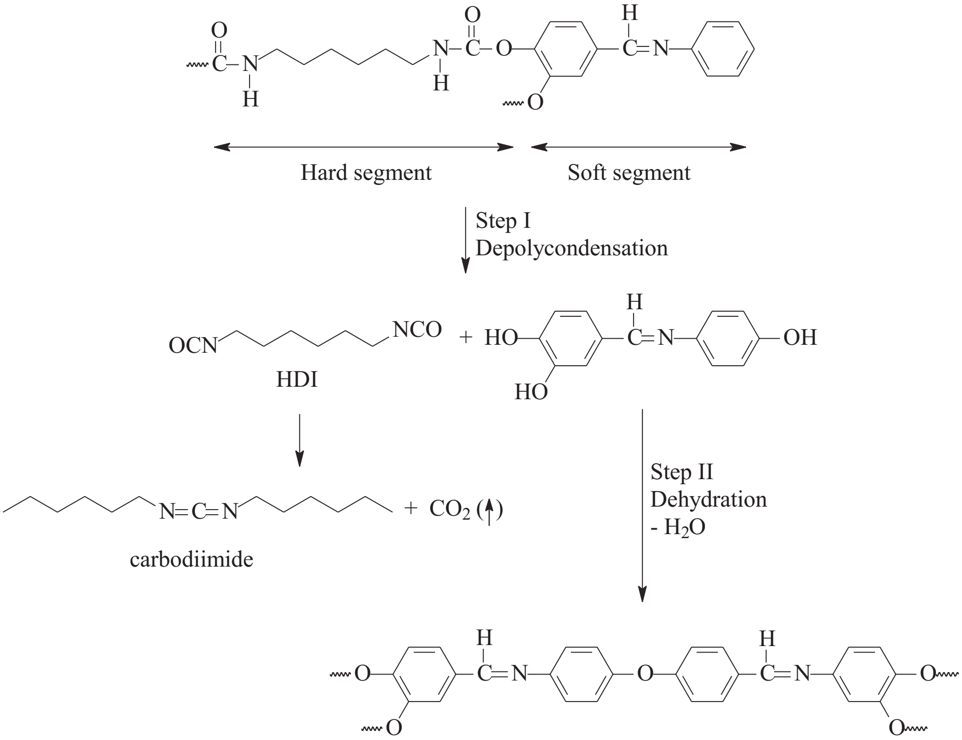


Fig. 10. Photographs of various steps of 3-DHBHDI thermal degradation



Scheme B. Thermal degradation steps of 3-DHBHDI-4AP

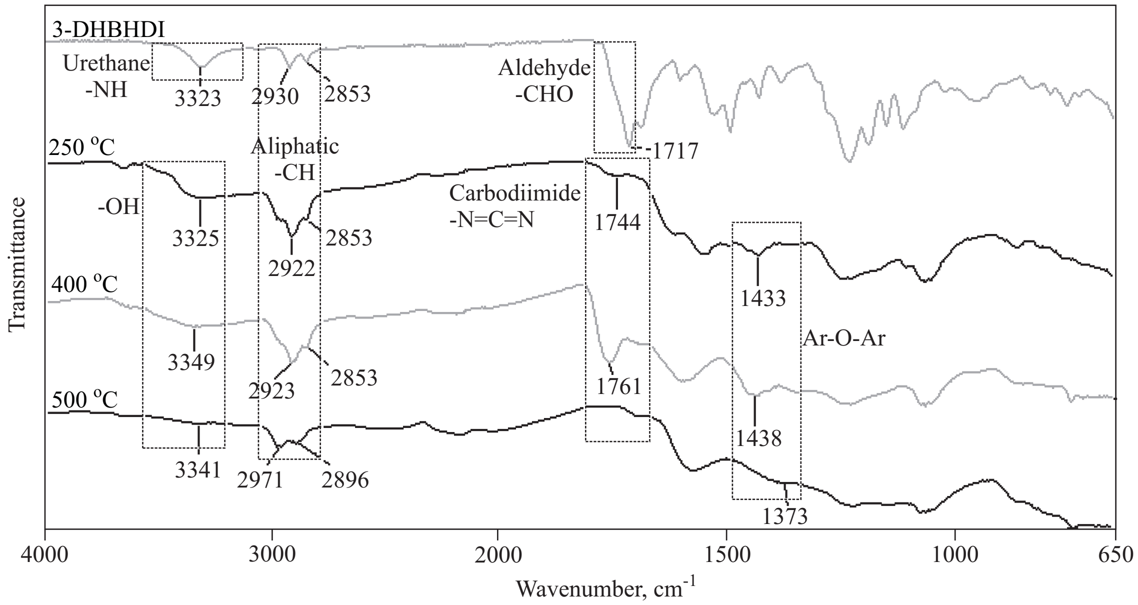


Fig. 11. FT-IR spectra of 3-DHBHDI after heating up to various temperatures

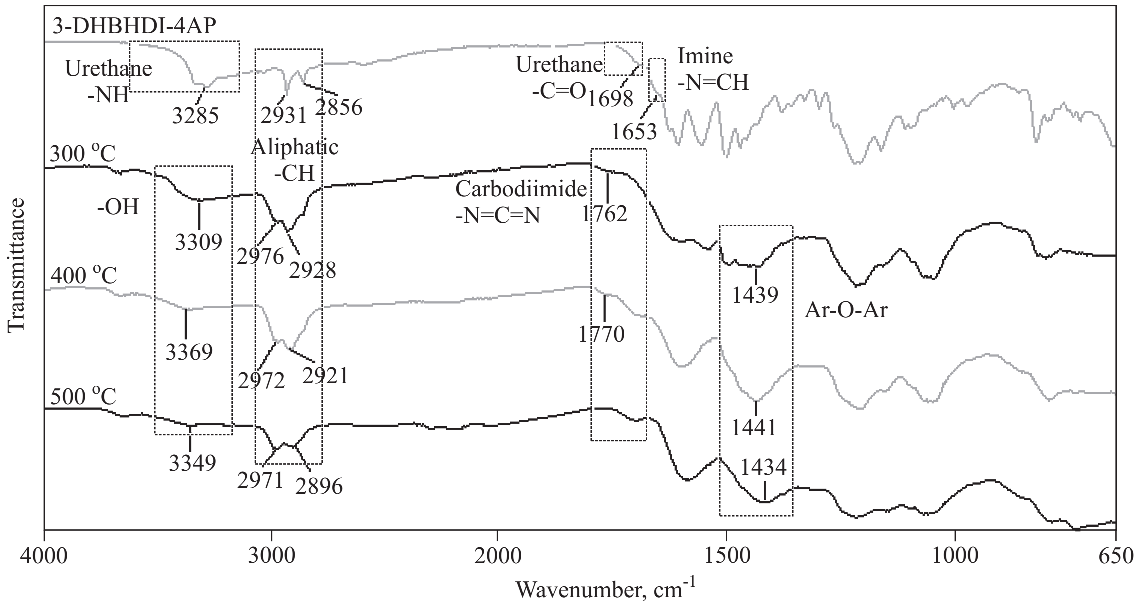


Fig. 12. FT-IR spectra of 3-DHBHDI-4AP after heating up to various temperatures

As it is known the thermal degradation of PURs occurs in two to three steps [30—33]. The example of such process for 3-DHBHDI-4AP is presented in Scheme B. The first step is a depolycondensation process that is associated with 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 step of degradation include decomposition of the soft segment by dehydration process. The thermal stability of PURs depends primarily on the polymerization ⇆ depolymerization equilibria with participation of the functional groups in the polymer molecule [34, 35]. The isocyanate formed during thermal decomposition may be dimerized to carbodiimide. Carbodiimide can then react with urethane groups to form a cross linked structure.

To explain the thermal degradation steps of the synthesized 3-DHBHDI, 3-DHBHDI-4AP, and P-3-DHBHDI-4AP, FT-IR spectra of the products after heating up to various temperatures are given in Figures 11—13. At the spectra of 3-DHBHDI characteristic carbodiimide (-N=C=N) peak is observed at 1744 cm^{-1} for 250 °C, and 1761 cm^{-1} for 400 °C, which agree with the literature values [36]. At 500 °C this peak disappears because of deformation of the -N=C=N bond to form new volatile products. Similarly, at the spectra of 3-DHBHDI-4AP and P-3-DHBHDI-4AP, these peaks appear at 1762 and 1760 cm^{-1} for 300 °C, and at 1770 and

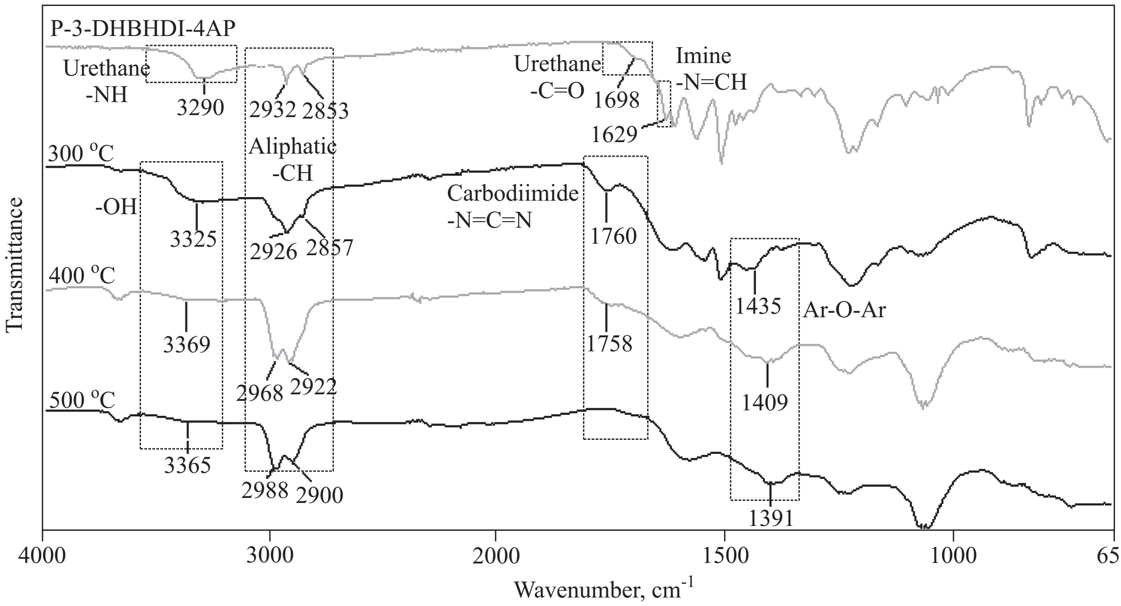


Fig. 13. FT-IR spectra of P-3-DHBHDI-4AP after heating up to various temperatures

1758 cm^{-1} for 400 °C, respectively and disappear at 500 °C. Additionally, after the depolymerization step with heating up to higher temperatures -OH functionalized obtained compounds are expected to form new ether-bridged structures with dehydration [36]. As it can be seen in Figs. 11—13, when 3-DHBHDI, 3-DHBHDI-4AP and P-3-DHBHDI-4AP are heated up to 250 and 500 °C, respectively, new broad absorption bands appear at 1391—1444 cm^{-1} indicating the Ar-O-Ar ether bond formation. Also the intensities of -OH stretch vibrations at 3309 and 3369 cm^{-1} decrease due to the dehydration.

During the first thermal degradation step the -NH peak disappears with appearing of the -OH peak due to the depolymerization and is followed by -OH peak decreasing with increasing temperature as a result of the dehydration and polyether formation (Scheme B). This suggestion could be also confirmed by calculation of the peak integrations of -OH stretch vibrations formed after the depolymerization. The -OH peak areas of 3-DHBHDI, 3-DHBHDI-4AP and P-3-DHBHDI-4AP after exposing to different temperatures are calculated using Perkin-Elmer spectrum software (Perkin-Elmer Ltd., USA) [37]. Obtained results are shown in Figure 14. Area of the -OH peaks decrease as temperature increases because of the dehydration of the diol/triol created in the polyether formation. This is also the evidence of the proposed thermal degradation mechanism.

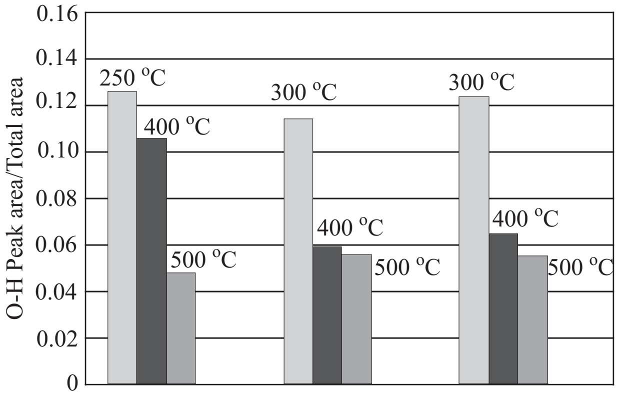


Fig. 14. Calculated O-H peak areas of 3-DHBHDI, 3-DHBHDI-4AP, and P-3-DHBHDI-4AP at different temperatures

CONCLUSIONS

New PUR, PAMUs and their polyphenol derivatives were synthesized by polycondensation, graft copolymerization and oxidative polycondensation reaction, respectively. Hexamethylene diisocyanate (HDI) was used as the comonomer agent of PUR. The obtained polymers were characterized by UV-vis, FT-IR, NMR and SEC analyses. The fluorescence spectra of the synthesized compounds obtained in DMF solutions show that the novel PAMUs derived by grafting of 2-aminophenol onto PUR are highly fluorescent and can be used in preparation of the alternative yellowish emitting diodes. However, TGA results showed that the PAMUs derived from 2-aminophenol had relatively lower thermal stabilities in comparison to the others. Thermal degradation steps of 3-DHBHDI, 3-DHBHDI-4AP, and P-3-DHBHDI-4AP were clarified using the FT-IR spectra of the degraded forms at various temperatures. Physical change of 3-DHBHDI was displayed at various temperatures showing that the color of 3-DHBHDI changed from light to dark forms as a result of the thermal degradation. DSC results showed that the new PAMUs have T_g values between 138 and 214 °C. Consequently, because of the fine thermal properties the synthesized compounds can be promising candidates for aerospace applications and they can be used to produce temperature-stable materials.

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