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Synthesis and characterization of new self-colored thermally stable poly(amide-ether-urethane)s based on an azo dye and different diisocyanates

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Abstract

In this work, four series of new self-colored segmented polymeric dyes were successfully synthesized via the reaction of an azo-based diacid, different diisosyanates and polyethylene glycol with molecular mass of 400 (PEG-400), under microwave irradiation via diisocyanate route. The polymers were characterized using FT-IR, ^{1}H NMR, UV−vis spectroscopy and flourimetery. The inherent viscosities of the poly(amide-ether-urethane)s (PAEU)s were in the range of 0.28−0.75 dL/g. Thermal properties of the PAEUs were evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). In terms of dye migration character, the PAEUs with a covalent molecule of dye are proven to have much lower thermal migration values (Mp%) than those of simple mixing of polymer and dyestuff. Solvent resistance and solvent migration of resulting colored copolymers were also compared with monomeric dye in different solvents. The resulting copolymers showed good viscosities, solvent and thermal migration resistance and good thermal stability.

Keywords: Azo dye; Dye migration; Isocyanate route; Microwave irradiation; Self-colored poly(amide-ether-urethane); UV−vis

1. Introduction

The topic of intrinsically colored polymers has received attention recently; polymeric pigments can be regarded as insoluble polymers which have a chromophoric centre within their structure. Four classes arise:

(a) Polymers, which as a result of secondary reaction become intrinsically colored;
(b) polymeric pigments derived from the formation of color sites within a substrate where hitherto they were absent such as the action of reactive dyes on natural polymers;
(c) macromolecules which are formed as a result of addition polymerization reactions in which one of the monomers is colored;
(d) intrinsically colored polymers resulting from stepwise polymerization reactions, such as the product of the reactions of multifunctional colored compounds. Within this category are the anthraquinones, azo compounds and phthalocyanines, etc. [1].

Thus, the design and synthesis of bi-functional colorants has received considerable attention because such colorants can be utilized as monomers for functional polymers via polyaddition and polycondensation reactions [2]. Owing to the inherent non-leaching behavior and good light fastness combined with the special properties of polymers [3,4], there has been much emphasis given to the synthesis of polymers containing chromophoric groups [5−9], for

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example, the aromatic azo group which can form the part of the main chain.

In addition, the aromatic azo group is of special interest because of the existence of *cis–trans* isomerism and its effect on the photochromic properties of the polymers. Therefore, polymers that contain the azo group have potential use in a variety of applications [5], such as materials with liquid-crystal [10,11] or non-linear optic properties [12]. Azobenzene-containing materials are photochromic and reversibly switch between two spectroscopically distinct forms by use of light. Thus azobenzene-based polymers are interesting due to their photoresponsive behavior which can be utilized in optical switches, optical data recording or optical information storage [13–15].

Polyurethanes (PU)s are thermoplastic elastomers that comprise repeating hard and soft segments; therefore, they possesses good mechanical properties and are widely used in synthetic leathers, fibres and adhesives [16]. For a colored PU leather, which is mostly made by non-woven fabrics coated with a mixture of pigment and PU resin, this has a lack of brightness and poor rubbing resistance. In addition, the elastic PU fibre is usually dyed with an acid dye or a disperse dye at a high temperature of 90–100 °C and a long time of 50–60 min, which will waste energy and time [17–19]. The use of dispersed pigments for coloring PU products gives rise to some problems such as limited attainable shade, nucleating effect, cleaning equipments, compatibility with polymeric products, wash fastness, migration and so on. Thus, the use of PU bonded dyes or reactive dyes offers lots of advantages [3,20,21].

On the other hand, industrial use of radiation as an alternative to thermal heating of the polymerization process has generated interest because of the faster time and improved efficiency. Recently there has been growing interest in applying microwave energy to synthetic polymer chemistry [22]. In this field, microwave energy has been utilized for the curing of polymers such as epoxy resins [23,24], polyurethanes [25,26] and for the imidization of polyamic acids [27].

In this article we wish to report the synthesis of modified thermally stable PUs with amide linkage, as well as with a covalent bond of dye molecule, by direct reaction of an azobenzene diacid, different diisocyanates and PEG polyether polyol. These self-colored PAEUs were prepared under facile and rapid microwave irradiation. The effects of different reaction conditions such as irradiation time, reaction catalysts, polymerization methods (one step vs. two step), reaction solvent and changes in the structure of diisocyanates on the polymer chain growth as well as their properties were investigated. The effects of introduction of diacid-based azo dye on different properties of resulting PAEUs such as thermal, solvent and spectroscopic properties were also studied.

2. Experimental section

2.1. Materials

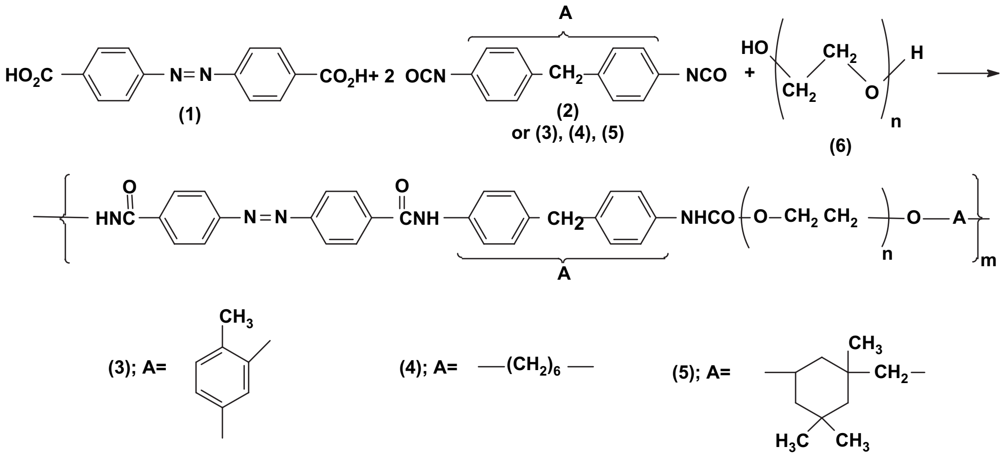
All chemicals were purchased from Aldrich, Riedel-deHaen AG, Fluka and Merck. 4,4′-methylene-bis-(4-phenylisocyanate) (MDI) (**2**), a high purity Aldrich product, was used without further purification. 2,4-Tolylene diisocyanate (TDI) (**3**) (Merck), hexamethylene diisocyanate (HDI) (**4**) (Merck), and isophorone diisocyanate (IPDI) (**5**) (Fluka) were employed as received. PEG-400 (Riedel-deHaen) was dried under vacuum at 80 °C for 8 h. *N*-Methyl pyrrolidone (NMP), and pyridine (Py) (Merck) were distilled under reduced pressure over BaO (Riedel-deHaen). 4,4′-Azodibenzenedicarboxylic acid (ABCA) (**1**) was prepared according to a typical procedure that was previously reported [28].

2.2. Instruments and measurements

Proton nuclear magnetic resonance ^{1}H NMR (500 MHz) spectra were recorded on a Bruker (Germany) Avance 500 instrument in DMSO-d_6 at room temperature (RT). Multiplicities of proton resonance were designated as broad (br), singlet (s), and multiplet (m). FT-IR spectra were recorded on a Jasco FT-IR Spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave-number (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon-Fensk Routine Viscometer (Germany). DSC data were recorded on a DSC-PL-1200 instrument under N_2 atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI). Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. A sample was first scanned from RT to 160 °C and maintained for 1 min followed by quenching to −50 °C at a cooling rate of 10 °C/min, and then a second heating scan was used to measure sample's glass transition temperatures of soft (T_{g_s}) or hard segments (T_{g_h}), respectively. TGA data for polymers were taken on a Perkin Elmer Thermal Analyser under N_2 atmosphere by IPPI. The microwave apparatus used for the polycondensation was a Samsung (South Korea) microwave oven (2450 MHz, 900 W). Absorbency measurement was performed by a single beam Spectrone-USA-model 4001-4, 250 V Spectrophotometer. A double beam Jasco V-570, UV–vis–near IR, Spectrophotometer was used to record the absorption spectra over a wavelength range of 190–600 nm. Quartz cuvettes were used for measurements in solution via $l = 1$ cm. Fluorescence of dye solutions was studied with a Jasco FP-750 Spectrofluorometer, PMT detector. Emission spectra were recorded over a wavelength range of 200–700 nm with excitation and emission slit width 3 nm and scanning speed of 150 nm/min.

2.3. Polymer synthesis

The PAEUs were prepared by the following general procedure (with P-M-4 as an example): into porcelain dish were placed ABCA (0.0802 g, 2.973×10^{-4} mol), PEG-400 (0.1186 g, 2.973×10^{-4} mol), MDI (0.1484 g, 2.93×10^{-4} mol) and 0.7 mL of NMP 4% (NMP containing 4% w/w $CaCl_2$) was added. The mixture was completely ground for 2 min at RT. Then it was irradiated in the microwave oven for 4 min at 100% of its power. The resulting product was isolated by the addition of 20 mL of distilled water/methanol mixture (30/70) and



Scheme 1. One-step synthesis of PAEUs by the reaction of diacid ABCA (**1**), PEG-400 and different diisocyanates.

followed by trituration. It was then filtered, and purified by two times precipitation from NMP into methanol (solvent- and non-solvent method) and dried at 80 °C for 8 h *in vacuo*; this yielded 0.2384 g (74%) of orange P-M-4 (the abbreviation stands for PAEU-diisocyanate-number of sample).

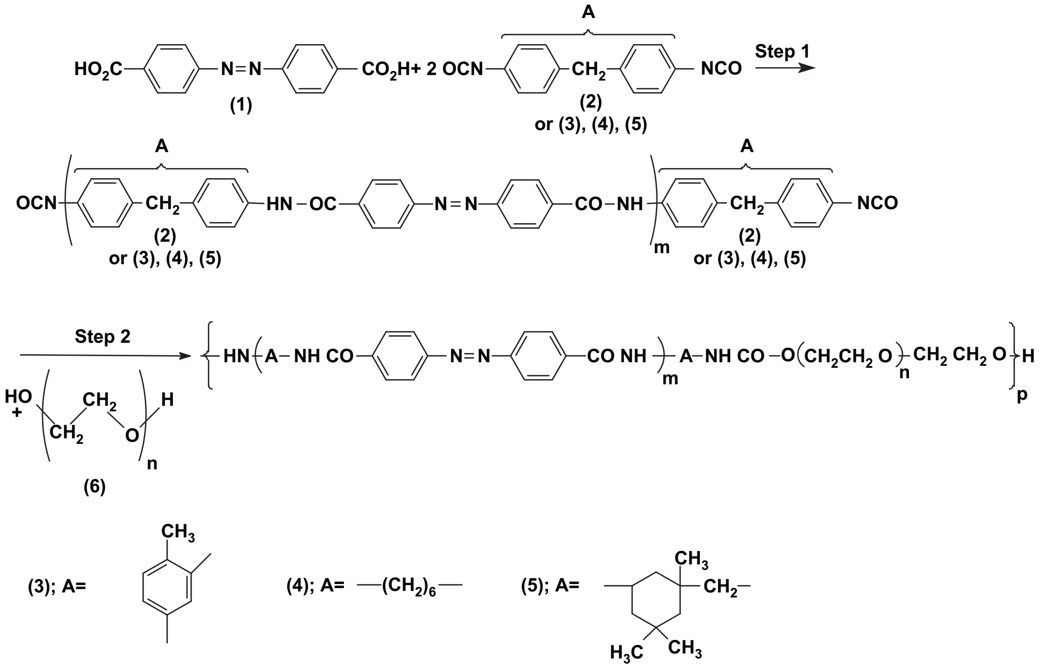
The above polymerization was repeated, but the reaction mixture was irradiated in the presence of dibutyltin dilurate (DBTDL), or Py as a catalyst.

3. Results and discussions

3.1. Polymer synthesis

The PAEU multiblock copolymers based on PEG polyether polyol and an azo-based diacid were prepared according to Schemes 1 and 2 by one-step as well as two-step methods. In these reactions PEG-400 as soft segment and ABCA were reacted with 2 mol excess of different diisocyanates in NMP or NMP 4% in the presence of different catalysts or without catalyst, respectively. This method furnished copolymers whose polyamide blocks are connected with urethane linkages (polymers 1–19, Tables 1–6).

The one-step copolymerization reactions were first performed by azo diacid (**1**), PEG-400 and MDI under different reaction conditions such as irradiation power, irradiation time, reaction catalysts including DBTDL, Py, or without catalyst, reaction solvent (NMP or NMP *n*% $CaCl_2$) and the amount of solvent. Tables 1 and 2 represent part of data related to these studies due to the reactions in NMP and NMP 4% as solvents. It was found that by increasing the ratio of $CaCl_2$ up to 4% (w/w) the viscosity and yield of the resulting PAEUs increased. It can be due to low solubility of ABCA in NMP, especially at RT (Fig. 1).



Scheme 2. Two-step synthesis of PAEUs. Step 1: reaction of diacid ABCA (**1**), and different diisocyanates, molar ratio (1:2), preparation of NCO-terminated oligoamide. Step 2: chain extension reaction of NCO-terminated oligoamide with PEG-400 polyether polyol.

Table 1
One-step copolymerzation reaction of MDI, diacid (**1**) and PEG-400 in the presence of different catalysts, at 100% of power and 4–5 min irradiation time in NMP as a solvent

Polymer	Non-solvent	Catalyst	Yield (%)	η_{inh} (dL/g)[d]
P-M-1[a]	MeOH/H_2O	No	35	0.38
P-M-2	MeOH/H_2O	Py[b]	40	0.28
P-M-3	MeOH/H_2O	DBTDL[c]	37	0.31

[a] Poly(amide-ether-urethane) based on MDI, the first entry, etc.

[b] Pyridine.

[c] Dibutyltin dilurate.

[d] Inherent viscosity – measured at a concentration of 0.5 (g/dL) in 4% (w/w) LiCl/DMF as solvent.

Table 2
One-step copolymerzation reaction of MDI, diacid (**1**) and PEG-400 in the presence of different catalysts, at 100% of power and 3–4 min irradiation time in NMP 4% as a solvent

Polymer	Non-solvent	Catalyst	Yield (%)	η_{inh} (dL/g)[d]
P-M-4[a]	MeOH/H_2O	No	74	0.56
P-M-5	MeOH/H_2O	Py[b]	71	0.68
P-M-6	MeOH/H_2O	DBTDL[c]	71	0.63

[a] Poly(amide-ether-urethane) based on MDI, the 4th entry, etc.

[b] Pyridine.

[c] Dibutyltin dilurate.

[d] Inherent viscosity – measured at a concentration of 0.5 (g/dL) in 5% (w/w) LiCl/DMF as solvent.

Table 3
One-step copolymerzation reaction of TDI, diacid (**1**) and PEG-400 in the presence of different catalysts, at 100% of power and 6 min irradiation time in NMP 4% as a solvent

Polymer	Non-solvent	Catalyst	Yield (%)	η_{inh} (dL/g)[d]
P-T-7[a]	MeOH/H_2O	No	70	0.75
P-T-8	MeOH/H_2O	Py[b]	60	0.69
P-T-9	MeOH/H_2O	DBTDL[c]	55	0.69

[a] Poly(amide-ether-urethane) based on TDI, the 7th entry, etc.

[b] Pyridine.

[c] Dibutyltin dilurate.

[d] Inherent viscosity – measured at a concentration of 0.5 (g/dL) in 5% (w/w) LiCl/DMF as solvent.

Table 4
One-step copolymerzation reaction of HDI, diacid (**1**) and PEG-400 in the presence of different catalysts, at 100% of power and 4–5 min irradiation time in NMP 4% as a solvent

Polymer	Non-solvent	Catalyst	Yield (%)	η_{inh} (dL/g)[d]
P-H-10[a]	MeOH/H_2O	No	70	0.75
P-H-11	MeOH/H_2O	Py[b]	79	0.65
P-H-12	MeOH/H_2O	DBTDL[c]	84	0.42

[a] Poly(amide-ether-urethane) based on HDI, the 10th entry, etc.

[b] Pyridine.

[c] Dibutyltin dilurate.

[d] Inherent viscosity – measured at a concentration of 0.5 (g/dL) in 5% (w/w) LiCl/DMF as solvent.

Table 5
One-step copolymerzation reaction of IPDI, diacid (**1**) and PEG-400 in the presence of different catalysts, at 70% of power and 5–6 min irradiation time in NMP 4% as a solvent

Polymer	Non-solvent	Catalyst	Yield (%)	η_{inh} (dL/g)[d]
P-I-13[a]	MeOH/H_2O	No	89	0.38
P-I-14	MeOH/H_2O	Py[b]	84	0.40
P-I-15	MeOH/H_2O	DBTDL[c]	65	0.45

[a] Poly(amide-ether-urethane) based on IPDI, the 13th entry, etc.

[b] Pyridine.

[c] Dibutyltin dilurate.

[d] Inherent viscosity – measured at a concentration of 0.5 (g/dL) in 5% (w/w) LiCl/DMF as solvent.

The optimized reaction conditions including irradiation power (100%), reaction solvent (NMP 4%), and amount of solvent [2–2.5 (v/w) (solvent/solid)] were repeated for the synthesis of other copolymers with TDI, HDI and IPDI. Optimization of irradiation power and time was also performed in the case of each diisocyanates concerning viscosity and yield (Tables 3–5).

The two-step copolymerization reactions were performed according to the best reaction catalysts obtained for each diisocyanate under one-step method. Thus, PAEU multiblock copolymers based on MDI, IPDI, TDI, and HDI were prepared in NMP 4% as solvent, in the presence of Py, DBTDL or without catalyst (Table 6). It seems that two-step method does not have any superior effect on the viscosity and yield of resulting PAEUs compared to the one-step method.

It is worthy to mention that solution polymerization under classical heating method, except for MDI, gave unsatisfactory results especially in the case of aliphatic diisocyanates [29].

3.2. Thermal properties

The thermal behaviors of PAEUs P-M-5, P-T-8, P-H-11 and P-M-16 were evaluated by TGA and DSC in N_2 atmosphere at a heating rate of 10 °C/min.

Table 6
Two-step copolymerzation reaction of different diisocyanates, diacid (**1**) and PEG-400 (Scheme 2) at 100% of power in NMP 4% as a solvent

Polymer	Non-solvent	Catalyst	Step 1 irradiation time (min)	Step 2 irradiation time (min)	Yield (%)	η_{inh} (dL/g)[e]
P-M-16[a]	MeOH/H_2O	Py[b]	3	2 + 4[d]	74	0.70
P-T-17	MeOH/H_2O	No	3	2 + 4[d]	68	0.75
P-H-18	MeOH/H_2O	No	3	2 + 4[d]	73	0.63
P-I-19	MeOH/H_2O	DBTDL[c]	3	2 + 3[d]	79	0.40

[a] Poly(amide-ether-urethane) based on different diisocyanates, the 16th entry, etc.

[b] Pyridine.

[c] Dibutyltin dilurate.

[d] The chain extension step was first performed at 100% of power (2 min) then at 70% of power (3–4 min).

[e] Inherent viscosity; Measured at a concentration of 0.5 (g/dL) in 5% (w/w) LiCl/DMF as solvent.

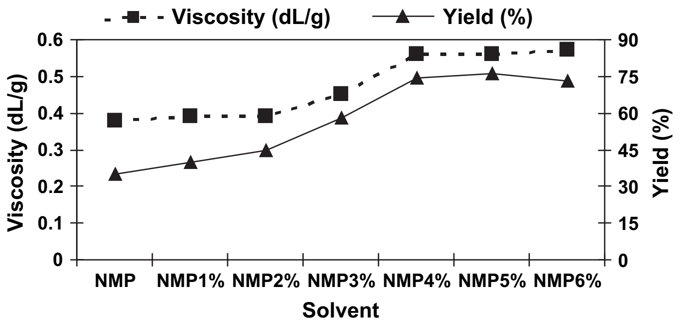


Fig. 1. The effect of $CaCl_2$ content of NMP (% w/w) as reaction solvent on the viscosity and yield of PAEUs based on MDI, one-step method with no catalyst.

TGA curves of PAEUs are given in Fig. 2. The $T_5\%$, $T_{10}\%$, and char yields are listed in Table 7. The first step in the thermal decomposition of these polymers is the elimination of the azo group as molecular nitrogen. This observation was also noted by Riordan and Blair [30] in the thermal degradation of polyamides containing azo groups. The $T_5\%$ for all the PAEUs ranged from 270 to 310 °C, and char residue ranged from 25 to 40%. Relying on $T_5\%$ it can be said that polymer based on the *meta*-azo linkage (P-T-8) is less thermally stable than those based on the *para*-azo or linear-azo linkage and this may be attributed to the difference in the stereoregularity, leading to more compact packing of the polymer chain in P-M-5, P-M-16 and P-H-11. As shown in Fig. 2 the char residue of polymers based on aromatic diisocyanates are more than the ones based on aliphatic diisocyanates.

Typical DSC diagrams for P-M-5, P-H-11 and P-M-16 are shown in Fig. 3. The DSC trace of P-M-5 (Fig. 3a) shows no transition associated with softening or melting that may be due to its more rigid structure than P-H-11. A smooth and broad base line change around 160 °C can be observed which was assigned to (T_{g_h}) of P-H-11. DSC trace of P-M-16 showed two transitions around 113 and 203 °C, assigned to (T_{g_s}) and (T_{g_h}), respectively (Fig. 3c). This shows relatively phase segregation of this polymer, prepared by two-step method, when compared to P-M-5, resulting from one-step method.

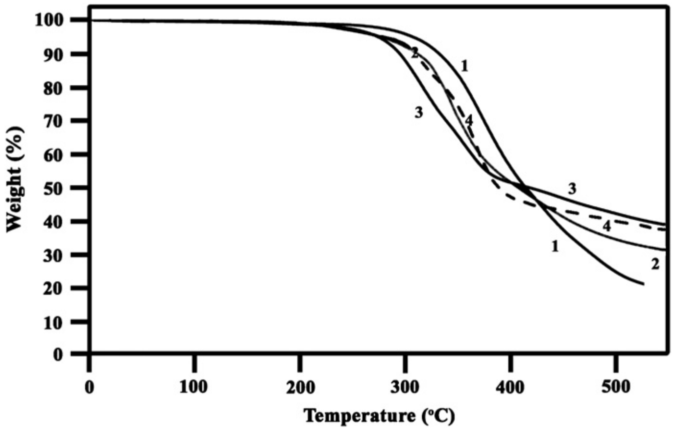


Fig. 2. TGA thermogram of PAEUs recorded at heating rate of 10 °C/min in N_2 atmosphere: (1) P-H-11, (2) P-M-5, (3) P-T-8 and (4) P-M-16.

Table 7
Thermal properties of PAEUs

Polymer	TGA data, $T_5\%$[a]–$T_{10}\%$[b] (°C)	Char yield[c] (%)	DSC[d], (T_{g_s})[e]–(T_{g_h})[f] (°C)
P-M-5	277–315	35	–[g]
P-M-16	277–316	40	113–203
P-T-8	275–295	43	–[g]
P-H-11	307–332	25	160

[a] Temperature at which 5% weight loss was recorded by TGA at heating rate of 10 °C/min in N_2 atmosphere.

[b] Temperature at which 10% weight loss was recorded by TGA at heating rate of 10 °C/min in N_2 atmosphere.

[c] Percentage of weight residue at 500 °C) in N_2 atmosphere.

[d] Center of the peak was recorded by DSC at heating rate of 10 °C/min) in N_2 atmosphere.

[e] Glass transition temperature of soft segment.

[f] Glass transition temperature of hard segment.

[g] No transition temperature was observed.

3.3. Investigation of dye thermal migration

To evaluate the dye migration of synthesized PAEUs, the percentage of dye migration (Mp(%)) was used according to the AATCC test method [19]. The glass plate shown as in Fig. 4 was coated with the self-colored P-M-4 (sample 1) to form a film of thickness 0.02 cm. Then region A was covered with a 2 cm diameter glass cover, but region B was left uncovered. After being warmed at 60 °C for 24 h in an oven, the diluted dye concentrations of region A and B in NMP (3×10^{-4} g/mL) were measured by a photometer. The Mp(%) is calculated as $Mp(\%) = [(C_B - C_A)/C_A] \times 100$, where C_A and C_B are the absorbances of the A and B area, respectively. The same experiments were performed with a sample (sample 2) prepared by simple mixing of azo diacid (**1**) and PU in NMP solution that was prepared by chain extension of NCO-terminated PEG-400 with 1,4-butandiol instead of (**1**), as well as a sample prepared by simple dissolving of ABCA in NMP (sample 3). It is found that the PAEU with covalent bond of dye molecule does have a better thermal migration property than those with simple mixture of dye and polymer (sample 2) or monomeric dye (sample 3) (see Table 8).

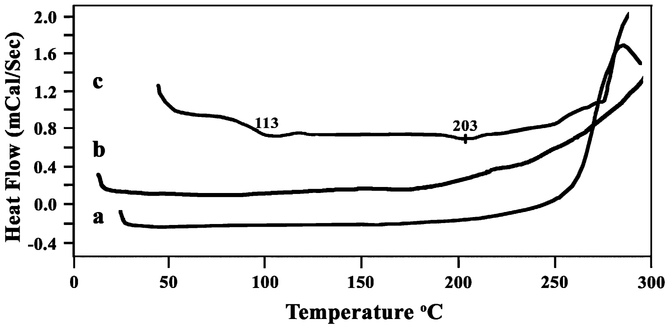


Fig. 3. DSC curves of (a) P-M-5, (b) P-H-11 and (c) P-M-16 under N_2 atmosphere at heating rate of 10 °C/min.

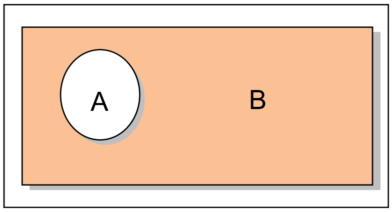


Fig. 4. The glass plate for the evaluation of dye thermal migration.

3.4. Investigation of dye solvent migration

Solubility properties and solvent wash-off resistance of dye of PAEUs were investigated in different solvents at RT or at 60 °C and changes in the intensity of UV–vis absorption peaks [31–33], as well as percentage of weight residue (%W_r) were followed for 2–5 months at different periods of time. The same experiments were performed on monomeric dye (**1**), in order to compare dye-loss of polymeric and monomeric dyes (Table 9). First, P-M-4 was freed from probable unbonded contaminant of azo dye by washing it in an aqueous solution of Na_2CO_3, H_2O and MeOH, respectively. Then 0.05 g of each sample was suspended in 10 mL of different solvents. After 2–5 months the weight residues of suspended polymers in different solvents were also measured and compared with monomeric dye (**1**). For example, Table 9 represents data related to: (1) absorption intensity of selected λ in each solvent for (**1**) and P-M-4, 2 h after immersion, as a measurement for their solubility properties; (2) absorption intensity of selected λ in each solvent for (**1**) and P-M-4, after 1 day immersion; (3) absorption intensity of selected λ in each solvent for (**1**) and P-M-4, after 1 week immersion; (4) absorption intensity of selected λ in each solvent for (**1**) and P-M-4, after 1 month immersion; and (5) %W_r of (**1**) and P-M-4 in each solvent after 2 and 3 months of immersion at RT. On the basis of data obtained from this study, polymeric dye has shown higher weight residue after 3 months in the mentioned solvents, and lower increase in the intensity of absorption peaks compared with monomeric dye. The difference in the solubility and solvent wash-off resistance of polymer and monomer (**1**) is also evident in Figs. 5 and 6. Also these figures compare the solvent wash-off resistance of P-M-4 and (**1**) for 5 months at different temperatures.

3.5. Spectroscopic characterization of PAEUs

Spectral data including ^{1}H NMR and FT-IR support the structural assignments for the PAEUs (Table 10, Figs. 7 and 8).

Table 8
Evaluation of dye thermal migration properties of PAEUs, measured at 300 nm in NMP 3% as solvent

Sample	C_A	C_B	Mp (%)[a]
P-M-4 (1)	0.41	0.43	4.8
PU + azo (2)	0.65	0.72	10.7
Azo diacid (3)	0.88	1	13.6

[a] The Mp(%) is calculated as $\text{Mp}(\%) = [(C_B - C_A)/C_A] \times 100$, where C_A and C_B are the absorbances of the A and B area, respectively.

Table 9
Comparison of solubility properties and solvent wash-off resistance of dye of P-M-4 and azo diacid (**1**)

Solvent	A[g] (P-M-4/1), 2 h	A (P-M-4/1), 1 day	A (P-M-4/1), 1 week	A (P-M-4/1), 1 month	%W_r[i] (P-M-4/1), 2 months/ 3 months
DMF[a]	0.95/1.39	0.63/1.03	0.65/1.95	0.68/2.02	(62/21)/(56/15)
H_2O[b]	0.09/0.39	0.11/1.03	0.15/2.17	0.18/3.20	(90/46)/(85/42)
Ethanol[c]	0.17/0.84	0.69/3.67 0.32/1.42[h]	2.77/4.16	3.03/5.02	(90/40)/(83/36)
Acetone[d]	0.05/0.59	0.24/3.19	0.8/3.69	1.21/4.21	(93/42)/(89/36)
THF[e]	0.20/0.79	1.32/4.21[e]	1.96/4.15	2.21/5.32	(94/67)/(91/60)
NaOH[f] (1 M)	0.19/1.21	0.54/3.45	0.57/3.47	0.87/4.02	(87/20)/(83/13)

[a] Measured at $\lambda = 458$ nm for P-M-4 and 455 nm for (**1**).
[b] Measured at $\lambda = 432$ nm.
[c] Measured at $\lambda = 335$ nm for P-M-4 and 340 nm for (**1**).
[d] Measured at $\lambda = 327$ nm for P-M-4 and 330 nm for (**1**).
[e] Measured at $\lambda = 362$ nm.
[f] Measured at $\lambda = 434$ nm.
[g] Absorbance.
[h] Measured at $\lambda = 365$ nm.
[i] $\%W_r = (W/W_0) \times 100$, W_0 = weight before immersion in a solvent at RT, W = weight after immersion in a solvent at RT.

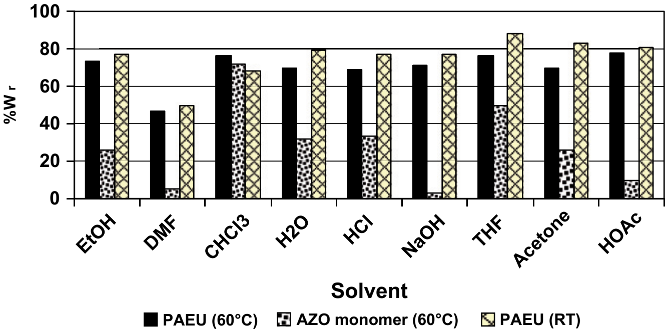


Fig. 5. The difference in solvent wash-off resistance of P-M-4 and monomer (**1**) after immersion in different solvents for 5 months (the parenthesis show temperature at which the sample had been immersed in a solvent).

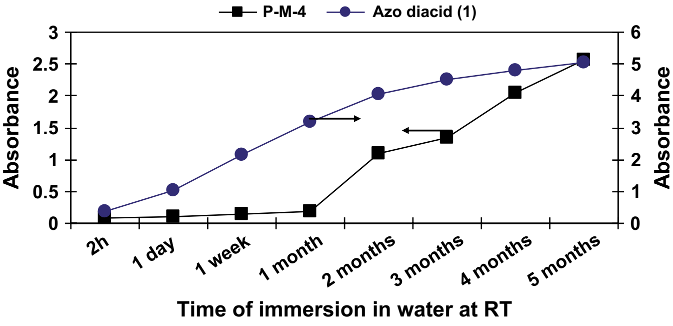


Fig. 6. Comparison of extent and rate of solvent wash-off resistance of P-M-4 and monomer (**1**) after immersion in water at RT during different periods of time for 5 months.

Table 10
FT-IR and ^{1}H NMR characterizations of PAEUs

P-M-4	FT-IR peaks (cm^{-1}): 3382 (m, br), 3104 (w), 3024 (w), 2946 (w), 2895 (w), 2835 (w), 1776 (w), 1717 (s), 1660 (s), 1597 (s), 1534 (s), 1509 (w), 1409 (m), 1379 (m), 1307 (s), 1234 (s), 1202 (m), 1179 (m), 1111 (w), 1090 (w), 1017 (w), 854 (w), 813 (w), 762 (w), 730 (w), 702 (w), 674 (w), 661(w), 634 (w), 607 (w), 560 (w), 511 (w)	^{1}H NMR peaks (ppm): 3.3–3.4 (m, br, CH$_2$ polyether), 3.6–3.8 (m, br, CH$_2$ polyether), 3.8 (s, br, CH$_2$ of MDI moiety), 7.07–8.2 (Ar–H), 8.2–9.0 (NH, amide and urethane)
P-T-8	FT-IR peaks (cm^{-1}): 3408 (m, br), 3296 (m, sh), 3024 (w), 2946 (w), 2925 (m), 2895 (w), 2835 (w), 1778 (w), 1720 (s), 1661 (s), 1599 (s), 1538 (s), 1506 (w), 1410 (m), 1384 (m), 1300 (s), 1233 (s), 1225 (m), 1200 (m), 1175 (m), 1119 (w), 1110 (w), 1090 (w), 1017 (w), 854 (w), 813 (w), 760 (w), 728 (w), 700 (w), 675 (w), 660(w), 633 (w), 605 (w), 553 (w), 500 (w)	^{1}H NMR peaks (ppm): 2.4 (S, br, CH$_3$, overlapped with DMSO-d_6), 3.5–4.3 (m, br, CH$_2$ polyether), 7.02–8.41 (Ar–H, NH)
P-H-12	FT-IR peaks (cm^{-1}): 3509 (w, sh), 3335 (m, br), 3108 (w), 3057 (w), 2933 (m), 2860 (m), 2625 (w), 1777 (m), 1720 (s), 1688 (s), 1641 (s), 1600 (s), 1530 (s), 1407 (m), 1378 (s), 1318 (s), 1251 (s), 1173 (m), 1103 (w), 1016 (w), 955 (w), 856 (w), 770 (w), 727 (w), 664 (w), 629 (w), 605 (w), 552 (w)	^{1}H NMR peaks (ppm): 1.2–1.4 (8H, br, CH$_2$), 2.5–2.9 (m, br, CH$_2$), 3.5 (m, br, CH$_2$, overlapped with H$_2$O), 4.1 (CH$_2$, br), 6.0–7.2 (NH amide and urethane), 7.2–8.2 (m, Ar–H)
P-I-13	FT-IR peaks (cm^{-1}): 3393 (m, br), 3112 (w, br), 2958 (m), 2926 (m), 2873 (m, sh), 1778 (w), 1719 (s), 1652 (m), 1646 (m), 1558 (m), 1540 (m), 1429 (w), 1400 (m), 1383 (s), 1311 (w), 1248 (w), 1198 (m), 1090 (w), 1085 (w), 1012 (w), 950 (m), 863 (w), 814 (w), 777 (w), 702 (w), 670 (w), 661(w), 643 (w), 607 (w), 598 (w), 560 (w), 540 (w), 511 (w)	^{1}H NMR peaks (ppm): 0.76–0.98 (m, 11H, CH$_3$, CH$_2$), 1.64 (d, br, 4H, CH$_2$), 2.5 (m, br, CH$_2$, overlapped with DMSO-d_6), 2.75 (m, br, CH), 3.36–3.55 (m, br, CH$_2$), 4.02 (m, CH$_2$), 5.56–6.67 (NH, br), 6.7–8.2 (m, Ar–H)

The data obtained with KBr disks, indicated the appearance of new absorption bands of amide and urethane functions and the absence of the original peaks arising from the COOH and NCO groups in the corresponding diacid (**1**) and diisocyanates precursors. For example, the FT-IR spectrum of P-M-4 exhibited characteristic absorption bands of the amide group around 3381 (N–H stretching) and 1660 cm^{-1} (C=O stretching), together with peaks at 1776 cm^{-1} (non-H-bonded C=O stretching, urethane), 1717 cm^{-1} (H-bonded C=O stretching, urethane). Moreover, characteristic absorption peaks at 1597 cm^{-1} C–N v + NH (amide II), 1534, 1509 cm^{-1} C=C, 1409 cm^{-1} –N=N–, 1307 cm^{-1} C–N v + NH (amide IV), 1234 cm^{-1} C–N v + NH (amide V), 1200, 1179, 1111 cm^{-1} C–O–C ether of PEG, 1090 cm^{-1} O=C–O–C, confirm its chemical structure (Table 10).

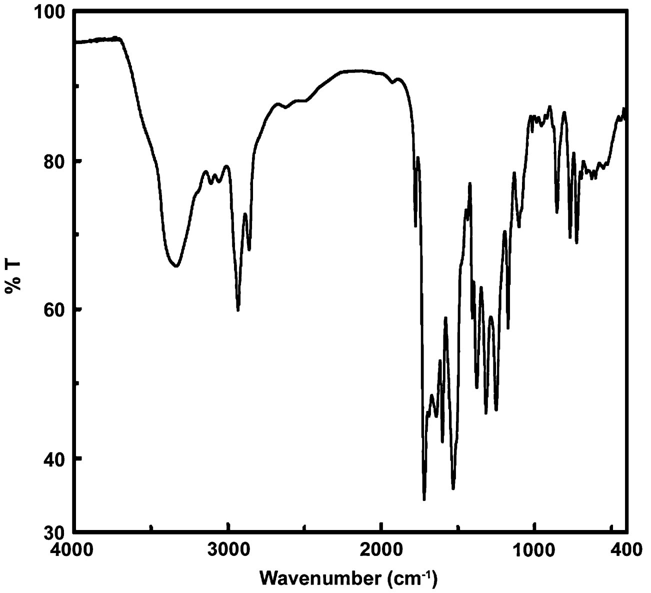


Fig. 7. FT-IR (KBr) spectrum of P-H-12.

The ^{1}H NMR spectrum of P-H-12 showed peaks that confirms its chemical structure. It showed peaks for CH$_2$ (1–3) in the region of 1.2–1.4 ppm. Peaks in the region of 2.5–2.9 and 3.5–4.1 ppm are related to CH$_2$ (4,5) and (6,7), respectively. The aromatic protons appeared in the region of 7.2–8.2 ppm. The peaks in the region of 6.0–7.2 ppm are assigned for NH of amide and urethane groups. Figs 7 and 8 represent FT-IR and ^{1}H NMR spectra of P-H-12, respectively.

3.6. UV–vis absorption and Fluorescence emission study

UV–vis absorption spectra of all PAEUs were recorded in DMF and their band positions and absorbance intensities are listed in Table 11. Polymers based on aromatic diisocyanates showed a hypsochromic shift in the position of their λ_{max} (about 14 nm) from 279–284 for P-H-12 and P-I-13 to 266–269 nm for P-M-4 and P-T-8 (Fig. 9). Also λ_{max} of all the PAEUs (266–284 nm) appeared at much lower wavelength than the azo monomer (300 nm).

Fluorescence emission phenomenon often occurs in cyclic, rigid molecules that contain π electrons, and is enhanced by the presence of electron-donating groups. Comparing the data in Table 11, it can be seen that ABCA showed stronger fluorescence intensity than P-M-4 (Fig. 10). This can be due to the presence of lower vibration structures in azo monomer (C=C, N=N) than that of P-M-4 (N–H, aliphatic C–H, amide and urethane C=O) as well as its rigid structure in comparison with P-M-4 having flexible moieties (C–O, CH$_2$) come from PEG segment. The peak positions of absorption and emission spectra of ABCA and P-M-4 are compared in Fig. 11, as well.

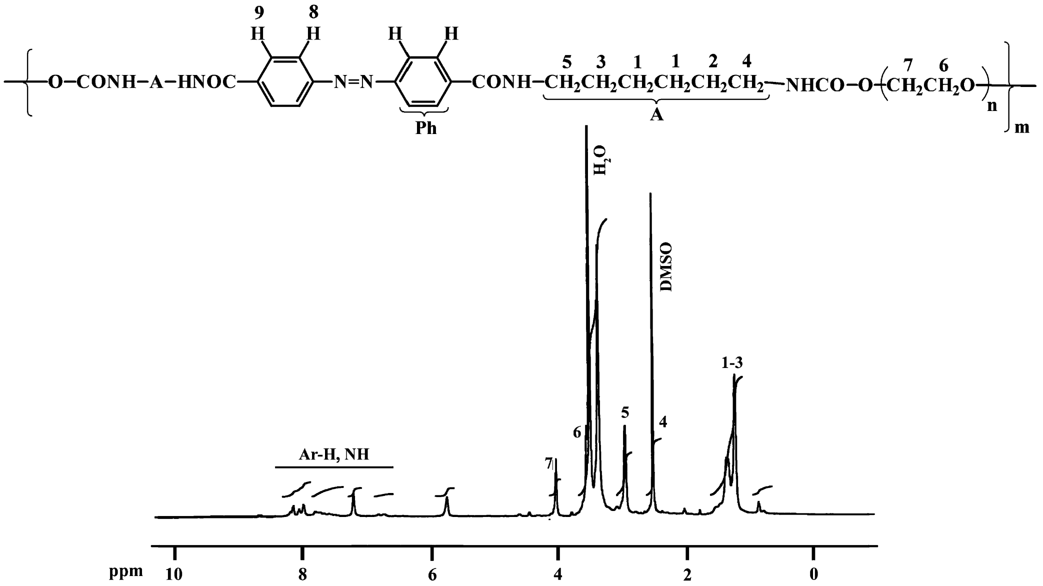


Fig. 8. ^{1}H NMR (500 MHz) spectrum of P-H-12 in DMSO-d_6 at RT (soluble fraction).

4. Conclusions

The data obtained from this study showed that microwave irradiation could be used effectively and easily for preparation of self-colored PAEUs. This method is more efficient than the conventional methods using classical heating. In order to obtain the best results for the polymerization of each diisocyanate, the reaction conditions were optimized for each of them. The resulting PAEUs containing a covalent bond of dye molecule showed better thermal and solvent migration properties than monomeric dye (**1**), as well as a sample prepared by physical mixing of PU with dye (**1**). Polymeric dyes have shown higher weight residue after 5 months even at 60 °C, as well as better solvent wash-off resistance compared to monomeric dye.

Table 11
Data related to absorption spectra of P-M-4, P-T-8, P-H-12, and P-I-13 in DMF solution as well as emission spectra of P-M-4 and diacid monomer (**1**)

Sample	UV study: λ (*A*)	Fluorescence study: λ (intensity)
P-M-4[a]	269 (1.39), 346 (0.3, br)	(1)[e] 307 (50), 348 (163), 436 (23), 531 (10), 631 (22), 675 (43) (2)[f] 347 (342), 383 (69), 403 (86), 686 (136)
P-T-8[b]	266 (1.33), 298 (0.53), 331 (0.40), 347 (0.32, sh), 366 (0.20, sh)	
P-H-12[c]	264 (1.09), 284 (1.23), 332 (0.88), 349 (0.74, sh), 367 (0.40, sh)	
P-I-13[d]	264 (0.82), 279 (0.85), 331 (0.54), 346 (0.48, sh), 365 (0.30, sh)	
Azo diacid[g] (**1**)	300 (1.3), 345 (0.5, br)	[h]298 (70), 339 (475), 351 (450), 403 (152, sh), 596 (160), 664 (165)

[a] Concentration = 2.5 × 10^{-4} g/mL.
[b] Concentration = 2 × 10^{-4} g/mL.
[c] Concentration = 2 × 10^{-4} g/mL.
[d] Concentration = 2.2 × 10^{-4} g/mL.
[e] Excited at 268 nm.
[f] Excited at 345 nm.
[g] Concentration = 2 × 10^{-4} g/mL.
[h] Excited at 300 nm.

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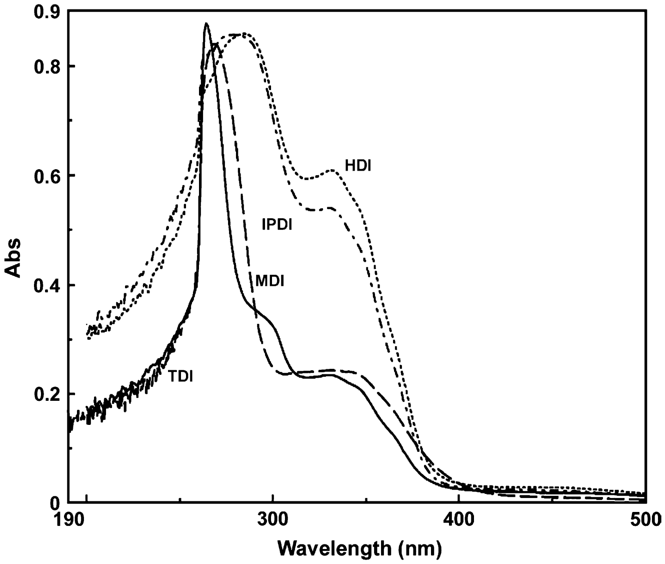

Fig. 9. Normalized absorption spectra of P-M-4 (MDI), P-T-8 (TDI), P-H-12 (HDI), and P-I-13 (IPDI) in dilute DMF solution.

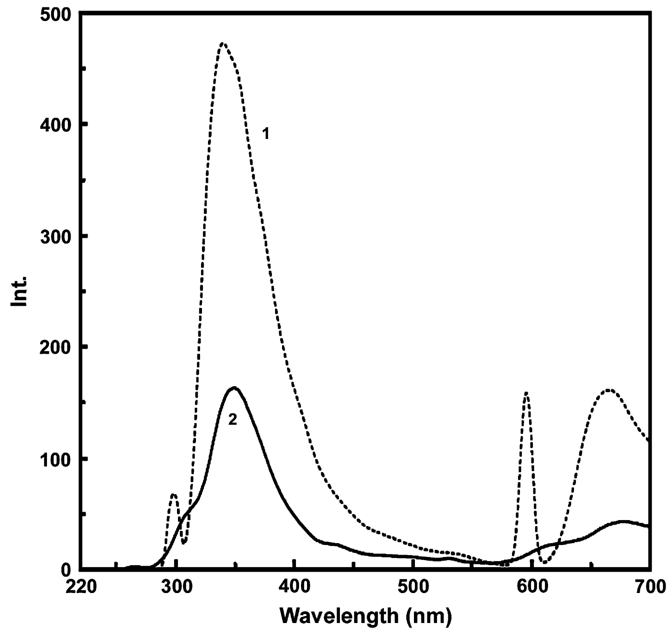

Fig. 10. Comparison of (1) emission spectra of ABCA excited at 300 nm and (2) emission spectra of P-M-4 excited at 267 nm.

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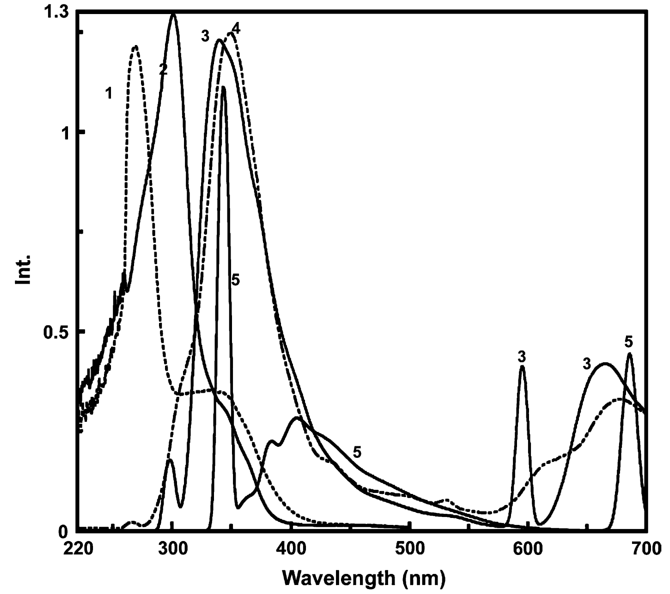

Fig. 11. Normalized absorption and normalized emission spectra of P-M-4 and ABCA in dilute DMF solution. (1) UV spectra of P-M-4, (2) UV spectra of ABCA, (3) emission spectra of ABCA excited at 300 nm, (4) emission spectra of P-M-4 excited at 267 nm, and (5) emission spectra of P-M-4 excited at 345 nm; comparing the peak positions.

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