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ORIGINAL PAPER

Synthesis of poly(urethane-urea) varnish bearing azobenzene chromophoric pendants

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Abstract A new diol with azoaromatic pendant was prepared by *N*-phenyl-4-amido-3,4-dichloromaleimide with 2-mercaptoethanol in the presence of NaOH, and used to obtain photosensible poly(urethane-urea) varnish. A poly(urethane-urea) varnish bearing azobenzene chromophores, based on a poly(ethylene adipate)diol (average molecular weight—2000), 4,4′-dibenzyldiisocyanate, diethylene glycol, trimethylolpropane, and afore-mentioned diol, were prepared and characterized. The polymers were characterized by FTIR spectroscopy, thermal analysis (DMA, DSC, and TGA), and the photochromic behavior by UV irradiation of thin films was discussed.

Keywords Poly(urethane-urea) · Azobenzene · Photosensitive polymers · Thermal behavior

Introduction

Synthesis and properties of polymeric materials containing different chromophores covalently attached to the polymer backbone have attracted an increasing interest in the recent years, not only for their photophysical properties but also for their applications [1–3]. Azobenzene is a typical photoresponsive unit showing the well-established reversible photopolymerization behavior among the variety of photo-active chromophores. Azobenzene-functionalized polymers are one of the actively studied subjects, and various polymers with azobenzene moiety have been reported

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[4–18]. Considering the great versatility of polyurethanes and their special properties, various monomeric and polymeric materials carrying azoaromatic chromophores were prepared and their photobehavior was studied taking into account the development of the new photochromic non-linear optical, liquid–crystal, or biological system [19–23].

Previously, we reported polyaminobismaleimide resin having urethane groups [24, 25], poly(ester-urethane-imide)s [26] and polyurethane-bismaleimide semi-interpenetrate materials [27]. Our research has focused upon incorporation of new chromophores, prepared by substitution reaction of dichloromaleimides containing azobenzene units into polyurethane.

Experimental

Measurements

The ATR-FTIR spectra were determined using a Bruker Vertex 70 Instruments equipped with a Golden Gate single reflection ATR accessory, spectrum range 600–4000 cm^{-1}.

The ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Bruker NMR spectrometer, Avance DRX 400 MHz, using DMSO-d_6 as solvents and tetramethylsilane as an internal standard.

Melting and softening points were determined using a Gallenkamp hot-block point apparatus.

Dynamic contact angles were performed by the Wilhelmy plate technique, using a Sigma 700 precision tensiometer produced by KSV Instruments. The sample plate dimensions were 50 × 8 mm, and rate of immersion-emersion was 5 mm/min in water. Immersion depth was 5 mm in standard conditions. All measurements were the average of three contact angle measurements of samples.

Dynamic mechanical experiments were made using a Diamond PerkinElmer instrument that applies a sinusoidal stress to the sample and measure the resulting strain. The force amplitude used was well within the linear viscoelastic range for all investigated samples. The thermo-mechanical properties were evaluated, starting from room temperature up to beyond the temperature corresponding to glass transition, at a heating rate of 4 °C/min and a frequency of 1 Hz, under nitrogen atmosphere. The size of films was of 10 × 10 × 0.5 mm for the tension attachment.

Thermogravimetric analysis (TGA) was performed under nitrogen flow (15 cm^3/min) at a heating rate of 20 °C/min from 25 to 550 °C with a Mettler Toledo model TGA/SDTA 851. The initial mass of the samples was 4–6 mg.

Differential scanning calorimetry (DSC) measurements were performed using a Mettler TA Instrument DSC 12E with a heating rate of 15 °C/min, in nitrogen.

Irradiations were carried out using a 500 W high pressure lamp and a proper filter ($\lambda = 365$ nm) at room temperature. The polymer film was prepared by coating the polymer solution in DMF ($c = 1$ g/dL) onto quartz plates and then allowed to dry at 50–55 °C under reduced pressure for 2–3 days.

Reagents and materials

The polyurethane component was prepared from:

- 4,4′-Dibenzyldiisocyanate (DBDI, local work), recrystallized from cyclohexane, $M = 264$, mp = 91 °C.
- Poly(ethylene glycol) adipate (PEGA, Baxenden) with a molar weight of 2000 and hydroxyl number $c_{OH} = 56$ mg KOH/g, with functionality of two, trimethylolpropane (TMP, Aldrich) and diethylene glycol (DEG, Aldrich) were used as received.
- 1,4-Diazabicyclo[2.2.2]octane (DABCO, Aldrich)
- Dimethylformamide (DMF, Aldrich) which was purified and dried by vacuum distillation on 4,4′-DBDI, bp = 153 °C.

The 4-amino-azobenzene was prepared from aniline, according to the literature procedure [28].

Synthesis of chromophore diol **4**

3,4-Dichloromaleimidobenzoic acid **(1)** was prepared from *p*-aminobenzoic acid and dichloromaleic anhydride in acetic acid according to the literature procedure [29] (mp = 315–319 °C; mp > 305 °C, [30]).

3,4-Dichloromaleimidobenzoic acid chloride **(2)** was prepared from **1** using thionyl chloride in toluene (mp = 225–228 °C [31]).

N-Phenyl-4-amido-azobenzene-3,4-(dichloro)maleimide **(3)** 0.01 mol of **2** in 100 mL acetone was cooled in an ice bath. Triethylamine (0.01 mol) as acid acceptor and a solution of 4-aminoazobenzene (0.01 mol) in 50 mL acetone were added. After stirring for 1 h at room temperature, the mixture was filtered, washed with water and methanol, and dried in a vacuum oven at 60 °C to give 3.6 g (yield 90%).

Analysis calculated for $C_{23}H_{14}N_4O_3Cl_2$ (465.271): C, 59.37; H, 3.03; N, 12.04; Cl, 15.24%. Found: C, 59.63; H, 2.97; N, 11.64; Cl, 15.43%.

IR (KBr, cm^{-1}): 1740, 1670, 1630, 1600, 1530, 1510, 1415, 1385, 1270, 1130, 990, 855, 750, and 695.

^{1}H-NMR (DMSO-d_6, TMS), δ (ppm): 10.72 (s, 1H, NH), 8.10 (2d, 4H, $J_1 =$ 8.4 Hz, $J_2 = 8.4$ Hz), 7.95 (d, 2H, $J = 8.4$ Hz), 7.88 (d, 2H, $J = 6.8$ Hz), 7.58 (m, 5H, $J_1 = 8.4$ Hz, $J_2 = 8$ Hz). ^{13}C-NMR (DMSO-d_6), δ (ppm): 120.43, 122.38, 123.50, 126.46, 126.52, 128.88, 129.96, 130.36, 131.67, 132.91, 135.15, 147.88, 152.03, 161.84, 165.52.

4-{3,4-bis[(2-hydroxyethyl)thio]-2,5-dioxo-2,5-dihydro-1*N*-pyrrol-1-yl}-*N*-{4-[(*E*)-phenyl diazenyl]phenyl}benzamide **(4)** was obtained by the Lynch method [32] through of reaction between dichloromaleimide (**3**) (1 mol) and 2-mercaptoethanol (2 mol) in the presence of an alcoholic NaOH solution. A detail synthetic method used to obtain compound **4** is described below. The flask was charged with 0.8 g (0.02 mol) of sodium hydroxide and 100 mL methanol and stirred for 30 min, and then 1.56 g (0.02 mol) of 2-mercaptoethanol was added. After 20 min of stirring,

50 mL solution of 4.65 g (0.01 mol) of dichloromaleimide **3** in DMF was added while vigorous stirring. The flask was gradually heated up to reflux and maintained at this temperature for 3 h. The reaction mixture was precipitated after cooling with water. The solid was filtered, washed with water and methanol, and dried at 60 °C in a vacuum oven for 12 h (yield 85%).

Analysis calculated for $C_{27}H_{24}N_4O_5S_2$ (548.617): C, 59.11; H, 4.41; N, 10.21; S, 11.69%. Found: C, 59.36; H, 4.56; N, 9.89; S, 11.52%.

IR (KBr, cm^{-1}): 3350, 2980, 1775, 1720, 1660, 1600, 1510, 1390, 1320, 1265, 1200, 1155, 1130, 1060, 1020, 845, 775, 750, 695, 555.

^{1}H-NMR (DMSO-d_6, TMS), δ (ppm): 10.71 (s, 1H, NH), 8.10 (2d, 4H, $J_1 = 8$ Hz, $J_2 = 8.8$ Hz), 7.95 (d, 2H, $J = 8.4$ Hz), 7.88 (d, 2H, $J = 8$ Hz), 7.56 (m, 5H, $J = 7.6$ Hz), 3.70 (t, 4H, $J = 6$ Hz), 3.45 (t, 4H, $J = 6$ Hz). ^{13}C-NMR (DMSO-d_6), δ (ppm): 34.15, 60.76, 120.50, 122.38, 123.50, 126.21, 128.75, 129.38, 131.05, 133.60, 134.61, 136.04, 142.27, 147.75, 152.05, 164.87, 165.26.

General procedure for the preparation of the polyurethane varnishes

Component I

PEGA (25 mmol), TMP (9 mmol) were dehydrated at 120 °C, for 4 h in vacuum, before use, they were dissolved in methylene chloride (48 g). To this solution, a mixture of DEG and monomer 4 (33 mmol) in molar ratio of 3:8, 26:7, and 3.3:0 was added, corresponding to a concentration of azobenzene monomer in polyurethane film of 15, 5, and 0%.

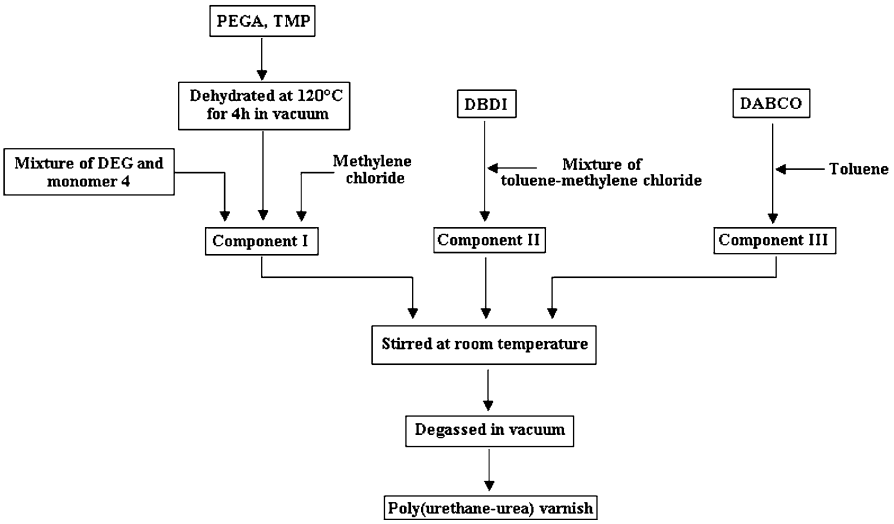
Component II

DBDI (15 g, 57 mmol) was dissolved in the toluene–methylene chloride mixture (85 g), in a weight ratio of 15:70. The formed solid was filtered.

Component III

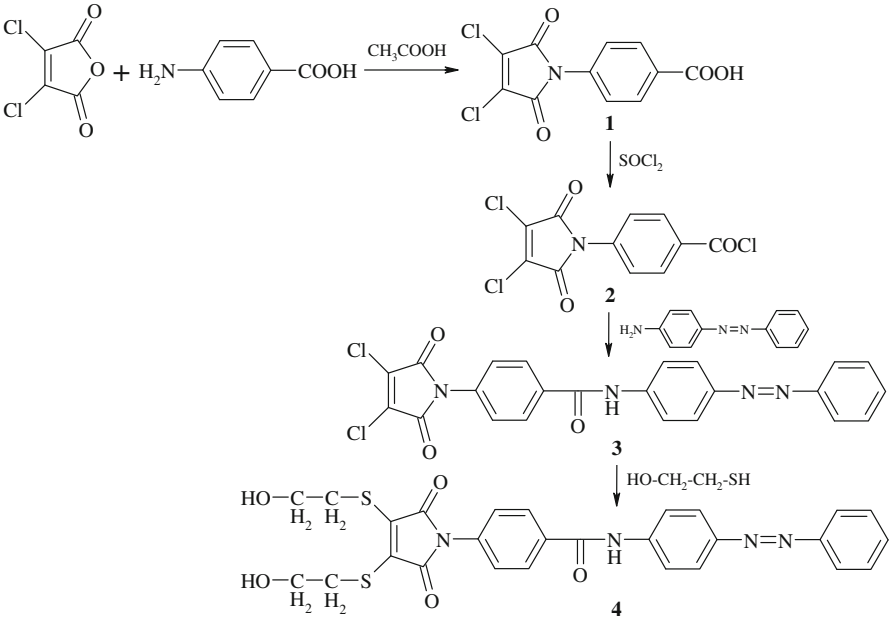
DABCO (3 g) was dissolved in toluene (97 g), heated at reflux until clear solution was obtained.

Component I and II was mixed in a weight ratio of 7:10, in the presence of component III (0.2–0.3 mL), at room temperature for 2.5–3 h. The polyurethane varnish was degassed in vacuum and quickly transferred to a glass plate, using a doctor blade ($e = 3$ mm). The solvent was evaporated in atmosphere at room temperature for 7 days. The film was removed from the glass plate by soaking it in the cold water. A schematic diagram for the preparation of the poly(urethane-urea) varnish is presented below.



Results and discussions

New diol maleimide chromophore (**4**) was prepared by substitution reaction between dichloromaleimide with azobenzene units (**3**) and 2-mercaptoethanol in the presence of alcoholic sodium hydroxide solution in accordance with Lynch method [32] (Scheme 1). The structure of compound **4** was identified by IR, ^{1}H-NMR, ^{13}C-NMR spectrometry, and elemental analysis. Elemental analysis data are in good



Scheme 1 Synthesis of the compound **4**

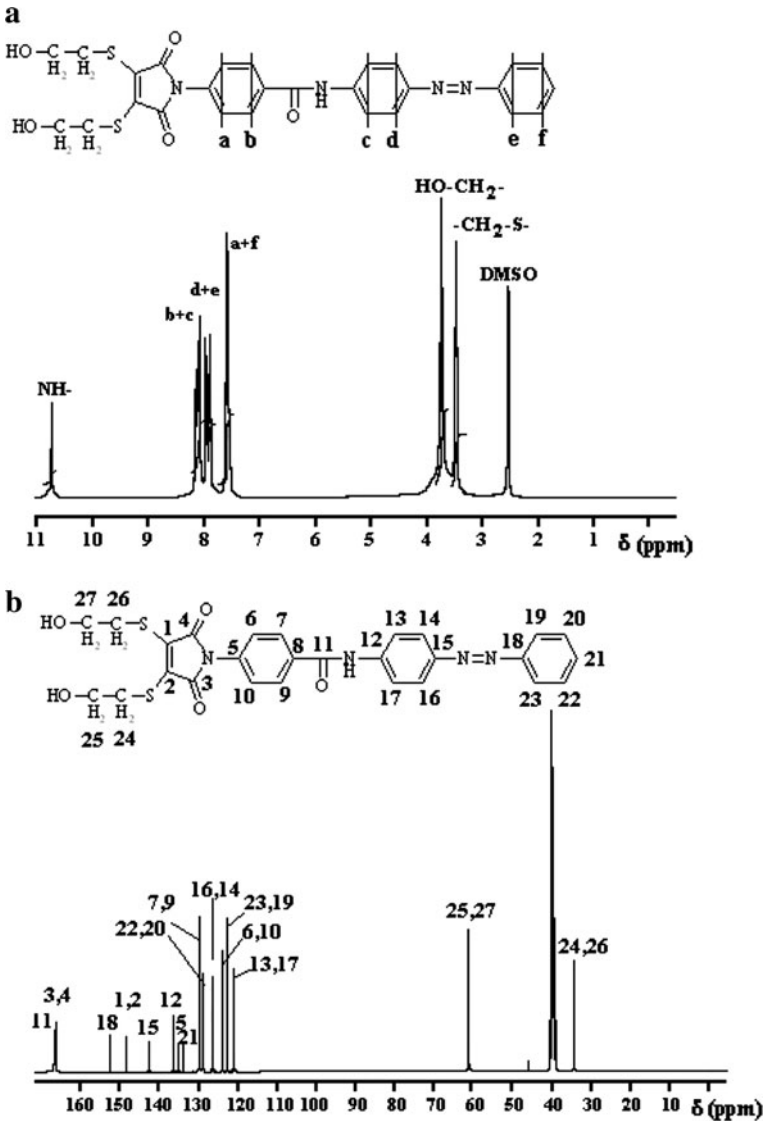


Fig. 1 ^{1}H-NMR (**a**) and ^{13}C-NMR (**b**) spectrum of compound **4**

agreement with the calculated values. The ^{1}-NMR (Fig. 1a) and ^{13}C-NMR (Fig. 1b) spectra confirmed their structure. The aromatic protons of compound **4** appeared as doublet and multiplet at 8.13–7.53 ppm. The methylene protons from 2-hydroxyethylthioether groups appeared as two triplets at 3.71 and 3.45 ppm, respectively, with coupling constant $J = 6$ Hz. ^{13}C-NMR spectrum shows signals for methylene carbons at 34.15 and 60.76 ppm, 12 signals for aromatic protons in the range 118.58

Table 1 Components of poly(urethane-urea)s

Sample	Component (mol)				
	DBDI	PEGA	Monomer 4	TMP	DEG
P-0	8.6	2.5	0	0.9	3.3
P-5	8.6	2.5	0.7	0.9	2.6
P-15	8.6	2.5	2.4	0.9	0.9

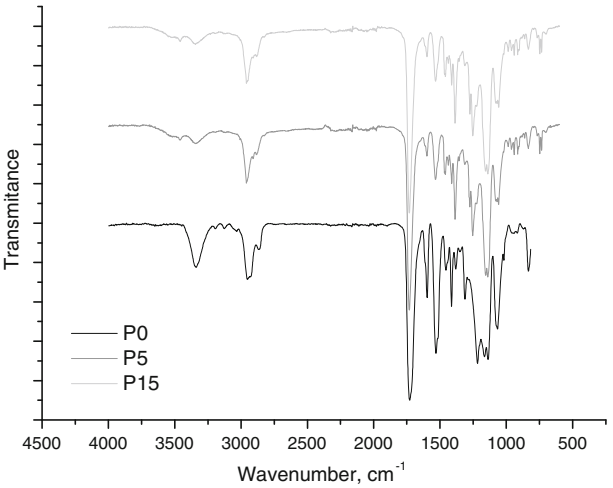


Fig. 2 ART-FTIR spectra of polymers

and 152.04 ppm, signals for –C=C maleimide, C=O maleimide, and CO amide at 147.88, 164.87, and 165.26, respectively (Fig. 1b).

The poly(urethane-urea) varnishes were prepared by the reaction of two components solution, one containing hydroxyl compound and the second *ortho*-component having diisocyanate, in the presence of DABCO as catalyst. The components of polymers P-(0, 5, 15) are presented in Table 1.

The ATR-FTIR spectra of the copoly(urethane-urea) films were performed on solvent cast thin films (Fig. 2). Absorption bands due to the NH stretching at 3350 cm^{-1} (hydrogen-bonded) and urethane, amide and maleimide carbonyl at 1750–1700 cm^{-1}, CH_2 stretching at 2857 cm^{-1} (symmetry) and 2950 (asymmetry), benzene C=C stretching at 1590 and 1415 cm^{-1}, and C–O–C stretching at 1210 cm^{-1} were observed. The reduced viscosities were ranged between 0.23 and 0.36 dL/g measured in DMF solution at 25 °C.

To examine the effect of hydrogen motions of maleimide-azoaromatic units on their photoisomerization, the kinetics of photochemic *trans* to *cis* and thermal *cis* to *trans* back isomerization in film state has been studied. Experiments by the mean of a high pressure Hg lamp were carried out to record the changes appearing in the electronic absorption spectra during UV irradiation. The azo polyurethane shows a strong absorption band centered at 353 nm, which is

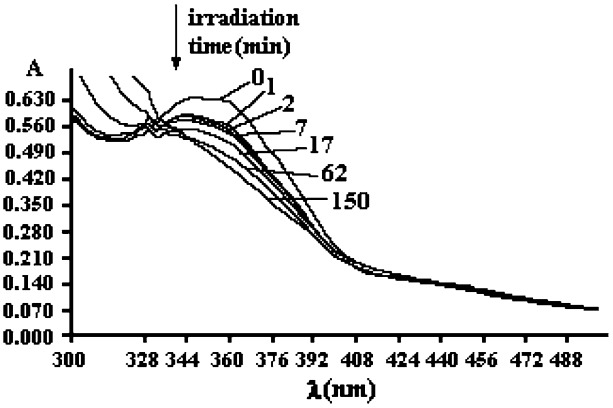


Fig. 3 Charge of UV–Visible spectrum of polymer film (P-5) by irradiation

assigned to a very intensive π–π^* transition of the azobenzene chromophore [33]. Following the evolution of photoprocesses in polymeric films (P-5) subjected to irradiation, it was observed that the absorption maxim at 353 nm corresponding to π–π^* transition decreased slowly as the UV light exposure time increased (Fig. 3).

This decrease leads to slower *trans–cis* photoisomerization of azo chromophores in the solid state.

Introduction of imidic monomer containing azobenzene groups in the backbone as chain extended does not affect much the mechanical behavior of polyurethane films obtained from diethylene glycol and chain extended. So, the stress–strain curves of polymers P-(0, 5, 15) were presented in Fig. 4.

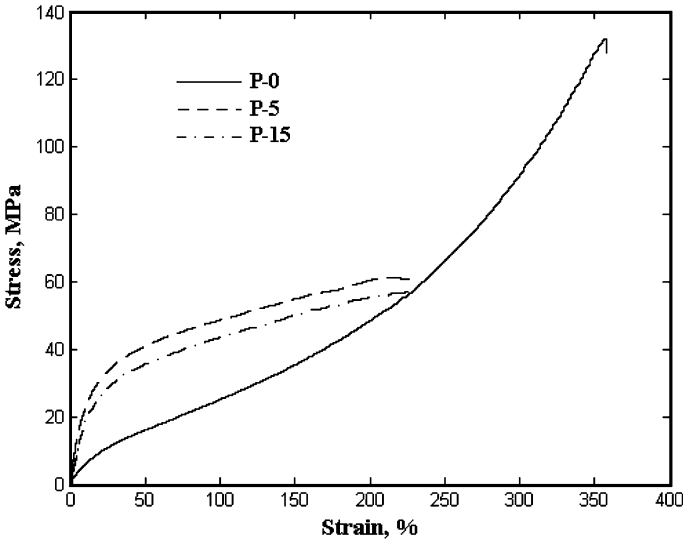


Fig. 4 Stress–strain curves of polymer films

Table 2 Tensile properties of poly(urethane-urea) films

Code	Tensile strength, MPa	Elongation at break, %	Modulus, MPa
P-0	13.23	358.15	7.02
P-5	6.10	228.87	32.20
P-15	5.50	206.01	33.67

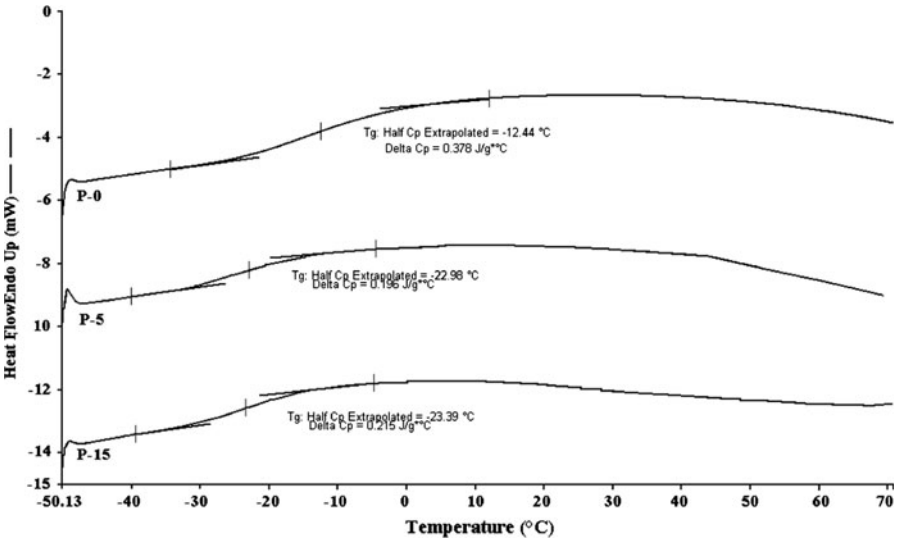


Fig. 5 DSC scans of polymer films

Most data appeared to follow the characteristic curves expected for elastomers; the stress increased relatively steeply at low strain, followed by a broad strain-softening zone, and a region of lower, but still positive slope, at intermediate strain. With the incorporation of imidic monomer in the segments of polyurethane, the modulus increases, and the elongation and strength at break decrease (Table 2).

Dynamic mechanical properties

Thermal and thermomechanical properties of poly(urethane-urea) films

The thermal behavior of poly(urethane-urea) films was investigated by DSC, DMA, and TGA measurements. The DSC traces of polymers P-(0, 5, 15) are given in Fig. 5, and are plotted as a function of temperature (Fig. 6). The data of thermal transitions (T_g), glass storage modulus at −50 °C ($E'(-50)$), rubbery modulus at 80 °C ($E'(80)$), and height of tan δ peak are presented in Table 3.

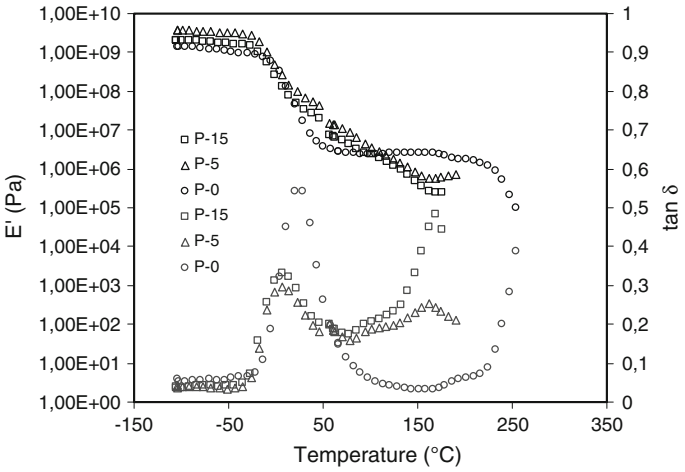


Fig. 6 Storage modulus (*black line*) and tan δ (*gray line*) profiles of polymer films

Table 3 Dynamic mechanical analysis of poly(urethane-urea) films

Code	T_α^{a} °C	T_g^{b} °C	$E'(-50\ °C)^{c}$ GPa	$E'(80\ °C)^{d}$ MPa	Height of tan δ	IDT[e] °C	Temperature of % weight loss[f], °C	
							5	10
P-0	−9.9	−12.4	1.10	2.58	0.537	316.5	324	P-0
P-5	−20.8	−22.8	1.71	3.92	0.326	302	312	P-5
P-15	−26.2	−23.4	3.20	7.80	0.284	302	312	P-15

[a] Glass transition temperature of soft segment of polymer by DMA measurement, corresponded to onset temperature of the decrease in E'

[b] Glass transition temperature of soft segment of polymer by DSC measurement

[c] Glass storage modulus at −50 °C

[d] Storage modulus at 80 °C (rubber state modulus)

[e] Initial decomposition temperature

[f] Temperature for 5 and 10% weight loss

Dynamic mechanical curves ($E' = f(T)$) of films exhibited a high plateau corresponding to the glassy state modulus due to the elastic energy stored in the crystalline and glass state amorphous domains and another plateau attributed to the rubbery state modulus due to the entropy owed to the two-phase structure of the material (Fig. 6). The values of T_α^{s} of films P-(0, 5, 15) corresponding to the relaxation associated with the glass transition of the soft phase, determined by onset temperature of the decrease in E', varied in the range of −9.9 and −26.2 °C (the minimum value belongs to film P-15). The storage modulus (E') of poly(urethane-urea) films decreased from 1.1–3.2 GPa to 2.58–7.8 MPa in the temperature range

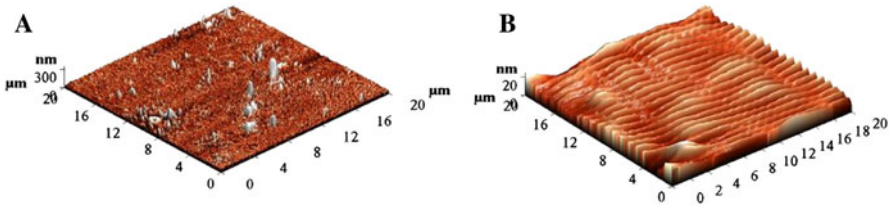


Fig. 7 Tapping-mode AFM 3D height image of films P-0 (**a**) and P-5 (**b**)

Table 4 Water contact angle of copoly(urethane-urea) films

Sample	θ_{adv} (°)	θ_{rec} (°)	Hysteresis (°)
P-0	71.23 ± 3.9	44.63 ± 0.58	26.60 ± 0.58
P-5	82.65 ± 1.51	51.95 ± 0.15	30.70 ± 0.15
P-15	87.91 ± 1.155	52.61 ± 0.015	35.30 ± 0.015

of −50 and 80 °C. As can be observed in Fig. 6, loss factor (tan δ) exhibited one maximum peak for films P-(0, 5, 15) and their height decreased with the increase in the maleimide chromophore (monomer 4). The thermal stability of films P-(5, 15) containing maleimide chromophore as chain extender is weaker than that of film P-0 based on the diethylene glycol as chain extender. Temperature for 10% weight loss of films P-(5, 15) ranged between 325 and 330 °C and for film P-0 was 340 °C (Table 3).

Surface characterization of poly(urethane-urea) films

Figure 7 shows two- and three-dimensional AFM image of film P-5. Surface morphology and external structure of films are investigated using AFM. AFM allows qualitative understanding of the external structure through direct observation.

Typical AFM height images for the films P-(0, 5) are shown in Fig. 7. As can be observed in Fig. 7, the difference of the surface roughness of the specimens is quite obvious. The surface roughness slightly decreased with the chain extender content.

Wettability could be estimated by the determination of the dynamic contact angle. Four samples were immersed and withdrawn into and out of the liquid simultaneously measuring the force acting on the samples. The advancing and receding contact angles were determined from the obtained force curve. Advancing and receding contact angle measurements on the casting films from polyurethanes based on monomer 4/dibenzyl diisocyanate/PEGA could provide more information on the hydrophilicity of films and hence their wetting ability. The advancing and receding contact angle increased with the increase of the amount of azobenzene maleimide diols content (**4**) for polymers P-(0, 5, 15) (Table 4).

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