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Synthesis and characterization of photoactive polyurethane elastomers with 2,3-dihydroxypyridine in the main chain

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Abstract Photoactive polyurethane elastomers with pyridine derivatives in the polymer backbone were synthesized by chain-extending isocyanate end-capped prepolymers with 2,3-dihydroxypyridine. The isocyanate-terminated prepolymers were obtained from poly(tetramethylene oxide) glycol of molecular weight 1400 (Terathane 1400) and 1,6-hexamethylene diisocyanate. The properties of the linear heterocyclic polyurethane were compared with properties of the crosslinked heterocyclic polyurethane obtained by chain extension with various crosslinkers. Heterocyclic polyurethane elastomers were characterized using Fourier transform infrared spectroscopy (FTIR), thermo-gravimetric analysis (TGA), dynamic mechanical analysis (DMA), contact angle measurements, and mechanical analysis. Static mechanical measurements showed greater elongation and tensile strength for polyurethanes with a lower content of heterocyclic groups in the hard segment. The static contact angles of the cast films of these polymers indicated that the nature of the hard segment influences the surface polarity. The dynamic mechanical spectra revealed that linear polymers have two transition temperatures as results from a clear phase separation caused by high-intermolecular hydrogen bonds in the regions of pyridine units and urethane groups. Polyurethane elastomer films with pyridine moieties in the main chain form a photosensitive material. If stored in laboratory conditions (light, ambient air atmosphere), the color of the films changes from white to black. These photo-induced structural changes are studied by H NMR measurements.

Introduction

Polyurethanes (PUs) are widely used because they have excellent properties which are determined by the chemical structure and morphology obtained during synthesis. The polyurethane morphology and properties can be optimized either by the introduction of new chemical structures in the backbone chains, which promote strong intermolecular association through physical crosslinks, or by chemical crosslinks that increase the structural integrity of the hard segment which results in improved properties [1–8].

Polyurethanes with hetero-aromatic groups in the main chain were used to improve the properties of polymers for high performance applications. Thus, using pyridine moieties as a typical hydrogen acceptor enables the creation of conjugated polymers with electro-conductive and photoconductive properties [9]. Pyridine is a hetero-aromatic group which can be found in natural and synthetic compounds. By introducing ionic moieties at the tertiary nitrogen during the chain extension stage, new products can be developed [10, 11].

Pyridine is an aromatic, heterocyclic ring with a pair of electrons localized in the sp^2 orbital of the nitrogen atom which determine improved electron-transporting properties in its polymers. The modification of their properties can be done through protonation or alkylation of the electron pair [12, 13]. Also, the sp^2 electron pair of the nitrogen atom of pyridine increases adhesion between substrates and improves the physico-mechanical and chemical resistance properties [14] and influences the photo-physical behavior of the materials [15].

In the pyridine group, 2,3-dihydroxypyridine is distinguishable due to its hydroxyl groups being in *ortho*-position relative to one another. When in excited state, hetero-aromatic compounds cause the shifting of the

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fluorescence band, which is important for the study of UV stabilization, stimulated radiation production or information storage [16–18]. In the polymeric matrix, photochromic behavior is related to the higher level of order of the molecular structure within phase-separated and self-assembled systems [19]. The chemical nature of the photochromic units from the polymer backbone or attached as side groups has been found to enhance the stability of molecular orientation. Also, the composition and nature of the whole polymer influence extension and kinetics in the case of photoinduced orientation [20, 21].

This article reports the synthesis of linear and cross-linked polyurethane elastomers containing pyridine moieties within the polyurethane backbone and the influence of the heterocyclic structural polyurethane formulation on the macromolecular properties. The results evidenced the formation of photosensitive elastomers, attested by the progressive change in color of the materials during storage. Polymeric materials that change color in response to various external stimuli can be used in various types of applications.

Experimental

Materials

Poly(tetramethy1ene oxide) glycol of a molecular weight of 1400 (Terathane 1400) (Aldrich, Switzerland) was dried in high vacuum for 2 h at 120 °C before use. All other chemicals were used as received.

2,3-dihydroxypyridine (DHPy), diethylene triamine, castor oil (CO), glycerin (Gly), and dimethylformamide (DMF) were purchased from Aldrich and 1,6-hexamethylene diisocyanate (HDI) was obtained from Fluka (Switzerland).

Synthesis of the polyurethane elastomers

These polyurethanes were synthesized in the absence of any catalyst and with equivalent weight ratios of poly(ether)-diol/HDI/diol and triol of 1/2/1 and 1/3/2 (Table 1).

The isocyanate end-caped prepolymer was prepared by reaction of the required amounts of dried Terathane 1400 and HDI, in a 250 mL glass reactor equipped with a mechanical stirrer, a drying tube connected to the vacuum pump and an oil bath, at 80 °C for 2 h. The prepolymer was chain-extended using the required amount of DHPy and DMF as the solvent at 80 °C for 2 h. The polyurethane product was cast onto cleaned glass plates and kept at 80 °C for 24 h in order to obtain flexible polyurethane films. Polyurethane films thus prepared were used for the determination of physico-mechanical properties and for the thermal resistance and optical behavior.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 Instrument equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the range of 600–4000 cm^{-1} with a nominal resolution of 4 cm^{-1}.

Thermogravimetric experiments took place in an air atmosphere through thermogravimetric analysis (TGA) using a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of the TGA scans was of 10 °C/min. The initial weight of the samples was about 50 mg and the temperature range 30–700 °C.

Dynamic mechanical properties measurement was performed with a dynamic mechanical analyzer (Perkin Elmer Diamond DMA) at a constant heating rate of 2 °C/min and 1 Hz, within a temperature range of −100 to 250 °C. The sample dimension was of $10 \times 10 \times 0.45$ mm^3 and the tests were performed in extension mode.

The mechanical properties were determined using a Shimadzu EZTest (Japan), equipped with a 5kN load cell. Dumbbell-shaped specimens were prepared using dies (75 × 12.5 × 4 mm; ISO 37 type 2). The test specimens that were cut from the samples were no more than 0.5 mm thick. The specimens were prepared so as to be free of surface roughness, fabric layers, etc. The tests were performed at room temperature (23 °C), with a cross-head speed of 50 mm/min. All the tests were conducted for five samples and the averaged-valued were reported.

Table 1 Formulations and hardness of the obtained heterocyclic polyurethane elastomers

Samples	Polyether/HDI/chain extenders molar ratio	Type of chain extenders	Hardness shore A
PU1	1:2:1	2,3-dihydroxypyridine	80
PU2	1:3:1	2,3-dihydroxypyridine	89
PU3	1:2:1	2,3-dihydroxypyridine + glycerin	73
PU4	1:2:1	2,3-dihydroxypyridine + diethylene triamine	66
PU5	1:2:1	2,3-dihydroxypyridine + castor oil	40

The surface tension of the polyurethane surfaces was measured by means of static contact angle using the sessile drop method on a Dataphysics Contact Angle System KSV Instruments LTD, Finland. Contact angle measurements were performed at room temperature using de-ionized water and ethylene glycol. Each contact angle measurement was recorded within the first 10–20 s following the placement of the sessile drop over a fresh surface region and repeated for cross-verification. The contact angle was measured with an accuracy of ±2°.

H NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) on polyurethane solutions in DMSO-d6 and chemical shifts are reported in ppm and refer to tetramethylsilane as internal standard.

Results and discussions

Infrared study

The infrared spectroscopy of polyurethanes is used particularly in the study of the hydrogen-bond interactions of the typical strong absorption bands at 3300–3500 cm^{-1} (N–H stretching vibration) and at 1650–1750 cm^{-1} for the carbonyl (C=O) stretching vibration which appear after the formation of urethane groups [22]. The FT–IR spectra of DHPy-polyurethane elastomers are shown in Fig. 1.

The absorption peaks for the stretching vibration of the pyridine ring clearly appear at the frequencies of 1570 and 820 cm^{-1} for linear polyurethanes (PU1, PU2). The intensity of these absorption peaks, which are assigned to the pyridine group, increases with the increase of DHPy content. The pyridine group in the polyurethane backbone strongly affects the hydrogen bonding in the polyurethane elastomers. These stretching vibration bands decreased in intensity with the incorporation of crosslinkers, indicating a hindering of the hydrogen-bonding process.

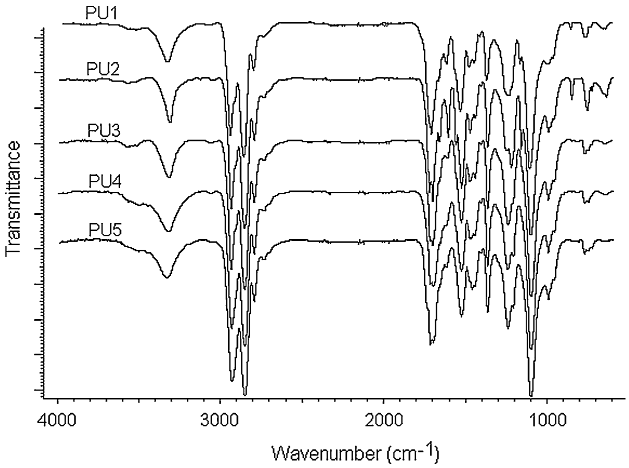


Fig. 1 FT–IR spectra of the synthesized polyurethane elastomers

The linear polyurethane with high content of DHPy (PU2) exhibits a splitting of the absorption peak of the carbonyl groups at 1680 and 1720 cm^{-1}. This can be explained by the strong hydrogen bonds which are formed between the C=O and N–H of the urethane groups and between the heteroatom of the pyridine ring and urethane N–H.

The C–O–C stretching of the polyurethane appears as a strong peak at 1100 cm^{-1} which proves that the ether group is also involved in H-bonding.

It can also be remarked that the N–H stretching vibration of the urethane group (at 3320 cm^{-1}) was made broader with the use of chemical crosslinks. This shows that crosslinking sites reduced freedom of movement of the molecular chains and thus more N–H groups were free from H-bonding.

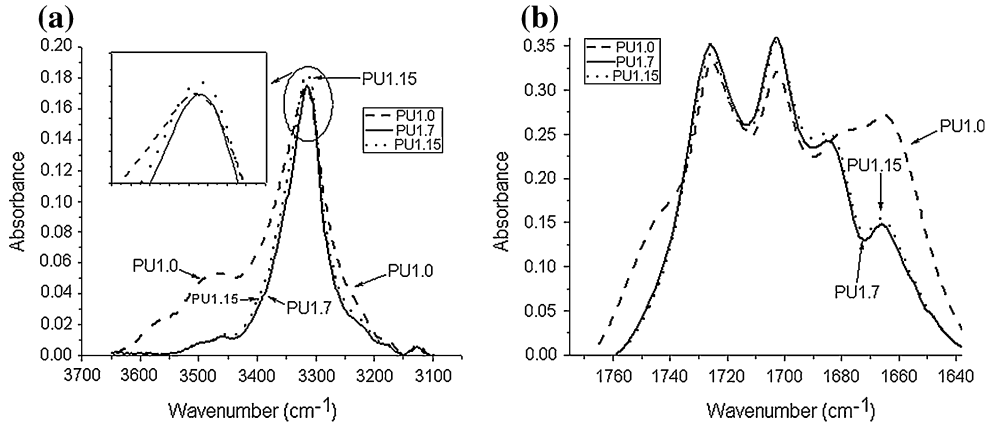
Figure 2 shows that, after 7 days of storage the shoulder at 1750 cm^{-1}, as well as the peaks at 1650 cm^{-1} and 3475 cm^{-1} have disappeared. This can be explained by the fact that the self-assemblage of the polyurethane matrix increases the hydrogen bonds between the N–H and the pyridine groups. The interaction split the hydrogen-bonded carbonyl band. Thus, the association of the N–H with pyridine groups favors ordered phase and promotes layer-packed units [23]. This implies that the urethane group can provide a large number of hydrogen donors and that the nitrogen atom of the pyridine ring has a great tendency to accept free H and thus the appearance of chromophore groups can be photoinduced within the molecular chain.

Thermal analysis

The thermal stability of the pyridine-based polyurethane with different formulations is determined by thermogravimetric analysis as given in Fig. 3.

The thermal analysis results indicated that initial decomposition temperatures are above 300 °C, which is attractive for the polymeric devices. The main decomposition started at about 300 °C and was complete around 500 °C. Polymers suffered the initial 10% weight loss in the range of 350–370 °C, indicating good thermal stability. As derived from the TGA curve, the maximum decomposition temperature ($T_{\max}$) of the polymers was in the range of 410–435 °C. The decomposition of the polymers in the final stage depends on the structure of the hard segments. In the case of polyurethanes with glycerin as crosslinker (PU3), weight loss is made more difficult because of the chemical cross-linking network, compared with linear polyurethanes or polyurethanes crosslinked with castor oil where dangling chain act as plasticizer. At 600 °C, the weight of the polymers had reduced to 9–17% of their

Fig. 2 Changes in the N–H (**a**) and C=O (**b**) spectra of the linear polyurethane (PU1) during storage in a laboratory environment. *Numbers* next to the sample designation indicate storage times in days



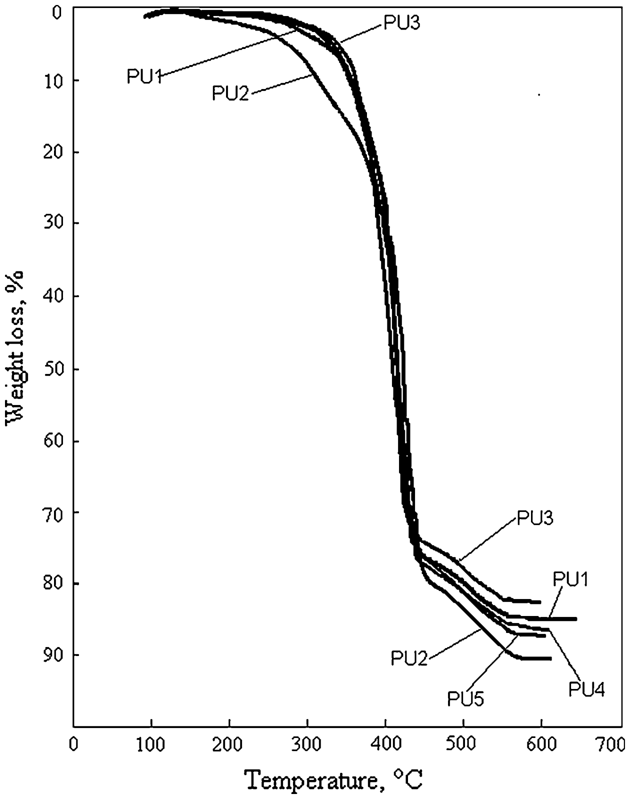


Fig. 3 TG curves of DHPy-based polyurethane films

initial weight, depending on the structure of the hard segments. These polyurethanes showed good thermal stability, which was a result of the incorporation of the rigid pyridine ring in the main chain. These results can be further improved by chemical crosslinking.

Dynamic mechanical analysis

Storage modulus (ε') and mechanical loss factor (tan *D*) curves as a variation of temperature for the various PU films are given in Fig. 4.

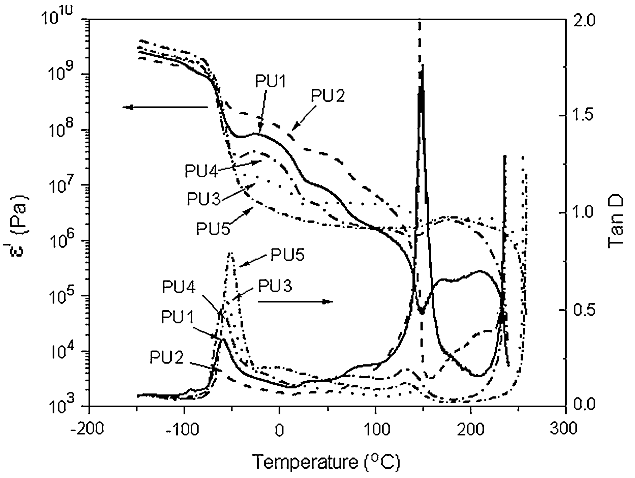


Fig. 4 The dependence of storage modulus (ε') and tan *D* on temperature for linear and crosslinked DHPy-based polyurethanes

The tan *D* values increased for samples that contain chemical crosslinks. The highest value is obtained in the case of the polyurethane crosslinked with castor oil. This is a result of the flexible nature of the dangling chains of castor oil. Crosslinkers shift the T_g values to higher values—from −64 °C (PU1) to −50 °C (PU5). The samples with chemical crosslinks exhibit a single T_g at around −50 °C. In the case of polyurethane than only had DHPy as a chain extender, two loss modulus peaks were observed, indicating phase separation. The peak at lower temperature is attributed to the glass transition of soft segments and the peak at higher temperature (120–150 °C) is due to the glass transition temperature of the hard phases [22]. The hard segments formed strong intermolecular interactions resulting in a largely ordered structure in this matrix phase. With the increase of the DHPy, the high temperature peak increases in intensity and the first peak decreases in intensity. This suggests that the hydrogen bonds have been formed predominantly between hard segments. The ordered structure of the hard phase in these PU is an effective source of strength for these samples.

Storage modulus (ε') versus temperature plots shows an almost continuous gradual decrease of ε' for polyurethanes with the highest DHPy content (PU2). This can be explained by the high interconnection between the molecular chains, generated through hydrogen bonds. The presence of the pyridine ring in the chain extender increases the stiffness of the polymer. On the contrary, for the polyurethane crosslinked with castor oil, ε' has an abrupt drop in the glass transition (T_g) region, followed by a large plateau region. This is a result of the disruptive effect of the dangling chains which cause a weaker packing cohesion of the hard domain due to hydrogen bond loss.

Mechanical properties

The stress–strain curves of the polyurethanes are presented in Fig. 5.

The linear polyurethanes which contain a high content of DHPy exhibited higher values of tensile strength and elongation (at break) compared to the chemically crosslinked samples. This is due to the nature of the pyridine compound chain extender—particularly their pair of electrons on the nitrogen atom—which allows for a higher degree of inter-cohesion bonding between the molecular chains. In PU2 the amount of hard domain with DHPy is very high, these areas representing physical multi-crosslinking points. The lowest value of tensile strength (2 MPa) was obtained in the case of polyurethanes crosslinked with castor oil (PU5). This indicates the plasticizing effect of their dangling chains.

With the increase of DHPy content, the tensile modulus at room temperature increases from 4.4 MPa (PU1) to 18.8 MPa (PU2) and elongation at break decreases.

These results are determined by the chemical structure of the DHPy which caused an increase in the stiffness of the material when introduced in the backbone chain. The dangling chains from the castor oil decrease tensile modulus values until 0.5 MPa (PU5). The different mechanical behavior is determined by the different hard segment chemical structure of polyurethane.

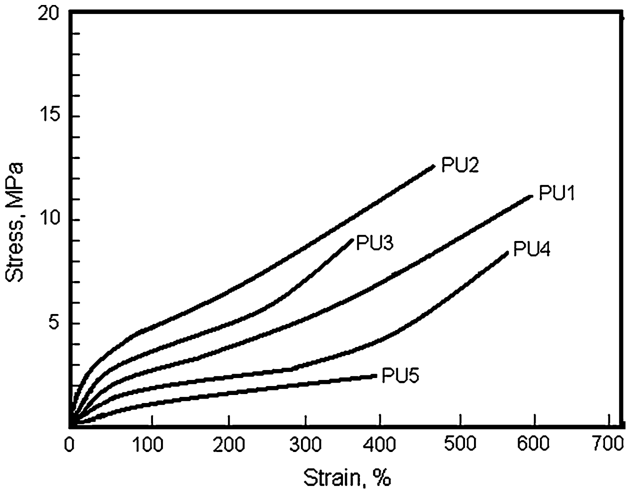


Fig. 5 Stress versus strain curves for the DHPy-polyurethane films

Contact angle measurements

The surface tension of the polymer surfaces was measured by means of static contact angle. The hydrophobic or hydrophilic properties of the polymer surface are important for establishing the biocompatibility of polymeric materials. The mobility and flexibility of the molecular chain makes its rearrangement possible, in order to create a rich hydrophilic or hydrophobic surface. This can also be determined through the variation of the hard segment structure [24]. The contact angle is composed of interactions of the three interfaces as described by Young's equation: [25]

$$\gamma_{SV} = \gamma_{SL+}\gamma_{LV}\cos(\theta) \quad (1)$$

where γ_{SV}, γ_{SL}, and γ_{LV} represent the interfacial tension of the solid/vapor, solid/liquid, and liquid/vapor interfaces. The equilibrium contact angle is represented by θ.

The measured contact angles of linear and crosslinked polyurethanes and the surface tension values are given in Tables 2 and 3, respectively.

The DHPy-based polyurethanes present a gradually declining hydrophilic character of the surface with the increase in DHPy content, so that PU2 has the highest value for water contact angle (119°). Also, the water contact angles increased from 90° for linear polyurethanes with a low content of DHPy (PU1) to 99° for polyurethanes with castor oil as crosslinker (PU5).

The differing contact angle values of the linear polyurethanes (PU1 and PU2) can be explained as the effect of the large interaction between molecular chains due to physical crosslinks of the wide hard segment and pyridine derivative, which hindered polar groups from migrating toward the polyurethane film surface. In the case of castor oil as crosslinker, it was hindered by the chemical crosslinks

Table 2 Contact angle (θ) and work of adhesion (W_a) values of the DHPy-based polyurethane films surfaces

Samples	Water		Ethylene glycol	
	θ (°)	W_a (mN/m)	θ (°)	W_a (mN/m)
PU1	90 ± 1	72.5	71 ± 1.8	63.8
PU2	119 ± 1.3	37.5	107 ± 1.7	34.3
PU3	94 ± 1.5	67.1	72 ± 2	63.2
PU4	92 ± 1.9	70.5	70 ± 1.2	64.5
PU5	99 ± 1.2	61.2	77 ± 1.1	58.9

Table 3 Interfacial tension for a solid–liquid system (γ_{sl}) in DHPy-based polyurethane films

Samples	λ_{sv}^{p} (mN/m)	λ_{sv}^{d} (mN/m)	γ_{sl} (mN/m)	
			Water	Ethylene glycol
PU1	6.5	14.9	21.7	5.6
PU2	1.3	5.1	41.7	20.1
PU3	3.3	19.2	28.3	7.4
PU4	4.6	17.9	24.9	6.1
PU5	2.3	18	31.8	9.4

p polar, *d* disperse

and hydrophobic nature of the castor oil. The increase in surface energy for PU5 can be explained by the introduction of polar functional groups provided by the castor oil.

The surface energy (γ_{SV}) is a results of disperse interactions and polar interactions [26].

$$\gamma_{SV} = \gamma_s^d + \gamma_s^p \qquad (2)$$

Polar interactions contain Coulomb interactions between permanent dipoles as well as interactions between permanent and induced dipoles. Dispersive interactions are caused by fluctuations in time of the charge distribution within the molecules [25].

The values of the surface tension tend to increase with the increase in DHPy content. The values of the contact angles may have varied due to differences in the chemical composition of the surface, but also due to differences in surface structure [27].

Optical properties

The activation of the photochemistry in the DHPy-based polyurethane films during laboratory storage is confirmed by the changes in color evolving from white to green, brown, and finally black (Fig. 6).

This change was obtained without modification of the ambient conditions, such as UV light exposure or temperature. If samples are stored in the same ambient conditions but in the dark there is no color change. We believe that this color change is induced by chemical modifications of the polymer systems with the creation of chromophore groups by de-protonation of the urethane N–H and formation of N–N bonds. The result is made possible by the DHPy hydroxyl groups, which are in *ortho*-position relative to one another.

H NMR study

The H NMR spectrum of PU1 showed peaks that confirms its chemical structure (Fig. 7). Peaks in the region of 1.22–2.2 ppm are related to H of CH_2 from PTMG and HDI. Peaks in the regions of 3 and 4 ppm are related to CH_2 bound up NH and O from urethane or ether, respectively. The aromatic protons appeared in the region of 5.5–7.9 ppm. The peaks in the region of 8.1–9 ppm are assigned to the NH of amide and urethane groups.

The structural changes during storage in laboratory environment were monitored by H NMR analysis of the PU1 sample at different storage times. After storage new peaks are generated and others disappear. Thus, after 20 days of

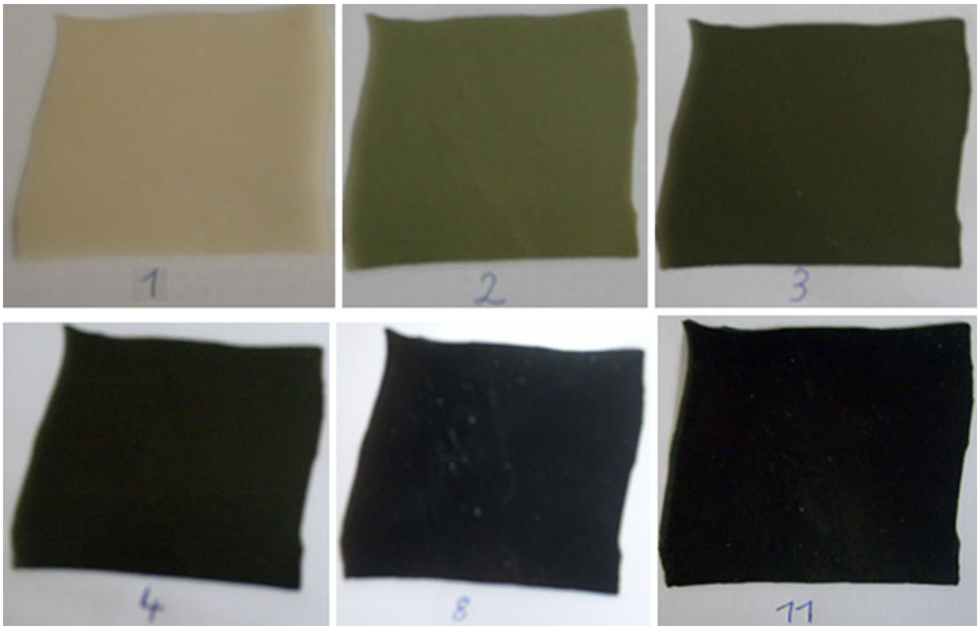


Fig. 6 Color changes of the linear DHPy-based polyurethane film (PU1) during laboratory storage. The *numbers* at the bottom of each sample represent storage days

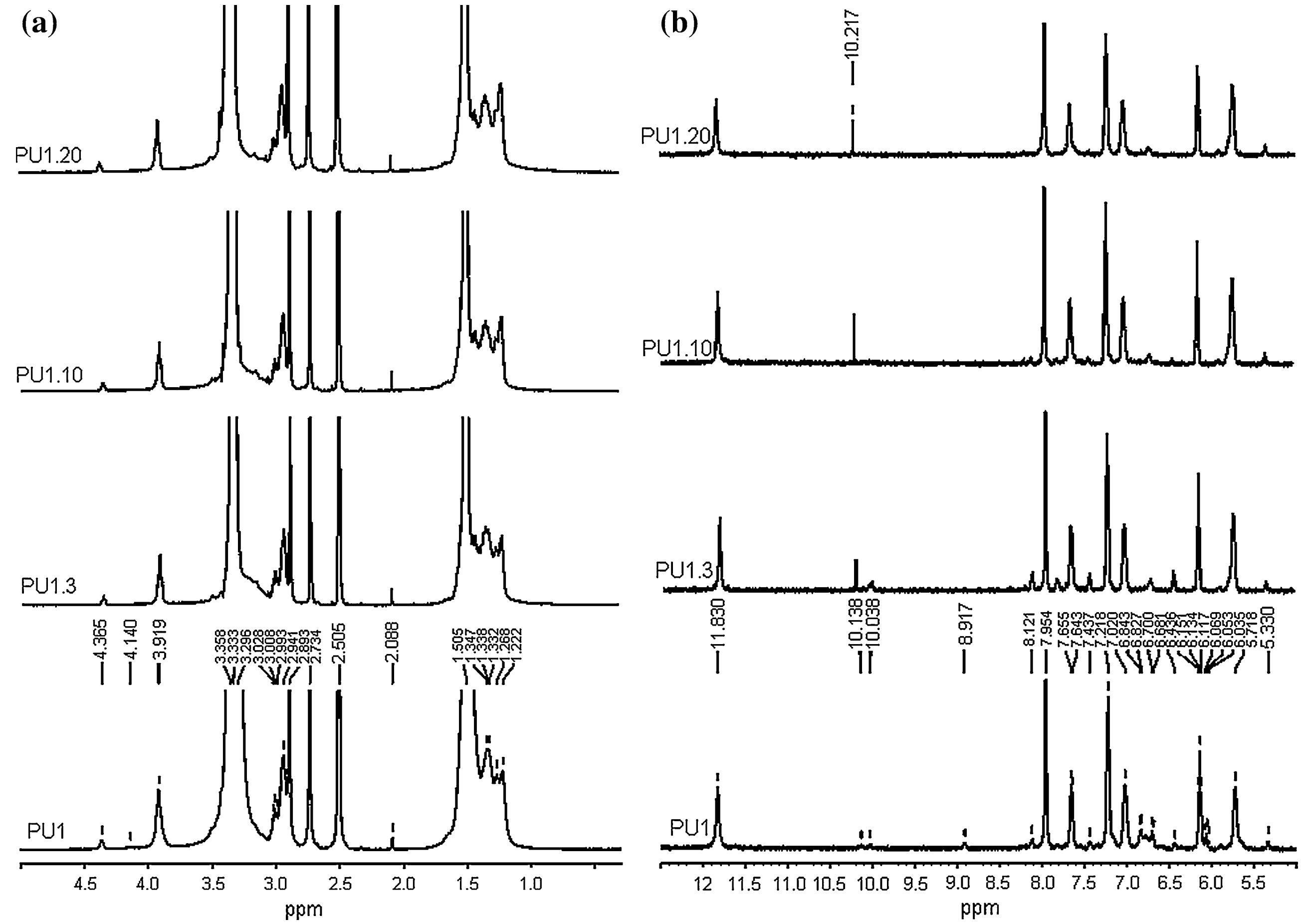


Fig. 7 H NMR spectra of PU1 in the aliphatic field (**a**) and aromatic field (**b**). *Numbers* next to the sample designation name indicate storage time (1–20) in days

storage the signal of the urethane proton (NH–CO–O) at 8.12 ppm totally disappeared. The lost of the NH proton shows the N-modification of the PU. The urethane N–H group is a proton donor and the heteroatom N from pyridine is an acceptor. The ortho-position of the dihydroxy pyridine provides the appropriate steric structure for the formation of the N–N bonds between urethane groups.

From the H NMR spectra (Fig. 7), we observed the disappearance of the peak at 10.038 ppm after 10 days of storage and the increase of the peak at 10.138 with the storage time. The upward trend of the aromatic protons on the pyridine ring and of the urethane group suggests a change in the electron density of the aromatic rings. The pyridine moiety seems to play an important role in the coloration process.

Also, new peaks appeared in the H NMR spectra in the range of 1.2–1.5 ppm. The peaks at 1.36–1.44 ppm can be assigned to the methylenes of the HDI and PTMO, respectively. The ratio of both areas was reduced from 111 to 66 after 20 days of storage.

These results indicate that the urethane bond suffers changes during storage of the polymer films. The signal at 1.22 showed an intensification of such changes with the increase of the storage time.

The proton intra- and inter-chain migration was possible because the polymer chains were aggregated within close proximity of each other. The decrease in area ratio or disappearance of the urethane NH peaks after storage indicates the amount of proton migration. On the basis of the ortho position of the pyridine urethane, the action of light results in a weakened NH bond due to resonance with the electron-withdrawing pyridine nitrogen. The equilibrium state is obtained through formation of the inter-chain N–N group.

Conclusions

DHPy-based polyurethane elastomers were synthesized from different chain extenders and different crosslinkers in various amounts. Static measurements showed higher tensile strength and elongation for linear polyurethane films. High contact angles of the cast films of linear polyurethane with high content of DHPy indicated the existence of strong interconnections due to the chain extender structure that modified surface polarity.

The main factor responsible for the photo-behavior of the polyurethane films stored in a light-exposed environment is the migration of the proton from urethane units to the pyridine nitrogen atom and the formation of chromophore units between polyurethane chains due to the specific ortho-structure of DHPy. No color changes were observed in the dark-kept samples. These differences in the color change rate between the light and non-light exposed samples suggest that light plays a primary role in this process.

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