



# Synthesis and characterization of novel linear and cross-linked polyurethane urea elastomers with 2,3-diaminopyridine in the main chain

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## Abstract

Novel polyurethane urea containing pyridine moieties in their main chains have been prepared by a two-step solution polymerization procedure. These polyurethane urea elastomers were synthesized by chain-extending isocyanate end-capped prepolymers with 2,3-diaminopyridine and different cross-linkers. The isocyanate-terminated prepolymers were obtained from poly(tetramethylene oxide) glycol of molecular weight 1400 (Terathane 1400) and 1,6-hexamethylene diisocyanate. Including pyridine derivatives into the structural compositions leads to a change in properties that were investigated using Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), mechanical measurements and contact angle and fluorescence analysis. The results show that intermolecular hydrogen bonds have formed between pyridine groups and urethane or urea groups, affecting all the obtained properties.

## Keywords

polyurethane urea, diaminopyridine, cross-linkers, mechanical properties, thermal behavior

## Introduction

Polyurethane urea elastomers are an important class of copolymers that have superior extensibility, toughness and durability compared with conventional polyurethanes. This is a result of the higher cohesiveness given by the urea linkages in the hard segment and of the degree of microphase separation being different from that of similar polyurethanes. Polyurethane urea morphology is affected by the chemical structure and stoichiometric ratio of the components, by the molecular weight and distribution of the segment as well as by the method used in the preparation of the polymer. The enhancement of the morphology and properties of such materials is significantly influenced by the new chemical structure of the chain extender from the hard domain, which promotes strong intermolecular association through physical cross-links. Also, the hard segment chemical cross-links increase structural integrity, improving both the working temperature range and mechanical properties.<sup>1–8</sup>

One way that can be used to improve the thermal and mechanical properties of the polyurethane urea is changing the chemical structure of the hard segment by introducing stable aromatic heterocyclic rings into the polymer backbone

chains.<sup>2,9,10</sup> Thus, using pyridine moieties as a typical hydrogen acceptor enables the creation of conjugated polymers with electroconductive and photoconductive properties.<sup>11,12</sup> Pyridine is a heteroaromatic ring which can be found in natural and synthetic compounds. In addition, by introducing ionic moieties at the tertiary nitrogen during the chain extension stage, new products can be developed.<sup>13,14</sup>

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, adhesion between substrates and improves the physicomaterial and chemical resistance properties. The introduction of a heterocyclic ring such as pyridine in the main chain of a polymer also leads to high

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**Table 1.** Formulations of the obtained 2,3-diaminopyridine (DAPy)-polyurethane urea elastomers.

Samples	Polyether/HDI/ chain extenders molar ratio	Type of chain extenders
PUU1	1:2:1	2,3-diaminopyridine
PUU2	1:3:2	2,3-Diaminopyridine
PUU3	1:2:1	2,3-Diaminopyridine + glycerin
PUU4	1:2:1	2,3-Diaminopyridine + diethylene triamine
PUU5	1:2:1	2,3-diaminopyridine + castor oil
PUU6	1:2:1	2,3-diaminopyridine + pyrogallol

thermal stability derived from the pyridine aromatic molecular symmetry.<sup>15–17</sup>

This article reports the synthesis of novel polyurethane urea that incorporates pyridine moieties into the main chain with the objective of increasing thermal stability and mechanical properties. To examine the effect of the pyridine content and cross-linker structure the obtained polyurethane urea were examined by Attenuated total reflectance (ATR)-Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile testing and surface properties evaluation.

## Experimental

### Materials

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

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

### Synthesis of the polyurethane urea elastomers

We obtained polyurethane urea with similar flexible segments and different rigid blocks. The polyurethane urea was synthesized using the compositions given in Table 1. Figure 1 shows the basic reactions involved in the preparation of the polyurethane urea.

The isocyanate end-capped 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 Isocyanate (NCO)-prepolymer was chain extended using the required amount of DAPy with DMF as the solvent at 80°C for 2 h. The polyurethane urea product was cast onto clean glass

plates and kept at 80°C for 24 h in order to obtain flexible polyurethane urea films.

### Measurements

FT-IR 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<sup>-1</sup> with a nominal resolution of 4 cm<sup>-1</sup>.

Thermogravimetric experiments took place in an air atmosphere through TGA using a DERIVATOGRAPH 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°C–700°C.

DSC measurements of the synthesized materials were performed on a DSC-7 Perkin-Elmer at a heating rate of 10°C/min. The thermal transition behavior was studied in a temperature range of –100°C to 40°C. Tests were conducted on samples of about 10 mg that were gradually heated in order to observe the glassy transition temperature (*T<sub>g</sub>*). The DSC experiments were carried out with a liquid nitrogen cooler in a helium atmosphere.

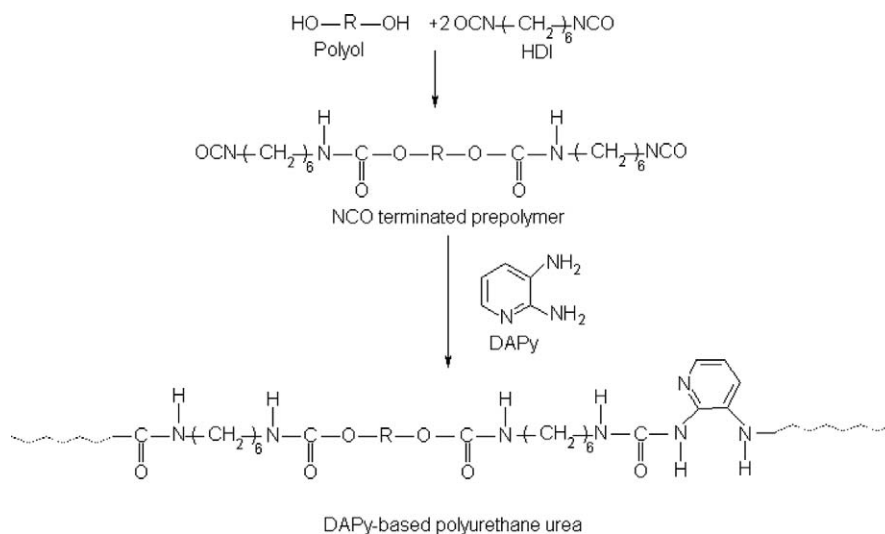
The mechanical properties were determined using a Shimadzu EZTest (Japan), equipped with a 5 kN load cell. Dumbbell-shaped specimens were prepared using dies (75 × 12.5 × 4 mm; ISO 37 type 2). The test specimens that were cut from the samples were no more than 0.5 mm thick. The specimens were prepared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

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 deionized 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°.

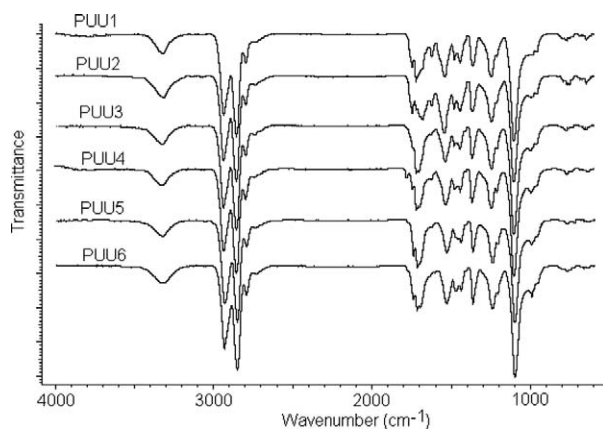
Fluorescence spectra were obtained at room temperature on a LS55 PerkinElmer spectrometer (Shelton, USA). The fluorescence spectra were measured at a 300 nm excitation and for emission wavelengths of 300–550 nm.

## Results and discussion

The properties of the polyurethane urea are determined by the composition of the hard and soft segments. The introduction of a heterocyclic ring, urea groups and chemical cross-links into the backbone chain via chain extenders provides additional interchain stiffness which enhances polymer properties. Thus, the hydrogen bonds determine



**Figure 1.** Schematic representation of DAPy-based polyurethane urea synthesis. DAPy: 2,3-diaminopyridine.



**Figure 2.** FT-IR spectra of the synthesized DAPy-polyurethane urea elastomers. FT-IR: Fourier transform infrared spectroscopy; DAPy: 2,3-diaminopyridine.

increased mutual attractions within the hard segments domain. These are studied by infrared spectroscopy, particularly the hydrogen bond interactions of the typical strong absorption bands at 3300–3500  $\text{cm}^{-1}$  (N-H stretching vibration) and at 1600–1800  $\text{cm}^{-1}$  for the carbonyl (C=O) stretching vibration which appear after the formation of urethane and urea groups.<sup>18</sup> The FT-IR spectra of DAPy polyurethane urea elastomers are shown in Figure 2.

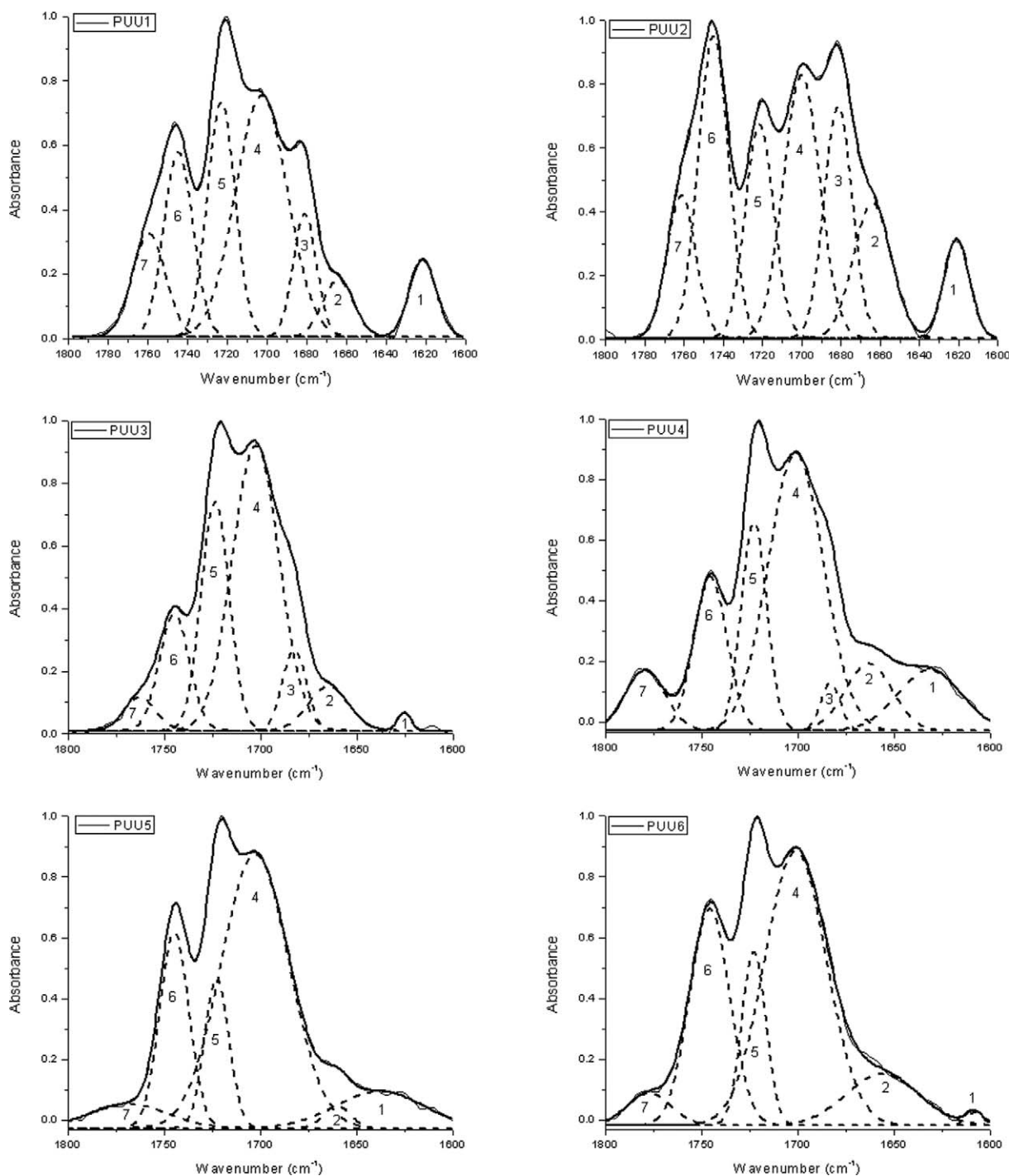
The absorption peaks for the stretching vibration of the pyridine ring clearly appear at the frequencies of 1537  $\text{cm}^{-1}$  and 793  $\text{cm}^{-1}$  for linear polyurethanes (PUU1, PUU2), thus shifting to lower frequencies than polyurethanes obtained with 2,3-dihydroxypyridine.<sup>12</sup> The intensity of the absorption peak from 1537  $\text{cm}^{-1}$  increases with the DAPy content. The pyridine and urea groups from the

polyurethane backbone strongly affected the hydrogen bonding in the polyurethane urea elastomers. These stretching vibration bands decreased in intensity with the incorporation of cross-linkers, indicating a hindering of the hydrogen-bonding process. The C–O–C stretching of the polyurethane urea appears as a strong peak at 1100  $\text{cm}^{-1}$ .

The microphase separation—which determines the final properties—can be measured by the hydrogen bonds between the N-H group and carbonyl of the urethane or urea and ether oxygen of the polyether soft segment. In the spectra of polyurethane urea, the individual peak positions of the bands at 1600–1800  $\text{cm}^{-1}$  (amide I carbonyl stretching vibrations) were identified by Fourier self-deconvolution. The deconvoluted bands of the carbonyl stretching region are shown in Figure 3.

The linear polyurethane urea that contains only DAPy (PUU1 and PUU2) as chain extender exhibits absorption stretching vibrations of urea carbonyl group peaks at 1664  $\text{cm}^{-1}$  (hydrogen-bonded urea C=O) and 1683  $\text{cm}^{-1}$  (free urea C=O). By increasing the urea linkage in the polymer structure, the area percentage of these peaks increases from 5% (PUU1) to 12% (PUU2) which confirms that hydrogen bonds enhance hard segment connections (Table 2). Additionally, the absorption peak from 1622  $\text{cm}^{-1}$  can be explained by the strong hydrogen bonds that form between the heteroatom of the pyridine ring and urethane N–H. The urethane group can give way to a large number of N–H ···N–Py hydrogen bonds.

The urethane carbonyl stretching vibrations present a peak from 1745  $\text{cm}^{-1}$  and 1700  $\text{cm}^{-1}$  corresponding to the free urethane carbonyl groups and hydrogen-bonded urethane carbonyl groups. The stretching vibrations at 1720  $\text{cm}^{-1}$  and 1761  $\text{cm}^{-1}$  can be associated with ordered and, respectively, disordered hydrogen-bonded carbonyl.



**Figure 3.** Deconvoluted FT-IR spectra of pyridine-based polyurethane urea: carbonyl stretching region. Solid line: recorded spectra; dashed line: resolved peaks; FT-IR: Fourier transform infrared spectroscopy.

The frequencies of the disordered hydrogen-bonded carbonyl vary according to the used cross-linker structure. A comparison of the percentage area reveals that the hard segment structure sets the proportion of hydrogen-bonded urethane and urea carbonyl groups. If the degree of hydrogen bonding and ordering of the carbonyl groups increases, it results in an enhanced

phase-separated microstructure and better mechanical properties (PUU3, PUU5, PUU6).

The use of a diamine chain extender determines an increase in polymer backbone urea linkages which provide more hydrogen bonding between the carbonyl and NH groups, enhancing microphase separation.<sup>19</sup> Also, the association of the N-H with the pyridine group

**Table 2.** The position of the peaks and their areas for the carbonyl stretching regions of the prepared pyridine-based polyurethane ureas.

Sample code	Peak positions, $\text{cm}^{-1}$ (% area)						
	1	2	3	4	5	6	7
PUU1	1621 (6)	1664 (5)	1681 (8)	1703 (36)	1723 (19)	1744 (16)	1759 (10)
PUU2	1621 (6)	1664 (12)	1681 (15)	1700 (22)	1721 (14)	1745 (21)	1761 (10)
PUU3	1625 (1)	1664 (6)	1682 (7)	1702 (47)	1723 (23)	1745 (12)	1762 (4)
PUU4	1631 (11)	1663 (9)	1682 (2)	1700 (42)	1722 (15)	1745 (14)	1779 (7)
PUU5	1638 (10)	1660 (2)	–	1702 (55)	1722 (11)	1745 (17)	1768 (5)
PUU6	1608 (1)	1655 (11)	–	1701 (48)	1722 (12)	1745 (24)	1777 (4)

favors ordered phase and promotes layer-packed units.<sup>20</sup>

### Thermal behavior

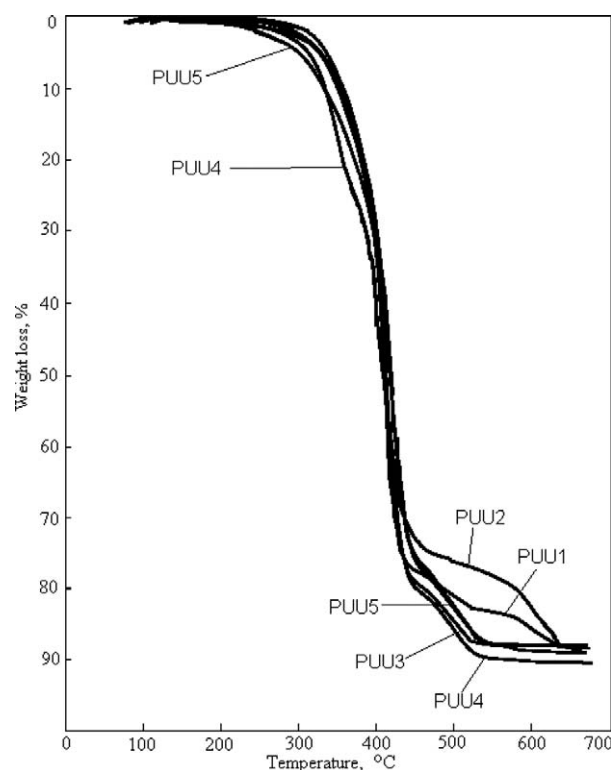
Because hard segment structure strongly influences the first stage of the thermal degradation, the introduction of heterocyclic diamine into the backbone chain was performed in order to increase the thermal stability of the polyurethane urea. The thermal stability of the pyridine-based polyurethane urea with different hard segment composition was evaluated based on the TGA data as given in Figure 4.

The polyurethane urea exhibits better thermal stability than polyurethanes obtained with 2,3-dihydroxy pyridine as chain extenders,<sup>12</sup> as a result of the high concentration of urea bonds that improve thermal stability. Also, the polyurethane urea with higher content of DAPy (PUU2) showed better stability in the last stage of the thermal degradation (after 450°C). If the complete decomposition of chemically cross-linked polyurethane urea took place around 550°C, the uncross-linked samples (PUU1 and PUU2) showed a complete decomposition at around 650°C. This shows a higher amount, and at the same time stronger hydrogen bonds that increase intermolecular chain connections.

Polymers suffered the initial 10% weight loss in the range of 370°C–380°C, indicating very good thermal stability. The initial weight loss takes place at lower temperatures for samples cross-linked with castor oil (PUU5) due to the presence of dangling chains in their structure acting as plasticizers.

At 700°C, the weight of the polymers was reduced to 9%–12% of their initial weight, depending on the structure of the hard segments. The polyurethane urea showed good thermal stability due to the incorporation of the rigid pyridine ring and urea groups into the main chain.

It is known that the chemical structure of the hard segment determines the flexibility or stiffness of the main chain and the types of physical interactions between functional groups. The thermal behavior of different polyurethane urea samples was studied with DSC and the obtained thermograms are shown in Figure 5.

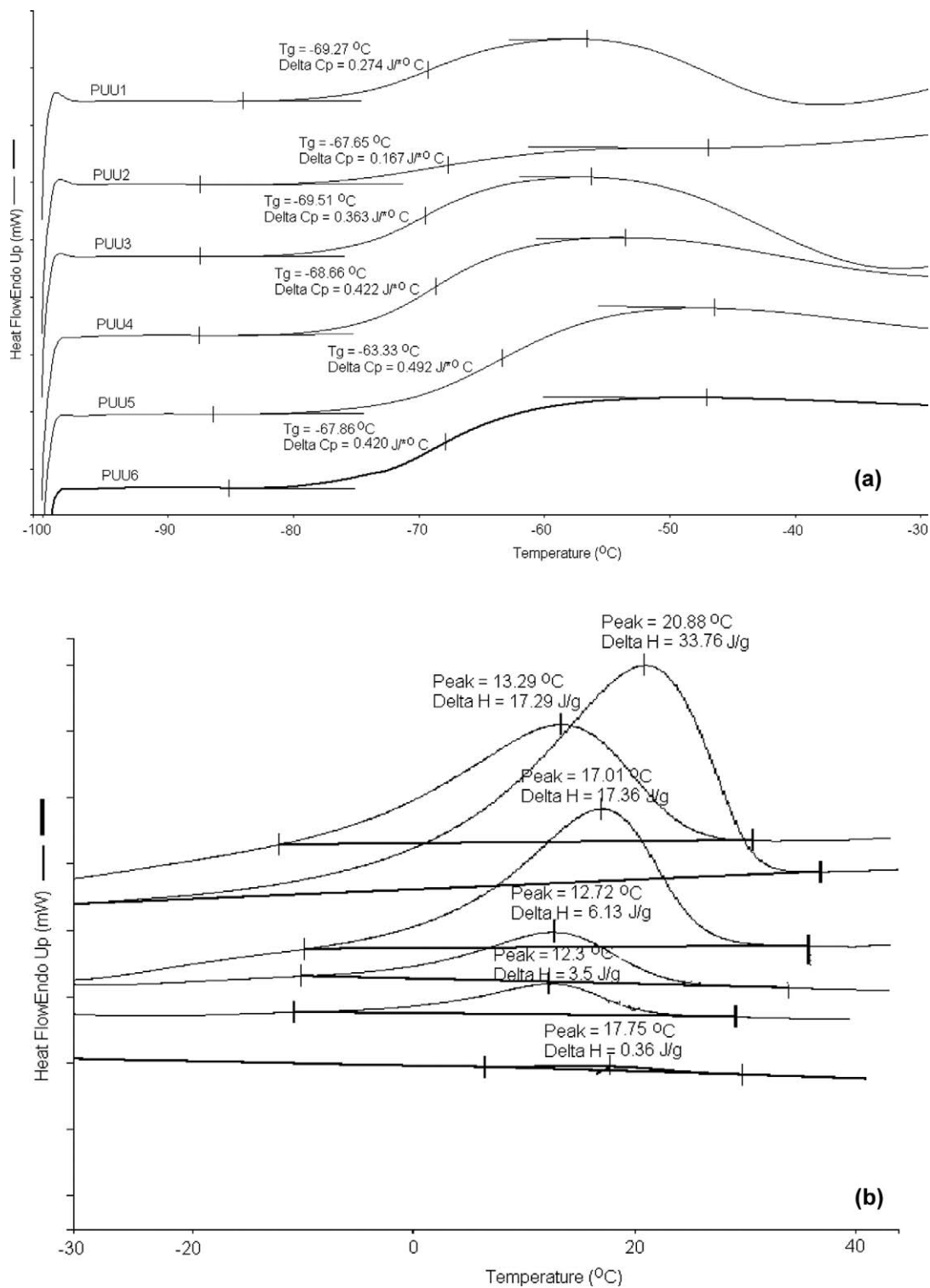


**Figure 4.** TG curves of DAPy-based polyurethane urea films. TG: thermogravimetric; DAPy: 2,3-diaminopyridine.

The obtained results indicate that the glass transition temperature of the soft segments slightly increases with the increase in DAPy content from  $-69^{\circ}\text{C}$  to  $-67^{\circ}\text{C}$  (PUU1 vs PUU2). The  $T_g$  of the soft segments is close to the  $T_g$  of polyols (about  $-70^{\circ}\text{C}$ ), indicating that the hard and soft segment phases should be significantly phase separated.

However, because all synthesized polyurethane urea used the same type and length of polyol, the variation in chain mobility can be attributed to the structure of the hard segment. The chemically cross-linked network of the hard segment weakened the flexibility of the soft segments, so that  $T_g$  was improved. This indicates that a chemically cross-linked structure of the hard segments prevents the formation of a significant number of hydrogen bonds

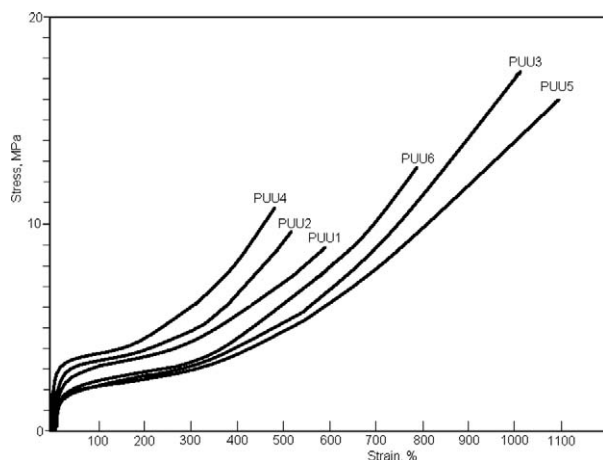




**Figure 5.** DSC thermograms of (a) glass transition and (b) melting soft segments of the DAPy-based polyurethane urea films. DSC: differential scanning calorimetry; DAPy: 2,3-diaminopyridine.

between the hard and soft segment. The variation in the polymer glass transition temperatures is in good agreement with the FT-IR investigation results of hydrogen bonding between the hard and soft segments.

Also, the small endothermic peaks appearing in DSC results may be related to the melting of the soft segment ordered structure. The endothermic transitions around 12°C–20°C could be associated with the breakdown of



**Figure 6.** Stress vs strain curves for the DAPy-polyurethane urea films.

DAPy: 2,3-diaminopyridine.

hydrogen bonding between the polyurethane/urea and ether bonds. The  $\Delta H$  associated with this transition was higher for PUU1, PUU2 and PUU3. This was a result of the high content of DAPy which enhances hard segment cohesion by hydrogen bonding interaction. Also, the presence of glycerol in PUU3 increases the mobility of the molecular chains increasing the ordering of polymer segments. The lowest value (0.36 J/g) was obtained for samples with pyrogallol as cross-linker due to its aromatic rigid structure. This prevents the ordering of polymer main chain segments via hydrogen bonds.

### Mechanical properties

The stress-strain curves of the polyurethane urea are presented in Figure 6.

The linear polyurethane urea which contains a high content of DAPy (PUU2) exhibited higher values of tensile strength and a slight decrease in elongation (at break) compared to polyurethane urea with lower content of DAPy (PUU1). This is due to the increased amount of pyridine and urea groups from the DAPy chain extender which allows for a higher degree of interchain cohesion by hydrogen bonding. The lower strain at break (450%) was obtained in the case of polyurethane urea cross-linked with diethylene triamine (PUU4). This is a result of PUU4 having formed the highest amount of urea groups that increase physical cross-linking. In this case, the modulus exhibits a high value (37 MPa) due to the reinforcing effects of the urea groups. The highest stress and strain at break values were obtained for samples cross-linked with glycerol and castor oil (PUU3 and PUU5). This indicates that DAPy decreases the plasticizing effect of castor oil dangling chains. The samples cross-linked with pyrogallol (PUU6) obtained lower values due to the aromatic chemical

**Table 3.** Contact angle ( $\theta$ ) and work of adhesion ( $W_a$ ) values of the 2,3-diaminopyridine (DAPy)-based polyurethane urea films surfaces.

Samples	Water		Ethylene glycol	
	$\theta(^{\circ})$	$W_a$ (mN/m)	$\theta(^{\circ})$	$W_a$ (mN/m)
PUU1	$82 \pm 1.1$	82.1	$72 \pm 1.4$	62.8
PUU2	$84 \pm 1.2$	79.3	$58 \pm 1.5$	72.8
PUU3	$78 \pm 1.2$	87.2	$73 \pm 1.2$	61.6
PUU4	$91 \pm 1.5$	70.8	$72 \pm 1.2$	62.2
PUU5	$95 \pm 1.4$	65.3	$72 \pm 1.3$	62.3
PUU6	$90 \pm 1.2$	71.9	$68 \pm 1.2$	65.5

**Table 4.** Interfacial tension for a solid-liquid system ( $\gamma_{sl}$ ) in 2,3-diaminopyridine (DAPy)-based polyurethane urea films.

Samples	$\lambda_{sv}^p$ (mN/m)	$\lambda_{sv}^d$ (mN/m)	$\gamma_{sl}$ (mN/m)	
			Water	Ethylene glycol
PUU1	16.9	6.3	13.8	8.3
PUU2	5.7	23.2	22.5	4.1
PUU3	25.1	2.8	13.5	14.2
PUU4	6.3	14	22.2	6.1
PUU5	2.8	19.6	29.8	8.1
PUU6	5	18.2	24.1	5.7

p: polar; d: disperse.

structure of pyrogallol which caused an increase in material stiffness when introduced in the backbone chain.

### Surface properties

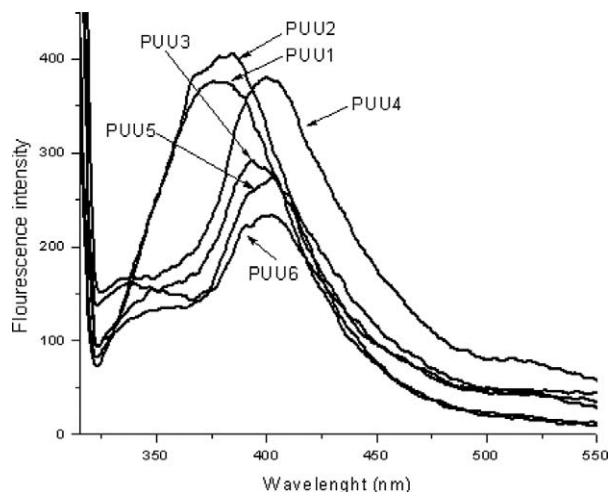
The hydrophobic or hydrophilic properties of the polymer surface are important for establishing water resistance and the degree of biocompatibility of polymeric materials. This can be measured by contact angle and surface energy. Changes in contact angle value are influenced by the film surface chemical structure which is a result of the free movement of the polar groups toward the film surface. This can be determined through the variation in the hard segment structure.<sup>21</sup> The contact angle is composed of interactions of the three interfaces as described by Young's equation<sup>22</sup>

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

where  $\gamma_{SV}$ ,  $\gamma_{SL}$  and  $\gamma_{LV}$  represent the interfacial tension of the solid/vapor, solid/liquid and liquid/vapor interfaces.

Contact angle measurements were made on the surface of the polyurethane urea films in order to estimate the influence of hard segment structure on their wettability and surface energy.

The water contact angle and surface tension measurements of polyurethane urea are shown in Tables 3 and 4.



**Figure 7.** Fluorescence emission spectra of DAPy-polyurethane urea films excited at 300 nm. DAPy: 2,3-diaminopyridine.

The water contact angle slightly increases with the increase in DAPy content from 82° to 84° (PUU1 vs PUU2). This results in increased hydrogen bonding interactions. A lower value of the contact angle was obtained for samples cross-linked with glycerol 78° (PUU3). This can be explained by the fact that chemical cross-links hindered the formation of all possible hydrogen bonds, yet the materials retained enough flexibility to allow polar groups to reach film surface. The highest water contact angle (95°) was obtained for samples cross-linked with castor oil (PUU5) as a result of the hydrophobic nature of castor oil.

Similar behavior was also obtained for the interfacial tension within the film-water system (Table 4). The values of the surface tension increase with the increase in DAPy content from 13 to 22 mN/m (PUU1 vs. PUU2). The high hydrogen bonding of the hard segment led to a higher degree of phase separation that hindered polar group movement. Higher values were obtained for samples cross-linked with castor oil and pyrogallol (PUU5 and PUU6). In the case of pyrogallol this is a result of the rigid aromatic structure of the cross-linker.

The fluorescence spectra of the DAPy-based polyurethane urea are shown in Figure 7.

Fluorescence intensity increases with the increase in DAPy content. The highest fluorescence intensity was obtained with the highest content of DAPy (PUU2). All cross-linked samples exhibited lower fluorescence intensity because the cross-linkers increase the efficiency of the interchain crossing process. Also, the fluorescence spectra shift from 376 nm (PUU1) to 402 nm (PUU5, PUU6) when DAPy content and chemical cross-linking increase.

The fluorescence spectra behavior can be explained by charge migration from the urethane, urea and heterocyclic

groups. The proton density of the urethane nitrogen atom decreases and thus the number of charges increases for the nitrogen atom of the pyridine ring. In this case the pyridine rings become strongly interconnected with the urethane and urea groups by H bonds. The optical properties of the polyurethane urea films depend on the connectivity of the pyridine rings from the polymer backbone which is in turn enhanced by hydrogen bonding and by the nature of the chemical cross-links.

## Conclusion

Novel polyurethane urea elastomers containing 2,3-diamino pyridine in the backbone chain were synthesized and characterized. The properties depended on the strength of the intermolecular hydrogen bonds between pyridine moieties, urethane and urea groups due to the flexibility of the polymer matrix being determined by cross-linker structure. This explains the good thermal behavior of these polyurethane ureas. Flexible cross-linkers lead to higher tensile strength and elongation. The high contact angles of the cast films indicated the existence of strong interconnections due to the diamino pyridine structure that modified surface polarity.

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