Thermally reversible cross-linked poly(ether-urethane)s

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Received 6 February 2013; accepted in revised form 14 April 2013

Abstract. Cross-linked poly(ether-urethane)s were prepared by Diels-Alder (DA) reaction of the furan-containing poly(ether-urethane) to bismaleimides and showed thermal reversibility evidenced by differential scanning calorimetry and attenuated total reflectance in conjunction with Fourier transform infrared spectroscopy (ATR-FTIR). The furan-containing poly(ether-urethane)s were synthesized by the polyaddition reaction of 1,6-hexamethylene diisocyanate (HMDI) or 4,4'-dibenzyl diisocyanate (DBDI) to poly(tetramethylene ether) glycol (PTMEG having $M_n = 250, 650, 1000, 1500$ and 2000) and 2-[*N,N*-bis(2-methyl-2-hydroxyethyl)amino]furfuryl as chain extender by the solution prepolymer method. The molar ratio of isocyanate: PTMEG:chain extender varied from 2:1:1 to 4:1:3, which produces a molar concentration of furyl group ranging between $3.65 \cdot 10^{-4}$ and $1.25 \cdot 10^{-3}$ mol/g.

Keywords: thermal properties, polyurethanes, Diels-Alder reaction, networks

1. Introduction

The application of reversible Diels-Alder (rDA) chemistry to the dynamic covalent assembly of organic materials has been only recently explored [1–4]. The number of DA reactions that undergo dynamically reversible adduct formation under mild conditions is, however, limited and there is an increasing interest in expanding the set of dynamic covalent DA reactions [5–8].

Over the past 10 years several groups have explored the use of reversible DA adduct formation in the design and synthesis of new organic materials, the most of such studies utilize the reactivity of electron-rich furan derivatives and electron-poor maleimide derivatives [9]. The DA cycloaddition of furan and maleimide can be accomplished at or slightly above room temperature, while the rDA reaction is performed at elevated temperatures.

Thermally rDA reactions have been used in numerous studies including polymer synthesis [10–17], dendrimers [18–21], epoxy resins [22–25], cross-linked polymer networks [26–30], organic-inor-

ganic polymer hybrids [31–33], surfactants [34], surface modification [35, 36] and remendable self-healing polymers [37]. Due to the fact that these reactions can proceed under mild conditions without a catalyst, they are attractive for designing covalently reversible bonds with furan and maleimide functional groups which are responsible for association and disassociation [35, 37, 38].

Polyurethanes are widely used in high resiliency flexible foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting components, high performance adhesives, surface coatings and sealants, Spandex fibers, seals, gaskets, carpet underlay, and hard plastic parts (such as for electronic instruments). For the manufacture of polyurethanes, two groups of at least bifunctional substances are needed as reactants: 1) isocyanate groups (diisocyanates, polyisocyanates), and 2) active hydrogen atoms (polyols, glycols, triols etc.). Two side reactions can occur during polyurethane synthesis: formation of

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both allophanate and biuret linkages from isocyanate functionality and an already existing urethane link. Both reactions not only affect stoichiometry, but also introduce branching, yielding cross-linked species. Polyurethanes can thus be formed through the branching and cross-linking. Due to these types of cross-links that are typically present in polyurethane, the polyurethane materials become difficult to melt process and difficult to remove once it is potted.

Taking advantage of experimental conditions, we report the formation of poly(ether urethane) networks with reversibly removable properties. Our approach to removable polymer networks is the introduction of chemically labile linkages within cross-linked polymeric networks. We have explored the DA cycloaddition reactions between bis-maleimide and furyl monomers or polymers [39–42]. The mechanical measurements showed a greater elongation at break for obtained polyurethane networks, elongation which can be even nine times higher than that of previously obtained polyurethane networks by Diels-Alder reaction [41].

2. Experimental part

2.1. Measurements

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

The proton nuclear magnetic resonance (^1H -NMR) spectra were recorded on a Bruker NMR spectrometer, Avance DRX 400 MHz, using CDCl_3 and DMSO-d_6 as solvent and tetramethylsilane as an internal standard.

Differential scanning calorimetry (DSC) measurements were conducted on a DSC 200 F3 Maia (Netzsch, Germany). About 9 mg of sample were heated in pressed and punched aluminum crucibles at a heating rate of $10^\circ\text{C}/\text{minute}$. Nitrogen was used as inert atmosphere at a flow rate of 100 mL/minute .

Thermogravimetric analysis (TGA) was conducted on a STA 449 F1 Jupiter device (Netzsch, Germany). Around 10 mg of each sample was heated in alumina crucibles at a heating rate of $10^\circ\text{C}/\text{min}$. Nitrogen was used as inert atmosphere at a flow rate of 50 mL/min .

The reduced viscosity of polyurethane was measured ($c = 0.5 \text{ g/dL}$, $25 \pm 0.2^\circ\text{C}$) in DMF using an Ubbelohde viscometer.

Gel permeation chromatographic (GPC) analyses were carried out on a PL-EMD 950 Evaporative light Detect instrument using *N,N*-dimethylformamide (DMF) as the eluant and standard polystyrene sample for calibration.

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 $50 \times 8 \text{ mm}$ and rate of immersion-emersion was $5 \text{ mm}/\text{min}$ in water. Immersion depth was 5 mm in standard conditions. All measurements were the average of 3 contact angle measurements of samples.

Stress-strain measurements were performed on a test apparatus, Shimadzu AGS-J, cell load 1 kN. Measurements were run at an extension rate of $10 \text{ mm}/\text{min}$, at room temperature 23°C . All samples were measured three times and the averages were obtained.

2.2. Reagents and materials

Dibutyltin dilaureate (Aldrich, 95%), dimethylformamide (DMF, Aldrich, 99%), poly(tetramethylene ether) glycol (PTMEG) (Terathane-250, -650, -1000, 1500 and -2000) (Aldrich), 2-furfuryl amine (Aldrich), epoxy propane (Aldrich), 1,6-hexamethylene diisocyanate (HDMI) (Aldrich) were used as received. 4,4'-Dibenzylidiisocyanate (DBDI) (Savinesti, Romania) was purified before use by recrystallization from anhydrous cyclohexane ($mp = 89\text{--}90^\circ\text{C}$), 4,4'-bismaleimido-diphenylmethane (**A**) was synthesized from 4,4'-diaminodiphenylmethane and maleic anhydride in a two-step method described in the literature [43] and recrystallized from toluene ($mp = 158\text{--}159^\circ\text{C}$). The oligoether urethane bis-maleimide (**B**) was synthesized from Terathane-650 and 4-maleimidophenyl isocyanate by the method described in the literature [41].

Synthesis of

2-[*N,N*-bis(2-methyl-2-hydroxyethyl)amino]furfuryl

This material was prepared according to the modified method described in the literature [44]. To a solution of epoxy propane (11.6 g, 0.2 mol) in toluene (80 mL), 2-furfuryl amine (9.3 g, 0.1 mol) and acetic acid (1 mL) were added. The mixture was stirred and refluxed for 3 hours. The solvent was evaporated out using a rotary evaporator. The crude product was washed with 50 mL cyclohexane three

times. After drying under vacuum at 50°C for 36 hours, a viscous liquid product was obtained.

Analysis calculated for $C_{11}H_{19}NO_3$ (213.273): C, 61.95; H, 8.98; N, 6.56%. Found: C, 62.13; H, 9.02; N, 6.48%.

1H -NMR ($CDCl_3$), δ (ppm): 1.12 (d, 6H, CH_3), 2.38–2.62 (m, 4H, CH_2 protons), 3.58 (s, 2H, OH protons), 3.75 (s, 2H, CH_2 protons), 3.83 (m, 2H, CH–N protons), 6.18 (s, 1H, 3-furfuryl proton), 6.30 (s, 1H, CH-furfuryl), 7.37 (s, 1H, C_5 of furan).

Synthesis of poly(ether-urethane)s containing furan ring PU-(1-12)

The polyurethanes were synthesized by the conventional two-step method under an inert atmosphere of high purity nitrogen in a 100 mL three-neck round bottomed flask equipped with a stirrer and a thermometer. A 10% w/v solution of poly(tetramethylene ether) glycol (PTMEG) in *N,N'*-dimethylformamide (DMF) was mixed with the catalyst, dibutyltin dilaureate (about 0.5 wt%) at 40°C for 30 minutes to obtain a homogeneous solution. In the first step, an excess of diisocyanate was added to obtain an isocyanate-terminated prepolymer (at several NCO/OH ratio of 2, 3 and 4) and the reaction was left for 2 hours at 80°C. The prepolymer solution was cooled at 60°C and chain extension step was performed adding stoichiometric amount of 2-[*N,N'*-bis(1-methyl-2-hydroxyethyl)amino]furfuryl in 5 mL DMF under nitrogen and stirring for

2 hours at 60°C. The solution was cooled (25°C) and the polymer was precipitated in cool distilled water and washed with methanol at room temperature. The sample was then dried at 50°C for 24 hours under reduced pressure. The polyurethane films were cast from 8 wt% solution of the polymer in DMF.

IR (KBr, cm^{-1}): 3395, 2968, 2932, 2885, 1833, 1632, 1502, 1454, 1411, 1375, 1337, 1279, 1147, 1067, 1013, 949, 838, 732 and 599.

Synthesis of polyurethane networks NPU-(1-12)A,B

To a solution of polyurethane (1.2 g) in DMF (10 mL), a stoichiometric bismaleimide monomer (**A** or **B**) was added. The mixture was stirred at 60°C for 2 hours and the solution was cast on Teflon Petri dish and the solvent was evaporated at 60°C for 24 hours. The obtained polymer films were used for all characterizations. NPU, before crosslinking, were soluble in aprotic dipolar solvents at room temperature. After crosslinking, when the samples were immersed in aprotic dipolar solvents, polyurethane networks swelled. At 140°C, the networks became soluble as a result of the de-crosslinking at this temperature.

3. Results and discussion

Polyurethanes containing furan moieties PU-(1-12) were prepared by the two-step method in DMF solution, by the reaction of DBDI or HMDI with

Figure 1. Synthesis of poly(ether-urethane) networks

Table 1. The composition of polyurethanes and their networks

Sample	R ₁	M _{PTMEG}	Isocyanate:PTMEG:chain extender	R ₂
PU-0-1		2000	2:1:1	–
NPU-1A			2:1:1	–CH ₂ –
NPU-1B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-2		1500	2:1:1	–
NPU-2A			2:1:1	–CH ₂ –
NPU-2B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-3			3:1:2	–
NPU-3A			3:1:2	–CH ₂ –
NPU-3B			3:1:2	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-4		1000	4:1:3	–
NPU-4A			4:1:3	–CH ₂ –
NPU-4B			4:1:3	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-5		650	2:1:1	–
NPU-5A			2:1:1	–CH ₂ –
NPU-5B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-6		250	2:1:1	–
NPU-6A			2:1:1	–CH ₂ –
NPU-6B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-7	–(CH ₂) ₆ –	2000	2:1:1	–
NPU-7A			2:1:1	–CH ₂ –
NPU-7B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-8		1500	2:1:1	–
NPU-8A			2:1:1	–CH ₂ –
NPU-8B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-9		1000	2:1:1	–
NPU-9A			2:1:1	–CH ₂ –
NPU-9B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-10		650	2:1:1	–
NPU-10A			2:1:1	–CH ₂ –
NPU-10B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-11		250	2:1:1	–
NPU-11A			2:1:1	–CH ₂ –
NPU-11B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–
PU-12		250	2:1:1	–
NPU-12A			2:1:1	–CH ₂ –
NPU-12B			2:1:1	–HN–OOC–PTMEG ₆₅₀ –COO–NH–

PTMEG (having number-average molecular weight of 250, 650, 1000, 1500 and 2000) and 2-[*N,N*-bis(2-methyl-2-hydroxyethyl)amino]furfuryl in molar ratio of 2:1:1, 3:1:2 or 4:1:3 as represented in Figure 1 and Table 1. The FT-IR and ¹H-NMR spectroscopy were used to investigate the formation of polyurethanes. Typical infrared spectra of synthesized polyurethanes are shown in Figure 2. They did not show the absorption band at 2270 cm^{–1} associated with isocyanate group. The ATR-FTIR spectra of the polyurethane elastomers **PU-(1-12)** exhibited the bonds typical for the polyurethanes. As can be observed in Figure 2 the intensity of the absorption bands at 1105 cm^{–1} corresponding to ether linkage decreased with decreasing the number-average molecular weight of PTMEG. The same behavior could be observed in the case of the

Figure 2. The ATR-FTIR spectra of polyurethanes

absorption band characteristic to the vibration of methylene group. These phenomena were expected

since a lower number-average molecular weight of PTMEG used in synthesis led to a decrease of the ether linkages and methylene groups ratio in the polyurethane structure.

The ^1H -NMR spectra of polyurethanes presented suitable signals for NH from urethane groups, CH_3 , CH_2 from polyether glycol and diisocyanate, aromatic protons from DBDI structures, furan protons from chain extender. Representative ^1H -NMR spectra of **PU-7** and **PU-12** were presented in Figure 3. The protons corresponding to the furyl group appeared at 6.38, 6.27 and 7.57 ppm, the protons specific to the NH from aliphatic structure from **PU-12** at 7.01 ppm and those specific to the aromatic structure from **PU-7** appeared at 6.29, 6.40, 7.57 and 9.41-9.46 ($-\text{NH}-\text{C}_6\text{H}_4-$) ppm. The ratio between integral area of furan and isocyanate protons of the obtained polymers is in agreement with the composition of the mixture used for synthesis (isocyanate:chain extender of 1:2).

The composition and inherent viscosity of **PU-(1-12)** were presented in Table 1 and Table 2. The cal-

Table 2. Properties of polyurethanes **PU-(1-12)**

Sample	$\eta_{\text{inh}}^{\text{a}}$ [dL/g]	M_w^{b}	PDI ^c	Hard segment content [%]	Furyl monomer content [mol/g]
PU-1	0.33	38 303	1.28	27.54	$3.65 \cdot 10^{-4}$
PU-2	0.63	37 877	1.34	33.63	$4.46 \cdot 10^{-4}$
PU-3	0.54	20 124	1.28	45.52	$7.35 \cdot 10^{-4}$
PU-4	0.41	21 447	1.30	53.34	$9.38 \cdot 10^{-4}$
PU-5	0.37	24 204	1.28	43.18	$5.74 \cdot 10^{-4}$
PU-6	0.43	22 306	1.28	53.90	$7.18 \cdot 10^{-4}$
PU-7	0.23	21 116	1.27	75.25	$10.08 \cdot 10^{-4}$
PU-8	0.58	26 023	1.28	21.62	$3.92 \cdot 10^{-4}$
PU-9	0.83	34 049	1.27	26.90	$4.88 \cdot 10^{-4}$
PU-10	0.51	17 519	1.29	35.56	$6.45 \cdot 10^{-4}$
PU-11	0.78	23 857	1.35	45.90	$8.33 \cdot 10^{-4}$
PU-12	0.45	22 950	1.27	68.82	$12.50 \cdot 10^{-4}$

^aInherent viscosity measured in DMF solution at 25°C

^bThe weight-average molecular weight

^cPolydispersity index

Figure 3. The ^1H -NMR spectra of **PU-7** and **PU-12**

culated hard segment content (as calculated from the initial composition) varied between 21.62 to 75.25% and the furfuryl monomer content varied in the range of $3.65 \cdot 10^{-4}$ – $12.50 \cdot 10^{-4}$ mol/g. The inherent viscosity measured in DMF solution at 25°C varied between 0.23 and 0.83 dL/g and decreased as the molar ratio of isocyanate:PTMEG:chain extender increases from 2:1:1 to 4:1:3. The weight-average molecular weight and polydispersity index were recorded on a PL-EMD 950 Evaporative light Detect instrument and reported in Table 2. As can be seen from Table 2, the weight-average molecular weight and polydispersity index decreased as the molar ratio of isocyanate:PTMEG:chain extender increased and the molecular weight of PTMEG decreased in the case of **PU-(1-7)**. Weight-average molecular weights and the polydispersity index of the polyurethanes were in the range of 17519–38303 and 1.27–1.35, respectively.

The polyurethane networks **NPU-(1-12)A,B** were prepared by the Diels-Alder crosslinking reaction of **PU-(1-12)** to 4,4'-bismaleimidodiphenylmethane (**A**) or oligoether urethane bismaleimide (**B**), as represented in Figure 1. The composition of polymers and networks is presented in Table 1.

The ATR-FTIR spectra of networks (Figure 4) showed the disappearance of the furan ring breathing absorption band at 1012 cm^{-1} and the appearance of new bands at 1775 cm^{-1} (C=O cycloadduct) and 1192 cm^{-1} (C–N–C succinimide ring from cycloadduct) attributed to the furan-maleimide cycloadduct [45]. The shifting absorption band characteristic to the carbonyl group to lower wavenumbers represents another confirmation of the formation of

the Diels-Alder cycloadduct. Also, it was observed a change in the absorption bands characteristic to the non-bonded and bonded urethane C=O at 1680 – 1720 cm^{-1} .

3.1. Thermal properties

Urethanes are known to be relatively thermally unstable materials and the decomposition temperature of the urethane bond depends on the polyurethane structure. Thus, the polyurethanes and their corresponding networks based on alkyl structure (**PU-** and **NPU-(8-12)**) presented a better thermal stability than the ones based on aryl structure (**PU-** and **NPU-(1-7)**). There have been proposed three mechanisms for the decomposition of urethane bonds: dissociation to isocyanate and alcohol, formation of primary amine and olefin, and formation of secondary amine and carbon dioxide. These reactions may proceed simultaneously or separately. Figure 5 presents the thermal degradation curves of polyurethane networks **NPU-(1-2,5-7)A**. As can be seen the decomposition of the urethane bonds proceeded in two stages, meaning that two of the reactions mentioned above were overlapping. These two stages ranged between 202 – 398°C (Table 3). At higher temperatures, the decomposition stage was due to the degradation of PTMEG chain and to the other units from the polyurethane network, and ranged between 381 – 517°C . As expected, the weight loss corresponding to the first two stages increased with decreasing the number-average molecular weight of PTMEG since the urethane linkages ratio in network was higher. On the other hand the weight loss of the third stage decreased due to the fact that

Figure 4. The ATR-FTIR spectra of networks

Figure 5. The TGA curves of **NPU-(1-7)A** with a isocyanate:PTMEG:chain extender molar ratio of 2:1:1

Table 3. The thermogravimetric data of PU and NPU

Sample	Weight loss/decomposition temperature [%/°C]			Y _c ^a [°C]
	Step I	Step II	Step III	
NPU-1A	4.20/216–286	13.08/332–370	70.12/402–466	11.88
PU-2	16.00/220–340	52.00/390–465	18.40/470–550	6.00
NPU-2A	4.90/160–279	17.30/329–371	64.78/398–475	12.80
NPU-2B	5.20/208–281	22.40/312–379	34.40/396–460	8.00
NPU-5A	3.76/209–285	24.40/313–376	55.54/398–494	15.25
NPU-6A	13.00/189–290	33.22/320–378	36.00/409–482	16.90
PU-7	14.00/200–278	42.80/312–392	30.80/409–492	11.30
NPU-7A	13.50/215–287	35.16/308–370	31.00/398–455	18.70
NPU-7B	8.70/213–274	36.50/318–371	38.10/410–483	15.60
PU-10	23.20/245–367	45.60/360–446	10.00/455–600	6.00
NPU-10A	26.80/240–350	43.60/383–455	92.00/460–580	11.20
NPU-10B	30.00/260–380	46.40/385–460	16.00/465–600	5.00

^aChar yield at 600°C

this decomposition step was due mainly due to the degradation of PTMEG chains.

Figure 6 shows the thermal behavior of the weight loss curves of **PU-7**, **NPU-7A** and **NPU-7B**. The shape of the weight loss curves of all samples was almost identical. The increase of the weight loss in the degradation second step of **NPU-7B** was due to the presence of the soft segment from bis-maleimide.

DSC analysis provided the information on the glass transition, crystallization, melting endotherms and also the rDA reaction of networks (Figure 7 and Figure 8). The DSC data are compiled in Table 4. Figure 7 present DSC curves of networks based on polyurethanes **PU-(1-7)** and bismaleimide **A** (Figure 7a) or **B** (Figure 7b). DSC curves of **NPU-(2-7)A** (Figure 7a) exhibited the glass transition temperature corresponding to the soft segment, the glass

Table 4. Thermal behavior of polyurethane networks

Sample	T _{g ss} ^a [°C]	T _{cryst ss} ^b [°C]	T _{melt ss} ^c [°C]	T _{g network} ^d [°C]	T _{rDA} ^e [°C]	ΔH _{rDA} ^f [J/g]
NPU-2A	–64.47	–	–2.58	–	120.14	–12.96
NPU-3A	–62.86	–	–	54.80	109.55	–44.38
NPU-4A	–66.18	–	–	53.32	112.44	–38.84
NPU-5A	–59.36	–	–	–	116.21	–3.44
NPU-6A	–36.06	–	–	53.11	109.12	–18.79
NPU-7A	–	–	–	52.06	104.25	–22.29
NPU-8A	–72.25	–34.54	22.72	–	117.46	–16.74
NPU-9A	–68.31	–	2.59	–	150.49	–
NPU-10A	–57.76	–	–	–	116.17	–
NPU-11A	–45.32	–	–	–	117.71	–30.65
NPU-12A	12.32	–	–	–	112.35	–91.16
NPU-1B	–69.25	–23.05	16.34	50.98	106.21	–2.40
NPU-5B	–56.08	–	–	46.20	121.17	–3.06
NPU-6B	–32.29	–	–	41.93	108.89	–13.76
NPU-7B	–	–	–	20.51	109.18	–46.73
NPU-8B	–72.34	–36.00	17.65	–	115.46	–6.95
NPU-9B	–69.93	–	8.20	–	109.82	–63.92
NPU-10B	–60.73	–	–	46.08	113.18	–13.02
NPU-11B	–48.69	–	–	48.05	113.05	–14.62
NPU-12B	8.34	–	–	–	113.44	–44.91

^aGlass transition temperature of soft segment polyurethanes^bCrystallization temperature of soft segment polyurethanes^cMelting temperature of soft segment polyurethanes^dGlass transition temperature of networks^eTemperature corresponding to retro Diels-Alder reaction^fHeat of the retro Diels-Alder reaction

transition temperature corresponding to networks and endothermic transition temperature corresponding to the rDA process, and varied in the range of -36.06 and -66.18°C , 50 – 55°C and 104 – 120°C , respectively. The networks based on PTMEG hav-

ing number-average molecular weight of 250 , **NPU-7A**, did not show T_g for soft segment. The rDA process energy ranged between -3.44 and -44.38 J/g depending on the number-average molecular weight of PTMEG and the isocyanate: PTMEG:chain extender molar ratio. DSC curves for networks **NPU-(1-7)B** showed the same transitions and endothermic process whose maximum temperature ranged between 106 – 121°C . On the DSC curves of polyurethane networks **NPU-(1-7)A,B** there can be observed that when decreasing the number-average molecular weight of PTMEG the T_g of network and T_g of the soft segment increased due to the fact that as the PTMEG chain's length decreases, its mobility decreases too, leading this way to a higher glass transition temperature. The decrease of the T_g of soft segment when increasing the number-average molecular weight of PTMEG indicates that longer soft segments present a better phase separation in the corresponding poly-

Figure 6. The TGA curves of **PU-7** and its corresponding networks

Figure 7. The DSC curves of networks based on DBDI; (a) with bismaleimide **A**; (b) with bismaleimide **B**

Figure 8. The DSC curves of networks based on HMDI; (a) with bismaleimide **A**; (b) with bismaleimide **B**

urethane network [46]. Also, by increasing the molar ratio (amount of chain extender) the crosslinking density increases (this was evidenced by the disappearance of melting endotherm of the soft segment) and the glass transition temperature of network slightly decreases, probably due to the longer segment lengths between network points.

The DSC curves of polyurethane networks **NPU-(8-12)A,B** are represented in Figure 8a and 8b. There can be observed that the curves presented the same characteristics as the ones of **NPU-(1-7)A,B**. Also, there can be noticed that using DBDI instead of HMDI in the synthesis of polyurethanes leads to a higher glass transition temperature of the soft segment.

Regarding the crystallization and melting processes from both Figures 7 and Figure 8 one can see that only the DSC curves of **NPU-(1,8)A,B** which contain PTMEG having the number-average molecular

weight of 2000 presented the crystallization exotherm, while the melting endotherm was present on the DSC curves of polyurethane networks which had PTMEG with the number-average molecular weight of 2000 and 1500. In the case of the networks with lower number-average molecular weight of PTMEG none of these processes could be observed, their molecular weight being too low to evidence a crystallization process [47].

3.2. Thermoreversibility of the networks

The DSC and ATR-FTIR methods were applied to evaluate the thermoreversibility of the networks. The thermoreversibility of the network (**NPU-11A**) was evidenced by applying multiple heating-cooling cycles in a differential scanning calorimeter. Thus, there can be observed that the endothermic peak characteristic to the retrodiene process appeared on all three heating curves, the maximum

Figure 9. The DSC scans of **NPU-11A**: h1 – the first heating run; h2 – the second heating run and h3 – the third heating run; c1 – the first cooling run; c2 – the second cooling run

Figure 10. The ATR-FTIR spectra of **NPU-11A**: a – initial; b – at 150°C; c – after cooling; d – recovery (after heat treatment at 80°C for 6 hours)

of the endothermic peak having almost the same value around 116–118°C (Figure 9). The cooling curves presented an exothermic peak with a maximum around 92–96°C, exotherm which is specific to the dienic process of regeneration of the furan-maleimide cycloadduct.

The thermoreversibility of **NPU-11A** was also confirmed by ATR-FTIR spectroscopy (Figure 10). So, recording the spectrum for this compound at 130°C (Figure 10 curve b) we can observe that it was not present anymore the characteristic band of cycloadduct at 1775 cm⁻¹ and also that the band attributed to the carbonyl stretching vibration shifted to higher values (1714 cm⁻¹). The –C–N–C– absorption band from succinimide at 1197 cm⁻¹ disappeared too due to the debonding of the cycloadduct in maleimide and furyl groups. After cooling the sample and recording again the spectrum, we could see that the carbonyl band shifted back to lower val-

Figure 11. The ¹H-NMR spectra of Diels-Alder cycloaddition after different time periods: (a) **PU-7B**; (b) after 10 h at 60°C (**NPU-7B**); (c) retro-DA (**PU-7B** + bismaleimide **B**)

ues (1711 cm⁻¹) and the appearance of the band at 1775 cm⁻¹ corresponding to the cycloadduct and the one at 1197 cm⁻¹ attributed to –C–N–C– from succinimide (Figure 10 curve c). After heating the sample at 80°C for 6 hours in an oven the carbonyl band shifts back to its initial value (1708 cm⁻¹) due to the complete recovery of the cycloadduct when an appropriate time was accorded to the dienic reaction took place (Figure 10 curve d).

The reaction between furyl and maleimide groups was carried out at different temperatures (60 and 140°C) in DMSO-d₆ (NMR tube under nitrogen atmosphere) allowing real-time ¹H-NMR character-

ization. The evolution of ^1H -NMR spectra were shown in Figure 11. Figure 11a represents the ^1H -NMR spectrum of **PU-7B**. After reacting **PU-7B** with bismaleimide **B** at 60°C for 10 h, part of formed network becomes insoluble; the ^1H -NMR spectrum exhibits new signals at 6.65–6.43, and 5.45–5.17 ppm assigned to exo/endo protons 2, 3, and 1 of DA adduct, respectively, along with the existing peaks at 7.57 ppm attributed to protons a from furyl unit, and at 6.42–6.25 ppm ascribed to protons b and c of furyl group (Figure 11 (b)). After complete Diels-Alder reaction, the sample became a gel and the ^1H -NMR spectrum could not be recorded. After the sample was heated at 140°C , the corresponding

^1H -NMR spectrum exhibited the signals characteristic to the bismaleimide **B** (7.14 ppm assigned to the proton d) and **PU-7B** (Figure 11c).

3.3. Surface characterization of the networks

The dynamic contact angles of the polyurethanes and polyurethane networks were measured using Wilhelmy plate technique. The advancing contact angle values measured in water and ethylene glycol and the hysteresis values are given in Table 5. The free surface energies were calculated according to Owens and Wendt equation (Equation (1)):

$$(1 + \cos\theta)\gamma_L = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^p + \gamma_L^p)^{1/2} \quad (1)$$

Table 5. Contact angle in water and ethylene glycol and dispersive and polar components of free energy of PU and NPU films

Sample	$\theta_{\text{adv water}}^{\text{a}}/\text{hysteresis}$	$\theta_{\text{adv EG}}^{\text{b}}/\text{hysteresis}$	$\Delta G_{\text{h}}^{\text{c}}$		Free surface energy ^d		
			Water	EG	γ^{d}	γ^{p}	$\gamma = \gamma^{\text{d}} + \gamma^{\text{p}}$
PU-1	91.85/32.26	81.56/50.76	0.365	1.631	5.642	11.420	17.062
PU-2	87.26/22.60	75.78/22.60	0.248	1.235	6.801	13.217	20.018
PU-3	93.35/34.09	78.90/34.09	0.371	1.100	9.227	7.923	17.409
PU-4	85.66/36.77	76.68/38.21	0.669	1.110	4.932	16.246	21.178
PU-5	92.89/26.14	82.51/36.34	0.207	0.788	5.659	10.789	16.448
PU-6	96.98/43.48	73.98/34.38	0.522	1.023	19.188	2.603	21.791
PU-8	87.00/29.07	84.73/26.80	0.406	1.148	1.240	21.487	22.727
PU-9	84.10/29.96	76.43/37.31	0.420	1.071	4.094	18.473	22.567
PU-10	70.57/18.30	64.30/18.30	0.435	1.250	3.583	30.856	34.439
PU-11	76.97/23.64	64.01/30.25	0.481	1.192	8.269	19.063	27.332
PU-12	89.19/34.81	76.82/46.08	0.543	–	7.494	11.419	18.913
NPU-1A	87.41/20.76	84.14/58.37	0.209	2.051	1.622	20.202	21.824
NPU-2A	77.20/29.55	75.78/29.25	0.687	1.010	1.181	30.421	31.602
NPU-3A	86.88/31.65	75.00/43.21	0.492	1.501	7.162	13.138	20.300
NPU-4A	73.42/16.91	63.81/27.77	0.356	1.050	9.666	24.951	30.617
NPU-5A	83.29/28.38	73.50/34.88	0.480	1.064	5.606	17.177	22.783
NPU-6A	84.16/28.78	70.81/15.43	0.470	0.862	8.544	13.723	22.267
NPU-8A	89.87/31.53	77.84/38.71	0.399	1.084	7.167	11.277	18.444
NPU-9A	91.59/45.35	82.24/20.53	0.805	0.292	4.948	12.258	17.206
NPU-10A	92.30/30.34	82.58/52.81	0.307	1.713	5.185	11.584	16.769
NPU-11A	82.28/25.43	71.74/35.50	0.418	0.954	6.210	17.242	23.452
NPU-12A	86.03/29.71	74.03/37.15	0.449	1.167	7.249	13.572	20.866
NPU-1B	88.84/31.47	81.31/31.49	0.425	2.368	3.825	15.377	19.202
NPU-2B	75.05/19.93	56.84/19.93	0.405	1.642	13.106	16.362	29.468
NPU-4B	90.60/36.63	91.62/71.54	0.526	2.650	0.278	22.079	22.357
NPU-5B	85.88/29.50	70.60/35.61	0.447	1.233	10.354	11.285	21.630
NPU-6B	82.47/31.56	76.61/43.25	0.606	1.413	3.051	21.370	24.420
NPU-7B	86.19/31.20	74.95/35.47	0.489	1.035	6.650	14.060	20.710
NPU-9B	81.79/27.11	74.24/39.62	0.479	1.256	3.472	21.220	24.692
NPU-10B	88.80/36.70	82.59/36.70	0.574	–	3.261	16.184	19.445
NPU-11B	88.39/45.53	67.65/53.08	0.954	–	16.544	6.698	23.153
NPU-12B	83.37/27.71	78.16/36.63	0.459	1.045	3.812	19.438	23.250

^aAdvanced contact angle measured in water

^bAdvanced contact angle measured in ethylene glycol

^cMolar free energy of hysteresis

^dCalculated from the dispersive (γ^{d}) and polar (γ^{p}) components

where θ represents the advancing contact angle value, γ_L is the free surface energy of the liquid, γ_L^d and γ_L^p are the dispersive and polar components of the free surface energy of the liquid, and γ_s^d and γ_s^p are the dispersive and polar components of the free surface energy of the polyurethane/polyurethane network films.

The molar free energies of hysteresis, quantitatively correlation to surface interaction of the hysteresis, were also calculated using Equation (2):

$$\Delta G_h = -RT \ln \left(\frac{\sin \theta_{\text{rec}}}{\sin \theta_{\text{adv}}} \right) \quad (2)$$

where ΔG_h is the molar free energy of hysteresis and θ_{adv} and θ_{rec} represent the advancing and receding dynamic contact angle values [48].

As can be observed, in the case of polyurethanes, the contact angle value depended on the nature of the isocyanate used in synthesis. Thus, **PU-(8-12)** had lower dynamic contact angle values than the corresponding **PU-(1-7)**, due to the hydrophilic behavior of the aliphatic diisocyanate [49]. The contact angle value decreased when crosslinking **PU-(1-7)** with bismaleimides, while the free surface energy increased. On the score of crosslinking, the majority of the carbonyl and NH groups are not implied in hydrogen bonds anymore, thus being able to contribute to the increase of the hydrophilicity of the surface of polyurethane networks comparing with the ones of the polyurethanes. In the case of **NPU-(8-12)** the contact angle value increased comparing with the corresponding polyurethane (in most of the cases), even when the free surface energy increased. This fact can be due to the roughness of the surface, which is known to reduce the effective area of the contact angle, leading this way to higher values of it. As can be seen in Table 5 in the case of **PU-(8-12)** the surface roughness (given by the hysteresis value) increased when crosslinking with bismaleimides [50].

In most of the cases the polar component's value was higher than the dispersive one's indicating that the dipolar forces and the hydrogen bonds played an important role in the structure of the polyurethanes and polyurethane networks. The value of the molar free energy of hysteresis was higher in ethylene glycol than that in water, in most of the cases, suggesting that the contribution of dipolar forces and hydrogen bonds in water was more pregnant in ethylene glycol [48].

3.4. Mechanical properties

The investigated mechanical properties of the polyurethanes and polyurethane networks were: breaking strength and elongation and Young's modulus. By crosslinking the polyurethanes with bis-maleimides there could be observed an increasing of the breaking elongation, elongation which can be even forth times higher (Figure 12a). The results of physico-mechanical measurements of poly(ether-urethane)s evidenced a slight increase of the tensile strength from 5.51 to 6.30 MPa, and a decrease of the elongation at break (from 243.10 to 128.46%), for a rate of reagents from 2:1:1 to 3:1:2. The breaking strength increased when crosslinking with bis-maleimides increased, which was more pronounced

Figure 12. The mechanical properties of polyurethanes and their networks: (a) stress-strain diagram for **PU-2** and its corresponding networks; (b) strength at break of polyurethanes and their networks; (c) modulus of **PU-(2-7)** and **NPU-(2-7)A**

when using the aromatic bismaleimide (Figure 12b). The isocyanate:PTMEG:chain extender molar ratio used in this reaction also influenced the breaking strength. As can be seen in Figure 12b, an increase of the isocyanate and chain extender amount led to a decrease of the breaking strength. The Young's modulus of polyurethanes and polyurethane networks had the same behavior as breaking strength and elongation, meaning that it increased after crosslinking with bismaleimides (Figure 12c). Instead, unlike breaking strain, the modulus of the polyurethane networks increased when increasing the used isocyanate amount in synthesis, from 20.69 to 83.54 MPa for **NPU-A** and 8.28 to 57.60 MPa for **NPU-B**.

4. Conclusions

Thermally reversible cross-linked poly(ether-urethane)s were prepared by the Diels-Alder crosslinking reaction of the furan-containing poly(ether-urethane) to bismaleimides. The glass transition temperature of the soft segment of DBDI-networks was higher than that of HDMI-networks and for both types of networks it decreased with increasing the molecular weight of PTMEG.

The thermal stability of networks was given by the both bismaleimide and isocyanate structure. The thermoreversibility of the networks was evidenced by both DSC and ATR-FTIR spectroscopy. The contact angle values of networks increased or decreased compared to that of polyurethanes depending on the isocyanate structure used in the synthesis. The bismaleimide structure and the used isocyanate:PTMEG:chain extender molar ratio influenced the mechanical properties of networks. By crosslinking the polyurethanes with bismaleimides there could be observed an increasing of the breaking elongation, elongation which can be even forth times higher than that of the initial polyurethane (900%).

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