Polyurethanes based on thermoreversible networks designed by Diels-Alder reaction

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Abstract. Urethane bismaleimides (BMIs) were used in order to obtain crosslinked structures by their reaction with an aromatic trifuran compound. The Diels-Alder (DA) reaction between the maleimide and furan moieties was investigated using proton nuclear magnetic resonance (^1H -NMR) spectroscopy for a model compound (CTF), due to the fact that the networks are insoluble in usual NMR solvents. The structure of the networks was confirmed by infrared spectroscopy. Thermal properties were investigated (by means of differential scanning calorimetry (DSC) and thermogravimetical analyses (TGA)) and compared with the ones of similar compounds, previously obtained from the same BMIs and a different trifuran compound (which contains tertiary nitrogen in its structure). Mechanical and rheological properties were also investigated. The influence of the nature of the polyol from the BMIs structure and/or the influence of using a trifurylic compound with or without tertiary nitrogen on the properties of the crosslinked networks were also discussed.

Keywords: thermal properties, Diels-Alder reaction, polyurethanes, network, thermoreversibility

1. Introduction

Polyurethanes appeared as a Bayer’s response to the successful development of high molecular weight polyamides by E.I. Dupont, given the competition between the two companies. The need for PUs steadily increased ever since then, because of its high abrasion, chemical resistance, flexibility, and good mechanical property [1]. Nowadays they are considered one of the most versatile polymeric materials class since they can be used in many forms and in a large number of applications including elastomers [2–5], flexible and rigid foams [6–8], biomedical applications [9–11], adhesives and coatings [12–14], polymers for electronics [15], etc. The reaction between diisocyanates or multiisocyanates and di- or polyols generates polyurethanes with different molecular structures varying from linear to crosslinked ones depending on the structure, functionality and stoichiometry of the reactants. These thermosetting

polymers cannot be reprocessed or reused if, according to the desired applications, chemical crosslinkers are used [16]. For de-crosslinking of polyurethane networks, dynamic covalent chemistry is used, especially by means of the DA and retro-DA (rDA) reactions [17]. Due to its reversibility the DA reaction also represents a choice to create self-healing properties for polymer networks [18].

Concerning polyurethane, the DA reaction was employed in thermally remendable linear polymers [19–22] and thermally reversible networks [23–27]. The latter were designed in three different ways: i) by polymerization reaction of monomers containing maleimide-furan cycloadduct [26, 28], ii) by crosslinking of linear polyurethane containing furan or maleimide pendant groups [27, 29, 30] and iii) by cycloaddition DA reaction between polyurethane containing furan end groups and multimaleimide monomers [19, 23–25, 31–33].

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In a previous work we synthesised polyurethane networks (NPU) from a trifurylic compound containing a tertiary nitrogen and urethaneic bismaleimide and studied their thermal properties [34]. Taking into account the fact that the DA reaction could be affected by the presence of the tertiary nitrogen which can activate the maleimide double bond (leading to the homopolymerization of bismaleimides) [35], in this work we prepared analogues networks from the same BMI and a different trifurylic compound (without tertiary nitrogen) in order to see how this influences their properties. Additionally to the thermal properties, the mechanical and rheological ones were studied and also the crosslinking densities were evaluated.

2. Experimental part

2.1. Measurements

The Fourier transform infrared (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 (Rheinstetten, Germany), using CDCl_3 and $\text{DMSO}-d_6$ as solvent and tetramethylsilane as an internal standard.

DSC measurements were conducted on a DSC 200 F3 Maia (Netzsch, Germany). A mass of 10 mg of each sample was heated in pressed and pierced aluminium 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 heat flow versus temperature was recorded. The baseline was obtained by scanning the temperature domain of the experiments with an empty pan. The enthalpy was calibrated with indium according to standard procedure.

The rheological measurements were performed using a controlled stress Bohlin CVO Rheometer (Malvern Instruments UK) with parallel plate geometry (60 mm diameter and 500 μm gap) and thermal control by Peltier effect. The experiments were carried out within the linear viscoelastic regime under the dynamic oscillation mode using a 1 rad/s frequency. Experiments were run from 70 to 140°C at a $1^\circ\text{C}/\text{min}$ heating rate constant.

TGA experiments were conducted on a STA 449 F1 Jupiter apparatus (Netzsch, Germany). 10 mg of sample was heated in an open alumina crucible in nitrogen atmosphere with a flow rate of 50 mL/min. A heating rate of $10^\circ\text{C}/\text{min}$ was applied.

Stress-strain measurements were performed on a test apparatus, Shimadzu AGS-J, cell load 1kN (Japan). Measurements were run at an extension rate of 10 mm/min, at room temperature 23°C . All samples were measured three times and the averages were obtained. The samples were 3 mm width, and 0.05–0.15 mm thickness; the gauge length was 20 mm.

The swelling degree (D_s) was measured by soaking a film (width 5 mm, length 5 mm, thickness 0.1–0.15 mm) in water, NMP/water (vol./vol. 1/1), Dioxane/water (vol./vol. 1/1), NMP, or Dioxane at room temperature for 70 h using the following equation: $D_s [\text{wt}\%] = 100(w_1 - w_0)/w_0$, where w_0 is the initial weight of the film and w_1 is the weight of the swollen film after soaking.

2.2. Reagents and materials

2-Furfurylamine, 2-furfuryl alcohol, 2-furfuryl glycidyl ether, bis(2-aminopropyl)polypropylene glycol-block-polyethylene glycol-block-propylene glycol, $M_n = 1900$ (Jeffamine ED-2003) (Aldrich), polyethylene glycol 2000 (PEG-2000), 20% solution of triphenylmethane triisocyanate in methylene chloride, triethylamine purchased from Aldrich Company and used as received. Dimethylformamide (DMF), chloroform, dichloromethane were distilled before uses.

Synthesis of bismaleimide containing urethane moieties BMI-(a-e)

The bismaleimide **BMI-(a-e)** were prepared from polyester glycols (poly(ethylene adipate) PEA-2000, poly(buthylene adipate) PBA-2000, polycaprolactone diol PCD-2000), poly(tetramethylene ether) glycols (PTHF-2000) or Jeffamine ED-2003 with 4-maleimidophenyl isocyanate according to a method described elsewhere [34, 36]. The structures of **BMI-(a-e)** are presented in Table 1.

Preparation of trifuran compounds TF-(1,2)

Synthesis of **TF-1** was described in our previous article [34]

Tris(2-furylmethyl)[methanetoilyltris(4,1-phenylene)] triscarbamate, **TF-2** was prepared by the addition reaction of triphenylmethane triisocyanate to 2-furfuryl alcohol in molar ratio of 1:3. A typical procedure is presented below. To a solution of 20% triphenylmethane triisocyanate (0.0272 mol, 50 mL) in methylene chloride and DMF (50 mL), 2-furfuryl alcohol (0.0818 mol, 7.15 mL) and four drops of triethylamine as catalyst were added and the solution was

Table 1. Structures of BMI-(a-e)

BMI	R1	
a		PEA-2000
b		PBA-2000
c		PCD-2000
d		PTHF-2000
e	$m \approx 39, l + n \approx 6$	Jeffamine 1900

Table 2. Composition of polyurethane networks

TF	R2	BMI	NPU
1		a	1a
		b	1b
		c	1c
		d	1d
		e	1e
2		a	2a
		b	2b
		c	2c
		d	2d
		e	2e

stirred at 60 °C for 4 hours. The methylene chloride was evaporated out with a rotary evaporator and the solution in DMF was precipitated in methanol, washed with methanol and dried at 60 °C for 12 hours in a vacuum oven.

TF-2 gives a brown solid, 95% yield.

FTIR spectrum (KBr [cm⁻¹]): 3390, 3313, 1713, 1595, 1526, 1412, 1315, 1220, 1046, 817, and 744.

¹H-NMR spectrum (DMSO-*d*₆, TMS), δ [ppm]: 9.73 (s, NH), 7.72 (s, 3H, C₄-H furan ring), 7.38 (d, *J* = 8.0 Hz, 6H, aromatic protons), 7.01 (d, *J* = 8.0 Hz, 6H, aromatic protons), 6.50–6.28 (d, 6H, =CH–CH= from furan ring), 5.39 (s, 1H, CH), 5.12 (s, 6H, CH₂-furan).

Synthesis of model compound

The model compound (**CTF**) was prepared by the cycloaddition reaction of **TF-2** to p-acetyl phenyl-maleimide in molar ratio of 1:3, in THF at reflux for 20 hours.

CTF

¹H-NMR spectrum (DMSO-*d*₆, TMS), δ [ppm]: 9.74 (s, 3H, NHCOO), 8.09–8.07 (d, 6H, aromatic protons *ortho*–CO–CH₃), 7.36–7.40 (dd, 12H, 6H, aromatic protons *ortho* imide and 6H aromatic protons *ortho*–NH), 7.01 (s, 6H, aromatic protons *ortho*–CH), 6.72–6.62 (dd, 6H, –CH=CH– *endo+exo* cycloadduct), 5.42 (s, 1H, >CH–phenyl), 5.30 (s, 3H, –CH cycloadduct), 4.99–4.48 (m, 6H, –CH₂– *exo+endo* cycloadduct), 3.90–3.67 (dd, >CH–CH< *endo* cycloadduct), 3.24–3.22 (d, >CH–CH< *exo* cycloadduct), 2.62 (s, 9H, –CH₃).

Synthesis of polyurethane networks NPU-1,2(a-e)

All adducts were synthesized from stoichiometric amount of the furan functional groups (**TF-1,2**) and bismaleimide **BMI-(a-e)**. The mixture was stirred at 110 °C for 1 hour in a necked flask in DMF under nitrogen atmosphere. Then, the temperature was

decreased at 80 °C and maintained for 6 hours. Finally the polymer solution was cast on glass plates at 80 °C and maintained for 10 hours. The thickness of films was about 0.7–1.2 mm.

3. Results and discussion

The DA reaction of the trifuran compounds **TF-(1,2)** and urethane bismaleimides **BMI-(a-e)**, as depicted in Figure 1 and Table 1 and 2, was used in order to obtain crosslinked thermoreversible polyurethane networks **NPU-1,2(a-e)**. Since the crosslinked networks are insoluble in NMR solvents, for facilitating the investigation by NMR spectroscopy of the DA and retro-DA reactions of trifuran compound with bismaleimide, a model compound, **CTF**, was synthesized (Figure 2). The spectral results confirmed the expected structure. So, in the ^1H -NMR spectrum of compound **CTF** (Figure 3a) it was observed the presence of both *endo* and *exo* forms of DA adduct: the H4 *exo* protons appear at 3.22–3.24 ppm, while the *endo* ones are present at 3.67–3.90 ppm, the *exo* and *endo* protons from the CH_2 linked to the adduct are between 4.99–4.48, the *exo/endo* H3 protons are those at 5.29 and 5.4–5.44 ppm and H1,H2 *endo/exo* appear at 6.62–6.72 ppm. The *exo* form of cycloadduct is formed majority since its formation is thermodynamically favoured. When heating **CTF** at 150 °C for 1 hour the retrodienic reaction takes place and the debonding of the cycloadduct was evidenced in the ^1H -NMR spectrum by the disappearance of the characteristic protons' chemical shifts.

The ^{13}C -NMR spectrum of compound **CTF** (Figure 3b) and the one of the debonded adduct (**CTF**

heated at 150 °C) confirm the formation of the *exo/endo* forms of the cycloadduct and the occurrence of the rDA reaction.

In order to demonstrate the occurrence of DA reaction when obtaining the crosslinked networks a $9 \cdot 10^{-3}$ mol/L solution in $\text{DMSO}-d_6$ of **BMI-d** and **TF-2** was prepared and the ^1H -NMR was recorded. Then the mixture was heated at 80 °C for 5 h and the spectra were recorded after each hour of reaction. The spectra are represented in Figure 3c, and the appearance of characteristic peaks of the cycloadduct can be observed. The reaction was not completed for the NMR experiment due to the insolubility of the final product, so in the spectra from Figure 3c there is a mixture of initial monomers and **NPU-2d**.

The structure of the network films was studied with ATR-FTIR spectroscopy. In Figure 4 there are represented for exemplification the spectra of **NPU-1(a-e)**. The formation of the cycloadduct is confirmed by the appearance of the absorption peak characteristic to

Figure 2. Synthesis of model compound **CTF**

Figure 1. Synthesis of **NPU-1,2(a-e)** networks

Figure 3. a) ^1H -NMR spectra of model compound (initially and at 150°C), b) ^{13}C -NMR spectra of model compound (initially and at 150°C), c) ^1H -NMR spectra representing the DA reaction evolution for **NPU-2d**; the assignment of the cycloadduct's protons is similar as in the case of **CTF** (Figure 3a)

Figure 4. ATR-FTIR spectra of networks **NPU-1(a-e)**

urethane groups). The CO absorption band for networks based on polyester diols appeared shifted to $1723\text{--}1733\text{ cm}^{-1}$ in comparison with that of cycloadducts based on polyether diols which appeared around $1709\text{--}1715\text{ cm}^{-1}$.

3.1. DSC

DSC analysis was utilised in order to get information about the glass transitions, crystallization, melting endotherms and also the thermoreversible character of the crosslinked networks (Figure 5 and 6) and the obtained data for **NPU-2(a-e)** are listed in Table 3, **NPU-1(a-e)** were discussed in our previous work. The DSC scans for the compounds are represented in Figure 5. One can observe the presence of two processes during the heating of all samples: first the glass transition of the soft segments (from the polyol of urethane BMI) followed by the disconnection of the Diels-Alder cycloadduct. The glass transition temperature of the soft segment varied between -75.10 and -15.78°C . The PTHF based network present the lowest T_g of the soft segment due to a better micro-phase separation comparing with the polyesters based networks. The T_g of the soft segment increases in the order $\text{PTHF} < \text{PBA} < \text{PCD} < \text{PEA} < \text{Jeffamine}$, the same variation in different compounds based on these polyols being previously observed [37]. **NPU-2(b-d)** networks based on PBA, PCD and PTHF also present an exothermic peak between -20.68 and 22.67°C indicating the crystallization of soft segments followed by an endotherm ranged between $12.25\text{--}44.32^\circ\text{C}$ appeared due to the melting of crystalline domains of soft segments. The last endotherm, ranged between $138.9\text{--}141.64^\circ\text{C}$, appears on the DSC curves of all the samples suggesting the debonding of the DA adduct. The enthalpy of this process is about $7.8\text{--}17.87\text{ J/g}$. Comparing the two series of networks,

L1 it as a shoulder at 1776 cm^{-1} . Also there can be ob-
 L2 served the disappearance of the absorption band spe-
 L3 cific to the furan ring breathing (at about 1013 cm^{-1}).
 L4 Other peaks specific to the structures **NPU-1(a-e)**
 L5 can be also observed at 1517 cm^{-1} (disubstituted
 L6 phenyl ring), around 1100 cm^{-1} (C–O–C of polyol ure-
 L7thane bismaleimide), 3330 and 1544 cm^{-1} (NH of

Figure 5. DSC scans for NPU-2(a-e)

Figure 6. DSC heating-cooling-heating curves for NPU-2e and cooling curve for NPU-1e

Table 3. Thermal behaviour of polyurethane networks

Sample	$T_{g\ ss}^a$ [°C]	T_{cryst}^b [°C]	T_{endo}^c [°C]	T_{rDA}^d [°C]	ΔH_{rDA}^e [J/g]
NPU-1a	-25.80	—	36.49	125.27	58.20
NPU-1b	-45.98	—	40.20	123.14	28.49
NPU-1c	-34.57	—	52.19	118.88	45.52
NPU-1d	-74.49	-33.50	9.68	130.58	79.76
NPU-1e	-40.35	—	—	136.52	19.85
NPU-2a	-22.02	—	—	140.48	17.87
NPU-2b	-47.47	7.38	40.28	138.90	7.80
NPU-2c	-39.76	22.67	44.32	139.53	15.47
NPU-2d	-75.10	-20.68	12.25	141.36	9.07
NPU-2e	-15.78	—	—	141.64	12.95

^aGlass transition temperature of soft segment of polyurethanes^bCrystallization temperature of soft segment of polyurethanes^cEndothermal peak temperature attributed to the melting of soft segment of polyurethanes^dEndothermal peak temperature corresponding to rDA process^eHeat of rDA process

there can be noticed that the use of **TF-2** instead of **TF-1** in the synthesis of networks leads to a higher rDA temperature of networks which varies in the range of 138.90 and 141.64 °C. The obtained values of the T_{rDA} for the crosslinked networks were higher than the ones of similar networks from other studies [38, 39].

The thermally reversible character of the compounds can be evidenced with DSC by applying multiple heating-cooling cycles to the sample. In Figure 6 is represented a heating-cooling-heating cycle for **NPU-2e**. The reproducibility of the endothermic peak from the heating curves demonstrates the thermoreversibility of the network. When heating the sample up to 190 °C the disconnection of the cycloadduct takes place with the formation of maleimide and furan groups. If cooling down the sample the above mentioned groups come close together and the reconnection of adduct is possible [37, 40, 41]. This is

Figure 7. Picture demonstrating the thermoreversibility of samples **NPU-1,2d**

evidenced by the exothermic peak which appears on the cooling curve. In the second heating, the breaking of the adduct takes place in the same temperature range as in the case of the first heating.

The thermoreversibility of the networks can be also observed in Figure 7 where one can see that the network film is insoluble in DMSO at room temperature, after keeping the sample for 5 minutes at 160 °C it solubilizes (we obtain a liquid) due to the debonding of the DA adducts with the disruption of the network. Then, if keeping the solution 2 h at 80 °C the reformation of the networks takes place because of the DA reaction of maleimide and furan groups, obtaining a gel.

3.2. Rheological behaviour

The gel point in rheological experiments is determined using various methods, according to different definitions [42, 43]: the divergence point or fixed level of the viscosity [44, 45], the crossover point of the dynamic storage modulus (G') and loss modulus (G'') [46], or the point at which the loss tangent becomes independent of testing frequency [47–50]. The gel point for **NPU-2d**, as the crossover point of G' and G'' appears at 116.5 °C as can be seen in Figure 8a. Initially, G' is lower than G'' indicating the viscous nature of the sample; during the heating process both G' and G'' increased gradually. After the gel point, the storage modulus value surpasses the loss modulus ones, suggesting the switch to the dominant elastic properties of the sample. The rheological measurements were done using the starting monomers and the reaction proceeded in the instrument. So, first the DA reaction took place and the viscosity increased. Then, we suppose a competition between the DA and rDA reactions proceeded, explaining this way the increasing trend of viscosity. One can also observe in the DSC experiments that on the heating/cooling curves the values of the endothermal and exothermal domains overlap. Other rheological studies from the literature on DA networks were done by cooling the debonded crosslinked networks [51]. For comparing the two series in Figure 8b the viscosity of **NPU-1e** and **NPU-2e** vs. time is represented. One can see that in the case of the network based on the trifurylic compound with tertiary nitrogen (**NPU-1e**) the gelation begins earlier, at a lower temperature and finishes at a higher one than in the case of **NPU-2e** network. So, the Diels-Alder reaction needs a longer time to proceed. This fact was also confirmed by the DSC

Figure 8. a) Dynamic storage modulus (G') and loss modulus (G'') evolution with increasing temperature for **NPU-2e**, b) Viscosity vs temperature curves for **NPU-1,2e**

experiment, where on the cooling curves of these samples (Figure 6) the exothermic peak corresponding to dienic reaction is larger in the case of **NPU-1e**.

3.3. TGA

Table 4 present the parameters extracted from the thermo gravimetric analyses, while the TG and DTG curves of the new networks are depicted in Figure 9. From the figure, as well from the table, the influence

Figure 9. TG and DTG curves for **NPU-2(a-e)**

of the structural nature of the substituents on the thermal stability may be observed. So, degradation begins faster in the case of **NPU-2d** based on the **BMI** which contains poly(tetramethylene ether) glycol, while **NPU-2b** (obtained from the maleimide with poly(buthylene adipate)) is stable up to 221 °C. **NPU-2a** has the highest char yield and **NPU-2b** the lowest. The thermal decomposition stages are similar to those of **NPU-1(a-e)** described in our previous work [34]. The IDT of the new synthesised networks compared with **NPU-1(a-e)** series are lower due to higher urethane group concentrations.

3.4. Mechanical properties

Young's modulus, maximum strength and maximum strain of all the samples are shown in Figure 10 and Table 5. When using **TF-2** in the synthesis of **NPU** instead of **TF-1** the flexibility of the molecular chains decreased due to the introduction of aromatic rings and also to the higher number of hydrogen bonds. Therefore, the Young's moduli of **NPU-2(a-e)** are higher than the ones of the corresponding **NPU-1**

Table 4. The thermogravimetric data for the polyurethane networks

Sample	IDT ^a [°C]	Decomposition temperature range (weight losses) [°C] [%]			Y _c ^b (700 °C) [%]
		stage I	stage II	stage III	
NPU-2a	204.46	228.69 (6.15)	325.12 (9.01)	406.52 (45.89) 452.56 (13.25)	26.66
NPU-2b	221.11	232.84 (4.40)	374.25 (64.50)	463.97 (11.39)	10.92
NPU-2c	215.67	233.04 (4.44)	409.03 (54.07)	469.98 (9.71)	17.71
NPU-2d	197.01	216.63 (3.75)	348.26 (20.62)	423.45 (58.39)	16.26
NPU-2e	200.00	300.00 (6.00)	440.00 (72.00)	—	21.00

^aInitial decomposition temperature by TGA measurements

^bChar yield at 700 °C

Figure 10. Mechanical properties of the samples a) Maximum stress and strain, b) Young modulus

Table 5. The mechanical properties of the polyurethane networks

Sample	Max. stress [MPa]	Max. strain [%]	Modulus [MPa]
NPU-1a	3.63	78.15	53.06
NPU-1b	10.60	229.68	23.91
NPU-1c	8.26	40.70	222.30
NPU-1d	6.54	260.70	3.65
NPU-1e	3.54	270.00	2.66
NPU-2a	5.63	27.30	395.00
NPU-2b	9.80	28.90	413.00
NPU-2c	10.32	2.12	642.03
NPU-2d	9.27	30.55	377.24
NPU-2e	5.75	50.13	323.00

networks. Also, the **NPU-2** films have higher values of the stress than the corresponding **NPU-1** ones. As expected, the strain varies opposite to the stress and Young's modulus since a less rigid structure can suffer a higher deformation.

3.5. Swelling properties

The crosslinking density was evaluated from the swelling degree values (an increase in the swelling degree shows a decrease of the crosslinking density) [17]. The measurements were done for **NPU1,2-d** and the data are presented in Figure 11. As can be seen **NPU-1d** has a higher swelling degree in all solvents compared to **NPU-2d** suggesting a higher crosslinking density for the latter one. These results are in agreement with T_{IDA} from the DSC study which is also higher for **NPU-2** series related to the **NPU-1** one. If the D_s values of the same film are compared, D_s of both samples increased with decreasing polarity of the solvent. The polyurethane networks obtained have a higher crosslinking density comparing with similar ones presented in literature [52].

Figure 11. D_s values of **NPU-1,2d** in water, water/NMP (1/1), water/dioxane (1/1), NMP and dioxane

4. Conclusions

New thermoreversible polyurethane networks based on A_2B_3 monomers were successfully obtained. Their thermal, rheological and mechanical properties were studied. The crosslinking density was estimated from the degree of swelling and the **NPU-2d** was found to have a higher crosslinking density than **NPU-1d**. The thermoreversibility of the networks was observed by different methods (DSC, solution properties). By changing the trifurylic compound, the time necessary for the DA reaction to proceed decreased as proved by DSC and rheological studies. The presence of tertiary nitrogen in the structure of the crosslinked polyurethane networks influences the viscosity in the retrodieneic domain of temperature probably due to the activation of free maleimide groups crosslinking. That is why in the rheological measurements the viscosity for **NPU-1e** increases when the one of **NPU-2e** reaches a plateau. Another effect of replacing the TF compound is the increase of the rDA temperature and the decrease of the initial decomposition temperature.

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