

Dedicated to Professor Alexandru T. Balaban  
on the occasion of his 85th anniversary

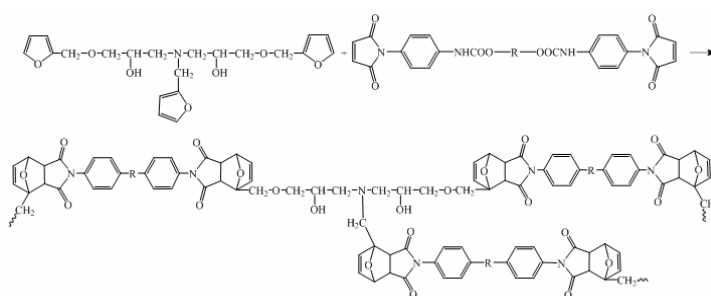
## THERMAL PROPERTIES OF THERMORENSPONSIVE NETWORKS BASED ON POLYURETHANES

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The synthesis of Diels-Alder (DA) adducts from stoichiometric quantities of urethane bismaleimide and new trifuran compound was investigated. Precursors of the DA reaction were first synthesized and their structures were determined by <sup>1</sup>H-NMR and ATR-FTIR spectra. To facilitate investigation by NMR spectroscopy of the DA and retro-DA reaction between trifuran compound and bismaleimide, a model compound was synthesized. TGA and DSC measurements were used to characterize their thermal properties.



### INTRODUCTION

Polyurethane chemistry is considered one of the most versatile chemistries for polymer materials. Due to the ability to adopt polyurethanes molecules structures to specific property requirements, different types can be synthesized and used in a variety of applications including elastomers,<sup>1-4</sup> flexible and rigid foams,<sup>5-7</sup> biomedical applications,<sup>8-10</sup> adhesives and coatings.<sup>11-13</sup> Polyurethanes are generally obtained from the reaction between diisocyanates or multiisocyanates and di- or polyols and can be built in a large variety of molecular structures varying from linear to crosslinked ones depending on the structure, functionality and stoichiometry of the reactants. When chemical crosslinkers are introduced,

according to the desired applications, these thermosetting polymers cannot be reprocessed or reused.<sup>14</sup> To produce the de-crosslinking of polyurethane networks, dynamic covalent chemistry is used, especially by means of the DA and retro-DA (rDA) reactions.<sup>15</sup> Concerning polyurethane, the DA reaction was employed in thermally remendable linear polymers<sup>16-19</sup> and thermally reversible networks.<sup>20-24</sup> The latter were designed in three different ways: i) by polymerization reaction of monomers containing maleimide-furan cycloadduct,<sup>23,25</sup> ii) by crosslinking of linear polyurethane containing furan or maleimide pendant groups<sup>24,26</sup> and iii) by cycloaddition DA reaction between polyurethane containing furan end groups and multimaleimide monomers.<sup>16,20-22,27-28</sup>

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The key of our previous networks was to obtain the linear polyurethanes bearing furan or maleimide pendant groups and then crosslink them with bismaleimide or bifuran compounds to form crosslinked polyurethane networks containing DA furan-maleimide cycloadducts.<sup>24,26,29</sup>

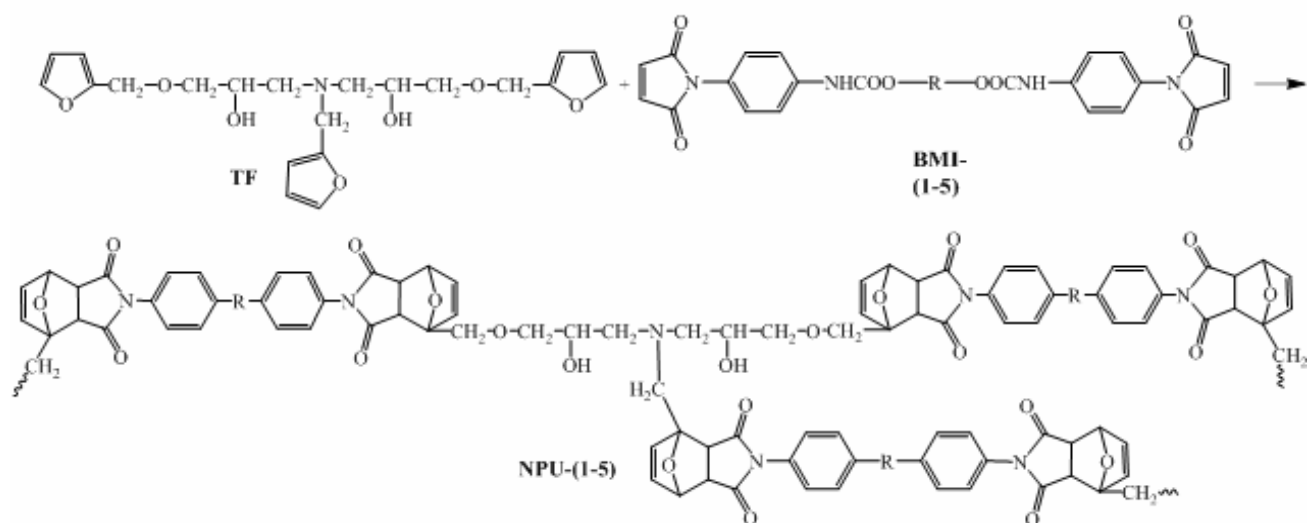
The purpose of this paper is to elaborate reversible crosslinkable polyurethane networks from  $A_nB_m$  monomers, containing multifunctional maleimide or furan groups, using DA reaction (where the crosslinked structures are essentially due to the DA links) and to study their thermal properties.

## RESULTS AND DISCUSSION

The synthesis route employed for the preparation of crosslinked self-healing polyurethane networks **NPU-(1-5)** involved a DA reaction of the trifuran compound **TF** and urethane bismaleimides **BMI-(1-5)**, as depicted in Scheme 1. Thermal properties (melting point, endothermal peak temperature, exothermal peak temperature) are shown in Table 1.

The DSC curves of **BMI-(1-5)** studied by DSC measurements using a Mettler TA Instrument DSC 12E with a heating rate of 6°C/min in nitrogen, in the temperature range of 20-300°C, presented an endothermic peak in the temperature range of 33.1-50°C and an exothermic peak between 140-294°C.

To facilitate the investigation by NMR spectroscopy of the DA and retro-DA reactions of trifuran compound with bismaleimide, a model compound, **CTF**, was synthesized (Scheme 2) and its structure was determined by <sup>1</sup>H-NMR spectroscopy, the spectral results confirming the expected structure. Thus, in the <sup>1</sup>H-NMR spectrum of compound **CTF** it was observed the disappearance of the signals corresponding to C<sub>5</sub> protons at 7.56-7.62 ppm, the shifting of signals specific to the furyl group protons from 6.25-6.43 ppm to 6.58 ppm and the appearance of new signals attributed to the bridge protons at 5.23-5.37 ppm and *exo/endo* protons from furan-maleimide cycloadduct at 3.80-3.08 ppm. In the spectrum recorded for this compound at 160°C, the appearance of the peaks attributed to the free maleimide and furan groups could be observed.



where R is: 1=PEA-2000, 2=PBA-2000, 3=PCD-2000, 4=PTHF-2000, 5=Jeffamine 1900

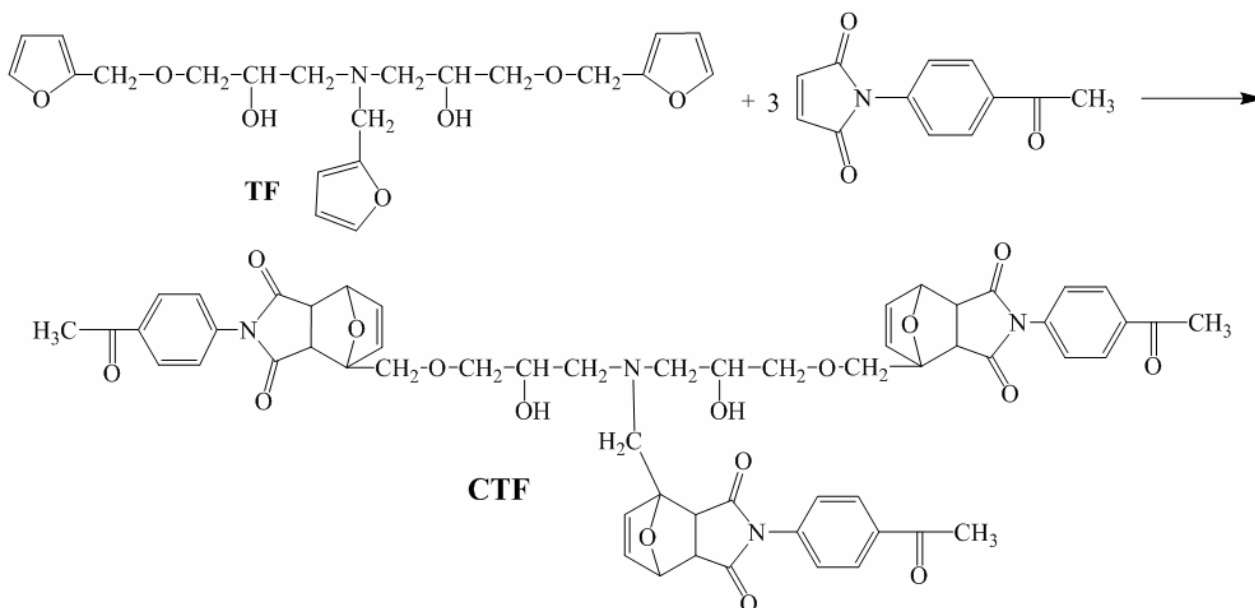
Scheme 1 – Synthesis of polyurethane networks.

Table 1

Properties of bismaleimides **BMI-(1-5)**

Sample	R <sub>1</sub>	Melting point <sup>a</sup> (°C)	T <sub>endo</sub> <sup>b</sup> (°C)	T <sub>exo</sub> <sup>c</sup> (°C)
<b>BMI-1</b>	PEA-2000	55-60	42	140
<b>BMI-2</b>	PBA-2000	65-70	50	140
<b>BMI-3</b>	PCD-2000	46-52	37	294
<b>BMI-4</b>	PTHF-2000	94-102	39	280
<b>BMI-5</b>	Jeffamine 1900	55-69	33.1	278

<sup>a</sup> Determined visually in a capillary tube melting point apparatus, <sup>b</sup>Endothermal peak temperature by DSC, <sup>c</sup>Exothermal peak temperature by DSC



Scheme 2 – Synthesis of model compound.

The  $^{13}\text{C}$ -NMR spectrum of compound **CTF** showed the disappearance of signals characteristic to the carbon from furyl groups at 152.36, 143.43, 110.87 and 109.79 ppm and the carbons from maleimide double bonds at 135.11 ppm and the appearance of a new signal at 174.17 ppm attributed to the C=O from furan-maleimide cycloadduct.

DSC analysis, conducted on a DSC 200 F3 M in the range temperature of  $-100$  and  $200^\circ\text{C}$ , provided the information on the glass transitions crystallization, melting endotherms and also the retrodienic reaction of networks (Fig. 1). The DSC data are compiled in Table 2. The DSC curves of networks **NPU-(1-5)** based on urethane bismaleimide and **TF** (Fig. 1) exhibited a glass transition temperature corresponding to the soft segments, an endothermic peak temperature attributed to the melting of soft segments and an endothermic transition temperature due to the rDA process, which varied in the range of  $-25.50$  and  $-74.49^\circ\text{C}$ ,  $9.68$ - $52.19^\circ\text{C}$  and  $118.88$ - $136.52^\circ\text{C}$ , respectively. The rDA process energy ranged between  $19.85$  and  $79.79$  J/g depending on the structure of bismaleimide **BMI-(1-5)**.

Regarding the crystallization and melting process, from Fig. 1 one can see that only the DSC curves of networks which containing PEA, PBA, PCD and PTHF presented the melting endothermic peak and the network **NPU-4** based on PTHF-2000 also showed the exothermic peak assigned to the crystallization of soft segment around  $-33.50^\circ\text{C}$ .

DSC method also reveals useful insights on the thermally reversible character of compounds.<sup>26</sup> Fig. 2 indicates, as an exemplification, the two temperature cycles of structures **NPU-5**. The thermally remendable character of the studied sample is demonstrated by the reproducibility of the endothermic process characteristic to the rDA reaction on the heating curves. This is due to structural disconnection into maleimide and furan moieties. The material thermally heals itself upon cooling via reconnection of diene and dienophile moieties by the DA reaction.<sup>30-32</sup> Processes enthalpies yielded similar values in the case of rDA reaction of  $19.85$  Jg $^{-1}$  and  $18.33$  Jg $^{-1}$  (Fig. 2). Process's enthalpy values for the DA reaction, upon cooling, was  $-0.5$  Jg $^{-1}$  for sample **NPU-5**. These aspects highlight the advantages and accessibility of the DA reaction as preferred over bondbreaking degradation reaction.<sup>31-34</sup>

The main characteristic parameters extracted from the TGA data are given in Table 2 and the DSC curves were presented in Fig. 3. By analyzing the table, one may observe that the thermal stability of the studied compounds varies depending on the structural nature of the substituents (PEA, PBA, PCD, PTHF). Most of the samples exhibit three stages of thermal decomposition. According to the literature, the first stage may be attributed to the retrodienic reaction and isocyanate and alcohol formation by urethane bond dissociation, while the next stages were described by partial polyols and maleimide cross-linked structures decomposition.<sup>26</sup>

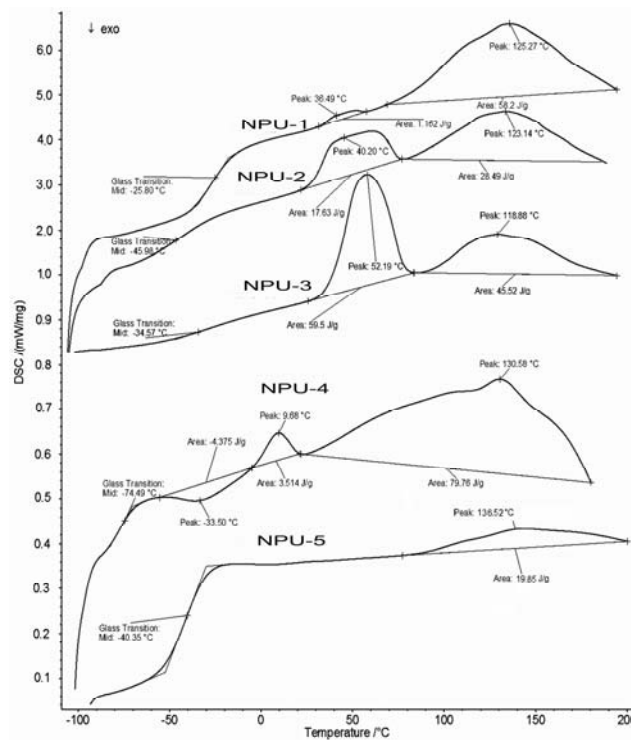


Fig. 1 – The DSC curves for the networks.

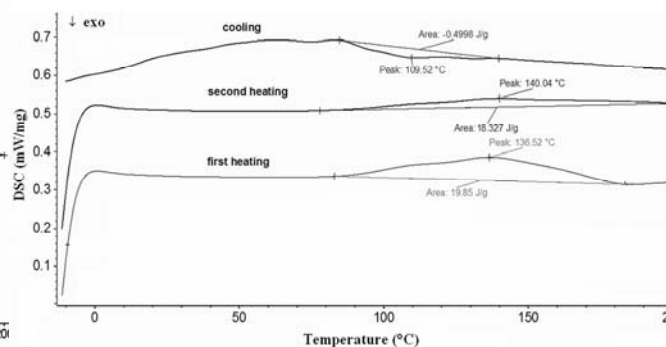


Fig. 2 – The DSC heating-cooling-heating cycle for NPU-5.

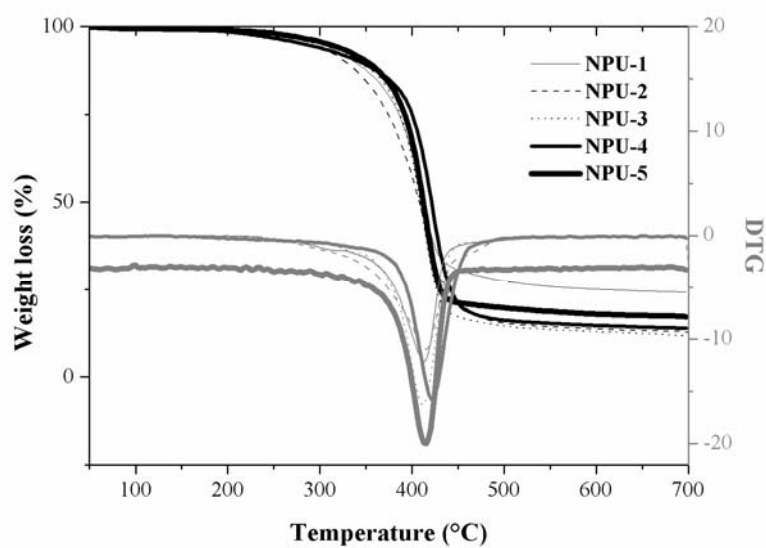


Fig. 3 – The TGA profiles of NPU-(1-5).

Table 2

The thermal data for the networks

Sample	IDT <sup>a</sup> (°C)	Decomposition temperature range, °C (weight losses, %)			Y <sub>c</sub> <sup>b</sup> (%)	T <sub>g,ss</sub> <sup>c</sup> (°C)	T <sub>endo</sub> <sup>d</sup> (°C)	T <sub>rDA</sub> <sup>e</sup> (°C)	ΔH <sub>rDA</sub> <sup>f</sup> (J/g)
		stage I	stage II	stage III					
NPU-1	249.60	249.60-294.74 (2.87)	294.74-358.07 (10.49)	358.07-435.35 (61.42)	24.02	-25.80	36.49	125.27	58.20

Table 2 (continued)

<b>NPU-2</b>	268.60	268.59-339.46 (11.62)	339.46-433.03 (61.13)	433.03-475.06 (13.11)	12.74	-45.98	40.20	123.14	28.49
<b>NPU-3</b>	262.30	262.30-372.67 (15.91)	372.67-436.33 (70.78)	-	11.38	-34.57	52.19	118.88	45.52
<b>NPU-4</b>	196.98	196.98-380.31 (15.97)	380.31-454.59 (69.29)	-	13.66	-74.49	9.68	130.58	79.76
<b>NPU-5</b>	245	245-350 (8.00)	350-480 (74.00)	-	17	-40.35	-	136.52	19.85

<sup>a</sup>Initial decomposition temperature by TGA measurements; <sup>b</sup>Char yield at 700°C; <sup>c</sup>Glass transition temperature of soft segment of polyurethanes; <sup>d</sup>Endothermic peak temperature attributed to the melting of soft segment of polyurethanes; <sup>e</sup>Endothermic peak temperature corresponding to rDA process; <sup>f</sup>Heat of rDA process

The mass loss in the first stage of thermal decomposition ranges between 2.87% and 15.97%. One must not exclude the possibility of the rDA reaction to generate some free maleimide and furan groups during heating, which contribute to the mass loss. Furthermore, self-addition and cross-linking reactions may occur between free maleimide groups leading to enhancement of thermal stability.<sup>26</sup> Thus, where the IDT exhibit an increasing trend, this may not be generally just due to mostly the substituent's nature. The second thermal degradation stage is the main one, where the highest mass loss occurs. The second and third stage (where present) are due to overlapping of complex decomposition processes generated by random chain scissions. Such processes correspond to degradation of polyols and cross-linked structure decomposition.

## EXPERIMENTAL

**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<sup>-1</sup>. The proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on a Bruker NMR spectrometer, Avance DRX 400 MHz, using CDCl<sub>3</sub> and DMSO-d<sub>6</sub> 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°C/min. Nitrogen was used as inert atmosphere at a flow rate of 50 mL/min. The temperature against heat flow was recorded. The baseline was obtained by scanning the temperature domain of the experiments (between -100 and 300°C) with an empty pan. The enthalpy was calibrated with indium according to standard procedure. TGA experiments were conducted on a STA 449 F1 Jupiter apparatus (Netzsch, Germany). 10 mg of sample was heated from 25 to 700°C in an open alumina crucible in nitrogen atmosphere with a flow rate of 50 mL/min. A heating rate of 10°C/min was applied.

**Reagents and Materials.** 2-Furfurylamine, 2-furfuryl alcohol, 2-furfuryl glycidyl ether, bis(2-aminopropyl)polypropylene

glycol-block-polyethylene glycol-block-propylene glycol, Mn=1900 (Jeffamine ED-2003) (Aldrich), polyethylene glycol 2000 (PEG-2000), triethylamine purchased from Aldrich Company and used as received. Dimethylformamide (DMF), chloroform, dichloromethane were distilled before uses.

**Synthesis of bismaleimide containing urethane moieties BMI-(1-5).** The bismaleimide **BMI-(1-5)** 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.<sup>35</sup> The properties of bismaleimides **BMI-(1-5)** are listed in Table 1. The bismaleimides **BMI-(1-4)** were synthesized and reported in our previous papers.<sup>19,35</sup> Bismaleimide **BMI-5** was obtained by the reaction of 4-maleimidophenyl isocyanate with Jeffamine ED-2300 in dichloromethane to give a yellow wax by crystallization from dichloromethane, 91% yield.

<sup>1</sup>H-NMR spectrum (DMSO-d<sub>6</sub>, TMS), δ (ppm): 8.63 (s, CONH), 7.46 (d, *J* = 8.8 Hz, 4H, aromatic protons), 7.22 (d, *J* = 8.8 Hz, 4H, aromatic protons), 7.16 (s, 4H, maleimide protons), 6.03 (d, CO-NH-CHCH<sub>3</sub>-), 4.15 (m, 2H, NH-CH<sub>2</sub>CH<sub>3</sub>-CH<sub>2</sub>-), 3.81 (m, 4H, CO-NH-CHCH<sub>3</sub>-CH<sub>2</sub>-O), 3.51 (m, CH<sub>2</sub>-O of polyethylene glycol block and CH<sub>2</sub>-O of polypropylene glycol block), 1.26 (t, CO-NH-CHCH<sub>3</sub>-), 1.06 (d, CH<sub>3</sub>-CH<).

**Preparation of trifuran compound TF.** TF was prepared by the reaction of 2-furfuryl glycidyl ether and 2-furfurylamine in molar ratio of 2:1, in toluene, according to a method described in the literature.<sup>15</sup>

TF gives yellow oil, 92% yield. <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, TMS), δ (ppm): 7.38 (s, 2H, C<sub>5</sub>-H furanic ring), 7.34 (s, 1H, C<sub>5</sub>-H furanic ring), 6.29-6.3 (dd, 5H, -CH=CH- furan protons), 6.17 (d, 1H, furan ring-CH<sub>2</sub>-NH-), 4.47 (s, 4H, -O-CH<sub>2</sub>-), 3.83 (N-CH<sub>2</sub>-furan ring), 3.71 (m, 2H, -CH<sub>2</sub>-CH(OH)-), 3.35-3.49 (m, 4H, -O-CH<sub>2</sub>-CH), 3.24 (s, 2H, OH), 2.03-2.63 (m, N-CH<sub>2</sub>-CH(OH)-)

**Synthesis of model compound.** The model compound was prepared by the cycloaddition reaction of TF to *p*-acetyl phenylmaleimide in molar ratio of 1:3, in THF at reflux for 20 hours. <sup>1</sup>H-NMR spectrum (DMSO-d<sub>6</sub>, TMS), δ (ppm): 8.06 (d, 6H, aromatic protons), 7.41 (d, 4H, aromatic protons *exo* cycloadduct), 7.28 (d, 2H, aromatic protons *endo* cycloadduct), 6.58 (s, 6H, -CH=CH- of cycloadduct), 5.37 (s, H<sub>endo</sub>, -CH-O of cycloadduct), 5.23 ((s, H<sub>exo</sub>, -CH-O of cycloadduct), 4.53-4.39 (d, H<sub>exo</sub> and H<sub>endo</sub> -O-CH<sub>2</sub>-cycloadduct), 4.19 (d, 2H, CH-OH), 3.80-3.40 (cycloadduct-

CH<sub>2</sub>-N< *endo+exo*, OCH<sub>2</sub>-CH(OH) *endo+exo* and CH of succinimide cycloadduct *endo*), 3.26 (d, 4H, -OC-CH<sub>2</sub>-N<), 3.08 (2H, CH of succinimide cycloadduct *exo*), 2.62 (t, 9H, -CO-CH<sub>3</sub>).

**Synthesis of polyurethane networks NPU-(1-5).** All adducts were synthesized from stoichiometric amount of the furan functional groups (TF) and bismaleimide BMI-(1-5). 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.

## CONCLUSIONS

A series of five new thermoreversible polyurethane networks was successfully synthesised by means of Diels-Alder reaction. The investigation by NMR spectroscopy of the DA and retro-DA reactions of trifuran compound with bismaleimide was facilitated by synthesising a model compound and the spectral data were in concordance with the expected structure. The thermo remendable character was evidenced by the endothermic peak characteristic to the rDA reaction from the DSC curves of the networks and also by the reproducibility of the dienic reaction in the heating-cooling-heating cycle. The thermogravimetric analyses revealed a two or three stage decomposition mechanism, depending on the nature of the polyol from the network's structure.

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