

Dedicated to the memory of
Professor Eugen Segal (1933-2013)

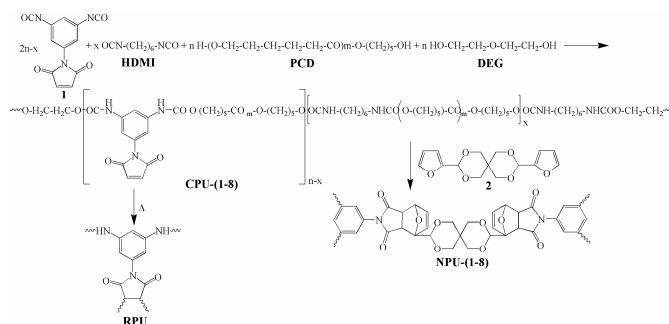
COPOLY(ESTER-URETHANE) NETWORKS CONTAINING THERMOREVERSIBLE BONDS

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Received April 29, 2014

Copoly(ester-urethane)s containing maleimide groups were prepared by polyaddition reaction of two diisocyanates, namely 1,6-hexamethylene diisocyanate (HDMI) and 5-maleimidoisophthalic diisocyanate, to polycaprolactone diols of molecular weight 1250 and 2000 g/mol and diethylene glycol as chain extender by the solution prepolymer method. The cross-linked copoly(ester-urethane) networks and copoly(ester-urethane) containing Diels-Alder (DA) reversible bonds were synthesized by thermal or Diels-Alder addition crosslinked of copoly(ester-urethane) containing maleimide groups. The structures of copolyurethanes and networks were confirmed by FTIR and ¹H-NMR spectroscopy. The thermal behaviour of polymers was studied by thermogravimetric analysis and differential calorimetric measurements.



INTRODUCTION

Recently, polymers containing reversible bonds have drawn much attention in terms of their responsiveness against external stimuli. Beside the multitude of papers that have been published in this area, a number of reviews also exist that focus on various aspects of the research, from both the synthetic chemistry and materials engineering points of view,¹⁻⁴ and a comprehensive book on the subject has been released.⁵ Over the past ten years several groups have explored to use of reversible Diels-Alder cycloadducts in the design and synthesis of new organic materials.⁶ Thermally retro-Diels-Alder (rDA) reactions have been used

in numerous studies including polymer synthesis,⁶⁻¹³ dendrimers,¹⁴⁻¹⁷ epoxy resins,¹⁸⁻²¹ cross-linked polymer networks,²²⁻²⁷ organic-inorganic polymer-hybrids,²⁸⁻³⁰ surfactants,³¹ surface modification,³²⁻³³ and remendable self healing polymers.³⁴ Due to the fact that these reactions can proceed under mild conditions without catalyst they are attractive for designing covalently reversible bonds with furan and maleimide functional groups which are responsible for association and dissociation.^{32, 34-35}

By taking advantage of this mechanism, we have developed thermoreversible network polymers using functional polymers containing furan groups and bismaleimide crosslinkers,³⁶⁻³⁷ maleimide functional polymers and bisfuranic

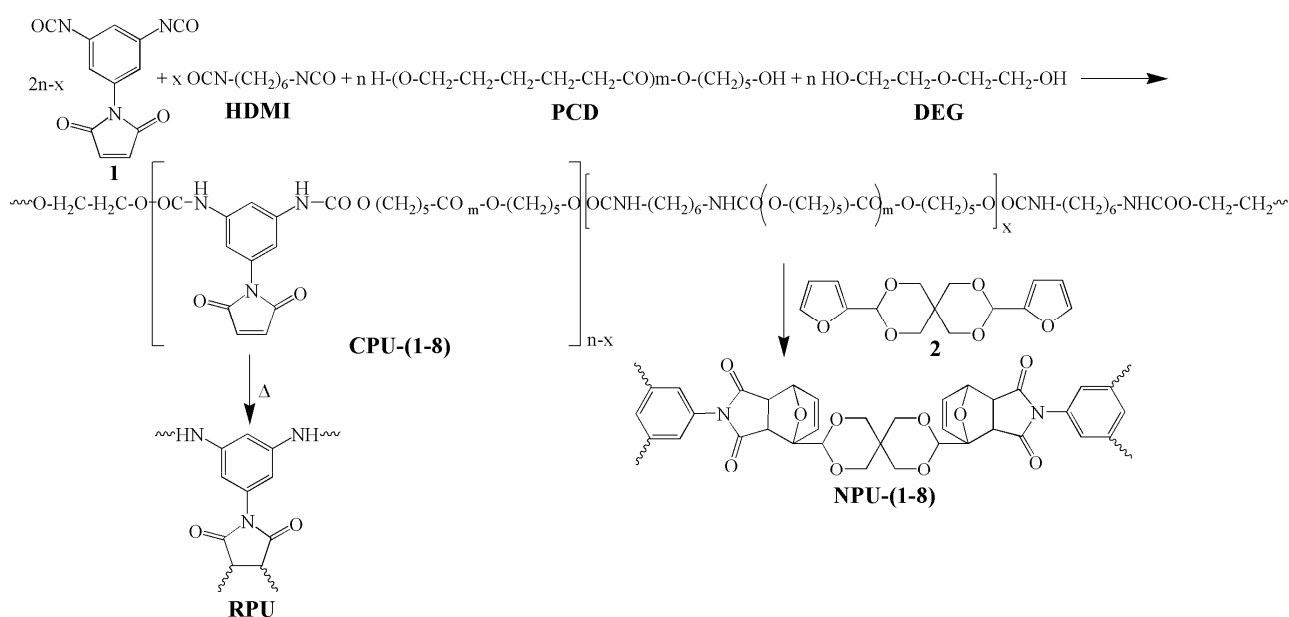
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monomers,³⁸ and monomers containing furan-maleimide cycloadducts.³⁹⁻⁴⁰ In this article, we describe the synthesis, recyclability and physical properties of DA networks polymers derived from copoly(ester-urethane) oligomers having maleimide side groups and bisfuryl monomer. The cross-linking of the polyurethane structure was performed by cycloaddition DA reaction of maleimide groups to bisfuryl monomer. These networks contain two kinds of reversible bonds that are DA bonds and supramolecular hydrogen bonds (between C=O and NH groups from urethane structure).

RESULTS AND DISCUSSION

CPU-(1-8) were prepared by conventional two stage method in DMF solution from a mixture of HMDI and **1**, PCD, DEG as chain extender and DBTL as catalyst (Scheme 1). The composition of copolymers and soft segment content were presented in Table 1.

The ATR-FTIR and ¹H-NMR spectroscopy was used to investigate the formation of structures. Typical IR spectra for **CPU-2**, **NPU-2** and **RPU-2** (**CPU-2** treated at 210°C) were presented in Fig. 1. They do not show the absorption band at 2270 cm⁻¹ associated with isocyanate groups. The FTIR spectrum of **CPU-2** presented the characteristic absorption bands at 3331 (assigned to -NH urethane groups), 3102, 2944 and 2863 (associated with asymmetric and symmetric -CH₂ groups), 1720 (due to the free -C=O from ester, imide and urethane groups), 1613, 1550 (corresponding to CO-N from urethane groups), 1460, 1435, 1420, 1366, 1239 and 1188, 1164 and 1045 (assigned to ester groups of PCD), 1093 (attributed to stretching of the ether groups), 961, 828 and 699 cm⁻¹. The absorption band at 3102, 1720, 1613, 1396, 828 and 699 cm⁻¹ were assigned to maleimide groups. The spectrum of **NPU-2** compared with that of **CPU-2** showed a reducing of absorption bands intensity and the disappearance of absorption bands at 3102 and 828 cm⁻¹ and the appearance of new bands at 1778, 1193 cm⁻¹ specific to furan-maleimide cycloadduct.³⁶



Scheme 1

Table 1

Composition of **CPU-(1-8)**

Sample	M _{n,PCD}	Monomer 1 (mol)	HMDI (mol)	PCD (mol)	DEG (mol)	Soft segment (%)
CPU-1	1250	2	0	1	1	66.97
CPU-2	2000	2	0	1	1	76.44
CPU-3	1250	1	1	1	1	70.24
CPU-4	2000	1	1	1	1	79.07
CPU-5	1250	1.5	0.5	1	1	68.57
CPU-6	2000	1.5	0.5	1	1	77.73
CPU-7	1250	0.5	1.5	1	1	72.09
CPU-8	2000	0.5	1.5	1	1	80.45

A typical $^1\text{H-NMR}$ spectrum of **CPU-3** is presented in Fig. 2 and it exhibited the characteristic peaks at 1.20-1.60 ($-\text{CH}_2-$ from PCD and HDMI), 2.25-2.30 ($-\text{CH}_2-\text{COO}$ from PCD), 3.40-3.45 ($-\text{CH}_2-\text{NH}-$ from HDMI), 3.50-3.53 ($-\text{CH}_2-\text{O}-$ from DEG), 3.61 ($-\text{CH}_2-\text{O}-$ from PCD), 4.13 ($-\text{CH}_2-\text{OOCNH}-$), 4.55-4.58 ($-\text{CH}_2-\text{OOCNH}-$ from urethane-DEG), 7.11 ($-\text{CH}=\text{}$ of maleimide), 7.16 ($-\text{NHCOO}-$), 7.72 ($-\text{CH}=\text{}$ aromatic), 7.90 ($-\text{CH}=\text{}$ aromatic), 8.20 (phenyl- $\text{NH}-\text{CO}$) ppm. The

percentages share of characteristic groups protons of copolymers calculated from $^1\text{H-NMR}$ peaks and the stoichiometric ratios of monomer used in the synthesis are listed in Table 2. Some discrepancies between experimental and calculated data may result from the reactivity difference of diisocyanates. All copolymers were soluble in dipolar aprotic solvents and inherent viscosity ranged between 0.28 and 0.68 dL/g (Table 2).

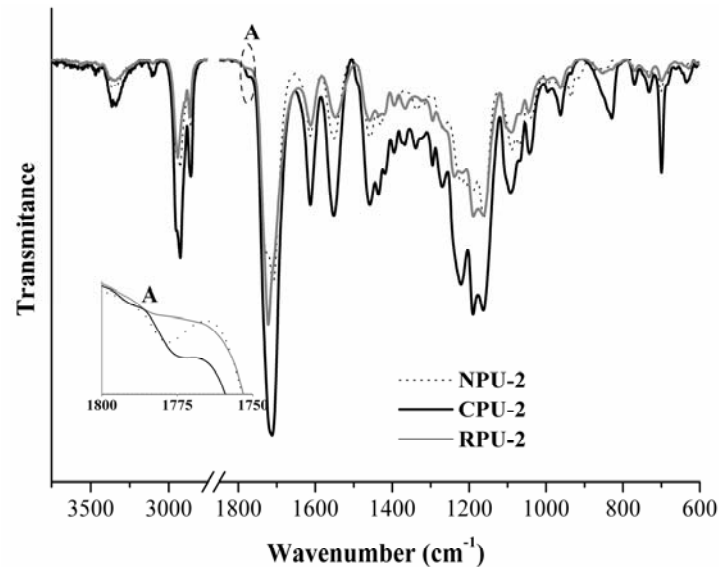


Fig. 1 – The FTIR spectra of CPU-2, NPU-2 and RPU-2.

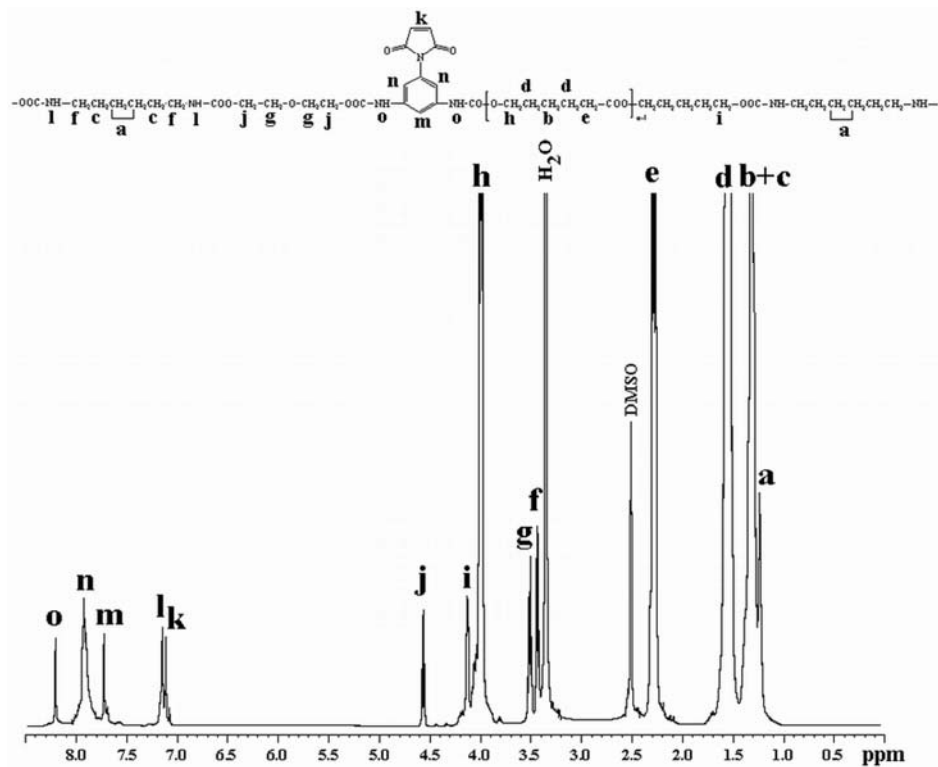


Fig. 2 – The $^1\text{H-NMR}$ spectrum of CPU-3.

Table 2
Contents of characteristic groups in polyurethanes (%)

Sample	Groups ^a												η_{inh}^b (dL/g)
	-CH ₂ -CO-		-CH ₂ -O-OC-		-CH ₂ -OOC-NH-		-NH-phenyl-		-CH ₂ -NH-		-CH=CH-		
	C	E	C	E	C	E	C	E	C	E	C	E	
CPU-1	16.83	16.38	16.83	16.41	1.98	1.87	1.98	1.89	0	0	1.98	1.88	0.39
CPU-2	15.15	14.89	15.15	15.01	3.03	2.98	3.03	3.01	0	0	3.03	3.00	0.28
CPU-3	16.26	15.98	16.26	16.02	1.90	1.81	0.96	0.89	0.96	0.89	0.96	0.89	0.47
CPU-4	14.40	14.13	14.40	14.08	2.88	2.73	1.42	1.37	2.88	2.83	1.42	1.39	0.43
CPU-5	16.54	16.32	16.54	16.26	1.95	1.92	1.46	1.41	0.97	0.93	1.46	1.41	0.53
CPU-6	14.76	14.57	14.76	14.58	2.95	2.88	2.21	2.17	1.47	1.41	2.21	2.18	0.49
CPU-7	16.00	15.83	16.00	15.92	1.88	1.79	0.47	0.41	2.82	2.79	0.47	0.41	0.68
CPU-8	14.03	13.78	14.03	13.85	2.80	2.73	0.70	0.68	4.21	4.18	0.70	0.68	0.57

^aC – calculated from stoichiometric ratio, E – estimated from ¹H-NMR data; ^bInherent viscosity

Table 3
Thermal properties of CPU-(1-8)

Sample	T _g ^a (°C)	T _{m1} ^b (°C)	ΔH_1^c (J/g)	T _{m2} ^b (°C)	ΔH_2^c (J/g)	T _{exo} (°C)	ΔH_{exo}^c (J/g)
CPU-1	-44.19	-	-	50.62	24.30	274.42	-39.84
CPU-2	-36.17	-	-	19.91	16.93	258.92	-43.22
CPU-3	-47.38	26.43	3.59	52.02	23.70	216.39	-24.37
CPU-4	-42.89	-	-	53.82	43.32	229.21	-10.02
CPU-5	-40.07	-	-	54.22	30.97	268.18	-29.79
CPU-6	-49.17	28.74	7.74	52.18	19.62	218.49	-15.40
CPU-8	-49.04	22.20	0.84	51.82	37.8	225.96	-27.03

^aThe glass transition temperature; ^bThe melting temperature of soft segment; ^cThe heat of melting and exothermal process

Thermal behaviour of CPU was investigated by DSC measurements. The DSC curves of CPU are presented in Fig. 3 and the corresponding data in Table 3. The DSC scans of CPU-(1-8) showed three thermal transition temperatures ranging between -49.17 and -36°C (assigned to the glass transition of soft segment), 26-54°C (due to the melting of soft segment) and 216-268°C (attributed to the thermal polymerization of maleimide groups).

Thermal behaviour of NPU was investigated by DSC and TGA measurements. The DSC scans of NPU-(1-8) showed a unimodal or bimodal endothermic peak in the range of 60-180°C attributed to rDA reaction. In addition, NPU-(3, 5-8) showed a glass transition of networks ranging between 107.72 and 119.98°C before the endothermic peak characteristic to the retrodionic process. ΔH of endothermic process was situated between 2.99 and 22.34 J/g and varied depending on molar ratio of **1** and molecular weight of polyol. The presence of *exo-endo* isomers mixture determined the appearance of the bimodal endothermic peak characteristic to the depolymerization reaction.³⁸

Thermal decomposition data of NPU-(1-8) are presented in Table 4. As expected, the hard

segments were less thermostable, depending on the isocyanate nature. So, the onset decomposition temperature (IDT) for NPU-(1-2) ranged between 217 and 225°C, while for the samples based on mixture of **1:HDMI** (1:1) the values increased to 250-254°C. The DTG curves of NPU-(1-8) indicated three stages of thermal decomposition, the latter two partially overlapped. The first stage showed a large amount of weight loss (Table 4). The rDA reaction occurred during the heating process and generated some free maleimide and furan groups in the sample, which contributed to the weight loss mentioned above. On the other hand, the self-addition and cross-linking reactions occurring between some free maleimide groups led to an increase of polymer thermal stability and a decrease of their weight loss during the second and third stage of thermal decomposition, evidenced by the low values of $Y_{c,600}$.

At the same time, all the processes mentioned above may overlap with complex decomposition processes generated by random chain scission. These processes consist of the urethane depolymerization and ester bonds decomposition in the first stage of thermal decomposition, while the cleavage of hard segments occurred during the second and third stages.³⁸

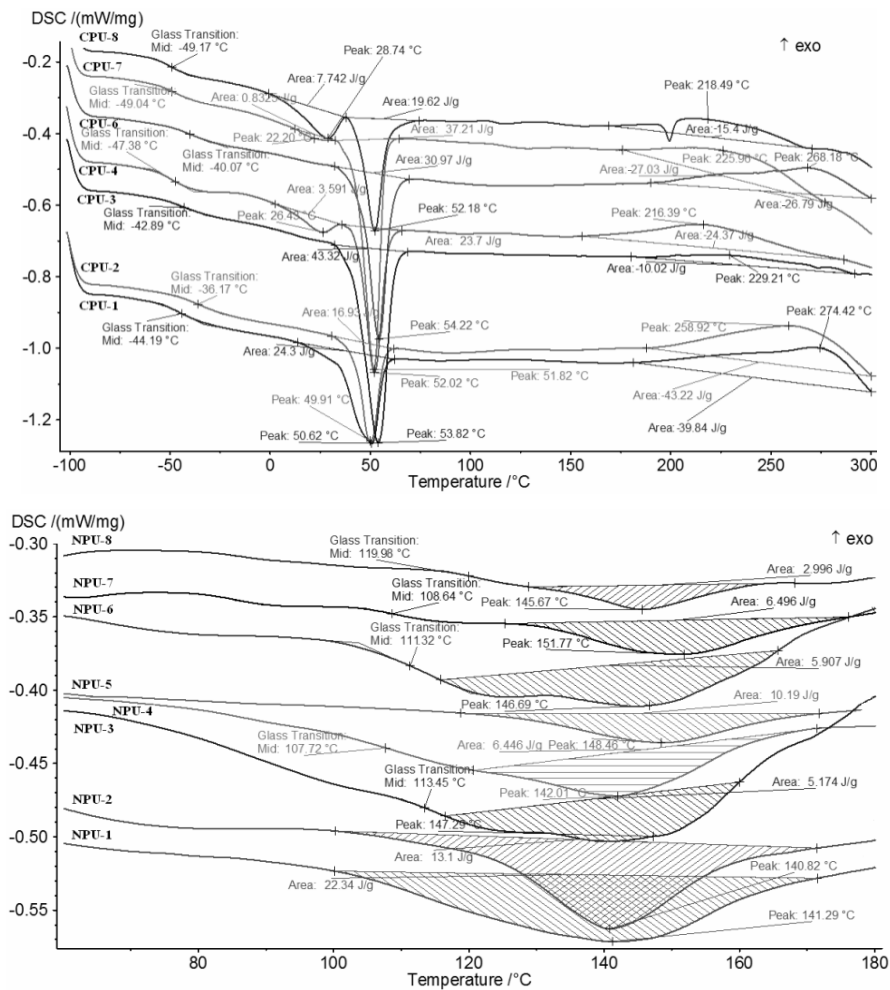


Fig. 3 – The DSC scans of CPU-(1-8) and NPU-(1-8).

Table 4

Thermogravimetric data, mechanical properties and the water contact angle of NPU-(1-8)

Sample	IDT (°C)	PDT _{max1} /Δw ₁ (°C/%)	PDT _{max2} /Δw ₂ (°C/%)	PDT _{max3} /Δw ₃ (°C/%)	Y _{c 600} (%)	Tensile strength (MPa)	Strain (%)	Modulus (MPa)
NPU-1	225.37	333.00/53.62	415.80/13.00	457.78/14.50	18.00	8.30	59.37	127.20
NPU-2	217.54	330.04/71.90	-	-	26.90	8.40	66.62	97.27
NPU-3	254.55	312.96/20.11	356.18/50.28	451.49/12.60	16.00	13.15	78.13	63.42
NPU-4	250.23	348.40/78.01	446.73/9.10	-	12.00	11.13	321.34	56.42
NPU-5	245.85	345.89/50.00	418.50/14.30	454.70/14.00	20.70	6.84	101.80	274.70
NPU-6	248.83	340.10/54.30	411.33/15.00	455.34/12.00	17	12.53	88.13	89.60
NPU-7	249.34	346.60/73.34	445.07/16.80	-	8.85	4.30	17.13	123.00
NPU-8	270.61	354.30/78.12	449.94/12.15	-	8.71	4.64	16.06	111.60

PDT_{max} –maximum decomposition temperature; Δw - weight loss at corresponding decomposition stage; Y_{c 600} – char yield at 600°C

The DSC and ATR-FTIR methods were applied to evaluate the thermoreversibility of NPU. The thermoreversibility of the network NPU-4 was evidenced by applying two heating-cooling cycles in the temperature range of 70-180°C (Fig. 4). Thus, there can be observed that the endothermic peak characteristic to the retro-DA process

appeared on all heating curves, the maximum temperature of the endothermic peak has almost the same value around 150°C. The cooling curve showed an exothermic peak corresponding to the DA process with a maximum around 130°C.

In addition, the thermoreversibility of NPU-4 was confirmed by ATR-FTIR spectroscopy (Fig.

5). So, recording the spectrum for this compound at 160°C, we could observe that the characteristic band of cycloadduct at 1774 cm⁻¹ was not present anymore and also that the band attributed to the stretching vibrations shifted to higher values (1724 cm⁻¹). The C-N-C absorption band at 1190 cm⁻¹ specific to cycloadduct disappeared and new bands at 955 and 828 cm⁻¹ corresponding to furan and maleimide groups appeared. After cooling the sample and recording again the spectrum, we could see that the carbonyl band shifted back to lower value and the bands at 1774 and 1190 cm⁻¹ attributed to the cycloadduct reappeared. After heating the sample at 100°C for 4 hours in an oven,

the carbonyl band shifted back to its initial value (1710 cm⁻¹), due to complete recovery of the cycloadduct when an appropriate time was accorded to the dienic reaction took place (Fig. 5, curve d).

Tensile properties of **NPU-(1-8)** are presented in Table 4. The tensile strength values of networks were relatively low, ranging between 4.30 and 13.15 MPa, except **NPU-(3, 4, 6)**, presumably to the low intramolecular forces, lack of crystallization during stretching. The elongations at break were below 100%, except **NPU-4**, which exhibited the higher value (321.34%), probably due to its more regular structure.

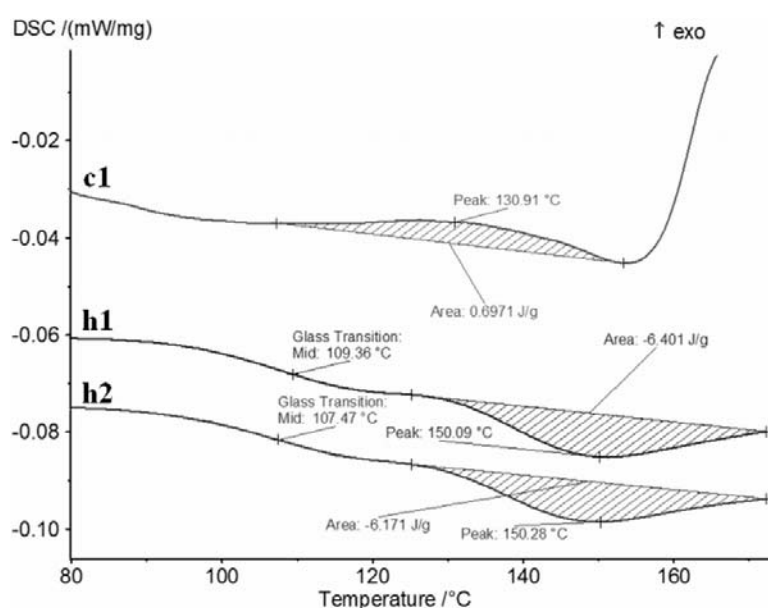


Fig. 4 – The DSC scans of NPU-4; h1, h2-the first and the second heating run, respectively; c1-the first cooling run.

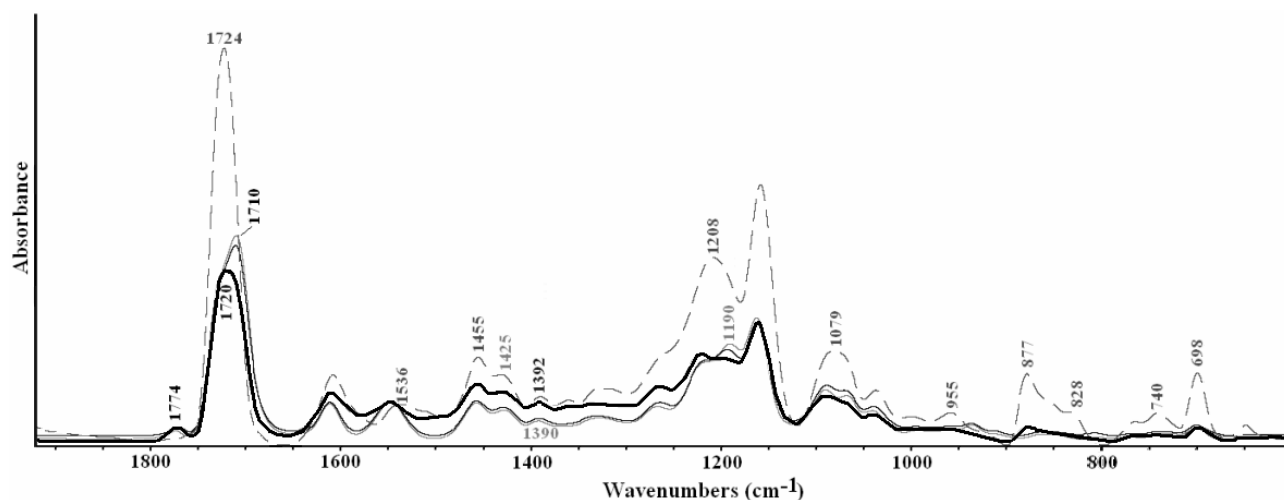


Fig. 5 – The ATR-FTIR spectra of NPU-4: black line – initial; dotted line – at 160°C; thick black line – after cooling; grey line – recovery.

EXPERIMENTAL

Measurements. The FTIR spectra were recorded on a Bruker Vertex 70 spectrophotometer. The ¹H-NMR spectra were recorded on a Bruker NMR spectrometer, Avance DRX 400 MHz, using DMSO-d₆ as solvents and tetramethylsilane as an internal standard. Melting and softening points were determined with a Gallenkamp hot-block point apparatus. Thermogravimetric measurements (TGA) were conducted on a STA F1 449 Jupiter device (Netzsch, Germany). Around 10 mg of each sample was heated in alumina crucibles at a heating rate of 10°C/min. Nitrogen was used as inert atmosphere at a flow rate of 50 mL/min. Differential scanning calorimetry (DSC) measurements were done using a Mettler TA Instrument DSC 12E with a heating rate of 10°C/min, in nitrogen. The inherent viscosities of the polymer solutions (measured at a concentration of 0.5 g/dL) in DMF were determined at 25°C using an Ubbelohde suspended level viscometer. Stress-strain measurements were performed on a test apparatus, Shimadzu AGS-J, cell load 1kN. Measurements were run at an extension rate of 50 mm/min, at room temperature 23°C. All samples were measured three times and the averages were obtained.

Reagents and Materials. Dibutyltin dilaurate (DBDTL, Aldrich, 95%), polycaprolactone diols of molecular weight 1250 and 2000 (PCD, Sigma-Aldrich), diethylene glycol (DEG, Aldrich), dimethylformamide (DMF, Aldrich), and 1,6-hexamethylene diisocyanate were used as received. 5-Maleimidoisophthalic diisocyanate (**1**) was prepared according to a method described in our previous papers.^{38, 41} 3,9-Di-2-furyl-2,4,8,10-tetra-spiro [5,5] undecane (**2**) was prepared by acetalization of pentaerythritol with 2-furaldehyde according to a method described in the literature.⁴²

Synthesis of copoly(ester-urethane)s containing maleimide groups in side chain CPU-(1-8). The copoly(ester-urethane)s were prepared by a conventional two-step method under inert atmosphere of highly pure nitrogen in a 100 ml three-necked round bottomed flask equipped with a magnetic stirrer, thermometer and condenser. To a 10 % w/v solution of PCD in dry DMF and DBDTL (10⁻² mol/L) as catalyst, an excess (2:1) of mixture of monomer **1** and HDMI was added (NCO:OH ratio = 2). The composition of initial components is described in Table 1. The solution was stirred at 60°C for 2 hours and an isocyanate terminated prepolymer was obtained. In a second step, a stoichiometric amount of dried DEG in DMF (3 mL) was added, and the stirring continued at 60°C for 4 hours. Then, the solution was precipitated in methanol and dried at 50°C for 24 hours under reduced pressure.

Synthesis of copolyurethane networks NPU-(1-8). To a solution of CPU-(1-8) (1 g) in DMF (10 ml), a stoichiometric amount of monomer **2** in DMF (3 mL) was added. The mixture was stirred at 60°C for 4 hours and casted on a Teflon Petri dish and the solvent was evaporated at 60°C for 24 hours. The film was removed by soaking in cold water and dried at 50°C for 24 hours under reduced pressure.

CONCLUSIONS

New copoly(ester-urethane) networks based on two diisocyanates, PCD and diethylene glycol as chain extender were prepared. The formation of structures was confirmed by ATR-FTIR and

¹H-NMR spectroscopy. The DSC measurements of copolymers revealed the presence of three thermal transitions assigned to the glass transition and melting of soft segment and the thermal polymerization of maleimide groups. The DSC scans of networks showed a unimodal or bimodal endothermic peak attributed to rDA reaction. The thermostability of networks depended on the aliphatic isocyanate amount. The thermoreversibility of networks was evidenced by the DSC and ATR-FTIR methods. The mechanical properties of the networks exhibited moderate values due to the presence of bulky bridges between polyurethane chains which prevents the formation of packed structures.

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