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Synthesis, Chemical Structure and Properties of Cross-linked Poly(esterurethanes) Based on Unsaturated Oligo(alkyleneester)diols

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Abstract: The cross-linked poly(esterurethanes) (PEU) based on unsaturated oligo(alkyleneester)diol (OAE) are presented. OAE was prepared from adipic acid, maleic anhydride and ethylene glycol and then characterized by elemental analysis, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy in account of double bonds and -COOH end groups. The synthesis of PEU was conducted in two steps. In the first step the prepolymers, containing free NCO or OH groups, were obtained via the reaction of OAE with 4,4`-diphenylmethane diisocyanate (MDI) used in excess. The cross-linking was achieved in the next step, in which the prepolymers were dissolved in methyl methacrylate (MMA) of concentrations in the range of 30 to 50 wt% in the presence of 1 wt% of methyl ethyl peroxide and 0.003 wt% of cobalt (II) 2-ethylhexanoate. It is proved that both chemical structure and MDI content in prepolymer influence the static and dynamic mechanical properties and thermal stability of the poly(esterurethanes).

Introduction

Unsaturated polyurethanes (uPUR), containing double bonds from polyesters soft segments [1-3], chain extenders [4, 5] or pendant groups [6-12], belong to a new class of elastomers. Their importance in macromolecular chemistry follows from their possible applicability in syntheses of cross-linked polymers. Such compounds exhibit good mechanical properties as well as considerable hydrolytical and chemical stability.

So far, many different methods for cross-linking of uPUR have been created. One of the most common is based on the reaction of hydrogen atoms, present in urethane groups, with free isocyanate groups coming from di- or triisocyanate. In this reaction one obtains the allophanate groups contributing to the spatial structure of PUR [13, 14].

The other method for synthesizing cross-linked polyurethanes utilizes triisocyanurates [15-17]. Elastomers containing isocyanurate rings constitute a wide group of materials with interesting thermal and mechanical properties. Their thermal stability is strictly connected with the presence of the isocyanurate rings while the mechanical properties strongly depend on the cross-linking density.

The PUR cross-linking process follows not only from the formation of allophanate groups, but also from a sulphur vulcanization of unsaturated urethane elastomers [4]. This method originates from the sulphur vulcanization of natural or synthetic rubber. The dynamic progress in this field was initiated in 1839 by Goodyear, who described the process of the sulphur vulcanization of the natural rubber in the presence of accelerators and activators for the curing process. The accessibility of ingredients, simple technology, and advantageous properties of the sulphur cured polyurethanes presents a wide range of the possible applications.

Quite recently a progress in the synthesis of UV-curable polymers could be observed. Oprea et al. [7, 8] have described two representations of this group, namely poly(urethane-urea-acrylates) (PUUA) and poly(urethane-urea-methacrylates) (PUUMA). These polymers were prepared in the polymerization process of isocyanate terminated prepolymers with the hexamethylenediamine and the acrylic or methacrylic acid. These works described the mechanical and thermal properties of cross-linked polyurethanes. In particular, the authors have shown that the presence of urea groups influences the material rigidity and cause phase separation. Moreover, further research has revealed that tensile strength and thermal stability is strictly connected with the cross-linked density [9, 10].

The next group of cross-linked urethane polymers studied in the literature were poly(ester-siloxane)urethanes (PES) [18-20]. The usage of poly(dimethylsiloxane) as co-monomer in the synthesis of the unsaturated polyurethanes allowed the production of a new group of materials particularly applicable in technology and medicine. A wide structural variety of the mentioned polymers allowed choosing one with the required mechanical, thermal and thermo-mechanical properties. However, the studies on the tensile strength of PES demonstrated that these parameters largely depend on their chemical composition and hard segments content.

In this paper we present results of studies on synthesis and physical-chemical properties of cross-linked poly(esterurethanes). The PEU are synthesized via an innovative method using the unsaturated oligo(alkyleneester)diol and methyl methacrylate as a cross-linking agent. In our analysis we have focused on the influence of PEU chemical structure on thermal, mechanical and dynamic-mechanical properties. In particular, the influence of such parameters is examined as a function of MDI and MMA content. The obtained results indicate their wide applicability as constructional materials in Materials Engineering.

Results and discussion

Characterization of oligo(alkyleneester)diol

Oligo(alkyleneester)diol was characterized by elemental analysis (Tab. 1) and measurements of the contents of –OH (EWOH) and –COOH (AN) groups. The double bonds contents in OAE were characterized by the iodine number (IN) (Tab. 2). The results indicate that the synthesis of the unsaturated oligo(alkyleneester)diol involves glycol addition to double bonds of OAE (see Scheme I) as a side reaction. In this reaction we obtained the non-linear products with double bonds content of about 76% of the value calculated for a linear product. This fact was also confirmed by elemental analysis.

The presence of the functional groups in OAE was confirmed by the FT-IR spectrum, presented in Fig. 1. The intense bands at 1732cm^{-1} and 1261cm^{-1}, characteristic for –C=O and –C-O groups, revealed the presence of the ester groups in these oligomers. The absorption bands at 1645cm^{-1} and 979cm^{-1}, corresponding to stretching vibrations of *C=C* and C=C-*C-H* groups, are the evidence of double bonds present in OAE. Moreover, the peak at 3500cm^{-1} prove the presence of OH end-groups in oligo(alkyleneester)diol.

Tab.1. C, H contents in oligo(alkyleneester)diol revealed in elemental analysis.

	Elemental analysis			
OAE	C[a]	H[a]	C[b]	H[b]
	(%)		(%)	
	52.28	5.93	52.35	6.01

[a] found value, [b] calculated value

Tab. 2. Properties of synthesized oligo(alkyleneester)diol.

OAE	EWOH (mg KOH/g)	AN (mg KOH/g)	IN[a] (g I_2/100g)	IN[b] (g I_2/100g)
	143.3	1.5	57.2	74.8

[a] found value, [b] calculated value

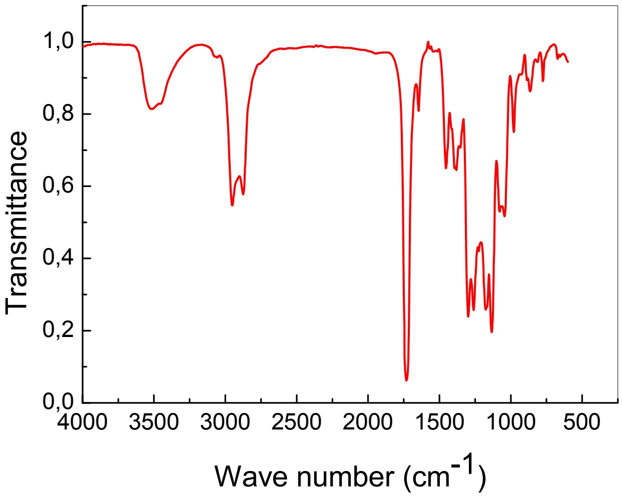
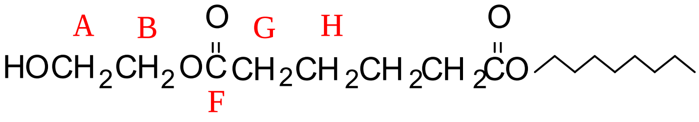


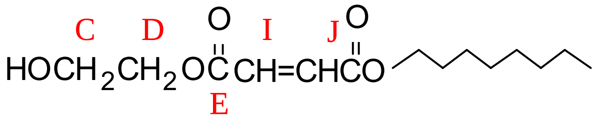
Fig. 1. FT-IR spectrum of OAE.

The structure and purity of the unsaturated oligomers is also confirmed by Heteronuclear Single Quantum Correlation (HSQC), Heteronuclear Multiple Bond Correlation (HMBC) and Correlation Spectroscopy (^{1}H COSY) spectra analysis (see Figs. 2-4). The results of spectral analysis indicate that the possible structures of OAE are as follows:

- glycol one side bonded with adipic acid (H_a) or fumaric acid (H_f):

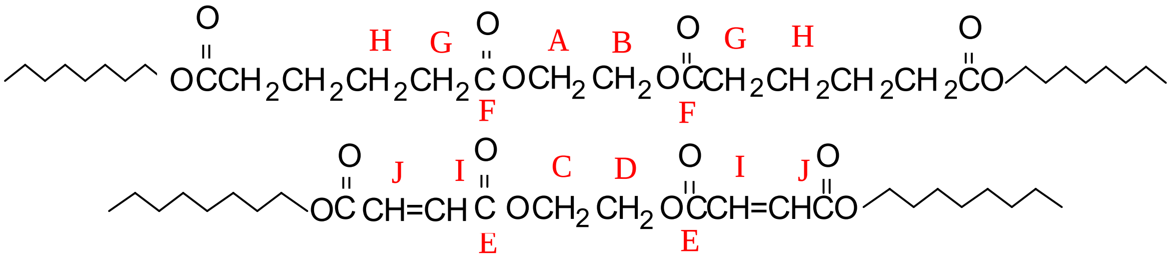


$$\overset{A}{HOCH_2}\overset{B}{CH_2}O\underset{F}{\overset{O}{\overset{\|}{C}}}\overset{G}{CH_2}\overset{H}{CH_2}CH_2CH_2\overset{O}{\overset{\|}{C}}O$$

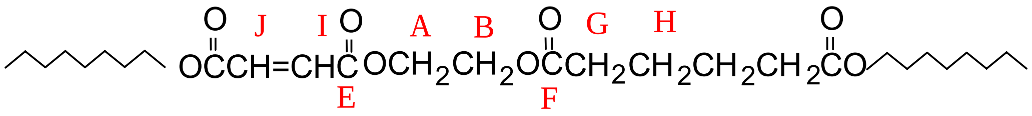


$$\overset{C}{HOCH_2}\overset{D}{CH_2}O\underset{E}{\overset{O}{\overset{\|}{C}}}\overset{I}{CH}=\overset{J}{CH}\overset{O}{\overset{\|}{C}}O$$

- glycol double-side bonded with adipic acid (H_{aa}) or fumaric acid (H_{ff}):



- glycol double-side bonded with adipic acid and fumaric acid (H_{af}) simultaneously:



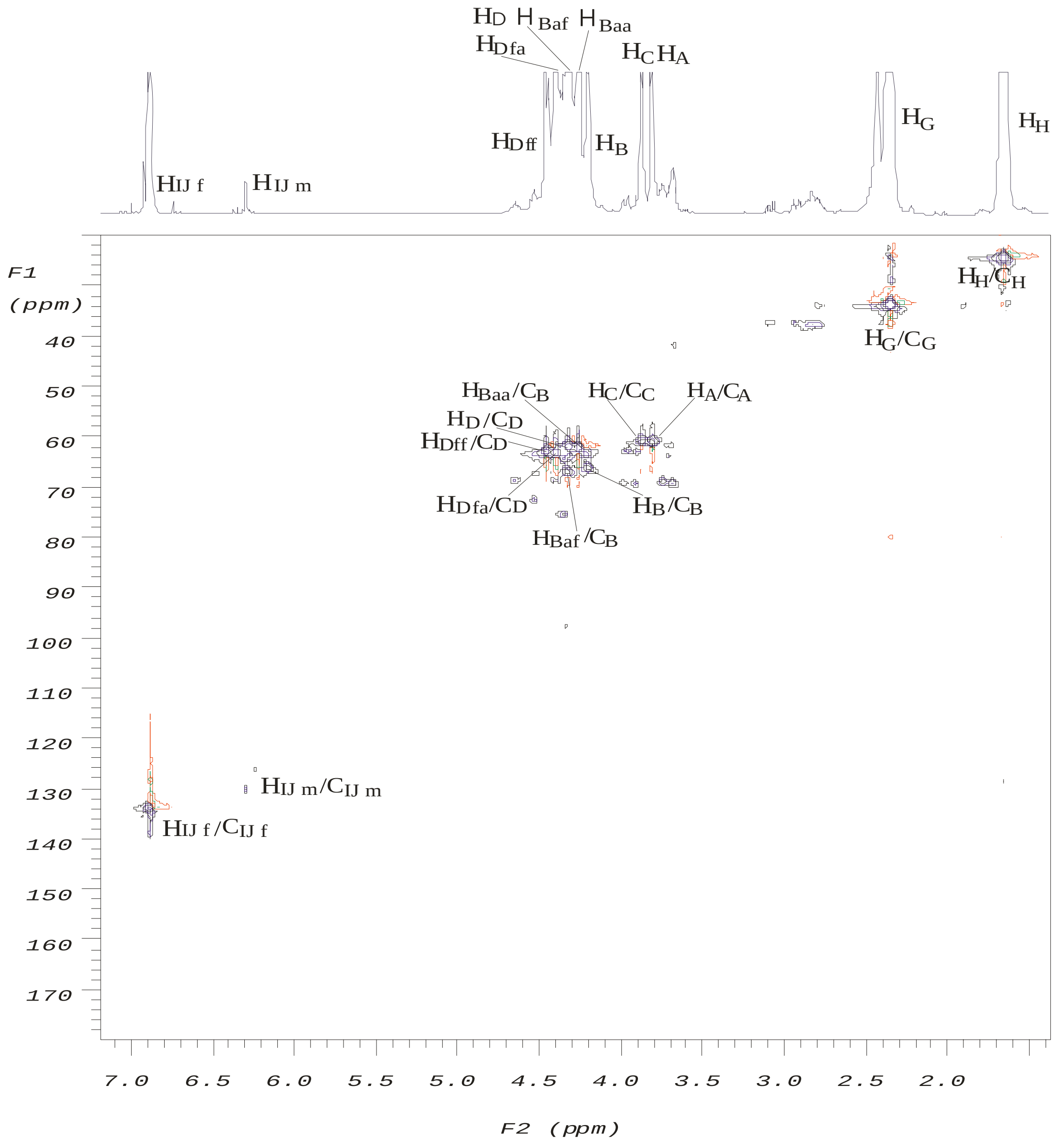
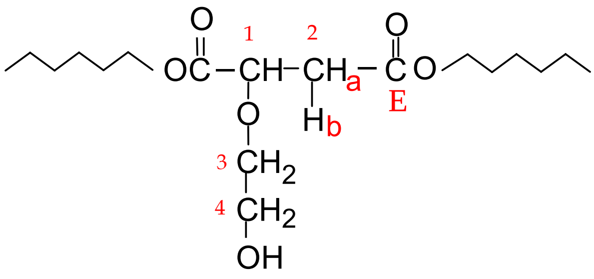


Fig. 2. HSQC spectra of oligo(alkyleneester)diol.

Another proof of the glycol addition to OAE is the HMBC correlation spectra, where signals: $H_{2b}/C1$, $H_{2a}/C1$, H_{2b}/C_E, H_{2a}/C_E are present. Therefore the only possible structure of the product is the one shown in the Scheme I (see also Fig. 3).



Scheme I. The glycol addition to OAE product.

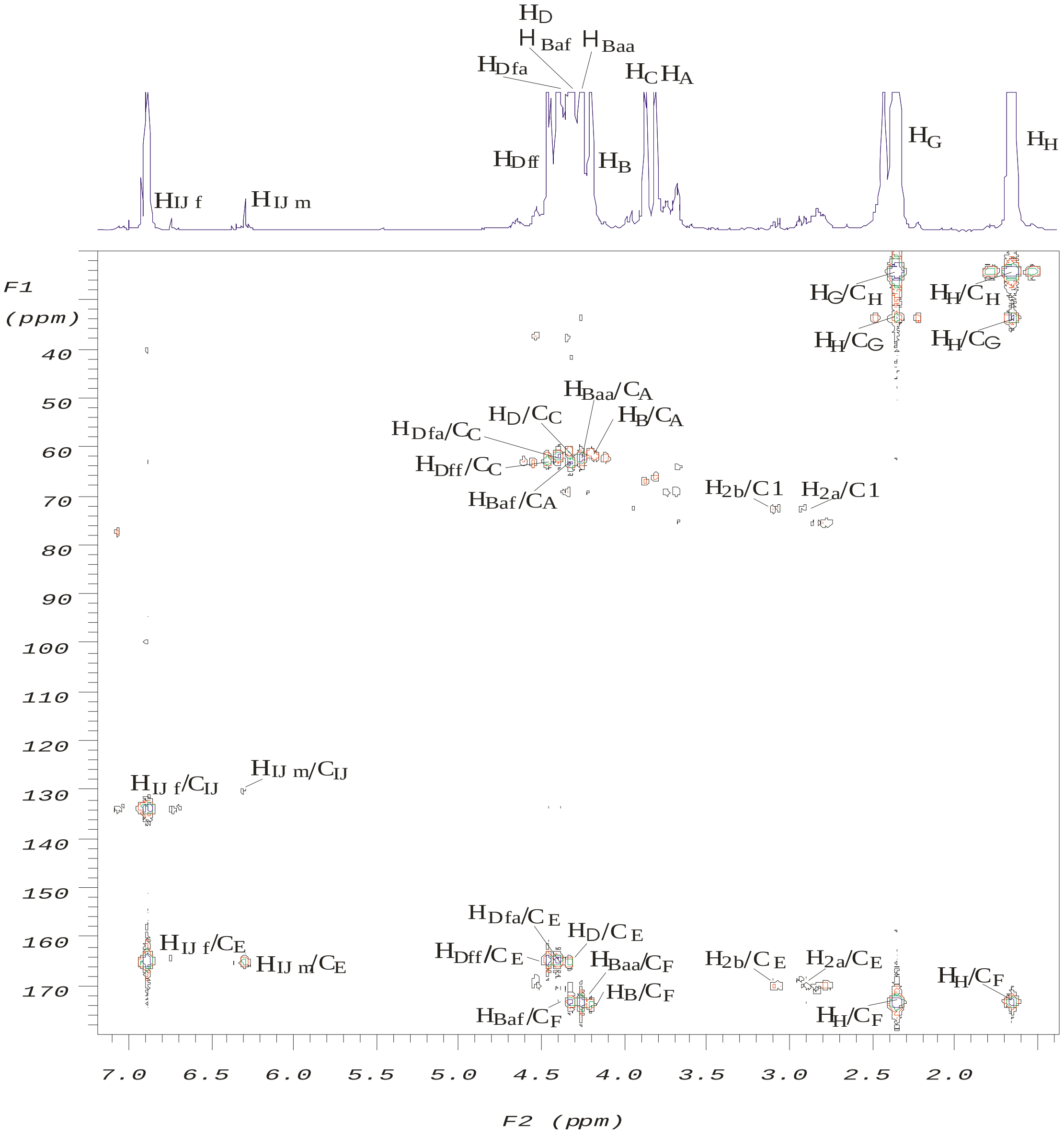


Fig. 3. HMBC spectra of oligo(alkyleneester)diol.

The results of NMR spectra as well as double bonds content measurements and the elemental analysis lead to the conclusion that the synthesized oligo(alkyleneester)diol is a branched unsaturated polyester.

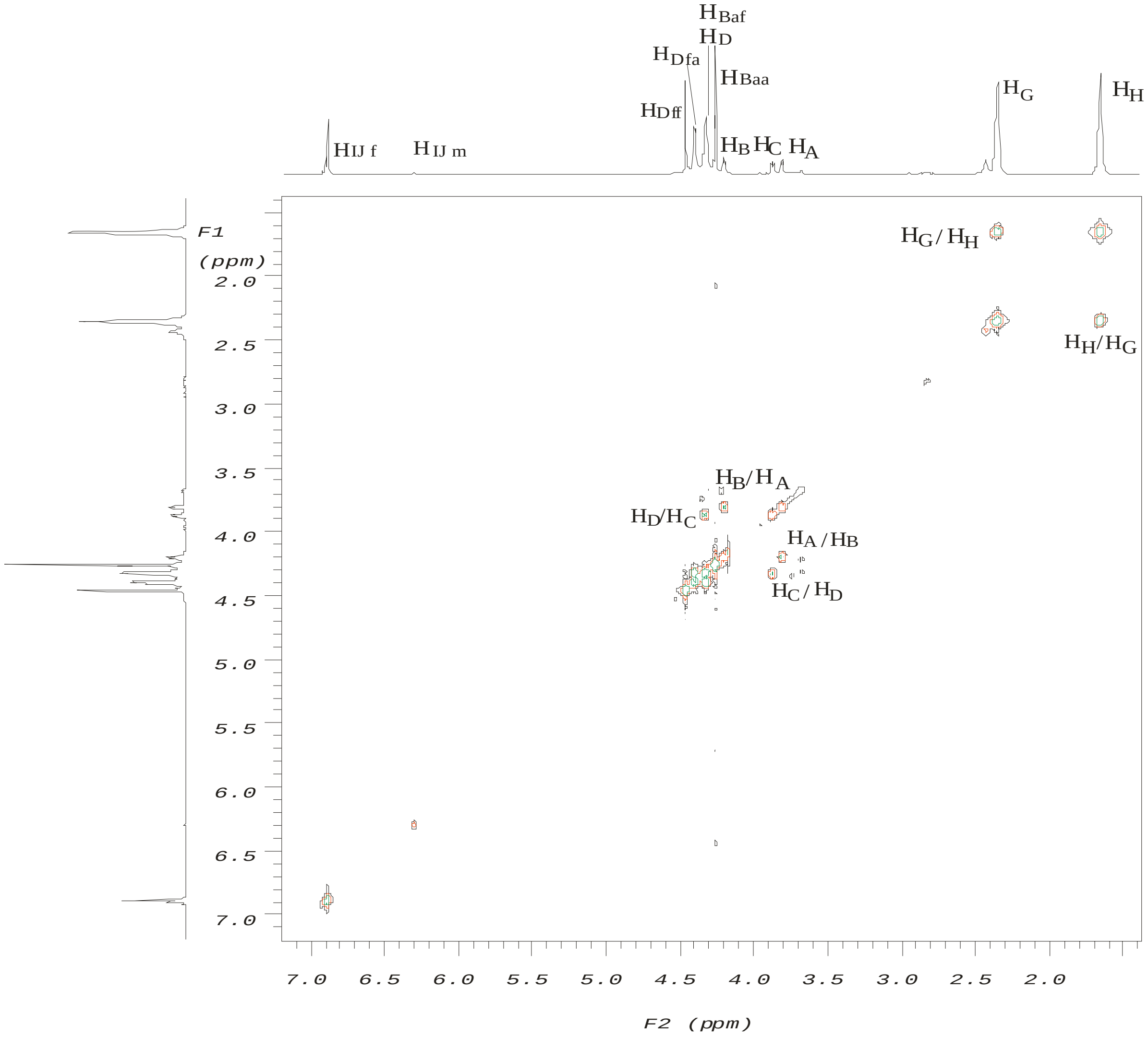


Fig. 4. ^{1}H COSY spectra of oligo(alkyleneester)diol.

Characterization of poly(esterurethanes)

The presence of the functional groups in PEU was confirmed by the FT-IR spectra analysis (Fig. 5). The intensive peak located at 3349cm^{-1}, characteristic for –NH absorption bands, proves the presence of urethane groups in PEU structure. The bands at 1531cm^{-1} and 1377cm^{-1} correspond to C-N stretching vibrations. Furthermore, the bands at 1728cm^{-1}, 1154cm^{-1} and 1075cm^{-1}, which originate from C=O and C-O-C groups, respectively, reveal the presence of ester groups in poly(esterurethanes). Moreover, for poly(esterurethanes) containing free isocyanate groups (PEU **I-III**) the band at 2283cm^{-1} is observed. Furthermore, the absorption bands around 1648cm^{-1} and 978cm^{-1} ($\nu C{=}C$ and $\gamma C{=}C\text{-}H$) suggest the presence of double bonds in the cross-linked polyurethanes.

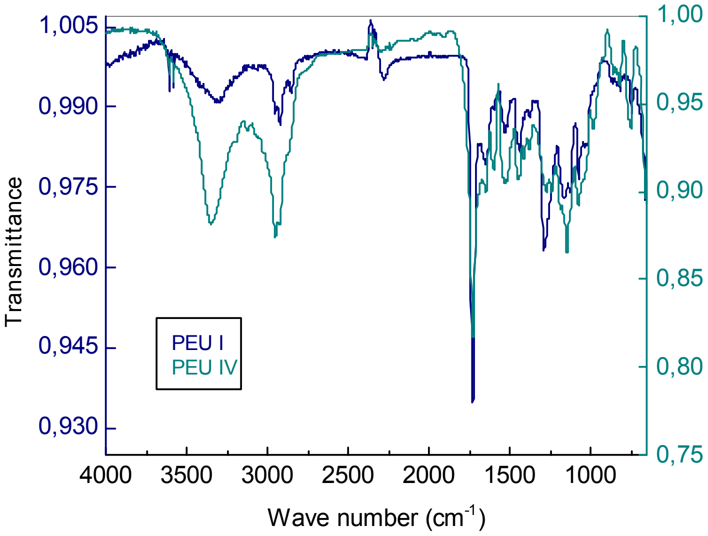


Fig. 5. FT-IR spectra of PEU I and PEU IV.

To obtain information about the thermal stability of the poly(esterurethanes), thermogravimetric analysis in a nitrogen atmosphere was carried out. The PEU initial decomposition temperatures, defined as 5% and 10% of the weight decrease ($T_{5\%}$, $T_{10\%}$) and temperatures of maximal rate of decomposition (T_{max}) are presented in Table 3. Cross-linked polyurethanes remain stable up to 300°C and reveal a single peak in the DTG-curve in the range of 406°C to 422°C (T_{max}). Thermogravimetric analysis simultaneously showed that PEU synthesized with the molar excess of OH groups (PEU V-VI) are more stable than PEU synthesized with the NCO groups molar excess (PEU I-III). The increase of the methyl methacrylate content as a cross-linking agent leads to the increase of the initial decomposition temperature of PEU. Furthermore, obtained results suggest that PEUs with the lower cross-linking density (PEU V, VI) are thermally more stable. The most probable explanation of this fact may come from the weak thermal stability of urethane and allophanate groups generated in the reaction of MDI and OAE [21].

Tab. 3. Thermal properties of cross-linked poly(esterurethanes).

	PEU							
	I	II	III	III a	III b	IV	V	VI
$T_{5\%}$ (^{O}C)	303.2	299.2	302.6	309.5	327.7	295.5	317.8	313.3
$T_{10\%}$ (^{O}C)	322.3	319.1	323.7	335.5	355.9	319.2	338.9	335.8
T_{max} (^{O}C)	409.3	406.6	410.1	416.6	417.9	412.8	422.4	418.7

The PEU study of the stress-strain properties (Table 4) shows a clear dependence of the tensile strength and elongation at break on the chemical structure and cross-linked density. Poly(esterurethanes) synthesized from prepolymers with NCO groups in molar excess (PEU I-III) had higher tensile strength than their analogues obtained from prepolymers with OH groups in molar excess (PEU V-VI). This result can be attributed to the cross-linking allophanate groups. Furthermore, the tensile strength of PEU increases with MMA contents in PEU. On the other hand poly(esterurethanes) synthesized from prepolymers with OH molar groups excess (PEU V-VI) proved to be more flexible.

Tab. 4. PEUs tensile strength (σ) and elongation at break (ε_r).

	PEU							
	I	II	III	III a	III b	IV	V	VI
$\sigma \pm SD^a$ (MPa)	31.6±1.4	28.3±0.7	27.2±3.9	27.4±5.9	35.0±5.5	22.3±3.3	22.0±2.4	20.3±0.2
$\varepsilon_r \pm SD^a$ (%)	15.3±4.1	55.3±3.7	99.0±15.5	34.0±9.9	59.0±12.7	135.0±15.5	264.0±5.3	257.0±9.9

[a] SD – standard deviation

Figs. 6, 7, 8 presents the dependence of the storage modulus (G′), loss modulus (G″) and loss tangent (tanδ) of selected cross-linked poly(esterurethanes) on temperature. The results of DMTA demonstrate the influence of chemical composition of PEU on the dynamic-mechanical properties. In the rubber elasticity region the effects of cross-linking of PEU are visible (Fig. 6). Poly(esterurethanes) synthesized by using methyl methacrylate as a curing monomer are more stable in comparison with the reference materials without cross-linking (PEU 0).

Temperature dependencies of the loss modulus G″ (Fig. 7) show single maxima at: 19.4°C, 20.9°C, 22.8°C, 16.3°C, 13.5°C, 6.4°C for PEU II, PEU III, PEU IIIb, PEU IV, PEU V, and PEU 0, respectively. On these curves, as in the case of the function G′(T), the effect of cross-linking is visible.

The glass transition temperatures (T_g), measured as maximum of tanδ(T) curve (Fig. 8), was found at: 33.5°C, 39.7°C, 44.6°C, 30.3°C, 33.7°C, and 15.4°C for PEU II, PEU III, PEU IIIb, PEU IV, PEU V, and PEU 0, respectively. The values of T_g of PEU exhibit the influence of MMA content and [NCO/OH] molar ratio on their properties. Moreover the magnitudes of tanδ peak values are similar and indicate no phase separation in the cross-linked poly(esterurethanes).

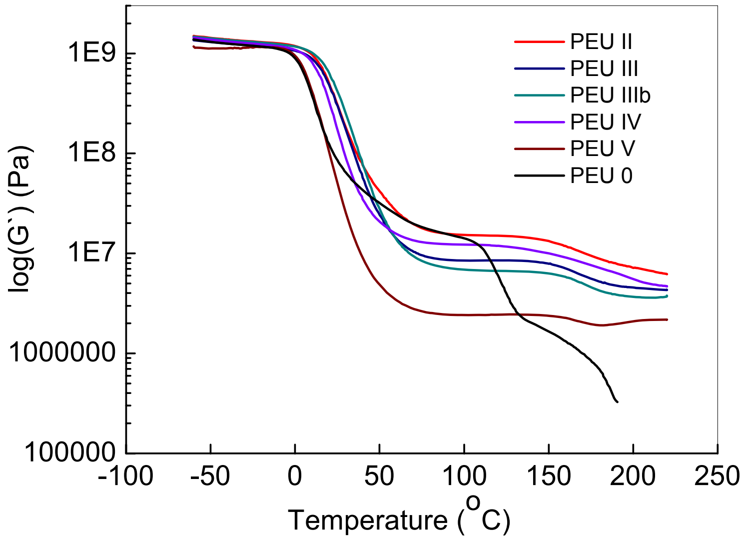


Fig. 6. Dynamic storage moduli (G′) of PEU as functions of temperature.

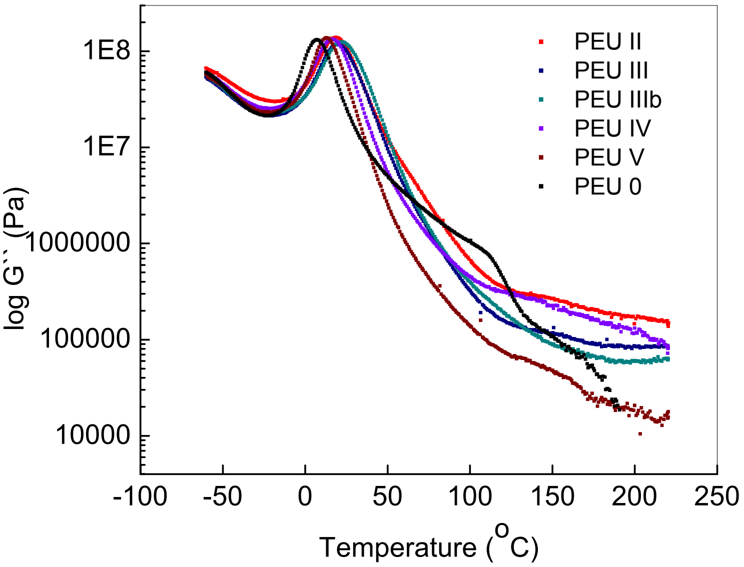


Fig. 7. Dynamic loss moduli (G″) of PEU as functions of temperature.

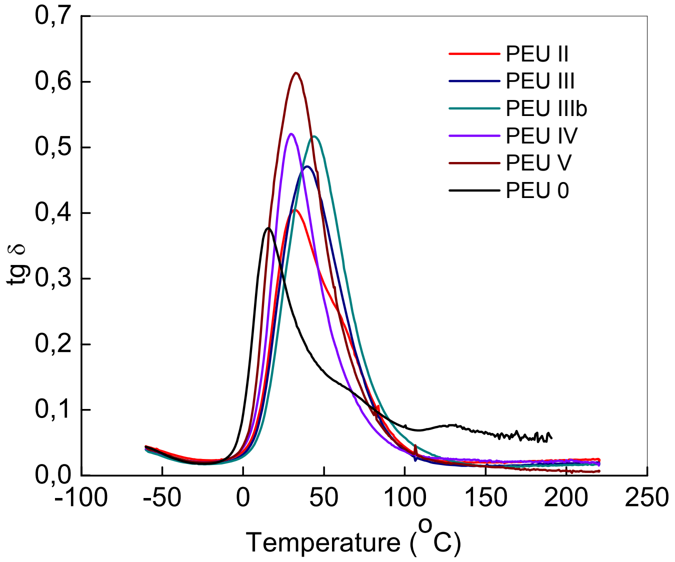


Fig. 8. Loss tangents (tanδ) of PEU as functions of temperature.

The average-number molecular weight (M_c) between cross-links in PEU was calculated using equation (5) [22] with the quantity G' obtained from DMTA. The values of M_c, presented in Table 5, show that the cross-links in poly(esterurethanes) come from the reaction of unsaturated polyurethanes with methyl methacrylate as well as the reaction of free isocyanate with urethane groups. The latter of the mentioned reactions leads to the formation of cross-linking allophanate groups. Poly(esterurethanes) synthesized from prepolymers with NCO groups molar excess (PEU I-III) have higher cross-link density in comparison to PEU synthesized from prepolymers with OH groups molar excess (V, VI). This follows from the presence of allophanate groups in the PEU structure, since they participate in the formation of polymer space.

Tab. 5. Average-number molecular weight (M_c) between cross-links in PEU.

PEU	G`(Pa)>T_g	T (K)	M_c
I	$1.04{\cdot}10^7$	373.0	380
II	$1.53{\cdot}10^7$	373.5	259
III	$8.49{\cdot}10^6$	373.3	460
III a	$9.39{\cdot}10^6$	373.3	423
III b	$6.88{\cdot}10^6$	373.4	575
IV	$1.23{\cdot}10^7$	373.0	321
V	$3.42{\cdot}10^6$	373.3	1158
VI	$2.42{\cdot}10^6$	373.2	1636

Conclusions

Our investigations confirm that unsaturated oligo(alkyleneester)diol is a suitable substrate in the synthesis of cross-linked poly(esterurethanes).

The curing method applied to the prepolymer obtained from oligo(alkyleneester)diol leads to the cross-linked poly(esterurethanes). The investigated polymers belong to a new group of cross-linked materials. Our research revealed that their properties strongly depend on the chemical structure of prepolymers, MMA contribution, and cross-links density. In particular the thermal stability and flexibility increases for polymers synthesized using OH-terminated prepolymers, while the tensile strength increases with the higher content of MDI units in the structure of the polyurethanes.

The Dynamic Mechanical Thermal Analysis shows the behavior typical for one-phase systems. Furthermore, the study of the dynamic-mechanical properties demonstrates that cross-linked poly(esterurethanes) are less temperature sensitive in comparison with the non cross-linked polymers. Additionally the experiments proved the influence of cross-links density on thermal and dynamic mechanical properties. Along with the decrease of the average-number molecular weight between cross-links in PEU one can observe enhancement of their mechanical properties and simultaneously aggravation of thermal properties. The last property depends on the chemical structure of cross-linking bonds.

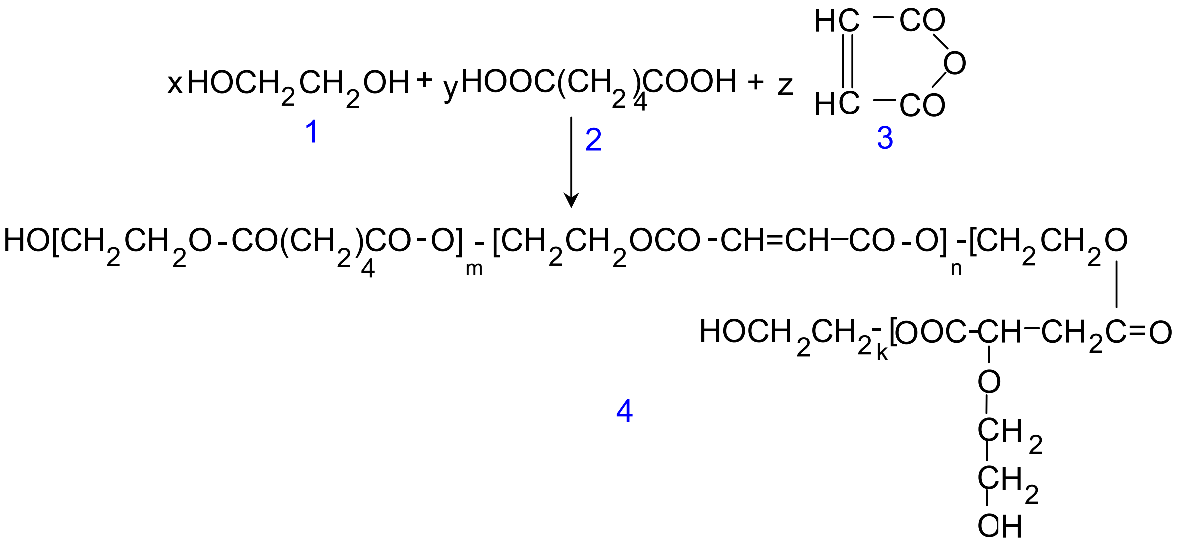
Experimental part

Materials

Adipic acid (Sigma-Aldrich), maleic anhydride (Sigma-Aldrich) were used as received without further purification. Glycol ethylene (POCh) was purified by distillation under reduced pressure (1.4hPa) (bp 117118°C). 4,4`-diphenylmethane diisocyanate (Borsdochem) was used after being filtrated in melt while methyl methacrylate (Sigma-Aldrich) was used after being washed in 10% NaOH solution and distilled water to remove the inhibitor and dehydrated over anhydrous $MgSO_4$. Hydroquinone (POCh), initiator: methyl ethyl peroxide (36% solution in dimethyl phthalate) and accelerator: cobalt (II) 2-ethylhexanoate were used in commercial form.

Synthesis of oligo(alkyleneester)diol

The unsaturated oligo(alkyleneester)diol (4) was synthesized by the polycondensation reaction of 2.4 mol of ethylene glycol (1), 1 mol of adipic acid (2) and 1 mol of maleic anhydride (3) (see Scheme II). The synthesis was carried out in the presence of hydroquinone (0.015 wt %), which was used as inhibitor. Four-necked reactor equipped with mechanical stirring, thermometer, nitrogen inlet tube, and a reflux condenser was used for preparation of OAE. In order to prove the progress of the polycondensation acid number of the mixture was measured. The reaction was carried out in the nitrogen atmosphere at a temperature of 190°C for 40h under normal pressure. When the concentration of –COOH groups in the reaction mixture had reached a nearly constant level the synthesis was continued under reduced pressure (1.4 hPa) for 24h until OAE with –COOH contents below 2mgKOH/g was obtained.



Scheme II. Synthesis of oligo(alkyleneester)diol (OAE).

Synthesis of poly(esterurethanes)

The synthesis of poly(esterurethanes) was carried out in two steps. In the first step prepolymers with a molar excess of NCO or OH groups (Tab. 6) were prepared from OAE and 4,4`-diphenylmethane diisocyanate. Three-necked reactor equipped with mechanical stirring, thermometer, and calcium chloride tube was used for preparation of PEU. The reactions were conducted at a temperature of 60°C for 1h with constant stirring and controlled by the determination of NCO groups' concentration. The latter was carried out by the titration after the reaction with N-dibutylamine [23]. In the second step the obtained prepolymers were dissolved in methyl methacrylate, which was used as a cross-linking monomer in concentrations from 30 to 50 wt% (see Tab. 6). The prepared mixtures were placed in mould and heated at the temperature of 80°C for 24h. The PEU curing process was carried out in the presence of 1 wt% of the methyl ethyl peroxide and of 0.003 wt% of the cobalt (II) 2-ethylhexanoate.

Tab. 6. Composition of the PEUs.

PEU	MDI content (g)	OAE content (g)	MMA content* (wt %)
I	11.3750	17.5925	30
II	10.6500	22.0100	30
III	10.6750	27.5900	30
III a	10.6750	27.5900	40
III b	10.6750	27.5900	50
IV	7.8000	24.1800	30
V	6.5750	30.5350	30
VI	5.5250	34.1775	30

* MMA % w/w per OAE

Titration methods

- Acid number measurements

Acid number (AN) is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number was measured in a typical procedure. A known amount (~0.5g) of OAE sample was dissolved in 30 cm^3 of acetone and titrated with 0.1 mol/dm^3 KOH (water solution) in the presence of phenolphthalein as a colour indicator. Acid number value was calculated using the following equation:

$$AN = \frac{NKOH \cdot a \cdot V}{m} \qquad (1)$$

where: V- is the volume of KOH solution (cm^3), m-mass of sample (g), a=56.1.

- Measurements of hydroxyl group content

Content of hydroxyl groups (EWOH) in OAE was measured by a titration method. A known amount of OAE (~0.5g) was dissolved in 5cm^3 of the mixture, which was prepared of 40 cm^3 of xylene, 5 cm^3 of acetic anhydride and 0.2 cm^3 of sulphuric acid. Samples were heated under reflux for 0.5 h. Thereafter 1 cm^3 of pyridine was added and the heating was continued for 10min. After that 50 cm^3 of distilled water was added and the solutions were titrated with 0.5 mol/dm^3 KOH (water solution) in the presence of phenolphthalein as colour indicator. Hydroxyl number was calculated using the following equation:

$$EWOH = \frac{(V_1 - V_2) \cdot a \cdot NKOH}{m} \qquad (2)$$

where: V_1- is the volume of KOH solution for titration of the blank (cm^3) ,V_2- is the volume of KOH solution for titration of the specimen (cm^3), m-mass of sample (g), a=56.1.

- Iodine number measurements

Iodine number was measured by a titration method. Known amount of OAE (~0.2g) was dissolved in 15 cm^3 of acetone, 25 cm^3 of 1 mol/dm^3 KOH solution and mixed for 1 h. After that it was titrated with 0.5 mol/dm^3 HCl solution in the presence of phenolphthalein till the colour disappeared. Thereafter the solution was diluted to 100 cm^3 and 15 cm^3 of this solution was moved to the flask and again diluted to 20 cm^3. Then 10 cm^3 of NaBr saturated solution, 5 g NaBr(s) and 25ml solution of Br_2 in methanol were added [24]. The next step of the procedure was to add 75 cm^3 of methanol and 15 cm^3 of 15 wt % KI (water solution). Obtained mixtures were titrated with 0.1 mol/dm^3 $Na_2S_2O_3$ (water solution) to disappearance of colour. Iodine number, characterizing the double bond content, was calculated using the following equation:

$$IN = \frac{(V_1 - V_2) \cdot b}{m} \tag{3}$$

where: V_1-$Na_2S_2O_3$ solution required for titration of the blank (cm^3), V_2-$Na_2S_2O_3$ solution required for titration of the specimen (cm^3), m-mass of sample (g), b=1.269.

- Determination of NCO group concentration

Determination of NCO group concentration was performed by a titration method. Prepolymer in amount of 0.5 g was dissolved in 10 cm^3 of 0.5 mol/dm^3 dibutylamine in chlorobenzene solution. Thereafter 30 cm^3 of acetone and Bromophenol Blue were added and titrated with 0.1 mol/dm^3 HCl (water solution) till a yellow colour. NCO concentration was calculated using the following equation:

$$NCO = \frac{x \cdot (V_1 - V_2)}{m} \tag{4}$$

where: V_1- is the volume of HCl solution for titration of the blank (cm^3) ,V_2- is the volume of HCl solution for titration of the specimen (cm^3), m-mass of sample (g), x=0.42.

Measurements

Elemental analysis was carried out using Elementary Anallyser EA 1108 apparatus. Infrared spectroscopy (IR) analyses of the oligo(alkyleneester)diol and poly(esterurethanes) were acquired from thin films on NaCl disc, using Bruker IFS66 spectrophotometer.

NMR spectra were recorded in $CDCl_3$ solution using Varian Unity Plus apparatus, with the frequency of 500 MHz.

Thermogravimetric analyses were performed on Pyris 1 TGA apparatus (Perkin Elmer) in nitrogen atmosphere in the temperatures ranging from 50°C to 600°C at the heating rate of 10°C min^{-1}.

Tensile properties were measured using tensile tester FPZ 100 (Rauensstein, Germany) at speed of 300 mm/min at ambient temperature.

Dynamic Mechanical Thermal Analysis (DMTA) was performed using Ares Solids Rheometer in the temperatures ranging from -60°C to 220°C at the heating rate of 5°C min^{-1}, with the frequency of 10 Hz.

Average-number molecular weight (M_c) between cross-links in PEU was calculated using the following equation:

$$M_C = \frac{\rho \cdot R \cdot T}{G^{`}} \tag{5}$$

where: ρ – polymer`s density (g/cm^3), R - universal gas constant (R=8.314 Jmol^{-1}K^{-1}) T – temperature (K), G′ – dynamic storage moduli (Pa).

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