LIDIA JASIŃSKA, BOGUMIŁA MASIULANIS *)

Gdańsk University of Technology
Faculty of Chemistry
Department of Polymer Technology
ul. G. Narutowicza 11/12, 80-852 Gdańsk, Poland

Synthesis, physical and chemical properties of polyetherurethanes modified by natural antioxidant

Summary — New polyetherurethanes (PEUR), modified by α-tocopherol (vitamin E) have been obtained. This natural antioxidant has been bounded with macromolecules as a chain branch, through ether linkage or through urethane group, using two kinds of synthesized monomers in PEUR preparation. The properties of modified PEUR have been compared with PEUR synthesized from the same basic substrates, only: poly(oxytetramethylene)glycol, 4,4'-methylene bis(cyclohexylene isocyanate) and 1,4-butanediol. Tensile strength, hardness and absorption of water and sunflower oil have been measured. The chemical stability of PEUR in Ringer's solution and in phosphate buffer (pH = 7.4) has been investigated by measurements of weight loss at time to six weeks. Such investigation in water hydrogen peroxide solution (30 wt. %) and thermogravimetric analysis in air atmosphere and inspection of the changes of infrared spectra after isothermal oxidative ageing at 100 ^{o}C have allowed to state that chemically bounded α-tocopherol improved the resistance of PEUR to oxidation.
Key words: modified polyetherurethanes, α-tocopherol, physical properties, thermooxidative resistance, chemical resistance.

SYNTEZA, FIZYCZNE I CHEMICZNE WŁAŚCIWOŚCI POLIETEROURETANÓW MODYFIKOWANYCH ZA POMOCĄ NATURALNYCH PRZECIWUTLENIACZY

Streszczenie — Otrzymano nowe polieterouretany (PEUR) modyfikowane α-tokoferolem (witamina E). Ten naturalny przeciwutleniacz związany został z makrocząsteczkami w postaci bocznych odgałęzień poprzez wiązanie eterowe lub uretanowe zależnie od użytego w syntezie PEUR jednego z dwóch rodzajów otrzymanych uprzednio monomerów (tabela 1). Właściwości modyfikowanych PEUR porównano z właściwościami ich niemodyfikowanych odpowiedników otrzymanych z tych samych podstawowych substratów: glikolu polioksytetrametylenowego, 4,4'-metylenobis(cykloheksylenoizocyjanianu) i 1,4-butanodiolu. Polimery charakteryzowano mierząc wytrzymałość na rozciąganie i twardość (tabela 3) oraz absorpcję wody i oleju słonecznikowego (tabela 4). Odporność chemiczną PEUR badano oznaczając okresowo ubytki masy na skutek inkubowania przez 6 tygodni w roztworze Ringers'a i buforze fosforanowym o pH = 7,4 (rys. 5) oraz inkubacji w 30 % roztworze wodnym nadtlenku wodoru (rys. 6). Badania skutków inkubacji w roztworze nadtlenku wodoru, jak również analiza termograwimetryczna w atmosferze powietrza oraz analiza zmian widm w podczerwieni po izotermicznym starzeniu oksydacyjnym w temp. 100 ^{o}C (tabela 5 i 6, rys. 2 i 3) pozwoliły stwierdzić, że α-tokoferol związany chemicznie z PEUR poprawia jego odporność na utlenianie.
Słowa kluczowe: modyfikowane polieterouretany, α-tokoferol, właściwości fizyczne, odporność termooksydacyjna, odporność chemiczna.

Polyetherurethanes (PEUR) and poly(etherurethaneureas) (PEURU) are produced and still used now as biomaterials, simultanously with poly(carbonateurethanes) (PCUR). These polymers are characterized by good mechanical properties, good hydrolytical stability and good hemo- and biocompatibility in comparison to other polymers. The advantage of PEUR is greater flexibility of the soft polyether segments, which is related with the higher mobility of the ether than carbonate linkages. However, PEUR in opposition to PCUR shows lower resistance to oxidation. Cracks observed on the surface of the long time implants made of PEUR [1] were caused by polymer degradation, initiated, according to the last hypothesis, by oxidation of the carbon atoms vicinal to oxygen atom of ether bonds [2, 3]. This reaction follows in organism by action of oxygen radicals released by macrophages and other living cells, activated through excitement by the material of implant [4].

*) Author for correspondence; e-mail: masiulan@urethan.chem.pg.gda.pl

With the aim to improve the oxidative resistance, PEUR were synthesized from polyetherdiols of lower content of the ether bonds. Instead of the commonly emplyed poly(oxytetramethylene)glycol (PTMG), macrodiols that have 6, 8 or 10 methylene groups between the ether oxygen were used [5]. On the base of measurements of the fail stress after treatment by hydrolytic media and hydrogen peroxide media, there was found that these new PEUR were significantly more resistant in relation to PEUR obtained from PTMG, which initial fail stress was however much greater [5].

Coury *et al.* developed biostable polyurethanes from aliphatic diisocyanate and aliphatic diols which not contained any ester or ether bonds [6]. These materials were performed *in vivo* with no sign of degradation after 12 weeks of implantation but exhibited poor flex fatigue and low wet tensile strength [6].

Modification of polyurethanes using fluorocompounds [7] or polysiloxane compound [8, 9], which migrate to the surface of these polymers, led to increase its hydrophobic character and to improvement of the resistance to the action of the substances released in living tissues.

The natural anti-oxidant present in organism is α-tocopherol (vitamin E) which plays the role of a scavenger of the free oxidative radicals and counteracts ageing and damaging of the cell membranes by inhibition of the oxidation of polyunsaturated lipids connected with proteins [10].

Santerre and colleagues obtained blends of PCUR with a special surface modifying macromolecule (SMM). Basic PCUR was prepared from haxane diisocyanate, polycarbonate diol and 1,4-butanediol and SMM was synthesized using polycarbonate diol, lysine diisocyanate (LDI) and fluoroalcohol. After derivatizing the LDI pendant ester group, vitamin E was coupled to this SMM [11]. Gel permeation chromatography (GPC) measurements of molecular weight and scanning electron microscopy investigations of morphological changes were performed before and after incubation of the blends in solution prepared of sodium hypochlorite. There was shown that SMM containing vitamin E was able to consume HOCI and its blend with PCUR demonstrated greater resistance to oxidizing degradation than PCUR itself and than blend of PCUR and SMM of only fluorine tails [11].

Schubert *et al.* used vitamin E (as a 5 wt. % admixture) to modification of PEUR. The obtained blend indicated significantly less oxidation after *in vivo* experience and the reduction of the leucocytes activity suggested also better biocompatibility of this material [12, 13].

Ortiz, Vazquez *at al.* obtained and investigated acrylic biomaterials with chemically bounded vitamin E of antioxidant properties [14, 15].

Vesicle systems of antioxidative activity on lionelic acid were prepared by polymerization of amphiphilic methacryloic monomers, containing vitamin E bounded by ether linkage [16].

The aim of this work was obtaining of PEUR of better resistance to oxidation and hydrolysis through modification of the typical PEUR chain by chemically bounded α-tocopherol. We describe the synthesis of two kinds of novel monomers containing chemicaly coupled α-tocopherol and synthesis and some physical and chemical properties of PEUR obtained with these monomers.

EXPERIMENTAL

Materials

In the syntheses of monomers with bounded α-tocopherol and in the synthesis of PEUR we used the following substrates:

— α-Tocopherol [2, 5, 7, 8-tetramethyl-2-(4', 8', 12'--trimethyltridecyl)-6-chromanol, formula (I) in eq. (1)] supplied by Aldrich was dehydrated by heating at temp. 60 °C under reduced pressure (1.4 hPa), for 3h, in a vacuum rotator.

— 3-Chlor-1,2-propanediol [formula II in eq. (1)] delivered by Aldrich was dehydrated by azeotropic distillation with benzene and next distillation under reduced pressure at temp. 119—120 °C.

— 1,1,1-Tris(hydroxymethyl) propane (trimethylolpropane, TMP) purchased from Aldrich was dehydrated by heating in a vacuum rotator at temp. 60 °C for 3h.

— Poly(oxytetramethylene)glycol (PTMG), trade name Terathane 2000, product of Du Pont supplied by Aldrich, characterized by $\overline{M}_n$ = 2050 g/mol was filtrated in melt and dehydrated by heating and mixing at 80—90 °C for 3h, under reduced pressure (1.4 hPa).

— 1,4-Butanediol (1,4-BD) from BASF was dehydrated by azeotropic distillation and purified by distillation under reduced pressure.

— 4,4'-Methylenebis(cyclohexyl isocyanate), mixture of isomers (HMDI) delivered by Aldrich was distilled under reduced pressure at temp. 200 °C.

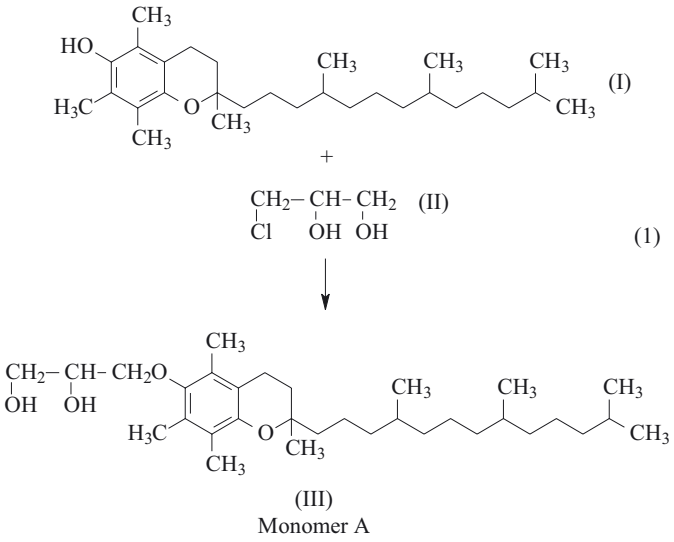
— Stannous 2-ethylhexanoate (Stannous octoate) from Sigma was used as catalyst in commercial form.

— Solvents: ethyl alcohol (POCh), hexan (Merck), acetone (POCh), diethylether (POCh) were purified by distillation and *N*,*N*-dimethylformamide (DMF, POCh) was dehydrated over P_2O_5 and distilled under reduced pressure.

— Sunflower oil (Zakłady Tłuszczowe, Kruszwica, Poland).

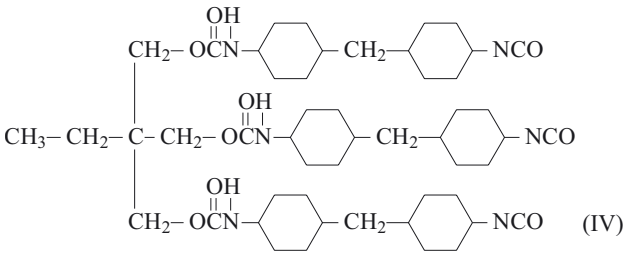
Synthesis of 2,3-dihydroxypropyl-α-tocopherol ether (monomer A)

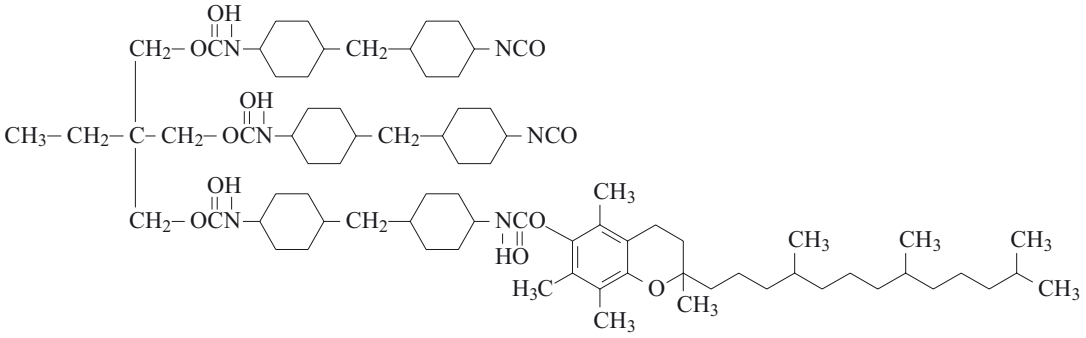
The aim of O-alkylation of α-tocopherol, described below, was the synthesis of diol [monomer A, formula (III)] according to equation (1), which could be able to react together with PTMG with NCO groups and form the prepolymer in synthesis with the molar excess of HMDI.



taken in the molar ratio 3:1. This reaction, in DMF solution (35 wt. % of substrates), at temp. 85—90 °C was controlled by determination of NCO groups concentration, by titration after reaction with *N*-dibutylamine [17].

In the second step to the solution of triisocyanatourethane α-tocopherol was added at temp. 60 °C, in the molar ratio of OH to NCO groups 1:3. The reaction was





continued at temp. 85—90 °C in argon atmosphere to the disappearance of OH band at IR spectrum (3500 cm^{-1}). The most probable product of this reaction is derivative with two free isocyanate groups [formula (V)].

To solution of 0.1 mole of α-tocopherol in 60 cm^3 of EtOH the solution of 0.125 mole of NaOH in 20 cm^3 of water was added with stirring and heating at argon atmosphere 75 °C/10 min. Next, the solution of 0.12 mole of 3-chlor-1,2-propanediol was added and the reaction was conducted at argon atmosphere at 75 °C for 24 h (S method) or 46 h (L method). In the longer (L) synthesis two portion of 0.02 mole Na_2CO_3 were added.

The reaction progress was controlled by thin layer chromatography (TLC). After synthesis the solution was filtrated from NaCl, which was rinsed by EtOH. Both solutions were poured together, diluted with 60 cm^3 of water and extracted with diethyl ether. The separated ether-phase was dehydrated over anhydrous $MgSO_4$, filtrated and ether was distilled off. The product obtained was purified by column chromatography and the separation was controlled by TLC. The fractions with monomer A were joined and the solvents were distilled off. Monomer A had at temp. >23 °C the form of high viscosity oil and at lower temperature — waxy form. The yield of the syntheses was 32 % and 50 % applying S and L methods, respectively.

Synthesis of the isocyanatourethane derivative of α-tocopherol (monomer B)

In the first step of this synthesis the triisocyanatourethane [formula (IV)] was obtained from HMDI and TMP,

Synthesis of PEUR

The synthesis of PEUR was conducted by a two step method using substrates listed in Table 1. In the first step the prepolymers containing free isocyanate groups were prepared by reaction of PTMG and HMDI taken in a molar excess of NCO groups (PEUR-3 and PEUR-4, Table 1) or with using additionally the monomer A (PEUR-1, Table 1) or monomer B (PEUR-2, Table 1). The reac-

Table 1. Substrates for syntheses of PEUR samples

Symbol of sample	Molar ratio of the monomer reactive groups					PTMG content wt. %
	first step				second step	
	OH in PTMG	NCO in HMDI	OH in monomer A	NCO in monomer B	OH in 1,4-BD	
PEUR-1	1	4.2	0.2	—	3	62.7
PEUR-2	1	5.7	—	0.3	5	46.7
PEUR-3	1	4.8	—	—	3.8	61.6
PEUR-4	1	7	—	—	6	46.4

tions followed in a presence of 0.1 wt. % of the catalyst, at temp. up to 95 °C, under reduced pressure and were controlled by IR spectroscopy (to disappearance of OH band at 3500 cm^{-1}). In the second step the obtained prepolymers, after dissolving in DMF (to concentration 80 wt. %) reacted with 1,4-BD at 70 °C during 1.5 h, in equivalent ratio of NCO and OH groups, in argon atmosphere.

Forming of PEUR films

PEUR were processed into films by pouring the polymer solutions into a running centrifuge drum (1000 rpm/min), covered by polytetrafluorethylene layer (PTFE). The antiadhesion layer of PTFE was, unfortunately, not sufficiently thick to make the sand-blast cleaned aluminum drum wholly smooth. Solvent was evaporated in argon atmosphere at temp. up to 70 °C. Next PEUR were gradually heated in a vacuum dryer (1.4 hPa) at 50 °C (2 h), 70 °C (2 h), 90 °C (2 h), 110 °C (2 h) and finally at 130 °C (3—5 h) in the case of PEUR non-modified and PEUR obtained using of monomer A or finally at 130 °C (9—12 h) in the case of PEUR synthesized with monomer B. This heating process enabled full evaporation of the solvent and total reaction of NCO groups (disappearance of NCO band at 2264 cm^{-1}).

Before investigation of the properties, PEUR films of thickness 0.2—0.5 mm were stored for at least one week at room temperature.

Methods

Thin Layer Chromatography (TLC) was carried out on the aluminum plates covered by Kieselgel 60 F_{254} (Merck) with use of the mixture of hexane and acetone (10:2 v/v) as the mobile phase. The chromatograms were observed under UV lamp (CAMAG) at 254 nm with use of α-tocopherol as the reference material.

Liquid/solid chromatography in a glass column (35 mm of diameter) was carried out with use of Kieselgel 0.08 mm (Merck) as the stationary phase and the mixture of hexane and acetone (10:2 v/v) as the mobile phase. The mass ratio of the separated substances to Kieselgel was 1:10. The fractions were controlled by TLC as was described earlier.

^1H NMR spectra were recorded in solution of dimethylsulphoxide (DMSO) using Varian Unity Plus apparatus, with the frequency of 500 MHz, in the Laboratory of NMR Spectroscopy at the Gdańsk University of Technology.

Infrared Spectroscopy (IR) analyses of the prepolymers and PEUR were acquired from their films on NaCl disc (after evaporation of the solvent at temp. 50 °C under reduced pressure 1.4 hPa for 30 min) using Bruker IFS66 spectrophotometer.

The stress-strain properties were tested at room temperature with the help of tensile tester FPZ 100 (Rauenstein, Germany) using film samples of dimensions 120×10 mm with traversing length of 50 mm and thickness of 0.2 to 0.5 mm, at the extension rate of 4.5 mm/s.

The hardness was determined with Shore A durometer (VEB Thûr. Industrial Rauenstein) for samples consisting of several layers of the films after 15 s pressing of the needle.

Thermogravimetric Analysis (TGA) was carried out with the temperature growth from 20 °C to 600 °C and the rate of heating 6 deg/min using Pyris 1 TGA apparatus (Perkin Elmer) for the samples of mass 3 mg, in a steady flow of air.

Investigation of the resistance of PEUR to accelerated thermooxidative ageing was carried out by measuring of the absorption of selected bonds from IR spectra (on NaCl disc), acquired before and after heating of the polymer film at 100 °C in the chamber with the forced flow of air, for 24 h. With use of the base line method [18], absorption of the ether bonds ($A_{C\text{-}O\text{-}C}$) at 1110 cm^{-1} and absorption of the carbonyl groups ($A_{C=O}$) at 1716 cm^{-1} were measured and compared, both in regard to absorption of CH_2 groups (A_{CH_2}) of β position to the ether bonds at 2930 cm^{-1} [19, 20], by determination of ratios

$$\frac{A_{C-O-C}}{A_{CH_2}} \quad \text{and} \quad \frac{A_{C=O}}{A_{CH_2}}$$

Investigation of the chemical stability of PEUR was conducted using the following aqueous solutions, prepared as in [21]:

— Ringer's solution (9 g of NaCl, 0.42 g of $NaHCO_3$, 0.24 g of $CaCl_2$ and 1 g of glucose in 1000 cm^3 of distilled water),

— phosphate-buffered saline of pH = 7.4 (the separately prepared solutions of Na_2HPO_4 (28.4 g) and $Na_2HPO_4 \cdot H_2O$ (27.6 g) in 1000 cm^3 and 0.9 wt. % solution of NaCl in water were mixed in the volume proportion 77:23,

— hydrogen peroxide solution (30 wt. % of H_2O_2 in water).

The dry samples of PEUR films (2.5 cm in diameter) were weighted with accuracy of 0.0002 g and incubated in solutions at temp. 37 °C up to six weeks. After every week 3—5 of each kind of samples were taken out, rinsed by distilled water and dried to constant weight (50 °C/1.4 hPa) to determine the weight loss. The solutions over samples were changed to a fresh after every week.

To determine water and sunflower oil sorption, five dry samples of PEUR were weighted with accuracy of 0.0002 g and separately maintained in redistilled water or in sunflower oil for 24 h at temp. 37 °C. After removing, the samples were impressed between the filter paper and immediately weighted. The average values of percentage increase in weight were counted.

RESULTS AND DISCUSSION

Chemical structure of monomers with bounded α-tocopherol

The structure of the monomer A [formula (III) in eq. (1)] used to synthesis of PEUR-1 (Table 1) was confirmed by ^{1}H NMR spectrum (Fig. 1) in which the characteristic chemical shifts of the protons from OH groups (4.55 ppm; 4.90 ppm) and shifts of the protons from α-tocopherol structure are visible: 0.82 ppm (m, 12H, CH_3: 4'a, 8'a, 12'a, 13'), 1.08-1.35 ppm (m, 21H, CH and CH_2: 1', 2', 3', 4', 5', 6', 7', 8', 9', 10', 11', 12'), 1.18 ppm (s, 3H, CH_3:2a), 1.48 ppm (m, 2H, CH_2:3), 1.72 ppm (m, 2H, CH_2:4), 1.98 ppm (s, 3H, CH_3:8b), 2.0 ppm (s, 3H, CH_3:7a), 2.02 ppm (s, 3H, CH_3:5a), 3.45 ppm (m, 2H, CH_2:12), 3.58 ppm (m, 1H, CH:11), 3.79 ppm (m, 2H, CH_2:10), 2.5 ppm (DMSO).

In the described conditions of TLC retention coefficient R_f = 0.218 for monomer A and R_f = 0.593 for α-tocopherol were designated.

Owing to use of the trifunctional isocyanate [formula (IV)] in the reaction with α-tocopherol to obtaining of monomer B, there was the possibility, that beside of the structure specified by formula (V) also di- or triurethane compounds could also arise. However, because of the molar ratio of OH to NCO groups was 1:3, as well as because of the steric hindrance, the structure (V), monourethane diisocyanate, was the most probable in the monomer B. Estimated content of NCO groups in the product of this reaction — 14.4 wt. % was very close to the theoretical value (13.7 wt. %) and was taken into account when counting of the quantity of substrates in the synthesis of PEUR-2.

The substrates for syntheses of obtained PEUR as well as non-modified PEUR-3 and PEUR-4 are presented

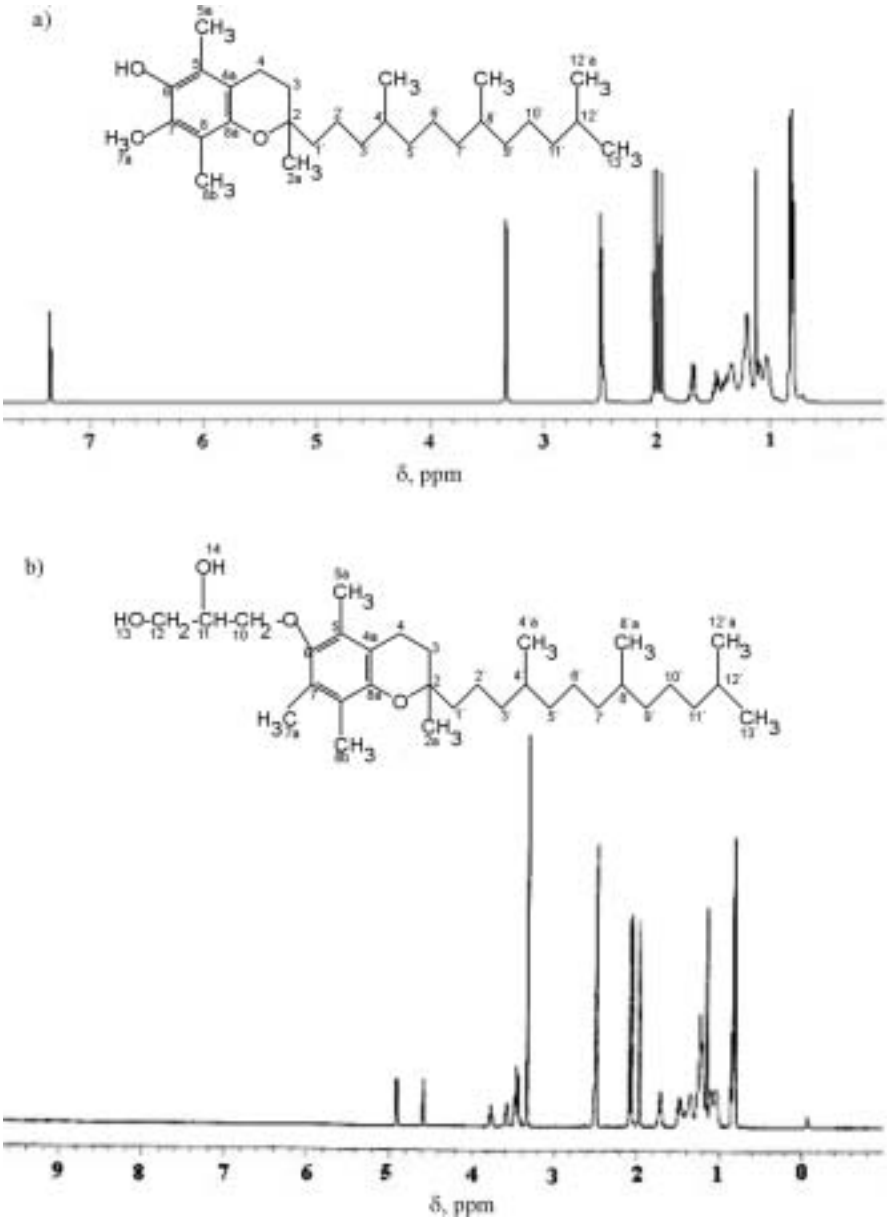
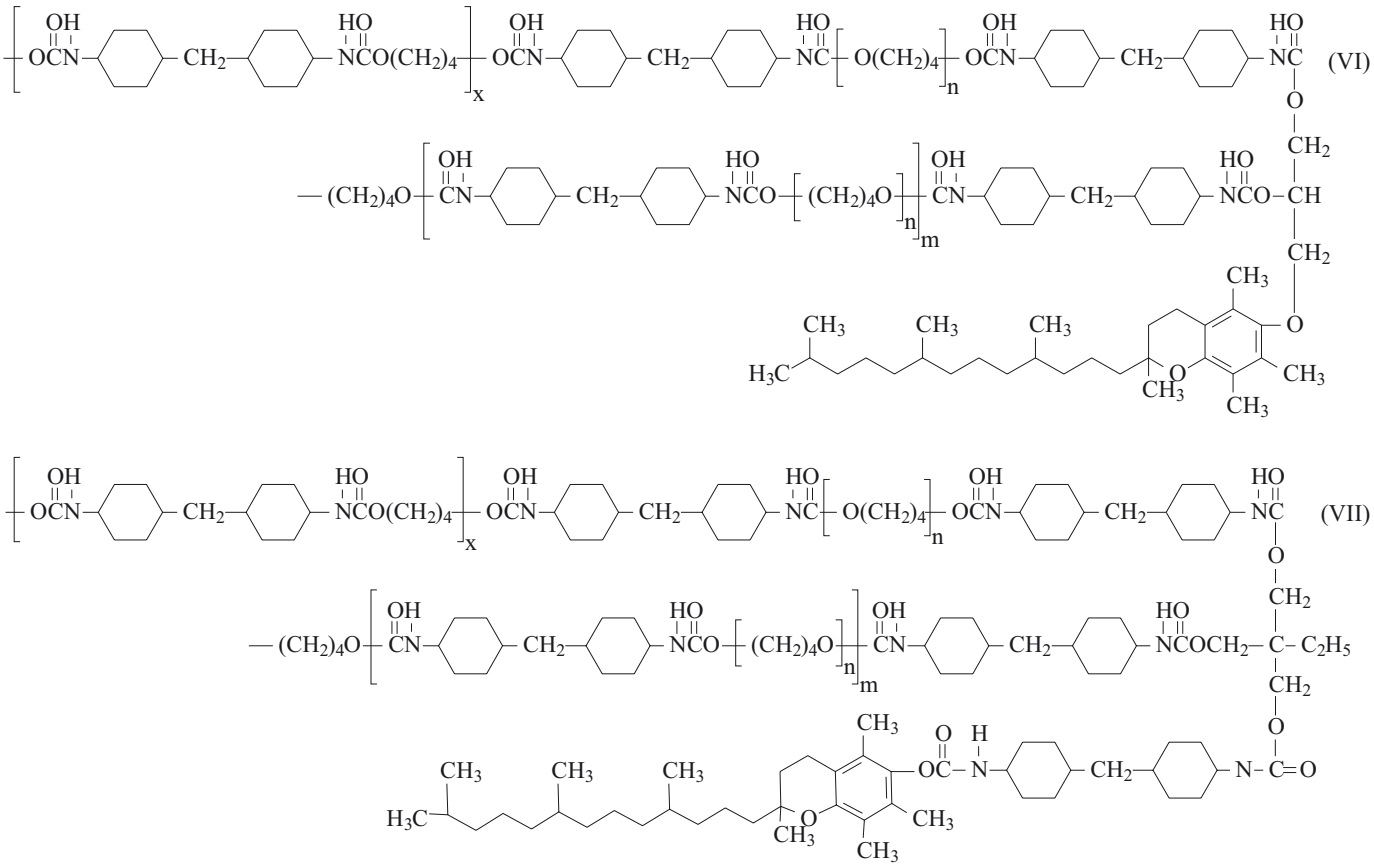


Fig. 1. ^{1}H NMR spectra of: a) α-tocopherol, b) 2,3-dihydroxypropyl-α-tocopherol-ether



in Table 1. Scheme of PEUR-1 structure obtained with monomer A is shown as formula (VI) and the main PEUR synthesized with use of the monomer B (PEUR-2) is given as the structure specified by formula (VII). Both modified PEUR-1 and PEUR-2 contained 2.5 wt. % of α-tocopherol structure. The characteristic bands from IR spectra of obtained PEUR confirming the proposed structure are listed in Table 2.

T a b l e 2. Characteristic of IR absorption bands observed for the groups from monomers and PEUR

Wave Number, cm^{-1}	Kind of vibration[a)]	Group from the chain
3500	ν(O-H)	hydroxyl (-CH_2OH)
3320	ν(N-H)	urethane (-NHCOO-)
2930	ν_a(C-H)	β-CH_2- of PTMG
2854	ν_s(C-H)	β and α-CH_2- of PTMG
2796	ν_s(C-H)	α-CH_2- of PTMG
2264	ν_a(N=C=O)	isocyanate
1740—1690	ν(C=O)	urethane (-NHCOO-)
1448	δ(C-H)	-CH_2-
1367	ω(C-H)	-CH_2-
1110	ν(C-O-C)	ether $(CH_2)_4$-O-$(CH_2)_4$

[a)] ν — stretching vibrations, ν_a — asymmetric vibrations, ν_s — symmetric vibrations, δ — bending vibrations, ω — wagging vibrations.

Physical properties of obtained PEUR

Hardness and stress-strain properties of obtained PEUR (Table 3) were dependent on participation of the soft PTMG segments and hard segments from 1,4-BD and HMDI and also on the monomers with bounded α-tocopherol. If the part of PTMG in PEUR was the same (PEUR-1 and PEUR-3 or PEUR-2 and PEUR-4, respectively) the presence of α-tocopherol led to decrease in hardness and to increase in maximal elongation. This modifying compound plays the role of the internal plasticizer in obtained PEUR.

Tensile strength of our PEUR would be probably improved when the centrifuge barrel of much smoother surface could be used to form the films.

T a b l e 3. Hardness and stress-strain properties of modified and non-modified PEUR

PEUR	Hardness °Shore A	Tensile strength at break ± *SD*[b)], MPa	Relative elongation at break ± *SD*[b)], %	Tension set ± *SD*[b)], %
PEUR-1	67	5.2 ± 0.6	240 ± 8.5	8.4 ± 2.2
PEUR-2	80	11.3 ± 0.9	144 ± 10.2	21.8 ± 6.4
PEUR-3	68	8.0 ± 1.2	210 ± 6.6	13.5 ± 2.0
PEUR-4	87	9.1 ± 0.8	45 ± 6.3	3.0 ± 1.2

[b)] *SD* — standard deviation.

Determination of water and sunflower oil sorption indicated the dependence of these properties on PTMG and α-tocopherol contents (Table 4). Generally, water sorption by PEUR was very small (0.78—1.06 %). Lower

density and particularly the affinity to fats were the reasons of the greater sunflower oil sorption by PEUR modified by α-tocopherol in comparison to oil sorption by non-modified PEUR of the same PTMG content. Non--modified PEUR-4, of the highest content of hard segments from 1,4-BD and HMDI was characterized by the least sunflower oil sorption. Oil sorption by PEUR-3 of the higher PTMG-segments content was only a little lower than oil sorption by PEUR modified by α-tocopherol (PEUR-1 and PEUR-2).

T a b l e 4. Water and sunflower oil sorption in PEUR

Symbol of sample	Water sorption wt. %	Sunflower oil sorption, wt. %
PEUR-1	0.78	18.0
PEUR-2	1.06	16.7
PEUR-3	0.94	16.5
PEUR-4	0.79	7.4

The investigations of fats sorption by PEUR modified by α-tocopherol should be extended in continuation of this work because for the biomedical implants greater sorption of fats is disadvantageous. It may lead to decrease in mechanical strength and to change of the implant's shape. In some application in medicine, for instance as the microcapsules, swelling of the polymeric vesicles by fats in the organism may be advantageous for the diffusion of the bioactive substances included in them.

Thermooxidative stability of PEUR on the base of dynamic TGA

Soft polyether segments in obtained polymers are of the least thermooxidative stability. Initial decomposition temperatures, determined as the corresponding to 5 % and 10 % of the weight loss (T_5 and T_{10}, respectively) were dependent upon the weight parts of these segments (Table 5). This dynamic thermogravimertic analysis of PEUR showed simultaneously that modification of PEUR by bounded α-tocopherol led to incerease in the initial temperatures of thermal decomposition in air atmosphere, what was probably related to better oxidative resistance of the modified PEUR in comparison to the suitable non—modified PEUR.

T a b l e 5. Thermogravimetric analysis of PEUR

Symbol of sample	T_5, °C	T_{10}, °C	T_{1max}, °C
PEUR-1	288	302	321
PEUR-2	302	311	320
PEUR-3	280	300	322
PEUR-4	274	294	322

TGA showed that from two kinds of obtained modified PEUR, for PEUR-2 in which α-tocopherol is bounded by urethane bond, T_5 and T_{10} are higher than corresponding temperatures for PEUR-1 with α-tocopherol bounded by the ether linkage. The positive influence of α-tocopherol-structure on thermostability of PEUR is assigned to higher temperatures of the initial decomposition of PUER-2 in relation to PEUR-4 though PEUR-2 with α-tocopherol structure contains a small quantity of aromatic-aliphatic urethane bonds, known from lower thermostability than aliphatic urethane bonds, present as the main in all PEUR obtained.

Temperatures corresponding to the first peak of maximal rate of decomposition (T_{1max}) were practically the same for modified and non-modified PEUR.

Resistance of PEUR to isothermal oxidative ageing

Oxidative ageing of the polyether segments in polyurethanes leads to decrease in the quantity of ether bonds (C-O-C) and to increase in the quantity of carbonyl groups (in keton or carboxyl groups) [4].

Such ageing conducted in this work for selected PEUR at temp. 100 °C, in a chamber with forced flowing air for 24 h, showed that α-tocopherol bounded with PEUR chain protected, as antioxidant, the carbon atoms in the α-position to ether bonds. IR absorption of β CH_2 groups, which was practically constant, was used as the reference for calculation of changes of C-O-C and C=O absorption by base line method. The results of these measurements are listed in Table 6. As it was stated the absorption of ether bonds and carbonyl bonds of PEUR-1 and PEUR-2, modified by 2.5 wt. % of bounded α-tocopherol was practically unchanged. For non-modified PEUR-3 and PEUR-4 followed decrease in the ether bonds absorption and, the most visible, increase in carbonyl bonds absorption.

T a b l e 6. Changes of the absorption of the ether bonds and keton/carboxyl carbonyl bonds after thermooxidative ageing of PEUR

Symbol of sample	$A_{C-O-C} / A_{\beta CH_2}$		$A_{C=O} / A_{\beta CH_2}$	
	before ageing	after ageing	before ageing	after ageing
PEUR-1	0.80	0.86	1.42	1.17
PEUR-2	0.78	0.84	0.73	0.76
PEUR-3	1.00	0.56	0.72	1.83
PEUR-4	0.72	0.66	0.99	1.47

Figure 2 shows the IR spectra before and after isothermal oxidative ageing of PEUR-1 and in Figure 3 corresponding spectra are visible for PEUR-3, non-modified by α-tocopherol and showing very close PTMG ratio to PEUR-1.

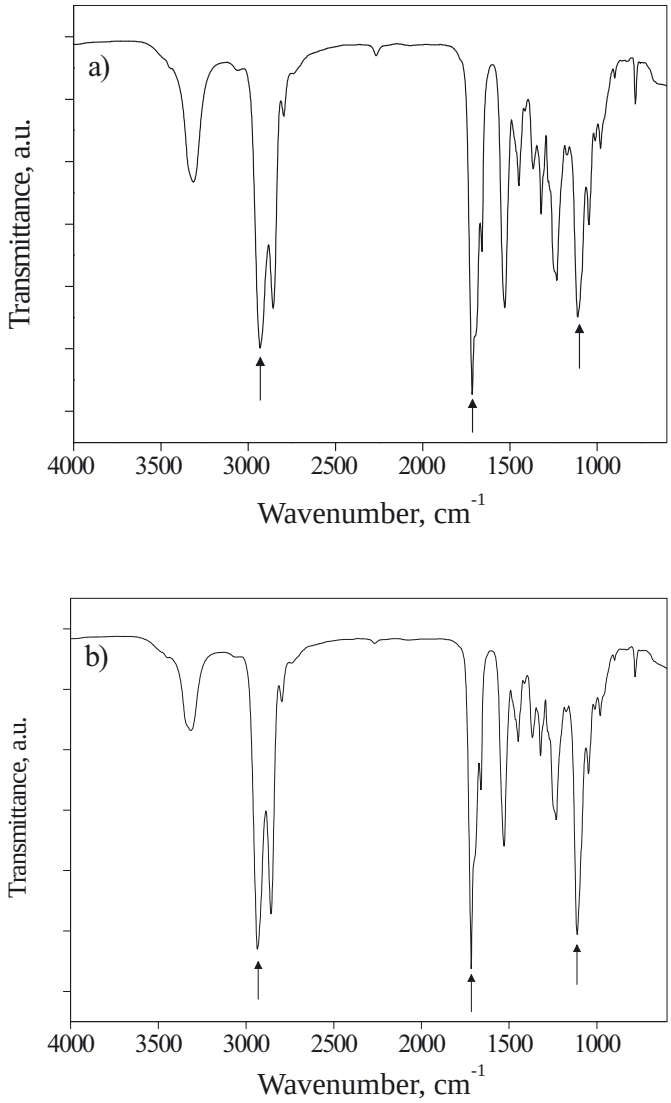


Fig. 2. IR spectra of PEUR-1: a) before ageing, b) after ageing at 100 °C for 24 h in flowing air

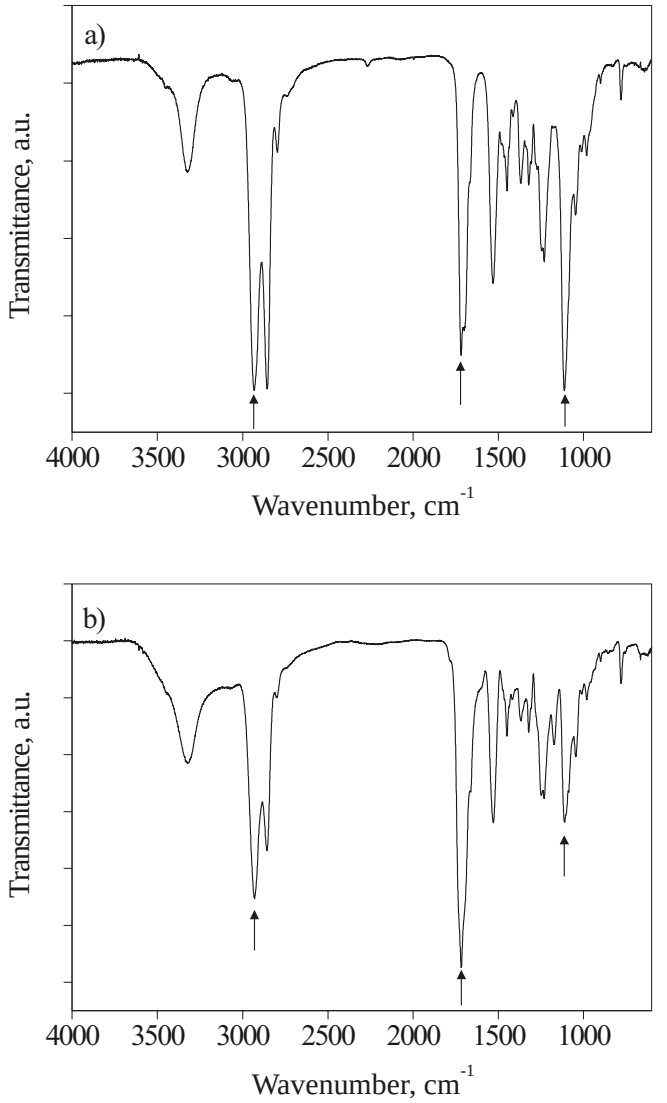


Fig. 3. IR spectra of PEUR-3: a) before ageing, b) after ageing at 100 °C for 24 h in flowing air

Chemical stability of PEUR in selected aqueous solution

Weight loss of the selected PEUR in six weeks time acting of the Ringer's solution, phosphate buffer (pH = 7.4) and 30 wt. % of hydrogen peroxide solution are presented in Fig. 4—6, respectively. The first two solutions are very often used to characteristics of the biomaterial's stability, as simulating the conditions in the organism. The behavior in H_2O_2 solution gives the possibility of evaluation of PEUR resistance to oxidative degradation.

After incubation in the Ringer's solution (Fig. 4), PEUR-1 and PEUR-2 modified by α-tocopherol and non-modified PEUR-3 showed very small loss of weight (from 0.3 to 0.4 %). This decrease was settled in time of first three weeks, in which the loss of weight of modified PEUR was higher than for non-modified PEUR. It may be related to the lower density of modified PEUR and easier penetration of the Ringer's solution into film and removing the substances becoming on account of influence of this solution.

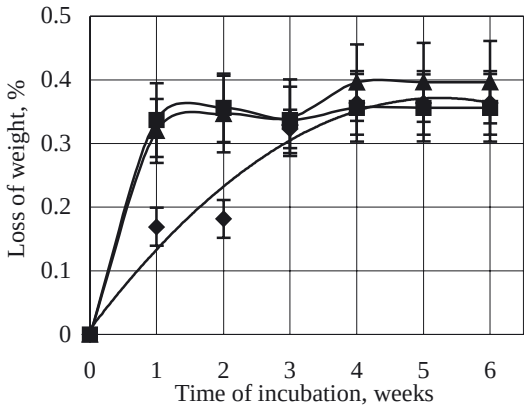


Fig 4. Weight loss of PEUR after incubation in Ringer's solution: ■ — PEUR-1, ▲ — PEUR-2, ♦ — PEUR-3

In the phosphate buffer (Fig. 5), the least decrease in weight (*ca*. 0.2 %) was determined for PEUR-2 modified

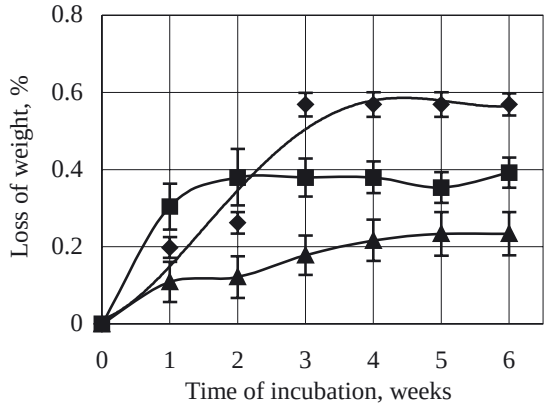


Fig. 5. Weight loss of PEUR after incubation in phosphate saline buffer (pH = 7.4): ■ — PEUR-1, ▲ — PEUR-2, ♦ — PEUR-3

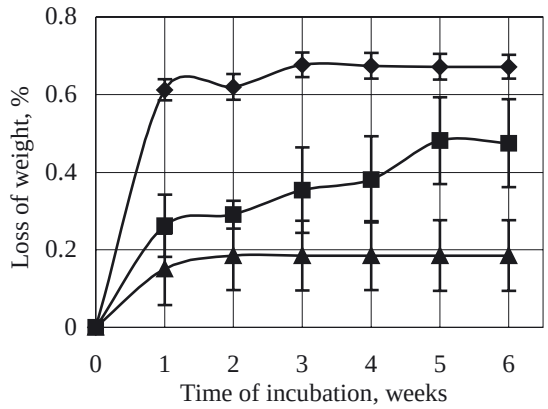


Fig. 6. Weight loss of PEUR after incubation in hydrogen peroxide solution: ■ — PEUR-1, ▲ — PEUR-2, ♦ — PEUR-3

by α-tocopherol with use of monomer B in synthesis and of lower content of PTMG segments. In these buffer the greatest loss of weight was measured for non-modified PEUR-3, settled as 0.6 % after three weeks of incubation.

During all six weeks of incubation in the hydrogen peroxide solution, PEUR-1 and PEUR-2 modified by 2.5 wt. % of bound α-tocopherol were more resistant according to mass change than non-modified PEUR-3 (Fig. 6). The least change of weight (0.2 %) was indicated for PEUR-2 of lower PTMG content and obtained with use of monomer B in which α-tocopherol was bound by urethane bond.

CONCLUSIONS

On the base of the results of the investigation of thermooxidative ageing and stability in H_2O_2 solution it could be stated that modification of polyetherurethanes by chemically bounded α-tocopherol gives the possibility to improve the oxidative stability of these polymers. It is necessary to extend these investigations on synthesis of PEUR modified by α-tocopherol and investigation of their properties with use of the other methods of oxidation and hydrolytical stability, with adequate controlling. To find what quantity of bounded α-tocopherol is optimum to play good antioxidant role and to prevent the degradation of polyetheruretanes would be also necessary.

REFERENCES

1. Szycher M., Reed A. M., Siliciano A. A.: *J. Biomat. Appl.* 1991, **6**, 110.
2. Carson J. R., Edwards A.: *Urethanes Technology*, December 1999/January 2000, p. 24.
3. Tanzi M. C., Mantovani D., Petrini P., Guidoin R., Laroche G.: *J. Biomed. Mater. Res.* 1997, **36**, 550.
4. Wu Y., Sellitti C., Anderson J. M., Hiltner A., Lodoen G. A., Payet C. R.: *J. Appl. Polym. Sci.* 1992, **46**, 201.
5. Gunatillake P. A., Meijs G. F., Rizzardo E., Chatelier R. C., Mc Carthy S. J., Brandwood A., Schindhelm K.: *J. Appl. Polym. Sci.* 1992, **46**, 319.
6. Pinchuk L.: *J. Biomater. Sci. Polymer Edn.* 1994, **6**, 225.
7. Tang Y. W., Santerre J. P., Labow R. S., Taylor D. G.: *J. Biomed. Mater. Res.* 1997, **35**, 371.
8. Lim F., Yang C. Z., Cooper S. L.: *Biomaterials* 1994, **15**, 408.
9. Lemm W.: „Polyurethanes in Biomedical Engineering", Elsevier, Amsterdam 1984, p. 103.
10. Moszczyński P., Pyć R.: „Biochemia Witamin", Chapter II, PWN Warszawa 1999, p. 73.
11. Ernsting M. J., Labow R. S., Santerre J. P.: *J. Biomater. Sci. Polymer Edn.* 2003, **14**, 1411.
12. Schubert M. A., Wiggins M. J., Schaefer M. P., Hiltner A., Anderson J. A.: *J. Biomed. Mater. Res.* 1995, **29**, 337.
13. Schubert M. A., Wiggins M. J., De Fife K. M., Hiltner A., Anderson J. A.: *J. Biomed. Mater. Res.* 1996, **32**, 493.
14. Ortiz C., Vazquez B., San Roman J.: *Polymer* 1998, **39**, 4107.
15. Vazquez B., Ortiz C., San Roman J., Plasencia M. A., Lopez-Bravo A.: *J. Biomat. Appl.* 2000, **15**, 118.
16. Cho J., Kim Y-D.: *Macromol. Symp.* 1997, **118**, 631.
17. Roth H.: *Microchimica Acta* 1958, **6**, 766.
18. Rabek J. F.: „Experimental Methods in Polymer Chemistry", John Wiley and Sons, Chichester-New York-Brisbane-Toronto 1980, p. 241.
19. Wu Y., Sellitti C., Anderson J. M., Hiltner A., Lodeon G. A., Payet C. R.: *J. Appl. Polym. Sci.* 1992, **46**, 201.
20. Zieliński W., Rajca A.: „Metody spektroskopowe i ich zastosowanie do identyfikacji związków organicznych", WNT Warszawa, 1995.
21. Thomas V., Jayabalam M., Sandhya S.: *J. Biomat Appl.* 2000, **15**, 86.

Received 7 XII 2004.