Comparison of hydrolytic resistance of polyurethanes and poly(urethane-methacrylate) copolymers in terms of their use as polymer coatings in contact with the physiological liquid

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PU elastomers were synthesized using MDI, PTMO, butane-1,4-diol or 2,2,3,3-tetrafluorobutane-1,4-diol. Using the same diisocyanate and polyether reagents urethane segments were prepared, to be inserted in the poly(urethane--methacrylate) copolymers. Bromourethane or tetraphenylethane-urethane macroinitiators were used as transitional products reacting with MMA according to the ARGET ATRP. 1H and 13C NMR spectral methods, as well as DSC and TGA thermal methods, were employed to confirm chemical structures of synthesised elastomers and copolymers. To investigate the possibility of using synthesized polymers as biomaterials a research on keeping them in physiological liquid at 37°C was performed. A loss in weight and ability to sorption of water was determined and by using GPC the molecular weight changes were compared. Additionally, changes in the thermal properties of the samples after exposure in physiological liquid were documented using both the TGA and DSC methods. The studies of surface properties (confocal microscopy and SFE) of the obtained polymers were performed. The structure of the polymer chains was defined by NMR. Possible reasons of hydrolysis were discussed, stating that new copolymers are more resistant and polar biomaterials can be less interesting than elastomers.

Keywords: coatings, polyurethane elastomers, poly(urethane-methacrylate) block copolymers, ARGET ATRP, biomaterials, hydrolytic resistance.

INTRODUCTION

Today there is no doubt that the structure of segmented polyurethanes (PU) with its attendant strong polar interactions, dispersion interactions strengthened with the presence of a network of hydrogen bonds formed within the flexible and rigid segments, particularly between these segments is favorable for creating the phases of varying degrees of structured[1]. It turns out that this order is critical for a number of physicochemical, mechanical and biological properties, important for the application of these polymers in various fields of technology and medicine[2–4]. Meanwhile, in the present investigation, we focused on the synthesis of PU elastomer coatings with increased hydrophobicity. Also it is possible to consider applying of this type of coatings as special protective coatings to polar materials for example, old prints, wood, ceramics as well as biomaterials. Therefore, influences among the functional groups of polyurethane and the coating material are contributing to a significant increase of the adhesion, which as a result creates possibilities to obtain the tight adjoining, protecting the surface. In the latter case it is significant for obtaining durable polyurethane elastomers, also characterized by high resistance to biodegradation in conditions of their long contact with physiological liquids and tissues of living organisms. For a long time a series of commercially available polyurethane biomaterials has been known[5–8]. Also a lot of methods of the structural PU modification were developed aiming at, e.g. changes of their features generally hydrophilic to more hydrophobic by introducing apolar segments of siloxane or fluoroether[9–11]. This is the road that leads to significant changes in both the internal structure of the PU elastomer and hydrophobi-

zation of its surface[12]. Given the noted in recent years, significant progress in the use of new methods of atom transfer radical polymerization (ATRP), the use of some of them in obtaining urethane-acrylic copolymers synthesized in the restricted grade through an incorporation of unsaturated segments capable of radical crosslinking e.g. terminated polybutadiene polyols or low molecular weight isocyanate prepolymers extenders such as e.g. hydroxyethyl acrylate seems promising[13].

Realizing this concept we synthesized new types of poly(urethane-methacrylate) copolymers, using the specially made urethane macroinitiators: bromine and tetraphenylethane, capable of reacting with methacrylate monomers[14]. Polyurethane structures affect the improvement in mechanical properties of that kind of copolymers, while segments of poly(methyl methacrylate) (PMMA) are used to hydrophobization of PU surface, which result from the presence of apolar methyl groups in PMMA chain. Similarly to PU elastomers also poly-(urethane-acrylate) copolymers are finding application as biomaterials, among others biocompatible implant in tissue engineering[15], hydrophobic antimicrobial coating[16] and drug delivery in the form of appropriately formed micellar structures[17]. An effective control above the length of the block, which can be achieved using the methods of controlled radical polymerization (CRP), is of key importance[14, 18].

However, as part of the presented work we carried out the comparative study of these materials in terms of their resistance to hydrolytic degradation in the environment of physiological liquid similar to the blood plasma, similarly as described in works[19–21].

As reference material we used the synthesized by us PU elastomers, prepared by classical prepolymer me-

thod, of the same as the above copolymers diisocyanate (MDI) and polyol (PTMO), which were extended by butane-1,4-diol, or it's fluorinated analogue 2,2,3,3-tetra-fluorobutane-1,4-diol. Therefore, the primary objective of this study was to verify whether, and if so, to what extent the newly synthesized poly(urethane-methacrylate) copolymers with increased hydrophobicity are resistant to hydrolytic degradation as compared to conventional PU elastomers including their fluorinated analogues synthesized with MDI, PTMO and butane-1,4-diol or 2,2,3,3-tetrafluorobutane-1,4-diol.

EXPERIMENTAL

Material

4,4'-Methylene diphenyl diisocyanate (MDI), dibutyltin dilaurate (DBTDL), α-bromoisobutyryl bromide (BB; 98%), ethylene glycol (99.9%) and copper(0) metal turnings ($\geq$ 99%) were used as received from Sigma-Aldrich Inc., St. Louis, USA. Polyoxytetramethylene glycol of molecular weight 1000 (PTMO; Merck, Darmstadt, Germany) was purified by heating at 105°C under vacuum for 3 h before use. Benzophenone (99%; ABCR GmbH, Karlsruhe, Germany), methyl methacrylate (MMA; 99%; Sigma-Aldrich, USA), CuCl$_2$ (97%; Sigma-Aldrich, USA) and PMDETA ($\geq$ 98%; Merck, Germany) were used without further purification. Butane-1,4-diol (BD), 2,2,3,3-tetrafluorobutane-1,4-diol (TFBD) were used as received from Sigma-Aldrich Inc., St. Louis,

Synthesis methods

PU elastomers were synthesized in a two-step polyaddition process. The first stage includes synthesis of urethane–isocyanate prepolymer terminated by –NCO groups from diisocyanate (MDI) and polyol (PTMO 1000), in the presence of MEK. The reaction was conducted at 40°C for 1 h, followed by 2 h at 65°C, in order to bring the content of the unreacted –NCO groups in the reaction mixture to half of their initial values. This process can be approximately illustrated by the following reaction:

$$(1)$$
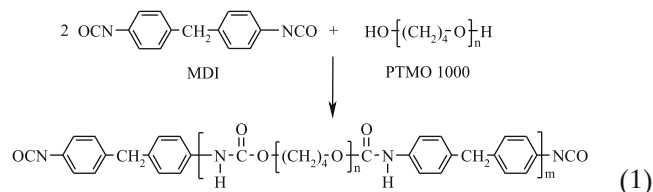
where: $n = 13$–14, $m = 5$–6.

In scheme (1) a secondary reaction of the allophanate formation reaction was omitted, which occurred under these conditions to a very small extent. The second stage involved in the chain extension of the created prepolymer by using TFBD or BD, also in MEK solution having a concentration of about 50 wt%, and at the molar ratio of –NCO to –OH groups of 1:1. The DBTDL was added as the catalyst at the level of 0.1 wt%, in relation to the PTMO. The extension reaction was carried out at 65°C until a complete reaction of the free –NCO groups (over 2 h). The extension of the prepolymer can be approximately illustrated by the following reaction:
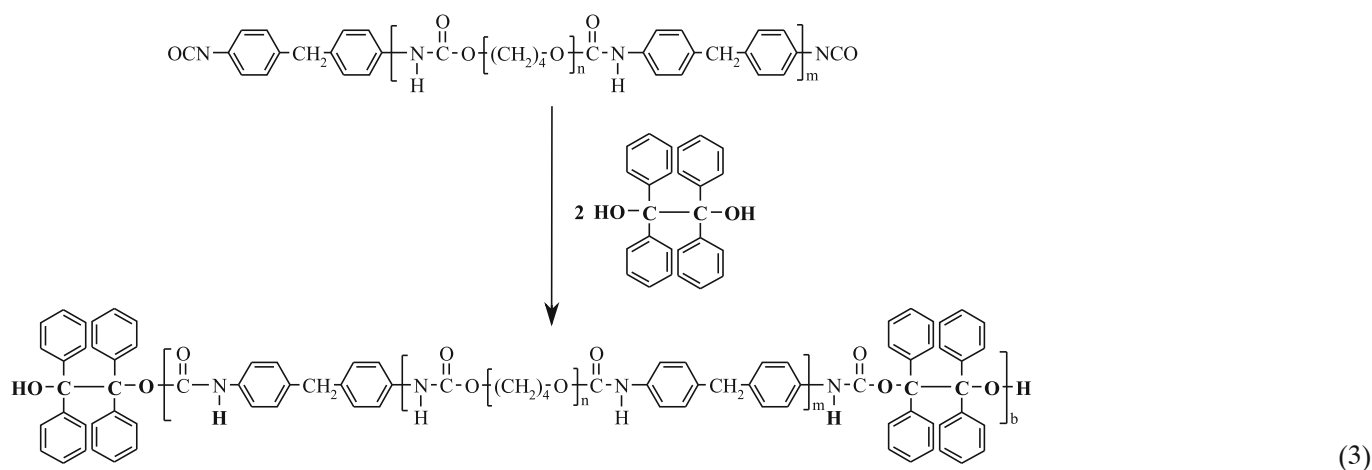

$$(2)$$
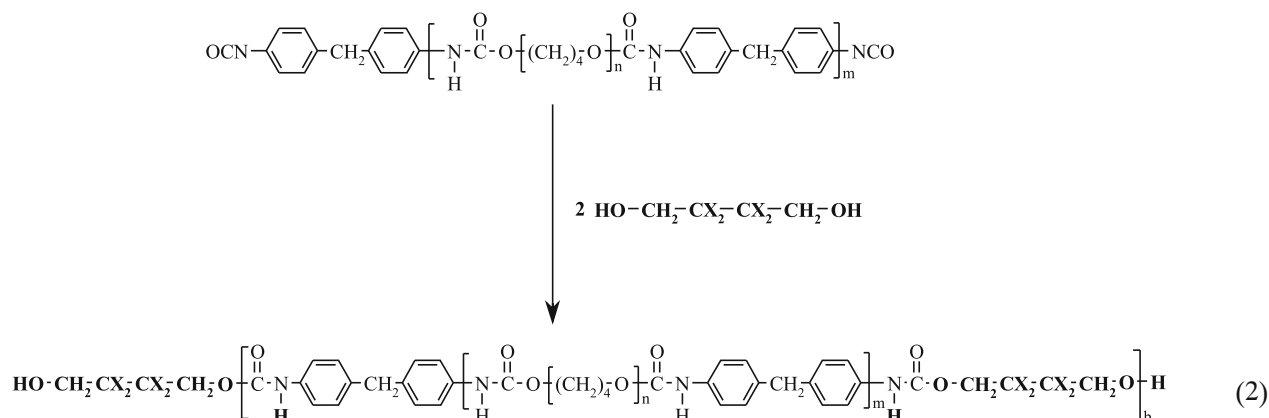
USA. Tetraphenylethane-1,2-diol (TPED) was prepared from benzophenone and 2-propanol as reported in the literature[22]. 2-Hydroxyethyl-2'-methyl-2'-bromopropionate (HMB) was prepared from ethylene glycol and α-bromoisobutyryl bromide as reported in the literature[14]. Acetonitrile (99.5%), methanol (99.9%), acetone (99.5%) and 2-propanol (99%) were obtained from Chempur, Piekary Śląskie, Poland. Analytical grade *N,N*-dimethyl-formamide (DMF; Sigma-Aldrich, USA) and methyl ethyl ketone (MEK; Sigma-Aldrich, USA), were distilled and the middle portions were used after storing over type 4 Å molecular sieves. Analytical reagents: Dibutylamine (Sigma-Aldrich), chlorobenzene, distilled and dried by type 4 Å molecular sieves (Chempur), HCl 0,1n (POCH), diiodomethane, formamide (Sigma-Aldrich), physiologic salt solution (Baxter).

where: X denotes H in the case of BD ($b = 5$) or F in case of TFBD ($b = 1$–2).

In practice this reaction is more complex and it constitutes the arrangement of the following reactions of urethane-isocyanate oligomers with BD or TFBD substrate, or with transitional products of the type of urethane oligomers terminated with –OH groups[23]. The task of DBTDL catalyst, was to accelerate reactions occurring in subsequent steps, leading to the PU, about the more great molecular weight. The resulting PU process solutions in MEK were poured onto poly(tetrafluoroethylene) plates, with the help of the applicator with a slot width of 1 mm, thus forming the membrane which was dried in a vacuum oven at 80°C for 6 h. The resulting films were then subjected to seasoning under room temperature for 10 days, and then removed without distortion from poly(tetrafluoroethylene) plates, yielding PU films used for the test.

Poly(urethane-methacrylate) copolymers were synthesized in a three-step process, consisting of a two-stage polyaddition and controlled radical reaction of connecting acrylic segments.

The first stage includes a synthesis of prepolymer from MDI and PTMO, carried out in a manner similar to the case of the PU elastomers. In the second stage at 65°C the resulting prepolymer is reacted with TPED or HMB, at the equimolar ratio of –NCO to –OH groups using DBTDL as a catalyst, getting macroinitiators in MEK solution, appropriately urethane-tetraphenylethane (TPE-PU-TPE) or bromourethane (MBP-PU-MBP) containing 0 wt% content of –NCO groups[14]. The TPE-PU-TPE macroinitiator synthesis process is presented by the following scheme:

(5)

where: R denotes part of the structure coming from TPE-PU-TPE or MBP-PU-MBP.

The resulting copolymer deposites were precipitated from the reaction mixture with methanol, and then washed with acetonitrile to remove from them a possible content of PMMA homopolymer.

The resulting copolymers were dried in a vacuum oven at 80°C for 6 h, then dissolved in acetone and as 50 wt% solutions were distributed on the surface of
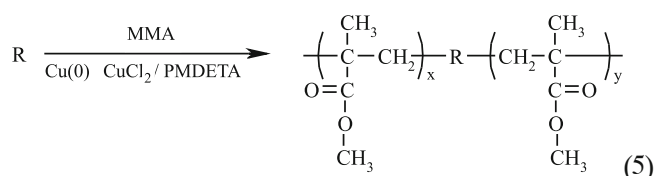

(3)

where: $b = 2$.

Meanwhile, the MBP-PU-MBP macroinitiator synthesis process is presented by the scheme:

(4)
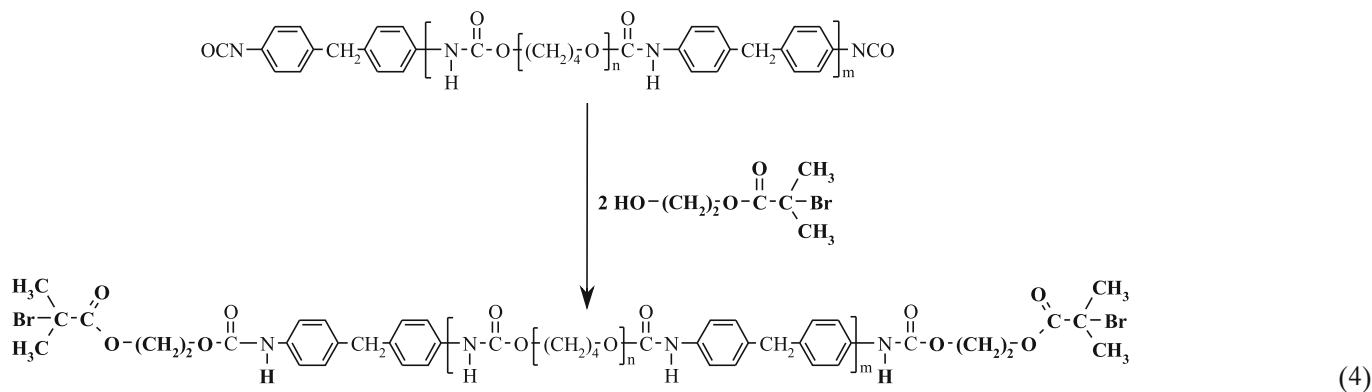
The third stage included a 30 h synthesis of tri-block copolymers by using ARGET ATRP method, in the presence of limited amount of air and with a very small (370 ppm) amount of copper catalyst. In this case, substrates were previously received TPE-PU-TPE and MBP-PU-MBP macroinitiators, as well as MMA. The reactions were carried out in the presence of a reducing metal Cu(0) and the $CuCl_2$/PMDETA catalyst complex in DMF environment[14]. In the case of the TPE-PU-TPE macroinitiator the reaction from MMA was performed at 80°C (reported now for the first time), while the MBP-PU-MBP macroinitiator at 100°C. The scheme below presents the polymerization process:

poly(tetrafluoroethylene) plates, and then dried in a vacuum oven at 80°C for 6 h. The resulting films were then subjected to seasoning under room temperature for 10 days, and then removed without distortion from poly(tetrafluoroethylene) plates, yielding copolymer films used for the test.

Chemical compositions of prepared elastomer and copolymer samples in the form of thin films are presented in Table 1.

Hydrolytic degradation study

Samples of the obtained polymers were subjected to hydrolytic degradation test at 37°C in an incubator for a period of 8 weeks in an environment similar to the physiological fluid of the blood plasma[20]. The loss in

Table 1. The chemical composition of synthesized polyurethane elastomers and poly(urethane-methacrylate) copolymers based MDI diisocyanate and PTMO polyol

Sample No.	Type of polymer	Type of diol	Monomer	Characteristic of molecular weights						Surface free energy parameters [mJ/m²] standard deviation						Surface roughnes grade parameters [μm]			
				before exposure			after exposure			before exposure			after exposure			before exposure		after exposure	
				M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	γs	γs^d	γs^p	γs	γs^d	γs^p	R_a	R_z	R_a	R_z
PU-1-E	PU elastomer	BD	–	36100	46200	1.280	32320	49000	1.516	43.08 *0.09*	39.50 *0.09*	3.58 *0.01*	45.19 *0.10*	40.46 *0.10*	4.73 *0.01*	0.023	0.037	0.142	0.247
PU-2-E	PUF elastomer	TFBD	–	11900	17600	1.479	11900	17700	1.487	28.31 *0.08*	25.54 *0.08*	2.77 *0.01*	29.92 *0.04*	26.87 *0.04*	3.05 *0.01*	0.032	0.033	0.213	0.241
PU-3-K	poly (urethane-metha-crylate) copolymer	TPED macrodiol	MMA	23820	36350	1.526	23720	36350	1.532	43.04 *0.11*	39.33 *0.11*	3.71 *0.02*	43.13 *0.10*	39.23 *0.10*	3.90 *0.02*	0.251	0.252	1.518	1.521
PU-4-K		HMB macrodiol	MMA	17400	38800	2.230	17350	38700	2.231	42.00 *0.08*	40.28 *0.08*	1.72 *0.01*	42.14 *0.06*	40.21 *0.05*	1.93 *0.01*	0.254	0.254	1.368	1.371

weight of the samples $\Delta m/m_o$ (%) was calculated using the following formula:

$$\frac{\Delta m_i}{m_{i,0}} = \frac{m_{i,0} - m_{i,t}}{m_{i,0}} \cdot 100\% \qquad (6)$$

where $m_{i,0}$, $m_{i,t}$ denotes the weight of dry sample i, before and after degradative incubation at time t.

The physical state of the surface of polymer samples before and after hydrolytic degradation was compared by using confocal microscopy with the optical 3D NanoFocus system.

Water sorption study

Water sorption S_i (%) was calculated according to the analogous equation (6), in which the $m_{i,t}$ – in this case is the weight of polymer sample immediately after removal from saline, after the degradative incubation at time t, drained in the filter paper.

Characterization techniques of the polymer structures

^{1}H and ^{13}C NMR spectra were taken with the use of the spectrometer FT-NMR Bruker Avance 500II (Bruker, Karlsruhe, Germany). The PU sample and copolymers were dissolved in DMSO-d_6/h-DMSO and the solutions with the concentration of about 0.2 g/dm³ were prepared. TMS was used as a standard.

Number-average (M_n) and weight-average (M_w) molecular weights and molecular weight distribution (MWD) were determined by GPC using a Viscotek T60A system (Viscotek, Houston, USA) equipped with a triple detector: refractometric (RI), light scattering (LS) and viscosity detector (DV). Separations were made at 25±0.1°C on a GMHHRL column packed with TSK-gel of pore diameter 5 μm Thoso-Haas, and Styragel 1 and 2 Waters. The THF flow rate was 1 mL/min. Column calibration was performed using typical polystyrene standards. The operation of the chromatograph was controlled by original computer software TRISEC Data Acquisition System by Viscotec Corporation.

Confocal microscopy

The physical state of the surface of polymer samples before and after hydrolytic degradation was compared using confocal microscopy with the optical *3D NanoFocus* system (Oberhausen, Germany) using the 320 x 320 mm objectives and magnification 50x. The nanometer precision resolution is based on the innovative confocal Multi--Pinhole-Technology in combination with the piezo module. Light source is a high efficiency LED, λ = 505 nm. Image acquisition module from *NanoFocus* system is a

fast digital camera with progressive scan technology, up to 55 fps, 512 x 512 Pixel, 10 bit and firewire.

With the use of the confocal microscopy the parameters of surface roughness grade of polymer coating before and after hydrolytic degradation were determined. Values of the coefficients of roughness R_a (arithmetic mean deviation of the assessed profile) and R_z (maximum height of the profile within a sampling length) were obtained from the *μsurf Premium software*.

Method for determination of components of surface free energy for solids

The physical parameters of the surface energy of a solid γ_S were found on the basis of the Owens-Wendt method which assumes that the surface free energy $\gamma_{S,L}$ may be presented as a sum of two components[24]:

$$\gamma_{S,L} = \gamma_{S,L}^d + \gamma_{S,L}^p \qquad (7)$$

where: $\gamma_{S,L}^d$ denotes surface energy connected with dispersion interactions and $\gamma_{S,L}^p$ – surface energy connected with polar acid-base interactions.

Equation (7) is generally applicable both to a solid phase, and the subscript of S is used then, and to a wetting liquid (standard liquid or tested liquid), with the subscript of L. The surface free energy (*SFE*) parameters for solids (*S*) and for liquids (*L*) interacting with those solids should satisfy the Owens-Wendt equation:

$$\gamma_L \cdot \frac{1 + \cos \Theta}{2} = \sqrt{\gamma_S^d \cdot \gamma_L^d} + \sqrt{\gamma_S^p \cdot \gamma_L^p} \qquad (8)$$

where Q is the experimentally found contact angle between a liquid drop and a solid surface under investigation. So, contact angles Θ were first measured for the surfaces of cationomer coatings with the use of 2 pairs of model liquids (water-diiodomethane) with known parameters of γ_L, γ_L^d and γ_L^p (Table 2)[25]. Then, equation (8) was used to calculate the values of γ_S^d and γ_S^p for the studied cationomers. The values of γ_S were calculated from equation (7).

The contact angles Θ were measured with the use of the method suggested by Zisman[26], i.e. by means of an optical goniometer (*Cobrabid Optica* – Warsaw) with a digital camera installed in the axial direction of its lens.

Table 2. Surface properties of model measuring liquids[25]

Model measuring liquid	Surface free energy parameters [mJ/m²]		
	γ_L	γ_L^d	γ_L^p
Water	72.8	21.8	51.0
Diiodomethane	50.8	48.5	2.3

Thermal analysis

Thermal gravimetric analysis of the samples of the obtained PU elastomer and poly(urethane-methacrylate) copolymer films before and after incubation was carried out using TGA/DSC1 thermobalance from Mettler Toledo. TG; $Dm/m = f(T)$ and DTG; $dm/dT = f(T)$ were derived. The measurement conditions were as follows: sample weight ~1.5 mg, gas flow –50 cm³/min, aluminium pan. The measurements were taken within the temperature range of 25–550°C, at a constant heating rate of 10 deg/min, in nitrogen.

A Mettler Toledo type 822[e] differential calorimeter (DSC) with Star[e] System software was employed to analyze the thermal properties of cured samples. The samples (10–40 mg) were placed in aluminum crucibles and placed in the measuring chamber. Initially, samples of the elastomers were heated up to 220°C at the rate of 10°/min to eliminate stresses, which possibly could be left after the molding process, and then they were cooled down to –60°C. After another 10 min, their progressive heating was initiated at the rate of 10 deg/min. The measurements were taken within the temperature range of from –60 to 220°C, in the environment of nitrogen, which was passed at the rate of 30 cm³/min. Meanwhile, in the case of copolymers measurements were taken within the temperature range of from –90 to 150°C.

RESULTS AND DISCUSSION

The chemical structures of the synthesized polyurethane elastomers (PU-1-E and PU-2-E) and poly(urethane--methacrylate) copolymers (PU-3-K and PU-4-K) were confirmed by ¹H NMR (Fig. 1, Table 3) and ¹³C NMR spectroscopy (Table 4). In the case of copolymer PU-3-K and PU-4-K, similar structures have been characterized respectively at work[22] and[14], but they are not the same results as the ones obtained by using other catalyst complexes.

Figure 2 shows structural fragments, which make the chains of (a–c) PU-1-E elastomer, (a, b, d) PU-2-E elastomer, (a, b, e) PU-3-K copolymer and (a, b, f) PU-4-K copolymer. These results of ¹H NMR and ¹³C NMR spectroscopy show that PU elastomers and poly-(urethane-methacrylate) copolymers were successfully synthesized.

For the initial assessment of the suitability of polyurethane as biomaterial there is an important test of resistance to hydrolytic degradation under the conditions similar to those existing in the body, or for example during the incubation in physiologic salt solution having an ionic strength similar to blood plasma. The change of mass of the test material over a longer period of time – at least several weeks has been observed as the basic criterion for such resistance. The results of performed examinations are shown in Figure 3.
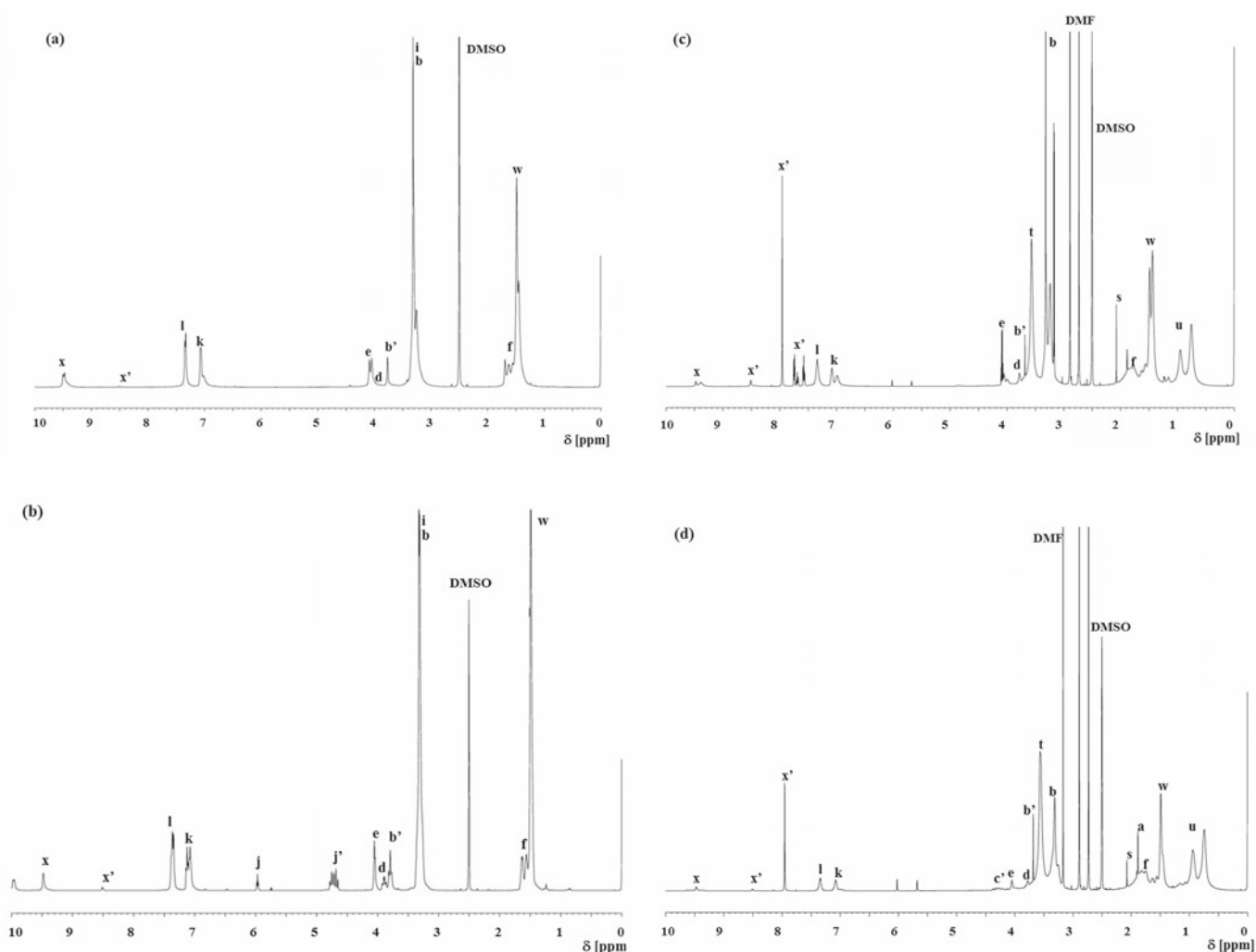

Figure 1. ¹H NMR spectra of (a) PU-1-E elastomer, (b) PU-2-E elastomer, (c) PU-3-K copolymer and (d) PU-4-K copolymer

They showed that in spite of the relatively small loss in weight of less than 1%, the values of the parameter synthesized PU elastomers were characterized by a significantly greater weight loss (about 1%) than the poly-(urethane-methacrylate) copolymers. If the mass loss of the PU-2-E sample obtained with TFBD is clearly smaller than the corresponding PU without fluorine, which is explained more hydrophobic of chains containing the fluorinated segments, meanwhile PU-3-K and PU-4-K copolymers exhibit a similar resistance to the hydrolytic degradation in studied conditions. The above results correspond to the results of determinations of sorption of water, which for PU is approximately 2.5% (for the fluorine-containing PU 2.05%), and for copolymers is at a range of 0.6–0.7%, which is presented in Figure 4.

The examined PU, although they are linear polymers about mainly of physical networks, resulting from the presence of hydrogen bonds, practically do not absorb water, so are strongly hydrophobic material in their mass.

Research carried out by NMR spectroscopy confirmed that the fundamental structure of these chains did not change during the incubation of samples in the physio-

Table 3. ^{1}H NMR data of polyurethane elastomers (PU-1-E and PU-2-E) and poly(urethane-methacrylate) copolymers (PU-3-K and PU-4-K)

Type of nucleus ^{1}H by Figure 1.	PU-1-E	PU-2-E	PU-3-K	PU-4-K
	Chemical shift [ppm]			
a	–	–	–	1.88–1.90
c'	–	–	–	4.32–4.37
x	9.47–9.50	9.48	9.35–9.50	9.49
x'	8.50	8.50	7.95–8.50	8.00–8.49
l	7.33–7.35	7.34–7.36	7.34	7.34
k	7.07	7.07–7.14	6.99–7.08	7.07
d	3.77	3.77–3.82	3.78	3.77
i	3.32	3.33	–	–
b	3.32	3.33	3.32	3.32
w	1.49	1.49	1.44–1.49	1.49
b'	3,68	3,68	3.58	3,68
f	1.62–1.64	1.62–1.64	1.56–1.71	1.57–1.64
e	4.05–4.09	4.04–4.05	4.01–4.05	4.04
w'	1.45	–	–	–
b"	3.24	–	–	–
j	–	5.96–5.98	–	–
j'	–	4.65–4.78	–	–
t	–	–	3.71	3.56
s	–	–	2.01–2.15	2.07
u	–	–	0.75–1.26	0.74–1.28

Table 4. ^{13}C NMR data of polyurethane elastomers (PU-1-E and PU-2-E) and poly(urethane-methacrylate) copolymers (PU-3-K and PU-4-K)

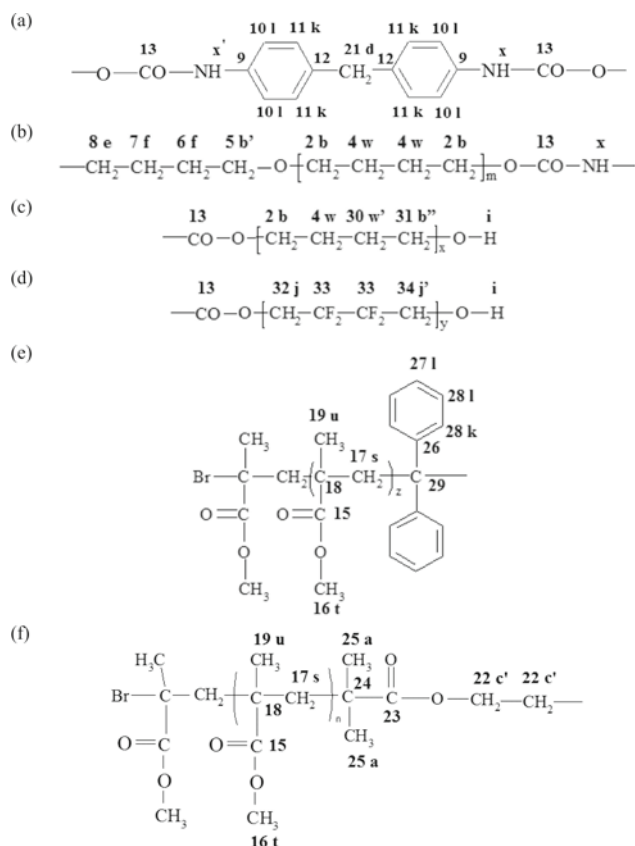| Type of nucleus ^{13}C by Figure 1.	PU-1-E	PU-2-E	PU-3-K	PU-4-K
	Chemical shift [ppm]			
21	40.00	39.00	38.94–39.94	38.93–39.93
13	153.46	153.48	162.10	162.20
9	135.31	135.14	135.59	135.66
10	118.15	118.51–118.19	117.98–118.17	118.16
11	128.68	128.72–128.88	128.49	125.65–128.73
12	138.92	137.58	137.56	137.06
2	69.60	69.67	69.65	69.62
4	25.97	25.99	25.99	25.99
5	69.34	69.38	69.37	69.36
6	25.45	25.49	25.48	25.48
7	25.64	25.65	25.65	25.65
8	63.79	63.81	63.69	63.81
30	25.15	–	–	–
31	63.58	–	–	–
32	–	69.31	–	–
33	–	58.44–59.08	–	–
34	–	63.80	–	–
15	–	–	176.08	177.27
16	–	–	51.52	51.62
17	–	–	52.65	53.58
18	–	–	43.82	43.81–44.18
19	–	–	16.01–21.01	15.89–18.51
29	–	–	83.40	–
28	–	–	129.51	–
27	–	–	126.12	–
26	–	–	136.93	–
25	–	–	–	30.67
24	–	–	–	48.50
23	–	–	–	176.07–177.27
22	–	–	–	63.81

(a)

Figure 2. Chemical structure of (a–c) PU-1-E elastomer, (a, b, d) PU-2-E elastomer, (a, b, e) PU-3-K copolymer and (a, b, f) PU-4-K copolymer
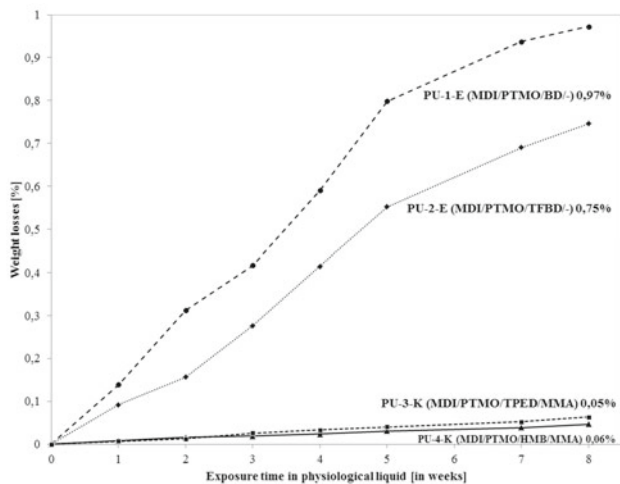

Figure 3. Relations of the weight losses [%] from the exposure time of films of PU elastomers and poly(urethane--methacrylate) copolymers in physiological liquid
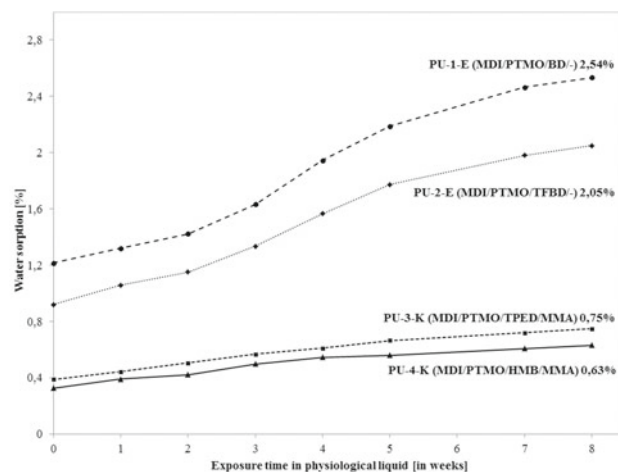

Figure 4. Relations of the water sorption [%] from the exposure time of films of PU elastomers and poly(urethane--methacrylate) copolymers in physiological liquid

logic salt solution, but about the course of degradation – although to a limited extent – shows the character of the molecular weight distribution of studied polymers derived from GPC chromatograms. The stated lack of significant differences in the NMR spectres of samples before and after exposure in the physiologic salt solution, which suggests that any structural changes are of very subtle nature, and it can be demonstrated only in the course of further quantitative analyzes.

M_n values and the determined degrees of polydispersity values of the studied polymers are given in Table 1. It is obvious that the applied method of the calibration of GPC columns based on polystyrene standards, isn't a reliable method for assessing the absolute values of the molecular weights of the resulting polymers, especially for poly(urethane-methacrylate) copolymers, of which fragments of chains differing in the polarity are probably in the different degree soluble in average polar eluent, which is THF. For this reason, the values of M_n and M_w may be lowered. This remark also applies to the apolar polyurethanes containing fluorine. However, the results of determination degrees polydispersity of molecular weights are rather correct and show that the values of M_w/M_n for the tested polyurethanes after exposition increase, but the increase for the copolymers is slight, which confirms their very favorable resistance to the effect of physiologic salt solution.

SFE measurements provide additional information relating to the surface of the tested samples (Table 5). They show that the polarity of the PU elastomers and
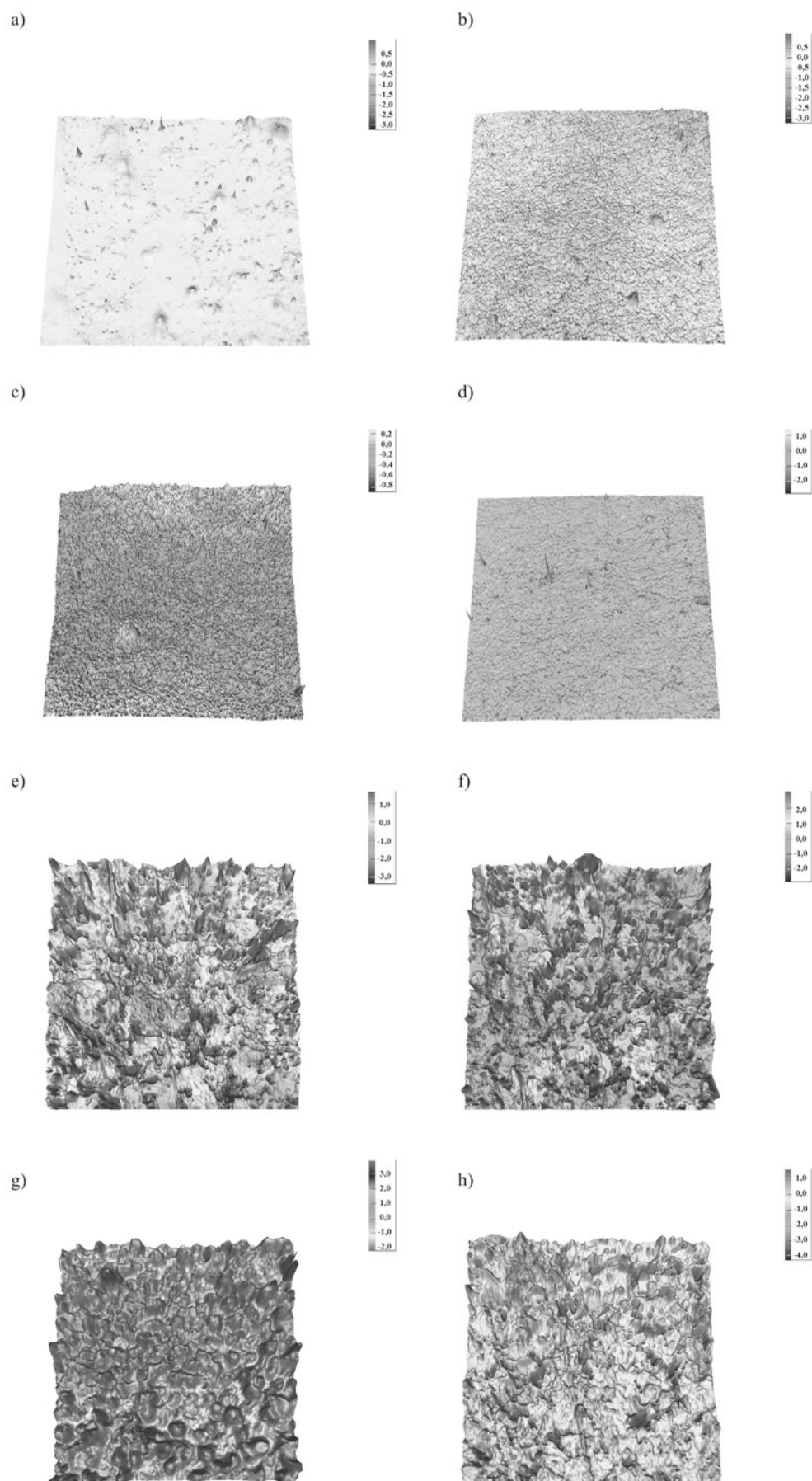
Table 5. Experimental values of contact angles, parameters of SFE as calculated by Owens-Wendt method for PU elastomers and poly(urethane-methacrylate) copolymers before and after exposure in physiologic salt solution

Sample No.	Experimental values of contact angles Θ [°] *Standard deviation*		Parameters of *SFE* [mJ/m²] *Standard deviation*		
	before exposure/after exposure				
	Model measuring fluids		γ_L^d	γ_L^p	γ_L
	CH₂I₂	Water			
PU-1-E	33.27/30.74 *1.357/1.650*	79.79/76.69 *0.893/0.747*	39.50/40.46 *0.09/0.10*	3.58/4.73 *0.01/0.01*	**43.08/45.19** *0.09/0.10*
PU-2-E	60.99/58.93 *1.246/0.643*	91.45/90.10 *1.253/0.536*	25.54/26.87 *0.08/0.04*	2.77/3.05 *0.01/0.01*	**28.31/29.92** *0.08/0.04*
PU-3-K	34.14/32.10 *1.550/1.268*	81.24/80.42 *1.744/1.973*	39.33/39.23 *0.11/0.09*	3.71/3.90 *0.02/0.02*	**43.04/43.13** *0.11/0.10*
PU-4-K	35.35/35.26 *1.030/0.507*	84.20/83.48 *1.700/1.735*	40.28/40.21 *0.08/0.05*	1.72/1.93 *0.01/0.01*	**42.00/42.14** *0.08/0.06*

Figure 5. Confocal images of the elastomers PU-1-E (a, b), PU-2-E (c, d) and copolymers PU-3-K (e, f), PU-4-K (g, h), in physi-ologic salt solution, were taken for the objects 320×320 μm and with magnification 50×

poly(urethane-methacrylate) copolymers is similar, and their value of the *SFE* is $\gamma_S = 42–43$ *mJ/m²*, in addition with a dominant contribution from dispersion interactions γ_S^d (90%), than the polar γ_S^d (below 10%). However, PU containing fluorine is definitely more hydrophobic: $\gamma_S = 28$ *mJ/m²*. This confirms the strong influence of fluorine on the change of the character of the polymer surface, described in our earlier work[27, 28]. However, there is no doubt – in view of the precision of the performed measurements – that *SFE* values of the surface of PU elastomer samples after incubation in physiologic salt solution grow about a few *m*J/m², and of copolymers only to a little, although clearly marked degree. As expected, the increase of γ_S^p component is relatively greater than the γ_S^d component, although the dispersion influences in each of the analyzed cases make a much greater contribution to the *SFE* of studied coatings. It can be concluded that the PU hydrolysis conditions are conducive to the formation of polar groups on the surface of polymer samples. Most likely, these groups are formed by hydrolysis of urethane bonds, always present in small quantities in PU urea bonds, as well as by limited hydrolysis of the ether bonds.

The hydrolysis of the above mentioned segments and bonds, has even a small effect on the morphology of the sample. On the first layer of polymer coating hydrolytic degradation takes place and with time, also within the interior of the sample. These changes can be imaged using a confocal microscope. The resulting images confirm the more diversified shape of the surfaces in the samples subjected to the hydrolytic degradation, but it is definitely more visible in the case of the samples of poly(urethane-methacrylate) copolymers, in spite of small changes in *SFE*. However, it must be noted that the surface morphology of these samples was also before degradation – as can be seen in Figure 5 – more diversified, and their surface is rougher, which is indicated by R_a and R_z parameters, determined by using the confocal microscope (Table 1). The values of these parameters for a given coating prepared from the given polymer after degradation is approximately 6 times higher, which can be explained as a result of grooving of the surface by rinsing of the hydrolysis products. The diverse morphology of PU coatings, and coatings derived from poly(urethane--methacrylate) copolymers is probably a result of the greater phase separation of generally polar segments derived from polyurethane and more hydrophobic polymethacrylic segments, than flexible polyol segments and and rigid urethane segments typical for PU elastomers. In addition, the information about possible changes in the structure and morphology of the studied samples can be obtained by analyzing their thermal resistance. The
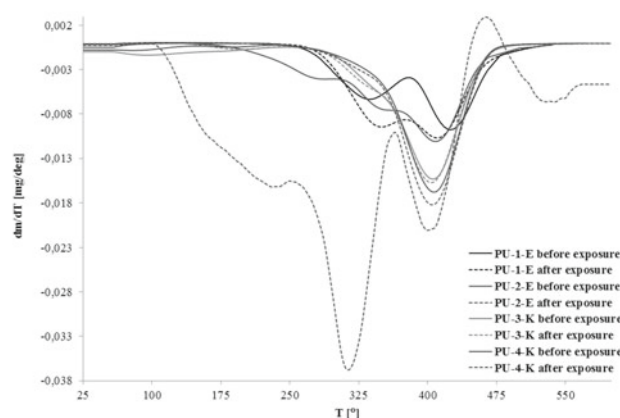

Figure 6. DTG thermograms for PU elastomers and poly--(urethane-methacrylate) copolymers before and after exposure in physiologic salt solution

TG and DTG thermograms for the samples before and after exposures were similar in nature, and only accurate quantitative analysis has revealed a small, but significant differences (Fig. 6). The results of these determinations are shown in Table 6.

The most complex thermal decomposition was observed for the PU-2-E fluorinated elastomer sample. It proceeded in three stages. In the first-stage (T = 278°C) the polymer has already lost about 17% mass. In the second-stage degradation occurs quickly, while in the third-stage destruction is already very deep and probably includes not only the polar aromatic urethane segments, but also more stable ether segments. From this point, in the decomposition of PU-1-E elastomer only 2 stages can be identified, a very rapid weight loss with a deep rapid degradation in the range of 300–400°C.

PU-2-E sample after exposure is less stable and its decomposition begins at 230°C. Also at a slightly lower temperature, but with similar performance about 51% losses of mass – as in samples before exposure – there are II and III stages degradation of this sample. Thermal decomposition of PU-1-E sample after exposure already occurs more quickly, i.e. with the greater loss of the mass, but the second-stage (for this sample it is indeed the first-stage) occurrs at a higher temperature by 10 deg (344°C), and the third-stage (for this sample it is also the second-stage) similarly has a significantly higher loss of the mass (about 50%), but it is noted at 407°C. The above analysis shows indirectly both significant differences in the mechanisms of the degradation of PU-1-E and PU-2-E samples, but also subtle, yet detectable changes in resistance of the elastomers after exposure in physiologic salt solution, which in turn proves the occurrence of certain structural changes, in addition differences in the course of exothermic effects recorded on the DTA

Table 6. Thermal stability of the PU elastomers and poly(urethane-methacrylate) copolymers before and after exposure in physiologic salt solution

| Sample No. | I stage degradation | | | | II stage degradation | | | | III stage degradation | | | | Summary mass loss in T = 600°C (%) | |
| | before exposure | | after exposure | | before exposure | | after exposure | | before exposure | | after exposure | | | |
	Mass loss [%]	T [°C]	Mass loss [%]	T [°C]	Mass loss [%]	T [°C]	Mass loss [%]	T [°C]	Mass loss [%]	T [°C]	Mass loss [%]	T [°C]	before exposure	after exposure
PU-1-E	–	–	–	–	32.22	333	40.99	344	49.70	422	52.04	407	87.92	93.03
PU-2-E	16.65	278	16.74	230	51.36	336	51.37	313	51.36	404	51,37	398	97.44	98.32
PU-3-K	–	–	–	–	15.25	329	16.08	327	81.20	406	80.44	404	96.45	96.52
PU-4-K	–	–	–	–	–	–	–	–	95.29	409	95.30	408	95.29	95.30

thermograms, in the range of registered degradation temperatures, evidenced by the changes in the structure which are difficult to detect such low inherently sensitive NMR method. From an analysis of the TG and DTG thermograms of poly(urethane-methacrylate) copolymer samples it results that the thermal decomposition occurrs definitely differently from PU elastomers, i.e. in one (PU-4-K) or in two (PU-3-K) clearly and explicitly registered stages, and there is practically no difference in the resistance to the thermal degradation of the samples before and after exposure in physiologic salt solution. It is very beneficial for potential applications of these copolymers as biomaterials, because it indicates about the structural stability of these polymers during their exposure to the conditions that may cause the effects of hydrolytic degradation.

DSC thermograms for the samples before and after exposures were similar in nature, which is reflected by
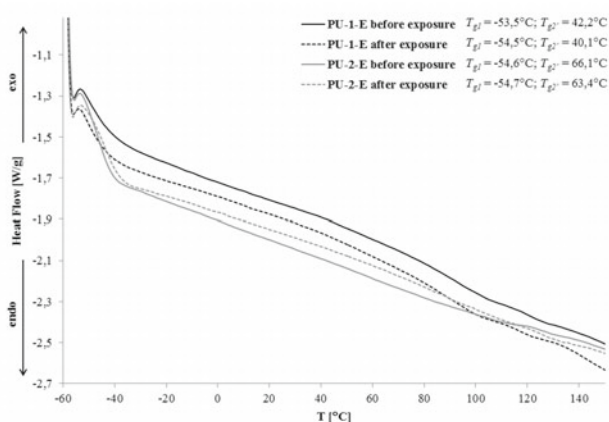

Figure 7. DSC thermograms for PU elastomers before and after exposure in physiologic salt solution
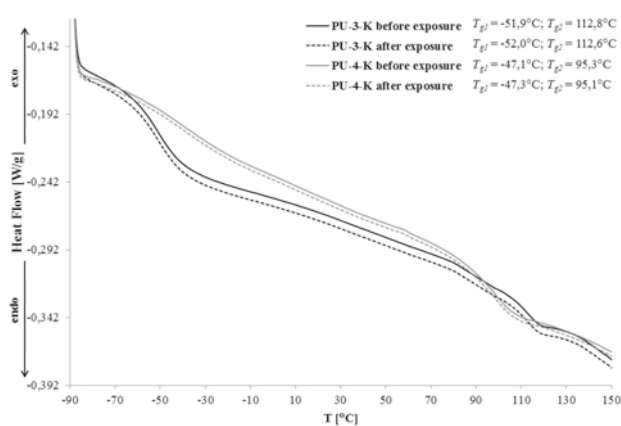

Figure 8. DSC thermograms for poly(urethane-methacrylate) copolymers before and after exposure in physiologic salt solution

virtually unchanged glass transition temperature values for positive and negative values Figure 7 and 8. As shown in Figure 7, the T_{g1} of the flexible polyol segments present in PU-1-E and PU-2-E elastomers are observed at –54 and –55°C, respectively. The T_{g2} of the rigid urethane segments is observed at 42 and 66°C, respectively. Furthermore, in the case of tri-block copolymers (Fig. 8) the DSC method analysis indicated a limited miscibility of phases containing rigid and flexible segments (forming the chain of the polymers under synthesis):

two separate areas were present, to which distinct ranges of glass transition temperatures (T_g) were assigned: T_{g1} = –47 – –52°C (corresponding to transitions in the flexible segments) and T_{g2} = 95 – 113°C (characteristic for phase transitions occurring within the rigid PMMA segments introduced into the PU macroinitiator chain).

CONCLUSIONS

The performed examinations confirm the described in the literature, good resistance to hydrolysis of PU elastomer synthesized with MDI, PTMO and BD. For this reason, coating made from PU elastomers is applied as special protective coatings to the materials of the natural origin and as biomaterials. However, they are definitely polar coatings with the *SFE* value above 40 *mJ*/m². Replacing part of hydrogen atoms by fluorine atoms by using as an efficient chains extension of urethane–isocyanate prepolymers TFBD in place of BD, causes substantial reduction of the polarity (*SFE*<30 *mJ*/m²), but at the same time the morphology of the sample surface becomes more diverse, the roughness of the coating grows, which may be disadvantageous for the applications of this type of PU (here we omit the issues of the possible harmful effects of fluoride on the human body, which wasn't the subject of our discussion). The applied research methods: gel permeation chromatography, confocal microscopy and thermogravimetric analysis allowed to demonstrate significant differences in the resistance to hydrolysis in the physiologic salt solution of these polymers, although the changes in their chemical structure are slight: the change in the weight of the samples during storage in the physiologic salt solution didn't exceed 1%, and water absorption – 2.5%. This kind of hydrolysis probably happens in the most vulnerable on structural changes places of polyurethanes, even though the initial structure of macromolecules and the segmented construction of PU can be considered to be generally stable, due to the structural and morphology analysis carried out by NMR and DSC methods.

On the above background, poly(urethane-methacrylate) copolymers as new materials synthesized by ARGET ATRP method in the presence of limited amount of air – allowing to control the size and polydispersity molecular weight of the polymer – create potential options for use as biomaterials with a slightly less polarity than PU elastomers. Here, there are great opportunities for further structural changes. Replacement of the urethane segments by more hydrophobic methacrylic segments contributes to an increase in the resistance to the hydrolysis of such block copolymers. The surface morphology of these materials is required in further research. Meanwhile, the confocal microscopy method demonstrated that it is highly variable, which has a large influence to the quality of biomaterial, because in the places of the inequality or structural dislocation, and faults of the phases built from the segments of different polarity the degradation processes can be initiated, causing pathological changes in the organ tissues being in contact with these areas.

ACKNOWLEDGMENT

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