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Influence of the content of hard segments on the properties of novel urethane–siloxane copolymers based on a poly(ϵ -caprolactone)-*b*-poly(dimethylsiloxane)-*b*-poly(ϵ -caprolactone) triblock copolymer

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Abstract: A series of novel thermoplastic urethane–siloxane copolymers (TPUSs) based on a α,ω -dihydroxy-[poly(ϵ -caprolactone)-*b*-poly(dimethylsiloxane)-*b*-poly(ϵ -caprolactone)] (α,ω -dihydroxy-PCL-PDMS-PCL) triblock copolymer, 4,4'-methylenediphenyl diisocyanate (MDI) and 1,4-butanediol (BD) was synthesized. The effects of the content (9–63 mass %) of hard urethane segments and their degree of polymerization on the properties of the segmented TPUSs were investigated. The structure, composition and hard segment degree of polymerization of the hard segments were examined using ¹H- and quantitative ¹³C-NMR spectroscopy. The degree of crystallinity of the synthesized copolymers was determined using wide-angle X-ray scattering (WAXS). The surface properties were evaluated by measuring the water contact angle and water absorption. In the series of the TPUSs, the average degree of polymerization of the hard segments was varied from 1.2 to 14.4 MDI-BD units. It was found that average values from 3.8 to 14.4 MDI-BD units were effective segment lengths for crystallization of hard segments, which resulted in an increase in the degree of microphase separation of the copolymers. Spherulite-like superstructures were observed in copolymer films by scanning electron microscopy (SEM), which are believed to arise from the crystallization of the hard segments and/or PCL segments, depending on the content of the hard segments. The surface of the copolymers became more hydrophobic with increasing weight fraction of PDMS. The synthesized copolymers based on a PCL-PDMS-PCL segment showed good thermal stability, which increased with increasing content of soft

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PDMS segments, as was confirmed by the value of the starting temperature of thermal degradation.

Keywords: urethane–siloxane copolymers; polyaddition; hard segment content; quantitative ^{13}C -NMR spectroscopy; thermal properties; X-ray scattering.

INTRODUCTION

Thermoplastic polyurethane elastomers (TPUs) have been used extensively as biomaterials because of their biocompatibility and good mechanical properties. TPUs are multiblock copolymers composed of rigid polyurethane sequences, hard segments (HS) connected *via* flexible soft segments (SS). A variety of aliphatic and aromatic diisocyanates with diol or diamine chain extenders have been employed for hard segment formation in polyurethane materials based on polyether or polyester macrodiols (typically of molecular weight $1000\text{--}5000\text{ g mol}^{-1}$) as the soft segment components.

The favorable physical properties of segmented TPUs are the consequence of microphase separation between the segments. The thermodynamic incompatibility of the hard and soft segments at low temperatures results in phase separation and, consequently, in the formation of a domain structure. It is believed that the hard segments, either glassy or crystalline with a melting temperature (T_m) above ambient temperature, form domains of approximately a few to tens of nanometers in size. These hard domains separate from the soft segments, which are usually formed of either low glass transition temperature (T_g) amorphous or low T_m crystalline segments. Their two-phase microstructure imparts excellent mechanical properties.^{1,2} TPUs that are made of crystallizable HS and SS resemble a unique crystalline–crystalline multiblock copolymer, where crystallization of each segment provides nanoscale confinement of the other. The morphology of semicrystalline TPU block copolymers is determined by the following factors: block lengths, chemical composition, the thermodynamic incompatibility between the constituent blocks and crystallization of crystallizable blocks.^{3–5}

The introduction of poly(dimethylsiloxane) (PDMS) into a polyurethane chain has the advantage of imparting some of the attractive properties of PDMS to the new polyurethane materials, such as high flexibility, biocompatibility, excellent thermal, oxidative and hydrolytic stability and low surface energy.^{6–11} PDMS prepolymer used for the preparation of siloxane–urethane copolymers have number average molecular weight (\bar{M}_n) values in the range $1000\text{--}5000\text{ g mol}^{-1}$. Due to substantial difference between the solubility parameters of PDMS and urethane hard segments, materials based on siloxane–urethane copolymers display the presence of microphase morphology. Early attempts of incorporating PDMS into a polyurethane backbone were unsuccessful due to the difficulty in the synthesis of TPUs with acceptably high molecular weights from a mixture of polar and non-polar components.¹² However, a mixed or special type of polyol

was used in order to increase the compatibility of the reaction mixture and, therefore, to achieve higher molecular weights and better mechanical properties.^{13–18}

In the past few years, significant research has been devoted to understand the correlation between microstructure and properties of segmented polyurethanes.^{19,20} Maafi *et al.* concluded that the structure of TPUs synthesized by two-step polyaddition method was more regular with narrower HS size distribution compared to the one-step method.²¹ Barreiro *et al.* studied the microstructure of poly(ester-urethane)s by experimental determination of the distribution of hard segments length using methods based on the hydrolysis of the polymer and subsequent size exclusion chromatography (SEC) analysis of the hydrolyzed products.²² However, until now ¹³C-NMR spectroscopy was used to examine the sequence distribution of hard segments in polyurethane copolymers in only a few research papers.^{23,24}

In a previous paper, the optimization of the synthesis of TPUSs with a high PCL-PDMS-PCL content was described.²⁵ In the present work, a series of novel urethane-siloxane copolymers based on an α,ω -dihydroxy-PCL-PDMS-PCL triblock copolymer, 4,4'-methylenediphenyl diisocyanate (MDI) and 1,4-butanediol (BD) was investigated. The triblock prepolymer contained terminal crystallizable poly(ϵ -caprolactone) blocks and a central poly(dimethylsiloxane) block. The combination of the properties of PCL and PDMS makes these block copolymers excellent candidates for employment as surface modifying additives in pharmaceutical and biomaterial applications.^{26–28} The content of hard MDI-BD segments in the polymer chains was varied from 9 to 63 mass %. Simultaneously, the length of the hard segments increased with increasing HS content. In this study, an analysis of the microstructure, *i.e.*, the determination of the distribution of hard segments length by quantitative ¹³C NMR spectroscopy, of urethane-siloxane copolymers is given. Hence, the influences of the content and average degree of the repeating units (MDI-BD) of the hard segments on the thermal, morphological and some physical properties of the synthesized TPUSs are presented in this paper.

EXPERIMENTAL

Materials

α,ω -Dihydroxy-(PCL-PDMS-PCL) (supplied by ABCR, Germany, $\bar{M}_n = 5700\text{--}6900$ g mol⁻¹) was dried at room temperature under vacuum for 2 h. The (\bar{M}_n) of the α,ω -dihydroxy-(PCL-PDMS-PCL), determined by ¹H-NMR spectroscopy, was 6100 g mol⁻¹. The molecular weights of the central PDMS block and the terminal poly(ϵ -caprolactone) sequences were 2000 and 2050 g mol⁻¹, respectively. 4,4'-Methylenediphenyl diisocyanate (MDI) (supplied by Aldrich), with an isocyanate content of 33.6 wt. %, was used as received. 1,4-Butanediol (BD) (from Aldrich) was purified by vacuum distillation. *N,N*-Dimethylacetamide (DMAc) (from Across) was dried over calcium hydride and then distilled under vacuum. The solvent tetrahydrofuran (THF) (supplied by J. T. Baker) was dried over lithium aluminum hydride and

distilled before use. Stannous octanoate ($\text{Sn}(\text{Oct})_2$) (purchased from Aldrich) was used as the catalyst without further purification.

Synthesis of polyurethane samples

The thermoplastic polyurethane copolymers were prepared by a two-step catalyzed polymerization in solution, starting from 4,4'-methylenediphenyl diisocyanate, 1,4-butanediol and α,ω -dihydroxy-(PCL-PDMS-PCL). All the copolymers were synthesized in the same manner under the optimal polymerization conditions:²⁵ the molar ratio of NCO/OH groups was 1.05/1, the amount of the catalyst was 0.15 mol % $\text{Sn}(\text{Oct})_2/\alpha,\omega$ -dihydroxy-(PCL-PDMS-PCL) and a mixture of DMAc/THF (1/1 v/v) was employed as the solvent. As an example, the synthesis of a copolymer with 87 mass % soft segment is described. A four necked round-bottom flask equipped with a mechanical stirrer, an inlet for dry argon, a reflux condenser and a dropping funnel was charged with 18.300 g (3.0 mmol) of α,ω -dihydroxy-(PCL-PDMS-PCL), 1.575 g (6.3 mmol) of 4,4'-methylenediphenyl diisocyanate, 60 mL of DMAc and 60 mL of THF. The flask was heated to 80 °C on a silicone oil bath and the reaction was started by the introduction of 0.29 mL of a solution of stannous octanoate in DMAc/THF (1.8 mg, 4.5×10^{-3} mmol of $\text{Sn}(\text{Oct})_2$). The reaction mixture was stirred for 40 min at 80 °C to prepare the NCO-terminated prepolymer. The content of NCO during reaction was determined using the dibutylamine back-titration method.²⁹ The reaction was stopped when the theoretical NCO content was attained (1.27 mass %).²⁵ For chain extension, a dilute solution of BD (0.540 g, 6.0 mmol) in DMAc/THF was added dropwise to the prepolymer with the addition of a second portion of MDI (0.785 g, 3.1 mmol) dissolved in DMAc/THF. The reaction was continued at the same temperature for 24 h. The viscous polymer solution was precipitated into methanol/water (1/1 v/v) and the polymer was filtered off and dried to constant weight in a vacuum oven at 40 °C for 3 days. Polyurethane films were prepared from a 10 mass % solution in DMAc and cast onto a Teflon[®] plate. The solvent was evaporated for 48 h at 40 °C in a force-draft oven. The films were obtained under vacuum at 40 °C for 24 h (0.4–0.5 mm thick) and stored in a desiccator.

Characterization

The NMR experiments were performed on Bruker Avance 500 spectrometer equipped with 5 mm inverse detection z -gradient probe. The ^1H - and ^{13}C -NMR spectra (at 500.13 and 125.75 MHz, respectively) were measured at 25 °C using $\text{DMSO}-d_6$ as the solvent. Chemical shifts are given on the δ scale relative to the residual DMSO signal. The copolymers were dissolved in $\text{DMSO}-d_6$ at 50 °C at a concentration of 10 % (w/v). The quantitative ^{13}C -NMR spectra were obtained using the gated decoupling method under the following conditions: pulse delay time of 10 s, an acquisition time of 1.10 s, a pulse width of 16.8 μs , a spectral width of 29.8 kHz and the number of scans was between 7000 and 21000.

The viscosities of solutions of the copolymers in DMAc were measured at 25 °C using an Ubbelohde viscometer. The intrinsic viscosities were calculated from these measurements.

Wide angle X-ray scattering (WAXS) was performed using a Diffractometric System APD 2000 diffractometer with CuK_α radiation using a copper anode (tube: 40 kV, 30 mA, $\lambda = 0.154178$ nm). The diffraction patterns were obtained in the Bragg angle range of 5–60°. The scan speed was 0.02 s per step in all measurements. The peaks in diffraction patterns were fitted by the Voigt deconvolution technique, using the Peakfit program, resulting in the areas of peaks. The percent crystallinity was calculated by peak deconvolution and subsequent determination of the relative areas under the amorphous halo and the crystalline peaks of the

X-ray diffraction pattern. The ratio of the area under the crystalline peaks to the total (amorphous + crystalline) area gave the degree of crystallinity.

The thermal stability of the copolymers was determined using TGA Q500 V6.3 Build 189 instrument in the temperature range from 25 to 700 °C, at a heating rate of 10 °C min⁻¹. The TGA scans were recorded under a dynamic nitrogen atmosphere with a gas flow rate of 50 mL min⁻¹. The average weight of the samples was about 10 mg.

The free or "air exposed" and cross-section morphology of the copolymer films was analyzed by field emission scanning electron microscopy (SEM). The samples were adhered to aluminum sample holders and sputter coated with Au to a thickness of *ca.* 5 nm (BAL-TEC SCD 005). The samples were then inserted into a JEOL JSM-6460LV microscope and the microphotographs were obtained at a working distance of *ca.* 14 mm at an acceleration voltage of 20 kV.

Water contact angle (WCA) measurements of the polymer films were realized in a Krüss DSA100 instrument using the sessile drop method. Single drops of distilled water with a volume of 20 µL were deposited on the film surface and the contact angles were measured after 30 s. All measurements were performed in air, at a temperature of 26 °C. The WCA measurements on polymer films were used to evaluate the surface properties and the wettability of the polymers by means of the sorption rate after 10 min (WCA_{10}) of deposition of the water droplet on the film surface. In all cases, at least five measurements were performed and the average contact angle was calculated.

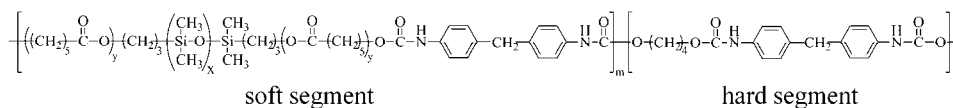
To determine equilibrium water content of the synthesized TPUSs, polymer films were immersed in phosphate buffered saline (PBS, pH 7.4) at 37 °C, for 2.5, 5, 8, 24, 26, 28 and 48 h, respectively. At each time point, the samples were removed and blotted lightly with filter paper to remove excess water. The weight of the hydrated samples was then determined and the water absorption was calculated as follows: $(w - w_0) \times 100 / w_0$, where w is the maximum wet weight measured and w_0 is the weight of the dry sample.

RESULTS AND DISCUSSION

A series of novel TPUSs was synthesized using PCL-PDMS-PCL as the soft segment component and MDI and BD as the hard segment components. The chemical structure of the synthesized polyurethanes is shown in Scheme 1. The samples were synthesized by a two-step polyaddition reaction in solution under optimized conditions.²⁵ In the synthesis of the TPUSs, the PCL blocks served as a compatibilizer between the non-polar PDMS blocks and the polar comonomers, MDI and BD. The TPUSs were synthesized first using an NCO-terminated prepolymer obtained from α,ω -dihydroxy-(PCL-PDMS-PCL) with slight excess of MDI and then chain extended with 1,4-butanediol to prepare the final TPUSs. The molar ratio of the α,ω -dihydroxy-(PCL-PDMS-PCL), MDI and BD was varied from 1:2:1 to 1:27:26 (Table I). The hard segment content of TPUSs was in the range of 9 to 60 mass %. The yields of the synthesized copolymers after precipitation were in the range of 85–93 % (Table I).

The structure and composition of the TPUSs

The molecular structure of the polyurethanes was investigated by ¹H and ¹³C NMR spectroscopy.



Scheme 1. The chemical structure of the synthesized polyurethane copolymers based on soft PCL-PDMS-PCL and hard MDI-BD segments.

TABLE I. Composition of the reaction mixture and the copolymers, the average degree of polymerization of the hard segments, intrinsic viscosities, yields and degree of crystallinity determined by WAXS of the synthesized TPUSs

Sample	Molar ratio ^a	Fraction of MDI-BD, HS units		L_n (HS) ^d	$[\eta]$ dL g ⁻¹	Yield ^e %	X_c / % (WAXS)
		mass % ^b	mass % (NMR) ^c				
TPUS-9	1:2:1	8.8	8.5	1.2	0.50	87	40
TPUS-13	1:3:2	13.2	15.3	1.7	0.55	85	36
TPUS-17	1:4:3	17.2	17.2	1.9	0.58	88	30
TPUS-21	1:5:4	20.9	19.9	3.8	0.61	90	26
TPUS-30	1:8:7	30.1	29.4	4.0	0.64	91	8 ^f ; 25 ^g
TPUS-40	1:12:11	39.5	38.4	4.7	0.67	91	9 ^f ; 16 ^g
TPUS-50	1:18:17	49.7	48.4	10.2	0.74	93	10 ^f ; 7 ^g
TPUS-60	1:27:26	59.8	62.6	14.4	0.83	92	13 ^f ; 5 ^g

^aPCL-PDMS-PCL:MDI:BD in the reaction mixture; at a 1.05 molar ratio of NCO/OH groups; ^bpredetermined by the composition of the reaction mixtures; ^cdetermined by ¹H-NMR spectroscopy; ^ddetermined by quantitative ¹³C-NMR spectroscopy; ^ecalculated after precipitation of the copolymers; ^fdegree of crystallinity of the MDI-BD segments; ^gdegree of crystallinity of the PCL segments

The ¹H-NMR spectra of the copolymers showed characteristic signals at chemical shift values: -0.04 ppm of the Si-CH₃ protons; 0.43 ppm of the Si-CH₂ protons; 1.27 ppm of the central CH₂ protons from the ϵ -caprolactone residues and the central CH₂ protons from the PDMS propylene groups; 1.51 ppm of the internal CH₂ protons from the ϵ -caprolactone residues; 2.25 ppm of the CH₂-COO protons from the ϵ -caprolactone residues; 3.96 ppm of the terminal CH₂ protons from the ϵ -caprolactone residues; 3.77 ppm of the CH₂ protons from the MDI residues; 1.70 and 4.09 ppm of the central and terminal CH₂ protons of the BD residues, respectively; 3.40 ppm of the CH₂-OOC protons from the PDMS propylene groups; 7.08 and 7.34 ppm of the aromatic protons and 8.50 and 9.50 ppm of the -NH urethane protons.

As an example, the ¹H-NMR spectrum of TPUS-60 is shown in Fig. 1.

The ¹³C-NMR spectra showed characteristic signals at the chemical shift values: 0.2 ppm of the SiCH₃ carbon; 24.1, 24.9 and 27.8 ppm of the central and internal CH₂ carbons from the ϵ -caprolactone residues; 60.4 and 63.5 ppm of the terminal CH₂ carbons from the PDMS propylene groups and terminal CH₂ carbons from the ϵ -caprolactone residues; 33.4 ppm of the CH₂-COO carbons from the ϵ -caprolactone residues; 25.3 and 63.7 ppm of the central and terminal CH₂ carbons from the BD residues; 40.0 ppm of the CH₂ carbon from the MDI resi-

dues; 153.6 and 172.7 ppm of the carbonyl carbons from the urethane and esters groups, respectively; 118.6, 129.1, 135.5 and 137.1 ppm of the aromatic carbons.

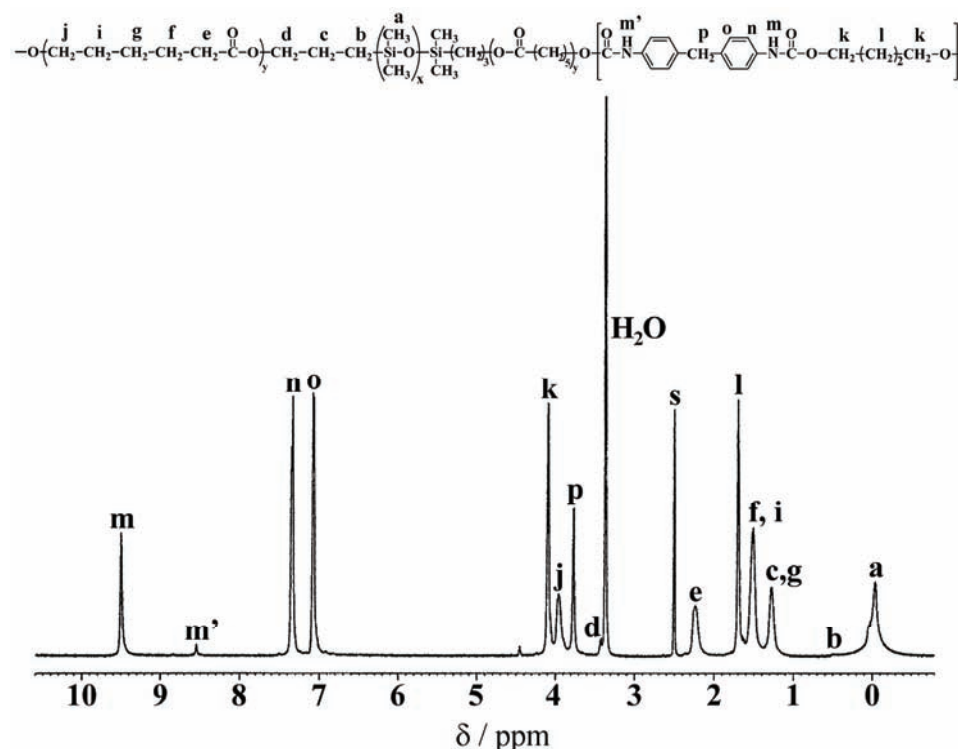


Fig. 1. $^1\text{H-NMR}$ Spectrum of the polyurethane copolymer with 40 mass % PCL-PDMS-PCL.

The composition of the polyurethanes, *i.e.*, the content of hard and soft segments, was calculated from the $^1\text{H-NMR}$ spectra as the relative intensities of the methyl proton signals arising from the $-\text{SiCH}_3$ groups and the aromatic proton signals from the MDI moieties. Thus, the mole and weight fraction of hard and soft segments were calculated, using the formulas:

$$x_{\text{HS}} = \frac{\frac{I(\text{Ar-H})}{8}}{\frac{I(\text{SiCH}_3)}{6X_x + 6} + \frac{I(\text{Ar-H})}{8}} \quad x_{\text{SS}} = 1 - x_{\text{HS}}$$

$$w_{\text{HS}} = \frac{x_{\text{HS}} M_{\text{HS}}}{x_{\text{HS}} M_{\text{HS}} + x_{\text{SS}} M_{\text{SS}}} \quad w_{\text{SS}} = 1 - w_{\text{HS}}$$

where: x_{HS} and x_{SS} are the mole fractions of hard and soft segments, respectively; w_{HS} and w_{SS} are the weight fractions of hard and soft segments, respec-

tively; $M_{HS} = 340 \text{ g mol}^{-1}$, the molecular weight of an MDI-BD unit; $M_{SS} = 6350 \text{ g mol}^{-1}$, molecular weight of a PCL-PDMS-PCL segment and $\bar{X}_x = 25.3$, the degree of polymerization of the PDMS-block in the prepolymer.

The theoretical and experimental mass % contents of the hard segments of the synthesized copolymers are presented in Table I. These results show that the weight fractions of the hard segments obtained from the $^1\text{H-NMR}$ analysis were in the range from 8.5 to 62.6 mass %. The obtained values of the weight fraction of the hard segments were in good agreement with values predetermined from the reaction mixture composition. For all the samples, except for TPUS-60, the disagreement was in the range of experimental error. It could be concluded that the composition of the polyurethanes was in good agreement with those expected from the composition of the feed, except for that of TPUS-60.

The NMR analysis showed that the syntheses of the polyurethane copolymers were successful, resulting in TPUSs with different lengths of the hard segments. The length of the hard segments in copolymer chains is defined as the number of repeating units $(\text{MDI-BD})_n$ (where $n = 1, 2, 3, 4, \dots$) and is designated as $L_n(\text{HS})$. The length of the hard segments, *i.e.*, the average degree of polymerization, $L_n(\text{HS})$, was calculated from the results of quantitative $^{13}\text{C-NMR}$ spectroscopy, which are given in Table I. The $^{13}\text{C-NMR}$ spectra of the non-protonated aromatic region for polyurethane copolymers with different HS content are shown in Fig. 2, from which it could be seen that the peaks of the original symmetrical aromatic carbon atoms contained in MDI split and different signals (**r**, **r'** at 134.9–135.5 ppm and **t**, **t'** at 137.1–137.7 ppm) resulted due to the existence of MDI-BD and MDI-PCL linkages.^{23,24} In addition, two signals, one at δ 152.5 and the other at δ 153.4 ppm that are related to $-\text{NHCOO}-$ were found, which could be attributed to the $-\text{NHCOO}-$ formed by reaction of MDI with 1,4-butanediol and with ϵ -caprolactone, respectively. The $L_n(\text{HS})$ was calculated from the ratio of the integral of the aromatic carbon signal from the MDI connected to 1,4-butanediol (**r**, Fig. 2) and that of the aromatic carbon signal from the MDI connected to ϵ -caprolactone (**r'**, Fig. 2). The synthesized TPUSs showed that the average hard segment lengths increased from 1.2 to 14.4 MDI-BD units with increasing HS content. According to the obtained results, $^{13}\text{C-NMR}$ analysis provides a relatively simple and reliable method to determine the microstructure of TPUS copolymers.

The results of the intrinsic viscosity, $[\eta]$, measurements of the polyurethanes are presented in Table I. The intrinsic viscosities values were between 0.50 and 0.83 dL g^{-1} . Increasing content of hard segments in the copolymer, *i.e.*, a decrease in the flexibility of the copolymer chains, led to an increase of the intrinsic viscosity.

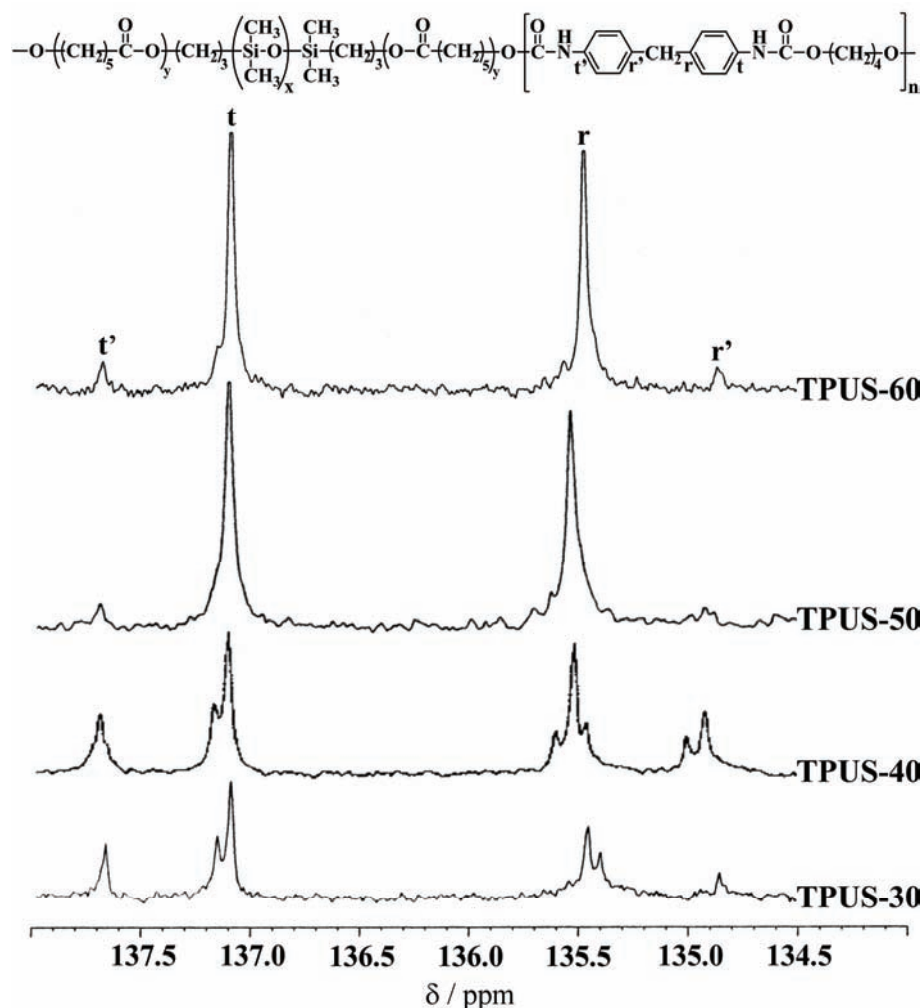


Fig. 2. Comparison of quantitative ^{13}C -NMR spectra of the polyurethane copolymers in the aromatic region showing the splitting for the non-protonated carbons.

Sequence length distribution of the TPUSs

In this study, the hard-segment length distribution in the obtained polyurethane copolymers was analyzed according to the Peebles statistical procedure,³⁰ assuming that the polyurethanes were formed by polyaddition reaction without side reactions and under stoichiometric conditions, and with the relative reactivity of the MDI groups $\mu = 1$. The calculated hard-segment length distributions are presented as weight and mole fraction distributions. Plots of the two distribution functions for several reaction mixture compositions are shown in Fig. 3.

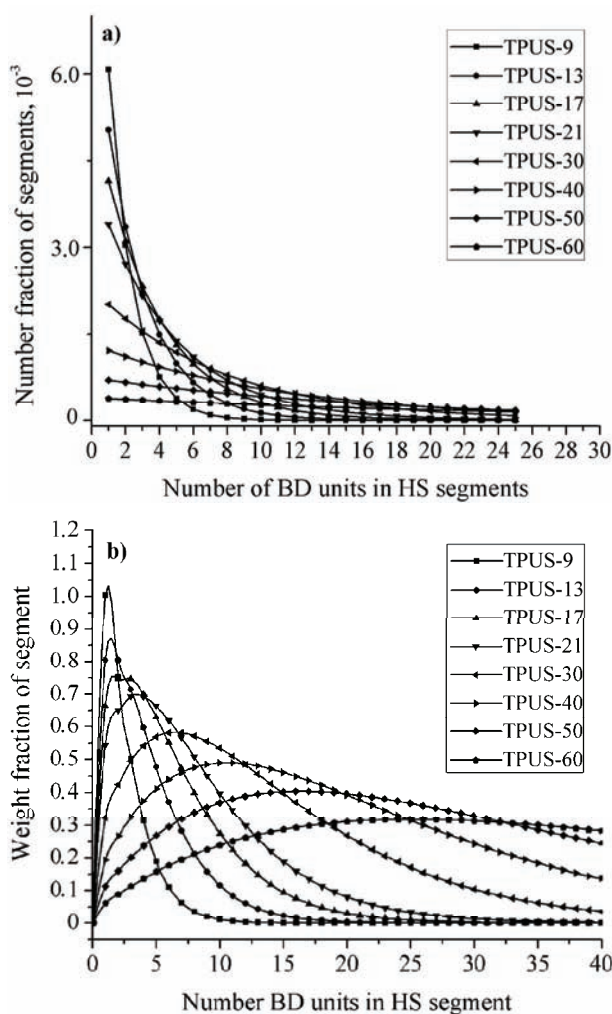


Fig. 3. Number fraction distribution curve (a) and weight fraction distribution curve (b) of the hard segment length for the TPUS copolymers.

The distribution of the sequence lengths, as was previously reported,³⁰ followed the most probable form:

$$P_i = C_1(1-p)^2 p^{i-1}$$

where P_i is the concentration of sequence lengths that contain exactly i extenders (BD) and $i+1$ MDI units, C_1 is the initial concentration of BD.

The weight fraction distributions were calculated from the weight fraction of MDI residues containing BD units, $(i+1) P_i / A_1$, and the weight fraction of the internal diisocyanate units X_1^{int}/A_1 , both normalized to the initial concentration of MDI, A_1 .

It can be seen that on a number basis there were more lone MDI units than any other HS units regardless of the copolymer composition. The weight fraction distribution shows that the most probable segment length increased from 2 to 26 with increasing hard segment content from 9 to 63 mass %. The average segment length was below 5 for the copolymers with a hard segment content of less than 40 mass %. The content of one MDI unit in the copolymer chains was reduced with increasing hard segment content. In addition, the polydispersity of the HS distribution increased with increasing hard-segment content. Higher contents of hard segments introduce longer sequence lengths into the polymer chains, which would promote microphase separation.

WAXS Analysis of the TPUSs

The information on the crystalline structure of the synthesized copolymers was obtained from WAXS measurements. The diffraction diagrams for the polyurethanes are shown in Fig. 4, from which it can be seen that all the TPUSs displayed three crystalline peaks at 2θ values of 21.31–21.66, 22.06–22.30 and 22.99–23.98°. The X-ray diffraction pattern of the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer displayed an amorphous halo from the PDMS block and three peaks at 2θ values of 21.21, 21.85 and 23.56°, which originated from the PCL blocks. For poly(ϵ -caprolactone), PCL, the presence of only one crystalline system, ortho-rhombic, was reported.³¹ Based on the combined X-ray and electron diffraction data, the unit cell of poly(MDI-BD) is triclinic with dimensions $a = 5.33$ Å, $b = 5.26$ Å, $c = 38.68$ Å, $\alpha = 113.6^\circ$, $\beta = 116.0^\circ$, $\gamma = 94.4^\circ$.³²

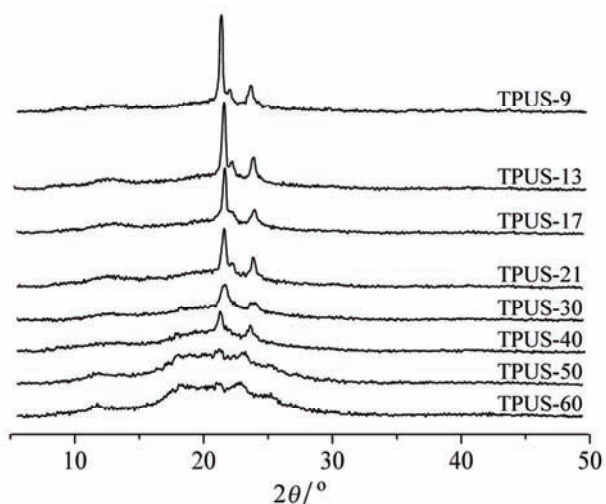


Fig. 4. X-Ray diffraction patterns of the synthesized polyurethane copolymers.

From the X-ray data and the peak positions in the diffractograms of the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer and TPUS copolymers, it may be

stated that the soft PCL-PDMS-PCL segments in the TPUSs formed a crystalline structure. This is due to crystallization resulting from the PCL component in the soft segments. The diffractograms of the TPUSs were very similar to the diffractogram of the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer and the main peaks occurred at almost the same 2θ values. Shifts in the peaks positions were observed for every copolymer, which could be attributed to deformations of the unit cell due to constraints imposed by the segmented structure and strong hydrogen bonds. In addition, it is visible that with increasing content of hard segments in the polymers, the areas of the crystalline peaks were reduced compared to the peaks from the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer. The X-ray diffraction patterns of the TPUS-30, TPUS-40, TPUS-50 and TPUS-60 samples displayed additional, not very sharp, peaks at 2θ 19.39 and 25.24°. ⁷ These peaks positions were reported in the literature for MDI-BD crystallinity. In all the TPUS diffractograms, an amorphous halo at 2θ 12° due to the presence of the PDMS blocks was also observed. The behavior clearly demonstrates that the PDMS blocks formed a completely separated phase in the copolymers at room temperature.

The WAXS analyses confirmed that the hard MDI-BD segments partially contributed to the total degree of crystallinity of the TPUS samples with a hard segment content between 20 and 63 mass %. It can be concluded that the average degree of polymerization from 3.8 to 14.4 MDI-BD units were effective segment lengths for the formation of crystalline hard segments. The degrees of crystallinity, X_c^{WAXS} , of the polyurethanes were in the range from 17 to 40 % (Table I), while the degree of crystallinity of the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer was 57 %. The value of degree of crystallinity of the HS tended to increase with increasing content of the hard segment length while the value of degree of crystallinity of the PCL-segments tended to decrease with increasing content and average degree of polymerization of HS (Fig. 5). The fact that the WAXS degree of crystallinity decreased with increasing weight fraction of MDI-BD hard segments in TPUSs was confirmed by the results of DSC analysis (to be published elsewhere). The total degree of crystallinity for TPUS-60, calculated from the DSC results, was the lowest in the series of copolymers and was around 30 %, from which it can be concluded that the presence of the hard segments probably disturbed the crystal growth of the PCL-segments. The synthesized TPUSs that consisted of crystallizable hard MDI-BD and soft PCL-PDMS-PCL segments were double crystalline copolymers.

A decrease in the crystallinity of segmented polyurethanes was previously reported for copolymers with different segment lengths of PCL,^{33,34} but a systematic verification of the influence of the polyurethane hard segment length on the morphology of the PCL-block was not addressed. In a general way, the observed decrease in the degree of crystallinity of the PCL phase with increasing

urethane content in the copolymers can be explained in terms of the restrictions introduced by the covalent linkages and, more importantly, by the presence of strong interchain interactions through hydrogen bonding.^{35,36}

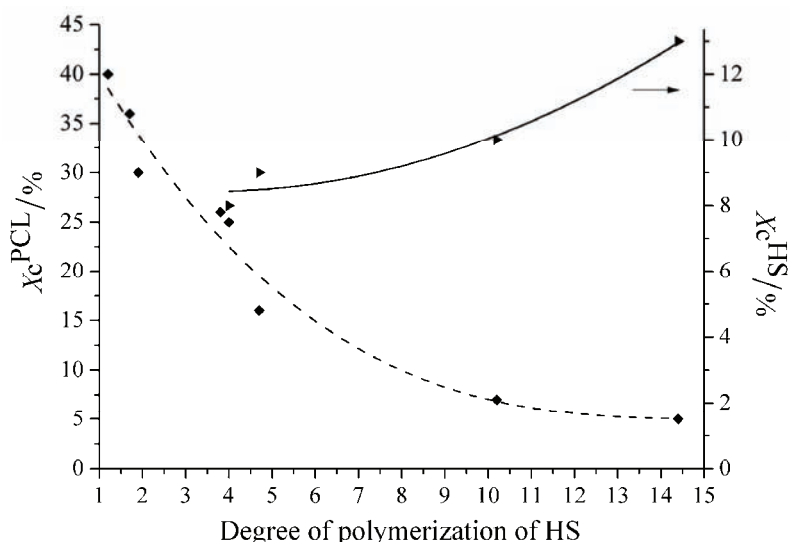


Fig. 5. Change in the degree of crystallinity of the PCL and hard segments determined by WAXS, as a function of the average degree of polymerization, L_n , of the hard segments.

TG analysis of the TPUSs

The thermal stability and degradation behavior of the synthesized polyurethanes were investigated by thermogravimetric analysis under a nitrogen atmosphere. The TG curves for the TPUSs with different contents of hard segments in the integral and differential form are shown in Figs. 6a and 6b, respectively. The characteristic temperatures for weight losses of 5 %, 50 % and 90 % as well as the residual weight at 600 °C are considered. The obtained results are given in Table II. The $T_{5\%}$ value is considered to represent the beginning of degradation.

The degradation of the copolymers commenced between 281 and 316 °C. From these data, it could be concluded that the thermal stability of the synthesized TPUSs depended strongly on the concentration of the urethane groups and decreased with increasing hard segment content in the copolymers. In addition, the temperature of 50 % weight loss in the TPUS series decreased with increasing content of hard segments. The thermally weakest link in polyurethane copolymers is the urethane bond, which starts to dissociate at around 200 °C. Three mechanisms of decompositions of urethane bonds have been suggested and the reactions may proceed simultaneously: dissociation to the original polyol and isocyanate, formation of a primary amine, an alkene, and carbon dioxide, and formation of a secondary amine and carbon dioxide.³⁷

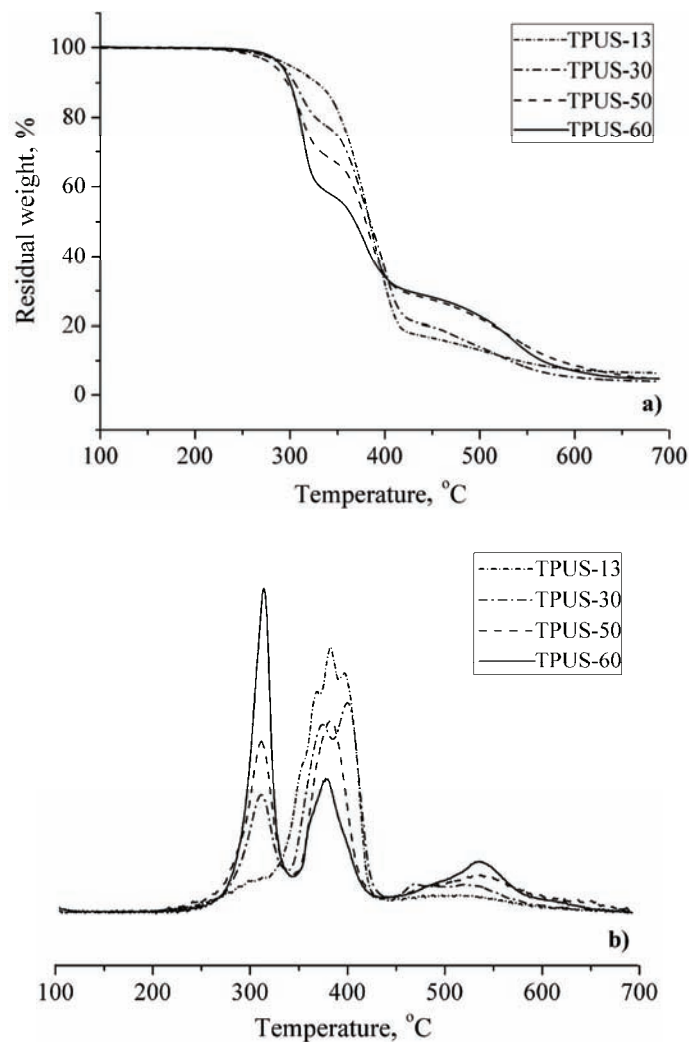


Fig. 6. TG and DTG curves for the polyurethane copolymers recorded at a heating rate of 10 °C under a nitrogen atmosphere.

The shapes of the weight loss curves of all the synthesized TPUSs were similar and overall differences in thermal stability appeared when the hard segment content increased. The thermal degradation of the synthesized TPUSs was a three-step process under a nitrogen atmosphere (Fig. 6b). The thermal degradation of the copolymers commenced *via* the decomposition of the urethane bonds, followed by degradation of the soft segments. Further decomposition in the region between 500 and 600 °C correlates with the aromatic content in the polyurethanes.^{37,38} The obtained results indicated that TPUSs based on PCL-PDMS-

-PCL are sufficiently stable to be melt processed, for example, by injection molding and extrusion.

Table II. Thermal stability of the synthesized TPUSs under a nitrogen atmosphere

Sample	$t_{5\%}$ °C	$t_{50\%}$ °C	$t_{90\%}$ °C	t_{\max} °C	Residual weight at 600 °C, %
TPUS-9	316	391	536	319/379/397/514	6.8
TPUS-13	306	391	548	310/376/391/515	7.6
TPUS-17	298	384	–	316/375/395/490	10.7
TPUS-21	301	394	538	316/374/399/525	6.8
TPUS-30	298	391	538	317/379/404/519	5.4
TPUS-40	286	386	555	313/383/538	6.3
TPUS-50	283	381	585	314/382/538	8.7
TPUS-60	281	367	555	318/382/538	4.8
α,ω -dihydroxy-(PCL-PDMS-PCL)	258	364	520	280/345/397/490	7.4

The residual weights of the TPUS samples at 600 °C ranged from 4.8 to 10.7 % (Table II). The residual weight originated mainly from the “organic”-fraction (MDI-BD and PCL), while the poly(dimethylsiloxane) chains under a nitrogen atmosphere degraded by depolymerization, giving cyclosiloxanes as the degradation products.³⁹

It could be concluded that introduction of siloxane prepolymer with terminal PCL sequences enhanced the thermal stability in comparison with TPUs based on poly(caprolactone)-*b*-poly(tetrahydrofuran)-*b*-poly(caprolactone) diol (PCL-PTHF-PCL).⁴⁰

Morphological investigation of the TPUSs by SEM

The “air” surface of the obtained films was investigated by SEM to observe any possible superstructure. The SEM microphotographs of the synthesized TPUSs and the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer are shown in Fig. 7. The SEM microphotograph of α,ω -dihydroxy-(PCL-PDMS-PCL) exhibited a spherulitic structure typical for a semicrystalline polymer. The SEM microphotographs of the polyurethane films displayed a distinct spherulitic-like structure. There was a significant difference in the morphology between the copolymers with 9–20 and 30–63 mass % hard segments. For this reason, microphotographs of TPUSs at different magnifications are shown in Fig. 7.

The polyurethane samples with a hard segment content below 30 mass % showed a spherulite-like structure that is believed to arise from the crystallization of the PCL segments only, which was also suggested by the WAXS results. The mean size of the PCL crystalline superstructures in the prepolymer was 125 μm , while in the polyurethanes with a hard segment content below 30 mass %, it was in the range 46 – 64 μm . With increasing hard segment content, an enhancement in the crystallinity of the hard domains was evidenced. Due to this, at hard seg-

ment contents above 30 mass %, the visible ball-like structure probably arose from crystallization of both hard and PCL segments, which could lead to spherulitic structures. The interconnection of the crystallites, visible in SEM the micrographs, was most likely the consequence of the increasing length of the hard MDI-BD segments (Fig. 7). The main size of these crystalline superstructures in the TPUSs with more than 30 mass % hard segment was in the range 1 – 14 μm . The lack of crystalline fibrillar growth in these structures might be due to non-uniformity of the hard segment lengths in the mentioned samples, thereby impeding longer range ordering, but this is only a supposition.⁴¹

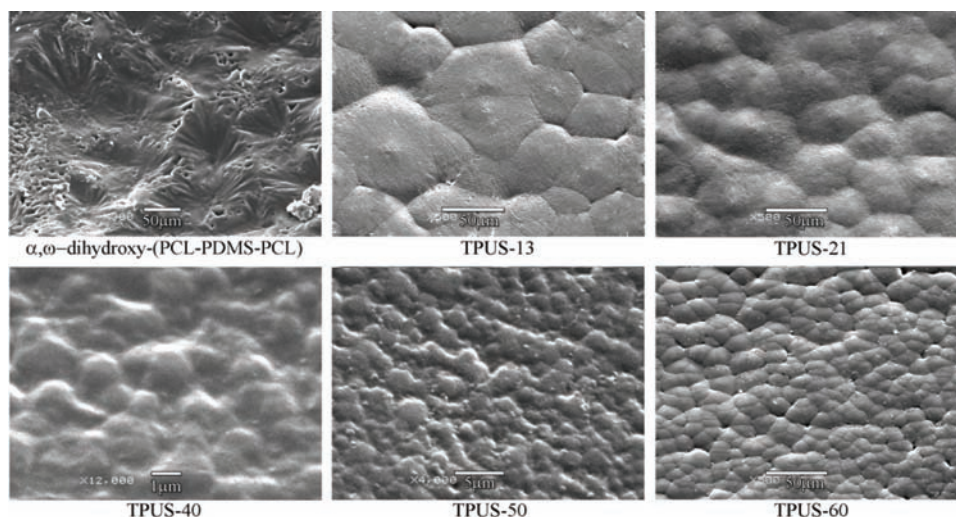


Fig. 7. SEM Microphotographs of the air surface of films of the polyurethanes and the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer.

In addition, Fig. 8 shows the cross-sectional morphologies of polyurethane copolymers with different HS contents. In addition, it could be seen that the TPUSs show a unique structure with spherulitic-like structure in the longitudinal cross-section.⁴² The average spherulite sizes in the TPUS copolymers were 2–4 μm . The spherulites of α,ω -dihydroxy-(PCL-PDMS-PCL) were 136 μm in size. The smaller size of the spherulites in the copolymer than in prepolymer can be explained by the introduction of the urethane block in polymer chains that restricts crystallization of the PCL-segments.

Water contact angle of the TPUSs

Special attention was focused on the wettability of the polyurethane surface, evaluated by water contact angle measurements (WCA). A water contact angle of 90° or more indicates a non-wetting surface. The relationship between the water contact angle and hard segment content is shown in Fig. 9, from which it can be seen

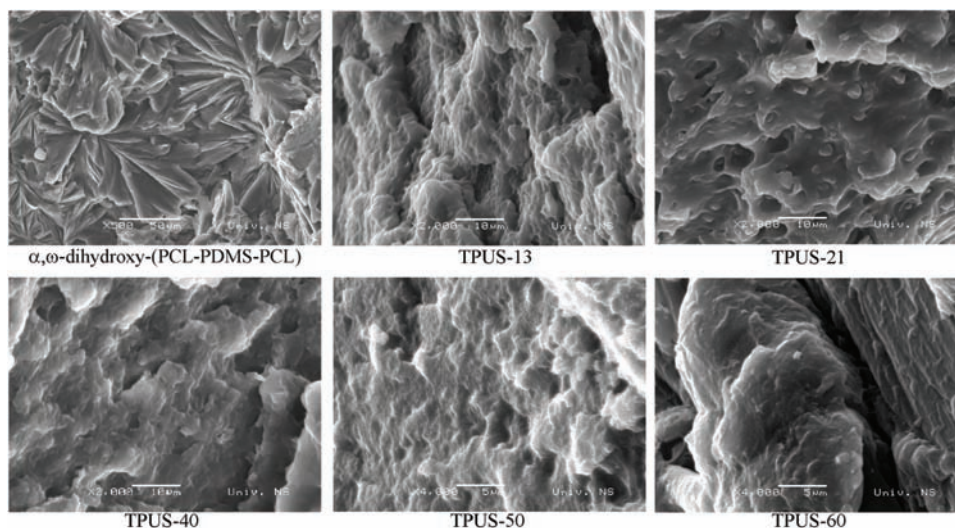


Fig. 8. SEM Microphotographs of the cross-section of films of the polyurethanes and the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer.

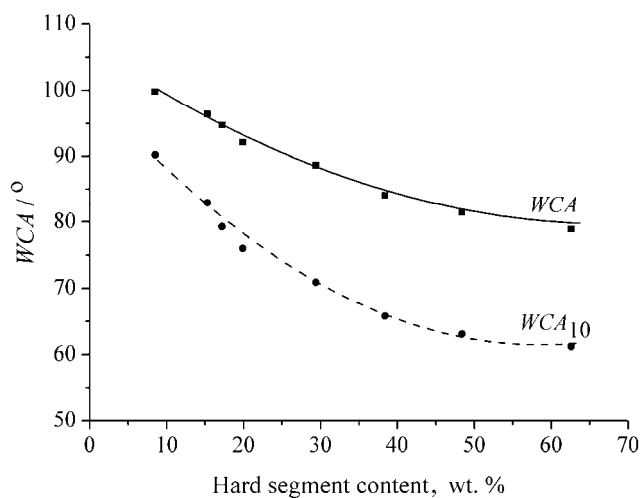


Fig. 9. Static water contact angle (WCA) and sorption rate (WCA_{10}) of the polyurethanes vs. hard segment content determined by $^1\text{H-NMR}$ spectroscopy.

that the value of the WCA for the TPUSs increased from 78.9 to 99.8° with increasing content of PDMS in the copolymers. The wettability of the copolymers decreased, *i.e.*, the hydrophobicity increased, with increasing weight fraction of PDMS. The water absorption rates of the TPUS samples, WCA_{10} , were measured after 10 min of the deposition of the water drop on the sample surface (Fig. 9), indicating that polyurethanes with higher HS contents absorbed the water drop more rapidly, decreasing their original values by 9.6 for TPUS-9 and 17.7 for TPUS-60. Thus, the polyurethanes with higher PDMS contents are more hydro-

phobic. The obtained results may be ascribed to the migration tendency of PDMS to the surface of the TPUSs, caused by the very low surface energy of PDMS.²⁶ The water contact angles for the TPUS-40, TPUS-50 and TPUS-60 samples were comparable with the contact angles of TPUs used in commercial implantable devices (75–80°) and culture grade polystyrene (80–85°).⁴³

Water absorption of the TPUSs

Water uptake for the TPUS samples in PBS at 37 °C as a function of time is shown in Fig. 10. The obtained results showed that water absorption increased slightly with increasing immersion times. The water uptake of the TPUS samples after 24 h was between 1.42 and 2.90 %, while it was 1.50 % for the prepolymer. The value of the water uptake for the TPUSs increased with decreasing content of PDMS in the copolymers. This occurred because PDMS in copolymer formed a hydrophobic surface, which caused the reduction in the water uptake of TPUSs. All the synthesized TPUSs absorbed water. However, in comparison with polyurethanes based on more hydrophilic polyols reported by other authors,⁴⁴ the synthesized TPUSs were considered rather hydrophobic due to the hydrophobic nature of the PDMS and poly(ϵ -caprolactone). Therefore, polyurethanes based on PDMS with its potent water resistant properties demonstrated a great promise for use as medical implant.¹¹

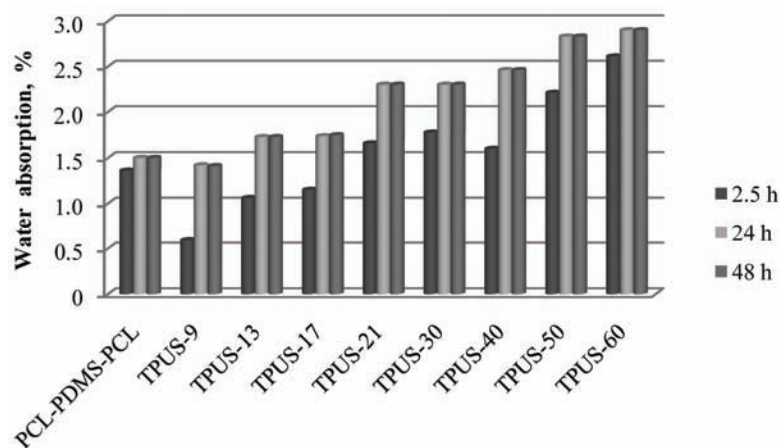


Fig. 10. Water absorption in dependence of the immersion time of the synthesized polyurethanes and α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer.

CONCLUSIONS

In order to investigate the influence of the hard segment length, *i.e.*, the average degree of polymerization, L_n , (MDI-BD) on the properties of TPUSs, novel thermoplastic siloxane–urethane copolymers based on biocompatible PCL-PDMS-PCL as soft segments with varying contents of hard segments were syn-

thesized. The weight fractions of the hard segments in the TPUS copolymers were in the range from 9 to 63 mass % and the average degree of polymerization of the hard segments varied between 1.2 and 14.4 MDI-BD units and was lower compared to the statistically calculated values. The increase in the HS degree of polymerization with hard segment content indicated that the chain-extension step in the synthesis of TPUSs was successful. The degree of crystallinity calculated from WAXS data was in the range from 17 to 40 %. The TPUS series represents a class of crystalline-crystalline block copolymers that consist of crystallizable hard and soft segments. Due to the increase in the degree of polymerization of the hard MDI-BD segments, the degree of crystallinity of the HS increased. It was found that an average number between 3.8 and 14.4 repeating MDI-BD units were effective segment lengths for a crystalline hard segment to be formed. As the HS content increased, there was a marked decrease in SS crystallinity. SEM images confirmed the presence of a spherulitic morphology, which arises from the crystallization of the hard segments and/or PCL segments depending on the content of the hard segments. The surface of the copolymers became more hydrophobic with increasing weight fraction of PDMS. The obtained results indicated that TPUSs based on soft PCL-PDMS-PCL segments are sufficiently stable to be melt processed, for example, by injection molding and extrusion. The synthesized TPUSs thus combine chemical, thermal, surface and morphological properties that might be employed in future biomedical applications.

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ИЗВОД

УТИЦАЈ САДРЖАЈА ТВРДОГ СЕГМЕНТА НА СВОЈСТВА НОВИХ УРЕТАН-СИЛОКСАНСКИХ КОПОЛИМЕРА НА БАЗИ ПОЛИ(ϵ -КАПРОЛАКТОН)-*b*-ПОЛИ(ДИМЕТИЛСИЛОКСАН)-*b*-ПОЛИ(ϵ -КАПРОЛАКТОНА)

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У овом раду приказана је структура и нека својства серије нових термопластичних уретан-силоксанских кополимера (TPUSs) на бази α,ω -дихидрокси-[поли(ϵ -капролактон)-*b*-поли(диметилсилоксан)-*b*-поли(ϵ -капролактон)] триблок кополимера (α,ω -дихидрокси-PCL-PDMS-PCL), 4,4'-метиленидифенилдиизоцијаната (MDI) и 1,4-бутандиола (BD). Испитан је утицај садржаја уретанског тврдог сегмента (9–63 мас. %) и његове дужине, тј. степена полимеризације, изражене преко броја MDI-BD остатака, на својства сегментираних TPUSs. Структура, састав и степен полимеризације тврдог сегмента су испитани помоћу ¹H- и квантитативне ¹³C-NMR спектроскопије. Степен кристаличности кополимера је одређен методом дифракције X-зрака на великим угловима (WAXS). Површинска својства кополимера су

испитана одређивањем контактних углова са водом и мерењем апсорпције воде. У серији кополимера дужина тврдог сегмента изражена преко броја понављајућих MDI-BD јединица је варирана од 1,2 до 14,4. Утврђено је да тврди сегменти са 3,8 до 14,4 понављајућих MDI-BD јединица ефикасно кристалишу, што је резултовало у повећању степена микрофазне сепарације кополимера. SEM анализа је показала присуство сферулитне структуре у кополимерним филмовима, која највероватније потиче од кристализације тврдих и/или PCL сегмената, зависно од садржаја тврдих сегмената. Хидрофобност површине кополимера је расла са повећањем масеног удела PDMS-а у одговарајућем узорку. Синтетисани полиуретани на бази PCL-PDMS-PCL показују повећање термичке стабилности са повећањем садржаја меких PDMS сегмената, што је потврђено порастом почетне температуре деградације, одређене TG анализом.

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