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Original scientific paper

Structural, thermal and surface characterization of thermoplastic polyurethanes based on poly(dimethylsiloxane)

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Abstract: In this study, the synthesis, structure and physical properties of two series of thermoplastic polyurethanes based on hydroxypropyl-terminated poly-(dimethylsiloxane) (HP-PDMS) or hydroxyethoxypropyl-terminated poly-(dimethylsiloxane) (EO-PDMS) as soft segments, and 4,4′-methylenediphenyl diisocyanate and 1,4-butanediol as hard segments were investigated. The polyurethanes were synthesized by two-step polyaddition in solution. The effects of the type and content of PDMS segments on the structure, thermal and surface properties of copolymers were studied by ^{1}H-, ^{13}C-nuclear magnetic resonance (NMR) spectroscopy and two-dimensional NMR spectroscopies (heteronuclear multiple bond correlation (HMBC) and rotating-frame nuclear Overhauser effect (ROESY)), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray scattering (WAXS), scanning electron microscopy (SEM) and water contact angle and water absorption measurements. Thermal properties investigated by DSC indicated that the presence of soft PDMS segments lowers the glass transition and melting temperatures of the hard phase as well as the degree of crystallinity. SEM analysis of the copolymers with a lower soft segment content confirmed the presence of spherulite superstructures, which arise from the crystallization of the hard segments. When compared with polyurethanes prepared from HP-PDMS, the copolymers synthesized from EO-PDMS with the same content of the soft segments had a higher degree of crystallinity, better thermal stability and a less hydrophobic surface. The obtained results showed that the synthesized polyurethanes had good thermal and surface

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properties, which could be further modified by changing the type or content of the soft segments.

Keywords: thermoplastic polyurethanes; poly(dimethylsiloxane); 2D NMR spectroscopy; thermal properties, surface properties.

INTRODUCTION

Thermoplastic polyurethane elastomers (TPUs) represent a group of heterogeneous biomaterials that have found a wide range of biomedical applications owing to their excellent mechanical properties, ability to be easily processed and relatively good biocompatibility.[1] TPUs are multi-block copolymers composed of a high molecular weight macrodiol, called a soft segment (SS), and a hard segment (HS) composed of a diisocyanate and a low molecular weight diol. The thermodynamic incompatibility between the hard and the soft segments results in a microphase separation at room temperature. Micro-domains rich in hard segments resulted from intermolecular interactions (*e.g.*, crystallization, hydrogen bonds), form so-called physical crosslinks and guarantee good mechanical strength, while the soft amorphous phase improves the flexibility of the polymeric material. By varying the type and molecular weight of the macrodiol, the chemical structure and symmetry of the diisocyanate, the HS/SS ratio, the polymerization method, and the crystallizability of both hard and soft segments, the mechanical and physical properties of TPUs could be tuned to the targeted values for specific clinical applications.[2–7]

Poly(dimethylsiloxane)s (PDMSs) were used as soft segments in various TPUs because of their low-temperature flexibility, high thermal and oxidative stability, good biocompatibility, water repellency, low surface tension, ultraviolet resistance, and high permeability of many gases.[8–11] At the beginning, TPUs based on PDMS exhibited poor mechanical properties due to the large differences between the solubility parameters of PDMS and the comonomers, which led to phase separation during the polyaddition reaction. However, in numerous subsequent papers, the preparation of thermoplastic polyurethane and polyurea copolymers based on the end-functionalized PDMS macrodiols, such as hydroxyhexyl-, aminopropyl-, and methylaminopropyl-PDMS, with a high molecular weight and good mechanical properties, were reported.[12–14] In order to avoid or reduce phase separation during the synthesis of PDMS-containing TPUs, several concepts were reported in the literature.[15–18] These concepts included mixing PDMS with conventional polyether or polyester macrodiols, the introduction of polar functionality into the PDMS, and use of PDMS–polyether or PDMS–polyester copolymers. In order to enhance the biostability of TPUs derived from the ethoxypropyl–PDMS macrodiol, reduction of the second polyether or polyester comonomer in the soft segment mixture is desirable.[19,20] TPUs containing PDMS segments have been employed in various biomedical applications,

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because they can significantly reduce nonspecific protein adsorption and thrombus formation.[21] In the past few years, a significant amount of research has been realized to understand the correlation between the microstructure and properties of TPUs because these factors are important for achieving the ideal properties for specific medical applications. According to the literature, the type of SS, chemical composition, surface hydrophilicity, degree of crystallinity, and surface topography have great effects on the biocompatibility of TPUs.[22–26]

Recently, an extensive study was published on the thermal, mechanical, surface, and biocompatibility properties of a series of TPUs based on poly(ε-caprolactone)-*b*-poly(dimethylsiloxane)-*b*-poly(ε-caprolactone) (PCL-PDMS-PCL) as soft segments with different hard segment contents.[27] The synthesized samples were double crystalline block-copolymers in which both hard and soft segments were crystallized. It was found that the degree of crystallinity, storage modulus, hardness, hydrophobicity, and the degree of microphase separation of copolymers all increased with increasing HS content. It was also found that the presence of the crystallizable PCL segments in the SS improved the biocompatibility of TPUs and that the copolymers, with a good microphase separation and having a non-toxic nature, might have potential application as implants in medicine. The combination of good elastomeric properties and biocompatibility of polyurethanes and PDMS makes these block copolymers excellent candidates for drug encapsulation and biomedical applications.

In the present study, two series of PDMS-based thermoplastic polyurethanes (TPUSs) with different ratios of hard to soft segments were synthesized by a two-step polyaddition reaction in solution. These two series differed in the type of functionality of the terminated PDMSs, which were incorporated into the polyurethane backbone as flexible segments. In the first series, a hydroxypropyl-terminated PDMS was employed for the synthesis of the novel TPUSs, while in the second series hydroxyethoxy propyl-terminated PDMS was used. The structures of the TPUSs were characterized by ^{1}H-, ^{13}C-nuclear magnetic resonance (NMR) spectroscopy and 2D-NMR, *i.e.*, COSY (correlation spectroscopy), HMBC (heteronuclear multiple bond correlation) and ROESY (rotating-frame nuclear Overhauser effect spectroscopy). The degree of crystallinity was determined by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS) analysis, while the thermal properties were examined by DSC and thermogravimetric analysis (TGA). The surface properties were investigated by scanning electron microscopy (SEM), and water contact angle and water absorption measurements. The effects of the type and content of the soft segments on the structural, thermal, morphological and some physical properties of TPUSs are presented.

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EXPERIMENTAL

Materials

α,ω-Bis(hydroxypropyl)poly(dimethylsiloxane) (HP-PDMS) and *α,ω*-bis[3-(2-hydroxyethoxy)propyl]poly(dimethylsiloxane) (EO-PDMS), supplied from ABCR, were dried over molecular sieves (0.4 nm) before use. The number average molecular weights, $\bar{M}_n$, of the HP-PDMS and EO-PDMS were calculated from ^{1}H-NMR spectroscopy results. The $\bar{M}_n$ of the prepolymer HP-PDMS was 960 g mol^{-1}, and for the prepolymer EO-PDMS 1000 g mol^{-1}. 4,4′-Methylenediphenyl diisocyanate (MDI) (from Aldrich) with an isocyanate content of 33.6 wt. % was used as received. 1,4-Butanediol (BD) (from Aldrich) was distilled and dried over molecular sieves before use. *N,N*-Dimethylacetamide (DMAc) (from Acros) was dried for 24 h over calcium hydride and distilled under reduced pressure before use. Tetrahydrofuran (THF) (from J. T. Baker) was dried over lithium aluminum hydride and distilled before use. Stannous octanoate ($Sn(Oct)_2$; from Aldrich), was used as a dilute solution in an anhydrous mixture of THF/DMAc (1:1, *V*/*V*).

Synthesis of the TPUSs

The TPUSs were synthesized by a catalyzed two-step polymerization in solution. The reactants were MDI, BD and *α,ω*-bis(3-hydroxypropyl)PDMS (TPUS1 series) or bis[3-(2-hydroxyethoxy)propyl]PDMS (TPUS2 series). Both series consisted of five samples prepared with different contents of soft segments. The last two numbers in the name of the TPUSs represent the weight percent of the hard segment. The molar ratio of the reacting –NCO groups (from MDI) and –OH groups (from the BD and PDMS prepolymer) was 1.05. The catalyst was stannous octanoate (0.15 mol % $Sn(Oct)_2$/PDMS prepolymer), while a mixture of DMAc/THF (1/1, *V*/*V*) was employed as the solvent.

The polymerization reactions were performed in a four-neck, round-bottom, Pyrex reaction flask equipped with a mechanical stirrer, an inlet for dry argon, a reflux condenser and a dropping funnel. A typical reaction procedure was as follows: the desired amounts of PDMS prepolymer and MDI were dissolved in DMAc/THF in the flask at room temperature and then heated up to 80 °C (for the TPUS1 series) or 40 °C (for the TPUS2 series) under an argon atmosphere. The reaction was started by the introduction of a solution of catalyst in DMAc/THF. The reaction mixture was stirred for 20 min at 80 °C (for the TPUS1 series) or 30 min at 40 °C (for the TPUS2 series) to prepare the NCO-terminated prepolymer, *i.e.*, until the theoretical NCO content was attained. The change in the NCO content during the reaction was monitored using the standard dibutylamine back-titration method.[28] In the second stage of the reaction, a dilute solution of BD in DMAc/THF was added drop-wise to the NCO-terminated prepolymer and the reaction was continued at 80 °C for 24 h (TPUS1 series) or at 50 °C for 24 h (TPUS2 series). The final polymer concentration was 25 wt. % for the TPUS1 and 15 wt. % for the TPUS2 samples. The reaction mixture was cooled down to room temperature and the copolymers were precipitated into a methanol/water (1/1, *V*/*V*) mixture, then washed several times with methanol, filtered and dried to a constant weight in a vacuum oven at 40 °C for 2 days. The yields of copolymers after precipitation in methanol/water mixture were in the range of 78.4–92.1 % for the TPUS1 samples and 86.5–94.2 % for the TPUS2 samples (Table I).

Preparation of TPUS films

The films were prepared by pouring the TPUS solution in DMAc (10 wt. %) onto a Teflon® dish (diameter 5 cm) and drying at 40 °C in a force-draft oven for 48 h. The films (typically about 0.5 mm thick) were then dried under vacuum at 40 °C for 24 h and stored in a desiccator at room temperature before characterization.

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Characterization

The NMR experiments were performed on Bruker Avance 500 spectrometer equipped with 5 mm inverse detection *z*-gradient probe. The ^{1}H- and ^{13}C-NMR spectra (at 500.13 and 125.75 MHz, respectively) were measured at 25 °C using DMF-d_7 as the solvent. Chemical shifts are given on the δ scale relative to the solvent DMF signal. The quantitative ^{13}C-NMR spectra were obtained using the inverse gated decoupling method under the following conditions: pulse delay time, 10 s; acquisition time 1.10 s; pulse width, 16.8 μs; spectral width, 29.8 kHz and number of scans, ≈10000. The 2D NMR experiments, such as COSY, HMBC and ROESY were performed with standard Bruker pulse sequences. COSY was collected with eight scans per 512 increments, while HMBC and ROESY were collected with 16 scans per 512 increments.

TABLE I. Composition of the reaction mixture and the copolymers, the average degree of polymerization of the hard segments and yields of the synthesized TPUSs

Polymer	Molar ratio[a]	SS, mol % (in feed)[b]	SS, mol % (NMR)	SS, mol % (in feed)[b]	SS, mol % (NMR)	L_n (HS) (NMR)[c]	Yield, %
TPUS1-20	1:2:1	50.0	41.4	78.1	71.5	1.3	78.4
TPUS1-35	1:3:2	33.3	30.2	64.0	60.6	2.0	88.3
TPUS1-45	1:4:3	25.0	23.8	54.3	52.7	2.9	90.2
TPUS1-50	1:5:4	20.0	19.5	47.1	46.2	3.4	91.7
TPUS1-55	1:6:5	16.7	16.5	41.6	41.2	3.9	92.1
TPUS2-20	1:2:1	50.0	54.9	78.6	78.2	1.4	86.5
TPUS2-35	1:3:2	33.3	36.9	64.8	63.3	2.1	89.9
TPUS2-45	1:4:3	25.0	27.5	55.1	54.7	3.0	92.6
TPUS2-50	1:5:4	20.0	21.2	47.9	45.2	3.5	93.1
TPUS2-55	1:6:5	16.7	23.0	42.4	40.4	4.4	94.2

[a]PDMS:MDI:BD in the reaction mixture at a 1.05 molar ratio of NCO/OH groups; [b]predetermined by the composition of the reaction mixtures; [c]determined by quantitative ^{13}C-NMR spectroscopy

The intrinsic viscosities ([η]) were measured in an Ubbelohde viscometer at 25 °C using DMAc as the solvent.

A Waters 1525 GPC system (Waters, Milford, MA), consisting of two Styragel columns (HR 1 and HR-5E columns, 4.6 mm×300 mm each, Waters, Milford, MA) connected in series, a binary HPLC pump, a Waters 717 plus autosampler and a Waters 2414 refractive index detector, and BreezeTM software were used to compute molecular weight distribution of the TPUS1 samples. Sample solutions of the TPUS1 series in THF at a concentration of 10 mg mL^{-1} were filtered through a 0.45 μm hydrophobic fluoropore (PTFE) filter (Millipore Corporation, Bedford, USA) before injection into the GPC system and eluted with THF at 40 °C at a flow rate of 0.3 mL min^{-1}. The system was calibrated with a number of polystyrene standards ranging from 3680 to 570000 g mol^{-1}. It is important to note that due to the insolubility of the TPUS2 samples in THF, DMAc was used as the mobile phase. The GPC chromatograms of TPUS2 samples were obtained on a Waters 600E instrument equipped with a refractive index detector and three Supelco Pl-Gel columns under similar conditions.

The DSC measurements were conducted on a DSC Q1000V9.0 Build 275 thermal analyzer. The TPUSs were analyzed under a dynamic nitrogen atmosphere (flow rate: 50 mL min^{-1}) in the temperature range from –90 to 230 °C at a heating and a cooling rate of 10 and 5 °C

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min^{-1}, respectively. The weight of the samples was approximately 5 mg. All details of the calculation of degree of crystallinity from DSC results, are described in the literature.[17,27]

TGA was performed using a TGA Q500 V6.3 Build 189 instrument under a dynamic nitrogen atmosphere (flow rate: 50 mL min^{-1}), in the temperature range from 25 to 700 °C at a heating rate of 10 °C min^{-1}. The average weight of the samples was around 10 mg.

The WAXS measurements were realized using a Diffractometric System APD 2000 diffractometer with Cu K_α radiation using a copper anode (tube: 40 kV, 30 mA, λ = 0.154178 nm). The diffraction patterns were obtained in the Bragg angle range of 5–50°. The scan speed was 0.02 s per step for all measurements. The degree of 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 scanning electron microscopy (SEM) microphotographs were obtained on JEOL JSM-6460LV instrument, at a working distance of *ca.* 14 mm and an accelerating voltage of 20 kV.

The water contact angles were determined on Krüss DSA100 using the sessile drop method. The measurements were performed at 22 °C, 30 s after deposition of single drops (20 μL) on the sample surface. The average value of five measurements was used.

Water absorption was investigated at room temperature by sample immersion in phosphate buffered saline (PBS, 1.5 mM KH_2PO_4, 6.5 mM Na_2HPO_4, 2.7 mM KCl, 0.14 M NaCl, pH 7.4, Acros Organics) at 37 °C, for 1, 2.5, 4, 6, 24, 28 and 48 h. At each time point, the samples were removed and blotted with filter paper to remove excess water and weighed. The average value of three measurements for each sample was used. The weight percent of the water absorption was calculated as follows:

$$\text{Water absorption} = 100\frac{w_t - w_0}{w_0}$$

where w_t is the weight of the hydrated sample after time t and w_0 is the weight of the dry sample.

RESULTS AND DISCUSSION

Two series of thermoplastic polyurethane copolymers based on α,ω-bis(3-hydroxypropyl)PDMS or α,ω-bis[3-(2-hydroxyethoxy)propyl]PDMS as soft segments and MDI–BD as hard segments were synthesized by catalyzed two-step polyaddition in solution under optimized conditions. Each series was composed of five samples of different soft segment contents (40–80 wt. %). The molar ratio of the PDMS prepolymer, MDI and BD, predetermined by the composition of the reaction mixture, was varied from 1:2:1 to 1:6:5 (Table I). The chemical structures of the segmented TPUSs based on HP-PDMS and EO-PDMS are presented in Fig. 1. The content and the type of the soft segments were varied to investigate the influence of these variables on some properties of the synthesized TPUSs, which could be optimized and adjusted for a specific medical application of the copolymers.

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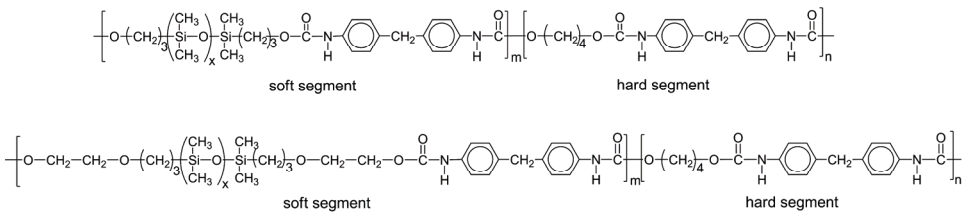

Fig. 1. Chemical structures of the polyurethane copolymers based on HP-PDMS or EO-PDMS soft segments.

Synthesis of TPUSs using an end-functionalized PDMS as a single soft segment is very difficult to realize, due to the extremely high immiscibility of polar urethane components with a non-polar PDMS prepolymer. In the synthesis of the second series samples, the terminal ethoxy units served as compatibilizers between the non-polar PDMS macrodiol and the polar comonomers, *i.e.*, MDI and BD. Optimization of the reaction conditions was performed at different times of the polyaddition reaction, at different reaction temperatures (40, 60 and 80 °C), and at different concentrations of reactants in the reaction mixture (15, 20 and 25 wt. %). The course of the first stage of the polyaddition was monitored using the standard dibutylamine back-titration method. Theoretically, the end of the first stage of the reaction was at 5.8 wt. % (TPUS1 samples) and at 5.6 wt. % (TPUS2 samples) of free NCO groups. According to the titration results, the reaction was very rapid and the values were attained after 20 and 30 min for TPUS1 and TPUS2 samples, respectively. Progress of the second stage of polyaddition reaction was assessed through the changes of intrinsic viscosities of the final copolymers. The optimal reaction temperatures to obtain the highest intrinsic viscosities were 80 °C for the TPUS1 and 40 °C for TPUS2 series. The optimal concentrations of reactants to obtain the highest intrinsic viscosity were 25 wt. % for the TPUS1 samples and 15 wt. % for the TPUS2 samples and the optimal time for the second stage of the reaction was 24 h for all the samples. These results indicate that the prepolymer EO-PDMS reacts more rapidly with MDI and BD than the HP-PDMS prepolymer, probably due to the presence of terminal ethoxy units. DMAc/THF (1/1, *V*/*V*) mixture was shown to be an excellent reaction medium for all the syntheses in this study.

NMR analysis of the structure and composition of the TPUSs, the intrinsic viscosity measurements and GPC analysis

In order to investigate the molecular structure of the synthesized TPUSs, ^{1}H-NMR, ^{13}C-NMR, and the two-dimensional NMR (COSY, HMBC and ROESY) analyses were performed. Representative ^{1}H-NMR spectra of the TPUSs with 45 wt. % HP-PDMS and 80 wt. % EO-PDMS soft segments are shown in Fig. 2.

In ^{1}H-NMR spectra, the signals of the $SiCH_3$ protons appeared in the region 0.2–0.3 ppm. The methylene protons attached to the silicon were at 0.62 ppm, and

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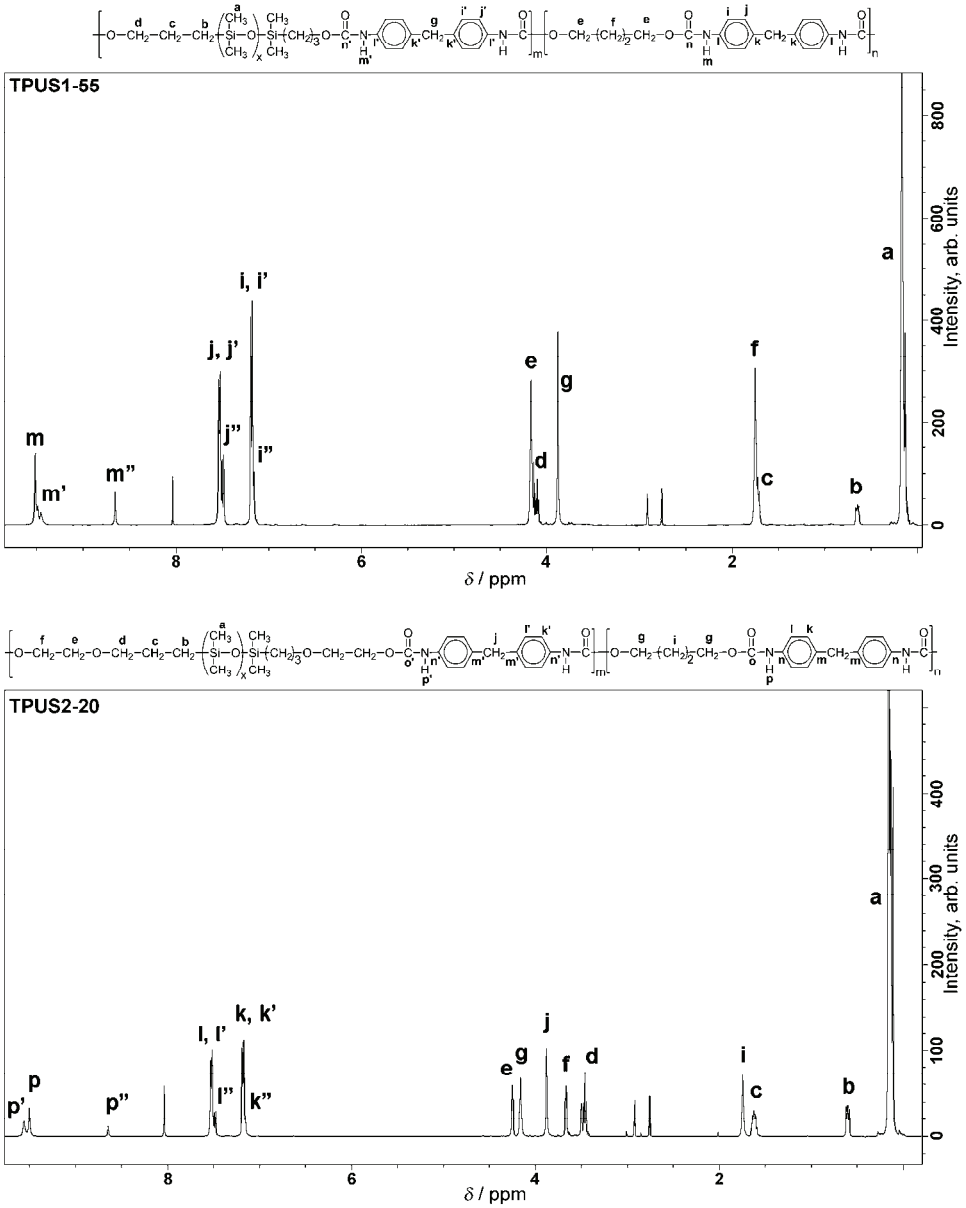

Fig. 2. ^{1}H-NMR spectra of the TPUSs with 45 wt. % of HP-PDMS and with 80 wt. % of EO-PDMS soft segments.

the central methylene protons from PDMS propylene groups were at 1.60 ppm. The signals of the methylene protons from PDMS propylene groups connected to the oxygen atom appeared at 3.55 ppm. The proton resonances at 1.77 and 4.16

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ppm originated from the central and terminal methylene groups from the BD residues. The signal of the methylene protons from the MDI residues appeared at 3.88 ppm. Proton resonances at 7.18 and 7.51 ppm from the aromatic protons, and at 8.64, 9.50 and 9.56 ppm from the urethane –NH protons in the soft and hard segments were observed. In ^{1}H-NMR spectra of the samples from the TPUS2 series, the signals of the methylene protons from the ethylene oxide residue appeared at 3.67 and 4.25 ppm.

The composition of TPUSs was determined from the ^{1}H-NMR spectra as the relative intensities of the Si–CH_3 protons signals and signals of the aromatic protons arising from the MDI moiety. The mole and weight fractions of the soft and hard segments were calculated using these formulas:

$$x_{SS} = \left[\frac{\left(\frac{I(\mathrm{SiCH_3})}{6\bar{X}_x + 6} \right)}{\left(\frac{I(\mathrm{Ar\text{-}H}}{8} \right)} \right]; \; x_{HS} = 1 - x_{SS}$$

$$w_{SS} = \frac{x_{SS} M_{SS}}{\left(x_{SS} M_{SS} + x_{HS} M_{HS} \right)}; \; w_{HS} = 1 - w_{SS}$$

where: x_{SS} and x_{HS} are the mole fractions of the soft and hard segments, respectively; w_{SS} and w_{HS} are the weight fractions of the soft and hard segments, respectively; M_{SS}, 1210 or 1250 g mol^{-1}, represents the molecular weights of the soft segments, *i.e.*, MDI–HP-PDMS and MDI–EO-PDMS segments, respectively; M_{HS}, 340 g mol^{-1}, is the molecular weight of the MDI–BD unit; $\bar{X}_x$, 10.6 and 9.95, stands for the degrees of polymerization of the PDMS-block in the HP-PDMS and EO-PDMS prepolymers, respectively.

The values for the weight fraction of the soft segment ranged from 41.2 to 71.5 % for TPUS1 samples and from 40.4 to 78.2 % for TPUS2 samples, which is relatively in agreement with the values predetermined from the composition of the reaction mixtures (except for TPUS1-20 sample, Table I). However, the experimentally determined copolymer composition was in a slightly better agreement with the theoretical numbers calculated from the composition of the feed for TPUS2 series in comparison to TPUS1 series. It could be concluded that the EO-PDMS soft segments are efficiently incorporated into the polyurethane chains due to the presence of terminal ethoxy units in the soft segment.

The length of the hard segments, *i.e.*, the average degree of polymerization, L_n(HS), was calculated from the results of quantitative ^{13}C-NMR spectroscopy, the results of which are given in Table I. The quantitative ^{13}H-NMR spectra showed splitting from the non-protonated aromatic carbons of MDI in the *ipso* position relative to the urethane group and different signals at 134.9–135.5 and 137.1–137.7 ppm, resulting from the existence of MDI–BD and MDI–ethylene

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oxide linkages. The average length of the hard segments was calculated as the ratio of the integral of aromatic carbon signal from MDI associated with BD and the sum of integrals of the two aromatic carbon signals from MDI associated with ethylene oxide: one from the original soft segment and one from the extended soft segment. Therefore, this calculation takes into account chain extension in the soft segment. The degree of polymerization of the MDI–BD segments in the macromolecular chain increased with decreasing soft segment content from 1.3 to 3.9 for samples in the TPUS1 series and from 1.4 to 4.4 for samples in the TPUS2 series. The experimental values of L_n were in relatively good agreement with L_n(HS) values determined by the composition of the reaction mixture (L_n in the range 1–5), except for the TPUS1-55 and TPUS2-55 samples.

The chemical shifts observed in the ^{13}C-NMR spectra of the copolymers at 0.8 and 1.8 ppm were from carbon atoms from the $SiCH_3$ groups. The central methylene carbon atoms and methylene carbon atoms attached to the silicon from the PDMS propyl groups appeared at 14.9 and 22.0 ppm. The terminal methylene carbon atoms from the PDMS propyl groups appeared at 62.1 ppm. The signals of the central and terminal methylene carbon atoms from the BD residue appeared at 26.7 and 65.0 ppm, respectively. The carbon atom from the methylene group from MDI residue appeared at 41.2 ppm. The signals from the carbonyl atoms at 154.1 and 155.0 ppm originated from the urethane groups. The signals from the aromatic carbons appeared at 119.5, 130.1, 136.9 and 139.0 ppm. The carbon atoms of methylene groups from the ethylene oxide residues appeared at 69.8 and 74.5 ppm only for samples in the TPUS2 series.

To the best of our knowledge, no studies have been published in which the structures of these particular TPUS copolymers were investigated in detail by 2D NMR spectroscopy. The assignments of the proton and carbon resonances within the structures of the samples from both series, which belong to the aromatic protons and carbons, the carbonyl carbons and urethane –NH protons, were resolved in HMBC and ROESY experiments.

The HMBC and ROESY spectra of TPUS1-55 are shown in Figs. 3 and 4, respectively. The resonances for the Hc and Hd signals that were overlapped with Hf and He signals were identified from COSY (spectrum is not presented) based on Hc–Hb and Hc–Hd correlations, respectively. The aromatic carbons in the hard and soft segments were deduced from HMBC based on the correlations Hj–Cj, Hj′–Cj′, Hj″–Ck″, Hi–Cl, Hi′–Cl′ and Hi″–Cl″. The position of the urethane carbonyl from the soft segment at 153.9 ppm was confirmed by HMBC correlation between Hm″–Hn″. The urethane –NH protons from the hard and soft segments were identified by HMBC based on Hm–Cl and Hm″–Cl″ correlations. Furthermore, the urethane –NH protons from the hard and soft segments were assigned by ROESY correlations through space between Hm–Hf, Hm–He, Hm′–Hc and Hm″–Hj″. These results suggest that chain extension in the first phase of reaction

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occurred to some extent (these signals are labeled with ″, which refers to extension of soft segments) and consequently two types of –NH urethane signals in the soft segments appeared.

The HMBC and ROESY spectra of TPUS2-20 are shown in Figs. 3 and 4, respectively. The position of the urethane –NH protons in the hard segment at 9.50 ppm was confirmed by ROESY correlations between Hp–Hg and Hp–Hi, while the position of the urethane –NH protons in the soft segment at 8.64 and 9.56 ppm was confirmed by ROESY correlations between Hp″–Hl″, Hp′–Hd, Hp′–Hf, Hp′–He, and Hp′–Hl′. The urethane –NH protons, aromatic and carbonyl signals from the soft and hard segments were identified by HMBC based on the correlations Hp″–Cn″, Hp″–Co″, Hp′–Cl′, Hp–Cn and Hp–Cl, respectively. The NMR results confirmed that MDI moieties were incorporated into the polymer chains, both in the hard and soft segments. The presence of two types of –NH urethane signals, aromatic and carbonyl signals in the soft segments for both TPUS2 and TPUS1 samples suggest that the chain extension reaction occurred after the first phase of the polyaddition. The extent of the chain extension in soft segments ranged from 18.4 to 22.1 % for the TPUS1 samples and from 7.3 to 14.4 %

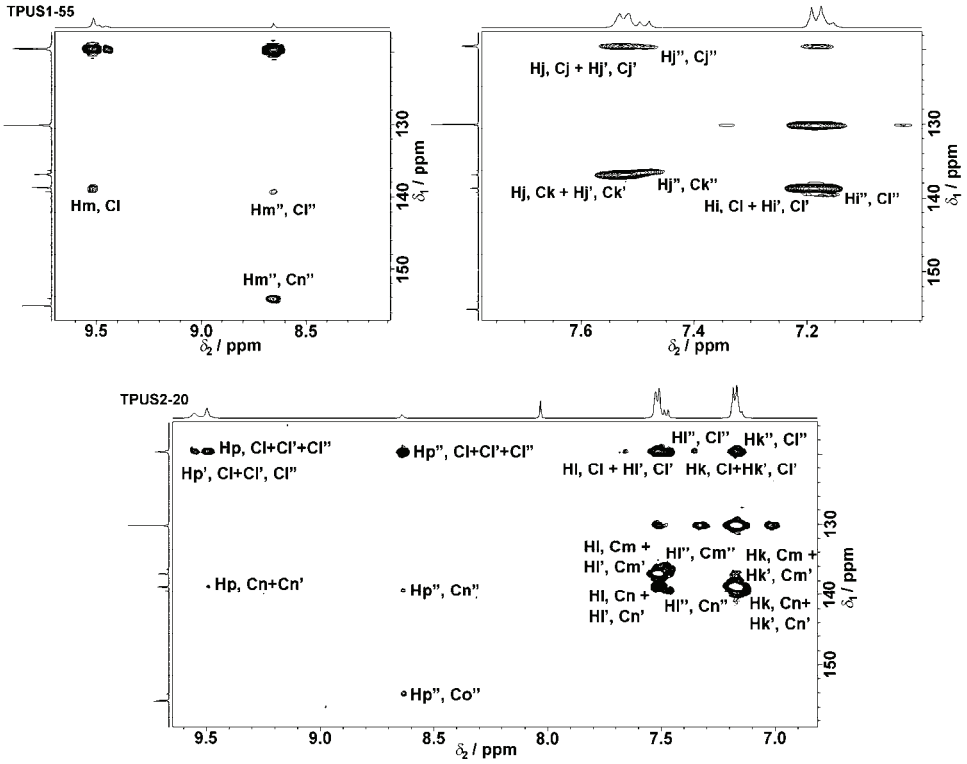

Fig. 3. HMBC spectra of the TPUSs with 45 wt. % of HP-PDMS and with 80 wt. % of EO-PDMS soft segments.

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for the TPUS2 samples. These results were obtained from the ^{1}H-NMR spectra based on the relative intensities of the –NH urethane proton signal arising from the chain extension in the soft segments and all the –NH urethane protons signals from the hard and soft segments and are in agreement with literature data.[27] It was previously found that the polydispersity of the NCO-terminated prepolymer after the first stage of the reaction mainly affects the increase of randomness in polyurethane chains and therefore increased polydispersity of the HS length.[27] Thus, chain extension after the first phase of the polyaddition has a significant influence on the structure and composition of the final copolymers.

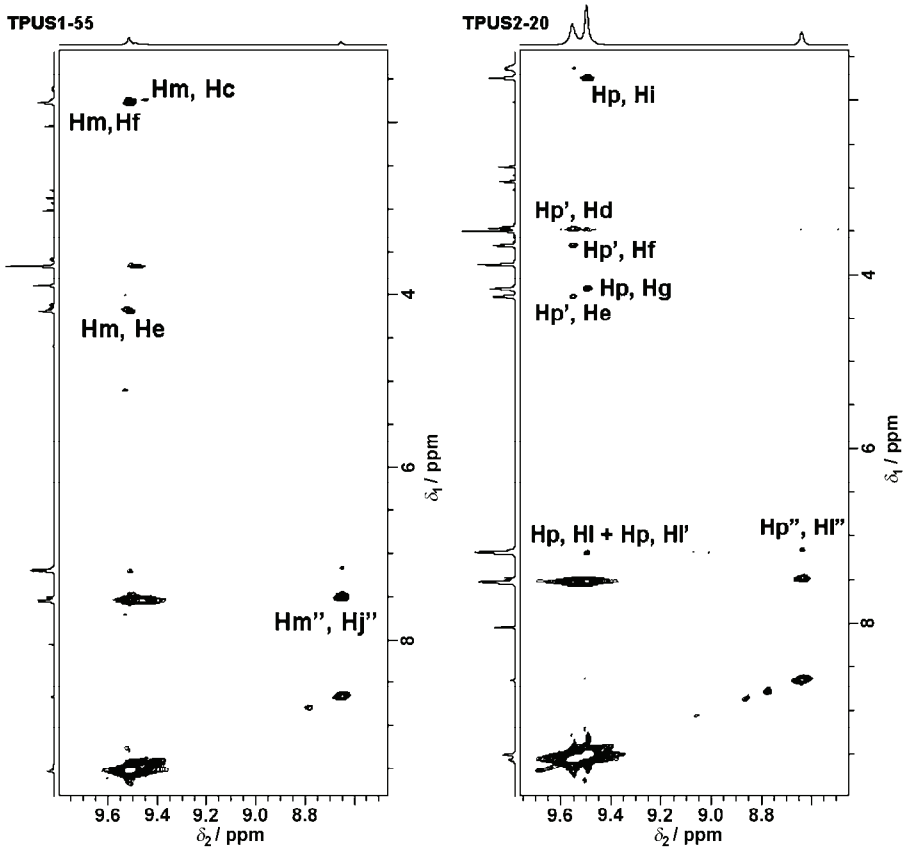

Fig. 4. ROESY spectra of the TPUSs with 45 wt. % of HP-PDMS and with 80 wt. % of EO-PDMS soft segments.

The results of the intrinsic viscosity measurements and GPC analysis of the TPUSs are listed in Table II. The intrinsic viscosities of the TPUSs ranged from 0.42 to 0.56 dL g^{-1} in the first series and from 0.59 to 0.69 dL g^{-1} in the second series. It seems that the intrinsic viscosity increases with decreasing content of

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PDMS segments. The number average molecular weights ($\bar{M}_n$) of the TPUS1 samples, determined by GPC, ranged from 20050 to 30650 g mol^{-1}, with a polydispersity index between 2.3 and 3.0. The $\bar{M}_n$ values of the TPUS2 samples ranged from 22630 to 37760 g mol^{-1} with a polydispersity of 1.9–2.7. The GPC chromatograms of the copolymers exhibited only one peak with a shape that corresponded to a typical high molecular weight product of a step-growth polymerization. The intrinsic viscosity and $\bar{M}_n$ values were slightly higher for the TPUS2 series samples in comparison to those in the TPUS1 series.

TABLE II. Results of GPC analysis and intrinsic viscosities of the synthesized TPUSs

Polymer	$\bar{M}_n$ / g mol^{-1}	$\bar{M}_w$ / g mol^{-1}	$\bar{M}_w/\bar{M}_n$	$[\eta]$ / dL g^{-1}
TPUS1-20	30650	70580	2.3	0.42
TPUS1-35	21690	52060	2.4	0.45
TPUS1-45	23940	58570	2.5	0.52
TPUS1-50	20050	60750	3.0	0.53
TPUS1-55	20650	54640	2.7	0.56
TPUS2-20	26080	61380	2.3	0.59
TPUS2-35	22630	44460	1.9	0.62
TPUS2-45	32290	83470	2.6	0.63
TPUS2-50	37510	103510	2.7	0.65
TPUS2-55	37760	92930	2.4	0.69

Thermal analysis

The TPUSs were semi-crystalline polymers, the melting, crystallization and glass transition temperatures of which were measured by DSC. The obtained DSC thermograms of selected TPUSs recorded during the second heating run are shown in Fig. 5 and the results are summarized in Table III.

TABLE III. Thermal properties and degree of crystallinity, determined by DSC and WAXS analyses, of selected TPUSs

Polymer	T_{gHS} °C	T_{mHS} °C	ΔH_m J g^{-1}	T_{cHS} °C	ΔH_c J g^{-1}	X_c %	X_c^{HS} %	X_{cWAXS} %
TPUS1-20	25	155	0.80	40	4.5	0.88	3.39	6.2
TPUS1-45	65	203	17.0	160	18.6	18.9	36.5	18.1
TPUS1-55	71	205	24.8	164	32.5	27.2	45.5	26.4
TPUS2-20	32	157	3.9	84	5.1	4.3	19.5	6.5
TPUS2-45	37	186	17.5	93	5.8	19.6	42.3	18.5
TPUS2-55	48	191	26.0	94	8.7	28.5	47.8	27.7

The DSC curves show high-temperature transitions corresponding to the melting and crystallization temperatures of the hard MDI–BD segments. The melting and crystallization temperatures of the hard segments depend on the type of soft segments and on the average sequence length of the crystallizable units (Table III). Simultaneously, it seems that the melting and crystallization tempera-

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tures of the HP-PDMS-based TPUSs were slightly higher than those of the polyurethanes in the EO-PDMS series, as shown in Fig. 5. As the soft segment content decreased, the melting and crystallization temperatures were shifted to the higher value, which indicates better ordering of the hard domains.

These results show that the enthalpy of melting (ΔH_m) and enthalpy of crystallization (ΔH_c) increased with decreasing weight fraction of the soft segments.

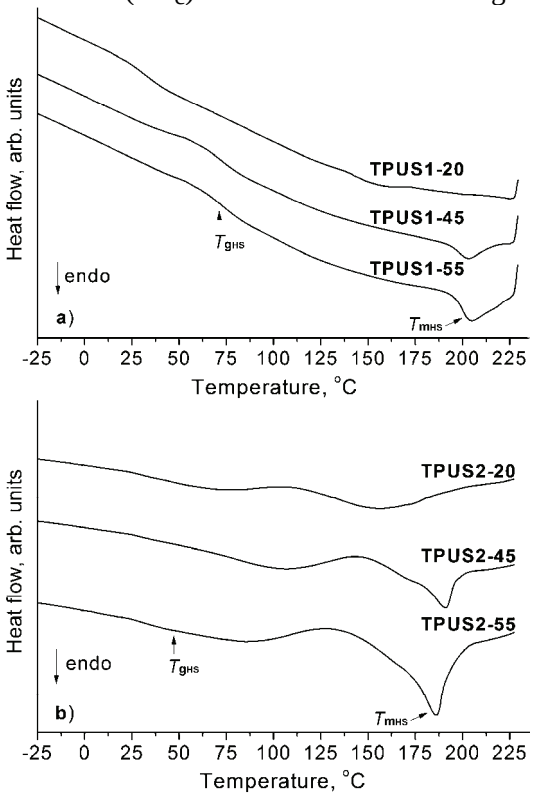

Fig. 5. DSC thermograms recorded during the second heating run of selected TPUSs.

The total degree of crystallinity (X_c) ranged from 0.9 to 27.2 % for TPUS1 samples and from 4.3 to 28.5 % for TPUS2 samples, depending on the soft segment content and ΔH_m. The degree of crystallinity (X_c^{HS}), which was calculated based on the weight fraction of the hard segments in the TPUSs ranged from 3.39 to 45.5 % for the TPUS1 and from 19.5 to 47.8 % for the TPUS2 samples. These results indicate that the hard segments in the copolymers could not crystallize completely and that some short hard segments were incorporated into the amorphous phase. The X_c and X_c^{HS} values are higher for the samples in TPUS2 series in comparison with TPUS1 samples, probably due to the lower extent of the chain extension reaction after the first stage of the polyaddition for the TPUS2 samples. It was found that the side reaction led to further decrease in the length

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of the hard segments for the TPUS1 samples (Table I) and, therefore, to a lower degree of crystallinity. These results are in agreement with previous reports[27,29] that the occurrence of the side reaction could degrade the thermoplastic properties of the hard phase by decreasing the degree of crystallinity and phase separation.

The DSC results show that even hard segments with only one MDI–BD unit can form a crystalline structure. According to the literature, hard segments with more than three MDI–BD units could form stable crystals.[18,27,30] Altogether, these data suggest that HS with an average length of 1 to 5 MDI–BD units can crystallize (Table III).

The glass transition temperatures of the hard segments (T_{gHS}) ranged from 25 to 71 °C for samples in the TPUS1 series and from 32 to 48 °C for samples in the TPUS2 series. Similar results were reported for other MDI–BD-based polyurethanes.[20,31–33] The T_g of the high molecular weight MDI–BD homopolymer is 110 °C, and since the mean hard segment sequences for TPUSs are relatively short (Table I), the hard domain T_g would be expected to be lower than 110 °C.[33] As shown in Table III, the values of T_{gHS} increase with decreasing PDMS content. This is attributed to an increase in the physical cross-links that restricts the molecular motion of the polymer chains and leads to an increase in T_{gHS}. The T_g values of the hard segments were lower for the samples of the TPUS2 series, which indicates mixing of the amorphous hard segments with the terminal ethoxy units of the soft segment.

The thermal stability of the synthesized TPUSs was investigated by thermogravimetric analysis under a dynamic nitrogen atmosphere. The obtained TG and thermogram derivative (DTG) curves for the copolymers are presented in Fig. 6, and characteristic temperatures of thermal degradation, residual weight at 650 °C and temperatures at which maximum degradation occurred are listed in Table IV. Under the given experimental conditions, thermal degradation of these samples was expected to begin between 269 and 289 °C (temperatures at 5 % weight loss). According to the obtained results, thermal degradation mechanism of the synthesized TPUSs is quite complex and both thermal stability and thermal degradation mechanism are influenced by the type and content of the SS. Thermal stabilities of the samples in the TPUS2 series were higher than those of the samples in the TPUS1 series. Furthermore, the results obtained by TG analysis showed that on increasing the soft segment content, the thermal stability of the investigated samples increased. Thermal stabilities of the synthesized TPUSs based on EO-PDMS were similar to those of other polyurethanes derived from the PDMS macrodiol[34] and slightly higher than those of some poly(urethane–urea)s based on PDMS.[35]

Three peaks corresponding to the temperatures of a maximum rate of weight loss were evident in the DTG curves (Fig. 6, Table IV), indicating that the thermal

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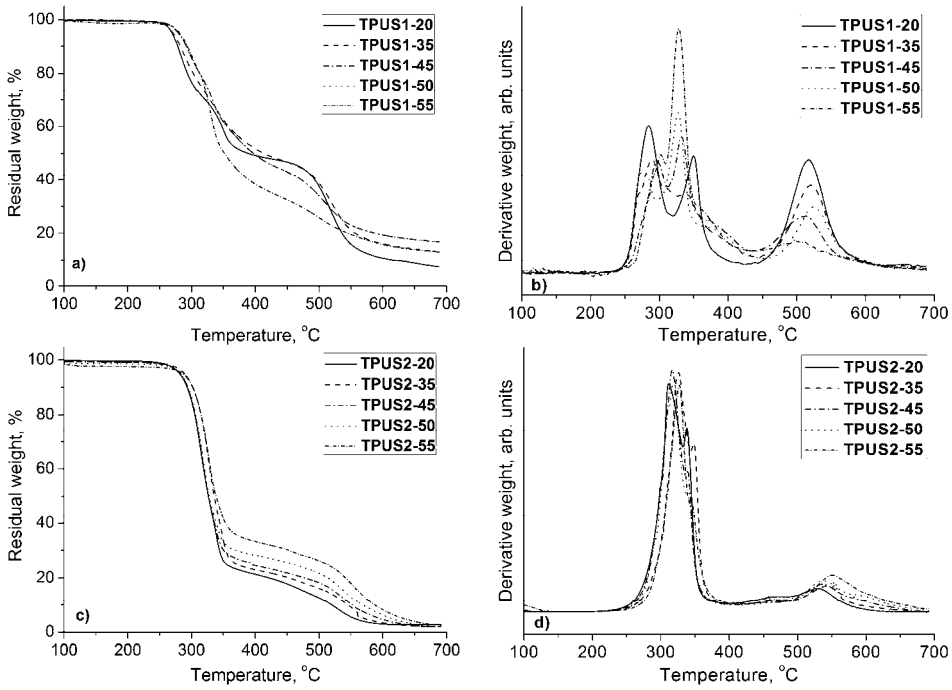

Fig. 6. TG and DTG curves for the TPUSs recorded at a heating rate of 10 °C min^{-1} under a dynamic nitrogen atmosphere.

degradation of these TPUSs is, at least, a three-step process under nitrogen. The first step of thermal degradation occurred in the hard segment by decomposition of the urethane bonds (the thermally weakest link in TPUSs), resulting in dissociation to the original macrodiol and isocyanate and to the formation of a primary or secondary amine, an alkene and carbon dioxide.[36–38] According to the results presented in Table IV, the temperatures corresponding to the maximum rate of thermal degradation in the first step are in the 275–298 °C range for the TPUS1 samples and in the 313–325 °C range for the TPUS2 samples. In the second step of thermal degradation, the PDMS components decomposed (324––351 °C for the TPUS1 samples and 338–345 °C for the TPUS2 samples), while the decomposition of the aromatic compounds occurred in the temperature region between 500 and 600 °C (494–524 °C for the TPUS1 samples and 530–549 °C for the TPUS2 samples).

The residual weights at 650 °C of the samples in TPUS1 series ranged from 8.6 to 17.6 %, whereas the residual weights at 650 °C of the samples in the TPUS2 series ranged from 0.05 to 3.7 % (Table IV). The values of the residual weight at 650 °C suggest that TPUSs with the higher SS content generally have a smaller residue. The residual weight under nitrogen originated mainly from the MDI–BD fraction, which could be explained by the degradation mechanism of

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PDMS chains under a nitrogen atmosphere that occurs after disruption of the urethane bonds. The degradation occurs through depolymerization with the formation of cyclosiloxanes, which are thermally more stable than linear poly-(dimethylsiloxane)s.[39]

TABLE IV. Results of thermogravimetric analysis under a dynamic nitrogen atmosphere

Polymer	$T_{5\%}$ / °C	$T_{10\%}$ / °C	$T_{50\%}$ / °C	$T_{85\%}$ / °C	DTG_{max} / °C	Residual weight at 650 °C, %
TPUS1-20	269	279	385	555	284 / 351 / 517	8.6
TPUS1-35	271	277	413	622	284 / 333 / 517	14.1
TPUS1-45	275	288	388	684	293 / 330 / 510	17.6
TPUS1-50	279	277	396	685	275 / 324 / 524	17.6
TPUS1-55	281	290	390	617	298 / 324 / 494	13.8
TPUS2-20	281	293	327	478	313 / 338 / 530	0.05
TPUS2-35	289	302	331	507	322 / 343 / 535	2.2
TPUS2-45	282	294	330	530	322 / 345 / 537	2.5
TPUS2-50	282	295	331	544	325 / 344 / 539	3.1
TPUS2-55	286	302	335	560	325 / 345 / 549	3.7

WAXS analysis

The synthesized polyurethanes were characterized by WAXS analysis and the degrees of crystallinity, X_{cWAXS}, determined by deconvolution of the signals belonging to the crystalline and amorphous parts, are presented in Table III. The X-ray diffractograms obtained for selected TPUSs are shown in Fig. 7. The diffraction profiles of TPUSs exhibited weak peaks at 2θ values of 19° and 24°, which correspond to the crystallinity of the hard MDI–BD segment.[40–42] Figure 7 clearly shows that the relative intensity of polyurethanes increased with the decreasing SS content in TPUSs. Shifts in the peak's 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. Based on 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, α = = 113.6°, β = 116.0°, γ = 94.4°.[43] For copolymers, two amorphous halos were also observed at 2θ 12° arising from the phase-separated PDMS segments and at 2θ 20° arising from non-PDMS segments. The crystallinity of the copolymers was clearly facilitated by the strong segregation of the PDMS and MDI–BD segments. The degree of crystallinity ranged from 6.2 to 26.4 % for the TPUS1 samples and from 6.5 to 27.7 % for the TPUS2 samples. The WAXS degrees of crystallinity decreased with the increasing weight fraction of soft segments, similarly to the degrees of crystallinity determined by DSC. The obtained results showed that degree of crystallinity did not significantly change by varying the type of soft segments. Based on the degree of crystallinity values, the total degree

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of crystallinity in the TPUSs almost exclusively depended on the weight fraction of the SS content.

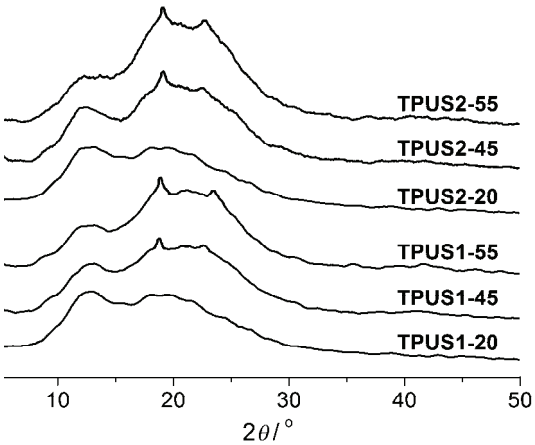

Fig. 7. X-ray diffraction patterns of selected TPUSs.

Water contact angle and water absorption

The wettability of TPUSs was investigated by static contact angle measurements. The water contact angle is indicative of the hydrophobicity of a surface, whereby a water contact angle of 90° or more indicates a non-wetting surface. The water contact angles were found to increase with increasing PDMS content in both series (Fig. 8). This may be attributed to the hydrophobic character of PDMS and its surface activity.[34,44] Thus, PDMS can migrate to the surface of samples due to its lower surface energy in comparison to the surface energy of a polyurethane. The observation of surface segregation of a low surface energy segment, such as PDMS, was reported for PDMS-containing polyurethane copolymers.[8,34,44] The TPUSs with a higher content of soft PDMS segments have a more hydrophobic surface and better water resistance. The higher water contact angles obtained for the HP-PDMS containing TPUSs indicate the presence of a larger hydrophobic surface compared to the EO-PDMS-based TPUSs.

The bulk hydrophobicity of the prepared copolymers was quantified by measuring the amount of absorbed water at 37 °C. As shown in Fig. 9, the water absorption increased slightly at longer immersion times with the maximum water uptake value being attained after 24 h. The values of water uptake of the TPUSs after 24 h ranged from 0.5 to 1.47 % for the TPUS1 series and from 0.74 to 1.61 % for the TPUS2 series. The TPUSs based on HP-PDMS exhibited lower water uptakes compared with the samples based on EO-PDMS. The water uptake of the TPUSs decreased with increasing content of PDMS, which formed a hydrophobic surface that caused the reduction in the water uptake values of the copolymers. In comparison with polyurethanes prepared from the more hydrophilic

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macrodiols reported by other group,[45] the synthesized TPUSs were considered rather hydrophobic due to the hydrophobic character of the PDMS. Therefore, thermoplastic polyurethanes based on PDMS with good waterproof properties show great promise for use as medical implants.[11]

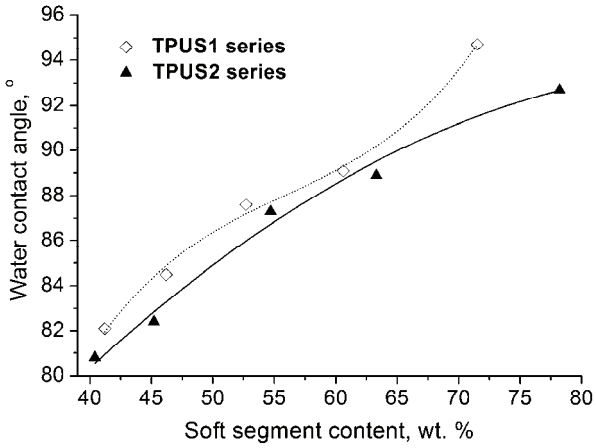

Fig. 8. Water contact angle of the TPUSs *vs*. soft segment content determined by ^{1}H-NMR spectroscopy.

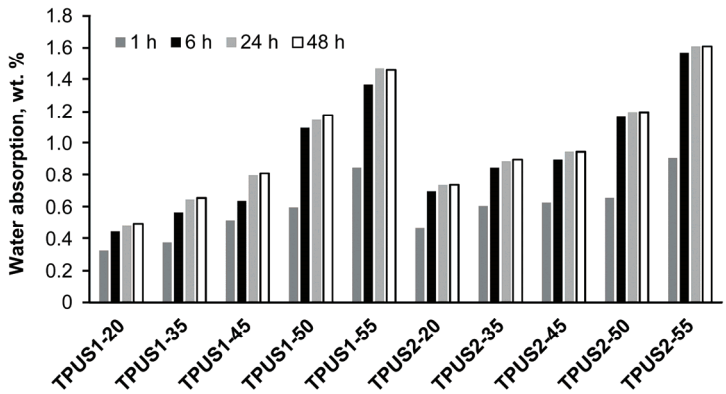

Fig. 9. Water absorption by TPUSs as a function of immersion time.

SEM analysis

The surface morphology of the synthesized TPUSs was examined by SEM (Fig. 10). SEM microphotographs of samples with 45 and 55 wt. % of the soft segment revealed a rather uniform surface with microphase separation. These TPUSs showed a spherulite-like structure that is believed to arise from the crystallization of the hard segments, which was also suggested by the DSC and WAXS results. The lack of crystalline fibrilar growth in these structures might be

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due to the non-uniformity of the lengths of the hard segments in the mentioned samples, thereby impeding longer range ordering, but this is only a supposition.[46] The main size of these crystalline superstructures in TPUSs varied between 2 and 8 μm. With decreasing SS content, an enhancement in the crystallinity of the hard domains was evidenced, but still the highest value of the main spherulite size was observed for samples TPUS1-55 and TPUS2-55. Samples TPUS1-20 and TPUS2-20 displayed phase mixing morphology and these samples showed increased homogeneity and surface smoothness. From these results and the water contact angle measurements, it could be concluded that the surface of the TPUSs with higher PDMS contents is more hydrophobic, because of the low surface tension of the PDMS segments and their ability to migrate to the surface.

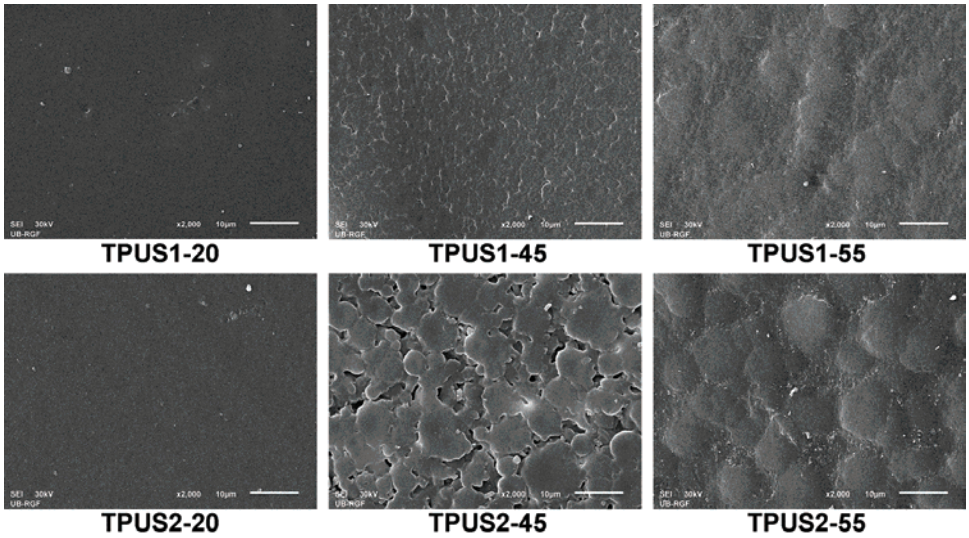

Fig. 10. SEM microphotographs of films prepared from TPUS copolymers.

The results indicate that TPUSs have good microphase separation, as well as surface and thermal properties, which could be tailored to the requirements for biomedical application, such as biomedical devices for short- and long-term uses, by changing the type of soft segments and the PDMS content. It was found that all the TPUSs were sufficiently stable to be melt processed, for example, by injection molding and extrusion. Furthermore, TPUSs based on EO-PDMS are less hydrophobic and have higher crystallinity, which would promote better cell attachment and growth on the polymer surface.[27] Therefore, TPUSs based on EO-PDMS soft segments could be expected to improve the adhesion of endothelial cells on the surface of the copolymers and consequently their biocompatibility due to the presence of ethylene oxide terminal units in the soft segments. The synthesized TPUSs based on the HP-PDMS and EO-PDMS thus combine

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various chemical, surface and thermal properties that could be used for different biomedical applications, such as biomedical devices for short- and long-term uses, respectively.

CONCLUSIONS

The synthesis and the structural, thermal and surface characterization of polyurethane copolymers prepared from different types of soft PDMS segments and with varying PDMS contents were presented herein. Two series of medium molecular weight copolymers based on hydroxypropyl-terminated PDMS or hydroxyethoxypropyl-terminated PDMS as the soft segments were synthesized by a two-step polyaddition in solution. The multiblock structure of the synthesized TPUSs was confirmed by ^{1}H-, ^{13}C- and 2D-NMR spectroscopy. Based on the results of ^{1}H-NMR spectroscopy, the composition of the copolymers was found to be close to the composition of the feed, with a slightly better efficiency of EO-PDMS segment introduction into the polymer chains. Quantitative ^{13}C-NMR analysis confirmed that the chain extension occurred after the first stage of polyaddition reaction, with a higher degree of chain extension in the soft segment found in the copolymers based on HP-PDMS compared to those based on EO-PDMS. The TPUSs were semi-crystalline polymers, in which the hard segment, with an average length of crystallization from 1 to 5 MDI–BD units, crystallized. The melting temperature, glass transition temperature and the degree of crystallinity of the copolymers decreased with increasing content of soft PDMS segments. The X-ray diffraction patterns indicated that the hard MDI–BD segments in the TPUSs crystallized in a triclinic crystal lattice, similarly to the MDI–BD homopolymer. The synthesized TPUSs with a lower soft segment content showed a spherulite-like structure that is believed to arise from the crystallization of the hard segments. SEM analysis and water contact angle experiments showed that, due to hydrophobic character of PDMS and its low surface tension, samples with the higher PDMS contents had more hydrophobic surfaces. Compared to the HP-PDMS-containing TPUSs, the samples prepared from EO-PDMS have a higher degree of crystallinity, better thermal stability and less hydrophobic surfaces. It could be concluded that the inclusion of the PDMS prepolymer with a terminal ethoxy units resulted in slightly improved miscibility of the reaction mixture and therefore to better thermal and surface properties. In addition, the structural, thermal and surface properties of the synthesized TPUSs could be tailored by changing the type or content of the soft segment and adjusted to the requirements for biomedical applications. The impact of different types of soft PDMS segments on the microstructure–mechanical property relation and biocompatibility behavior of TPUSs will be discussed in further publications.

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ИЗВОД

СТРУКТУРНА, ТЕРМИЧКА И ПОВРШИНСКА КАРАКТЕРИЗАЦИЈА ТЕРМОПЛАСТИЧНИХ ПОЛИУРЕТАНА НА БАЗИ ПОЛИ(ДИМЕТИЛСИЛОКСАНА)

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У овом раду су испитивани синтеза, структура и физичка својства две серије термопластичних полиуретана са меким сегментима на бази хидроксипропил терминираног поли(диметилсилоксана) (HP-PDMS) и хидроксиетоксипропил терминираног поли-(диметилсилоксана) (EO-PDMS), и тврдим сегментима на бази 4,4′-метилендифенил--диизоцијаната и 1,4-бутандиола. Свака серија се састојала од узорака који имају различит садржај меког сегмента. Полиуретани су синтетисани двостепеним поступком полиадиције у раствору. Утицај врсте и садржаја PDMS сегмената на структуру, термичка и површинска својства кополимера је испитан помоћу ^{1}H-NMR, ^{13}C-NMR, дводимензионалне NMR (HMBC и ROESY) спектроскопије, GPC, DSC, TGA, WAXS, SEM и одређивањем контактних углова са водом и мерењима апсорпције воде. Термичка својства испитана DSC методом указују да присуство меких PDMS сегмената снижава температуре остакљивања и топљења тврде фазе, као и степен кристалиничности. SEM анализа кополимера са ниским садржајем меког сегмента потврђује постојање сферулитне морфологије, која потиче од кристализације тврдих сегмената. У поређењу са полиуретанима на бази HP-PDMS, синтетисани кополимери на бази EO-PDMS имају већи степен кристалиничности, бољу термичку стабилност и мање хидрофобну површину. Добијени резултати су показали да синтетисани полиуретани имају добра термичка и површинска својства, што се може даље модификовати променом врсте или садржаја меког сегмента.

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