The effect of polar solvents on the synthesis of poly(urethane–urea–siloxane)s

MILICA BALABAN[1], VESNA ANTIĆ[2*#], MARIJA PERGAL[3#],
IOLANDA FRANCOLINI[4], ANDREA MARTINELLI[4] and JASNA DJONLAGIĆ[5#]

[1]*University of Banja Luka, Faculty of Science, Banja Luka, Bosnia and Herzegovina,*
[2]*University of Belgrade, Faculty of Agriculture, Belgrade, Serbia,* [3]*University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia,* [4]*University of Rome "Sapienza", Dept. of Chemistry, Rome, Italy and* [5]*University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia*

Abstract: Segmented poly(urethane–urea–siloxanes) (PUUS) based on 4,4′-methylene diphenyl diisocyanate–ethylene diamine (MDI–ED) hard segments and hydroxypropyl-terminated poly(dimethylsiloxane) (PDMS, $\overline{M}_n$ = 1000 g mol⁻¹) soft segments were prepared under various experimental conditions. The copolymers with constant molar ratio of hard and soft segments (PDMS:MDI:ED = 1:2:1; 20 wt. % of the hard segments) were synthesized in two different solvent mixtures, by a two-step polyaddition procedure. The first one was tetrahydrofuran/*N,N*-dimethylacetamide (THF/DMAc) with different co-solvent ratios (1/1, 1/2 and 1/9, v/v), whereas the second one was tetrahydrofuran/*N*-methylpyrrolidone (THF/NMP, 1/9, v/v). The reaction conditions were optimized by varying the co-solvents ratio, the concentration of the catalyst, the initial monomer concentration, as well as the time of the first and the second step of the reaction. The effects of the experimental conditions on the size of the PUUS were investigated by gel permeation chromatography (GPC) and dilute solution viscometry. The copolymers with the highest molecular weights were obtained in the THF/NMP mixture (1/9, v/v). The structure and composition of the copolymers were determined by ¹H-NMR and FTIR spectroscopy. The morphology of the synthesized copolymers was investigated by atomic force microscopy (AFM), while the thermal properties were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The surface properties were evaluated by measuring the water contact angle (WCA). The copolymers exhibited phase-separated microstructure and were stable up to 200 °C in nitrogen.

Keywords: urethane–urea–siloxane copolymers; two-step polyaddition; reaction conditions; optimization; thermal properties; microphase separation.

INTRODUCTION

Poly(urethane–urea) (PUU) copolymers represent an important subclass of segmented polyurethanes (PU) in which diamines are used as the chain extenders rather than diols. The soft segments in both PU and PUU copolymers are usually aliphatic polyesters or polyethers with number average molecular weights in range from 1000 to 5000 g mol^{-1}, while the hard segment content is between 15 and 40 wt.%. Due to the stronger hydrogen bonding in the hard domains, the PUU possess improved mechanical properties compared to conventional thermoplastic PU.[1–4]

Segmented PU and PUU with polydimethylsiloxane (PDMS) as the soft segment (PUS and PUUS, respectively) have found substantial interest because of the many unique properties of the PDMS segments, including low glass transition temperature, low surface energy, high permeability to many gases, biocompatibility and thermal stability, which made them suitable for applications such as elastomers, coatings and biological implants.[5,6] The extremely large differences in the solubility parameters of PDMS and urethane and urea groups (15.6, 37.2 and 45.6 J$^{1/2}$ cm$^{-3/2}$, respectively),[7] which results in almost complete phase separation between the hard and soft segments in copolymer, together with strong hydrogen bonding which occurs in the hard segments, should lead to improved mechanical properties of PUUS copolymers. However, the initial attempts to synthesize PDMS-based poly(urethane–urea)s resulted in copolymers with rather low molecular weight and poor mechanical properties, mainly due to solubility problems during synthesis.[6,7]

The solvent mixture usually used for the synthesis of PUUSs is THF/DMAc, tetrahydrofurane/*N*,*N*-dimethylacetamide, of different co-solvent ratios. DMAc is responsible for the dissolution of polar monomers and segments, while the presence of THF is necessary because of the dissolution of the non-polar PDMS segments.[8–10] The use of 2-propanol (2-PA) as a solvent for the preparation of the PDMS–urea copolymers with high urea contents and high molecular weights has also been demonstrated.[11,12] Considering the large difference in polarity between the urethane/urea hard segments and the siloxane soft segments, there are now two general approaches to the synthesis of PUUS copolymers. The first involves the presence of polyether- or polyester-segments as co-soft segments, in order to improve miscibility of PDMS with the urethane and urea units.[13–15] The presence of the second soft segment, which has the ability to form hydrogen bonds with the hard segments, leads to extensive phase mixing of the hard and the soft segments and to a deterioration in mechanical properties, due to the decrease of the phase separation in the copolymers.[16,17] In addition, it was established that typical aliphatic polyether and polyester soft segments are susceptible to oxidative and hydrolytic degradation *in vivo*, which restricts their long-term use as biomedical implants.[18]

The second approach to the synthesis of segmented PUUSs is based on using end-functionalized PDMS as a single soft segment, whereby the terminal units attached to the ends of the siloxane oligomers act as a "compatibilizer" between the highly polar urethane/urea hard segments and the non-polar siloxane soft segments.[6,14] Over the years, the use of hydroxybutyl-, hydroxyhexyl-, as well as aminopropyl- and secondary aminoalkyl-terminated PDMS oligomers for the preparation of polyurethane, polyurea and poly(urethane–urea) copolymers has been reported.[12,19,20] Recently, segmented PUUS based on fluorinated hydroxypropyl-terminated PDMS were prepared.[21] Generally, the synthesis of segmented PUUS is very difficult to realize due to the extremely high immiscibility of the highly polar combination of urethane/urea hard segments with non-polar siloxane soft segments, regardless of the kind of used end-functionalized PDMS. The selection of the appropriate solvent is critical to promote solubilization and to prevent premature precipitation of the growing chains, thus ensuring copolymers of high molecular weight.

This work focused on the synthesis of PUUS copolymers derived from hydroxypropyl-terminated PDMS as the soft segment and 4,4′-methylene diphenyl diisocyanate–ethylene diamine (MDI–ED) as the hard segment. The molar ratio of the reacting monomers was constant (PDMS:MDI:ED = 1:2:1), which resulted in the copolymers with the predetermined content of the hard segments of 20 wt. %. The copolymers were prepared in two different solvent mixtures, DMAc/THF and NMP/THF. The aim of this work was to optimize the experimental conditions for the synthesis of PUUS in order to obtain high-molecular weight copolymers. The effects of the co-solvents ratio, the catalyst concentration, the reaction time and the initial monomer concentration in the reaction mixture on the molecular weigh were studied. The goal was to compare molecular weights of the PUUS obtained in the DMAc/THF mixtures, which are usually used for the synthesis of this kind of copolymers, with those of the products obtained in more polar NMP/THF solvent combination. The structure of the obtained copolymers was characterized by NMR and FTIR spectroscopy, while their thermal properties were studied by DSC and TG analysis. The morphology of the PUUSs was investigated by AFM. It was also investigated whether the small variation in the structure and composition of the copolymers synthesized under different experimental conditions had an influence on their properties.

EXPERIMENTAL

Materials

$α,ω$-Dihydroxypropyl-poly(dimethylsiloxane) ($α,ω$-dihydroxypropyl-PDMS, $\bar{M}_n$ = 1000 g mol^{-1}, from ABCR) was dried over molecular sieves. The structure and the number-average molecular weight of PDMS were confirmed by ^{1}H-NMR spectroscopy. 4,4′-Methylene diphenyl diisocyanate (MDI, from Aldrich) with an isocyanate content of 33.6 wt. %, and ethylene diamine (ED, from Zorka, Serbia), were used as received. *N,N*-Dimethylacetamide

(DMAc, from Acros) was dried over calcium hydride and distilled under vacuum. *N*-Methyl-pyrrolidone (NMP, from Acros) was purified by low-pressure distillation prior to use. Tetra-hydrofuran (THF, from J. T. Baker) was dried over lithium aluminum hydride and distilled before use. The stannous octanoate ($Sn(Oct)_2$) catalyst was obtained from Aldrich and used without further purification. The catalyst was used as a dilute solution (0.01 g cm^{-3}) in an anhydrous mixture THF/DMAc (1/1, v/v) or THF/NMP (1/9, v/v).

Synthesis

Two series of the PUUS copolymers were prepared by a two-step polyaddition procedure in solution, using *α,ω*-dihydroxypropyl-PDMS, MDI and ED as chain extenders. The first series was synthesized in a mixture of THF and DMAc (1/1, 1/2 or 1/9, v/v), while the second series was obtained in a mixture of THF and NMP (1/9, v/v). All copolymers were prepared at a constant molar ratio of the reacting monomers (PDMS:MDI:ED = 1:2:1), which resulted in a content of hard segments of 20 wt. %. The reaction temperature was varied from 40 to 80 °C, while the catalyst concentration was varied between 0 and 0.10 mol % $Sn(Oct)_2$, based on PDMS.

For all the used combinations of the reaction conditions, the time of the first reaction step was determined in preliminary experiments, by the standard dibutylamine back-titration me-thod.[22] The reaction time of the first step was measured from the moment of completion of the addition of the solution of PDMS and $Sn(Oct)_2$ into the solution of MDI. The second step (chain-extension) was performed for 1 or 3 h. The exceptions were the experiments in which optimization of the reaction time of the second step was performed, when reaction was extended up to 8 h. The initial concentration of the monomers in the reaction mixture was varied between 7.5 and 25 wt. % (Table I).

TABLE I. Reaction conditions for the synthesis of PUUSs at 40 °C, intrinsic viscosities, the results of the GPC and ^{1}H-NMR analysis and yields of the copolymers

Sample[a]	Time of 1st step min	$[\eta]$ dL g^{-1}	$\bar{M}_n$ g mol^{-1}	$\bar{M}_w$ g mol^{-1}	$\bar{M}_w/\bar{M}_n$	Content HS, mol % (NMR)[b]	Content HS, wt. % (NMR)[b]	l HS[c]	Yield[d] %
				Series I					
PUUS7.5-0.1	27	0.15	9400	20420	2.17	52.5	21.5	1.1	62
PUUS10-0.1	20	0.17	8250	16300	1.97	41.9	15.2	0.7	84
PUUS10-0.05	25	0.18	7800	14500	1.86	33.6	11.1	0.5	79
PUUS15-0.1	15	0.15	8050	14400	1.79	43.4	16.0	0.8	83
PUUS15-0.05	20	0.18	9020	16750	1.86	48.2	18.7	0.9	90
		(0.22)	(12200)	(25230)	(2.07)	(55.8)	(23.9)	(1.3)	(88)
PUUS15-0	29	(0.24)	(12440)	(25650)	(2.06)	(60.3)	(27.3)	(1.5)	(85)
PUUS15A--0.05[e]	17	(0.25)	(14300)	(28730)	(2.01)	(54.8)	(23.1)	(1.2)	(90)
PUUS15B-0[f]	29	(0.28)	(18500)	(73500)	(3.97)	(60.1)	(27.2)	(1.5)	(89)
				Series II					
PUUS10-0.05	19	0.19	8230	13850	1.68	42.0	15.2	0.7	86
PUUS15-0.05	17	0.23	11050	19500	1.76	54.0	22.6	1.2	89
PUUS25-0.05	15	0.28	13040	25120	1.92	45.7	17.3	0.8	91
		(0.29)	(19540)	(58100)	(2.97)	(51.2)	(20.7)	(1.0)	(93)

[a]The values without brackets are for an extension step of 1 h, while the values in brackets are for an extension step of 3 h; [b]calculated according to 1 soft segment; [c]the HS content predetermined by the composition of the reaction mixtures was 50 mol % and 20 wt. %; [d]calculated after precipitation of the copolymer; [e]solvent mixture: THF/DMAc (1/2, v/v); [f]solvent mixture: THF/DMAc (1/9, v/v)

A typical synthesis for the sample PUUS15-0.05 from Series I, in THF/DMAc (1/1, v/v), at a concentration of the catalyst of 0.05 mol % and the concentration of the monomers of 15 wt. %, is described herein. The reaction was performed in a four-necked round-bottomed flask equipped with an overhead stirrer, a dry argon inlet, a reflux condenser and a dropping funnel. In the first step the solution of 5.00 g (5.0 mmol) PDMS in 33.2 cm^3 of THF/DMAc (1/1, v/v) and the catalyst (1.0 mg, 2.5·10^{-3} mmol) was slowly added from the dropping funnel into the flask containing required amount of MDI (2.50 g, 10.0 mmol) and 16.6 cm^3 of THF/DMAc (1/1, v/v). The solution of MDI had previously been heated to 40 °C in a silicone oil bath. The reaction mixture was stirred for 20 min at 40 °C to prepare the isocyanate-terminated prepolymer. After the theoretical NCO content of 5.60 wt. % in the reaction mixture was reached, the prepolymer was chain-extended by the dropwise addition of the stoichiometric amount of ED (0.30 g, 5.0 mmol) in 2.0 cm^3 of solvent mixture, and the reaction was continued at the same temperature for 3 h. The synthesized copolymer was precipitated into methanol/water (1/1) solution, filtered and dried to the constant weight in a vacuum oven at 40 °C. The yields of synthesized PUUS copolymers after precipitation in methanol/water mixture were in the range of 79–93 %, except for sample PUUS7.5-0.1 (62 %) (Table I).

Film preparation

The copolymer films (0.2–0.3 mm thickness) utilized for characterization were cast from NMP solution (10 wt. %) into Teflon molds. First, the solvent was slowly evaporated for 48 h at 40 °C in a force-draft oven. The obtained films were dried under vacuum at 40 °C for 48 h.

Characterization methods

The ^{1}H-NMR spectra were recorded on a Bruker Avance 500 spectrometer (500.13 MHz) equipped with 5 mm inverse detection *z*-gradient probe at 25 °C using DMSO-d_6 as solvent.

The FTIR spectra were recorded on an ATR-IR Nicolet 380 instrument with a diamond crystal of refractive index 2.4 and an incidence angle of 45°. All spectra were collected using 64 scans in the spectral region between 4000 and 400 cm^{-1}, at a resolution of 4 cm^{-1}.

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

The GPC measurements were conducted using a Waters 600E instrument equipped with a refractive index detector, on three Supelco Pl-Gel columns connected in line (crosslinked polystyrene with pore sizes of 10^{-5}, 10^{-6} and 10^{-7} m). NMP was used as the mobile phase at 60 °C, with a flow rate of 1.5 cm^3 min^{-1}. The volume of the sample solutions (1 wt. % in NMP) injected was 60 μL in all cases. The system was calibrated with a number of polystyrene standards (from Sigma-Aldrich) ranging from 1700 to 55100 g mol^{-1}.

Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC822 thermal analyser, under a nitrogen atmosphere, at a heating rate of 10 °C min^{-1} and the cooling rate of 40 °C min^{-1} over a temperature range from –150 to 200 °C. The weight of the samples was approximately 5 mg.

The thermal stabilities of the polymers were determined using a Mettler-Toledo DSC822 thermal analyser in the temperature range from 25 to 600 °C, at heating rate of 10 °C min^{-1}. The TG scans were recorded under dynamic nitrogen atmosphere at flow rate of 50 cm^3 min^{-1}. The average weights of the samples were around 3 mg.

Water contact angle (WCA) measurements of the polymer films were realized employing a Krüss DSA100, using the sessile drop method. Single drops of distilled water with a volume of 20 μL were deposited on the polymer film surface and the contact angles were measured at

26 °C after 30 s by means of a camera connected to software for image analysis. The contact angle values were obtained from the average of five measurements.

The surface topography of the PUUS samples was observed by atomic force microscopy (AFM). The AFM characterizations were performed with an AutoProbe CP-Research SPM (TM Microscopes-Veeco) instrument using 90 μm large area scanner. Measurements were performed in air using the contact AFM mode. Veeco phosphorus (n) doped silicon contact metrology probes-model MPP-31123-10 with an Al reflective coating and a symmetric tip were used.

Sample designation

The samples are denoted by 'PUUS' with two numbers denoting the initial monomer concentration and the catalyst concentration in the reaction mixture. For example, PUUS7.5-0.1 means that the initial monomer concentration in the reaction mixture was 7.5 wt. %, while the catalyst concentration was 0.1 mol % $Sn(Oct)_2$, based on PDMS. The samples that were prepared in the THF/DMAc mixtures at co-solvent ratios different to 1/1, v/v, are additionally denoted as "A" (THF/DMAc = 1/2, v/v) and "B" (THF/DMAc = 1/9, v/v).

RESULTS AND DISCUSSION

Determination of the optimal conditions for the synthesis of PUUSs

The PUUS copolymers were synthesized by the two-step polyaddition method ("prepolymer method"), as shown in Scheme 1.

The hard segment content of 20 wt.%, predetermined by the composition of the reaction mixtures, was calculated based on the copolymer structure given in Scheme 1. In this way, only the portion of MDI that reacted with diamine contributes to the hard segments, while the other MDI portion that reacted with the PDMS prepolymer gives the soft segments.

Two series of the copolymers with constant hard segment content (20 wt. %) were prepared in different solvent mixtures: THF/DMAc (1/1, 1/2 or 1/9, v/v) and THF/NMP (1/9, v/v). In the first step of the reaction, isocyanate-terminated prepolymer was prepared by reaction of MDI in an excess with PDMS, *i.e.*, the mole ratio of NCO and OH groups was 2:1. The required reaction time for the first step had previously been determined in separate experiments for all the employed combinations of the reaction conditions, using the standard dibutylamine back-titration method. The time of the first reaction step was the time required to reduce the concentration of the NCO groups to half of the initial value, and it is given in Table I. In the second step, the prepolymer was chain-extended with the stoichiometric amount of ED under various experimental conditions. The influence of the concentration of the catalyst and monomer in the reaction mixture, as well as the time of the second reaction step, on the molecular weight of the resulting copolymers was studied in order to determine the optimal experimental conditions for the synthesis of PUUS. The molecular weights of PUUS were monitored by measuring the intrinsic viscosity of the copolymer solutions and by GPC. The most important results of the optimization in THF/DMAc and THF/NMP

Scheme 1. The synthesis of the PUUS.

are summarized in Table I. The copolymers prepared in the THF/DMAc and THF/NMP solvents mixture are assigned as Series I and Series II, respectively. All syntheses given in Table I were realized at 40 °C.

Series I

The experiments in the first series commenced in the solvent mixture THF/ /DMAc (1/1, v/v). This solvent mixture is, with various volumetric ratios of co-solvents, usually used for the synthesis of the PDMS-based segmented poly(urethane–urea)s.[8–10] In the beginning, the influence of the reaction temperature on the time required to complete the first step of reaction, *i.e.*, the reaction between PDMS and MDI, was investigated. The dependence of the concentration of NCO groups on the time at different temperatures (40, 60 and 80 °C) is shown in Fig. 1. The initial NCO content in the reaction mixture was 11.2 wt. % and ideally it should have decreased to 5.6 wt. %, *i.e.*, to half of the initial value. However, due to the presence of excess of isocyanate and traces of moisture, side reactions occurred (allophanate and biuret). Consequently, the NCO groups reacted further and their concentration decreased to below the theoretical value, as can be seen in Fig. 1. The first step was generally very fast, especially at temperatures at 80 and 60 °C, when it was completed in 7 or 12 min, respectively. If the first step proceeds very rapidly, the possibility of the side reactions is also pronounced, which acts adversely on the molecular weight and the structure of the copolymers.
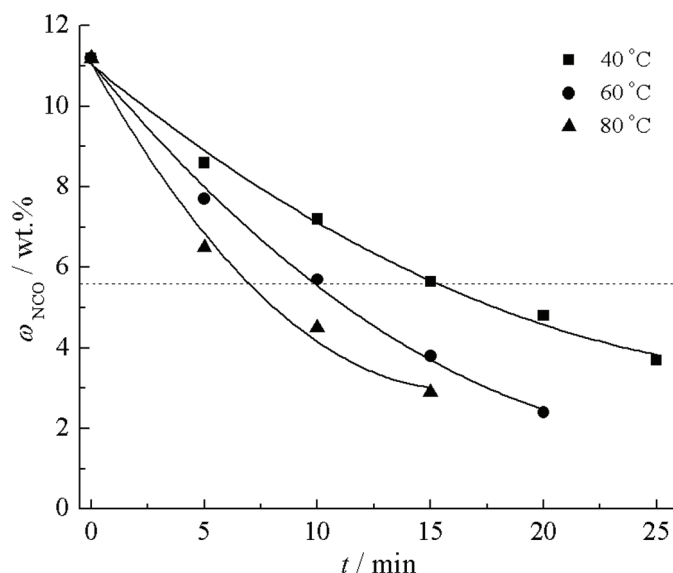

Fig. 1. The concentration of NCO groups as a function of the time of the first reaction step, for the syntheses in THF/DMAc (1/1, v/v) solvent mixture, at different temperatures (40, 60 and 80 °C) and at constant concentration of the monomers (15 wt. %) and catalyst (0.1 mol %).

When the reaction was performed at 40 °C, the reaction was completed in 15 min, which is a reasonable time for the first step. For these reasons, it was decided to perform all further reactions at 40 °C. It was also demonstrated that the time of the first reaction step was shorter with higher concentrations of catalyst and monomers in the reaction mixture (Table I).

The effect of the reaction time of the second phase on the size of the obtained PUUSs, at different concentrations of the catalyst and monomers in the reaction mixture, was also investigated. When the second phase (*i.e.*, the chain-extension step) lasted 1 h, the values of the intrinsic viscosity of all samples synthesized in THF/DMAc (1/1, v/v) were similar (0.15–0.18 dL g^{-1}, Table I), regardless the concentration of the catalyst or the monomers in the reaction mixture. By increase the reaction time of the second phase to 3 h, both the intrinsic viscosity and the molecular weight of the copolymers increased (the values given in brackets in Table I). In addition, it was noticed that a copolymer with a slightly higher molecular weight was obtained in the absence of the catalyst. This can be explained by side-reactions, which occur to a higher degree in the presence of the catalyst, leading to a reduction of the molecular weight. The effect of the time of the second step of reaction on the intrinsic viscosity of PUUSs, with a monomer concentration of 15 wt. % and without the catalyst is shown in Fig. 2. Increasing the reaction time to above 3 h (to 6 and 8 h) provoked a decrease in the viscosity, as it can be seen in Fig. 2. This is probably due to the longer exposure of the copolymer to traces of moisture, *i.e.*, its hydrolysis, and again due to the side-reac-
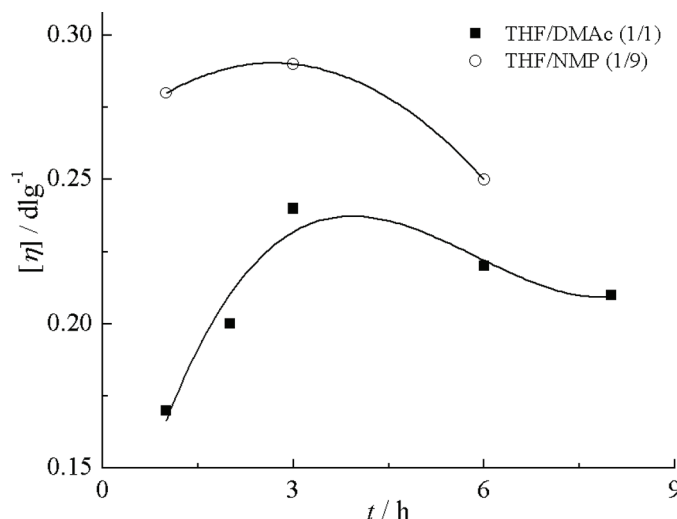

Fig. 2. The effect of the time of the second step on the intrinsic viscosity of PUUSs prepared in THF/DMAc (1/1, v/v at a monomer concentration of 15 wt.% without catalyst) and THF/NMP (1/9, v/v, at a monomer concentration of 25 wt.% and a catalyst concentration of 0.05 mol%) reaction mixtures.

tions of the isocyanate groups, which are related to a disruption of the stoichiometry, and are more pronounced during prolonged polymerization time. The highest values of intrinsic viscosity and molecular weight in the 1/1 (v/v) THF//DMAc mixture were obtained for the sample PUUS15-0, synthesized without the catalyst, with the initial concentration of monomers of 15 wt. % and the time of the second step of 3 h. Intrinsic viscosity of the sample PUUS15-0 amounted 0.24 dL g^{-1}, while the number average molecular weight determined by GPC was 12440 g mol^{-1} (Table I).

In the presence of the highest catalyst concentration (0.1 mol %), a slow decrease in the molecular weights of the copolymers (from 9400 to 8050 gmol^{-1}) with increasing monomer concentration (samples PUUS7.5-0.1, PUUS10-0.1 and PUUS15-0.1) was observed. The highest molecular weight of the sample PUUS7.5-0.1, obtained with the lowest monomer concentration, could be a consequence of polymer fractionation during precipitation and the loss of low molecular weight fractions, as was supported by the low polymer yield (62 %). Further decreases in molecular weight (samples PUUS10-0.1 and PUUS15-0.1) could be explained by the higher probability of side reactions at the highest catalyst concentration of 0.1 mol %, with increasing the monomer concentration. The side reactions were less pronounced at the lower catalyst concentration of 0.05 mol %, and an increase of the molecular weight of the copolymer could be observed with increasing monomer concentration (samples PUUS10-0.05 and PUUS15-0.05).

As was already stated, a key factor for the successful synthesis of PDMS-based poly(urethane–urea)s is the proper selection of the solvent. During the chain extension step in the 1/1 (v/v) THF/DMAc solvent mixture, an undesirable macroscopic separation of the reaction mixture was observed, as well as a premature precipitation of the copolymer, which resulted in low molecular weight of the copolymers. It is obvious that the employed solvent mixture was not polar enough to dissolve efficiently the growing copolymer chains. To overcome this problem, it was decided to increase the proportion of polar DMAc in the mixture.

The increase in the proportion of DMAc to 1/2 (v/v) THF/DMAc led to optically clearer, but not perfectly homogeneous reaction mixture, and to a certain increase in both the intrinsic viscosity and molecular weight of the obtained copolymers, in comparison with the syntheses in 1/1 (v/v) THF/DMAc (Table I). A further increase in the proportion of the polar co-solvent to the ratio 1/9 (v/v) THF/DMAc led to copolymer precipitation in the presence of the catalyst, very soon after the chain extender had been added. It was not possible to analyze this sample because it was not completely soluble in NMP, used for both the viscosity and GPC measurements. All previous samples were completely soluble in NMP, but only partially soluble in DMAc.

Then a new copolymer was prepared under the same conditions, in 1/9 (v/v) THF/DMAc mixture, but without the catalyst. The reaction mixture was clear

and homogeneous in this case, and consequently, the molecular weight of obtained copolymer was significantly higher. It was noticed that a molecular weight of the copolymer increased from 12440 to 18500 g mol^{-1} when the THF/DMAc ratio was changed from 1/1 to 1/9, at an initial monomer concentration of 15 wt. % in the absence of the catalyst in both cases. A further increase in the proportion of DMAc would be unfavorable because it would lead to a reduction in the solubility of the siloxane prepolymer in the reaction mixture. A certain minimum concentration of THF in the solvent mixture was necessary to maintain the PDMS molecules in solution until they had completely reacted with MDI.

Furthermore, the synthesis with monomer concentrations higher than 15 wt. % (for instance with 25 wt. %) was not successful, since precipitation of the copolymer again occurred.

According to the presented results, the copolymer with the highest molecular weight in Series I was obtained when the following reaction conditions were employed in the second phase of the synthesis: a reaction time of 3 h; a ratio of THF/DMAc co-solvents 1/9 (v/v); a monomer concentration of 15 wt. % and in the absence of the catalyst.

However, further attempts to synthesize PUUSs with a content of the hard segment higher than 20 wt.% under these conditions, again resulted in the premature precipitation of copolymers from the reaction mixture. It could be concluded that DMAc as a co-solvent is not sufficiently polar to provoke dissociation of the very strong hydrogen bonding between the urea groups, the concentration of which in the polymer chain increases with increasing hard segment content.

Series II

As was shown above, increasing the proportion of the more polar DMAc in the mixture with THF did not lead to the desired increase in molecular weight of PUUSs. In most cases, the reaction mixtures were turbid during the synthesis, due to precipitation of the copolymer, and consequently the viscosities and molecular weights of obtained samples were rather low. To overcome these problems, it was decided to replace DMAc as the polar component in the solvent mixture with NMP. NMP is also an aprotic solvent which is often used for the synthesis of thermoplastic poly(urethane–urea)s,[15] polyureas,[23,24] poly(amide–urea)s,[25] and poly(ester–urea)s,[26] but is slightly more polar than DMAc.[27]

To study the effect of the change of polar component of the reaction solvent, on the molecular weight of PUUSs, Series II was prepared in a THF/NMP (1/9, v/v) solvent mixture. Analogously to Series I, the time that was required to complete the first step of reaction was independently determined for all the syntheses and these values are given in Table I. The reaction time was found to decrease (from 19 to 15 min) with increasing concentration of both catalyst and reactants,

similar to when the THF/DMAc solvent mixtures were used. It was also registered that the rate of the reaction between PDMS and MDI was significantly higher in the THF/NMP mixture and showed less dependence on the initial concentration of monomers.

In Series II, the effect of the monomer concentration in the reaction mixture and reaction time of the second phase on the intrinsic viscosity and molecular weight of the obtained copolymers was investigated. The results are presented in Table I and Fig. 2. Unlike the syntheses in THF/DMAc, the reactions in THF/ /NMP proceeded in a perfectly clear solution after the addition of chain extender and precipitation was not observed regardless of any change in the reaction conditions. The molecular weight of the copolymers synthesized at reaction time of 1 h with a catalyst concentration of 0.05 mol % increased significantly with the concentration of the monomers in the reaction mixture, as was found for Series I. Moreover, in this solvent mixture, it was possible to synthesize PUUSs at a higher initial concentration of the monomers, *i.e.*, 25 wt. %. The values of $\bar{M}_n$ were 8230, 11050 and 13040 g mol^{-1} for monomer concentrations of 10, 15 and 25 wt. %, respectively (Table I). The reaction mixtures were perfectly homogeneous throughout the reactions and no precipitation was observed with any of the monomer concentrations polymerized in THF/NMP. Similar to Series I, a further increase of the reaction time to 3 hours resulted in increased viscosity and molecular weight of the copolymer to 19540 g mol^{-1} when the synthesis was performed at a monomer concentration of 25 wt. % in the presence of 0.05 wt. % of the catalyst. When the reaction time was increased to 6 hours, the viscosity of the copolymer decreased, *i.e.*, the trend was very similar to that in Series I (Fig. 2).

Despite the higher molecular weights obtained without a catalyst in the mixture of THF/DMAc (Table I), the syntheses in the THF/NMP mixture were performed in the presence of the catalyst because it was believed that the control of the reaction would be better. As will be shown later, the copolymer composition, *i.e.*, the hard segment content was determined by analysis of the ^{1}H-NMR spectra of the obtained copolymers. A better agreement with theoretical hard segment content was obtained for the samples that were synthesized in the presence of the catalyst than without (Table I).

Generally, the molecular weights of the PUUSs of Series II were higher than those prepared in the THF/DMAc mixture under the same conditions. The differences were more obvious with increasing concentration of the monomers in the reaction mixture, which was a consequence of better solubility of the PUUSs in THF/NMP than in THF/DMAc. This also shows that besides the choice of solvent, a very important factor for the successful synthesis of PUUS copolymers is a higher concentration of the monomers in the reaction mixture.

The yields of synthesized PUUS copolymers after precipitation in methanol/water mixture were between 62 and 90 % in Series I, while in Series II they

ranged between 86 and 93 %. The highest yield of 93 %, as well as the highest number average molecular weight of 19540 g mol^{-1} was obtained for the sample PUUS25-0.05 synthesized in the THF/NMP mixture. The polydispersity index was about 2 in most cases (Table I), indicating typical products of step polymerrization.

Based on all the results presented herein, it could be concluded that the optimal experimental conditions for the synthesis of PUUSs are THF/NMP (1/9, v/v) solvent mixture, a temperature of 40 °C, a catalyst concentration of 0.05 mol % and a reaction time of the second step of 3 h.

The structure and composition of PUUSs

The structure of the copolymers was verified by ^{1}H-NMR and ^{13}C-NMR spectroscopy. The ^{1}H-NMR spectrum of the PUUS25-0.05 sample from Series I is shown in Fig. 3.
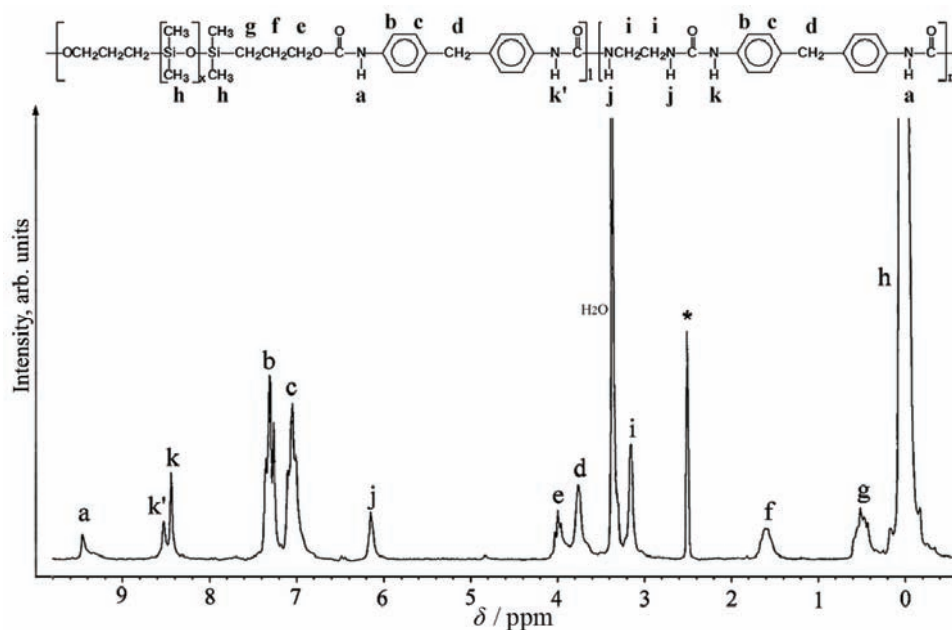

Fig. 3. ^{1}H-NMR Spectrum of the sample PUUS25-0.05 (the reaction time of the second step was 3 h).

In the ^{1}H-NMR spectrum the following characteristic signals were observed: 0.04 ppm of the Si–CH$_3$ protons; 0.53, 1.60 and 3.99 ppm of the CH$_2$ protons from the PDMS propylene residue; 3.15 ppm of the CH$_2$–CH$_2$ protons from the ethylene diamine residue; 3.75 ppm of the MDI methylene protons and 7.04 and 7.30 ppm of the aromatic protons from the MDI residue; 6.14 ppm of the NH urea protons next to ethylene diamine residue; 8.44 and 8.52 ppm of the NH

protons next to the aromatic rings, from the hard and soft segments, respectively; and 9.46 ppm of the NH urethane protons.

The content of hard segments was calculated from the ^{1}H-NMR spectra from the ratio of intensities of the aliphatic proton signals from the ED residues and the methyl proton signals from the –SiCH$_3$ groups, according to the following formulas:

$$x_{HS} = \frac{\dfrac{I(CH_2 - CH_2)}{4}}{\dfrac{I(SiCH_3)}{6 \cdot \overline{X}_X + 6} + \dfrac{I(CH_2 - CH_2)}{4}}; \quad x_{SS} = 1 - x_{HS}$$

$$w_{HS} = \frac{x_{HS} \cdot M_{HS}}{x_{SS} \cdot \overline{M}_{SS} + x_{HS} \cdot M_{HS}}; \quad w_{SS} = 1 - w_{HS} \; w_{SS} = 1 - w_{HS}$$

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 the hard and soft segments, respectively; $M_{HS} = 310$ g mol^{-1}, molecular weight of the MDI–ED unit; $\overline{M}_{SS} = 1250$ g mol^{-1}, molecular weight of the PDMS–MDI unit; $\overline{X}_X = 11.3$, the degree of polymerization of the PDMS prepolymer.

The experimental contents of the hard segments of the synthesized copolymers are presented in Table I. Better agreement of the experimental contents of the hard segments with the content predetermined by the composition of the initial reaction mixtures (20 wt. %) was obtained for the samples synthesized when the second step lasted 3 h. The highest deviation was observed for the samples synthesized without catalyst – the wt. % of HS was 27.3 and 27.2 for the samples PUUS15-0 and PUUS15B-0 from Series I. This was probably the result of the thermal instability of the hydroxypropyl end groups of the siloxane prepolymer under the polymerization conditions. Earlier studies showed that hydroxypropyl end groups undergo a cyclization reaction when heated, thereby losing their functionality and reactivity.[28–30] In the absence of the catalyst, the hydroxypropyl end groups preferentially degraded rather than reacted with the present NCO groups. This further suggests that the presence of the catalyst is very important for fast building of urethane bonds between MDI and PDMS residues, and for obtaining the predicted copolymer composition. The lengths of the hard segment, *l*(HS), calculated as the number of MDI–ED units per one soft segment, are also given in Table I. The values of *l*(HS) were in range from 0.5 to 1.5, while the theoretical value, predetermined by the composition of the reaction mixture, was 1MDI–ED unit per 1 soft segment.

The molecular structure of the copolymers was also confirmed by FTIR spectroscopy. Characteristic absorption bands appeared at 2960 and 2905 cm^{-1} (ν_s and ν_{as} of C–H), 1595 and 1410 cm^{-1} ($\nu_{(C=C)arom}$), 1538 and 1510 cm^{-1}

(Amide II bands), 1303 cm^{-1} (Amide III band). The presence of the bands at 1072 and 1015 cm^{-1} ($\nu_{(Si–O–Si)}$), 1258 cm^{-1} $\gamma_{(Si–CH_3)}$ and 792 cm^{-1} $\delta_{(Si–CH_3)}$ confirmed the incorporation of the PDMS soft segments into the copolymer chains.

It is well established that the morphologies and the physical properties of segmented poly(urethane–urea)s mainly depend on the extent of hydrogen bonding between the copolymer chains.[31–34] There are two regions in the FTIR spectrum related to the hydrogen bonding of the hard segments. The first is the absorption region at 1620–1760 cm^{-1}, corresponding to stretching vibrations of the C=O groups, where multiple bands were found. An intensive peak located at 1634 cm^{-1} is assigned to ν(C=O) absorbance of the ordered hydrogen-bonded urea bonds, while the absorption peaks at 1733 cm^{-1} ($\nu_{(C=O)non-bonded\ urethane}$), 1708 cm^{-1} ($\nu_{(C=O)hydrogen-bonded\ urethane}$), 1694 cm^{-1} ($\nu_{(C=O)non-bonded\ urea}$) and 1670–1680 cm^{-1} ($\nu_{(C=O)hydrogen-bonded\ urea,\ disordered}$) appear as small shoulders. The C=O region of the spectra of the samples was fitted by the Gaussian deconvolution technique, using the PeakFit v4.12 (SeaSolve Software Inc.) program, whereby the locations and areas of each of these bands was given (Table II). The Gaussian deconvolution procedure showed very good agreement between observed and generated values (Fig. 4). The C=O and N–H stretching regions of the FTIR spectra of selected PUUS samples are shown in Figs. 5a and 5b, respectively. In the carbonyl region of FTIR spectra of the PUUS copolymers, the C=O absorption peak of hydrogen bonded urea dominated (Fig. 5a) and its area ranged from 49 to 59 %.

TABLE II. Curve fitting results (area, %) for the C=O stretching region of the FTIR spectra of some of the synthesized PUUSs

Sample	ν / cm^{-1}					$X_{b,UT}$	$X_{b,UA}$	$X_{o,UA}$	$X_{d,UA}$
	1733	1708	1694	1670–1680	1634		%		
Series I (the reaction time of the second step was 3 h)									
PUUS15-0.05	11.5	19.8	4.6	5.2	58.9	63.3	93.3	85.7	7.6
PUUS15-0	12.0	22.6	6.0	6.9	52.5	65.3	88.4	80.3	9.2
PUUS15A-0.05	10.4	25.8	9.5	4.1	50.3	71.3	85.1	78.7	6.4
PUUS15B-0	12.8	22.4	4.5	7.3	53.0	63.6	93.1	81.8	11.3
Series II									
PUUS15-0.05 (1 h)	12.2	27.1	6.7	4.6	49.4	69.0	89.0	81.4	7.6
PUUS25-0.05 (1 h)	12.6	25.1	8.5	3.9	49.9	66.7	86.4	80.1	6.2
PUUS25-0.05 (3 h)	11.4	24.7	7.6	3.1	53.2	68.4	88.1	83.3	4.8

FTIR Spectroscopy has also been used for the analysis of phase separation in PU and PUU copolymers. The degree of phase separation is reflected in the size and perfection of the domains. The success in the utilization of FTIR spectroscopy for investigating phase separation depends on the existence of bands sensitive to mixed and phase separated states. It was proposed that the degree of microphase separation in poly(urethane–urea) copolymers could be assessed

based the degree of hydrogen bonding of the urea C=O, whereby the extent of microphase separation is directly related to the intensity of the ordered urea absorbance at 1634 cm^{-1}. Simultaneously, the relative intensity of the absorbance of disordered hydrogen bonded urea carbonyls is a measure of the phase mixing between the hard and soft segments.[35–37] The degree of hydrogen bonding of urethane groups ($X_{b,UT}$) and urea groups ($X_{b,UA}$), as well as the percentage of ordered ($X_{o,UA}$) and disordered ($X_{d,UA}$) urea–urea hydrogen bonds were calculated in following way:[21]

$$X_{b,UT} = \frac{Area\left(1708 \text{ cm}^{-1}\right)}{Area\left(1708 \text{ cm}^{-1}\right) + Area\left(1733 \text{ cm}^{-1}\right)}$$

$$X_{b,UA} = \frac{\Sigma\, Area\left(\text{bonded}\right)}{\Sigma\, Area\left(\text{bonded}\right) + Area\left(1694 \text{ cm}^{-1}\right)}$$

$$X_{o,UA} = \frac{Area\left(1634 \text{ cm}^{-1}\right)}{\Sigma\, Area\left(\text{bonded}\right) + Area\left(1694 \text{ cm}^{-1}\right)}$$

$$X_{d,UA} = \frac{Area\left(1670-1680 \text{ cm}^{-1}\right)}{\Sigma\, Area\left(\text{bonded}\right) + Area\left(1694 \text{ cm}^{-1}\right)}$$
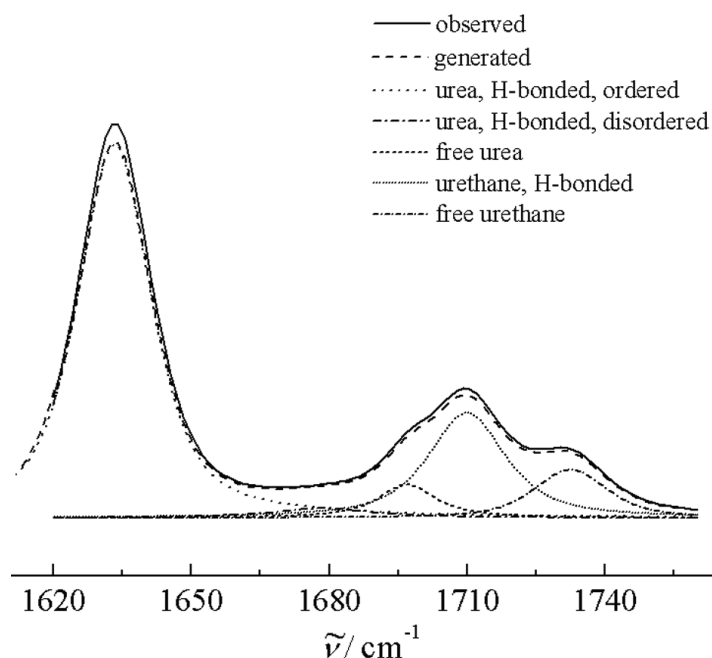

Fig. 4. Deconvolution of the carbonyl absorbance region of the FTIR spectrum for sample PUUS25-0.05 (reaction time of the second step was 3 h).

The Σ *Area*(bonded) is given as the sum of the areas at 1634 cm^{-1} (ordered hydrogen bonded urea bonds) and at 1670–1680 cm^{-1} (disordered hydrogen-bonded urea bonds):

$$\Sigma\,Area\left(\text{bonded}\right) = Area\left(1634\text{ cm}^{-1}\right) + Area\left(1670-1680\text{ cm}^{-1}\right)$$
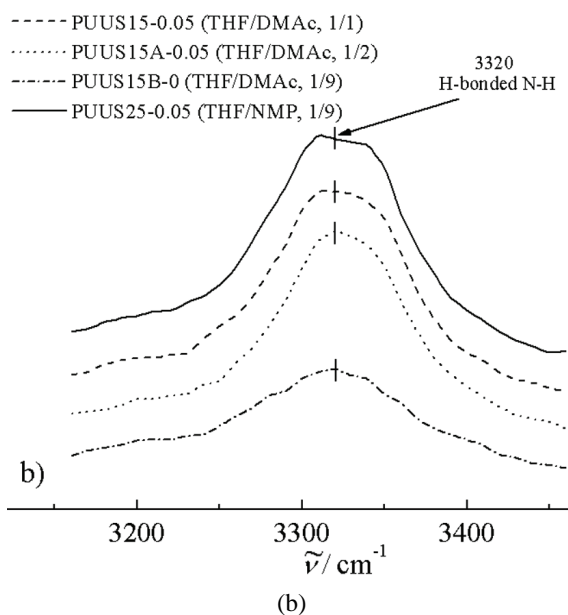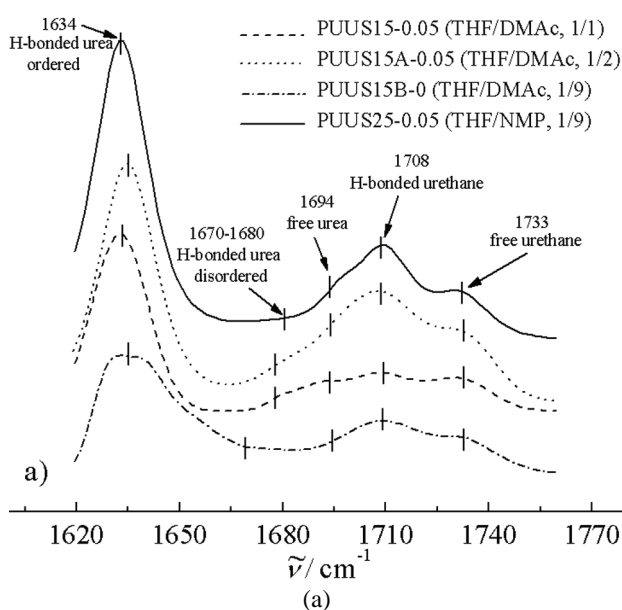

Fig. 5. FTIR Spectra of selected PUUS copolymers in the C=O (a) and N–H (b) stretching region (the reaction time of the second step was 3 h).

The results of these calculations for the prepared copolymers are given in Table II. It can be seen that the $X_{o,UA}$ values referring to urea ordered hydrogen bonding were similar in all samples and ranged from 79 to 86 %, indicating a high degree of microphase separation in the PUUS copolymers. The percentages of disordered hydrogen bonding urea, $X_{d,UA}$, ranged from 4.8 to 11.3 %, whereby somewhat higher values of $X_{d,UA}$ were calculated for the PUUS15-0 and PUUS15B-0, copolymers obtained without a catalyst in the mixture of THF/DMAc. This confirms the earlier conclusion that better control of reaction was enabled by the presence of the catalyst.

The second region related to hydrogen bonding was the N–H stretching region between 3100 and 3500 cm^{-1}, where a single peak centered at 3320 cm^{-1} was observed. This absorbance was assigned to the stretching vibrations of hydrogen-bonded N–H in both the urea and urethane units, indicating that all N–H groups in the PUUSs participated in hydrogen bonding. Using the Peakfit program, it was not possible to separate the peaks of disordered, hydrogen bonded N–H groups and free N–H groups, which for the PUU copolymers are characterized by absorbances at 3390 and 3450 cm^{-1}, respectively.[33] However, by comparison of the absorbance shape and intensity in this region, some qualitative assessment can be given.[37] Namely, the shapes and relative intensities of N–H absorbances were similar for most samples with a relatively sharp band at 3320 cm^{-1}, indicating a similar degree of phase separation (Fig. 5b). The broadening of the N–H band observed for the PUUS15B-0 sample implies a certain increase of phase mixing between the hard and soft segments, which is consistent with the previous analysis of the C=O region.

Thermal properties of the PUUSs

The results of DSC (first scan) and TG analyses of the PUUS synthesized in different solvent mixtures are summarized in Table III. In the DSC thermograms of PUUSs (Fig. 6), the glass transition temperatures of the soft segments were observed in the range from –112 to –99 °C, indicating that the PDMS was microphase separated from the hard segment phase. A relatively broad endothermic peak was observed between 50 and 68 °C. According to Seymour and Cooper, this peak relates to disruption of short-range ordering between the hard segments, *i.e.*, to dissociation of the hydrogen bonds.[38] The changes of the enthalpies of the endothermic peaks were in range from 0.83 to 1.22 J g^{-1}. In the second scan, this endothermic peak was not present, indicating that it was not possible to reform hydrogen bonds during the relatively fast cooling of the sample in the calorimeter.[39] For this reason, the first scan is presented in Fig. 6. The values of the glass transition temperatures of the soft segment did not changed significantly in the second scan.

TABLE III. DSC and TGA data of selected PUUSs under a nitrogen atmosphere (the reaction time of the second step was 3 h)

| Sample[a]	Reaction solvent	T_g (PDMS) °C	T, endo-peak °C	$T_{5\%}$ °C	$T_{10\%}$ °C	$T_{50\%}$ °C	$T_{90\%}$ °C	DTG_{max} °C	Residual weight at 600 °C, %
PUUS10-0.05	THF/DMAc 1/1	–109	50	219	256	348	579	278/349/473	7.7
PUUS15-0.05	THF/DMAc 1/1	–99	58	252	269	374	610	287/361/489	11.5
PUUS15-0	THF/DMAc 1/1	–112	52	216	271	374	537	291/348/472	1.3
PUUS15A-0.05	THF/DMAc 1/2	–107	56	256	276	373	592	288/352/488	8.9
PUUS25-0.05	THF/NMP 1/9	–99	68	163	239	380	556	285/338/472	1.4
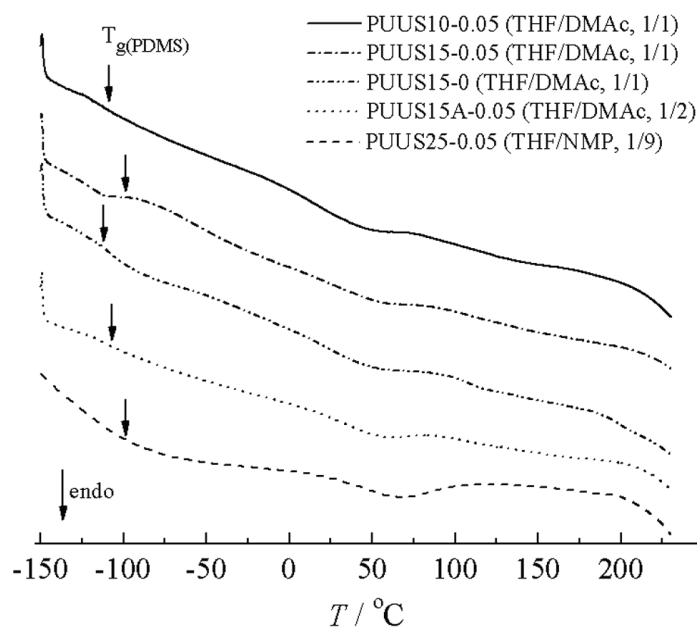
Fig. 6. DSC Analysis of selected PUUS copolymers (the reaction time of the second step was 3 h).

High temperature transitions were not detected in DSC thermograms, since the thermal degradation of the urea and urethane bonds begins around 200 °C, before melting the hard segments of the PUUS. This corresponds to the results of the TG analysis and to the proposed mechanism of degradation of poly(urethane––urea)s.[40]

The thermal stability and degradation behavior of the synthesized PUUSs were investigated by thermogravimetric analysis under a nitrogen atmosphere.

The TG and DTG curves (Fig. 7) indicate that thermal degradation occurs in three steps. The characteristic temperatures for weight losses of 5, 10, 50 and 90 %, respectively, as well as the residual weight at 600 °C are considered. The $T_{5\%}$ value is considered to represent the beginning of mass loss. The results show that
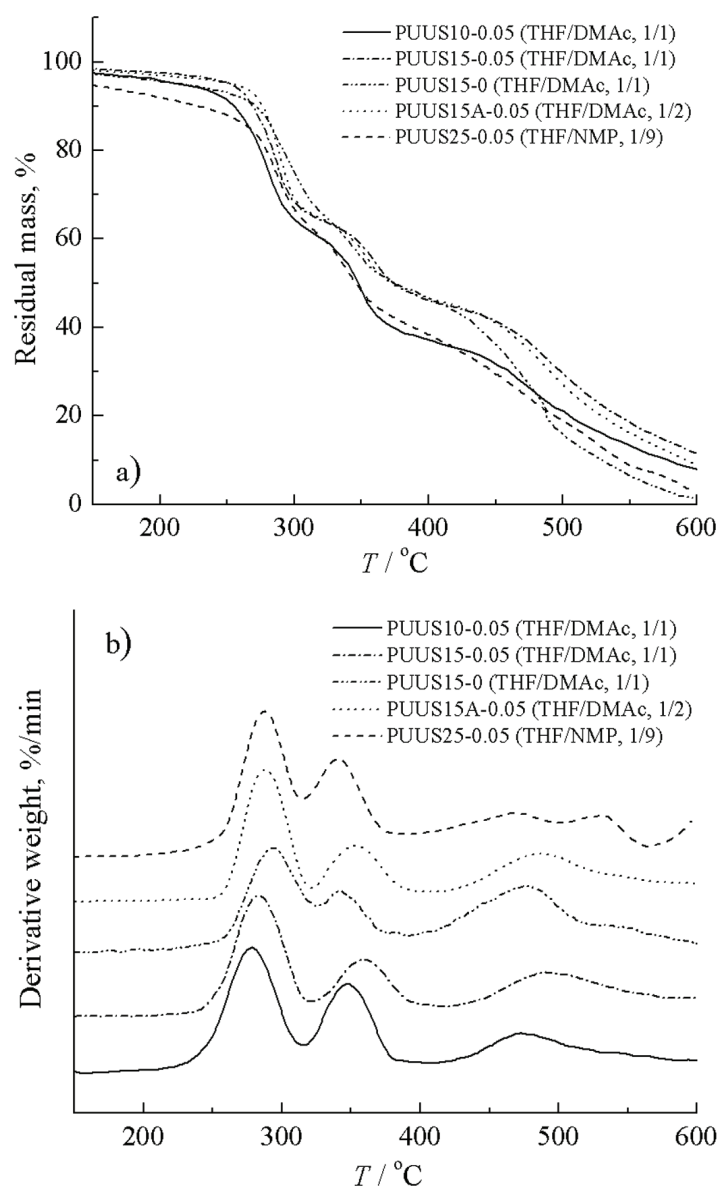

Fig. 7. TG and DTG analysis of selected PUUS copolymers (the reaction time of the second step was 3 h).

degradation of copolymers commenced above 200 °C, with the exception of the sample PUUS25-0.05, synthesized in THF/NMP, which lost 5 % of its weight by 163 °C (Table III). In this case, the weight loss begins at a lower temperature probably due to the presence of traces of NMP solvent in the sample, which is low volatile solvent and because of that cannot be easily removed from the sample. The temperatures of the maximal rate of degradation occurred around the same value for all samples, regardless of the reaction solvent (Table III).

It is well known that the thermally weakest link in polyurethane copolymers is the urethane bond, which commences 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.[41]

The thermal degradation of the synthesized PUUSs was a process, which occurred in three main steps under a nitrogen atmosphere. The thermal degradation of the copolymers commenced with decomposition of the urethane and urea bonds (the first and the second main DTG peaks), followed by degradation of the soft PDMS segments (the third DTG peak, between 400 and 500 °C). Further decomposition in the region between 500 and 600 °C corresponds to carbonization of the aromatic structures of MDI.[41,42]

The residual weights of the PUUS samples at 600 °C ranged from 1.4 to 11.5 % (Table III). The residual weight originated mainly from the "organic"-fraction (MDI–ED), while the PDMS chains under a nitrogen atmosphere degraded by depolymerization, giving cyclosiloxanes as the degradation products.[5]

Water contact angle of the PUUSs

Special attention was focused on the wettability and hydrophobicity of the PUUSs surface, through the measurement of the static water contact angle (WCA). The determined values of the WCA for the PUUS copolymers are reported in Table IV. A water contact angle of 90° or higher indicates a non-wetting (hydrophobic) surface. The values of the WCA for the PUUSs were in a very narrow range from 87.4 to 91.3°, which could be explained by the similar contents of hard and soft segments. Thus, the surfaces of the obtained copolymers were on the border between weak hydrophilic and weak hydrophobic. In an environment other than water, they could rearrange very rapidly from hydrophilic to hydrophobic and *vice versa*, in dependence on the polarity of the surrounding environment. In an environment more polar than water, the hard segments are on the top of the surface, while a non-polar environment causes migration of the PDMS, which covered most of the surface of the PUUSs. This behavior is due to the very low surface energy of PDMS. As a comparison, the values of the water contact angle for thermoplastic poly(urethane–siloxane) elastomers, based on

MDI, BD and α,ω-dihydroxy-[poly(caprolactone)–poly(dimethylsiloxane)–poly-(caprolactone)] (1:2:1 molar ratio of the reactants) were in the range from 93.7 to 99.9°, and these copolymers were considered to be hydrophobic.[43] Similarly, the contact angles of poly(ester–siloxane)s based on poly(butylene terephthalate) as the hard segments and poly(caprolactone)–poly(dimethylsiloxane)–poly(caprolactone) as the soft segments were in the range from 97 to 125°, depending on the hard to soft segment ratio, which classified these copolymers again as hydrophobic.[44]

TABLE IV. WCA values for selected PUUS

Sample	Contact angle, °
Series I (the reaction time of the second step was 3 h)	
PUUS15-0.05	87.4±1.5
PUUS15-0	89.0±1.4
PUUS15A-0.05	91.3±1.7
PUUS15B-0	89.8±1.0
Series II	
PUUS15-0.05 (1h)	89.5±1.1
PUUS25-0.05 (1h)	88.6±0.8
PUUS25-0.05 (3h)	90.8±0.9

Topographical investigation of the PUUSs by AFM

The morphology of the PUUS copolymers was investigated by AFM. A contact mode AFM image of the surface topology of the sample PUUS25-0.05 is presented in Fig. 8. The distribution of hard and soft phases of the copolymer surface was analyzed by 3D- and 2D-topographic images. Based on prior studies, it is known that the bright regions represent the hard phase (hard ordered domains or crystalline regions in a copolymer), while the darker regions represent the soft PDMS phase. The AFM images clearly showed that the PUUS copolymers formed a two-phase microstructure and crystallized in the form of sphere-
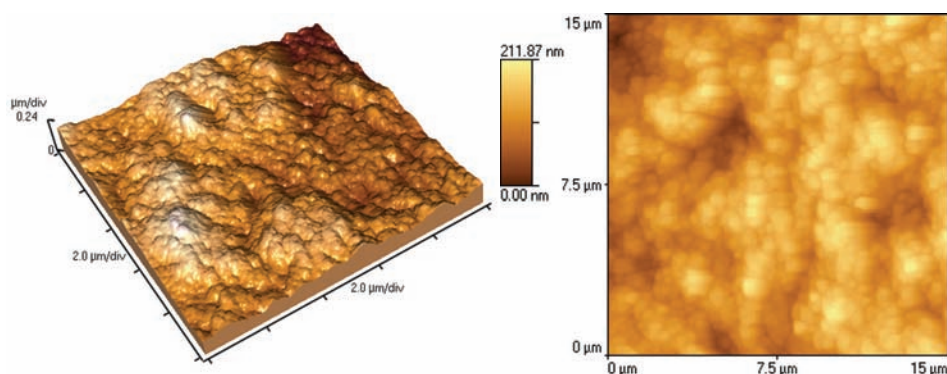

Fig. 8. 3D- and 2D-AFM images of the sample PUUS25-0.05 (size 15 μm).

litic superstructures. The average diameter of the hard segment domains, dispersed in the soft PDMS matrix was about 600 nm. AFM also confirmed that the hard-segment had a crystalline structure, which was not observed by DSC since the degradation of copolymers began before melting.

CONCLUSIONS

Segmented PUUSs were prepared by a two-step polymerization procedure in two different reaction mediums. It was demonstrated that the more polar THF/ /NMP mixture was a better solvent system for the synthesis of PUUSs than THF/ /DMAc. Copolymers with higher molecular weight were obtained in the THF/ /NMP mixture. It was also shown that not only was the solvent selection an important factor for the successful synthesis of the PUUS copolymers, but also a higher concentration of the monomers in the reaction mixture. Based on the obtained results, it was concluded that the following conditions were optimal for the synthesis of PUUSs in THF/NMP mixture: a temperature of 40 °C, a catalyst concentration of 0.05 mol % (calculated to PDMS), a monomer concentration of 25 wt. % in the reaction mixture and a reaction time for the second step of 3 h. The structure and composition of the PUUSs were confirmed by ^{1}H-NMR and FTIR spectroscopy. Small variations in the structure were obtained in dependence on the reaction conditions applied for the synthesis. A better agreement of the experimental hard segment content, determined by analysis of ^{1}H-NMR spectra of copolymers, with the theoretical hard segment content was obtained for the samples that were synthesized in the presence of catalyst than in its absence. FTIR Spectroscopy was employed for an analysis of the phase separation in the PUUS copolymers. It was calculated that the fraction of ordered hydrogen-bonded urea groups ranged from 79 to 86 %, indicating a high degree of microphase separation in the PUUS copolymers. DSC and AFM analysis also revealed that the copolymers show a phase-separated structure. The glass transition temperatures of the soft segments were observed in the range from –112 to –99 °C and a relatively broad endothermic peak was observed between 50 and 68 °C, which was related to the disruption of short-range ordering between hard segments. Thermal gravimetric analysis under nitrogen showed that the PUUSs were stable up to 200 °C. Since the values of the water contact angle were about 90°, the copolymers could possess slightly hydrophilic or hydrophobic surface properties, depending on the surrounding environment. The synthesis of a series of PUUS copolymers of different composition, *i.e.*, different hard/soft segment ratio, under the optimal conditions presented in this manuscript will be the subject of future work. Moreover, the influence of the structure and composition on the properties of the obtained copolymers will be investigated.

ИЗВОД

УТИЦАЈ ПОЛАРНИХ РАСТВАРАЧА НА СИНТЕЗУ ПОЛИ(УРЕТАН–УРЕА–СИЛОКСАНА)

МИЛИЦА БАЛАБАН[1], ВЕСНА АНТИЋ[2], МАРИЈА ПЕРГАЛ[3], IOLANDA FRANCOLINI[4], ANDREA MARTINELLI[4] и ЈАСНА ЂОНЛАГИЋ[5]

[1]*Универзишеш у Бањој Луци, Природно–машемашички факулшеш, Бања Лука, Босна и Херцеговина,* [2]*Универзишеш у Беоīраду, Пољоūривредни факулшеш, Беоīрад,* [3]*Универзишеш у Беоīраду, Инсшишуш за хемију, шехнолоīију и мешалурīију, Беоīрад,* [4]*University of Rome "Sapienza", Deptartment of Chemistry, Rome, Italy* и [5]*Универзишеш у Беоīраду, Технолошко–мешалуршки факулшеш, Беоīрад*

Сегментирани поли(уретан–уреа–силоксани) (PUUS), са тврдим сегментима на бази 4,4′-метилендифенилдиизоцијаната и етилендиамина (MDI–ED) и меким сегментима на бази хидроксипропил-терминираног поли(диметилсилоксана) (PDMS, $\overline{M}_n =$ = 1000 g mol^{-1}), синтетисани су под различитим експерименталним условима. Кополимери са константним молским односом тврдих и меких сегмената (PDMS:MDI:ED = 1:2:1; 20 мас. % тврдих сегмената), синтетисани су у две различите смеше растварача као реакционог медијума, методом двостепене полиадиције. Прва комбинација растварача је била смеша тетрахидрофурана (THF) и *N*,*N*-диметилацетамида (DMAc), док је у другом случају коришћена смеша THF-а и *N*-метилпиролидона (NMP). Реакциони услови су оптимизовани у погледу односа ко-растварача, концентрације катализатора, почетне концентрације мономера и времена одигравања прве и друге фазе реакције. Испитан је утицај примењених експерименталних услова на величину PUUS применом гел-пропусне хроматографије (GPC) и вискозиметрије разблажених раствора [*η*]. Кополимери највећих моларних маса су добијени у смеши THF/NMP (1/9, v/v). Структура и састав кополимера су окарактерисани ^{1}H-NMR и FTIR спектроскопијом. Морфологија синтетисаних кополимера је испитана микроскопијом атомских сила (AFM), док су термичка својства испитана диференцијалном скенирајућом калориметријом (DSC) и термогравиметријском анализом (TGA). Површинска својства кополимера су испитана одређивањем контактних углова са водом (WCA). Кополимери су показали двофазну микроструктуру и били су стабилни до 200 °C у атмостери азота.

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