

Synthesis and Characterization of Novel Urethane-Siloxane Copolymers with a High Content of PCL-PDMS-PCL Segments

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ABSTRACT: Novel polyurethane copolymers derived from 4,4'-methylenediphenyl diisocyanate (MDI), 1,4-butanediol (BD) and α,ω -dihydroxy-[poly(caprolactone)-poly(dimethylsiloxane)-poly(caprolactone)] (α,ω -dihydroxy-(PCL-PDMS-PCL); $M_n = 6100 \text{ g mol}^{-1}$) were synthesized by a two-step polyaddition reaction in solution. In the synthesis of the polyurethanes, the PCL blocks served as a compatibilizer between the nonpolar PDMS blocks and the polar comonomers, MDI and BD. The synthesis of thermoplastic polyurethanes (TPU) with high soft segment contents was optimized in terms of the concentrations of the reactants, the molar ratio of the NCO/OH groups, and the time and temperature of the polyaddition reaction. The structure, composition, and hard MDI/BD segment length of the synthesized polyurethane copolymers were determined by ¹H, ¹³C-NMR, and two-dimensional correlation (COSY, HSQC, and HMBC) spectroscopy, while the hydro-

gen bonding interactions in the copolymers were analyzed by FT-IR spectroscopy. The influence of the reaction conditions on the structure, molecular weight, thermal, and some physical properties was studied at constant composition of the reaction mixture. A change in the molar ratio of the NCO/OH groups and the reaction conditions modified not only the molecular weight of the synthesized polyurethanes, but also the microstructure and therefore the thermal and physical properties of the copolymers. It was demonstrated that only PCL segments with high soft segment contents crystallize, thereby showing spherulitic morphology. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2715–2730, 2011

Key words: segmented polyurethanes; synthesis; structure; α,ω -dihydroxy-[poly(caprolactone)-poly(dimethylsiloxane)-poly(caprolactone)]; thermal properties

INTRODUCTION

Segmented thermoplastic polyurethane elastomers (TPUs) are an important class of polymeric materials consisting of thermodynamically incompatible hard and soft segments. The soft segments usually consists of polyether or polyester macrodiols of moderate molecular weight (1000 to 5000 g mol⁻¹), whereas the hard segments consist of the diisocyanate component and a low molecular weight chain extender (usually a diol or diamine). The thermodynamic incompatibility of the hard and soft segments at low temperatures results in phase separation and, consequently, in a domain structure. The hard segments form glassy or crystalline domains, which act

as physical crosslinking points among the flexible soft segment chains. The two-phase microstructure of TPUs imparts excellent mechanical properties. The properties of TPUs depend on many variables, such as the chemical structure of each type of segment, the molecular weight of the soft segments, the hard/soft segment content ratio, etc.^{1–4} In addition, it is well known that the polymerization method and preparation conditions affect the microstructure and the mechanical properties of TPUs.^{5–12}

Biocompatibility, unique chemistry and processability make polyurethanes ideal for numerous medical applications. Polyether- and polyester-based thermoplastic polyurethanes were the first to be used in biomedical applications; however, it is well known that they are susceptible to degradation by oxidation or hydrolysis.²

Siloxane-containing TPUs have been studied during the last 30 years.¹³ Polyorganosiloxanes were chosen as the soft segments because of their good thermal and oxidative stability, water repellency, low glass transition temperature, low surface energy,

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physiological inertness, and high gas permeability.^{13,14} Poly(dimethylsiloxane) (PDMS) is well known for its excellent biostability and biocompatibility as many copolymers based on PDMS have been synthesized and studied for various biomedical applications in recent times.^{15–17} Similar to conventional polyether- and polyester-based TPUs, PDMS prepolymers with \overline{M}_n values in the range 1000 to 5000 g mol⁻¹ are widely utilized in siloxane-urethane copolymers. The introduction of nonpolar PDMS into the polyurethane backbone has been demonstrated to be difficult because of its poor compatibility with the urethane components. The first attempts to synthesize PDMS-based TPUs resulted in copolymers with poor mechanical properties, which was attributed to the low molecular weight and also to the absence of intersegment hydrogen bonding between PDMS and the hard segments.¹⁸ To overcome this, a second soft segment macrodiol can be added to interject chemical species of intermediate polarity between the hard and PDMS soft segments.^{19–24} It has been established that terminal units attached to the ends of PDMS prepolymer can act as a “compatibilizer” between the polar hard and the nonpolar PDMS segments.¹³ In numerous articles, the preparation of thermoplastic polyurethane and polyurea copolymers based on end-functionalized PDMS prepolymers, such as hydroxyhexyl, aminopropyl, methylaminopropyl PDMS, with high molecular weight were reported.^{25–29} High molecular weight siloxane-based urethane and urea copolymers with good thermal and mechanical properties can be prepared by stoichiometric reaction of diisocyanates and PDMS prepolymers, without any chain extender^{26,30,31} or by the conventional prepolymer method through the employment of chain extenders.^{28,32}

In this paper, the use of a biocompatible triblock prepolymer ($\overline{M}_n = 6100$ g mol⁻¹) consisting of terminal crystallizable poly(ϵ -caprolactone) blocks and a central poly(dimethylsiloxane) block in the synthesis of polyurethanes is presented. The combination of the properties of PCL and PDMS, such as biocompatibility and slow enzymatic degradation rates, makes these block copolymers excellent candidates for surface modifying additives, drug encapsulation, and biomaterial applications.^{33–35} Incorporation of a high content of siloxane segments into the backbone of TPUs significantly improves their biostability.¹⁹

The synthesis and characterization of these novel thermoplastic polyurethanes based on soft PCL-PDMS-PCL and hard MDI/BD segments are presented in this article. The influence of the reaction conditions on the structure, molecular weight, thermal, and some physical properties of the segmented TPUs with high contents of PCL-PDMS-PCL segments are presented.

EXPERIMENTAL

Materials

α,ω -Dihydroxy-(PCL-PDMS-PCL) (from ABCR, $\overline{M}_n = 5700$ – 6900 g mol⁻¹) was dried at room temperature under vacuum for 2 h. The number-average molecular weight (\overline{M}_n) of the α,ω -dihydroxy-(PCL-PDMS-PCL), determined by ¹H-NMR spectroscopy, was 6100 g mol⁻¹ and this value was used in the calculations of the composition of reaction mixtures for the synthesis of the polyurethane copolymers. The calculation of \overline{M}_n of the PCL-PDMS-PCL was based on the number-average molecular weight value of the central PDMS block. Detailed explanation of the segment length calculation in prepolymer are given in the section NMR analysis of the structure and composition of the TPUs in the Results and Discussion. The molecular weight of the central PDMS block was $\overline{M}_{n\text{PDMS}} = 2000$ g mol⁻¹, while the molecular weight of the terminal poly(caprolactone) sequences was $\overline{M}_{n\text{PCL}} = 2050$ g mol⁻¹; 4,4'-Methylenediphenyl diisocyanate (MDI), higher than 98% (from Aldrich) with an isocyanate content of 33.6 wt %, determined by the standard dibutylamine back-titration method, was used as received. Then 1,4-butanediol (BD) (from Aldrich) was distilled and dried over molecular sieves (0.4 nm) before use. *N,N*-dimethylacetamide (DMAc) (from Across) 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 THF/DMAc (1 : 1 v/v).

Synthesis of TPUs

The thermoplastic polyurethanes (TPUs) were synthesized by a catalyzed two-step polymerization in solution. The reactants were MDI, BD and α,ω -dihydroxy-(PCL-PDMS-PCL) ($\overline{M}_n = 6100$ g mol⁻¹). The molar ratio of the reacting –NCO groups (from MDI) and –OH groups (from BD and α,ω -dihydroxy-(PCL-PDMS-PCL)) was varied (1.0, 1.05, and 1.1). The catalyst was stannous octanoate (0.15 mol % Sn(Oct)₂/ α,ω -dihydroxy-(PCL-PDMS-PCL)), while a mixture of DMAc/THF (1/1 v/v) was employed as the solvent.

All the syntheses were performed in a four-neck round-bottom flask equipped with a mechanical stirrer, an inlet for dry argon, a reflux condenser and a dropping funnel. The flask was placed in a silicone oil bath. The synthesis of the copolymer with molar ratio of α,ω -dihydroxy-(PCL-PDMS-PCL) : MDI : BD = 1 : 2 : 1 (i.e., 91.2 wt % soft PCL-PDMS-PCL segments) with a 1.05 molar ratio of NCO/OH groups

(i.e., for TPU-10), is described. The starting reaction mixture: 21.35 g (3.5 mmol) of α,ω -dihydroxy-(PCL-PDMS-PCL), 1.85 g (7.4 mmol) of MDI, 70 mL of DMAc, and 70 mL of THF was charged into the flask at room temperature and then heated up to 80°C under an argon atmosphere. The reaction was started by the introduction of 0.34 mL of catalyst solution in DMAc/THF (2.1 mg, 5.3×10^{-3} mmol of Sn(Oct)₂). The first phase of the polyaddition was realized at 80°C for 40 min under continuous stirring, to form the NCO-terminated prepolymer. The change in the NCO content during the reaction was monitored using the standard dibutylamine back-titration method.³⁶ For chain extension, a solution of BD 0.315 g (3.5 mmol) in 3.6 mL of DMAc/THF was added dropwise to the prepolymer and the reaction was continued for 24 h at the same temperature. The final polymer concentration was about 15.2% (w/w). The reaction mixture was cooled down to room temperature and the copolymer was precipitated into a methanol/water (1/1 v/v) solution, then washed with methanol several times, filtered and dried to constant weight in a vacuum oven at 40°C for 3 days. The yields of synthesized polyurethanes after precipitation in methanol/water mixture were in the range of 76 to 85% (Table I).

To test the TPU properties, 10 wt % solutions in DMAc were prepared and cast onto a Teflon® dish. From the solutions, thin films (0.4–0.5 mm) were obtained by slow evaporation of the solvent for 48 h at 40°C in a force-draft oven and then the films were dried under vacuum at 40°C for 24 h.

Characterization

NMR experiments were performed on Bruker Avance 500 spectrometer equipped with 5 mm inverse detection z-gradient probe. The ¹H and ¹³C-NMR spectra (at 500.13 and 125.75 MHz, respectively) were measured at 25°C using DMSO-*d*₆ as the solvent. Chemical shifts are given on the δ scale relative to the DMSO-*d*₆ signal. Two-dimensional NMR experiments (COSY, HSQC, and HMBC) were performed with standard Bruker pulse sequences. COSY and HSQC were collected with eight scans per 512 increments, while HMBC was collected with 16 scans per 512 increments.

The infrared spectra were taken in the attenuated total reflection (ATR) mode using a NICOLET 380 FT-IR spectrometer equipped with a Smart Orbit ATR attachment containing a single-reflection diamond crystal. The angle of incidence was 45 degrees and the refractive index was 2.4. The scanning range was from 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹ and 64 scans were collected for each sample.

The intrinsic viscosities, $[\eta]$, of the TPUs were measured in DMAc at 25°C using an Ubbelohde viscometer. For each TPU sample, four dilutions of different concentrations (from 0.5 to 0.3 g dL⁻¹) were measured.

The GPC chromatograms were obtained on a Waters 600E instrument equipped with a refractive index detector and three Supelco PI-Gel columns connected in line (crosslinked polystyrene with pore sizes of 10⁻⁵, 10⁻⁶, and 10⁻⁷ m) at 40°C. DMAc at a

TABLE I
Composition of the Copolymers, Conditions of Synthesis, and the Intrinsic Viscosities, Yields and ¹H NMR Analysis of the Synthesized TPUs

Polymer	Composition molar ratio ^a	Conc. of react. (wt %)	Time (II phase), h ^b	T (°C)	$[\eta]$ (dL g ⁻¹)	Soft segment, mole % ^c (NMR)	Soft segment, wt % ^c (NMR)	L_n (HS)	Yields, % ^d
TPU-1	1:2:1	15.2	2.42	40	0.29	34.9	90.9	–	79
TPU-2	1:2:1	19.4	2.25	40	0.25	34.1	90.6	–	79
TPU-3	1:2:1	25.1	1.83	40	0.23	33.5	90.4	–	76
TPU-4	1:2:1	15.2	10	40	0.33	33.5	90.0	1.9	79
TPU-5	1:2:1	15.2	24	40	0.37	39.1	92.3	2.1	80
TPU-6	1:2:1	15.2	48	40	0.37	38.9	91.5	2.1	80
TPU-7	1:2:1	15.2	24	80	0.36	27.4	87.6	1.4	81
TPU-8	1:2.1:1	15.2	24	40	0.42	37.8	91.9	1.7	83
TPU-9	1:2.1:1	15.2	24	60	0.45	36.4	91.4	1.3	82
TPU-10	1:2.1:1	15.2	24	80	0.50	36.5	91.5	2.3	85
TPU-11	1:2.1:1	15.2	48	80	0.49	36.5	91.5	2.3	85
TPU-12	1:2.2:1	15.2	24	80	0.31	24.7	85.9	0.9	84

^a α,ω -dihydroxy-(PCL-PDMS-PCL):MDI:BD; NCO/OH = 1 from TPU-1 to TPU-7; NCO/OH = 1.05 from TPU-8 to TPU-11; NCO/OH = 1.1 for TPU-12.

^b Time of the first phase of the polyaddition 40 min except for TPU-2 and TPU-3 (30 and 20 min., respectively).

^c Mole and weight % of soft segment, predetermined by the composition of the reaction mixtures, were 25.0 and 91.2 respectively.

^d Calculated after precipitation of the copolymers.

flow rate of $1.5 \text{ cm}^3 \text{ min}^{-1}$ was used as the eluent and narrow molar weight distribution polystyrene samples as calibration standards. An amount of $50 \text{ }\mu\text{L}$ of sample solution in DMAc (0.5–1 wt %) were injected. The number-average (\overline{M}_n) and weight-average (\overline{M}_w) molecular weights and polydispersity indexes were evaluated from these measurements.

Differential scanning calorimetry (DSC) was performed using a "Setaram Instrument DSC 151R." The DSC scans were recorded under a helium atmosphere (flow rate 25 mL min^{-1}) at a heating and cooling rate of 10 and 5°C min^{-1} , respectively, (two scans were run for each sample). The samples were analyzed in the temperature range from -150 to 100°C for the determination of the melting point (T_m) and the crystallization point (T_c), as well as the glass transition temperature (T_g) of the copolymers. The weight of the samples was approximately 20 mg .

Wide angle X-ray scattering (WAXS) was performed using a Diffractometric System APD 2000 diffractometer with Cu- K_α radiation using a copper anode (tube: 40 kV , 30 mA , $\lambda = 0.154178 \text{ nm}$). The diffraction patterns were obtained in the Bragg angle range of 5 to 60 degrees. The scan speed was 0.02 s per step in all measurements. From the WAXS data, the percent crystallinity was calculated by peak deconvolution and subsequent determination of the relative areas under the amorphous halo and the crystalline peaks of the X-ray diffraction pattern. The ratio of the area under the crystalline peaks to the total (amorphous + crystalline) area gave the degree of crystallinity.

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

Water contact angle measurements of the polymer films were measured in a Krüss DSA100 using the sessile drop method. Single drops of distilled water with a volume of $20 \text{ }\mu\text{L}$ 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.

RESULTS AND DISCUSSION

In this article, the synthesis and characterization of novel thermoplastic polyurethanes based on soft

PCL-PDMS-PCL and hard MDI/BD segments are presented. The TPUs with high soft segment (SS) contents were synthesized by catalyzed two-step polyaddition in solution (DMAc/THF). In the synthesis of TPUs, the PCL blocks served as compatibilizers for the nonpolar PDMS blocks and the polar comonomers, MDI and BD. The effects of the concentration of reactants, molar ratio of NCO/OH groups, and time and temperature of the polyaddition reaction on the formation of the polyurethanes were investigated to determine the optimal conditions for the preparation of these copolymers.

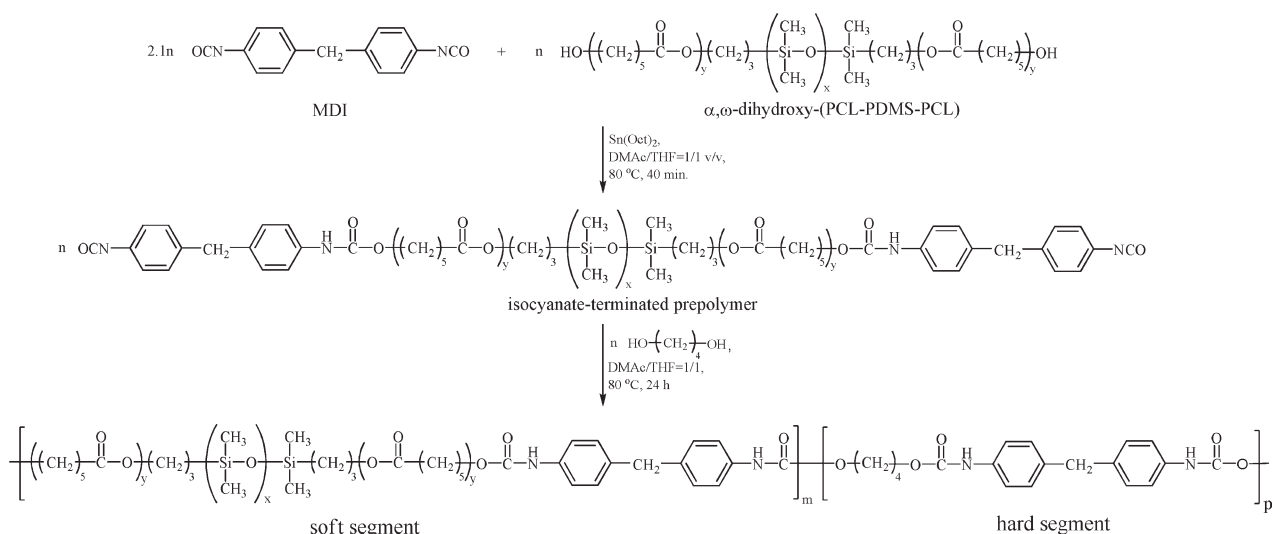
Twelve TPU copolymers with a high content of PCL-PDMS-PCL as the soft segments and MDI/BD as the hard segments were synthesized by a two-step polyaddition reaction in solution. The reaction was catalyzed by the addition of $0.15 \text{ mol } \%$ $\text{Sn}(\text{Oct})_2$, calculated to α,ω -dihydroxy-(PCL-PDMS-PCL). The reaction pathway for the synthesis of the TPUs with a molar ratio of α,ω -dihydroxy-(PCL-PDMS-PCL) : MDI : BD = $1 : 2 : 1$ (i.e., $91.2 \text{ wt. } \%$ PCL-PDMS-PCL segments) at a 1.05 molar ratio of NCO/OH groups is shown in Scheme 1. The isocyanate-terminated prepolymer was first synthesized from α,ω -dihydroxy-(PCL-PDMS-PCL) with an excess of MDI. The initial molar reactant ratio of MDI/ α,ω -dihydroxy-(PCL-PDMS-PCL) was 2.1 . The excess of MDI enables a prepolymer with NCO groups at both chain ends to be obtained. The first polyaddition step was realized at 80°C , for 40 min under an argon atmosphere. In the second step, the isocyanate-terminated prepolymer was extended with 1,4-butanediol at 80°C for 24 h to prepare the final TPUs.

Optimization of the synthesis of TPUs

In this study, the effects of the concentration of the reactants, the molar ratio of NCO/OH groups, and the time and temperature of the polyaddition reaction, on the formation of the TPUs, at almost a constant composition of the reaction mixture, were investigated. The molar ratios of α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer, MDI, and BD are presented in Table I.

The study of the influence of all the previously mentioned reaction parameters on the molecular weight of the TPUs is of practical importance.^{5–12} Its importance lies in the fact that if the reaction parameters can be proven to be deciding, then the properties of TPUs could be controlled and adjusted to any specific application, simply by optimizing the conditions of the TPU synthesis. Therefore, one of the aims of this study was to determine which reaction conditions have an influence on the molecular weight of TPUs.

The following types of experimental conditions were examined:



Scheme 1 Reaction scheme for the synthesis of polyurethane copolymers based on MDI, BD, and α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer.

1. Influence of the concentration of the reactants (15.2, 19.4, and 25.1 wt % in the reaction mixture) at an NCO/OH molar ratio of 1.0, at 40°C.
2. Influence of the chain extension time (2 h 25 min, 10, 24, and 48 h) at an NCO/OH molar ratio of 1.0, at 40°C.
3. Influence of the reaction temperature (40, 60, and 80°C) at an NCO/OH molar ratio of 1.05.
4. Influence of the NCO/OH molar ratio (1.0, 1.05, and 1.1) at 80°C.

The critical choice in the synthesis of the TPUs was deciding the reaction solvent, because of the large difference in the solubility parameters of the siloxane and urethane components. A mixture THF/DMAc (1 : 1 v/v) is known to be good solvent for the synthesis of PDMS-based polyurethane.⁶ This solvent mixture also proved itself to be excellent in the syntheses examined in the present study because during the whole course of the syntheses, the reaction mixtures were and remained homogeneous and optically clear.

Influence of the concentration of reactants

The course of the first step of the polyaddition was monitored using the standard dibutylamine back-titration method (Fig. 1). The progress of the second step of the polyaddition was assessed from the changes in the IR absorption band at 2260 cm^{-1} , assigned to the free NCO groups and by the dibutylamine back-titration method of the reaction mixture during TPU synthesis (Fig. 1).³⁶ The intrinsic viscos-

ities of the final copolymers were also determined (Table I and Fig. 2).

Theoretically, the first phase of the reaction ends at 1.27 wt % of free NCO groups. According to the results of the titration, it was found that the reaction was very rapid and that this value was attained after 40, 30, and 20 min, for reactant concentrations of 15.2, 19.4, and 25.1 wt %, respectively. The presence of free NCO groups (at 2260 cm^{-1}) which terminated the prepolymer chain ends was confirmed by FT-IR spectroscopy. In the first phase of the reaction, it is very important to prevent side reactions, such as trimerization and allophanate formation. These side reactions would lead to functionalities higher than 2, resulting in branching or even crosslinking of the polyurethane. After optimization of the first phase of the reaction, the second phase was also

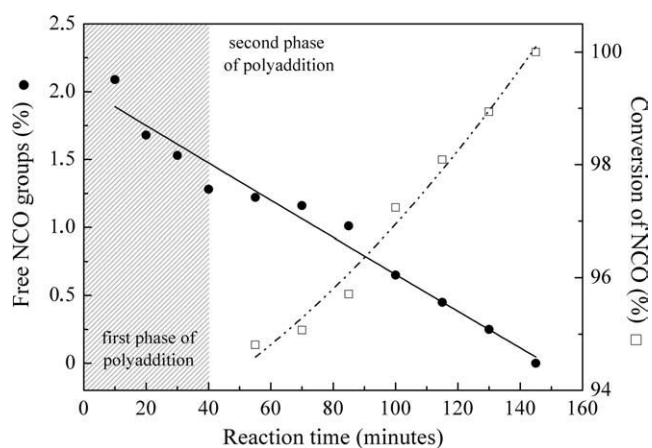


Figure 1 Monitoring of the progress of the polyaddition reaction with time, by the dibutylamine back-titration at a reactant concentration of 15.2 wt %.

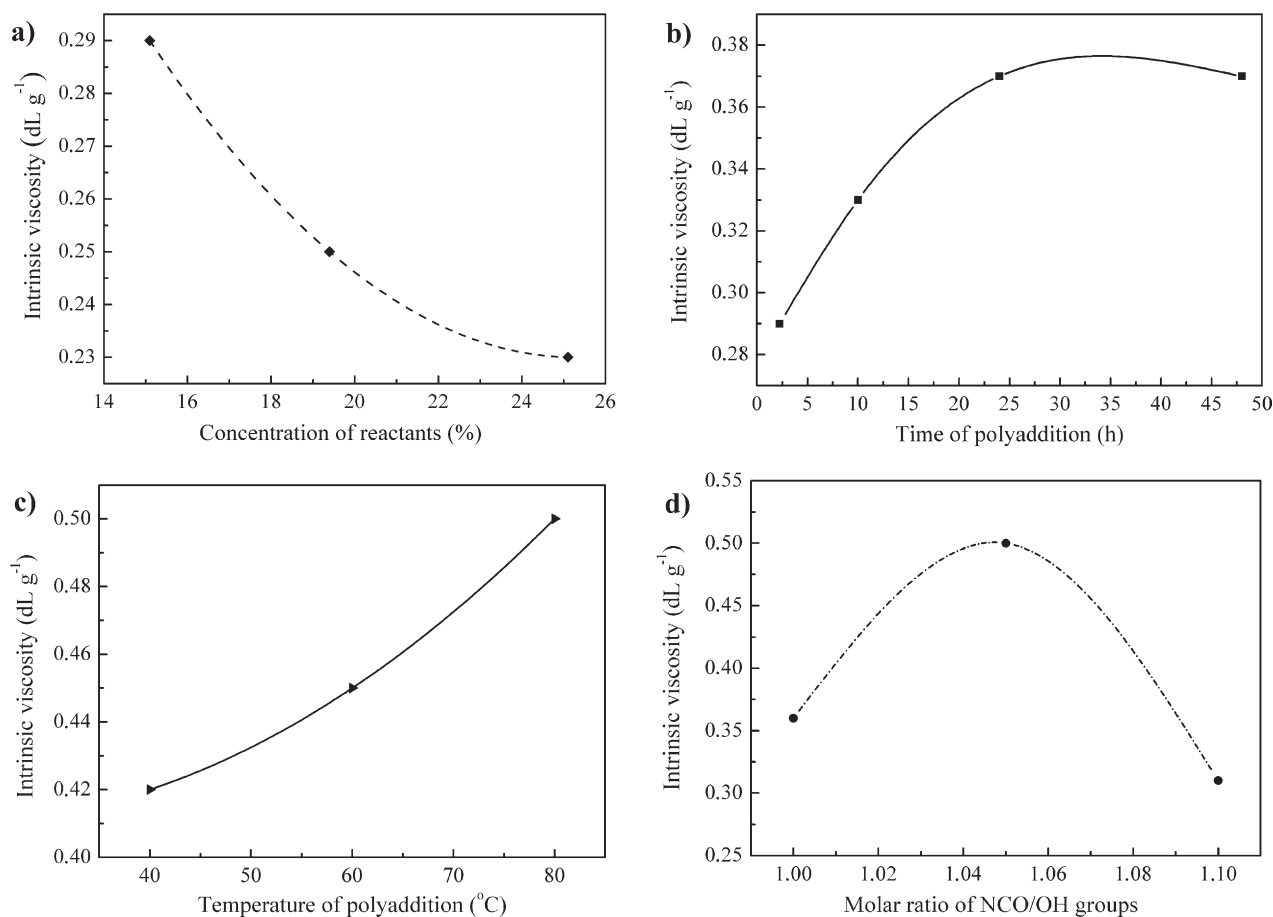


Figure 2 The dependence of the intrinsic viscosity of the TPUs on the reaction conditions: a) concentration of reactants in solution; b) time of the second stage of the polyaddition at 1.0 molar ratio NCO/OH; c) temperature during the second stage of polyaddition at a 1.05 molar ratio NCO/OH; d) molar ratio of NCO/OH at 80°C.

optimized. The optimal duration of the second phase of the reaction, determined by the dibutylamine back-titration method, was 2 h 25 min, 2 h 15 min, and 1 h 50 min reactant concentrations 15.2, 19.4, and 25.1 wt %, respectively, (Table I). The second phase of reaction proceeded faster with higher concentrations of the reactants, as was also observed in the first phase. The same results were obtained by FT-IR spectroscopy. From Figure 2, it can be seen that the optimal concentration of reactants to obtain the highest intrinsic viscosity in the reaction mixture was 15.2 wt %. From these results, it was concluded that the optimal time of the first phase of reaction was 40 min (the TPU-1 sample).

Influence of the chain extension (second phase) time

From Table I, it can be seen that the samples TPU-4, TPU-5, and TPU-6 were synthesized under the same conditions as the sample TPU-1, with only one exception that the second phase of the reactions were longer. The intrinsic viscosity of these four samples was measured. From Figure 2, it can be

seen that the intrinsic viscosity of the copolymers increased with duration of the second phase of the reaction (2 h 25 min; 10 and 24 h) from 0.29 to 0.37 dL g⁻¹. It was established that the intrinsic viscosity did not change after 24 h (Table I). FT-IR spectroscopy and the titration method showed that the end of the second phase of reaction was after 2 h 25 min. However, since the intrinsic viscosity of the copolymers increased with duration of the second phase of the reaction, it could be concluded that FTIR and the titration method were not sensitive enough to detect unreacted NCO groups. By changing the temperature of the polyaddition reaction from 40 to 80°C, the intrinsic viscosity did not change, as can be seen from the results for the sample TPU-7, for which the second phase of the reaction was 24 h at 80°C, with an NCO/OH molar ratio of 1.0 (Table I).

Influence of the reaction temperature

To further optimize the reaction conditions, three samples with a 1.05 molar ratios of NCO/OH groups (TPU-8, TPU-9, and TPU-10) were

synthesized at different reaction temperatures (Table I). The values of the intrinsic viscosity increased with increasing temperature (Fig. 2). From the obtained results, it could be concluded that the reaction conditions for the synthesized TPU-10 sample were in this case optimal. It is obvious from Figure 2 that the reaction temperature is a very important parameter and has a great influence on the intrinsic viscosities of the obtained polyurethanes.

Influence of the molar ratio of NCO/OH groups

The molar ratio of the isocyanate and hydroxyl groups is another critical control variable for polyurethane reactions,^{5,11} as summarized in Table I. This parameter proved to be important for the reaction conversion and optimization of the physical properties of the copolymers. The optimal molar ratio of NCO/OH groups for the polyaddition reaction, that provided highest intrinsic viscosities, was 1.05. From Figure 2, it can be seen that a molar ratio of NCO/OH groups higher than 1.05 (for TPU-12 sample; Table I), led to a decrease in the intrinsic viscosity of the resulting copolymer. A slight excess of isocyanate (1.05) is necessary to obtain the best possible molecular weight. This is attributed to compensation of isocyanates that are consumed during the copolymer synthesis, probably due to hydrolysis of isocyanate groups. Another possible reason is the impurities in commercially available MDI. The obtained results are in agreement with previously reported ones and the conclusion reached that a higher than stoichiometric NCO/OH molar ratio yields higher molecular weights and better mechanical properties of the resulting polymers.⁵

In conclusion, it was found that the optimal conditions for the synthesis of polyurethanes based on PCL-PDMS-PCL segments are: concentration of reactants 15 wt %, time of the first step and the second step of the reaction 40 min and 24 h, respectively, reaction temperature 80°C and molar ratio of isocyanate to hydroxyl groups 1.05.

NMR analysis of the structure and composition of the TPUs

The molecular structures of the synthesized polyurethanes were investigated by ¹H, ¹³C-NMR, and two-dimensional correlation (COSY, HSQC, and HMBC) spectroscopy. A typical ¹H-NMR spectrum of TPU-10 is shown in Figure 3(a). The spectrum of the copolymer showed the characteristic signals: methyl protons of the Si-CH₃ groups appeared at δ = -0.02 ppm, protons from the methylene groups which were attached to the silicon at δ = 0.51 ppm, central methylene protons from the PDMS propylene groups and central methylene protons from the

ε-caprolactone residues at δ = 1.31 ppm and internal methylene protons from the ε-caprolactone residues at δ = 1.54 ppm. The signals of the methylene protons from the ε-caprolactone residues which were attached to the carbonyl group appeared at δ = 2.18 ppm, while the terminal methylene protons from the ε-caprolactone residues appeared at δ = 3.98 ppm. Protons of methylene groups from the 4,4'-methylenediphenyl diisocyanate appeared at δ = 3.79 ppm. The central and terminal methylene protons from the BD residues appeared at δ = 1.70 and 4.09 ppm, respectively. The signals of the methylene protons from the PDMS propylene groups which were connected to ester oxygen atoms appeared at δ = 3.40 ppm. Proton resonances at δ = 7.08 and 7.33 ppm from the aromatic protons, and at δ = 8.49 and 9.32 ppm from the -NH urethane protons were observed.

The molar and weight fractions of the hard and soft segments were calculated from the ¹H-NMR spectra, as the relative intensities of the methyl proton signals arising from the -SiCH₃ groups and the aromatic proton signals from the MDI moiety.

$$x_{\text{HS}} = \frac{I(\text{Ar-H})}{\frac{I(\text{SiCH}_3)}{6 \cdot \bar{X}_n + 6} + \frac{I(\text{Ar-H})}{8}}; \quad x_{\text{SS}} = 1 - x_{\text{HS}}$$

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

where x_{HS} and x_{SS} are the mole fractions of the hard and soft segments, respectively; w_{HS} and w_{SS} are the weight fractions of the hard and soft segments, respectively; $M_{\text{HS}} = 340 \text{ g mol}^{-1}$, molecular weight of the MDI/BD unit; $M_{\text{SS}} = 6350 \text{ g mol}^{-1}$, molecular weight of the PCL-PDMS-PCL segment; $\bar{X}_n = 25.3$, the degree of polymerization of the PDMS-block in the prepolymer.

The number average molecular weight, \bar{M}_n , of the PCL-PDMS-PCL prepolymer was calculated based on \bar{M}_n value of the central block of PDMS. In addition, the degree of polymerization of the PDMS-block in the prepolymer was determined from the ¹H-NMR spectrum of prepolymer, as the relative intensities of the Si-CH₃ protons signals and the -COOCH₂- protons arising from the PDMS propylene groups which were connected to ester oxygen atom. The PCL block length was estimated taking into account the areas of the Si-CH₃ protons signals and the -CH₂COO- protons in the ε-caprolactone residue which were connected to ester carbonyl group. The degree of polymerization obtained for each block was 25.3 (PDMS) and 17.8 (PCL) and the estimation of the number average molecular weight of the α,ω-dihydroxy-(PCL-PDMS-PCL) prepolymer taking into account the relative chemical composition was 6100 g mol⁻¹.

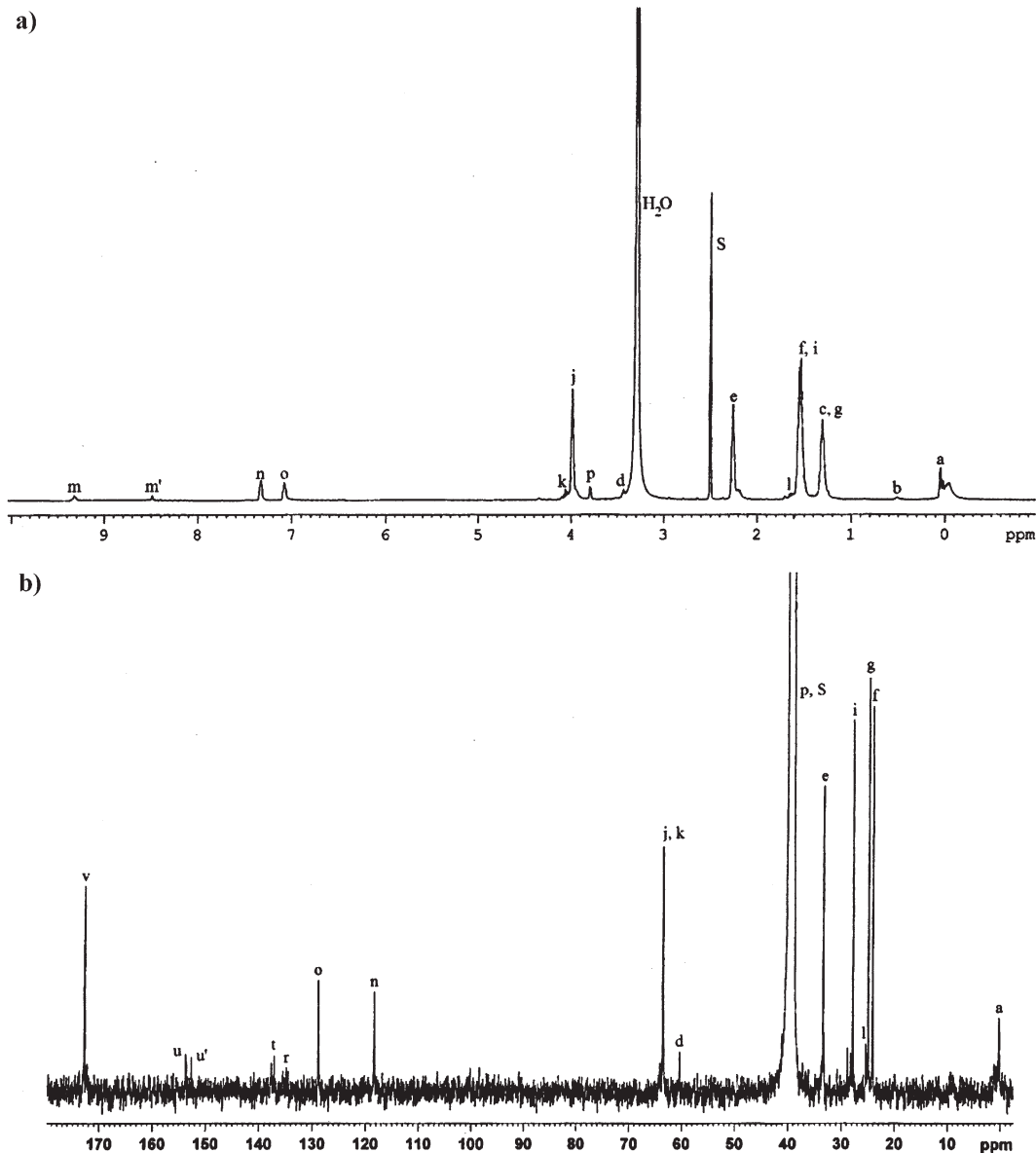
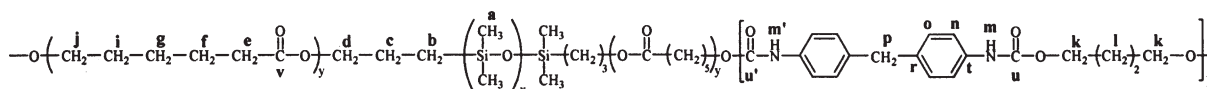


Figure 3 a) ¹H-NMR and b) ¹³C-NMR spectrum of the polyurethane sample TPU-10.

The experimental wt % content of the soft segments of the synthesized copolymers is presented in Table I, while the theoretical wt %, calculated from the composition of the reaction mixtures, was 91.2. These results show that the weight fractions of the soft segments were in the range from 85.9 to 92.3 wt %. The composition of the copolymers was in relatively good agreement with those expected from the composition of the feed. The greatest difference in the experimental composition was obtained for the TPU-5, TPU-7, TPU-10, and TPU-12 samples. These results show that reaction temperature and molar ra-

tio of NCO/OH groups had the greatest impact on the copolymer composition.

The lengths of the hard segments, L_n (HS), were calculated from ¹H-NMR spectroscopy and are shown in Table I. It is already known that the hard segment length can be calculated based on the ¹³C-NMR spectrum, taking into account the integrals of the aromatic carbon signals from the MDI units which are connected to the hard and soft segments.^{37,38} In the present case, the ¹³C-NMR signals of the aromatic carbon atoms were of rather low intensity because of the low content of hard segments

in the synthesized copolymer samples. Consequently, integration of such signals would be very unreliable. For this reason, the hard segment length, L_n (HS), was calculated based on the $^1\text{H-NMR}$ spectra, from the ratio of the integral of the $-\text{NH}$ proton signal from the MDI, which originated from the 1,4-butanediol, and the integral of $-\text{NH}$ proton signal from the MDI connected to the ϵ -caprolactone. Generally, the length of the hard segment in TPU copolymers depends on the kind and molar ratio of the compounds used in the reaction and also on the conversion during the reaction. The copolymers synthesized in this work showed very similar hard segment lengths, which are in the range from 0.9 to 2.3 MDI/BD units, due to the almost constant polyurethane composition.

A typical $^{13}\text{C-NMR}$ spectrum of TPU-10 is shown in Figure 3(b). The chemical shifts in the $^{13}\text{C-NMR}$ spectrum of the copolymer at $\delta = 0.3$ ppm were from carbon atoms from the SiCH_3 groups. The central and internal methylene carbon atoms from the ϵ -caprolactone residue appeared at $\delta = 24.2, 24.9,$ and

27.9 ppm. The terminal methylene carbon atom from the PDMS propyl groups and the terminal methylene carbon atom from the ϵ -caprolactone residues appeared at $\delta = 60.4$ and 63.6 ppm, respectively. The signal at $\delta = 33.4$ ppm was from methylene carbon atoms from the ϵ -caprolactone residues which were attached to the carbonyl groups. The signals of the central and terminal methylene carbon atoms from the BD residue appeared at $\delta = 25.3$ and 63.7 ppm, respectively. The carbon atom from the methylene group from 4,4'-methylenediphenyl diisocyanate appeared at $\delta = 39.5$ ppm. The signals from the carbonyl atoms at $\delta = 153.8$ and 172.9 ppm originated from the urethane and esters groups, respectively. The signals from the aromatic carbons appeared at $\delta = 118.4, 128.9, 135.5,$ and 137.4 ppm.

The assignments of the carbon and proton resonances with the structures shown in Figure 3 were confirmed by two-dimensional NMR spectroscopy. The COSY, HSQC, and HMBC spectra are shown in Figure 4. The chemical shifts of some missing signals in the ^{13}C spectrum and/or barely visible

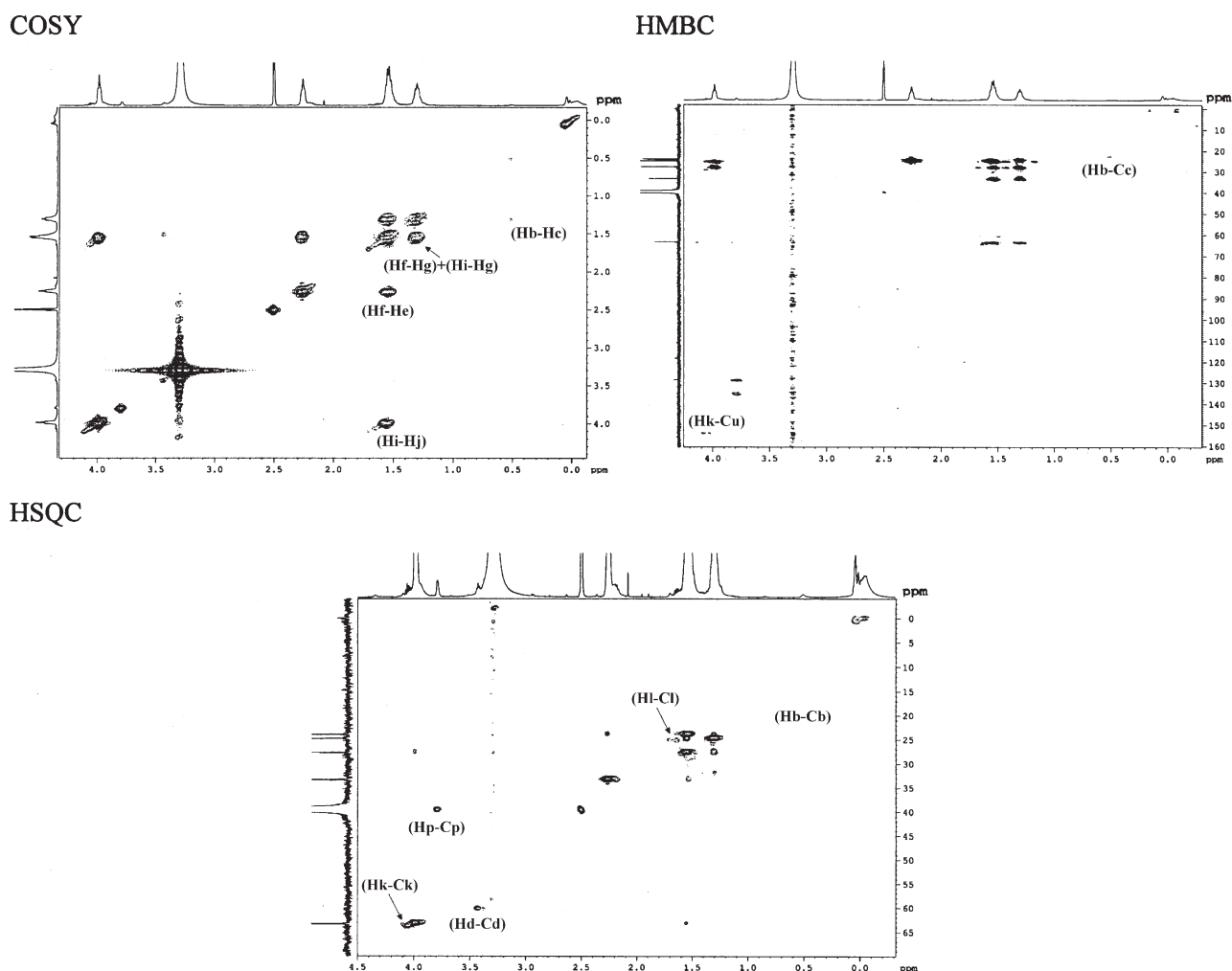


Figure 4 Two-dimensional-NMR spectra of the polyurethane sample TPU-10.

TABLE II
Curve Fitting Results for the C=O and N-H Stretching Regions of the FT-IR Spectra of the Synthesized TPUs

Polymer	% Area CO _{free urethane} (1733 cm ⁻¹)	% Area C=O _{PCL} (1722 cm ⁻¹)	% Area C=O _{segment mixing} (1716 cm ⁻¹)	% Area CO _{urethane-H bonding} (1700 cm ⁻¹)	% Area NH _{free urethane} (3435 cm ⁻¹)	% Area NH _{urethane-H bonding} (3320 cm ⁻¹)
TPU-5	24.3	50.7	21.7	3.3	9.7	90.3
TPU-6	22.2	48.9	25.8	3.0	10.3	89.7
TPU-7	22.1	50.5	24.3	3.1	10.1	89.9
TPU-8	25.9	50.3	20.6	3.1	9.7	90.3
TPU-9	18.9	53.5	24.8	2.7	7.9	92.1
TPU-10	27.2	52.0	17.2	3.7	8.1	91.9
TPU-11	24.0	50.7	21.5	3.7	11.6	88.4
TPU-12	21.5	57.5	17.5	3.5	11.4	88.6

in the ¹H spectrum (**b**, **d**, **l**, **k**) were deduced from HSQC correlations. Furthermore, the signal of **p** in the ¹³C spectrum was also deduced from HSQC since it overlapped with those from DMSO. The signal of **c**, absent in the ¹³C and overlapped in the ¹H and HSQC spectra, was identified from HMBC and COSY. The overlapped signals of **f** and **i** in the ¹H spectrum were resolved from COSY correlations. The urethane carbonyl atom at $\delta = 153.6$ bonded to a BD moiety showed HMBC correlations between C_u and H_k. From this it follows that the signal of carbonyl urethane group which is connected to the soft segment was observed at $\delta = 152.7$ ppm.

FT-IR spectroscopy of TPUs

The structures of the synthesized polyurethane copolymers were also verified by FTIR spectroscopy. The bands around 3320 cm⁻¹ (H-bonded urethane N-H stretch), 1733 cm⁻¹ (free urethane C = O), and 1700 cm⁻¹ (H-bonded urethane C = O) were assigned to the urethane linkage. The amide II and amide III bands for polyurethanes appeared at 1535 cm⁻¹ and 1260 cm⁻¹. The carbonyl groups of the PCL soft segments had a characteristic band at 1722 cm⁻¹. The intensive bands at 1016 and 1080 cm⁻¹ correspond to Si-O-Si and C-O-C groups in the copolymers. The rest of the bands at 2960, 2945, and 2865 cm⁻¹ were assigned to the presence of symmetric and asymmetric CH₂ groups, while the bands at 1597 and 1415 cm⁻¹ were assigned to the aromatic C = C.

FTIR spectroscopy has been used occasionally to estimate the degree of phase separation for TPU copolymers.³⁹ Hydrogen bonding exists in polyurethane copolymers, and involves the urethane NH group as the donor, and the urethane carbonyl or the ester carbonyl (in poly(ester-urethane)s) as the acceptor.

The synthesized TPU exhibited four absorbance peaks in the CO region: hydrogen-bonded carbonyl groups in the ordered hard domains at 1700 cm⁻¹, free (nonbonded) carbonyl groups at 1733 cm⁻¹,

hydrogen-bonded carbonyl groups in the disordered domains at 1716 cm⁻¹, and carbonyl groups from the PCL segments at 1722 cm⁻¹. Similarly, in the -NH stretching region, two distinct bands at 3320 cm⁻¹ and 3435 cm⁻¹ are observed. The CO and NH regions were fitted by the Gaussian deconvolution technique, using the Peakfit program, resulting in the locations and areas of each of these bands (Table II). Deconvolution of the carbonyl group absorbance region for the TPU-10 sample is shown in Figure 5. The carbonyl region in FTIR spectra was divided on four absorbance peaks with fixed position, in which C = O (PCL) dominated and other were hidden or appeared as peak shoulders. The Gaussian deconvolution procedure was performed using the Peakfit program, which showed very good agreement between the observed and generated values. In the carbonyl region, the C = O (PCL) absorption peak was the main peak, the area of which in the FTIR TPUs spectra ranged from 49 to 58%. The fit standard error was in the range from 0.00013 to 0.0028 and $r^2 > 0.994$.

A single stretching band was observed near 3320 cm⁻¹ corresponding to the hydrogen bonded

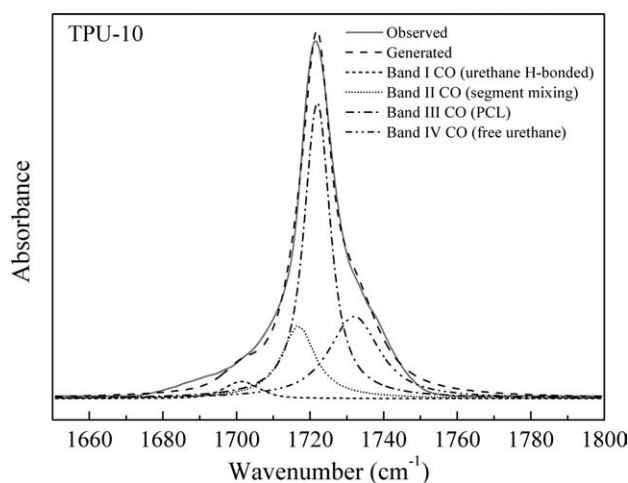


Figure 5 FT-IR spectrum of TPU-10, showing the absorbance region of the carbonyl groups (bands I-IV).

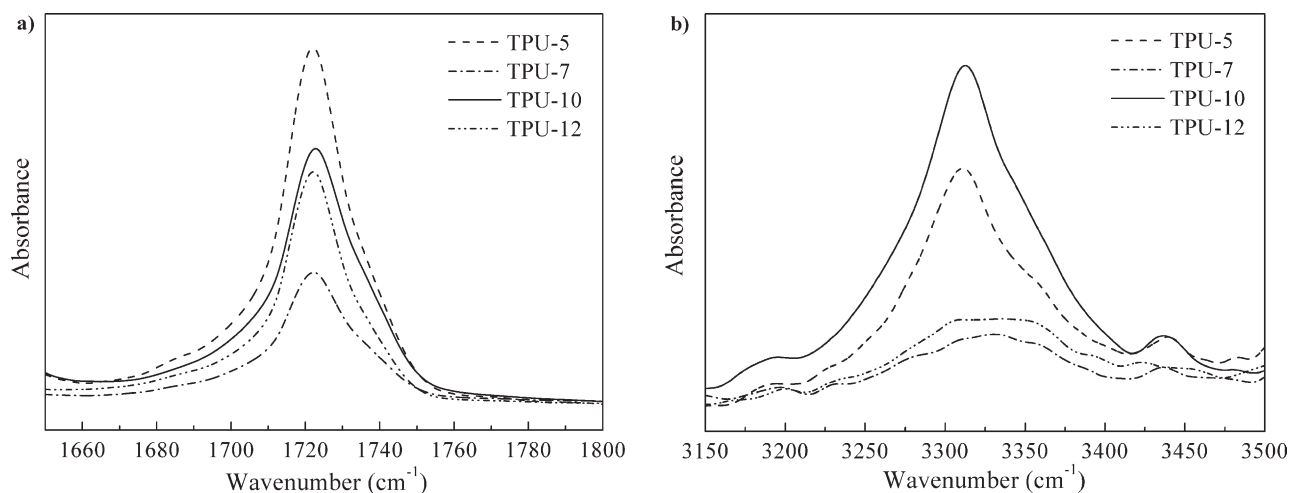


Figure 6 FT-IR spectra of (a) the C = O stretching region from 1650 to 1780 cm^{-1} and (b) the N-H stretching region from 3150 to 3500 cm^{-1} for some of the synthesized TPUs.

NH stretching vibration. A weak free NH stretching band absorbing at 3435 cm^{-1} was observed in all samples (Fig. 6). This indicates that most of the NH groups (88.4–91.2%) in the synthesized polyurethanes were involved in hydrogen bonds. As shown in Figure 6, the intensity of hydrogen bonded NH peak was increased for samples TPU-5 and TPU-10 due to the increase in hard-soft segment microphase separation. The band of the H-bonded N-H groups shifted to lower wavenumbers as the urethane groups became ordered, for TPU-5 and TPU-10 in comparison with TPU-7 and TPU-12. The shapes of the absorbance in this region were similar for TPU-5 and TPU-10 while broad peaks were observed in this region for TPU-7 and TPU-12.

The fraction of hydrogen bonded carbonyl groups was somewhat higher for TPU-10 than for the other TPUs. In addition, the fraction of urethane CO at 1716 cm^{-1} , corresponding to the disordered hard domains, was for synthesized TPUs in the range from 17.2 to 25.8% indicating existence of the certain phase mixing between hard and soft segments. The

TABLE III
GPC Analysis of the Synthesized TPUs

Polymer	\bar{M}_n (g mol^{-1})	\bar{M}_w (g mol^{-1})	\bar{M}_w/\bar{M}_n
TPU-1	19,800	33,400	1.7
TPU-2	19,400	34,900	1.8
TPU-3	14,400	28,300	2.0
TPU-4	19,000	35,600	1.9
TPU-5	20,500	38,700	1.9
TPU-6	16,500	30,600	1.9
TPU-7	19,000	35,400	1.9
TPU-8	20,600	37,400	1.8
TPU-9	22,200	41,400	1.9
TPU-10	34,300	53,300	1.6
TPU-11	26,000	37,800	1.6
TPU-12	15,900	31,100	2.0

obtained results led to the conclusion that substantial hydrogen bonding must occur between the urethane N-H and ester linkages in the soft segments. Incomplete domain separation resulting in hard segments dispersed in the soft segment matrix, and in hydrogen bonding at the soft-hard interface was the suggested explanation. The obtained FT-IR results also showed that a temperature of 80°C and a molar ratios of NCO/OH groups of 1.05 are essential for obtaining a copolymer with a better microphase-separated structure (TPU-10).

GPC analysis of the TPUs

The molecular weights obtained from GPC for the synthesized TPUs are summarized in Table III and representative chromatograms are shown in Figure 7. From Figure 7 it can be seen that TPU-10 sample has unimodal molecular weight distribution, while other synthesized TPU samples have small

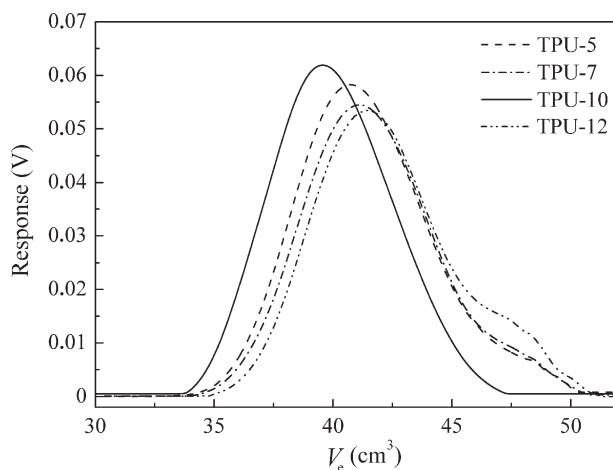


Figure 7 GPC chromatograms of some of the synthesized TPUs.

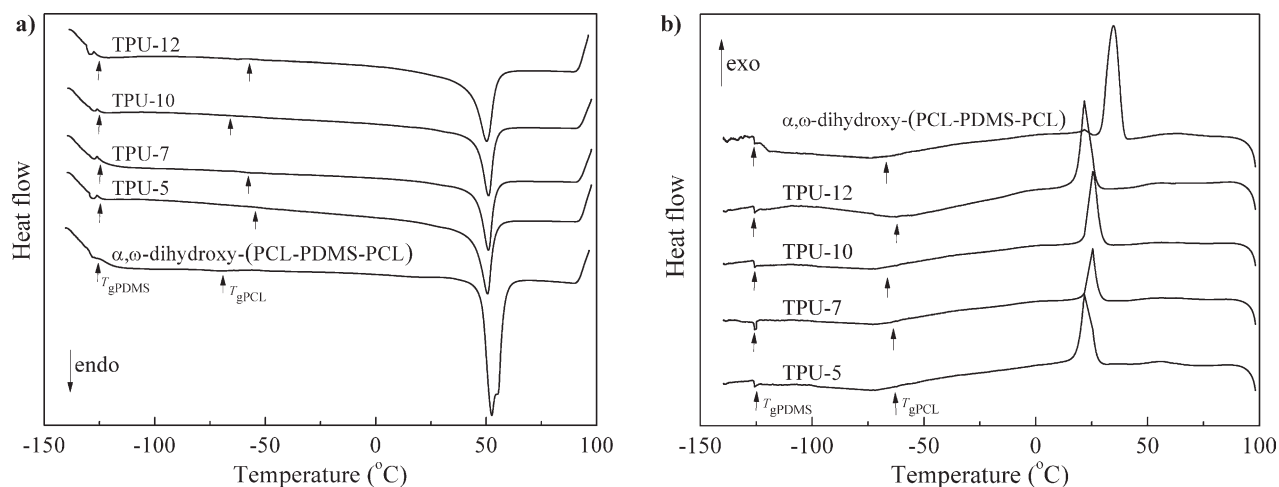


Figure 8 DSC thermograms of the synthesized TPUs obtained during: (a) second heating run and (b) cooling run.

shoulder due to the presence of low-molecular weight oligomers. The number-average molecular weights (\bar{M}_n) of the synthesized copolymers with a high SS content are in the range from 14400 to 34300 g mol⁻¹, with a polydispersity index ranging from 1.6 to 2.0. The \bar{M}_n values of the synthesized TPUs were consistent with their intrinsic viscosity values. The values of molecular weights varied with changes in the reaction conditions and molar ratio of NCO/OH groups. The highest value of \bar{M}_n was obtained for the TPU-10 sample. The GPC results showed that the molar ratio of the NCO/OH groups (1.05), the temperature of polyaddition reaction (80°C), the time of reaction (about 25 h) and the reactant concentration (15.2 wt %) had a critical influence on the growth of the molecular weight of the TPU-10 copolymer. From these results, it can be concluded that optimal conditions for the synthesis of TPU-10 could be employed in the further syntheses of TPUs having different hard and soft segments contents.

To prepare higher molecular weight TPUs with good mechanical properties, the chain extension should be more efficient. It might be envisaged that the chain extension in the preparation of high molecular weight TPUs could be more effective if the second stage of polyaddition reaction were realized in the presence of a more polar solvent, such as DMAc,

DMF or NMP, or in a mixture with a higher content of DMAc (such as DMAc/THF, 9 : 1 v/v).

Thermal properties of TPUs

The synthesized polyurethanes are semicrystalline polymers, the melting, crystallization, and glass transition temperatures of which were observed by DSC analysis. The DSC measurements were performed between -150 and 100°C using the so-called triple cycle, heating-cooling-heating, to determine the melting temperature (T_m), the enthalpy of melting (ΔH_m), the crystallization temperature (T_c), the enthalpy of crystallization (ΔH_c), and the degree of crystallinity of the TPU samples and, for the sake of comparison, of the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer. The results are presented in Figure 8(a,b) and Table IV. DSC thermograms of the synthesized TPUs obtained during second heating run show one clear endotherm, attributed to the T_m of the SS. The melting temperatures of the PCL-segments in the TPUs were between 49°C (for TPU-7) and 51°C (for TPU-10 sample). The slight increase in T_m is the consequence of the increasing degree of regularity of the crystallites and somewhat better microphase separation. The melting and the crystallization temperatures of PCL-segments in the copolymers were lower than those of the α,ω -dihydroxy-(PCL-PDMS-PCL)

TABLE IV
DSC Results and Water Static Contact Angle of some of the Synthesized TPUs

Polymer	T_m (°C)	ΔH_m (J g ⁻¹)	T_{gPDMS} (°C)	T_{gPCL} (°C)	T_c (°C)	ΔH_c (J g ⁻¹)	X_c^{PCL} (%)	Contact angle (deg)
TPU-5	50.6	42.4	-123.9	-54.7	21.7	38.6	46.1	97.0 ± 1.6
TPU-7	49.4	41.0	-121.9	-57.7	23.6	38.0	47.0	94.0 ± 1.4
TPU-10	51.2	42.9	-124.6	-61.9	25.7	40.4	47.1	99.9 ± 0.9
TPU-12	50.3	39.1	-123.4	-55.8	21.5	39.1	45.7	93.7 ± 0.5
α,ω -dihydroxy-(PCL-PDMS-PCL)	51.8	57.9	-126.6	-69.1	34.1	55.5	58.1	98.9 ± 1.1

prepolymer. This can be explained by the introduction of covalent bonds between the PCL-segments and the urethane blocks, which restricts both the phase separation and crystallization of the PCL-segments.⁴⁰

The DSC results showed that the hard segments could not form a crystalline structure, probably because of their short chain length and lack of organization. To form hard segment crystals in MDI-based polyurethanes, the segments need to be of a sufficient length. It is known that hard segments consisting of more than three MDI units can form stable crystals.⁴¹

The degree of crystallinity of the PCL segment, (X_c^{PCL}), of the TPUs was calculated by means of the following equation:

$$X_c^{\text{PCL}} = \Delta H_m / w \Delta H_m^{\theta}$$

where ΔH_m is the enthalpy of the melting of TPU samples, w is the weight fraction of PCL segments determined by ¹H-NMR spectroscopy, and ΔH_m^{θ} is the theoretical values of the enthalpy of the melting of perfectly crystalline PCL homopolymer, calculated based on the group contribution method ($\Delta H_m^{\theta} = 148.2 \text{ J g}^{-1}$).⁴²

The degree of crystallinity of PCL segments (X_c^{PCL}) in the TPUs was in the range from 45.7 to 47.1% (in the second heating run), which means that ~ 46 wt % of the PCL segments in polyurethane crystallized.

Segmented polyurethanes that consist of amorphous HS and crystallizable SS segments belong to amorphous-semicrystalline multi-block copolymers. They exhibit considerable morphological structures on nanoscale as a result of two competing self-organizing mechanisms: crystallization and microphase separation. Crystallization and morphology of semicrystalline block copolymers has attracted much attention and several reviews have been published recently.^{43,44}

Semicrystalline block copolymers that consist of chemically different segments can self-assemble into various nanostructures in melt, depending on the segregation strength χN (where χ and N represent the Flory-Huggins interaction parameter and the degree of polymerization, respectively), and volume or weight ratio of the constituent components. The morphology of semicrystalline block and multiblock copolymers is determined by the thermodynamic incompatibility between the constituent blocks and by the crystallization of one or more blocks.^{43,44}

The Flory-Huggins interaction parameter χ , was calculated through the equation $\chi = V_u(\delta_1 - \delta_2)^2 / RT$, where the arbitrary reference volume V_u was conveniently selected as $100 \text{ cm}^3 \text{ mol}^{-1}$, R is the universal gas constant, T is the absolute temperature and the solubility parameters of the hard segment (com-

posed of one BD and two MDI units), PCL, and PDMS units of soft segments are 11.9, 8.55, and 7.3 (cal cm^{-3})^{1/2}.⁴⁵

The estimation of χN of the α,ω -dihydroxy-(PCL-PDMS-PCL) triblock copolymer ranged from 9.3 to 7.9 at room temperature and at 10°C above the T_m of the PCL homopolymer, respectively, suggesting that the sample exhibited a homogeneous mixed phase ($\chi N < 10.5$) according to the mean-field theory. The results are in agreement with those of Childs et al.³³ who report that α,ω -dihydroxy-(PCL-PDMS-PCL) triblock copolymers are either mixed in the melt or weakly segregated. We roughly estimated that χN for the HS-PCL segments in the TPUs is in the range from 1.4 to 3.7 (at 10°C above the T_m of the PCL segment) and the average degree of polymerization of HS (from 0.9 to 2.3), thus, they form a homogeneous mixed melt. It could be concluded that the PCL sequences of the SS phase crystallized from homogeneous mixed phase.

The glass transition temperature, T_g , of the PCL segments in the synthesized polyurethane copolymers was between -55 and -62°C (in the second heating run) while for α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer, it was -69°C . The T_g 's of the PCL segments were present in the heating run, although not so pronounced as in the cooling run, as is shown in Figure 8(a,b). The T_g of the amorphous PDMS-phase in the synthesized TPUs was between -122 and -125°C , while this value was lower in the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer, i.e., -127°C . It was also reported that pure PCL-PDMS-PCL triblock copolymer formed a two-phase morphology and exhibited two glass transitions—one of the siloxane segment at -128°C and the other at -72°C of the amorphous PCL-segment, and a melting point of poly(ϵ -caprolactone) at $+54.6^\circ\text{C}$.⁴⁶ The obtained results indicated a slight increase of the glass transition temperature of the PCL segments of the copolymers in comparison to the T_g of the PCL in the prepolymer, due to a relatively small amount of hard segment mixing within the soft domain.

Waxes analysis of the TPUs

The wide-angle X-ray diffraction (WAXS) results are presented in Figure 9. The presence of only one crystalline system, *ortho*-rhombohedral was reported for poly(ϵ -caprolactone).⁴⁷ Based on X-ray diffraction data, the unit cell of poly(MDI-BD) is triclinic with dimensions $a = 5.33 \text{ \AA}$, $b = 5.26 \text{ \AA}$, $c = 38.68 \text{ \AA}$, $\alpha = 113.6$, $\beta = 116.0$, $\gamma = 94.4$ degrees.⁴⁸ The characteristic peaks for the copolymer TPU-10 were at $2\theta = 21.31$, 22.06 , and 23.72 degrees while α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer displayed an amorphous halo from the PDMS block and three peaks at 2θ values of 21.21 , 21.85 , and 23.56 degrees, which

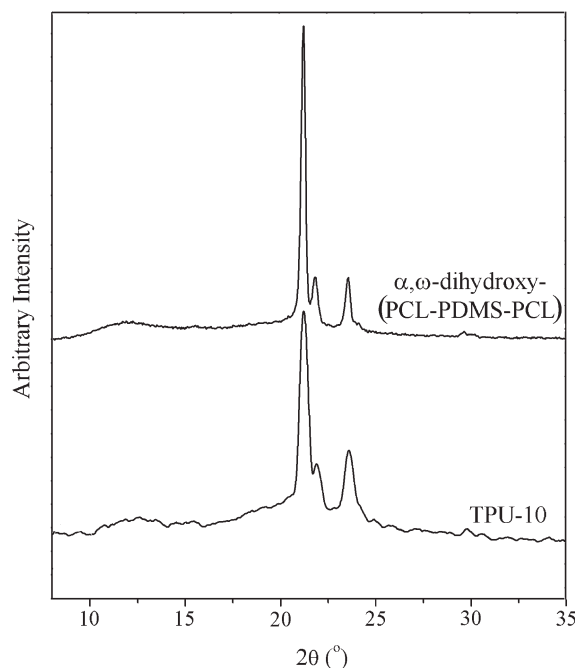


Figure 9 X-ray diffraction patterns of the TPU-10 sample and the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer.

originated from the PCL block. The diffractograms of the TPUs were very similar to the diffractograms of the prepolymer, the main peaks occurring at almost the same 2θ values as those of the prepolymer. From the X-ray data, it may be concluded that the soft PCL-PDMS-PCL segments in the TPUs formed a crystalline structure. This is due to crystallization resulting from the PCL sequences. In the diffractograms of the TPUs, an amorphous halo (≈ 12 degrees) due to the presence of the PDMS block was also observed. The degrees of crystallinity, X_c^{WAXS} , of the TPUs were about 40%, while the degree of crystallinity of the prepolymer was 57%. No MDI/BD crystallinity was detected by WAXS analysis. This implies that either the crystalline dimensions of hard segments are not large enough to be detected or that the number density of the crystallites is low.⁴⁹ These results were consistent with the data obtained by DSC.

Morphological investigation of TPUs by SEM

The surface morphology of TPU films was investigated by SEM. The SEM microphotographs of the TPU-10 sample and the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer are shown in Figure 10. The SEM microphotographs of α,ω -dihydroxy-(PCL-PDMS-PCL) and the copolymer films clearly show a spherulitic structure typical for semicrystalline polymers.⁵⁰ In addition, the SEM microphotographs showed that the copolymers had distinct microphase separation. The spherulitic-like structures are believed to arise

from the crystallization of the PCL sequences. The average size of the PCL spherulites in prepolymer was 125 μm , while in the TPU 64 μm .

In addition, Figure 10 shows the cross-sectional morphologies of the copolymer and the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer. Also, it could be seen that the copolymer show a unique spherulitic-like structure in the longitudinal cross section.⁵¹ The average spherulite size of the TPUs was about 3 μm . The spherulites of the α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer were 136 μm in size. The smaller size of the spherulites in the copolymer than in prepolymer can be explained by the introduction of the urethane block in polymer chains that restricts crystallization of the PCL segments.

Hydrophobic properties of TPUs

To evaluate the degree of hydrophobicity and wettability of the TPUs, static contact angles in water were measured. The determined values of the water contact angles for the copolymers are reported in Table IV. A water contact angle of 90 degrees or higher indicates a nonwetting surface. The value of the water contact angle for the TPUs was in the range from 93.7 to 99.9 degrees while for α,ω -dihydroxy-(PCL-PDMS-PCL) the value was 98.9 degrees. Thus the obtained TPUs could be considered to be hydrophobic. This behavior is due to the very low surface energy of PDMS, which migrates to the surface and covers most of the surface of the TPUs. The copolymer TPU-10, synthesized under the optimal conditions, a consequence of the better microphase separation, showed the highest value of contact angle, 99.9 degrees. Thus, PDMS-containing polyurethanes with their potential water resistant properties demonstrated great promise for use as implant material. As a comparison, the contact angles of poly(ester-siloxane)s based on poly(butylene terephthalate) (PBT) as the hard and PCL-PDMS-PCL as the soft segments were in the range from 97 to 125 degrees,⁵² while the contact angles of TPUs with different hard to soft segment weight ratios were between 79 and 100 degrees. The later will be discussed in detail in a further publication. In both the latter cases, the contact angle value, i.e., hydrophobicity, increased with increasing of PDMS content.

CONCLUSIONS

Novel siloxane-urethane copolymers based on MDI/BD as the hard and high content of PCL-PDMS-PCL as the soft segments were successfully synthesized by two-step polyaddition reactions in solution. It was found that the optimal polymerization conditions are: concentration of reactants 15 wt %, time of

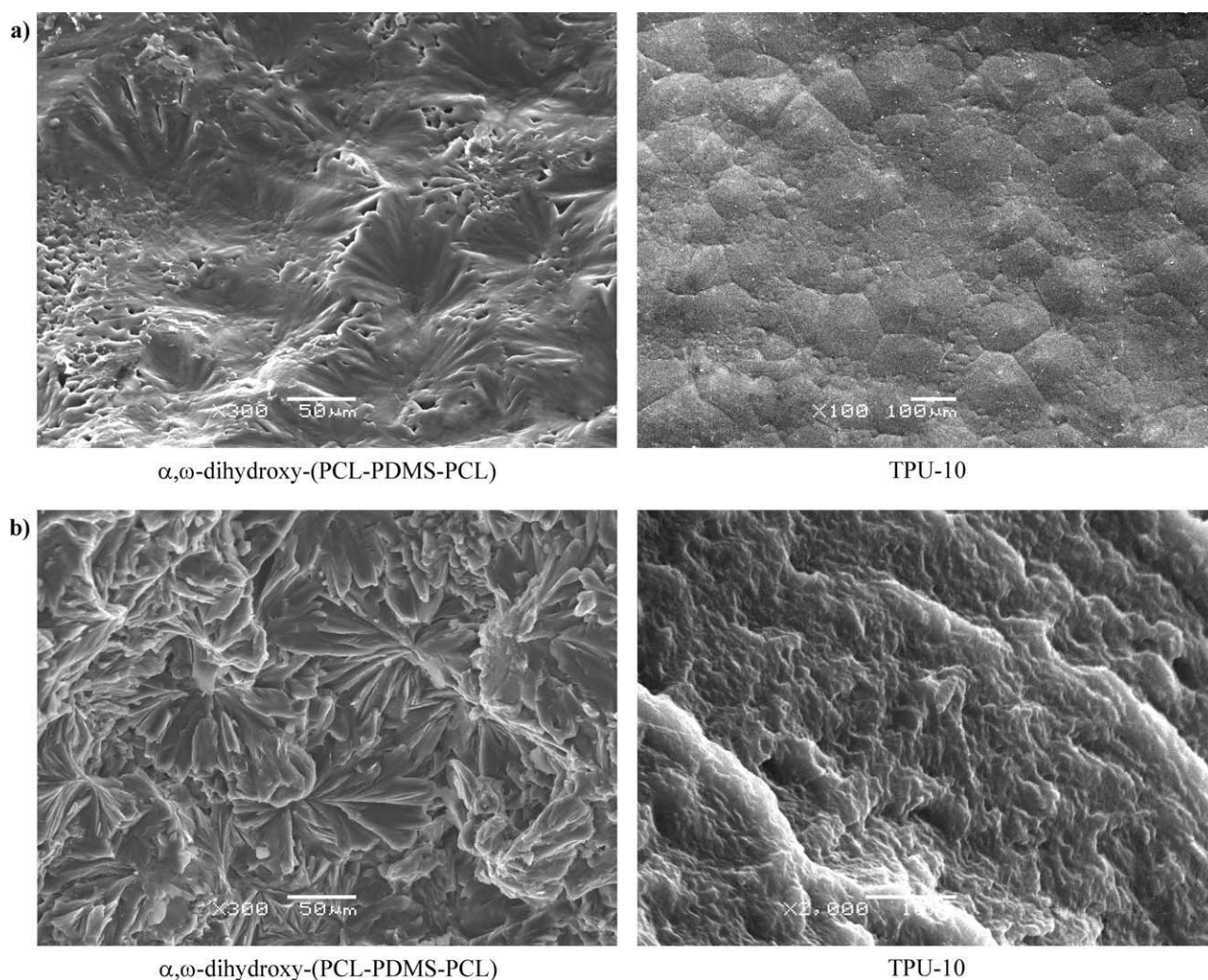


Figure 10 SEM microphotographs of the air surface a) and cross section b) of TPU-10 films and α,ω -dihydroxy-(PCL-PDMS-PCL) prepolymer films.

the first step of the reaction 40 min and time the second step of reaction of 24 h, reaction temperature of 80°C and molar ratio of isocyanate to hydroxyl groups of 1.05. Under the optimal conditions, the copolymer with the highest molecular weight (\overline{M}_n (TPU-10) = 34,300 g mol⁻¹) and best microphase-separated structure was obtained. The multiblock structure of the synthesized siloxane-urethane copolymers was confirmed by ¹H, ¹³C-NMR, and two-dimensional (COSY, HSQC, HMBC) spectroscopy. FT-IR analysis showed that, since almost all the -NH groups were hydrogen bonded in synthesized TPUs while the carbonyl groups of the urethane linkages were not, some carbonyl groups of the ester moieties in the soft segments may also have been involved in hydrogen bonding. DSC and WAXS results showed that PCL segments crystallized, whereas the hard segments containing two MDI/BD units could not form a crystalline structure, probably because of their short chain length. SEM

images confirmed the presence of a spherulitic morphology, which arises from the crystallization of the PCL segments. The thermal and physical properties of the copolymers were slightly affected by molecular weight and microphase separation. Copolymer TPU-10, synthesized under the optimal conditions, due to a better microphase separation, showed a higher melting temperature, a lower glass transition temperature, and the highest value of the contact angle with water. As a consequence of the increased microphase separation the thermal properties and stiffness of the copolymer were slightly better.

The synthesized TPUs based on PCL-PDMS-PCL segments are hydrophobic thermoplastic copolymers that could be considered for use in numerous applications, for example as medical implants. The influence of different contents of soft PCL-PDMS-PCL segments on the microstructure-mechanical property relationships and biocompatibility behavior of TPUs will be discussed in further publications.

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