Variable Hard Segment Length in Poly(urethane urea) through Excess of Diisocyanate and Vapor Phase Addition of Water

J. O. Basse Asplund,*,† Tim Bowden,† Torbjörn Mathisen,‡ and Jöns Hilborn*,†

Department Materials Chemistry, Uppsala University, Lägerhyddsvägen 1, 751 21 Uppsala, Sweden, and Radi Medical Systems AB, Palmbladsgatan 10, 754 50 Uppsala, Sweden

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ABSTRACT: Poly(urethane urea)s with hard segments derived only from diisocyanate linked via urea linkages were synthesized using a new and simple one-pot method. The creation of urea linkages were done via creating the amine in situ by adding water in vapor phase slowly and continuously. This synthesis method eliminates the tedious control to approach stoichiometry, is less sensitive to impurities, involves no intermediate isolation steps, and does not involve any chain extender. A study using a two-armed poly(ϵ-caprolactone) as soft segment and methyl 2,6-diisocyantohexanoate (LDI) as the hard segment was performed. The length of the hard segment was varied from 4.8 to 11.6 LDI units. Stress−strain measurements showed an increase in elastic modulus, 146 to 235 MPa, when increasing the hard segment length, while the elongation at break decreased, 980 to 548%. IR spectroscopy showed an increase in hydrogen bonding when increasing the hard segment length. The synthesis was also shown to be applicable to common diisocyanates such as HDI, TDI, and MDI.

Introduction

In this article we present a one-pot synthesis of a poly(urethane urea) (PUU) that eliminates tedious approaches to control stoichiometry, is less sensitive to impurities, and involves no isolation of intermediates. The hard segment of the PUU can easily be varied in length and is derived only from diisocyanate, linked together via urea linkages.

Polyurethanes (PU) are a very versatile class of polymer, found in a wide range of applications such as mattresses, paints, car bumpers, shoe soles, and artificial heart valves. When found as thermoplastic elastomers, polyurethanes contain a soft segment, acting as a spring, and a hard segment holding the material together through physical cross-linking.

Two strategies of synthesizing polyurethanes are (1) using a soft segment consisting of a polyester, polyether, or polycarbonate and a diisocyanate, and then chain extend the polymer with a shorter diol or diamine, and (2) using a fictionalized soft segment and synthesize the reactive groups in situ by use of protecting groups. The former is the general procedure used, and common diisocyanates include 4,4′-methylbis(phenyl)-diisocyanate (MDI), 1,3-toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), and methyl 2,6-diisocyanatehexanoate (LDI).[1−4] Chain extenders are commonly 1,4-butanediol or ethylenediamine, used to give urethane and urea linkages, respectively.[1−3] By variation of the soft segment component, using different diisocyanates, and using a diol or diamine as a chain extender, the properties of the material can be altered. Of particular interest are the extent of phase separation and the composition of the hard segment controlling the secondary forces between these. It has been shown that urea linkages give stronger hydrogen bonding than the corresponding urethane linkage due to the two −NH groups in urea.[5−7]

Versteegen et al. employed the latter technique and took advantage of the boc protecting group and were able to produce isocyanates and amines in situ, creating monodisperse hard segments.[8] While others have studied systems with a distribution of urea groups in the hard segment,[9,10] Versteegen et al. studied the hydrogen-bonding strength for poly(ether urea)s with an exact number of urea groups.[8] Through their elegant multiple synthesis, they could study the effect of increasing hydrogen-bonding sites on mechanical properties and processability. Sung et al. and Yilgör et al. synthesized their systems with multiple urea groups by adding diisocyanate and chain extender in different proportions, resulting in a polydisperse hard segment,[9,10] Yilgör et al. have also explored the possibility of using water as a chain extender to synthesize low molecular weight products.[11] The use of a protecting group strategy involves multiple steps and purification, while using diisocyanate and chain extender requires great care to control stoichiometry. The latter is due to that the molecular weight of the soft segment cannot be determined exactly and that the system is sensitive to protic impurities that can consume functional groups.

There is always a search for more simple methods of synthesizing polymers, especially where the properties can easily be tailored. In this article we present a new and simple way of synthesizing non-cross-linked poly(urethane urea)s, where the hard segment derives only from diisocyanate and whose length can be altered. The synthesis is a one-pot reaction and requires minimal monitoring. Importantly, the rate-determining step is the addition of water, which is done slowly and continuously, reaching perfect stoichiometry, and high molecular weight polymer. Practically, the dissolved soft segment is added to an excess of diisocyanate in a three-necked round-bottom flask, and water is supplied in the vapor phase. Solvent can be added as the viscosity increases and to facilitate formation of a high molecular weight product. In short, the reactants are added to a reaction flask, the vapor is “switched on”, and the polymerization continues until a desired viscosity is reached. This novel method of synthesizing PUU was employed using poly(ϵ-caprolactone) as the soft segment and four different diisocyanates, two aromatic, MDI and TDI, and two aliphatic, HDI, and LDI. A more thorough study was done on the system with LDI, for future studies where the potentially biodegradable PUU are of interest.[12,13] Four different lengths of the hard segment were

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† Uppsala University.

‡ Radi Medical Systems AB.

* To whom correspondence should be addressed. E-mail: basse@polymer.uu.se, jons.hilborn@polymer.uu.se.

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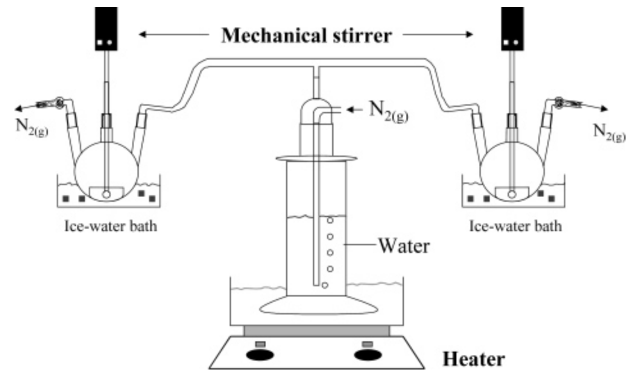


Figure 1. Reaction setup for two parallel PUU synthesis via water vapor addition.

synthesized and characterized with focus on hydrogen-bonding, thermal, and mechanical properties.

Experimental Section

Materials. LDI (Kyowa Hakko Europe GmbH) was distilled at 100 °C and 0.1 Torr. HDI (>99%, Fluka), MDI (98%, Merck), and 2,4-TDI (80%, Merck) were all used as received. ϵ-Caprolactone (Sigma Aldrich) was distilled at reduced pressure from CaH_2, and 1,4-butanediol (Merck) was distilled at reduced pressure. Both were stored in a glovebox. Stannous 2-ethylhexanoate ($Sn(Oct)_2$) (Sigma Aldrich) was used as received but opened inside the glovebox, and 1,4-diazabicyclo[2.2.2]octane (DABCO) (Merck) was sublimated at reduced pressure. *N*,*N*-Dimethylformamide (DMF) (HPLC, Sigma Aldrich) and chloroform-*d* ($CDCl_3$) (Chemtronica) were kept over molecular sieves (4 Å). Chloroform (Sigma Aldrich), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Acros), methanol (Sigma Aldrich), D_2O (Chemtronica), 1,1,1,3,3,3-hexafluoro-2-propanol-d_2 (HFIP-d_2) (Acros), and phosphorus pentoxide (P_2O_5) (Fluka) were used as received.

Synthesis of Poly(ϵ-caprolactonediol). The soft segment, poly(ϵ-caprolactonediol) was synthesized, initiated from 1,4-butanediol. To an oven-dried (220 °C) 250 mL round-bottom flask cooled under argon was added 25.6 g (0.225 mol) of ϵ-caprolactone, 0.68 g (7.6 mmol) of 1,4-butanediol, and 0.12 g (0.30 mmol) of $Sn(Oct)_2$ added inside a glovebox. The flask was sealed and brought outside the box, and the polymerization was conducted at 110 °C in an oil bath for 24 h. Chloroform (50 mL) was used to dissolve the polymer before precipitation in 500 mL of methanol. The filtered product was dried in a vacuum over P_2O_5 (yield 85%, $\bar{M}_w$ (GPC) of 6000 g/mol, $\bar{M}_n$ (NMR) of 4600 g/mol and PDI 1.22). ^{1}H NMR ($CDCl_3$): δ 4.05 (t, 2H, CH_2O), 3.64 (t, 2H, CH_2OH end-group), 2.30 (t, 2H, CH_2CO), 1.62 (m, 4H, CH_2), and 1.38 (m, 2H, CH_2).

Synthesis of Poly(urethane urea). For the LDI−PCL system, four different poly(urethane urea)s with different lengths of the hard segment were synthesized. The target lengths of the hard segment were 6, 10, 12, and 15 LDI units. For HDI it was 10 while for the aromatic, MDI and TDI, the target hard segment $\overline{DP}$ was limited to 4, to avoid gelation during synthesis. The effect of adding water in vapor phase is that stoichiometry is approached slowly and continuously. As a comparison, two PUU were synthesized where the water was added in the liquid phase. In the first case all the water was added at the same time, and in the second case it was added dropwise from a standard solution over a period of 2 h.

Prepolymer Syntheses. In a typical experiment were 1.61 g (7.60 mmol) of LDI and 5.30 g (1.14 mmol) of PCL, dissolved in DMF (20 mL) and added to a dry 250 mL three-necked round-bottom flask, giving a molar ratio of 6.7:1 (LDI:PCL). The PCL was added dropwise over 3 h, and the reaction was left overnight with stirring.

Poly(urethane urea) Synthesis. To the prepolymer 0.44 g (3.9 mmol) of DABCO dissolved in DMF (5 mL) was added. The water vapor apparatus was connected as shown in Figure 1; the oil bath temperature was set to 40 °C and the nitrogen gas flow to a few bubbles/s. To minimize side reactions and to attract the water vapor, an ice−water bath was placed under the reaction flask. As the polymerization continued and the viscosity increased, DMF was added to facilitate formation of high molecular weight product. The viscosity started to increase after 5 h, and the synthesis was terminated after 11 h. A total amount of 17 mL of DMF was added. The product was precipitated with water using a mixer and then filtered. To remove DMF from the precipitated polymer, it was stirred in hot water overnight. The filtered polymer was dried in a vacuum over P_2O_5 (yield 87%) ^{1}H NMR PCL−LDI (HFIP-d_2): δ 4.67 (m, 1H, NCHCOO), 4.55 (m, 2H, CH_2O), 4.21 (s, 3H, CH_3O), 3.57 (m, 2H, NCH_2), 2.81 (t, 2H, CH_2CO), and 2.38−1.65 (m, 12H, CH_2). The synthesis of PCL−HDI followed the same procedure as just described (yield 82%). ^{1}H NMR PCL−HDI (HFIP-d_2): δ 4.56 (m, 2H, CH_2O), 3.57 (m, 4H, CH_2N), 2.81 (t, 2H, CH_2CO), and 2.2−1.76 (m, 14H, CH_2).

Aromatic PUU tended to form physical gels when reaching stoichiometry. To facilitate inherent viscosity measurements and film casting, the synthesis was therefore interrupted prior to gel formation. To obtain samples for DSC measurements, some of the polymer solution was precipitated in water and dried in a vacuum over P_2O_2.

PUU Synthesis Using Water in Liquid Phase. The prepolymer synthesis was done as described above by adding dissolved PCL dropwise to a 6-fold excess of LDI. The calculated amount of deionized water (DIW) needed was based on the assumption that one-sixth of the isocyanates had reacted with the PCL during the prepolymer synthesis.

Poly(ϵ-caprolactone) (2.4 g, 0.40 mmol) was dissolved in DMF (7 mL) and added to 0.52 g (2.5 mmol) of LDI (LDI:PCL 6.1:1) dropwise over 3 h. DABCO (0.14 g, 1.3 mmol) dissolved in DMF (2 mL) was added to the prepolymer followed by DIW (0.037 g, 2.0 mmol). Precipitation of the polymer was done with water; the isolated product was washed in hot water overnight and then dried in a vacuum over P_2O_5. The product was insoluble in chloroform, DMF, DMSO, and HFIP, and the isolated yield was 87%.

A standard solution of DIW in DMF was prepared with a water concentration of 2.07 mmol/g. Poly(ϵ-caprolactone) (3.5 g, 0.58 mmol) dissolved in DMF (8 mL) was added dropwise to LDI (0.75 g, 3.6 mmol) (LDI:PCL 6.12:1) followed by the addition of DABCO (0.2 g, 2 mmol) dissolved in DMF. The standard solution (1.42 g, 2.94 mmol water) was then added over 2 h. When the viscosity increased, DMF (2 mL) was added. The polymer was isolated by precipitation with water, filtered, washed in hot water overnight, and dried in a vacuum over P_2O_5, resulting in a 92% isolated yield. ^{1}H NMR PCL−LDI (HFIP-d_2): δ 4.67 (m, 1H, NCHCOO), 4.55 (m, 2H, CH_2O), 4.21 (s, 3H, OCH_3), 3.59 (m, 2H, NCH_2), 2.81 (t, 2H, CH2CO), and 2.33−1.71 (m, 12H, CH_2).

Characterization by NMR. The compositions of the poly(ϵ-caprolactone) (PCL) and the poly(urethane urea)s (PUU) were determined by ^{1}H NMR at 400 MHz (JEOL ECP-400). $CDCl_3$ was used for PCL and HFIP-d_2 for the PUU. For the latter, a capillary with D_2O was inserted into the NMR tube to lock the NMR signal. The average degree of polymerization ($\overline{DP}$) for the PCL diol was determined using eq 1

$$\overline{DP}_{\mathrm{PCL}} = 2\,\frac{I(\delta 2.30)}{I(\delta 3.64)} \tag{1}$$

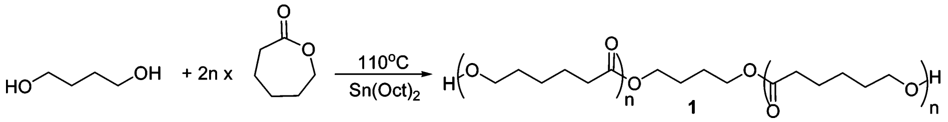
where the resonance $I(\delta 3.64)$ (t, 2H, CH_2OH) is from the end group of PCL and $I(\delta 2.30)$ (t, 2H, CH_2CO) is from the main chain of PCL. The length of the diisocyanate segment (DI) was calculated from eq 2

$$\overline{DP}_{\mathrm{DI}} = \overline{DP}_{\mathrm{PCL}}\,\frac{I(\delta_{\mathrm{DI}})}{I(\delta 2.30)} \tag{2}$$

For LDI and HDI δ_{DI} 3.58 (t, 2H, CH_2NH) was used; however, the aromatic systems were not soluble, and their composition could not be determined.

Molecular Weight and Inherent Viscosity Measurements. The molecular weight of PCL was determined using a Waters Alliance

Scheme 1. Synthesis of Poly(ϵ-caprolactonediol) Using 1,4-Butanediol as Initiator



GPCV2000 system with Millennium software. The system included Waters Styragel HR5E-HR4-HR1 columns, viscometer, and a RI detector. The measurement was done in chloroform at 40 °C at a flow rate of 1 mL/min. Calculations were done using polystyrene standards.

Inherent viscosity (*IV*) was conducted for the poly(urethane urea)s. Samples were dissolved in 10 mL of HFIP, giving a concentration of 0.1 g/100 mL, and filtered using a PTFE 0.45 μm filter. A viscometer from Schott (ViscoClock) was used together with an Ubbelohde capillary 0_c. The water bath held a temperature of 25 °C, and each sample was measured four times. PUU from aromatic diisocyanates were not soluble when precipitated and dried; therefore, the *IV* was determined by extracting a sample from the polymerization solution (DMF) and diluting it to the desired concentration. The inherent viscosity was calculated using eq 3:

$$IV = \frac{\ln\left(\frac{t_p}{t_s}\right)}{C_p} \tag{3}$$

where t_p is the time, in seconds, for the polymer solution and t_s is the time for the solvent. C_p is the polymer concentration in g/dL.

Thermal Analysis. Glass transition temperature (T_g) and melting temperature (T_m) were measured using a TA Instruments DSC Q1000 at a rate of 10 °C/min and cycled between −80 and 120 °C for PCL and between −80 and 180 °C for the poly(urethane urea)s. Sample masses were approximately 4 mg, and the calculations were based on the second heating.

Tensile Properties. The aliphatic PUU were cast from a 7 wt % HFIP solution onto glass substrates with a doctor blade. The films were air-dried for 24 h, and to remove solvent residues, the films were placed in a vacuum oven for 48 h at room temperature. For the aromatic derived PUU, the films were cast from the polymerization solution using a doctor blade, necessary due to lack of solubility when precipitated and dried. The films were air-dried for 48 h and vacuum-dried for 10 days.

Because of the risk of pinholes formed in the film during casting, scanning electron microscopy (Philips XL30 ESEM-FEG) was used to verify that no defects were present. A thin layer of gold was applied through sputtering. Both surfaces and cross section were studied.

Five to eight dog-bone shaped samples (width 11 mm, length 23 mm) were punched out, and the thickness was measured using a micrometer screw, 12−18 μm (aliphatic PUU) and 23−32 μm (aromatic PUU). Stress−strain properties were determined at a deformation rate of 100 mm/min using an Instron 5544 with Merlin software.

Characterization of Hydrogen Bonding by FTIR. To study hydrogen bonding between carbonyl (C=O) and amide (N−H) groups for the LDI−PCL system, an FTIR (Perkin-Elmer, Spectrum One) with a ZnSe crystal was used. Samples were taken from the films, described previously, used for mechanical measurements, and were scanned 64 times at a resolution of 2 cm^{-1}.

Results and Discussion

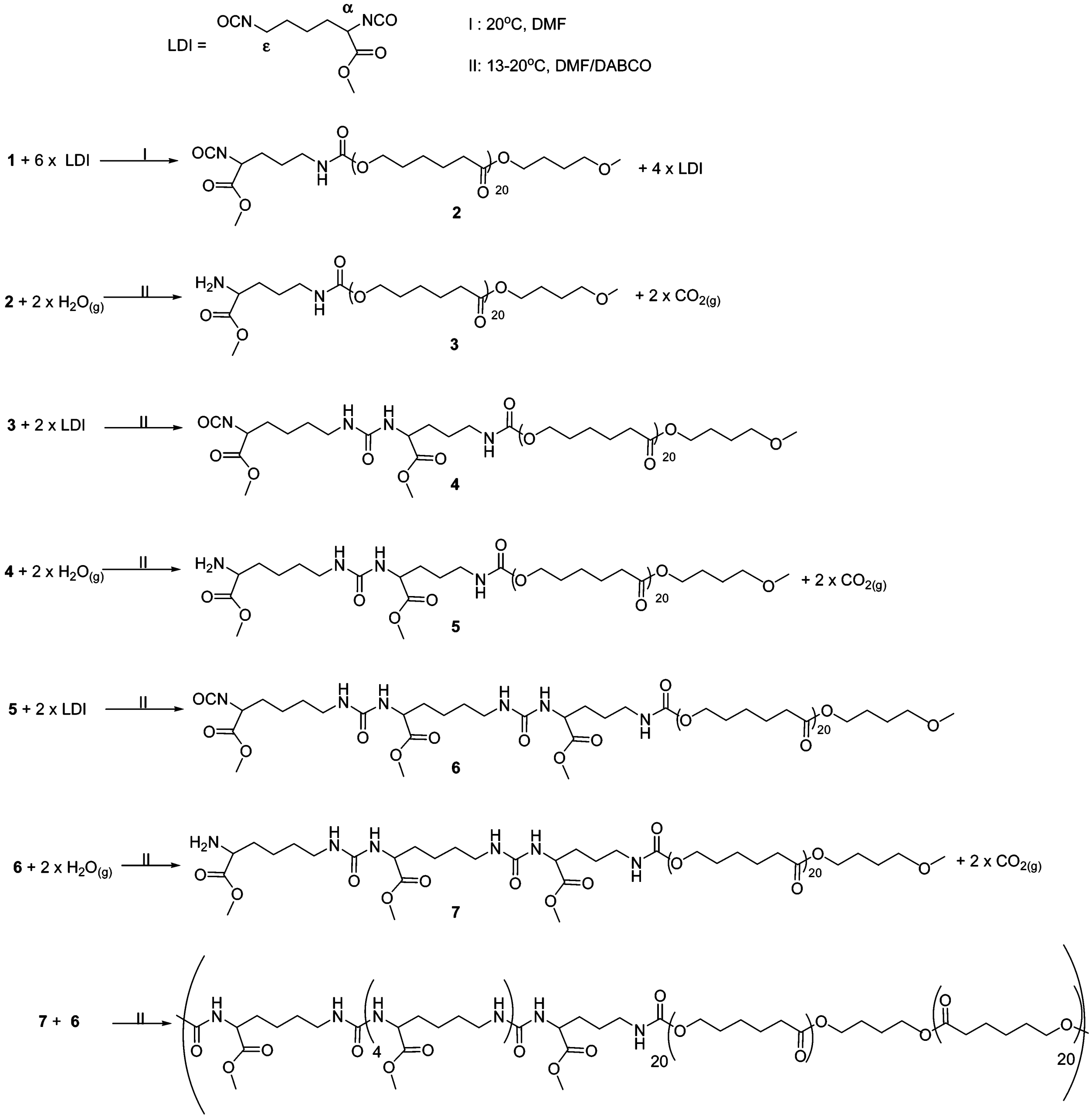
Chemical Composition and Hard Segment Length. A novel and simple way of synthesizing PUU in a one-pot reaction is presented. The setup, Figure 1 (showing two parallel synthesis), contains only two three-necked round-bottom flasks, each equipped with an overhead stirrer. The flasks are connected to a gas bubble flask containing water. Nitrogen is passed through the water, during heating, and carries the water vapor to the reaction flask containing the reactants, diisocyanate and poly(ϵ-caprolactone).

Poly(ϵ-caprolactone) (**1**) synthesis, Scheme 1, was successful and gave a $\bar{M}_w$ of 6000 g/mol, PDI of 1.22 (GPC), and a $\overline{DP}$ of 40 (NMR). A schematic reaction scheme of the PUU synthesis is shown in Scheme 2. The scheme shows a general reaction but should not be considered as the only route. The hard segment synthesis shows only α-to-ϵ coupling between two LDI, but α-to-α and ϵ-to-ϵ couplings are also possible. A prepolymer, **2**, was synthesized by the addition of the poly(ϵ-caprolactone) diol, **1**, dissolved in DMF to an excess of diisocyanate, giving an isocyanate-terminated prepolymer. The addition was done dropwise over 3 h to avoid the formation of monoblocks comprised of LDI units. They correspond to single LDI units, which have reacted with two soft-segment units. Hard-segment formation started upon the addition of water vapor. When isocyanate reacts with water, it forms the corresponding amine (**3**) and carbon dioxide. The amine can then react with another isocyanate and form a urea linkage (**4**). When approaching stoichiometry almost all the excess of isocyanate has reacted (**6**), and when adding more water the final isocyanates will react linking the chains together, resulting in high molecular weight polymer.

NMR together with *IV* showed that the syntheses of the poly(urethane urea)s were successful, resulting in PUU with four different lengths of hard segment (Figure 2). The lengths of the hard segments were calculated and are shown in Table 1. The four LDI-based poly(urethane urea)s showed hard segment lengths from just under 5 (4.8) LDI units to almost 12 (11.6) LDI units (denoted LDI 4.8 to LDI 11.6), and all showed inherent values above 2 dL/g. The poly(urethane urea) with HDI had a segment length of 9.7 HDI units (denoted HDI 9.7) and an inherent viscosity of 3.54dL/g. The aromatic PUU could be kept in solution from the polymerization but when precipitated and dried they could not be redissolved completely, a result of the strong secondary forces found in aromatic PUU. Since the synthesis was interrupted prior to stoichiometry, the inherent viscosities were lower for the aromatic PUU, MDI 4* 0.63 dL/g and TDI 4* 0.72 dL/g. Measuring molecular weight and *IV* for polymers with strong secondary forces like hydrogen bonding is delicate. The hydrogen bonding can create agglomerates internally or externally, resulting in data that are difficult to interpret. The results presented here give though a hint to the molecular size of the synthesized polymers.

The reason why the target values for the hard segment were not reached could be due to formation of dimers or trimers of diisocyanates; nonetheless, it has been shown that the hard segment length can easily be varied. All polymers were prepared in yields of more than 80%. To be able to evaluate the advantage of adding the water in vapor phase in a continuous manner, two reference synthesizes were done where the water was added in liquid phase. LDI and PCL were added in 6:1 proportion in the same way as for the vapor phase addition synthesis. When adding all the water at once, the solution became greenish and then turned brown; the isolated product could not be dissolved and thereby not analyzed with solution demanding techniques. When adding the water from a standard solution (2.07 mmol/mL in DMF), the isolated product was soluble and showed a

Scheme 2. Synthesis of Poly(urethane urea) with a Hard Segment Containing Five Urea Groups[a]



[a] The scheme only shows hard segment growth in one direction of the two-armed poly(ϵ-caprolactone).

lower inherent viscosity, 0.84 g/dL, than the correspond PUU, synthesized with vapor phase addition. When using a standard solution, the addition is much more local and excess is easily achieved in that region and stoichiometry is passed.

Result of Molecular Weight and Hydrogen Bonding. The aliphatic PUU all showed high elongation at break, 540−980% (Table 2). The LDI−PCL system also showed that altering the hard segment length varied the stress−strain properties. When increasing the length of the hard segment, the elongation at break decreased while the elastic modulus increased, which corresponds well with what Sung et al. have reported.[9] A poly(urethane urea) with HDI in the hard segment gave a lower elastic modulus and higher strain at break than the corresponding LDI, 89 MPa (LDI 9.8, 211 MPa) and 857% (LDI 9.8, 712%). This does not correspond with earlier studies that show that asymmetrical diisocyanates yield materials with lower modulus.[14] Even though the aromatic PUU had lower *IV*, they showed high elongation at break, 804% (TDI 4) and 347% (MDI 4). The slower evaporation when casting the films from DMF allows the phase separation to be more pronounced, which would explain the lower elastic modulus for the aromatic PUU.

When studying hydrogen bonding with IR spectroscopy there are two major regions of interest: the carbonyl region located between ~1620 and 1760 cm^{-1} and the N−H (amide I) region found between 3100 and 3500 cm^{-1} (Figure 4).

Table 3 shows the frequencies from the IR spectra performed on films from the LDI−PCL. No peaks from "free" carbonyl or from disordered urea carbonyl could be seen. The carbonyl urea peak around 1630−1640 cm^{-1} shifted toward lower frequencies as the hard block length increases (Table 3). According to Coleman and Painter, stronger hydrogen bonding will lead to a decrease in frequency for the carbonyl and the amide I peak while the amide II peak should increase in frequency.[13] This tendency is seen in Table 3; when increasing the hard block length, the amide II peak shifts from 1559 to 1569 cm^{-1} while the carbonyl peak shifts from 1639 to 1631

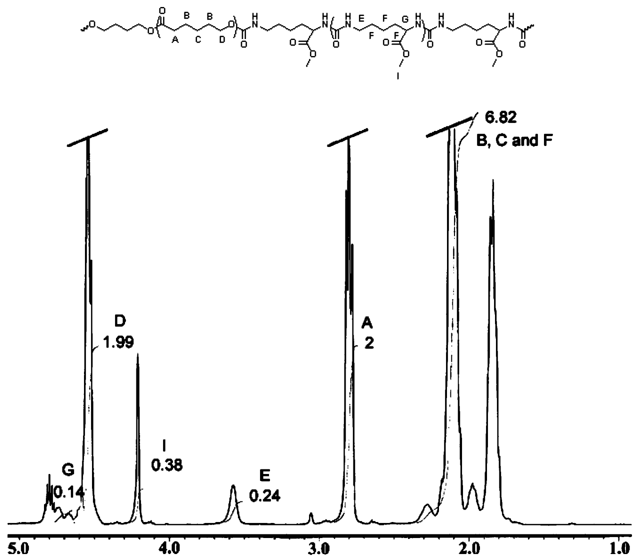


Figure 2. NMR of PCL−LDI with a hard segment length of 4.8 LDI units.

Table 1. Average Degree of Polymerization of the Hard Segment, Hard Segment Content, Inherent Viscosity, and Isolated Yield

polymer	target length	hard segment content (%)	length (NMR)	*IV* (dL/g)	isolated yield (%)
PCL			40[b]	0.28	85
LDI 4.8	6.7	18	4.8	2.21	87
LDI 8.0	10.1	27	8.0	2.04	82
LDI 9.8	12.0	31	9.8	2.31	88
LDI 11.6	15.1	35	11.6	2.52	86
HDI 9.7	10.7	31	9.7	3.54	82
TDI 4*[a]	3.9			0.72	81
MDI 4*[a]	4.2			0.63	86

[a] Interrupted synthesis and hard segment length not confirmed. [b] Average degree of polymerization.

Table 2. Mechanical Properties for the Aliphatic PUU; Results Are Shown as Mean Values with Standard Deviation in Parentheses

polymer	hard segment content (%)	elongation at break (%)	*E* modulus (MPa)	tensile stress at break (MPa)
LDI 4.8	18	980 (156)	146 (12)	32 (6.0)
LDI 8.0	27	801 (113)	179 (20)	30 (10)
LDI 9.8	31	712 (29)	211 (22)	44 (4.2)
LDI 11.6	35	548 (56)	235 (31)	32 (3.4)
HDI 9.7	31	857 (83)	89 (12)	49 (5.1)
TDI 4*[a]		804 (30)	124 (28)	33 (5.7)
MDI 4*[a]		347 (62)	43 (11)	6.6 (0.9)

[a] Interrupted synthesis and hard segment length not confirmed.

cm^{-1}. In the amide I region there is also a shift to lower frequency, and a sharper peak was seen on increasing the hard block length, emphasizing stronger hydrogen bonding. LDI 9.8 showed the lowest frequency and the sharpest peak, indicating stronger and more ordered hydrogen bonding.[15,16]

Glass Transition and Melting Point. The thermal properties were calculated on the basis of the second heating after heating to 180 °C and cooling to −80 °C. The melting temperatures, T_m, presented here are for the soft segment and are the peak values, and the glass transition temperature, T_g, is for the soft segment since no transition was seen for the hard segment. All systems showed a weak T_g around −60 °C, which was attributed to the soft PCL segment (Table 4). No trend for the soft segment T_g could be seen when increasing the hard segment content which, according to Yang et al.,[17] should increase the T_g. The higher T_g for the PUU from aromatic diisocyanates is in accordance with what Lee et al. showed when they compared glass transition of PU from aromatic and aliphatic diisocyanates.[1]

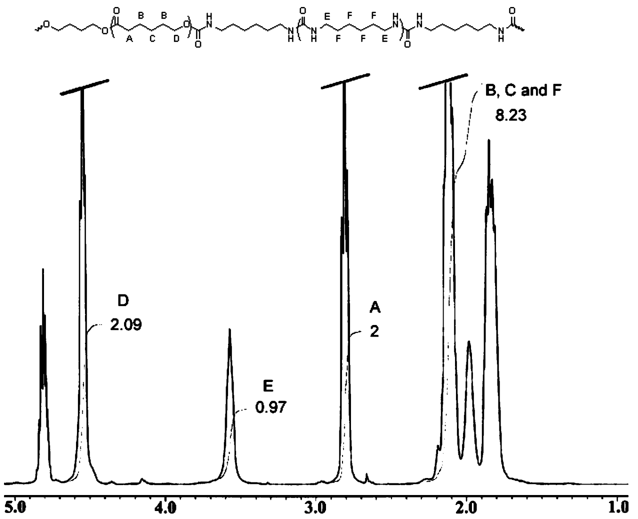


Figure 3. NMR of PCL−HDI with a hard segment length of 9.7 HDI units.

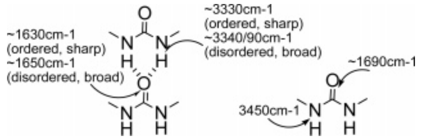


Figure 4. Origin of IR spectra for urea groups, hydrogen bonded (left) and free (right).

Table 3. Amide and Carbonyl Peaks from PUU Films

PUU	amide I peak (cm^{-1})	amide II peak (cm^{-1})	carbonyl peak (cm^{-1})
LDI 4.8	3362	1559	1639
LDI 8.0	3353	1559	1638
LDI 9.8	3343	1569	1631
LDI 11.6	3348	1562	1635

Table 4. Thermal Properties during Second Heating

polymer	T_g (°C)	T_m (°C)	crystallinity (J/g)
PCL	−64.2	52.6	73.8
LDI 4.8	−59.8	47.4	33.6
LDI 8.0	−62.4	43.1	29.8
LDI 9.8	−61.3	40.6	28.1
LDI 11.6	−58.9	38.8	25.0
HDI 9.7	−58.8	32.6	25.6
TDI 4*[a]	−57.4	42.2	37.9
MDI 4*[a]	−57.0	41.1	30.2

[a] Interrupted synthesis and hard segment length not confirmed.

For the soft segment, T_m decreased with the hard segment length, going from 47 to 39 °C when going from 4.8 to 11.6 LDI units (Figure 6). The same trend was seen when studying crystallinity. This corroborates increased phase mixing and thereby hydrogen bonding between urea and ester groups. The melting temperature should theoretically not change when changing the hard segment length, but the hard segment domains interfere and disturb the soft segment domains (vide supra). Since the volume fraction of PCL decreases with increasing hard segment content, this is expected. When comparing different diisocyanates with similar hard segment lengths, one can see that the melting temperature was lower when HDI was used compared with LDI 9.8. This trend was also seen for the two aromatic diisocyanates, TDI and MDI, when compared with LDI 4.8 (Table 4).

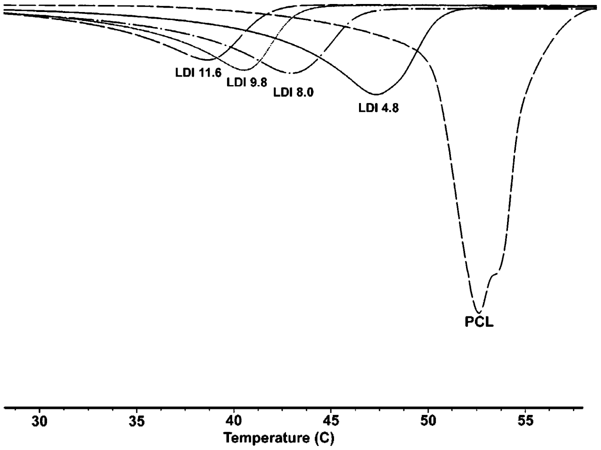


Figure 5. DSC curves showing melt transitions for PUU. To the left, LDI:PCL systems with increasing hard segment length and pure PCL.

Conclusion

A simple one-pot reaction has been developed for the synthesis of poly(urethane urea). The hard segment is built up during the addition of water in the vapor phase, creating the amine in situ and thereby linking diisocyanates together via urea linkages. Synthesizing the same PUU by adding the water all at once or dropwise from a standard solution resulted in an insoluble PUU and a PUU with lower inherent viscosity, respectively. This synthetic method avoids intermediate isolation steps, and by adding the water continuously and slowly, the addition becomes the rate-determining step and the problem with careful control of stoichiometry is eliminated. Here we have demonstrated, for the first time, the synthesis of a non-cross-linked poly(urethane urea) with a hard segment derived only from diisocyanate with no chain-extender added. Not only can the properties be altered via varying the soft segment, diisocyanate, or chain extender, but also by easily synthesizing different lengths of hard segment. Through this technique a new simple tool for tailoring properties of PUU is provided.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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