Synthesis and Characterization of Segmented Copoly(ether urea)s with Uniform Hard Segments

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ABSTRACT: Employing protective group strategy and novel isocyanate chemistry, segmented copoly(ether urea)s with uniform hard segments were prepared. Amine-terminated poly(tetrahydrofuran) served as the soft segment of these polymers. The size of the hard segments and the number of urea groups it contains were varied systematically, and their influence on the properties was investigated. The strength of hydrogen bonding between the urea groups in monodisperse hard segments containing exactly 1 to exactly 4 urea groups was studied by infrared spectroscopy and compared with materials containing polydisperse hard segments. The strength of hydrogen bonding in polymers possessing exactly two urea groups per hard segment resulted in an optimal balance between excellent mechanical properties and good processability and solubility.

1. Introduction

Thermoplastic elastomers (TPEs) are polymers that combine advantages of both thermoplastics and elastomers.[1] In general, their specific properties are a result of their morphology. At ambient temperature, physical cross-links in the amorphous matrix give the material its elastomeric, rubberlike properties. At higher temperatures, these physical cross-links are broken due to their reversibility, and the material can be processed easily. In many thermoplastic elastomers, the reversible cross-links originate from crystallization of one of the blocks of the segmented copolymer. These “hard” blocks are generally polyester,[1,2] polyamide,[3] or polyurethane[4] segments. At low temperatures, crystalline domains account for the mechanical stability of the material; however, above the melting point of the hard block, a polymer melt is obtained.

Among segmented copolymers, thermoplastic elastomeric polyurethanes (TPUs) are the most widely used. The TPU consists basically of three building blocks: a long-chain diol, normally with a polyether or polyester backbone; a diisocyanate, and a chain extender, e.g., water, a short-chain diol, or a diamine. TPU’s are often prepared via a one-pot procedure, in which the long-chain diol is first reacted with an excess of the diisocyanate to form an isocyanate-functionalized prepolymer, which is subsequently reacted with the chain extender, resulting in the formation of the high molecular weight polyurethane. This synthetic procedure to prepare TPUs has the intrinsic disadvantage that it leads to a statistical distribution in the lengths of the hard segments.[5] As a result, the phase separation of these block copolymers is incomplete. Part of the hard blocks, in particular the shorter segments, are dissolved in the soft phase, causing an increase in the glass transition temperature, which is undesirable for the low-temperature flexibility of the material. The polydispersity of the hard segment is manifested in a broad melting range and a rubbery plateau that is dependent on temperature. To improve these properties, and to get more insight into the structure−properties relationship, block copolymers containing hard segments of uniform length have been prepared in the past.[6,7] These studies showed that uniform hard blocks leads to polymers with better properties, which are less temperature dependent.

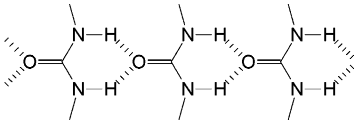

Figure 1. Bifurcated hydrogen-bonding motif of urea derivatives.

Several types of hard blocks have been used to reach this objective, such as non-hydrogen-bonding polyurethanes,[6a,b] normal polyurethanes,[6c,d,f] and poly(urethane urea)s.[6e] Niesten et al. used hard blocks based on uniform aramid units[7] and have shown that these units form perfect crystals which melt in a narrow temperature region. Most TPEs containing uniform hard blocks were prepared by fractionation of a mixture of hard block oligomers and subsequent copolymerization of the uniform hard oligomer of a specific length with the prepolymer. This procedure is hampered by the low solubility of—especially the longer—oligomers and the difficulty in fractionating oligomers that are different in length but similar in chemical structure.

Urea groups are excellent functionalities for use in hard blocks of thermoplastic elastomers because they are known to associate via bifurcated hydrogen bonds (Figure 1).[8] The hydrogen bond strength exceeds that of amides and urethanes. Many researchers utilized the strong association between urea groups to obtain gelling agents.[9]

Thermoplastic elastomers containing urea groups have been prepared before,[10] but few examples are known of TPEs possessing hard blocks comprising solely urea groups.[11] Yilgör et al. described segmented poly(dimethylsiloxane) and poly(ethylene oxide) based urea copolymers and studied their behavior in detail.[11a−e] These polymers were prepared by chain extension of amine-terminated prepolymers with diisocyanates. However, their synthetic strategy does not allow the prepa-

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ration of uniform hard blocks possessing more than two urea groups.

In this paper, we present the synthesis of segmented block copolymers possessing uniform (monodisperse) hard blocks based on urea groups, making use of a protective group strategy and employing di-*tert*-butyl tricarbonate, a mild and selective reagent for the formation of isocyanates that was recently developed by us.[12] Poly(tetrahydrofuran) (pTHF) was used as the soft segment since it is commercially available in a variety of molecular weights and may be prepared on a laboratory scale via a cationic ring-opening polymerization of tetrahydrofuran.[13]

2. Experimental Section

General Methods and Instrumentation. NMR spectra were recorded on a Varian Inova 500 MHz spectrometer, a Bruker 400 MHz spectrometer, and a Varian Gemini 300 MHz spectrometer. Infrared spectra were measured on a Perkin-Elmer 1600 FT-IR. Size exclusion chromatography (SEC) was performed on a Shimadzu LC10-AT, using a Polymer Laboratories Plgel 5 μm Mixed-D column, a Shimadzu RID-6A detector, and *N*-methylpyrrolidone as eluent. Molecular weights were calculated relative to polystyrene standards. MALDI−TOF spectra were obtained at a Perseptive Biosystems Voyager DE-Pro MALDI−TOF mass spectrometer (accelerating voltage, 20 kV; grid voltage, 74.0%; guide wire voltage, 0.030%; delay, 200 ms; low mass gate, 900 amu). Samples for MALDI−TOF were prepared by adding a solution of the polymers in THF (20 μL, $c = 1$ mg/mL) to a solution of α-cyano-4-hydroxycinnamic acid in THF (10 μL, $c = 20$ mg/mL) and subsequent thoroughly mixing. This mixture (0.3 μL) was brought on a sample plate, and the solvent was evaporated. Size exclusion chromatography (SEC) was performed on a Shimadzu LC10-AT, using a Polymer Laboratories Plgel 500 A column, a Shimadzu SPD-10AV UV−vis detector, and chloroform as eluent. Polystyrene standards were used for calibration.

Materials. Di-*tert*-butyl tricarbonate, **4**, was prepared according to literature procedure.[12] Bis(3-aminopropyl)poly(tetrahydrofuran) with molecular weights 350 and 1100 g/mol, poly(tetrahydrofuran) with molecular weights 2000 and 2900 g/mol, and poly(ethylene oxide) with molecular weight 2000 were purchased from Aldrich. PTHF/EO_{4000}, a random copolymer of THF and EO in a ratio of 90:10, was kindly provided by Prof. Dr. Doetze Sikkema (Akzo-Nobel). 1,4-Diisocyanatobutane, borane−tetrahydrofuran complex (1 M in THF), and sodium hydride (60% dispersion in mineral oil) were purchased from Aldrich, 1,3-diaminopropane was from Acros, 1,2-ethylenediamine was from Janssen, and 1,5-diaminopentane and 1,6-diisocyanatohexane were from Fluka.

Bis(2-cyanoethyl)poly(tetrahydrofuran), 2. Poly(tetrahydrofuran)diol, $M_n = 2000$ g/mol (20.00 g, 10.0 mmol), and 15-crown-5 (44 mg, 0.2 mmol) were dissolved in acrylonitrile (40 mL) and cooled in an ice bath. Sodium hydride (8 mg 60% dispersion in mineral oil, 0.2 mmol) was added to the solution, and the reaction mixture was stirred at 0 °C for about 15 min, after which the reaction mixture turned slightly yellow. At this point, the reaction was quenched by addition of a drop of concentrated hydrochloric acid. The solution was concentrated, and the residue was taken up in dichloromethane (100 mL) and centrifuged at 4500 rpm. The mixture was decanted, filtered, and concentrated in vacuo. The product was obtained as a slightly yellow, viscous liquid, which slowly crystallized (20.13 g, 96%). ^{1}H NMR ($CDCl_3$): δ 3.62 (t, 4H, OCH_2CH_2CN), 3.51 (t, 4H, $CH_2OCH_2CH_2CN$), 3.40 (br t, 106H, $OCH_2CH_2CH_2CH_2O$ main chain), 2.59 (t, 4H, CH_2CN), 1.60 ppm (br m, 110H, $OCH_2CH_2CH_2CH_2O$ main chain). ^{13}C NMR ($CDCl_3$): δ 117.7 (CN), 71.0 ($CH_2OCH_2CH_2CN$), 70.4 ($OCH_2CH_2CH_2CH_2O$ main chain), 65.1 (OCH_2CH_2CN), 26.3 ($OCH_2CH_2CH_2CH_2O$ main chain), 18.7 ppm (CH_2CN). FT-IR (ATR): ν 2939, 2855, 2161 (w, C≡N stretching), 1367, 1103 cm^{-1} (C−O stretching).

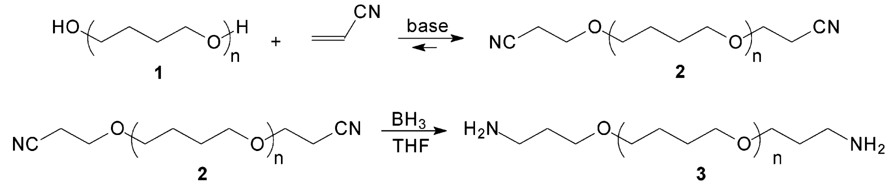
Bis(3-aminopropyl)poly(tetrahydrofuran), 3. To a solution of borane−tetrahydrofuran complex (80 mL of 1 M THF, 80 mmol) in dry THF (240 mL) was added slowly bis(2-cyanoethyl)poly(tetrahydrofuran), **2** (20.00 g, 9.5 mmol), dissolved in dry THF (160 mL) at 0 °C. The solution was stirred for 30 min at 0 °C, after which it was heated to reflux for 4 h. The reaction mixture was cooled to 0 °C, and methanol (80 mL) was added dropwise (be careful: hydrogen gas evolution). Hydrochloric acid (4 mL, 37% in water) was added slowly, and the reaction mixture was stirred for 1 h and subsequently evaporated to dryness under reduced pressure. Trimethyl borate was removed by three coevaporations with methanol (3 times 100 mL). To the viscous liquid was added sodium hydroxide solution (150 mL, 1 M in water), and this was extracted with diethyl ether (3 times 300 mL). The combined organic layers were dried with sodium sulfate and filtered, and the solvent was evaporated on a rotary evaporator without putting the flask in the water bath. During the evaporation, the polymer precipitated from the cold solution and was obtained as a white powder (18.74 g, 93%). ^{1}H NMR ($CDCl_3$): δ 3.49 (t, 4H, $OCH_2CH_2CH_2NH_2$), 3.41 (br. t, 138H, $OCH_2CH_2CH_2CH_2O$ main chain), 2.79 (t, 4H, CH_2NH_2), 1.71 (t, 4H, $OCH_2CH_2CH_2NH_2$), 1.62 (br m, 142H, $OCH_2CH_2CH_2CH_2O$ main chain), 1.1 ppm (br s, 4H, NH_2). ^{13}C NMR ($CDCl_3$): δ 70.5 ($OCH_2CH_2CH_2CH_2O$ main chain), 68.8 ($OCH_2CH_2CH_2NH_2$), 39.7 (CH_2NH_2), 33.6 ($OCH_2CH_2CH_2NH_2$), 26.4 ppm ($OCH_2CH_2CH_2CH_2O$ main chain). FT-IR (ATR): ν 3564, 3539, 2941, 2862, 1492, 1372, 1107, 996 cm^{-1}. MALDI−TOF $[M + Na^+]$ = Calcd $155.1 + n \times 72.0$ Da. Obsd: $155.9 + n \times 72.0$ Da. SEC (phenyl urea derivative): $M_n = 3769$ g/mol, PDI = 1.5.

$pTHF_{1100}$-U. Bis(3-aminopropyl)poly(tetrahydrofuran), $M_n = 1100$ g/mol (2.00 g, 1.82 mmol), was dissolved in chloroform (20 mL), and a solution of di-*tert*-butyl tricarbonate (0.48 g, 1.82 mmol) in chloroform (4 mL) was injected into this solution at 20 °C. The reaction mixture was stirred for 2 h at 20 °C and subsequently evaporated to dryness under reduced pressure. The product was obtained as a very viscous colorless oil. ^{1}H NMR (DMSO): δ 3.33 (60H, CH_2O), 2.95 (4H, CH_2N), 1.50 ppm (65H, $CH_2CH_2CH_2$). FT-IR (ATR): ν 3350 (N−H stretching), 2938, 2853, 1637 (C=O stretching), 1568, 1366, 1103 cm^{-1} (C−O stretching). SEC (NMP, rel to PS): $M_n = 68 \times 10^3$ g/mol.

$pTHF_{1100}$-U-C_2H_4-U. *Via Route A (Scheme 3)*. Bis(3-aminopropyl)poly(tetrahydrofuran), $M_n = 1100$ g/mol (0.50 g, 0.45 mmol), was dissolved in chloroform (10 mL), and a solution of di-*tert*-butyl tricarbonate (0.235 g, 0.91 mmol) in chloroform (1 mL) was injected into this solution at 20 °C. The reaction mixture was stirred for 30 min. 1,2-Ethylenediamine (0.0269 g, 0.45 mmol) in chloroform (3 mL) was added dropwise at 20 °C, and the solution was stirred for 1 h, and subsequently partly concentrated, and methanol (1 mL) was added. The product was precipitated in pentane (50 mL), filtered, and dried in vacuo. It was obtained as white, fluffy, elastic fibers (0.47 g, 86%). ^{1}H NMR (DMSO): δ 5.91 (4H, NH), 3.34 (59H, CH_2O), 2.99 (8H, CH_2N), 1.51 ppm (56H, $CH_2CH_2CH_2$). FT-IR (ATR): ν 3329 (N−H stretching), 2937, 2854, 1615 (C=O stretching), 1589 1366, 1105 cm^{-1} (C−O stretching). SEC (NMP, rel to PS): $M_n = 41 \times 10^3$ g/mol.

$pTHF_{1100}$-U-C_4H_8-U (= $pTHF_{1100}$-U_2). *Via Route B (Scheme 3)*. Bis(3-aminopropyl)poly(tetrahydrofuran), $M_n = 1100$ g/mol (10.00 g, 9.09 mmol), was dissolved in chloroform (100 mL) and a solution of 1,4-diisocyanatobutane (1.40 g, 9.99 mmol) in chloroform (40 mL). About 75% of the latter solution was added to the former solution at once, and the rest was added dropwise at 20 °C. The solution was stirred for 1 h, and subsequently partly concentrated, and methanol (5 mL) was added. The product was precipitated in hexane (500 mL), filtered, and dried in vacuo. It was obtained as white, fluffy, elastic fibers (10.62 g, 93%). ^{1}H NMR ($CHCl_3$): δ 5.4−4.8 (4H, NH), 3.41 (58H, CH_2O), 3.25 (4H, $OCH_2CH_2CH_2N$), 3.17 (4H, $NCH_2CH_2CH_2CH_2N$), 1.74 (4H, $OCH_2CH_2CH_2N$), 1.62 (58H, $OCH_2CH_2CH_2CH_2O$), 1.50 ppm (4H, $NCH_2CH_2CH_2CH_2N$). FT-IR (ATR): ν 3324 (N−H stretching), 2940, 2854, 1615 (C=O stretching), 1580 1365, 1104 cm^{-1} (C−O stretching).

Scheme 1. Synthesis of Amine-Terminated Prepolymers 3



SEC (NMP, rel to PS): $M_n = 42 \times 10^3$ g/mol, $\rho = 0.98$ g/cm^3.

4-(*tert*-Butoxycarbonylamino)-1-butylamine, 5. Di-*tert*-butyl dicarbonate (14.40 g, 50 mmol) was dissolved in chloroform (100 mL) and added dropwise to a solution of 1,4-diaminobutane (17.60 g, 200 mmol) in chloroform (150 mL) at 0 °C. The suspension was stirred overnight at 20 °C. The reaction mixture was washed three times with water (100 mL), and the product was extracted by hydrochloric acid solution (100 mL 1 M in water). The aqueous layer was isolated, basified by addition of sodium hydroxide solution (10 mL 10 M in water), and subsequently extracted 3 times with dichloromethane (3 times 100 mL). The combined organic layers were dried with sodium sulfate and filtered, and the dichloromethane was removed under reduced pressure. Recrystallization of the product from diisopropyl ether gave the pure product as colorless crystals (7.80 g, 80%, with respect to di-*tert*-butyl dicarbonate); $T_m = 84$ °C. ^{1}H NMR ($CDCl_3$): δ 4.71 (s, 1H, N*H*Boc), 3.13 (q, 2H, BocNH−CH_2, $J = 6.2$ Hz), 2.71 (t, 2H, H_2NCH_2, $J = 6.6$ Hz), 1.57−1.46 (m, 4H, $CH_2CH_2CH_2$), 1.44 (s, 9H, CH_3), 1.28 ppm (s, 2H, NH_2). ^{13}C NMR ($CDCl_3$): δ 155.8 (*C*═O), 79.0 (($CH_3)_3C$), 41.9 (CH_2NHBoc), 40.5 (CH_2-NH_2), 31.0 (CH_2CH_2NHBoc), 28.5 (CH_3), 27.6 ppm (CH_2CH_2-NH_2). FT-IR (ATR): ν 3359 (N−H stretching), 1689 (C═O stretching), 1521, 1167 cm^{-1}. Anal. Calcd (%) for $C_9H_{20}N_2O_2$ (188.27): C, 57.42; H, 10.71; N, 14.88. Found (%): C, 56.65; H, 10.62; N, 14.58.

***O,O′*-Bis(4-(*tert*-butoxycarbonylamino)butylureido)-poly(tetrahydrofuran), 7.** Di-*tert*-butyl tricarbonate **4** (1.03 g, 3.94 mmol) was dissolved in chloroform (20 mL), and 4-(*tert*-butoxycarbonylamino)-1-butylamine **5** (0.74 g, 3.94 mmol) in chloroform (4 mL) was injected in this solution at 20 °C. The reaction mixture was stirred for 30 min to yield isocyanate **6**. Subsequently, bis(3-aminopropyl)poly(tetrahydrofuran), $M_n =$ 1100 g/mol (2.00 g, 1.82 mmol), in chloroform (8 mL) was added, and the solution was stirred for 1 h at 20 °C, after which it was concentrated in vacuo (2.75 g, 99%). ^{1}H NMR ($CDCl_3$): δ 5.4 (br s, 2H, N*H*Boc), 4.8 (br s, 4H, N*H*C═ON*H*), 3.53 (t, 4H, $OCH_2CH_2CH_2N$), 3.42 (br m, 60H, $OCH_2CH_2CH_2CH_2O$), 3.31 (t, 4H, $OCH_2CH_2CH_2N$), 3.16 (m, 8H, $CH_2CH_2CH_2CH_2N$), 1.80 (qui, 4H, $OCH_2CH_2CH_2N$), 1.62 (br m, 70H, $OCH_2CH_2CH_2$-CH_2O), 1.50 (m, 4H, $NCH_2CH_2CH_2CH_2N$), 1.44 ppm (s, 18H, CH_3). FT-IR (ATR): ν 3357, 1680, 1626, 1579, 1520, 1365, 1102 cm^{-1}.

***O,O′*-Bis(4-aminobutylureido)poly(tetrahydrofuran), 8**. *O,O′*-Bis(4-(*tert*-butoxycarbonylamino)butylureido)poly(tetrahydrofuran), **7** (6.80 g, 8.95 mmol), was dissolved in dichloromethane (10 mL), and trifluoroacetic acid (5 mL) was added. The reaction mixture was stirred at 20 °C overnight. Dichloromethane and trifluoroacetic acid were removed under reduced pressure, and the residue was redissolved in dichloromethane (50 mL) and washed with sodium hydroxide solution (50 mL 1 M in water). The aqueous layer was extracted two more times with dichloromethane (two times 50 mL). The combined organic layers were dried with sodium sulfate and filtered, and the dichloromethane was removed under reduced pressure. The product was obtained as a waxy solid (4.90 g, 85%). ^{1}H NMR ($CDCl_3$): δ 4.9−4.7 (d br s, 4H, N*H*C═ON*H*), 3.50 (t, 4H, $NCH_2CH_2CH_2O$, $J = 5.9$ Hz), 3.41 (br m, 70H, OCH_2CH_2-CH_2CH_2O), 3.27 (q, 4H, $OCH_2CH_2CH_2N$, $J = 6.2$ Hz), 3.27 (q, 4H, (C═O)$NHCH_2CH_2CH_2CH_2N$, $J = 5.9$ Hz), 2.71 (t, 4H, NH_2CH_2, $J = 6.8$ Hz), 1.75 (qui, 4H, $NCH_2CH_2CH_2O$, $J = 6.3$ Hz), 1.62 (br m, 70H, $OCH_2CH_2CH_2CH_2O$), 1.50 (m, 8H, $NHCH_2CH_2CH_2CH_2N$), 1.03 ppm (s, 4H, NH_2). FT-IR (ATR): ν 3327, 2938, 2859, 1616, 1587, 1365, 1106 cm^{-1}.

pTHF$_{1100}$-U$_3$. *O,O′*-Bis(4-aminobutylureido)poly(tetrahydrofuran), **8** (0.50 g, 0.368 mmol), was dissolved in chloroform (5 mL), and di-*tert*-butyl tricarbonate (0.19 g, 0.735 mmol) in chloroform (1 mL) was injected into this solution at 20 °C. The reaction mixture was stirred for 30 min, and methanol (3 mL) was added, immediately followed by *O,O′*-bis(4-aminobutylureido)poly(tetrahydrofuran), **8** (0.50 g, 0.368 mmol), in chloroform (3 mL). The reaction mixture was stirred for 1 h at 20 °C and subsequently precipitated in pentane (100 mL). The product was obtained as a white fluffy powder (0.89 g, 88%). ^{1}H NMR (10% TFA in $CDCl_3$): δ 3.71 (64H, CH_2O), 3.45 (4H, $OCH_2CH_2CH_2N$), 3.32 (8H, $NCH_2CH_2CH_2CH_2N$), 1.99 (4H, $OCH_2CH_2CH_2N$), 1.73 ppm (71H, $OCH_2CH_2CH_2CH_2O$ + $NCH_2CH_2CH_2CH_2N$). FT-IR (ATR): ν 3324, 2940, 2854, 1615, 1576 1366, 1105 cm^{-1}.

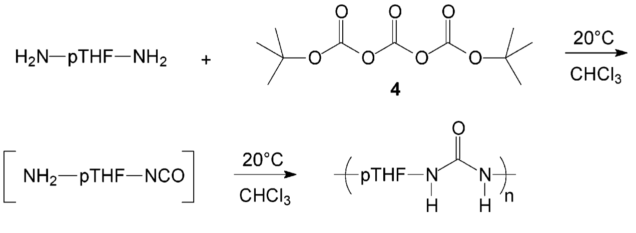
pTHF$_{1100}$-U$_4$. *O,O′*-Bis(4-aminobutylureido)poly(tetrahydrofuran), **8** (0.50 g, 0.368 mmol), was dissolved in chloroform (7 mL) and methanol (3 mL). 1,4-Diisocyanatobutane (0.0567 g, 0.405 mmol) was dissolved in chloroform and added dropwise to the former solution at 20 °C. Subsequently, the reaction mixture was stirred for 1 h. The viscous solution was poured into heptane, and the suspension was stirred for 3 h. Then it was allowed to settle, the liquid was decanted, and the product was dried under reduced pressure. It was obtained as a rubbery solid (0.40 g, 73%). ^{1}H NMR (10% TFA in $CDCl_3$): δ 3.71 (66H, CH_2O), 3.45 (4H, $OCH_2CH_2CH_2N$), 3.31 (12H, $NCH_2CH_2CH_2CH_2N$), 1.98 (4H, $OCH_2CH_2CH_2N$), 1.72 ppm (73H, $OCH_2CH_2CH_2CH_2O$ + $NCH_2CH_2CH_2CH_2N$). FT-IR (ATR): ν 3323, 2940, 2855, 1616, 1574 1368, 1104 cm^{-1}.

pTHF$_{1100}$-U$_{2PD}$. Bis(3-aminopropyl)poly(tetrahydrofuran), $M_n = 1100$ g/mol (2.00 g, 1.79 mmol), and 1,4-diaminobutane (0.158 g, 1.79 mmol) were dissolved in chloroform (20 mL). A solution of di-*tert*-buty tricarbonate (0.94 g, 3.58 mmol) in chloroform (3 mL) was injected into this solution at 20 °C. The reaction mixture was stirred for 1 h at room temperature, during which the solution formed a gel. Methanol (5 mL) was added, and the solution was partly concentrated and then precipitated in pentane (150 mL). The product was obtained as white, fluffy, elastic fibers (2.02 g, 90%). ^{1}H NMR ($CDCl_3$/methanol-d_4): δ 3.34 (80H, CH_2O), 3.21 (4H,), 3.13 (4H, NCH_2-$CH_2CH_2CH_2N$), 1.75 (4H, $OCH_2CH_2CH_2N$), 1.64 (77H, OCH_2-$CH_2CH_2CH_2O$), 1.49 ppm (4H, $NCH_2CH_2CH_2CH_2N$). FT-IR (ATR): ν 3326 (N−H stretching), 2939, 2853, 1620 (C═O stretching), 1579 1366, 1104 cm^{-1} (C−O stretching). SEC (NMP, rel to PS): M_n = n.d.

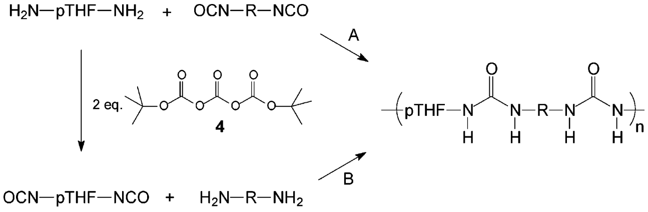
3. Results

3.1. Synthesis. For the preparation of pTHF-based thermoplastic elastomers with hard blocks comprising solely urea groups, amine-terminated pTHF was required. A route to obtain these prepolymers by end group modification was optimized (Scheme 1). Cyanoethylation[14] of hydroxy end groups of pTHF **1** by reaction with acrylonitrile yielded the prepolymers with nitrile functionalities **2**. The reaction was catalyzed by either potassium hydroxide or sodium hydride in an amount of 1 mol %. Next, the nitrile groups of **2** were hydrogenated to yield the amine-terminated prepolymers **3**.[15] Since catalytic hydrogenation and reduction with $LiAlH_4$ were unsuccessful, this hydrogenation was carried out with borane in THF. After several coevaporations with methanol and hydrochloric acid to remove boron−nitrogen complexes, the product was obtained as

Scheme 2. Synthesis of PTHF$_{1100}$-U



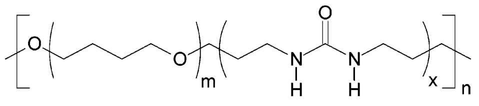
Scheme 3. Two Routes toward PTHF$_{1100}$-U-*R*-U



a white powder. Characterization by ^{1}H NMR, ^{13}C NMR, FT-IR, SEC, and MALDI−TOF MS proved the proposed structure of **3** and showed a degree of functionalization of more than 97%.

Prepolymers with a range of molecular weights were prepared and were used for the synthesis of thermoplastic elastomeric polyurethanes.

Thermoplastic elastomers with one to four urea groups in the hard segment were prepared using the di-*tert*-butyl tricarbonate reagent,[12] in combination with a protective group strategy for the polymers with 3 or 4 urea groups. These polymers are schematically denoted as pTHF$_y$-U$_x$, in which x is the number of urea groups in the hard block and y the number-averaged molecular weight of the pTHF soft block.



pTHF$_y$-U$_x$

The synthesis of pTHF1100-U, a polymer with exactly one urea group in the hard block, is shown in Scheme 2. Amine-terminated prepolymer, pTHF, with molecular weight of 1100 g/mol was reacted with 1 equiv of di-*tert*-butyl tricarbonate (**4**) per two amine groups. The formed isocyanate groups react immediately with another amine group, resulting in a single urea group. After workup, the product was obtained as a viscous liquid in a yield of 97% and with $M_w = 68 \times 10^3$ g/mol based on SEC.

Polymers pTHF$_{1100}$-U$_2$ having a hard block comprising exactly two urea groups separated by 2−6 methylene groups were synthesized by chain extension of the amine-terminated prepolymer with the appropriate diisocyanate (method A) or by reacting the isocyanate-terminated prepolymer with a diamine (method B) (Scheme 3), depending on the availability of the diisocyanate. The chain extender was added dropwise to a solution of the prepolymer in CHCl$_3$, to ensure the exact 1 to 1 ratio of both functional groups in the equivalence point of the reaction, thus obtaining a maximum degree of polymerization. Monitoring the disappearance of the isocyanate band with infrared spectroscopy followed the extent of the reaction.

The polymers were obtained in good yields with molecular weights ranging from 20×10^3 to 55×10^3 g/mol. All polymers were obtained as highly elastic fluffy fibers. Solution casting of the polymers from chloroform solution gave completely transparent elastic films, in contrast to pTHF$_{1000}$-U with one urea group, which was obtained as a viscous liquid at room temperature.

To study the influence of the molecular weight of the prepolymer (soft block), amine-terminated prepolymers with varying molecular weights were chain extended by reaction with 1,4-diisocyanatobutane. These polymers are schematically denoted as e.g. pTHF$_{1100}$-U$_2$. After precipitation, the polymers were obtained as white, elastic, fluffy fibers, except for pTHF$_{350}$-U$_2$, which was obtained as a powder. The molecular weight of this polymer was also considerable lower than that of the other polymers, probably caused by the low functionality of the starting amine-terminated prepolymer.

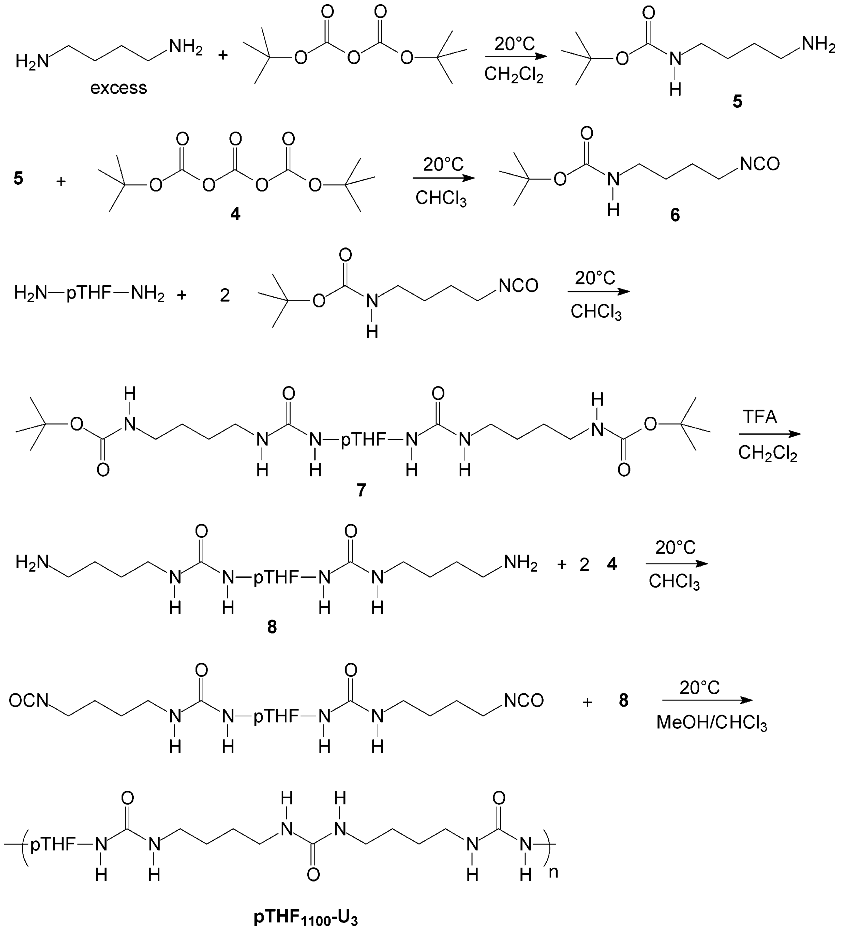
Although the copoly(ether urea)s with two urea groups in the hard block possess already highly elastic properties, we also aimed at synthesizing a polymer comprising three urea groups in the hard block, pTHF$_{1100}$-U$_3$, since it will have a higher melting temperature of the hard block. The synthetic strategy to achieve this goal is outlined in Scheme 4. The first step was the monoprotection of 1,4-diaminobutane by reaction with di-*tert*-butyl dicarbonate. After several extractions and a recrystallization 4-(*tert*-butoxycarbonylamino)-1-butylamine (**5**) was obtained in a yield of 80%. Reaction of the remaining amine group with di-*tert*-butyl tricarbonate gave isocyanate **6** within 15 min in a quantitative yield.

Isocyanate **6** was reacted with the amine-terminated pTHF$_{1100}$, and in the next step the protective group was removed by treatment with trifluoroacetic acid (TFA), yielding the amine-terminated prepolymer **8** with one urea group at both end groups. Reaction of **8** with 2 equiv of di-*tert*-butyl tricarbonate (**4**) gave the corresponding isocyanate-terminated prepolymer, and polycondensation with amine-terminated prepolymer **8** resulted in the segmented copolymer with exactly three urea groups in the hard block. During this step some methanol was added to avoid gelation. After precipitation of the product in pentane, the polymer was obtained as a white fluffy powder. Solution-casting of the product gave a transparent flexible film. The molecular weight could not be determined by SEC, since the polymer was insoluble in the eluent NMP.

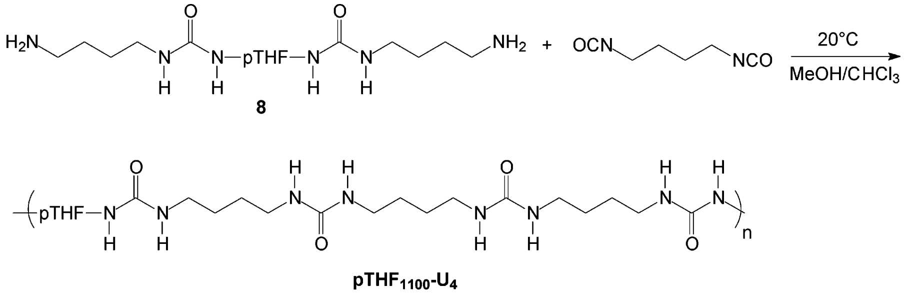
The synthesis of a segmented copoly(ether urea) having a hard block containing exactly four urea groups in the hard block, pTHF$_{1100}$-U$_4$, is a straightforward continuation of the synthesis of the one with three urea groups. Amine-terminated prepolymer **8** was reacted with 1,4-diisocyanatobutane in a mixture of methanol and chloroform (Scheme 5). Because of the very strong interaction between this hard block comprising four urea groups, the solution became highly viscous, and this hampered the precipitation of the product in heptane. The polymer was obtained as a rubbery solid. The molecular weight could not be determined by SEC since the polymer was insoluble in the eluent NMP.

Finally, a segmented copoly(ether urea) with a polydisperse hard block with on average two urea groups, pTHF$_{1100}$-U$_{2PD}$, was synhesized to study the influence of the uniformity of the hard block. This polymer was prepared by adding di-*tert*-butyl tricarbonate **4** (half an equivalent of per amino group) to an equimolar mixture of amino-terminated pTHF$_{1100}$ and 1,4-diaminobutane (Scheme 6). Assuming equal reactivity of the amino groups of the prepolymer and diaminobutane, a random

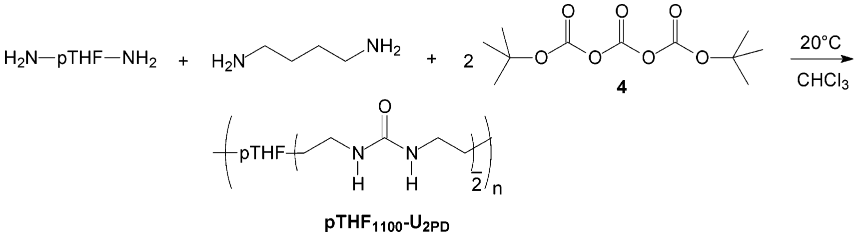
Scheme 4. Synthesis of a Polymer Comprising Three Urea Groups per Hard Block, PTHF$_{1100}$-U$_3$



Scheme 5. Synthesis of a Polymer Comprising Four Urea Groups per Hard Block, PTHF$_{1100}$-U$_4$



Scheme 6. Synthesis of Polymer with Polydisperse Hard Block, PTHF$_{1100}$-U$_{2PD}$



distribution of the hard block length will be obtained. The polymer was obtained as white, elastic, fluffy fibers by precipitation in pentane. The material was moderately soluble in chloroform−methanol mixtures but insoluble in NMP, hampering the determination of its molecular weight.

3.2. Hydrogen Bonding within Block Copoly(ether urea)s. Infrared spectroscopy is a helpful tool for studying the extent of hydrogen bonding of several hydrogen-bonding groups.[11f,16] Coleman and Painter reported on a temperature-dependent infrared study of a polyurea and model ureas.[16a] They concluded that the frequency of both the N−H and the C=O (amide I) vibration depend strongly on the hydrogen-bonding nature of the urea groups (Figure 2).

If the hydrogen-bonding strength between urea groups increases, the frequency of both the N−H and C=O vibrations decreases, in contrast to the amide II band (a combined N−H bending and C−N stretching vibration) at approximately 1575 cm^{-1}, which increases in

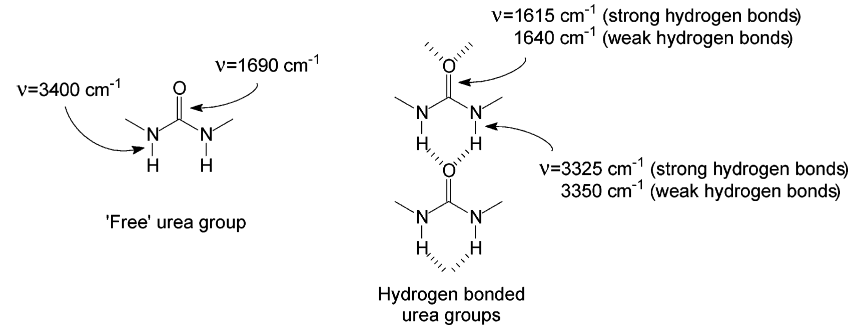


Figure 2. Characteristic infrared bands for urea groups.

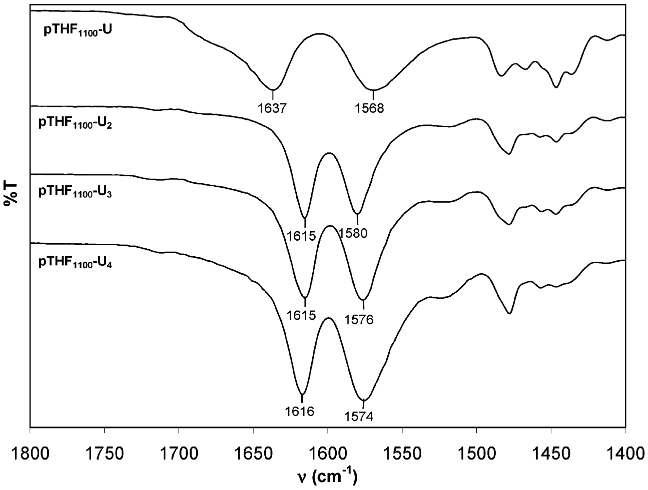


Figure 3. Carbonyl region of infrared spectra of copoly(ether urea)s.

Table 1. Synthesis of Amine-Terminated Prepolymers 3

prepolymer	M_n (g mol^{-1})	M_w/M_n	yield (%)
pTHF$_{350}$	350	1.8	
pTHF$_{1100}$	1100	1.7	
pTHF$_{2000}$	2500	1.5	86
pTHF$_{2900}$	5200	1.5	90
PTHF/EO$_{4000}$[a]	4500	1.4	89

[a] Random copolymer of tetrahydrofuran and ethylene oxide.

Table 2. Synthesis of PTHF-U$_2$ with Varying Size of Soft and Hard Segments

spacer R	soft block	method	yield (%)	M_w (10^3 g/mol)[a]
n-C$_2$H$_4$	pTHF$_{1100}$	B	80	41
n-C$_3$H$_6$	pTHF$_{1100}$	B	86	47
n-C$_4$H$_8$	pTHF$_{350}$	A	83	8.5
n-C$_4$H$_8$	pTHF$_{1100}$	A	89	42
n-C$_4$H$_8$	pTHF$_{2000}$	A	85	53
n-C$_4$H$_8$	pTHF$_{2900}$	A	84	32
n-C$_4$H$_8$	PTHF/EO$_{4000}$	A	93	58
n-C$_5$H$_{10}$	pTHF$_{1100}$	B	84	32
n-C$_6$H$_{12}$	pTHF$_{1100}$	A	89	43

[a] Measured by SEC, with NMP as solvent, relative to polystyrene standards.

frequency. Thus, the position of these bands is a direct indication of the strength of hydrogen bonding. Furthermore, competitive hydrogen bonding between urea and ether groups in the soft block, so-called mixing of hard and soft phases, was quantified. It is more practical to use the carbonyl stretching vibration since this band is narrower than the N−H stretching vibration, and it shifts more upon increase of the hydrogen-bonding strength. In our copolymers, the absence of any carbonyl groups other than from the urea groups, such as urethanes, amides, or esters, is advantageous, allowing an unambiguous analysis of the hydrogen bonds.

The block copoly(ether urea)s show a remarkable difference in their physical properties. The polymer with only one urea group in the hard block, pTHF$_{1100}$-U, possesses hardly any mechanical properties; it was obtained as a viscous liquid. This is an indication of the absence of stable cross-links at room temperature. In the infrared spectra this is evidenced by the position of the carbonyl stretching vibration at 1637 cm^{-1} (Figure 3 top), corresponding to weakly hydrogen-bonded urea groups. Apparently, one single urea group is not sufficient to form stable cross-links by strong hydrogen bonds. Hence, this unit cannot form a hard block. However, for the sake of conformity, we like to use this term here.

The segmented copolymers with two urea groups in the hard block (Table 2) possess very intriguing elastic properties. The fibers are shape-persistent and not tacky. The infrared spectrum of pTHF$_{1100}$-U$_2$ (Figure 3) shows a strong, sharp peak at 1615 cm^{-1}, indicative of strong hydrogen bonding between urea groups. No other peaks corresponding to weakly hydrogen bonded and free urea groups were observed. Thus, two urea groups in the hard blocks induce strong association and stable cross-links at room temperature. The length of the spacer between the urea groups (Table 2) has no effect on the nature of hydrogen bonding. In all these polymers, strong hydrogen bonding is present according to infrared spectroscopy.

Table 2 shows the different soft blocks that were used in the segmented polymers with two urea groups in the hard block. Upon comparison of the FT-IR spectra of the polymers with different soft block length, no difference is observed for the position of the carbonyl stretching vibration. However, the intensity of this peak varies considerably since the concentration of urea groups depends on the molecular weight of the soft block.

The copoly(ether urea)s having three and four urea groups in the hard block show comparable FT-IR spectra as the polymers with two urea groups (Figure 3). The intensity of the bands corresponding to urea groups increases with increasing number of urea groups. The position of the amide I band does not change upon introducing more than two urea groups, indicating no change in hydrogen-bonding strength. The amide II band shifts slightly and broadens; the reason for this is unclear.

To compare the hydrogen bonding in the uniform hard blocks with the polydisperse ones, part of the infrared spectra of polymers pTHF$_{1100}$-U$_2$ and pTHF$_{1100}$-U$_{2PD}$ is shown in Figure 4. Both polymers have the same overall composition, which is reflected by the equal intensity

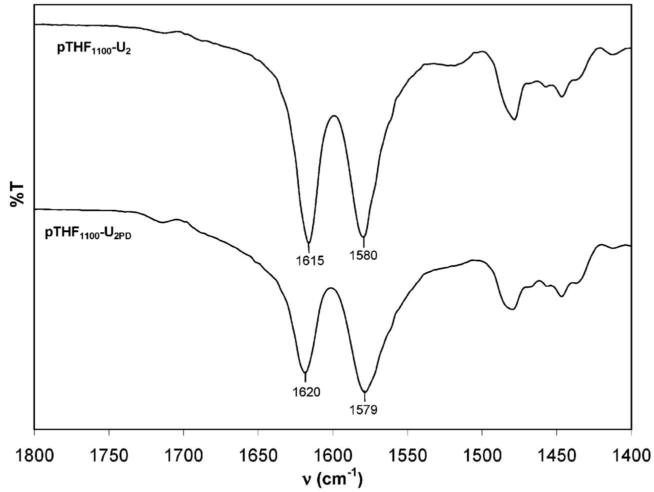


Figure 4. Carbonyl region of infrared spectra of copoly(ether urea)s: uniform hard block (top) and polydisperse hard block (bottom).

of the different functional groups in the polymer. However, the polymer with the polydisperse hard block shows a broader peak corresponding to the carbonyl of the urea group compared to the uniform hard block. This indicates a distribution in hydrogen-bonding strengths within the polydisperse hard blocks. The position of this peak is also at higher frequency (1620 cm^{-1} vs 1615 cm^{-1}, respectively), which denotes that, on average, the hydrogen bonding in the polydisperse hard blocks is weaker than in the uniform hard blocks. This confirms our hypothesis that uniform hard blocks associate stronger than polydisperse hard blocks.

3.3. Flow Temperatures. Thermoplastic elastomers possess elastic properties at ambient temperatures and thermoplastic properties at temperatures above the melting point of the thermoreversible cross-links. The flow temperatures of the different block copoly(ether urea)s were determined by optical microscopy. The temperatures at which the material lost its dimensional stability, the flow temperature, are depicted in Figure 5. Since we are interested in the material properties at and above ambient temperature, the lower limit of the desired flow temperature range is room temperature, and the upper limit is 200 °C, which is the decomposition temperature of the urea groups.[17] This window is indicated by the two dotted horizontal lines.

Figure 5a shows the flow temperature of the material as a function of the number of methylene units within the aliphatic, linear spacer between the urea groups. The polymers with an *even* number of methylenes systematically have a higher flow temperature compared to those with an *odd* number. This is often observed in such a homologous series, including the [*n*]-nylons and [*n*]-polyurethanes.[18] The polymer with a butylene spacer ($n = 4$) has the highest flow temperature, and this is one of the reasons for us to study this hard segment in more detail.

In Figure 5b, the influence of the number of urea groups in the hard block is depicted. As discussed before, the polymer with only one urea group shows viscous flow even below room temperature. Incorporation of one additional urea group makes the material elastomeric and increases the flow temperature to about 140 °C. The melting of the hard blocks is completely reversible. Increasing the number of urea groups in the hard block to three or four results in polymers that do not flow below 200 °C. Above this temperature, degradation starts to occur. This was evidenced by discoloration and fuming of the sample. Although both materials started to flow when heated slightly above 200 °C for prolonged times, this process was not reversible, which is also an indication of degradation. The polymer with a polydisperse hard block (on average two urea groups) shows a flow temperature only slightly lower than the one with exactly two urea groups.

In Figure 5c, the flow temperature as a function of soft block length is shown for the polymers with two urea groups separated by a butylene spacer in the hard block. The flow temperature decreases with increasing soft block length. This is a general trend observed for segmented copolymers and is explained by the solvent effect proposed by Flory.[19] Upon dilution of the crystallizable hard segment, the size of the crystals will become smaller and hence its melting point decreases. Thus, varying the soft block length enables us to alter the flow temperature of the material.

4. Conclusions

Using an optimized two-step synthesis, consisting of cyanoethylation followed by hydrogenation with borane, α,ω-diamino-poly(tetrahydrofuran)s are readily obtained in excellent yields on a 50 g scale from commercially available hydroxy-terminated prepolymers. The amine-terminated pTHF prepolymers are convenient materials for use as the soft block in block copoly(ether urea)s with hard blocks consisting of exactly 1−4 urea groups. The

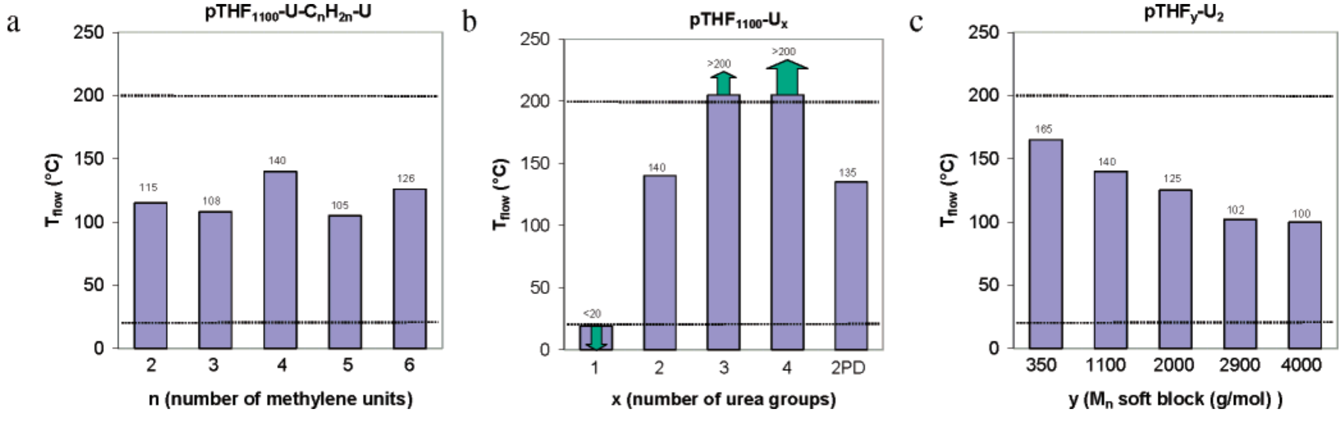


Figure 5. Flow temperature of block copoly(ether urea)s: (a) Dependence of flow temperature on number of methylene units between urea groups in hard block. (b) Dependence on number of urea groups in hard block. Urea groups are separated from eac other by four methylene units (2PD denotes a polymer with a polydisperse hard block with on average two urea groups). (c) Dependence of flow temperature on molecular weight of soft block.

number of urea groups in the hard blocks can be controlled exactly by employing novel isocyanate chemistry, using di-*tert*-butyl tricarbonate, and protective group strategy. The polymer having only one urea group in the hard block is a viscous liquid. Polymers having two urea groups in the hard block possess an optimal balance between mechanical properties and processability, as they are highly elastic and very soluble. Their synthesis is straightforward, as no elaborate protective group chemistry has to be employed. A number of polymers with varying spacers between the two urea groups and with different soft block lengths were prepared. The flow temperature of these materials ranged from 100 to 165 °C and decreased with increasing soft block length. Increasing the number of urea groups in the hard block to three or four gave insoluble gel-forming polymers that are hard to process. Apparently, the association between the hard blocks in these polymers is too strong.

The strength of hydrogen bonding of the urea groups in the polymers was monitored by infrared spectroscopy. This confirmed our observation that hydrogen bonding between hard blocks having only one urea group is weak. By increasing the number of urea groups to two or more, the association of the hard blocks increases, and strong hydrogen bonding is observed by FT-IR. Measurements on materials with two urea groups in the hard block shows that the length of the spacer has little influence on urea hydrogen bonding.

Comparison of the FT-IR spectra of a polymer possessing uniform hard blocks with one possessing a polydisperse hard block indicates a distribution of hydrogen-bonding strengths and weaker hydrogen bonding between the polydisperse hard blocks, illustrating the advantages of the well-defined character of these polymers. A more detailed study of the morphology, thermal behavior, and mechanical properties of these polymers will be discussed in a forthcoming paper.[20]

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