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Thermoplastic polyurethanes from β-methyl-δ-valerolactone-derived amidodiol chain extenders

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ABSTRACT

Here we describe the synthesis of thermoplastic polyurethanes (TPUs) from polyols and amidodiol chain extenders, each of which is prepared from glucose-derived β-methyl-δ-valerolactone (MVL). Utilizing these novel chain extenders, we prepared TPUs with *ca.* 42–44 wt% hard segment content, comprising 72–75 wt% MVL-derived atoms. This compares favorably with an analogous sample prepared using 1,4-butanediol as the chain extender having 57 wt%. These TPUs are ductile (600–900% strain at break) and have high tensile strength (14–33 MPa stress at break). By virtue of the nature of the diamidodiol used as chain extenders, the hard segments contain a greater density of hydrogen bonding −NHC(=O)− functional groups relative to those prepared using traditional short chain 1,n-alkanediols.

1. Introduction

Polyurethanes (PUs) comprise a diverse class of materials with myriad applications. The underlying chemical reaction used to synthesize these polymers (alcohol + isocyanate → urethane) is rapid, selective, and occurs under mild conditions. These features, along with the ready availability of a considerable array of polyols and isocyanates, have enabled polyurethanes to be prepared with an equally diverse array of properties. As with most conventional polymers, modern PUs are typically petroleum-derived and do not readily degrade. The wide-spread use of PUs therefore has a significant environmental impact from several perspectives. The development of alternatives that are bio-degradable and/or that are derived from renewable feedstocks is an important and growing area of investigation. Some have sought to address these issues by incorporating polyols into PUs that have been derived from renewable feedstocks such as vegetable oils [1–5]. While attractive from an availability and cost perspective, these need to be functionalized prior to polymerization (e.g., to ethoxylated polyols) [6,7]. Additionally, these vegetable oil-derived polyols are multifunctional, necessarily giving rise to cross-linked PUs, which are difficult to recycle. Other researchers have prepared PUs using polyols derived from terpenes [8,9] or from natural rubber [10].

In a recent approach [11] researchers have used poly(β-methyl-δ-valerolactone) (**2**, PMVL, Scheme 1A, gray arrows) as the polyol. PMVL is a rubbery polyester ($T_g \sim -52$ °C) that is easily prepared by bulk ring-opening polymerization of β-methyl-δ-valerolactone (**1**, MVL) [12]. This lactone can be efficiently prepared from mevalonate, which, in turn, is now available on large scale through an engineered strain of *E. coli* that uses glucose as its carbon source [12]. These polyols were incorporated into thermoplastic PUs (TPUs) and PU foams [11]. Notably, the resulting polymers could be recycled at the molecular level by thermal depolymerization with up to 97% recovery of the MVL. This represented a significant improvement over the state of the art in PU chemical recycling, since, unlike other recycling methods such as glycolysis [13] or hydrolysis [14], the polyester segment was almost fully recovered in the form of pure MVL. Moreover, commonly used polyol soft-segments are often based on non-depolymerizable backbones such as polyethers. These MVL-derived TPUs were prepared using diisocyanates; nearly all of the commonly used isocyanates in PU chemistry, including methylenediphenyl diisocyanate (MDI), are petroleum derived and considerably toxic. We hypothesized that, by using MVL-derived diol chain extenders (**4**, Scheme 1B) that also contained polar amide functional groups, we could prepare TPUs with excellent mechanical properties while reducing the overall isocyanate content [15]. This strategy would allow us to maintain (or increase) the density of polar −NHC(=O)− groups in the TPU hard segment, thereby increasing the overall fraction that is sustainably sourced and decreasing the proportion derived from isocyanate. Amide-containing diol chain extenders derived from (petroleum-based) ε-caprolactone and poly(caprolactone) polyols

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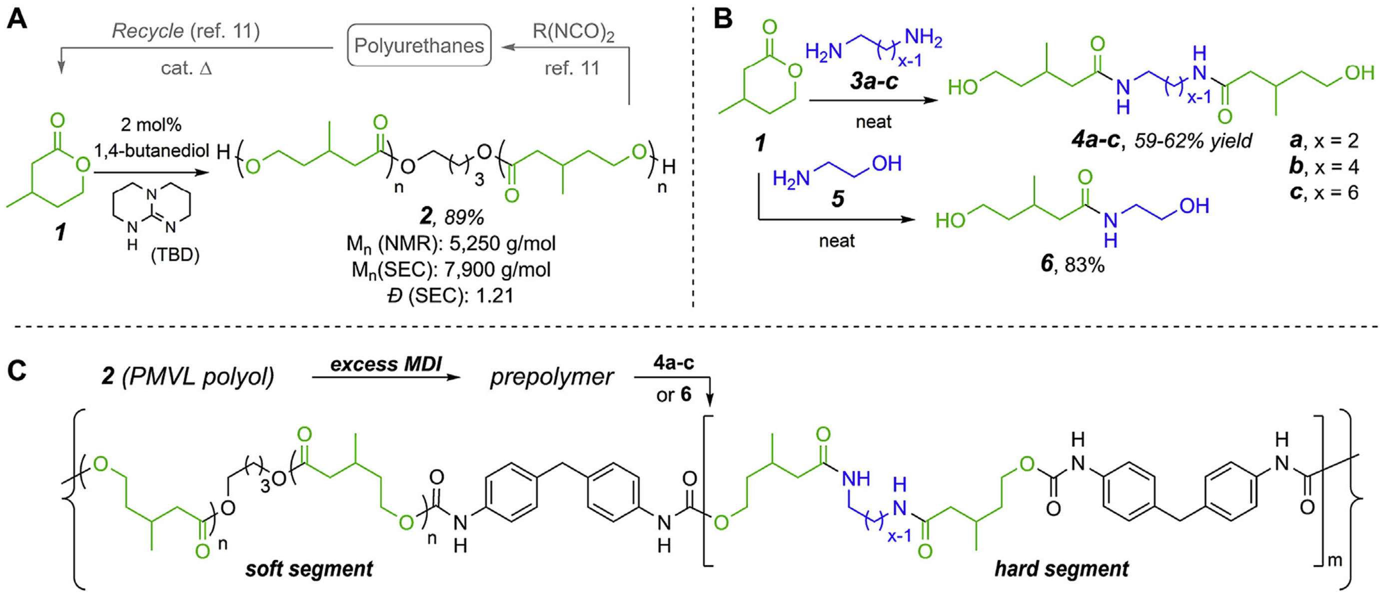

Scheme 1. (A) Synthesis of PMVL polyol (**2**). Similar PMVL polyols have been incorporated into recyclable polyurethanes [11]. (B) Synthesis of amidodiol chain extenders **4a**–**c** and **6**. (C) Synthesis of TPUs by a two-step process. Structure shown for chain extenders **4a**–**c**. MDI = 4,4′-methylenediphenyl diisocyanate.

have been used in TPUs [16]. Here we describe the preparation and characterization of TPUs using not only a PMVL polyol as the flexible soft-segment, but also amide-containing hard-segment chain extender moieties that are likewise derived from MVL.

2. Results and discussion

Polyols (more precisely, polymeric telechelic diols) were prepared in excellent yield by base-catalyzed ring-opening transesterification polymerization (ROTEP) of MVL using 1,4-butanediol as the initiator [11,12]. We preliminarily prepared and examined several TPUs that differed in the molecular weight of the polyol used as the soft segment. A TPU based on **2** (M_n ~5200 g mol^{-1}, Đ = 1.21, Scheme 1A) showed early promise, and this polyol was used as the precursor to all of the materials described here. The focus of these studies has been to explore the effect of the varying nature of the chain extenders **4a**–**4c** and **6** on TPU properties.

We prepared a series of potential chain extenders by reaction of MVL (**1**) with the α,ω-diamines **3a**–**c**. More specifically, the diamidodiol compounds **4a**–**c** (Scheme 1B) were prepared by treatment of **1** with 0.5 equivalents of the requisite diamine in the bulk and at ambient temperature. These products are crystalline and each was isolated in ~60% yield after 2 recrystallizations. Similarly, **1** was treated with ethanolamine (**5**) to give the monoamide diol **6** in 83% yield.

Having prepared **2** and the library of chain extenders, we turned our attention to the preparation of the TPUs themselves. This was accomplished using a standard two-step, one-pot approach in which the polyol, an excess of the isocyanate MDI, and Sn(2-ethylhexanoate)$_2$ (1 mol%) were combined and allowed to react to form a pre-polymer. In the second step, a sufficient quantity of the diol chain extender was added to balance the stoichiometry of –OH and –NCO groups; urethane formation ensued. The yield, number average molecular weight, dispersity, and glass transition temperature of each TPU produced by this approach are shown in Table 1. The T_g values of the five TPUs were similar, *ca.* −42 °C. This is slightly higher than the T_g of PMVL alone, which is not surprising, because the incorporation of PMVL into segmented PUs would be expected to restrict mobility. This trend has been observed previously with PMVL-derived TPUs [11].

Thermogravimetric analysis (TGA) of the TPUs (Fig. 1) revealed a considerably higher degradation temperature than that reported

Table 1
TPU synthesis,[a] composition, molecular weight, and thermal properties. Reaction and structure shown in Scheme 1C.

TPU[b]	Chain extender	Hard cont. (wt%)[c]	Yield (%)[d]	M_n (rel)[e]	Đ[e]	$T_{g,DSC}$ (°C)[f]	$T_{g,DMTA}$ (°C)[g]
TPU-4a	**4a**	41.7	90	140,000	1.31	−44	−39
TPU-4b	**4b**	42.8	70	110,000	1.28	−45	−40
TPU-4c	**4c**	43.9	87	160,000	1.34	−45	−39
TPU-6	**6**	36.5	83	240,000	1.28	−41	−36
TPU-BDO	**BDO**[h]	43.2	92	140,000	1.54	−41	–[i]

[a] Conditions: DMF, 60 °C.
[b] Each of the TPUs was prepared from the same sample of polyol **7**.
[c] Hard content = [mass of isocyanate + mass of chain extender]/[total mass]; each of the TPUs derived from one of **4a**–**c** and **6** was prepared using the same molar ratio of the three reactants.
[d] Yield of precipitated, dried polymer.
[e] As measured by GPC (DMF mobile phase, relative to polystyrene standards).
[f] Determined by DSC.
[g] Determined by DMTA, from the maximum of the loss modulus.
[h] BDO = 1,4-butanediol.
[i] We were unable to obtain a defect-free film for this sample.

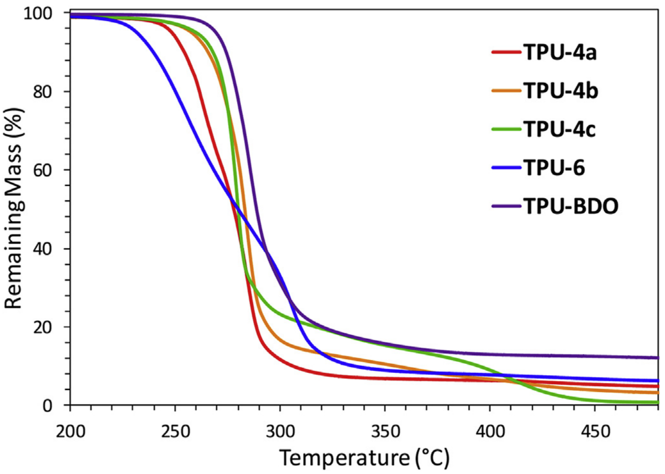

Fig. 1. TGAs of TPUs prepared from PMVL polyol and various chain extenders. Measurements were made from ambient temperature to 550 °C at a ramp of 10 °C min^{-1}; only regions of active mass loss are shown.

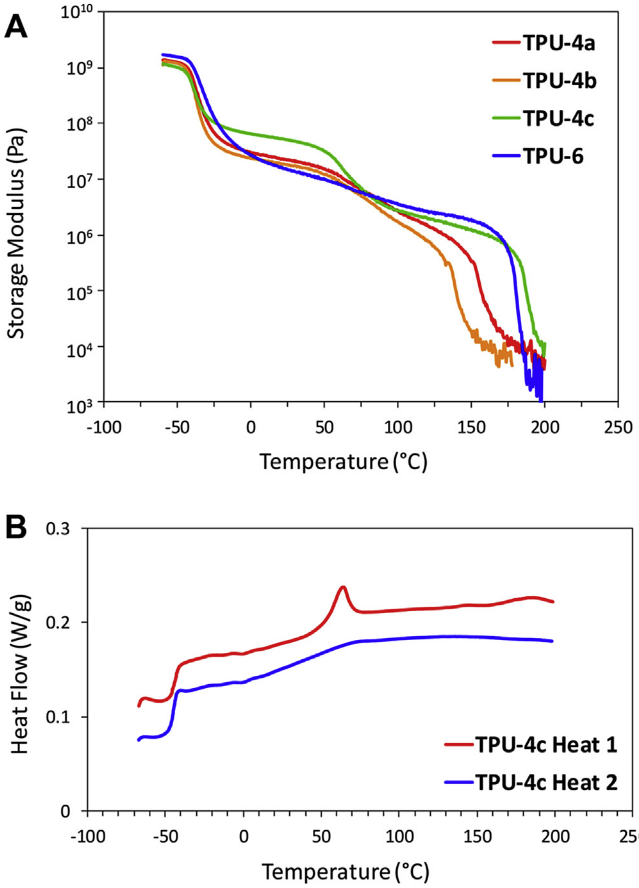

Fig. 2. (A) Temperature sweep DMTA analysis of the four amide-containing TPUs from −60 to 200 °C at 5 °C min^{-1}. The samples were analyzed at a strain rate of 0.05% and a frequency of 1 Hz. (B) DSC curves for **TPU-4c**. The curve "Heat 1" was the first heating ramp (at 10 °C min^{-1}) of a sample of polymer film, which was immediately cooled to −70 °C (at 5 °C min^{-1}) and a second heating curve (Heat 2) was recorded.

for the homopolymer PMVL (*ca.* 5% and 50% mass loss at 150 and 200 °C, respectively [11]). The opportunity for depolymerization from the terminus of PMVL with release of MVL (**1**) is quenched once the terminal hydroxyls of the polyol are capped as carbamates in the PUs. This behavior was also observed previously [11]. The shape of the TGA profile for each of the TPUs described here was influenced by the nature of the chain extender, even among the three extenders that are most similar in structure (i.e., **4a**–**c**; red, orange, and green, respectively). Because *N*-aryl/*O*-alkyl urethane linkages are known to thermally reverse at temperatures of *ca.* 200 °C [17], this process presumably initiates the degradation process. Because PMVL is thermally unstable at temperatures this high, once a carbamate-capped PMVL moiety reverts to the free alcohol, relatively rapid depolymerization will ensue. The lag in the final stages of mass loss increases for the TPUs made from the chain extenders having a longer 1,n-diamidoalkane core [$(CH_2)_2$ vs. $(CH_2)_4$ vs. $(CH_2)_6$]. However, this effect is of a greater magnitude than one might expect based only on the relatively small differences in wt% composition of **TPU-4a**, **TPU-4b**, and **TPU-4c** (mass of the chain extender varies from only 21–24 wt%). Seemingly the central diamido subunit is promoting different rates of thermal breakdown within the hard segment, leading to the fastest degradation to volatiles within **TPU-4a**.

The TPUs were then analyzed by dynamic mechanical thermal analysis (DMTA) in order to further characterize their mechanical and thermal properties (Fig. 2A). All four of the samples analyzed had a distinct T_g around −35 to −40 °C for the soft segment and eventually reached some temperature at which the material began to flow (*ca.* 130–180 °C). This flowing temperature (T_f) is likely due to the mixing of the discrete soft and hard block phases. It is also possible that the urethane linkages are exhibiting some reversion at these temperatures, contributing to the drop in modulus. However, *N*-aryl-*O*-alkyl urethanes do not typically undergo reversion until 200 °C [17], as previously discussed. Interestingly, three of the materials exhibited another transition around 70 °C, with **TPU-4c** having the most notable decrease in the modulus. It is fairly common for TPUs to exhibit three or more thermal transitions and it is often believed that the second is due to melting of the hard blocks [18]. Indeed, the first heating curve of the DSC analysis indicates a melting transition; however, no crystallization exotherm is visible upon cooling and this transition disappears on the second heating curve (Fig. 2B). Similar behavior for a comparable TPU has been reported and this suggests that crystallization of the hard segment in these TPUs is a slow process [19]. When our TPUs are allowed to age at room temperature for 2 days after erasing the thermal history, the second transition reappears (DSC), again consistent with slow crystallization.

To see if this transition similarly disappeared during DMTA, we cycled **TPU-4c** through heating and cooling, allowing it to equilibrate at 150 °C for 10 min in order to ensure that any thermal history was erased. Surprisingly, the thermal transition at 70 °C remains (see Figs. S4 and S5 for DMTA and DSC annealing experiments). Interestingly, the plateau modulus between the first and second thermal transitions is reduced after complete ablation of the thermal history. This reduction is likely due to the loss of crystallinity in the hard segment; we posit that a fraction of the modulus is re-attained upon cooling by reformation of amide/urethane hydrogen-bonds, albeit not in a crystalline state. Similar mechanical behavior was also observed in the TPU alluded to above [19].

The tensile properties of the TPUs were also studied by uniaxial extension tests (Fig. 3 and Table 2). These are elastic materials, showing strain at break on the order of 800–900% for all four TPUs studied. Stress at break ranged from 14 to 33 MPa, demonstrating that TPUs with high tensile strength can be prepared using these sustainable chain extenders. The elastic moduli for these materials ranged from *ca.* 9–38 MPa. We do note that there are differences in the molecular weight among the samples (in particular, **TPU-6**), which may account for some of the differences observed in the tensile properties.

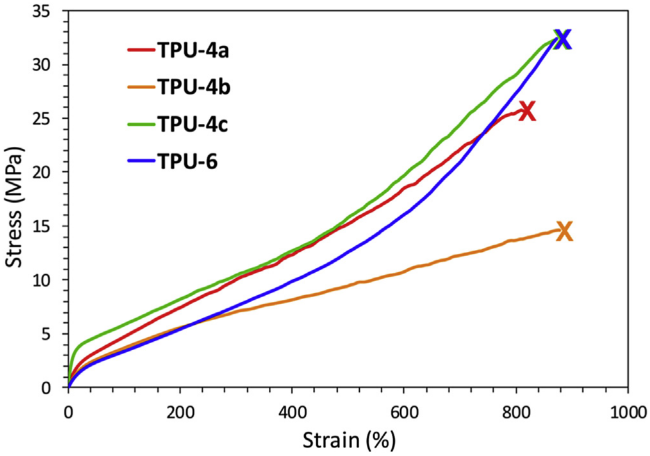

Fig. 3. Representative stress-strain curves for uniaxial extension tests of TPUs. Samples were elongated at 10 mm min^{-1} until break, which is marked as an X on the plot.

Table 2
Mechanical properties of the TPUs.

TPU (% hard contend)	σ_b (MPa)[a]	ε_b (%)[a]	E (MPa)[b]	Hysteresis after cycle (%)[c]				
				1	2	3	4	20
TPU-4a (42)	24 ± 2	790 ± 48	14 ± 1	43	29	27	27	26
TPU-4b (43)	14 ± 1	850 ± 90	10 ± 0.4	41	29	27	27	26
TPU-4c (44)	33 ± 2	920 ± 90	38 ± 4	63	45	43	43	40
TPU-6 (37)	30 ± 5	820 ± 80	8.6 ± 0.5	34	23	21	21	21

[a] Stress at break (σ_b) and strain at break (ε_b) were determined by uniaxial extension with a crosshead velocity of 10 mm min^{-1}.

[b] The modulus was determined by measuring the slope of the initial (linear) region of the stress-strain curve.

[c] Hysteresis measurements were taken by cycling between 0 and 50% strain at a rate of 60 mm min^{-1}.

We also examined the hysteresis behavior of several of the TPUs (Table 2 and Fig. 4). The hysteresis values correspond to the area between the increasing and decreasing stress-strain curve of each cycle (as a % of the total area under the increasing stress-strain curve). A representative set of curves (for **TPU-6**) is shown in Fig. 4. Typically, the energy loss decreased through the first few cycles and remained fairly constant thereafter; the difference between cycle 4 and cycle 20 (Table 2) is small for all four TPUs. This can also be seen by the similarity between cycles 10 and 20 in Fig. 4.

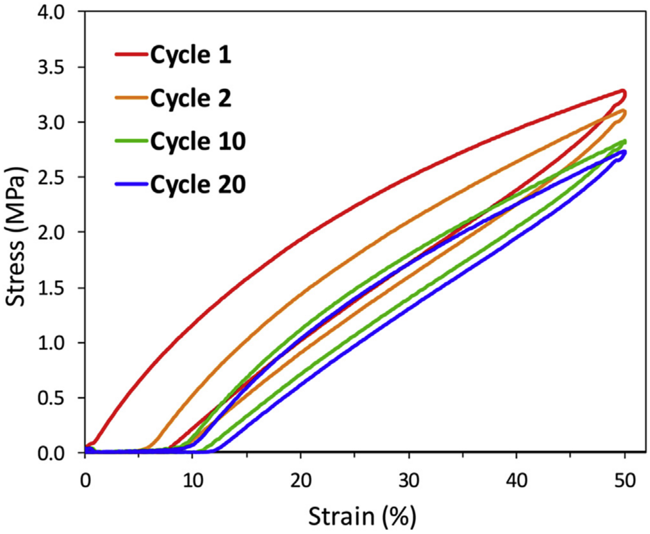

Fig. 4. Hysteresis curves for **TPU-6**. Sample was run to 50% strain at a strain rate of 60 mm min^{-1}.

Using the MVL-derived chain extenders **4a**–**c** and **6** is advantageous because a larger portion of the overall TPU mass comes from the bio-derived MVL. Namely, the wt% of atoms from MVL is 72–75% for **TPU-4a**–**c** vs. 57% for **TPU-BDO**. The hard segments in **TPU-4a**–**c**, which incorporate the diamidodiol chain extenders, contain two –NHC(=O)– moieties that contribute to the hydrogen bond network in the resulting TPUs. In fact, the molecular mass per H-bonding functional group (i.e., amide *or* urethane) present in the hard segment is lower for **TPU-4a**–**c** (135–150 amu per urethane/amide) than for **TPU-BDO** (170 amu per urethane)—that is, any of **TPU-4a**–**c** contains a higher density of H-bonds even though a lower % of isocyanate-derived mass.

Inherently, any thermoplastic with an accessible T_f is capable of being recycled into a new polymer by melt reprocessing, including TPUs. We sought to determine if these TPUs would also be chemically recyclable. This would be advantageous in settings where the initial TPU-based product could not be reprocessed into a similar value material (e.g., loss of substantial mechanical integrity or mixed with other polymeric impurities in a recycling stream). Indeed, these MVL-based TPUs are chemically recyclable by thermal depolymerization in a similar fashion as other MVL-based polymers previously reported [11,20]. Upon heating a sample of a TPU based on **4c** with a small amount of $Sn(Oct)_2$ catalyst under vacuum, we were able to collect MVL (*ca.* 98% pure) by distillation. The mass recovery of MVL was excellent (85%), considering the small scale (*ca.* 2 g) of the experiments.

3. Conclusions

In summary, we have prepared new thermoplastic polyurethanes incorporating the glucose-derived β-methyl-δ-valerolactone (MVL), in which *both* the soft segment polyols [11] and hard segment chain extenders are derived from MVL. Use of PMVL as the soft segment renders these polyurethanes chemically recyclable [11]. The novel MVL-derived amidodiol chain extenders **4a**–**c** and **6** arose by simply reacting MVL with a 1,n-diamine or ethanolamine, respectively. These were then used to prepare a series of TPUs. As demonstrated here, **TPU-4a**–**c** and **TPU-6** are appealing materials; they are elastic, tough, and exhibit thermal stability on par with related TPUs [11]. Furthermore, these materials contain a lower wt% of isocyanate, a correspondingly higher portion of bio-derived atoms, and a higher density of –NHC(=O)– functional groups in the hard segment. Altogether, these qualities make these materials an attractive addition to the existing collection of bio-derived TPUs [6,21].

4. Experimental section

4.1. Materials

All solvents were used as received from the manufacturer. Acetone (Certified ACS) for recrystallizations was purchased from Fisher. Dichloromethane (Stabilized/Certified ACS) was purchased from Fisher. Dimethylformamide was purchased from Aldrich (99.8%, anhydrous). Methanol (HPLC Grade) was purchased from Fisher. β-Methyl-δ-valerolactone (MVL) was prepared according to a previously reported procedure [11]. Ethylenediamine, 1,4-diaminobutane, and 1,6-diaminohexane were purchased from Sigma-Aldrich and used as received. Ethanolamine was purchased from Sigma-Aldrich and purified by azeotropic distillation with benzene, followed by distillation. TBD was purchased from Sigma-

Aldrich and purified by sublimation (70 °C at 100 mTorr) prior to use. 1,4-Butanediol was purchased from Sigma-Aldrich and dried over 4 Å molecular sieves for at least 1 week prior to use. Benzoic acid was purchased from Sigma-Aldrich and used as received. MDI was purchased from Sigma-Aldrich and purified by bulb-to-bulb vacuum distillation before use.

4.2. Instrumental methods

4.2.1. Nuclear magnetic resonance spectroscopy (NMR)

Spectra were collected on a Bruker Avance III or Avance II 500 (500 MHz) spectrometer. Chemical shifts for ^{1}H NMR in $CDCl_3$, DMSO-d_6, and CD_3OD (Cambridge Isotopes) are referenced to TMS (0.00 ppm), $CHD_2(S{=}O)CD_3$ (2.50 ppm), and CHD_2OD (3.31), respectively. Chemical shifts for ^{13}C NMR in $CDCl_3$, DMSO-d_6 and CD_3OD are referenced to $CDCl_3$ (77.16 ppm), $CD_3(S{=}O)CD_3$ (39.52 ppm), and CD_3OD (49.00), respectively. Resonances are reported in the following format: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^{1}H NMR assignments are indicated by the substructural environment (e.g., CH_aH_b).

4.2.2. IR spectroscopy (IR)

IR spectra were recorded with a Bruker Alpha Platinum ATR-FTIR instrument that uses a diamond single bounce crystal. The data are reported as the average of 32 scans.

4.2.3. Thermogravimetric analysis (TGA)

Performed on a TA instruments Q500 under an atmosphere of nitrogen and using a heating rate of 10 °C min^{-1}. Sample sizes were 15–20 mg.

4.2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry data were collected on a TA instruments Q-1000 under nitrogen. Samples were analyzed in hermetically sealed, aluminum pans. The reported T_g values were those observed during the first heating cycle, without erasing thermal history, so as to observe any morphological features at equilibrium. T_g values were identical to those measured during the second heating ramp, within error. The heating rate was 10 °C min^{-1} and the cooling rate was 5 °C min^{-1}.

4.2.5. Dynamic mechanical thermal analysis (DMTA)

[20] Performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) using rectangular films (*ca.* 0.5 mm (T) × 4 mm (W) × 12 mm (L)). DMTA experiments were conducted in tension film mode, where the axial force was first adjusted to 0.2 N of tension (sensitivity of 0.01 N) to ensure no buckling of the sample. The proportional force mode was set to force tracking to ensure that the axial force was at least 100% greater than the dynamic oscillatory force. The strain adjust was then set to 30% with a minimum strain of 0.05%, a maximum strain of 5%, and a maximum force of 0.2 N in order to prevent the sample from going out of the specified strain range. The sample was allowed to equilibrate at −60 °C for 10 min before ramping to 200 °C at a rate of 5 °C min^{-1}, with an oscillating strain of 0.05% and an angular frequency of 1 Hz. The T_g was calculated from the maximum value of the loss modulus. **TPU-4c** was also subjected to cyclical DMTA at 5 °C min^{-1} by ramping from −60 °C to 130 °C, cooling to −60 °C, heating to 150 °C, holding at 150 °C for 10 min, rapidly cooling to −60 °C (*ca.* 100 °C/min), and finally ramping to 150 °C.

4.2.6. Size exclusion chromatography (SEC)

The dispersity and number-average molar mass of the PMVL polyol were estimated using size exclusion chromatography with a $CHCl_3$ mobile phase. A flow rate of 1 mL min^{-1} and sample concentrations of *ca.* 2 mg mL^{-1} were used. The samples (50 μL injection volume) were passed through three successive PLgel Mixed C columns (7.5 mm id, 25 cm length) and observed with a refractive index detector (HP1047A). The values are reported relative to poly(styrene) standards. The number-average molar mass and dispersity of TPUs were estimated using size exclusion chromatography with a DMF mobile phase (containing 0.1 M LiBr). Again, a flow rate of 1 mL min^{-1} and sample concentrations of *ca.* 2 mg mL^{-1} were used. These samples (20 μL injection volume) were passed through two successive Styragel HT4 columns (7.8 mm id, 30 cm length). The values are again reported relative to poly(styrene) standards.

4.2.7. Tensile testing

Uniaxial extension data were recorded on a Shimadzu Autograph AGS-X Series tensile tester (Columbia, MD). Samples were observed at a constant crosshead velocity of 10 mm min^{-1} until failure. Data from these experiments are reported as the average and standard deviation from a minimum of 5 samples. Hysteresis tests were conducted on the same instrument. The samples were elongated to 50% strain at a constant crosshead velocity of 60 mm min^{-1} and then relaxed back to 0% strain at the same rate. This cycle was repeated 20 times for each sample. Hysteresis data are reported as the average from a minimum of 2 samples. Films of the all four TPUs were prepared by solvent casting according to the following procedure: A sample of precipitated polymer was dissolved in *ca.* 13 mL of DMF and poured into a cylindrical PTFE dish with diameter of *ca.* 7.5 cm. The dish was placed in a desiccator with the desiccator lid ajar. A slight vacuum (~200 torr) was applied, drawing an airflow over the surface of the polymer. After *ca.* 6 days the film was visibly dry, at which time the film was removed and further dried at 70 °C in a vacuum oven for 24 h. The film was allowed to stand at room temperature for at least 24 h before it was cut into bars for tensile testing. (Prior to testing, a sample of the film was analyzed by NMR spectroscopy in DMSO-d_6 to ensure that the DMF had been completely removed). This procedure produced films with thickness of 0.5 ± 0.1 mm.

4.3. Chain extender synthesis

4.3.1. N,N′-(ethane-1,2-diyl)bis(5-hydroxy-3-methylpentanamide) (4a)

A round-bottomed flask, equipped with a PTFE-coated magnetic stir bar, was charged with β-methyl-δ-valerolactone (20 g, 175 mmol, 2.05 equiv). The solution was stirred while ethylenediamine (1 equiv.) was added over *ca.* 5 min by syringe. An exotherm was observed, and the stirred mixture was allowed to cool to room temperature overnight, after which time it had solidified. The solid mass was dissolved in *ca.* 800 mL of hot acetone and allowed to cool slowly to room temperature. After several hours the flask was transferred to a freezer (−20 °C) to encourage further crystallization. After 2 days, the flask was removed from the freezer and the solids collected by vacuum filtration. The filter cake was washed 4–5 times with acetone (100–200 mL) and 3 times with hexanes (150 mL). The white crystalline product was dried under vacuum (15.2 g, 62% yield). mp: 96–101 °C.

4.4. Polymer synthesis

4.4.1. PMVL polyol **2**

In a dry-box 3-methyl-valerolactone (57.0 g, 500 mmol) and 1,4-butanediol (0.89 mL, 10 mmol, 2 mol%) were combined in an oven-dried jar containing a stir bar. The mixture was stirred until it became homogenous. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, 70 mg, 0.5 mmol, 0.1 mol%) was added in portions. The jar was tightly capped with a PTFE-lined cap, removed from the box, and vigorously stirred for 1 h at room temperature. The jar was then placed in a freezer (−20 °C) for 8 h. The jar was removed from the freezer and benzoic acid (3 mL, 1.0 M solution in $CDCl_3$) was added, followed by enough dichloromethane to bring the total volume to ~100 mL. The mixture was stirred with a glass stirring rod to mix the benzoic acid and dichloromethane while still cold in order to effectively quench TBD-promoted depolymerization. The mixture was separated into two roughly equal parts. Each was treated as follows: The solution was further diluted with dichloromethane (300 mL) and washed with 0.5 M aqueous NaOH (3 × 200 mL), 0.5 M aqueous HCl (200 mL), water (200 mL), and brine (200 mL). The organic phase was dried over $MgSO_4$ and filtered. At this point the two portions were combined and the solvent removed *in vacuo* to give the polyol (51.7 g, 89% yield). The number average molecular weight (M_n) was determined by NMR analysis to be 5250 g/mol. When the sample was analyzed by SEC ($CHCl_3$), the molecular weight was estimated to be 7900 g/mol and the polydispersity 1.21.

4.4.2. *TPU-4c*

In a dry-box, MDI (613 mg, 2.45 mmol, corresponding to an ~2 mol% excess of isocyanate relative to OH functional groups) was weighed into an oven-dried vial containing a stir bar. The PMVL polyol (FW = 5250 g/mol, 1.68 g, 0.320 mmol) and the diol chain extender **4c** (717 mg, 2.08 mmol) were each placed into a second and third vial. All three vials were capped with rubber septa and removed from the box. The vial with the isocyanate was partially submerged into a 60 °C oil bath and stirred. To this molten MDI was added *ca.* 12 mg (0.03 mmol, *ca.* 1 mol%) of $Sn(Oct)_2$. To the vial containing the polyol was added 2–2.5 mL of dimethylformamide. This solution was then added by syringe to the MDI over a period of about 30–45 s. The vial that had contained the polyol was rinsed with 1 mL of additional DMF, which was added to the reaction mixture. The mixture was stirred for 30–60 min at 60 °C. To the third vial, containing **4c**, was added 2 mL of DMF and the resulting solution was added dropwise to the reaction mixture over *ca.* 2 min. This vial was then rinsed with 1 mL of additional DMF, which was also added to the mixture. The reaction solution was stirred vigorously to achieve thorough mixing and then stirred for an additional 2 h at 60 °C. The reaction mixture was allowed to cool to room temperature and aged overnight at room temperature. The viscous mixture was diluted with 5 mL of DMF and slowly poured into 250 mL of stirred methanol. The precipitated polymer was rinsed several times with methanol and the solid material collected and dried under vacuum. This sample was held in a vacuum oven at 70 °C overnight. The resulting sample of polymer had a mass of 2.6 g (87% yield). ^{1}H NMR: (500 MHz, DMSO-d_6) See annotated spectrum in Fig. S39; ^{13}C NMR: (125 MHz, DMSO-d_6) See spectrum in Fig. S40; IR (neat): 3309, 2959, 2930, 2874, 1728, 1639, 1532, and 1222 cm^{-1}; T_g (measured by DSC): −44 °C; M_n (rel, SEC, DMF, PS standards): 163.4 kg/mol; $Đ$ (SEC, DMF): 1.34.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2017.01.042.

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