Tunable thermoplastic poly(ester-urethane)s based on modified serinol extenders

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SUPPLEMENTARY INFORMATION

EXPERIMENTAL

Materials

Tetrahydrofuran (THF), ethyl acetate, methanol, diethyl ether, dimethylsulfoxide (DMSO), sodium carbonate, sodium hydroxide and magnesium sulfate were purchased from Fischer Scientific. 2-Amino-1,3-propanediol, ethyl chloroformate, ethyl isocyanate and 1,8-diaza[5.4.0]undec-7-ene (DBU) were purchased from Sigma Aldrich. Poly(ε-caprolactone) (PCL) was obtained from Perstorp (CAPA\textsuperscript{TM} 2201A, \(M_w = 2,000\) g/mol, hydroxyl number = 54-58). Dicyclohexylmethane 4,4\textsuperscript{'}-Diisocyanate (H\textsubscript{12}MDI) was purchased from Tokyo Chemicals Industry Co. Ltd. and was distilled and stored under inert conditions. All chemicals were used as received unless otherwise stated.
Instrumental methods and general considerations

$^1$H and $^{13}$C NMR spectra were obtained on a Bruker DPX-400 spectrometer (400 MHz) at 293 K. All chemical shifts were reported as $\delta$ in parts per million (ppm) and referenced to the residual solvent signal (($\text{CD}_3$)$_2$SO: $^1$H, $\delta = 2.50$ ppm; $^{13}$C, $\delta = 39.52$). Gel permeation chromatography (GPC) was used to determine the dispersities ($D_M$) and molecular weights of synthesized polymers. GPC was conducted in dimethylformamide (DMF) using a Varian PL-GPC 50 system equipped with 2 × PLgel 5 µM MIXED-D columns in series and a differential refractive index (RI) detector at a flow rate of 1.0 mL min$^{-1}$. The systems were calibrated against Varian Polymer Laboratories Easi-Vial linear poly(methyl methacrylate) (PMMA) and analyzed by the software package Cirrus v3.3. Tensile data was obtained at ambient temperature by axially loading ‘dog-bones’ in a Tensiometric M100-1CT system with a load cell capacity of 1 kN and crosshead speed of 5 mm min$^{-1}$ with a premeasured grip-to-grip separation. All values reported were obtained from an average of 10 repeat specimens and the results were recorded using winTest v4.3.2 software. Molten polymer samples were molded into ‘dog-bones’ via compression molding at 100 °C using a PTFE mold and allowed to cool to ambient temperature. Static contact angle measurements were obtained using a KRUSS DSA10 drop shape analyzer and were processed using the software package DSA3 1.72b IEEE1394b. Each polymer was dissolved in minimal DMSO before being deposited as a thin film on a glass slide. The solvent was allowed to evaporate overnight before trace solvent was removed in vacuo. TPEU samples were allowed to anneal at 25 °C in an incubator for 5 days prior to analysis. Using a KRUSS DSA100 a 100 µL droplet of DI H2O was deposited onto the surface of the film and the measurement was taken immediately and analyzed using a sessile drop type with a polynomial (tangent 2) computational method. Dynamic mechanical thermal analysis (DMTA) data was obtained using a Mettler Toledo DMA 1 star system and was analyzed using the software package.
STARe V13.00a (build 6917). DMTA samples were analyzed by single cantilever bending, oscillating at a frequency of 5.0 and 0.5 MHz with a displacement of 10 mm between -80 and 180 °C at a heating rate of 2 °C min⁻¹. All polymers were analyzed using a Mettler Toledo DMA 1 Star system to determine the thermo-mechanical properties and glass transitions of the materials. Polymer samples were molded into ‘bars’ via compression molding using a PTFE mold and allowed to cool to ambient temperature. All TPEUs were annealed for 5 days in an incubator at 25 °C. Wide angle x-ray diffraction data was obtained using a Panalytical X’Pert Pro MPD equipped with a Cu Ka₁ hybrid monochromator (λ = 0.154 nm) as the incident beam optics and PiXcel detector was processed using OriginPro 8 software. Accelerated degradation studies were conducted under conditions previously reported by C X F Lam et al.¹ All polymers which could form ‘degradation disks’ were subjected to accelerated degradation studies (5M aq. NaOH). Polymer samples were molded into disks via compression molding at 100 °C using a PTFE mold and allowed to cool to ambient temperature. The disks were placed in individual vials containing 20 mL of 5M NaOH solution and incubated at 37 °C. The weight of the dried disks was measured periodically using an analytical balance.

General synthesis of protected 2-amino-diol extenders

Carbamate-protected (C₃c): The carbamate-protected 2-amino-1,3-propanediol extender (C₃c) was synthesized according to literature.² In a 1 L round bottom flask fitted with a magnetic stirrer bar, 2-amino-1,3-propanediol (10 g, 1.10 × 10⁻¹ mol) and Na₂CO₃ (25 g, 2.36 × 10⁻¹ mol) were dissolved in a mixture of deionized H₂O:THF (500 mL, 2:1 respectively). The solution was cooled on an ice-bath for 20 min before the addition of ethyl chloroformate (10.25 mL, 1.07 × 10⁻¹ mol) and allowed to stir for 2 h. The reaction mixture was removed from the ice-bath and allowed to warm to room temperature and was stirred overnight (~ 12
The desired product was extracted with ethyl acetate (6 × 300 mL), dried over MgSO₄ and filtered before all volatiles were removed in vacuo to yield an off white crystalline solid. The solid was sublimed to yield the pure product as a white crystalline solid. (15.07 g, yield 84%). Characterizing data was consistent with the previous report.² ¹H NMR (400 MHz, DMSO-d₆) δ 6.62 (d, ⁴J_H-H = 7.1 Hz, 1H), 4.54 (t, ⁴J_H-H = 5.3 Hz, 2H), 3.97 (q, ⁴J_H-H = 7.0 Hz, 2H), 3.50 – 3.28 (m, 6H), 1.15 (t, ⁴J_H-H = 7.1 Hz, 3H). ¹³C NMR (101 MHz, DMSO-d₆): δ 157.34 (s, C=O), 62.10 (s, CH₂), 61.60 (s, CH), 54.1 (s, CH₂), 14.60 (s, CH₃).

Urea-protected (C₃u): The urea-protected 2-amino-1,3-propanediol extender (C₃u) was synthesized according to literature.³ In a 1 L round bottom flask fitted with a magnetic stirrer bar, 2-amino-1,3-propanediol (10 g, 1.10 × 10⁻¹ mol) was dissolved in a mixture of methanol:THF (500 mL, 1:2 respectively). The solution was cooled on an ice-bath for 20 min before the addition of ethyl isocyanate (8.69 mL, 1.10 × 10⁻¹ mol) and allowed to stir for 15 min. The reaction mixture was removed from the ice-bath and allowed to warm to room temperature and was stirred for 4 h. The solvent was removed in vacuo and the white off-white solid was suspended and stirred in 400 mL of diethyl ether for 20 min before being collected by filtration. The white crystalline solid was dried in vacuo to yield the pure urea-protected extender as a fluffy white solid. (16.04 g, yield 90%). Characterizing data was consistent with the previous report.³ ¹H NMR (400 MHz, DMSO-d₆) δ 5.98 (t, ⁴J_H-H = 5.5 Hz, 1H), 5.64 (d, ⁴J_H-H = 7.8 Hz, 1H), 4.64 (t, ⁴J_H-H = 5.3 Hz, 2H), 3.55 – 3.45 (m, 1H), 3.44 – 3.27 (m, 4H), 3.05 – 2.93 (m, 2H), 0.97 (t, ⁴J_H-H = 7.2 Hz, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 157.85 (s, C=O), 60.47 (s, CH₂), 52.64 (s, CH), 33.92 (s, CH₂), 15.63 (s, CH₃).

**General synthesis of TPU from carbamate-protected extenders**

The TPU synthesis described is based on the synthesis of a polyurethane with a 30% hard-block composition using the C₃c extender.
In a clean and dry vial fitted with a magnetic stirrer bar, poly(ε-caprolactone) with a $M_W = 2,000$ g mol$^{-1}$ (PCL$_{2k}$) (1 g, $5 \times 10^{-4}$ mol) and DBU (3.73 µL, $6.9 \times 10^{-6}$ mol) were heated to 100 °C under a flow N$_2$ for 20 min to aid the reduction of water within the system. The molten mixture was cooled to 80 °C before the addition of H$_{12}$MDI (402 µL, $1.64 \times 10^{-3}$ mol). The reaction mixture was allowed to stir under N$_2$ for 40 min to allow for prepolymer formation before the addition of the C$_3$ extender (186 mg, $1.14 \times 10^{-3}$ mol). The polymerization was allowed to proceed for 2 h before being removed from the heat to retard further reaction. The molecular weight was analyzed via GPC and the unreacted isocyanate was quenched by washing the TPU in methanol before being dried in vacuo. $^1$H NMR (400 MHz, DMSO-$_d_6$) δ 7.22 – 6.64 (m, 1H), 4.08 – 3.72 (m, 8H), 3.55 – 3.01 (m, 3H), 2.27 (t, J = 7.2 Hz, 5H), 1.92 – 0.66 (m, 27H). $M_n = 110.5$ kg·mol$^{-1}$, $D_M = 1.98$ (RI detection, DMF GPC).

**General synthesis of TPUs from urea-protected C$_3$ extenders**

The TPU synthesis described is based on the synthesis of a polyurethane with a 30% hard-block composition using the C$_{3u}$ extender.

In a clean and dry vial fitted with a magnetic stirrer bar, poly(ε-caprolactone) with a $M_W = 2,000$ g mol$^{-1}$ (PCL$_{2k}$) (1 g, $5 \times 10^{-4}$ mol) and DBU (3.73 µL, $6.9 \times 10^{-6}$ mol) were heated to 100 °C under a flow N$_2$ for 20 min to aid the reduction of water within the system. The molten mixture was cooled to 80 °C before the addition of H$_{12}$MDI (402 µL, $1.64 \times 10^{-3}$ mol). The reaction mixture was allowed to stir under N$_2$ for 40 min to allow for prepolymer formation before the addition of a solution of C$_{3u}$ extender (185 mg, $1.14 \times 10^{-3}$ mol) dissolved in 150 µL of DMSO. The polymerization was allowed to proceed for 2 h before being removed from the heat to retard further reaction. The molecular weight was analyzed by GPC and any
unreacted isocyanate using IR spectroscopy, was quenched by washing the TPU in 50 mL of methanol before being dried in vacuo. $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 6.04 – 5.67 (m, 2H), 4.11 – 3.80 (m, 19H), 3.53 – 2.89 (m, 23H), 2.27 (m, 14H), 1.91 – 0.69 (m, 79H). $M_n = 100.9$ kg·mol$^{-1}$, $D_M = 2.10$ (RI detection, DMF GPC).

**Tensiometric analysis**

All TPUs were analyzed using an M100-1CT tensiometer to determine the tensile properties of the materials. Molten polymer samples were molded into ‘dog-bones’ via compression molding at 200 °C using a PTFE mold and allowed to cool to ambient temperature. All TPUs were annealed for 5 days in an incubator at 25 °C. The rate of elongation of each sample was 5 mm min$^{-1}$. Data was collected from ten repeats.

**Wide-angle x-ray diffraction**

Wide angle x-ray diffraction data was obtained using a Panalytical X’Pert Pro MPD equipped with a Cu Kα₁ hybrid monochromator ($λ = 0.154$ nm) as the incident beam optics and PiXcel detector was processed using OriginPro 8 software. Each polymer was compression molded into discs and allowed to anneal for 5 days in an incubator at 25 °C before standard “powder” 2θ-θ diffraction scans were carried out at room temperature in the angular range between 5° and 60° 2θ.

**Dynamic mechanical and thermal analysis (DMTA)**

Dynamic mechanical thermal analysis (DMTA) data was obtained using a Mettler Toledo DMA 1 star system and was analyzed using the software package STARe V13.00a (build 6917). DMTA samples were analyzed by single cantilever bending, oscillating at a frequency of 5.0 and 0.5 MHz with a displacement of 10 mm between -80 and 180 °C at a heating rate
of 2 °C min\(^{-1}\). All polymers were analyzed using a Mettler Toledo DMA 1 Star system to determine the thermo-mechanical properties and glass transitions of the materials. Molten polymer samples were molded into ‘bars’ via compression molding using a PTFE mold and allowed to cool to ambient temperature. All TPEUs were annealed for 5 days in an incubator at 25 °C.

**Degradation studies**

Accelerated degradation studies were conducted under conditions previously reported by Lam et al.\(^1\) All TPUs were subjected to accelerated degradation studies (5 M aq. NaOH). Polymer samples were molded into disks via compression molding at 200 °C using a PTFE mold and allowed to cool to ambient temperature. The disks were placed in individual vials containing 20 mL of 5 M NaOH solution and incubated at 37 °C with constant agitation at 60 rpm. The surface of the disks were ‘dab’-dried using KIMTECH SCIENCE\textsuperscript{TM} precision wipes in order to remove excess surface water before the weight was measured periodically using an analytical balance.

**REFERENCES**

Figure S1. GPC chromatograms (RI detection) (a) C_{3c} and (b) C_{3u} -based TPEUs in DMF against poly(methyl metacrylate) (PMMA) standards (Table 1).
Figure S2. FT-IR spectra of C$_3$c (black) and C$_3$u (red) extenders.

Figure S3. FT-IR spectra of C$_3$c-based TPEUs.
Figure S4. FT-IR spectra of C₃u TPEUs.

Figure S5. ¹H NMR spectra of (a) C₃c and (b) C₃u extenders (400 MHz, 25 °C, DMSO-d₆).
Figure S6. $^1$H NMR spectra of C$_{3c}$-based TPEUs (Table 1). (400 MHz, 25 °C, DMSO-$d_6$).
Figure S7. $^1$H NMR spectra of C$_{3u}$-based TPEUs (Table 1). (400 MHz, 25 °C, DMSO-$d_6$).

Figure S8. Exemplar stress-strain curves of 30C$_{3c}$-TPEU (Table 2). Experiments were conducted at ambient temperature (~ 25 °C) at an elongation rate of 5 mm min$^{-1}$ until failure.
Figure S9. Exemplar stress-strain curves of 45C$_3$-TPEU (Table 2). Experiments were conducted at ambient temperature (~ 25 °C) at an elongation rate of 5 mm min$^{-1}$ until failure.

Figure S10. Exemplar stress-strain curves of 60C$_3$-TPEU (Table 2). Experiments were conducted at ambient temperature (~ 25 °C) at an elongation rate of 5 mm min$^{-1}$ until failure.
Figure S11. Exemplar stress-strain curves of 30C₃u-TPEU (Table 2). Experiments were conducted at ambient temperature (~ 25 °C) at an elongation rate of 5 mm min⁻¹ until failure.

Figure S12. Exemplar stress-strain curves of 45C₃u-TPEU (Table 2). Experiments were conducted at ambient temperature (~ 25 °C) at an elongation rate of 5 mm min⁻¹ until failure.
Figure S13. Exemplar stress-strain curves of $60\text{C}_{3\alpha}$-TPEU (Table 2). Experiments were conducted at ambient temperature ($\sim 25^\circ\text{C}$) at an elongation rate of $5\text{ mm min}^{-1}$ until failure.

Figure S14. WAXD diffractograms for crystalline PCL ($M_w = 2,000\text{ g mol}^{-1}$)