Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

for:

Combining block copolymers and hydrogen bonding for poly(lactide) toughening

Paula A. Delgado, Marc A. Hillmyer*

Department of Chemistry, University of Minnesota,

207 Pleasant St. SE, Minneapolis, MN 55455, USA

Experimental Details

Materials

Acetoacetate guanidinum, methyl ethoacetate, and hexamethylene diisocyanate were purchased from Aldrich and were used as received. d,l-Lactide (99.5%) was provided by Ortec, Inc and was used as received. Tin(II) ethylhexanoate [$Sn(Oct)_2$] was purchased from Aldrich and vacuum distilled, Triazabicyclodecene (TBD) was purchased from Aldrich, sublimed, and recrystallized prior to use. HTPB was provided by Cray Valley (Krasol LBH-3000) and was used as received. Dichloromethane and toluene were purified by a commercial solvent purification system (MBraun).

Characterization

The ^{1}H NMR spectroscopy was performed on a Bruker Avance III operating at 500 MHz. Solutions were prepared in $CDCl_3$ (Cambridge Isotope Laboratories) at specified concentrations. All spectra were acquired at 20 °C with 100 scans and a relaxation delay of 10 s. Chemical shifts are reported in ppm with respect to the residual chloroform signal (7.26 ppm). NMR data processing was performed using ACD software. Variable temperature NMR was acquired in toluene-d_8 (Cambridge Isotope Laboratories) from 20 to 98 °C at 3.68 mM with 30 scans and a relaxation delay of 10 s. Each temperature was equilibrated for 15 min.

Size-exclusion chromatography was performed at 35 °C on a Hewlett- Packard (Agilent Technologies) 1100 series liquid chromatograph equipped with a Hewlett-Packard 1047A refractive index detector. The instrument operates using three Plgel 5 μm Mixed-C columns in series with molar mass range 400–400,000 g mol^{-1}. Chloroform was used as the mobile phase with an elution rate of 1 mL min^{-1}. LBL Samples were prepared by dissolving 1 mg of polymer in 1 mL of chloroform stirred for one to two hours and filtered through a 0.2 μm Teflon filter. Polystyrene standards (Polymer Laboratories) were used for calibration of molar mass. Due to the high UPy self-dimerization constant, polymers can aggregate at standard SEC concentrations (ca. 1 mg/mL) resulting in inconsistent molar mass values. To prevent this problem, the polymers were diluted (0.6 mg/mL) and stirred for two hours before SEC analysis. This technique resulted in reproducible molar mass values.

Small-angle X-ray scattering data was collected at the Advanced Photon Source (APS) at Argonne National Laboratories at Sector 5-ID-D beamline. The beamline is maintained by the Dow-Northwestern-Dupont Collaborative Access Team (DND-CAT). The source produces X-rays with a wavelength of 0.7293 Å. The sample to detector distance was 3.97 m and the detector radius is 81 mm.

Scattering intensity was monitored by a Mar 165 mm diameter CCD detector with a resolution of 2048 × 2048. The two-dimensional scattering patterns were azimuthally integrated to afford one-dimensional profiles presented as spatial frequency (*q*) versus scattered intensity.

Scanning electron microscopy was performed on a Hitachi S900 with a cold field emission gun (FEG). The instrument was operated using a 1.5 kV accelerating voltage. The samples were prepared by placing them on an aluminum sample mount shimmed with carbon tape followed by sputter coating with platinum (~2-3 nm). Pt was deposited using a VCR high-resolution indirect ion beam sputtering system.

Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments Q1000 series equipped with a liquid nitrogen cooling system (LNCS) at a heating rate of 10 °C min^{-1}. The instrument was calibrated using indium and as standard. All samples were prepared in hermetically sealed pans (3–6 mg) and were run under a nitrogen purge with an empty pan as a reference. The thermal history of the samples was erased by heating to 200 °C at a rate of 10 °C min^{-1} and isothermally annealing for 5 min. The samples were then cooled at 10 °C min^{-1} to -100 °C followed by a second heating cycle to 200 °C at a rate of 10 °C min^{-1}. Glass transition temperatures were obtained at the mid-point of each transition.

Tensile testing was conducted using dog-bone shaped bars. The shape was obtained after mold pressing the samples at 150 °C and subsequently quenching at a rate of 35 °C min^{-1}. Approximate dimensions: 0.7 mm (*T*) × 3 mm (*W*) × 25 mm (*L*). The samples were wrapped in aluminum foil and aged for 48 hours at 25 °C in a vial filled with dry DRIERITE. Tensile measurements were performed on a Rheometrics Scientific MiniMat instrument at 20 °C (uniaxial extension rate: 2.0 mm min^{-1}). Young's modulus and tensile tougheness values were calculated using Minimat software. Reported averages and standard deviations are the product of five samples.

Aging studies

Measurements by differential scanning calorimetry (DSC):

Samples were press molded at 150 °C for 5 minutes and subsequently quenched at a rate of 35 °C min^{-1}. Samples were then annealed at 40 °C (ΔT_g = -16 °C) in a vial filled with DRIERITE under vacuum before analyzing by DSC.

Measurements by mechanical testing:

Dog-bone shaped bars were prepared as described before. Bars were annealed at 40 °C (ΔT_g = -16 °C) with different aging times in a vial filled with DRIERITE under vacuum before tensile testing. Mechanical properties were averaged from five samples.

Synthesis of block copolymers

Synthesis of 2-amino-4-hydroxy-6-methylpyrimidine (uracylopyrimidine). As reported in literature,[1] acetoacetate guanidinum (7.9 g, 82.7 mmol), sodium bicarbonate (7.8 g) and absolute ethanol were refluxed on a Soxhlet system with K_2CO_3 in the thimble. After 30 min of reflux (80 ˚C), methyl ethoacetate (18.0 g, 138.3 mmol) dissolved in absolute ethanol (30 mL) was added to the system. The reaction was left at 80 ˚C overnight. The reaction mixture was then poured into water, where the product was filtered and dried under vacuum. Yield: 85%. ^{1}H NMR ($CDCl_3$; 25 °C): δ (ppm) = 10.81 (s, 1H), 6.58 (s, 2H), 5.39 (s, 1H), 1.98 (s, 3H). ^{13}C NMR ($CDCl_3$; 25 °C): δ (ppm) = 155.5, 107.3, 100.3, 62.0.

Synthesis of ureidopyrimidinone isocyanate (UPy-isocyanate). Prepared according to literature.[Error! Bookmark not defined.] In a drybox, uracylopyrimidine (2.94 g, 23.2 mmol) and hexamethylene diisocyanate (26.8g, 0.16 mol) were added to a 150 mL pressure vessel. The reaction mixture was heated to 100 °C for 17 h, after which it was allowed to cool to room temperature. Pentane was added to the solution, and the remaining solid was filtered and washed with cold pentane. The solid was dried under vacuum at 70 °C for one day. The purity of the compound was confirmed by elemental analysis. Yield: 99%. ^1H NMR ($CDCl_3$; 25 °C): δ (ppm) = 13.12 (s, 1H), 11.87 (s, 1H), 10.20 (s, 1H), 5.82 (s, 1H), 3.25-3.31 (m, 4H), 2.23 (s, 3H), 1.64 (m, 4H), 1.41 (m, 4H). ^{13}C NMR ($CDCl_3$; 25 °C): δ (ppm) = 172.8, 156.6, 154.6, 148.1, 106.0, 43.3, 39.9, 31.1, 29.2, 26.2, 19.1. $C_{13}H_{19}N_5O_3$: Calcd. C 52.23, H 6.53, N 23.88; Found C 53.05, H 6.33, N 24.11.

General synthesis of LBL copolymers

With the exception of monomer feed composition, the synthesis of LBL copolymers was identical for all samples in the series. In a dry box, degassed HTPB, $Sn(Oct)_2$, and toluene (80 mL) were added to a 150 mL pressure vessel equipped with a stir bar. The solids were allowed to stir for 30 min at room temperature, after which d,l-lactide was added. The pressure vessel was then removed from the dry box and placed in a 110 °C oil bath, where it was left for 4 h under vigorous stirring. After cooling the system, the pressure vessel was brought back into the dry box, and half of the reaction mixture was poured into a 100 mL round-bottom flask where it was allowed to cool to room temperature before precipitating into methanol. The other half was left for UPy-functionalization. The polymer was decanted, dissolved in methylene chloride, and precipitated into hexanes. It was then redissolved in methylene chloride (100 mL) and butylated hydroxyl toluene (1 wt%) was added. The mixture was then poured into a polypropylene container and allowed to dry under nitrogen flow overnight before drying in a vacuum oven at 80 °C for 4 days.

LBL(11-3.3-11): HTPB (1.54g); d,l-lactide (8.68g , 60.25 mmol); $Sn(Oct)_2$ (0.024g, 0.06 mmol). ^1H NMR (500 MHz, $CDCl_3$; 25 °C): δ (ppm) =7.00 [s, BHT], 5.10-5.98 [b, $-CH_2-C\underline{H}=CH-CH_2-$, $-CH_2-CH(C\underline{H}=CH_2)-$ and $-COC\underline{H}(CH_3)O-$ backbone], 4.49-5.10 [b, $-CH_2-CH(CH=C\underline{H_2})-$ backbone], 4.38 [m,

-CO$\mathit{C}\underline{\mathit{H}}$(CH$_3$)OH end group], 3.97-4.21 [b, PB-$\mathit{C}\underline{\mathit{H}_2}$-O-PLA) block junction], 2.75 [b, -COCH(CH$_3$)O$\underline{\mathit{H}}$ end group], 1.79-2.50 [CH$_2$-C$\underline{\mathit{H}}$(CH=CH$_2$)– and C$\underline{\mathit{H}_2}$-CH=CH-CH$_2$-], 1.37-1.81 [b, -COCH(C$\underline{\mathit{H}_3}$)O- backbone], 0.97-1.36 [b, -C$\underline{\mathit{H}_2}$-CH(CH=CH$_2$)- backbone]. Yield: 92%.

LBL(17-3.3-17): HTPB (0.752g); d,l-lactide (8.44g , 58.63 mmol); Sn(Oct)$_2$ (0.024g, 0.06 mmol).

^{1}H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 7.00 [s, BHT], 5.10-6.03 [b, -CH$_2$-C$\underline{\mathit{H}}$=CH-CH$_2$-, -CH$_2$-CH(C$\underline{\mathit{H}}$=CH$_2$)– and -CO$\mathit{C}\underline{\mathit{H}}$(CH$_3$)O- backbone], 4.85-5.10 [b, -CH$_2$-CH(CH=C$\underline{\mathit{H}_2}$)– backbone], 4.39 [m, -CO$\mathit{C}\underline{\mathit{H}}$(CH$_3$)OH end group], 3.98-4.23 [b, PB-$\mathit{C}\underline{\mathit{H}_2}$-O-PLA) block junction], 1.92-2.19 [CH$_2$-C$\underline{\mathit{H}}$(CH=CH$_2$)– and C$\underline{\mathit{H}_2}$-CH=CH-CH$_2$-], 1.40-1.85 [b, -COCH(C$\underline{\mathit{H}_3}$)O- backbone], 1.10-1.50 [b, -C$\underline{\mathit{H}_2}$-CH(CH=CH$_2$)- backbone]. Yield: 90%.

LBL(36-3.3-36): HTPB (0.43g); d,l-lactide (9.67g , 67.13 mmol); Sn(Oct)$_2$ (0.027g, 0.06 mmol).

^{1}H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 7.00 [s, BHT], 5.25-6.00 [b, -CH$_2$-C$\underline{\mathit{H}}$=CH-CH$_2$-, -CH$_2$-CH(C$\underline{\mathit{H}}$=CH$_2$)– and -CO$\mathit{C}\underline{\mathit{H}}$(CH$_3$)O- backbone], 4.85-5.25 [b, -CH$_2$-CH(CH=C$\underline{\mathit{H}_2}$)– backbone], 4.38 [m, -CO$\mathit{C}\underline{\mathit{H}}$(CH$_3$)OH end group], 3.99-4.29 [b, PB-$\mathit{C}\underline{\mathit{H}_2}$-O-PLA) block junction], 2.00-2.50 [CH$_2$-C$\underline{\mathit{H}}$(CH=CH$_2$)– and C$\underline{\mathit{H}_2}$-CH=CH-CH$_2$-], 1.40-2.05 [b, -COCH(C$\underline{\mathit{H}_3}$)O- backbone], 0.89-1.42 [b, -C$\underline{\mathit{H}_2}$-CH(CH=CH$_2$)- backbone]. Yield: 95%.

LBL(58-3.3-58): HTPB (0.29g); d,l-lactide (9.81g , 68.1 mmol); Sn(Oct)$_2$ (0.028g, 0.07 mmol).

^{1}H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 6.99 [s, BHT], 5.05-6.13 [b, -CH$_2$-C$\underline{\mathit{H}}$=CH-CH$_2$-, -CH$_2$-CH(C$\underline{\mathit{H}}$=CH$_2$)-, and -CO$\mathit{C}\underline{\mathit{H}}$(CH$_3$)O- backbone], 4.70-5.05 [b, -CH$_2$-CH(CH=C$\underline{\mathit{H}_2}$)– backbone], 4.37 [m, -CO$\mathit{C}\underline{\mathit{H}}$(CH$_3$)OH end group], 3.99-4.28 [b, PB-$\mathit{C}\underline{\mathit{H}_2}$-O-PLA) block junction], 0.98-2.55 [b, CH$_2$-C$\underline{\mathit{H}}$(CH=CH$_2$)-, C$\underline{\mathit{H}_2}$-CH=CH-CH$_2$-, -COCH(C$\underline{\mathit{H}_3}$)O-, and -C$\underline{\mathit{H}_2}$-CH(CH=CH$_2$)- backbone]. Yield: 93%.

LBL(80-3.3-80): HTPB (0.22g); d,l-lactide (9.89g , 68.6 mmol); Sn(Oct)$_2$ (0.028g, 0.07 mmol).

^{1}H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 7.00 [s, BHT], 4.60-6.48 [b, -CH$_2$-$\underline{\mathit{CH}}$=CH-CH$_2$-, -CH$_2$-CH(C$\underline{\mathit{H}}$=CH$_2$)-, and -CO$\mathit{C}\underline{\mathit{H}}$(CH$_3$)O- backbone], 4.70-5.05 [b, -CH$_2$-CH(CH=C$\underline{\mathit{H}_2}$)- backbone], 4.38 [m,

-CO$C\underline{H}$(CH$_3$)OH end group], 3.98-4.28 [b, PB-$C\underline{H_2}$-O-PLA) block junction], 0.80-2.65 [b, CH$_2$-C$\underline{H}$(CH=CH$_2$)-, C$\underline{H_2}$-CH=CH-CH$_2$-, -COCH(C$\underline{H_3}$)O-, and -C$\underline{H_2}$-CH(CH=CH$_2$)- backbone]. Yield: 90%.

LBL(85-3.3-85): HTPB (0.18g); d,l-lactide (9.92g , 68.9 mmol); Sn(Oct)$_2$ (0.028g, 0.07 mmol). ^{1}H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 6.99 [s, BHT], 4.95-5.80 [b, -CH$_2$-C$\underline{H}$=CH-CH$_2$-, -CH$_2$-CH(C$\underline{H}$=CH$_2$)-, and -CO$C\underline{H}$(CH$_3$)O- backbone], 4.75-5.05 [b, -CH$_2$-CH(CH=C$\underline{H_2}$)- backbone], 4.37 [m, -CO$C\underline{H}$(CH$_3$)OH end group], 3.95-4.25 [b, PB-$C\underline{H_2}$-O-PLA) block junction], 0.78-2.65 [b, CH$_2$-C$\underline{H}$(CH=CH$_2$)-, C$\underline{H_2}$-CH=CH-CH$_2$-, -COCH(C$\underline{H_3}$)O-, and -C$\underline{H_2}$-CH(CH=CH$_2$)- backbone]. Yield: 95%.

General synthesis of UPy-LBL copolymers

In a dry box, the ureidopyrimidinone-isocyanate synthon was added to the remaining half of the unquenched LBL copolymers. The pressure vessel was removed from the dry box and placed in a 110 °C oil bath for 15 min while stirring vigorously. The solution was allowed to cool to room temperature, and the polymer was precipitated twice into methanol (dissolving with methylene chloride). The polymer was precipitated from hexanes before dissolution in methylene chloride (100 mL). Butylated hydroxyl toluene (1 wt%) was added to the polymer solution. The mixture was then poured into a polypropylene container and allowed to dry under nitrogen flow overnight before drying in a vacuum oven at 70 °C for 4 days.

UPy-LBL(10-3.3-10): UPy-NCO (0.34g, 1.17 mmol). ^{1}H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 13.13 [s, =CH(CH$_3$)N$\underline{H}$- end group], 11.85 [s, =CN$\underline{H}$CO- end group], 10.12 [s, -CON$\underline{H}$CH$_2$- end group], 5.90 [s, -CO-C$\underline{H}$=C(CH$_3$)- end group], 5.10-6.20 [b, -CH$_2$-C$\underline{H}$=CH-CH$_2$-, -CH$_2$-CH(C$\underline{H}$=CH$_2$)-, and -CO$C\underline{H}$(CH$_3$)O- backbone], 4.60-5.10 [b, -CH$_2$-CH(CH=C$\underline{H_2}$)- backbone], 3.97-4.24 [b, -CO$C\underline{H}$(CH$_3$)O-C(O)NHCH$_2$- and PB-$C\underline{H_2}$-O-PLA block junction], 3.05-3.36 [b, -C$\underline{H_2}$-NHC(O)O- and -C$\underline{H_2}$-NHC(O)NH- end group], 2.58-1.90 [s, CH$_2$-C$\underline{H}$(CH=CH$_2$)-, C$\underline{H_2}$-CH=CH-CH$_2$- backbone], 0.80-1.90 [s, -COCH(C$\underline{H_3}$)O-, and -C$\underline{H_2}$-CH(CH=CH$_2$)- backbone]. Yield: 84%.

UPy-LBL(20-3.3-20): UPy-NCO (0.17g, 0.57 mmol).^{1}H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 13.16 [s, =CH(CH$_3$)N$\underline{H}$- end group], 11.89 [s, =CN$\underline{H}$CO- end group], 10.16 [s, -CON$\underline{H}$CH$_2$- end group], 5.92 [s, -CO-C$\underline{H}$=C(CH$_3$)- end group], 4.95 -6.01 [b, -CH$_2$-C$\underline{H}$=CH-CH$_2$-, -CH$_2$-CH(C$\underline{H}$=CH$_2$)-, and -COC$\underline{H}$(CH$_3$)O- backbone], 4.65-4.95 [b, -CH$_2$-CH(CH=C$\underline{H_2}$)- backbone], 3.96-4.31 [b, -COC$\underline{H}$(CH$_3$)O-C(O)NHCH$_2$- and PB-C$\underline{H_2}$-O-PLA block junction], 3.07-3.35 [b, -C$\underline{H_2}$-NHC(O)O- and -C$\underline{H_2}$-NHC(O)NH- end group], 2.25 [s, -CO-CH=C(C$\underline{H_3}$)- end group], 0.80-2.32 [b, CH$_2$-C$\underline{H}$(CH=CH$_2$)-, C$\underline{H_2}$-CH=CH-CH$_2$-, COCH(C$\underline{H_3}$)O-, and -C$\underline{H_2}$-CH(CH=CH$_2$)- backbone]. Yield: 82%.

UPy-LBL(36-3.3-36): UPy-NCO (0.10g, 0.33 mmol). ^{1}H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 13.15 [s, =CH(CH$_3$)N$\underline{H}$- end group], 11.88 [s, =CN$\underline{H}$CO- end group], 10.14 [s, -CON$\underline{H}$CH$_2$- end group], 7.00 [s, BHT], 5.92 [s, -CO-C$\underline{H}$=C(CH$_3$)- end group], 5.05-6.01 [b, -CH$_2$-C$\underline{H}$=CH-CH$_2$-, -CH$_2$-CH(C$\underline{H}$=CH$_2$)-, and -COC$\underline{H}$(CH$_3$)O- backbone], 4.72-5.05 [b, -CH$_2$-CH(CH=C$\underline{H_2}$)- backbone], 4.00-4.24 [b, -COC$\underline{H}$(CH$_3$)O-C(O)NHCH$_2$- and PB-C$\underline{H_2}$-O-PLA block junction], 3.08-3.36 [b, -C$\underline{H_2}$-NHC(O)O- and -C$\underline{H_2}$-NHC(O)NH- end group], 2.25 [s, -CO-CH=C(C$\underline{H_3}$)- end group], 0.78-2.44 [b, CH$_2$-C$\underline{H}$(CH=CH$_2$)-, C$\underline{H_2}$-CH=CH-CH$_2$-, COCH(C$\underline{H_3}$)O-, and -C$\underline{H_2}$-CH(CH=CH$_2$)- backbone]. Yield: 87%.

UPy-LBL(57-3.3-57): UPy-NCO (0.06g, 0.22 mmol). ^{1}H NMR (500 MHz, CDCl$_3$; 25 °C): δ (ppm) = 13.16 [s, =CH(CH$_3$)N$\underline{H}$- end group], 11.88 [s, =CN$\underline{H}$CO- end group], 10.16 [s, -CON$\underline{H}$CH$_2$- end group], 7.00 [s, BHT], 5.92 [s, -CO-C$\underline{H}$=C(CH$_3$)- end group], 5.05-6.29 [b, -CH$_2$-C$\underline{H}$=CH-CH$_2$-, -CH$_2$-CH(C$\underline{H}$=CH$_2$)-, and -COC$\underline{H}$(CH$_3$)O- backbone], 4.63-5.05 [b, -CH$_2$-CH(CH=C$\underline{H_2}$)- backbone], 3.97-4.36 [b, -COC$\underline{H}$(CH$_3$)O-C(O)NHCH$_2$- and PB-C$\underline{H_2}$-O-PLA block junction], 3.07-3.37 [b, -C$\underline{H_2}$-NHC(O)O- and -C$\underline{H_2}$-NHC(O)NH- end group], 2.25 [s, -CO-CH=C(C$\underline{H_3}$)- end group], 0.88-2.53 [b, CH$_2$-C$\underline{H}$(CH=CH$_2$)-, C$\underline{H_2}$-CH=CH-CH$_2$-, COCH(C$\underline{H_3}$)O-, and -C$\underline{H_2}$-CH(CH=CH$_2$)- backbone]. Yield: 80%.

UPy-LBL(80-3.3-80): UPy-NCO (0.05g, 0.17 mmol). ^{1}H NMR (500 MHz, $CDCl_3$; 25 °C): δ (ppm) = 13.12 [s, $=CH(CH_3)N\underline{H}-$ end group], 11.87 [s, $=CN\underline{H}CO-$ end group], 10.18 [s, $-CON\underline{H}CH_2-$ end group], 5.92 [s, $-CO-C\underline{H}=C(CH_3)-$ end group], 5.05-6.10 [b, $-CH_2-C\underline{H}=CH-CH_2-$, $-CH_2-CH(C\underline{H}=CH_2)-$, and $-COC\underline{H}(CH_3)O-$ backbone], 4.75-5.05 [b, $-CH_2-CH(CH=C\underline{H_2})-$ backbone], 4.00-4.56 [b, $-COC\underline{H}(CH_3)O-C(O)NHCH_2-$ and PB-$C\underline{H_2}$-O-PLA block junction], 3.04-3.50 [b, $-C\underline{H_2}-NHC(O)O-$ and $-C\underline{H_2}-NHC(O)NH-$ end group], 2.25 [s, $-CO-CH=C(C\underline{H_3})-$ end group], 0.75-2.40 [b, $CH_2-C\underline{H}(CH=CH_2)-$, $C\underline{H_2}-CH=CH-CH_2-$, $COCH(C\underline{H_3})O-$, and $-C\underline{H_2}-CH(CH=CH_2)-$ backbone]. Yield: 82%.

UPy-LBL(86-3.3-86): UPy-NCO (0.04g, 0.13 mmol). ^{1}H NMR (500 MHz, $CDCl_3$; 25 °C): δ (ppm) = 13.15 [s, $=CH(CH_3)N\underline{H}-$ end group], 11.88 [s, $=CN\underline{H}CO-$ end group], 10.16 [s, $-CON\underline{H}CH_2-$ end group], 5.93 [s, $-CO-C\underline{H}=C(CH_3)-$ end group], 4.58 -6.15 [b, $-CH_2-C\underline{H}=CH-CH_2-$, $-CH_2-CH(C\underline{H}=CH_2)-$, $-COC\underline{H}(CH_3)O-$, and $-CH_2-CH(CH=C\underline{H_2})-$ backbone], 3.95-4.60 [b, $-COC\underline{H}(CH_3)O-C(O)NHCH_2-$ and PB-$C\underline{H_2}$-O-PLA block junction], 3.01-3.60 [b, $-C\underline{H_2}-NHC(O)O-$ and $-C\underline{H_2}-NHC(O)NH-$ end group], 0.71-2.53 [b, $CH_2-C\underline{H}(CH=CH_2)-$, $C\underline{H_2}-CH=CH-CH_2-$, $COCH(C\underline{H_3})O-$, and $-C\underline{H_2}-CH(CH=CH_2)-$ backbone]. Yield: 85%.

Synthesis of poly(d,l-lactide) (PLA). In a dry box, benzyl alcohol (0.022 g, 2.00 mmol), dichloromethane (80 mL), and d,l-lactide (10.08 g, 70 mmol) were added to a 150 mL pressure vessel equipped with a stir bar. The solids were dissolved, and a solution of TBD (0.01 g in 2 mL of dichloromethane, 0.07 mmol) was added to the reaction mixture. The polymerization was allowed to proceed at room temperature for 1 h before quenching with benzoic acid (0.09 g, 0.7 mmol). The polymer was precipitated into methanol twice (dissolving in methylene chloride), precipitated in hexanes once, and finally dissolved in dichloromethane (100 mL). The solution was then poured into a polypropylene container and allowed to dry under nitrogen flow overnight before drying in a vacuum oven at 80 °C for 4 days. Yield: 97%.

Synthesis of UPy-poly(d,l-lactide) (UPy-PLA). In a dry box, benzyl alcohol (0.007 g, 0.06 mmol), $Sn(Oct)_2$ (0.014 g, 0.035 mmol), and toluene (40 mL) were added to a 150 mL pressure vessel equipped with a stir bar. The solids were allowed to dissolve, and d,l-lactide was added (5.04 g, 35 mmol) to the reaction mixture. The pressure vessel was then removed from the dry box and placed in a 110 °C oil bath, where it was left for 4 h while stirring vigorously. After cooling the system, the pressure vessel was returned to the dry box where ureidopyrimidinone-isocyanate (0.042 g, 0.14 mmol) was added. The pressure vessel was subsequently removed from the dry box and placed in a 110 °C oil bath for 15 minutes while stirring vigorously. The polymer was precipitated into methanol twice (dissolving in methylene chloride), precipitated in hexanes once, and finally dissolved in dichloromethane (100 mL). The solution was then poured into a polypropylene container and allowed to dry under nitrogen flow overnight before drying in a vacuum oven at 80 °C for 4 days. Yield: 87%.

Synthesis of LBzL.

Difunctional hydroxy-terminated PLA (LBzL) was synthesized as a polymer control. In a dry box, degassed 1,4-phenylenedimethanol (0.008 g by stock solution), dichloromethane (40 mL), and d,l-lactide (5.04 g, 35 mmol) were added to a 150 mL pressure vessel equipped with a stir bar. The solids were dissolved, and a solution of TBD (0.005 g in 2 mL of dichloromethane, 0.04 mmol) was added to the reaction mixture. The polymerization was then allowed to proceed at room temperature for 1 h before quenching with benzoic acid (0.04 g, 0.35 mmol). The polymer was precipitated into methanol twice and dissolved in dichloromethane (100 mL). The solution was then poured into a polypropylene container and allowed to dry under nitrogen flow overnight before drying in a vacuum oven at 80 °C for 4 days. Yield: 95%.

Synthesis of UPy-LBzL

UPy-LBzL is the difunctional UPy-functionalized PLA. In a dry box, 1,4-phenylenedimethanol (0.008 g by stock solution), $Sn(Oct)_2$ (0.014 g, 0.035 mmol), toluene (40 mL) were added to a 150 mL pressure vessel equipped with a stir bar. The solids were dissolved, and d,l-lactide was added (5.04 g, 35 mmol) to the reaction mixture. The pressure vessel was then removed from the dry box and placed in a 110 °C oil bath, where it was left for 4 h while stirring vigorously. After cooling the system, the pressure vessel was returned to the dry box where ureidopyrimidinone-isocyanate (0.08 g, 0.28 mmol) was added. The pressure vessel was subsequently removed from the dry box and placed in a 110 °C oil bath for 15 min while stirring vigorously. The polymer was precipitated twice from methanol and lastly with hexanes (redissolving with dichloromethane). After polymer decantation, it was dissolved in dichloromethane and poured into a polypropylene container, where it is allowed to dry under nitrogen flow overnight followed by a vacuum oven at 80 °C for 4 days. Yield: 85%.

Synthesis of UPy-PB. In a dry box, degassed HTPB (2.0 g), $Sn(Oct)_2$ (0.487 mg, 0.0012 mmol), and toluene (10 mL) were added to a 150 mL pressure vessel equipped with a stir bar. The solids were dissolved and ureidopyrimidinone-isocyanate (0.82 g, 2.76 mmol) was added. The pressure vessel was subsequently removed from the dry box and placed in a 110 °C oil bath for 15 minutes while stirring vigorously. The polymer was precipitated twice from methanol and lastly with hexanes (redissolving with dichloromethane). After polymer decantation, it was dried in a vacuum oven at room temperature for 4 days. Yield: 87%.

Synthesis of UPy-LBL with varying functionality

The UPy-LBL(80-3.3-80) series of polymers were synthesized from the same batch to ensure an identical monomer molar feed composition. UPy-functionalization was controlled by regulating the reaction time. Thus, in a dry box, degassed hydroxy-terminated polybutadiene (0.77 g), dichloromethane (280 mL), and d,l-lactide (34.58 g, 250 mmol) were added to a 500 mL round-bottom flask equipped with a stir bar. The solids were dissolved, and a solution of TBD (0.033 g in 5 mL of dichloromethane, 0.24 mmol) was added to the reaction mixture. The polymerization was allowed to proceed at room temperature for 1 h before distributing the reaction mixture in seven separate 150 mL pressure vessels. The UPy-LBL(80-3.3-80)-0 aliquot was quenched immediately after distribution by the addition of benzoic acid (0.04g, 0.35 mmol) without addition of ureidopyrimidinone-isocyanate. This polymer was precipitated and dried as described for UPy-LBL polymers, adding BHT (0.05 g) before drying the polymer. Ureidopyrimidinone-isocyanate (0.1 g, 2.4 mmol) was added to each of the remaining aliquots, and the polymerization was allowed to proceed at room temperature for the specified period of time (0, 3, 6, 9, 12 and 24 h). Every aliquot was quenched and precipitated as described for the UPy-LBL polymers, adding BHT (0.05 g) before drying. Overall yield: 82-85%.

Equations:

Equation (S1):

$$\bar{D}P_{PLA} = \left[I_{6-4.2} - \left(\bar{D}P_{1,4PB}\, x2 + \bar{D}P_{1,2PB} x3\right)\right] x\, \frac{1}{2}$$

Where $DP_{1,4PB}$ and $DP_{1,2PB}$ are 21.35 and 39.65 respectively

Equation (S2):

$$w_{PLA} = \frac{\bar{D}P_{PLA}}{\bar{D}P_{PLA} + \bar{D}P_{PB}}\, x\, 100\%$$

Equation (S3):

$$M_{nLBL} = \bar{D}P_{PLA}\, x\, 144 + 3300$$

Equation (S4):

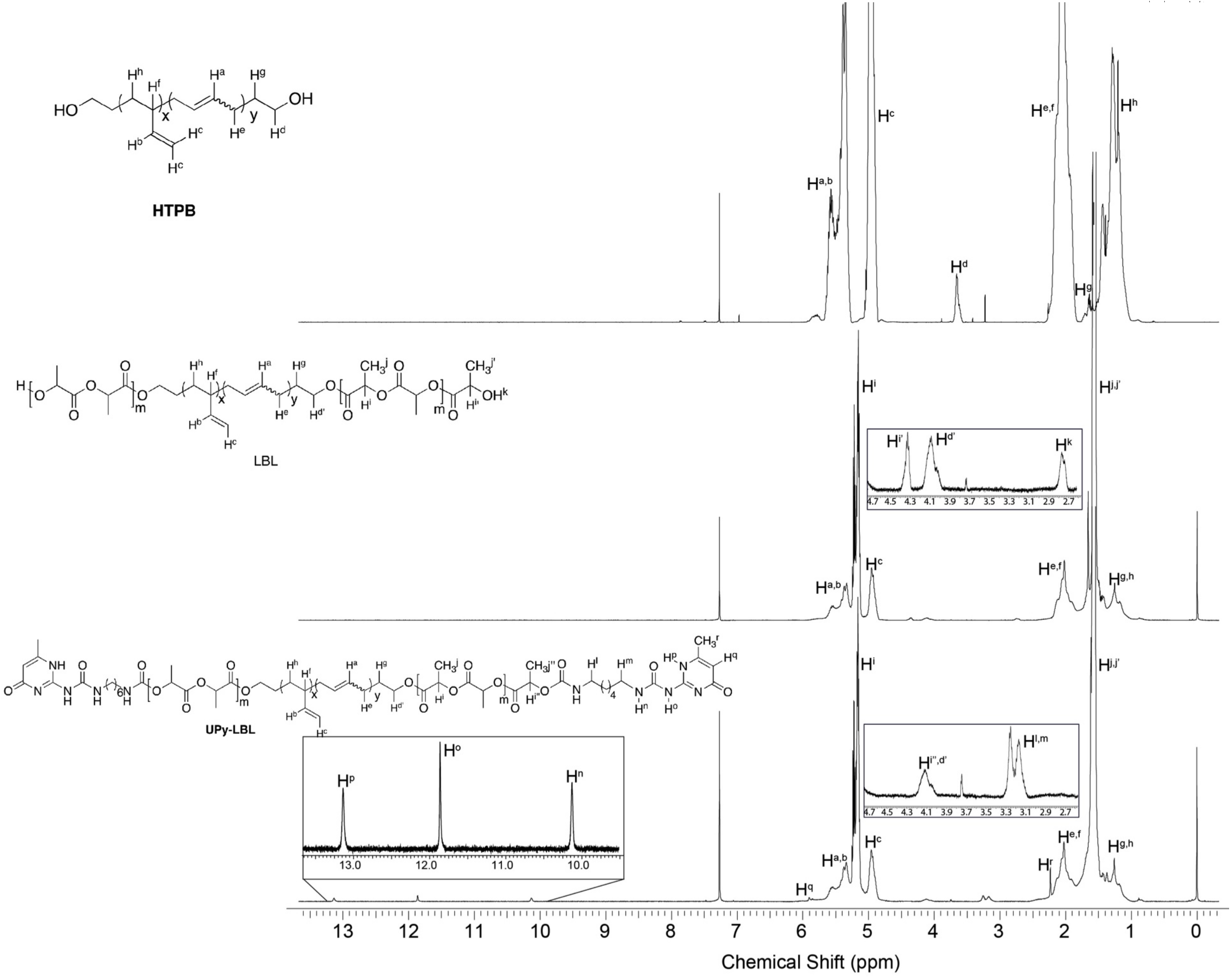
$$M_{nUPy-LBL} = \left(\bar{D}P_{PLA}\right) x\, 144 + 3300 + 2(293.3)$$

Equation (S5):

$$F = \frac{\frac{I_{3.05-3.45}}{8}}{\frac{I_{3.05-3.45}}{8} + \frac{I_{4.38}}{2}}\, x\, 2$$

F

L


HTPB
LBL
UPy-LBL
H^a,b
H^c
H^d
H^e,f
H^g
H^h
H^i
H^j,j'
H^i'
H^d'
H^k
H^g,h
H^q
H^r
H^i'',d'
H^l,m
H^p
H^o
H^n
Chemical Shift (ppm)
13 12 11 10 9 8 7 6 5 4 3 2 1 0

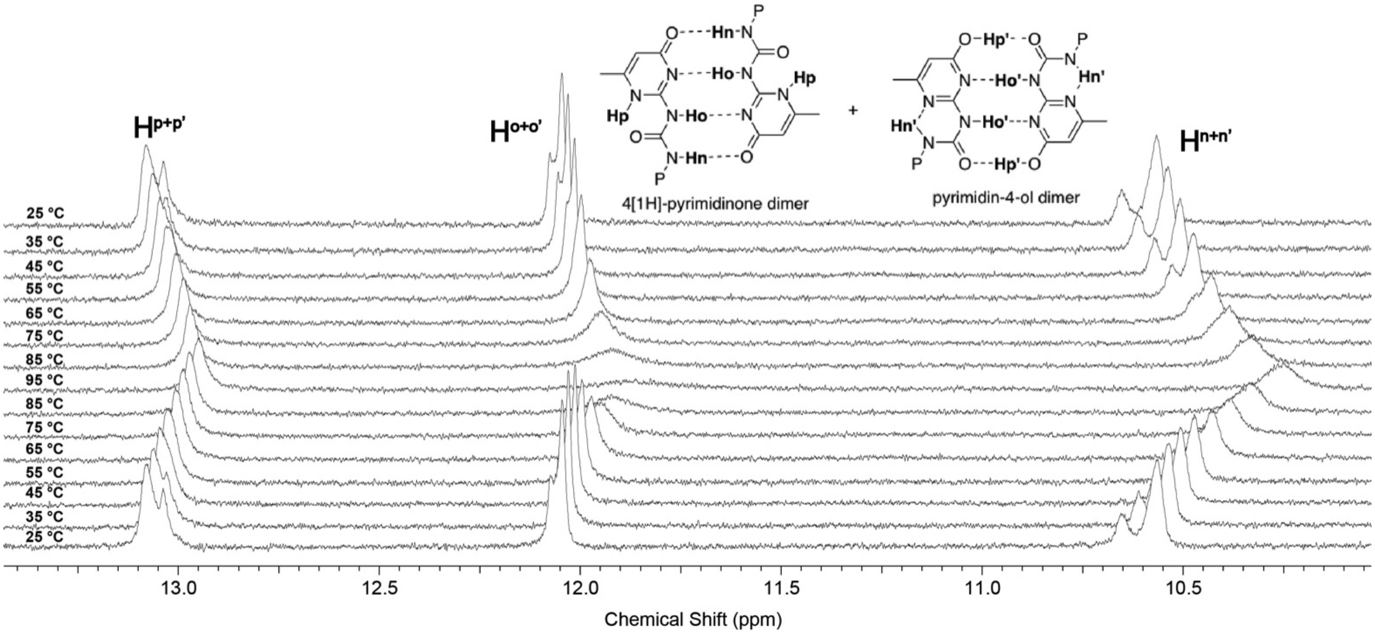


Figure S2. ^{1}H NMR spectra of UPy-LBL$_{(10\text{-}3.3\text{-}10)}$ as a function of temperature in Toluene-d$_8$ [3.68 mM].

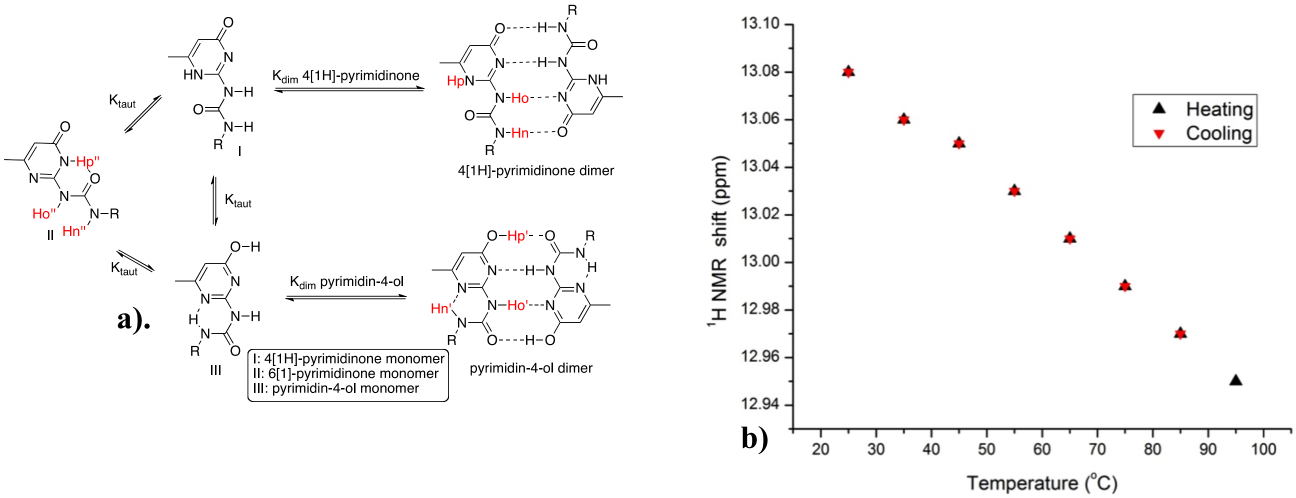


Figure S3. a) UPy mono- and dimer-tautomeric forms. b) ^{1}H NMR NH chemical shift of UPy-LBL$_{(10\text{-}3.3\text{-}10)}$ as a function of temperature in Toluene-d$_8$ [3.68 mM]

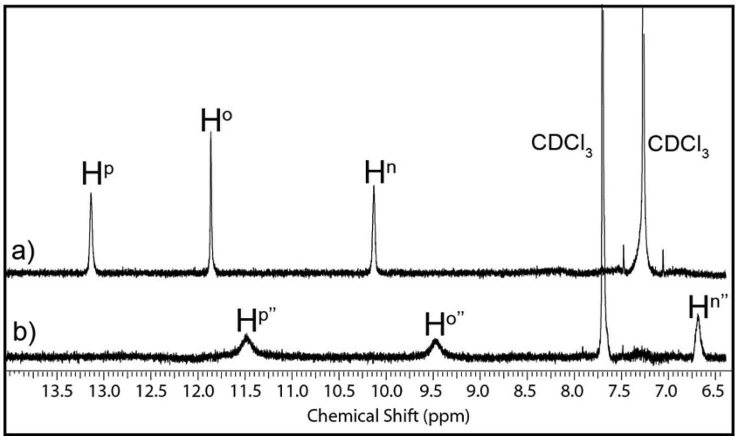


Figure S4. ^{1}H NMR spectra (NH region) of UPy-LBL$_{(10\text{-}3.3\text{-}10)}$. a) Spectrum in $CDCl_3$ [1.8 mM]. b) Spectrum in $CDCl_3$ after addition of 0.1 mL of DMSO.

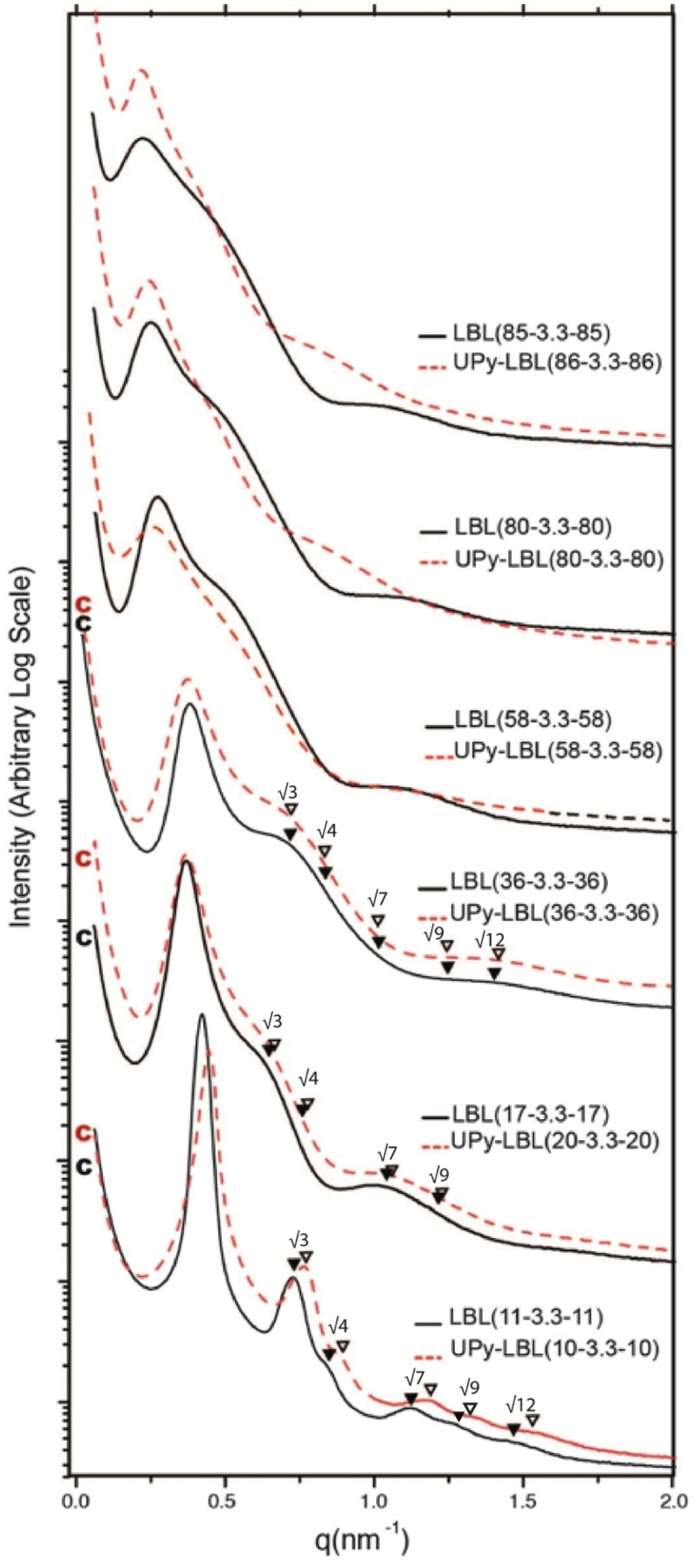


Figure S5. One-dimensional SAXS profiles for representative LBL triblock copolymers measured at 25 °C. Red dashed lines represent UPy-functionalized polymers. Bold and empty arrows indicate the predicted peak positions for the indicated morphologies (C = cylinders) for non-UPy and UPy-functionalized polymers respectively.

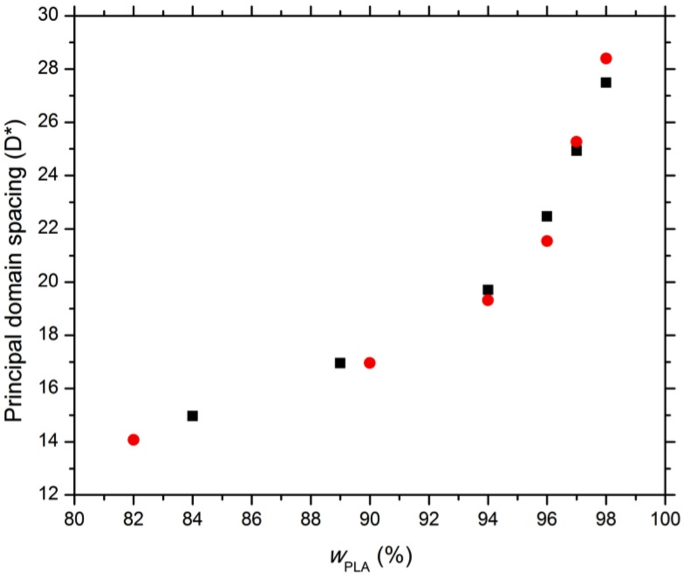


Figure S6. Principal domain spacing (D*) respects the molecular weight of synthesized polymers. Red dots represents the UPy-LBL polymers while the black dots denote the LBL analogous.

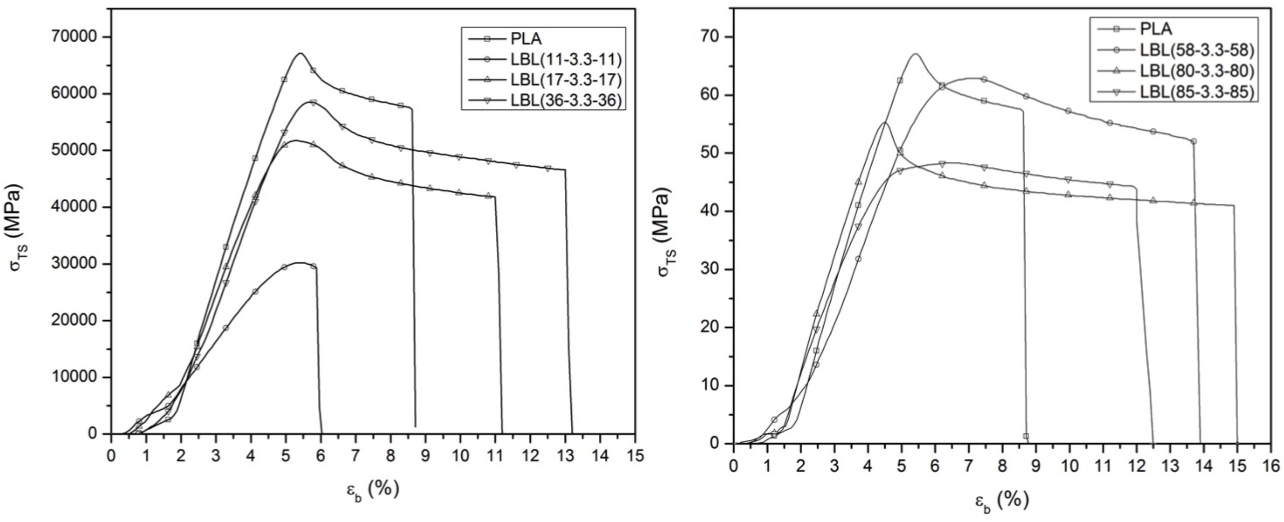


Figure S7. Representative engineering stress-strain curves of non-UPy functionalized polymers (LBL).

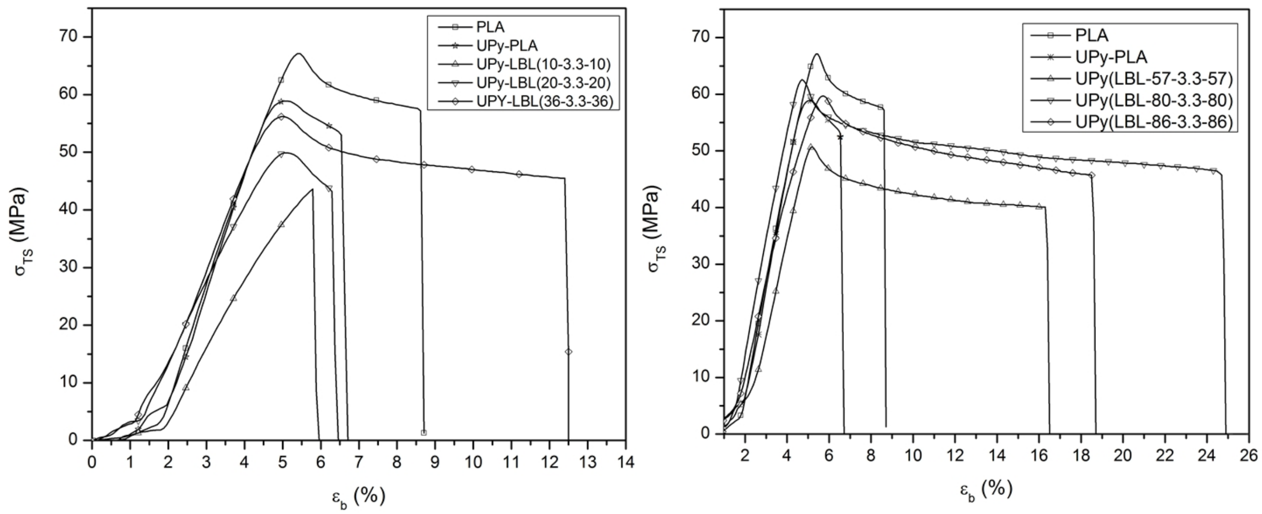


Figure S8. Representative engineering stress-strain curves of UPy-functionalized polymers (UPy-LBL).

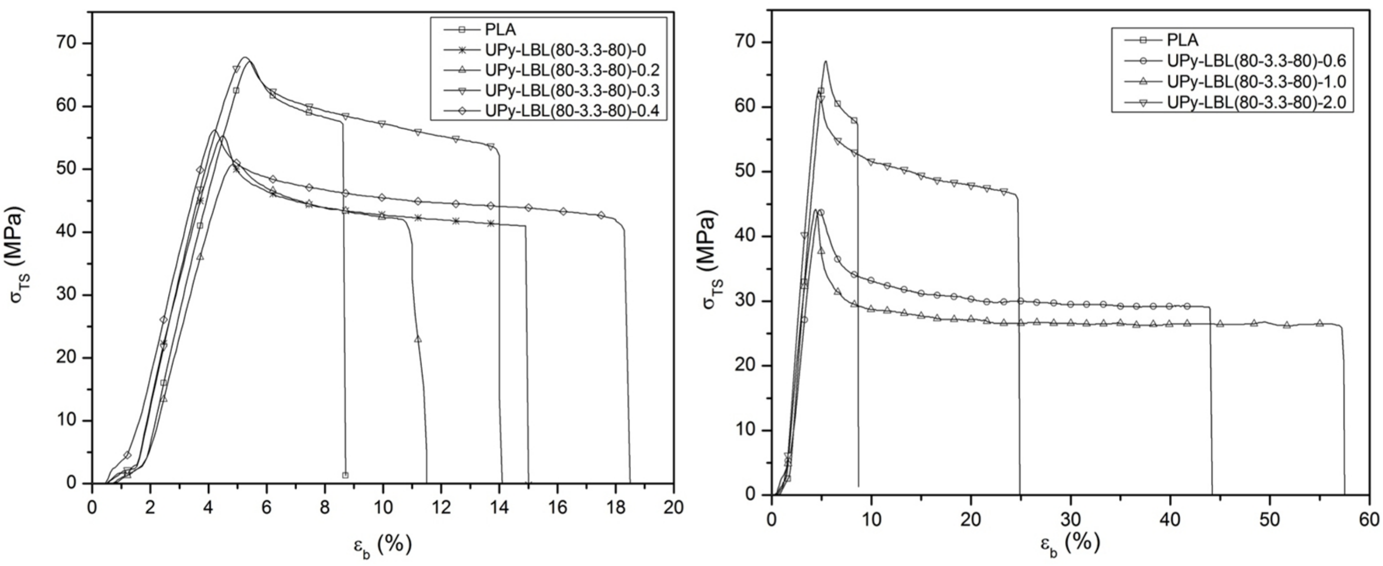


Figure S9. Representative engineering stress-strain curves of UPy-functionalized polymers.

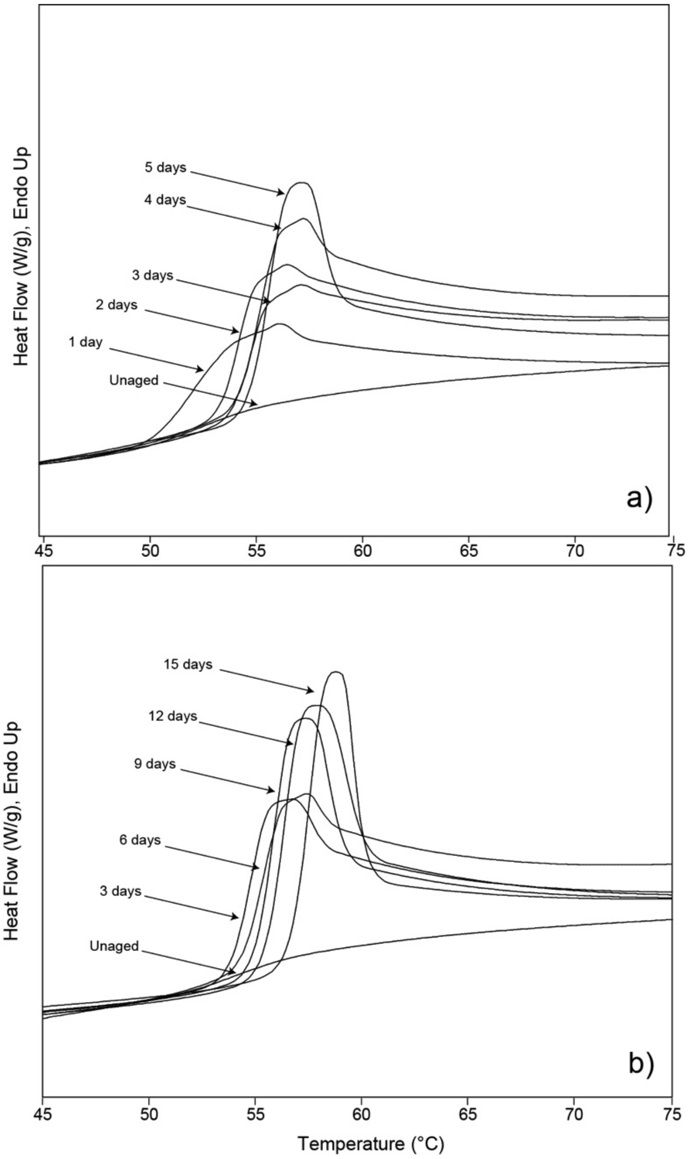


Figure S10. DSC heating thermograms of polymer UPy-LBL(80-3.3-80)-1.0 (10 ˚C/min). Polymer was annealed at 40˚C for the indicated aging time under inert atmosphere. a) First five days of aging b) representative thermograms of 15 days of aging.

References:

[1] F. H. Meijer, R. P. Sijbesma, H. Kooijman, A. L. Spek, E. W. Meijer, *J. Am. Chem. Soc.,* 1998, **120**, 6761–6769.