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Supporting Information for Manuscript Entitled with

A facile method to prepare high molecular weight bio-renewable poly(γ-butyrolactone) using a strong base/urea binary synergistic catalytic system

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Experimental Section

Materials.

Tetrahydrofuran (THF) was purified by purging with dry nitrogen, followed by passing through columns of activated alumina. Potassium methoxide (KOMe, 90+ %) was obtained from Alfa Aesar Co. Potassium *tert*-butoxide (tBuOK, 98 %) was purchased from Energy Chemical Co. γ-Butyrolactone (γBL) obtained from Aladdin Reagent Co. was stirred with CaH_2 for 24 hours, then distilled under reduced pressure and stored over activated 4 Å molecular sieves in a glove box. THF-d8 was stirred with Na/K alloy for 48 hours and then distilled under vacuum. The cyclic trimeric phosphazene base (CTPB) was synthesized according to the reported procedure.[1] 1-Phenyl-3-(4-(trifluoromethyl) phenyl) urea (U1),[2] 1-(4-chlorophenyl)-3-phenylurea

(U2),[3] 1-(4-chlorophenyl)-3-(4-methoxyphenyl) urea (U3),[4] 1, 3-diisopropylurea (U4),[5] 1-(4-chlorophenyl)-3-cyclohexylurea (U5),[6] 1-cyclohexyl-3-(4-methoxyphenyl) urea (U6)[7] and 1-cyclohexyl-3-phenylurea (U7)[8] were prepared based on the reported procedures from commercially available isocyanates and amines. 1, 3-Diphenylthiourea (TU1) was prepared by reacting phenyl isothiocyanate with aniline in a similar way to U2. Ureas and TU1 were dried under vacuum at 50 °C for at least 8 hours and then stored in a glove box. All commercially obtained reagents were used as received without further purification unless otherwise noted.

Instruments.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVNEO400ASCEND FT-NMR spectrometer at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts were reported in δ (ppm) relative to the residual deuterated solvent peak. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker Microflex LRF MS spectrometer equipped with a 337 nm nitrogen laser operating in a positive ion, linear mode. The sample solutions (10 mg/mL in THF), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) solution (50 mg/mL in THF) and sodium trifluoroacetate solution (5 mg/mL) were mixed in a volume ratio of 4:2:1, 1 μL of which was then deposited on the target plate and dried before measurement. Size exclusion chromatography (SEC) experiments were performed on a Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump and a model 1260 differential refractometer detector with using THF as mobile phase at a flow rate of 1.0 mL/min at 40 °C. One PLgel 5 μm guard column and three Mz-Gel SD_{plus} columns (10^3 Å, 10^4 Å, and 10^5 Å, linear range of MW = 1000 – $2*10^6$ Da) were connected in series. SEC experiments were also conducted on a SEC system equipped with Shimadzu LC-20AD pump and a Wyatt Optilab differential refractometer detector with using DMF as mobile phase at a flow rate of 1.0 mL/min at 40 °C. One Mz-Gel SD_{plus} guard column and three PLgel 5 μm columns (500 Å, 10^3 Å, 10^4 Å, linear range of MW = 500 – $1.7*10^6$ Da) were connected in series. The molecular weight and dispersity were calculated using 10

polystyrene standards with narrow molecular weight distribution as references. The sample concentration used for SEC analyses was 5-10 mg/mL. Differential scanning calorimetry (DSC) measurements were performed on a TA instrument DSC 25. Temperature was calibrated with an indium standard. Measurements were performed under N_2 atmosphere with a flow rate of 50 mL/min. Each sample with a mass of 5-10 mg was used for the measurement. The typical procedures for the measurements of PγBL samples were as follows: in the first heating scan, samples were heated from -85 °C to 100 °C at a heating rate of 10 °C/min and kept at 100 °C for 2 min to eliminate any thermal history. In the second heating scan, samples were cooled to -85 °C at 10 °C/min and then equilibrium at -85 °C for 2 min, and subsequently reheated to 100 °C at 10°C/min. Thermogravimetric analysis (TGA) measurements were performed on a TA Q50 thermogravimetric analyzer. The samples were heated from 40 °C to 500 °C at a heating rate of 10 °C/min under N_2 atmosphere with a flow rate of 50 mL/min. The mechanical tensile tests were performed on a Zwick Z005 tensile testing machine. Rectangular shaped specimens with dimensions of 75 mm length * 4 mm width * 0.6 mm thickness were prepared by hot press molding at 80 °C for 20 min and then cold press at room temperature for 10 min. The specimens were measured at room temperature using a crosshead speed of 20 mm/min. Young's moduli were calculated as the slope of stress-strain curves at strain below 1%. The stress at yield, elongation and stress at break and Young's moduli were reported as average values with standard deviations obtained from at least 5 specimens.

Table S1. Thermal properties of PγBL samples with varied molecular weights [a]

sample	Mn (kDa)	DSC							TGA	
		Cooling scan		Second heating scan						
		T_c (°C)	ΔH_c (J/g)	T_g (°C)	$T_{m,1}$ (°C)	$\Delta H_{m,1}$ (J/g)	$T_{m,2}$ (°C)	$\Delta H_{m,2}$ (J/g)	$T_{d,5\%}$ (°C)	$T_{d,max}$ (°C)
S1	4.8	21.6	56.1	-47.1	43.5	10.3	60.2	71.1	219.7	311.2
S2	12.1	14.6	53.4	-45.6	46.9	5.7	61.7	64.6	267.4	328.6

S3	16.3	5.3	49.6	-44.1	46.3	2.7	61.6	56.8	292.6	361.0
S4	23.3	6.1	48.2	-44.7	47.0	1.9	61.9	53.0	294.6	378.9

[a] The conditions for the preparation of samples: S1: Table 1, run 6; S2: Table 1, run 8; S3: Table 1, run 12; S4: Table 1, run 20.

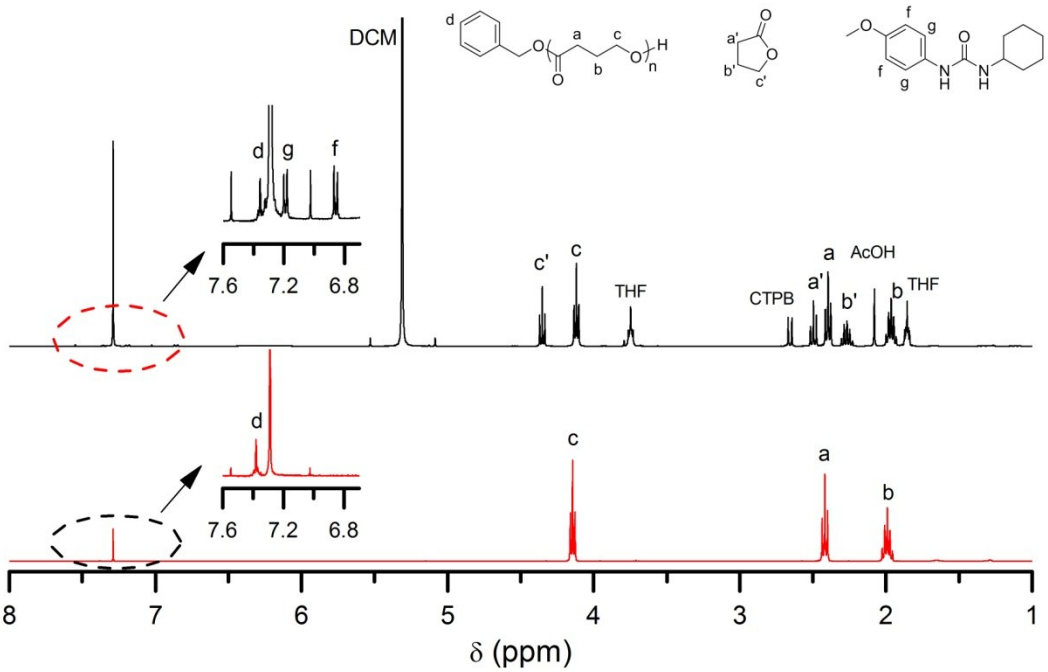

Figure S1. Stacked ^{1}H NMR spectra of reaction mixtures before precipitation (top) and obtained PγBL after precipitation (bottom) in $CDCl_3$ (Table 1, run 12).

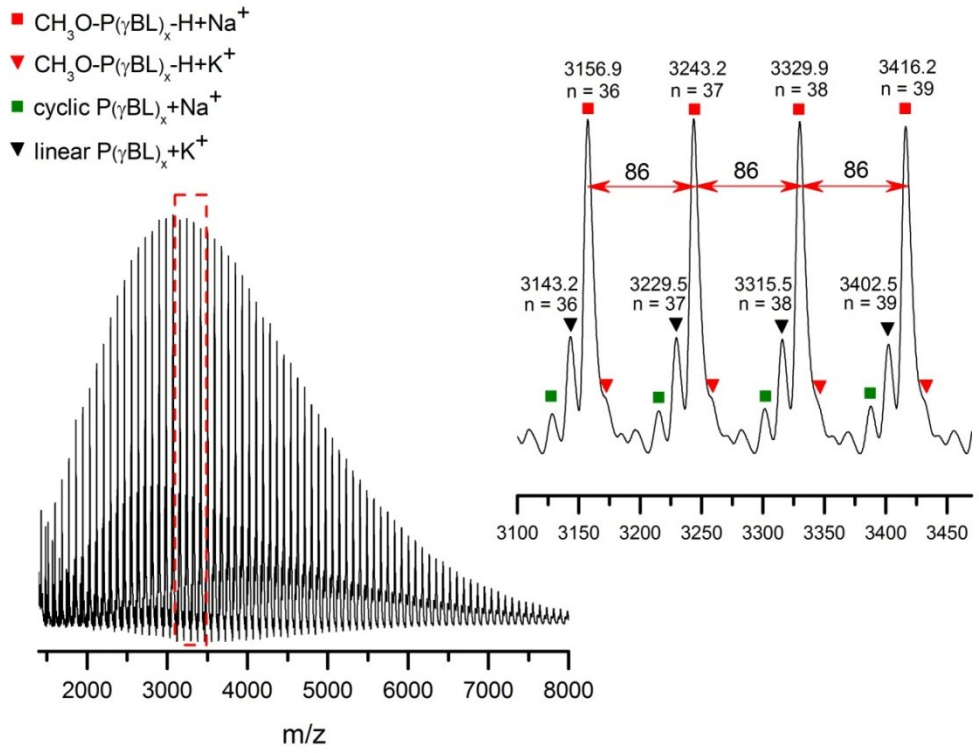

Figure S2. MALDI-TOF mass spectrum of PγBL catalyzed with KOMe alone (Table 1, run 1). ■ and ▼: linear PγBL with CH_3O/H chain ends, ■: cyclic PγBL with no chain ends, ▼: linear PγBL with acylated lactone/H chain ends.

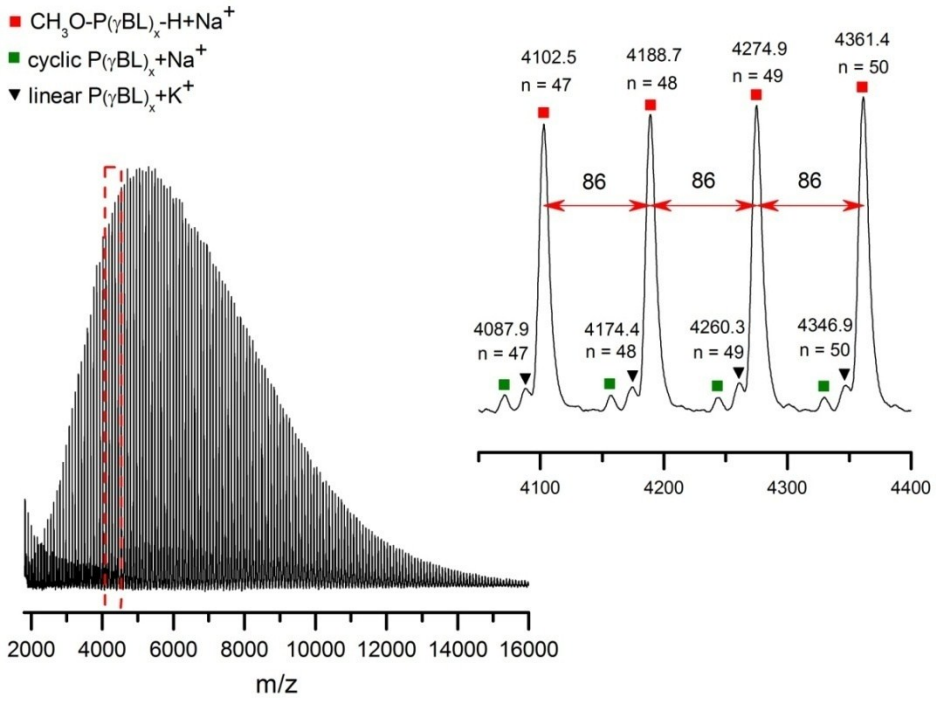

Figure S3. MALDI-TOF mass spectrum of PγBL catalyzed with KOMe/U7 (Table 1, run 8). ■: linear PγBL with CH_3O/H chain ends, ■: cyclic PγBL with no chain ends, ▼: linear PγBL with acylated lactone/H chain ends.

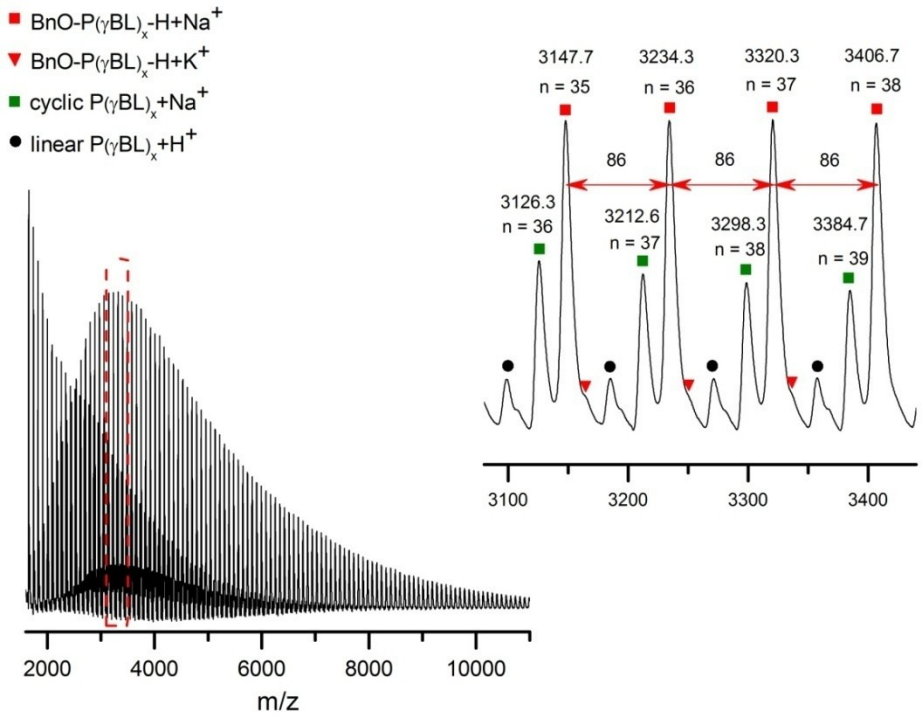

Figure S4. MALDI-TOF mass spectrum of PγBL catalyzed with CTPB alone (Table 1, run 11). ■ and ▼: linear PγBL with BnO/H chain ends, ■: cyclic PγBL with no chain ends, ●: linear PγBL with acylated lactone/H chain ends.

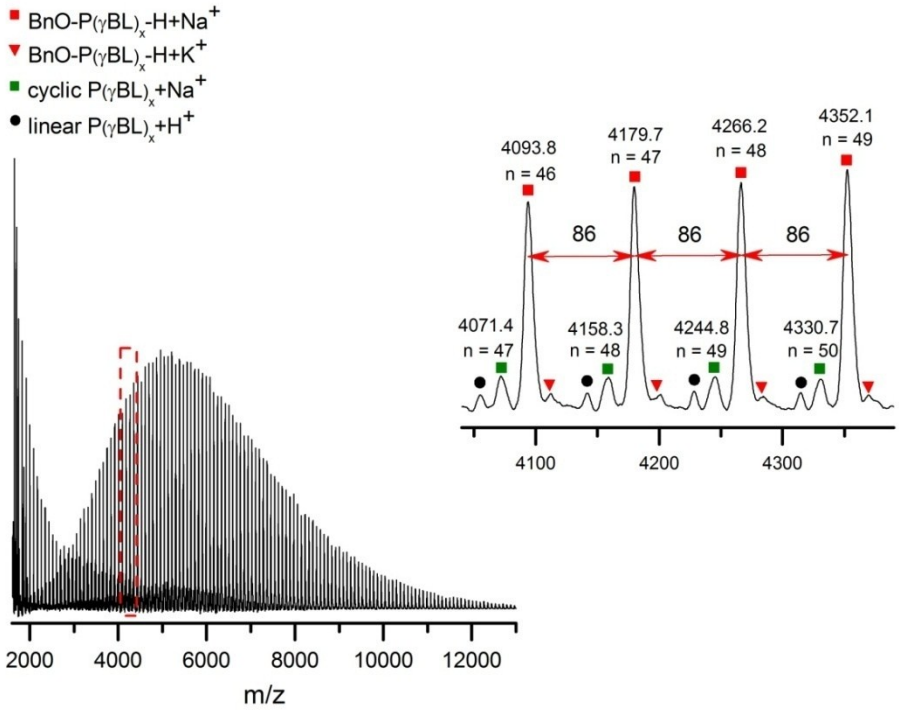

Figure S5. MALDI-TOF mass spectrum of PγBL catalyzed with γBL/CTPB/U6/BnOH = 1000/1/3/1 (Table 1, run 19). ■ and ▼: linear PγBL with BnO/H chain ends, ■: cyclic PγBL with no chain ends, ●: linear PγBL with acylated lactone/H chain ends.

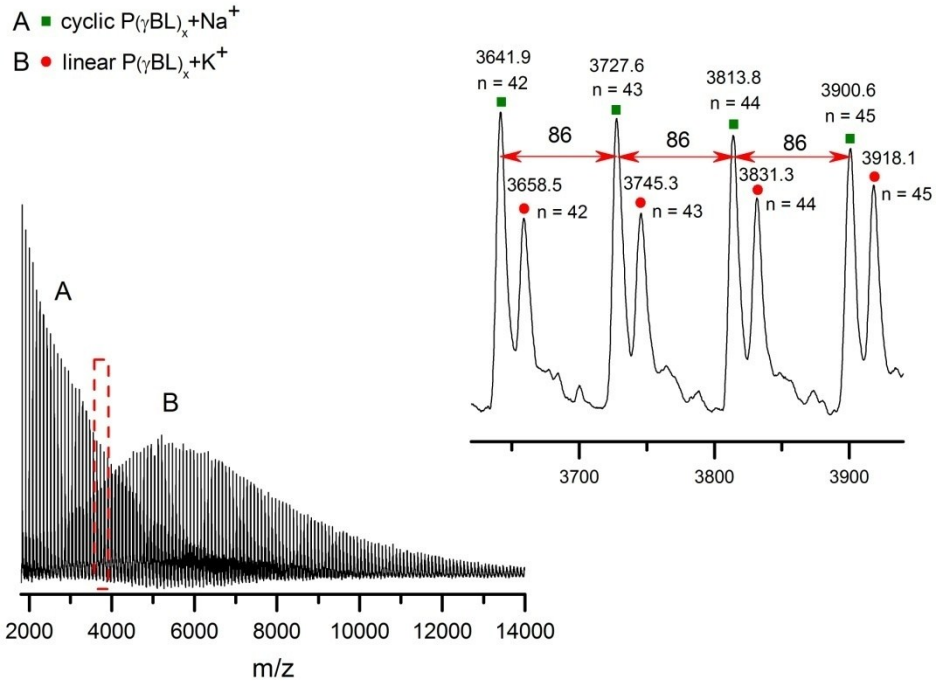

Figure S6. MALDI-TOF mass spectrum of PγBL catalyzed with γBL/CTPB/U6 = 300/1/3 (Table 1, run 22). Group A ■: cyclic PγBL with no chain ends, group B ●: linear PγBL with acylated lactone/H chain ends.

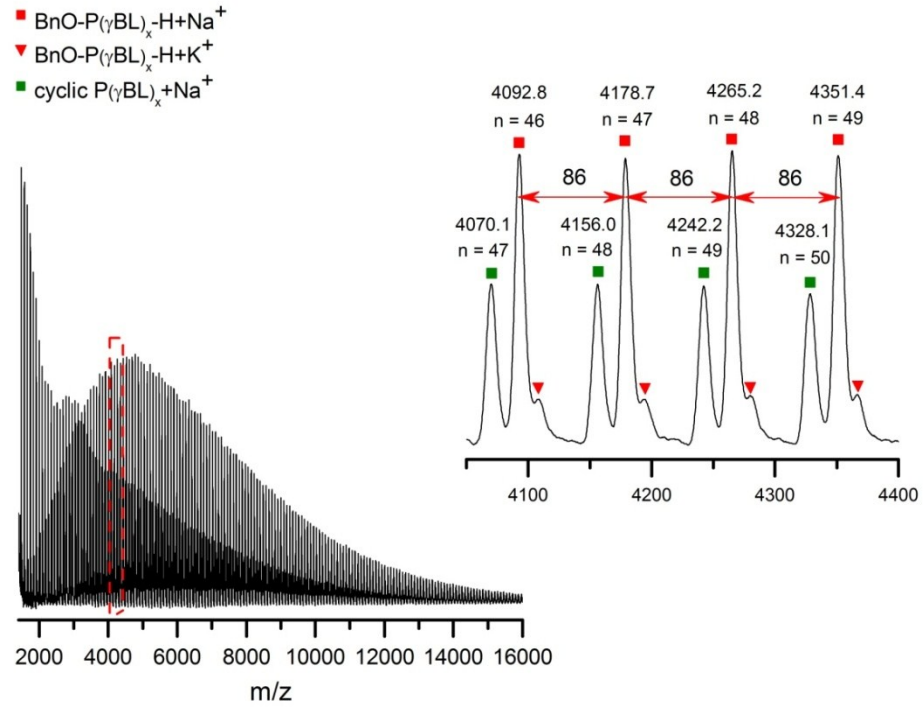

Figure S7. MALDI-TOF mass spectrum of PγBL catalyzed with γBL/CTPB/U6/BnOH = 300/1/3/1 (Table 1, run 12). ■ and ▼: linear PγBL with BnO/H chain ends, ■: cyclic PγBL with no chain ends.

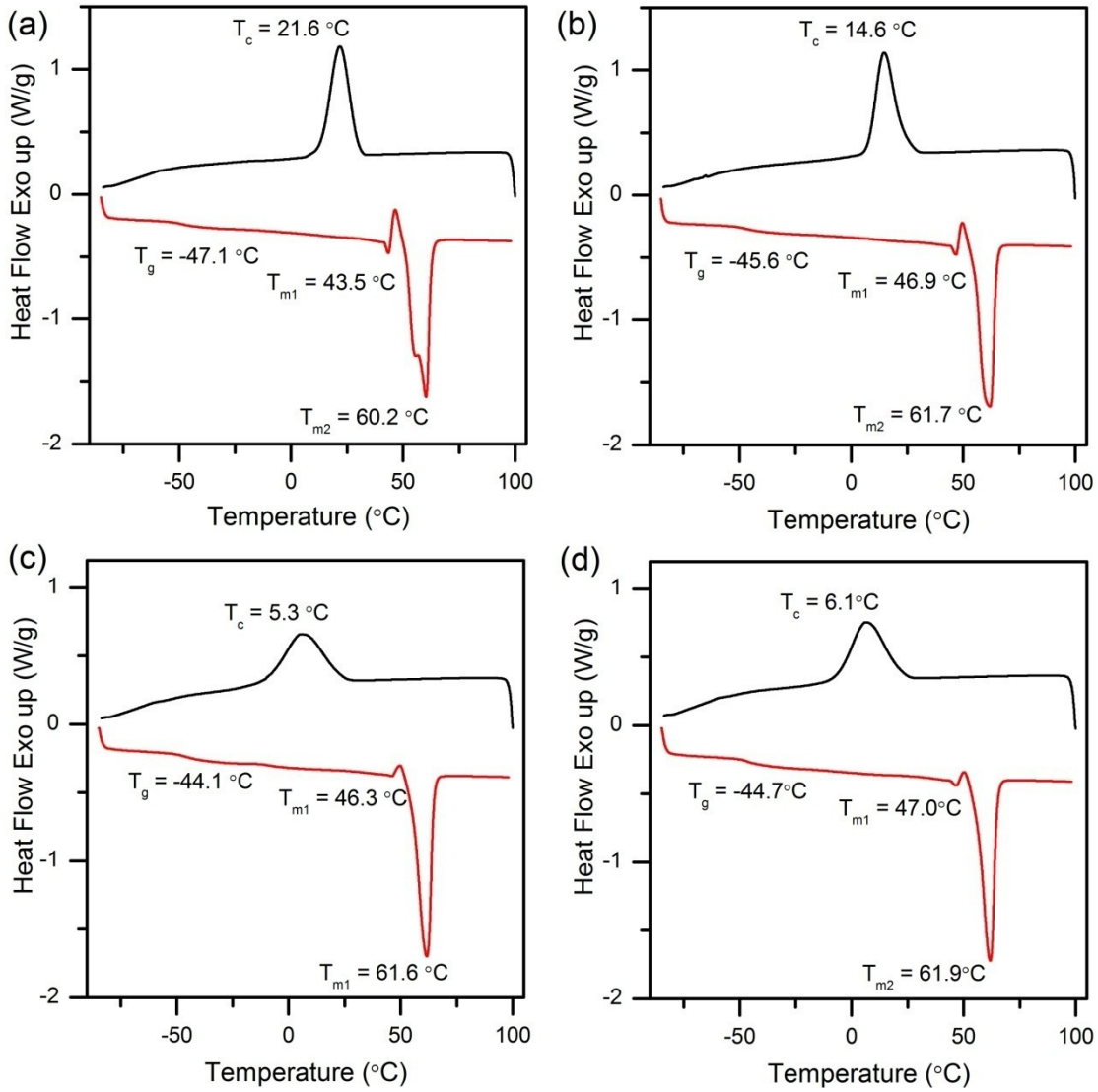

Figure S8. DSC curves of PγBL with varied molecular weights: (a) S1: 4.8 kDa, Đ=1.29, Table 1, run 6; (b) S2: 12.1 kDa, Đ=1.59, Table 1, run 8; (c) S3: 16.3 kDa, Đ=1.80, Table 1, run 12; (d) S4: 23.3 kDa, Đ=1.75, Table 1, run 20. Black line: cooling scans, red lines: second heating scans.

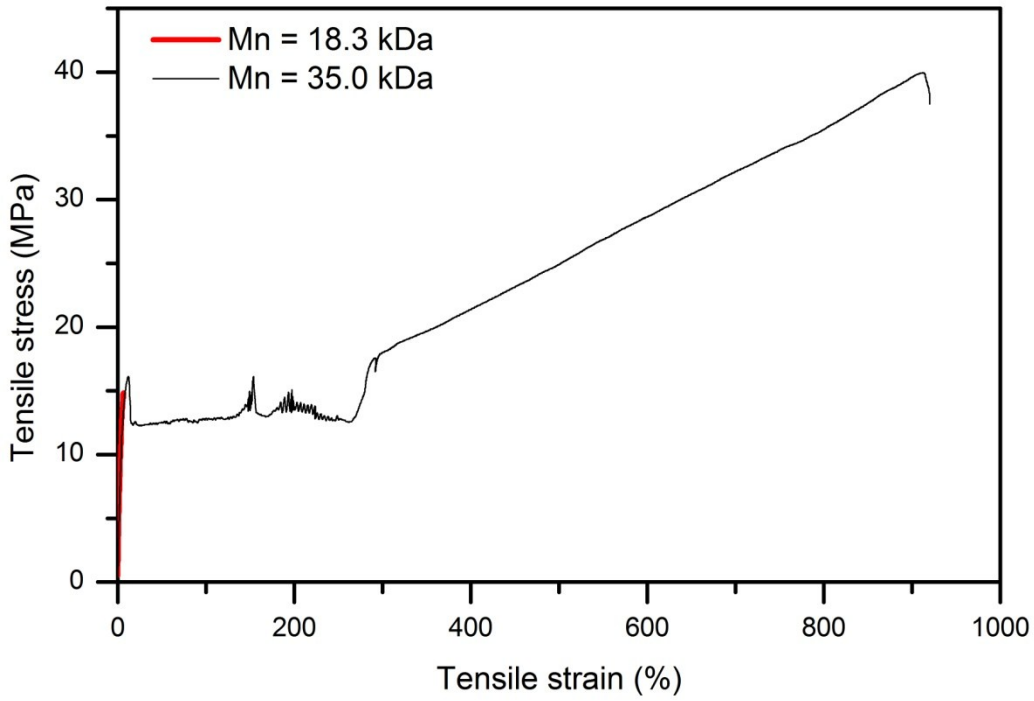

Figure S9. Stress-strain curve of PγBL with a M_n of 18.5 kDa (red line) and a M_n of 35.0 kDa (black line), respectively.

References

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