Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthetic Approach to Tailored Physical Associations in Peptide-Polyurea/Polyurethane Hybrids

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Table S1. Summary of relative PU and PUU components. #Molecular weight obtained from: *[1]H NMR, and ×Multi-angle light scattering (MALS). MALS was performed in a DMF solution with 0.05 M LiBr on an 18 angle Dawn Heleos II with Wyatt detector. Polarizability (dn/dc) was collected for Z20-20 (PU) (0.048 ml/g) and Z20-40 (PU) (0.078 ml/g) using variable concentrations.

Table 1 Sample	Peptide wt%	HS wt%	Modified HS wt%	PEG wt%	M_w (kg/mol)
Z20-PEG-Z20	76	0	0	24	13.9*
PEG-HDI (PU)	0	5	5	95	
Z20-20 (PU)	20	4	24	76	127.3×
Z20-40 (PU)	40	3	43	57	104.5×
Z20-60 (PU)	60	2	62	38	
PEG-HDO-BDO (PUU)	0	33	33	67	
Z20-25 (PUU)	25	33	57	43	
Z20-36 (PUU)	36	33	65	35	
Z20-50 (PUU)	50	33	84	16	

Equation S1. Modified hard segment content for PU samples.

$$\text{wt(\%) HS}_m = \frac{M_{DI} + M_{PZLY}}{M_{DI} + M_{PZLY} + M_{PEG}}$$

Equation S2. Modified hard segment content for PUU samples

$$\text{wt(\%) HS}_m = \frac{(n+1)M_{DI} + nM_{BDO} + M_{PZLY}}{(n+1)M_{DI} + nM_{BDO} + M_{PZLY} + M_{PEG}}$$

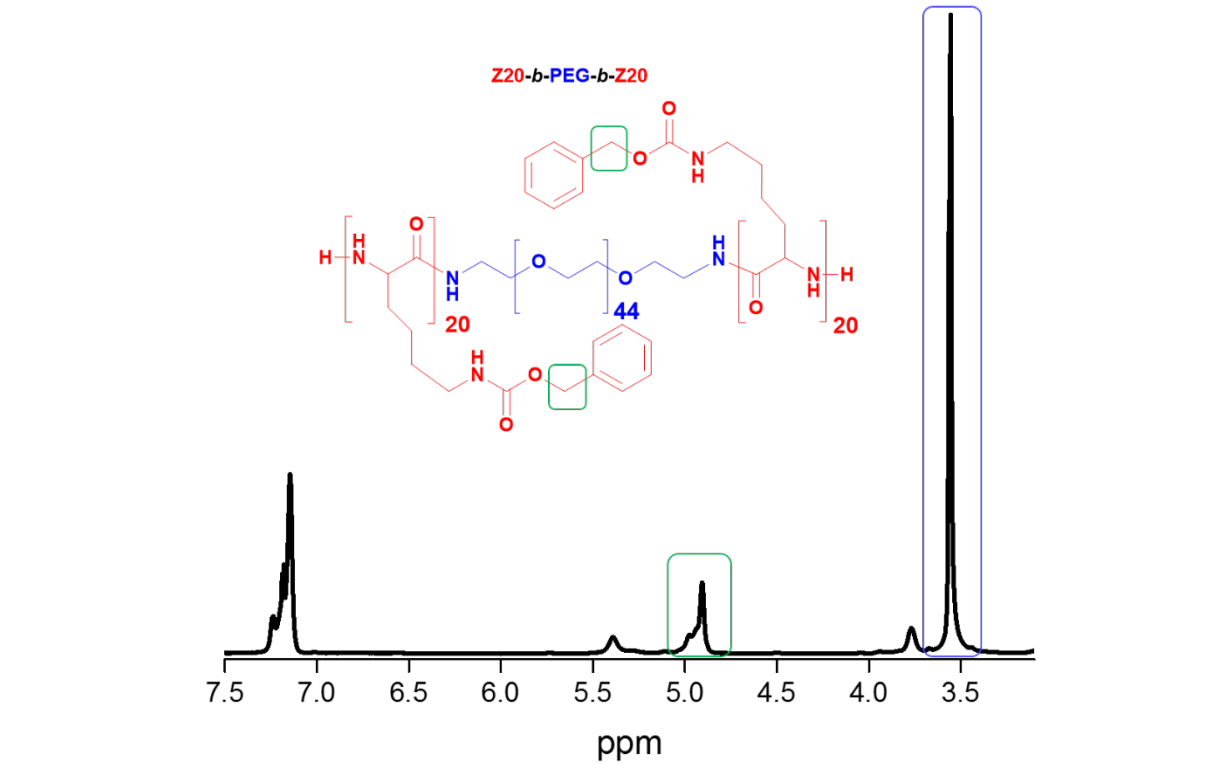

Figure S1. ^{1}H NMR recorded in CDCl3 (δ 7.26), of Z20-*b*-PEG-*b*-Z20 triblock with relative integrations used in the calculation of molecular weight. Integration of the peak at δ 3.6 (m, 308H) representing the PEG backbone is compared to the peak at δ 4.9 (m, 80H) to confirm the number of ZLY units present.

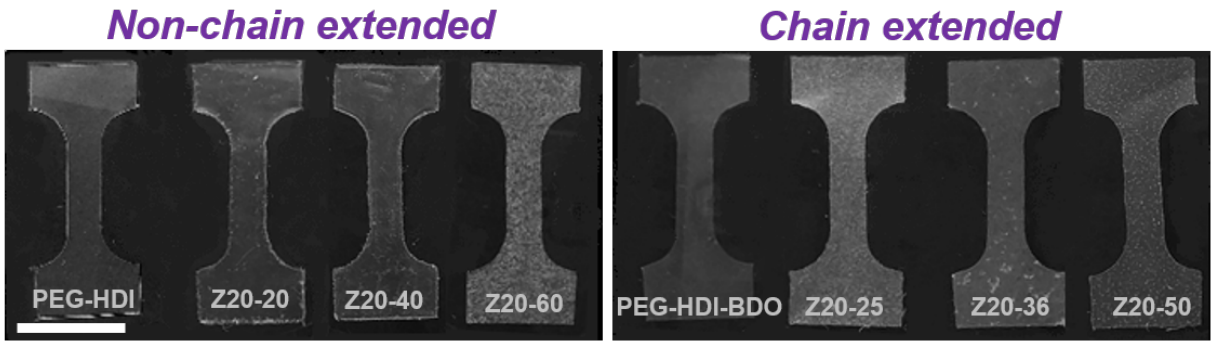

Figure S2. Dogbone films of PUs and PUUs. Films range in appearance from clear/colorless (PEG-HDI, PEG-HDI-BDO) to white/opaque (Z20-60 (PU), Z20-25 (PUU)). Scale bar is 1 cm.

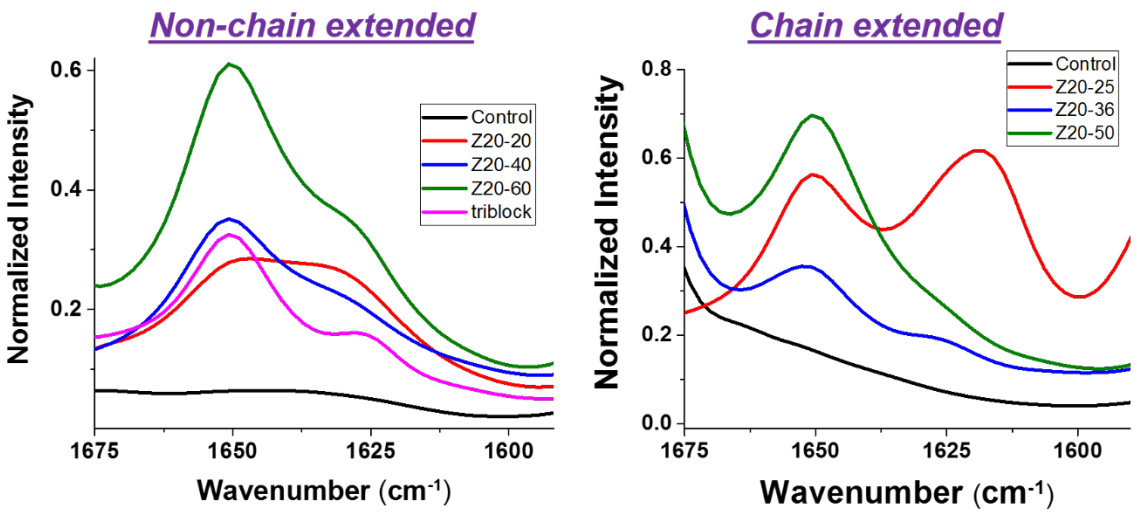

Figure S3. ATR-FTIR analysis of the carbonyl region for PZLY PUs and PUUs.

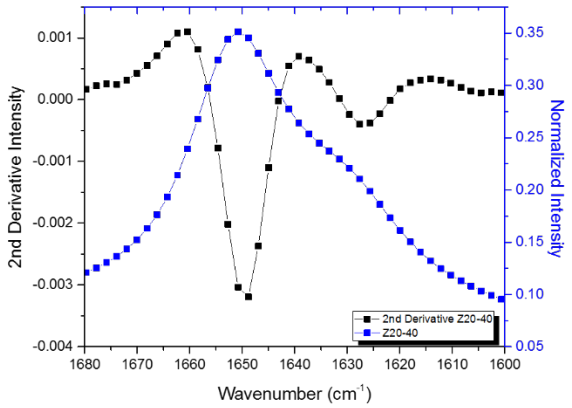

Figure S4. A demonstration of the neat ATR-FTIR spectra and 2nd derivative spectra of a Z20-40 (PU) film. As shown, the 2nd derivative allows separation of the β-sheet (1625 cm^{-1}) and α-helical (1650 cm^{-1}) peaks. The 2nd derivative spectrum is used to obtain the Gaussian fit parameters (peak width and peak position). These parameters are then used to fit the unmodified ATR-FTIR spectrum and calculate the peak area. Comparison of the peak areas provides the relative amounts of each secondary structure.

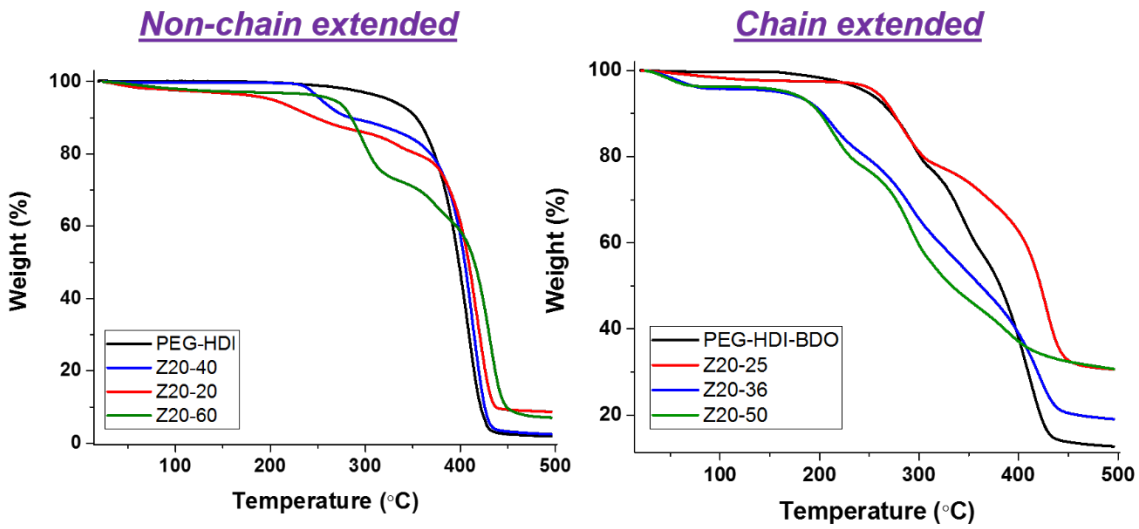

Figure S5. Thermogravimetric analysis of PUs and PUUs to determine degradation upon heating in a N_2 atmosphere at 10 °C/min. Degradation was apparent at 200 °C with onset temperatures ranging from 175 - 250 °C. In the PU control, only one degradation temperature is observed. Upon addition of PZLY, two degradation points are seen with the first degradation temperature attributed to peptide degradation and the second degradation temperature is related to decomposition of the urea bond. An additional degradation region is shown for the PUUs, which is correlated to urethane linkages from the BDO chain extension.

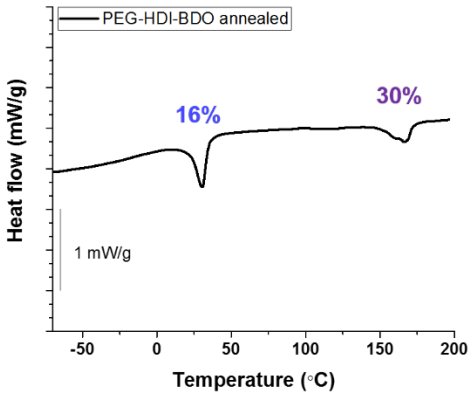

Figure S6. DSC of a control PEG-HDI-BDO film annealed for 2 hours at 100 °C. Hard segment endotherm (exotherm up) increased in crystallinity slightly from 26% (**Figure 3**) to 30%; however, the PEG crystallinity has decreased from 23% to 16% (**Figure 3**). Annealing would aid in better homogeneity of the hard block, promoting one hard segment T_m transition vs. multple hard block peaks seen in **Figure 3**. However, the overall phase separation post-annealing does not significantly improve.

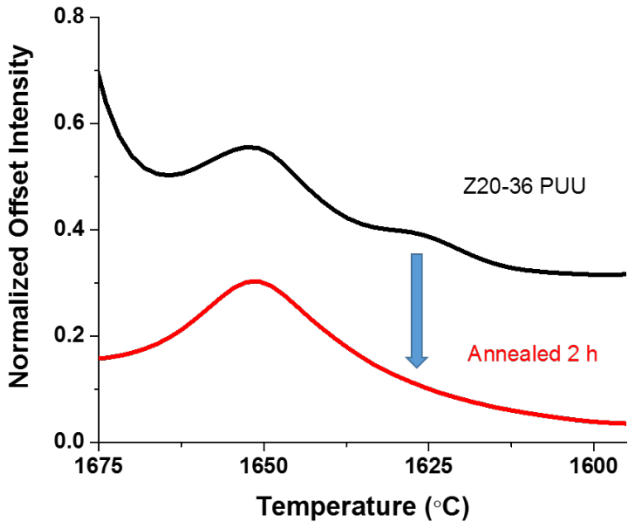

Figure S7. Reduction of β-sheet formation in Z20-36 PUU upon annealing at 100 °C for 2 h.

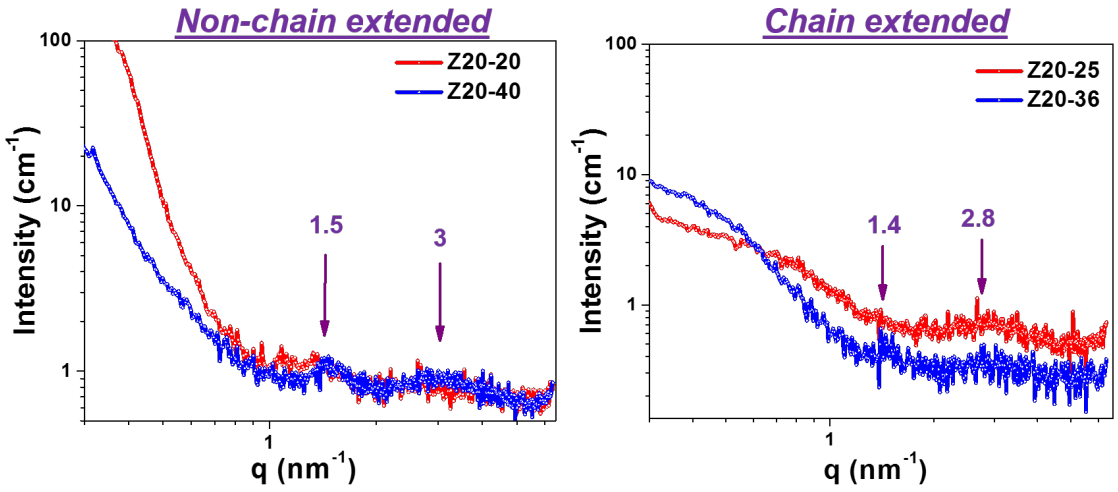

Figure S8. Zoomed in spectra of PZLY-PUs and PZLY-PUUs that highlight long-range ordering. Labeled are the reflection positions representing the appearance of a superstructure.