Electronic Supplementary Information

Emulsion-Templated Synthetic Polypeptide Scaffolds prepared by Ring-Opening Polymerization of *N*-Carboxyanhydrides

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<u>γ-Benzyl-L-glutamate *N*-carboxyanhydride (BLG NCA)</u>

^{1}H NMR (DMSO-d_6): δ = 2.02 (m, 2H, C**H**$_2$), 2.49 (m, 2H, C**H**$_2$), 4.48 (ddd, J_1 = 7.8 Hz, J_2 = 5.5 Hz, J_3 = 1.1 Hz, 1H, C**H**), 5.11 (s, 2H, benzyl C**H**$_2$), 7.37 (m, 5H, aryl C**H**), 9.11 (s, 1H, N**H**)

^{13}C NMR (DMSO-d_6): δ = 26.41 (C**H**$_2$), 29.07 (C**H**$_2$), 56.19 (C**H**), 65.70 (benzyl C**H**$_2$), 127.97 (aryl C**H**), 128.04 (aryl C**H**), 128.43 (aryl C**H**), 136.00 (aryl **C**), 151.84 (C**O**), 171.30 (C**O**), 171.68 (C**O**)
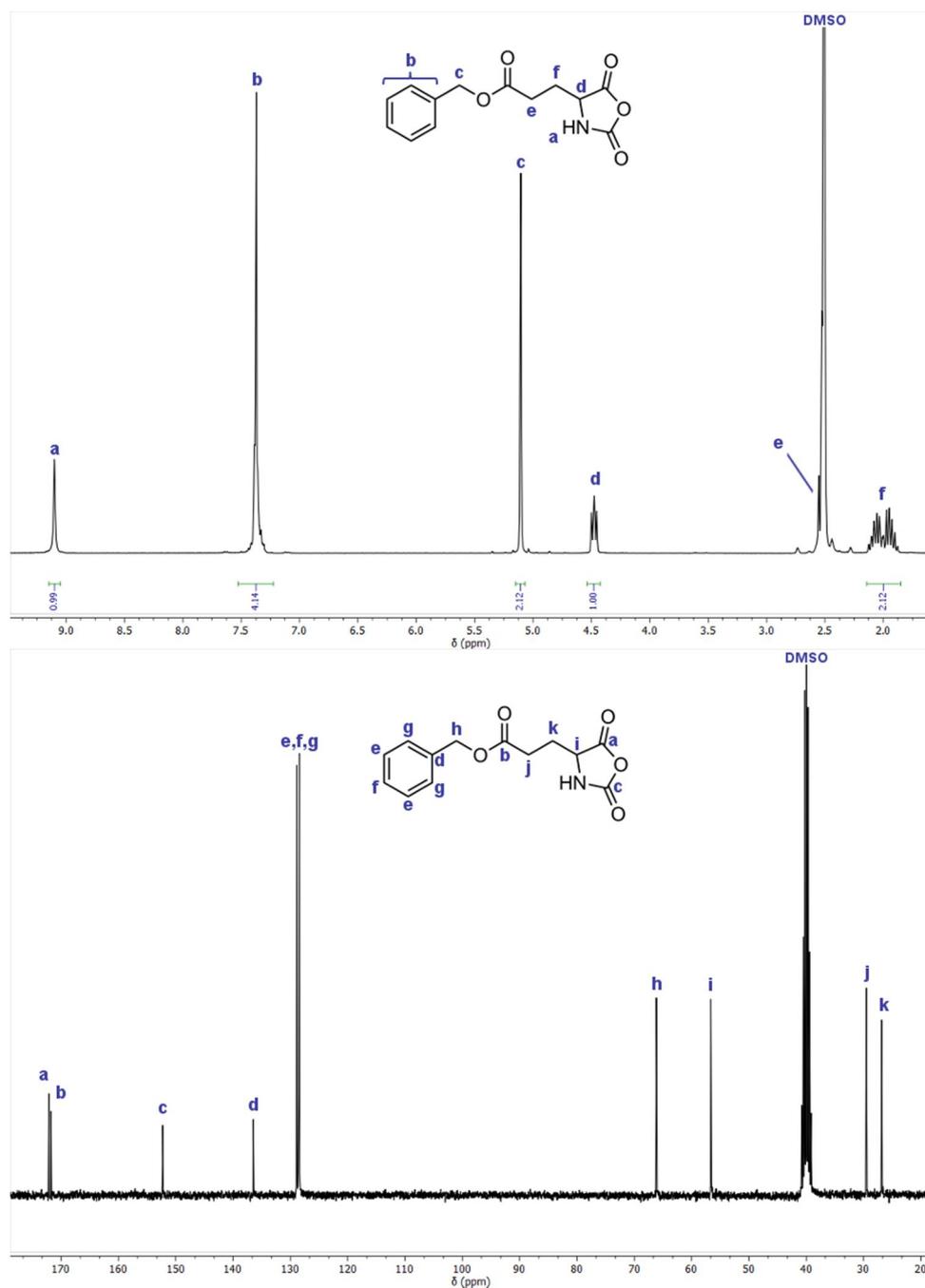
Fig. S1 (Top) ^{1}H and (bottom) ^{13}C NMR spectra of BLG NCA with signal assignation.

<u>L</u>-cystine di-*N*-carboxyanhydride (<u>L</u>-cystine NCA)

^{1}H NMR (DMSO-d_6): δ = 3.22 (m, 4H, **CH₂**), 4.79 (ddd, J_1 = 6.6 Hz, J_2 = 4.4 Hz, J_3 = 1.3 Hz, 2H, **CH**), 9.26 (s, 2H, **NH**)

^{13}C NMR (DMSO-d_6): δ = 38.99 (**CH₂**), 56.60 (**CH**), 151.69 (**CO**), 170.03 (**CO**)
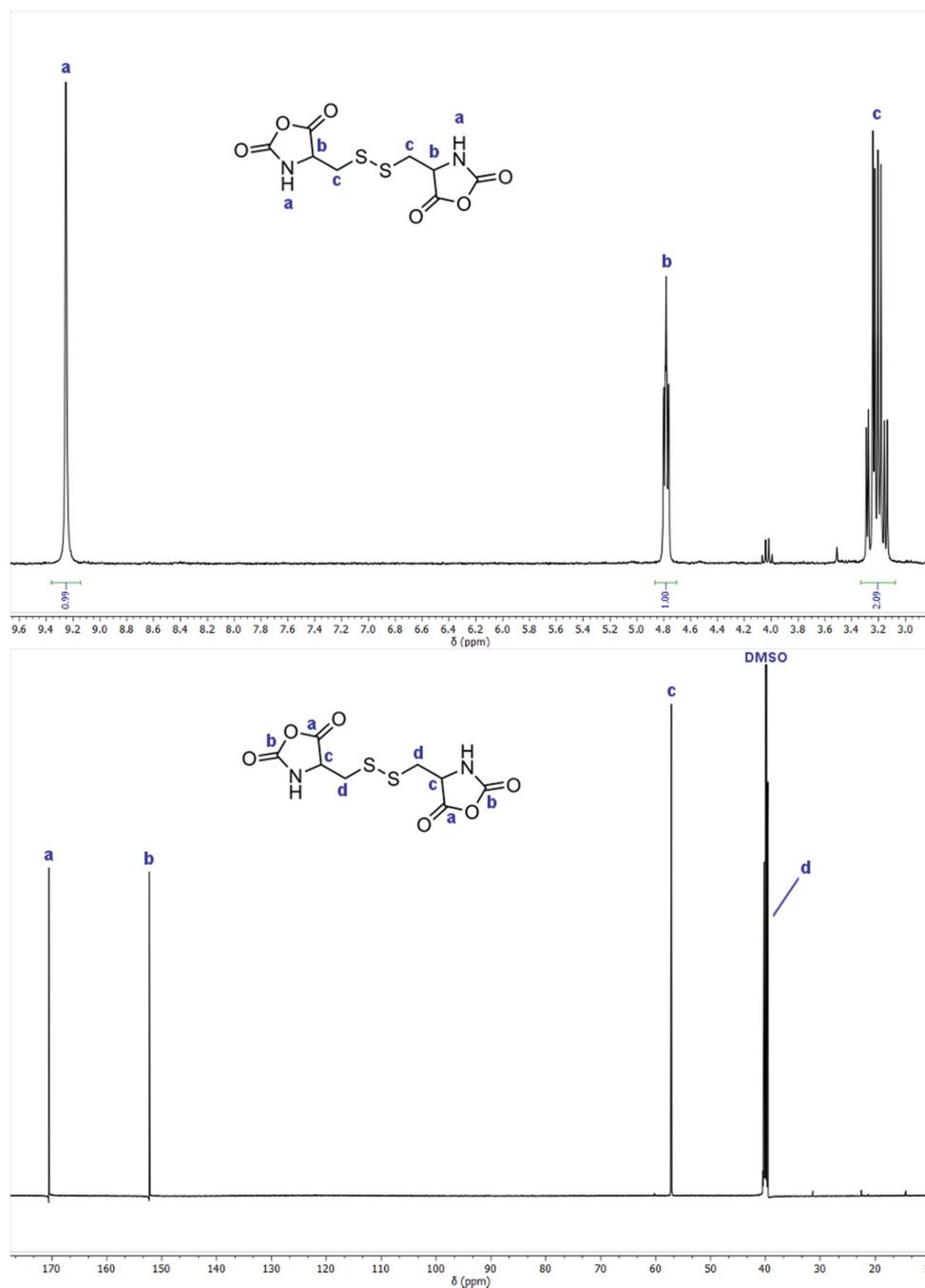
Fig. S2 (Top) ^{1}H and (bottom) ^{13}C NMR spectra of <u>L</u>-cystine NCA with signal assignation.

<u>N^ε-carbobenzyloxy-L-lysine N-carboxyanhdride (ZLL NCA)</u>

^{1}H NMR (DMSO-d_6): δ = 1.38 (m, 4H, **CH₂**), 1.70 (m, 2H, **CH₂**), 3.00 (q, J = 6.1 Hz, 2H, **CH₂**), 4.43 (ddd, J_1 = 6.5 Hz, J_2 = 5.2 Hz, J_3 = 1.1 Hz, 1H, **CH**), 5.01 (s, 2H, benzyl **CH₂**), 7.35 (t, 1H, N**H**), 7.34 (m, 5H, aryl **CH**), 9.08 (s, 1H, N**H**)

^{13}C NMR (DMSO-d_6): δ = 21.51 (**CH₂**), 28.68 (**CH₂**), 30.54 (**CH₂**), 39.83 (**CH₂**), 56.91 (**CH**), 65.03 (benzyl **CH₂**), 127.63 (aryl **CH**), 127.65 (aryl **CH**), 128.25 (aryl **CH**), 137.17 (aryl **C**), 151.88 (**CO**), 156.00 (**CO**), 171.56 (**CO**)
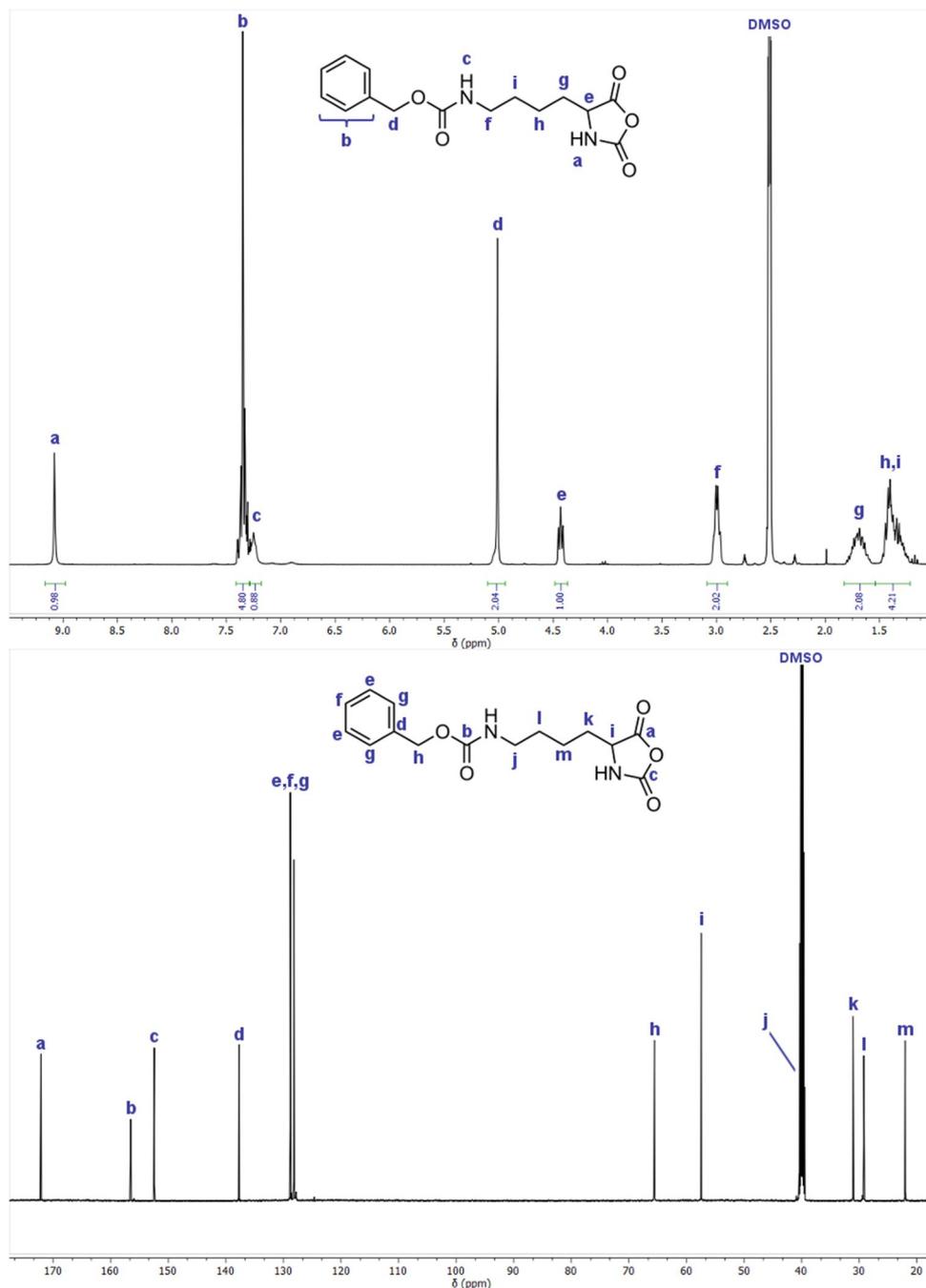
Fig. S3 (Top) ^{1}H and (bottom) ^{13}C NMR spectra of ZLL NCA with signal assignation.

Methylated Pluronic F-127 (F127-OMe)

^{1}H NMR (CDCl$_3$): δ = 1.08-1.18 (m, PPO C**H**$_3$), 3.38 (s, 3H, OC**H**$_3$), 3.30-3.61 (m, PPO C**H**, C**H**$_2$), 3.61-3.72 (m, PEO C**H**$_2$)
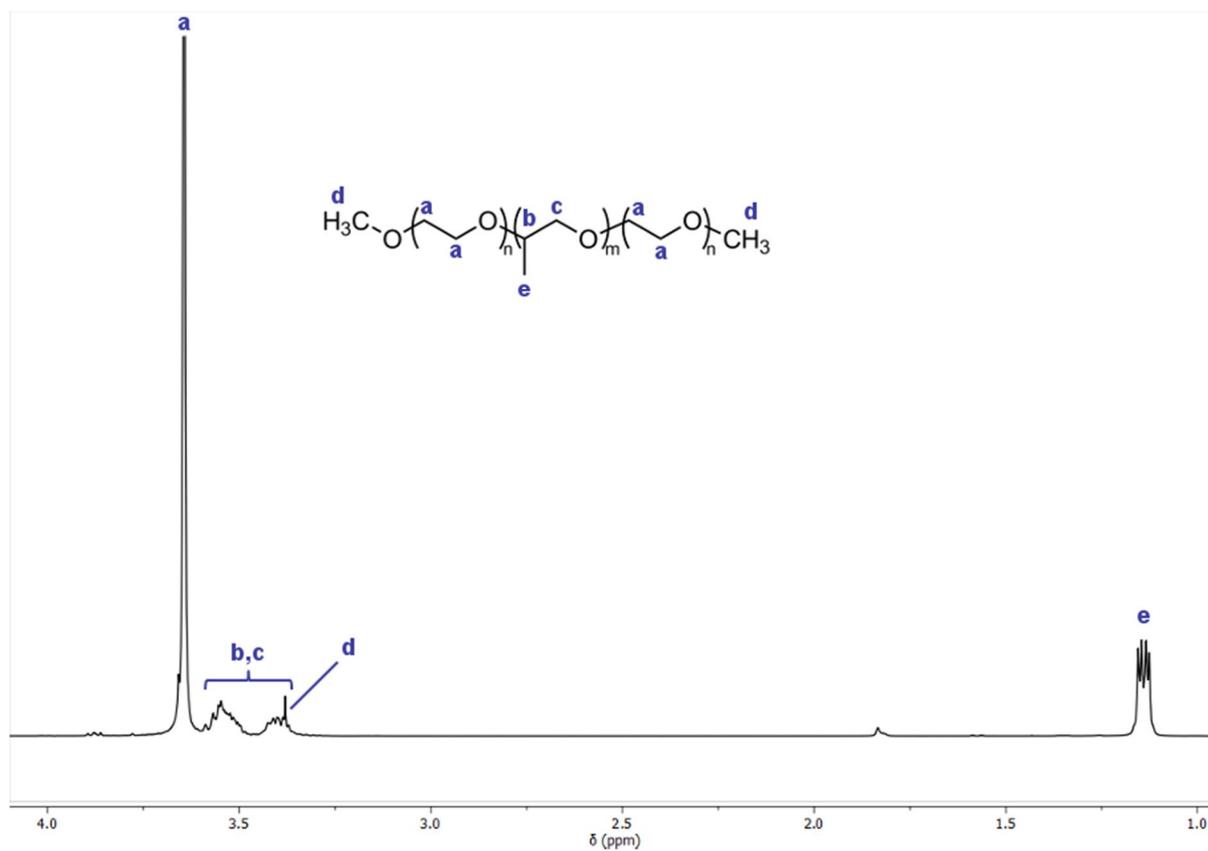
Fig. S4 ^{1}H NMR spectrum of Pluronic F127-OMe with signal assignation.

Table S1 Chemical composition of HIPEs used for the preparation of polyHIPEs.

	PBLG 80-10	PBLG 80-3	PBLG 85-3	PZLL 80-5.5	P(BLG-*co*-ZLL) 80-5
External phase, wt%					
DMF	20.86	21.34	16.76	20.18	20.99
BLG NCA	11.05	11.31	8.88	-	5.56
ZLL NCA	-	-	-	14.93	6.47
L-Cystine NCA	0.65	0.66	0.52	0.75	0.65
F127-OMe	3.26	1.00	0.78	1.97	1.68
DIPEA	0.03	0.03	0.02	0.10	0.06
Internal phase, wt%					
Petroleum benzine	64.16	65.66	73.04	62.07	64.58

Linear PBLG and PZLL

0.5 M solutions of BLG NCA and ZLL NCA in DMF were prepared and polymerized by the addition of 0.5 mol% DIPEA at room temperature for 24 hours. The full consumption of the monomer was confirmed by ^{1}H NMR. Polymer solutions were precipitated into 5.0 wt% aqueous NaCl solution. Filtered products were washed with distilled water, and dried in a desiccator until a constant weight was reached.

Polymerization kinetic study monitored by ^{1}H NMR

2.0 M solutions of BLG NCA and ZLL NCA in DMF were prepared and polymerized by the addition of 0.5 mol% DIPEA at room temperature. The aliquots were taken after 5 minutes, quenched with acetic acid-d_4, then diluted with DMSO-d_6, and immediately analyzed by ^{1}H NMR.

Vial inversion test

To observe the gelation of PZLL and PBLG polymers without the L-cystine crosslinker, the vial inversion tests of PBLG 80-3* and PZLL 80-5.5* HIPEs were performed. A vial containing the HIPE with added catalyst was turned upside-down after polymerizing for 15 min, 1 h, 24 h, 48 h, and 72 h. The PBLG HIPE stopped flowing after 15 min indicating the gelation. No gelation occurred in PZLL HIPE and it became extensively phase separated after 3 days with both phases still remaining liquid.

Fig. S5 Vial inversion of PZLL 80-5.5* (left) and PBLG 80-3* (right), both without the L-cystine crosslinker, after 72 h of polymerization.
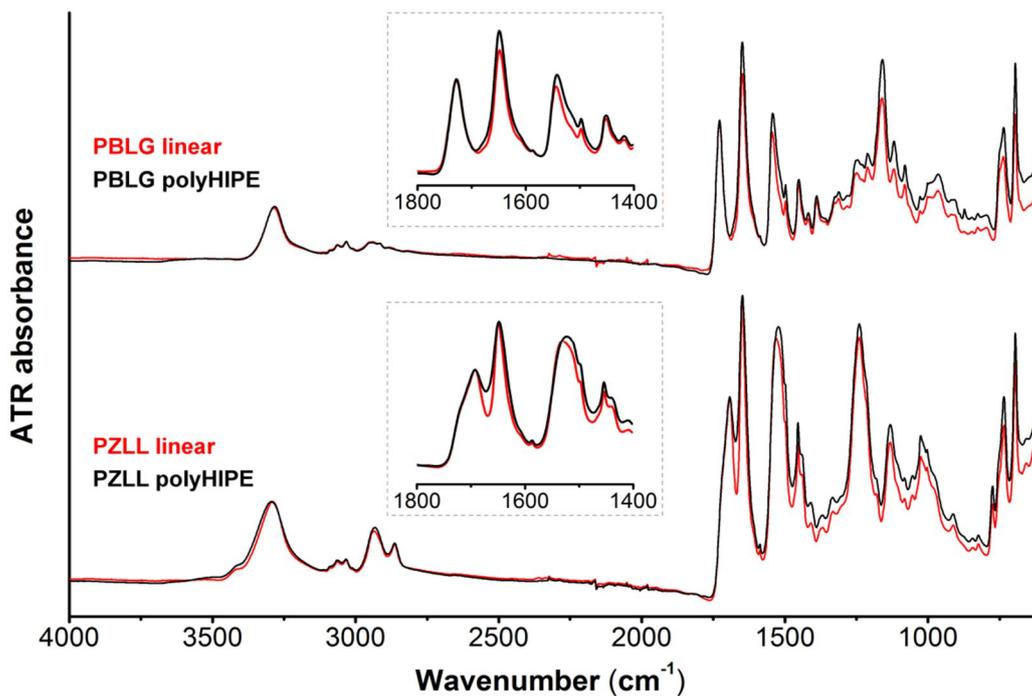
Fig. S6 Overlay of the FTIR spectra of (top) linear PBLG and PBLG 80-3 polyHIPE and (bottom) linear PZLL and PZLL 80-5.5 polyHIPE. The enlarged spectra show the carbonyl region, where no notable changes in the amide I and amide III bands are observed.
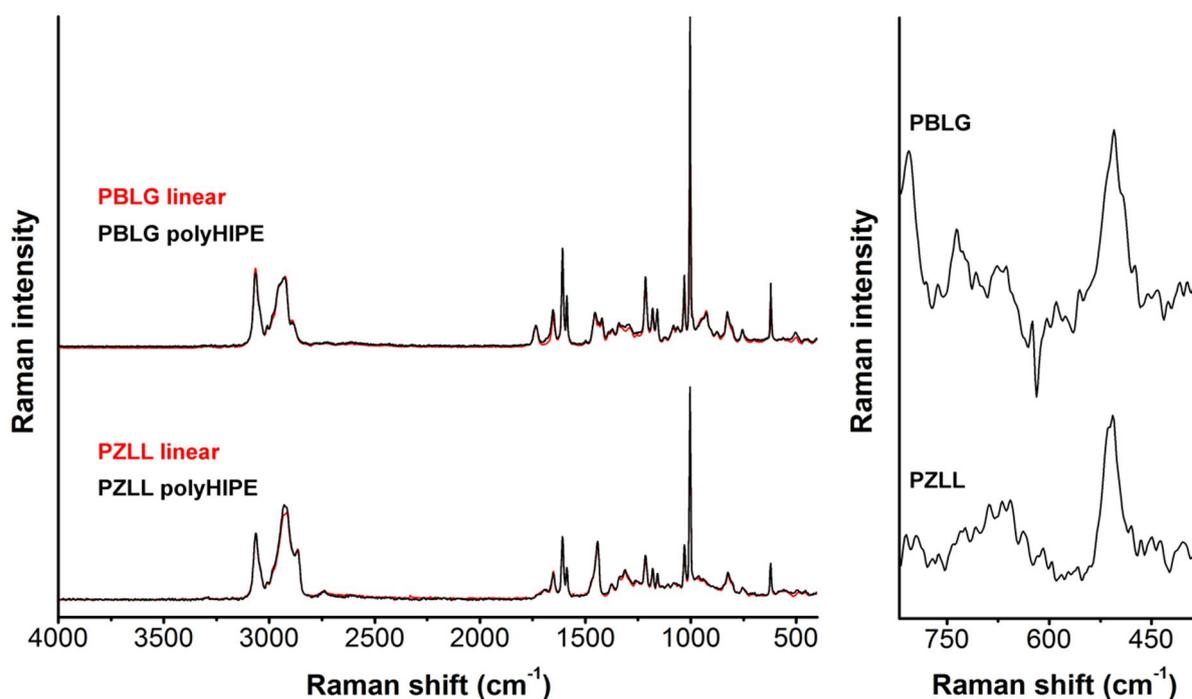
Fig. S7 (Left) Overlay of the Raman spectra of (top) linear PBLG and PBLG 80-3 polyHIPE and (bottom) linear PZLL and PZLL 80-5.5 polyHIPE. (Right) The enlarged regions of differential Raman spectra (Raman spectrum of the linear sample was subtracted from the Raman spectrum of the corresponding polyHIPE) show the signal corresponding to the stretching vibration of the disulfide bond of the L-cystine crosslinker.
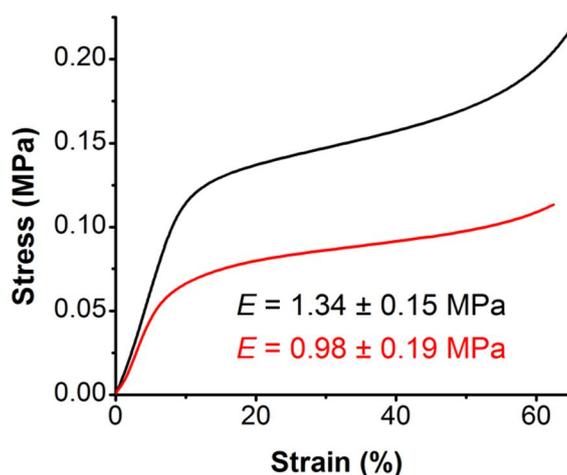
Fig. S8 Representative compressive stress-strain curves of polyHIPE PBLG 80-3 at 37 °C in dry state (black) and swollen in PBS (red). The average values of three in parallel measured samples and their standard errors are given.