Supplementary Information: Controlling Polymer Architecture to Design Dynamic Network Materials with Multiple Dynamic Linkers

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Determination of number average molecular weight (M_n) and composition by NMR

For typical PEA-UPyMA-FMA RAFT materials, peak at 3.36 ppm (PADTC-CH_2 at trithiocarbonate) was calibrated to 2H. Peaks centered at 5.0 ppm (FMA-furfuryl) was integrated and divided by 2 (2H from FMA) delivering the FMA units. The peaks near 3.20 ppm (UPyMA) were integrated and divided by 4 (2H from UPyMA urethane protons $\underline{CH_2}NHCOOCH_2$ and 2H from UPyMA urea protons $\underline{CH_2}NHCONH$) delivering the UPyMA units. The peak at 4.10 ppm was integrated, and the resulting integral at 4.1 ppm had the integral values of the peaks near 3.2 ppm subtracted (4H from UPyMA from CH_2 at UPyMA ester and CH_2 at UPyMA $NHCOO\underline{CH_2}$ urethane), and the remaining signal, divided by 2 (2H from EA CH_2 ester protons) delivering the EA units.

For the PEA-UPyMA-FMA FRP material, peak at 2.7 ppm (thioether R-S-$\underline{CH_2}$ from first added monomer) was calibrated to 2H. Peaks centered at 5.0 ppm (FMA-furfuryl) was integrated and divided by 2 (2H from FMA) delivering the FMA units. The peaks near 3.20 ppm (UPyMA) were integrated and divided by 4 (2H from UPyMA urethane protons $\underline{CH_2}NHCOOCH_2$ and 2H from UPyMA urea protons $\underline{CH_2}NHCONH$) delivering the UPyMA units. The peak at 4.10 ppm was integrated, and the resulting integral at 4.1 ppm had the integral values of the peaks near 3.2 ppm subtracted (4H from UPyMA from CH_2 at UPyMA ester and CH_2 at UPyMA $NHCOO\underline{CH_2}$ urethane), and the remaining signal, divided by 2 (2H from EA CH_2 ester protons) delivering the EA units.

M_n by NMR is typically calculated via multiplying monomer units by their respective molecular weights, a sum of the resulting values and the molecular weight of the chain transfer agent (PADTC or DDT) gives the experimental M_n value.

Supplemental Data:

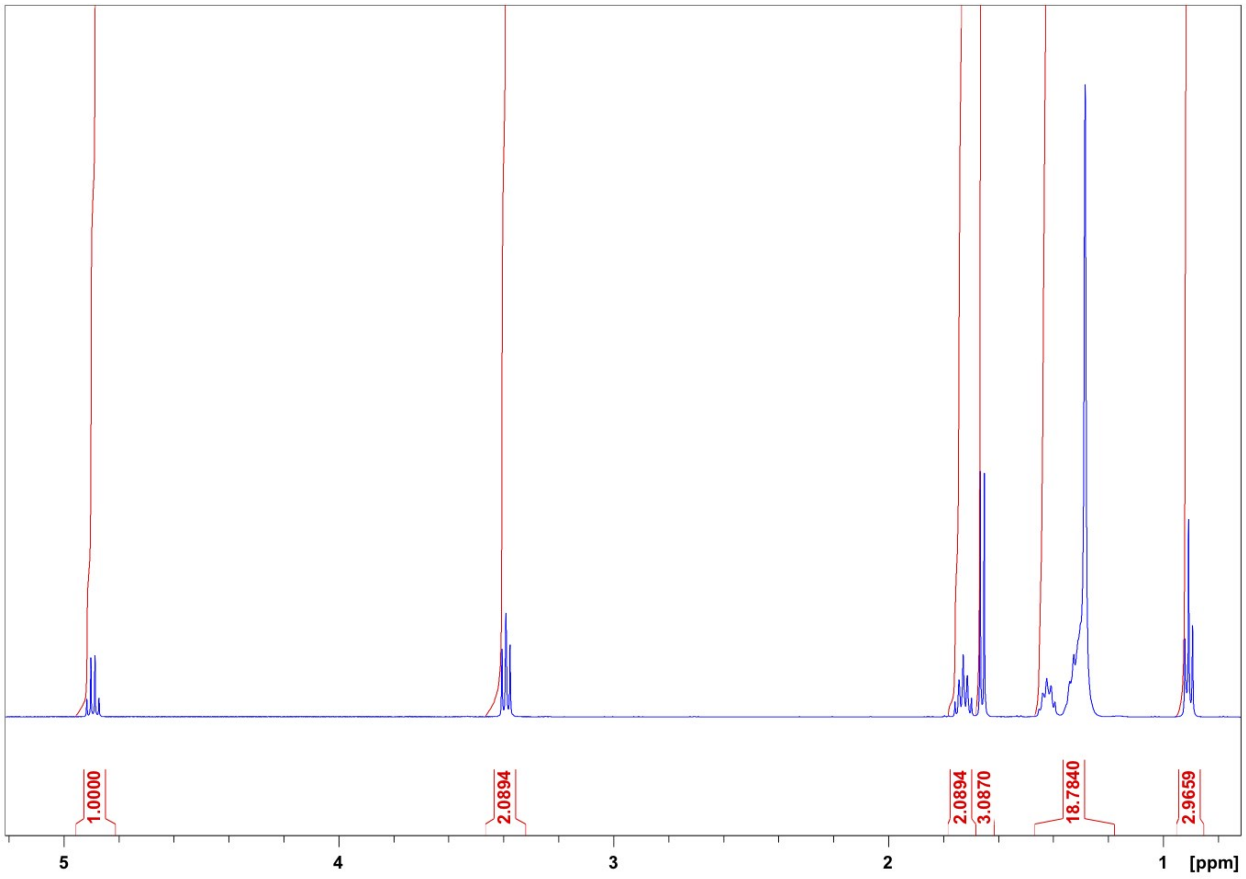

Figure S1: NMR spectrum of PADTC.

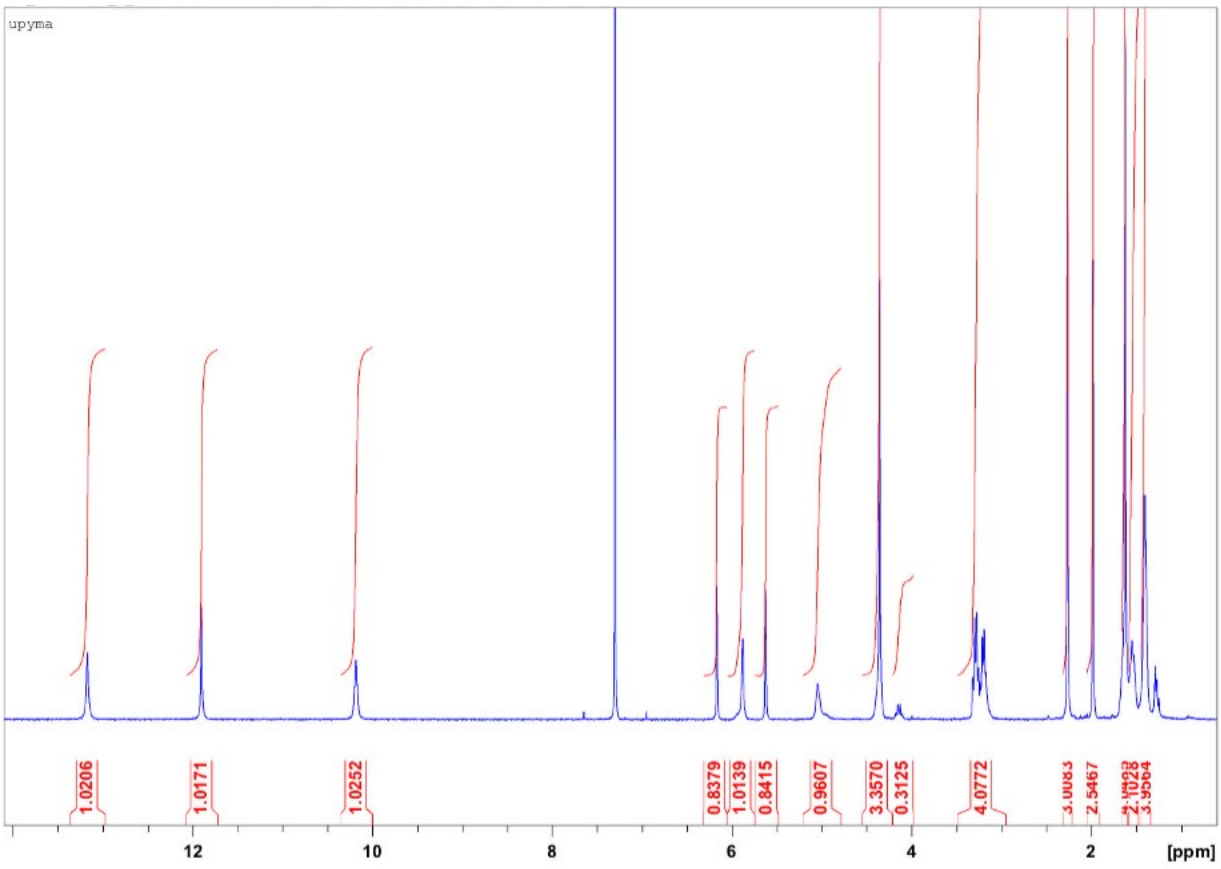

Figure S2: NMR spectrum of UPyMA.

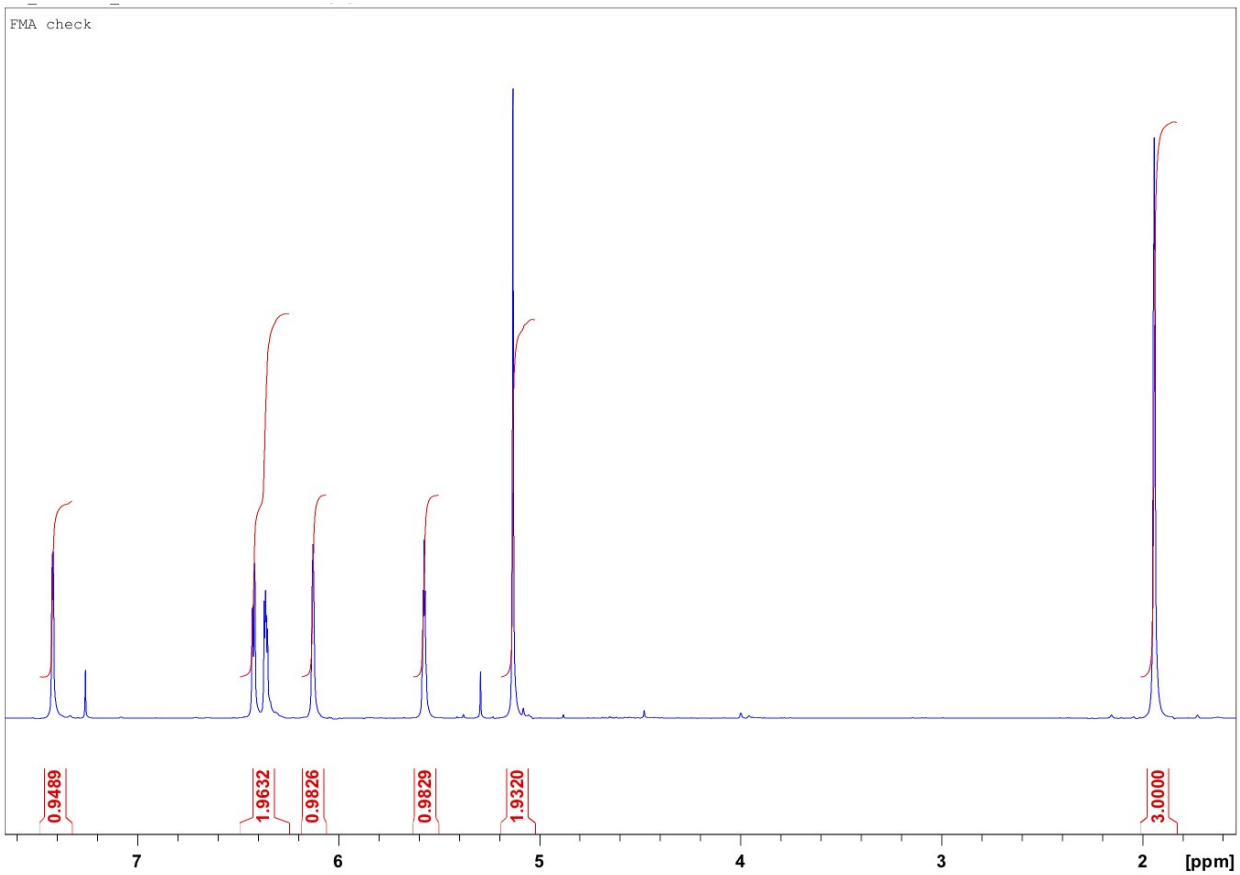

Figure S3: NMR Spectrum of FMA.

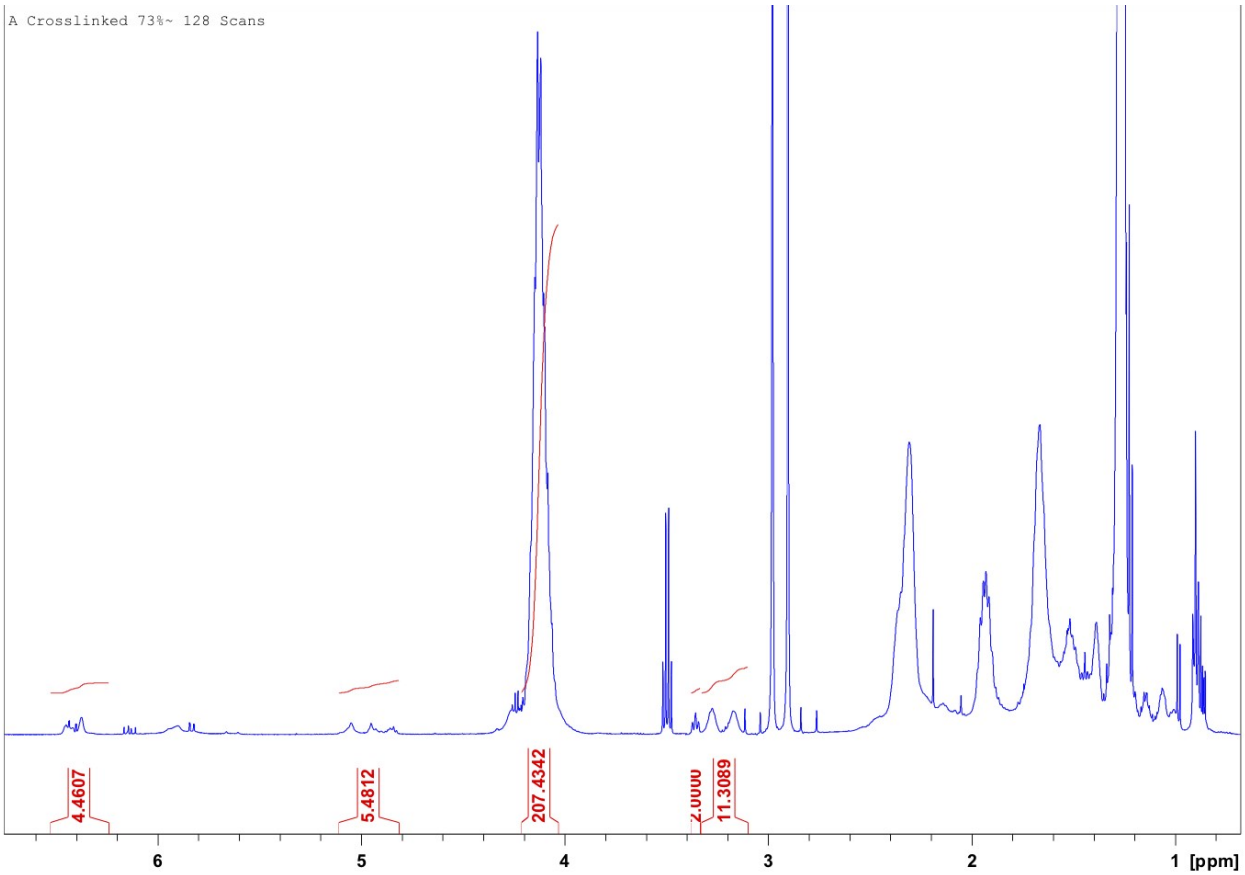

Figure S4: NMR Spectrum of PEA_{100}-$UPyMA_{2.5}$-$FMA_{2.5}$ made by RAFT

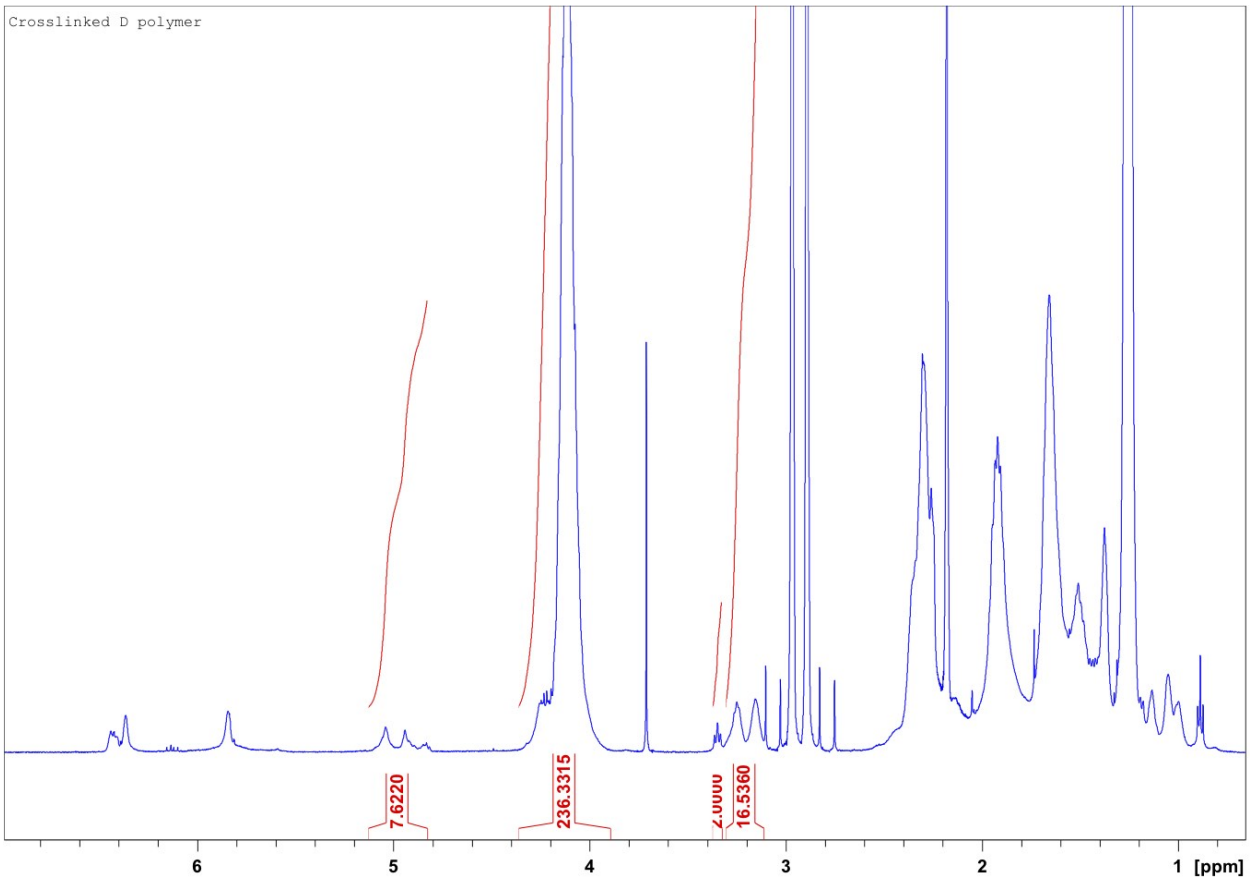

Figure S5: NMR Spectrum of PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$ made by RAFT

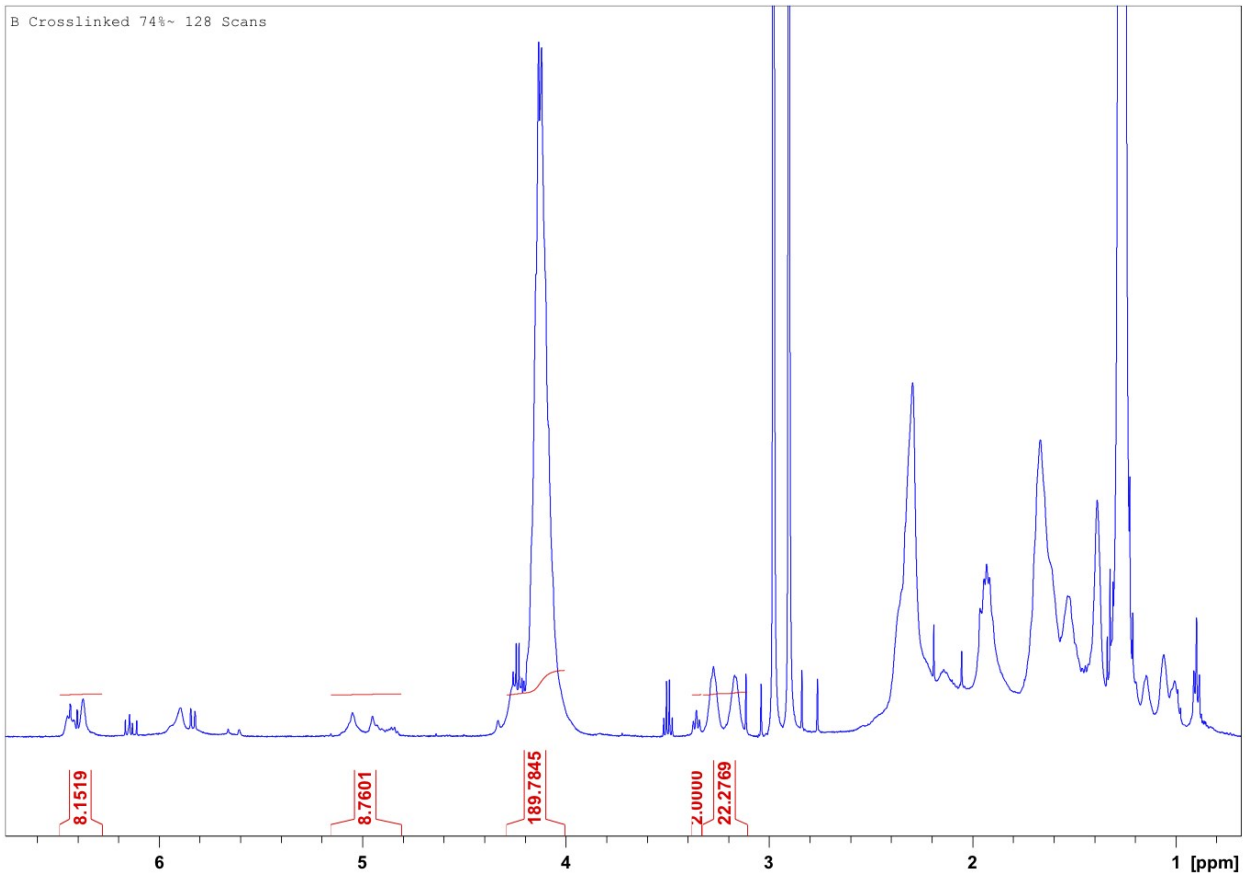

Figure S6: NMR Spectrum of PEA_{100}-$UPyMA_5$-FMA_5 made by RAFT

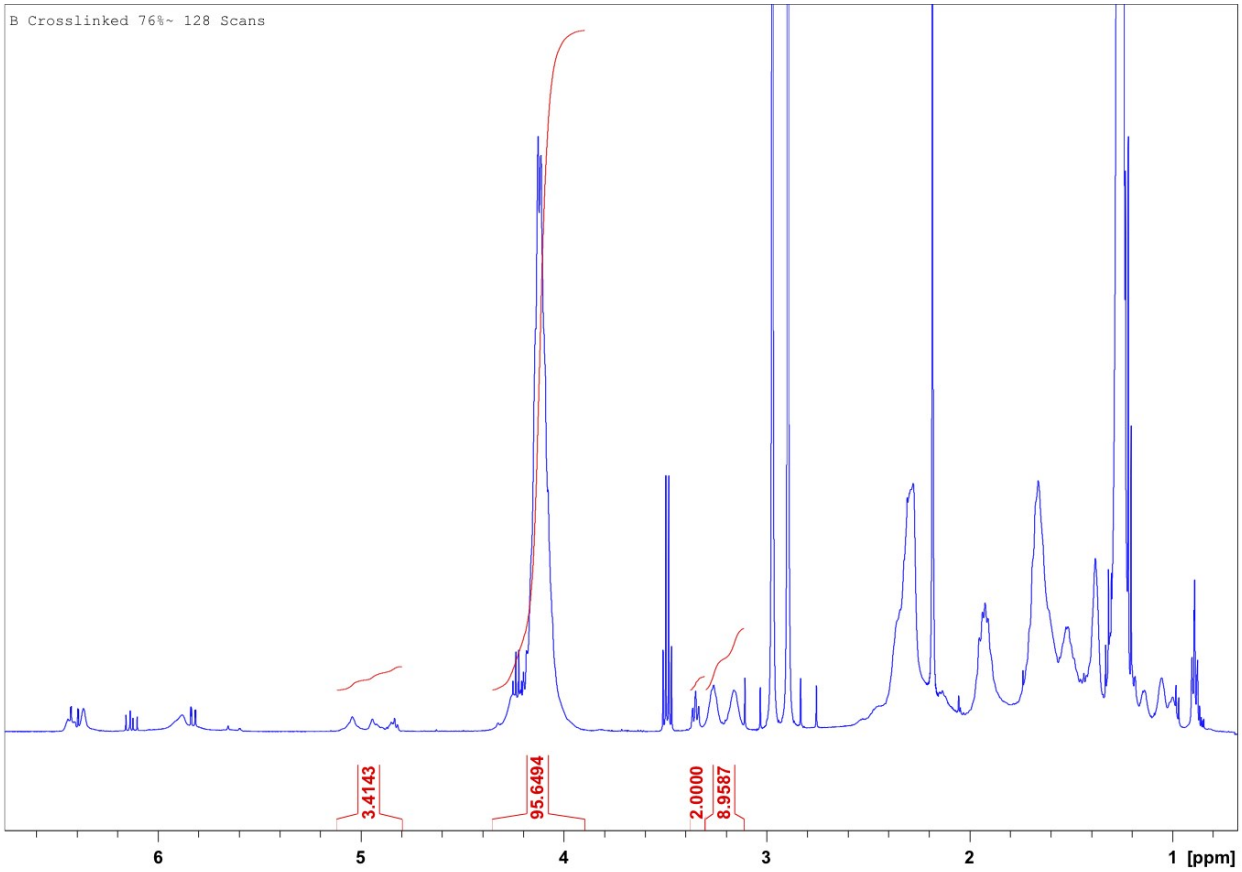

Figure S7: NMR Spectrum of PEA_{50}-$UPyMA_{1.9}$-$FMA_{1.9}$ made by RAFT

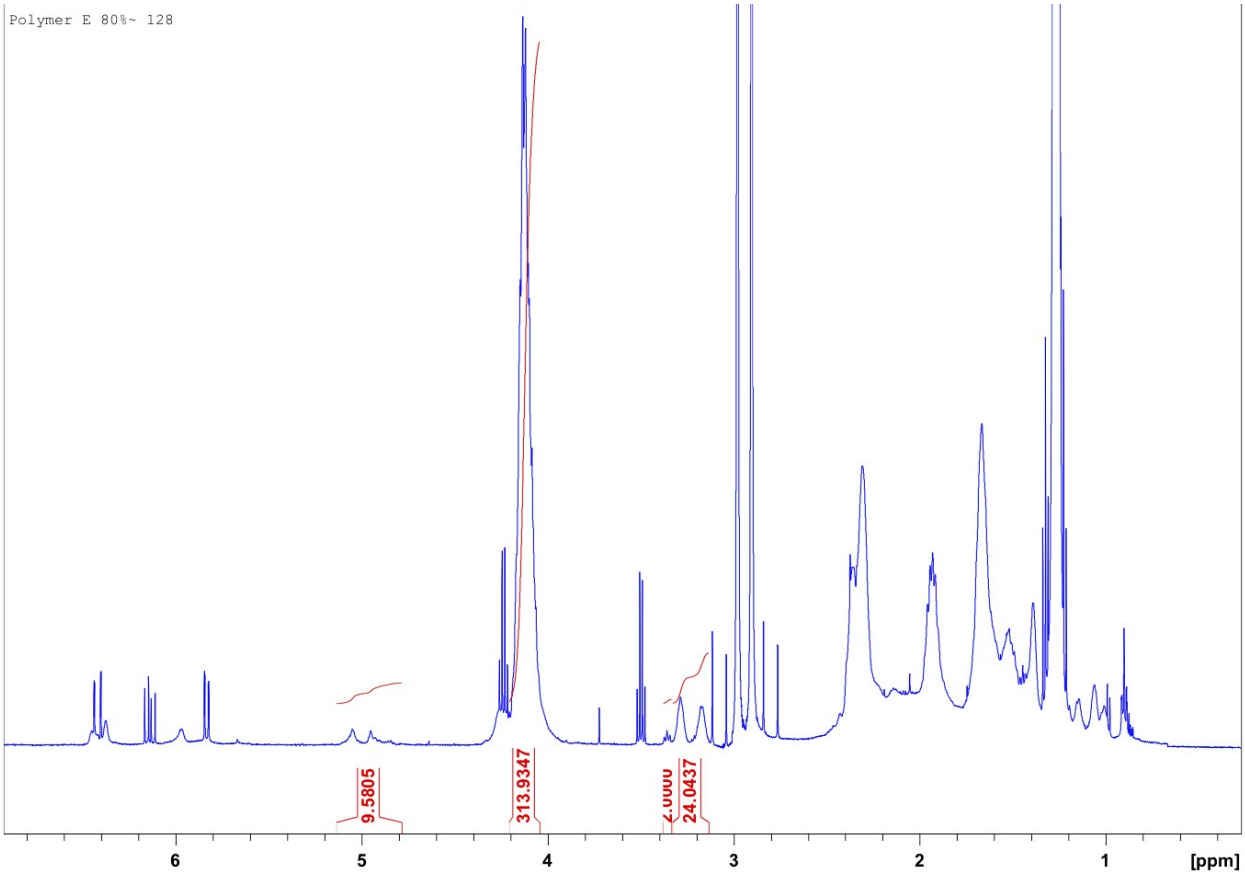

Figure S8: NMR Spectrum of PEA_{150}-$UPyMA_{5.6}$-$FMA_{5.6}$ made by RAFT

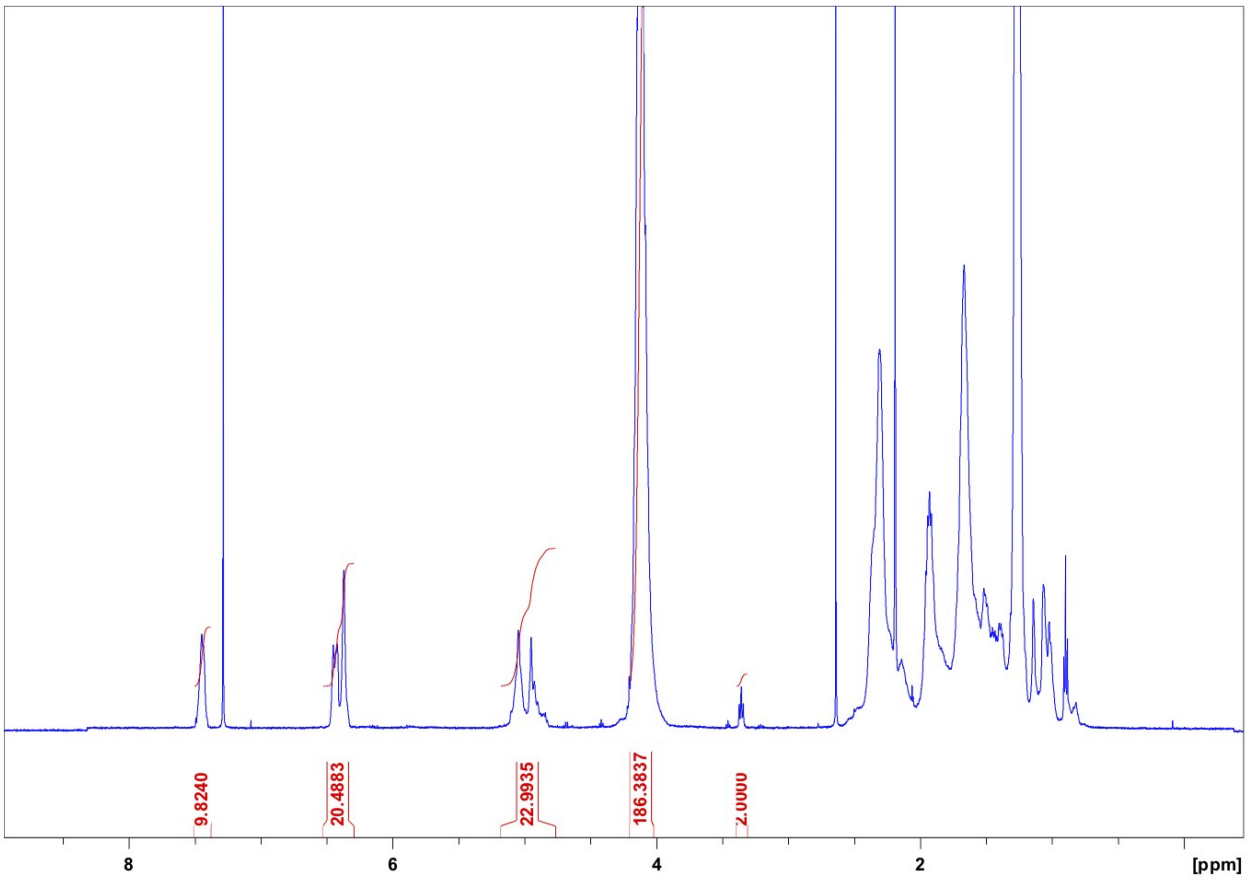

Figure S9: NMR Spectrum of PEA_{100}-$UPyMA_0$-FMA_{10} made by RAFT

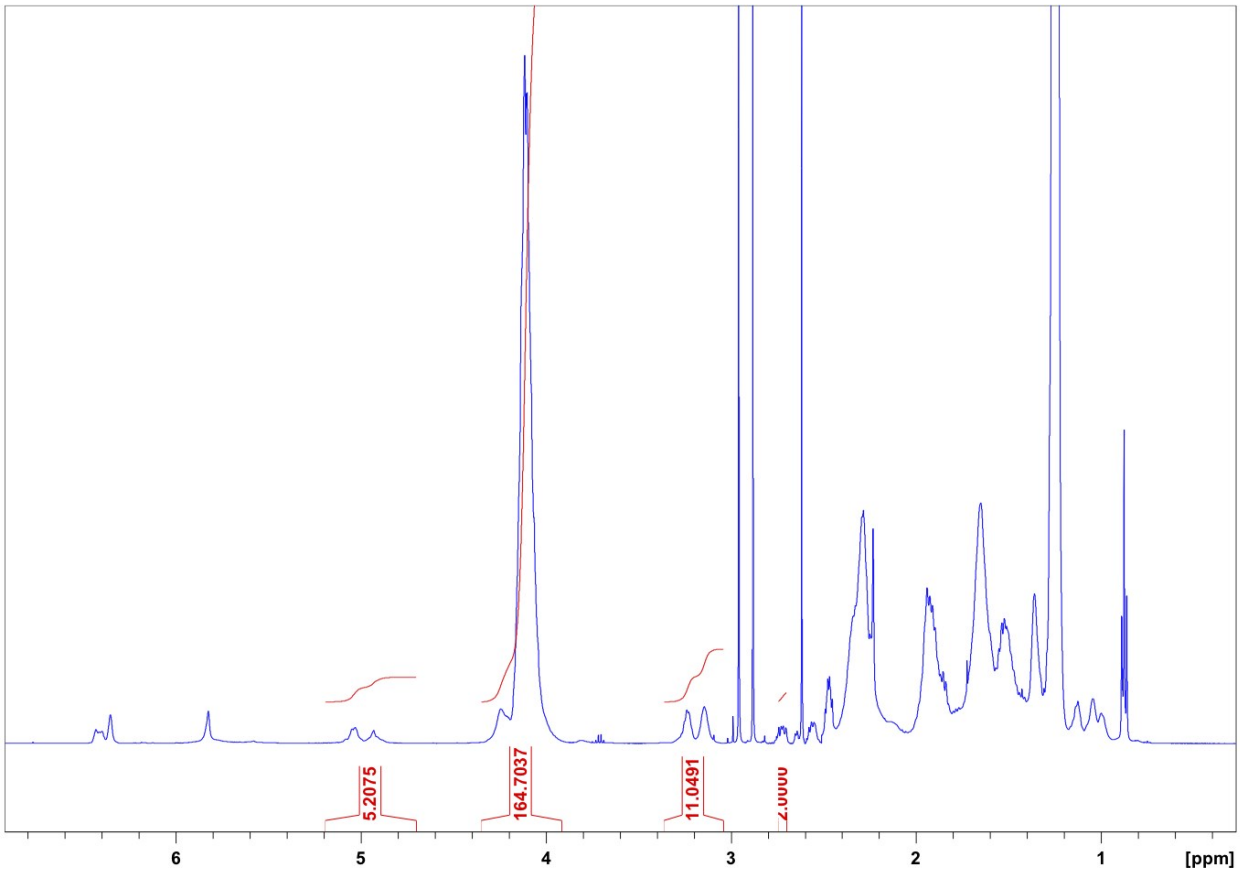

Figure S10: NMR Spectrum of PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$ made by FRP

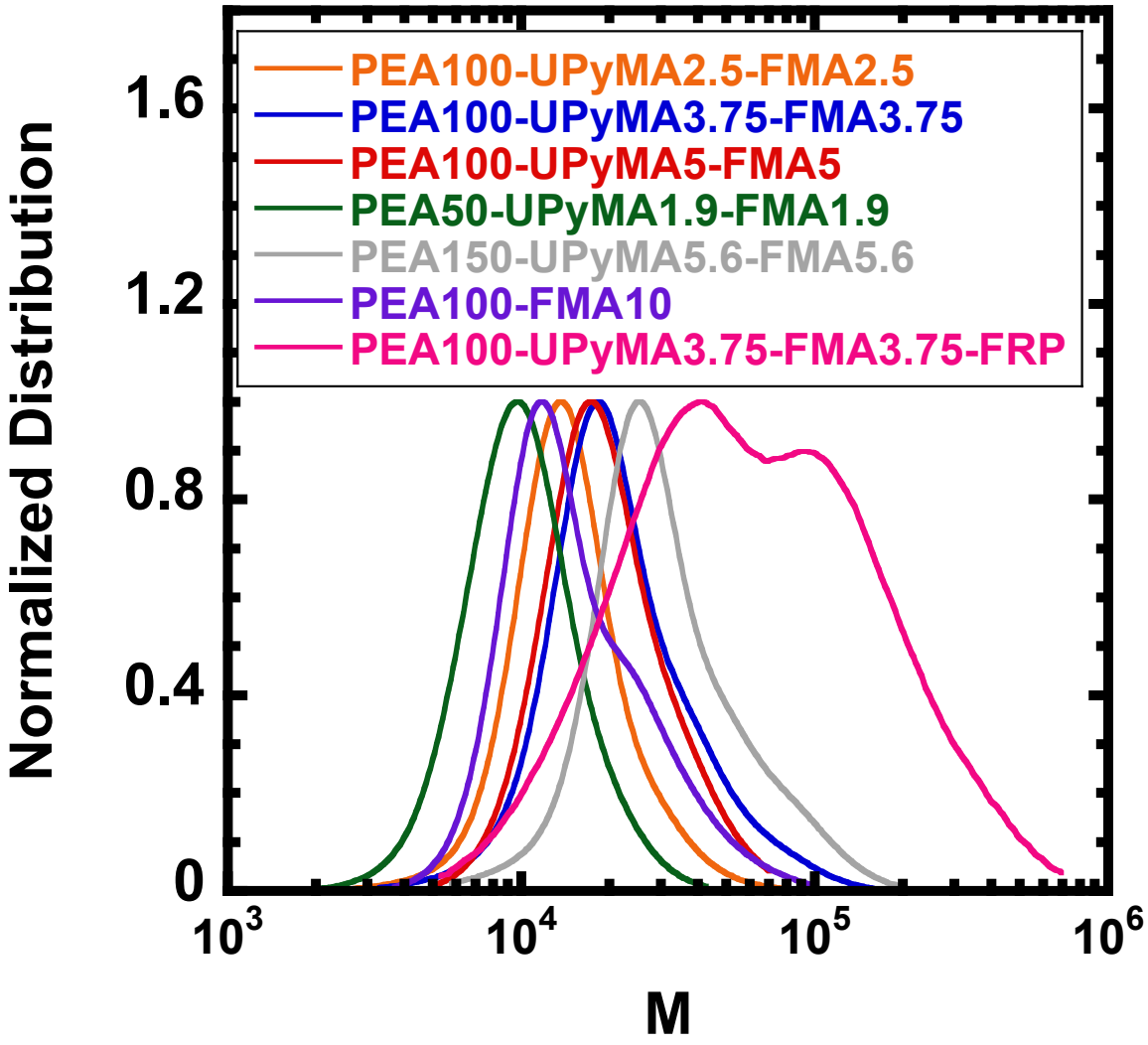

Figure S11: SEC traces of all polymers synthesized.

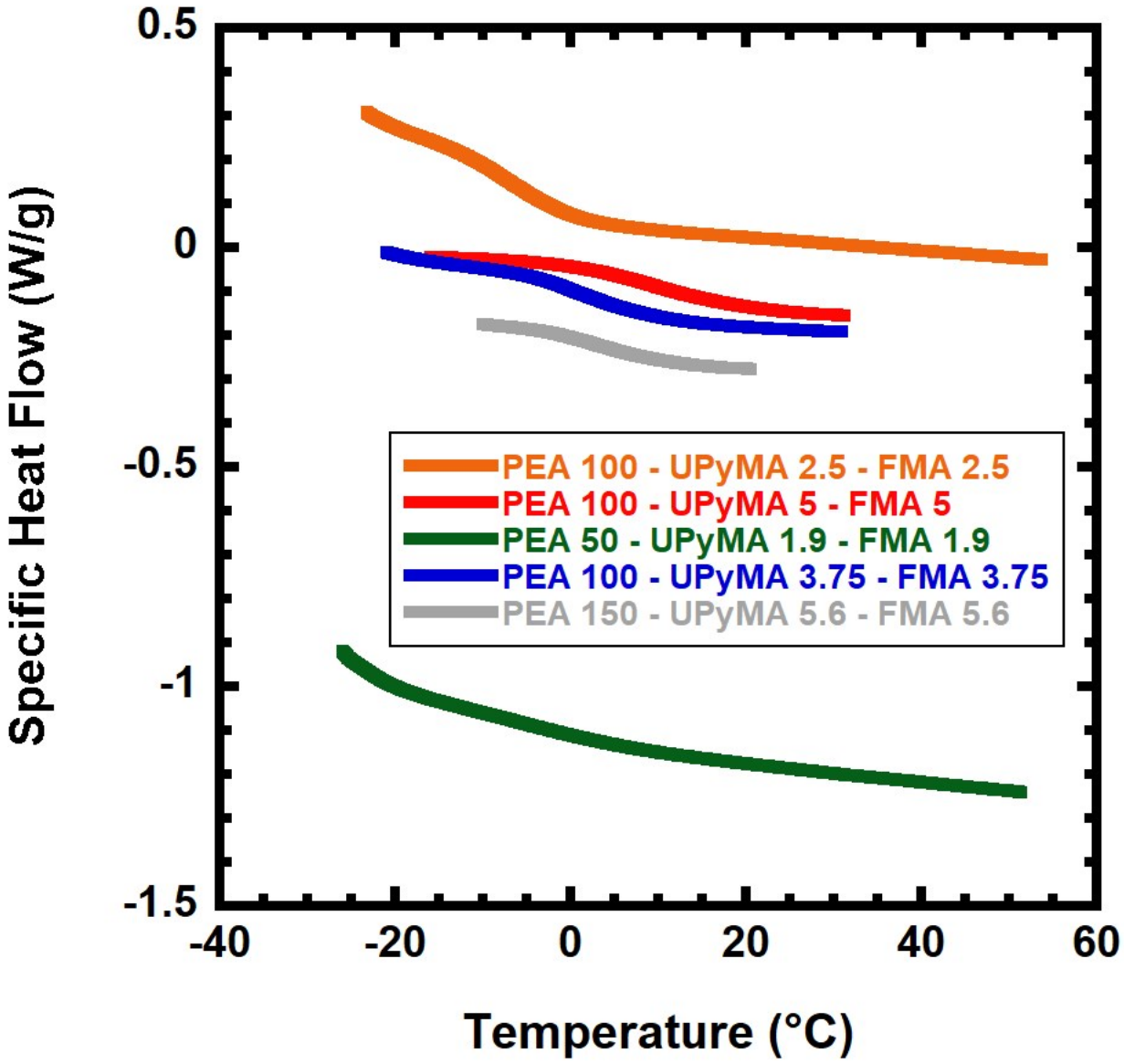

Figure S12: Typical DSC traces of each material studied.

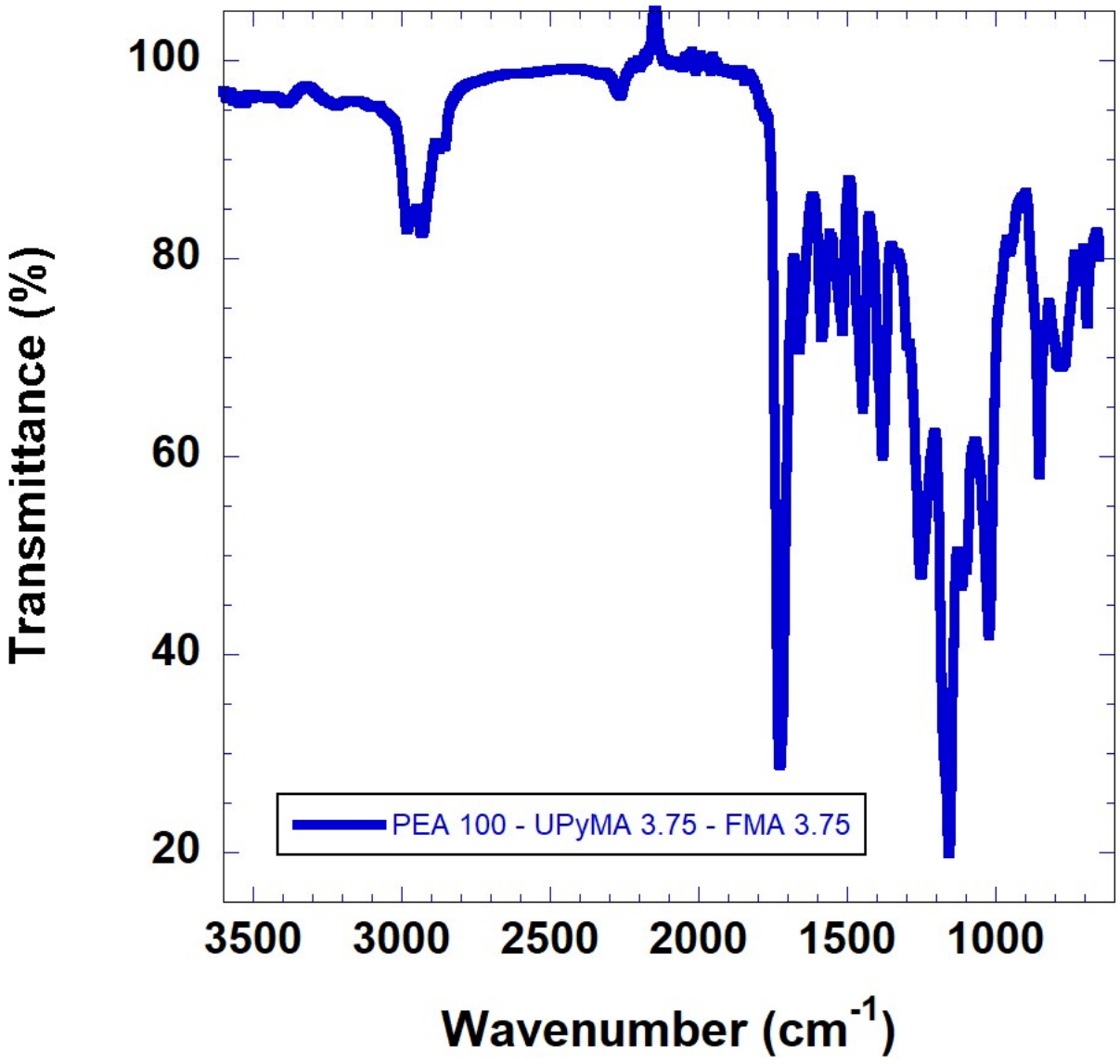

Figure S13: Infrared (IR) spectrum for PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$ material.

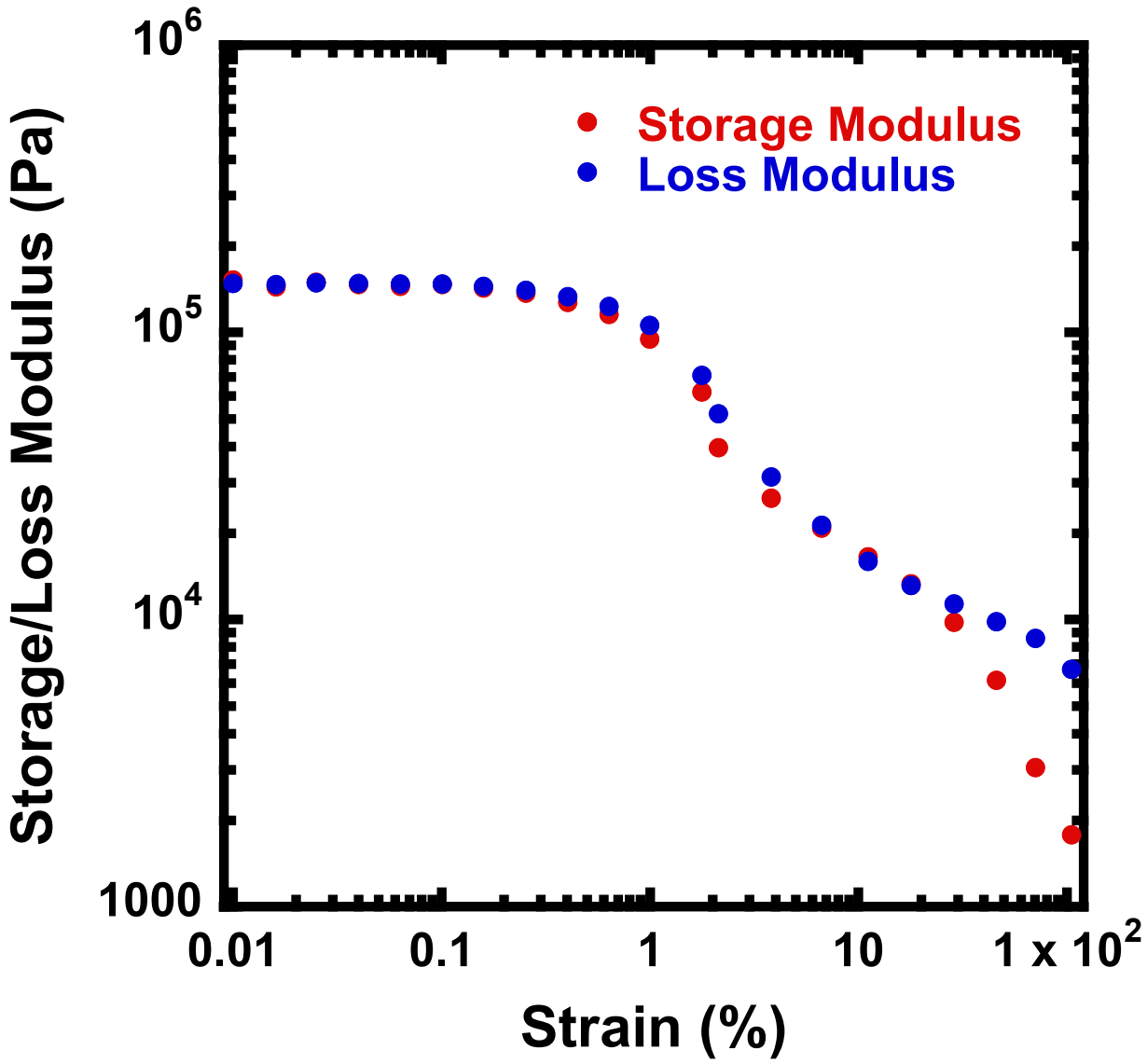

Figure S14: Rheological strain sweep of PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$ using a 1 Hz frequency at 25 °C.

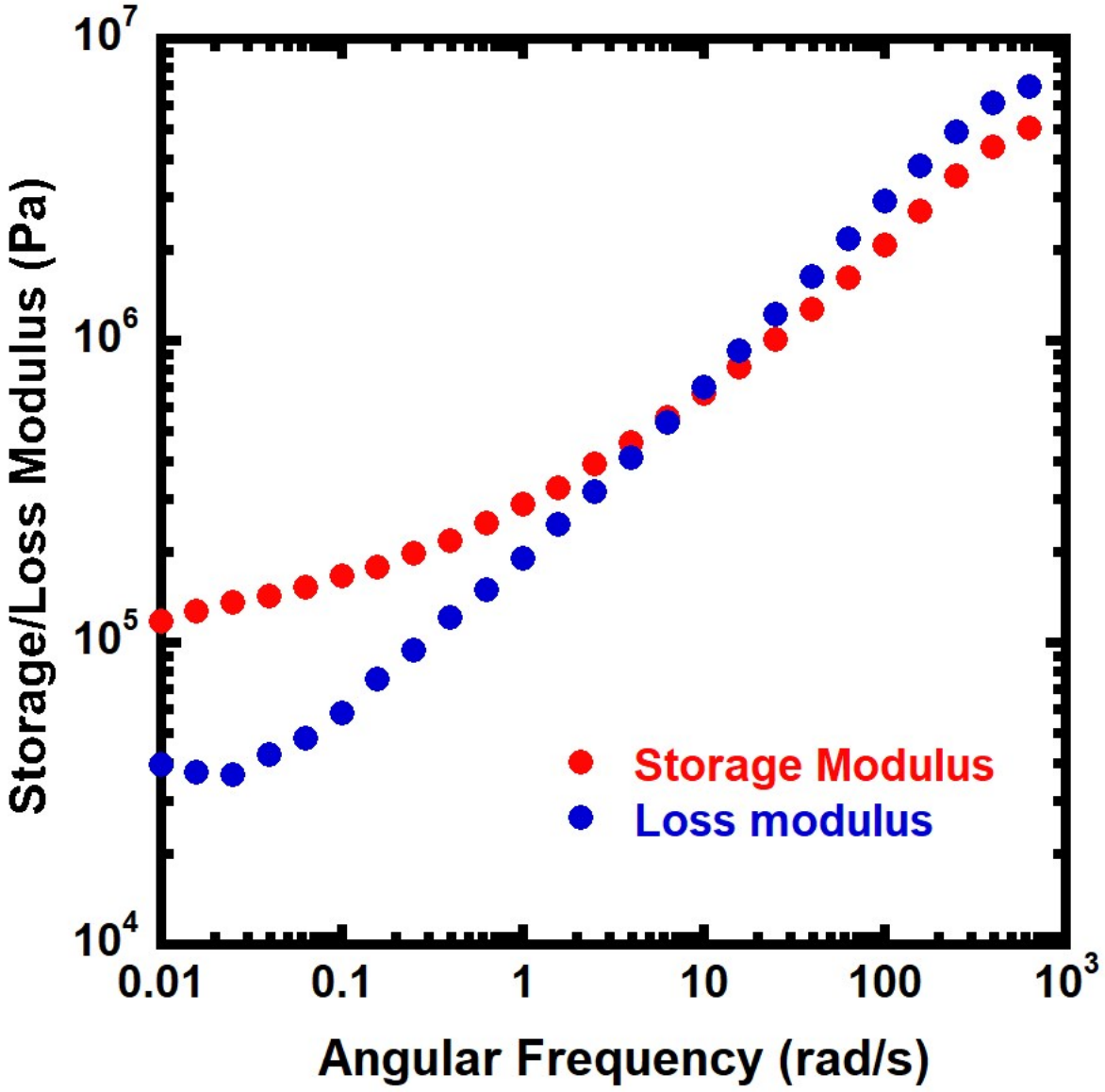

Figure S15: Rheological frequency sweep of PEA_{100}-$UPyMA_{2.5}$-$FMA_{2.5}$ using 0.1% strain at 25 °C.

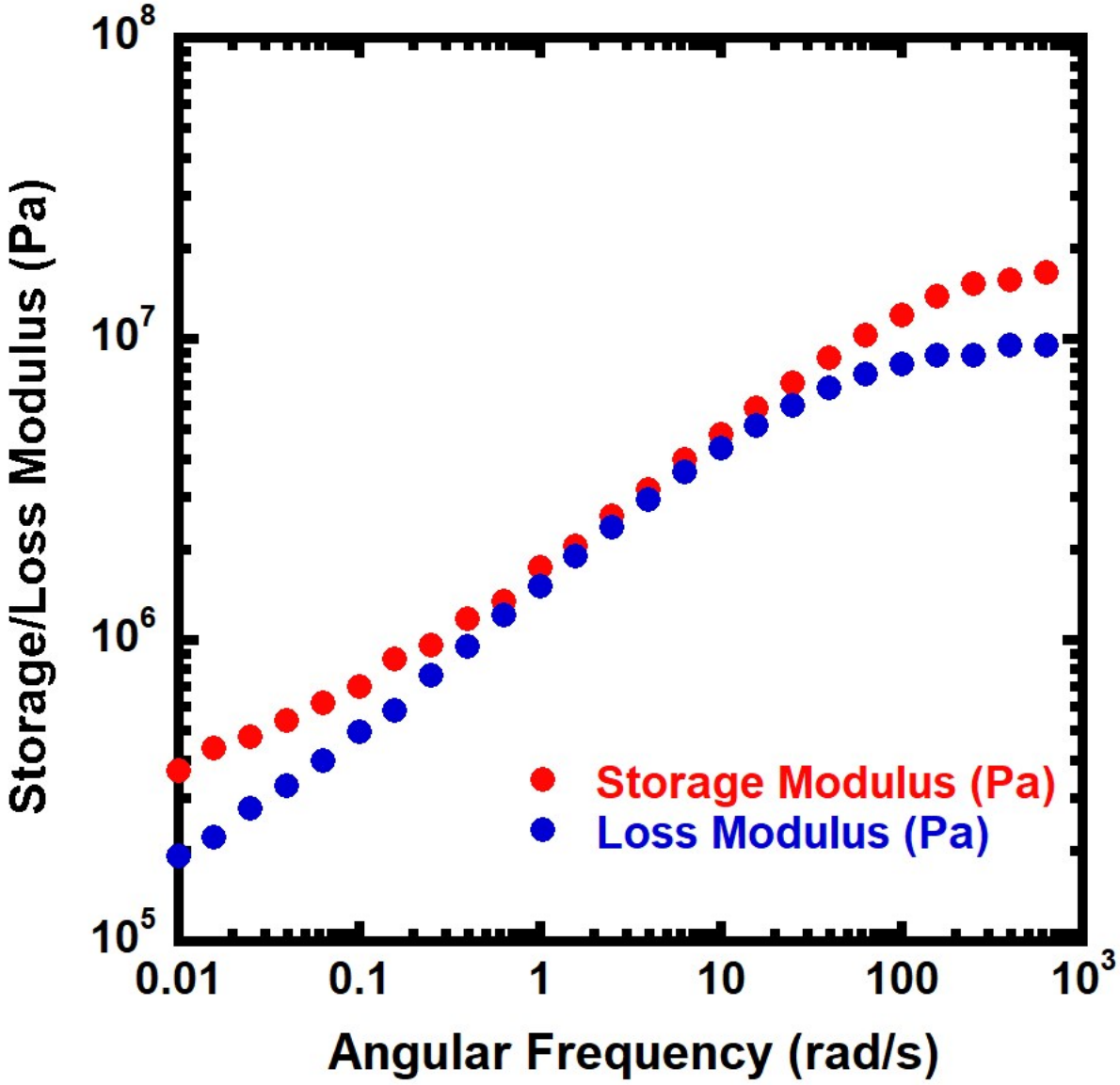

Figure S16: Rheological frequency sweep of PEA_{100}-$UPyMA_5$-FMA_5 using 0.1% strain at 25 °C.

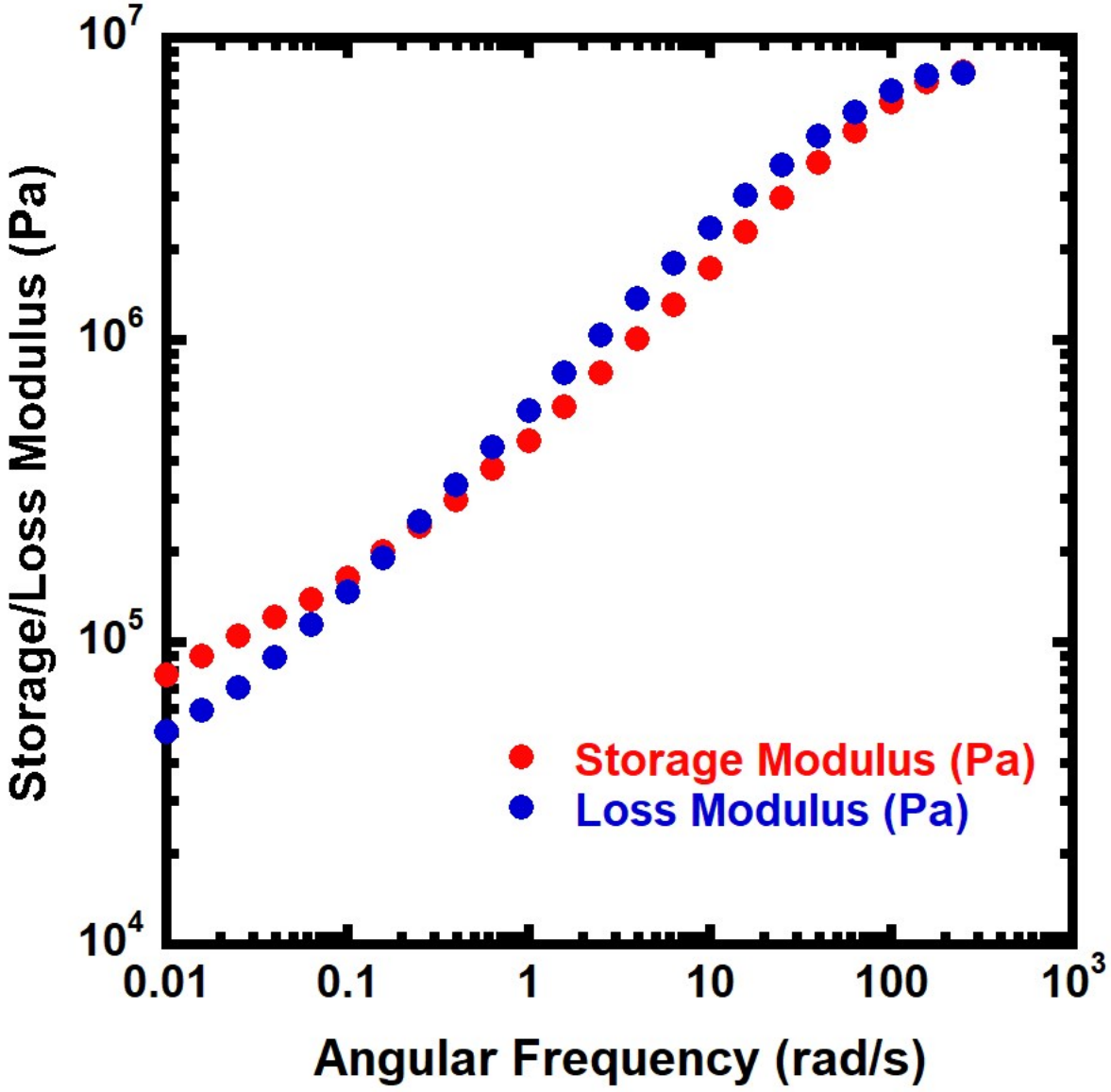

Figure S17: Rheological frequency sweep of PEA_{50}-$UPyMA_{1.9}$-$FMA_{1.9}$ using 0.1% strain at 25 °C.

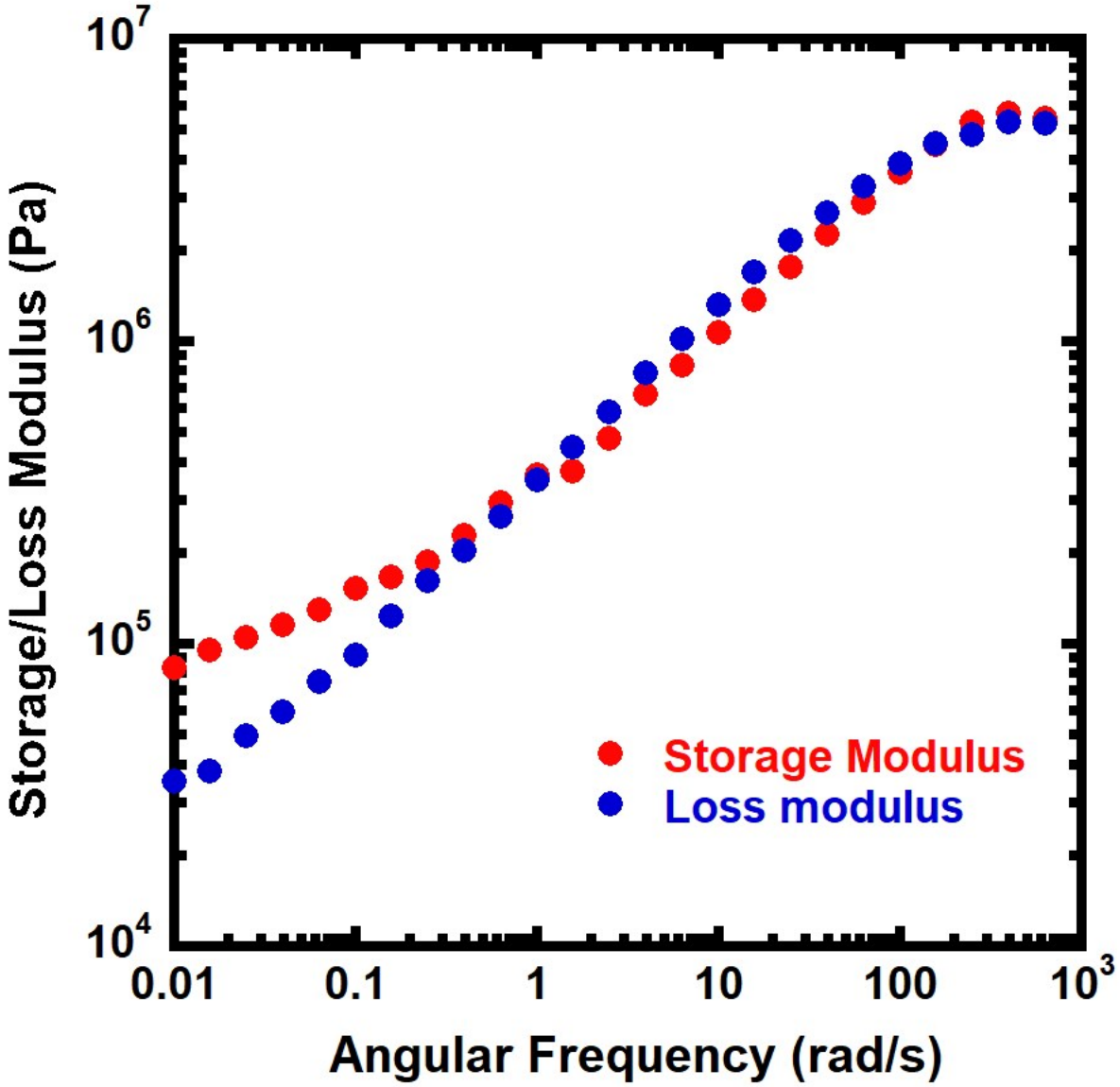

Figure S18: Rheological frequency sweep of PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$ using 0.1% strain at 25 °C.

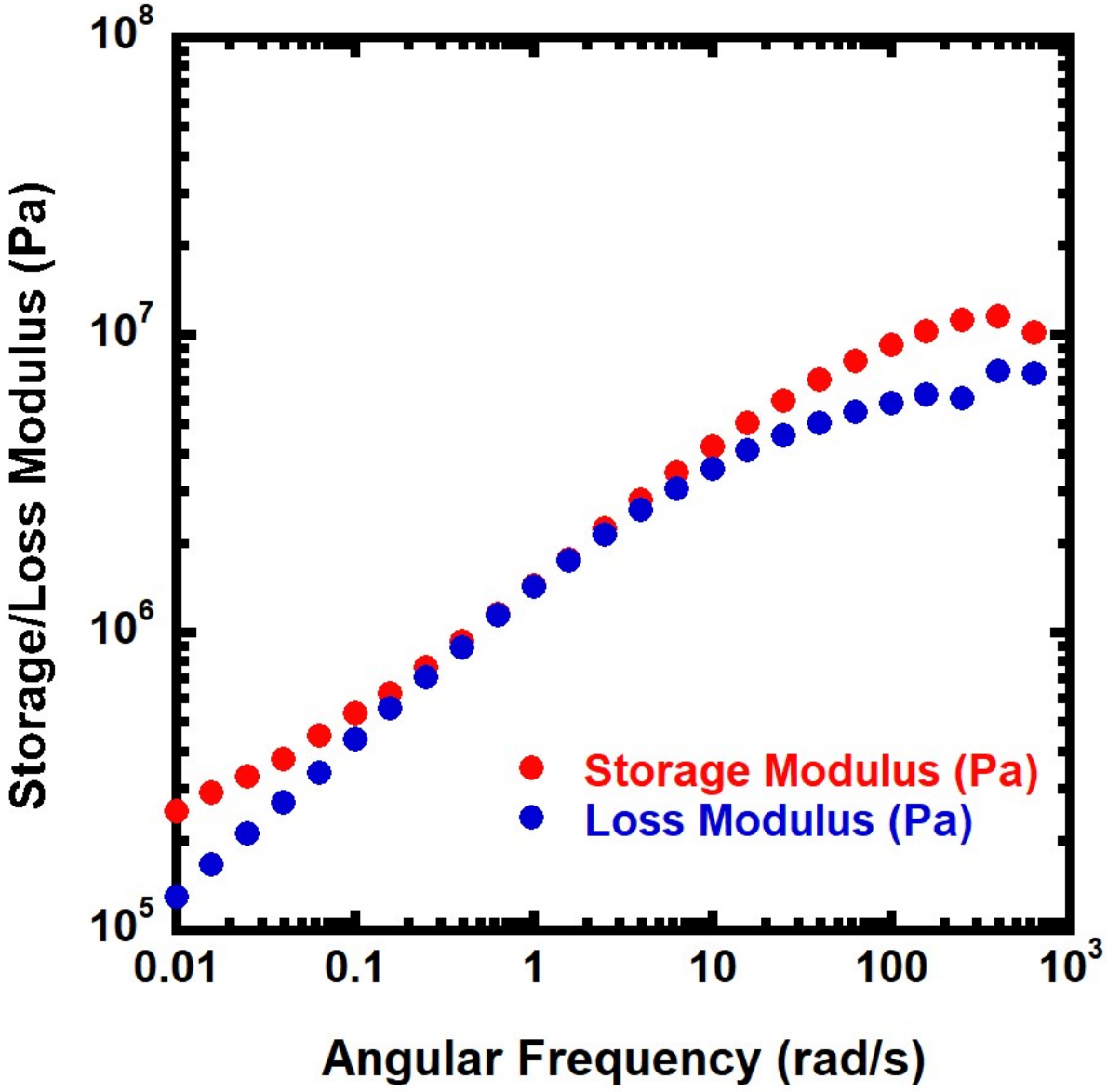

Figure S19: Rheological frequency sweep of PEA_{150}-$UPyMA_{5.6}$-$FMA_{5.6}$ using 0.1% strain at 25 °C.

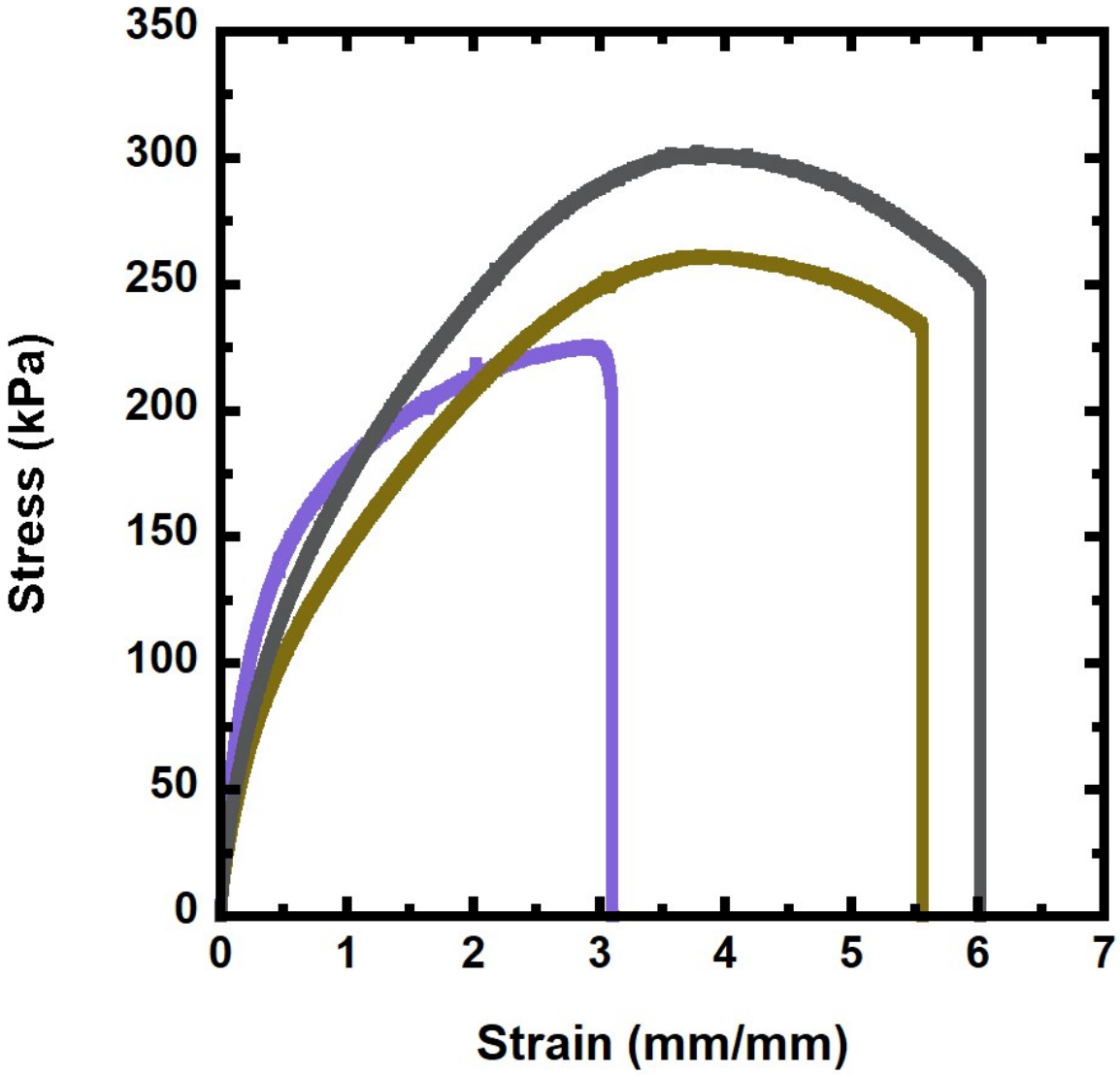

Figure S20: Uncut Variability of PEA_{100}-$UPyMA_{2.5}$-$FMA_{2.5}$.

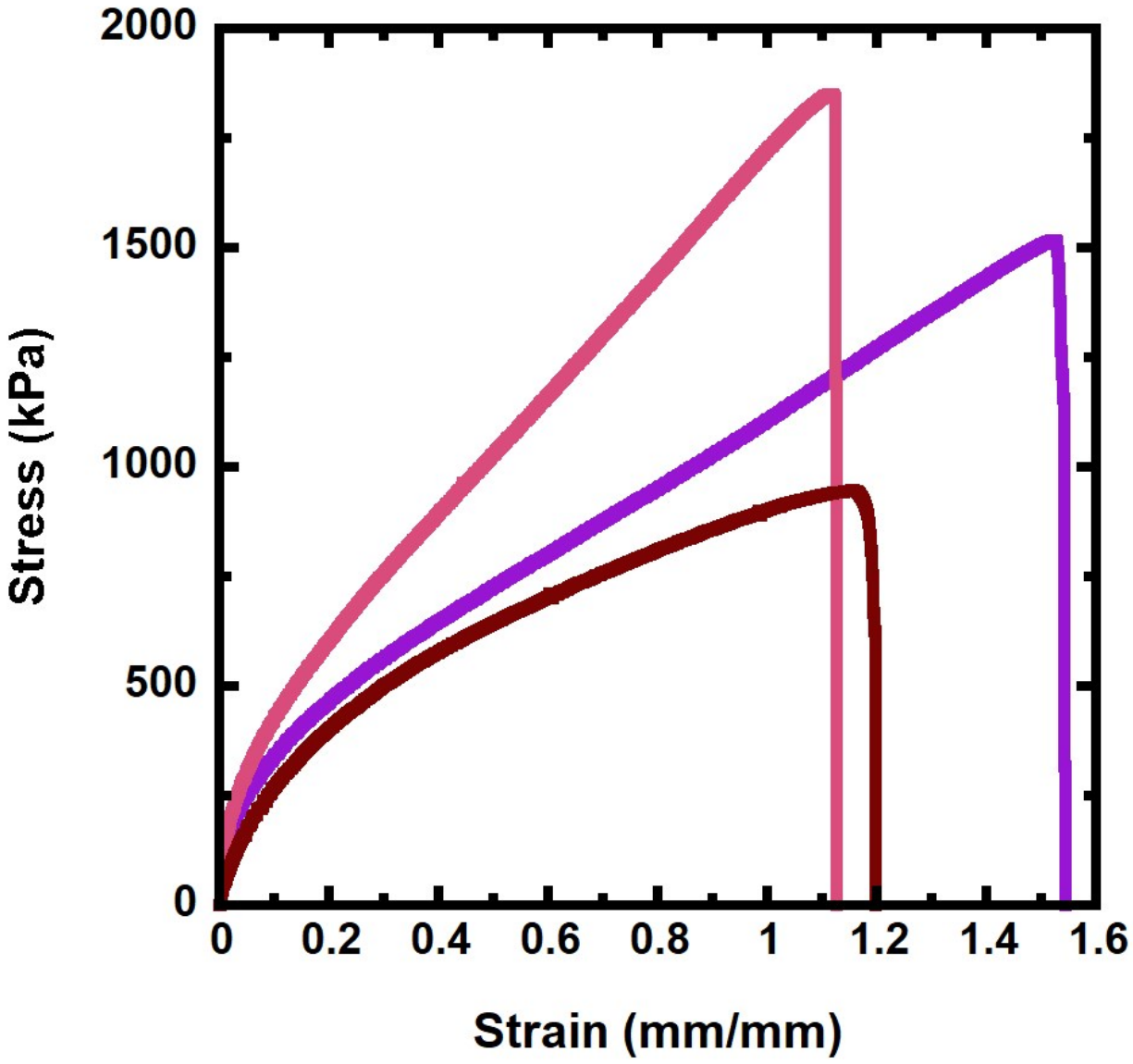

Figure S21: Uncut Variability of PEA_{100}-$UPyMA_5$-FMA_5.

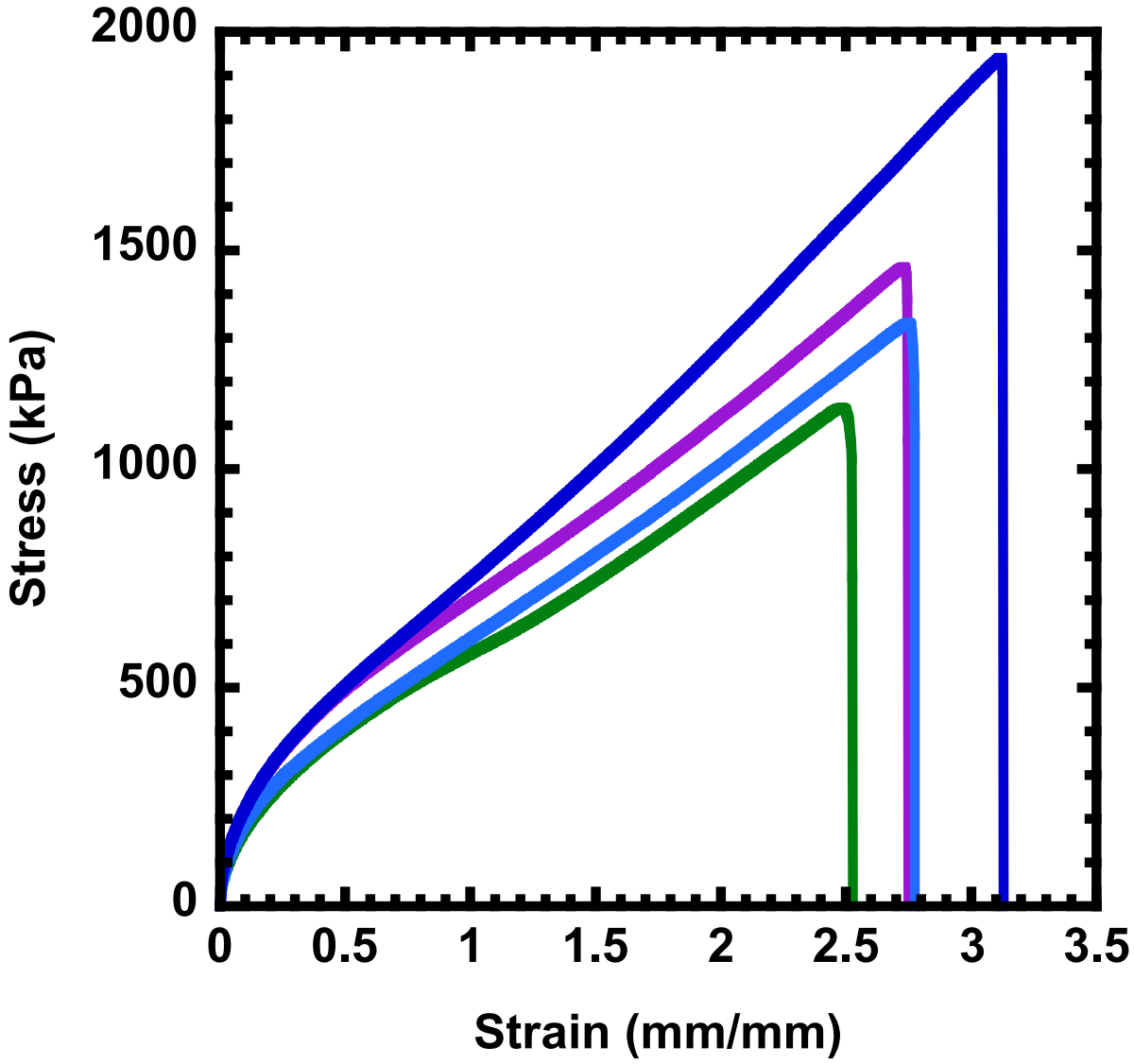

Figure S22: Uncut Variability of PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$.

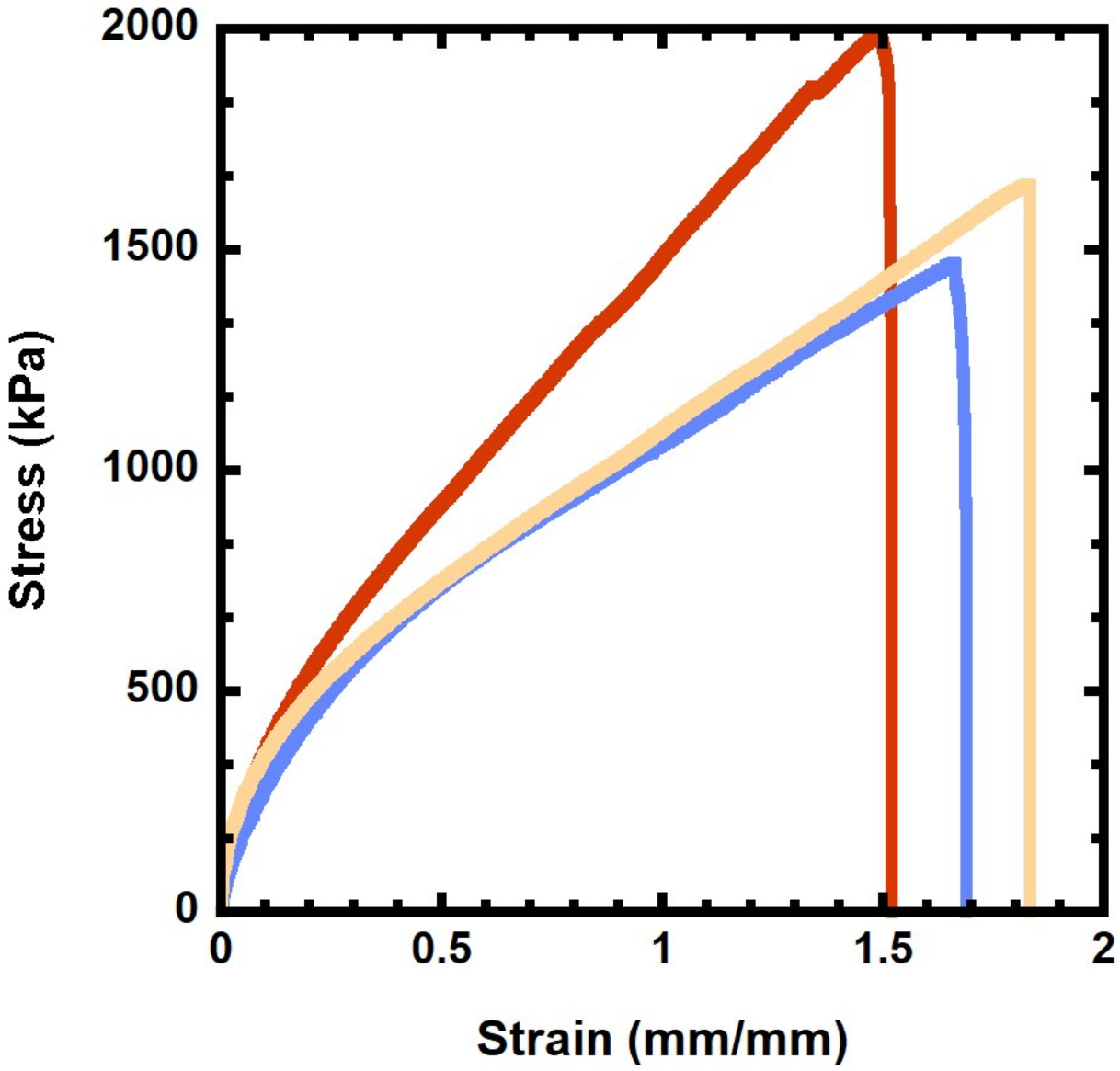

Figure S23: Uncut Variability of PEA_{150}-$UPyMA_{5.6}$-$FMA_{5.6}$.

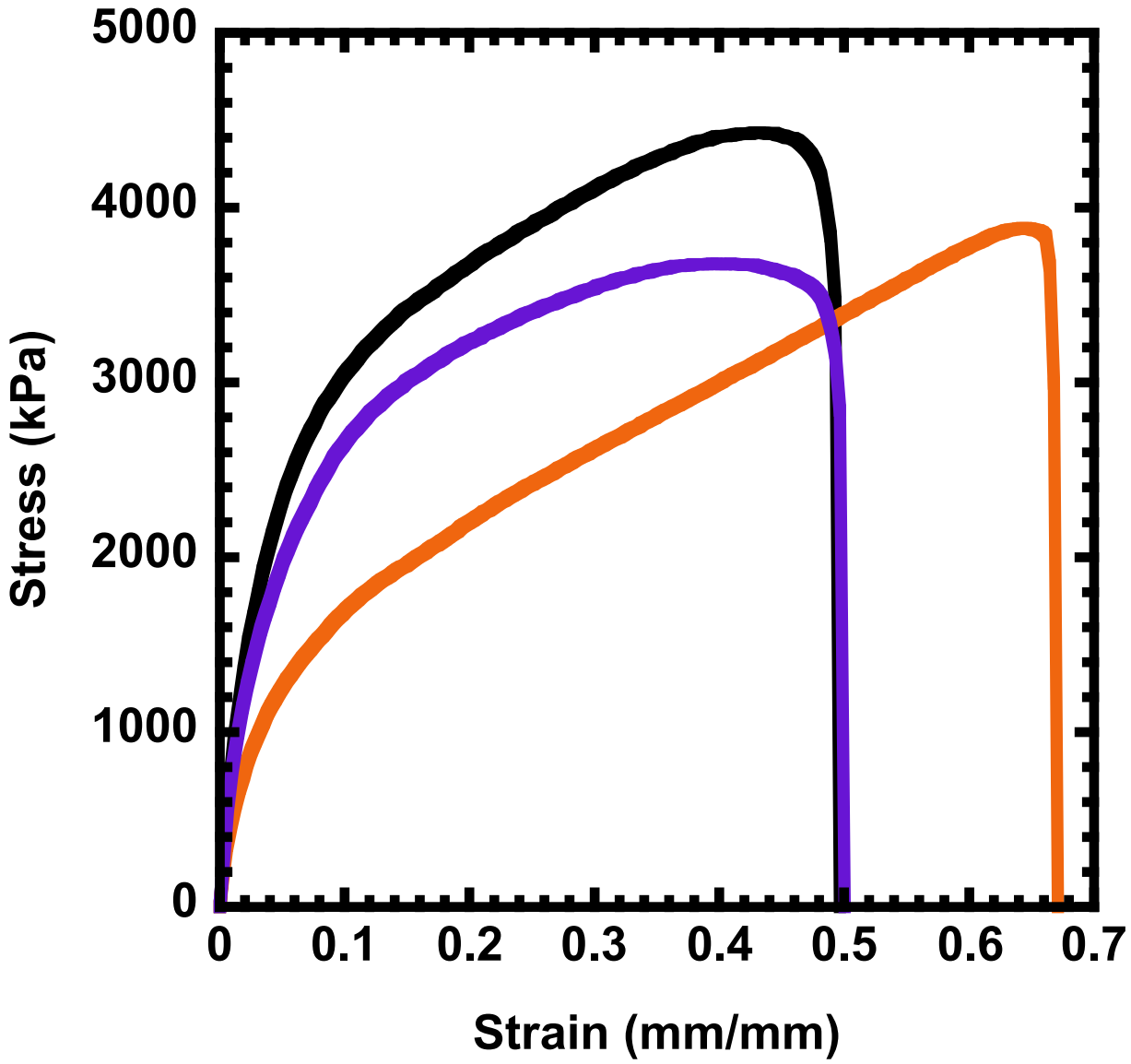

Figure S24: Uncut Variability of PEA_{100}-$UPyMA_0$-FMA_{10} materials.

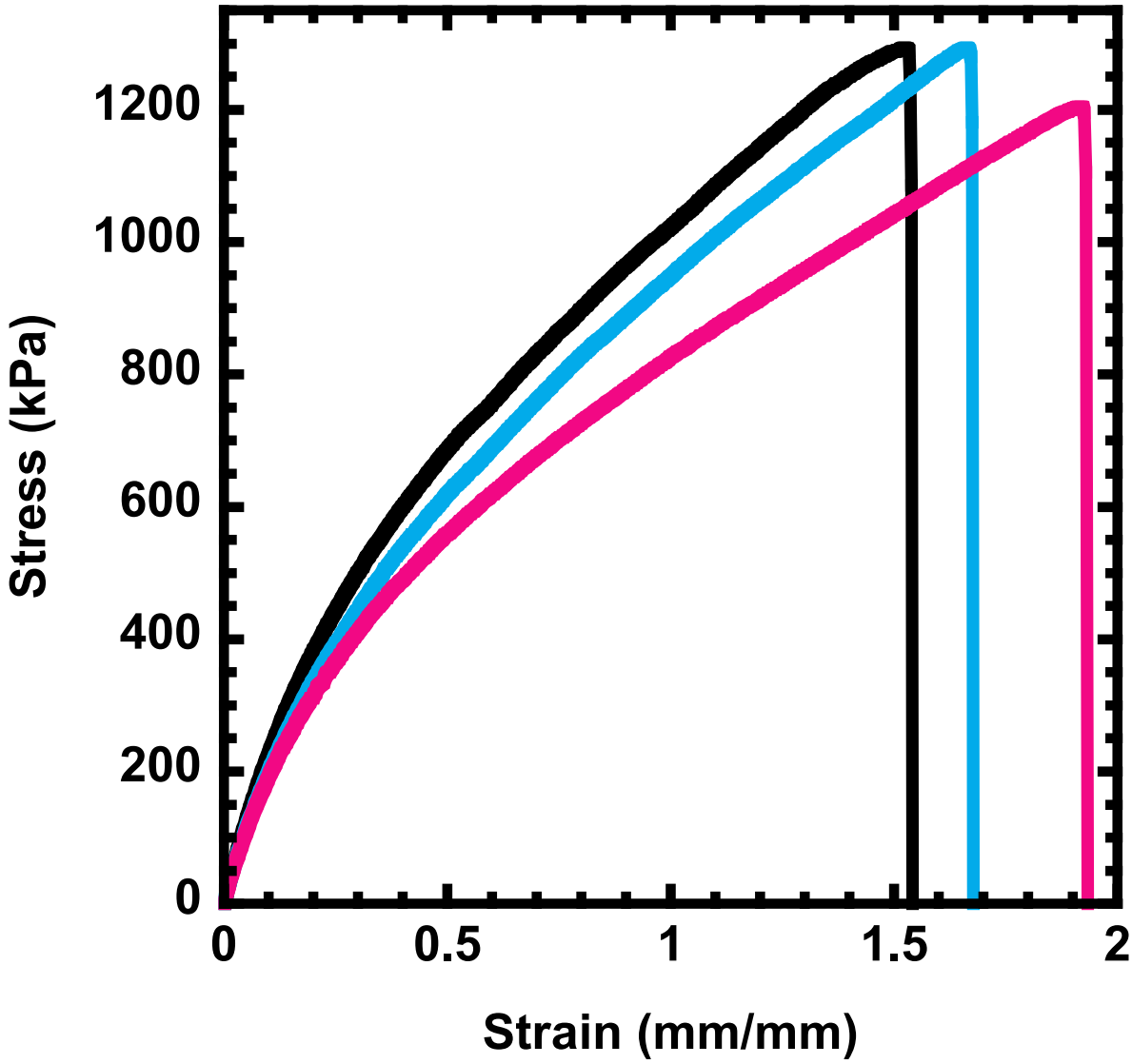

Figure S25: Uncut Variability of PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$-FRP materials.

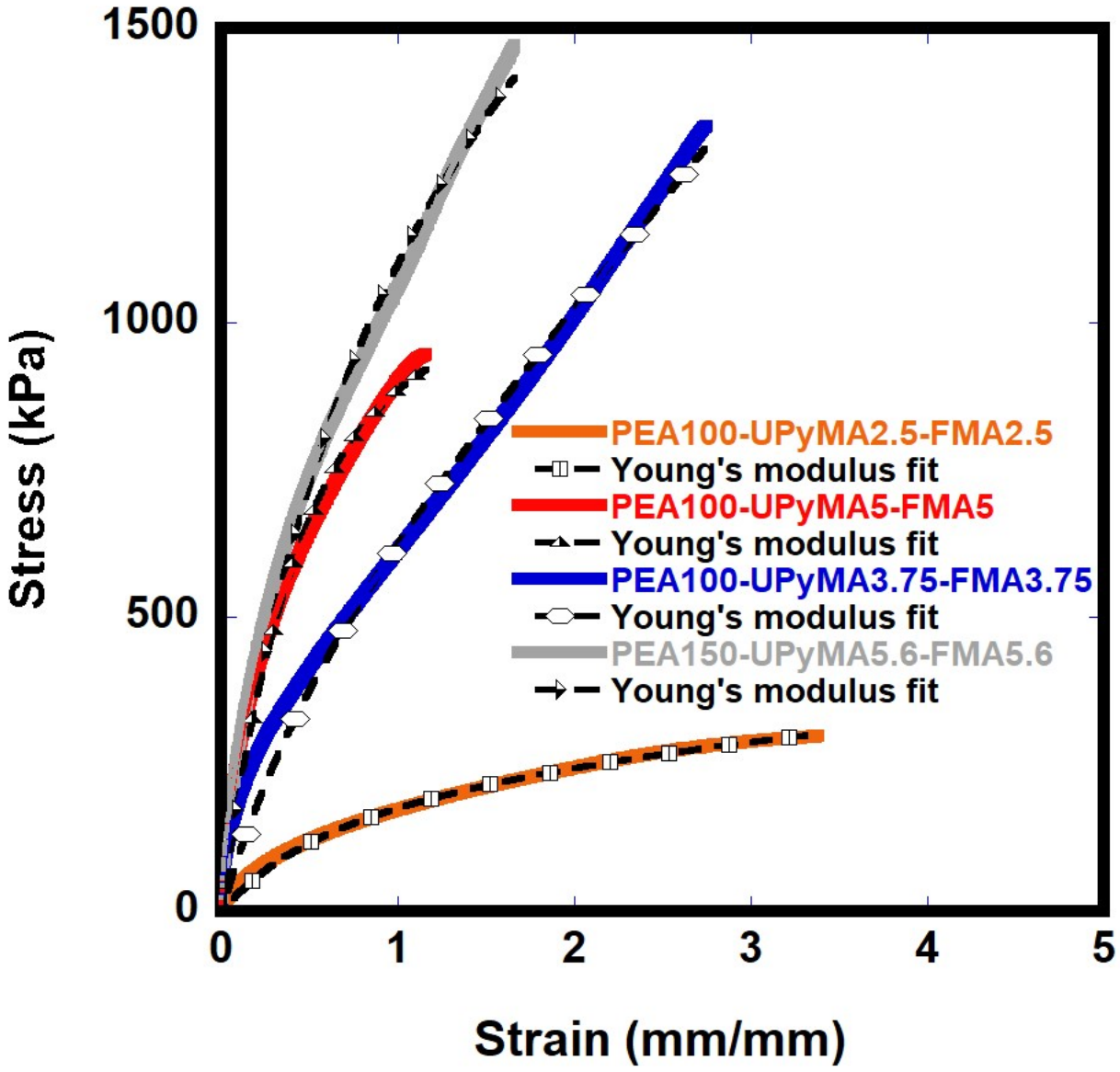

Figure S26: Fitted Young's modulus curves for typical each of the materials.

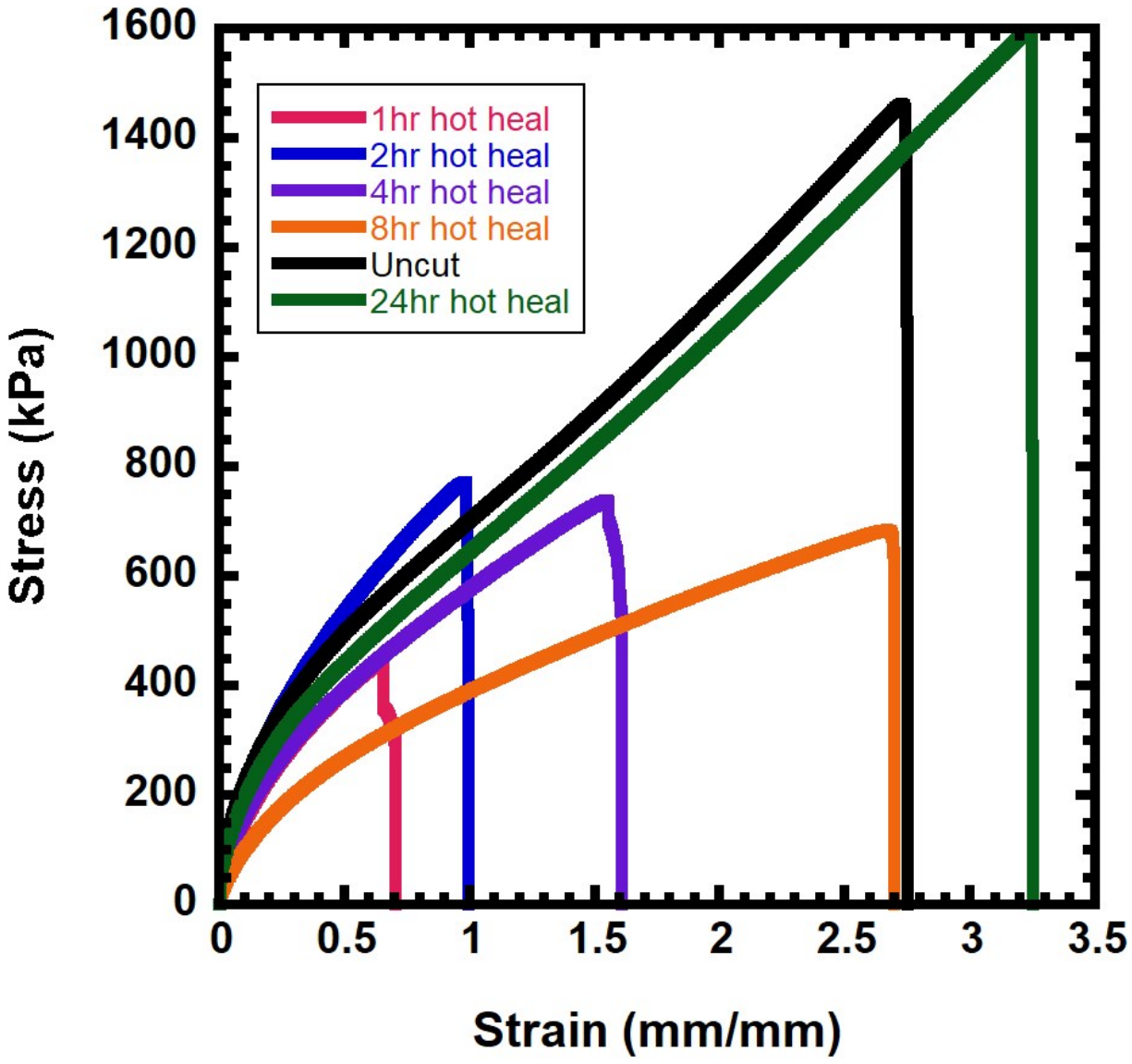

Figure S27: Self-healing properties of PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$ materials at 80 °C.

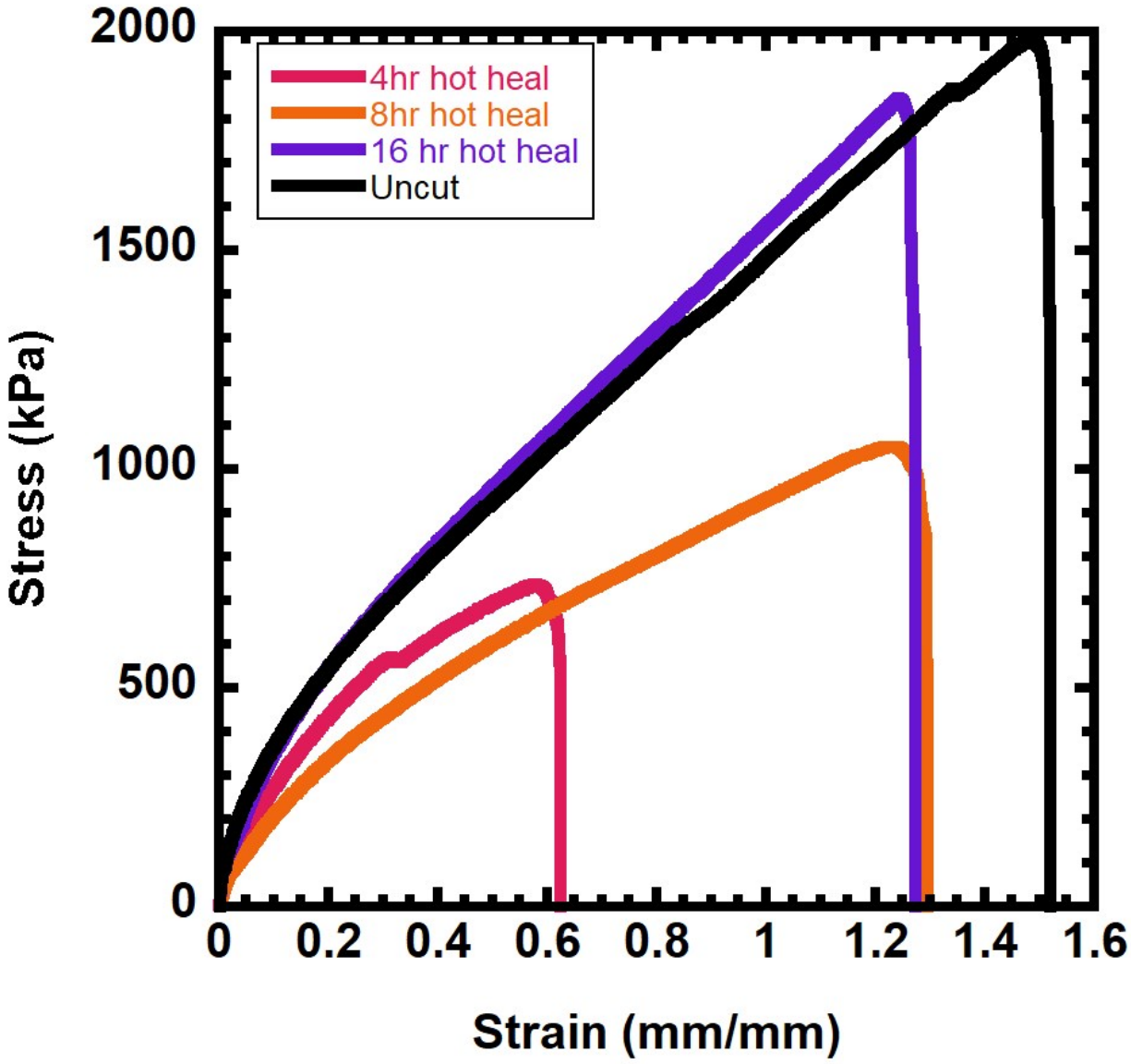

Figure S28: Self-healing properties of PEA_{150}-$UPyMA_{5.6}$-$FMA_{5.6}$ materials at 80 °C.

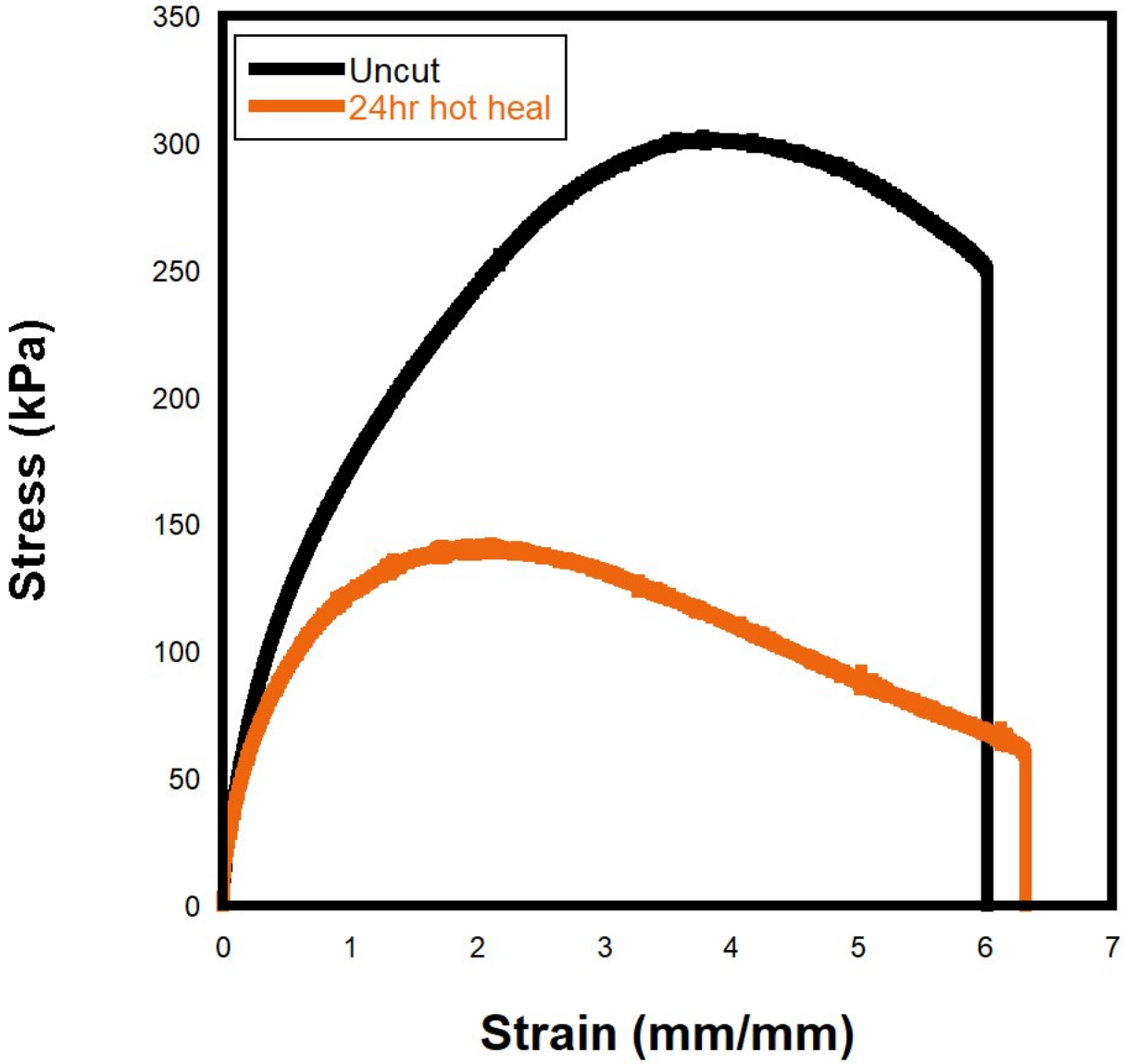

Figure S29: Self-healing properties of PEA_{100}-$UPyMA_{2.5}$-$FMA_{2.5}$ materials at 80 °C.

Table S1: Self-healing recovery of materials. a 24 h, b 16 h

Material	%Recovery Stress	%Recovery Strain
PEA_{100}-$UPyMA_{2.5}$-$FMA_{2.5}$ [a]	49	105
PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$ [a]	100	95
PEA_{100}-$UPyMA_{5}$-FMA_{5} [a]	109	118
PEA_{150}-$UPyMA_{5.6}$-$FMA_{5.6}$ [b]	93	84