Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information: Dual-Dynamic Interpenetrated Networks Tuned through Macromolecular Architecture

Borui Zhang, Jun Ke, Jafer R. Vakil, Sean C. Cummings, Zachary A. Digby, Jessica L. Sparks, Zhijiang Ye, Mehdi B. Zanjani, Dominik Konkolewicz*

Table S1. Composition (molar ratio), GPC calculated number average molecular weight (M_n), and GPC calculated dispersity values (M_w/M_n) of PEA-UPyA polymer.

Entry	Polymer	PADTC	AIBN	EA	UPyA	M_n	M_w/M_n
1	PEA_{100}-$UPyA_{5}$	1	0.2	100	5	64166	1.17
2	PEA_{100}-$UPyA_{7.5}$	1	0.2	100	7.5	87793	1.13
3	PEA_{100}-$UPyA_{10}$	1	0.2	100	10	91937	1.21
4	PEA_{50}-$UPyA_{3.75}$	1	0.2	50	3.75	9244	1.17
5	PEA_{150}-$UPyA_{11.25}$	1	0.2	150	11.25	26991	1.16

Table S2. Calculated units of UPyA and EA in PEA-UPyA polymer and related number average molecular weight (M_n) obtained from NMR.

Entry	Polymer	3.30-3.05 ppm	Units of UPyA	4.40-3.80 ppm	Units of EA	M_n by NMR
1	PEA_{100}-$UPyA_{5}$	21.8 protons	5.0	205.0 protons	100.5	12400
2	PEA_{100}-$UPyA_{7.5}$	31.4 protons	7.4	234.4 protons	115.2	14900
3	PEA_{100}-$UPyA_{10}$	54.0 protons	13.0	220.1 protons	108.0	16500
4	PEA_{50}-$UPyA_{3.75}$	23.0 protons	5.3	144.1 protons	70.1	9530
5	PEA_{150}-$UPyA_{11.25}$	44.0 protons	10.5	362.7 protons	179.4	22600

Table S3. Composition (molar ratio), reaction duration, GPC calculated weight average molecular weight (M_n), and GPC calculated dispersity values (M_w/M_n) of PEA-FMA polymer.

Entry	Polymer	PADTC	AIBN	EA	FMA	Duration	M_n	M_w/M_n
1	PEA_{100}-FMA_{5}	1	0.2	100	5	5 h	11725	1.05
2	PEA_{100}-$FMA_{7.5}$	1	0.2	100	7.5	6 h	10410	1.05
3	PEA_{100}-FMA_{10}	1	0.2	100	10	9 h	11354	1.06
4	PEA_{50}-$UPyA_{3.75}$	1	0.2	50	3.75	6 h	5520	1.08
5	PEA_{150}-$UPyA_{11.25}$	1	0.2	150	11.25	7 h	17860	1.09

Table S4. Calculated units of FMA and EA in PEA-FMA polymer and related number average molecular weight (M_n) obtained from NMR.

Entry	Polymer	5.10-4.80 ppm	Units of FMA	4.25-3.90 ppm	Units of EA	M_n by NMR
1	PEA_{100}-FMA_5	11 protons	5.5	194 protons	97.0	11000
2	PEA_{100}-$FMA_{7.5}$	15.2 protons	7.6	193.2 protons	96.6	11200
3	PEA_{100}-FMA_{10}	20.3 protons	10.2	185.3 protons	92.7	11300
4	PEA_{50}-$UPyA_{3.75}$	10.3 protons	5.2	109.6 protons	54.8	6670
5	PEA_{150}-$UPyA_{11.25}$	26.0 protons	13.0	382.0 protons	191.0	21600

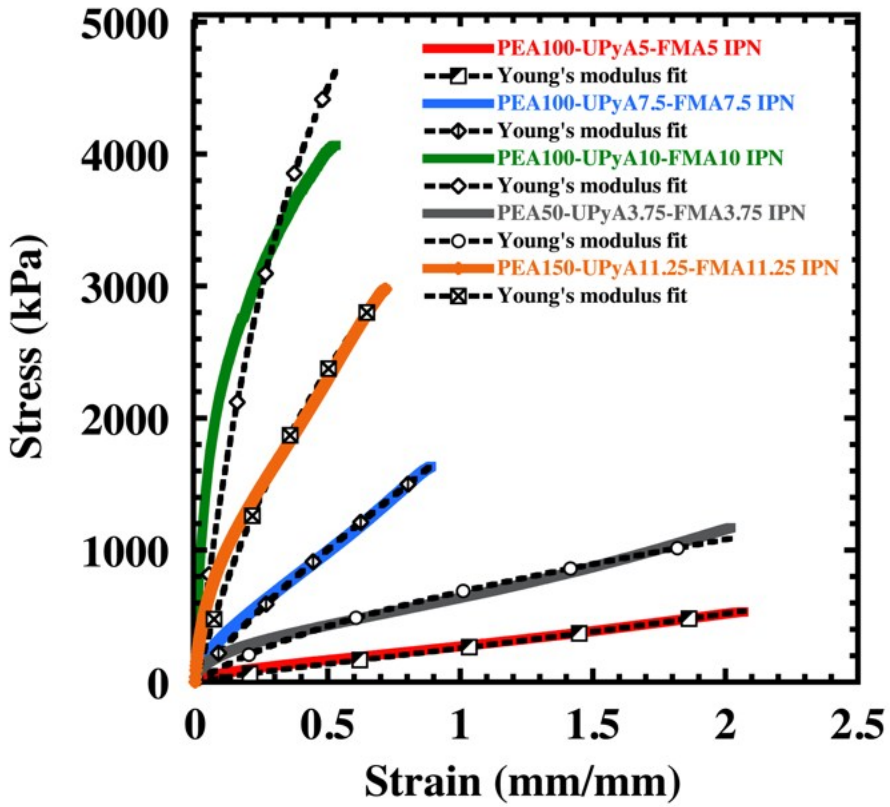

Figure S1. Fitted Young's modulus curves for each IPN materials.

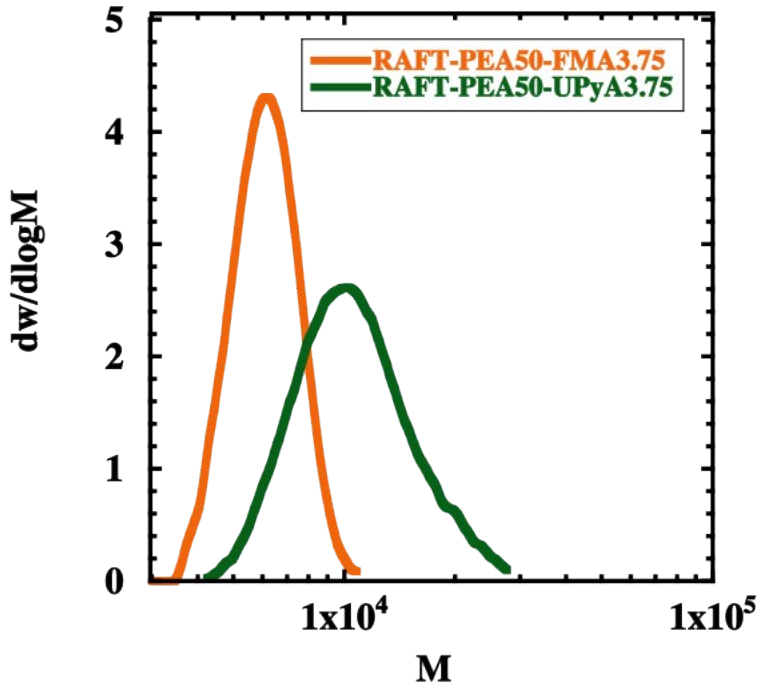

Figure S2. GPC traces of PEA_{50}-$FMA_{3.75,}$ and PEA_{50}-$UPyA_{3.75}$.

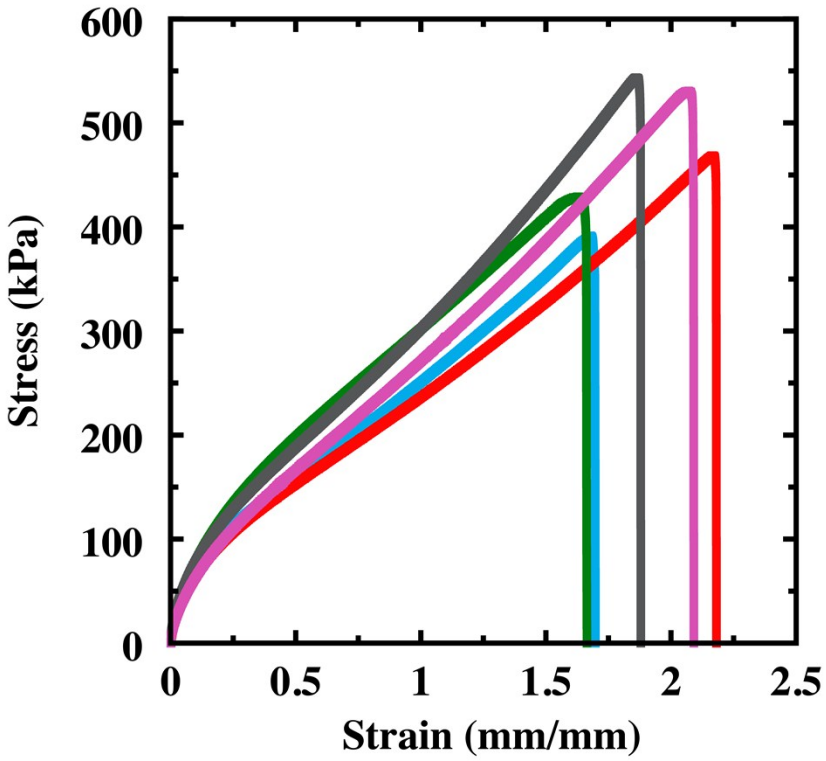

Figure S3. PEA_{100}-$UPyA_5$-FMA_5 uncut variability.

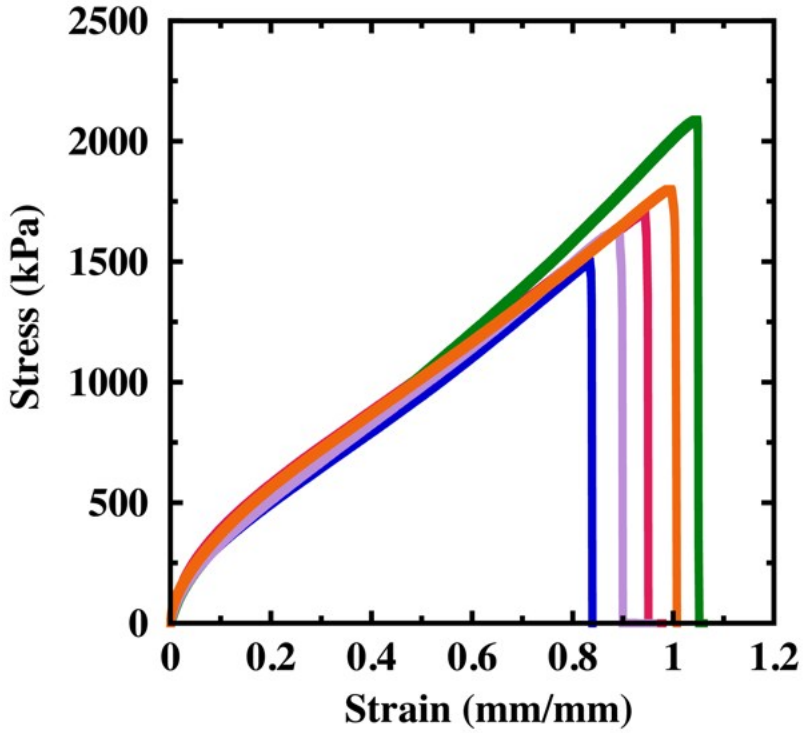

Figure S4. PEA_{100}-$UPyA_{7.5}$-$FMA_{7.5}$ uncut variability.

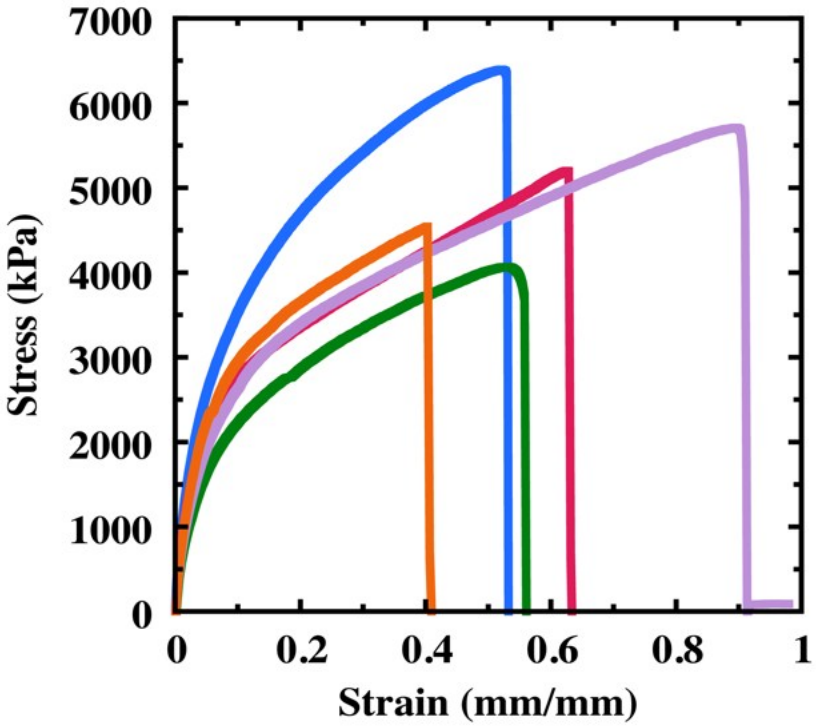

Figure S5. PEA_{100}-$UPyA_{10}$-FMA_{10} uncut variability.

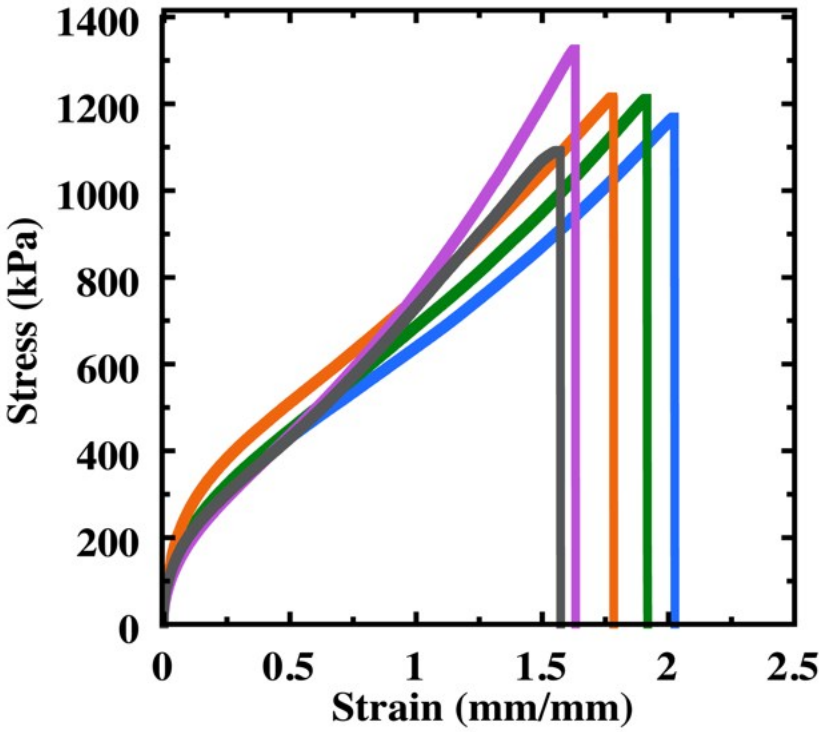

Figure S6. PEA_{50}-$UPyA_{3.75}$-$FMA_{3.75}$ uncut variability.

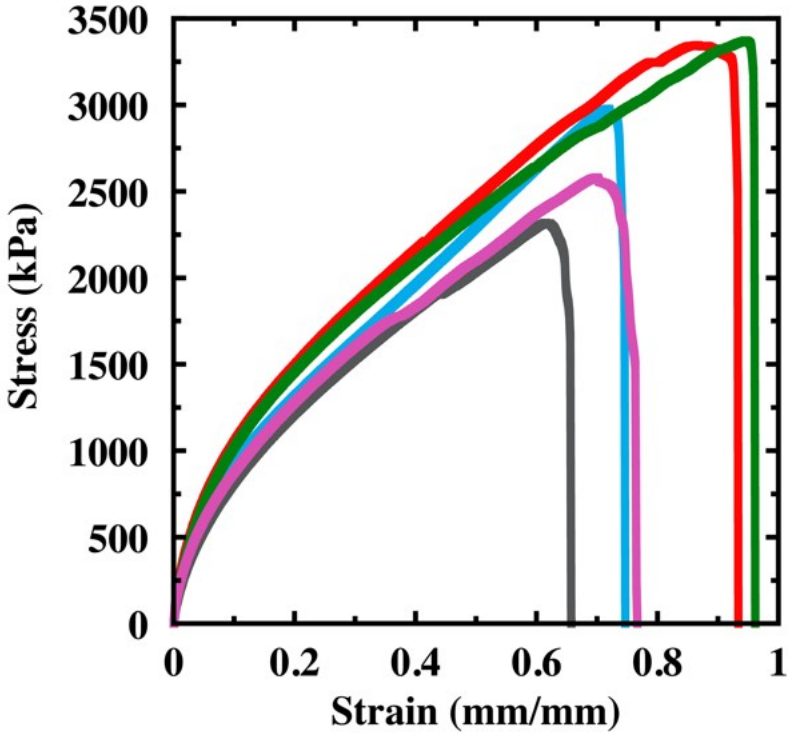

Figure S7. PEA_{150}-$UPyA_{11.25}$-$FMA_{11.25}$ uncut variability.

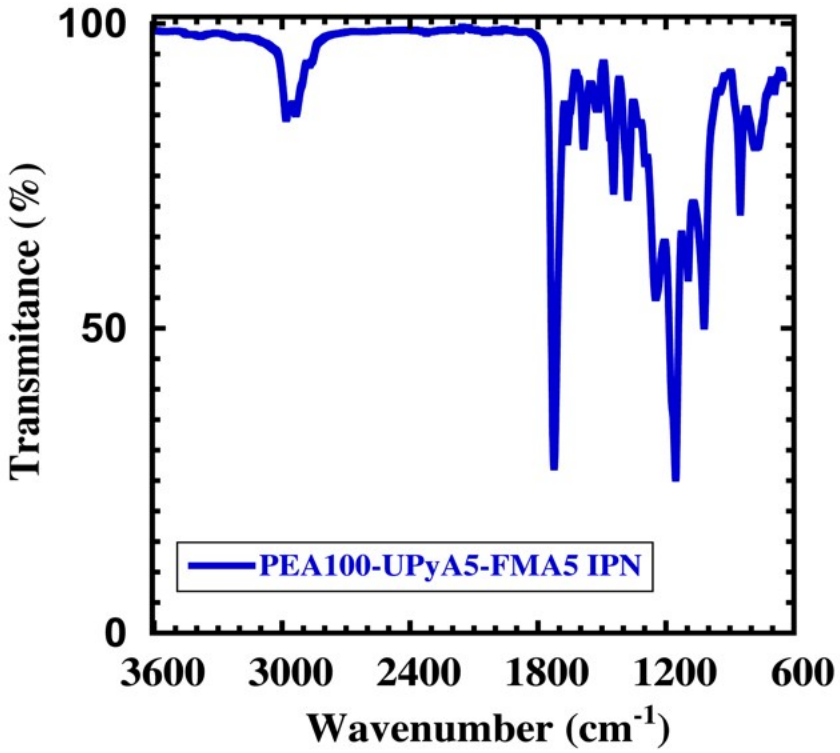

Figure S8. Infrared (IR) spectrum for PEA_{100}-$UPyA_5$-FMA_5 IPN material.

Table S5. IR assignment of PEA100-UPyA5-FMA5 IPN material.

Peak (cm^{-1})	Proposed Assignment	Reference
2981	C-H stretch	1
2936	C-H stretch	2, 3
1725	C=O ester stretch	3
1663	C=C stretch	1
1587	C=C bending	1
1446	C-H bending	1
1248	C-O antisymmetric stretching	3
1155	C-O symmetric stretching	3
1022	C-N stretch	1
852	C-H out of plane bending	1

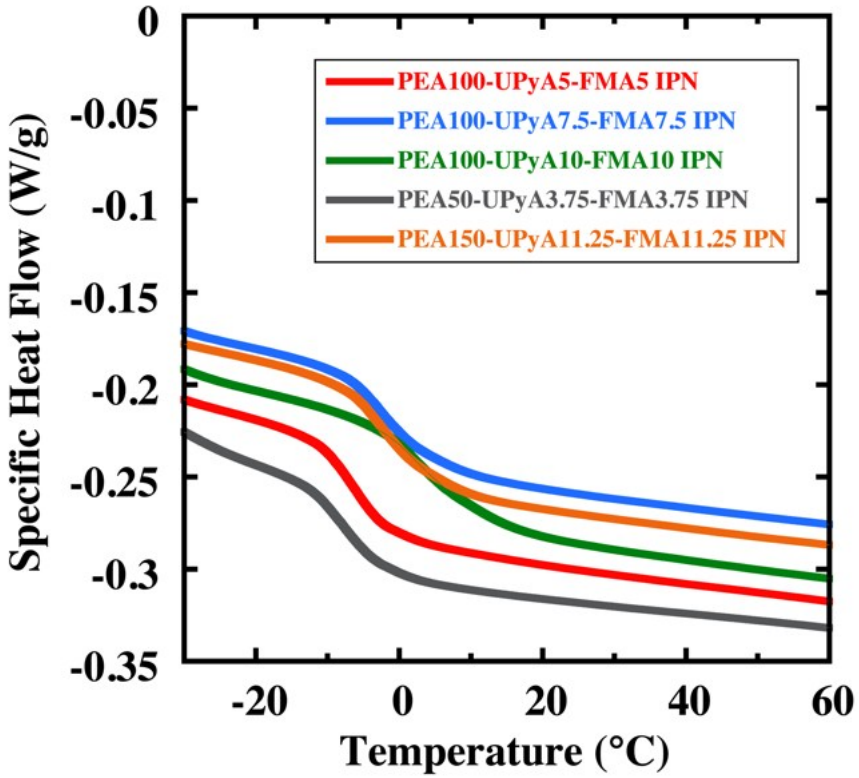

Figure S9. DSC traces of all five IPN materials.

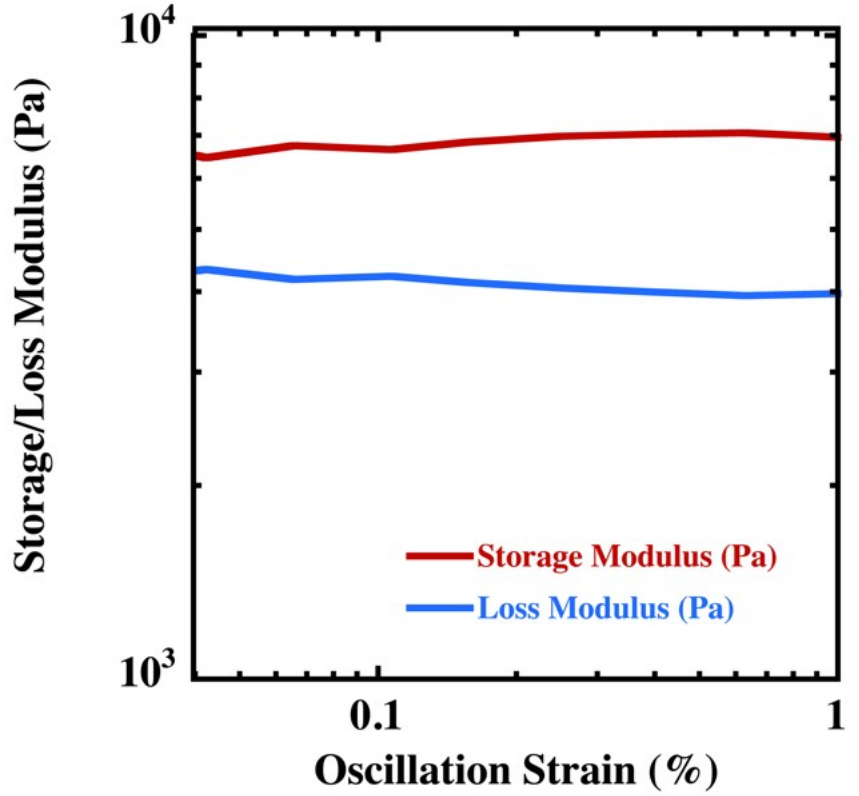

Figure S10. Rheological strain sweep of PEA_{100}-$UPyA_5$-FMA_5 IPN at angular frequency of 0.1 Hz.

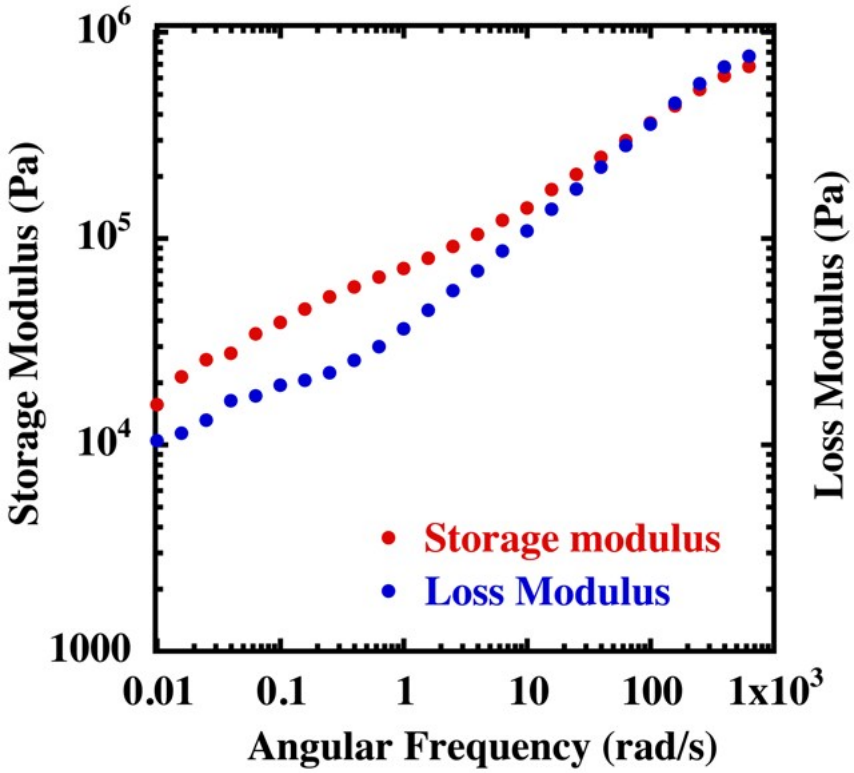

Figure S11. Rheological frequency sweep of PEA_{100}-$UPyA_5$-FMA_5 IPN using 0.1% strain and 0.1 Hz.

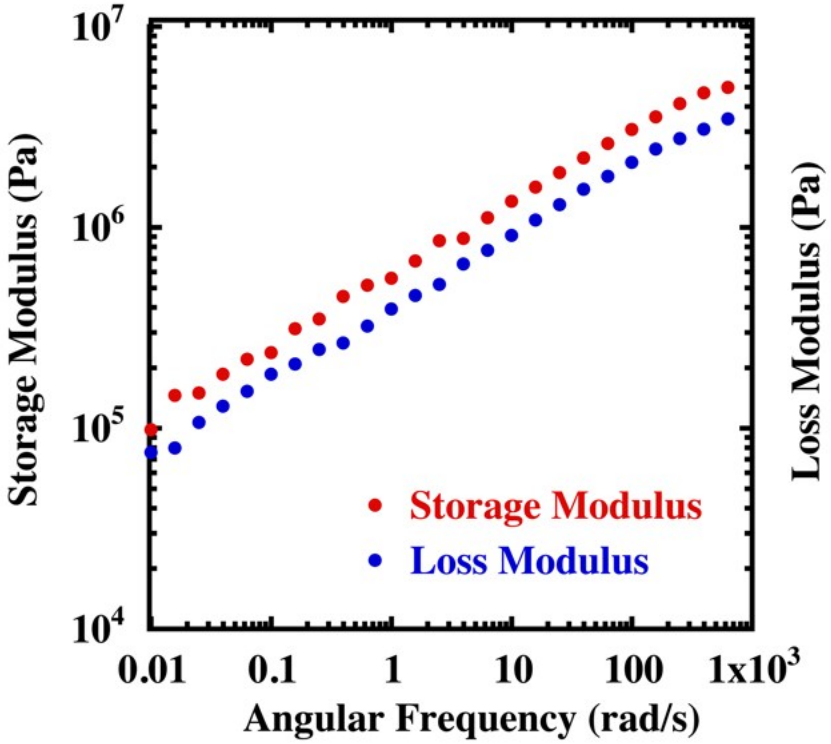

Figure S12. Rheological frequency sweep of PEA_{100}-$UPyA_{7.5}$-$FMA_{7.5}$ IPN using 0.1% strain and 0.1 Hz.

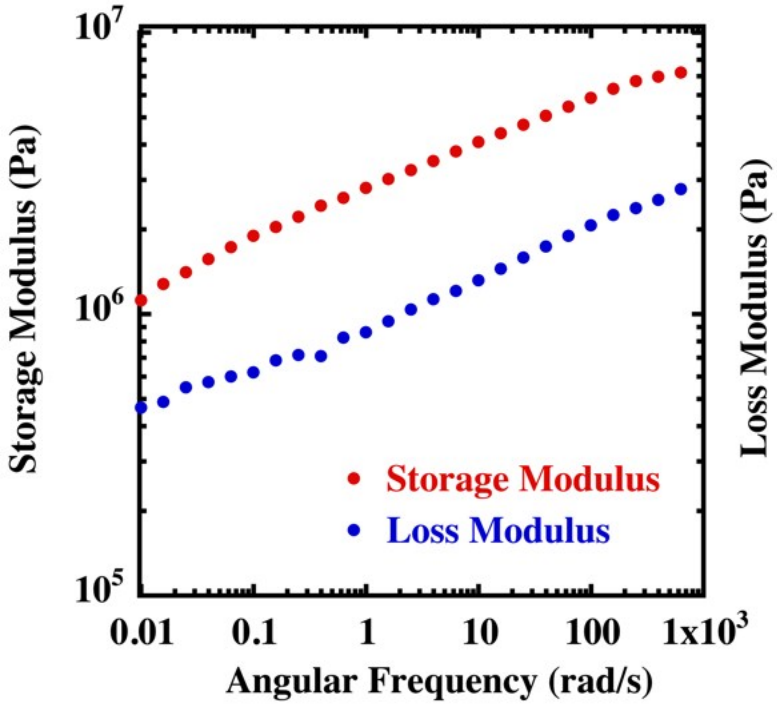

Figure S13. Rheological frequency sweep of PEA_{100}-$UPyA_{10}$-FMA_{10} IPN using 0.1% strain and 0.1 Hz.

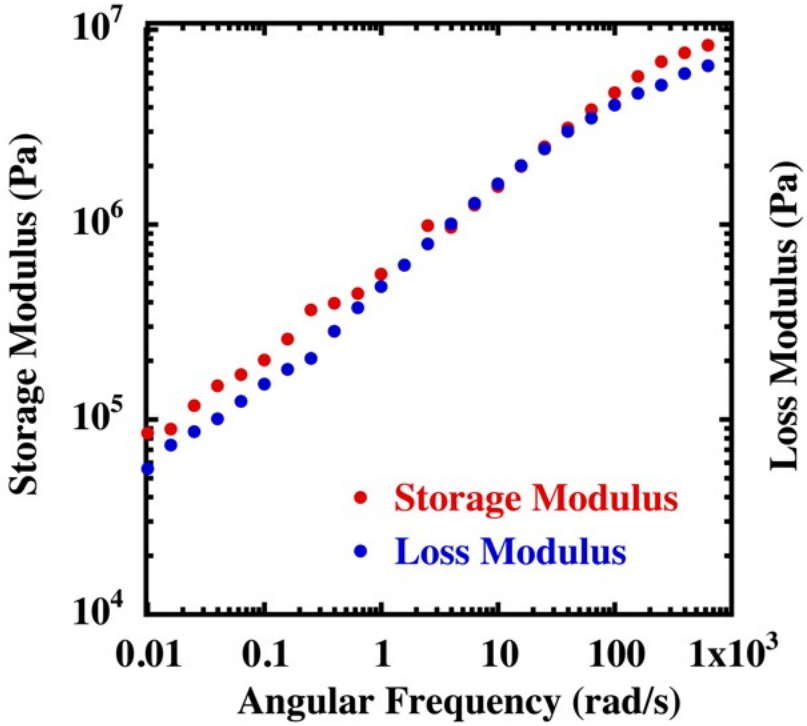

Figure S14. Rheological frequency sweep of PEA_{50}-$UPyA_{3.75}$-$FMA_{3.75}$ IPN using 0.1% strain and 0.1 Hz.

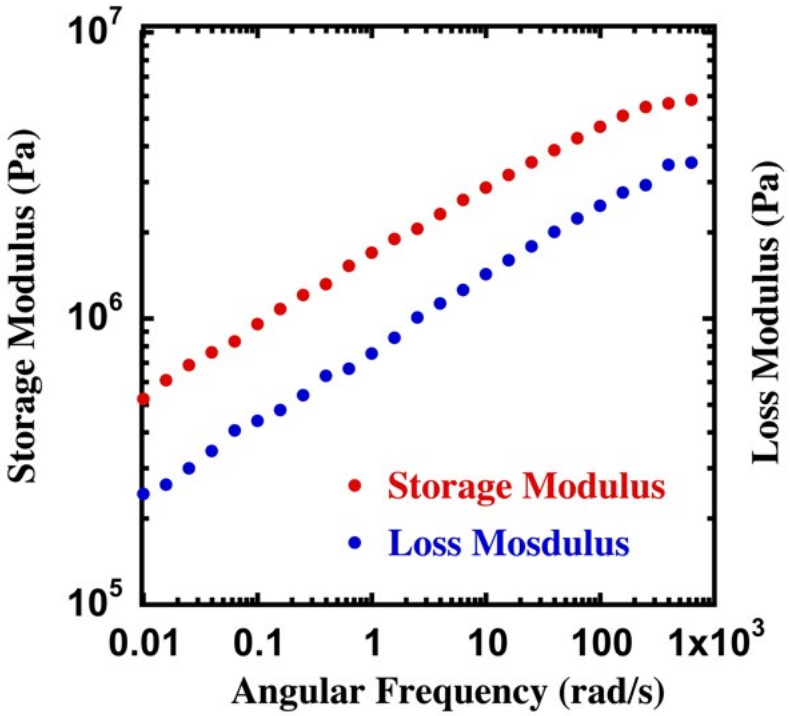

Figure S15. Rheological frequency sweep of PEA_{150}-$UPyA_{11.25}$-$FMA_{11.25}$ IPN using 0.1% strain and 0.1 Hz.

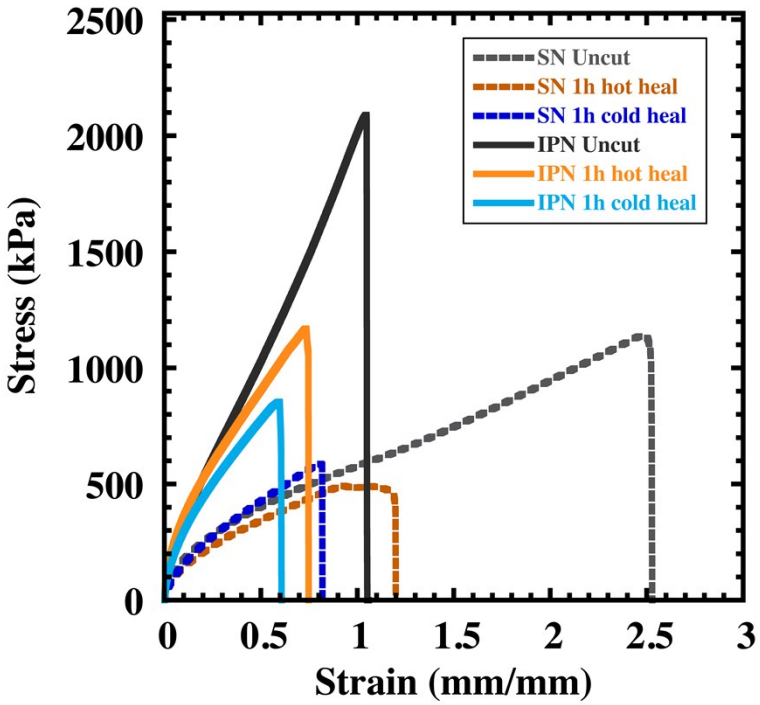

Figure S16. Typical stress vs strain curves for Uncut and 1 h cold and hot self-healing properties of PEA_{100}-$UPyA_{7.5}$-$FMA_{7.5}$ IPN and PEA_{100}-$UPyMA_{3.75}$-$FMA_{3.75}$ SN materials.

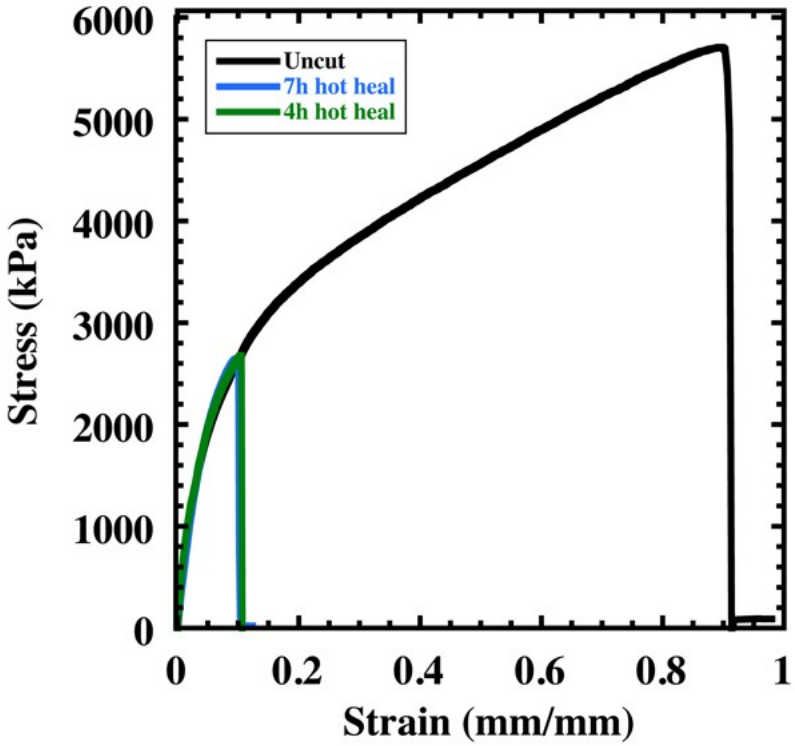

Figure S17. Self-healing properties of PEA_{100}-$UPyA_{10}$-FMA_{10} IPN materials at 90 °C. PEA_{100}-$UPyA_{10}$-FMA_{10} No self-healing was observed for the of PEA_{100}-$UPyA_{10}$-FMA_{10} materials at room temperature.

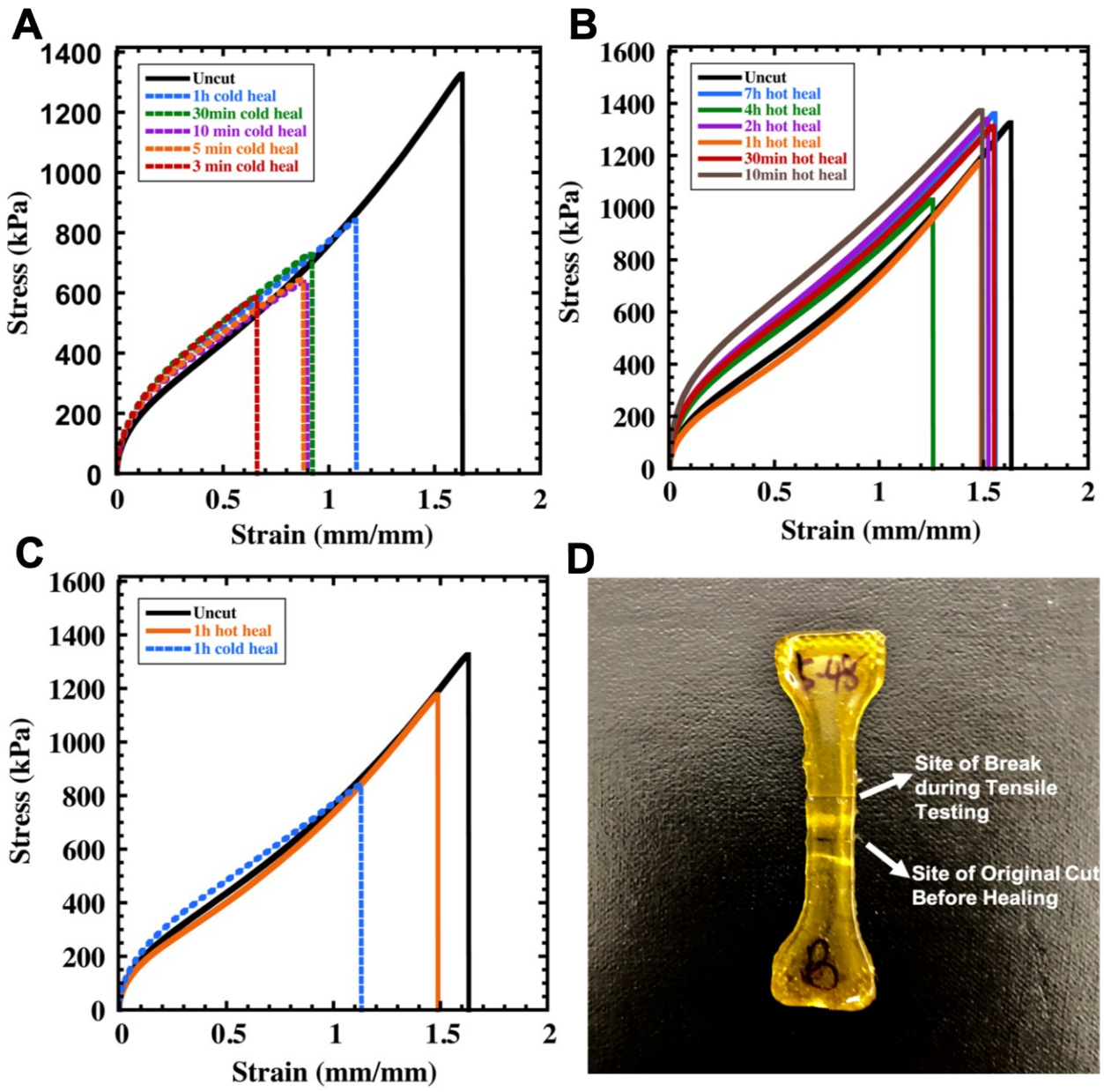

Figure S18. Self-healing properties of PEA_{50}-$UPyA_{3.75}$-$FMA_{3.75}$ IPN materials. (A) Typical stress vs strain curves after different healing time for cold heal of PEA_{50}-$UPyA_{3.75}$-$FMA_{3.75}$ IPN at room temperature. (B) Typical stress vs strain curves after different healing time for hot heal of PEA_{50}-$UPyA_{3.75}$-$FMA_{3.75}$ IPN at 90 °C. (C) Comparison of 1h hot heal stress-strain curve with 1 h cold heal stress-strain curve. (D) Photograph of a PEA_{50}-$UPyA_{3.75}$-$FMA_{3.75}$ IPN indicating site of original cut and break point during mechanical testing after 4h of healing at 90 °C.

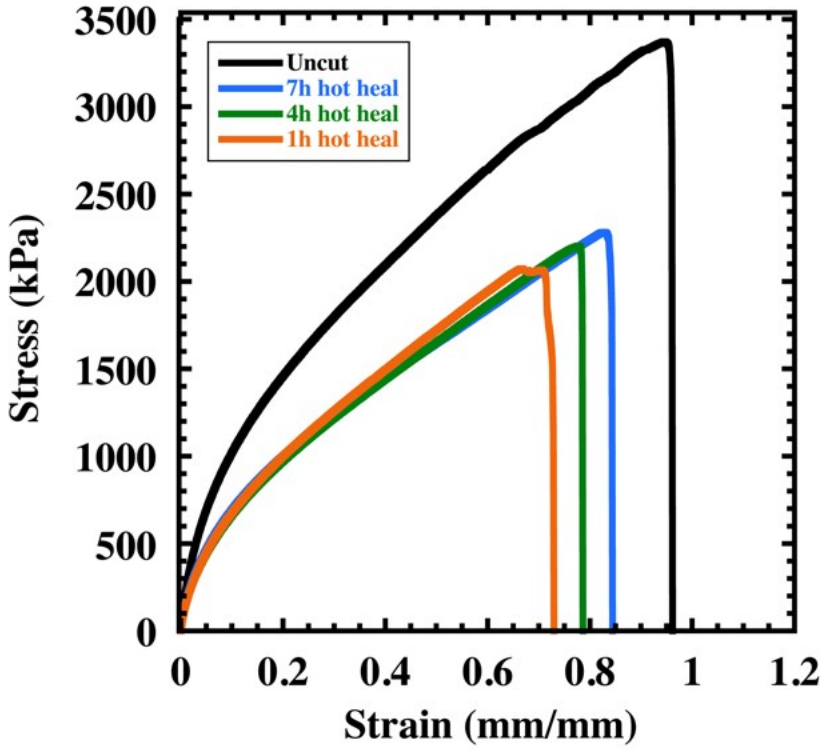

Figure S19. Self-healing properties of PEA_{150}-$UPyA_{11.25}$-$FMA_{11.25}$ IPN materials at 90 °C. They don't self-heal at room temperature.

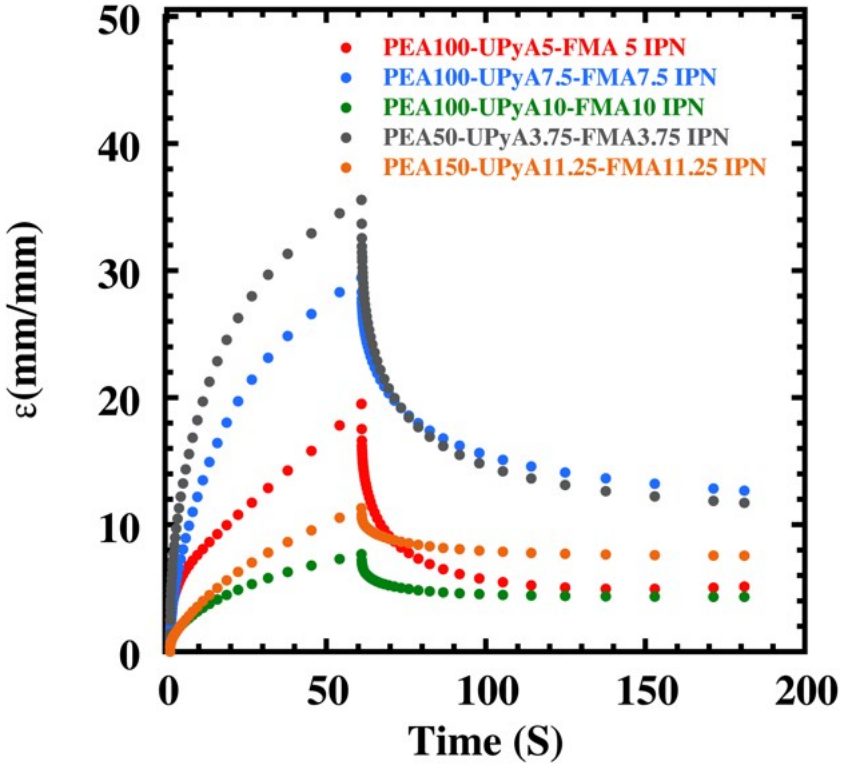

Figure S20. Creep deformation of all five IPN materials.

References

1. Palleros, D. R., *Experimental organic chemistry*. Wiley & Sons: 2000.
2. Vargün, E.; Usanmaz, A., Polymerization of 2-hydroxyethyl acrylate in bulk and solution by chemical initiator and by ATRP method. *J. Polym. Sci. A* **2005,** *43*, 3957-3965.
3. Wang, L.; Dong, W.; Xu, Y., Synthesis and characterization of hydroxypropyl methylcellulose and ethyl acrylate graft copolymers. *Carbohydr. Polym.* **2007,** *68*, 626-636.