Supplemental Information

Polyelectrolyte Complex Scaffoldings for Photocrosslinked Hydrogels

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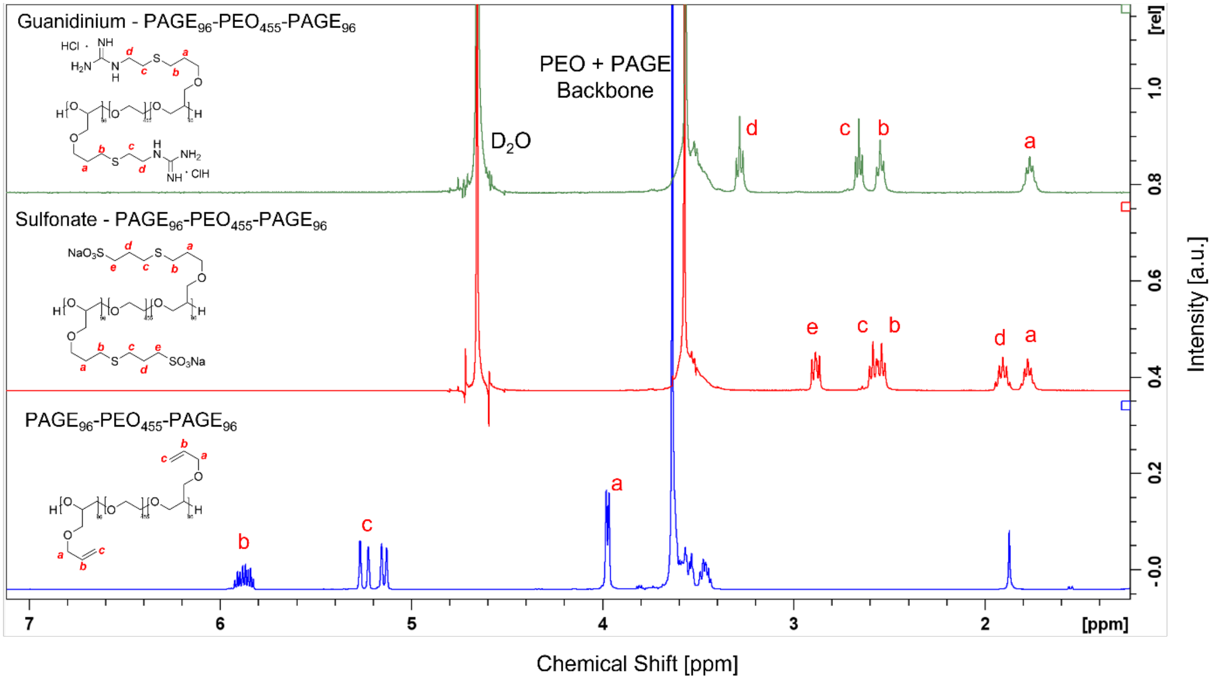
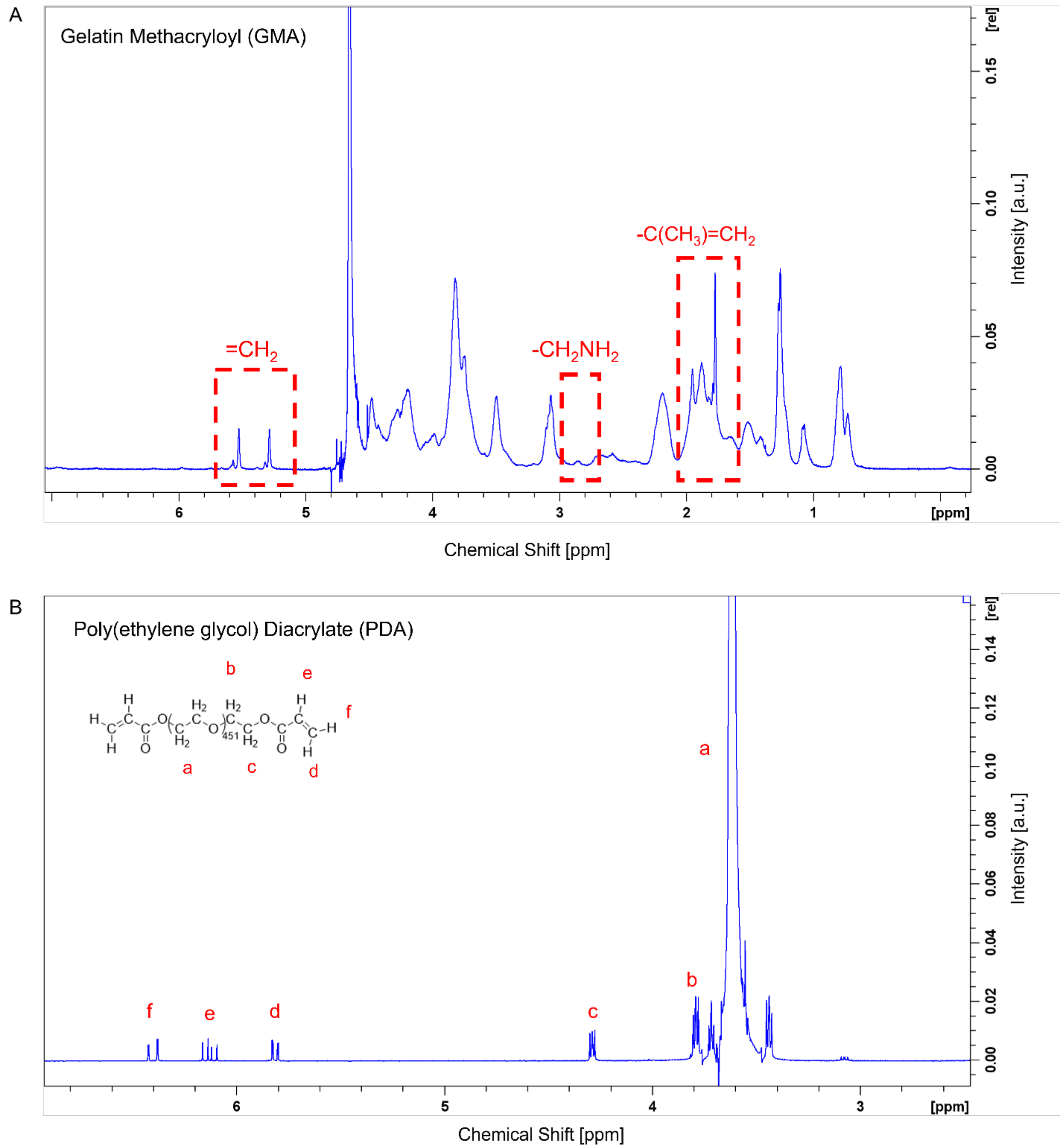


Figure S1. [1]H NMR spectra of $PAGE_{96}$-PEO_{455}-$PAGE_{96}$, sulfonate-functionalized $PAGE_{96}$-PEO_{455}-$PAGE_{96}$, and guanidinium-functionalized $PAGE_{96}$-PEO_{455}-$PAGE_{96}$.



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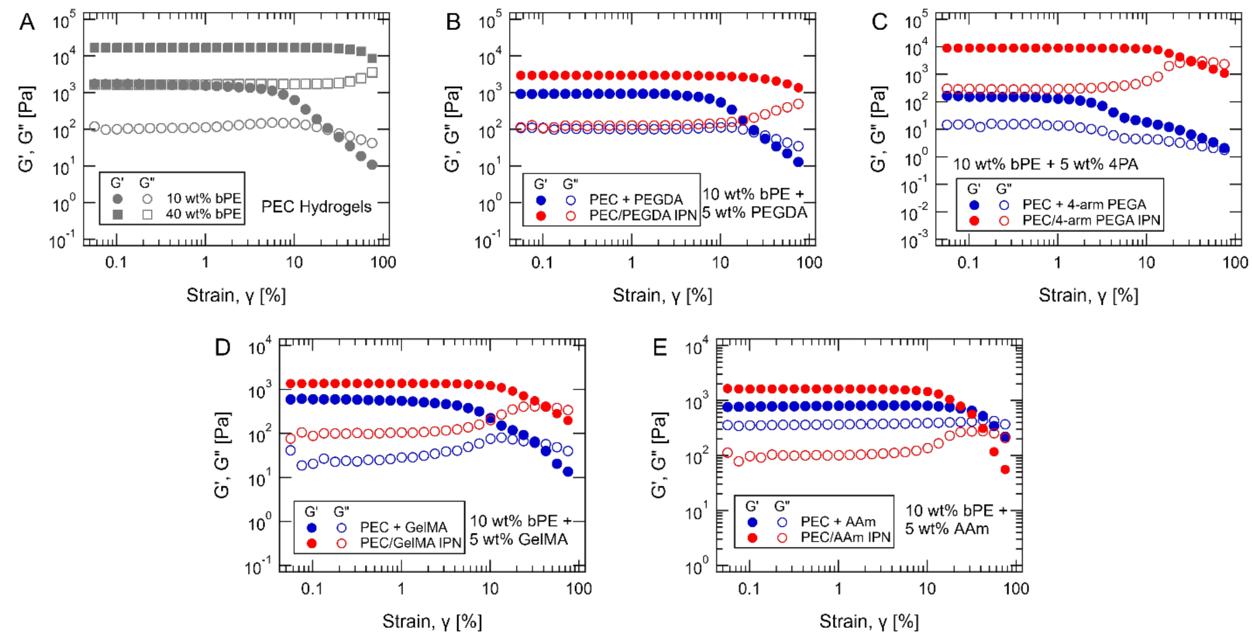


Figure S3. Representative amplitude sweeps showing G' and G'' as a function of strain for PEC, PEC + precursors, and IPN hydrogels. **(A)** PEC hydrogels with C_{bPE} = 10 wt% and 40 wt%. **(B)** PEC + PEGDA and PEC/PEGDA IPN hydrogels with C_{bPE} = 10 wt% and C_{PC} = 5 wt%. **(C)** PEC + 4-arm PEGPA and PEC/4-arm PEGPA IPN hydrogels with C_{bPE} = 10 wt% and C_{PC} = 5 wt%. **(D)** PEC+AAm and PEC/AAm IPN hydrogels with C_{bPE} = 10 wt% and C_{PC} = 5 wt%. **(E)** PEC+GelMA and PEC/GelMA IPN hydrogels with C_{bPE} = 10 wt% and C_{PC} = 5 wt%.

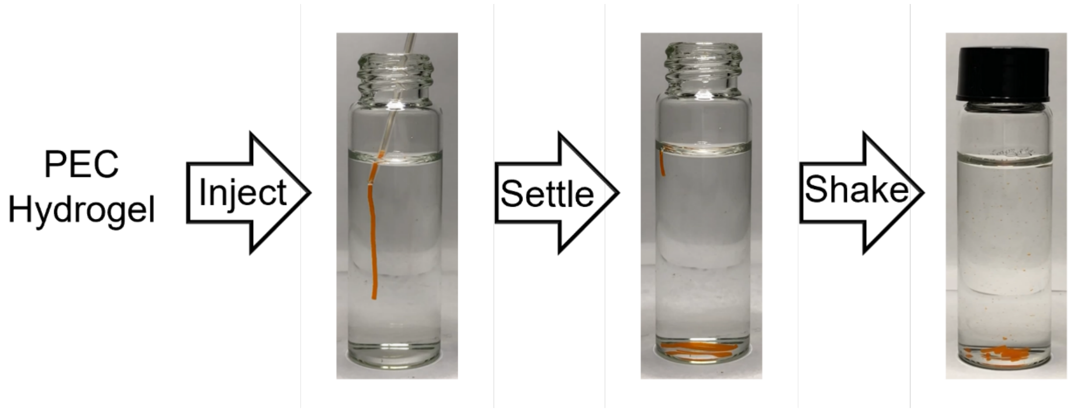


Figure S4. Photos showing injectability of polyelectrolyte complex (PEC) hydrogel and its interim resistance against dissolution upon shaking in water.

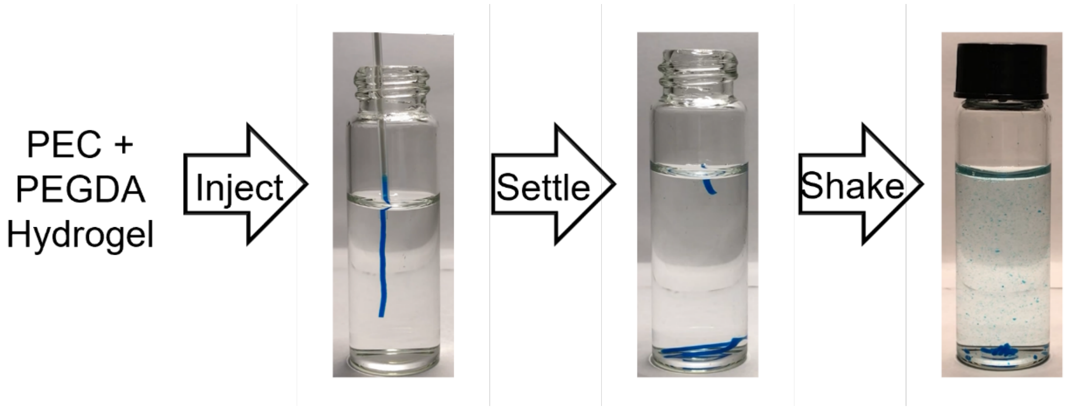


Figure S5. Photos showing injectability and interim insolubility of PEC+PEGDA hydrogel in water.

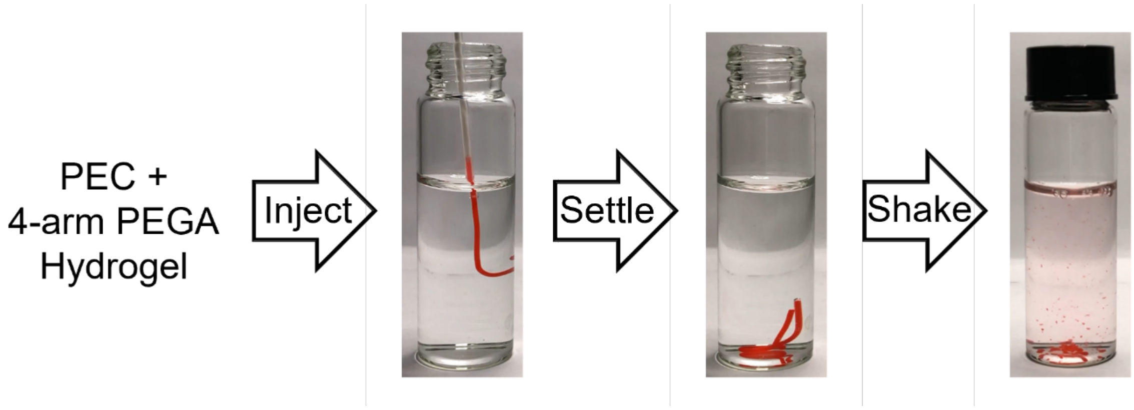
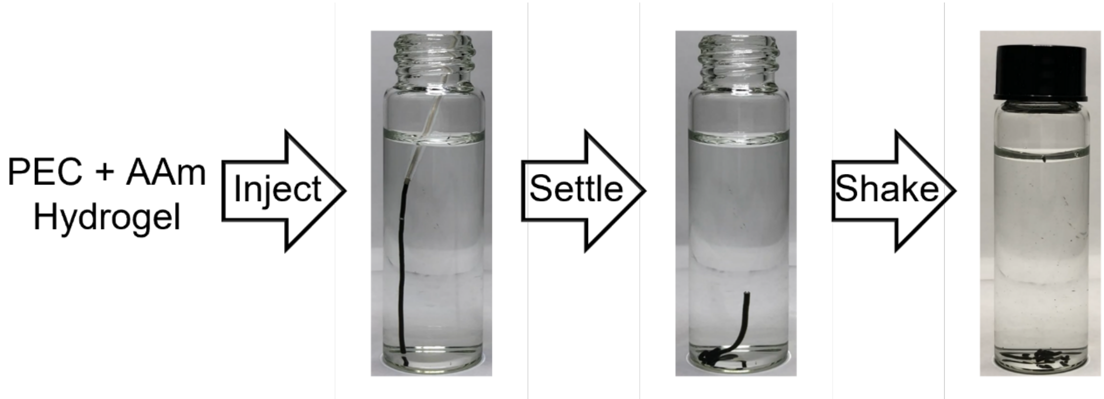


Figure S6. Photos showing injectability and interim insolubility of PEC+4-arm PEGA hydrogel in an aqueous environment.



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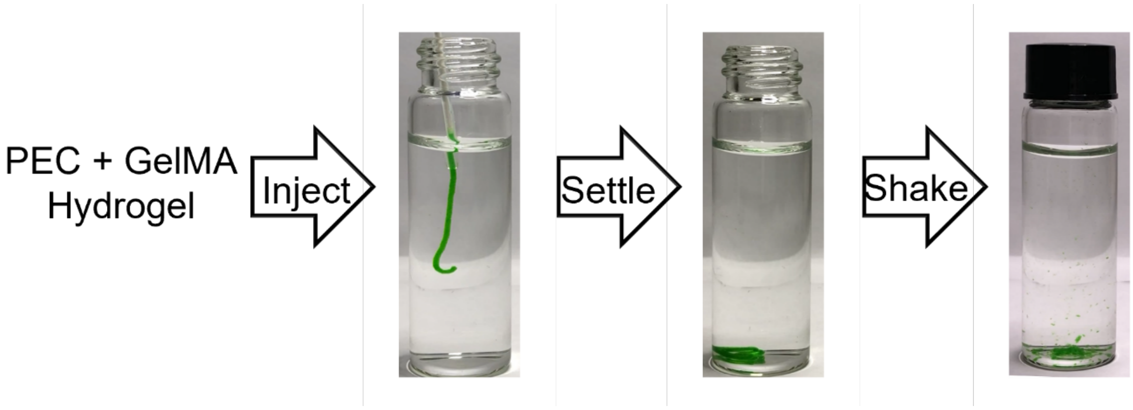

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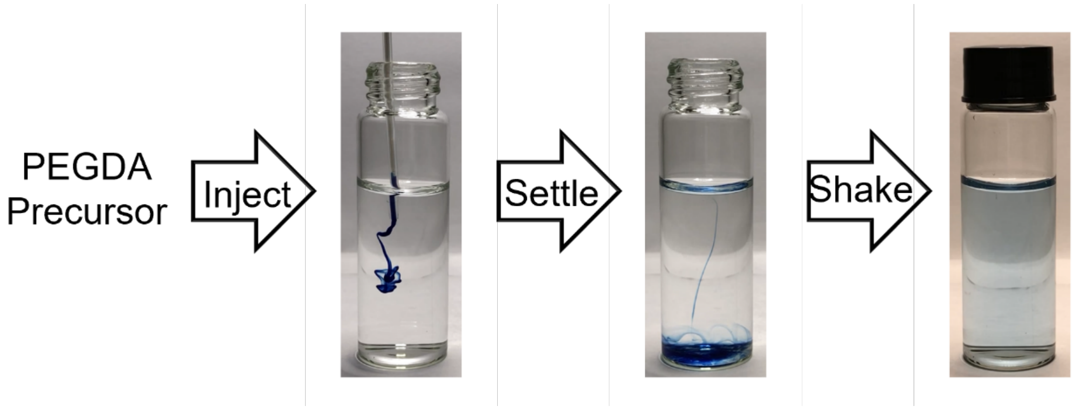

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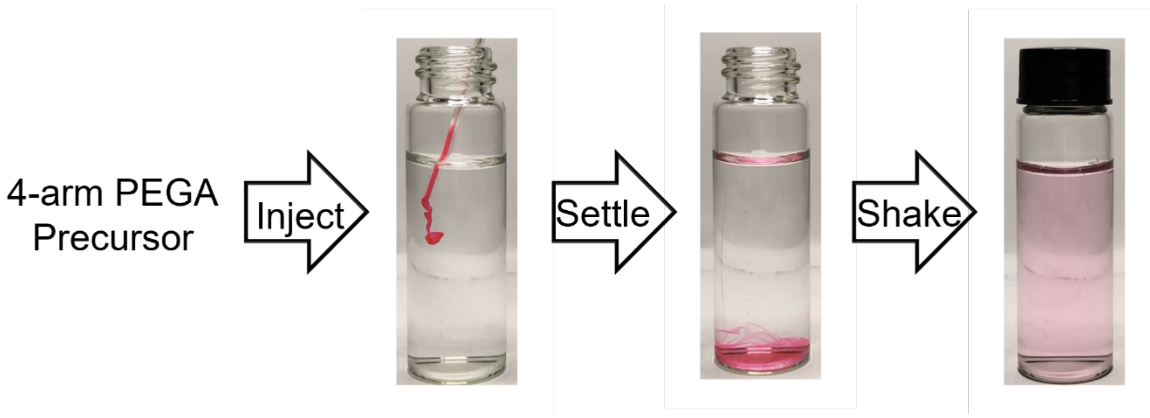

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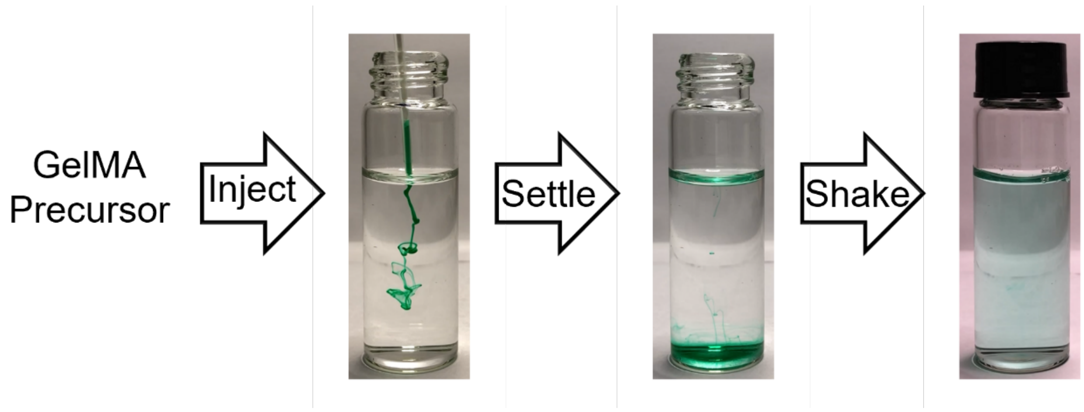

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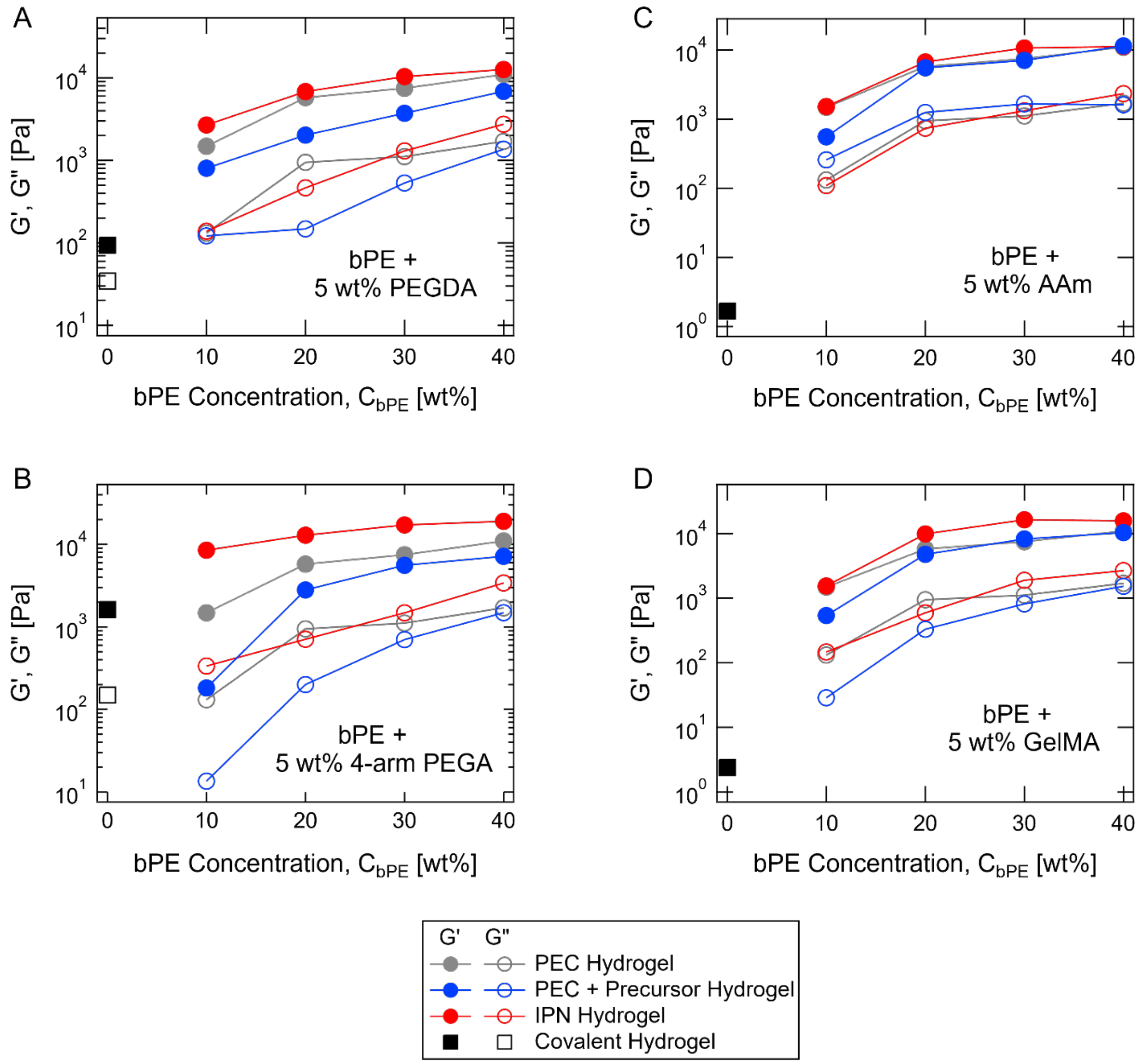

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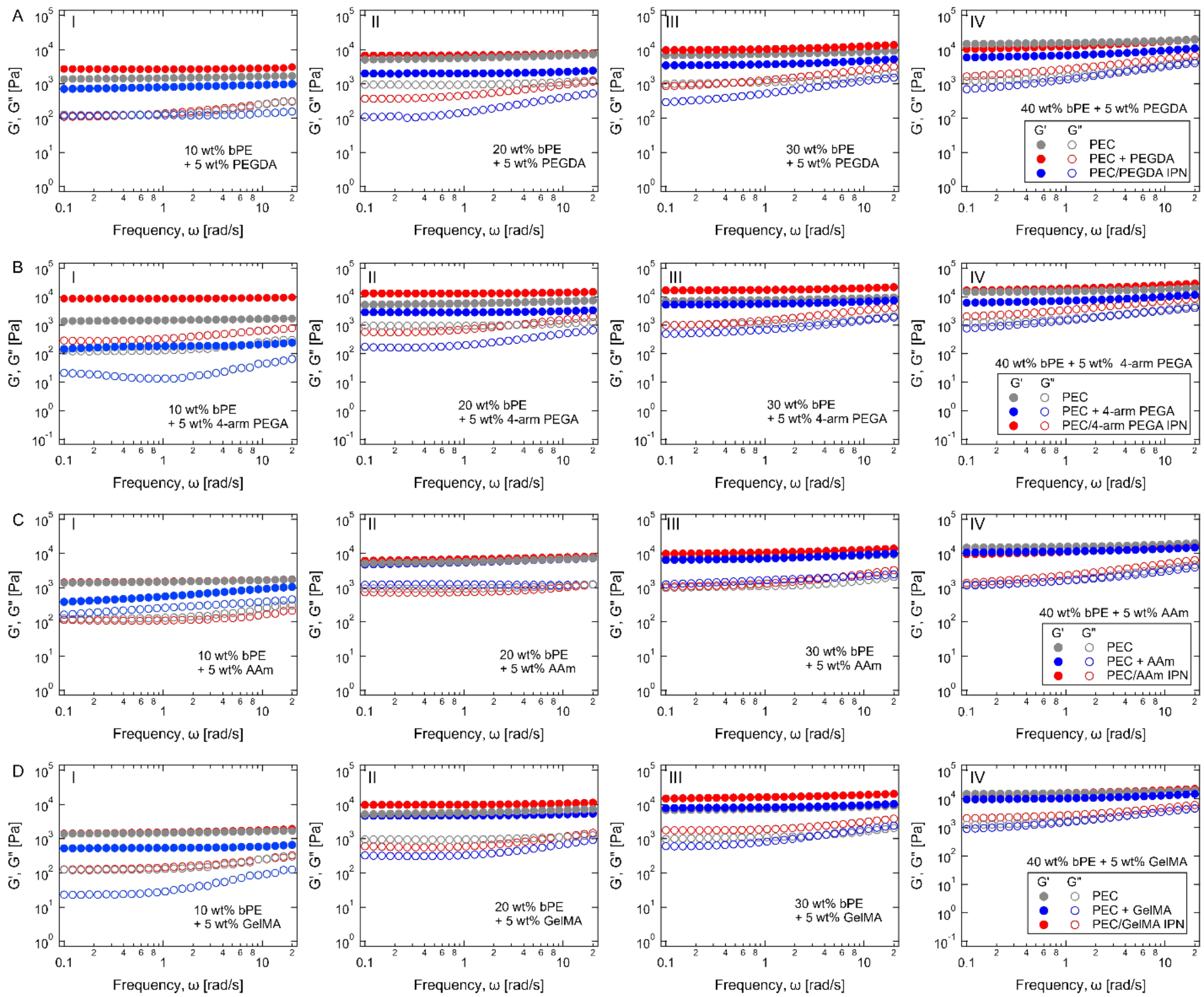

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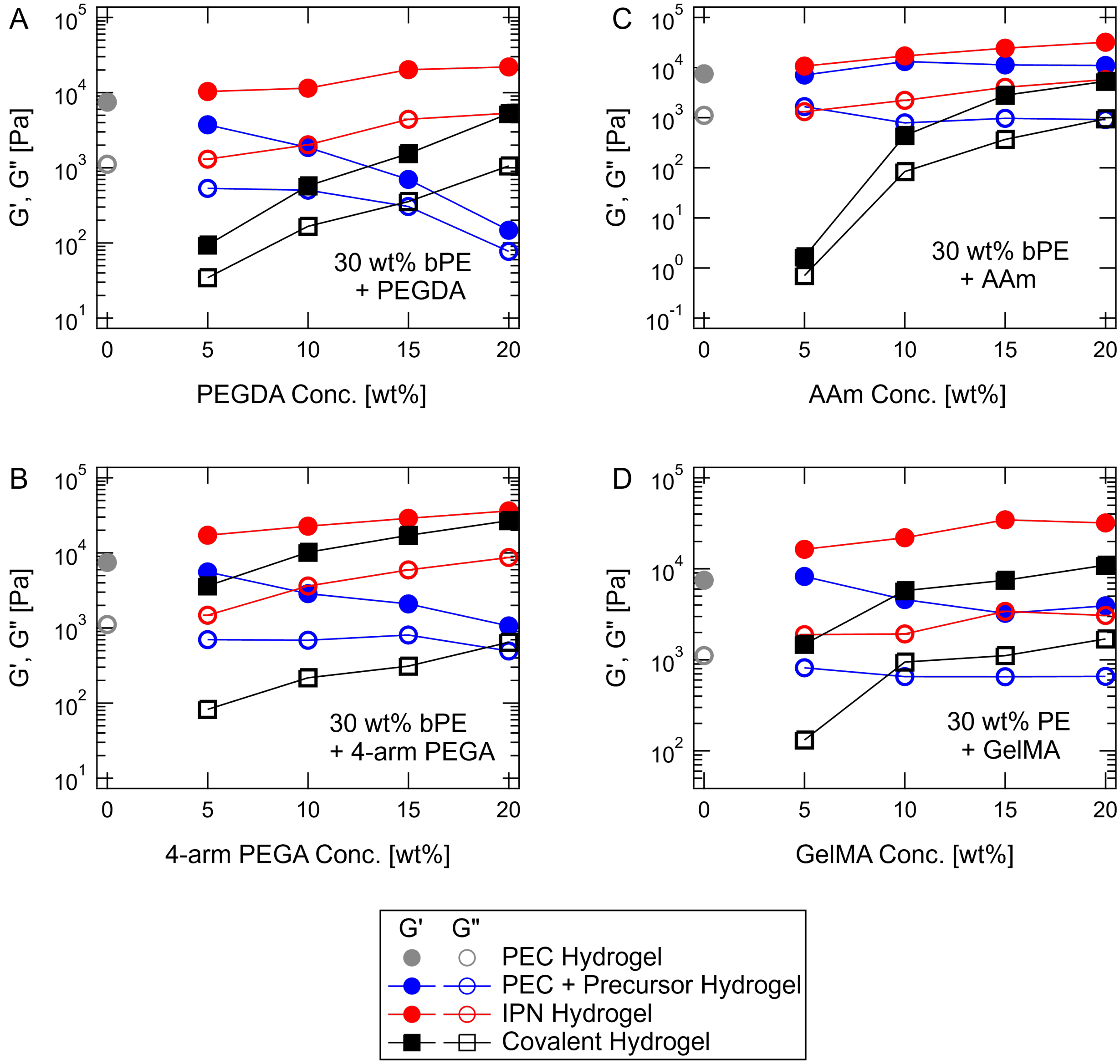

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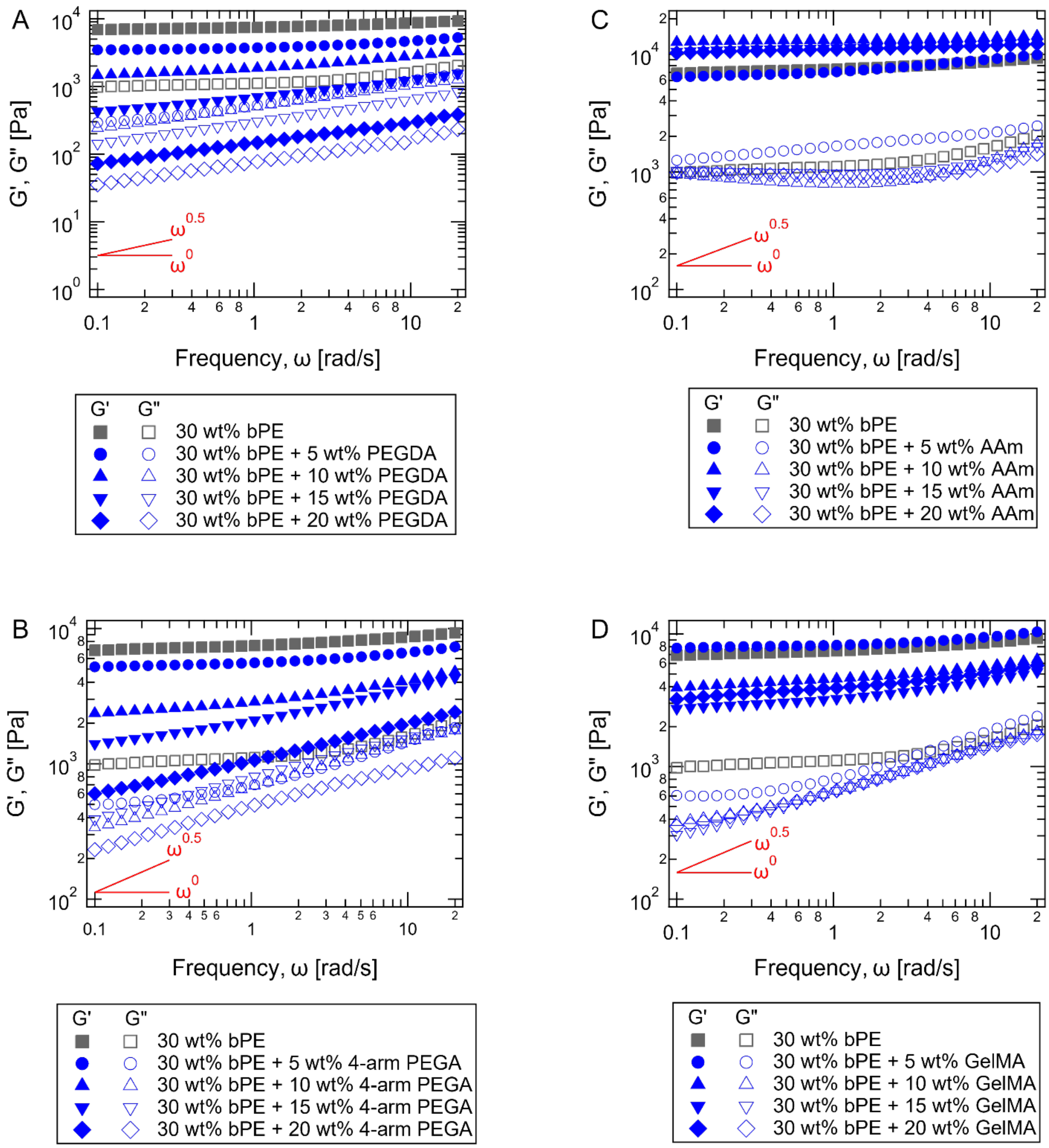

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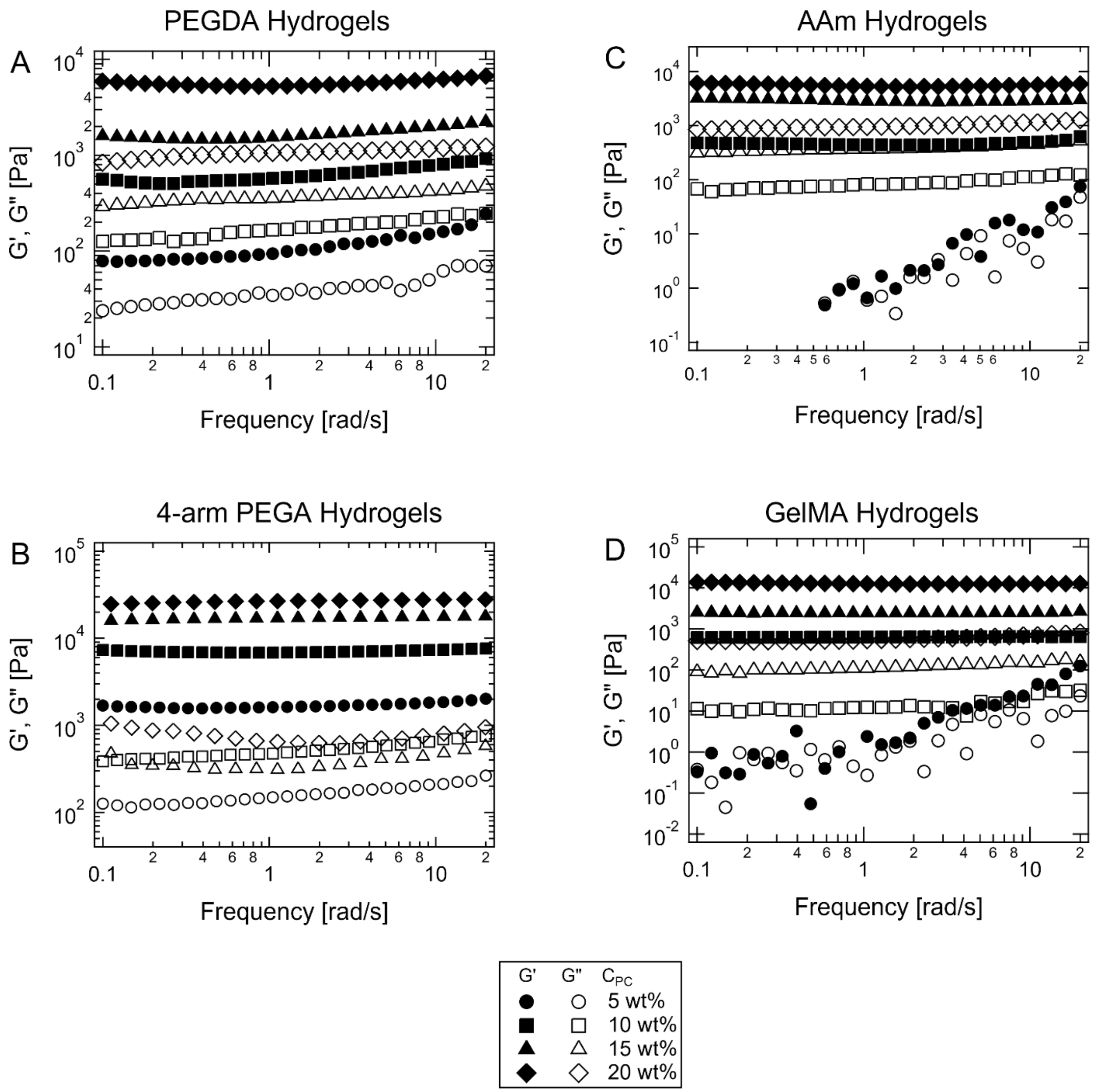

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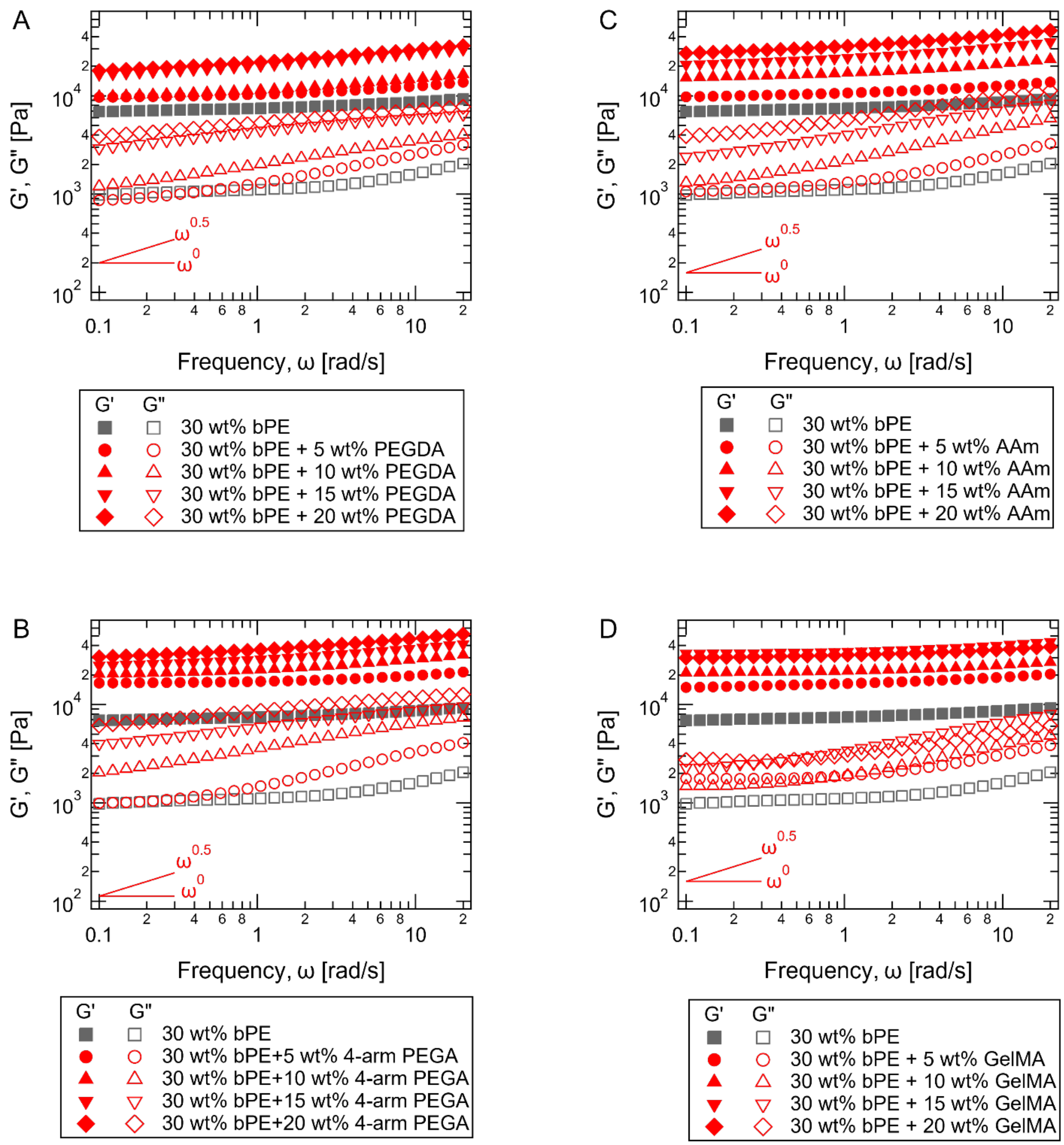

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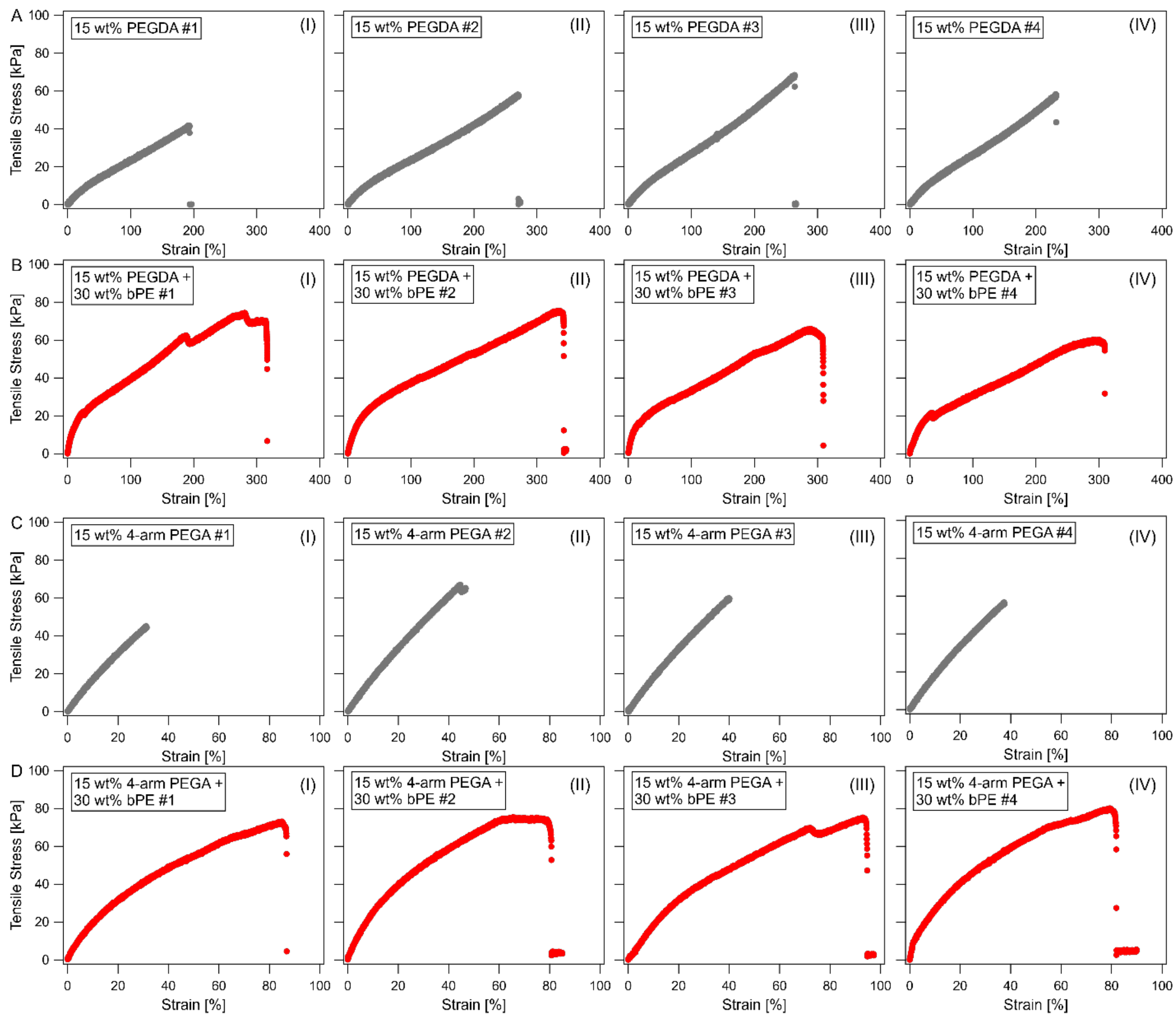

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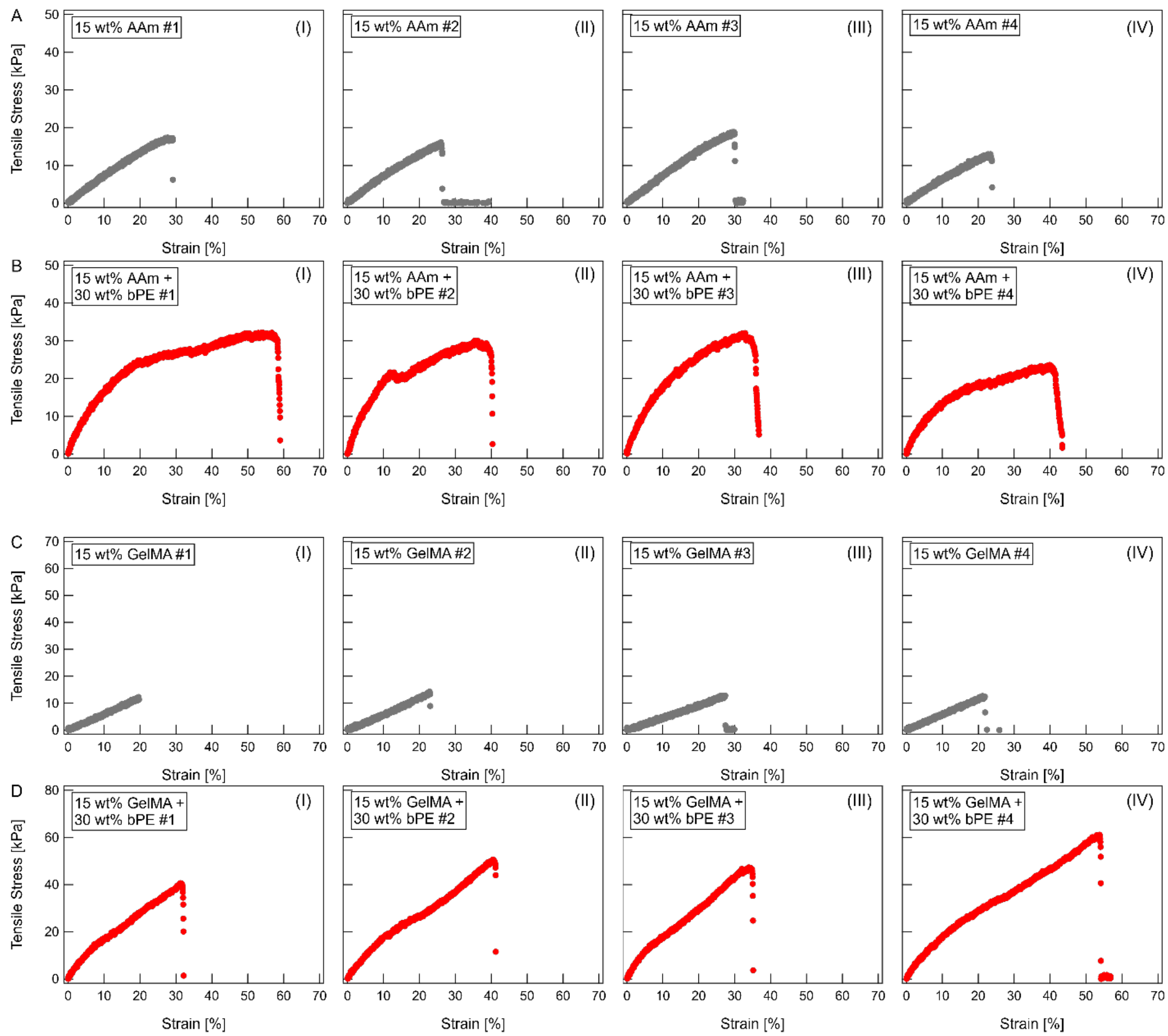

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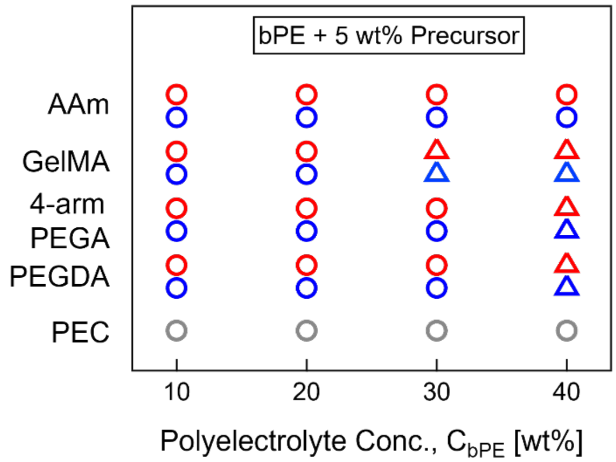

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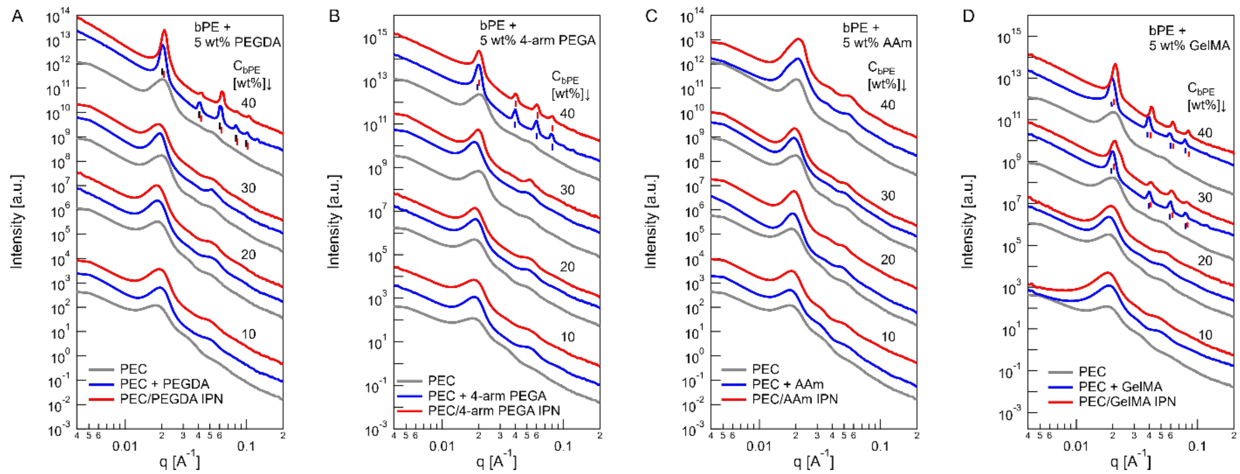

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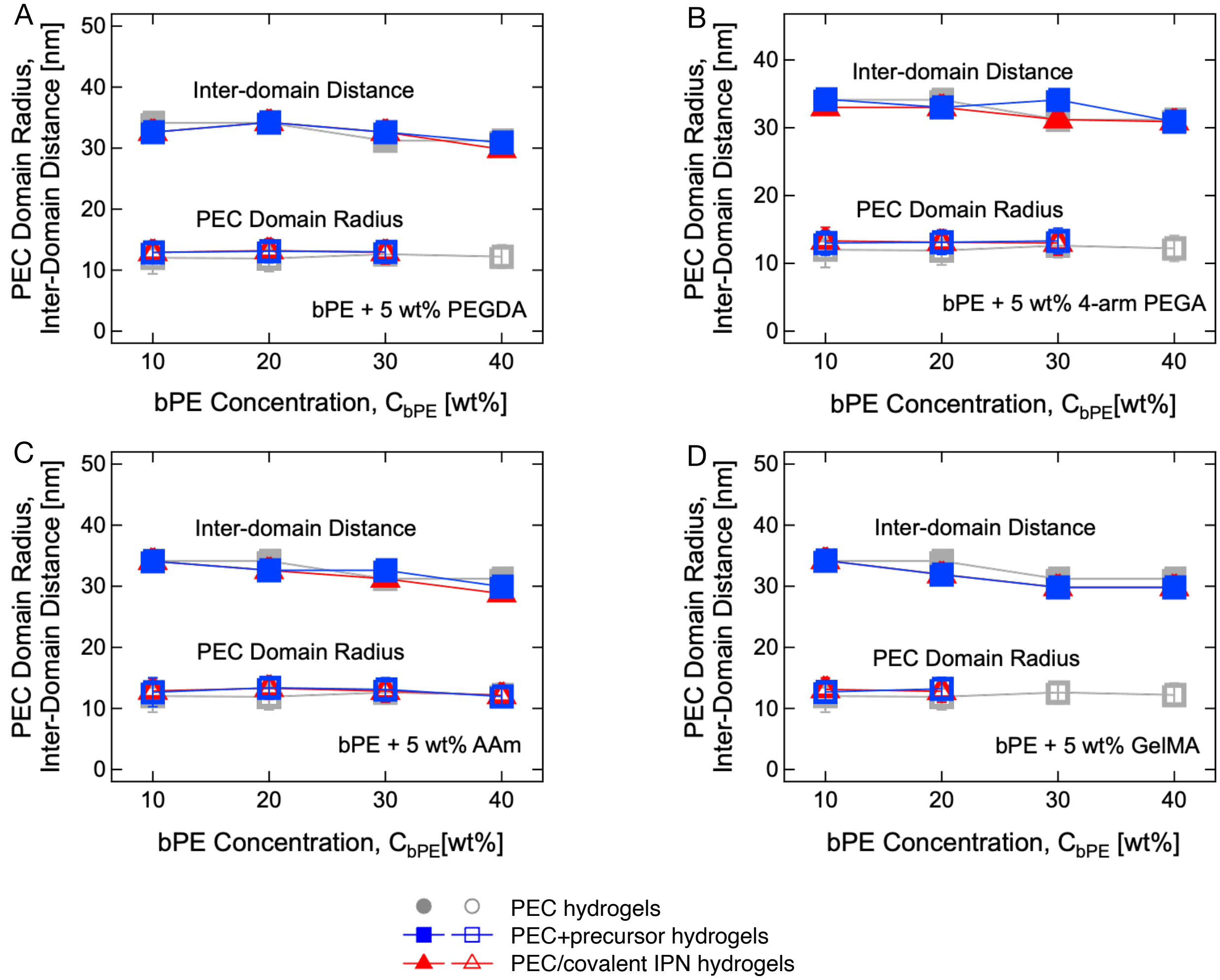

Figure S23. Attributes of the PEC domains (size and interdomain distance), as ascertained from the SAXS spectra, in the PEC (grey), PEC + precursors (blue), and IPN (red) hydrogels with varying bPE concentration. All PEC+precursor and IPN hydrogels contain 5 wt% precursor content. (A) PEGDA-based hydrogels, (B) 4-arm PEGA-based hydrogels, (C) AAm-based hydrogels, (D) GelMA-based hydrogels.

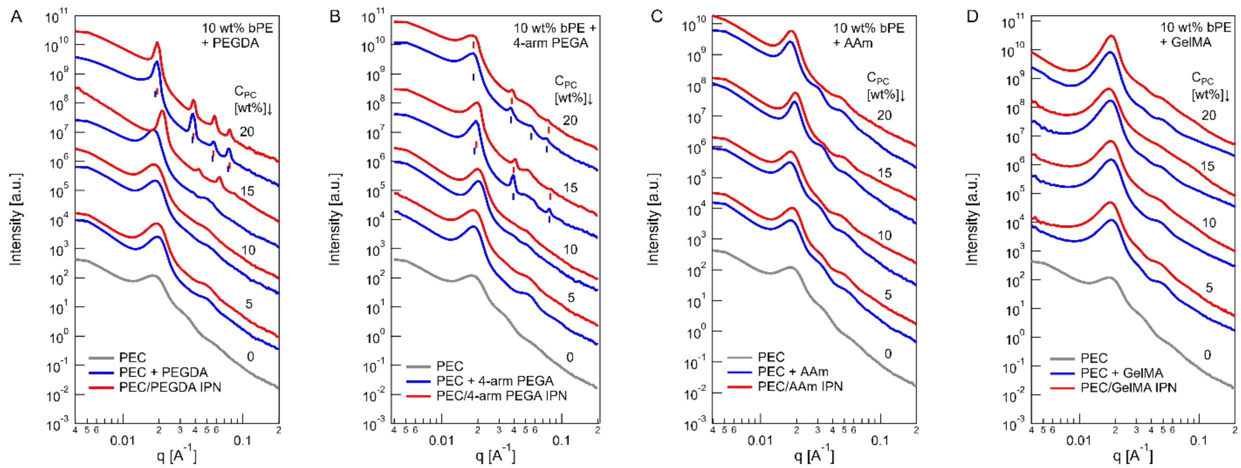

Figure S24. One-dimensional SAXS scattering $I(q)$ as a function of q for the PEC (grey), PEC + precursors (blue), and IPN (red) hydrogels with varying precursor concentration. Hydrogels contain 10 wt% tbPE content. (A) PEGDA-based hydrogels, (B) 4-arm PEGA-based hydrogels, (C) AAm-based hydrogels, (D) GelMA-based hydrogels. The SAXS scattering curves were shifted vertically for clarity. The details of Bragg peak positions are summarized in Table S1-S6.

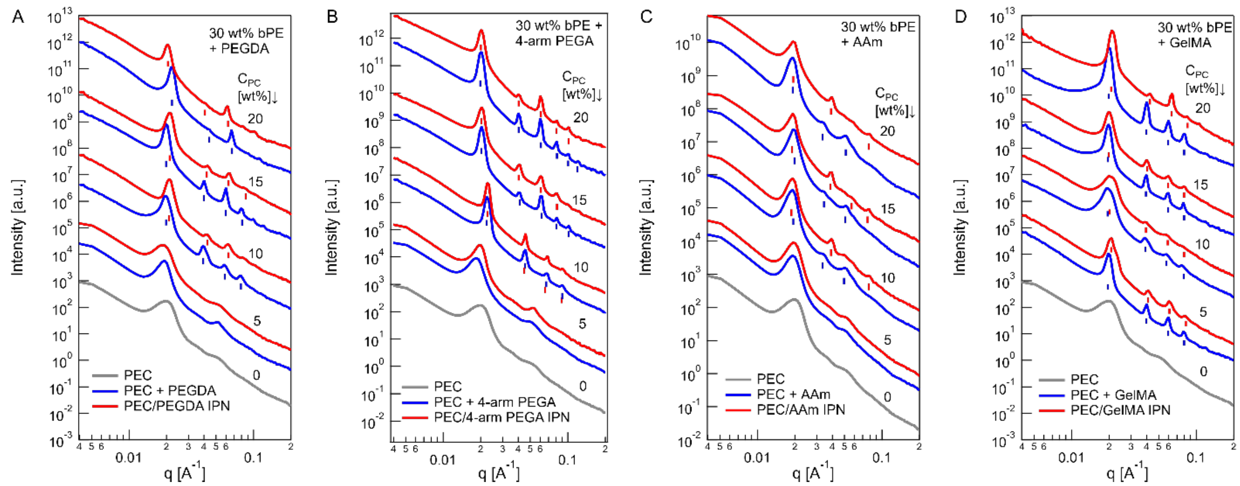

Figure S25. One-dimensional SAXS scattering $I(q)$ as a function of q for the PEC (grey), PEC + precursors (blue), and IPN (red) hydrogels with varying precursor concentration. Hydrogels contain 30 wt% tbPE content. (A) PEGDA-based hydrogels, (B) 4-arm PEGA-based hydrogels, (C) AAm-based hydrogels, (D) GelMA-based hydrogels. The SAXS scattering curves were shifted vertically for clarity. The details of Bragg peak positions are summarized in Table S1-S6.

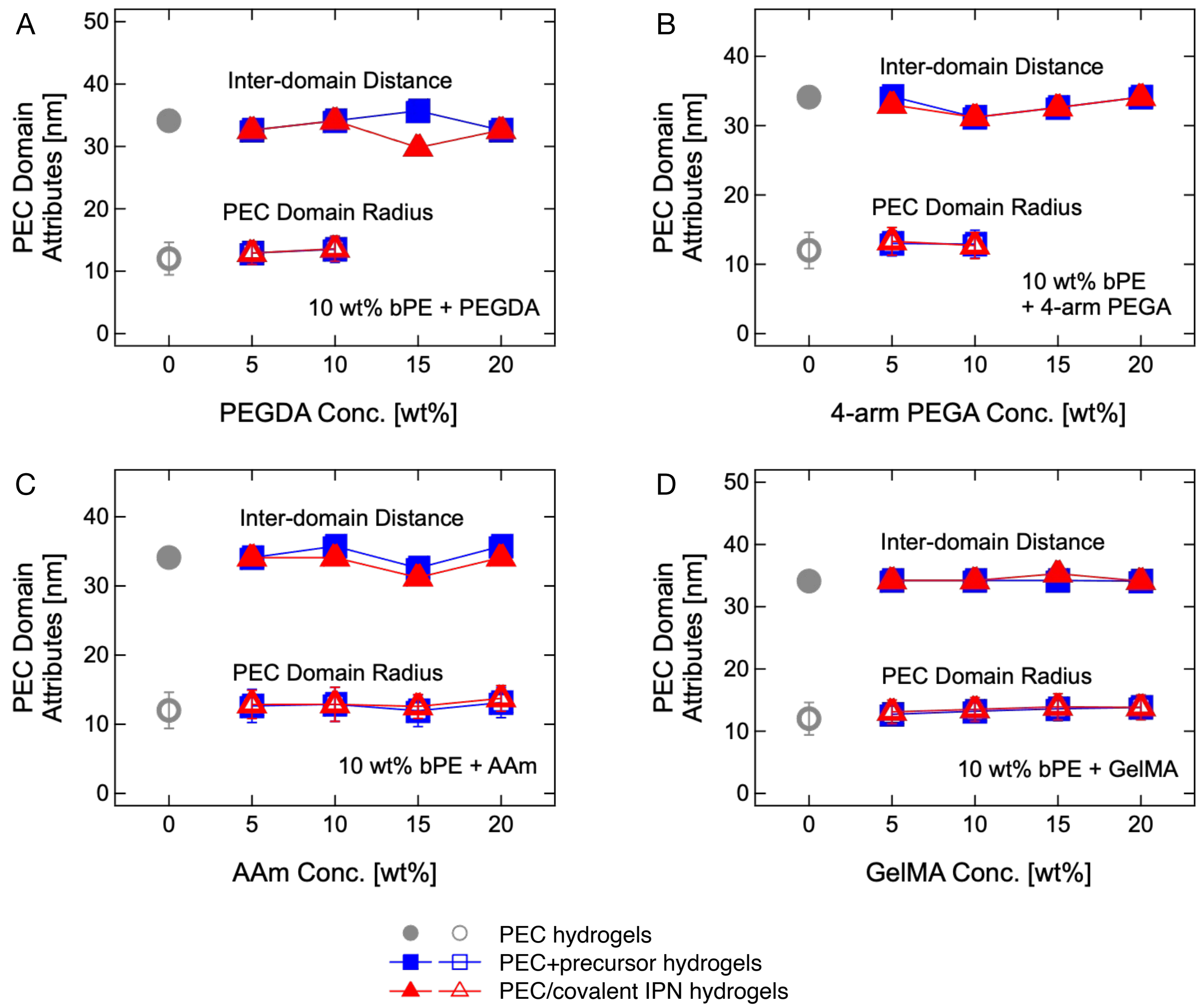

Figure S26. Attributes of the PEC domains (size and interdomain distance), as ascertained from the SAXS spectra, in the PEC (grey), PEC + precursors (blue), and IPN (red) hydrogels with varying precursor concentration. Hydrogels contain 10 wt% tbPE content. (A) PEGDA-based hydrogels, (B) 4-arm PEGA-based hydrogels, (C) AAm-based hydrogels, (D) GelMA-based hydrogels.

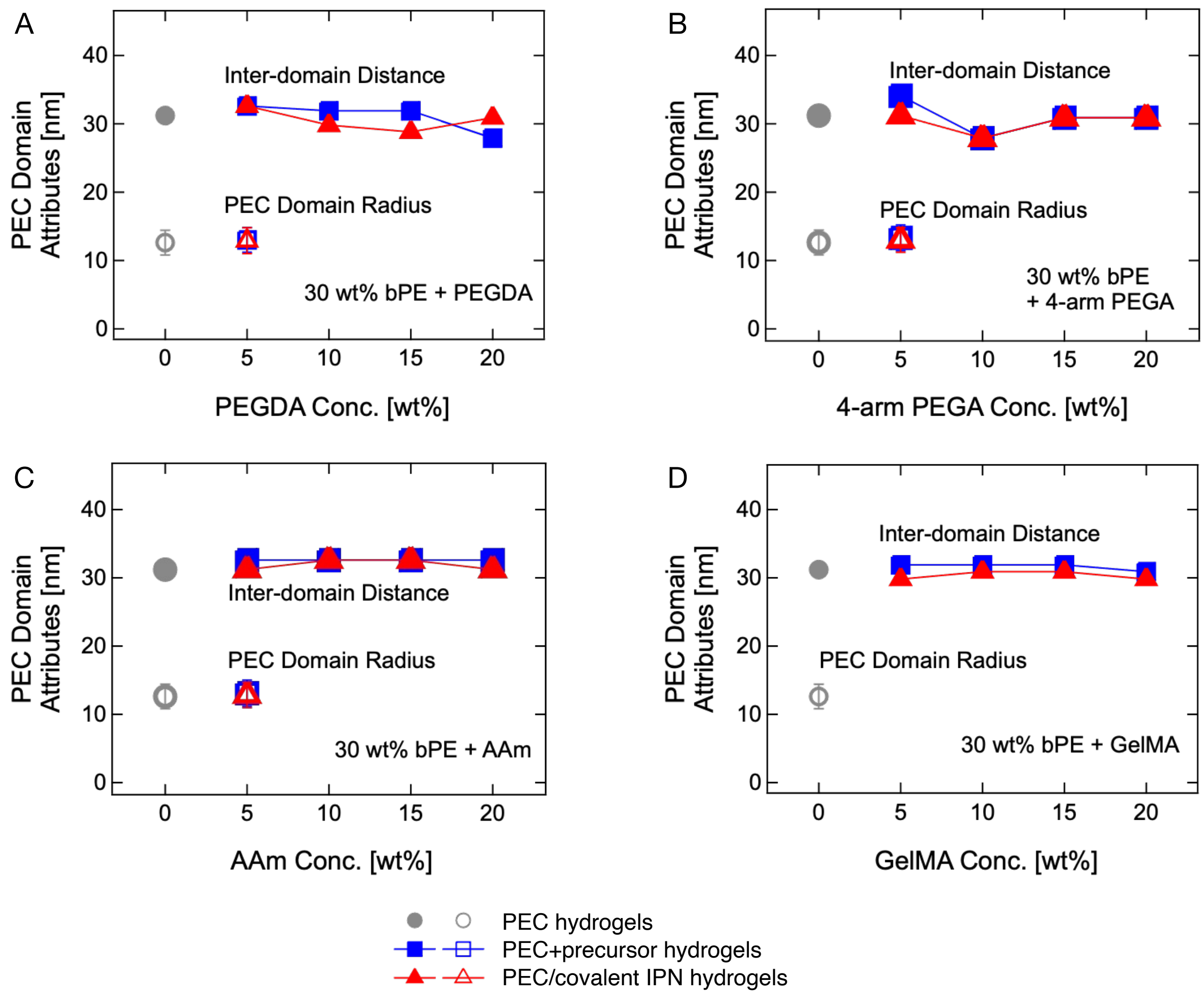

Figure S27. Attributes of the PEC domains (size and interdomain distance), as ascertained from the SAXS spectra, in for the PEC (grey), PEC + precursors (blue), and IPN (red) hydrogels with varying precursor concentration. Hydrogels contain 30 wt% tbPE content. (A) PEGDA-based hydrogels, (B) 4-arm PEGA-based hydrogels, (C) AAm-based hydrogels, (D) GelMA-based hydrogels. The SAXS scattering curves were shifted vertically for clarity.

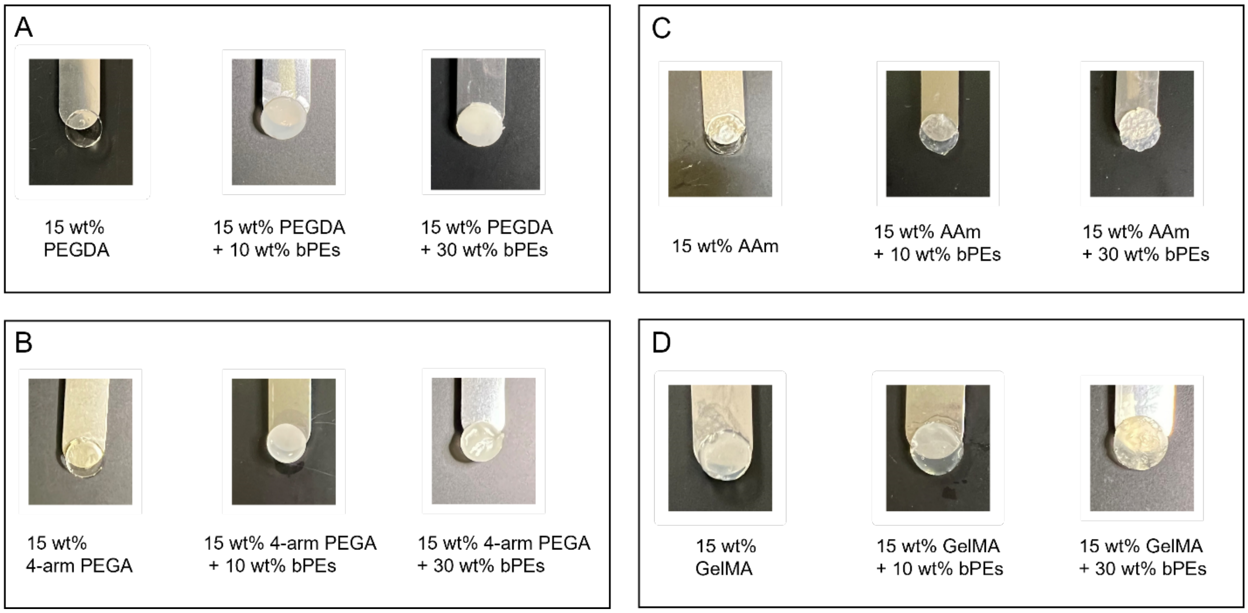

Figure S28. Photos of covalent and IPN hydrogels showing differences in optical density upon addition of tbPEs. All covalent hydrogels contained C_{PC} = 15 wt%. IPN hydrogels contained a constant C_{PC} = 15 wt% and varying C_{bPE} = 10 wt% or 30 wt%. (A) PEGDA-based hydrogels, (B) 4-arm PEGA-based hydrogels, (C) AAm-based hydrogels, (D) GelMA-based hydrogels.

Table S1. Bragg peak positions and microstructural details for PEC+4-arm PEGA hydrogels and PEC/4-arm PEGA IPN hydrogels with C_{bPE} = 30 wt%.

Hydrogel Description	q [Å^{-1}]	$\frac{q}{q^*}$	Expected $\frac{q}{q^*}$	Microstructure
PEC+4-arm PEGA hydrogels with C_{bPE} = 30 wt% and C_{PC} = 10 wt%, q^*= 0.0225 Å^{-1}	0.0459	2.04	2	LAM
	0.0689	3.06	3	
	0.0903	4.01	4	
PEC/4-arm PEGA IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 10 wt%, q^*= 0.0225 Å^{-1}	0.0459	2.04	2	LAM
	0.0689	3.06	3	
	0.0903	4.01	4	
PEC+4-arm PEGA hydrogels with C_{bPE} = 30 wt% and C_{PC} = 15 wt%, q^*= 0.0204 Å^{-1}	0.0415	2.04	2	LAM
	0.0622	3.06	3	
	0.0816	4.01	4	
	0.102	5.01	5	
PEC/4-arm PEGPA IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 15 wt%, q^*= 0.0204 Å^{-1}	0.0415	2.04	2	LAM
	0.0602	2.96	3	
	0.0816	4.01	4	
	0.102	5.01	5	
PEC+4-arm PEGA hydrogels with C_{bPE} = 30 wt% and C_{4PA} = 20 wt%, q^*= 0.0204 Å^{-1}	0.0401	1.97	2	LAM
	0.0602	2.96	3	
	0.0816	4.01	4	
	0.102	5.01	5	
	0.122	5.99	6	
PEC/4-arm PEGPA IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 20 wt%, q^*= 0.0204 Å^{-1}	0.0401	1.97	2	LAM
	0.0602	2.96	3	
	0.0816	4.01	4	
	0.102	5.01	5	
	0.124	6.09	6	

Table S2. Bragg peak positions and microstructural details for PEC+PEGDA hydrogels and PEC/PEGDA IPN hydrogels with C_{bPE} = 30 wt%.

Hydrogel Description	q **[Å^{-1}]**	$\frac{q}{q^*}$	**Expected** $\frac{q}{q^*}$	**Microstructure**
PEC+PEGDA hydrogels with C_{bPE} = 30 wt% and C_{PC} = 10wt%, q^*= 0.0197 Å^{-1}	0.0401	2.04	2	LAM
	0.0582	2.96	3	
	0.0789	4.01	4	
PEC/PEGDA IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 10 wt%, q^*= 0.0211 Å^{-1}	0.0429	2.04	2	LAM
	0.0622	2.96	3	
	0.0844	4.01	4	
PEC+PEGDA hydrogels with C_{bPE} = 30 wt% and C_{PC} = 15wt%, q^*= 0.0197 Å-1	0.0401	2.04	2	LAM
	0.0602	3.06	3	
	0.0789	4.01	4	
PEC/PEGDA IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 15 wt%, q^*= 0.0218 Å^{-1}	0.0429	1.97	2	LAM
	0.0644	2.96	3	
	0.0873	4.01	4	
PEC+PEGDA hydrogels with C_{bPE} = 30 wt% and C_{PC} = 20 wt%, q^*= 0.0225 Å^{-1}	0.0444	1.97	2	LAM
	0.0666	2.96	3	
PEC/PEGDA IPN hydrogels with C_{bPE} = 30 wt% and C_{pc} = 20 wt%, q^*= 0.0204 Å^{-1}	0.0415	2.04	2	LAM
	0.0622	3.06	3	

Table S3. Bragg peak positions and microstructural details for PEC+AAm hydrogels and PEC/AAm IPN hydrogels with C_{bPE} = 30 wt%.

Hydrogel Description	q **[Å^{-1}]**	$\frac{q}{q^*}$	**Expected** $\frac{q}{q^*}$	**Microstructure**	**Comments**
PEC+AAm hydrogels with C_{bPE} = 30 wt% and C_{PC} = 10 wt%, q^*= 0.0193 Å^{-1}	0.0343	1.78	1.73	HCP	
	0.0508	2.63	2.65		
PEC/AAm IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 10 wt%, q^*= 0.0193 Å^{-1}	0.0397	2.06	2	LAM	Missing peak at $3q^*$
	0.0788	4.09	4		
PEC+AAm hydrogels with C_{bPE} = 30 wt% and C_{PC} = 15 wt%, q^*= 0.0193 Å^{-1}	0.0343	1.78	1.73	HCP	
	0.0522	2.71	2.65		
PEC/AAm IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 15 wt%, q^*= 0.0193 Å^{-1}	0.0397	2.06	2	LAM	
	0.0578	3.00	3		
	0.0788	4.09	4		
PEC+AAm hydrogels with C_{bPE} = 30 wt% and C_{PC} = 20 wt%, q^*= 0.0193 Å^{-1}	0.0343	1.78	1.73	HCP	
	0.0508	2.63	2.65		
PEC/AAm IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 15 wt%, q^*= 0.0201 Å^{-1}	0.0397	1.97	2	LAM	Missing peak at $3q^*$
	0.0805	4.00	4		

Table S4. Bragg peak positions and microstructural details for PEC+GelMA hydrogels and PEC/GelMA IPN hydrogels with C_{bPE} = 30 wt%.

Hydrogel Description	q [Å^{-1}]	$\frac{q}{q^*}$	Expected $\frac{q}{q^*}$	Microstructure
PEC+GelMA hydrogels with C_{bPE} = 30 wt% and C_{PC} = 5 wt%, q^*= 0.0197 Å^{-1}	0.0401	2.04	2	LAM
	0.0602	3.06	3	
	0.0789	4.01	4	
PEC/GelMA IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 5 wt%, q^*= 0.0211 Å^{-1}	0.0415	1.97	2	LAM
	0.0602	2.86	3	
	0.0816	3.87	4	
PEC+GelMA hydrogels with C_{bPE} = 30 wt% and C_{PC} = 10 wt%, q^*= 0.0197 Å^{-1}	0.0387	1.97	2	LAM
	0.0582	2.96	3	
	0.0789	4.01	4	
PEC/GelMA IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 10 wt%, q^*= 0.0204 Å^{-1}	0.0401	1.97	2	LAM
	0.0582	2.86	3	
	0.0789	3.87	4	
PEC+GelMA hydrogels with C_{bPE} = 30 wt% and C_{PC} = 15 wt%, q^*= 0.0197 Å^{-1}	0.0401	2.04	2	LAM
	0.0602	3.06	3	
	0.0789	4.01	4	
PEC/GelMA IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 15 wt%, q^*= 0.0204 Å^{-1}	0.0401	1.97	2	LAM
	0.0602	2.96	3	
	0.0816	4.01	4	
PEC+GelMA hydrogels with C_{bPE} = 30 wt% and C_{PC} = 20 wt%, q^*= 0.0204 Å^{-1}	0.0429	1.97	2	LAM
	0.0644	2.96	3	
	0.0844	4.01	4	
PEC/GelMA IPN hydrogels with C_{bPE} = 30 wt% and C_{PC} = 20 wt%, q^*= 0.0211 Å^{-1}	0.0429	2.04	2	LAM
	0.0644	3.06	3	
	0.0844	4.01	4	

Table S5. Bragg peak positions and microstructural details for PEC+4-arm PEGA hydrogels and PEC/4-arm PEGA hydrogels with C_{bPE} = 10 wt% and 40 wt%.

Hydrogel Description	**q [Å^{-1}]**	$\frac{q}{q^*}$	**Expected** $\frac{q}{q^*}$	**Microstructure**	**Comments**
PEC+4-arm PEGA hydrogels with C_{bPE} = 10 wt% and C_{PC} = 15 wt%, q^*= 0.0193 Å^{-1}	0.0397	2.06	2	LAM	Missing peak at $3q^*$
	0.0788	4.09	4		
PEC/4-arm PEGA IPN hydrogels with C_{bPE} = 10 wt% and C_{PC} = 15 wt%, q^*= 0.0193 Å^{-1}	0.0397	2.06	2	LAM	Missing peak at $3q^*$
	0.0788	4.09	4		
PEC+4-arm PEGA hydrogels with C_{bPE} = 10 wt% and C_{PC} = 20 wt%, q^*= 0.0184 Å^{-1}	0.0374	2.03	2	LAM	
	0.0564	3.06	3		
	0.0737	4	4		
PEC/4-arm PEGA IPN hydrogels with C_{bPE} = 10 wt% and C_{PC} = 20 wt%, q^*= 0.0184 Å^{-1}	0.0383	2.08	2	LAM	Missing peak at $3q^*$
	0.0754	4.09	4		
PEC+4-arm PEGA hydrogels with C_{bPE} = 40 wt% and C_{PC} = 5 wt%, q^*= 0.0204 Å^{-1}	0.0401	1.97	2	LAM	
	0.0602	2.96	3		
	0.0789	3.87	4		
PEC/4-arm PEGA IPN hydrogels with C_{bPE} = 40 wt% and C_{PC} = 5 wt%, q^*= 0.0204 Å^{-1}	0.0401	1.97	2	LAM	
	0.0602	2.96	3		
	0.0816	4.01	4		

Table S6. Bragg peak positions and microstructural details for PEC+PEGDA hydrogels and PEC/PEGDA IPN hydrogels with C_{bPE} = 10 wt% and 40 wt%.

Hydrogel Description	q **[Å^{-1}]**	$\frac{q}{q^*}$	**Expected** $\frac{q}{q^*}$	**Microstructure**
PEC+PEGDA hydrogels with C_{bPE} = 10 wt% and C_{PC} = 20wt%, q^* = 0.0193 Å^{-1}	0.0383	1.99	2	LAM
	0.0564	2.93	3	
	0.0771	4.00	4	
PEC/PEGDA IPN hydrogels with C_{bPE} = 10 wt% and C_{PC} = 20 wt%, q^*= 0.0193 Å^{-1}	0.0383	1.99	2	LAM
	0.0578	3	3	
	0.0771	4	4	
PEC+PEGDA hydrogels with C_{bPE} = 40 wt% and C_{PC} = 5wt%, q^* = 0.0204 Å^{-1}	0.0415	2.03	2	LAM
	0.0602	2.96	3	
	0.0816	4.01	4	
	0.1020	5.01	5	
PEC/PEGDA IPN hydrogels with C_{bPE} = 40 wt% and C_{PC} = 5 wt%, q^*= 0.0211 Å^{-1}	0.0429	2.03	2	LAM
	0.0622	2.94	3	
	0.0844	4.00	4	
	0.1060	5.02	5	

Movie SM1. Video showing injectability of PEC hydrogels and their interim resistance against dilution and material loss in water.

Movie SM2. Video showing injectability of PEC+PEGDA hydrogels and their interim resistance against dilution and material loss in water.

Movie SM3. Video showing injectability of PEC+4-arm PEGA hydrogels and their interim resistance against dilution and material loss in water.

Movie SM4. Video showing injectability of PEC+AAm hydrogels and their interim resistance against dilution and material loss in water.

Movie SM5. Video showing injectability of PEC+GelMA hydrogels and their interim resistance against dilution and material loss in water.

Movie SM6. Video demonstrating immediate dilution of PEGDA precursors in water.

Movie SM7. Video demonstrating immediate dilution of 4-arm PEGA precursors in water.

Movie SM8. Video demonstrating immediate dilution of AAm precursors in water.

Movie SM9. Video demonstrating immediate dilution of GelMA precursors in water.