Supporting Information

Ultra-stiff and tough hydrogels based on small but strong hydrophobic associations *via* low-reactive hydrophilic monomer

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The conversions of monomers (IMA and AAm) during the radical copolymerization could be calculated by an established method.[1] As an illustration, the conversion of IMA at any AAm conversion during copolymerization with a ratio of monomers as $[IMA]_0/[AAm]_0$ = 0.77/0.39 were calculated step-by-step.

1. Assuming that the vinyl group in IMA has the same reactivity as that of ethyl methacrylate (EMA), the Q and e values of IMA are equal to that of EMA. Both EMA and AAm (Q, e) values are cited from Polymer Handbook,[2] and reactivity ratios were calculated on the basis of Alfrey-Price equations, as follows :

$$r_{IMA} = \frac{Q_{IMA}}{Q_{AAm}} exp[-e_{IMA}(e_{IMA} - e_{AAm})]$$

$$r_{AAm} = \frac{Q_{AAm}}{Q_{IMA}} exp[-e_{AAm}(e_{AAm} - e_{IMA})]$$

2. Based on the equations shown below, the variation of the molar fraction of unreacted IMA in the feed (f_{IMA}) as a function of total conversion ($Conv_{total}$) was calculated.

$$Conv_{total} = 1 - \frac{M}{M_0} = 1 - (\frac{f_{IMA}}{f_{IMA}^0})^{\alpha}(\frac{f_{AAm}}{f_{AAm}^0})^{\beta}(\frac{f_{IMA}^0 - \delta}{f_{IMA} - \delta})^{\gamma}$$

$$\alpha = \frac{r_{AAm}}{1 - r_{AAm}} \quad \beta = \frac{r_{IMA}}{1 - r_{IMA}} \quad \gamma = \frac{1 - r_{IMA}r_{AAm}}{(1 - r_{IMA})(1 - r_{AAm})} \quad \delta = \frac{1 - r_{AAm}}{2 - r_{IMA} - r_{AAm}}$$

where, the molar fraction of IMA in the initial monomer feed is f_{IMA}^0 = 1/(1+0.5)= 0.667, and the molar fraction of AAm in the initial monomer feed is f_{AAm}^0 = 0.5/(1+0.5) =0.333.

3. Knowing the variation of f_{IMA} and f_{AAm} = 1-f_{IMA} as a function of $Conv_{total}$, the conversions of IMA ($Conv_{IMA}$) and AAm ($Conv_{AAm}$) at any moment were calculated:

$$Conv_{IMA} = 1 - \frac{f_{IMA}(1 - Conv_{total})}{f_{IMA}^{0}}$$

$$Conv_{AAm} = 1 - \frac{f_{AAm}(1 - Conv_{total})}{f_{AAm}^{0}}$$

Water content measurement. The water content of the all hydrogels were calculated as water content (wt%)=$[(W_s - W_d)/W_s] \times 100\%$, where W_s is the weight of the water-equilibrated hydrogel and W_d is the weight of the hydrogels that were dried in a lyophilizer.

The swelling ratio measurement. The swelling ratio of P(IMA_1-co-AAm_1) hydrogel (S_w) under water was determined as $S_w = W_t/W_0$, in which W_t and W_0 were the weight at different immersing time and the initial one, respectively.

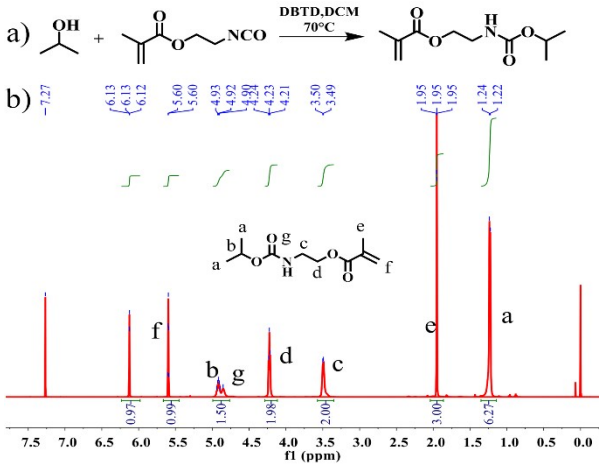

Fig. S1. (a) Synthetic route and (b) ^{1}H NMR spectrum of IMA.

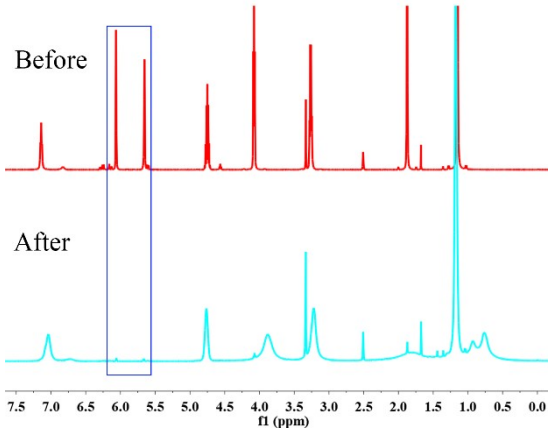

Fig. S2. ^{1}H NMR spectra of IMA before and after polymerization.

Table S1. Q, e values and the reactivity ratios of IMA and AAm.

	Q value	e value	Reactivity ratio
IMA	0.76	0.17	3.52
AAm	0.23	0.54	0.25

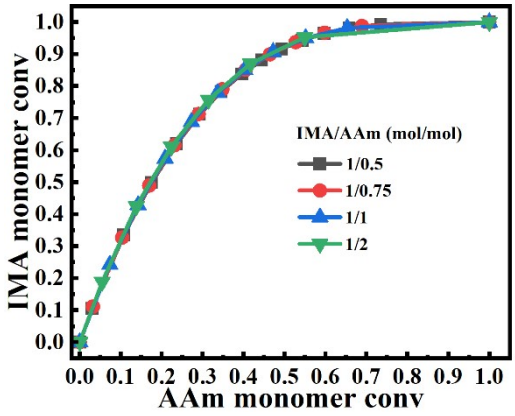

Fig. S3. Calculated results for IMA conversion versus the AAm conversion during the copolymerization of them.

Table S2. Preparation conditions of P(IMA_1-co-AAm_y)-m-n hydrogels.

Code	**IMA (mol/L)**	**AAm (mol/L)**	**MBAA (mol/L)**
PIMA	0.89	0	0.025
P(IMA_1-co-$AAm_{0.5}$)	0.77	0.39	
P(IMA_1-co-$AAm_{0.75}$)	0.72	0.54	
P(IMA_1-co-AAm_1)	0.67	0.68	
P(IMA_1-co-AAm_2)	0.54	1.08	
P(IMA-co-AAm)-0.5%	0.072	0.054	0.006
P(IMA-co-AAm)-1%			0.012
P(IMA-co-AAm)-3%			0.036
P(IMA-co-AAm)-4%			0.049
P(IMA-co-AAm)-9%	0.40	0.30	0.014
P(IMA4-co-AAm3)-19%	0.92	0.69	0.032
P(IMA4-co-AAm3)-24%	1.21	0.91	0.042

AIBN was used as initiator for all hydrogels with a concentration of 0.3 mol% with respect to the total monomer concentration.

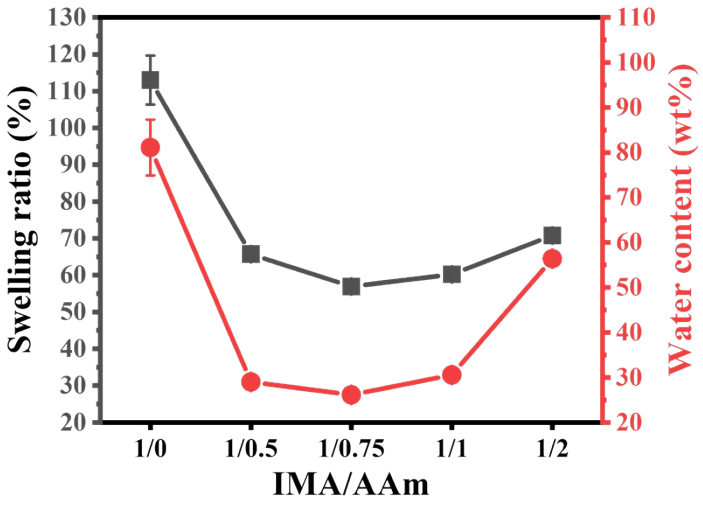

Fig. S4. The swelling ratios and water content of P(IMA-co-AAm) hydrogels with different IMA/AAm molar ratios.

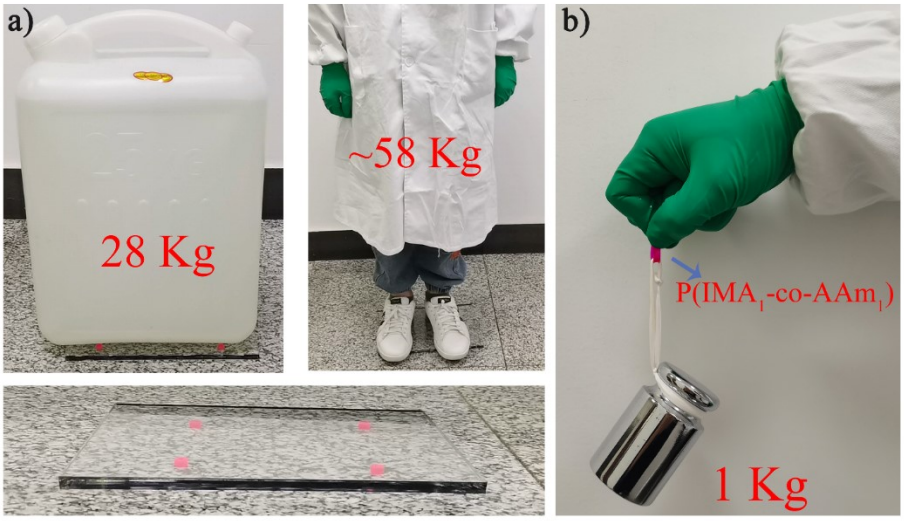

Fig. S5. Photos of $P(IMA_1\text{-co-}AAm_1)$ hydrogel (a) supports 28 kg of water or a person with weight of 58 kg without collapse, (b) lifts a weight of 1 kg without stretching.

Table S3. Tensile and compressive properties of different hydrogels.

Samples	Tensile					Compressive			Water content (wt%)
	Breaking stress (MPa)	Young's modulus (MPa)	Toughness (MJ/m^3)	Breaking strain (%)	Yield stress (MPa)	Stress at 85% compression (MPa)	Compressive modulus (MPa)	Toughness (MJ/m^3)	
P(IMA_1-co-$AAm_{0.5}$)	5.45±0.46	57.53±7.94	0.97±0.07	31.67±3.21	-	232.45±16.06	200.94±32.35	25.95±2.82	29.0±1.2
P(IMA_1-co-$AAm_{0.75}$)	4.48±0.22	48.39±3.89	19.80±0.30	466±19.30	3.95±0.12	140.39±9.89	57.57±1.32	16.83±0.78	26.7±0.2
P(IMA_1-co-AAm_1)	3.30±0.17	29.43±1.27	9.07±1.60	445±14.11	1.56±0.06	98.13±5.97	28.60±2.78	8.93±0.49	30.6±0.7
P(IMA_1-co-AAm_2)	0.64±0.09	0.60±0.06	1.61±0.44	399.5±20.8	-	10.52±1.50	0.33±0.03	0.90±0.07	56.4±0.3
P(IMA-co-AAm)-0.5%	1.63±0.07	47.14±3.37	0.74±0.05	38.67±5.13	-	64.07±6.80	26.82±1.35	7.55±0.56	44.3±2.3
P(IMA-co-AAm)-1%	3.05±0.11	43.03±1.25	5.00±0.37	192.67±21.73	3.65±0.17	109.18±11.39	46.56±8.93	12.71±0.78	36.3±1.5
P(IMA-co-AAm)-3%	4.26±0.07	56.64±5.69	17.18±0.76	458±12.58	3.75±0.12	166.86±4.31	76.02±8.01	18.69±0.85	26.0±0.3
P(IMA-co-AAm)-4%	4.04±0.07	54.40±3.08	13.50±1.07	396±31	3.63±0.11	193.16±14.71	106.5±7.61	24.53±5.27	25.3±1.5
P(IMA-co-AAm)-9%	2.68±0.21	43.21±2.13	0.83±0.06	34.33±2.08	-	66.67±9.67	40.72±0.71	8.66±0.81	41.4±0.6
P(IMA-co-AAm)-19%	4.92±0.06	49.09±1.68	19.32±0.15	459.33±18.50	3.46±0.27	179.66±19.26	59.72±1.93	18.45±0.28	26.0±0.8
P(IMA-co-AAm)-24%	4.87±0.07	40.89±2.38	18.80±0.26	459.67±9.07	3.37±0.15	144.55±10.10	33.41±6.29	14.69±0.73	25.9±0.2
Human cartilage[3-6]	8.1-40	58-228	-	80	-	14-59	8.1-20.1	-	60-80

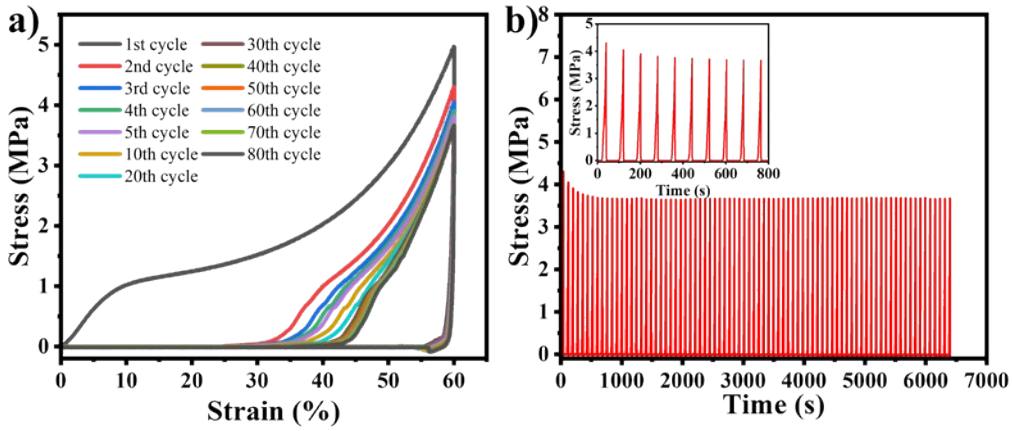

Fig. S6. (a) 80 successive compressive stress-strain curves and (b) stress-time cycles of P(IMA$_1$-co-AAm$_1$) with 60% strain. The inset was the first 10 compressive stress-time cycles.

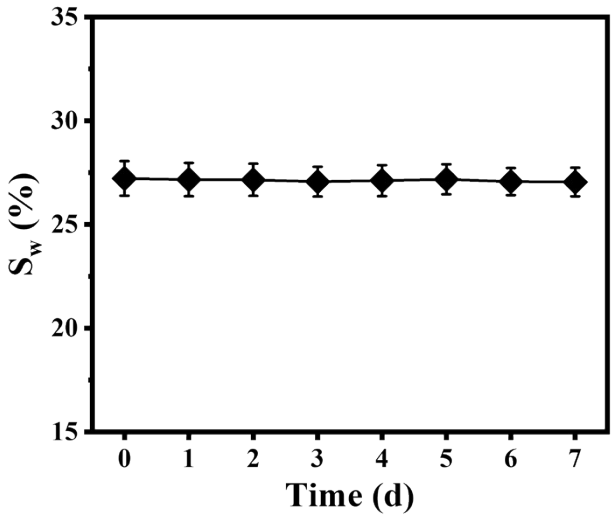

Fig. S7. The swelling ratios of P(IMA$_1$-co-AAm$_1$) hydrogel at different soaking times.

Fig. S8. Photos of P(IMA-co-AAm)-m-n hydrogels with different concentrations of (a) MBAA and (b) monomers.

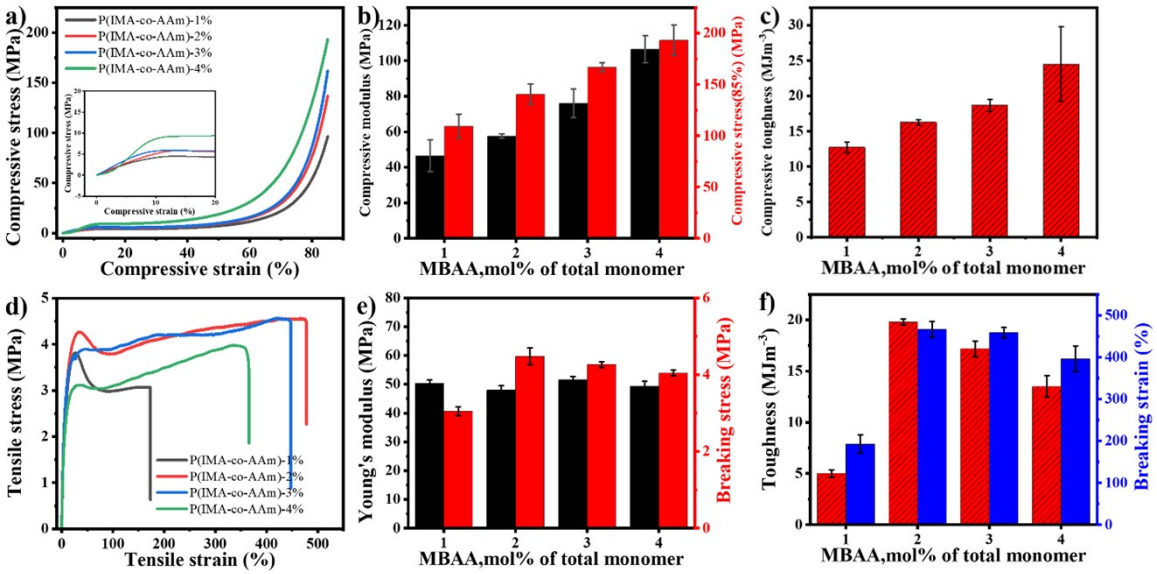

Fig. S9. (a) Compressive and (d) tensile stress–strain curves, (b) compressive modulus and stress at 85%, and (c) compressive toughness, (e) Young's modulus and breaking stress, (f) toughness and breaking strain of different MBAA (mol%/monomers) hydrogels.

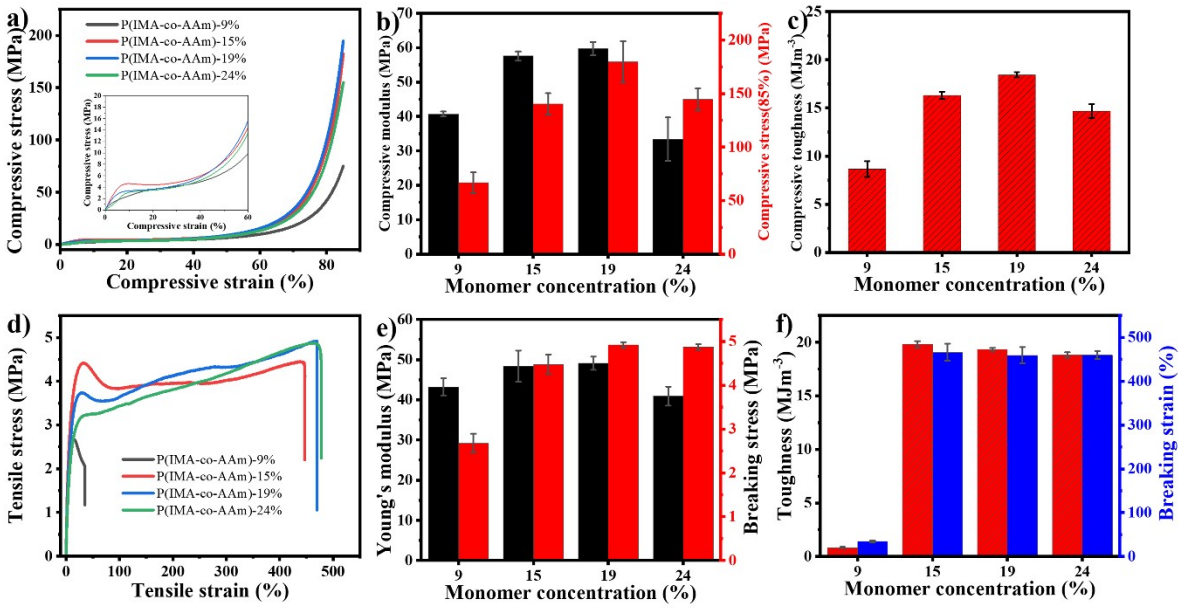

Fig. S10. (a) Compressive and (d) tensile stress–strain curves, (b) compressive modulus and stress at 85%, and (c) compressive toughness, (e) Young's modulus and breaking stress, (f) toughness and breaking strain of different monomer concentration hydrogels.

Table S4. Preparation conditions of other hydrogels.

Code	IMA (mol/L)	AAm (mol/L)	MBAA (mol/L)
P(IAA-co-AAm)	0.84	0.63	0.029
P(BMA-co-AAm)	1.02	0.77	0.036

AIBN was used as initiator for all hydrogels with a concentration of 0.3 mol% with respect to the total monomer concentration.

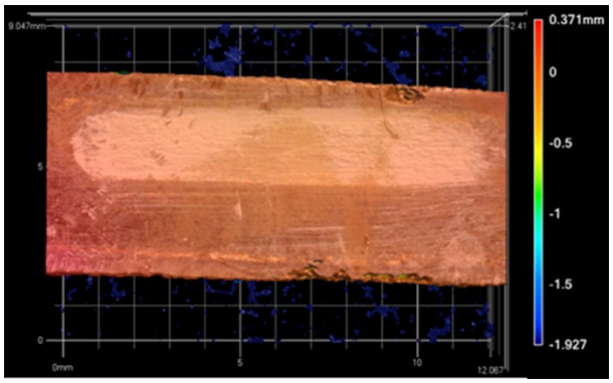

Fig. S11. 3D images of worn surfaces of the P(IMA_1-co-AAm_1) hydrogels under PBS solution lubrication.

References

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