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Supplementary Information

Stretchable, self-Healable, and adhesive ionogels formed *via* dual association of complex copolymers

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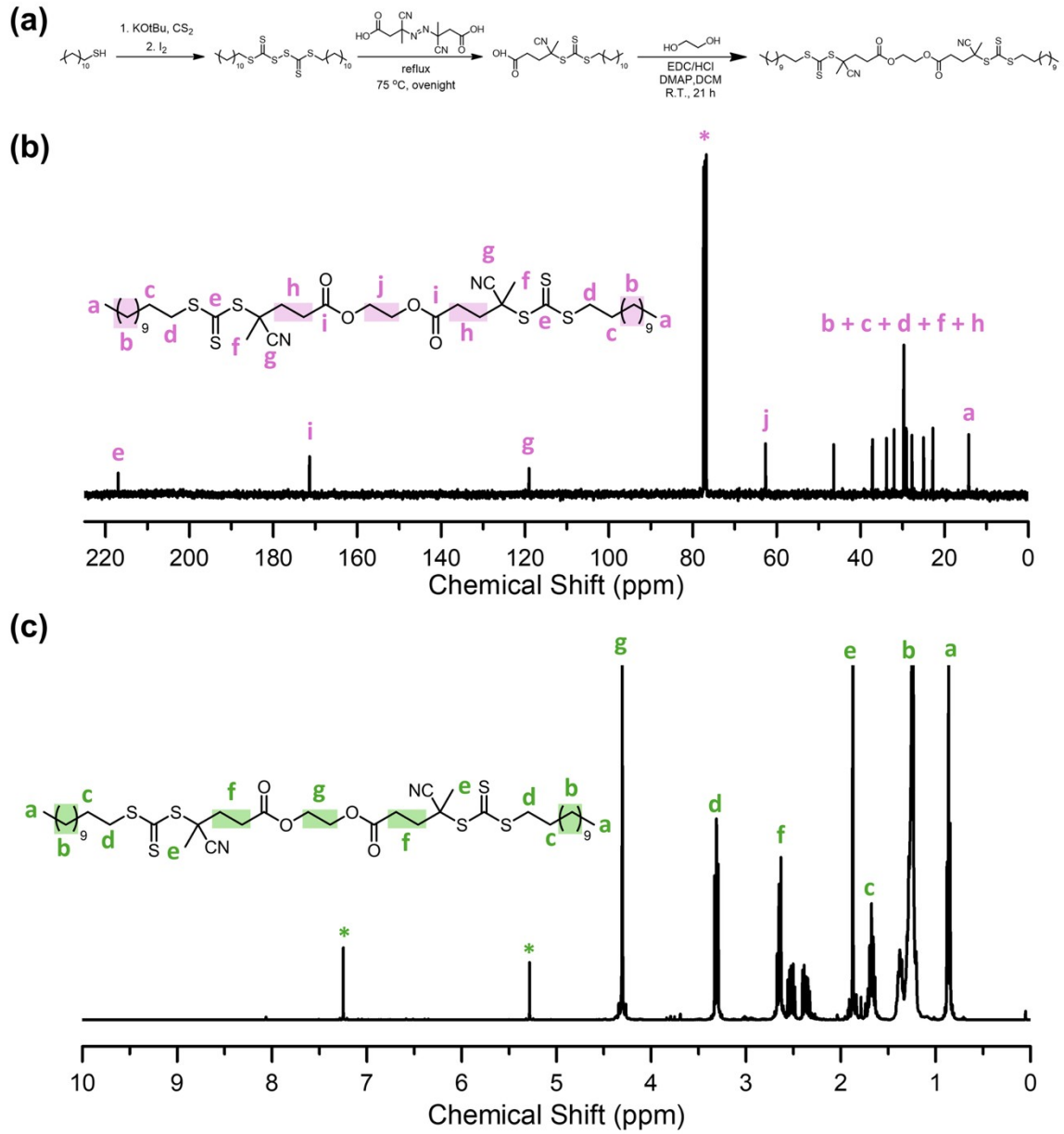

Figure S1. (a) Synthetic scheme of difunctional CTA-EG, (b) ^{13}C and (c) ^{1}H NMR spectra of CTA-EG.

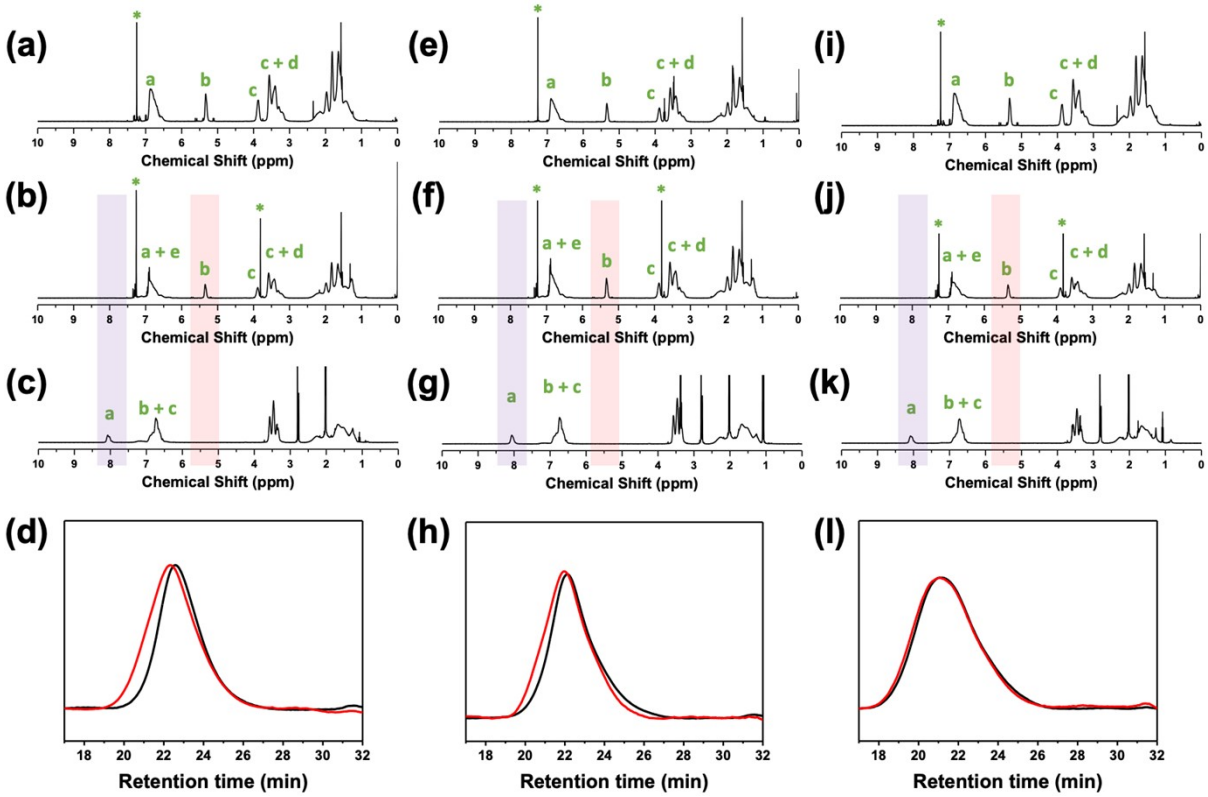

Figure S2. Representative ^{1}H NMR spectra of the copolymers, (a-c) PSHMS-85k, (e-g) PSHMS-98k, (i-k) PSHMS-136k, acquired at each synthetic step, and SEC traces of (d) PSHMS-85k, (h) PSHMS-98k, (l) PSHMS-136k before (black) and after the chain extension with *t*BS (red).

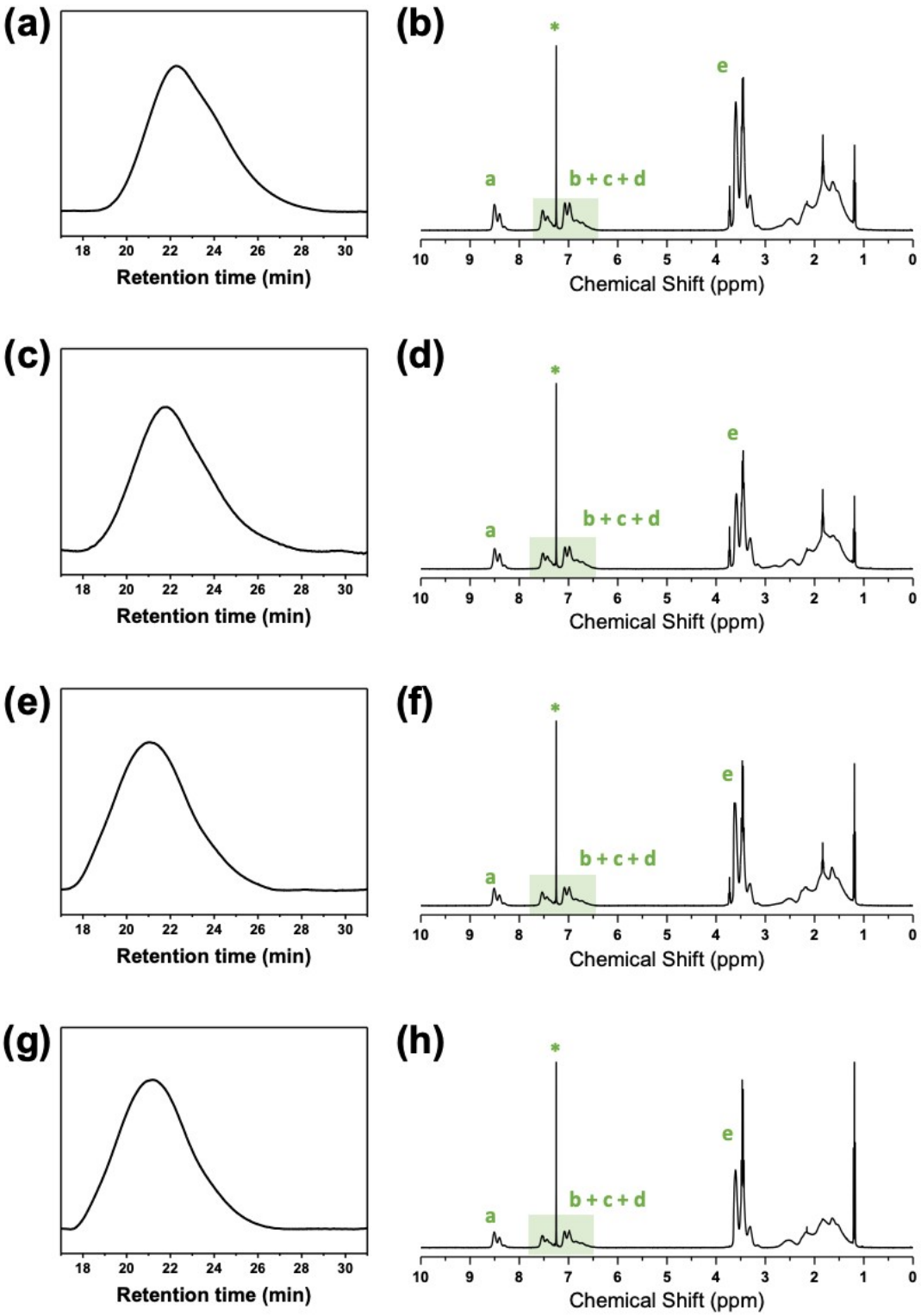

Figure S3. SEC traces and ^{1}H NMR spectra of (a) PVM-73k, (c) PVM-108k, (e) PVM-139k, (g) PVM-151k.

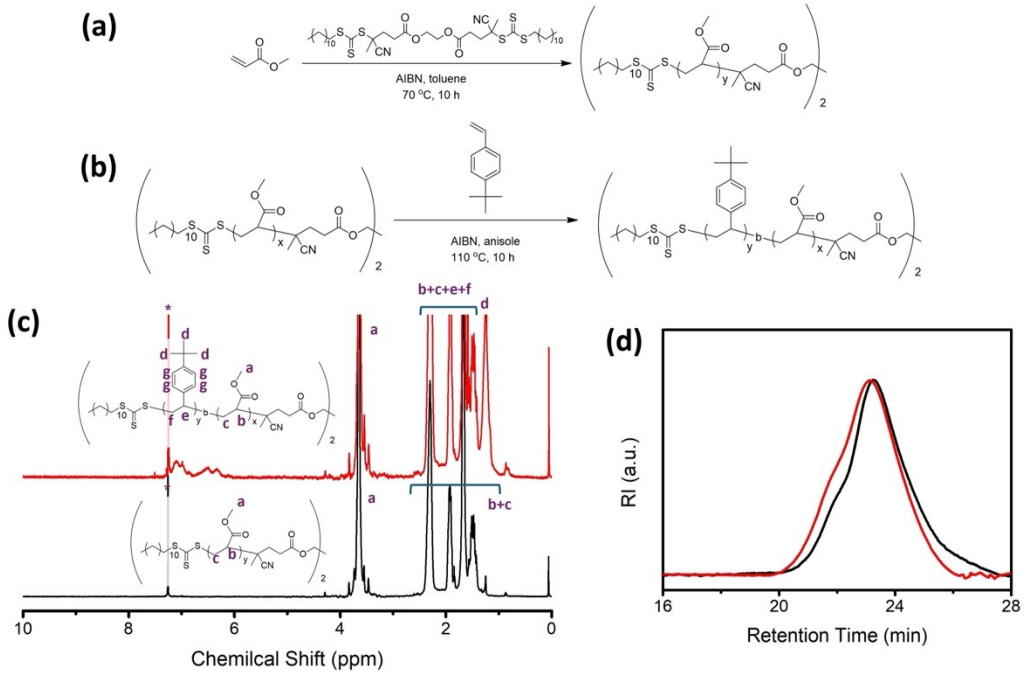

Figure S4. Synthesis of (a) poly(methyl acrylate) macro-RAFT agent and (b) poly(*tert*-butyl styrene-*b*-methyl acrylate-*b*-*tert*-butyl styrene), (c) ^{1}H NMR spectra and (d) SEC traces of PSMS before (black) and after chain extension with *t*BS (red).

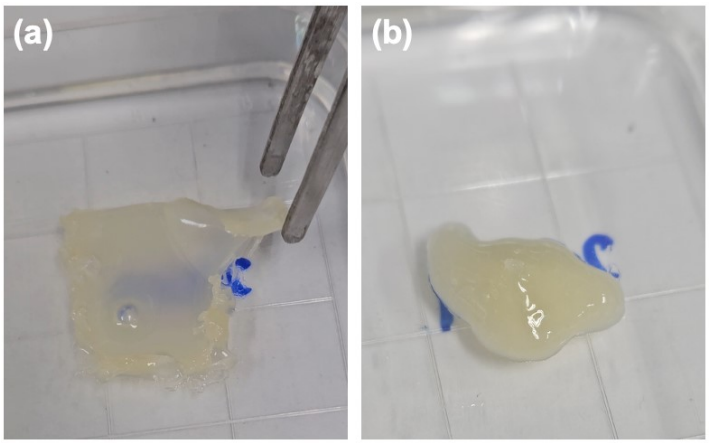

Figure S5. Photographs showing (a) as-fabricated ionogel with PSMS and PVM-87k, and (b) annealed ionogel at 50 ^{o}C for 24 h.

Table S1. M_n, $Đ$, and actual compositions under various reaction conditions for different POM and PVM samples.

Entry	[CTA-EG] : [AIBN] : [OTHPSt/2VP] : [MA]	$F_{OTHPSt/2VP}$: F_{MA}	Time (h)	Temp. (°C)	DP_{OTHPSt} or DP_{2VP}	DP_{MA}	M_n (kg/mol)	$Đ$
POM-65k	1 : 1 : 964 : 5000	0.356 : 0.644	4	70	180	325	64.5	1.42
POM-80k	1 : 1 : 723 : 3750	0.360 : 0.640	4	70	222	401	79.5	1.43
POM-87 k	1 : 1 : 723 : 3750	0.344 : 0.656	4	70	242	437	86.7	1.55
POM-113 k	1 : 1 : 964 : 5000	0.408 : 0.592	4	70	316	571	113	1.96
PVM-73k	1 : 1 : 1170 : 6500	0.299 : 0.701	24	70	237	555	73.9	1.82
PVM-87k	1 : 1 : 1170 : 6500	0.332 : 0.668	24	70	312	627	87.0	1.83
PVM-108k	1 : 1 : 1170 : 6500	0.332 : 0.688	24	70	367	809	108	2.09
PVM-139k	1 : 1 : 1440 : 8000	0.326 : 0.674	24	70	491	1015	139	2.24
PVM-151k	1 : 1 : 900 : 5000	0.342 : 0.658	24	70	559	1077	151	1.99

Table S2. M_n, $Đ$, and actual compositions under various reaction conditions for different PSOMS samples.

Entry	[POM] : [AIBN] : [*t*BS]	F_{tBS} : F_{OTHPSt} : F_{MA}	Time (h)	Temp. (°C)	DP_{tBS}	M_n (kg/mol)	$Đ$
PSOMS-85k	1 : 1 : 125	0.076 : 0.329 : 0.595	6	90	131	85.5	1.41
PSOMS-98	1 : 1 : 125	0.058 : 0 339 : 0.603	6	90	119	98.7	1.40
PSOMS-114k	1 : 1 : 125	0.062 : 0.323 : 0.615	6	90	167	114	1.52
PSOMS-136k	1 : 1 : 125	0.043 : 0.391 : 0.566	6	90	145	136	1.72

Table S3. Estimated healing efficiencies of fabricated HV11 ionogels using PVM-87k and PSHMS of which the molecular weight of PSHMS was varied.

	η_{stress} (%)		η_{strain} (%)		$\eta_{toughness}$ (%)	
Temperature Time	50 ℃ 36 h	50 ℃ 60 h	50 ℃ 36 h	50 ℃ 60 h	50 ℃ 36 h	50 ℃ 60 h
PSHMS-85k	45.0	74.2	53.4	58.7	23.1	35.4
PSHMS-98k	75.2	94.5	68.4	88.6	46.4	72.6
PSHMS-114k	86.9	96.5	79.2	92.8	60.1	87.4
PSHMS-136k	88.2	98.0	66.2	77.6	54.8	69.5

Additional Experimental Details

Synthesis of poly(tert-butyl styrene-b-methyl acrylate-b-tert-butyl styrene) (PSMS). Poly(methyl acrylate) (PMA) macro-RAFT agent was first synthesized via RAFT polymerization using a difunctional RAFT agent (CTA-EG), followed by chain extension with tert-butyl styrene (*t*BS) to obtain poly(*t*BS-*b*-MA-*b*-*t*BS) (PSMS). For the synthesis of the PMA macro-RAFT agent, methyl acrylate (MA, 1.03 g, 12.00 mmol), AIBN (0.002 g, 0.01 mmol), CTA-EG (0.01 g, 0.01 mmol), and toluene (1.03 g) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar. The reaction mixture was degassed by three freeze–pump–thaw cycles. Polymerization was then carried out at 70 °C for 10 h. The reaction was quenched by exposure to air. The mixture was diluted with THF and precipitated into excess methanol. The resulting light-yellow solid was collected by vacuum filtration and dried under vacuum at 30 °C for 24 h. For chain extension with *t*BS, the PMA macro-RAFT agent (0.42 g, 0.007 mmol), *t*BS (0.219 g, 1.37 mmol), AIBN (0.0011 g, 0.007 mmol), and anisole (2.54 g) were added to a 10 mL Schlenk flask. The solution was degassed by three freeze–pump–thaw cycles and placed in an oil bath preheated to 110 °C for 10 h. The polymerization was then quenched by exposure to air. The reaction solution was diluted with THF and precipitated into excess methanol. The resulting white solid, PSMS, was collected by vacuum filtration and dried under vacuum at 30 °C for 24 h.