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Supporting Information

for

Multimodal Underwater Adhesion Using Self-assembled Dopa-bearing ABA Triblock Copolymer Networks

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Detailed Experimental Methods

Reagents and chemicals. The following reagents were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used as received: poly(ethylene glycol) (PEG, molecular weight 10,000 g mol^{-1}); methacrylic acid *N*-hydroxysuccinimide ester (NHSMA); dopamine hydrochloride (Dopa); CuBr; 2,2'-bipyridine (bpy); 4-dimethylaminopyridine (DMAP); trimethylamine (TEA); 2-bromoisobutyryl bromide; 4-methylmorpholine; ethylene carbonate; chloroform; hexane; *N*,*N*-dimethylformamide (DMF) and neutral alumina.

Synthesis of poly(ethylene glycol)-based macroinitiator (Br-PEG-Br). PEG (10 g, 1.0 mmol, 1.0 equiv) and DMAP (0.2 g, 1.6 mmol, 1.6 equiv) were dissolved in 30 mL anhydrous chloroform. After degassing 1 h under nitrogen, the flask was placed in a water-ice bath and the solution was allowed to cool to 0 ^{o}C. Subsequently, TEA (0.28 mL, 2.0 mmol, 2.0 equiv) and 2-bromoisobutyryl bromide (0.3 mL, 2.4 mmol, 2.4 equiv) were added dropwise via a syringe under nitrogen. The reaction was stirred for 18 h as the temperature gradually increased from 0 ^{o}C to room temperature. The solution was precipitated in hexane. The crude product was re-dissolved in 30 mL anhydrous chloroform and washed twice using DI water.

The resulting mixture was dried by $MgSO_4$ and re-precipitated in hexane to obtain the final product. ^{1}H NMR (300 MHz, $CDCl_3$): 3.64 (s, 4H, $-OCH_2$ CH_2O-), 1.94 (s, 3H, $-CH_3$).

Synthesis of poly(NHSMA)-b-PEG-b-poly(NHSMA) triblock copolymer (ABA-Dopa(–)). A 10 mL Schlenk flask was charged with Br-PEG-Br (0.1 g, 0.0097 mmol, 1 equiv), NHSMA (0.267 g, 1.5 mmol, 150 equiv), bpy (0.006 g, 0.039 mmol, 4 equiv) and ethylene carbonate (0.38 g). The flask was immersed in liquid N_2 and then CuBr (0.0028 g, 0.019 mmol, 2 equiv) was added. Contents were degassed using three freeze-pump-thaw cycles and then heated to 110 °C in an oil bath for 20 min. The viscous solution was rapidly cooled in liquid N_2 and then diluted with 5 mL DMF. The product was precipitated in acetone, centrifuged, and dried in vacuum for 18 h. ^{1}H NMR (300 MHz, DMSO-d_6): 1.38 (br, 3H, $-CH_3$), 2.42 (br, 2H, $-CH_2C-$), 2.78 (d, 4H, $-CH_2CH_2-$), 3.50 (s, 4H, $-OCH_2CH_2O-$).

Synthesis of poly(NHSMA)-b-PEG-b-poly(NHSMA)-Dopa triblock copolymer (ABA-Dopa(+)). A 50 mL Schlenk flask was charged with ABA-Dopa(–) (0.1 g, 0.393 mmol, 1 equiv) dissolved in 5 mL DMF and bubbled with N_2 (g) for 1 h. Dopamine hydrochloride (0.746 g, 3.93 mmol, 10 equiv) was dissolved in 5 mL anhydrous DMF in another flask and bubbled with N_2 (g) for 1 h. 4-methylmorpholine (0.692 mL, 6.29 mmol, 16 equiv) was added to neutralize dopamine hydrochloride. After 1 h, the neutralized dopamine hydrochloride solution was injected into the polymer solution. Reaction times were selected between 6–24 h. The resulting solution was dialyzed (3.5 kD dialysis membrane, Spectra/Por®) in an acidic buffer (pH = 2, 0.01 M HCl) for 48 h and followed by lyophilizing.

^1H NMR (300 MHz, DMSO-d_6): 6.58 (s, H, $C_6H_2H(OH)_2$-), 6.81-6.70 (d, br, 2H, $C_6HH_2(OH)_2$-), 7.9 (s, br, H, $C_6H_3(OH)_2$- CH_2CH_2-NH-), 8.9 (d, br, 2H, -OH).

Chemical characterization. ^1H NMR (Bruker Avance 300 MHz spectrometer, Bruker Corporation, Billerica, MA, USA) was used to record polymer structure for Br-PEG-Br in $CDCl_3$ and for both ABA-Dopa(–) and ABA-Dopa(+) in DMSO-d_6. Molecular weight (*MW*) and molecular weight distribution (*MWD*, M_w/M_n) were determined by gel permeation chromatography (GPC) in a DMF phase containing 50 mM LiBr (flow rate: 1 mL min^{-1}) using PSS columns (PSS, Amherst, MA, USA) at 25 °C. The GPC system equipped with a Waters 515 HPLC pump and a Waters 2414 refractive index detector. Before the analysis, samples were filtered through neutral alumina. UV-vis spectroscopy (UV-2600, Shimadzu, Tokyo, Japan) was used to characterize conjugation ratios and the redox state of pendant catechol groups on ABA-Dopa(+) polymers.

Thermomechanical characterization. Thin films of polymer were prepared for various characterization techniques including uniaxial testing and dynamic mechanical analysis. Films were prepared by first preparing polymer solutions (20 wt%) of the ABA triblock polymers in DMF. The solvent was partially removed under vacuum at room temperature for 30 min. The film was then incubated in excess DI water for >4 h. Dynamic viscoelastic measurements of both ABA-Dopa(–) and ABA-Dopa(+) networks were performed by a RSA-G2 solids analyzer (TA Instruments, New Castle, DE, USA) with film tension clamp. ABA-Dopa(+) and ABA-Dopa(–) samples dedicated for mechanical characterization had dimensions of $l \times w \times t = 3 \times 3 \times 0.12\ mm^3$ and $3 \times 3 \times 0.06\ mm^3$, respectively. Storage modulus (E') and loss modulus (E'') as a function of ω from 0.1 to 100 rad s^{-1} were measured with an oscillatory strain of ± 0.5%. Tensile tests were performed by using Instron 5549 with a 10 N load cell and equipped with Bluehill 3 software (Norwood, MA, USA). Polymer networks were uniaxially strained at a rate of 2 mm min^{-1}. The mechanical properties of films composed of hydrated ABA-Dopa(+) networks were also measured at strain rates of 10 and 30 mm min^{-1}. A strain rate of 2 mm min^{-1} was used for cycle tests at strains of 10%, 50% and 80%. The stress relaxation properties of ABA-Dopa(+) were measured using an Instron 5549. Hydrated polymer networks were uniaxially strained to ε = 10% strain at a strain rate of 2 mm min^{-1}. Values of $\sigma(t)$ were then recorded for t = 0–700 sec when holding the 10% strain. Differential scanning calorimetry (DSC) measurements were performed using a TA-Q200 (TA Instruments, New Castle, DE, USA) using a heating rate of 10 °C min^{-1} and a temperature range between 20−350 °C for two sets of heating and cooling cycles. Representative thermograms were shown for the second heating cycle.

Force-distance measurements. Force-distance curves were measured using a custom-built instrument that contains a mechanical probe attached to a microcontroller and a 50 mN load cell (GSO-50, Transducer Techniques, Temecula, CA, USA). A planar glass probe with a diameter of 5 mm and a thickness of 1 mm was mounted to the load cell. Both polymer networks were prepared into substrates with a nominal diameter of D = 10 mm and a thickness of t = 0.05 mm for ABA-Dopa(+) and a diameter of D =10 mm and a thickness of t = 0.08 mm for ABA-Dopa(–). Samples were fixed to rigid polystyrene substrates. A 10 mN preload was exerted. Approach and retraction speeds were held constant for a given experiment and were chosen to be one of the following values: 2, 10, or 30 mm min^{-1}. The approach phase concluded after the appropriate value of preload was reached. The retraction phase immediately followed the approach phase. Force-displacement curves were recorded using custom-built LabVIEW software.

Additional Data

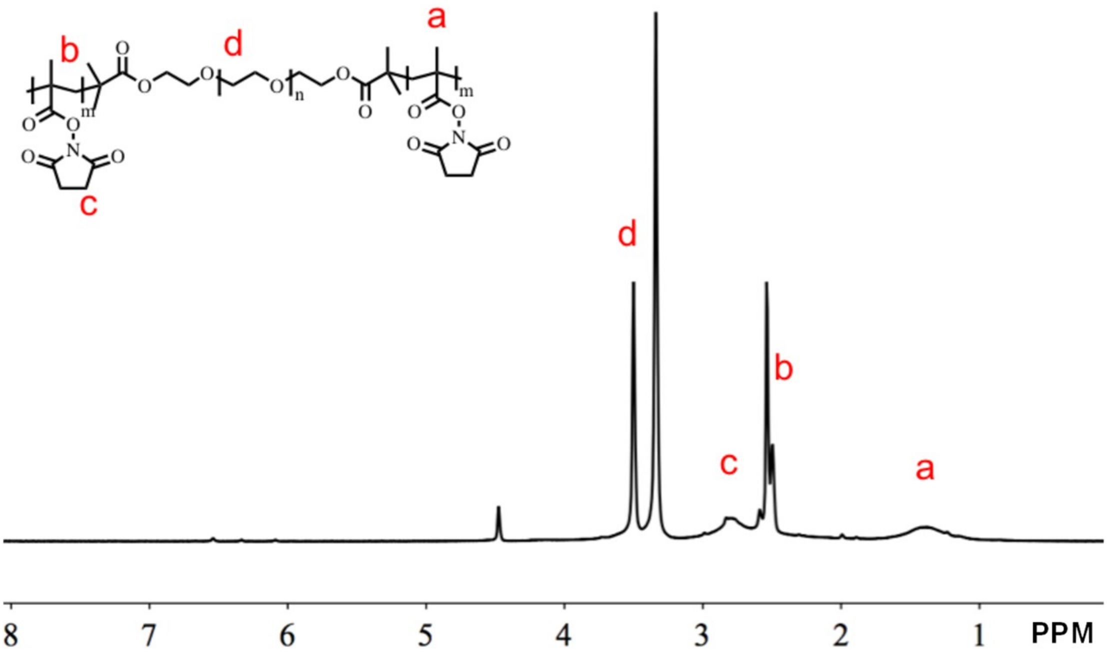

Fig. S1 ^{1}H NMR spectrum of ABA-Dopa(–) in DMSO-d_6.

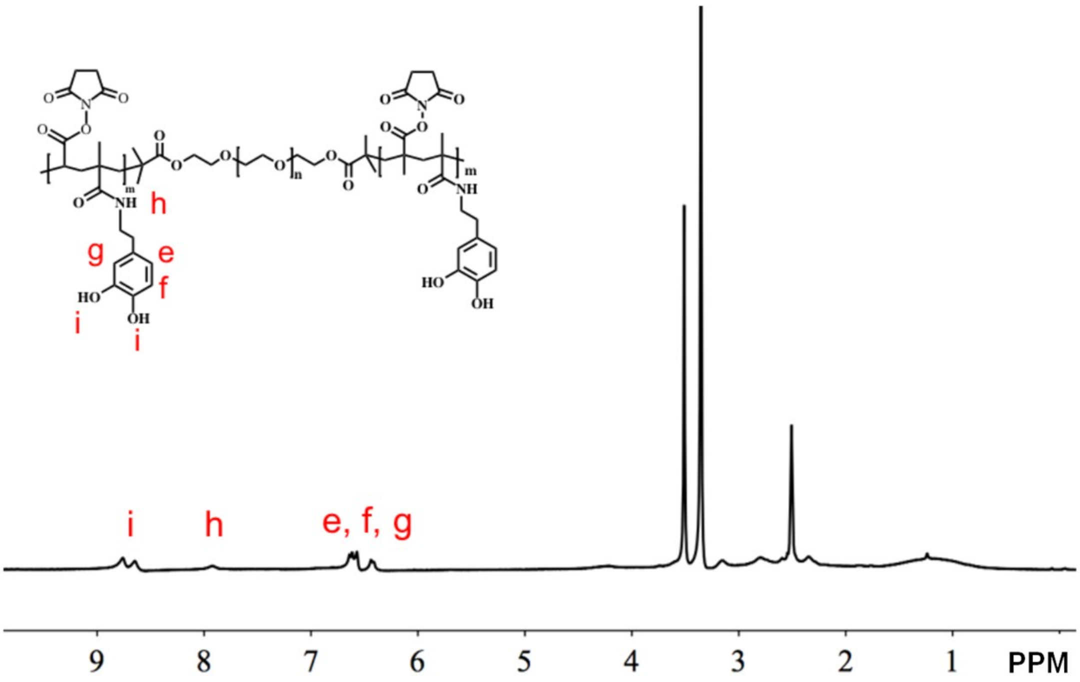

Fig. S2 ^{1}H NMR spectrum of ABA-Dopa(+) in DMSO-d$_6$.

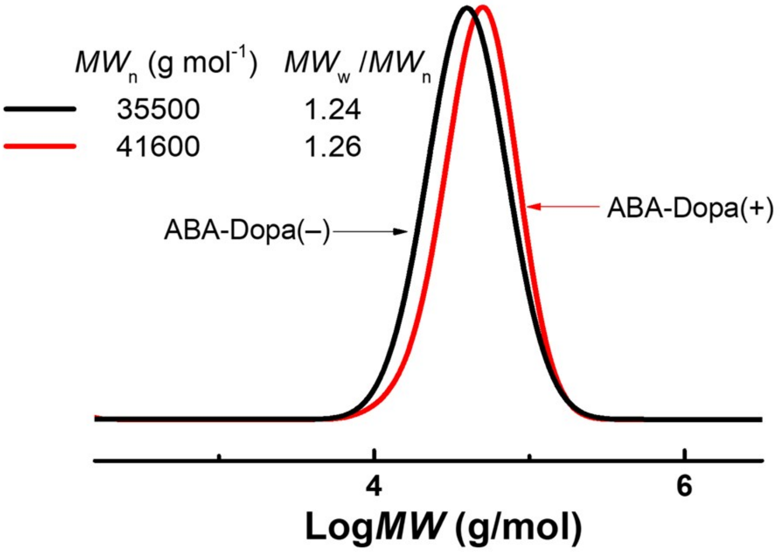

Fig. S3 Gel permeation chromatography traces of ABA-Dopa(–) and ABA-Dopa(+) copolymers.

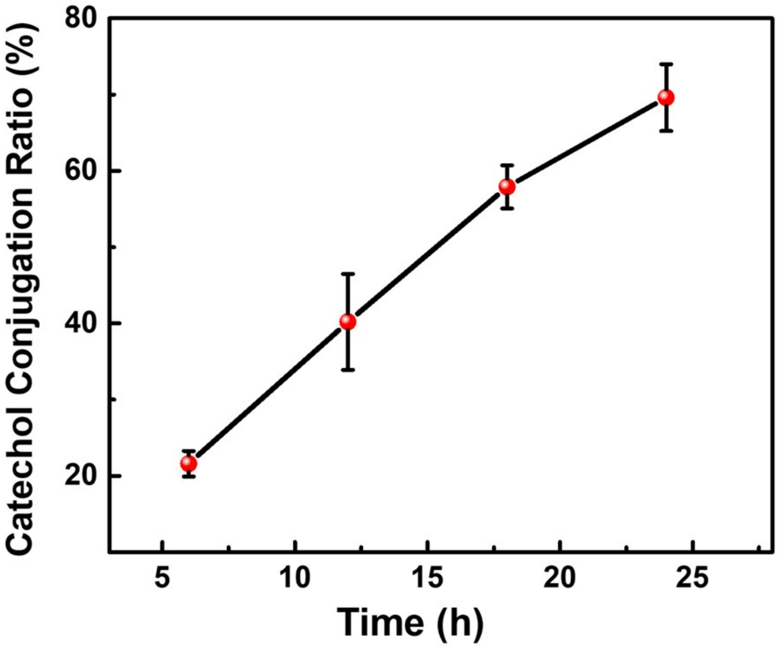

Fig. S4 Dopa conjugation ratio of ABA-Dopa(+) as a function of the reaction time for conjugation. Conjugation ratios are calculated on per NHSMA monomer basis.

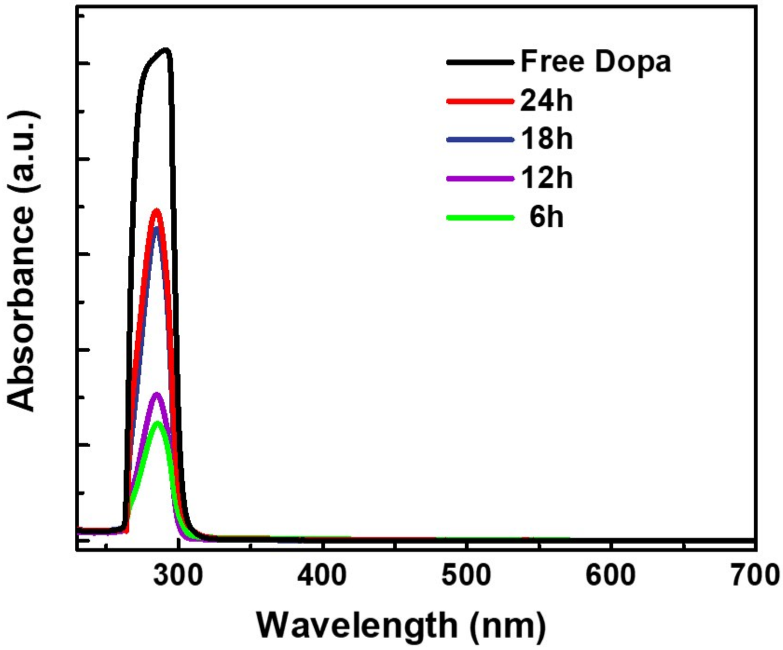

Fig. S5 UV-vis spectra of free Dopa compared to soluble ABA-Dopa(+) polymers that are prepared using conjugation reactions of increasing reaction time.

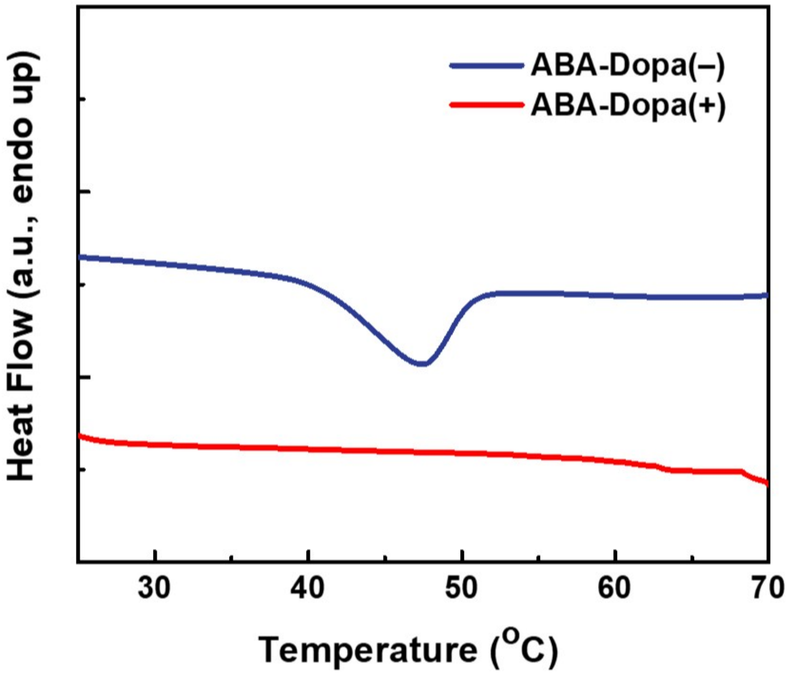

Fig. S6 DSC thermograms for both ABA-Dopa(–) and ABA-Dopa(+) networks.

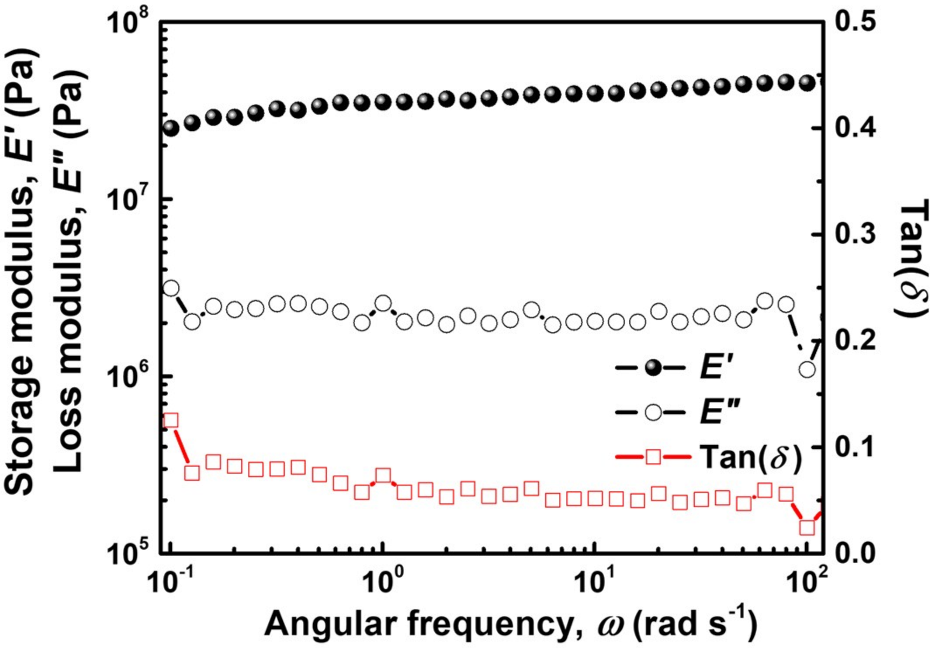

Fig. S7 Storage (E') and loss (E'') modulus are plotted as a function of angular frequency obtained from tensile oscillatory sweeps ($\varepsilon = 0.5\%$; $\omega = 0.01\text{–}100$ rad/s) for films composed of ABA-Dopa(–) triblock polymers. ABA-Dopa(–) films exhibit a solid-like behavior with a storage modulus of E' = 1–3 x 10^7 Pa and a loss modulus of E' = 2–3 x 10^6 , modest ranges across a broad spectrum of angular frequencies. Values for tan(δ) ranged from 0.05–0.1 over the range of tested angular frequencies. These data suggest that the mechanical properties of the network are dominated by the elastic response in networks composed of ABA-Dopa(–) polymers.

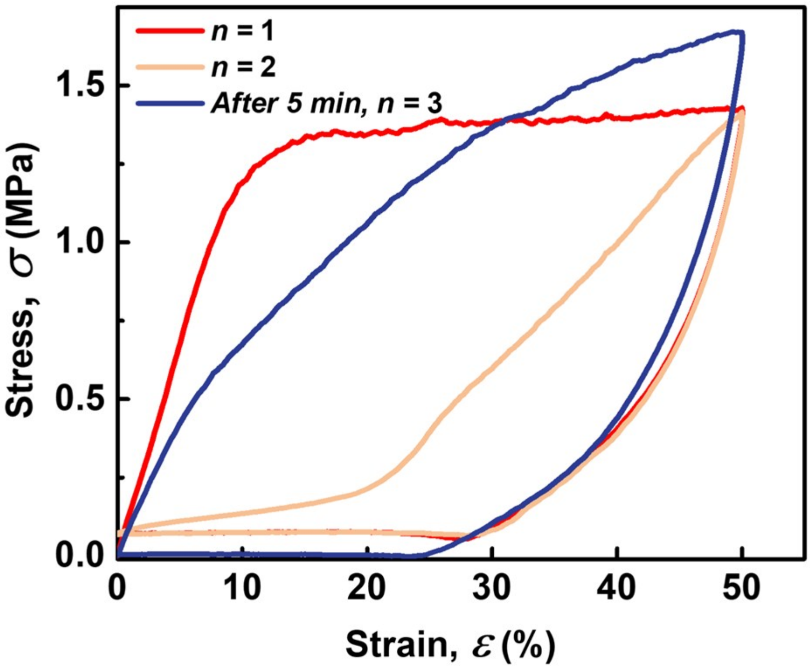

Fig. S8 Cyclic tensile curves of films prepared from ABA-Dopa(+) triblock polymers at a nominal strain of $\varepsilon = 50\%$: n = 1*;* n = 2; *After 5 min,* n = 3.

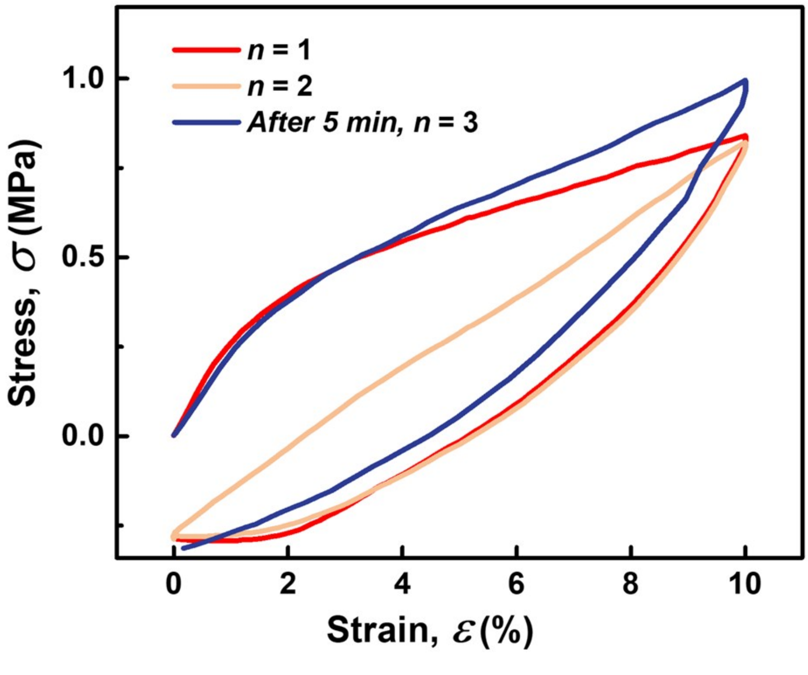

Fig. S9 Cyclic tensile curves of films prepared from ABA-Dopa(+) triblock polymers at a nominal strain of $\varepsilon = 10\%$: n = 1; n = 2; *After 5 min,* n = 3.

Table S1 Fitting parameters, relaxation time (τ) and nominal stress ($\bar{\sigma}$), for stress relaxation of networks composed of ABA-Dopa(+) triblock copolymers.

τ_1 (s)	τ_2 (s)	τ_3 (s)	$\bar{\sigma}_0$	$\bar{\sigma}_1$	$\bar{\sigma}_2$	$\bar{\sigma}_3$	R_j^2 (%)
0.76 ± 0.01	9.87 ± 1.48	114.28 ± 11.91	0.40 ± 0.04	0.27 ± 0.01	0.17 ± 0.01	0.15 ± 0.03	99.79 ± 0.27

Table S2 Mechanical properties of networks composed of either ABA-Dopa(–) or ABA-Dopa(+) copolymers under uniaxial strain as a function of strain rate.

Sample name	Strain rate, $\dot{\varepsilon}$ (mm min^{-1})	Young's modulus, E (MPa)	Breaking strength, σ_b (MPa)	Elongation at break, ε_b (%)	Work of extension at fracture, W_e (MJ m^{-3})
Dopa(–)	2	32.25 ± 4.74	0.84 ± 0.01	4.01 ± 1.53	0.025 ± 0.021
Dopa(+)	2	27.68 ± 2.79	1.09 ± 0.10	129.38 ± 23.89	1.55 ± 0.43
Dopa(+)	10	36.99 ± 4.97	1.36 ± 0.16	60.43 ± 28.75	0.83 ± 0.53
Dopa(+)	30	38.26 ± 3.05	1.61 ± 0.16	32.14 ± 9.91	0.50 ± 0.13

Table S3 Tensile work of extension (W_e) of ABA-Dopa(+) films at nominal strains of ε = 10%, 50%, and 80% as a function of strain cycle: $n = 1$, $n = 2$, and *After 5 min*, $n = 3$.

Tensile strain	$W_{n=1}$ (MJ m^{-3})	$W_{n=2}$ (MJ m^{-3})	$W_{\text{After 5 min}, n=3}$ (MJ m^{-3})
10%	0.053 ± 0.002	0.028 ± 0.004	0.046 ± 0.003
50%	0.52 ± 0.04	0.20 ± 0.04	0.48 ± 0.03
80%	1.0 ± 0.03	0.43 ± 0.03	0.85 ± 0.05

Table S4 Adhesive properties of networks composed of ABA-Dopa(–) and ABA-Dopa(+) copolymers as a function of retraction rate.

Sample	Retraction rate, v (mm min^{-1})	Adhesion stress, σ (kPa)	Work of adhesion, W_{ad} (kJ m^{-3})	Work of adhesion, W_{ad} (J m^{-2})
Dopa (–)	2, 10, 30	~0*	~0*	~0*
Dopa (+)	2	0.68 ± 0.07	2.46 ± 0.20	0.12 ± 0.01
Dopa (+)	10	0.51 ± 0.01	1.21 ± 0.02	0.06 ± 0.01
Dopa (+)	30	0.37 ± 0.01	1.19 ± 0.02	0.059 ± 0.01

*Below the detection limit of the instrument.

Table S5 Mechanical and adhesive properties of ABA-Dopa(+) (this work) compared to other previous Dopa based polymer networks.

Sample composition	**Dopa site**	**Cross-link method**	**Storage modulus, E' (Pa)**	**Toughness W_e, (MJ m^{-3})**	**Adhesive strength σ(kPa)**	**Work of adhesion, W_{ad} (J m^{-2})**
ABA-Dopa(+) (this work)	Side chain	Self-assembly	$(0.7–8) \times 10^7$	0.5-1.55	0.37-0.68	0.059-0.12
Dopa modified PEO-PPO-PEO[1]	End group	Self-assembly	1.3×10^4	N/A	N/A	N/A
4-arm catechol-terminated PEG[2]	End group	Fe^{3+}	$(0.3–10) \times 10^3$	N/A	N/A	N/A
Catechol-modified tetronic[3]	End group	$NaIO_4$	$(0.5–2) \times 10^4$	N/A	31-49[b]	1.21 ± 0.02[b]
P(HEMA-*co*-DMA)[4]	Side chain	PEG dimethacrylate	$(0.6–1) \times 10^4$	N/A	N/A	0.2-0.4[c]
DMA-AAPBA[a][5]	Side chain	UV	$(0.7–5) \times 10^4$	N/A	N/A	0.076-0.46[d]

[a] DMA-AAPBA is polymerized by dopamine methacrylamide (DMA) and 3-acrylamido phenylboronic acid (AAPBA).

[b] Measured using the lap shear method.

[c] The probe test was performed with a preload of 50 mN and a retraction rate of 0.01 mm/s.

[d] The probe test was performed in pH = 3 and pH = 9. Work of adhesion was analyzed based on JKR theory.

Additional References

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