

Electronic Supplementary Information

Controlling the mechanical properties of hydrogels via modulating the side-chain length

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Experimental section

Materials

Oligo(ethylene glycol) methyl ether methacrylate (OEG, average $M_n = 300$ g/mol, $n = 4$ or 5 ; $M_n = 500$ g/mol, $n = 8$ or 9 , $M_n = 950$ g/mol, $n = 19$ or 20), ethylene glycol dimethacrylate (EGDMA, 98%), and N,N,N',N' -tetramethyl ethylenediamine (TEMED, 99%) were purchased from Sigma-Aldrich. Ammonium peroxodisulfate (APS, 95%), acrylamide (AAM, 98%), N -isopropylacrylamide (NIPAM, 98%), and N,N' -methylenebis acrylamide (BIS, 99%) were purchased from Wako Pure Chemical Industries. All reagents were used as received.

Synthesis of the hydrogels

A series of pOEG-based gels, pNIPAM, pAAM, and copolymer gels were prepared using free-radical (co)polymerization. The monomers were dissolved in deionized water. The total monomer concentration of each solution was kept constant (1000 mM). EGDMA and APS (2 mM) were added to the solutions. These pre-gel solutions were then stirred and degassed with argon. To investigate the effect of cross-linker content on the mechanical properties of the gels, the amount of EGDMA was increased from 1 mM to 50 mM, where the monomer concentration was fixed at 1000 mM. Finally, TEMED (32 mM) was added to the solutions to initiate the polymerization. It should be noted here that pAAM gels were not formed when EGDMA was used as cross-linker, and thus EGDMA was replaced with BIS for the pAAM gels. The solutions were injected into a petri dish (2 mL) and maintained for 24 h to form gels. The polymerization was conducted at 20 °C.

Compression and cyclic compression tests

The compressive mechanical properties of the hydrogels were measured using a testing system (STB-1225S, A&D company Ltd.) in an unconfined compression mode between two impermeable parallel plates. Before commencing the compression test, a load of 0.01 N was applied to ensure complete

contact between the sample surface and plate. For the standard compression test, cylindrical samples were compressed at a strain rate of 1 mm/min with a 2.5 kN load cell up to a maximum 100% strain of the original heights. The engineering stress was calculated by dividing the recorded force by the initial cross-sectional area. The engineering strain under compression was defined as the change in height relative to the original height of the freestanding specimen. The compressive elastic modulus (G) was defined as the slope of the compressive stress-strain curve within the range of 10-20% strain. The compressive strength (σ_{st}) was defined as the maximum stress at 90% strain or at fracture, at which the stress decreased rapidly with increasing strain. These values were averaged by testing three gels of the same batch and the standard deviation is shown in the figures as error bars. The cyclic consecutive loading-unloading test was carried out without a waiting time for 10 cycles at a strain rate of 1 mm/min. The loading-unloading operations were repeatedly conducted on the same specimen with a strain of up to 50%. The dissipated energies (E_d) were calculated based on the area under the stress-strain curves at each maximum strain. The energy absorption of the hydrogel was derived from the cyclic compressive stress-strain relations. The hysteresis loop area, bounded by the loading-unloading curves, indicates the dissipated energy or adsorbed energy due to the viscous nature of the hydrogel. The compression energy (kJ/m^3), the total energy applied to the hydrogel during compression, is defined as the area between the loading curve and horizontal axis, while the relaxation energy (kJ/m^3) is the area between the unloading curve and horizontal axis. The dissipation energy (kJ/m^3) loss during the hysteresis cycle was calculated from the area under the hysteresis loop. The percentage of dissipation energy (%) was determined by dividing the dissipation energy (kJ/m^3) by the compression energy (kJ/m^3). In this study, to evaluate the mechanical stability, high mechanical stability was defined as the elastic modulus that does not change upon repeated use; thus, the elastic modulus of the gels at cyclic loading (G_c) was calculated from the slope of the loading curves within the range of 10-20% strain. For the shape-recovery properties, the residual strain (λ_r) was defined as the strain at zero stress of the unloading curves.

Temperature-dependent measurements of transmittance

To characterize the thermoresponsive behavior of the hydrogels, the temperature-dependent transmittance of the gels was measured using UV-vis spectroscopy (UV-1280, Shimadzu). The tested gels were prepared in a disposal cell (12.5×12.5×45 mm) and the wavelength used was 500 nm. The temperature was raised stepwise from 25 to 70 °C. We started each measurement at least 15 min after the temperature reached the target temperature to allow thermal equilibration of the sample.

Swelling tests and calculation of the crosslink density

To determine the crosslink density of the gels, swelling tests were conducted. For the preparation of the samples, the pre-gel solutions (10 mL) were divided into three glass petri dishes (1 mL), resulting in three gels of one composition. Each gel was permeated with 200 mL of deionized water and allowed to

stand for 7 or more days until equilibration. After that, the weight of the equilibrium-swollen gel was measured to determine the degree of swelling of the gel. When measuring the weight, the water on the surface of the gel was wiped off sufficiently prior to the measurement.

Here, to calculate the crosslink density of the gels by their swelling degree, we applied the Flory-Rehner equation with affine-model networks:^{1,2}

$$v_0 = \frac{[\ln(1 - \varphi_e) + \varphi_e + \chi \varphi_e^2]}{V_1 \left[\frac{1}{2} \left(\frac{\varphi_e}{\varphi_0} \right) - \left(\frac{\varphi_e}{\varphi_0} \right)^{1/3} \right]} \quad (1)$$

wherein v_0 is the number density of the effective elastic chains in the gel network, φ_e is the volume fraction of the polymer at the swelling equilibrium, χ is the Flory-Huggins interaction parameter, V_1 is the molar volume of the solvent (water), φ_0 is the volume fraction of polymer at the as-prepared state, and φ_e / φ_0 represents the swelling degree.

Then, φ_0 can be calculated according to:

$$\varphi_0 = \frac{[(W_m / d_m) + (W_c / d_c)]}{[(W_m / d_m) + (W_c / d_c) + W_s]} \quad (2)$$

where W_m , W_c , and W_s are the weight (gram) of the monomer, crosslinker agent, and solvent, respectively, while d_m and d_c are the specific gravity (g/cm^3) of the monomer and crosslinker agent, respectively.

According to Flory-Huggins theory, φ_e can be determined by assuming that the volume of the polymer does not change after reaching the swelling equilibrium:

$$\varphi_e = \frac{[(W_m / d_m) + (W_c / d_c)]}{[(W_m / d_m) + (W_c / d_c)] + [W_e - (W_m + W_c)]} \quad (3)$$

where W_e is the weight of the swollen gels, i.e., the total weight of water and polymers. For the calculation of v_0 , W_e was the average value of the measured three samples. In addition, the χ parameter was set to 0.48 based on literature precedents on pOEG-based and polyacrylamide derivatives.^{3,4}

Table S1. Conditions for the synthesis of homo-pOEG-based gels and control gels.

Code	OEG(S) ^a	OEG(M) ^a	OEG(L) ^a	NIPAM [mM]	EGDMA	AAM	BIS
OEG(S) E1	1000	-	-	-	1	-	-
OEG(S) E10	1000	-	-	-	10	-	-
OEG(S) E30	1000	-	-	-	30	-	-
OEG(S) E50	1000	-	-	-	50	-	-
OEG(M) E1	-	1000	-	-	1	-	-
OEG(M) E10	-	1000	-	-	10	-	-
OEG(M) E30	-	1000	-	-	30	-	-
OEG(M) E50	-	1000	-	-	50	-	-
OEG(L) E1	-	-	1000	-	1	-	-
OEG(L) E10	-	-	1000	-	10	-	-
OEG(L) E30	-	-	1000	-	30	-	-
OEG(L) E50	-	-	1000	-	50	-	-
NIPAM E1	-	-	-	1000	1	-	-
NIPAM E10	-	-	-	1000	10	-	-
NIPAM E30	-	-	-	1000	30	-	-
NIPAM E50	-	-	-	1000	50	-	-
AAM B1	-	-	-	-	-	1000	1
AAM B10	-	-	-	-	-	1000	10
AAM B30	-	-	-	-	-	1000	30
AAM B50	-	-	-	-	-	1000	50

^aOEG(S), OEG(M), and OEG(L) represent OEGMA with $n = 4$ or 5 , OEGMA with $n = 8$ or 9 , and OEGMA with $n = 19$ or 20 , respectively.

Table S2. Parameters obtained from the swelling tests; the volume fraction of the polymers at as-prepared state (φ_0) and equilibrium state (φ_e), as well as the effective crosslink density (ν_0) of the tested gels.

Code	φ_0	φ_e	φ_e / φ_0	ν_0 [$\mu\text{mol}/\text{mL}$]
OEG(S)E1	0.222	0.035 ± 0.001	0.159 ± 0.005	4.80 ± 0.35
OEG(S)E10	0.223	0.067 ± 0.003	0.301 ± 0.013	21.2 ± 2.26
OEG(S)E30	0.226	0.115 ± 0.008	0.885 ± 0.060	90.1 ± 18.4
OEG(S)E50	0.228	0.118 ± 0.004	0.896 ± 0.032	95.0 ± 10.4
OEG(M)E1	0.317	0.066 ± 0.002	0.207 ± 0.006	21.1 ± 1.40
OEG(L)E1	0.463	0.087 ± 0.004	0.189 ± 0.008	45.5 ± 4.71
OEG(L)E10	0.464	0.098 ± 0.005	0.210 ± 0.012	59.9 ± 8.17
OEG(L)E30	0.465	0.100 ± 0.004	0.215 ± 0.008	63.2 ± 5.56
OEG(L)E50	0.466	0.111 ± 0.011	0.239 ± 0.024	85.1 ± 20.3
NIPAM E1	0.473	0.073 ± 0.016	0.153 ± 0.033	31.6 ± 15.3
AAM B1	0.485	0.017 ± 0.004	0.035 ± 0.008	1.36 ± 15.3

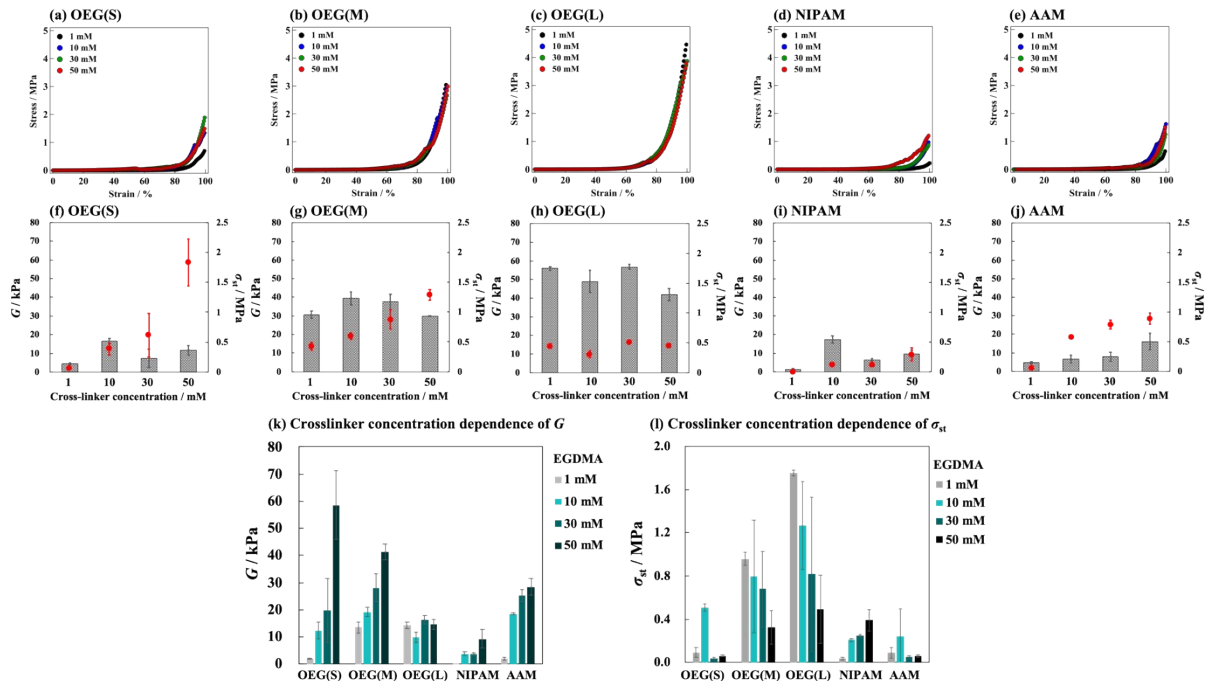


Figure S1. Stress-strain curves for the hydrogels with different crosslinker contents under uniaxial compression: (a) pOEG(S), (b) pOEG(M), (c) pOEG(L), (d) pNIPAM, and (e) pAAM. (f-j) The

compressive modulus, G (red circles, left axis) and strength, σ_{st} (black bars, right axis) of the corresponding hydrogels. (k)-(l) Dependence of G and σ_{st} on the crosslinker concentration.

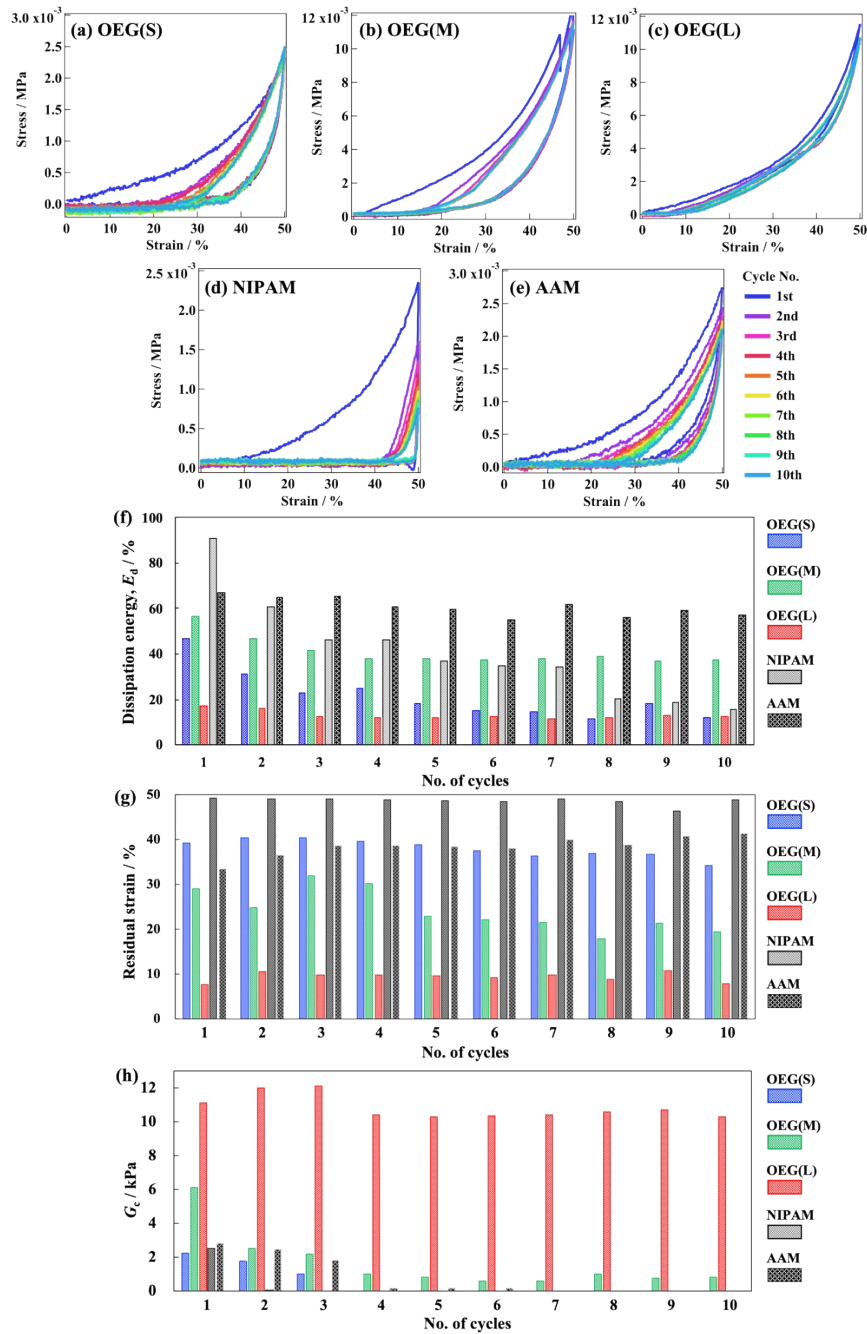


Figure S2. Cyclic compression stress-strain curves for ten successive loading-unloading cycles at 50% maximum strain for the (a) pOEG(S), (b) pOEG(L), (c) pOEG(L), (d) pNIPAM and (e) pAAM gels. (f) Percentage dissipation energy (E_d) for the tested gels after each cycle. (g) Residual strain (λ_r) obtained from the cyclic unloading curves. (h) Elastic modulus at the loading (G_c) of the tested gels. It should be noted that there is partially no data: G_c cannot be determined within the range of 10-20% strain due to the presence of residual strain above 20%. In this case, the residual strain of pOEG(L) gels was lower than those of other gels and did not depend on the number of cycles. In addition, G_c of the pOEG(L) gels was higher than those of other gels. These results indicate that the shape-recovery properties and

mechanical stability of the pOEG(L) are high. Moreover, these values also depend on the side-chain length, suggesting that the side-chain length also affects these properties.

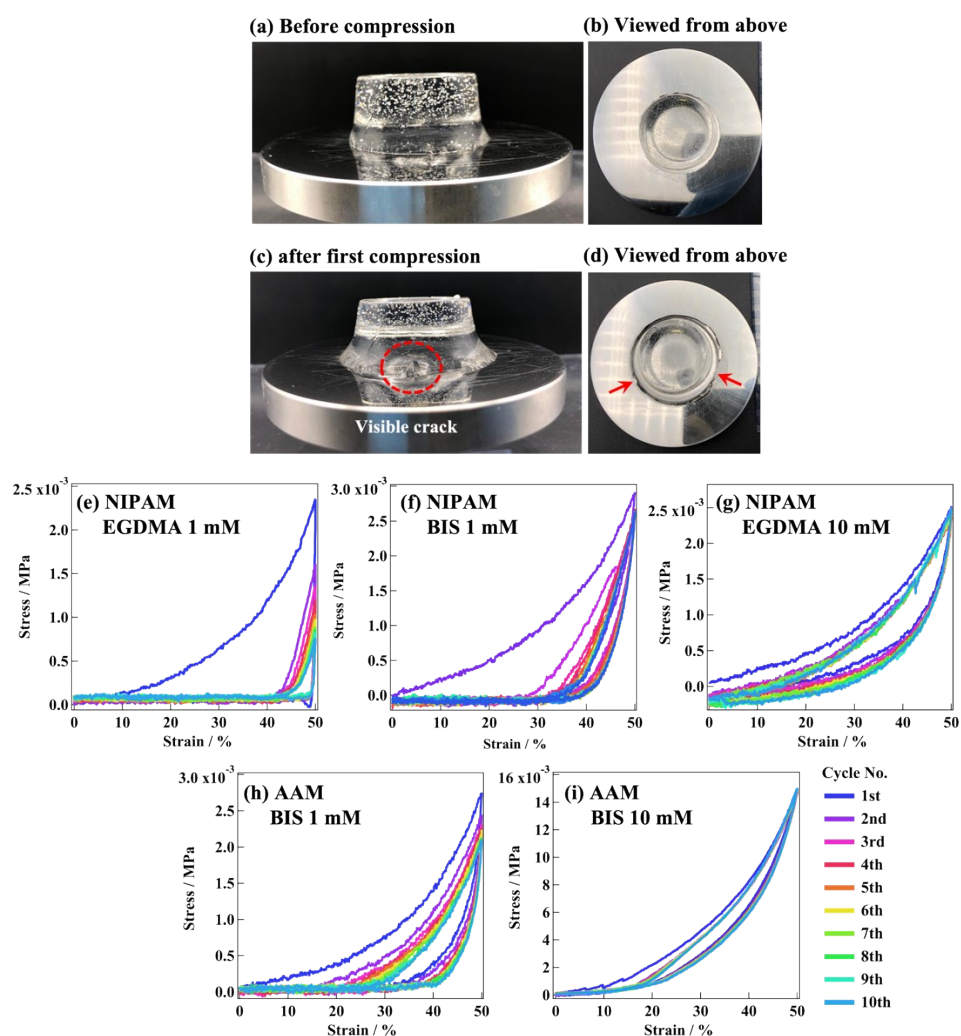


Figure S3. Photographs of pAAM gels (BIS 1 mM) before (a,b) and after (c,d) compression at 50% maximum strain; visible cracks were observed after the compression. The stress-strain curves for ten successive loading-unloading cycles at 50% maximum strain for the (e) pNIPAM (EGDMA 1 mM), (f) pNIPAM (BIS 1 mM), (g) pNIPAM (EGDMA 10 mM), (h) pAAM (BIS 1 mM), and (i) pAAM (BIS 10 mM) gels.

Table S3. Conditions for the synthesis of p(OEG(S)-*co*-OEG(L)) copolymer gels.

Code	Monomer concentration [mM]	Copolymerization ratio of OEG(S) and OEG(L)	OEG(S)	OEG(L) [mM]	EGDMA
OEG(S)	1000	10 : 0	1000	0	1
S7L3	1000	7 : 3	700	300	1
S5L5	1000	5 : 5	500	500	1
S3L7	1000	3 : 7	300	700	1
OEG(L)	1000	0 : 10	0	1000	1

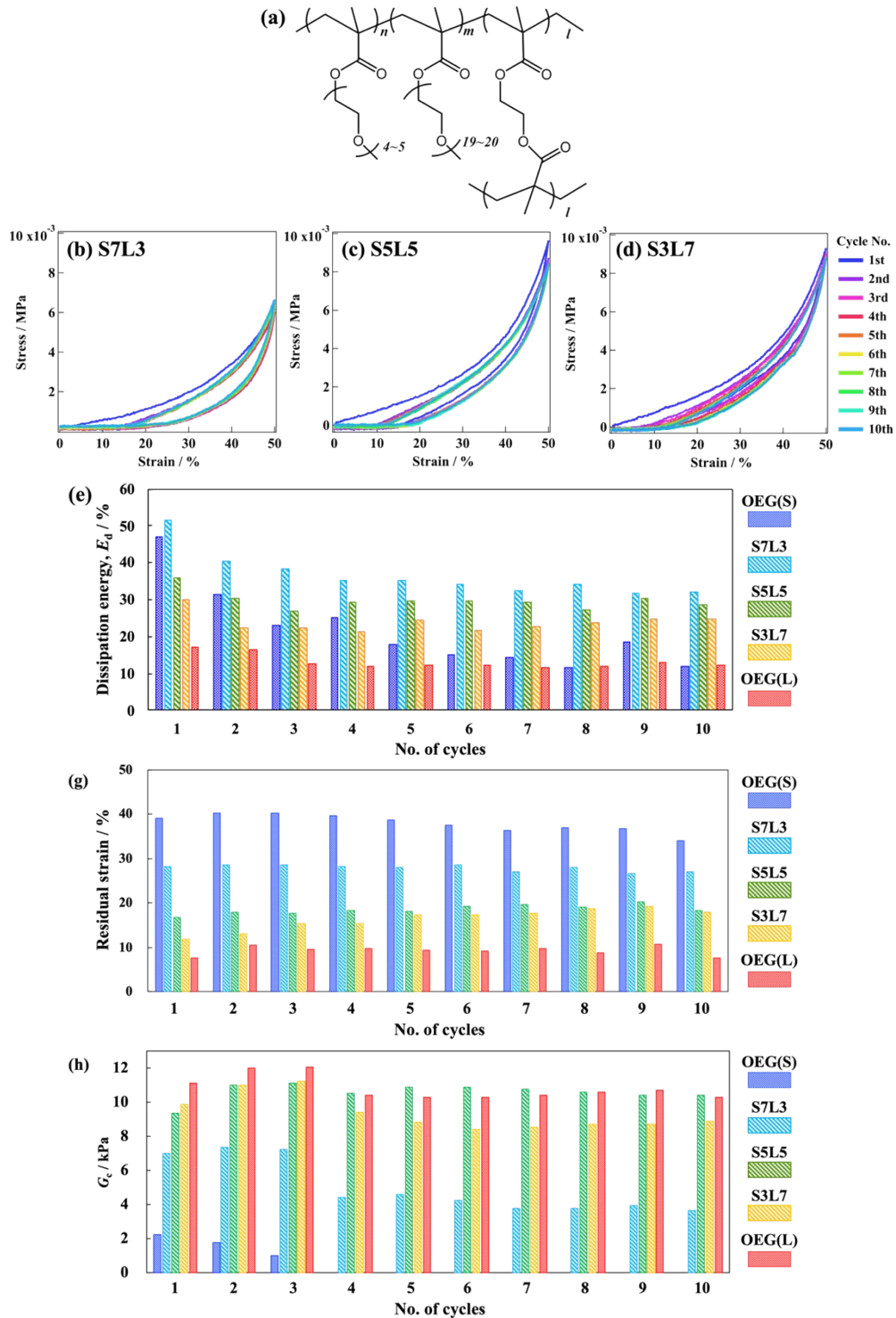


Figure S4. (a) Chemical structure of the p(OEG(S)-*co*-OEG(L)) copolymer hydrogels. Cyclic compression stress-strain curves for ten successive loading-unloading cycles at 50% maximum strain for the (b) S7L3, (c) S5L5, and (d) S3L7 copolymer gels. (e) Percentage dissipation energy (E_d) for the tested gels after each cycle. (g) Residual strain (λ_r) obtained from the cyclic unloading curves. (h) Elastic modulus at the loading (G_c) of the tested gels. It should be noted here that there is partially no data: G_c cannot be determined within the range of 10-20% strain due to the presence of residual strain above 20%.

Table S4. Conditions for the synthesis conditions of p(NIPAM-*co*-OEG(L)) copolymer gels.

Code	Monomer concentration [mM]	Copolymerization ratio of NIPAM and OEG(L)	NIPAM	OEG(L) [mM]	EGDMA
NIPAM	1000	100 : 0	1000	0	1
N95OEG5	1000	95 : 5	950	50	1
N90OEG10	1000	90 : 10	900	100	1
N70OEG30	1000	70 : 30	700	300	1
N50OEG50	1000	50 : 50	500	500	1
N30OEG70	1000	30 : 70	300	700	1
OEG(L)	1000	0 : 100	0	1000	1

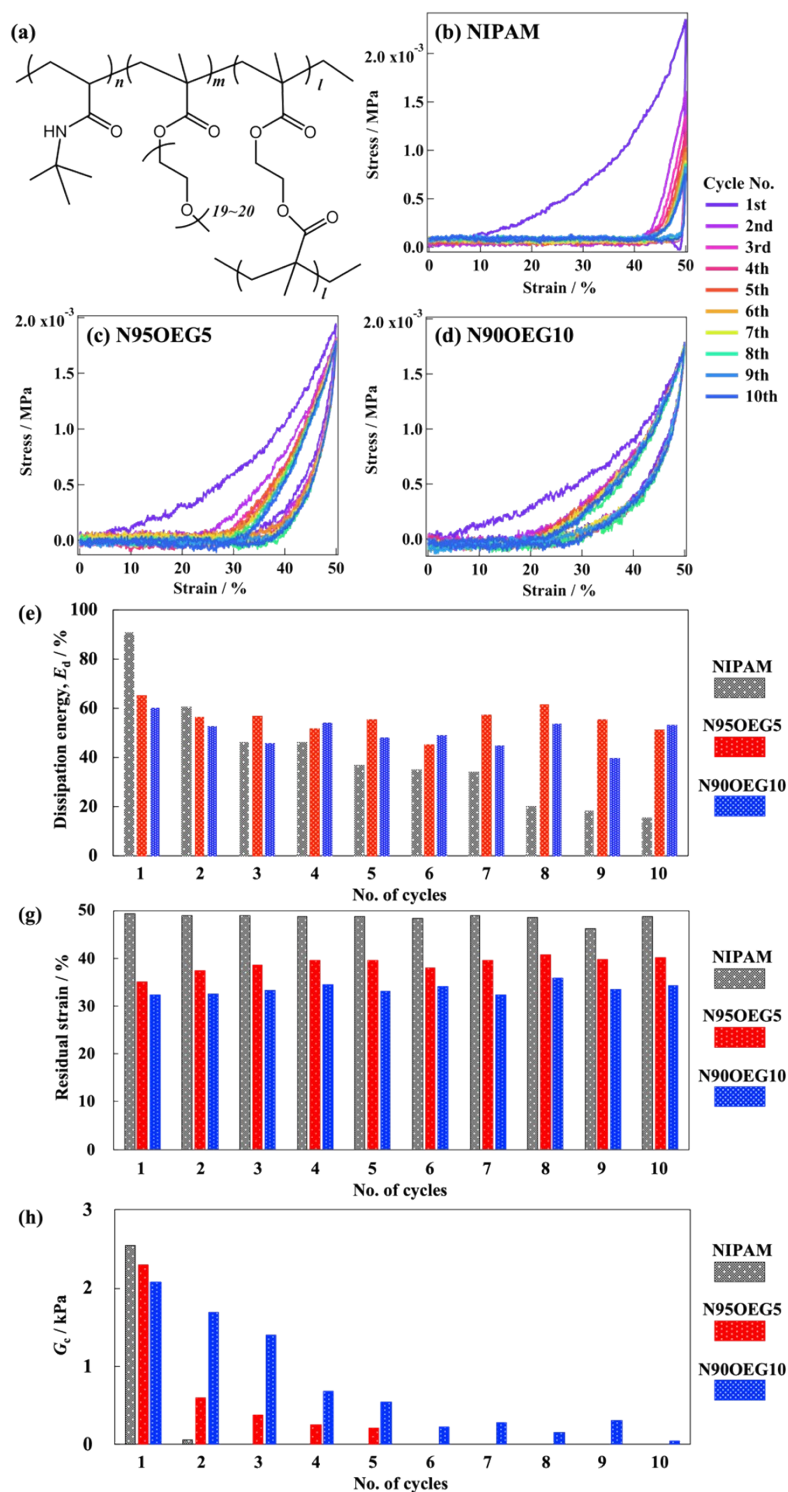


Figure S5. (a) Chemical structure of the p(NIPAM-co-OEG(L)) copolymer hydrogels. Cyclic compression stress-strain curves for the (b) NIPAM (c) N95OEG5, and (d) N90OEG10 gels for ten successive loading-unloading cycles at 50% maximum strain. (e) Percentage dissipation energy (E_d) for the tested gels after each cycle. (g) Residual strain (λ_r) obtained from the cyclic unloading curves. (h) Elastic modulus at the loading (G_c) of the tested gels. It should be noted here that there is partially no data: G_c cannot be determined within the range of 10-20% strain due to the presence of residual strain above 20%.

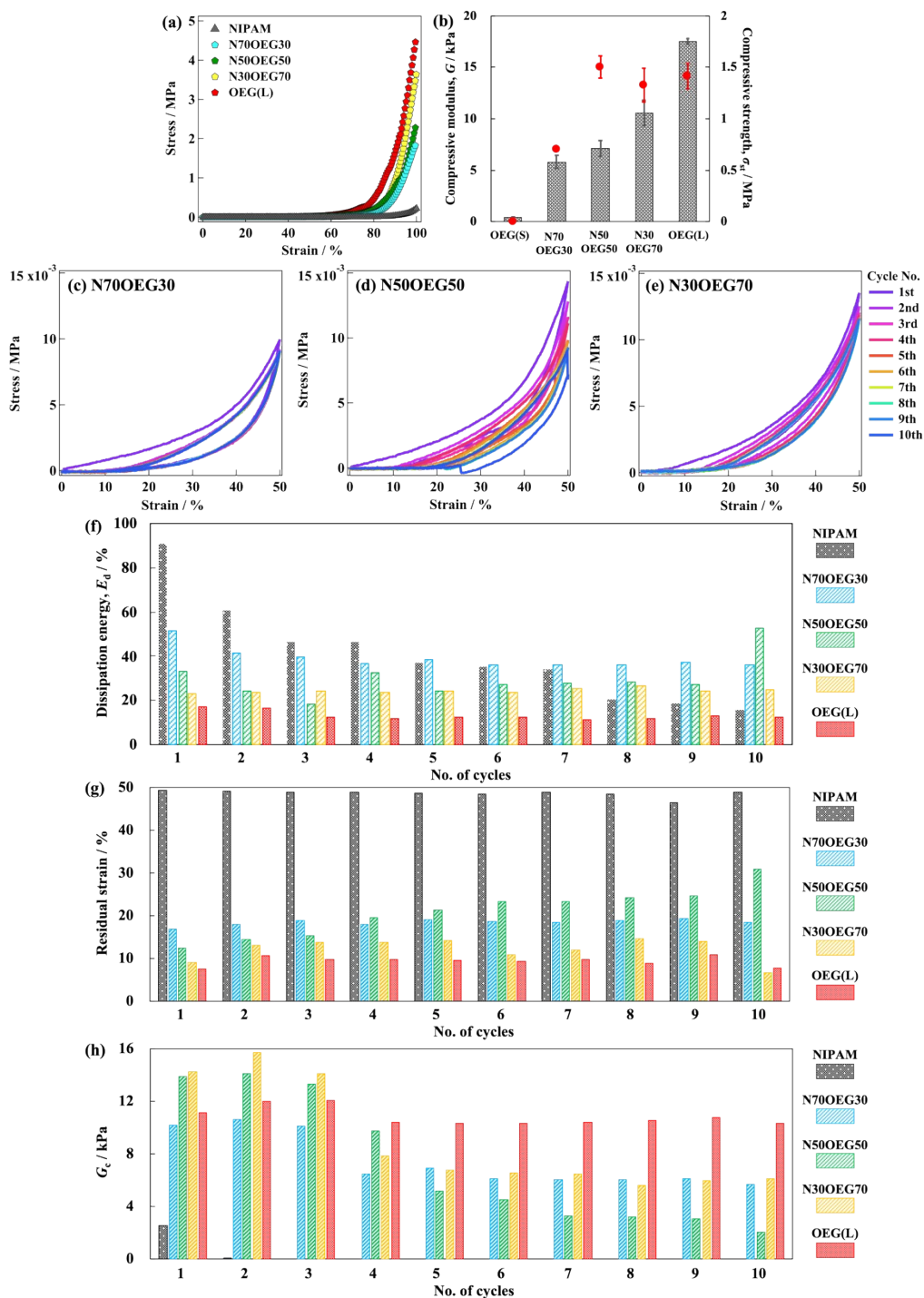


Figure S6. (a) Stress-strain curves for the p(NIPAM-co-OEG(L)) gels with different copolymerization ratios under uniaxial compression. (b) The compressive modulus, G (red circles, left axis) and strength, σ_{st} (black bars, right axis) of the p(NIPAM-co-OEG(L)) gels. The cyclic compression stress-strain curves for ten successive loading-unloading cycles at 50% maximum strain for the (c) N70OEG30, (d) N50OEG50, and (e) N30OEG70 gels. (f) Percentage dissipation energy (E_d) for the tested gels after each cycle. (g) Residual strain (λ_r) obtained from the cyclic unloading curves. (h) Elastic modulus at the loading (G_c) of the tested gels. It should be noted here that there is partially no data: G_c cannot be determined within the range of 10-20% strain due to the presence of residual strain above 20%.

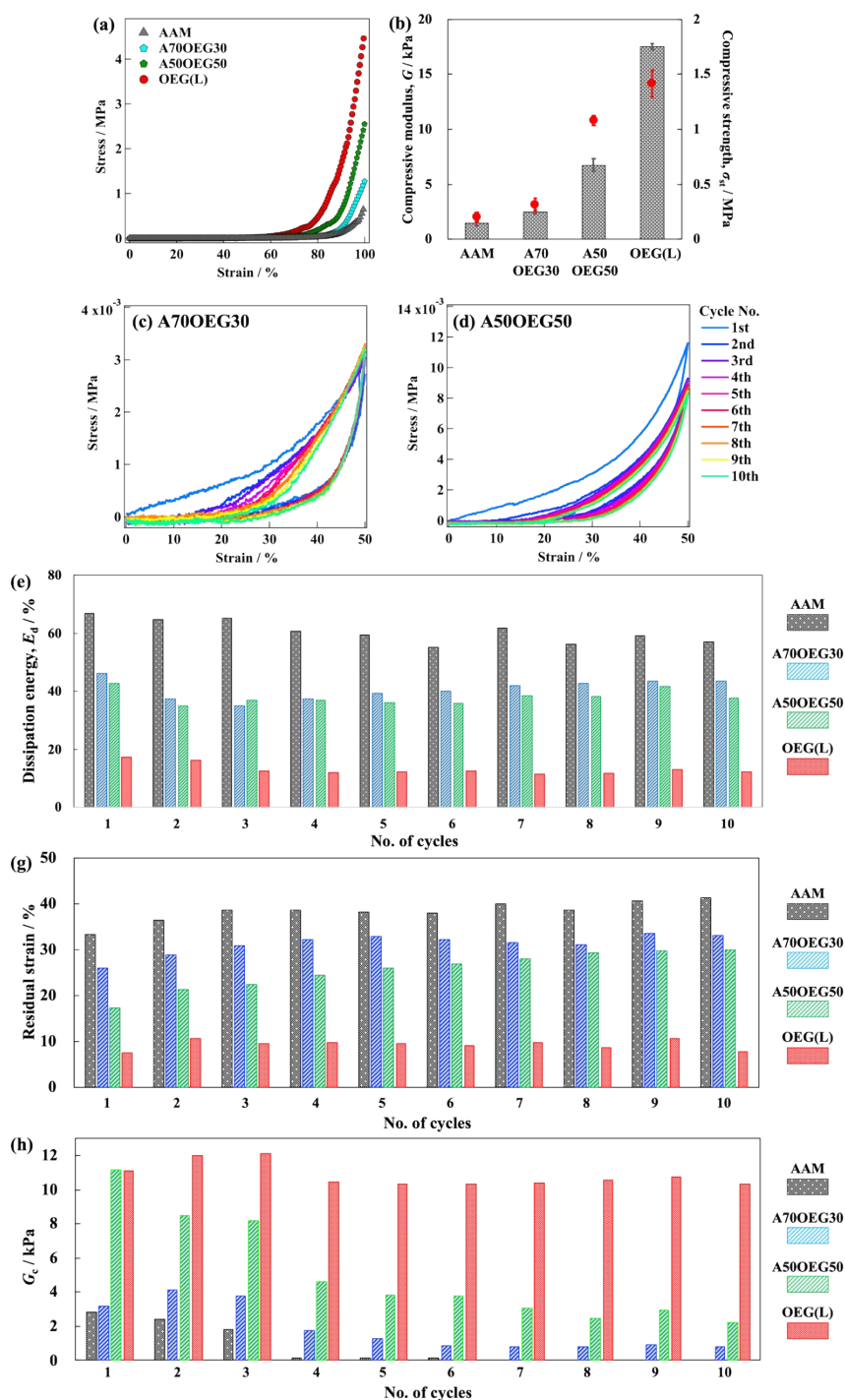


Figure S7. (a) Stress-strain curves for the p(AAM-co-OEG(L)) gels with different copolymerization ratios under uniaxial compression. (b) The compressive modulus, G (red circles, left axis) and strength, σ_{st} (black bars, right axis) of the p(AAM-co-OEG(L)) gels. Cyclic compression stress-strain curves for ten successive loading-unloading cycles at 50% maximum strain for (c) A70OEG30 and (d) A50OEG50. (e) Percentage dissipation energy (E_d) for the tested gels after each cycle. (g) Residual strain (λ_r) obtained from the cyclic unloading curves. (h) Elastic modulus at the loading (G_c) of the tested gels. It should be noted here that there is partially no data: G_c cannot be determined within the range of 10-20% strain due to the presence of residual strain above 20%.

References:

- [1] P. J. Flory, and J. Rehner, Jr., *J. Chem. Phys.*, 1943, **11**, 521-526.
- [2] T. Matsunaga, T. Sakai, Y. Akagi, U. Chung, and M. Shibayama, *Macromolecules*, 2009, **42**, 1344-1351.
- [3] A. D. Drozdov, *Gels*, 2021, **7**, 40.
- [4] Y. H. Bae, T. Okano, and S. W. Kim, *J. Polym. Sci. B. Polym. Phys.*, 1990, **28**, 923-936.