Electronic Supplementary Material (ESI) for Soft Matter.

Highly stretchable ionically crosslinked acrylate elastomers inspired by polyelectrolyte complexes

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S1. Materials and methods.

Materials. Ethyl acrylate (EA) and 2-hydroxyethyl acrylate (HEA) were purchased from TCI America. 4,4'-Azobis(4-cyanovaleric acid) (ABCVA), [2-(acryloyloxy)ethyl]trimethyl-ammonium chloride solution (ATMAC, 80 wt.% in H_2O), 3-sulfopropyl acrylate potassium (SPAP), acetone-d6 and deuterium oxide were purchased from Sigma-Aldrich. Acetonitrile was purchased from Fisher Chemical. N,N-dimethylformamide (DMF) was purchased from Macron. The dialysis tubing (12,000~14,000 Da) was purchased from Ward's Science. All the chemicals were used as received without further purification.

Synthesis of EA20+. 28.62 g EA (20 eq.) and 3.46 g ATMAC (1 eq.) were dissolved in a 300 mL mixed solvent of acetonitrile and water (v/v = 3:1) in a round-bottom flask. The solution was then put in an ice water bath and bubbled with argon for 30 min, after which the flask was heated and kept at 60 °C under N_2 atmosphere overnight. ABCVA (840 mg) was used as the initiator. The reaction mixture was later poured into dialysis tubing and dialyzed in water. The water was changed every 12 h at least 5 times. A rotation evaporator was used to remove the water, after which the product was redissolved in DMF and dried in a mold. The material was removed from the mold and dried in a vacuum oven at 60 °C for a day and later left in air for equilibration.

The synthesis of EA20-, EA10+, EA10-, EA5+ and EA5- follows the same procedure as EA20+, with different ingredient mass shown in the following table.

Table S1. The mass of ingredients used in the EA-based copolymer synthesis.

Copolymer name	EA	ATMAC	SPAP
EA20-	28.62 g (20 eq.)	-	3.32 g (1 eq.)
EA10+	27.32 g (10 eq.)	6.60 g (1 eq.)	-
EA10-	27.32 g (10 eq.)		6.34 g (1 eq.)
EA5+	25.04 g (5 eq.)	12.10 g (1 eq.)	-
EA5-	25.04 g (5 eq.)	-	11.62 g (1 eq.)

Synthesis of HEA5+.10.45 g HEA (5 eq.) and 4.36 g ATMAC (1 eq.) were dissolved in 300 mL water in a flask. The solution was then put in an ice water bath and bubbled with argon for 30 min, after which the flask was heated and kept at 60 °C under N_2 atmosphere overnight. ABCVA (300 mg) was used as the initiator. The reaction mixture was later poured into dialysis tubing and dialyzed in water. The water was changed every 12 h for at least 5 times. A rotation evaporator was used to concentrate the solution, after which the solution was dried in a mold. The material was removed from the mold and dried in a vacuum oven at 60 °C for a day and later left in air for equilibration.

The synthesis of HEA5- follows the same procedure as HEA5+, with ATMAC replaced by 4.18 g SPAP.

Synthesis of EA homopolymer. 30.04 g EA was dissolved in 300 mL acetonitrile in a flask. The solution was then put in an ice water bath and bubbled with argon for 30 min, after which the flask was heated and kept at 60 °C under N2 atmosphere overnight. ABCVA (840 mg) was used as the initiator. The reaction mixture was later poured into dialysis tubing and dialyzed in water. The obtained solid product was redissolved in DMF and dried in a mold. The material was removed from the mold and dried in a vacuum oven at 60 °C for a day.

EA20+/- assembly. 3.14 g of EA20+ and 3.86 g of EA20- were dissolved in a mixed solvent of acetonitrile and water (v/v = 3:1) separately. Then the two solutions were mixed and rigorously vibrated. The mixture was poured into dialysis tubing and dialyzed in water. The water was changed every 12 h at least 5 times. The obtained solid was swollen with DMF and dried in a mold. The material was removed from the mold and dried in a vacuum oven at 60 °C for a day and later left in air for equilibration.

The assembly of EA10+/- and EA5+/- follows the same procedure as EA20+/-, with different mix ratios shown in the following table.

Table S2. The mass of copolymers used in the EA-based complex assembly.

Material name	EA10+	EA10-	EA5+	EA5-
EA10+/-	2.79 g	4.21 g	-	-
EA5+/-	-	-	3.23 g	3.77 g

The assembly of HEA5+/- follows the same procedure as EA20+/-, with acetonitrile/water mixture replaced by water, and the mixing ratio is as follows: 3.54 g of HEA5+ and 3.46 g of HEA5-.

Mechanical tests. Mechanical tests were performed on a Zwick-Roell Z010 system with a 20 N capacity load cell (X-Force HP, Zwick-Roell). Rectangular specimens were prepared with a 4 mm-spaced double-razor cutter. The thickness was around 1 mm and was carefully measured before each test. The gauge length was set to be 20 mm. Monotonic tensile tests and cyclic loading tests were performed with displacement control using engineering strain. Engineering stress and strain were calculated from recorded force and travel during tests using the equations below. For the self-healing tests, each specimen was cut into two pieces, immediately reattached at the cut surfaces and placed in a rectangular mold of their original size. The tests were repeated three times. The test with intermediate final stretch was selected to plot.

$$\sigma_{\text{engineering}} = \frac{F}{\text{width} \times \text{thickness}}$$

$$\varepsilon_{\text{engineering}} = \frac{\text{travel}}{\text{gauge length}}$$

Fourier-transform infrared (FTIR) spectroscopy. The FTIR spectra of the materials were collected using a Bruker Vertex V80V Vacuum FTIR system with a deuterated triglycine sulfate (DTGS) detector at attenuated total reflection (ATR) mode. The spectral range of 4000~500 cm^{-1} was collected with 32 scans at a resolution of 4 cm^{-1}. Samples were measured right after cooling down to room temperature following removal from the vacuum oven.

Raman spectroscopy. The Raman spectra of the materials were collected using a Renishaw InVia Confocal Raman Microscope system. A 785 nm laser source was used for excitation at 10% power with 1200 l/mm grating. The spectral range of 3200~100 cm^{-1} was collected with 30 s exposure time and one accumulation. The calibration was performed referring to the 520.5 cm^{-1} line of silicon. Samples were measured right after cooling down to room temperature following removal from the vacuum oven.

Differential scanning calorimetry (DSC). Samples were loaded in Tzero hermetic aluminum pans and measured with a TA Instruments Q1000 MDSC system. They were measured with a heating rate of 10 °C/min and a cooling rate of 10 °C/min in the range of -50~110 °C for one heating-cooling-heating cycle. Data from the second heating ramp was shown. Glass transition temperatures (T_g) were determined from the inflection point of the curve.

X-ray photoelectron spectroscopy (XPS). Samples were analyzed using a Scienta Omicron ESCA-2SR with operating pressure ca. 1x10^{-9} Torr. Monochromatic Al Kα x-rays (1486.6 eV) were generated at 250 W (15 kV; 20 mA) with photoelectrons collected from a 2 mm diameter analysis spot. Photoelectrons were collected at a 0° emission angle with source to analyzer angle of 54.7°. A hemispherical analyzer determined electron kinetic energy, using a pass energy of 200 eV for survey scans and high resolution scans. A flood gun was used for charge neutralization.

^{1}H nuclear magnetic resonance (^{1}H-NMR). The ^{1}H-NMR spectra of copolymers were acquired with a Bruker Advance III HD 500 spectrometer with 16 scans, 30 s relaxation delay and 90° excitation pulse. EA20+ and EA10+ were dissolved in acetone-d6. EA5+, EA5-, HEA5+ and HEA5- were dissolved in deuterium oxide. The spectra use reference by solvent.

Small-angle X-ray scattering (SAXS). SAXS measurement was conducted using an Anton Paar SAXSess bench-top X-ray scattering system, which employed a line collimated beam at 0.1542 nm and a block camera setup for data collection. All samples were measured at 30°C, which is above the samples' glass transition temperatures. The samples were sandwiched between Kapton films, and all samples and backgrounds were scattered for 7 minutes. Kapton's scattering intensity with a peak at around 5 nm^{-1} was subtracted as a background from all samples. The experimental line collimated intensity $I_{exp}(q)$ is a function of point collimated intensity $I_0(q)$ such that [1,2],

$$I_{exp}(q) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_x(x)W_y(y)I_0\left(\sqrt{\left(\frac{\lambda a q}{2\pi} - y\right)^2 + x^2}\right)$$

$W_x(x)$ and $W_y(y)$ are the horizontal and vertical X-ray beam with horizontal vertical dimensions x and y. q is the scattering wave vector, and a is the sample-to-detector distance. Generalized indirect Fourier transformation (GIFT) was utilized to desmear $I_{exp}(q)$.

Dynamic mechanical analysis (DMA). DMA tests were performed on a TA Instruments DMA Q800 system. Temperature sweep experiments were conducted using film tension mode with the following parameters: 3 °C/min temperature sweep rate, 5 min soak time, 0.1% strain, and 1 Hz frequency. The temperature range is the exact range shown in our DMA plots. Rectangular specimens were prepared with a 4 mm-spaced double-razor cutter. The thickness was around 1 mm and was carefully measured before each test. The gauge length was set to be 20 mm.

Gel permeation chromatography (GPC). The molecular weight and polydispersity (PDI) of our copolymers were obtained by a Waters Ambient Temperature GPC. EA20+, EA20- and EA10- were measured with DMF (0.1% LiBr) as the eluent at a flow rate of 1 mL/min based on polystyrene standards. EA5 was measured with water (0.05% NaN_3) as the eluent at a flow rate of 1 mL/min based on poly(methacrylic acid) standards. Samples in DMF were prepared with a concentration of 3 mg/mL and samples in water were prepared with a concentration of 3 mg/mL. All samples were filtered through a 0.45 μm PTFE filter.

S2. Ionic ratio analysis.

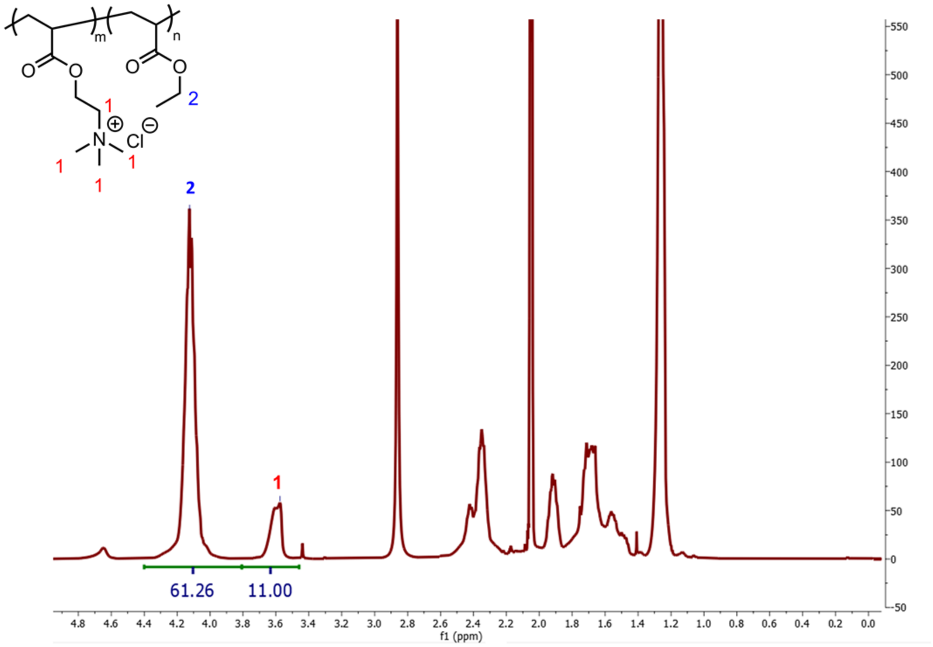

Figure S1 The ^{1}H-NMR spectrum of EA20+. The ionic:neutral ratio is determined to be 1:30.63.

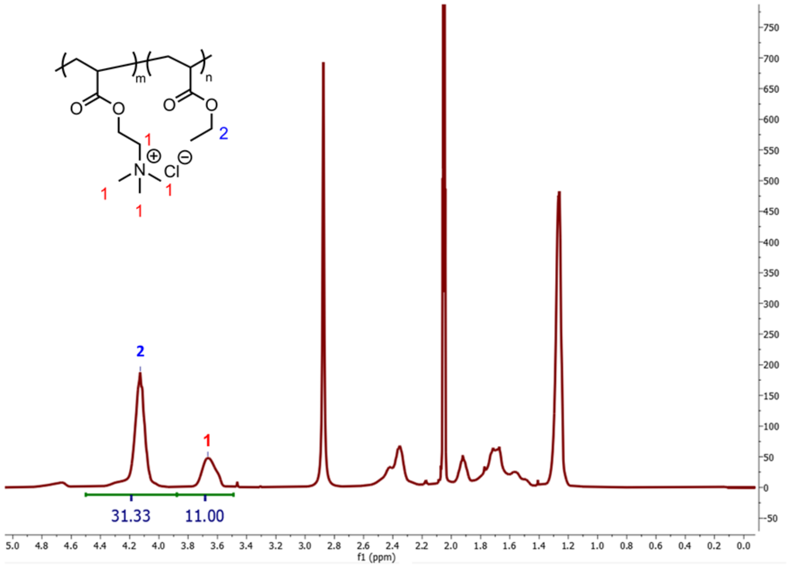

Figure S2 The ^{1}H-NMR spectrum of EA10+. The ionic:neutral ratio is determined to be 1:15.66.

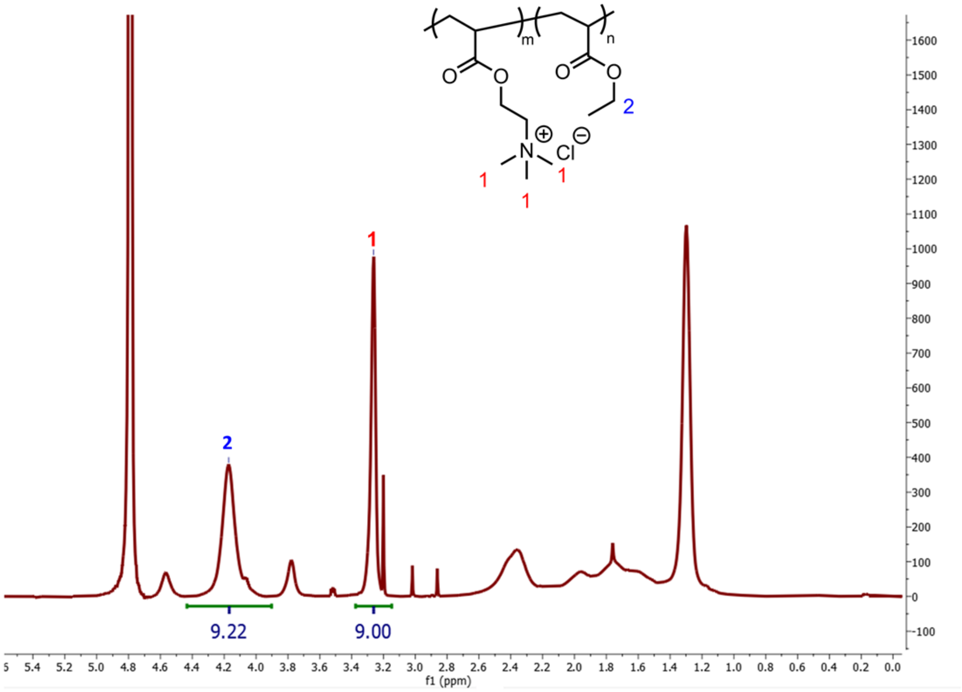

Figure S3 The ^{1}H-NMR spectrum of EA5+. The ionic:neutral ratio is determined to be 1:4.61.

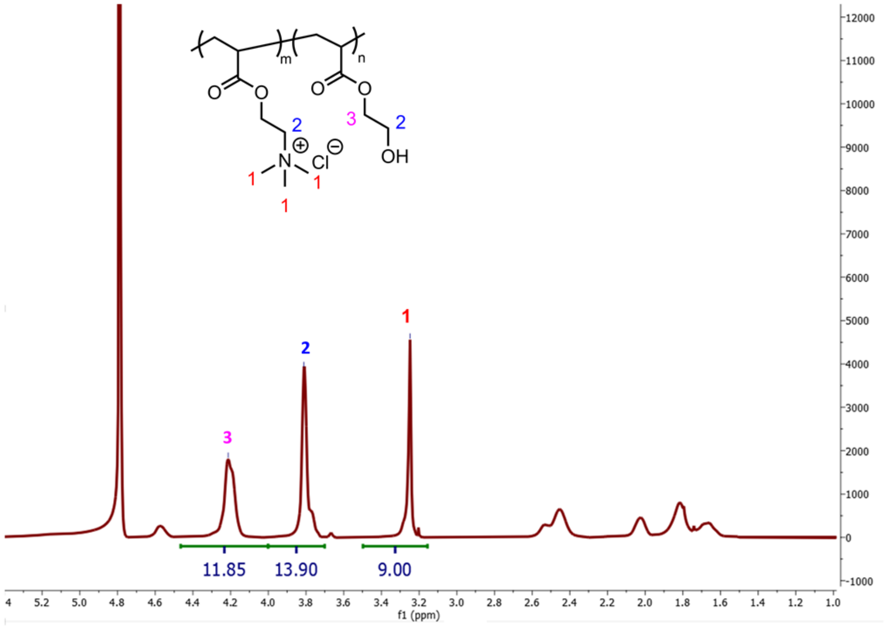

Figure S4 The ^{1}H-NMR spectrum of HEA5+. The ionic:neutral ratio is determined to be 1:5.92.

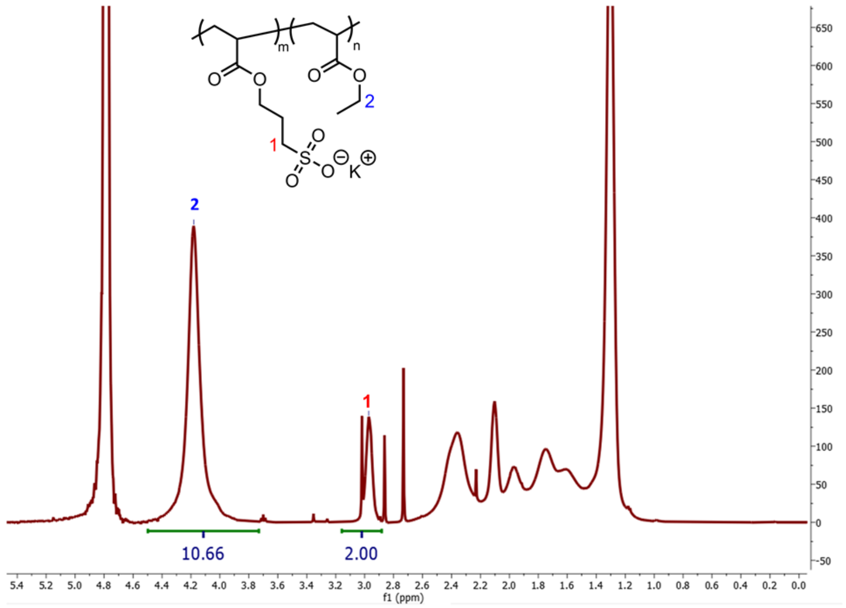

Figure S5 The ^{1}H-NMR spectrum of EA5-. The ionic:neutral ratio is determined to be 1:5.33.

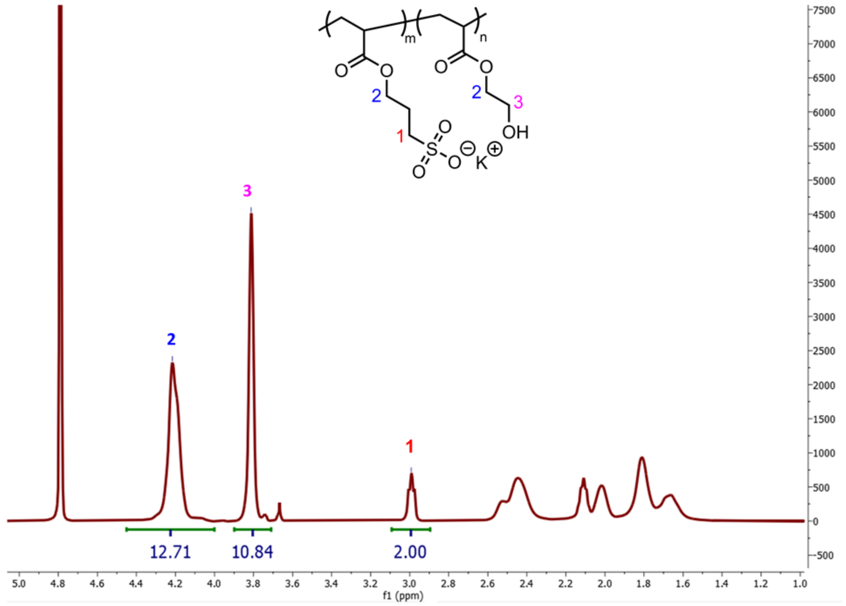

Figure S6 The ^{1}H-NMR spectrum of HEA5-. The ionic:neutral ratio is determined to be 1:5.42.

Table S3 XPS results of EA20- and EA10-.

Samples	Area *S*			Percentage of charged monomers (%)
	O (1s)	S (2s)	N (1s)	
EA20- (1)	824.29	4.51	2.40	2.36
EA20- (2)	897.89	5.71	2.63	2.74
EA20- (3)	836.81	5.25	1.44	2.69
EA10- (1)	789.10	7.10	1.40	3.93
EA10- (2)	798.65	7.21	1.11	3.94
EA10- (3)	836.44	7.75	1.87	4.06

We use the following equation to calculate the percentage of charged monomers:

$$\mathrm{SPAP\%} = \left(1 + \frac{\frac{S_{\mathrm{O}}}{2.93} - \frac{5S_{\mathrm{S}}}{1.43} - \frac{2S_{\mathrm{N}}}{1.8}}{\frac{2S_{\mathrm{S}}}{1.43}}\right)^{-1}$$

Then we use the average percentage of SPAP to calculate the ionic:neutral ratio. We have that this ratio for EA20- is 1:37.60 and for EA10- is 1:24.17.

It is worth noting that we synthesized the two polymers as random copolymers, and the percentage of the ionic monomer is relatively low. These two factors above should suppress surface phase separation, making the XPS measurement representative of the bulk polymer.

S3. Supplemental mechanical test results.

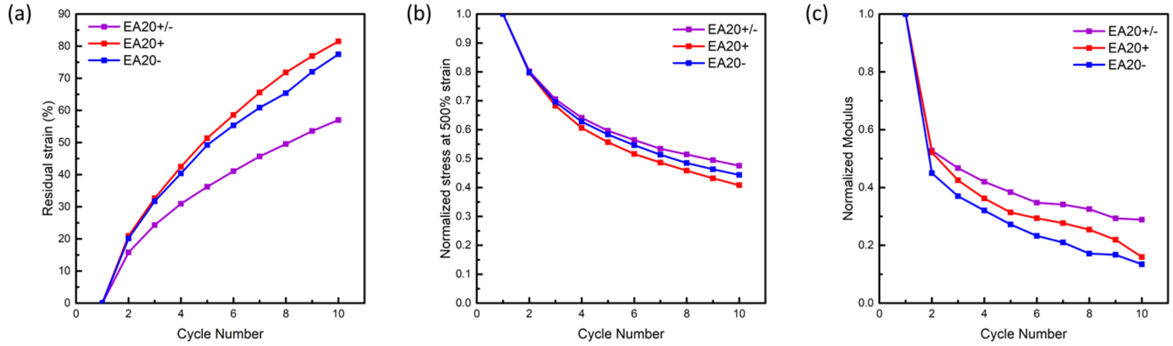

Figure S7 (a) Residual strain upon reloading, (b) normalized stress at 500% strain and (c) normalized modulus obtained from cyclic tensile loading tests at a 0.1 s^{-1} strain rate of EA20+/-, EA20+ and EA20-.

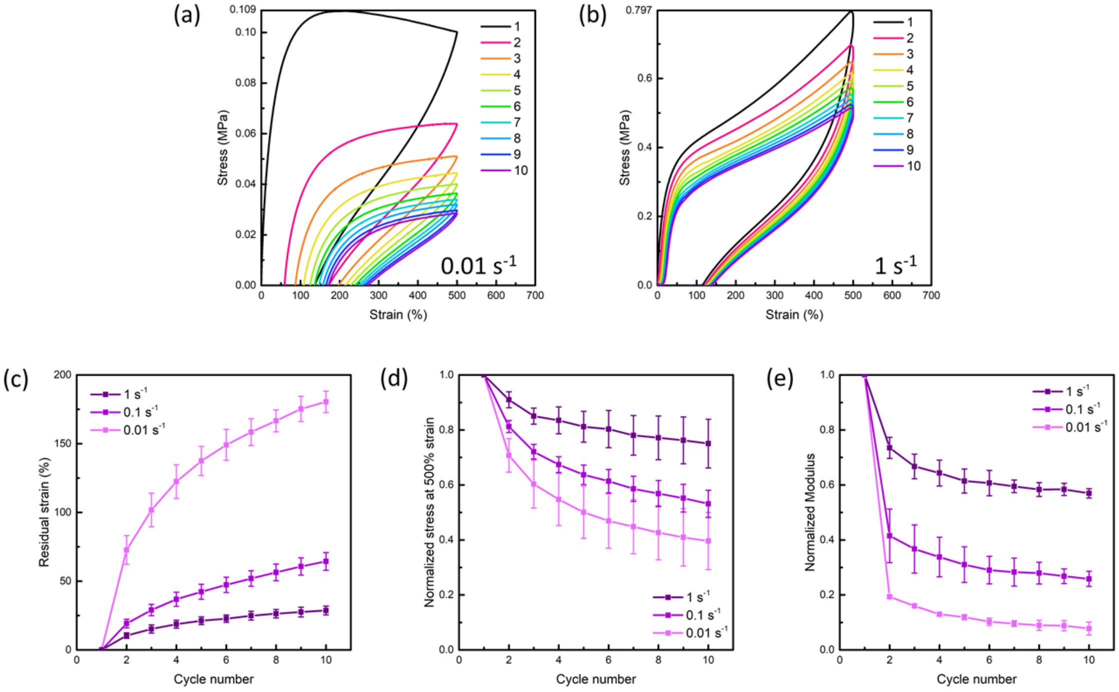

Figure S8 Repeated cyclic tensile test results of EA20+/- at different strain rates. (a,b) The stress-strain curves of tests at (a) 0.01 s^{-1} and (b) 1 s^{-1}. (c) Residual strain upon reloading, (d) normalized stress at 500% strain and (e) normalized modulus are obtained from the curves shown.

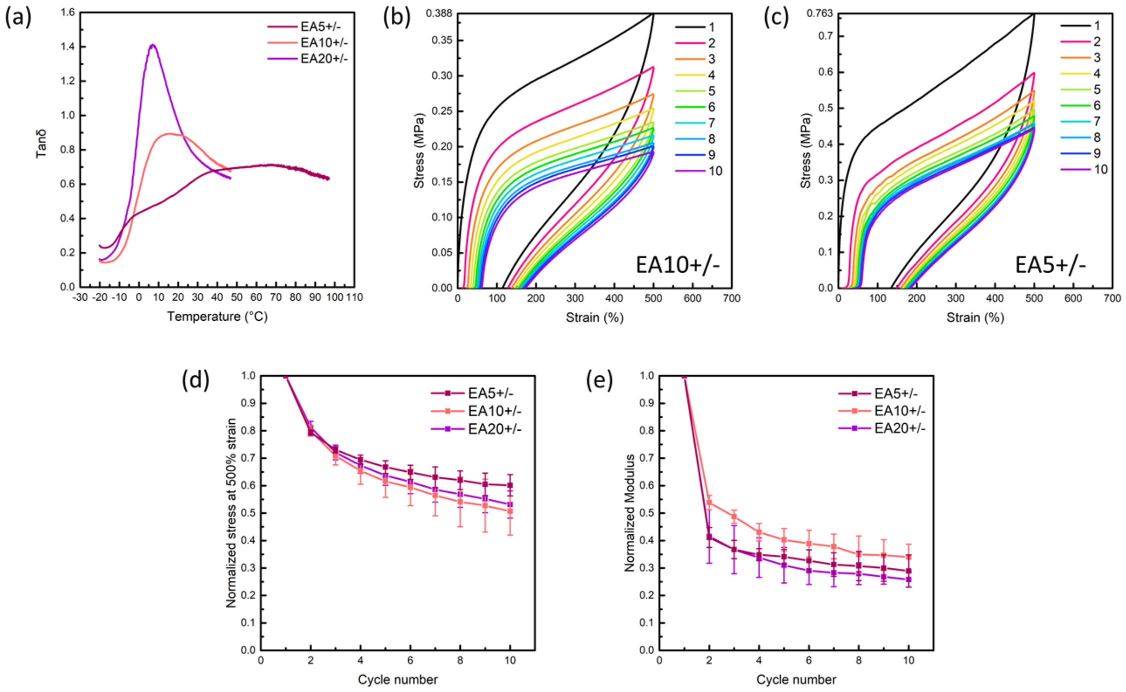

Figure S9 (a) Temperature dependence of tan□ of complexes with different ionic ratios. (b,c) The stress-strain curves of cyclic tensile tests at a 0.1 s^{-1} strain rate for (b) EA10+/- and (c) EA5+/-. (d) Normalized stress at 500% strain and (e) normalized modulus are obtained from the curves shown.

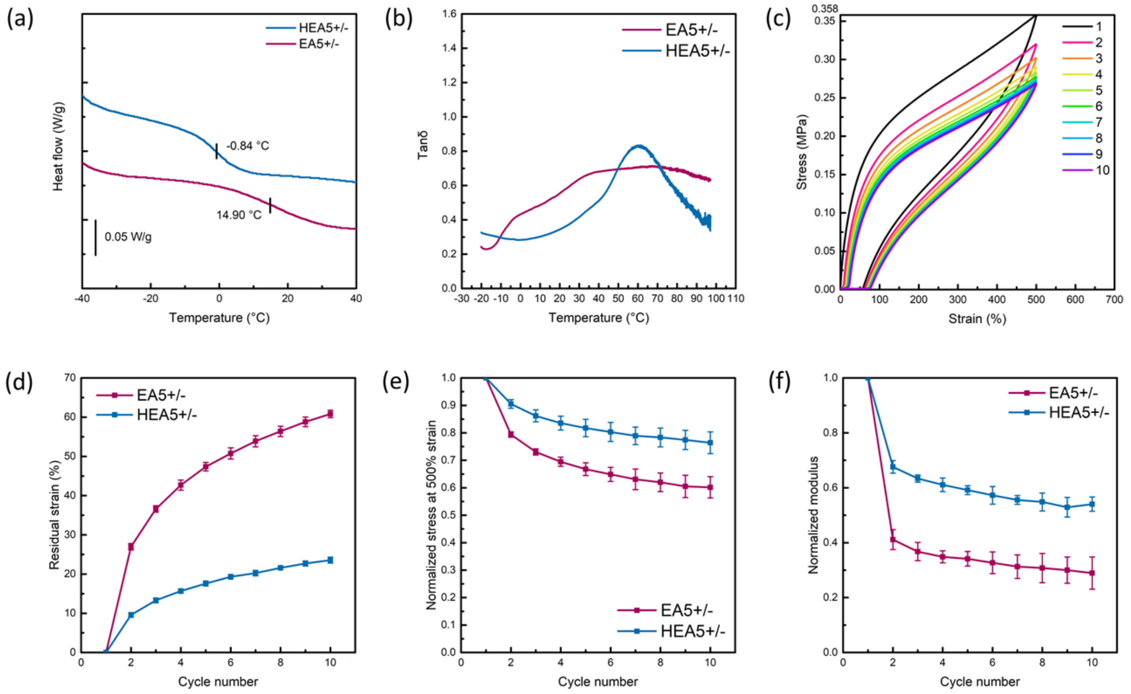

Figure S10 Comparison between EA5+/- and HEA5+/-. (a) Heat flow curves of the second heating scans with "exotherm up" from DSC. (b) Temperature dependence of tan□ from DMA. (c) The stress-strain curves of cyclic tensile tests at a 0.1 s^{-1} strain rate for HEA5+/-. (d) Residual strain upon reloading, (e) normalized stress at 500% strain and (f) normalized modulus are obtained from the cyclic tensile tests.

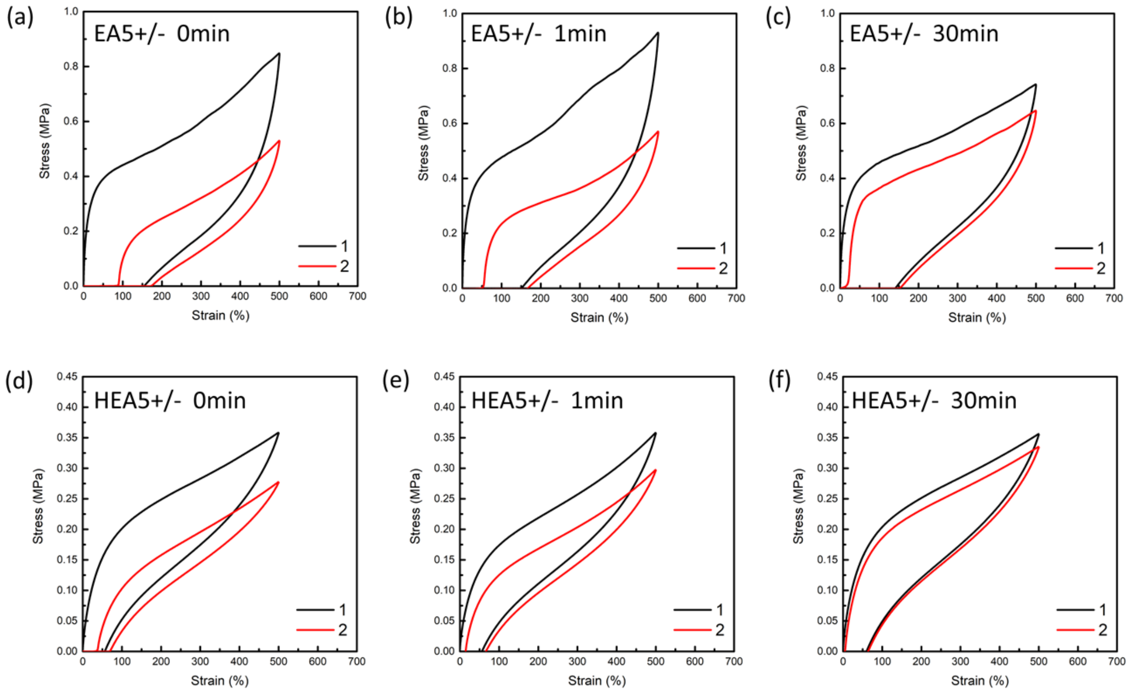

Figure S11 Cyclic tensile stress-strain curves of EA5+/- and HEA5+/- at a 0.1 s^{-1} strain rate with different waiting time between the first and the second. (a-c) Curves of EA5+/- with waiting time of (a) 0 min, (b) 1 min and (c) 30 min. (d-f) Curves of HEA5+/- with waiting time of (d) 0 min, (e) 1 min and (f) 30 min.

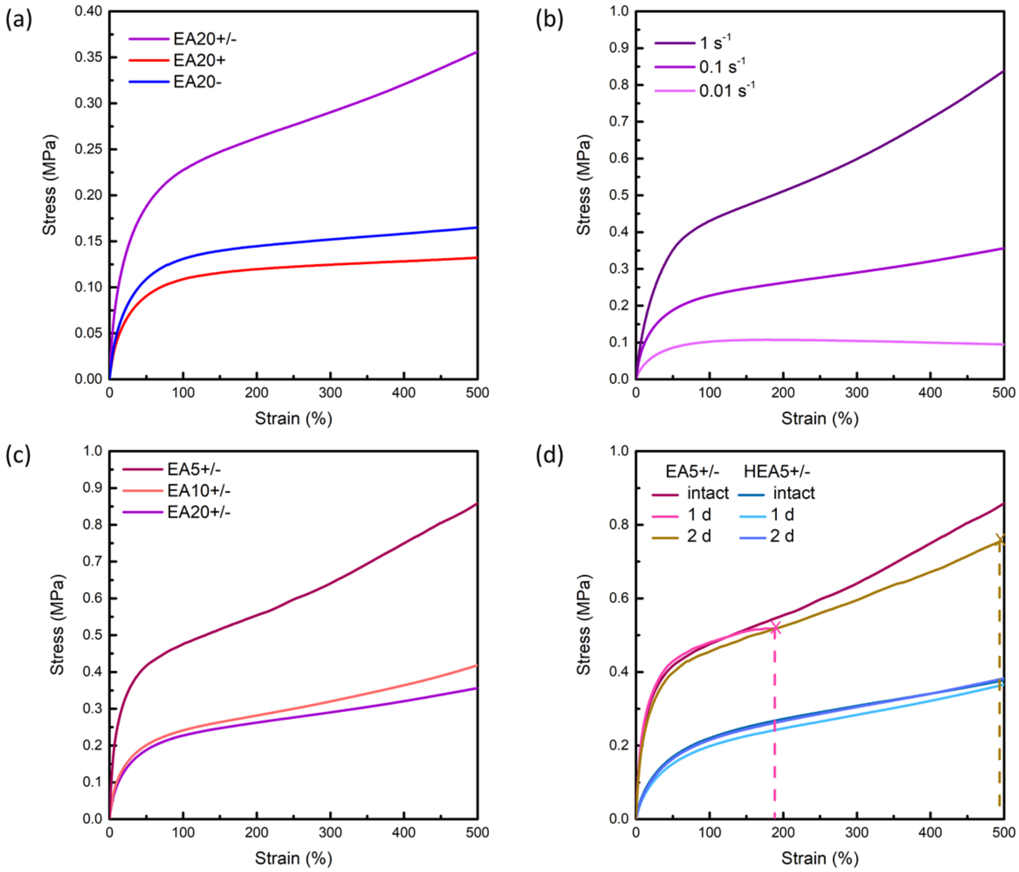

Figure S12 Zoomed-in versions of (a) figure 2c, (b) figure 3a, (c) figure 4c, and (d) figure 5a from the manuscript.

S4. Supplemental SAXS results.

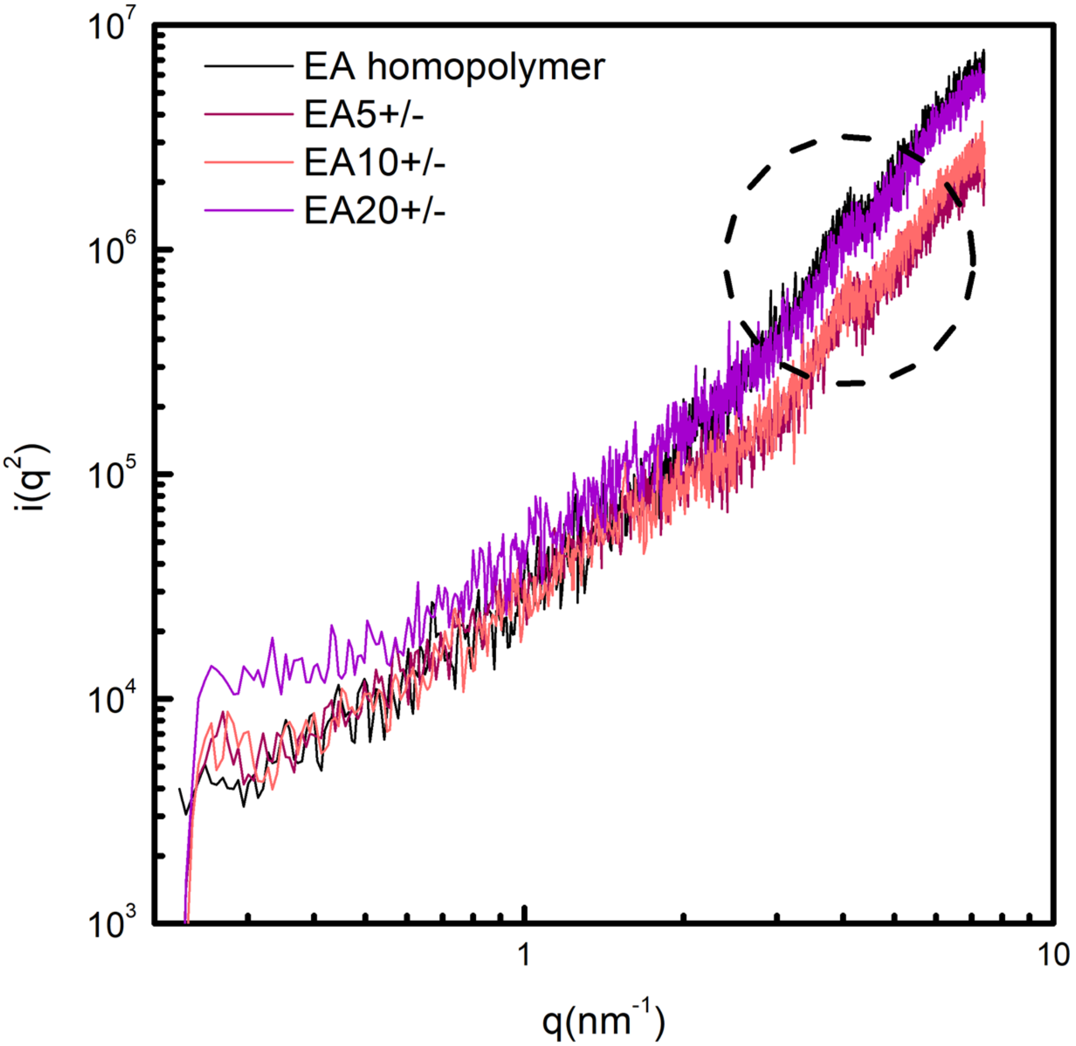

Figure S13 Kratky plot of the three EA complexes with different ionic ratios and of the EA homopolymer.

S5. Gel permeation chromatography results.

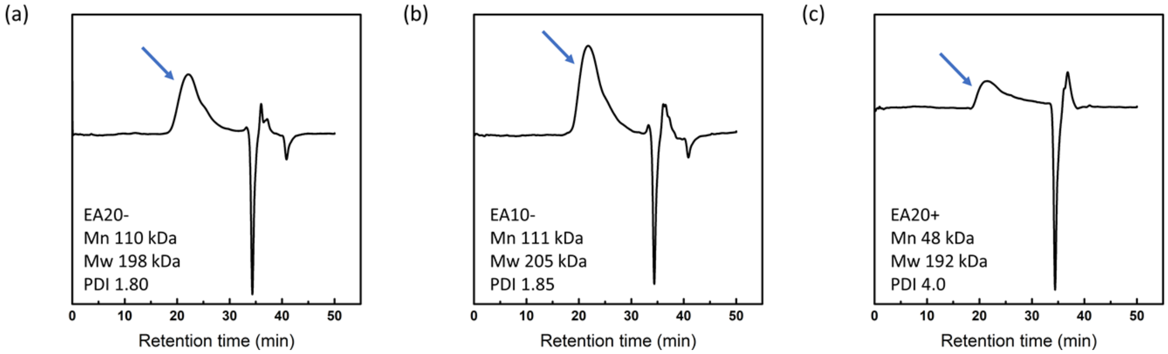

Figure S14 GPC plots of (a) EA20-, (b) EA10-, and (c) EA20+. The blue arrows indicate the polymer peaks.

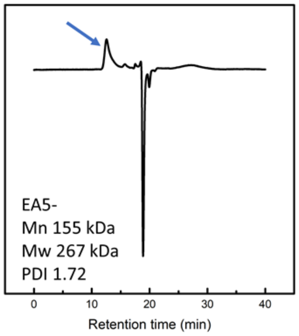

Figure S15 GPC plot of EA5-. The blue arrow indicates the polymer peak.

S6. Elemental analysis results.

Table S4 XPS results of EA5+/-, EA10+/- and EA20+/-.

Samples	Area/RSF			
	S (2s)	N (1s)	K (2s)	Cl (2p)
EA5+/-	8.82	7.95	No signal	1.30
EA10+/-	2.16	3.83	No signal	No signal
EA20+/-	2.45	2.58	No signal	No signal

Reference.

[1] Glatter, O., Kratky, O., Small Angle X-Ray Scattering; Academic Press: New York, 1982.

[2] Srivastava, S., Shin, J. H., Archer, L. A., Soft Matter, 2012, 8, 4097− 4108.