

## Supporting Information

for

### Environmentally Ion-Dissociable High-Performance Supramolecular Polyelectrolyte Plastics

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## Materials

2-Hydroxypropyltrimethyl ammonium chloride chitosan (HACS-Cl,  $\sim 1.5 \times 10^5$  g mol<sup>-1</sup>), sodium phytate (SP, 98%), and cellulose 2-(2-hydroxy-3-(trimethylammonio)propoxy) ethyl ether chloride (CHTM-Cl,  $\sim 4.3 \times 10^5$  g mol<sup>-1</sup>) were purchased from Shanghai Yuanye Bio-Technology Co., Ltd. Sodium methanesulfonate (> 98%), sodium 1-butanesulfonate (98%), sodium 1-octanesulfonate (98%), and sodium laurylsulfonate (98%) were purchased from Aladdin. (3-Acrylamide propyl) trimethylammonium chloride (TMPA-Cl, 75 wt% in water) was purified by filtering the solution through alkaline alumina column to remove the polymerization inhibitor. The seawater was obtained at 25 nautical miles from the coast of East China Sea. Other chemicals were purchased from Aladdin or Shanghai Yuanye Bio-Technology Co., Ltd. and used directly. The water used was purified by filtration through a Millipore Gradient system, giving a resistivity of 18.2 M $\Omega$  cm.

## Characterizations

All <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded on an Avance III HD400 spectrometer (Bruker) with D<sub>2</sub>O as the solvent. Supramolecular polyelectrolyte plastics were characterized using a Nicolet iS20 attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometer. UV-Vis spectra were measured using the UNICO2802 UV-Visible spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a TA Q5000IR TGA instrument under a nitrogen atmosphere to obtain the decomposition temperature ( $T_{d, 5\%}$ ) at 5% degradation of the polymers. Polymers with a weight of about 5-10 mg were slowly heated up from 40 to 700 °C with a rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere to explore the thermal stability. The surface chemical components of different films were analyzed by using X-ray photoelectron spectroscopy (XPS, Kratos Axis supra+). The data of hydrodynamic diameter ( $D_h$ ) and size distribution of polymers in solutions were obtained from dynamic light scattering (DLS) measurements using a Zetasizer (Malvern Zetasizer Nanoseries) at 25 °C. A commercial laser light

scattering spectrometer (ALV/DLS/ SLS-5022F) equipped with a multi- $\tau$  digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He–Ne laser ( $\lambda_0 = 632.8$  nm) was used to measure the weight-average molar mass of HACS-Cl and CHTM-Cl. The morphologies of the materials were characterized by the GeminiSEM 500 Schottky field emission scanning electron microscope, and the SEM samples were sprayed with gold before testing. The mechanical properties of the supramolecular polyelectrolyte plastics were measured using SANS TS7104 electronic testing instrument (SANS, China). The length, width, and thickness of the samples were measured by a digital caliper. All the mechanical tests were measured at least three times to rule out coincidences such as defects produced during the fabrication of the films. Supramolecular polyelectrolyte films were tested after standing at 25 °C and relative humidity (RH) of 50% for 24 h. The tensile speed was set to 10 mm min<sup>-1</sup>. Samples were cut into rectangles with a size of 30.0 × 4.0 mm. The thickness of the samples was all about 0.3 mm. For the single-edge notch tensile test, the sample size was about 60.0 mm × 5.0 mm × 0.5 mm. The specimens were notched to about 45%-55% of their width with a diamond saw, and then the notch was sharpened by using a razor blade. The displacement rate during the test was 10 mm min<sup>-1</sup>. To demonstrate the robust properties of the supramolecular plastic, the HACS-SP-C<sub>8</sub> film with the exterior size of about 30 mm × 30 mm × 3 mm and interior size of about 20 mm × 15 mm × 3 mm was employed to pull a car.

### **Fabrication of supramolecular polyelectrolyte plastics HACS-C<sub>x</sub>s**

Taking HACS-C<sub>8</sub> as an example, the typical synthetic process is as follows. The HACS-Cl (2000.0 mg, 5.02 mmol of repeat units) was first added to water (35.0 mL) to form an aqueous solution and sodium 1-octanesulfonate (2215.7 mg, 10.04 mmol) was separately dissolved in water (5.0 mL) at the same time. Then, the sodium 1-octanesulfonate solution was added to the HACS-Cl solution drop-by-drop under stirring, and white precipitates were observed to form immediately. Afterward, the collected white precipitates HACS-C<sub>8</sub> were rinsed three times with water to

remove excessive salts. The attained HACS-C<sub>8</sub> was dried in a vacuum oven at 70 °C and then ground into powders by using a pulverizer. Powder samples of HACS-C<sub>8</sub> (1000.0 mg) were weighed and added to water (1.86 mL) and allowed to stand for 12 h at 25 °C and RH of 45% ± 5%. Then, the HACS-C<sub>8</sub> (35 wt%) mixture was further hot-pressed at 60 °C and 15 MPa for 30 min using a flat-plate hot-pressing machine to obtain the supramolecular polyelectrolyte plastic.

### **Fabrication of the supramolecular polyelectrolyte plastic HACS-SP**

The HACS-Cl (2000.0 mg, 5.02 mmol of repeat units) was first added to water (35.0 mL) to form an aqueous solution and SP (1577.4 mg, 10.04 mmol) was separately dissolved in water (5.0 mL) at the same time. Then, the SP solution was added to the HACS-Cl solution drop-by-drop under stirring, the mixed solution was stirred for 30 min. Afterward, the pH of the mixed solution was adjusted to ~ 7 with a further stirring of the mixed solution for another 30 min. Then, the mixed solution was added to water (200.0 mL) drop-by-drop under stirring, and white precipitates were observed to form immediately. Then, the collected white precipitates HACS-SP were rinsed three times with water to remove excessive salts. The attained HACS-SP was dried in a vacuum oven at 70 °C, and then ground into powders by using a pulverizer. Powder samples of HACS-SP (1000.0 mg) were weighed and added to water (1.86 mL) and allowed to stand for 12 h at 25 °C and RH of 45% ± 5%. Afterward, the HACS-SP (35 wt%) mixture was further hot-pressed at 60 °C and 15 MPa for 30 min using a flat-plate hot-pressing machine to obtain the supramolecular polyelectrolyte plastic.

### **Fabrication of the supramolecular polyelectrolyte plastic HACS-SP-C<sub>8</sub>**

Taking HACS-SP-C<sub>8</sub> at pH ~ 7 as an example, the typical synthetic process is as follows. The HACS-Cl (2000.0 mg, 5.02 mmol of repeat units) was first added to water (35.0 mL) to form an aqueous solution and SP (772.9 mg, 5.02 mmol)

was separately dissolved in water (5.0 mL) at the same time. Then, the SP solution was added to the HACS-Cl solution drop-by-drop under stirring, and the mixed solution was stirred for 30 min. The mixed solution was added to water (200.0 mL) drop-by-drop under stirring, and white precipitates were observed to form immediately. Afterward, the collected white precipitates HACS-SP were rinsed three times with water to remove excessive salts. The white precipitates HACS-SP were put into a beaker (250.0 mL) with water (200.0 mL). Then, sodium 1-octanesulfonate (1107.9 mg, 5.02 mmol) was added into the beaker and stirred for 2 h. The white precipitates HACS-SP-C<sub>8</sub> were rinsed three times with water to remove excessive salts. The attained HACS-SP-C<sub>8</sub> was dried in a vacuum oven at 70 °C, and then ground into powders by using a pulverizer. Powder samples of HACS-SP-C<sub>8</sub> (1000.0 mg) were weighed and mixed with water (1.86 mL). The mixture was allowed to stand for 12 h at 25 °C and relative humidity of 45% ± 5%. Afterward, the HACS-SP-C<sub>8</sub> (35 wt%) mixture was further hot-pressed at 15 MPa under 60 °C for 30 min using a flat-plate hot-pressing machine to obtain the supramolecular polyelectrolyte plastic.

### **Dissociation kinetics of HACS-SP-C<sub>8</sub>**

HACS-SP-C<sub>8</sub> (80.0 mg) was placed in NaCl solution (0.45 M, 2.0 mL). An aliquot (200 μL) was taken from the solution at a predesigned time. Meanwhile, NaCl solution (0.45 M, 200 μL) was added to the solution to keep the total volume unchanged. First, NaCl solution (0.45 M, 200 μL) was dried and weighed as a blank control. Samples were then taken and dried at certain intervals, and the mass change was recorded.

## Supplementary Tables

**Table S1.** Exchange ratio of Cl<sup>-</sup> in HACS-Cl with sulfonates determined by XPS analyses.

	HACS-Cl	HACS-C <sub>1</sub>	HACS-C <sub>4</sub>	HACS-C <sub>8</sub>	HACS-C <sub>12</sub>
Cl <sup>-</sup>	0%	75%	80%	87%	100%

**Table S2.** Exchange ratio of Cl<sup>-</sup> of HACS-SP and HACS-SP-C<sub>x</sub>s determined by XPS analyses.

	HACS-Cl	HACS-SP	HACS-SP-C <sub>4</sub>	HACS-SP-C <sub>8</sub>	HACS-SP-C <sub>12</sub>
Cl <sup>-</sup>	0%	66%	98%	98%	93%

**Table S3.** Artificial seawater composition.<sup>S1</sup>

Salt	NaCl	MgCl <sub>2</sub>	MgSO <sub>4</sub>	CaCl <sub>2</sub>	KCl	NaHCO <sub>3</sub>	NaBr	Total
g kg <sup>-1</sup>	26.518	2.447	3.305	1.141	0.725	0.202	0.083	34.421

**Table S4.** Dissociation mole ratio of HACS-SP-C<sub>8</sub> in artificial seawater and seawater.

		White precipitate	HACS-SP-C <sub>8</sub>	Dissociation mole ratio
Artificial seawater	N:P	0.2:1.0	9.9:1.0	98%
Seawater	N:P	0.9:1.0	9.9:1.0	91%

Supplementary Figures

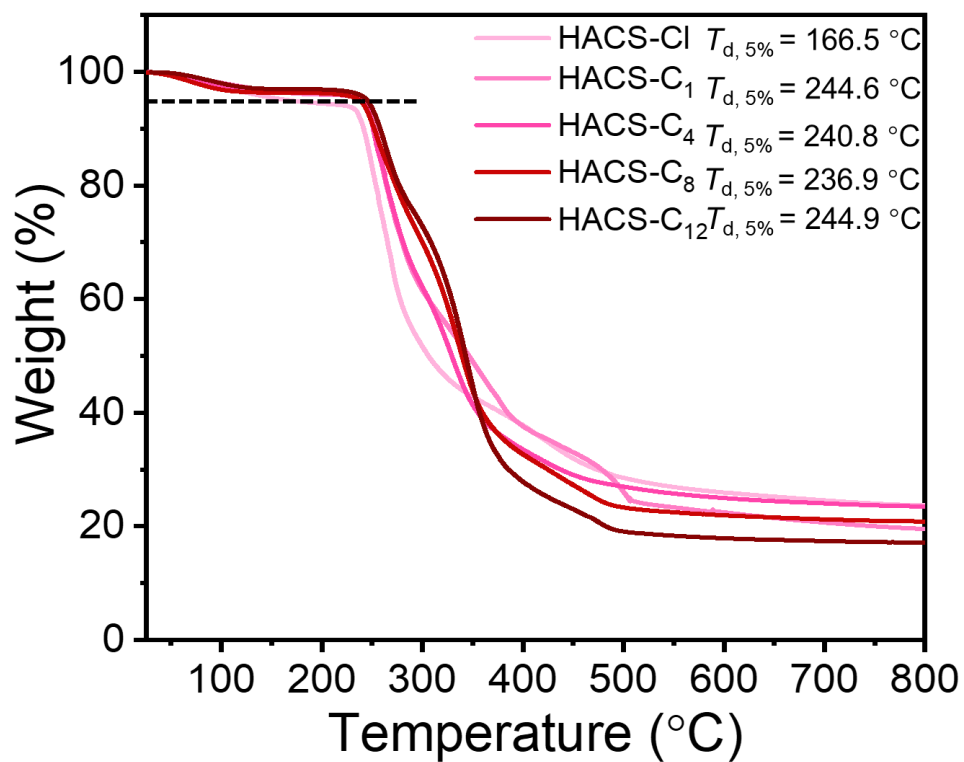
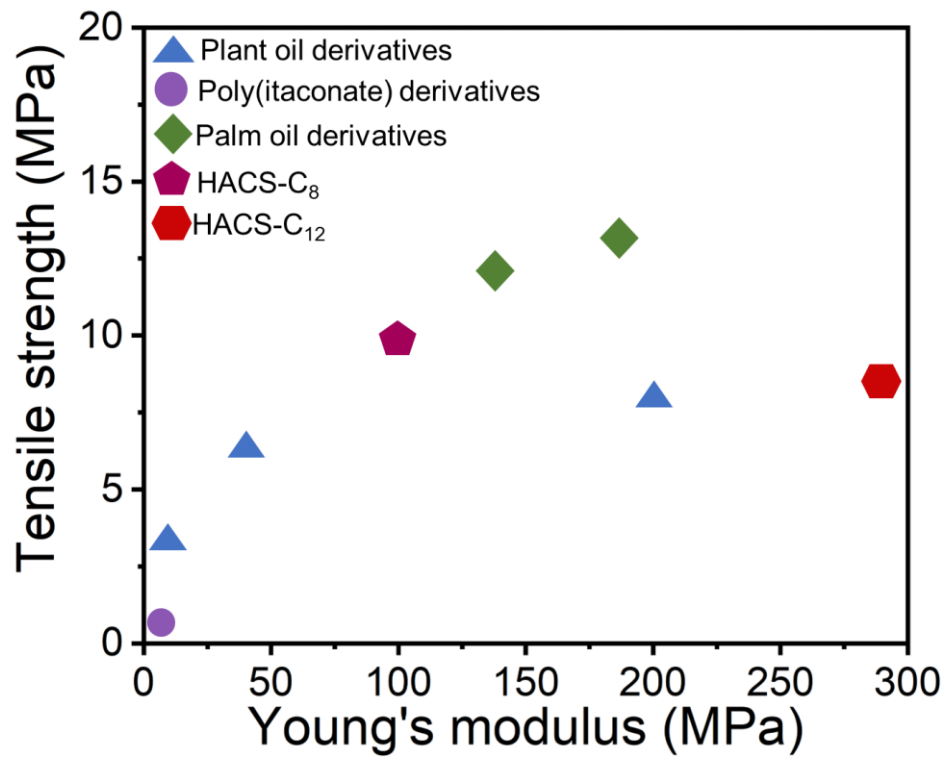


Figure S1. TGA curves of HACS-Cl and HACS-C<sub>x</sub>s.

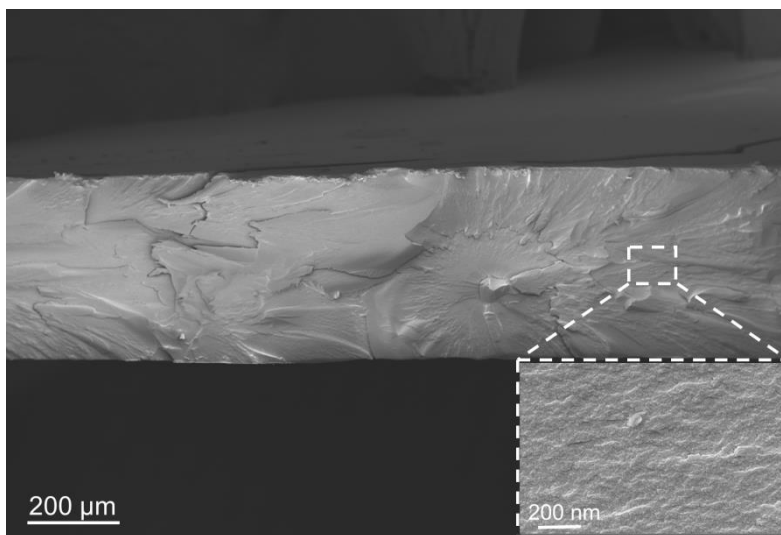




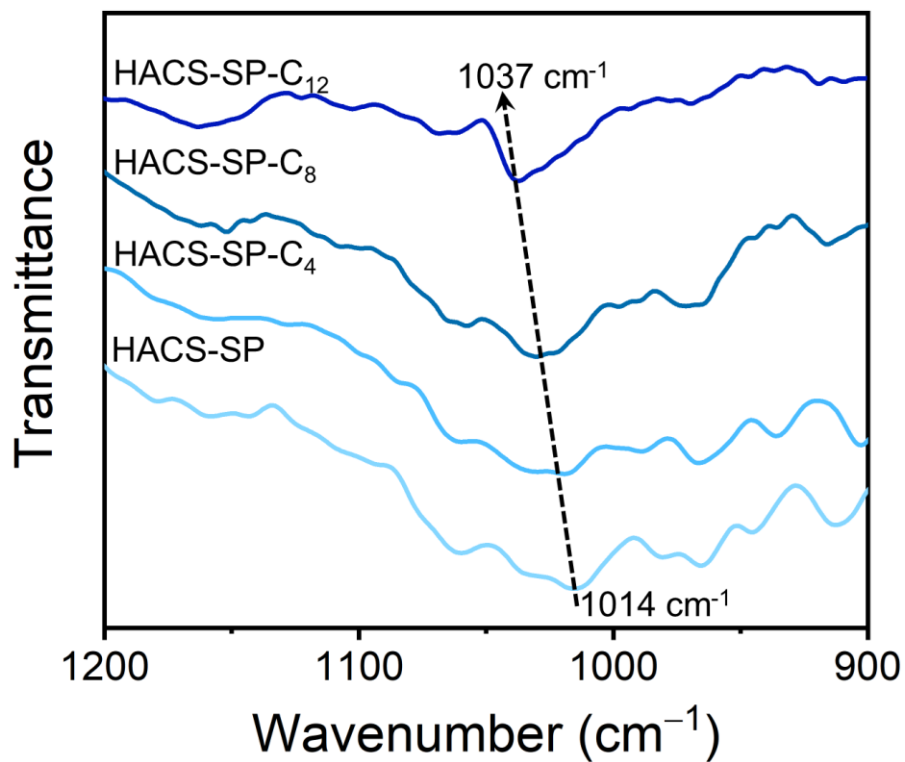
**Figure S2.** Comparison of the mechanical properties of HACS-C<sub>8</sub> and HACS-C<sub>12</sub> with common bio-based plastics from plant oils,<sup>S2, S3</sup> palm oil derivatives,<sup>S4</sup> or itaconic acids.<sup>S5</sup>



**Figure S3.** Photos of HACS-SP at pH ~ 2, pH ~ 7, and pH ~ 12.

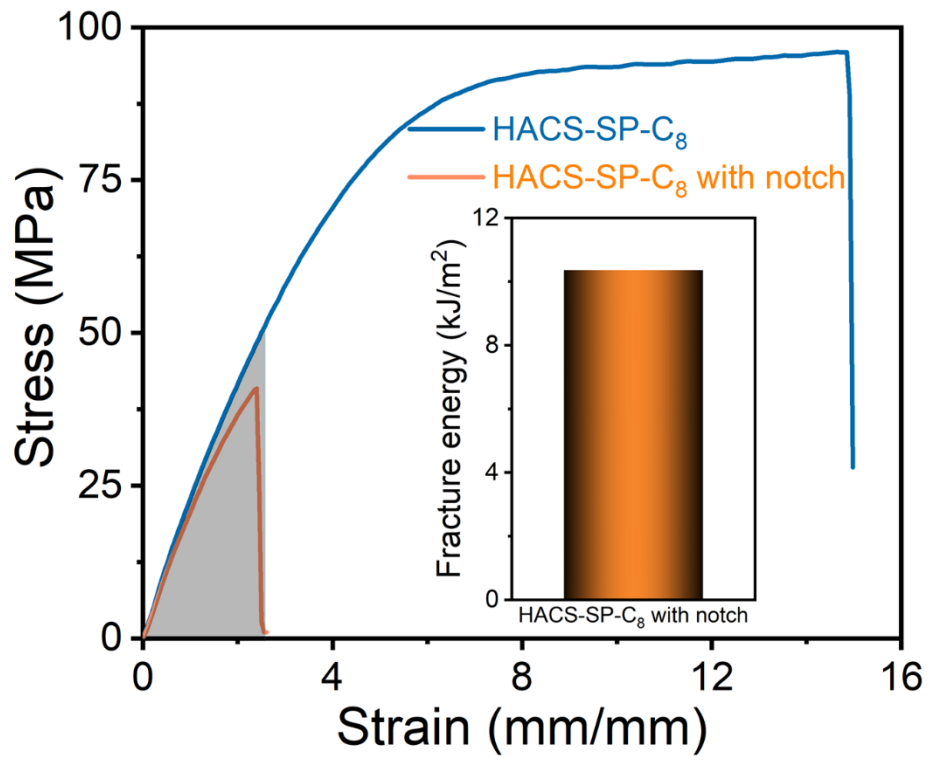


**Figure S4.** SEM images of the fracture cross-section of polyelectrolyte plastics. The inset shows the fracture cross-section at large magnifications.

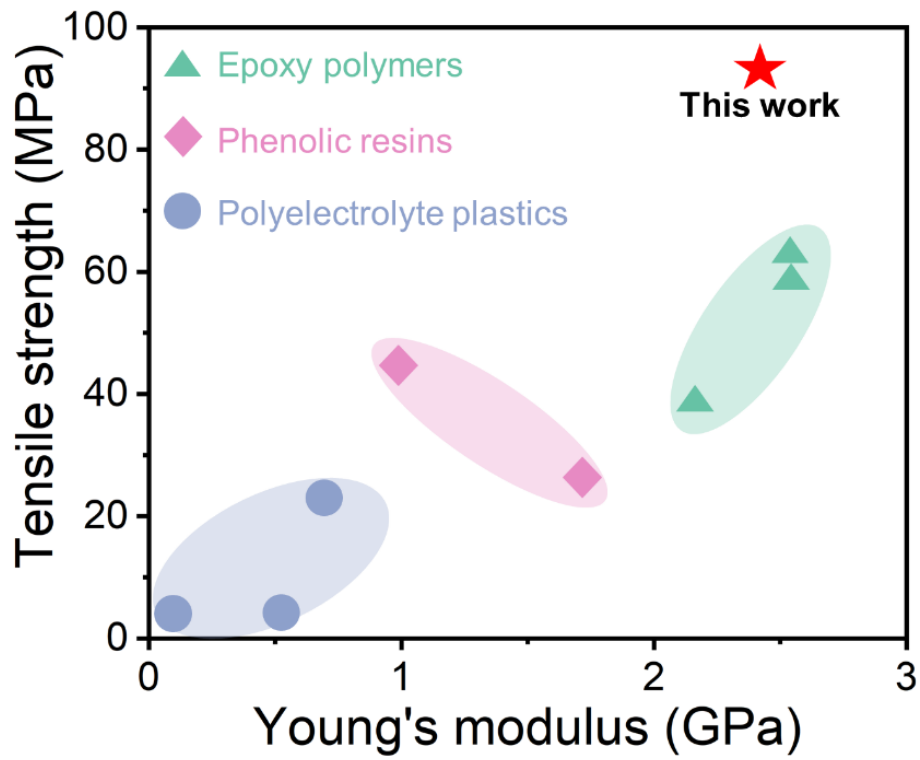


**Figure S5.** ATR-FTIR spectra of HACS-SP-C<sub>x</sub>s.

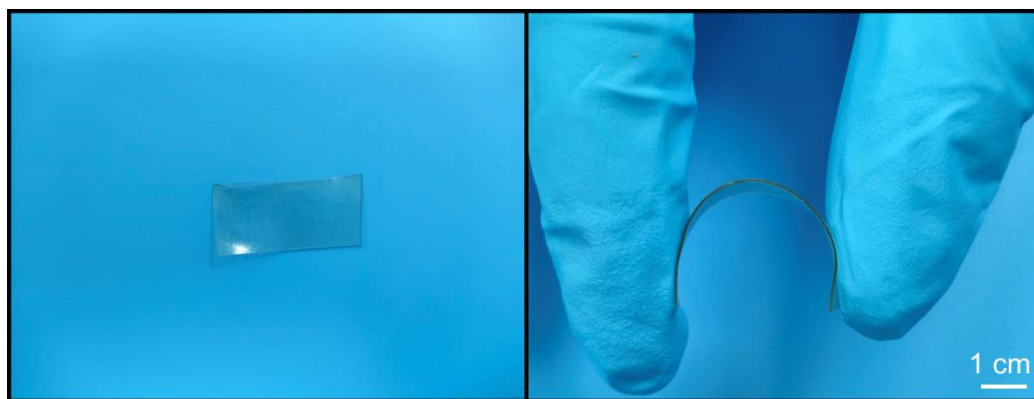
The band around 1014 cm<sup>-1</sup> corresponds to the stretching vibration of C–O bond in the C–OH groups. This band shifts to a higher wavenumber accompanying the exchange with sulfonate counterions with a longer hydrophobic chain, indicating a stronger disruption of the hydrogen bonds.<sup>56</sup>



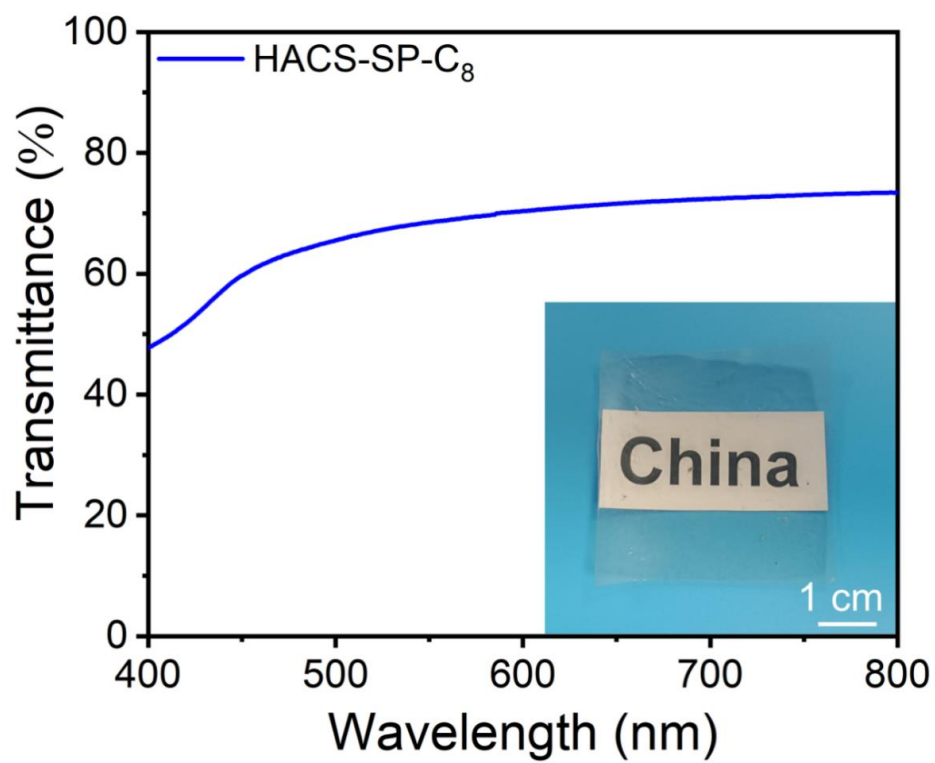
**Figure S6.** Representative stress-strain curves of HACSP-C<sub>8</sub> with or without notch with the inset showing the calculated fracture energy.



**Figure S7.** Comparison of mechanical properties of the supramolecular polyelectrolyte plastic HACS-SP-C<sub>8</sub> with epoxy,<sup>S7-S10</sup> phenolic resin,<sup>S11, S12</sup> and polyelectrolyte plastics.<sup>S13-S15</sup>

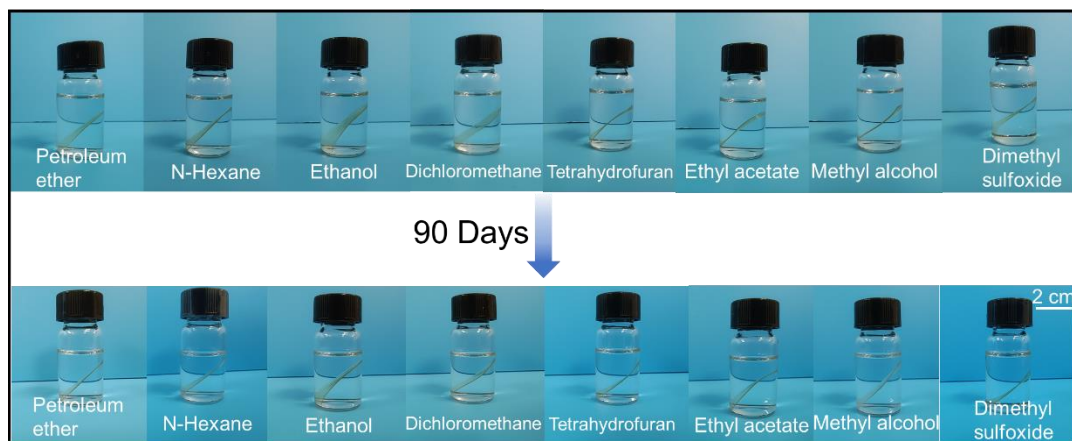


**Figure S8.** Photos showing the good flexibility of HACS-SP-C<sub>8</sub>.

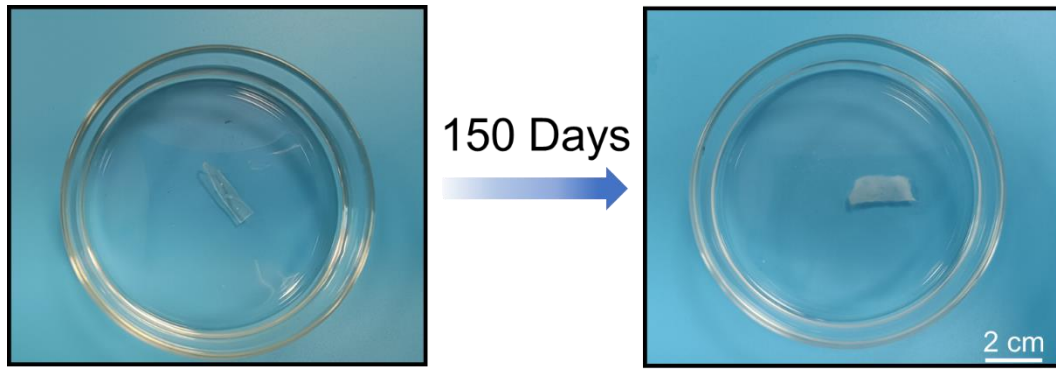


**Figure S9.** UV-Vis spectrum of HACS-SP-C<sub>8</sub>. The inset shows the transparency of the HACS-SP-C<sub>8</sub> film.

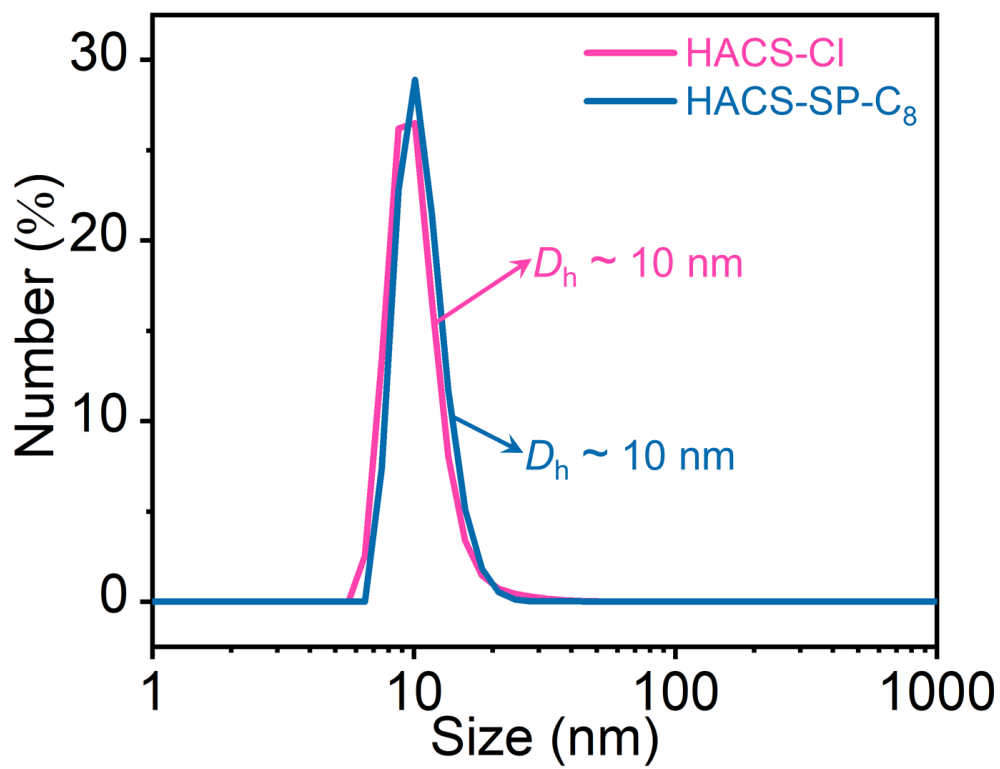




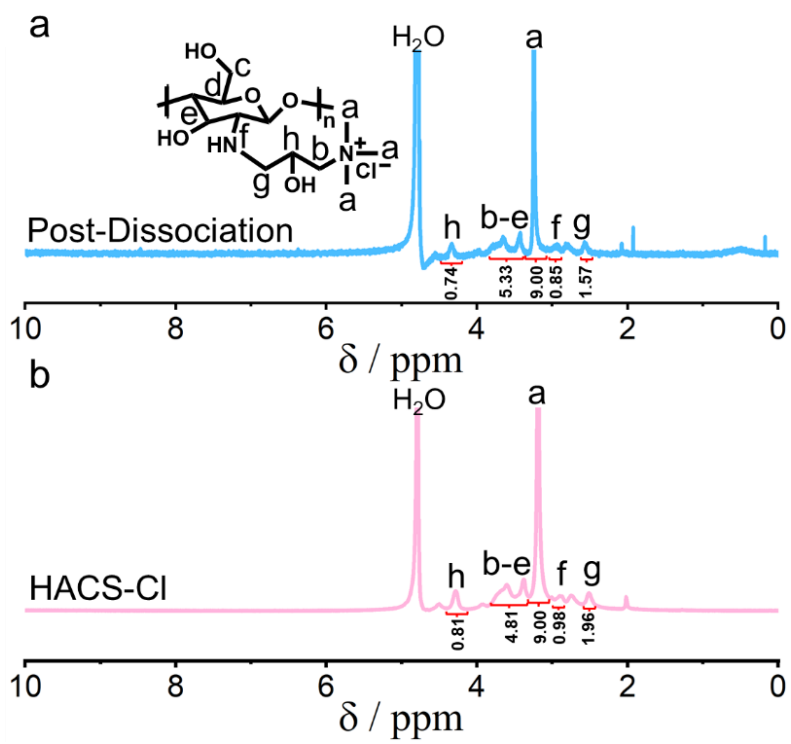
**Figure S10.** The chemical stability of HACSP-C<sub>8</sub> films in different organic solvents after 90 days at room temperature.



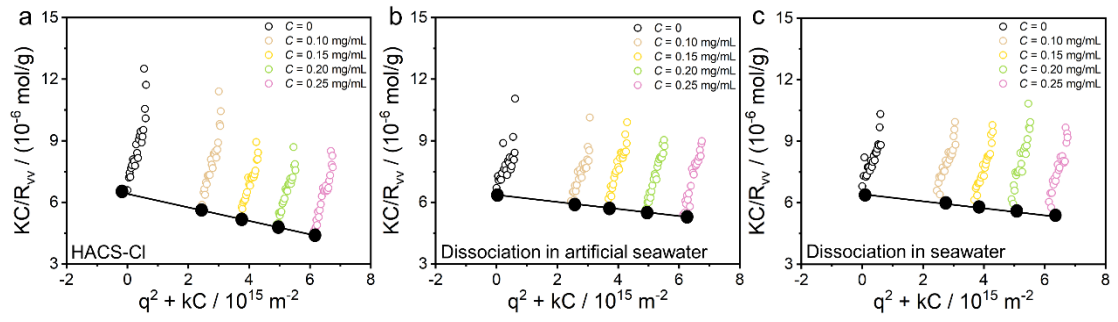
**Figure S11.** The stability of the HACs-SP-C<sub>8</sub> film in water after 150 days at room temperature.



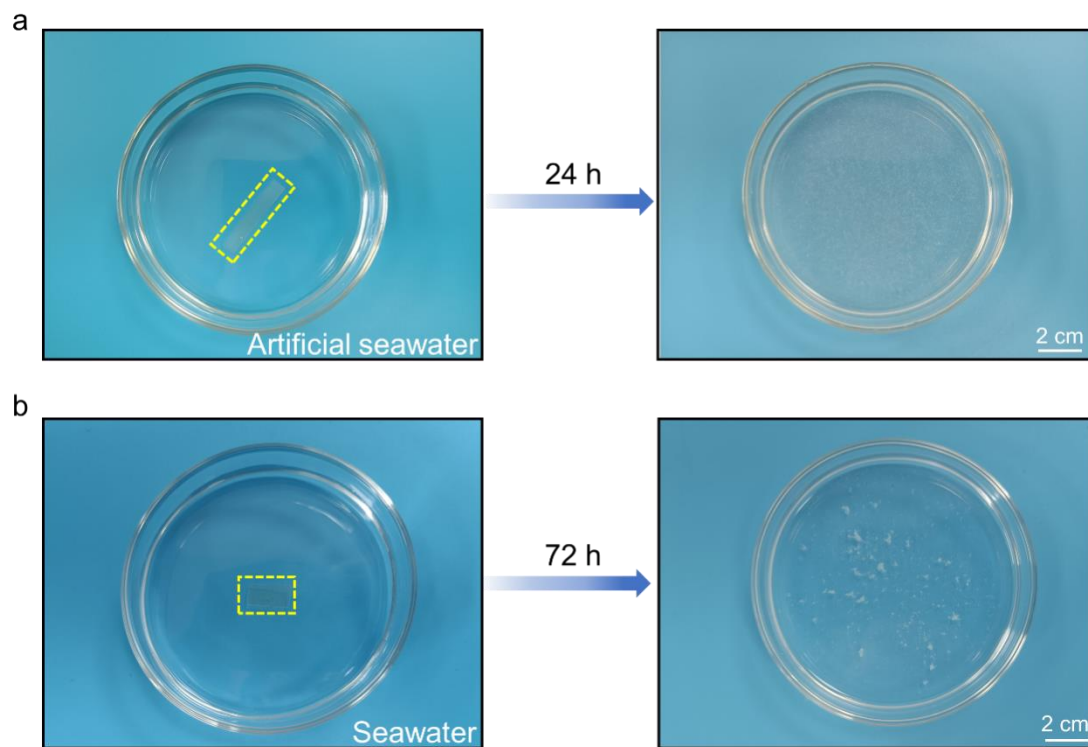
**Figure S12.** DLS analyses of HACS-Cl and the dissociated HACS-SP-C<sub>8</sub> film in artificial seawater, where the latter is measured after the dissociation of the HACS-SP-C<sub>8</sub> in the artificial seawater for 24 h.



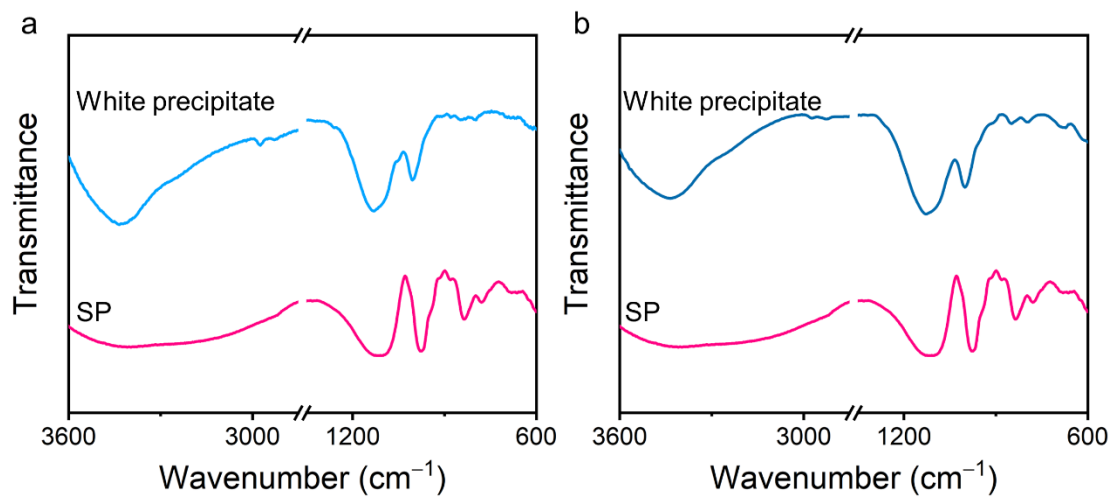
**Figure S13.**  $^1\text{H}$  NMR spectra of (a) HACS-Cl and (b) HACS-SP-C<sub>8</sub> after dissociation in seawater.



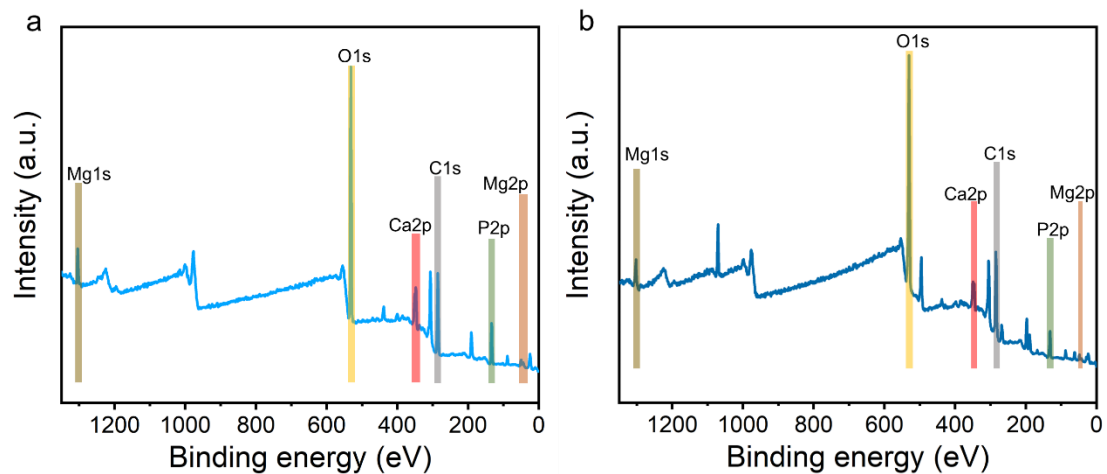
**Figure S14.** (a) Zimm plots of HACS-Cl. Zimm plots of (b) and (c) HACS-SP-C<sub>8</sub> after dissociation in artificial seawater and seawater.



**Figure S15.** (a) Photos showing the dissociation of the HACS-SP-C<sub>8</sub> film in artificial seawater. (b) Photos showing the dissociation of the HACS-SP-C<sub>8</sub> film in seawater.



**Figure S16.** (a) FT-IR spectra of SP and white precipitates found in the dissociated solution of the HACS-SP-C<sub>8</sub> film in artificial seawater. (b) FT-IR spectra of SP and white precipitates found in the dissociated solution of the HACS-SP-C<sub>8</sub> film in seawater. Here, the band around 1123 cm<sup>-1</sup> corresponds to the stretching vibration of P=O group in SP.



**Figure S17.** (a) XPS survey of white precipitates found in the dissociated solution of the HACS-SP-C<sub>8</sub> film in artificial seawater. (b) XPS survey of white precipitates found in the dissociated solution of the HACS-SP-C<sub>8</sub> film in seawater.



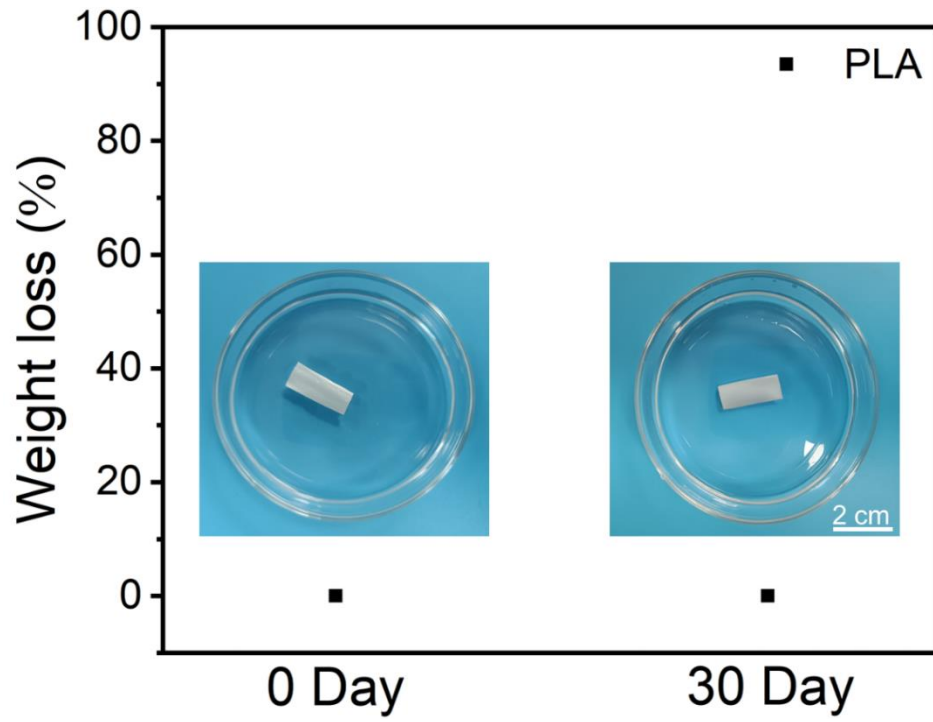
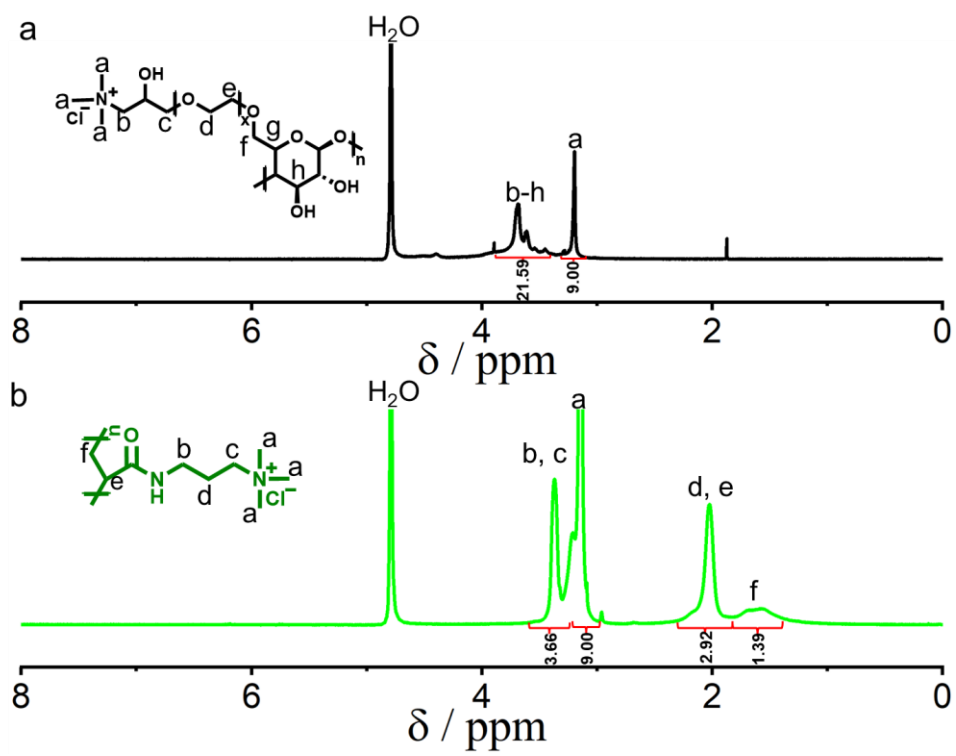


Figure S18. Photos and weight loss of PLA before and after 30 days in seawater.



**Figure S19.** Assigned  $^1\text{H}$  NMR spectra of (a) CHTM-Cl and (b) PTMPA-Cl in  $\text{D}_2\text{O}$ .

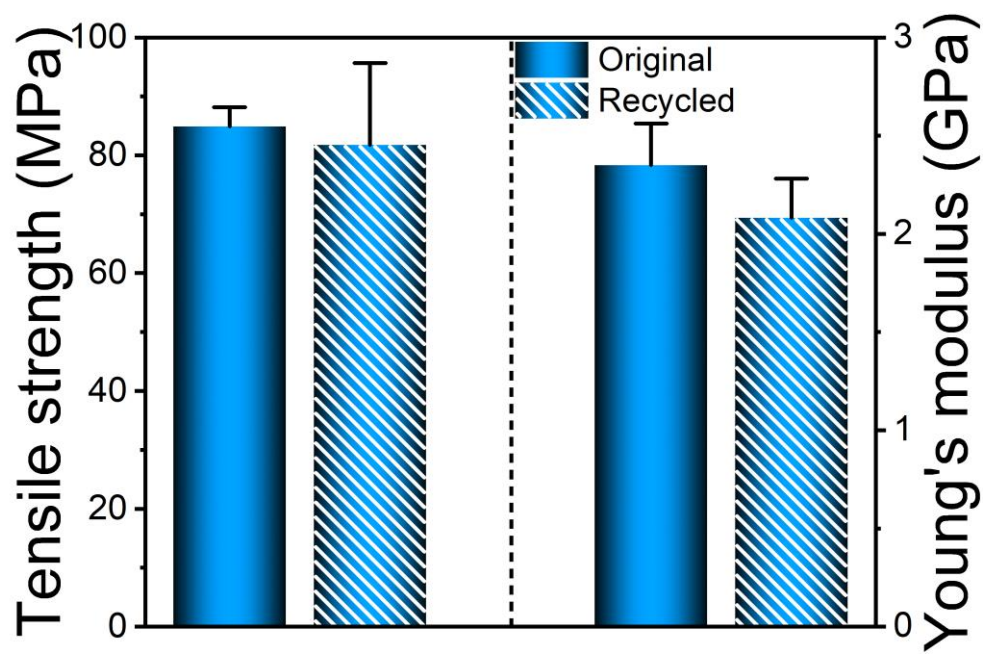
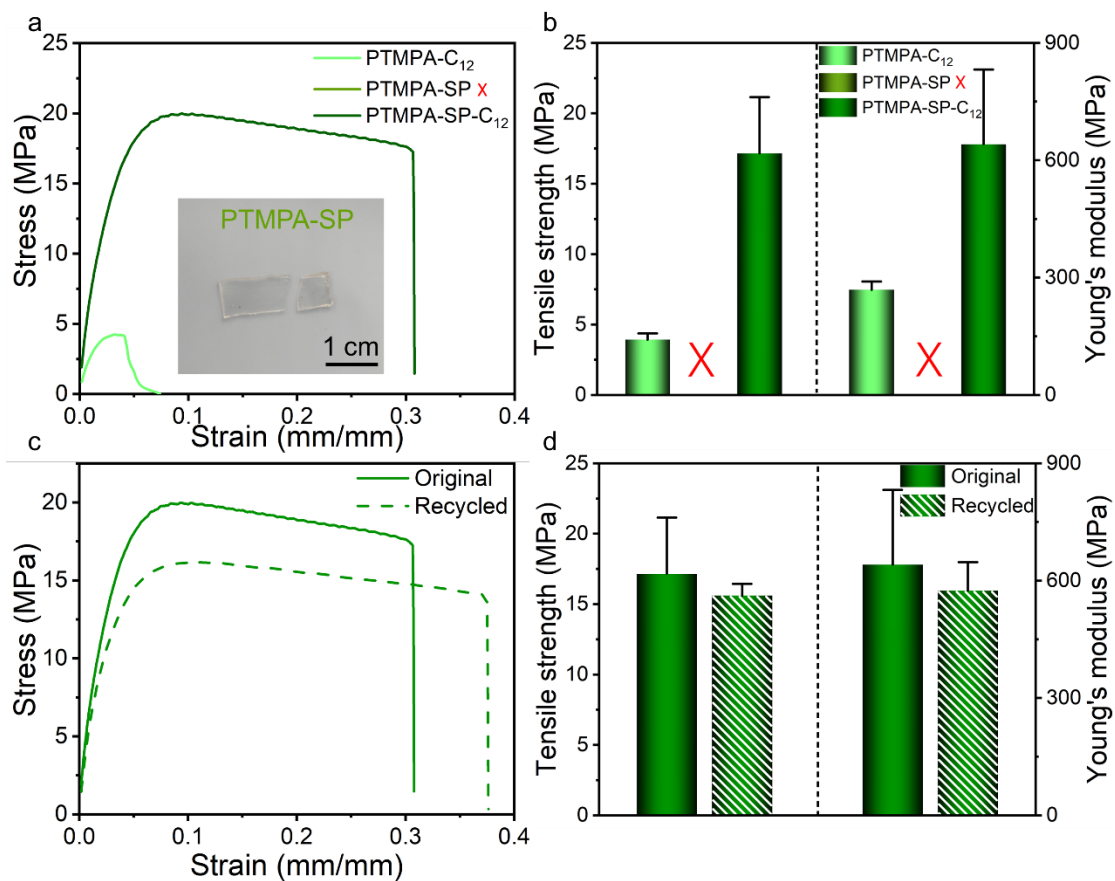
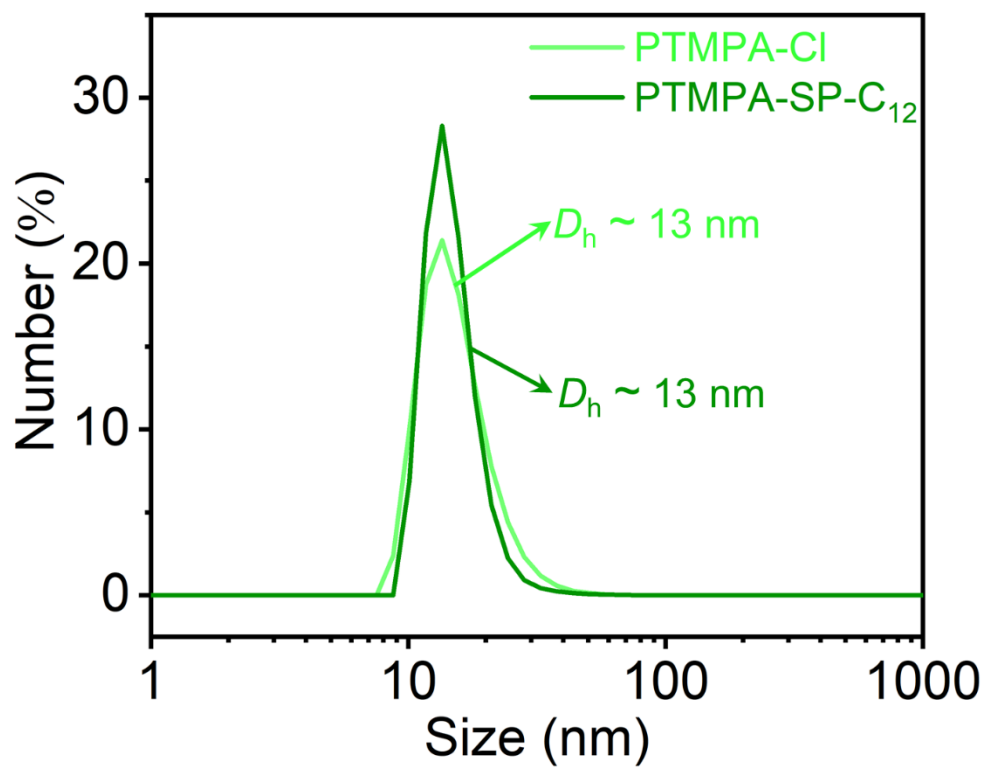


Figure S20. Tensile strengths and Young's moduli for CHTM-SP-C<sub>12</sub> before and after recycling.



**Figure S21.** (a) Representative stress-strain curves with the inset showing the broken PTMPA-SP film and (b) tensile strengths and Young's moduli for PTMPA-C<sub>12</sub>, PTMPA-SP, and PTMPA-SP-C<sub>12</sub>. The red cross means that PTMPA-SP is too brittle to be tested mechanically. (c) Representative stress-strain curves and (d) tensile strengths and Young's moduli for PTMPA-SP-C<sub>12</sub> before and after recycling.



**Figure S22.** The  $D_h$  and size distribution of PTMPA-Cl and PTMPA-SP-C<sub>12</sub> in 0.45 M NaCl solution, where the latter is measured after the dissociation of the PTMPA-SP-C<sub>12</sub> in the NaCl solution for 24 h.

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