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Title	Facile Tuning of Hydrogel Properties by Manipulating Cationic-Aromatic Monomer Sequences
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Citation	SCIENCE CHINA Chemistry, 64(9), 1560-1568 https://doi.org/10.1007/s11426-021-1010-3
Issue Date	2021-08-12
Doc URL	https://hdl.handle.net/2115/86544
Rights	The original publication is available at www.scichina.com and www.springerlink.com
Type	journal article
File Information	Supporting information.pdf,

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Facile Tuning of Hydrogel Properties by Manipulating Cationic-Aromatic Monomer Sequences

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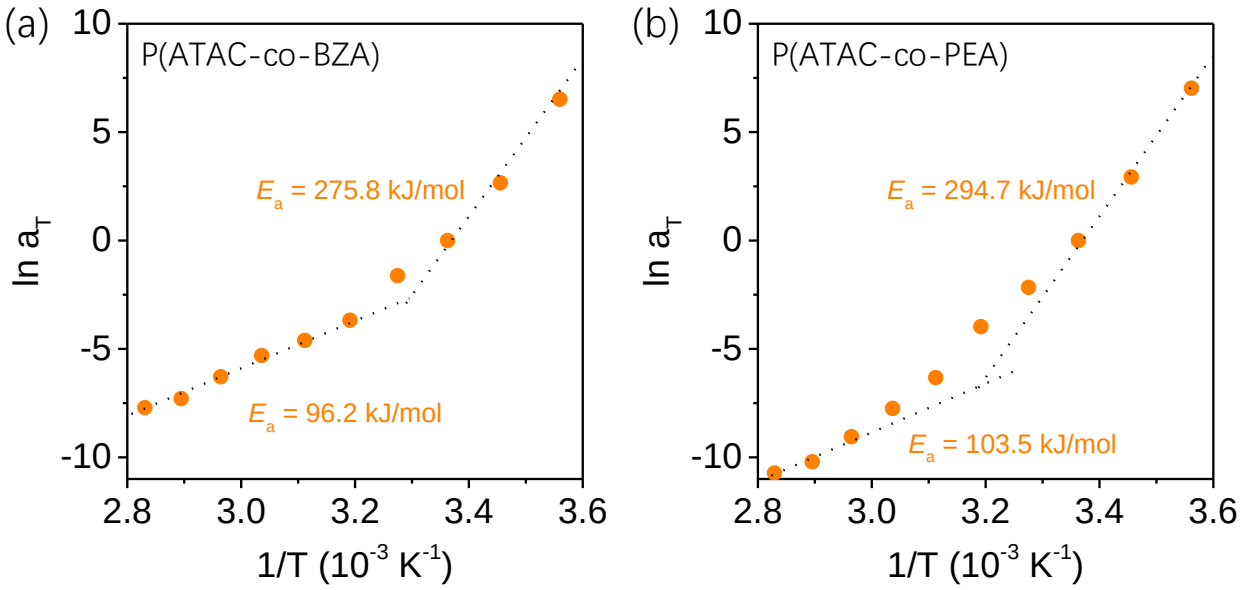

Figure S1. Arrhenius plot depicting the temperature dependence of the shift factors a_T for P(cation-adj-π) and P(cation-co-π) hydrogels in water. The apparent activation energy values were calculated from the slope of the curve.

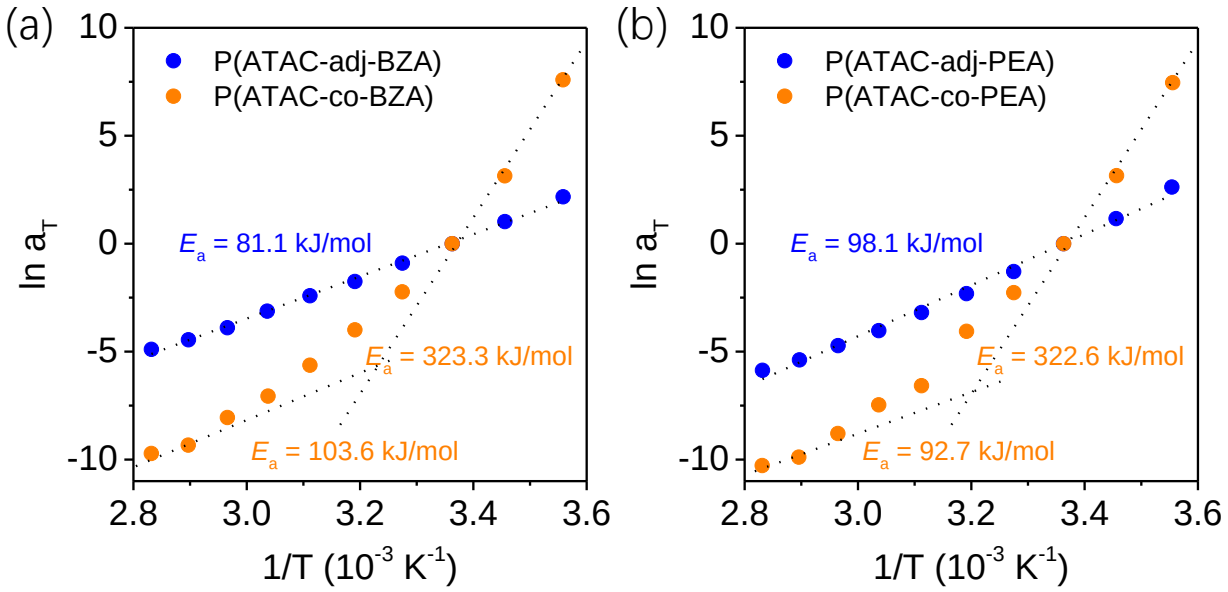

Figure S2. Arrhenius plot depicting the temperature dependence of the shift factors a_T for P(cation-adj-π) and P(cation-co-π) hydrogels in 0.7 M NaCl solution. The apparent activation energy values were calculated from the slope of the curve.

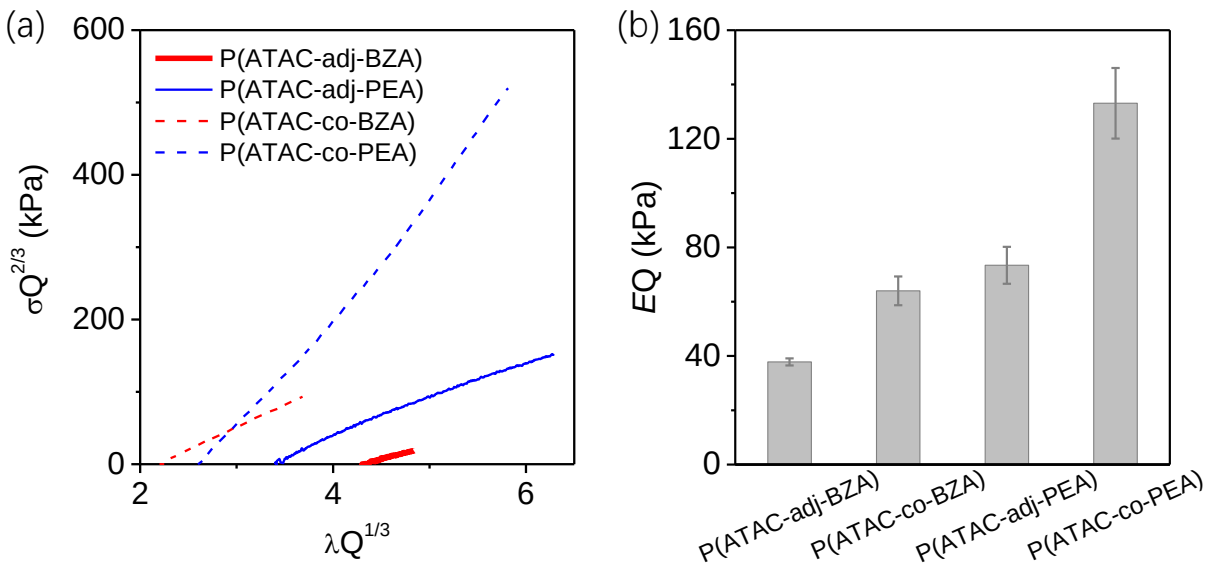

Figure S3. (a) Normalized tensile stress-strain curves of P(cation-adj-π) and P(cation-co-π) hydrogels in water. σ is the stress of hydrogels. λ is the extension ratio, which is related to the strain ε as λ = ε +1. Q is the volume swelling ratio of hydrogels relative to their as-prepared state. (b) Normalized Young's modulus of hydrogels in water.

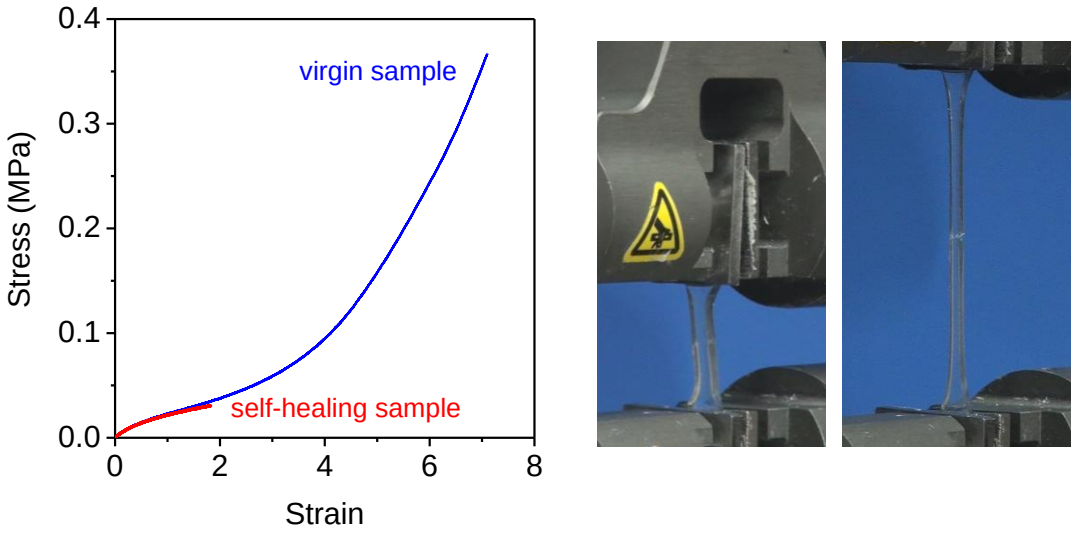

Figure S4. Tensile stress-strain curves of original and self-healed P(ATAC-adj-PEA) hydrogels and digital photos of self-healed P(ATAC-adj-PEA) hydrogels before and after stretch.

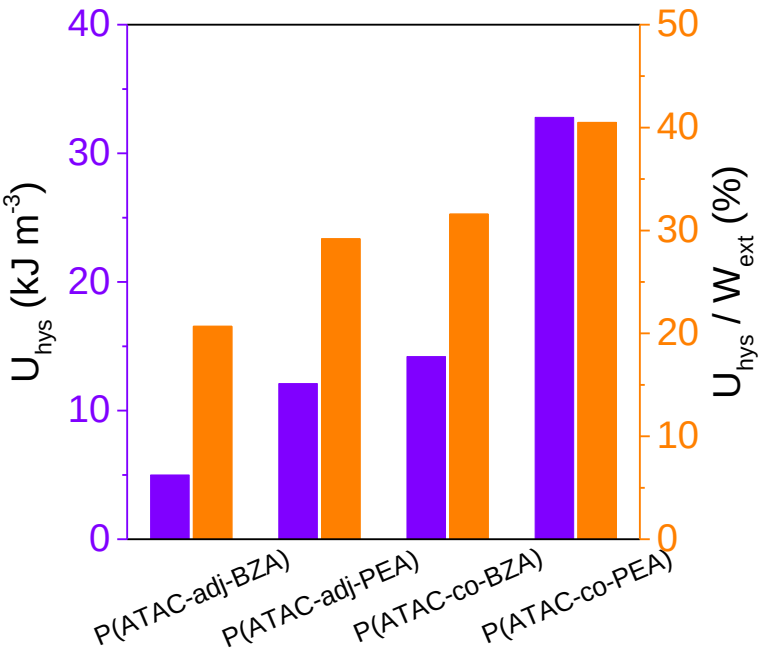

Figure S5. The energy dissipation U_{hys} and fraction of energy dissipation in relative to the total work applied (U_{hys} / W_{ext}) for P(cation-adj-π) and P(cation-co-π) hydrogels at a maximum strain of 200%. W_{ext} is estimated from the area under the loading curve of the virgin sample, and U_{hys} is from the hysteresis area of the virgin sample in Figure 8.

Table S1. The energy dissipation U_{hys} of P(cation-adj-π) and P(cation-co-π) hydrogels at a maximum strain of 200% under different recovery times. U_{hys} is the hysteresis area in Figure 8.

	P(ATAC-co-BZA) (kJ m^{-3})	P(ATAC-adj-BZA) (kJ m^{-3})	P(ATAC-co-PEA) (kJ m^{-3})	P(ATAC-adj-PEA) (kJ m^{-3})
Original	14.2	5.0	32.8	12.1
30 s	-	4.7	-	10.6
1 min	9.6	4.7	-	10.9
2 min	-	-	26.9	-
3 min	12.5	-	31.9	-

Instantaneous number-average sequence length of monomers $\langle N_M \rangle$ in polymer chains at different conversion point

Based on the free radical polymerization theory,[1] during the chain growth reaction, the probability of adding an M_1 monomer unit to an M_1 end chain, denoted as p_{11}, at any conversion point p, can be expressed as:

$$p_{11}(p) = \frac{r_1 f_1(p)}{r_1 f_1(p) + f_2(p)} \tag{S1}$$

Where conversion point p is the total conversion of monomers, r_1 is monomer reactivity ratio for the addition of monomer M_1 and M_2 to the M_1 end chain. $f_1(p)$ and $f_2(p)$ are the molar fraction of monomers M_1 and M_2 at conversion p, respectively. Similarly, the probability of adding an M_2 monomer unit to an M_2 end chain, denoted as p_{22}, can be expressed,

$$p_{22}(p) = \frac{r_2 f_2(p)}{r_2 f_2(p) + f_1(p)} \tag{S2}$$

Where r_2 is monomer reactivity ratio for the addition of monomers M_2 and M_1 to the M_2 end chain. The probabilities $(p_{M_1})_x$ and $(p_{M_2})_x$ of forming M_1 and M_2 sequences of length x are given by

$$(p_{M_1})_x = p_{11}^{x-1}(1 - p_{11}) \tag{S3}$$

$$(p_{M_2})_x = p_{22}^{x-1}(1 - p_{22}) \tag{S4}$$

The value of $(p_{M_1})_x$ and $(p_{M_2})_x$ at each point p is hence the instantaneous sequence length distribution. The instantaneous number-average sequence lengths of monomers M_1 and M_2 at conversion p, $\langle N_{M1} \rangle$ and $\langle N_{M2} \rangle$, respectively, are:

$$\langle N_{M_1} \rangle(p) = \frac{1}{1 - p_{11}(p)} \tag{S5}$$

$$\langle N_{M_2} \rangle(p) = \frac{1}{1 - p_{22}(p)} \tag{S6}$$

Therefore, the fraction of the number of M_1 in xM_1 segment to the total number of M_1 is

$$\phi_{M_1}(x) = \frac{x(p_{M_1})_x}{\sum x(p_{M_1})_x} = x p_{11}^{x-1}(1-p_{11})^2 \quad \text{(S7)}$$

Similarly, the fraction of the number of M_2 in xM_2 segment to the total number of M_2 is

$$\phi_{M_2}(x) = \frac{x(p_{M_2})_x}{\sum x(p_{M_2})_x} = x p_{22}^{x-1}(1-p_{22})^2 \quad \text{(S8)}$$

Calculation of percentage of monomer in adjacent location

Here we derived the equation for the percentage of monomer in adjacent sequence. For a segment with one M_1 sequence length (x = 1), all M_1 are adjacent to M_2, namely the percentage of M_1 in adjacent to M_2 is

$$({p_{M_1}}^{adj})_1 = 100\% \quad \text{(S9)}$$

When sequence length of M_1 is larger than 1 (x = 2, 3...), the percentage that M_1 is adjacent to M_2 for x sequence length is

$$({p_{M_1}}^{adj})_x = \frac{2}{x} \times 100\% \quad \text{(S10)}$$

Then the total percentage that M_1 is adjacent to M_2 in total number of M_1 is

$${P_{M_1}}^{adj} = \phi_{M_1}(x=1) \times ({p_{M_1}}^{adj})_1 + \sum_{x=2}^{n} [\phi_{M_1}(x) \times ({p_{M_1}}^{adj})_x] \quad \text{(S11)}$$

Similarly, the total percentage that M_2 is adjacent to M_1 in total number of M_2 is

$${P_{M_2}}^{adj} = \phi_{M_2}(x=1) \times ({p_{M_2}}^{adj})_1 + \sum_{x=2}^{n} [\phi_{M_2}(x) \times ({p_{M_2}}^{adj})_x] \quad \text{(S12)}$$

Based on the equation S11 and S12, the total percentage of M_1 and M_2 in adjacent location in polymer chains is

$$P_M{}^{adj} = \frac{[M_1]P_{M_1}{}^{adj} + [M_2]P_{M_2}{}^{adj}}{[M_1] + [M_2]} \quad \text{(S13)}$$

By using r_1, r_2 values in Table 1, and $f_1(p)$, $f_2(p)$ determined experimentally, we estimated conversion *p* dependence of $\langle N_{M1} \rangle$ and $\langle N_{M2} \rangle$ using Eqs. S5, S6 for equimolar ratio of ATAC-BZA pair and ATAC-PEA pair in different solvent, and the results are shown in Figure 2g and 2h. The percentage of adjacent sequence for equimolar ratio of ATAC-BZA pair and ATAC-PEA pair in DMSO were estimated from Equation S13 using r_1, r_2 values in Table 1.

References

1. Odian, G. Principles of Polymerization, 4th ed. *Wiley-Interscience: Hoboken, NJ* **2004**.