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Electronic Supplementary Information (ESI)

Macroscopic Assembling of Oppositely Charged Polyelectrolyte Hydrogels

Jinhui Li[a,b], Zuxiang Xu[a,b], Ying Xiao[b], Guorong Gao[b], Jing Chen[b], Jingbo Yin[a] and Jun Fu*[b]

[a]Department of Polymer Materials, School of Materials Science and Engineering, Shanghai University, Nanchen Road 333, Shanghai 200444.

[b]Cixi Institute of Biomedical Engineering & Polymers and Composites Division, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, 1219 Zhongguan West Road, Ningbo 315201.

*E-mail address: fujun@nimte.ac.cn

1. Synthesis of Pluronic F127 diacrylate (F127DA)

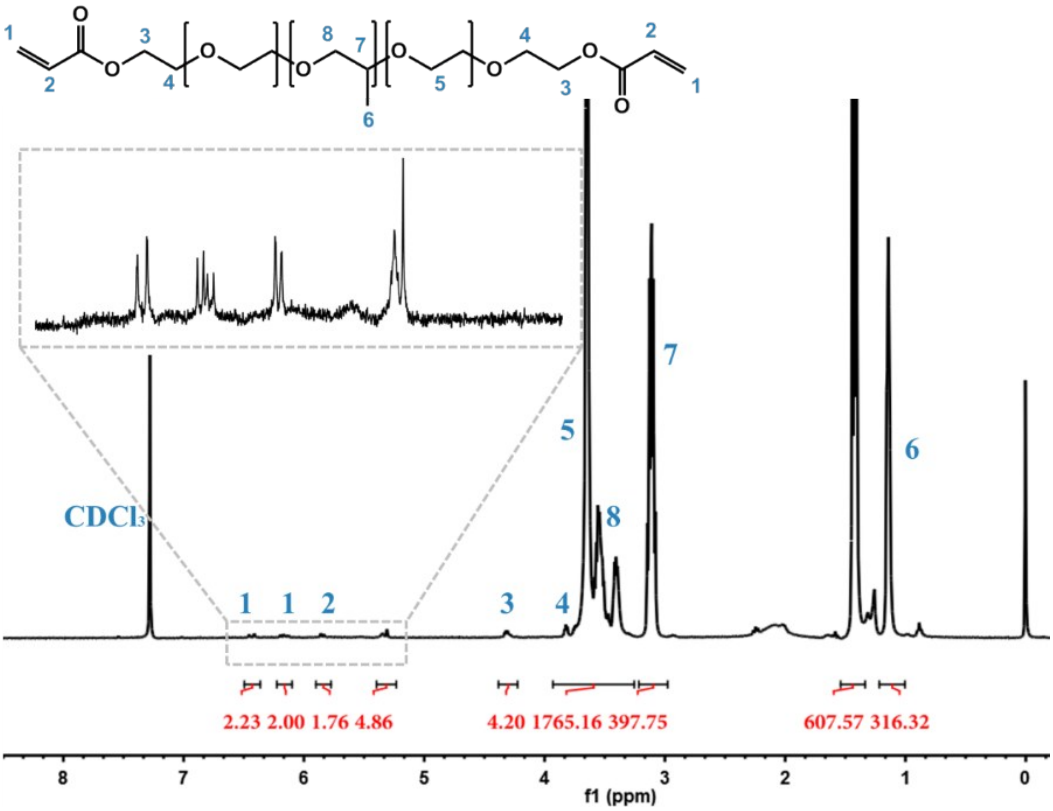

Fig. S1 ^{1}H NMR spectrum of the F127DA in $CDCl_3$ at 25 ^oC

2. Preparation of the polyelectrolyte hydrogels

Table S1 The formulations for the preparation of PAgel

	NaMAA (mg)	HEMA (g)	F127DA (mg)	H_2O (mL)	KPS (mg)	TEMED (μL)
$PAgel_{0.05}$	32 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10
$PAgel_{0.075}$	48 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10
$PAgel_{0.1}$	64 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10
$PAgel_{0.125}$	82 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10
$PAgel_{0.15}$	98 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10

Table S2 The formulations for the preparation of PCgel

	DMAEMA (mg)	HEMA (g)	F127DA (mg)	H_2O (mL)	KPS (mg)	TEMED (μL)
$PCgel_{0.1}$	47 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10
$PCgel_{0.2}$	94 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10
$PCgel_{0.3}$	141 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10
$PCgel_{0.4}$	188 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10
$PCgel_{0.5}$	235 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10
$PCgel_{0.6}$	282 ± 1	4.6 ± 0.01	50 ± 1	6	7 ± 1	10

3. Mechanical properties of $PAgel_{0.1}$ and $PCgel_{0.2}$ at different pH.

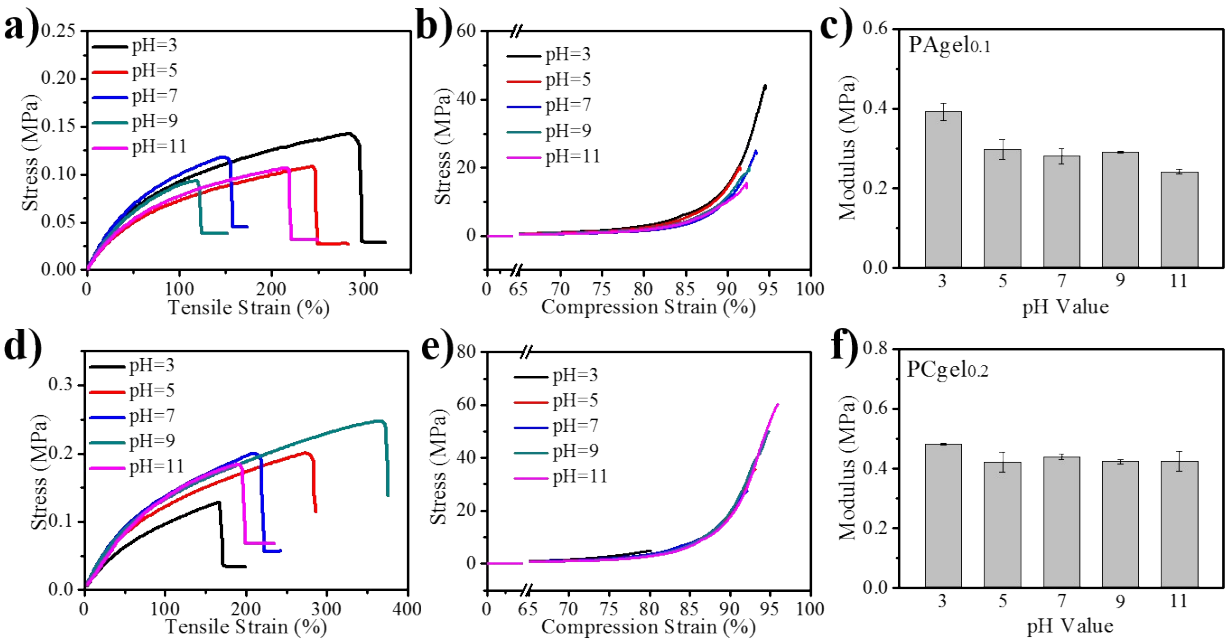

Fig. S2 (a)Typical tensile stress–strain curves, (b) typical compressive stress–strain curves and (c) modulus of $PAgel_{0.1}$ in different pH solutions. (d)Typical tensile stress–strain curves, (e) typical compressive stress–strain curves and (f) modulus of $PCgel_{0.2}$ in different pH solutions.

4. The effect of IS on the mechanical properties of hydrogels

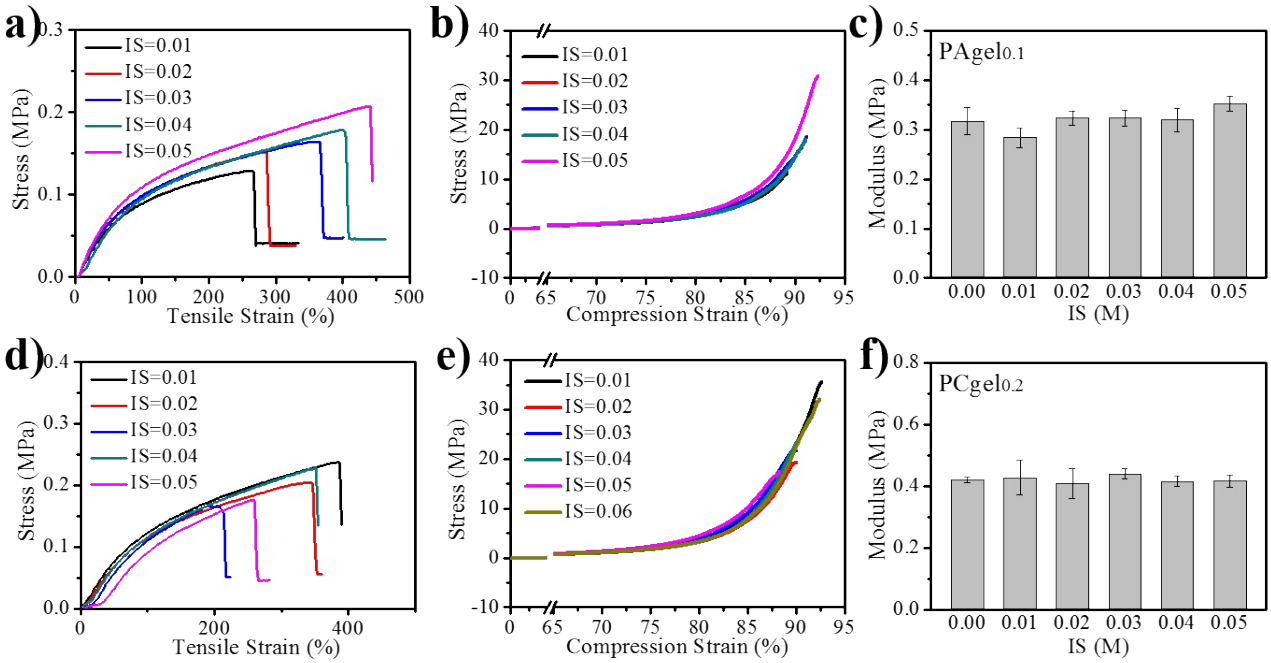

Fig. S3 (a) Typical tensile stress–strain curves, (b) typical compressive stress–strain curves and (c) modulus of $PAgel_{0.1}$ in different IS solutions. (d) Typical tensile stress–strain curves, (e) typical compressive stress–strain curves and (f) modulus of $PCgel_{0.2}$ at different IS.

Before the test, all the equilibrium swelling hydrogels were immersed in different IS solutions for 2 weeks. When IS was from 0 M to 0.05 M, the mechanical properties of hydrogels have little change (Fig. S3).

5. The C_w of the polyelectrolyte hydrogels

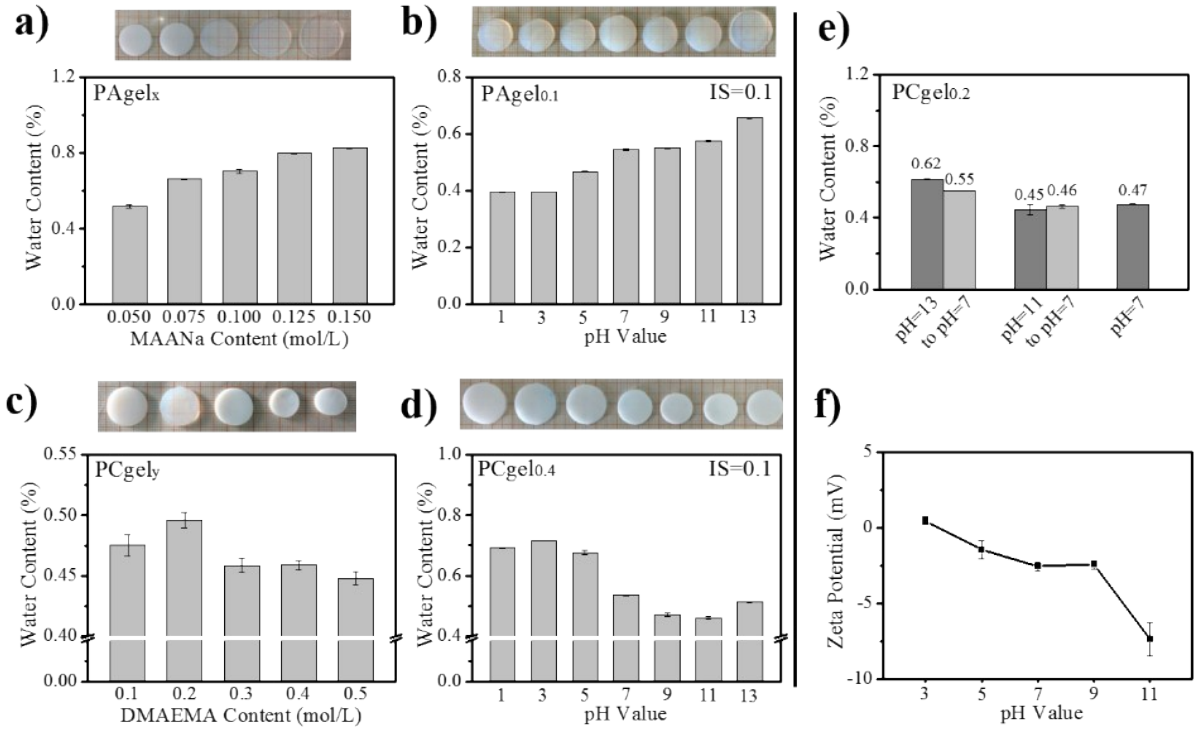

Fig. S4 The C_w of equilibrium swelling PAgel$_x$ with different (a) C_{MAA} and (b) pH. The C_w of equilibrium swelling PCgel$_y$ at different (c) C_D and (d) pH value. (e) The C_w of PCgel$_{0.2}$ were from pH=13 to pH=7, pH=11 to pH=7, and pH=7 solution. (f) Zeta potential of Pure HEMA hydrogel at different pH value. The ionic strength (IS) of all the solutions is 0.1 M.

The PAgel$_x$ gels appear opaque at low NaMAA content (C_M), while it becomes translucent and transparent with increasing C_M from 0.05 M to 0.15 M. The corresponding C_w of PAgel$_x$ was increased from 0.5 to 0.8. The appearance, volume and water content of the PAgel$_x$ gels are sensitive to pH. At pH 1 and 3, the C_w of PAgel$_{0.1}$ hydrogel is constant. With pH increasing from 3 to 7, the C_w of PAgel$_{0.1}$ was increased from 0.39 to 0.54. At pH 7 and 9, the C_w of PAgel$_{0.1}$ remained the same. Further increase of pH to 11 and 13 led to higher the C_w values.

Similarly, the DMAEMA content (C_D) and pH have influences on the PCgel$_y$ (Fig. S4c and d). The gels remained opaque in the C_D range from 0.1 M to 0.6 M and the C_w of PCgel$_y$ kept about 0.45. At pH 1, 3, and 5, the C_w of PCgel$_{0.4}$ remained about 0.69. As pH was increased from 5 to 9, the C_w of PCgel$_{0.4}$ was decreased from 0.67 to 0.47. When pH was increased from 9 to 11, the C_w remained constant, while it was increased a bit at pH 13. At pH < 7, the DMAEMA monomers are protonated to carry positive charges, and thus the gel is slightly deswelled. At pH > 7, the polymer network

becomes neutral, and thus the water content is decreased.

When hydrogels were immersed in pH=11 solution, the water content was increased. To further study this reason, the $PCgel_{0.2}$ were handled at pH = 13 and pH = 11, the C_w of these hydrogels, which were reswollen at pH = 7, were compared (Fig. S4e, f). When pH = 13, the C_w = 0.55, which is higher than hydrogel without immersing in pH = 13 solutions. A rapid decrease in zeta potential of pure HEMA hydrogel at high pH also due to the ester bond of hydrogels hydrolyzed.

6. The mathematical derivation of Equation 3

To further study the interface strength, the interface strength of assemblies was roughly described by an ideal charged plate model: $F = EQ$ (1), $E = \frac{U}{d} = \frac{4\pi kQ}{\varepsilon S}$ (2) and $C = \frac{\varepsilon S}{4\pi kd}$ (3). According to Equation (1), (2), and (3), the interface strength could be described by

$$\frac{F_{inter}}{S} = \frac{QE}{S} = \frac{QU}{Sd} = \frac{CU^2}{Sd} = \frac{\varepsilon SU^2}{4\pi kd^2 S} = \frac{\varepsilon(U_1 - U_2)^2}{4\pi kd^2} \tag{4}$$

$$\frac{F_{inter}}{S} = \frac{\sigma_+ \sigma_-}{2\varepsilon S^2} = \frac{\sigma_+ \sigma_-}{2\varepsilon d^2 S^2} = \frac{(U_1 - U_2)Q_+}{d} = \frac{(U_1 - U_2)Q_-}{d} \tag{5}$$

where F_{inter} is interface force, S is the contact area of two hydrogels, ε is the dielectric constant of solution between the two hydrogels, K is the electrostatic constant, d is the space of the two hydrogels. U_1 and U_2 are electric potentials of two hydrogels respectively. σ_+ and σ_- are the charge dentisy, Q_+ and Q_- are total quantity of electric charge on the surface which contain free charges and fixed charges.

7. The interface strengths of assemblies in detail

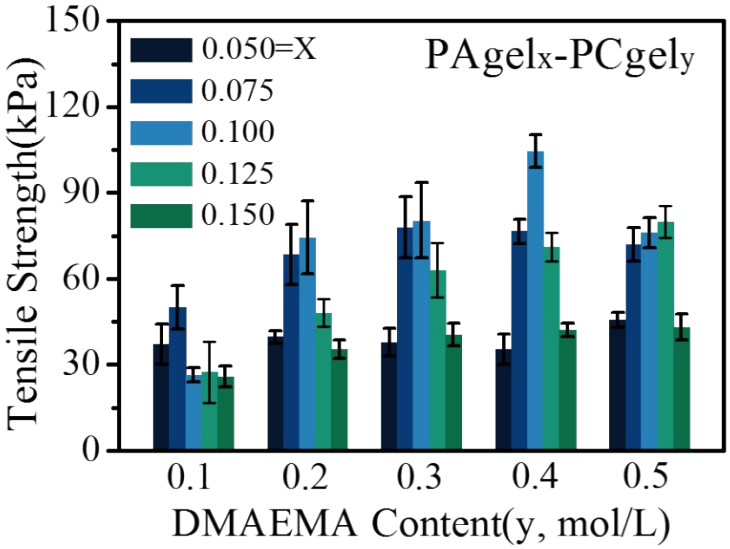

Fig. S5 The interface strength of assembly ($PAgel_x$-$PCgel_y$) in deionized water as a function of C_m.