Supporting Information

Zwitterionic copolymer additive architecture affects the membrane performance: Fouling resistance and surface rearrangement in saline solutions

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Keywords: Zwitterion; membrane; random copolymer; comb copolymer; fouling resistance

S1. Polymer Characterization

S1.1. Chemical characterization of PMMA-*r*-SB2VP copolymer

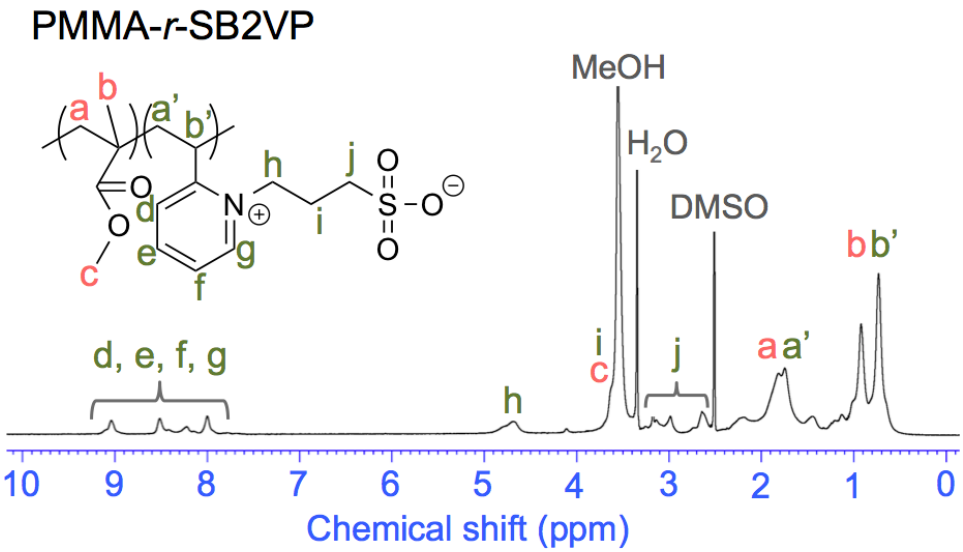

Fig. S1 ^{1}H-NMR spectrum of zwitterionic random copolymer PMMA-*r*-SB2VP

S1.2. Initiation efficiency of chlorine groups in backbone polymer PVDF-*co*-CTFE during ARGET-ATRP

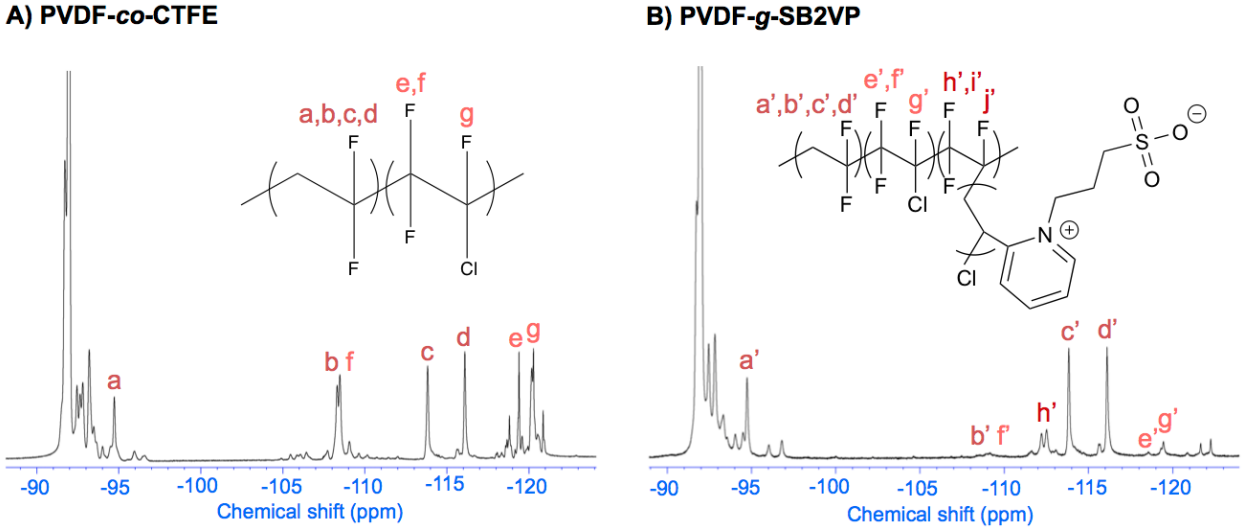

Fig. S2 ^{19}F-NMR spectra of (A) backbone copolymer PVDF-*co*-CTFE, and (B) comb copolymer PVDF-*g*-SB2VP

We determined the percentage of initiated chlorine as 85% by comparing the ^{19}F NMR spectra of the backbone PVDF-*co*-CTFE and product PVDF-*g*-SB2VP. We used the areas under the peaks b, f, c and d from the backbone PVDF-*co*-CTFE, and b', f', c' and d' from the product PVDF-*g*-SB2VP in our calculations performed by following the steps elaborated in a previous study.[1]

S1.3. Chemical characterization of PVDF-*g*-SB2VP copolymer after water wash

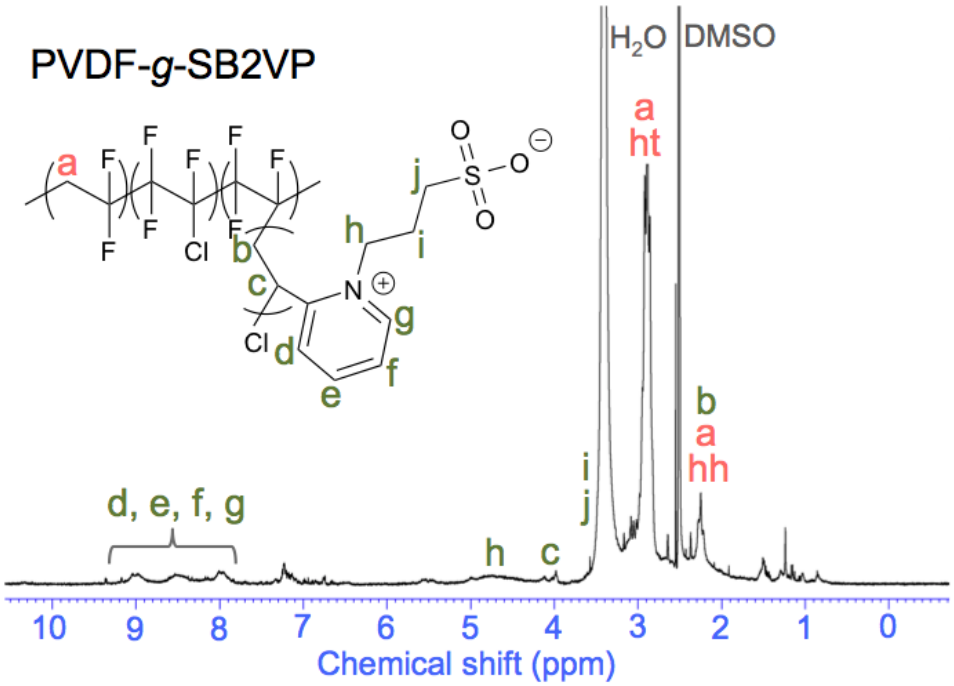

Fig. S3 ^{1}H-NMR spectrum of the zwitterionic copolymer PVDF-*g*-SB2VP after water wash

S2. Membrane Morphology

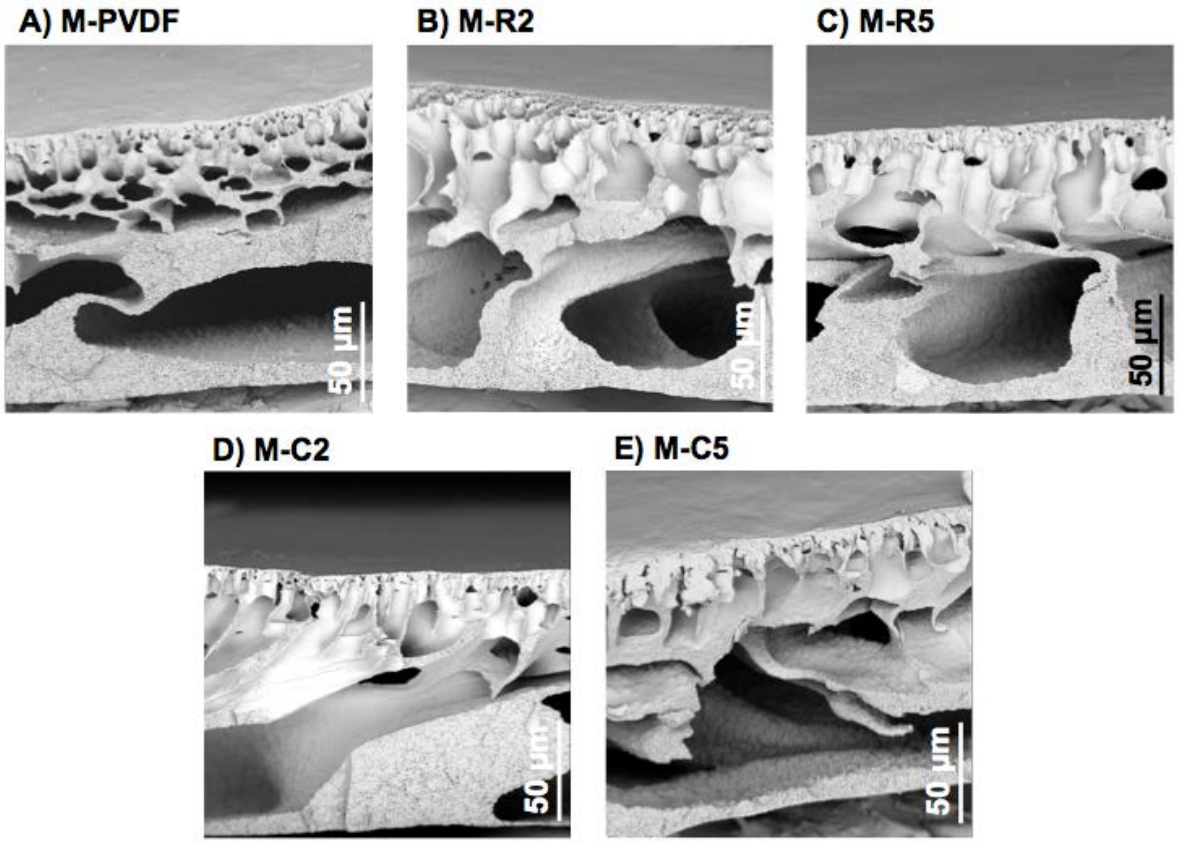

Fig. S4 Tilted cross-sectional SEM images showing the surface and cross-sectional morphologies of membranes

S3. Surface Hydrophilicity and Water Permeance

Table S1 Pure water permeances and captive bubble contact angles of blend membranes along with control M-PVDF

Membrane series	Membrane code	Contact angle (°)	Pure water permeance (L/m^2.h.bar)
Additive-free PVDF	M-PVDF	55 ± 4	24 ± 5
M-R	M-R2	44 ± 2	33 ± 5
	M-R5	34 ± 3	115 ± 7
M-C	M-C2	46 ± 4	28 ± 4
	M-C5	32 ± 3	112 ± 6

S4. Protein Rejection by the M-PVDF Membrane

Table S2 Rejection of three proteins by the M-PVDF membrane

Protein	Molar mass (kDa)	Hydrodynamic radius (nm)	Rejection (%)
Bovine serum albumin	66.5	3.5	100
Ovalbumin	42.7	2.8	97
β-Lactoglobulin	18.4	2	95
Cytochrome C	12.4	1.7	77

S5. Calculation of Molecular Sizes of SB2VP Monomer and Trimer

We used Molecular Modeling Pro software (ChemSW) to calculate the conformation of an SB2VP monomer and a PSB2VP trimer. First, local charges were calculated using Extended Huckel theory. Then, energy minimization was conducted while accounting for electrostatics and hydrogen bonding, with a dielectric constant of 80.4 (corresponding to water). We repeated the calculation three times, allowing moderate changes first and then refining the structure.

Using this method, we calculated the maximum dimension of an SB2VP monomer to be ~1.0-1.1 nm depending on conformation. Inter-atomic distance between the backbone carbon atoms to the farthest atom was typically on the order of 0.5-0.6 nm. In contrast, the maximum dimension of the trimer was ~1.8 nm, with the inter-atomic distance between the first backbone carbon (i.e. attachment to the PVDF backbone) to the farthest atom was ~1.2-1.3 nm.

S6. Oil Fouling Test

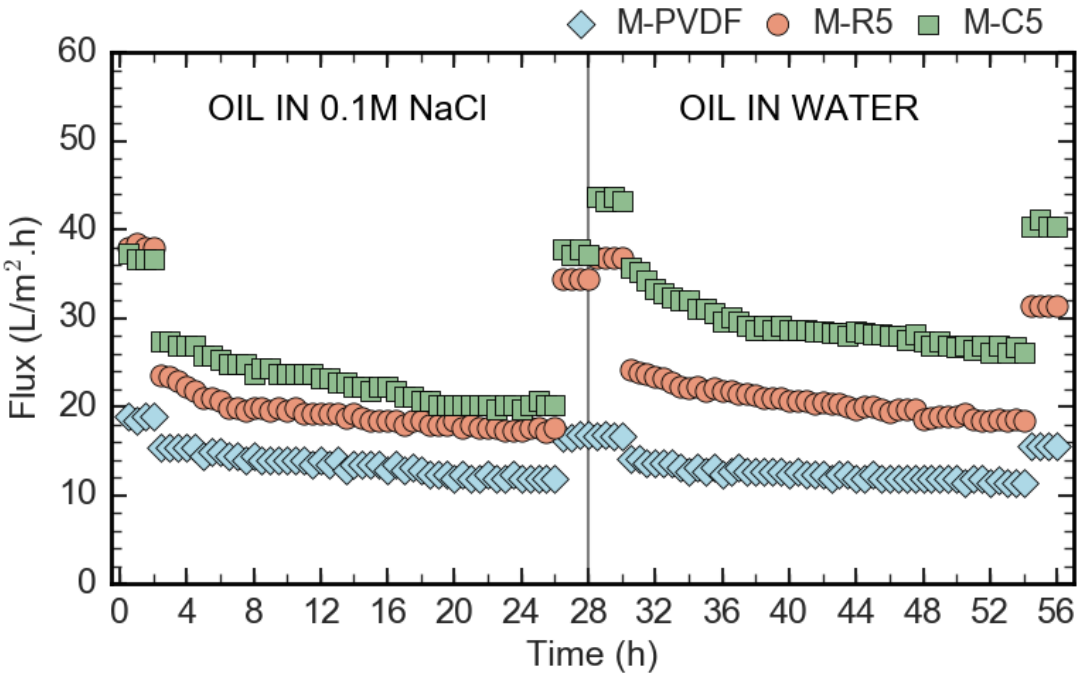

Fig. S5 Long-term oil fouling resistance by filtration of M-PVDF (10 psi), M-R5 (5 psi), and M-C5 (10 psi) membranes. The fluxes are plotted without normalizing.

S7. Protein Fouling Tests

S7.1. AFM detachment force measurements

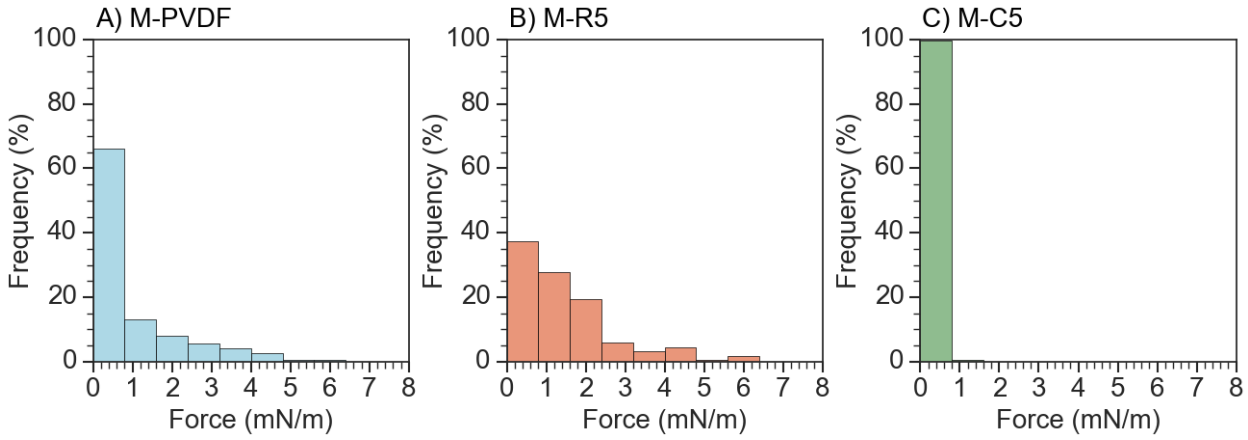

Fig. S6 Distributions of normalized detachment force measurements between the AFM particle (foulant) probe and membranes (A) M-PVDF, (B) M-R5, and (C) M-C5.

S7.2. Dynamic protein fouling test

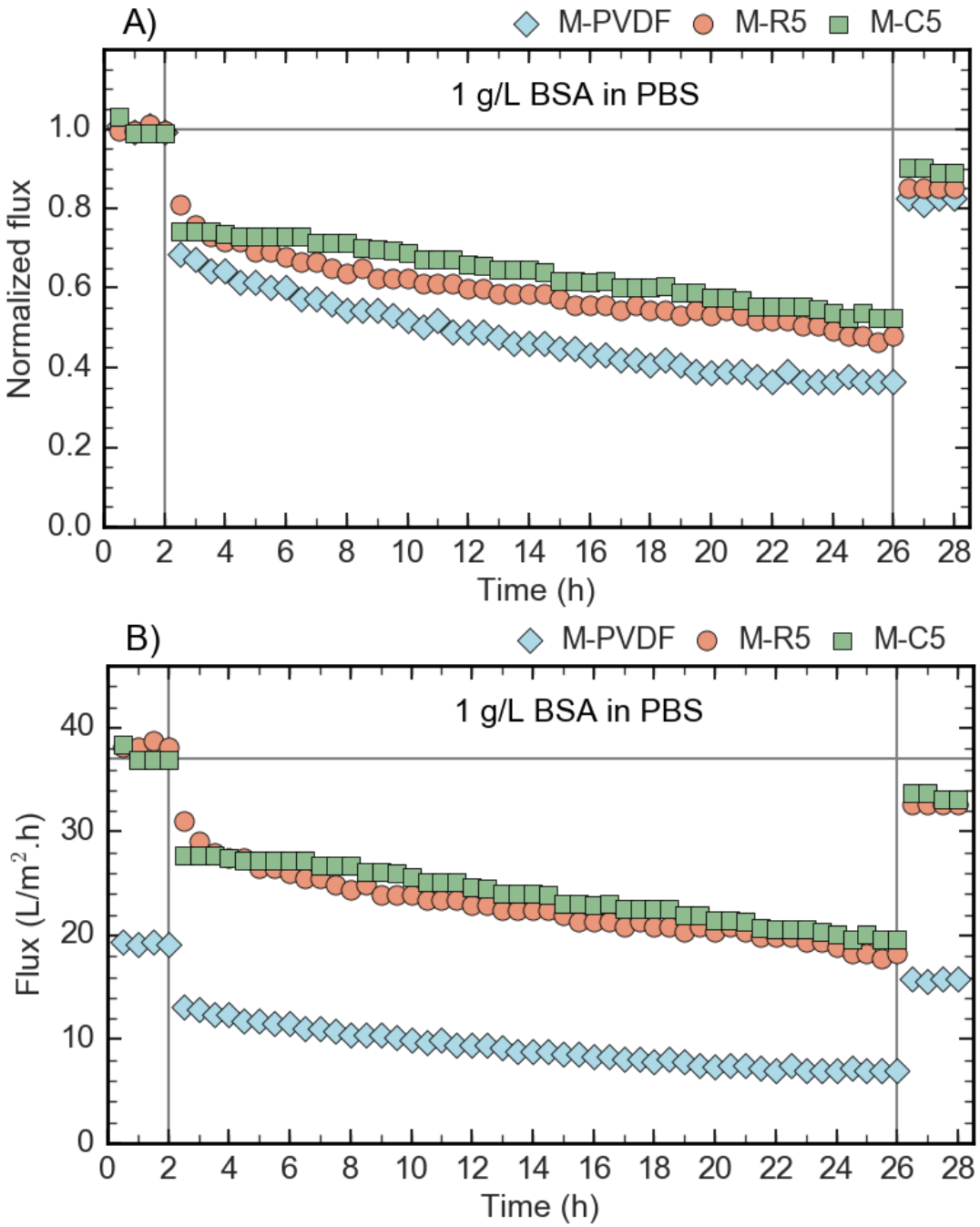

Fig. S7 Long-term protein fouling resistance by 24 h filtration of M-PVDF (10 psi), M-R5 (5 psi), and M-C5 (10 psi) membranes. The fluxes are plotted (A) after normalizing by the average initial flux of each membrane; 19 L/m^2.h for M-PVDF, 38 L/m^2.h for M-R5, and 37 L/m^2.h for M-C5, (B) without normalizing.

Notes and references

1 C. Vannucci, I. Taniguchi and A. Asatekin, *ACS Macro Lett.*, 2015, **4**, 872.