

Supporting Information for

Tuning Network Structures of Hydrophobic Hydrogels by Controlling Polymerization

Solvent

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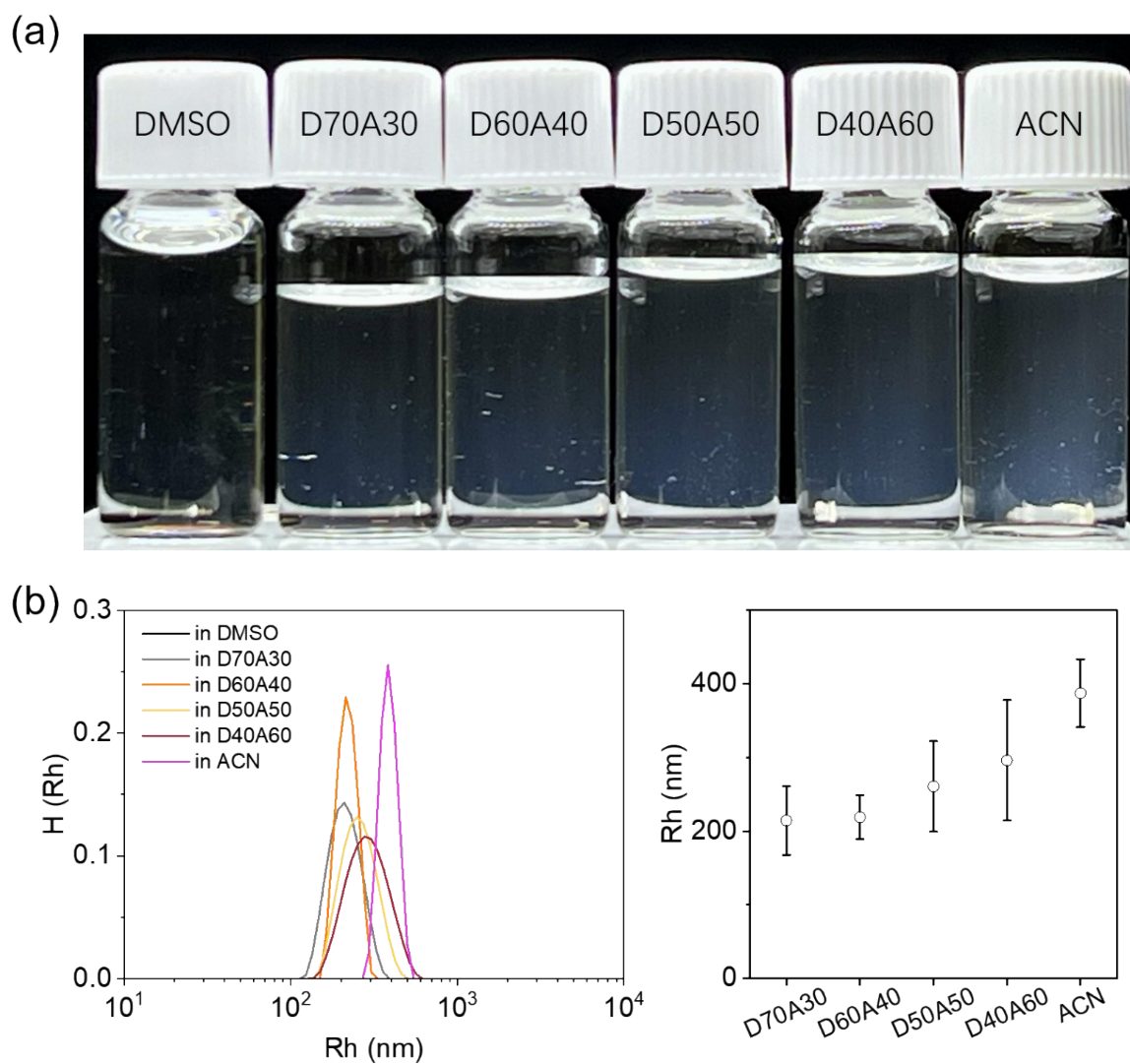


Figure S1. (a) Photos of precursor solutions with different reaction solvents. (b) Distributions of hydrodynamic radii of ATAC (0.5 M) and 4F (0.5 M) mixtures in the precursor solutions obtained from dynamic light scattering (DLS) measurement.

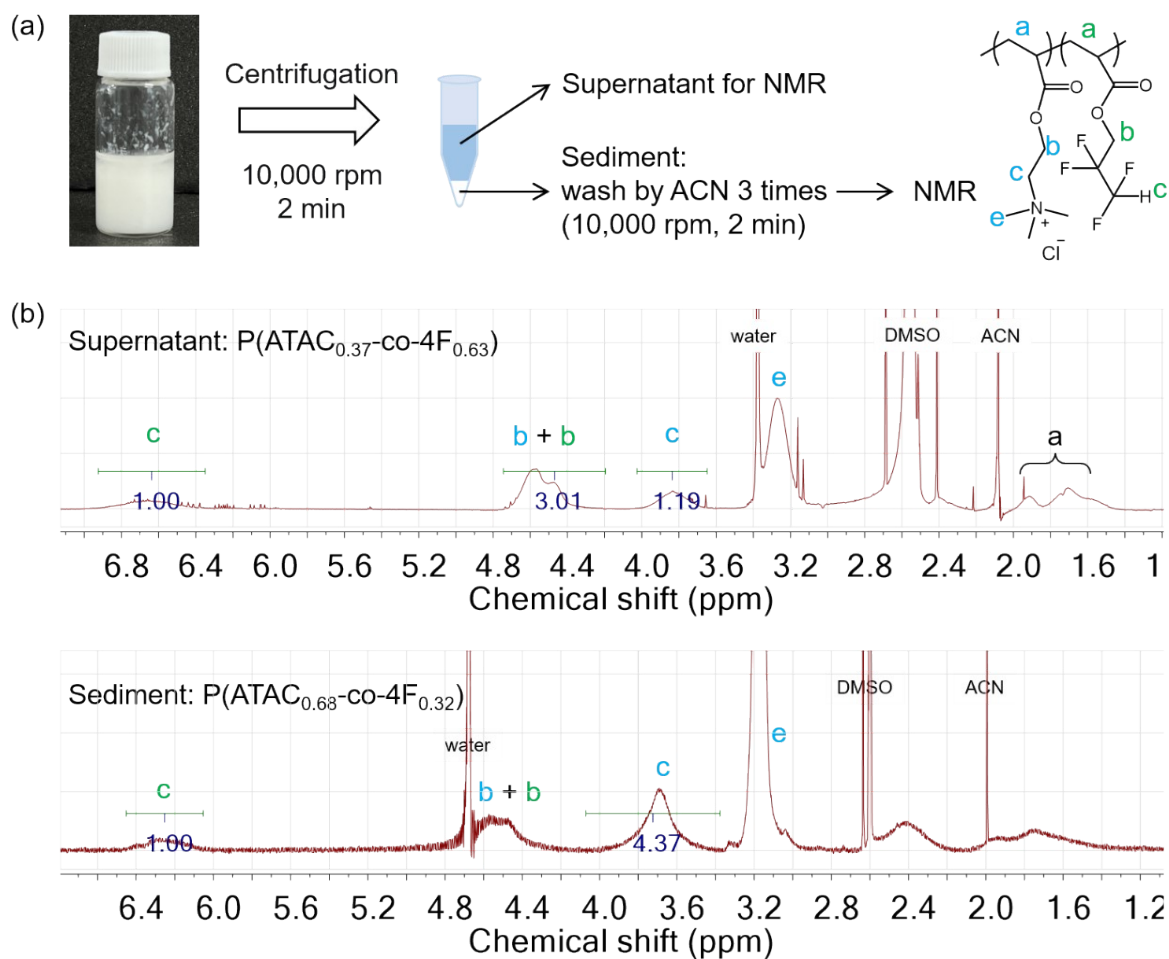


Figure S2. (a) Schematic illustration of separation of copolymers synthesized in the D60A40 solvent. (b) ^1H NMR spectrum of copolymers in supernatant and sediment, respectively. The supernatant was diluted by DMSO-d_6 , and the sediment was diluted by D_2O .

Table S1. Apparent reactivity ratios of monomers in different reaction solvents.

	DMSO	D70A30	D60A40	D50A50	D40A60	ACN
r_{ATAC}	1.02 ± 0.02	1.72 ± 0.10	3.74 ± 0.24	5.37 ± 0.62	7.65 ± 0.86	12.80 ± 1.20
$r_{4\text{F}}$	1.01 ± 0.02	1.01 ± 0.07	0.67 ± 0.07	0.31 ± 0.08	0.28 ± 0.08	0.001 ± 0.004
$r_{\text{ATAC}} \cdot r_{4\text{F}}$	1.03	1.74	2.51	1.67	2.14	0.013

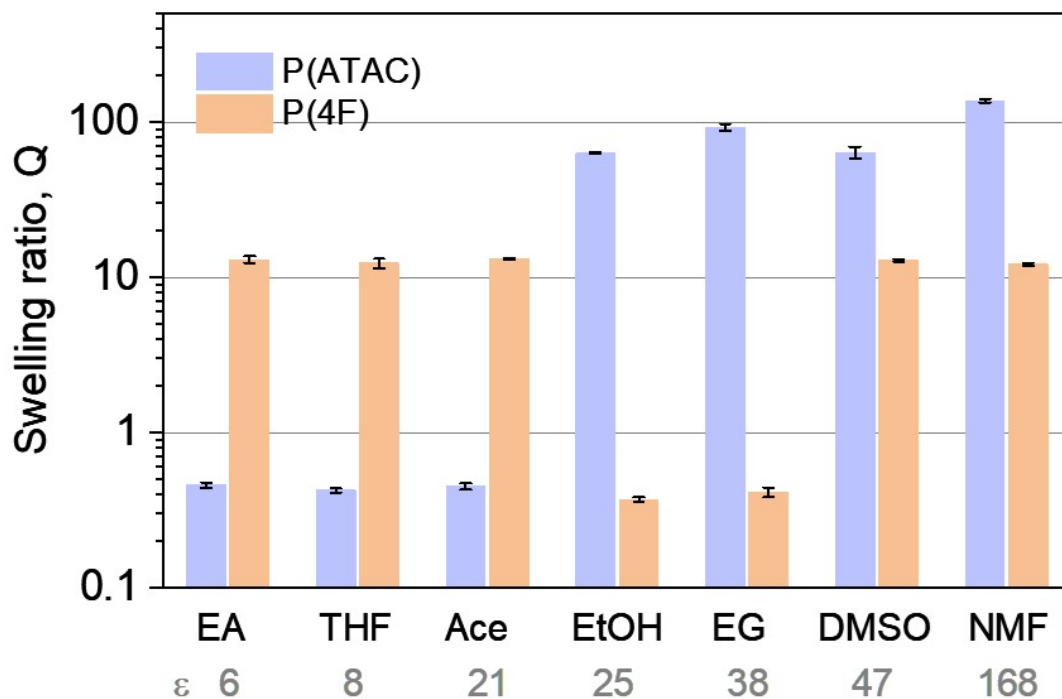


Figure S3. Volume swelling ratio Q of neat P(ATAC) and P(4F) gels with respect to their as-prepared states in different solvents.

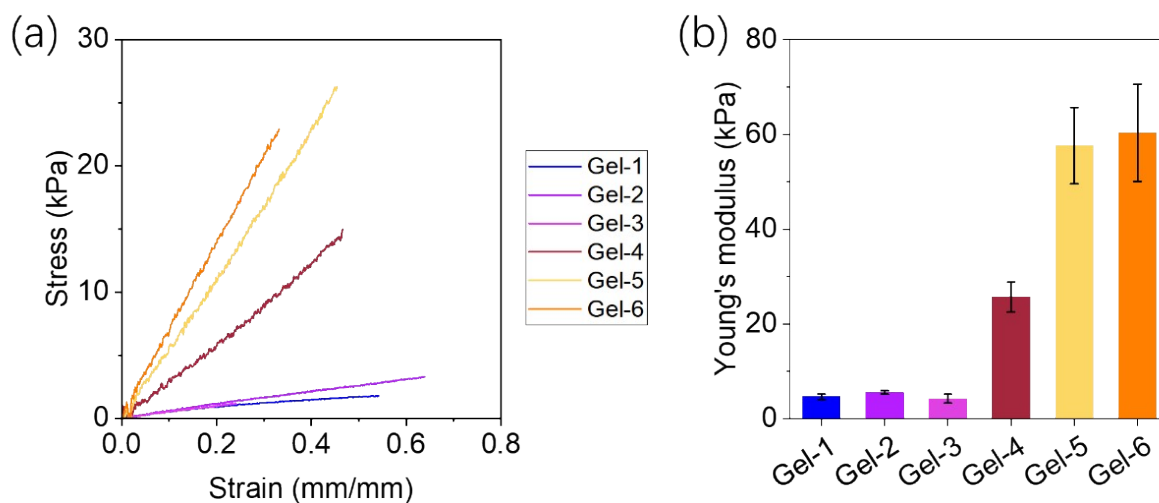


Figure S4. (a) Tensile stress-strain curves of hydrogels equilibrated in water (obtained at a strain rate of 0.14 s^{-1}). (b) Extracted Young's modulus of the hydrogels.

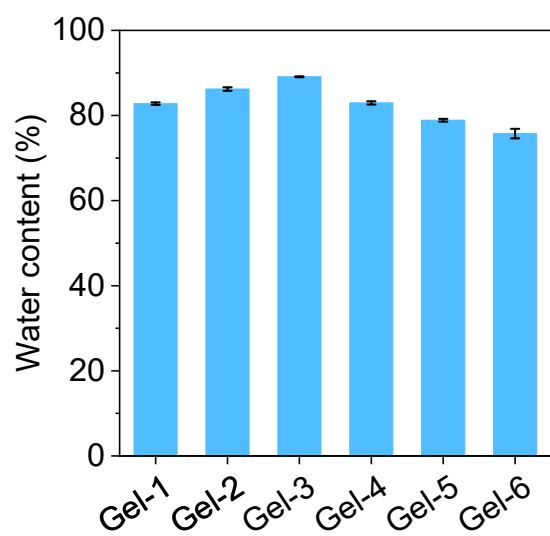


Figure S5. The water content of hydrogels equilibrated in 0.7 M NaCl solution.

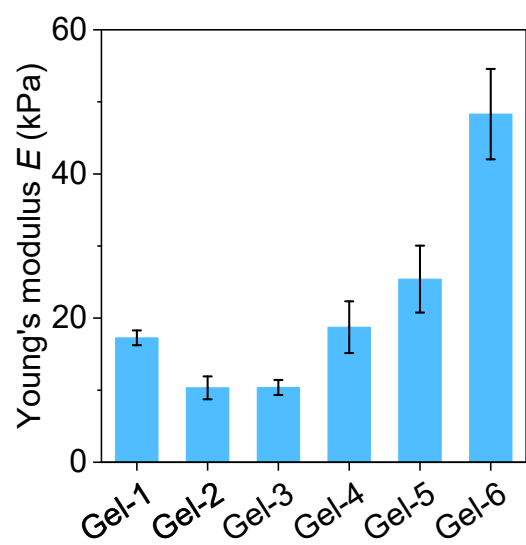


Figure S6. Young's modulus of as-prepared organogels.

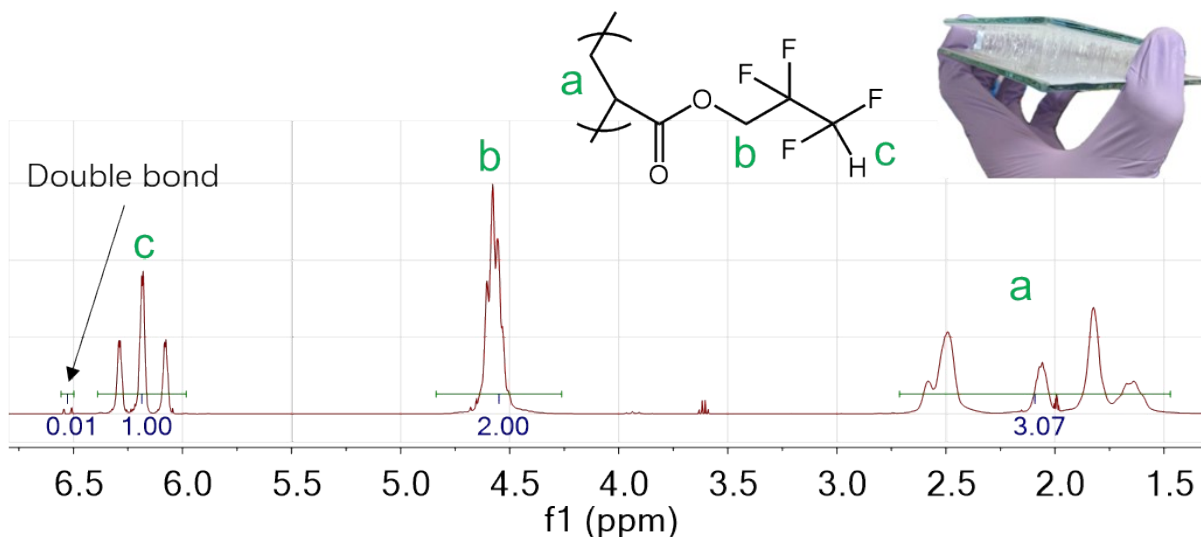


Figure S7. ¹H NMR spectrum of P(4F) in ACN. The precursor solution comprises 4F (2.4 M), the chemical crosslinker (MBAA, 2.4 mM), and the UV initiator (2-oxoglutaric acid, 6 mM). Following 11 hours of irradiation, a viscous solution was obtained (instead of a gel), as demonstrated in the inset digital photo. In contrast, utilizing DMSO under the same condition resulted in the formation of a gel. These outcomes suggest that despite nearly complete monomer consumption (~99%), the monomers fail to polymerize into long chains and establish a network in ACN. This phenomenon is attributed to the higher radical transfer ability of ACN compared to DMSO.