Electronic Supplementary Information

Associative Properties of Poly(ethylene glycol)-Poly(vinyl acetate) Comb-like Graft Copolymer in Water

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1. Flow curves of PEG-*g*-PVAc/H_2O binary systems

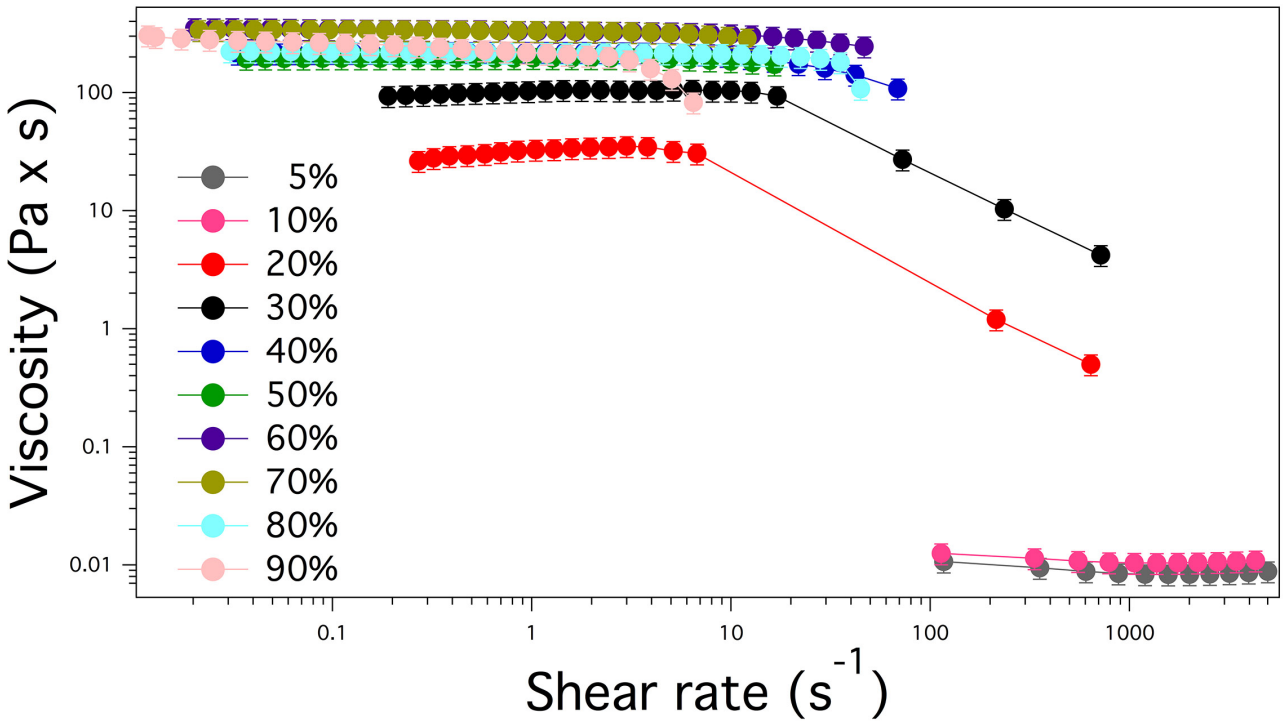


Figure SI1. Flow Curves of PEG-*g*-PVAc/H_2O binary systems. Polymer weight contents are indicated in the figure legend.

2. Amplitude sweep of PEG-*g*-PVAc/H_2O binary systems

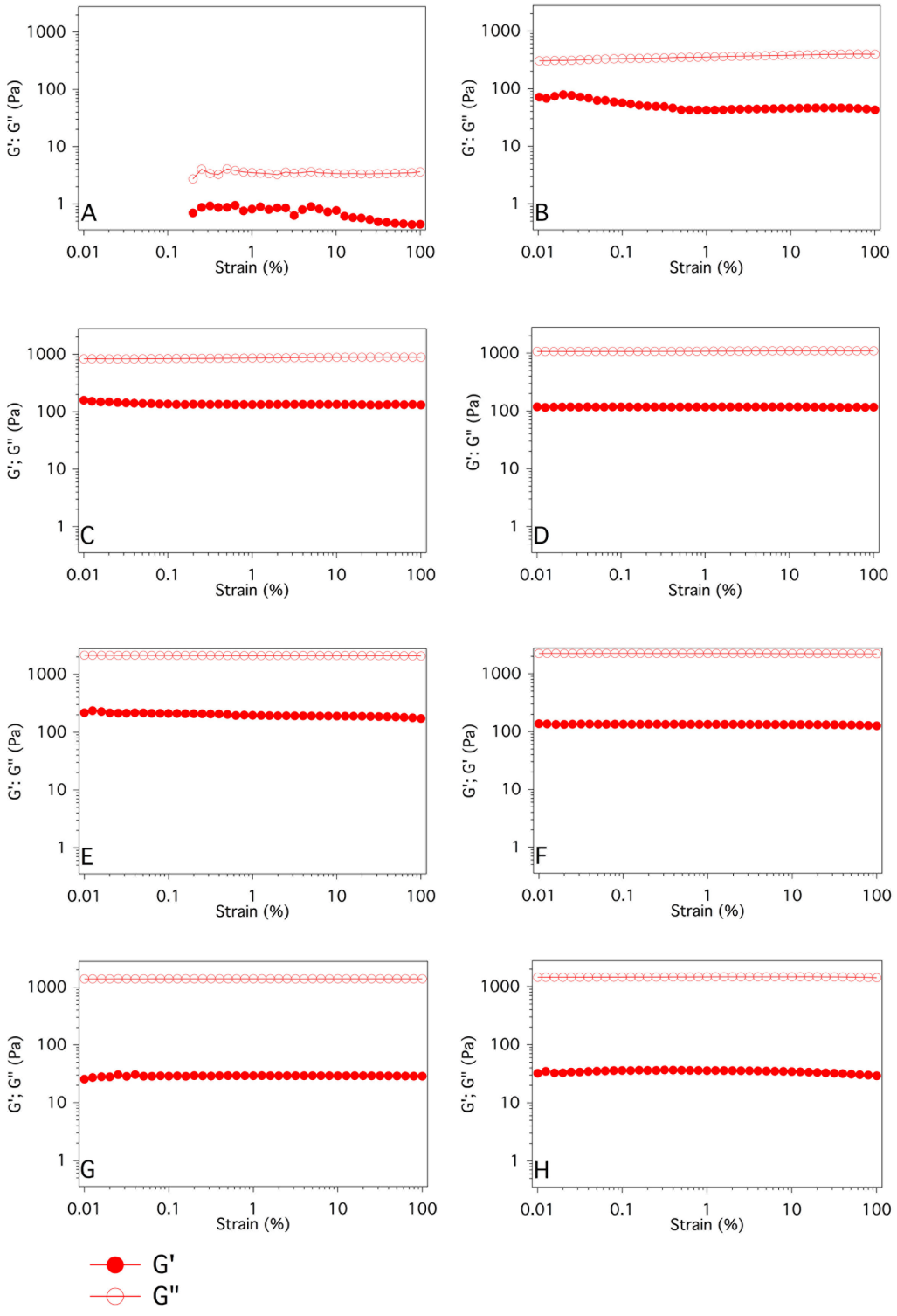


Figure SI2. Amplitude sweep of PEG-*g*-PVAc/H_2O binary systems containing 20 wt% (A), 30 wt% (B), 40 wt% (C), 50 wt% (D), 60 wt% (E), 70 wt% (F), 80 wt% (G), 90 wt% (H) polymer.

3. Frequency sweep of PEG-*g*-PVAc/H_2O binary systems

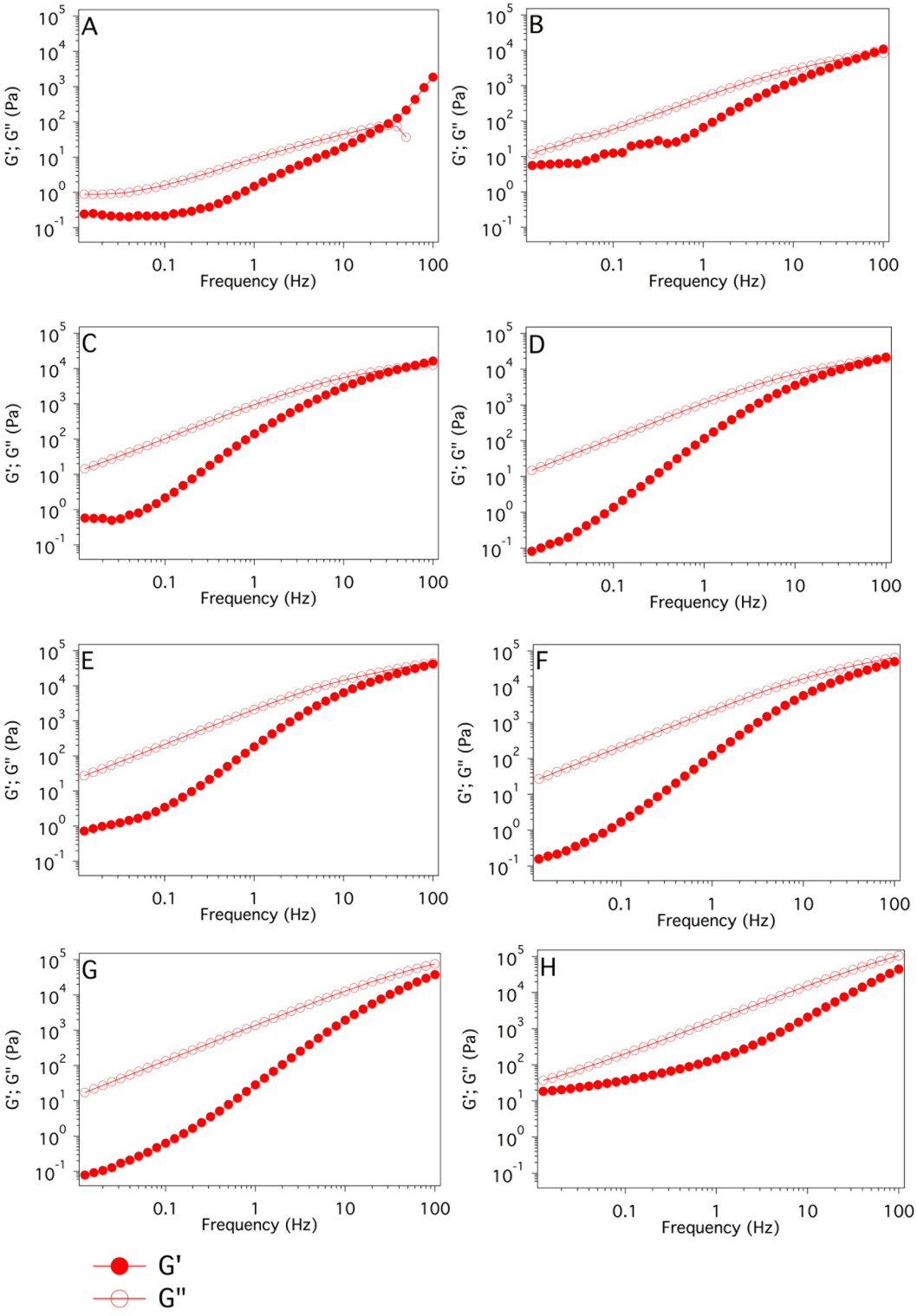


Figure SI3. Frequency sweep of PEG-*g*-PVAc/H_2O binary systems containing 20 wt% (A), 30 wt% (B), 40 wt% (C), 50 wt% (D), 60 wt% (E), 70 wt% (F), 80 wt% (G), 90 wt% (H) polymer.

4. Calculations for H_2O/EO molecular ratio in PEG-g-PVAc 60 wt%

In the DSC thermogram (heating step) for sample PEG-g-PVAc 60 wt% no endothermic peak relative to the fusion of bulk water is detected, meaning that all water molecules are bound to the polymer chains, reasonably to the PEG portion.

Considering 1 g of sample, 0.4 g are water and 0.6 g are polymer. PEG (Mw = 6 kDa) is 40 wt% of the total polymer weight, so the PEG weight in PEG-g-PVAc 60 wt% sample is 0.6 g* 0.4 = 0.24 g

The number of water molecules in 0.4 g is 0.4 g / 18 g/mol * 6.023 10^{23} molecules/mol = 1.34 10^{22} molecules.

The number of PEG molecules in 0.24 g is 0.24 g / 6000 g/mol * 6.023 10^{23} molecules/mol = 2.41 10^{19} molecules.

So, 1.34 10^{22} H_2O molecules/ 2.41 10^{19} PEG (Mw = 6 kDa) molecules ≈ 555 H_2O molecules per PEG 6 kDa chain.

In a PEG 6 kDa chain there are about 136 EO units, so 555/136 ≈ 4 H_2O molecules per EO unit.

5. DSC thermograms of PEG-*g*-PVAc/H_2O binary systems

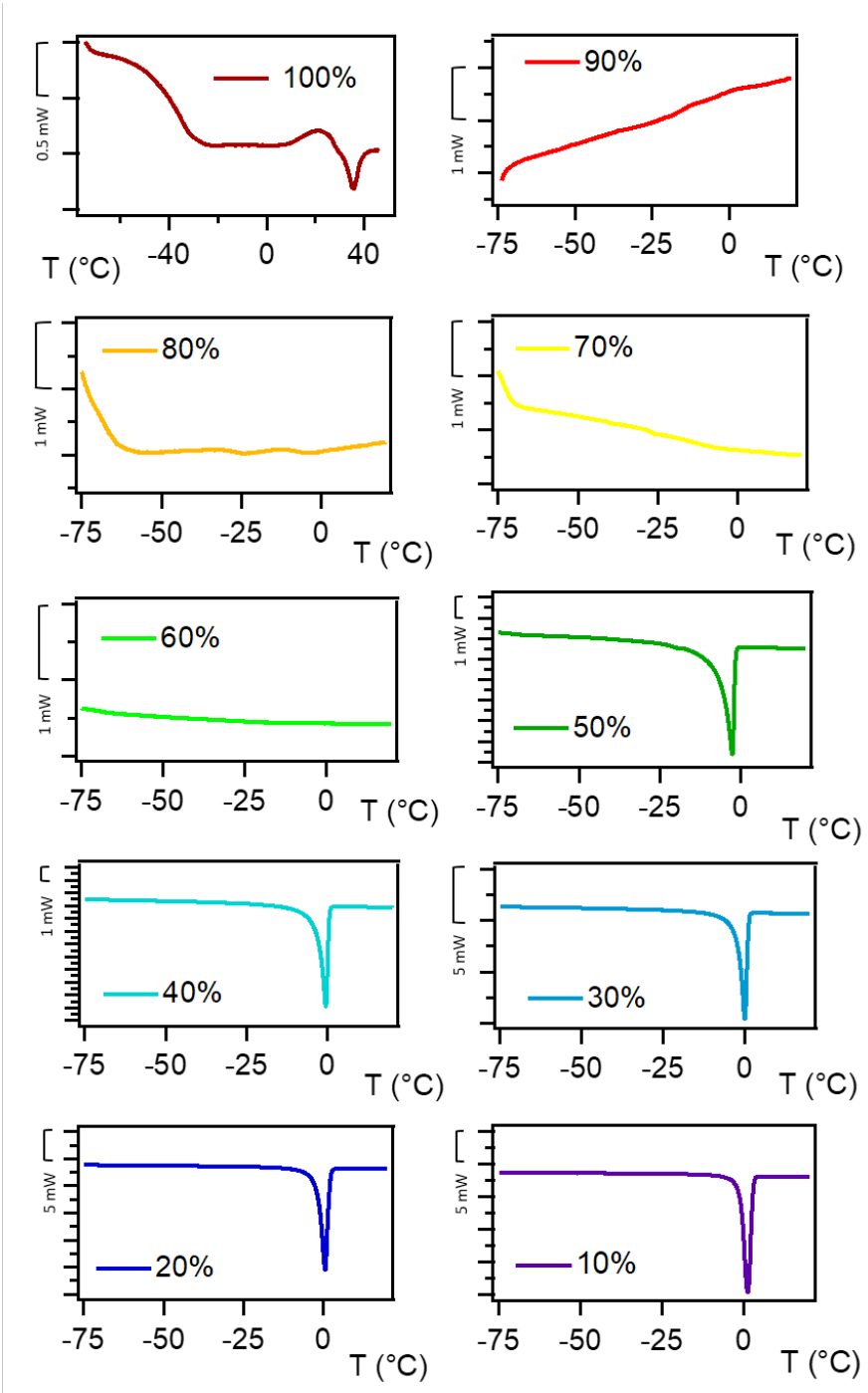


Figure SI4. DSC thermograms of PEG-*g*-PVAc in water in the 10-90% weight concentration range.

6. Summary of SAXS data fitting results

Table S1. Summary of salient parameters extracted from fitting of SAXS data as discussed in the main text.

	Schulz-spheres form factor		Two-Yukawa				Teubner-Strey					
PEG-g-PVAc content (wt%)	Sphere radius, r (Å) ± 0.6 Å	Schulz polydispersity, σ	K_1	Z_1	K_2	Z_2	a_2	c_1	c_2	Correlation length, ξ (Å) ± 0.6 Å	Repeat distance, *d* (Å) ± 0.6 Å	*d*/ξ
10	58	0.18	1.1	4.6	-1.1	3.6	-	-	-	-	-	-
20	58	0.18	-	-	-	-	0.16	-222.9	98775	119	182	1.5
30	58	0.18	-	-	-	-	0.08	-90.7	31481	135	163	1.2
40	58	0.18	-	-	-	-	0.07	-81.4	25682	144	156	1.1
50	58	0.18	-	-	-	-	0.17	-147.7	35745	143	137	1.0
60	-	-	-	-	-	-	0.28	-199.4	40497	115	125	1.1
70	-	-	-	-	-	-	0.27	-176.9	34538	94	122	1.3

7. SAXS patterns for PEG-*g*-PVAc 80 wt% and 90 wt% in water.

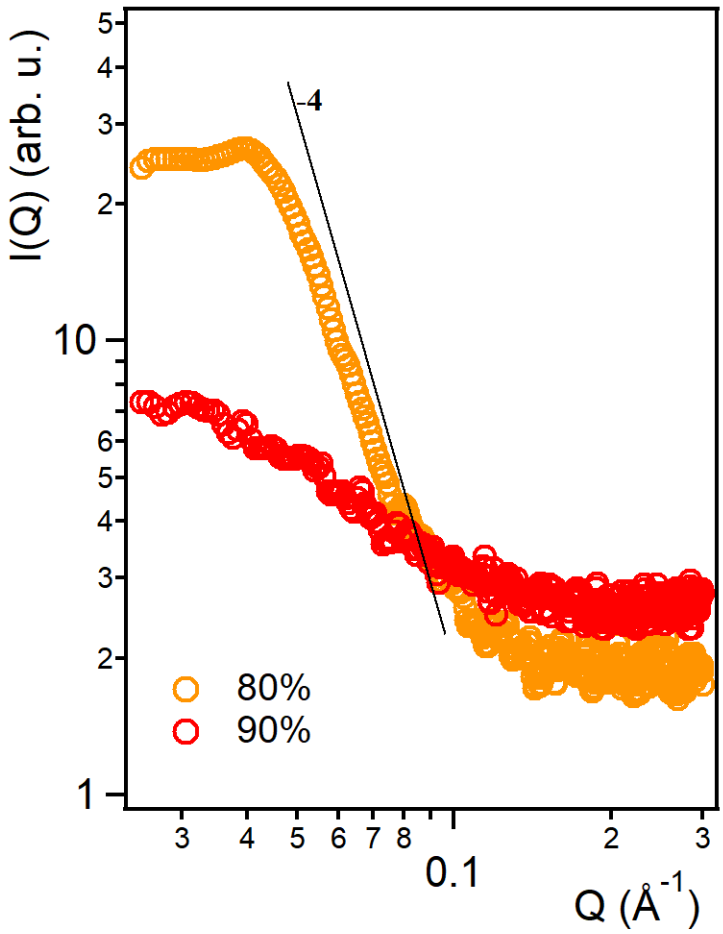


Figure SI5. Small-angle X-ray patterns for PEG-*g*-PVAc 80 wt% and 90 wt% in water.

8. SAXS curves of PEG-*g*-PVAc/H_2O binary systems at different temperatures

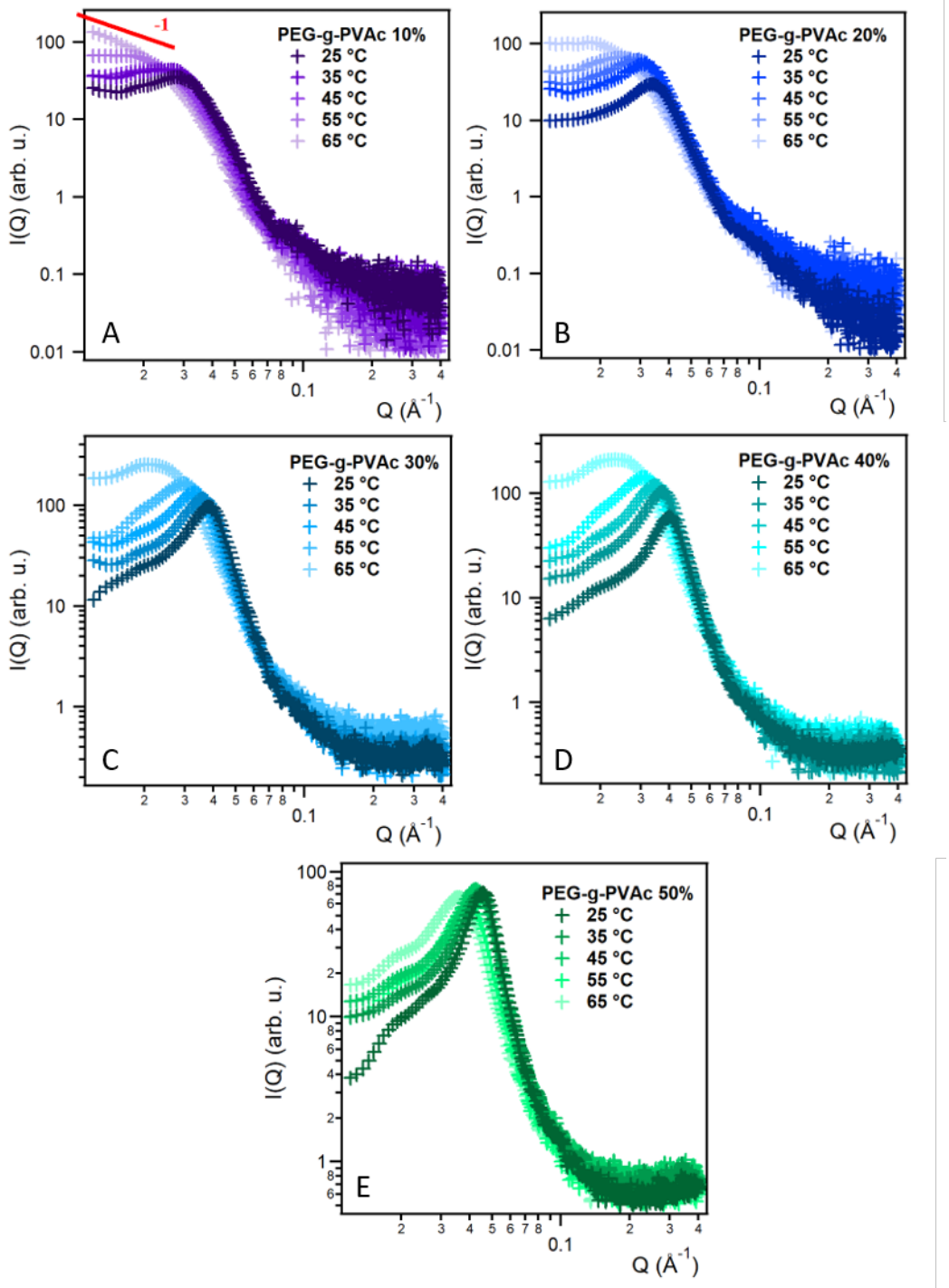


Figure SI6. Small-angle X-ray patterns for PEG-*g*-PVAc/water systems at: A) 10 wt%, B) 20 wt%, C) 30%, D) 40%, and E) 50% polymer, acquired on a temperature range between 25 °C and 65 °C.

9. Dissipative Particle Dynamics (DPD) Simulation Protocol

In our DPD simulations, every 3-5 heavy atoms are coarse-grained into one DPD bead using an in-house developed procedure. Every three water molecules are also coarse-grained into one DPD bead. Bead definitions are summarized in Table S1. Non-bonded interactions between beads follow the standard DPD potential,[1] in which a conservative intermolecular potential along with dissipative and random forces capture molecular interactions:

$$f_i = \sum_{j \neq i}(F_{ij}^C + F_{ij}^D + F_{ij}^R) \quad (1)$$

where f_i is the total force on bead i, and F_{ij}^C is the conservative force defined by a purely-repulsive soft-core potential that allows for larger time steps of picoseconds instead of the femtoseconds used in conventional MD simulations. The dissipative force (F_{ij}^D) and the random force (F_{ij}^R) take into account the fluctuations of energy and serve as the Langevine thermostat. Mathematically, each of these forces are defined as follows:

$$\begin{aligned} F_{ij}^C &= -a_{ij}\omega^C(r_{ij})\hat{r}_{ij} \\ F_{ij}^D &= -\gamma\omega^D(r_{ij})(v_{ij}\cdot\hat{r}_{ij})\hat{r}_{ij} \\ F_{ij}^R &= -\sigma\omega^R(r_{ij})\xi_{ij}\Delta t^{-1/2}\hat{r}_{ij} \end{aligned} \quad (2)$$

The repulsive parameters a_{ij} are dependant on the chemical identity of beads i, j. $\hat{r}_{ij}$ is a unit vector in the direction of r_{ij} and $r_{ij} = |r_i - r_j|$. The weight function ω^C is defined as:

$$\omega^C(r_{ij}) = \begin{cases} 1 - \frac{r_{ij}}{r_{cut}} & if\ 0 \leq r_{ij} \leq r_{cut} \\ 0 & if\ r_{ij} > r_{cut} \end{cases} \quad (3)$$

where r_{cut} is the truncation distance. The parameters σ, γ are set to obey the dissipation-fluctuation theorem with $\sigma^2 = 2\gamma$ and $\sigma = 3.56$. The quantity $v_{ij} = v_i - v_j$ is the relative velocity between beads i and j. ξ_{ij} is a Gaussian distributed random variable with zero mean and unit variance and Δt is the integration time step. The weight function ω^R is the same as ω^C. Finally, ω^D is defined as $\omega^D = (\omega^R)^2$.

The repulsive parameter $\boldsymbol{a_{ij}}$ is transferable by design, and is derived by relating to the Flory-Huggins χ parameters obtained using COSMO-RS theory.[2] The relation between the $\boldsymbol{a_{ij}}$ and the Flory-Huggins theory is outlined in this paper.[3] Transferable harmonic bonds and angles are defined as necessary, and parameterized to reproduce atomistic distributions obtained from COMPASS force field.[4] Further refinement of the DPD non-bonded parameters was applied to account for the pressure drop due to formation of bonds. All non-bonded and bonded parameters are summarized in the attached parameter file.

Table S2. DPD bead definition. {} indicates branching in the chemical structure.

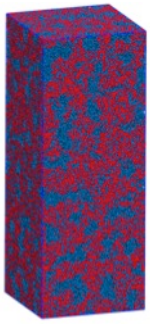
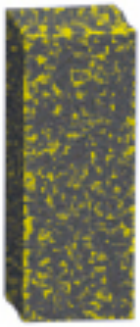
Bead name	Representing chemistry
WAT	Three water molecules
EO	Middle polyethylene glycol monomer: -O-CH_2-CH_2-
EOT	Terminal PEG monomer: -O-CH_2-CH_3
EOH	Terminal PEG monomer: -CH_2-CH_2-OH
EOB	Grafting point on PEG backbone: -CH_2-CH{}-O-
MVAc	Middle polyvinyl acetate monomer: -CH_2-CH{-O-C{=O}-CH_3}-
TVAc	Terminal polyvinyl acetate monomer: -CH_2-CH_2{-O-C{=O}-CH_3}

All simulations are performed using LAMMPS molecular dynamics package.[5] Initial configurations and molecular topologies are prepared using Culgi software (https://culgi.com). The truncation distance (r_{cut}) of the potential is set to 1, which is used to define the reduced length unit. In this work, we define the number density of water beads as ρ_{ref} = 5.0, with three water molecules in each bead. Hence, a DPD unit volume (r_{cut}^3) contains 15 water molecules. Given the macroscopic density of water, this volume corresponds to 15 × 30.07 Å^3. The unit length in our simulations hence corresponds to $\sqrt[3]{\upsilon_{ref}\rho_{ref}}$ = 7.66 Å 3 at a reference molecular volume υ_{ref} = 90.0 Å^3 (which is the volume of three water molecules under ambient conditions). We also opt for an energy unit that corresponds to T = 300 K at k_BT = 1, where k_B is Boltzmann constant. The DPD friction coefficient (γ) is set to 6.36. The non-bonded 1-4 interactions are not scaled. The DPD thermostat is used to keep the temperature constant at T = 1 (reduced units, corresponding to 300 K). The equation of motion is integrated using the Velocity-Verlet algorithm with a time step of 0.015 (reduced units). Further details on the choice of units and parameters are discussed in this paper.[6] The simulation box is rectangular 60×60×160 (reduced units), and periodic in all directions. The number of polymer chains varies between 26-129, and the number of

water beads is between 1 to 3 million, to retrieve polymer concentrations between 10 to 90 wt%. Polymers are simulated with polydispersity index of 1. All simulations start with a random configuration of polymers in water, and are relaxed for 1.5×106 steps in NPT ensemble with P = 41.89 (a preset reference pressure[3]) and pH = 7. The production run is 1.5×106 steps during which configurations are stored every 20000 timestep for post-simulation analysis. Visualization is performed by VMD software.

10. DPD Simulation Boxes

Table S3. DPD simulation boxes showing water (yellow), PEG-g-PVAc copolymer (grey), PEG only (blue), and PVAc only (red) at equilibrium.

[PEG-*g*-PVAc]	Simulation box	Polymer only
80%		
90%		

11. References

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