Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Computational Design of Janus Polymersomes with Controllable Fission from Double Emulsions

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S1. DPD fundamentals.

In DPD method, like molecular dynamics, the motion of all the DPD beads obeys Newton's equation of motion.

$$\frac{dr_i}{dt} = v_i, \qquad \frac{dv_i}{dt} = f_i/m_i \tag{S1}$$

where $\boldsymbol{r}_i$, $\boldsymbol{v}_i$ and m_i denote the position vector, velocity vector and mass of beads respectively, and $\boldsymbol{f}_i$ is the force acting on bead i. The force $\boldsymbol{F}_{ij}$ exerted on bead i by bead j is consisted of a conservative force F_{ij}^C, a dissipative force F_{ij}^D and a random force F_{ij}^R. Thus, the total force $\boldsymbol{f}_i$ is given by

$$f_i = \sum_{j \neq i} \left(F_{ij}^C + F_{ij}^D + F_{ij}^R\right) \tag{S2}$$

where the sum runs over all other beads within the cutoff radius r_c. And the conservative force F_{ij}^C, dissipative force F_{ij}^D and random force F_{ij}^R are given by

$$F_{ij}^C = \begin{cases} a_{ij}(r_c - r_{ij})e_{ij} & r_{ij} \leq r_c \\ 0 & r_{ij} > r_c \end{cases} \tag{S3}$$

$$F_{ij}^D = -\gamma \omega^D(r_{ij})(e_{ij} \cdot v_{ij})e_{ij} \tag{S4}$$

$$F_{ij}^R = \sigma \omega^R(r_{ij})\theta_{ij}e_{ij} \tag{S5}$$

where a_{ij} is a constant that describes the maximum repulsion between two interacting beads. r_{ij} is the distance between beads i and j. $e_{ij} = r_{ij}/r_{ij}$, $v_{ij} = v_i - v_j$, v_i *and* v_j are the velocities of beads i and j, respectively. γ and σ are the amplitudes of dissipative and random forces, respectively. θ_{ij} is a randomly fluctuating variable. ω^D and ω^R are r-dependent weight functions for dissipative and random forces, respectively. According to the fluctuation-dissipation theorem, $\omega_{ij}^D(r)=[\omega_{ij}^R(r)]^2$ and $\sigma^2=2\gamma k_B T$ (σ=3 and γ=4.5). The following simple form of ω^D and ω^R was chosen by Groot and Warren[1]:

$$\omega^D(r) = [\omega^R(r)]^2 = \begin{cases} (1 - r/r_c)^2 & r \le r_c \\ 0 & r > r_c \end{cases} \quad (S6)$$

Also, the chain beads of polymers are connected by a harmonic bond:

$$F_{ij}^B = -\sum_j C^B (r_{ij} - r_{eq}) e_{ij} \quad (S7)$$

where C^B and r_{eq} denotes the bond rigidity and the equilibrium bond length, respectively. Here, the most common and reliable values ($C^B = 4.0$ and $r_{eq} = 0$)[1-5] were adopted in our simulations.

The repulsive interaction parameters (a_{ij} in eq S3) can be estimated from the χ-parameter in Flory-Huggins theory according to the study of Groot and Warren[1] as follows:

$$a_{ij} = a_{ii} + 3.27\,\chi_{ij} \quad (S8)$$

S2. Finite size effect.

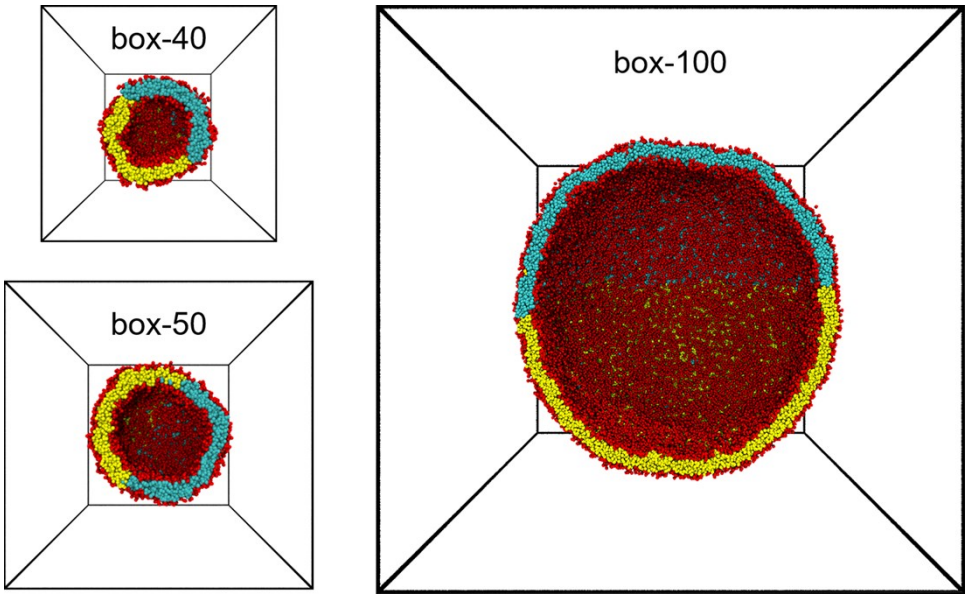

Fig. S1. Snapshots of Janus polymersomes obtained in different boxes sized $(40r_c)^3$, $(50r_c)^3$ and $(100r_c)^3$, respectively. Color code: block A, red; block B, cyan; block C, yellow.

S3. The stability of double emulsions.

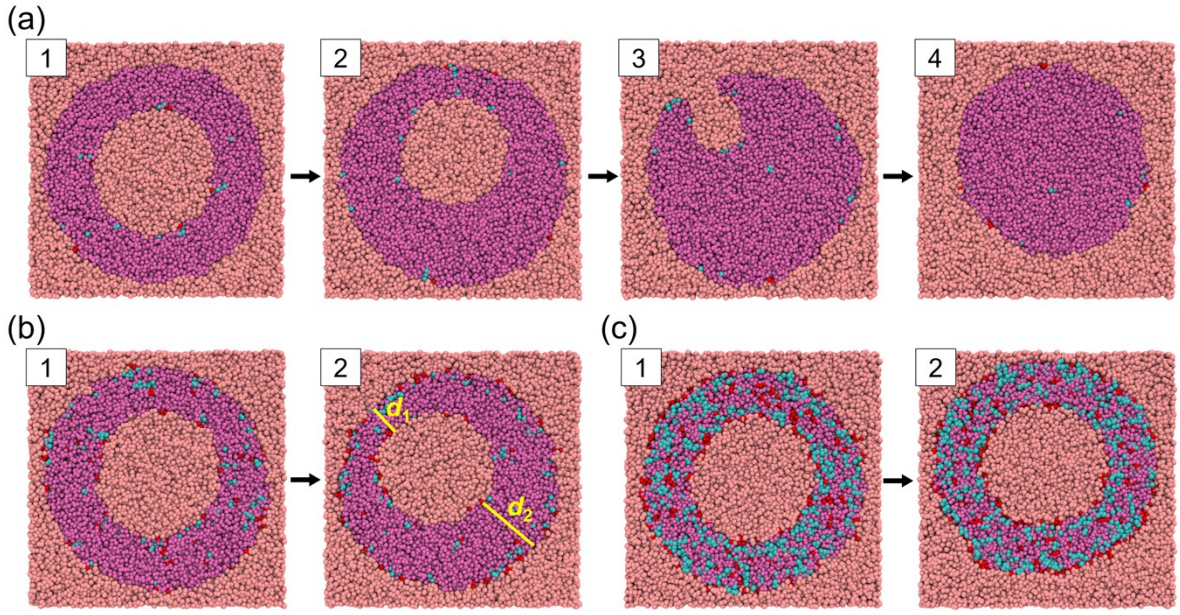

Fig. S2. Sequential sectional snapshots of the double emulsions with different A_4B_8 diblock copolymer concentrations ($\varphi_{polymer}$). (a) $\varphi_{polymer} = 0.02$, and the simulation times are 0, 2.0×10^5, 5.0×10^5, and 1.0×10^6 steps, respectively. (b) $\varphi_{polymer} = 0.10$, and the simulation times are 0 and 2.0×10^6 steps. d_1 and d_2 are the thickness of the oil phase in different positions. (c) $\varphi_{polymer} = 0.40$, and the simulation times are 0 and 2.0×10^6 steps. Color code: Water, pink; Oil, mauve; block A, red; block B, cyan.

S4. Dewetting of the double emulsion.

Table S1. Inner size (r_{in}), surface area (A) and the critical number of polymer chains (N_c) for different double emulsions.

r_{in}	6	8	10	12	14	16
A	452.4	804.2	1256.6	1809.6	2463.0	3217.0
N_c	1000	1500	2500	3500	5000	6500

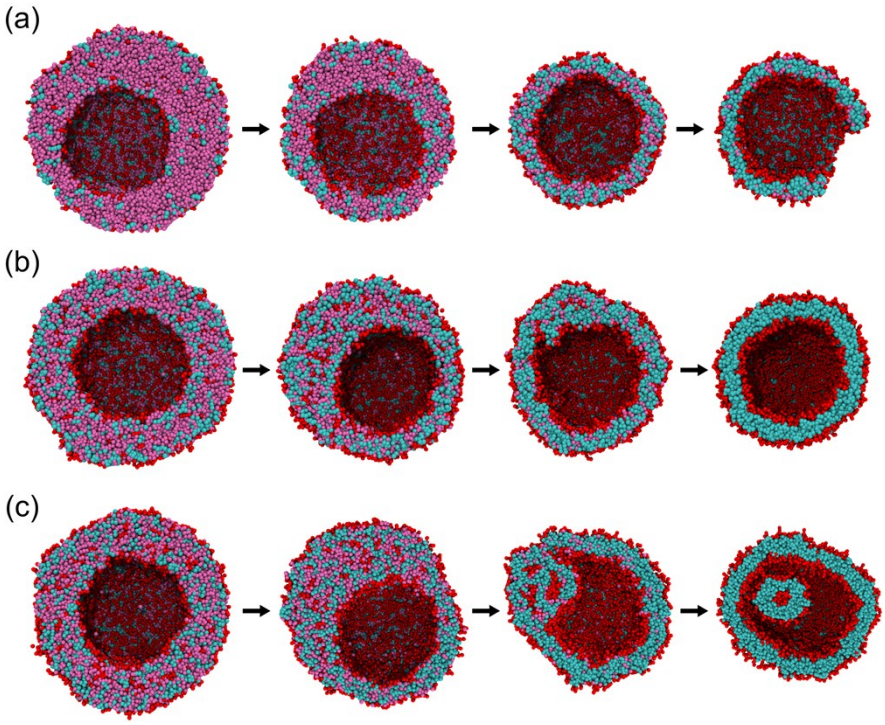

Fig. S3. Sequential sectional snapshots of the dewetting process with different polymer concentrations. (a) $N_{polymer}$ = 2000, and the simulation times are 0, 1.0 × 10^6, 2.0 × 10^6, and 2.5 × 10^6 steps, respectively. (b) $N_{polymer}$ = 3500, and the simulation times are 0, 1.0 × 10^6, 2.0 × 10^6, and 3.0 × 10^6 steps, respectively. (c) $N_{polymer}$ = 4500, and the simulation times are 0, 1.0 × 10^6, 1.6 × 10^6, and 3.0 × 10^6 steps, respectively. Water phase are omitted for clarity. Color code: Oil, mauve; block A, red; block B, cyan.

S5. Calculation of the degree of phase separation.

As shown in Fig. S5, the degree of phase separation (*dps*) of blocks B and C is defined as[6]

$$dps = 1 - \frac{\langle \rho_B \rho_C \rangle}{\sqrt{\langle \rho_B^2 \rangle \langle \rho_C^2 \rangle}}$$

where ρ_B and ρ_C are the number densities of beads B and C in the spherical space with each bead B or C as the origin and r_{cut} as the cutoff radius. $\langle \cdots \rangle$ is the ensemble average. $dps = 0$ means beads B and C mix perfectly, while $dps = 1$ is for complete phase separation.

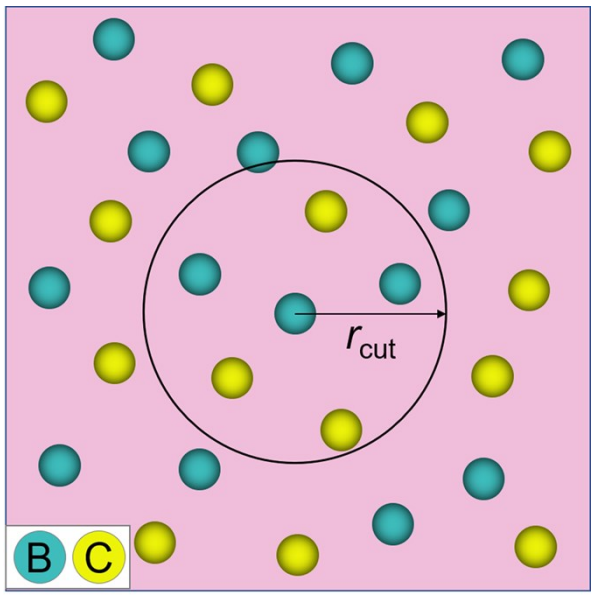

Fig. S4. Schematic diagram for the calculation of the degree of phase separation. Beads B and C are in cyan and yellow, respectively.

S6. Co-assembly of AB/AC blends through double emulsion.

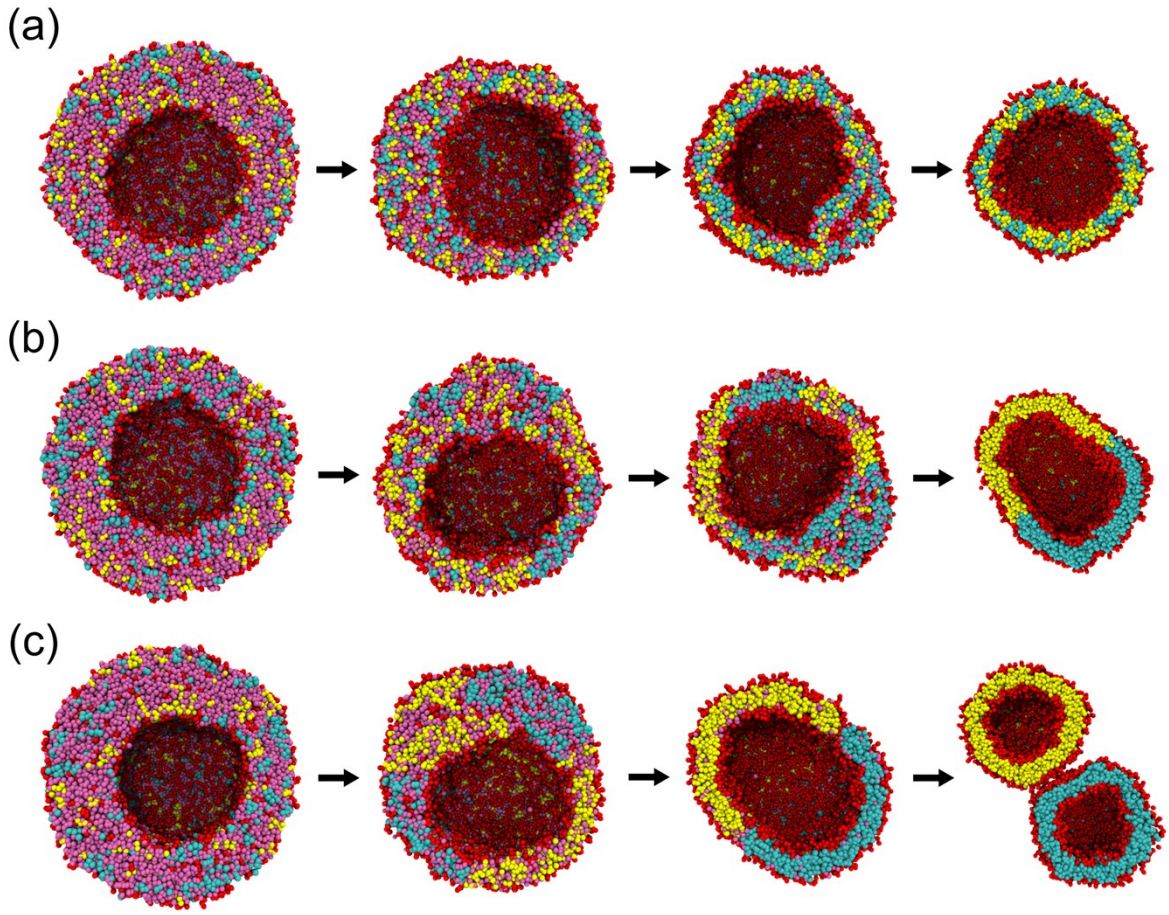

Fig. S5. Sequential sectional snapshots of the formation of two-component polymersomes with different values of a_{BC}. (a) a_{BC} = 25, and the simulation times are 0, 0.8 × 10^6, 1.2 × 10^6, and 2.0 × 10^6 steps, respectively. (b) a_{BC} = 30, and the simulation times are 0, 0.8 × 10^6, 1.2 × 10^6, and 2.0 × 10^6 steps, respectively. (c) a_{BC} = 40, and the simulation times are 0, 0.8 × 10^6, 1.2 × 10^6, and 2.0 × 10^6 steps, respectively. Water phase are omitted for clarity. Color code: Oil, mauve; block A, red; block B, cyan; block C, yellow.

S7. Co-assembly of AB/AC/BC blends through double emulsion.

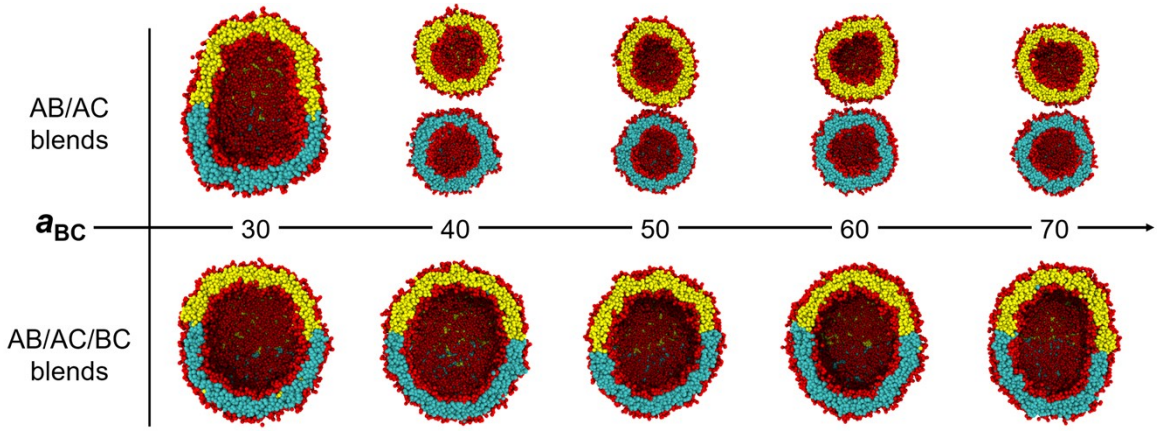

Fig. S6. Sectional snapshots of the vesicles obtained from AB/AC blends and AB/AC/BC blends with different values of a_{BC}. Color code: block A, red; block B, cyan; block C, yellow.

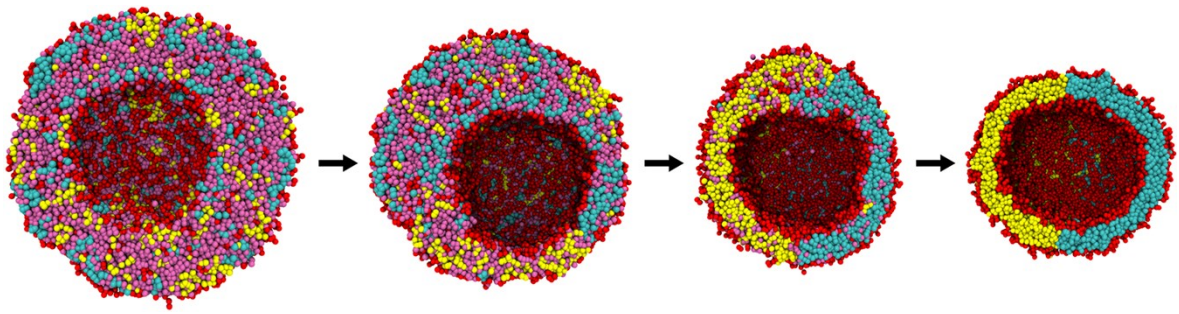

Fig. S7. Sequential sectional snapshots of the formation of Janus polymersome. The simulation times are 0, 0.6×10^6, 1.0×10^6, and 2.0×10^6 steps, respectively. Water phase are omitted for clarity. Color code: Oil, mauve; block A, red; block B, cyan; block C, yellow.

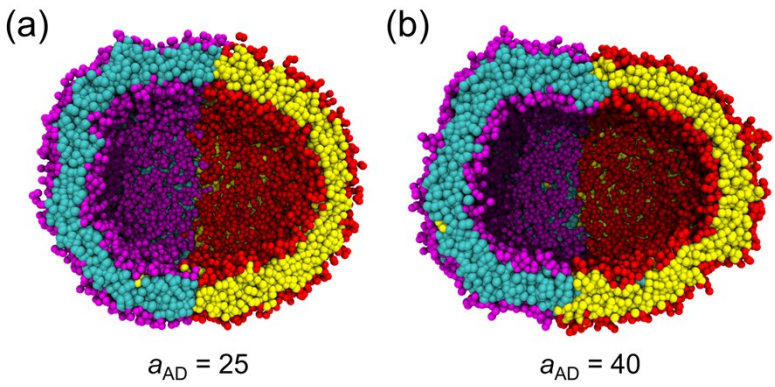

Fig. S8. Sectional snapshots of Janus polymersome formed through the co-assembly of AB/CD/BC blends with a_{AD} = 25 (a) and a_{AD} = 40 (b). Water phase are omitted for clarity. Color code: block A, red; block B, cyan; block C, yellow; block D, magenta.

S8. Effect of the number of BC.

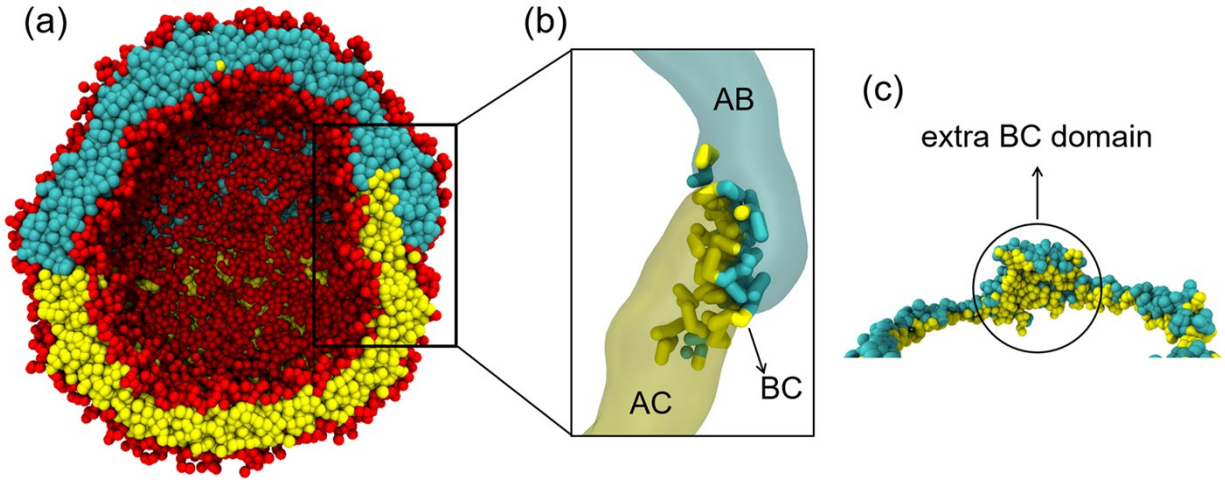

Fig. S9. (a) Sectional snapshot of the Janus polymersome obtained with N_{BC} = 285. (b) Enlarged detail the extra BC domain in the membrane. (c) Snapshot of the extra BC domain attached to the Janus ring. Color code: block A, red; block B, cyan; block C, yellow.

S9. Mean-square displacement curves of polymers.

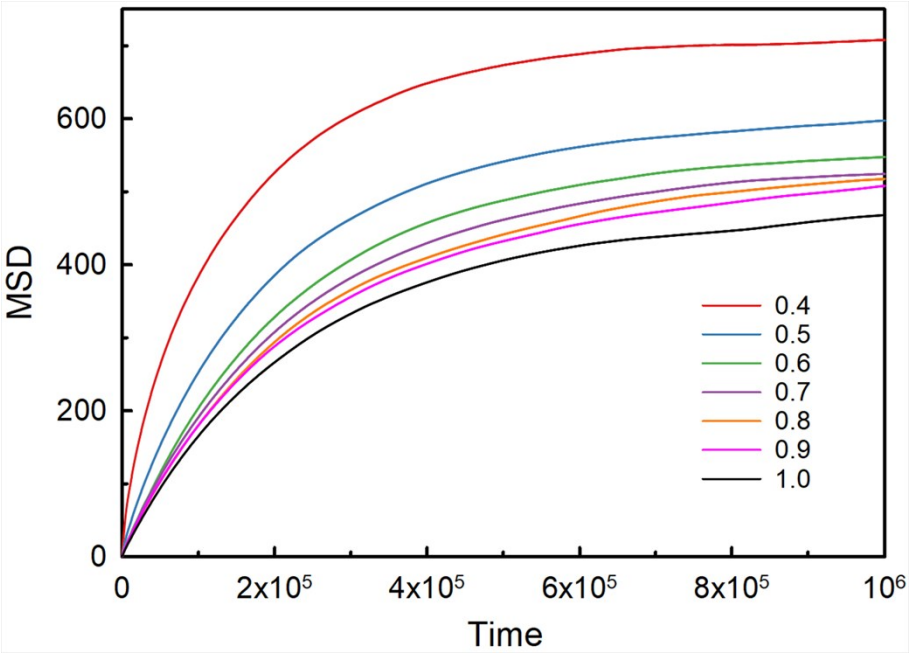

Fig. S10. Mean-square displacement (MSD) curves of polymers with different polymer concentrations.

S10. References.

(1) Groot, R. D.; Warren, P. B., Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation. *J. Chem. Phys.* **1997**, *107*, 4423-4435.

(2) Groot, R. D.; Rabone, K., Mesoscopic simulation of cell membrane damage, morphology change and rupture by nonionic surfactants. *Biophys. J.* **2001**, *81*, 725-736.

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(6) Lin, Y. J.; Jiménez-García, K.; Spielman, I. B., Spin–orbit-coupled Bose–Einstein condensates. *Nature* **2011**, *471*, 83-86.