Supplementary Information (SI) for Soft Matter.

Supplementary Material:

A Novel Microscopic Origin of Co-Nonsolvency

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I Details of the ternary Flory-Huggins theory

Here we describe how to calculate the free energy change (as well as its entropic and energetic contributions) during the liquid-liquid phase separation in the co-nonsolvency effect of homopolymer solutions using the ternary Flory-Huggins theory.

For the multi-chain system, in the framework of the Flory-Huggins theory, we may write the Helmholtz mixing free energy density for a homogeneous polymer solution in binary mixtures of S- and O-solvents as

$$\beta f = \frac{\phi_P}{N} ln\phi_P + \phi_S ln\phi_S + (1-\phi_P-\phi_S) ln(1-\phi_P-\phi_S) + \chi_{PS}\phi_P\phi_S \tag{1}$$

where k_B is the Boltzmann constant and T is the absolute temperature, ϕ_P and ϕ_S are the concentrations of polymer segments and S-solvent respectively, the concentration of O-solvent is thus $\phi_O=1-\phi_P-\phi_S$, N is the degree of polymerization of polymer, $\chi_{PS} = (z-2)\varepsilon_{PS} / k_B T$ is the Flory-Huggins parameter between monomer and S-solvent with ε_{PS} denoting the energy for each S-solvent/monomer contact and z=18 the lattice coordinate number for the single-site bond fluctuation model. Finally, the volumes of each monomer and each solvent molecular are set to be 1. The first three terms in Eq. (1) represent the mixing entropy and the last term denotes the enthalpy attraction between monomer and S-solvent. The competition between these two contributions determines whether a solution remains homogeneous or undergoes separation into coexisting phases. With Eq. (1), we may calculate the exchange chemical potential of polymer per monomer basis as

$$\frac{\mu_P}{k_B T} = \frac{1 + ln\phi_P}{N} - ln(1 - \phi_P - \phi_S) - 1 + \chi_{PS}\phi_P \tag{2}$$

and the exchange chemical potential of S-solvent as

$$\frac{\mu_S}{k_B T} = ln\phi_S - ln(1 - \phi_P - \phi_S) + \chi_{PS}\phi_P \tag{3}$$

The osmotic pressure is then given by

$$\beta\Pi = \frac{\phi_P}{N} - \phi_P - ln(1 - \phi_P - \phi_S) + \chi_{PS}\phi_P\phi_S \tag{4}$$

For appropriate parameters, a homopolymer solution may separate into an S-solvent-dilute phase (Phase I: with superscript I) and an S-solvent-concentrated phase (with superscript II). Denoting the concentration of species *i* in these two phases by ϕ_i^{I} and ϕ_i^{II} respectively, we can calculate the concentration by numerically solving the phase equilibrium conditions, $\mu_P(\phi_P^{\mathrm{I}}, \phi_S^{\mathrm{I}}) = \mu_P(\phi_P^{\mathrm{II}}, \phi_S^{\mathrm{II}})$, $\mu_S(\phi_P^{\mathrm{I}}, \phi_S^{\mathrm{I}}) = \mu_S(\phi_P^{\mathrm{II}}, \phi_S^{\mathrm{II}})$ and $\Pi(\phi_P^{\mathrm{I}}, \phi_S^{\mathrm{I}}) = \Pi(\phi_P^{\mathrm{II}}, \phi_S^{\mathrm{II}})$. We can use this method to construct the binodal in the polymer-S-solvent phase diagram.

On the other hand, if a system with initial concentrations of polymer and S-solvent being ϕ_P and ϕ_S is located in the phase separated region, it will separate into an S-solvent-dilute phase and a coexisting S-solvent-concentrated phase. Denoting the volume fraction of the S-solvent-dilute phase by *x*, the mass conservation law requires that $(1-x)\phi_i^{\mathrm{II}} + x\phi_i^{\mathrm{I}} = \phi_i$ with the concentrations of the *i*-th component in each of these two phases being ϕ_i^{I} and ϕ_i^{II} respectively. The difference in the Helmholtz free energy density is thus

$$\Delta f = xf(\phi_P^{\mathrm{I}}, \phi_S^{\mathrm{I}}) + (1-x) f(\phi_P^{\mathrm{II}}, \phi_S^{\mathrm{II}}) - f(\phi_P, \phi_S) \tag{5}$$

with *f* being given by Eq. (1).

Likewise, the energetic and entropic contributions in Δf are given respectively by

$$\Delta u = xu(\phi_P^{\mathrm{I}},\phi_S^{\mathrm{I}})+(1-x)u(\phi_P^{\mathrm{II}},\phi_S^{\mathrm{II}})-u(\phi_P,\phi_S) \tag{6}$$

and

$$\Delta s = xs(\phi_P^{\mathrm{I}},\phi_S^{\mathrm{I}})+(1-x)s(\phi_P^{\mathrm{II}},\phi_S^{\mathrm{II}})-s(\phi_P,\phi_S) \tag{7}$$

with u and s are given respectively by

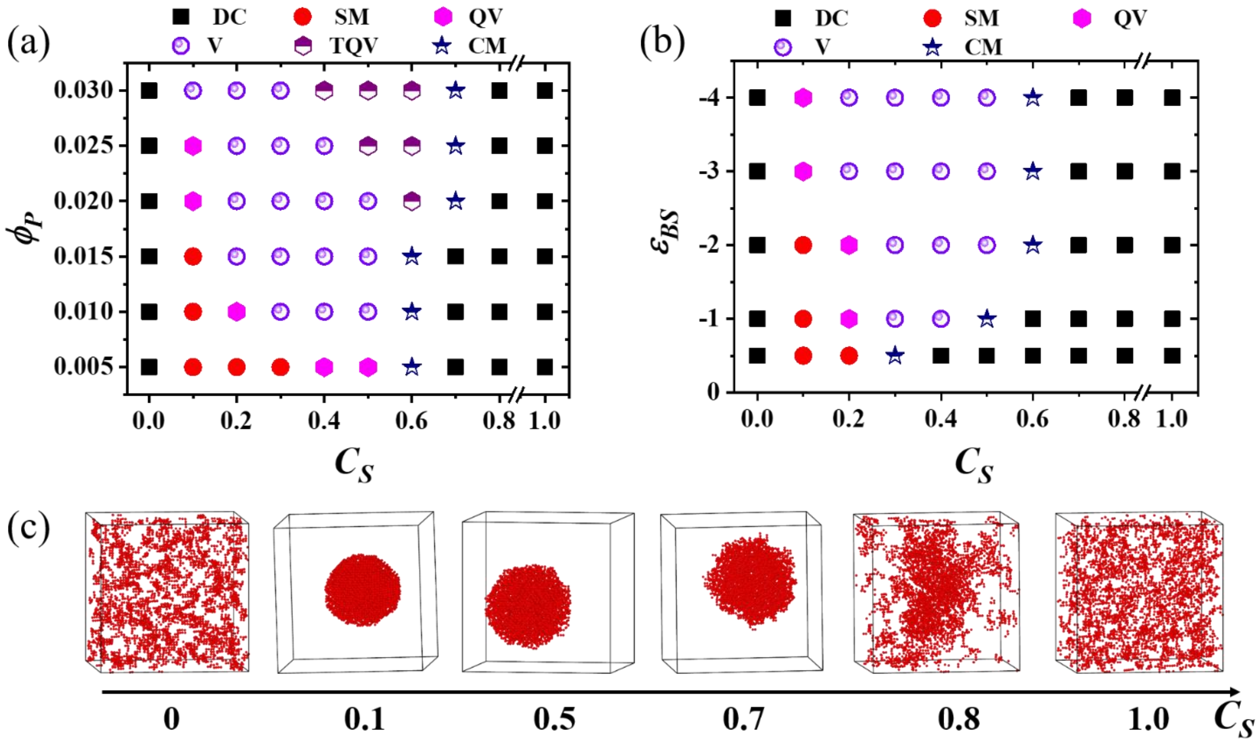
$$\beta u = \chi_{PS}\phi_P\phi_S \tag{8}$$

and

$$s/k_B = \frac{\phi_P}{N} ln\phi_P + \phi_S ln\phi_S + (1-\phi_P-\phi_S)ln(1-\phi_P-\phi_S) \tag{9}$$

To further evaluate the relative contributions of binary solvents in Δs, we also calculate the difference of mixing entropy density purely due to the binary solvents $\Delta s'$ in the same way as Δs with $s'/k_B = \phi_S ln\phi_S + (1-\phi_P-\phi_S)ln(1-\phi_P-\phi_S)$ by ignoring the first term in Eq. (9).

II Figures



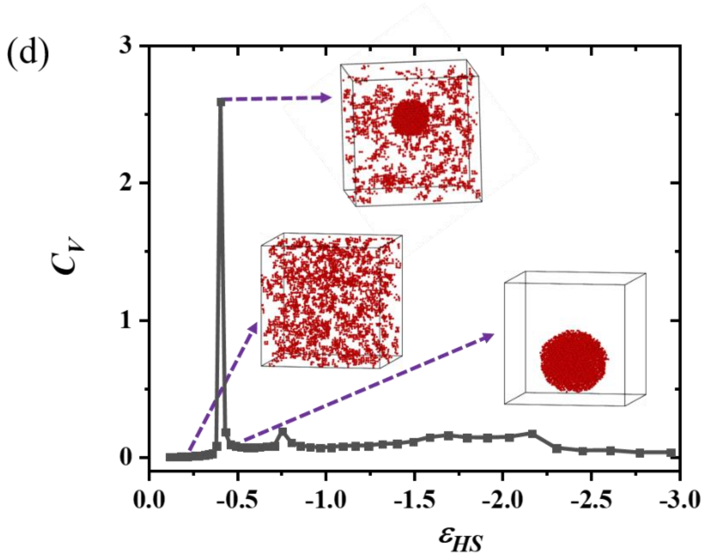


Figure S1 (a-c) The morphological phase diagrams of multi-chain systems. (a-b) For diblock copolymers, (a) in the C_S–ϕ_P plane at $\varepsilon_{BS} = -2$ and (b) in the C_S–ε_{BS} plane at $\phi_P = 0.01$. DC, SM, QV, V, TQV, and CM represent dispersed chains, spherical micelles, quasi-vesicles, vesicles, tubular quasi-vesicles, and compound micelles, respectively. (c) For homopolymers as a function of C_S at $C_P = 0.02$ and $\varepsilon_{HS} = -2.0$. (d) The specific heat curve in the space of ε_{HS} for multi-chain homopolymer systems with chain length $N = 10$, and $C_S = 0.1$, in the calculation, the effective temperature T' is related to ε_{HS} with $T' = 1/\varepsilon_{HS}$.

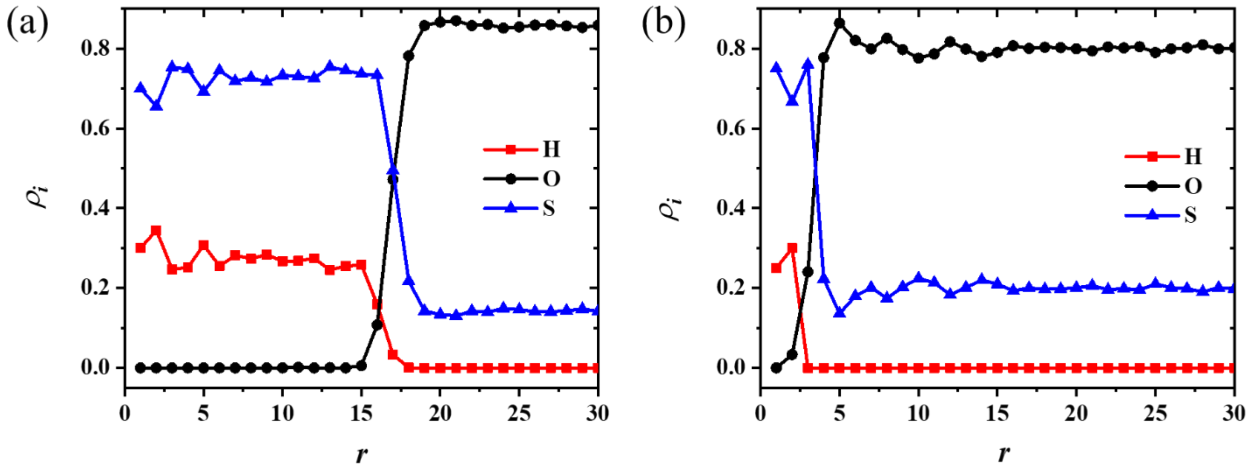


Figure S2 Typical radial density profiles for homopolymer systems with $C_S = 0.2$ and $\varepsilon_{HS} = -2.0$ of (a) multi-chains ($C_P = 0.02$) and (b) a single-chain.

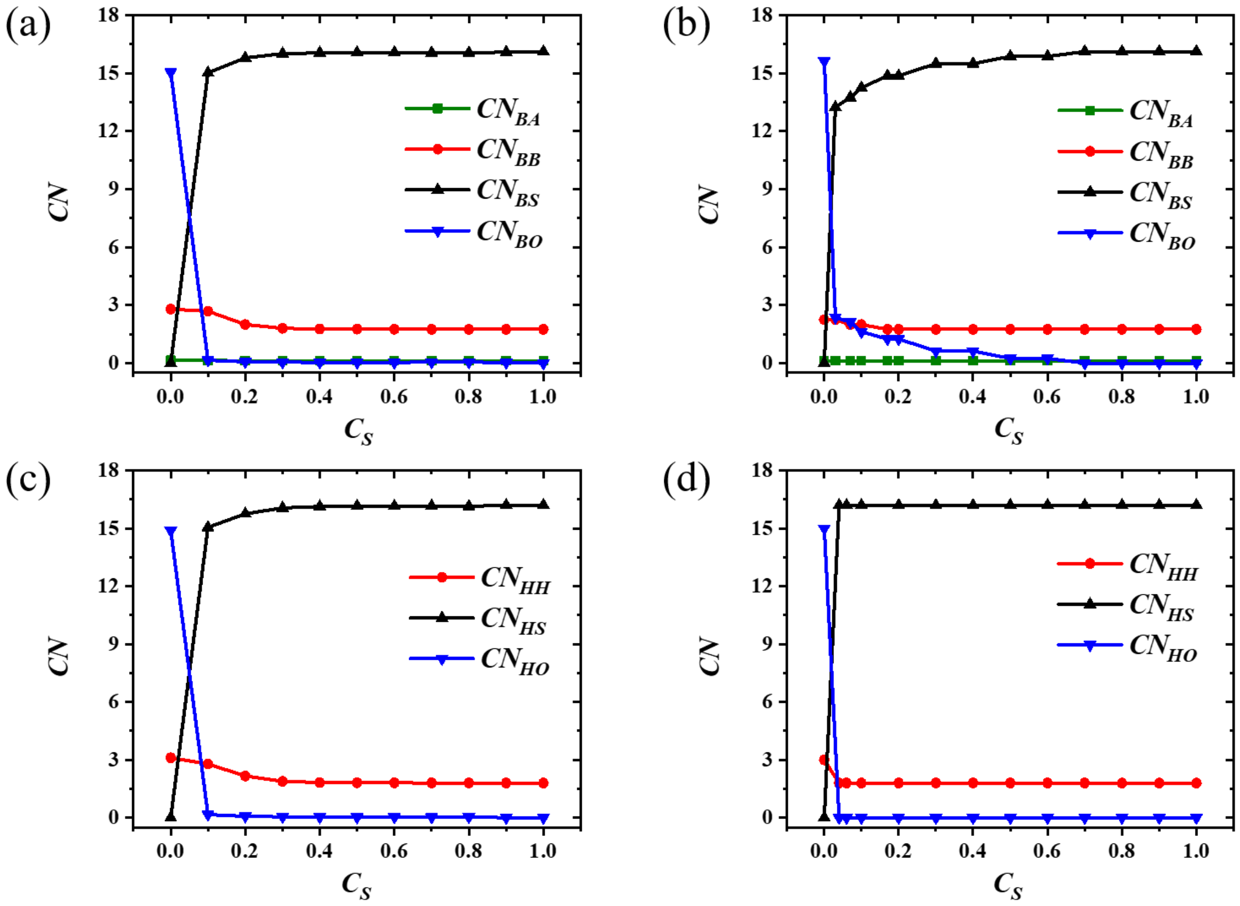


Figure S3 The C_S dependence of the average contact numbers of each B(H)-segment with all species in different systems with $\varepsilon_{BS} = \varepsilon_{HS} = -2.0$. (a, b) Copolymer with $f_A = 0.2$ and (c, d) homopolymer. (a, c) multi-chains ($C_P = 0.02$) and (b, d) a single-chain.

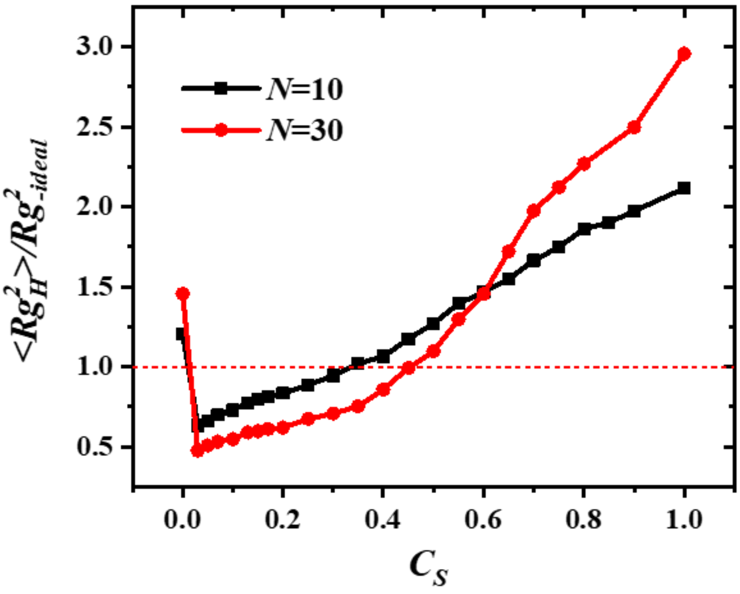


Figure S4 The C_S dependence of the normalized chain mean-square radius of gyration in single-chain homopolymer systems with $N = 10$ and $N = 30$.