I. SUPPORTING INFORMATION

A. Solvation free energy and its minimization procedure

Here we present the details of theoretical model omitted in the main text. We start from the solvation free energy of the polymer chain in the mixed solvent media

$$\Delta G_s = F_{id} + F_{ex} + PV_g - \mu_s N_s - \mu_c N_c,$$

where $V_g = 4\pi R_g^3/3$ is the volume of gyration of the polymer chain, R_g is the chain gyration radius, N_s and N_c are, respectively, the molecule numbers of the solvent and co-solvent in the gyration volume; F_{id} is the ideal free energy of the polymer chain and mixed solvent which can be calculated in the following way

$$F_{id} = \frac{9}{4}k_BT\left(\frac{6R_g^2}{Nb^2} + \frac{Nb^2}{6R_g^2}\right)$$
$$+N_sk_BT\left(\ln\frac{N_s\Lambda_s^3}{V_g} - 1\right) + N_ck_BT\left(\ln\frac{N_c\Lambda_c^3}{V_g} - 1\right), \tag{1}$$

where b is the bond length of the chain, k_B is the Boltzmann constant, N is the polymerization degree, T is the absolute temperature, Λ_s and Λ_c are the de Broglie wavelengths of the low-molecular weight species. The first term in (1) is the free energy of the ideal Gaussian polymer chain within the Fixman approximation [1–12]; P is the pressure imposed to the system which will be determined below. The interactions 'monomer-monomer', 'monomer-solvent', 'solvent-solvent', 'co-solvent-co-solvent', and 'solvent-co-solvent' are described by the WCA potentials

$$V_{ij}(r) = \left\{ \begin{array}{l} 4\epsilon_{ij}\left[\frac{1}{4} + \left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right], r < 2^{1/6}\sigma_{ij} \\ 0, r > 2^{1/6}\sigma_{ij} \end{array} \right\}.$$

Interaction monomer-co-solvent is described by the full Lennard-Jones potential

$$V_{pc}(r) = 4\epsilon_{pc}\left[\left(\frac{\sigma_{pc}}{r}\right)^{12} - \left(\frac{\sigma_{pc}}{r}\right)^{6}\right]. \tag{2}$$

Therefore, the excess free energy of polymer solution takes the form

$$F_{ex} = F_{ev} + F_{att}, \tag{3}$$

where F_{ev} is the contribution of the repulsive interactions in the gyration volume due to the excluded volume of the monomers and molecules of the low-molecular weight species which we determine through the Mansoori-Carnahan-Starling-Leland equation of state for the hard-spheres mixture (see below) with the effective diameters of species calculated in accordance with a well-known Barker-Henderson relation [14]:

$$d_i = \int_0^{2^{1/6}\sigma_{ii}} \left(1 - e^{-V_{ii}(r)/k_BT}\right) dr, \tag{4}$$

where $i = p, s, c$.

As it was mentioned in the main text, our model is fully corresponded to situation realized in MD simulation of Mukherji et al. [15]. Thereby, we neglected the attractive interactions 'solvent-solvent', 'solvent-co-solvent', 'solvent-monomer', 'co-solvent-co-solvent', and 'monomer-monomer', taking into account attractive interaction only between polymer and co-solvent within the standard mean-field approximation:

$$F_{att} = \rho_p\rho_c V_g \int d\mathbf{r}\Phi_{pc}(|\mathbf{r}|) = -\frac{32}{9}\sqrt{2}\pi\epsilon_{pc}\sigma_{pc}^3\rho_p\rho_c V_g, \tag{5}$$

where $V_g = 4\pi R_g^3/3$ is the gyration volume, ρ_p and ρ_c are, respectively, the number densities of monomers and co-solvent in the gyration volume; attractive part of the full Lennard-Jones potential according to the Weeks-Chandler-Anderson scheme [14] is

$$\Phi_{pc}(r) = \begin{cases} -\epsilon_{pc}, r < 2^{1/6}\sigma_{pc} \\ 4\epsilon_{pc}\left[\left(\frac{\sigma_{pc}}{r}\right)^{12} - \left(\frac{\sigma_{pc}}{r}\right)^6\right], r > 2^{1/6}\sigma_{pc} \end{cases}$$

.

Choosing the local mole fraction of co-solvent x_1 in the gyration volume and the gyration radius R_g as the order parameters, one can rewrite the solvation free energy in the following way

$$\Delta G_s(R_g, x_1) = \frac{9}{4}k_BT\left(\frac{6R_g^2}{Nb^2} + \frac{Nb^2}{6R_g^2}\right)$$
$$+\rho_1 V_g k_BT\left(x_1\left(\ln\left(\rho_1 x_1\Lambda_c^3\right) - 1\right) + (1 - x_1)\left(\ln\left(\rho_1(1 - x_1)\Lambda_s^3\right) - 1\right)\right)$$
$$+V_g\left(P(\rho, x, T) + f_{ex}(\rho, x_1, \rho_p, T) - \rho_1\left(\mu_s(\rho, x, T)(1 - x_1) + \mu_c(\rho, x, T)x_1\right)\right), \tag{6}$$

where $\rho_p = N/V_g$ is a monomer number density and $f_{ex}(\rho, x_1, \rho_p, T)$ is a density of excess free energy which has a form

$$f_{ex}(\rho, x_1, \rho_p, T) = \rho k_BTA(\rho, x_1, \rho_p) - \frac{32}{9}\sqrt{2}\pi\epsilon_{pc}\sigma_{pc}^3\rho_p\rho_1 x_1, \tag{7}$$

where the following short-hand notations are introduced

$$A(\rho, x_1, \rho_p) = -\frac{3}{2}\left(1 - y_1(\rho, x_1, \rho_p) + y_2(\rho, x_1, \rho_p) + y_3(\rho, x_1, \rho_p)\right) + \frac{3y_2(\rho, x_1, \rho_p) + 2y_3(\rho, x_1, \rho_p)}{1 - \xi(\rho, x_1, \rho_p)}$$

$$+\frac{3\left(1-y_1(\rho,x_1,\rho_p)-y_2(\rho,x_1,\rho_p)-\frac{y_3(\rho,x_1,\rho_p)}{3}\right)}{2(1-\xi(\rho,x_1,\rho_p))^2}+(y_3(\rho,x_1,\rho_p)-1)\ln(1-\xi(\rho,x_1,\rho_p)), \quad (8)$$

$$y_1(\rho,x_1,\rho_p)=\Delta_{cp}\frac{d_c+d_p}{\sqrt{d_pd_c}}+\Delta_{sp}\frac{d_s+d_p}{\sqrt{d_pd_s}}+\Delta_{sc}\frac{d_s+d_c}{\sqrt{d_cd_s}}, \quad (9)$$

$$y_2(\rho,x_1,\rho_p)=\frac{1}{\xi}\left(\frac{\xi_c}{d_c}+\frac{\xi_s}{d_s}+\frac{\xi_p}{d_p}\right)\left(\Delta_{cp}\sqrt{d_cd_p}+\Delta_{sp}\sqrt{d_sd_p}+\Delta_{sc}\sqrt{d_sd_c}\right), \quad (10)$$

$$y_3(\rho,x_1,\rho_p)=\left(\left(\frac{\xi_c}{\xi}\right)^{2/3}\left(\frac{\rho_1x_1}{\rho}\right)^{1/3}+\left(\frac{\xi_s}{\xi}\right)^{2/3}\left(\frac{\rho_1(1-x_1)}{\rho}\right)^{1/3}+\left(\frac{\xi_p}{\xi}\right)^{2/3}\left(\frac{\rho_p}{\rho}\right)^{1/3}\right)^3, \quad (11)$$

$$\Delta_{sp}=\frac{\sqrt{\xi_s\xi_p}}{\xi}\frac{(d_s-d_p)^2}{d_sd_p}\frac{\sqrt{\rho_1\rho_p(1-x_1)}}{\rho},\ \Delta_{cp}=\frac{\sqrt{\xi_c\xi_p}}{\xi}\frac{(d_c-d_p)^2}{d_cd_p}\frac{\sqrt{\rho_1\rho_px_1}}{\rho}, \quad (12)$$

$$\Delta_{cs}=\frac{\sqrt{\xi_c\xi_s}}{\xi}\frac{(d_c-d_s)^2}{d_cd_s}\frac{\rho_1}{\rho}\sqrt{x_1(1-x_1)} \quad (13)$$

$$\xi_s=\frac{\pi\rho_1(1-x_1)d_s^3}{6},\ \xi_c=\frac{\pi\rho_1x_1d_c^3}{6},\ \xi_p=\frac{\pi\rho_pd_p^3}{6}, \quad (14)$$

$$\xi=\xi(\rho,x_1,\rho_p)=\xi_s+\xi_c+\xi_p; \quad (15)$$

the local solvent composition x_1 in the gyration volume is introduced by the following relations

$$\rho_s=\frac{N_s}{V_g}=\rho_1(1-x_1),\ \rho_c=\frac{N_c}{V_g}=\rho_1x_1. \quad (16)$$

The local number density ρ_1 of binary mixture can be related with the bulk number density ρ and the monomer number density ρ_p through the incompressibility condition $\rho_1=\rho-\rho_p$.

The pressure in the bulk solution P in our model is determined by the the Mansoori-Carnahan-Starling-Leland equation of state:

$$\frac{P(\rho,x,T)}{\rho k_BT}=\frac{1+\xi(\rho,x,0)+\xi^2(\rho,x,0)-3\xi(\rho,x,0)(y_1(\rho,x,0)+y_2(\rho,x,0)\xi(\rho,x,0)+\frac{\xi^2(\rho,x,0)y_3(\rho,x,0)}{3})}{(1-\xi(\rho,x,0))^3}. \quad (17)$$

The chemical potentials of the solvent species can be calculated by the following obvious thermodynamic relations

$$\mu_c(\rho,x,T)=\frac{1}{\rho}\left(P(\rho,x,T)+f(\rho,x,T)+(1-x)\left(\frac{\partial f(\rho,x,T)}{\partial x}\right)_{\rho,T}\right), \quad (18)$$

$$\mu_s(\rho,x,T)=\frac{1}{\rho}\left(P(\rho,x,T)+f(\rho,x,T)-x\left(\frac{\partial f(\rho,x,T)}{\partial x}\right)_{\rho,T}\right), \quad (19)$$

where $f(\rho, x, T)$ is a density of Helmholtz free energy of the bulk solution which can be calculated as

$$f(\rho, x, T) = \rho k_B T \left(x \ln \left(\rho \Lambda_c^3 x \right) + (1-x) \ln \left(\rho \Lambda_s^3 (1-x) \right) \right) + \rho k_B T A(\rho, x, 0). \quad (20)$$

B. Connection with Flory theory

Here we present how our approach can be related to the classic Flory theory of a single flexible polymer chain in a good solvent. We rewrite the Gibbs free energy as follows:

$$\Delta G_s = \frac{9}{4} k_B T \left(\frac{6R_g^2}{Nb^2} + \frac{Nb^2}{6R_g^2} \right) + V_g \left(f_{mix} + P - \mu_s \rho_1 (1-x_1) - \mu_c \rho_1 x_1 \right), \quad (21)$$

where f_{mix} is the free energy density of three-component mixture of unbound particles. We consider the regime of expanded coil, i.e., when $6R_g^2/(Nb^2) \gg 1$ and $x_1 \simeq x$. In this case, the internal monomer number density is small, i.e $\rho_p \ll \rho$, so that $\rho_1 \simeq \rho$. Hence, we get in this approximation

$$f_{mix}(\rho, x_1, \rho_p, T) = f(\rho, x, T) + \frac{1}{2} B(\rho, x, T) \rho_p^2 + O(\rho_p^3), \quad (22)$$

where the second virial coefficient

$$B(\rho, x, T) = \frac{\partial^2 f_{mix}(\rho, x, 0, T)}{\partial \rho_p^2} \quad (23)$$

is introduced and $f(\rho, x, T)$ is determined by (20). Further, taking into account that $f + P - \mu_s \rho (1-x) - \mu_c \rho x = 0$, we arrive at the relation for the single chain free energy [16] which depends on the state parameters of solvent mixture only through the second virial coefficient of monomers B:

$$\Delta G_s = F_p(R_g) = \frac{9}{4} k_B T \left(\frac{6R_g^2}{Nb^2} + \frac{Nb^2}{6R_g^2} \right) + \frac{B(\rho, x, T) N^2}{2V_g}. \quad (24)$$

Minimization of the polymer free energy with respect to the gyration radius yields the classic Flory result

$$R_g \sim b^{2/5} B^{1/5} N^{3/5}. \quad (25)$$

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