Supporting Information

Effects of cosolvent partitioning on conformational transitions and tethered chain flexibility in spherical polymer brush

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1. Chemical potential of the monomer μ_M and interaction parameter χ^*_{eff}

The density of the interaction free energy per chain f_{Int} is given by

$$f_{Int} = \phi_A \ln\phi_A + (1-\phi_A-\phi_P)\ln(1-\phi_A-\phi_P) - \chi_A\phi_P(\phi_A+2\phi_B{}^2) - \frac{1}{2}\chi_{eff}\phi_P{}^2 \qquad \text{(S1)}$$

where the interaction parameter between monomers χ_{eff} is given by

$$\chi_{eff} = -12.974 + 0.0449597T + 17.92\phi_P - 0.056944\phi_P T + 14.814\phi_P{}^2 - 0.051419\phi_P{}^2 T \qquad \text{(S2)}$$

The chemical potential of the monomer μ_M is defined by

$$\mu_M = \frac{\partial F_{Int}}{\partial \phi_P} = k_B T V \frac{\partial f_{Int}}{\partial \phi_P} \qquad \text{(S3)}$$

Note that the partial derivative used to determine μ_M should be carried out with respect to the degree of polymerization *N*, rather than the volume fraction of the monomer ϕ_P. Thus, $f_{Int}(\phi_P)$ must be changed to $f_{Int}(V, N)$.

Substituting $\phi_p = a^3 N / V$ into eqn (S1), we obtain μ_M through the thermodynamic derivative of eqn (S3)

$$\mu_M = Vk_BT\frac{\partial f_{Int}(V,N)}{\partial N} = Vk_BT[(1-\phi_A-\frac{a^3N}{V})\frac{1}{1-\phi_A-\frac{a^3N}{V}}(-\frac{a^3}{V})$$
$$-\frac{a^3}{V}ln(1-\phi_A-\frac{a^3N}{V})+\chi_A\frac{a^3}{V}(\phi_A+2\phi_B{}^2) \tag{S4}$$
$$+\frac{1}{2}25.894(\frac{a^3N}{V})\frac{a^3}{V}-\frac{1}{2}0.0899194(\frac{a^3N}{V})\frac{a^3}{V}T-\frac{1}{2}53.76(\frac{a^3N}{V})^2\frac{a^3}{V}$$
$$+\frac{1}{2}0.170832(\frac{a^3N}{V})^2\frac{a^3}{V}T-\frac{1}{2}59.256(\frac{a^3N}{V})^3\frac{a^3}{V}+\frac{1}{2}0.205676(\frac{a^3N}{V})^3\frac{a^3}{V}T]$$

Substituting $\phi_p = a^3N/V$ into eqn (S4) and rearranging the consequent, we have

$$\frac{\mu_M}{k_BTa^3} = -1-\ln(1-\phi_A-\phi_P)-\chi_A(\phi_A+2\phi_B{}^2)+\frac{1}{2}\chi_{eff}^{*}\phi_p \tag{S5}$$

where the interaction parameter between monomers χ_{eff}^{*} is given by

$$\chi_{eff}^{*} = 25.894-0.0899194T-53.76\phi_P+0.170832\phi_PT-59.256\phi_P{}^2+0.205676\phi_P{}^2T \tag{S6}$$

2. Osmotic pressure of the brush Π_{Brush} and interaction parameter χ_{eff}^{**}

The free energy of the spherical brush per chain F_{Brush} is given by

$$\frac{F_{Brush}}{k_BT} = \frac{F_{Int}}{k_BT}+\frac{F_{Elas}}{k_BT}$$
$$= V[\phi_A\ln\phi_A+(1-\phi_A-\phi_P)\ln(1-\phi_A-\phi_P)-\chi_A\phi_P(\phi_A+2\phi_B{}^2)-\frac{1}{2}\chi_{eff}\phi_P{}^2] \tag{S7}$$
$$+\frac{3\pi^4H^5S}{320a^7p^2\tau N^4}(1+\frac{5H}{4R}+\frac{3H^2}{7R^2})$$

where $\phi_A = \frac{a_C{}^3n_A}{V}$, $\phi_B = \frac{a_C{}^3n_B}{V}$, and $\phi_P = \frac{a^3N}{V}$.

The osmotic pressure in the polymer brush Π_{Brush} is defined by

$$\frac{\Pi_{Brush}}{k_BT} = -\frac{\partial F_{Brush}}{k_BT\partial V} = -\left(\frac{\partial F_{Int}}{k_BT\partial V}+\frac{\partial F_{Elas}}{k_BT\partial V}\right) \tag{S8}$$

The interaction term $\frac{\partial F_{Int}}{k_BT\partial V}$ is obtained by

$$\frac{\partial F_{Int}}{k_B T\partial V} = \ln(1-\frac{a_c{}^3 n_A}{V}-\frac{a^3 N}{V})+\frac{a^3 N}{V}+\chi_A a^3 N[\frac{a_c{}^3 n_A}{V^2}+4\frac{(a_c{}^3 n_B)^2}{V^3}]$$
$$-\frac{1}{2}12.947\frac{(a^3N)^2}{V^2}+\frac{1}{2}0.0449597\frac{(a^3N)^2}{V^2}T+\frac{1}{2}35.84\frac{(a^3N)^3}{V^3}$$
$$-\frac{1}{2}0.113888\frac{(a^3N)^3}{V^3}T+\frac{1}{2}44.442\frac{(a^3N)^4}{V^4}-\frac{1}{2}0.154257\frac{(a^3N)^4}{V^4}T \quad \text{(S9)}$$

Substituting $\phi_A = \frac{a_C{}^3 n_A}{V}$, $\phi_B = \frac{a_C{}^3 n_B}{V}$, and $\phi_P = \frac{a^3 N}{V}$ into eqn (S9), we have

$$\frac{\Pi_{Int}}{k_B T} = -\frac{\partial F_{Int}}{k_B T\partial V} = -ln(1-\phi_A-\phi_P)-\phi_P-\chi_A\phi_P(\phi_A+4\phi_B{}^2)$$
$$-\frac{1}{2}[-12.947\phi_P{}^2+0.0449597\phi_P{}^2T+35.84\phi_P{}^3$$
$$-0.113888\phi_P{}^3T+44.442\phi_P{}^4-0.154257\phi_P{}^4T] \quad \text{(S10)}$$

The rearrangement of eqn (S10) leads to

$$\frac{\Pi_{Int}}{k_B T} = -\frac{\partial F_{Int}}{k_B T\partial V} = -ln(1-\phi_A-\phi_P)-\phi_P-\chi_A\phi_P(\phi_A+4\phi_B{}^2)-\frac{1}{2}\chi_{eff}^{**}\phi_P{}^2 \quad \text{(S11)}$$

where the interaction parameter between monomers χ_{eff}^{**} is given by

$$\chi_{eff}^{**} = -12.974+0.0449597T+35.84\phi_P-0.113888\phi_P T+44.442\phi_P{}^2-0.154257\phi_P{}^2T \quad \text{(S12)}$$

The elastic term $\frac{\partial F_{Elas}}{k_B T\partial V}$ is obtained by

$$\frac{\partial F_{Elas}}{k_B T\partial V} = \frac{\partial F_{Elas}}{k_B TS\partial H}$$
$$= \frac{3\pi^4 H^4}{64a^7 p^2\tau N^4}(1+\frac{3H}{2R}+\frac{3H^2}{5R^2}) \quad \text{(S13)}$$

and then

$$\frac{\Pi_{Elas}}{k_B T} = -\frac{3\pi^4 H^4}{64a^7 p^2\tau N^4}(1+\frac{3H}{2R}+\frac{3H^2}{5R^2}) \quad \text{(S14)}$$

Finally, the osmotic pressure in the spherical brush Π_{Brush} is

$$\frac{\Pi_{Brush}}{k_B T} = -\chi_A\phi_P(\phi_A+4\phi_B{}^2)-\ln(1-\phi_P-\phi_A)-\phi_P-\frac{1}{2}\chi_{eff}^{**}\phi_P{}^2$$
$$-\frac{3\pi^4 H^4}{64p^2a^7\tau N^4}(1+\frac{3H}{2R}+\frac{3H^2}{5R^2}) \quad \text{(S15)}$$

References

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