Supplementary Materials for

Folding Behaviors of Two-Dimensional Flexible Polymers

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This PDF file includes:

Supplementary Text 1

FIG. S1 to FIG. S3

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Details of simulation methods

Dissipative Particle Dynamics (DPD) is a coarse-grained molecular dynamics (MD) method that employs a momentum-conserving thermostat and soft repulsive interactions among beads to represent the clusters of molecules [1-3]. This approach allows the simulation of physical phenomena occurring on relatively large temporal and spatial scales and has proven to be particularly useful in studying the general properties of macromolecular systems [4-7]. Furthermore, the force depends only on the difference in bead position and velocity, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, which guarantees Galilean invariance [7],

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i \tag{S1}$$

and

$$m\frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i, \tag{S2}$$

where $\mathbf{r}_i$, $\mathbf{v}_i$ and $\mathbf{f}_i$ are, respectively, the position, velocity and force on the i-th bead with mass m at time t. The time evolution of the interacting beads obeys Newton's equations of motion. Espanol and Warren formulate the DPD model in terms of a stochastic differential equation [6],

$$f_i = \frac{d\mathbf{v}_i}{dt} = \sum_{j\neq i}\mathbf{F}_{ij}^{\mathrm{C}} + \sum_{j\neq i}\mathbf{F}_{ij}^{\mathrm{D}} + \sum_{j\neq i}\mathbf{F}_{ij}^{\mathrm{R}}. \tag{S3}$$

The right-hand side of Eq. (S3) amounts to the total force on the bead i due to pair-wise interactions with other beads in the system via conservative, $\mathbf{F}_{ij}^{\mathrm{C}}$, dissipative, $\mathbf{F}_{ij}^{\mathrm{D}}$, and random, $\mathbf{F}_{ij}^{\mathrm{R}}$, forces, which vanish beyond an interparticle distance $\mathbf{r}_{ij} = r_c$. The conservative force is a soft repulsion acting along the line of bead centers and is given by

$$\mathbf{F}_{ij}^{\mathrm{C}} = \begin{cases} \alpha_{ij}(1 - r_{ij}/r_c)\boldsymbol{e}_{ij}, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c, \end{cases} \tag{S4}$$

where α_{ij} is a maximum repulsion between beads i and j, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$, $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$. Note that, if species i and j are fairly compatible, $\alpha_{ij} = 25$. As incompatibility between i and j increases, α_{ij} increases. The solvent environment is changed by only tuning the interaction parameter α_{PS} (P denotes the 2D polymer and S denotes the solvent) in this letter. The random and dissipative forces constitute the DPD thermostat and are given by

$$\mathbf{F}_{ij}^{\mathrm{D}} = -\gamma\omega^{D}(r_{ij})(\mathbf{v}_{ij}\cdot\boldsymbol{e}_{ij})\boldsymbol{e}_{ij} \tag{S5}$$

and

$$\mathbf{F}_{ij}^{\mathrm{R}} = \sigma\omega^{R}(r_{ij})\zeta_{ij}\Delta t^{-1/2}\boldsymbol{e}_{ij}, \tag{S6}$$

with $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, ζ_{ij} is a symmetric random number with zero mean and unit variance. γ and σ are coefficients of the dissipative and random forces, which are related via the fluctuation-dissipation theorem [4]

$$\sigma^2 = 2\gamma k_B T, \tag{S7}$$

where k_B is the Boltzmann constant and T is the absolute temperature of the system. $\omega^D(r_{ij})$ and $\omega^R(r_{ij})$ are weight functions, defined as [3]

$$\omega^{\mathrm{D}}(r_{ij}) = [\omega^{\mathrm{R}}(r_{ij})]^2 = \begin{cases} (1 - r_{ij}/r_c)^2, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c. \end{cases} \tag{S8}$$

These forces are of short-range with a fixed cutoff distance r_c. Similar to MD simulations, DPD can capture the time evolution of a 2D polymer system through the numerical integration of the above equations of motion. The bonds between the beads in the polymer are described by the harmonic spring potential

$$U_{\mathrm{bond}}(r) = \frac{1}{2}k_b(r - r_0)^2. \tag{S9}$$

Here k_b is the bond force constant and r_0 is the equilibrium bond length. k_b and r_0 are set to 4.0 and 0.0. 2D polymers are flexible without angle bending potential.

In the standard DPD method, molecules are reduced by combining several atoms or groups of atoms into coarse-grained (CG) beads. We use coarse-grained beads to form a square network to simulate a single-layer 2D polymer. We then put the constructed single-layer 2D polymer and solvent beads S into 3D simulation boxes of different sizes to simulate and calculate the radius of gyration (R_g). The minimum size of the simulation box should be greater than twice the radius of gyration, and the number density ρ of the box is 3. In our simulations, we set the time step $\Delta t = 0.04$, a cutoff distance of $r_c = 1.0$, a mass of $m = 1.0$ and a temperature of $k_B T = 1.0$.

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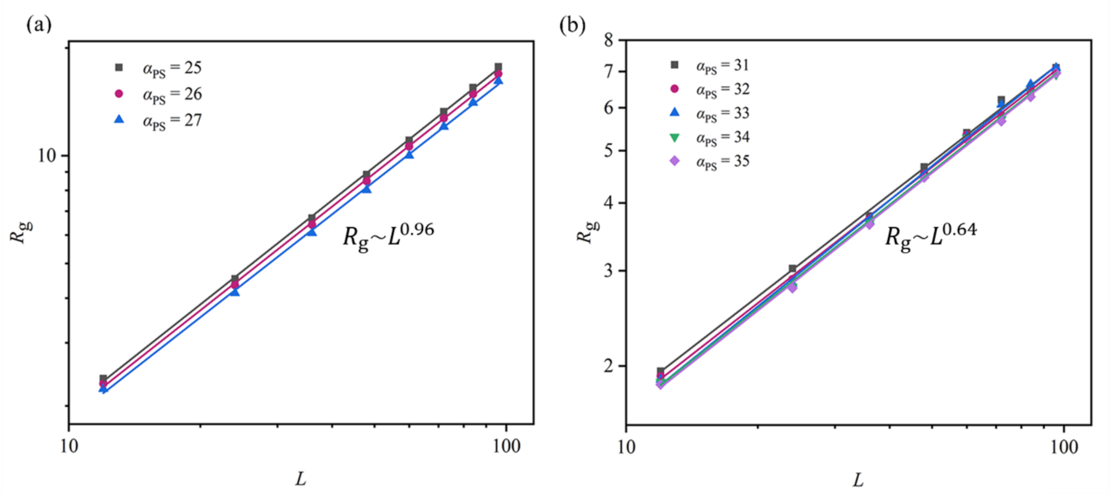

FIG. S1. The fitting relationship between the radius of gyration R_g and the size of 2D polymer L for various solvent conditions. (a) The fitting relationship at α_{PS} = 25, 26 and 27. (b) The fitting relationship for α_{PS} ranging from 31 to 35.

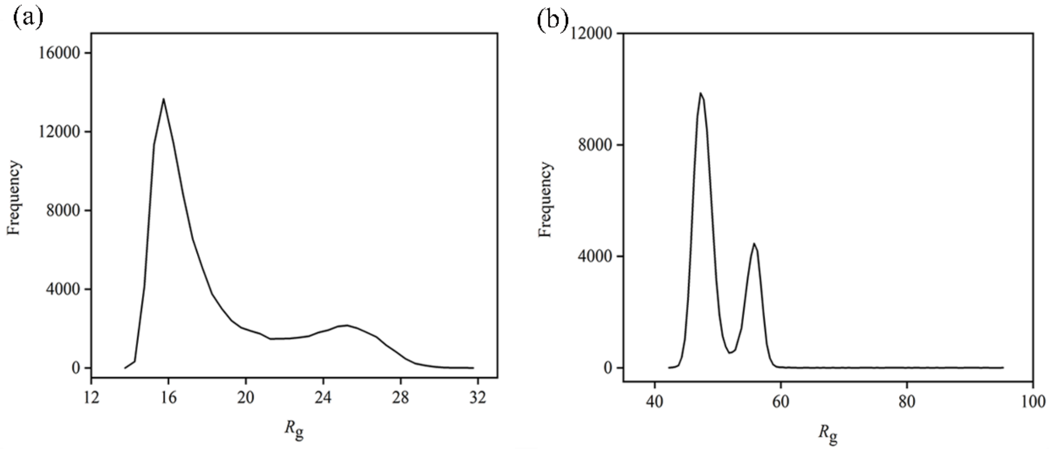

FIG. S2. The frequency distribution of the radius of gyration R_g when $\alpha_{\mathrm{PS}} = 29$. (a) When $\alpha_{\mathrm{PS}} = 29$, the frequency distribution of R_g when L value is 36. (b) When $\alpha_{\mathrm{PS}} = 29$, the frequency distribution of R_g when L value is 78.

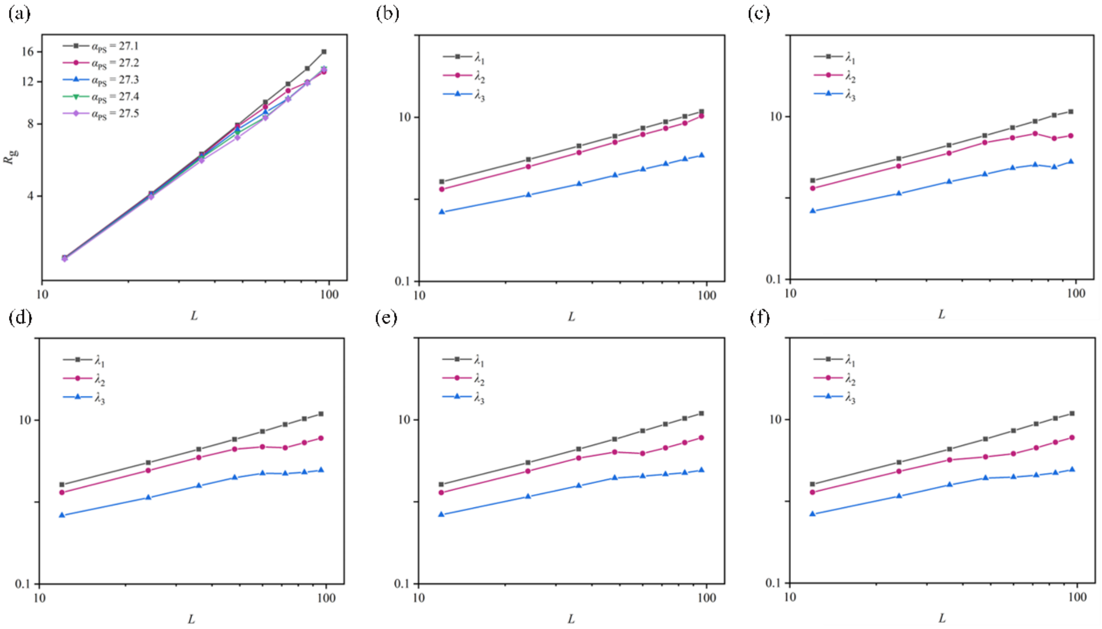

FIG. S3. The relationship of radius of gyration R, the eigenvalues of the radius of gyration tensor λ and the size of 2D polymer L. (a) The relationship of R_g and L, at different values of α_{PS} ranging from 27.1 to 27.5. (b), (c), (d), (e), (f) The relationship of the eigenvalues of the radius of gyration tensor and the size of 2D polymer, when α_{PS} = 27.1, 27.2, 27.3, 27.4 and 27.5.