Supporting Information

Regulation of the dynamics of polymer films by modifying stiffness and length of polymer brushes

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In our molecular dynamics simulations, the temperature is controlled using the Berendsen thermostat[1], which maintains the system temperature T_{sys} at the target bath temperature T by scaling the velocities of polymer monomers. To check our simulation results, we have also used the Nose–Hoover thermostat[2] to maintain the system temperature T_{sys}.

In the Berendsen thermostat, velocities are scaled at each integration step according to the relaxation of the system temperature toward the target temperature, following $dT_{sys}/dt = (T - T_{sys})/\tau$. Here, τ is the coupling time constant, which determines how tightly the bath and the system are coupled together.

Nose-Hoover thermostat does not control temperature by directly scaling velocities. Instead, it couples the system to a fictitious heat bath, which is introduced as an additional degree of freedom (often described as a "fictitious particle") in the extended system. By solving the equations of motion for this extended system, energy is exchanged between the system and the fictitious bath, maintaining a constant average temperature while allowing the correct fluctuations around the mean value, as required by the canonical ensemble. The Nose-Hoover thermostat introduces a bath viscous coefficient γ with a fictitious mass (Q), which controls the system temperature by changing the magnitude of γ. The dynamical equation of polymer monomers is

$$m\frac{d^2 r_i}{dt^2} = F_i - \gamma m v_i \quad . \tag{1}$$

And the evolution of the viscous coefficient is

$$Q\frac{d\gamma}{dt} = 3Nk_B(T_{sys} - T) \quad . \tag{2}$$

The fictitious mass Q is chosen as $Q = 3Nk_BT\tau^2_{\text{NH}}$ with τ_{NH} being a tunable relaxation time that controls the coupling strength between the system and the heat bath.

Simulations are performed for a polymer film using the same structural and interaction parameters as those adopted in Fig. 2 of the manuscript. Fig. S1 presents the temperature fluctuation around the target temperature $T = 1$ for both Berendsen and Nose-Hoover thermostats. For the Berendsen thermostat, the coupling time constant is set to $\tau = 1$ and 10, while for the Nose-Hoover thermostat, the relaxation time τ_{NH} is set to 1 and 3. In all simulation cases, the system temperature is well maintained around the preset target value.

Fig. S2 presents the layer-resolved dynamics of the polymer chains in the film obtained from the simulations with the Berendsen and Nose-Hoover thermostats. Nearly identical results are obtained with these two thermostats. The results indicate that the dynamical behavior of polymer chains in polymer films is insensitive to the choice of thermostat, verifying the reliability of our simulation settings and subsequent conclusions.

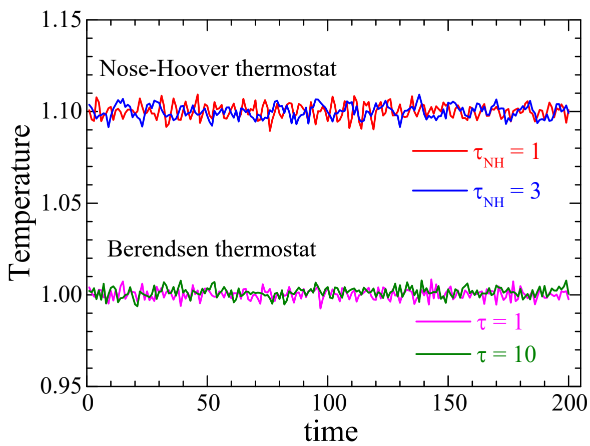

Fig. S1 Temperature evolution versus simulation time for the polymer film controlled by the Berendsen and Nose-Hoover thermostats at the target temperature $T = 1$. For clarity, the temperature curve of the Nose–Hoover thermostat is shifted upward by 0.1. All simulation parameters are identical to those used in Figure 2 of the manuscript.

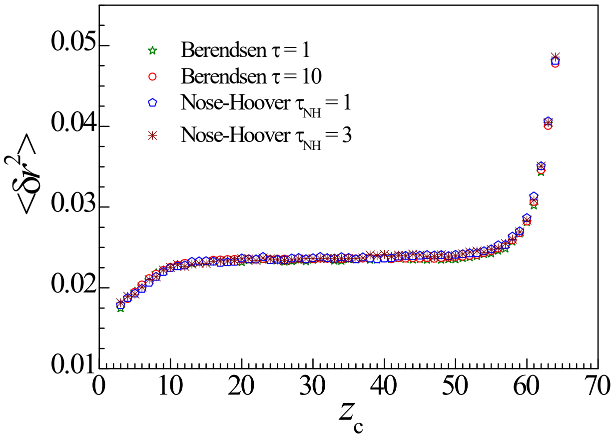

Fig. S2 Layer-resolved mean square displacement per unit time $<\delta r^2>$ of matrix polymers as a function of distance of their center-of-mass z_c from the substrate at $z = 0$ with different thermostat coupling time constant τ for Berendsen thermostat and different fictitious mass $Q = 3Nk_BT\tau^2_{NH}$ for Nose-Hoover thermostat. All simulation parameters are identical to those used in Figure 2 of the manuscript.

References

(1) H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola and J. R. Haak, Molecular dynamics with coupling to an external bath. *J. Chem. Phys.*, 1984, **81**, 3684−3690.

(2) D. J. Evans and B. L. Holian, The Nose−Hoover thermostat. *J. Chem. Phys.*, 1985, **83**, 4069−4074.