Supporting Information

Competitive adsorption and threading behavior in cyclic-linear polymer blend films supported on an attractive substrate

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1. Conformations and dynamics of flexible cyclic polymers in the melts

We have simulated the dependence of conformations and dynamics on polymer length N for flexible cyclic polymers in a melt at temperature $T = 1$. The density is set as 0.8. As shown in Fig. S1(a), the mean square radius of gyration exhibits the relation $\langle R_g^2 \rangle \sim (N-1)^{2\nu}$ with $\nu = 0.53$ and 0.47 for linear and cyclic polymers, respectively. The exponent ν values are consistent with those reported in the previous literature.[1] And the small ν value for the cyclic polymer manifests that topological constraint leads to more compact structures for cyclic polymers compared to linear analogues.[1,2]

For the dynamics of flexible cyclic polymers in the melt, we have calculated the mean square displacement of the center-of-mass of the cyclic polymers for a sufficiently long time starting from the equilibrium conformations: $\langle \Delta r^2(t) \rangle = \langle [\boldsymbol{r}_{cm}(t) - \boldsymbol{r}_{cm}(0)]^2 \rangle$, and $\boldsymbol{r}_{cm}(t)$ and $\boldsymbol{r}_{cm}(0)$ is the position vector of the center-of-mass of the cyclic polymers at time t and at initial time $t = 0$, respectively. As an example, the inset in Fig. S1(b) presents the evolution of $\langle \Delta r^2 \rangle$ of the flexible cyclic polymer of length $N = 32$ at temperature $T = 1$. Clearly, $\langle \Delta r^2 \rangle$ increases linearly with time t at a long time scale. Then the diffusion coefficient $D = \lim_{t\to\infty} \frac{\langle \Delta r^2(t) \rangle}{6t}$ can be obtained through a linear fitting in the long-time regime.

Fig. S1(b) presents the variation of D with N for the cyclic polymers. As the polymer length increases from 8 to 96, we observe a transition in the scaling behavior from $D \sim N^{-1}$ to $D \sim N^{-1.3}$. This transition is consistent with the previous MD simulation results for polyethylene (PE) melts.[1] And the deviation from the Rouse model for long N may be due to the threading between cyclic polymers.[1,2]

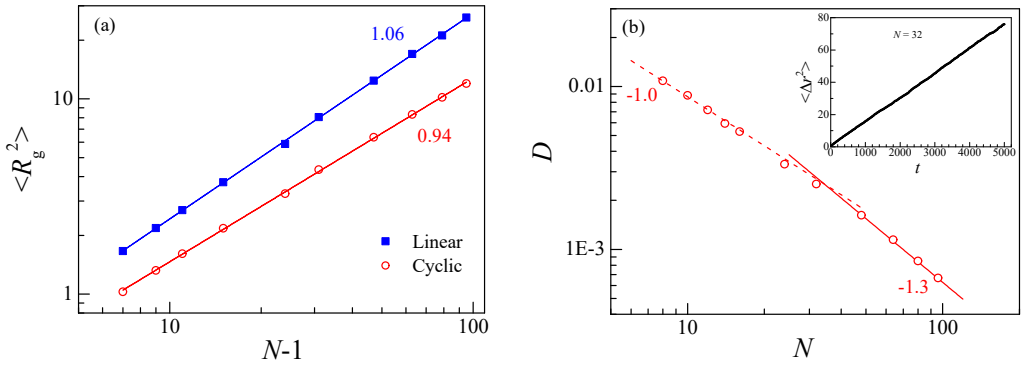

Fig. S1 (a) Log-log plot of the mean square radius of gyration $<R_g^2>$ versus the chain length, N–1, for flexible cyclic (open circles) and linear (solid squares) polymers in melts; (b) Log-log plot of the center-of-mass diffusion constant D versus the total number of monomers in the chain, N, for flexible cyclic polymers in melts. The straight solid lines in (a) are linear fitting results of $<R_g^2> \sim (N-1)^{2\nu}$ with $\nu = 0.53$ and 0.47 for linear and cyclic polymers, respectively. The dash and solid lines in (b) are $D \sim N^{-1}$ for short cyclic chains and $D \sim N^{-1.3}$ for long ones, respectively. Inset in (b): Plot of the mean square displacement $<\Delta r^2>$ versus time t for the flexible cyclic polymers of length $N = 32$. The concentration $c_p = 0.8$, and temperature $T = 1$.

2. Effect of topological structure on the diffusion of polymers.

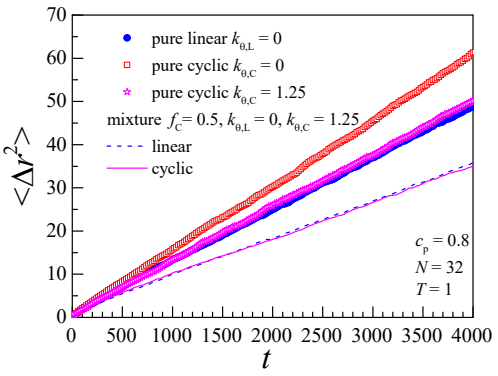

Fig. S2 Mean square displacement ($<\Delta r^2>$) of the center-of-mass of polymers in the bulk region of pure cyclic and pure linear polymer film, and a blend film of the fraction of cyclic chains $f_C = 0.5$. Chain length $N = 32$, the stiffness of linear chains $k_{\theta,L} = 0$, the stiffness of cyclic chains $k_{\theta,C} = 0$ and 1.25, temperature $T = 1$.

3. Effect of the fraction of cyclic chains in cyclic-linear polymer blend films.

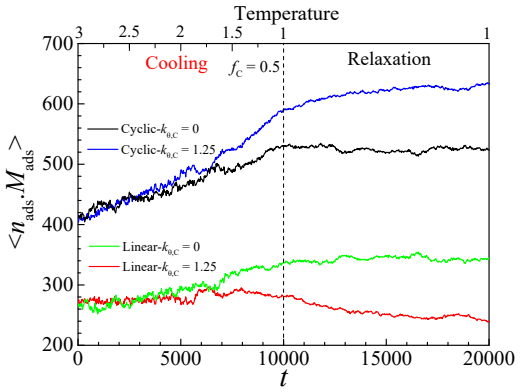

Fig. S3 Evolution of the number of adsorbed monomers ($<n_{ads}\cdot M_{ads}>$) for cyclic and linear chains in the blend film of the fraction of cyclic chains f_C = 0.5, when the equilibrated film at T = 3 is linearly cooled down to T =1, followed by subsequent relaxation at T = 1 for the stiffness of cyclic chains $k_{\theta,C}$ = 0 and 1.25. The stiffness of linear chains $k_{\theta,L}$ = 0.

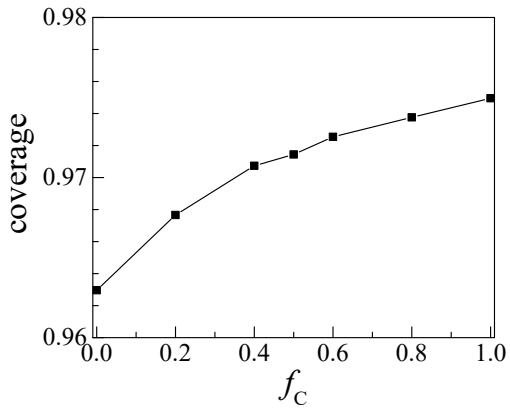

Fig. S4 Variation of the coverage of substrate surface, defined as the number of adsorbed monomers per substrate area, with the fraction of cyclic chains f_C in cyclic-linear polymer blend films. Chain length N = 32, the stiffness of cyclic and linear chains $k_{\theta,C}$ = 1.25 and $k_{\theta,L}$ = 0, respectively, temperature T = 1.

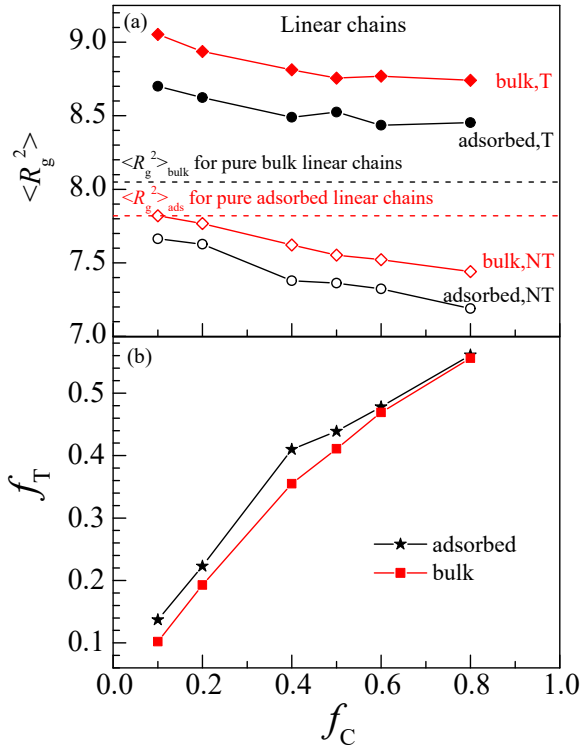

Fig. S5 Variations of the mean square radius of gyration $<R_g^2>$ of threading and non-threading linear chains (a) and the fraction of linear chains threading through cyclic chains f_T (b) on the fraction of cyclic chains f_C in cyclic-linear polymer blend films. Chain length $N = 32$, the stiffness of cyclic and linear chains $k_{\theta,C} = 1.25$ and $k_{\theta,L} = 0$, respectively, temperature $T = 1$.

4. Effect of the stiffness of cyclic chains in the cyclic-linear polymer blend film.

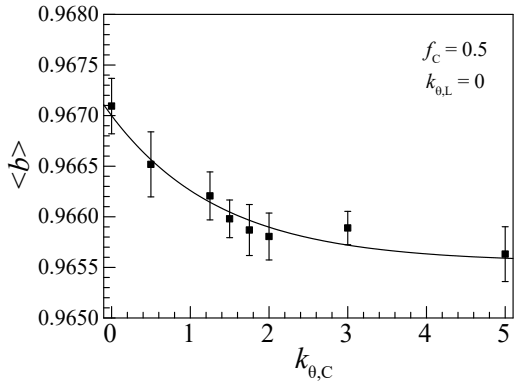

Fig. S6 Effect of the stiffness of cyclic chains ($k_{\theta,C}$) on the mean bond length (<b>) of cyclic chains in the blend film of $f_C = 0.5$. The solid line is a guide to the eye. The stiffness of linear chains $k_{\theta,L} = 0$, temperature $T = 1$.

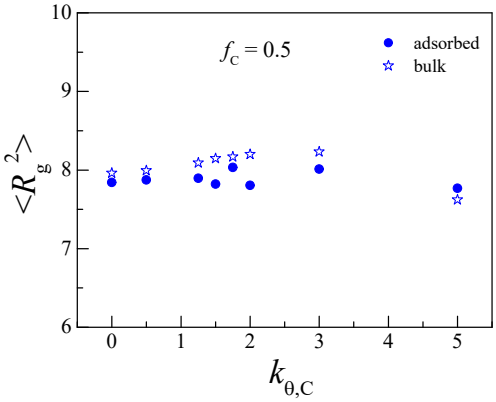

Fig. S7 Plot of the mean square radius of gyration $<R_g^2>$ of adsorbed and bulk linear chains versus the stiffness of cyclic chains $k_{\theta,C}$ in the cyclic-linear polymer blend films of $f_C = 0.5$. The stiffness of linear chains $k_{\theta,L} = 0$, chain length $N = 32$, temperature $T = 1$.

Table S1 Mean square radius of gyration of cyclic polymers adsorbed onto the substrate ($<R_g^2>_{ads}$) and in the bulk region ($<R_g^2>_{bulk}$) in cyclic-linear polymer blend film of $f_C = 0.5$ and in pure cyclic polymer film ($f_C = 1$) for different stiffness $k_{\theta,C}$ of cyclic polymer.

$k_{\theta,C}$	$<R_g^2>_{ads}$		$<R_g^2>_{bulk}$	
	$f_C = 0.5$	$f_C = 1$	$f_C = 0.5$	$f_C = 1$
0	4.37	4.27	4.42	4.29
0.5	5.07	4.92	5.01	4.84
1.25	7.17	6.86	6.47	6.18
1.5	8.42	7.95	7.12	6.80
1.75	11.28	9.86	7.82	7.42
2	14.34	13.58	8.53	8.14
3	16.58	15.56	11.62	11.50
5	18.02	17.62	18.13	17.93

References

1. K. Hur, R. G. Winkler and D. Y. Yoon, Comparison of ring and linear polyethylene from molecular dynamics simulations, *Macromolecules*, 2006, **39**, 3975–3977.
2. Y. Li, P. Yao and H. Guo, Non-Rouse behavior of short ring polymers in melts by molecular dynamics simulations, *Soft Matter*, 2023, **19**, 7161–7171.