

Electronic Supplementary Information for

Diffusion of polymer-grafted nanoparticles with dynamical fluctuations in unentangled polymer melts

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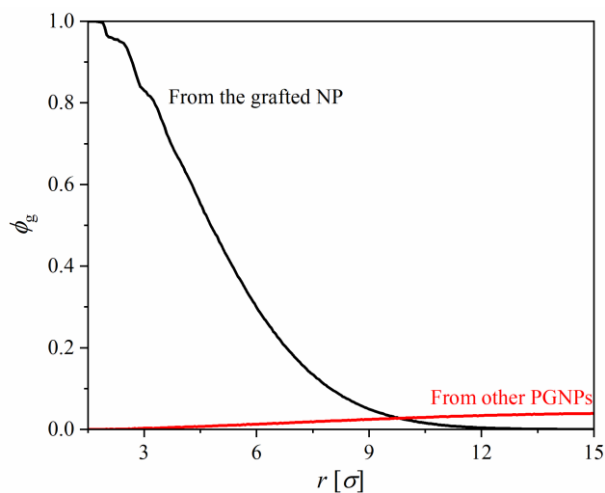


Fig. S1 Monomer number fraction as a function of radial distance from a reference nanoparticle (NP) center-of-mass for grafted chains on that NP (black) and from other polymer-grafted nanoparticles (PGNPs) (red) in system with $\Sigma_g = 0.96$ chain/ σ^2 , $N_g = 30$, and $N_m = 40$.

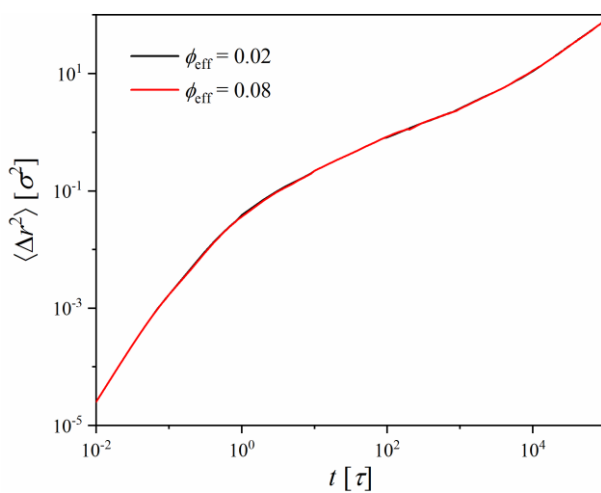


Fig. S2 Time dependence of the mean square displacements (MSDs) of the grafted NP center-of-mass in systems with $\Sigma_g = 0.96$ chain/ σ^2 , $N_g = 30$, and $N_m = 40$ at two different PGNP concentrations.

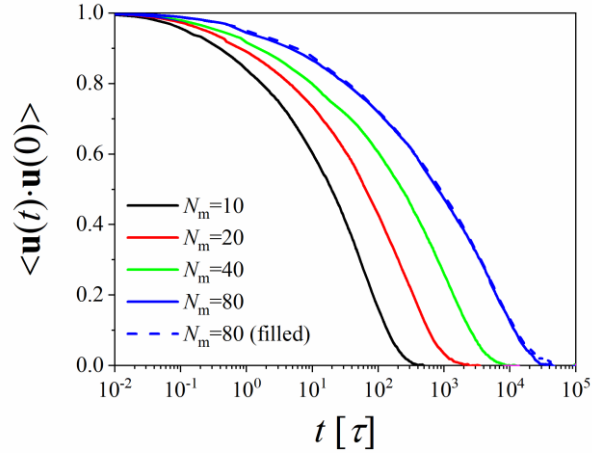


Fig. S3 Decay of the end-to-end vector autocorrelation function $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ of polymer chains with different lengths N_m as indicated, as a function of time t , in pure polymer melts (solid lines) and that in a filled system with $N_m = 80$, $N_g = 30$, and $\Sigma_g = 0.96$ chains/ σ^2 .

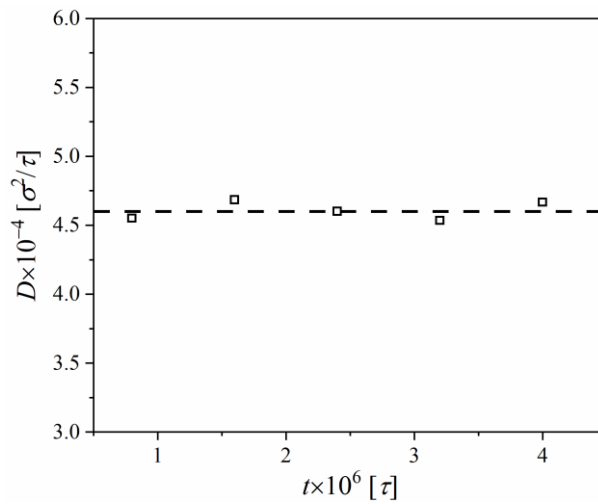


Fig. S4 No aging or change of PGNP mobility was observed for the system with $\Sigma_g = 0.96$ chain/ σ^2 , $N_g = 15$, and $N_m = 80$ after $10^5 \tau$ of pre-equilibration. The dashed line shows the ensemble-averaged diffusivity.

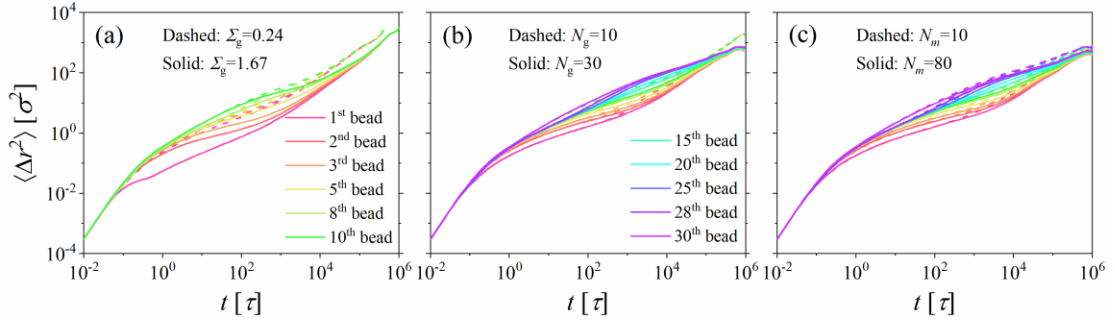


Fig. S5 Time dependence of the MSDs of monomers at different positions in grafted chains (from the grafting site to the free end) for different systems: (a) at fixed $N_g = 10$ and $N_m = 40$ but at different Σ_g , (b) at fixed $N_m = 40$ and $\Sigma_g = 0.96$ chains/ σ^2 but at different N_g , and (c) at fixed $N_g = 30$ and $\Sigma_g = 0.96$ chains/ σ^2 but at different N_m , as indicated.

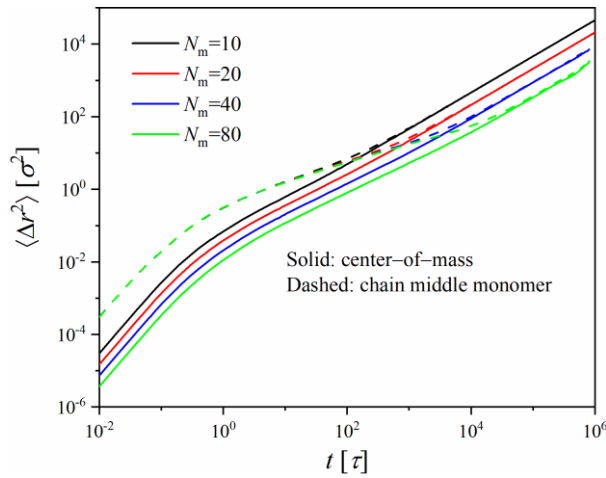


Fig. S6 MSDs of the chain middle monomer (dashed) and center-of-mass (solid) for matrix polymers of different chain lengths.

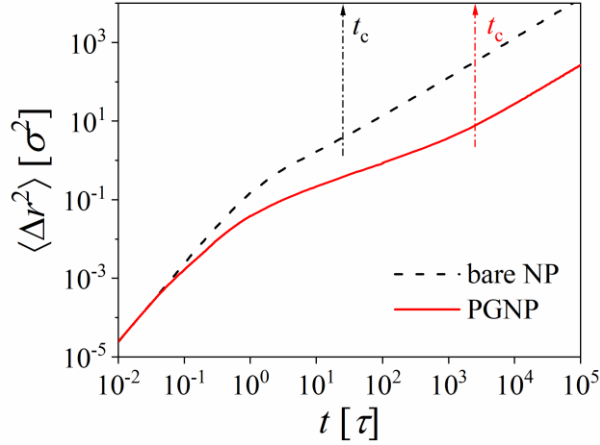


Fig. S7 Time dependence of the MSDs $\langle \Delta r^2 \rangle$ of the center-of-mass of PGNPs with $N_g = 10$ and $\Sigma_g = 0.96$ chains/ σ^2 and bare NPs in melts of $N_m = 40$.

Scaling relation between $\langle R_e^2 \rangle / \langle R_g^2 \rangle$ and Σ_g of grafted chains:

For polymer grafted on a sphere of radius R , if the size of a single chain R_e exceeds R , the situation is similar to that of a star polymer and can be described by the Daoud-Cotton picture,¹ as shown in Fig. S8. That is, the solid angle 4π is divided up into z conical sectors, so each chain grafted on the sphere has the same volume in which it can spread out. When we fill such a conical volume by blobs that touch each other, we clearly must have for the blob radius $\xi(r) \propto r/z^{1/2}$. Each blob contains $g(r) \propto \xi(r)^2$ monomers. According to the Daoud-Cotton picture, the blobs that correspond to one chain just fill one conical sector up to the brush height h . Then one can obtain the scaling relation $R_e \propto h \propto z^{1/4} N_g^{1/2} \propto \Sigma_g^{1/4} N_g^{1/2}$.² However, the consideration of R_g is more subtle since the chains are extended along the radial direction but be compressed along the lateral directions. In the radial direction, one still has $R_{gz} \propto h \propto \Sigma_g^{1/4} N_g^{1/2}$; while

in the lateral directions, $R_{gx} = R_{gy} \propto h/\Sigma_g^{1/2} \propto \Sigma_g^{-1/4} N_g^{1/2}$. Therefore, $\langle R_g^2 \rangle = \langle 2R_{gx}^2 + R_{gz}^2 \rangle = (a\Sigma_g^{-1/2} + b\Sigma_g^{1/2})N_g$, where a and b are the prefactors. The ratio of $\langle R_e^2 \rangle$ to $\langle R_g^2 \rangle$ then should be equal to $c/(a\Sigma_g^{-1} + b)$. If we change the form to be $\frac{\langle R_g^2 \rangle}{\langle R_e^2 \rangle} = \frac{a\Sigma_g^{-1} + b}{c} = A\Sigma_g^{-1} + B$, the value would decrease linearly with Σ_g . Therefore, the ratio of $\langle R_e^2 \rangle$ to $\langle R_g^2 \rangle$ of the grafted chains shows to be linear (the inset of Fig. 2a).

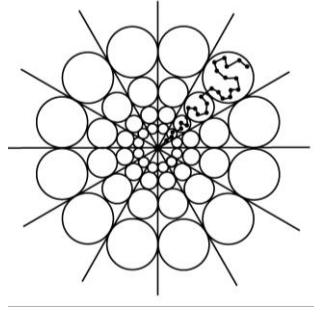


Fig. S8 Schematic construction of the Daoud-Cotton blob picture for star polymers. At a point-like center (or a small sphere), a total of z chains is grafted.²

Estimation of the local polymer monomeric viscosity:

Starting from equilibrated samples, nonequilibrium molecular dynamics simulations were performed to measure the rheological properties of neat polymer melts with chain lengths $N_m = 10, 20, 40,$ and 80 . SLLOD algorithm coupled with the “box deforming” technique was adopted to introduce a shear in x -direction and velocity gradient in y -direction.³ The shear rate $\dot{\gamma} = \partial v_x / \partial y$ was fixed at $10^{-5} \tau^{-1}$, which is low enough to reach the Newtonian plateaus for polymers with $N_m < 100$ and to obtain a zero-shear viscosity.^{4,5} The viscosity was calculated using $\eta = -\langle P_{xy} \rangle / \dot{\gamma}$, where

$\langle P_{xy} \rangle$ is the xy component of the pressure tensor. According to the Rouse assumption for unentangled polymers, i.e., the zero-shear viscosity is proportional to the chain length, $\eta \sim N_m$,⁶ we estimated the local viscosity at segmental scale by $\eta_0 = \eta/N_m$. The results are summarized in Table S1, from which we find the local polymer monomeric viscosity is about $\eta_0 \approx 1.4\tau\varepsilon/\sigma^3$.

Table S1 Rheological Properties from the Nonequilibrium Molecular Dynamics Simulations for Neat Polymer Melts with Different Chain Lengths.

N_m^a	$R_e^b [\sigma]$	$\eta^c [\tau\varepsilon/\sigma^3]$	$\eta_0^d [\tau\varepsilon/\sigma^3]$
10	3.4	13.71	1.37
20	5.1	27.65	1.38
40	7.4	57.67	1.44
80	10.7	95.26	1.19

^aLength of polymer chains. ^bEnd-to-end distance of polymer chains in equilibrium. ^cBulk polymer melt viscosity at a shear rate of $\dot{\gamma} = 10^{-5}\tau^{-1}$. ^dLocal polymer monomeric viscosity estimated using $\eta_0 = \eta/N_m$.

References

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