

Supporting Information

# Distinct Mechanical Properties of Nanoparticle-Tethering Polymers

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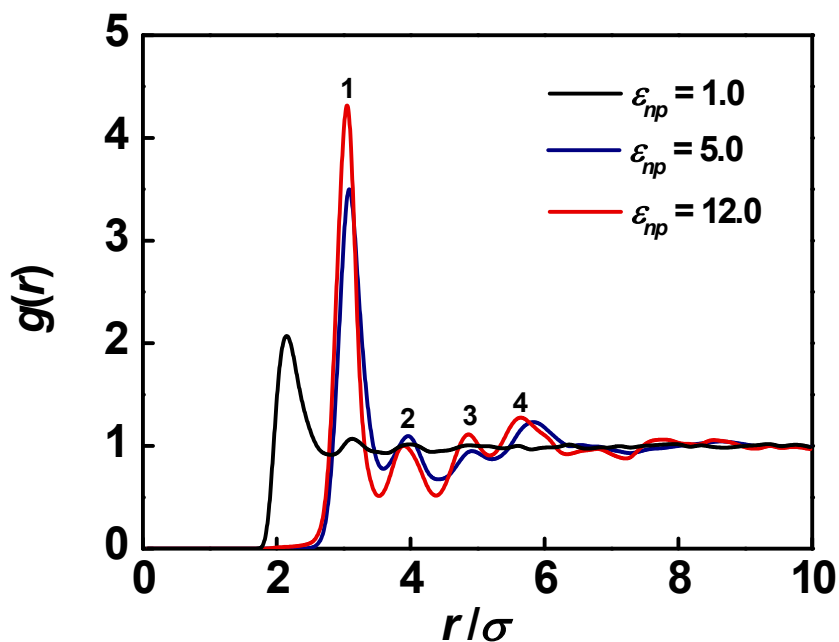
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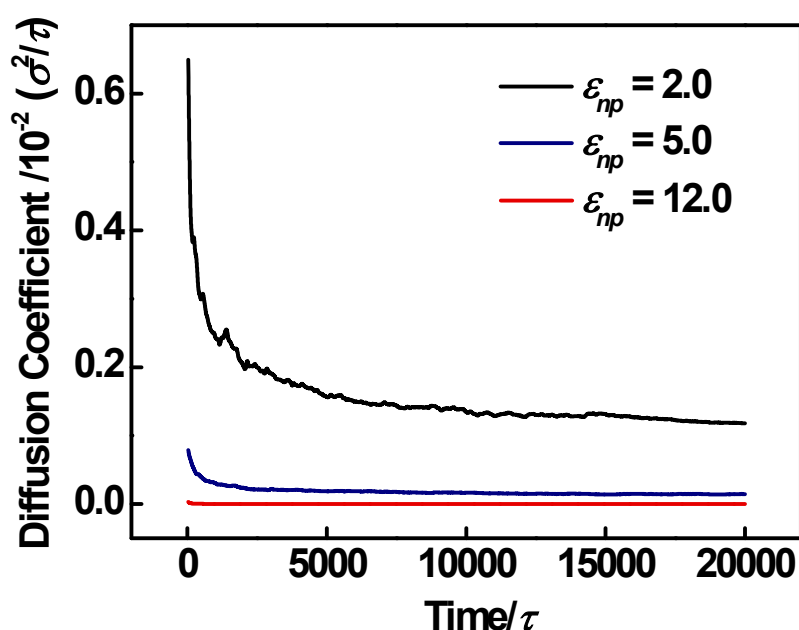
## 1. Effect of interaction strength $\epsilon_{np}$ on the stress-strain behavior of nanoparticle-tethering polymers

The pair correlation function  $g(r)$  was applied to further verify the packing structures of nanoparticles obtained by BOD. The peak position ratio of typical peaks in  $g(r)$  can determine the packing geometry.<sup>S1</sup> The results of  $g(r)$  at various  $\epsilon_{np}$  are shown in Figure S1. There is only one strong peak in  $g(r)$  at  $\epsilon_{np} = 1.0$ , while several peaks are exhibited at  $\epsilon_{np} = 5.0$  and 12.0. The typical peaks are numbered for larger  $\epsilon_{np}$ . The position ratio of typical peaks at  $\epsilon_{np} = 5.0$  and 12.0 is about  $1:\sqrt{2}:\sqrt{3}:2$ , indicating that the nanoparticles are packed approximately in a FCC manner (in accordance with the BOD results).



**Figure S1.** Pair correlation functions  $g(r)$  between the nanoparticles at various  $\epsilon_{np}$ . The typical peaks are numbered as 1, 2, 3, and 4 for larger  $\epsilon_{np}$ .

Figure S2 shows the diffusion coefficients of nanoparticles as a function of time at various  $\varepsilon_{np}$ . As can be seen, the diffusion coefficient decreases and finally arrives at a plateau for any  $\varepsilon_{np}$  with the evolution of time. The effect of  $\varepsilon_{np}$  on the diffusion coefficient of nanoparticles can be also viewed. At lower  $\varepsilon_{np}$  ( $\varepsilon_{np} = 2.0$ ), the diffusion coefficient is larger, and decreases more slowly with the time. With increasing  $\varepsilon_{np}$ , the diffusion coefficient decreases. At higher  $\varepsilon_{np}$  ( $\varepsilon_{np} = 12.0$ ), the diffusion coefficient is so small that the nanoparticles can be considered to be frozen.

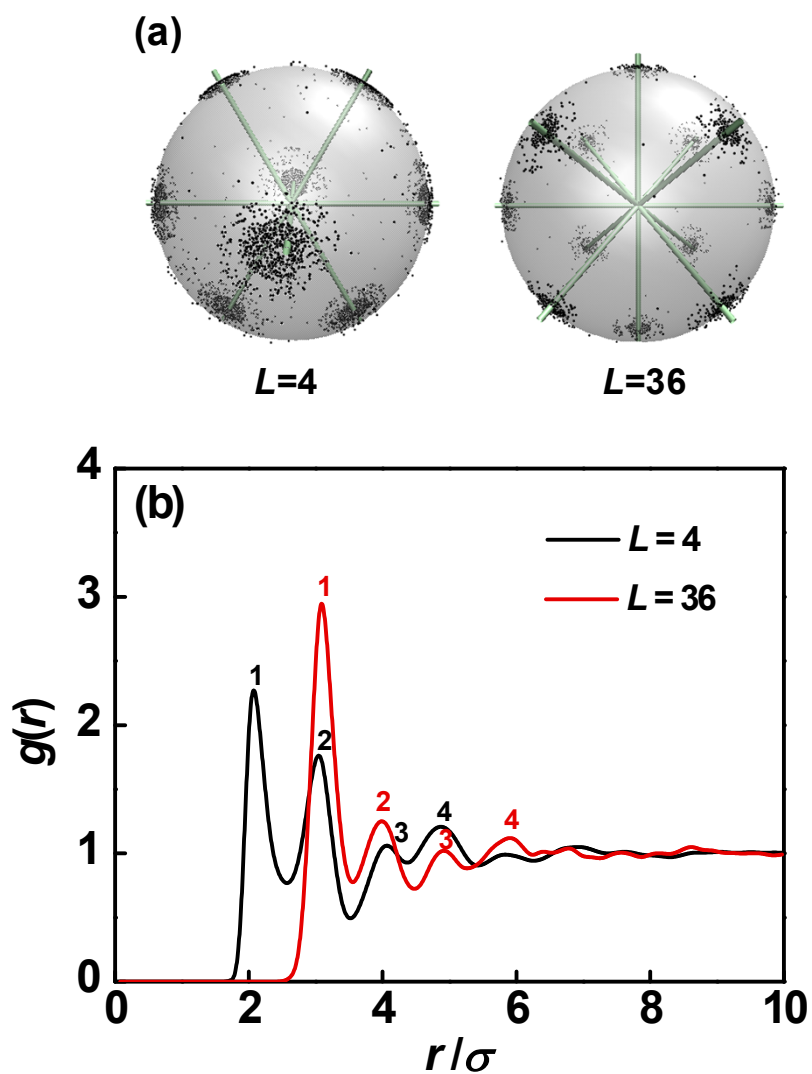


**Figure S2.** Diffusion coefficients of nanoparticles as a function of time at various  $\varepsilon_{np}$ .

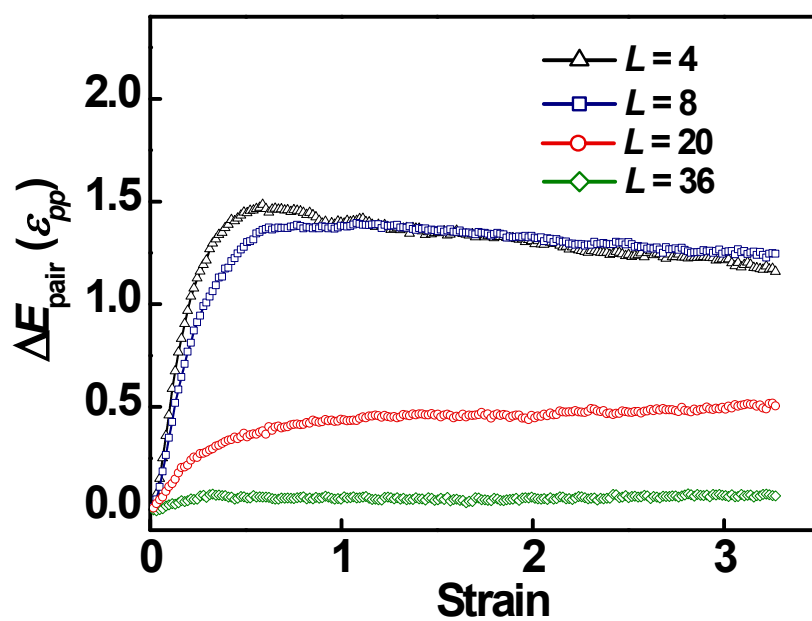
## 2. Effect of polymer length $L$ on the stress-strain behavior of nanoparticle-tethering polymers

Figure S3a and S3b shows the BOD of nanoparticles and the pair correlation function  $g(r)$  between the nanoparticles for various  $L$ , respectively. It can be seen that for  $L = 4$ , six point groups are distributed on the hexagon vertices and four point groups are located on the square vertices in the BOD, suggesting the nanoparticles approximately adopt a hexagonally closed packing manner.<sup>S2,S3</sup> For  $L = 36$ , the diagonal and square distribution of points in the BOD implies a FCC packing of nanoparticles, similar to the case of  $L = 24$  (Figure 2c). As shown in Figure S2b, for  $L = 4$  and 36, the  $g(r)$  has the typical peak position ratios  $1:\sqrt{2}:2:\sqrt{5}$  and  $1:\sqrt{2}:\sqrt{3}:2$ , respectively. Therefore, the hexagonally closed packing of nanoparticles for  $L = 4$  and the FCC packing of nanoparticles for  $L = 36$  were further confirmed.

Figure S4 shows the change of nonbonding potential  $\Delta E_{\text{pair}}$  between deformed and undeformed states with respect to the strain for various  $L$ . It can be seen, at smaller strain the nonbonding potential  $E_{\text{pair}}$  increases more remarkably for smaller  $L$ , resulting in larger enthalpy gain for smaller  $L$ . Therefore, the interaction enthalpy as well as the conformation entropy makes important contribution to the higher stress and modulus for smaller  $L$ . At larger strain, the value of  $\Delta E_{\text{pair}}$  for smaller  $L$  is still larger than that for larger  $L$ . Therefore, the enthalpy gain is still larger for smaller  $L$ . However, the entropy loss first increases then decreases with increasing  $L$ . It is shown that at larger strain, the stress first increases and then decreases with increasing  $L$  (Figure 5a). Therefore, the stress is dominated by the entropy for smaller  $L$ , while it is controlled by the cooperative action of entropy and enthalpy for larger  $L$ .



**Figure S3.** (a) BOD of nanoparticles for  $L = 4$  and  $L = 36$ . The solid lines indicate the BODs of ideal hexagonally closed packing and FCC packing structures. (b) Pair correlation functions  $g(r)$  between the nanoparticles for various  $L$ . The typical peaks are numbered as 1, 2, 3, and 4 for  $L = 4$  and  $L = 36$ .

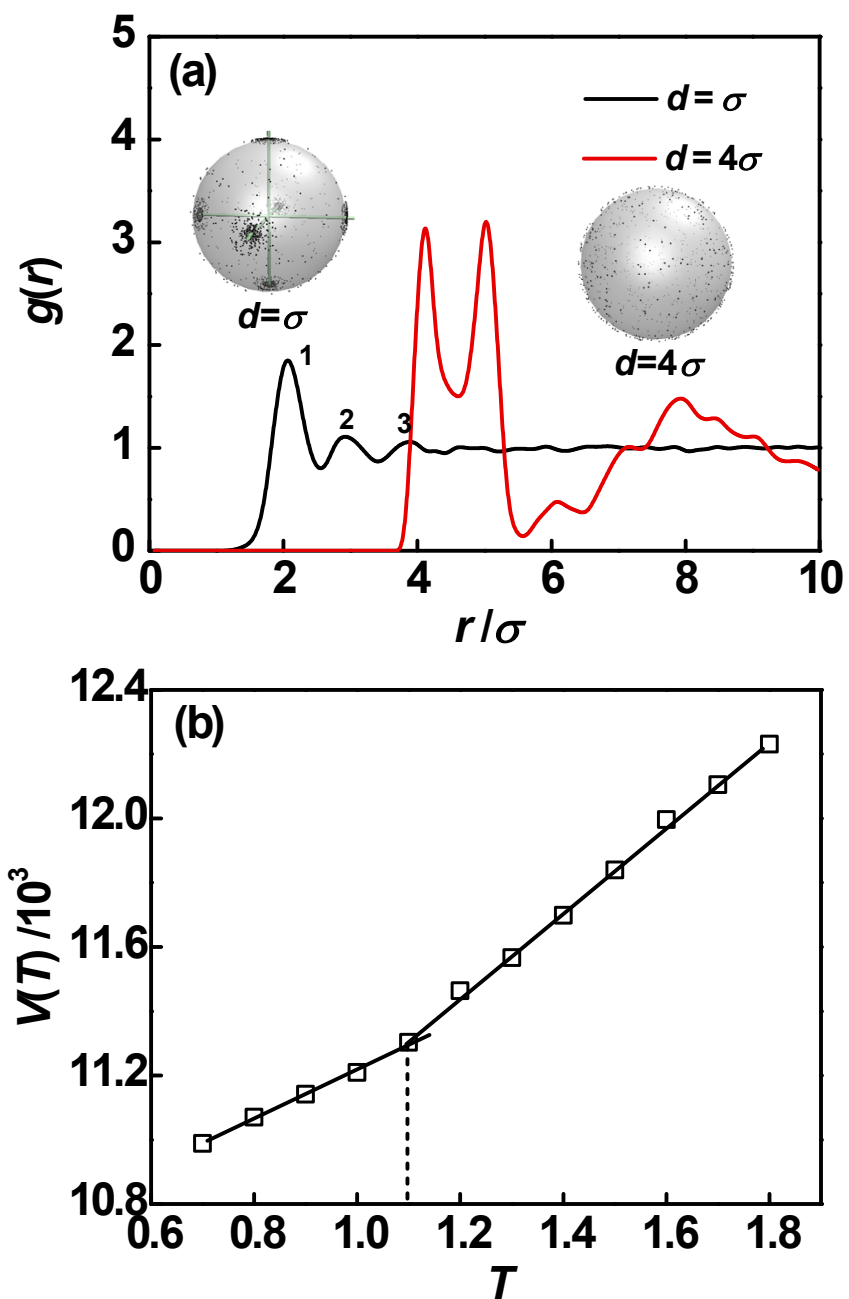


**Figure S4.** Change of nonbonding potential  $\Delta E_{\text{pair}}$  between deformed and undeformed states with respect to the strain for various  $L$ .

### 3. Effect of particle size $d$ on the stress-strain behavior of nanoparticle-tethering polymers

Figure S5a shows the pair correlation functions  $g(r)$  between the nanoparticles for various  $d$ . The insert shows the BOD of nanoparticles for  $d = \sigma$  and  $d = 4\sigma$ . In the BOD for  $d = \sigma$ , the projected points are approximately distributed in the form of point groups along the four-fold directions, indicating a non-perfect cubic-like packing for nanoparticles. This can be verified by the typical peak position ratio of  $1 : \sqrt{2} : 2$  in  $g(r)$ . With increasing  $d$  to  $4\sigma$ , there is no typical peak position ratio in  $g(r)$ , and the projected points are located randomly on the sphere surface in the BOD. Therefore, the nanoparticle packing is not ordered enough for  $d = 4\sigma$ .

In Figure 7a, the stress-strain curve for large nanoparticles ( $d = 4\sigma$ ) has an obvious yield point, exhibiting a glassy or crystalline feature. To explain this phenomenon, we examined the glass transition temperature for  $d = 4\sigma$ . The total volume  $V(T)$  as a function of  $T$  for  $d = 4\sigma$  is plotted in Figure S5b. As can be seen, the  $V(T)$  increases linearly with increasing  $T$  below or above a certain temperature. According to the intersections of fitted lines, the  $T_g$  is obtained to be about 1.1, which is higher than the examined temperature ( $T = 1.0$ ). Therefore, the stress-strain curve for  $d = 4\sigma$  exhibits a glassy feature.



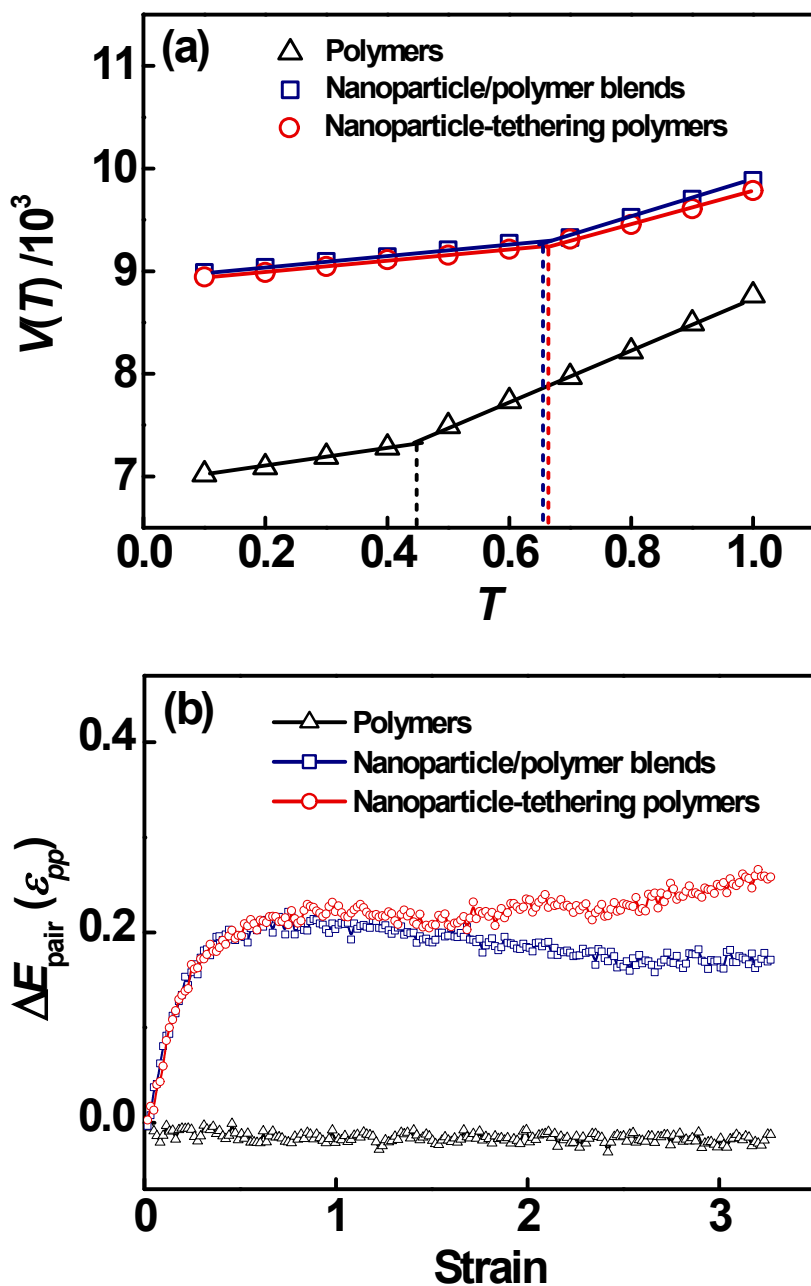
**Figure S5.** (a) Pair correlation functions  $g(r)$  between the nanoparticles for various  $d$ . The insert shows the BOD of nanoparticles for  $d = \sigma$  and  $d = 4\sigma$ . (b) Plot of the total volume  $V(T)$  versus  $T$  for the nanoparticle-tethering polymers with  $d = 4\sigma$ .



#### 4. Comparison with neat polymers and nanoparticle/polymer blends

We examined the glass transition temperatures for the neat polymers, nanoparticle/polymer blends, and nanoparticle-tethering polymers. Figure S6a shows the  $V(T)$  as a function of  $T$  for the neat polymers, nanoparticle/polymer blends, and nanoparticle-tethering polymers at  $T = 1.0$  and  $P = 0.0$ . By linear fitting, the  $T_g$  were estimated to be 0.45, 0.65, and 0.66 for the three systems. The  $T_g$  are all lower than 1.0, therefore these systems are in rubbery states at  $T = 1.0$ .

Figure S6b shows the changes of nonbonding potential  $\Delta E_{\text{pair}}$  between undeformed and deformed states for the neat polymers, nanoparticle/polymer blends, and nanoparticle-tethering polymers at  $T = 1.0$ . The  $E_{\text{pair}}$  almost has no increase for neat polymers, but increases rapidly with the strain at smaller strain for nanoparticle/polymer blends and nanoparticle-tethering polymers. The increase in  $E_{\text{pair}}$  for the nanoparticle/polymer blends and nanoparticle-tethering polymers are almost the same at smaller strain, but the  $\Delta E_{\text{pair}}$  for the nanoparticle-tethering polymers is larger than that for the nanoparticle/polymer blends. The larger  $\Delta E_{\text{pair}}$  leads to larger enthalpy gain. The enthalpy together with the entropy contributes to the highest stress for the nanoparticle-tethering polymers as shown in Figure 9a.



**Figure S6.** (a)  $V(T)$  versus  $T$  for the neat polymers, nanoparticle/polymer blends, and nanoparticle-tethering polymers at  $T = 1.0$  and  $P = 0.0$ . (b)  $\Delta E_{\text{pair}}$  versus the strain for the three systems. The polymer length was set to be 24, and the nanoparticle diameter was set to be  $2\sigma$ . The interaction strength between nanoparticles and polymers was  $\epsilon_{np} = 5.0$ .

## References

- [S1] C. J. Martinez, J. Liu, S. K. Rhodes, E. Luijten, E. R. Weeks and J. A. Lewis, *Langmuir*, 2005, **21**, 9978-9989.
- [S2] A. S. Keys, C. R. Iacovella and S. C. Glotzer, *J. Comput. Phys.*, 2011, **230**, 6438-6463.
- [S3] A. S. Keys, C. R. Iacovella and S. C. Glotzer, *Annu. Rev. Condens. Matter Phys.*, 2011, **2**, 263-285.