Supporting Information

Controlling the electrical conductive network formation in nanorod filled polymer nanocomposites by tuning nanorod stiffness

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The aggregation structure and the rotational diffusion of nanorod

Here, the number of the nanorods (NRs) for each system is 4500 (φ=4.40%). First, we calculated the end-to-end distance of NR $\left|\vec{R}_{ee}\right| = \left|\vec{r}_1 - \vec{r}_n\right|$, where $\vec{r}_1$ and $\vec{r}_n$ are the position vector of the first and the last beads of NR in Fig. S1. $\left|\vec{R}_{ee}\right|$ gradually increases from 4.63 for $K_{stiffness}$=0 to 8.29 for $K_{stiffness}$=100. Thus, the force constant $K_{stiffness}$ in Eq. (3) can be used to tune the NR stiffness, which is reflected by the increase of $\left|\vec{R}_{ee}\right|$.

Then we calculated the inter-nanorod radial distribution function (RDF) to characterize the NR dispersion state for systems with different NR stiffness ($K_{stiffness}$) in Fig. S2(a). The peak at $r = 1\sigma$ reflects the direct contact structure of NRs. And the peak at $r = 2\sigma$ reflects the NR aggregates sandwiched by one polymer layer. It is found that both the peaks at $r = 1\sigma$ and $r = 2\sigma$ decrease with increasing $K_{stiffness}$, which indicates a little aggregation of NRs. However, the dispersion of NRs is relatively uniform in the matrix because the height of the peaks is low (<1.0). To observe the NR dispersion state, the snapshots of NRs with different stiffness (φ=4.40%) are shown in Fig. S2(b). It clearly presents that the NRs gradually straighten with $K_{stiffness}$ and disperse uniformly in the matrix.

At last, we investigated the effect of NR stiffness ($K_{stiffness}$) on the rotational diffusion of NR.[1] The rotational diffusion of NR is defined as the time correlation function of the end-to-end vector of NR $\phi_{rot}(t) = \left\langle \vec{u}(t) \cdot \vec{u}(0) \right\rangle$, where $\vec{u}(t)$ denotes the end-to-end unit vector of NR at time t. As shown in Fig. S3, the rotational diffusion $\phi_{rot}(t)$ of NRs gradually decreases from 1.0 to 0 with the simulation time, which indicates that it gradually forgets its original position. This means that NRs experience enough relaxation within the simulation time. Following the work[2], we have calculated the rotational diffusion coefficient (D_r), which gradually decreases from $15.5*10^{-4}\tau^{-1}$, $12.2*10^{-4}\tau^{-1}$, $9.7*10^{-4}\tau^{-1}$, $7.35*10^{-4}\tau^{-1}$, $5.35*10^{-4}\tau^{-1}$ to $2.43*10^{-4}\tau^{-1}$ with the increase of $K_{stiffness}$ from 0, 1, 2, 5, 10 to 100, respectively.

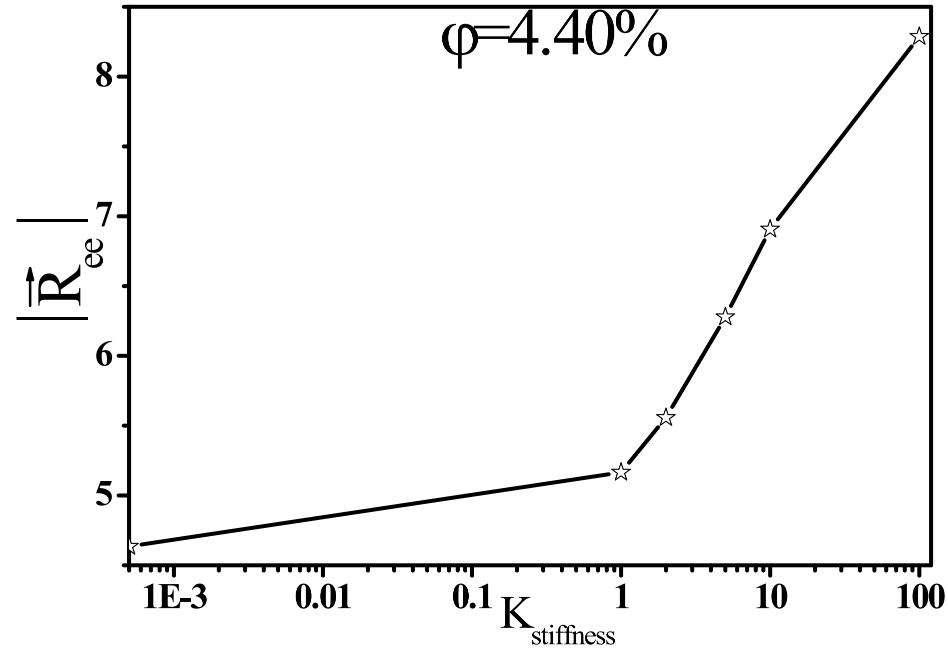


Fig. S1 The end-to-end distance $\left|\vec{R}_{ee}\right|$ of the nanorod with different stiffness ($K_{stiffness}$). (T^* =1.0)

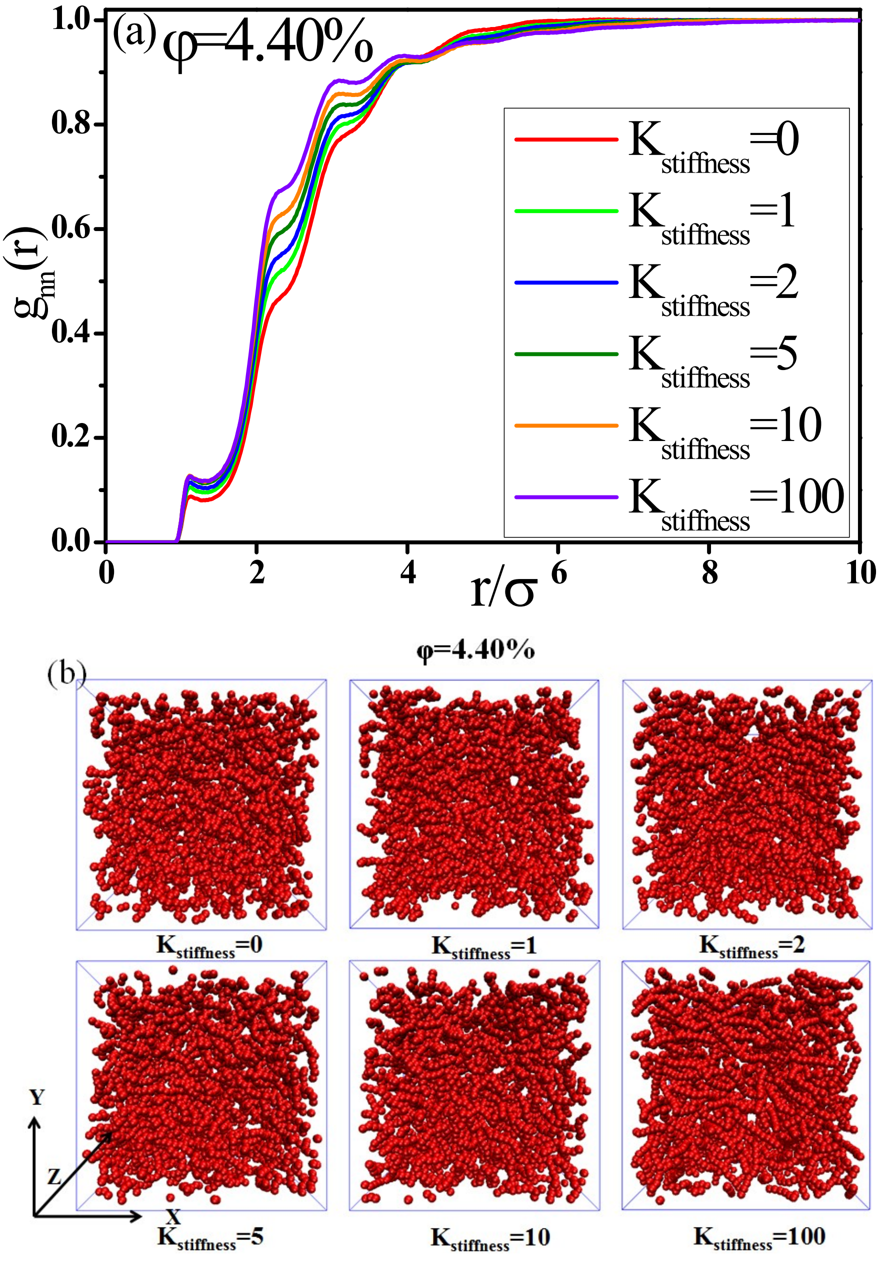


Fig. S2 (a) The RDF and (b) snapshots of the nanorod with different stiffness ($K_{stiffness}$) where the polymer chains are neglected for clarity. The red spheres denote the nanorods. (T^*=1.0, φ=4.40%)

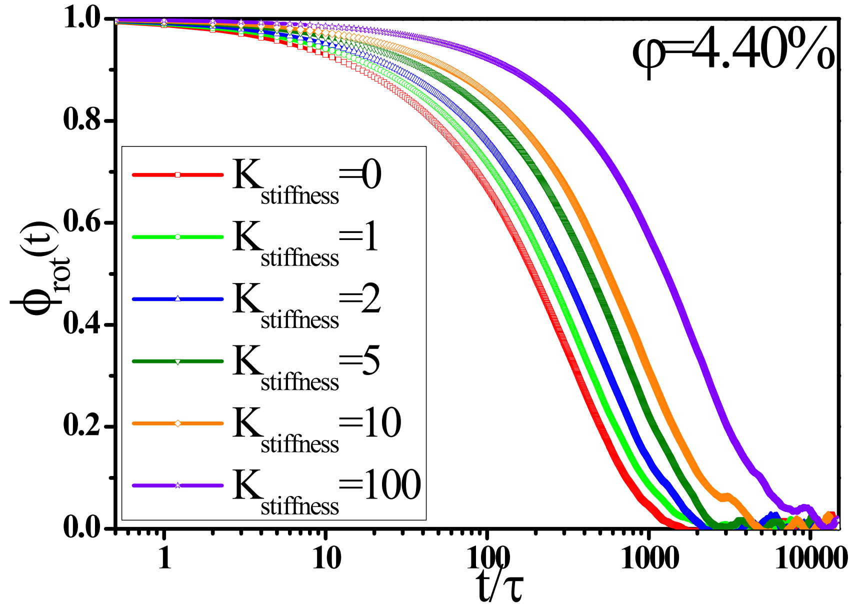
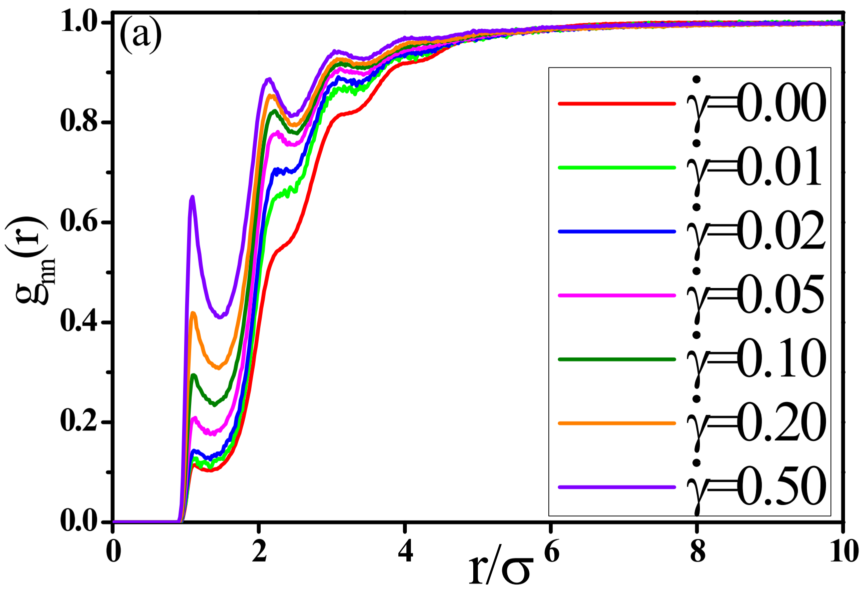


Fig. S3 The $\phi_{rot}(\mathrm{t})$ of the nanorod with different stiffness ($K_{stiffness}$). ((T^* =1.0, φ =4.40%)



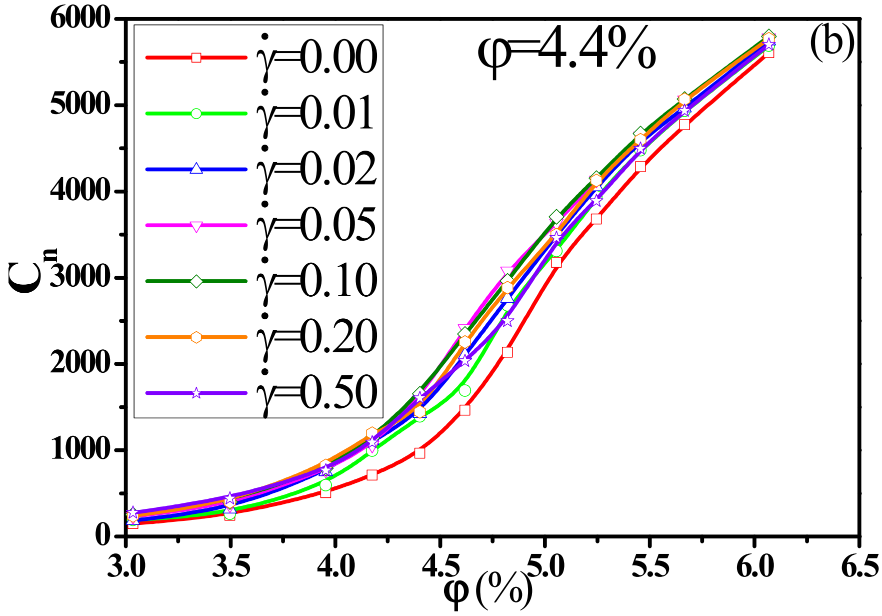


Fig. S4(a) The RDF and (b) the main cluster size C_n as a function of the nanorod volume fraction φ for different shear rates $\dot{\gamma}$. (T^* =1.0, $K_{stiffness}$=2)

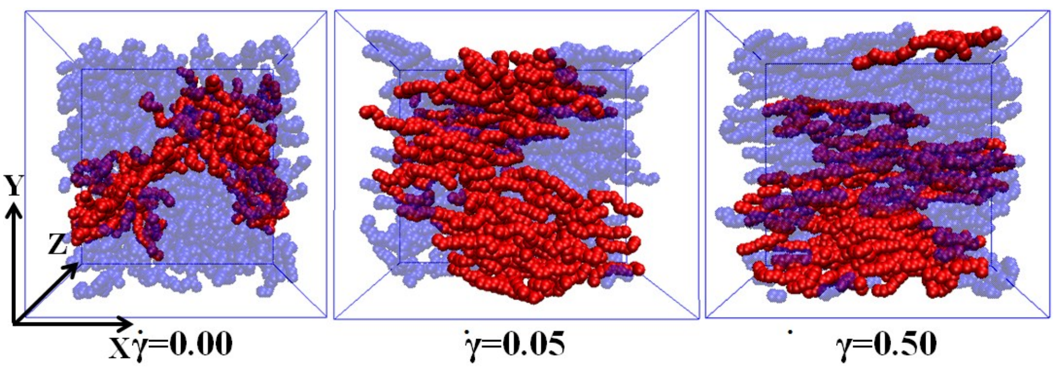


Fig. S5 Some typical snapshots for systems at three shear rates $\dot{\gamma}$. The red spheres denote the nanorods within the main cluster. The blue spheres are the other nanorods. X direction is the shear direction. (T^* =1.0, φ =4.40%, $K_{stiffness}$=2)

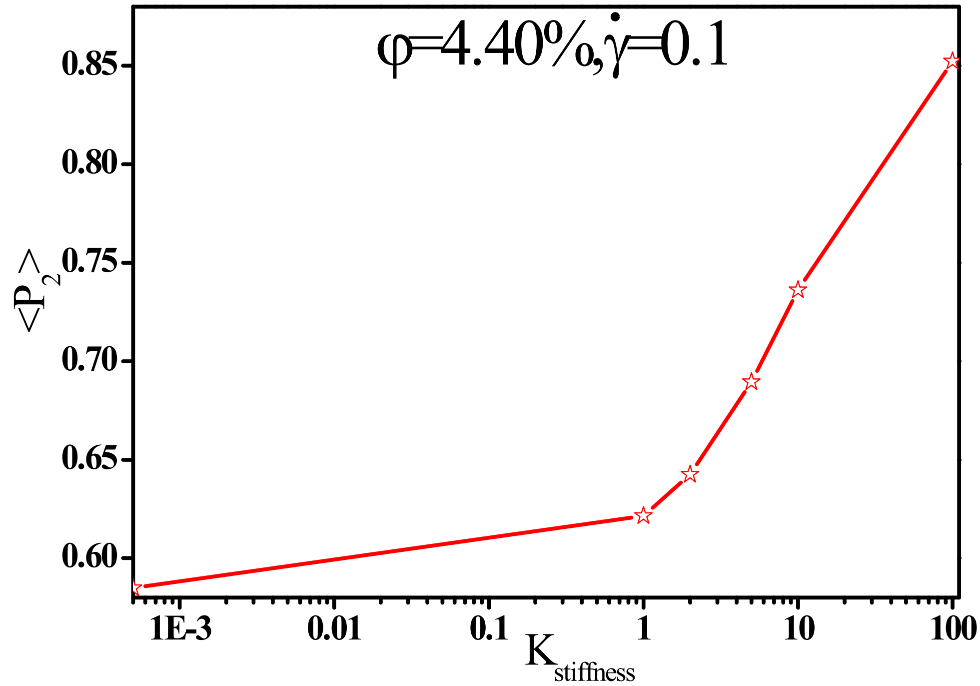


Fig. S6 The nanorod orientation $< P_2 >$ with respect to the nanorod stiffness ($K_{stiffness}$). (T^*=1.0, φ=4.40%, $\dot{\gamma}$=0.1)

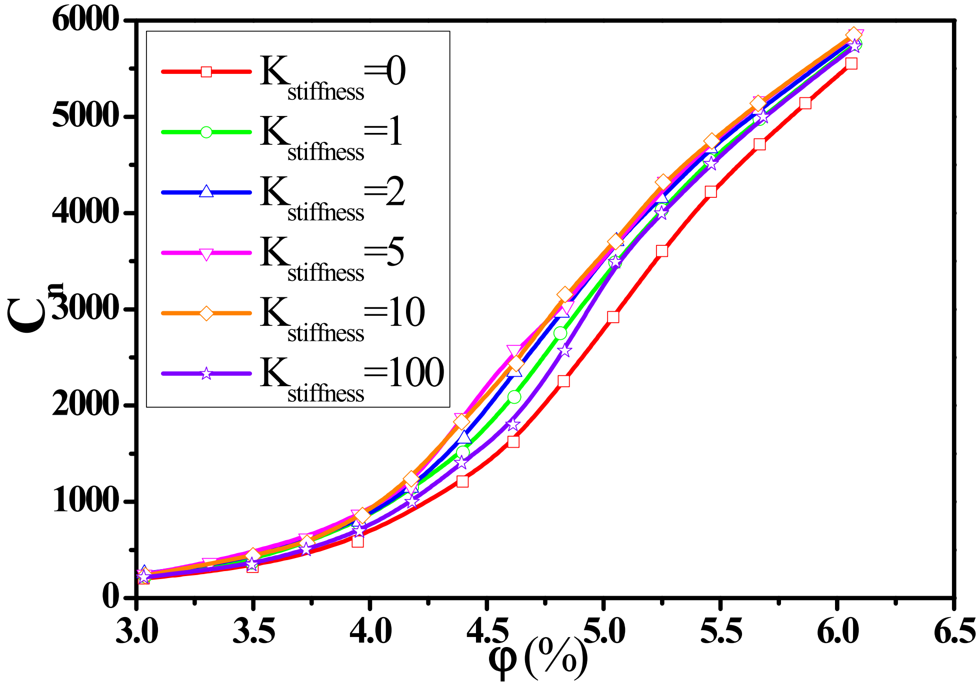


Fig. S7 Change of the main cluster size C_n as a function of the nanorod volume fraction φ for different nanorod stiffness ($K_{stiffness}$). (T^*=1.0, $\dot{\gamma}$=0.1)

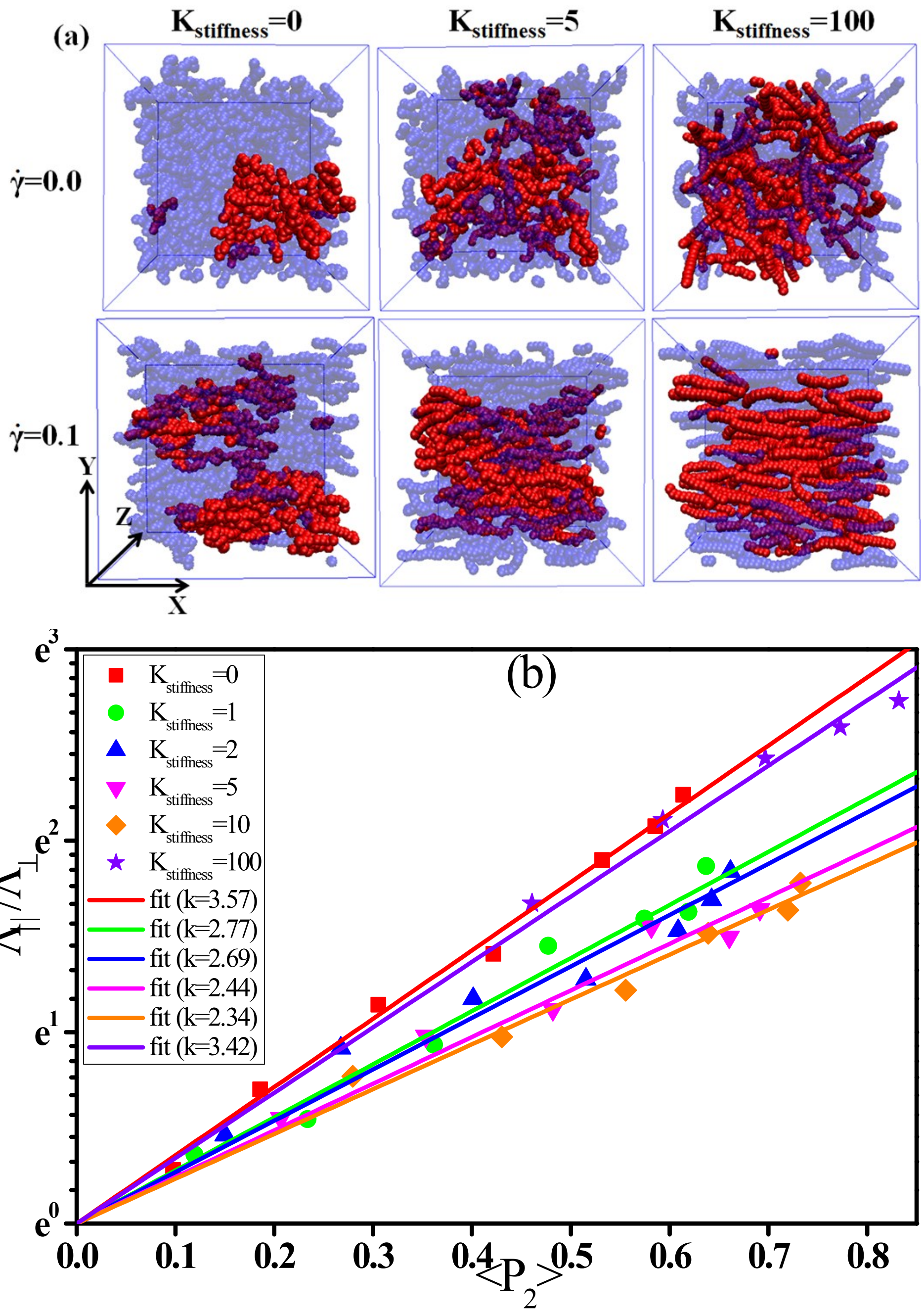


Fig. S8(a) Some typical snapshots for systems for different nanorod stiffness ($K_{stiffness}$) at two shear rates $\dot{\gamma}$= 0.0 and 0.1 (φ=4.40%). The red spheres denote the nanorods within the main cluster. The blue spheres are the other nanorods. X direction is the shear direction. (b) The linear relationship between the logarithm of anisotropy of conductive probability $\Lambda_{\parallel} / \Lambda_{\perp}$ and the orientation of nanorod $< P_2 >$ at φ=3.95%. (T^*=1.0)

References

1. M. J. Kim, H. W. Cho, J. Kim, H. Kim and B. J. Sung, *Physical Review E*, 2015, **92**, 042601.
2. T. Zhao and X. Wang, *Polymer*, 2013, **54**, 5241-5249.