Supporting Information

Molecular dynamics simulation of the electrical conductive network formation of polymer nanocomposites with polymer-grafted nanorod

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The aggregation structure of the nanorod in the matrix

First, we discussed the aggregation structure of the nanorod (NR) for different grafting density (N_g: 0, 2, 4, 6, and 8). The length L_g of grafted chains is 8. Here, each system contains 3500 NRs ($\varphi = 3.50\%$). It is reported that the NR dispersion state strongly depends on N_g, which results from the competition between the conformation entropy of grafted chains and the enthalpy between NRs.[1, 2] First, the inter-nanorod radial distribution function (RDF) is used to characterize the NR dispersion state in Fig. S2(a). Because of attractive interaction between NRs, NRs (N_g=0) tend to form the direct contact aggregation, which is proved by the high peak at $r = 1\sigma$. According to previous theories[1, 3] and experiment[4, 5], the aggregation of NRs is attributed to the depletion, which results in a fully entropic attraction between them. With increasing N_g, grafted chains repel the NRs apart. As a result, NRs gradually disperse into the matrix, which is reflected by the gradual decrease of the peak at $r = 1\sigma$. To intuitively observe the NR dispersion state, Figure S2(b) presents the snapshots of NRs for different N_g. At N_g=0, NRs are self-assembled to form the local order structure with NRs aligned side-by-side. High N_g gradually induces the local order structure of the NR aggregation break down. In summary, the NR dispersion state gradually changes from aggregation to relatively uniform distribution with increasing N_g. By employing the dissipative particle dynamics simulations[1], three different morphologies (aggregation, partial aggregation, dispersion) are observed with N_g, which is consistent with our simulation results.

From Fig. S2(b), we observed the obvious local order of the NR aggregation for

N_g=0. To better characterize it, the second Legendre polynomial ($< P_2(\mathrm{r}) >$) is calculated as a function of the distance between any two NRs, defined below:

$$< P_2(\mathrm{r}) >= (3 < \cos^2 \theta > -1) / 2 \quad (1)$$

where θ denotes the angle between the two end-to-end vectors of a pair of NRs. Averaged over all the NR pairs, $< P_2(\mathrm{r}) >$ is 1.0 for parallel alignment, 0.0 for random alignment, and -0.5 for perpendicular alignment. The local order of the NR aggregation is evaluated in Fig. S3(a). It reveals very strong orientational correlations for $N_g = 0$, which persists over relatively large distances. However, with increasing N_g, the peaks at $r < 4\sigma$ gradually decrease, which shows a weak orientational correlations and random distribution of NRs.

Then, we calculated the number of the nearest neighbor NRs surrounding one NR (N_{num}) at their separation less than 1.5σ in Fig. S2(a). Figure S3(b) presents the probability distribution P_N of N_{num} for different N_g. For $N_g = 0$, there are two obvious peaks of P_N, which are at N_{num}=3 and 4 respectively. These peaks actually reflect the local order of the NR aggregation structure. In addition, for $N_g = 0$, P_N at N_{num}=0 is about 0.08, which indicates that some isolated NRs still exit in the matrix. With the increase of N_g, the peak value of P_N increases. Meanwhile, N_{num} at the peak value of P_N gradually shifts from 4 to 1. These results further indicate that the local order structure is broken down. Accompanied by it, the NRs gradually disperse into the matrix and more single NR appears.

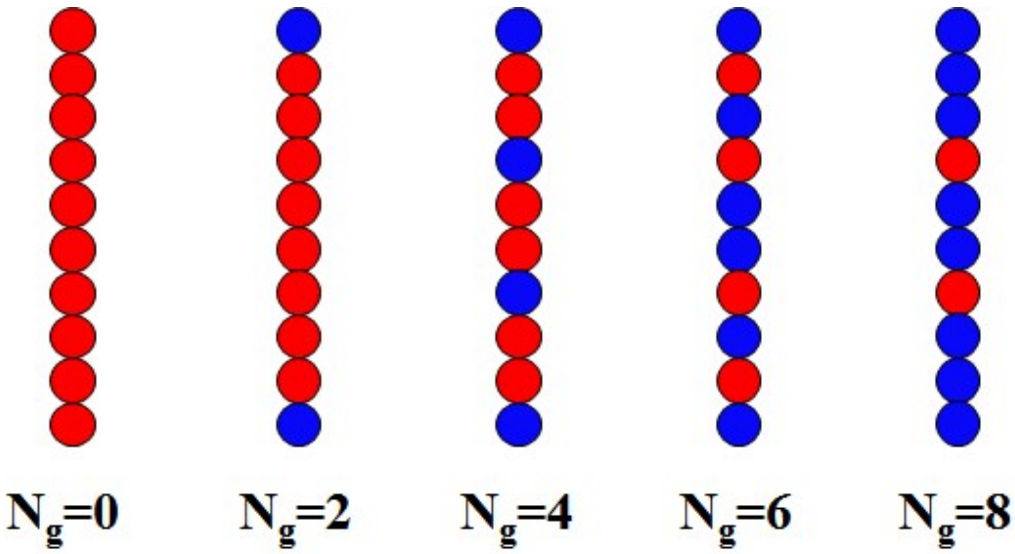

Fig. S1 The snapshots of nanorods with different grafting density (N_g). The blue spheres denote the grafted beads. The red spheres are the other beads. For clarity, the grafted chains are not presented.

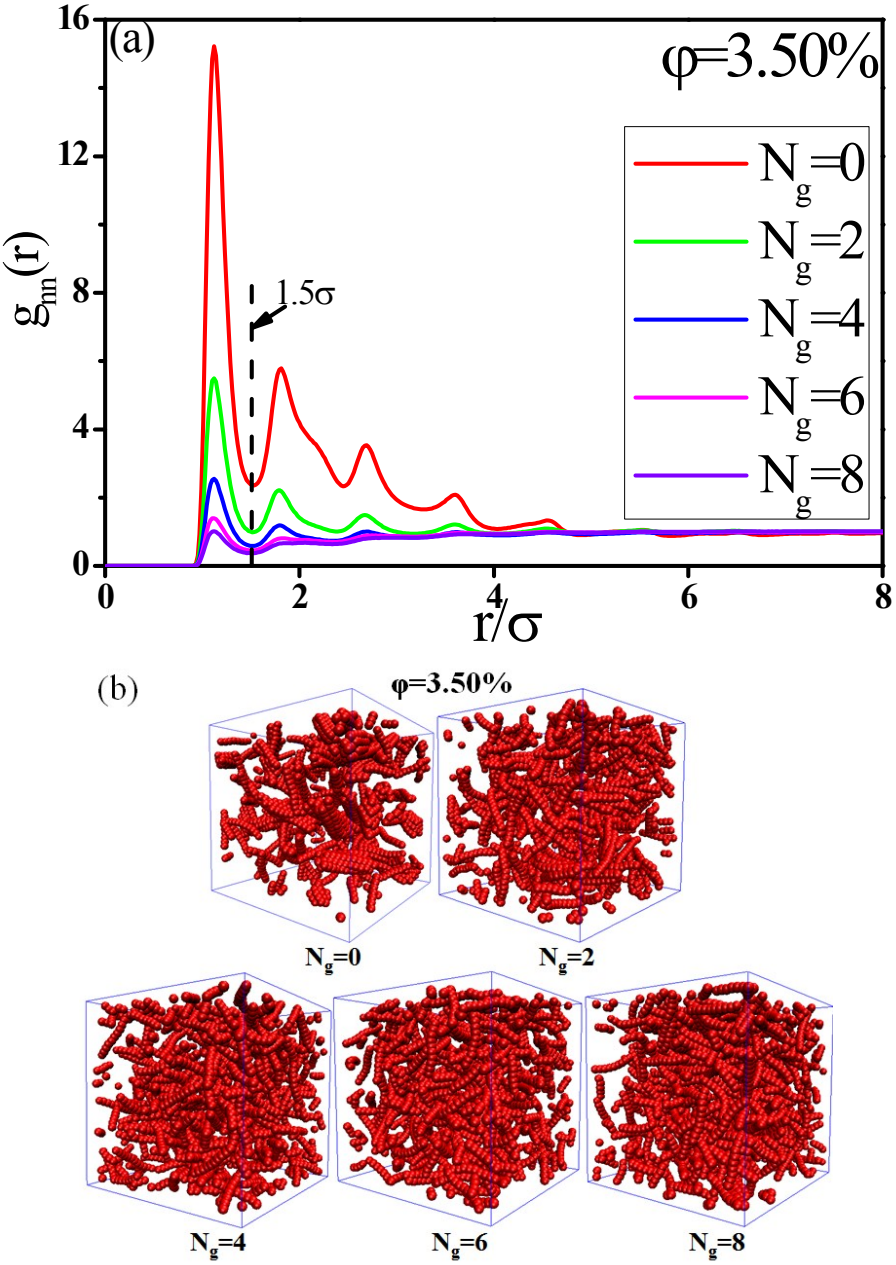

Fig. S2(a) RDF and (b) the snapshots of the nanorods with different grafting density (N_g) where the polymer chains are neglected for clarity at φ=3.50%. The red spheres denote the nanorods. (T^*=1.0, χ=0.0)

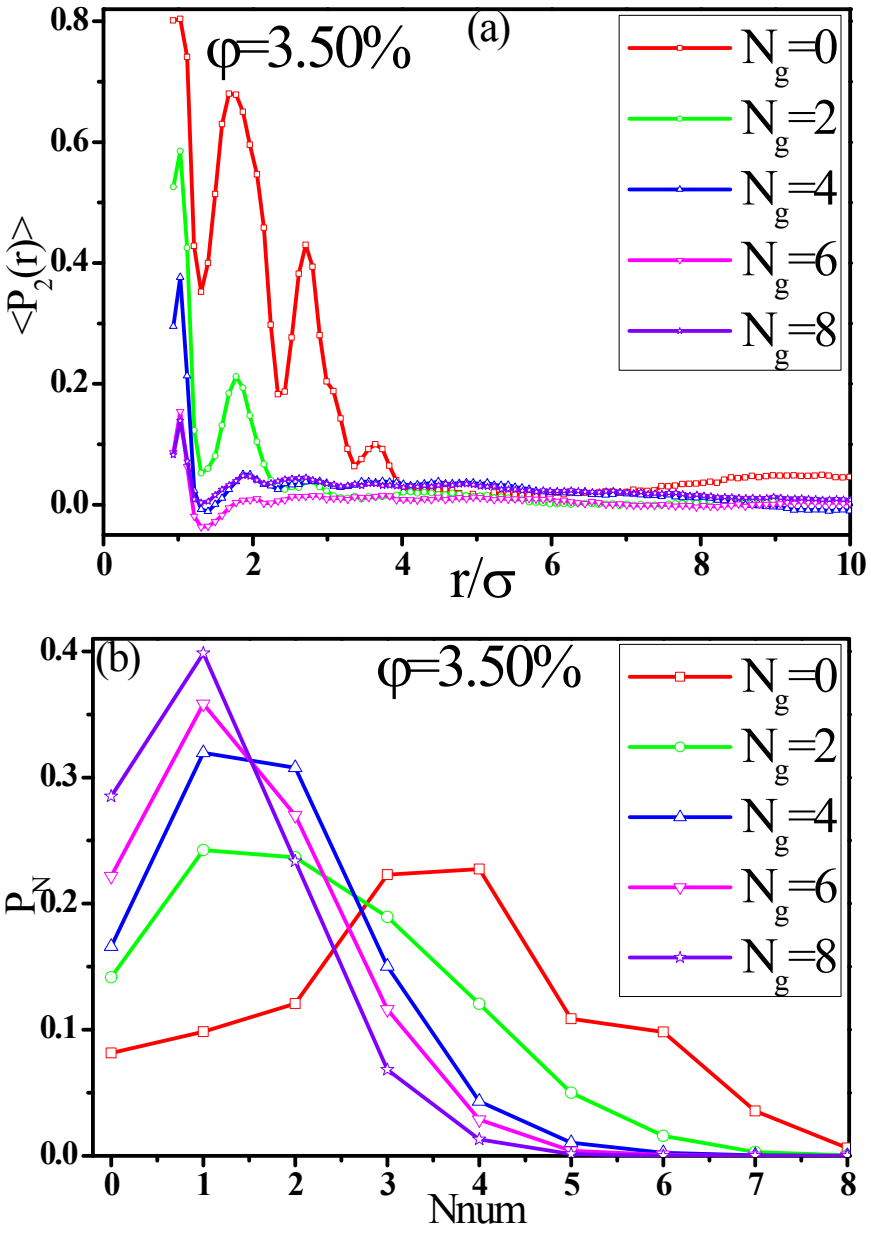

Fig. S3(a) The local order structure $< P_2(\mathrm{r}) >$ of the nanorod (NR) aggregation and (b) the probability distribution (P_N) of the nearest neighbor NRs surrounding one NR at a separation closer than 1.5σ (Nnum) for different grafting density (N_g). (T^* =1.0, χ=0.0)

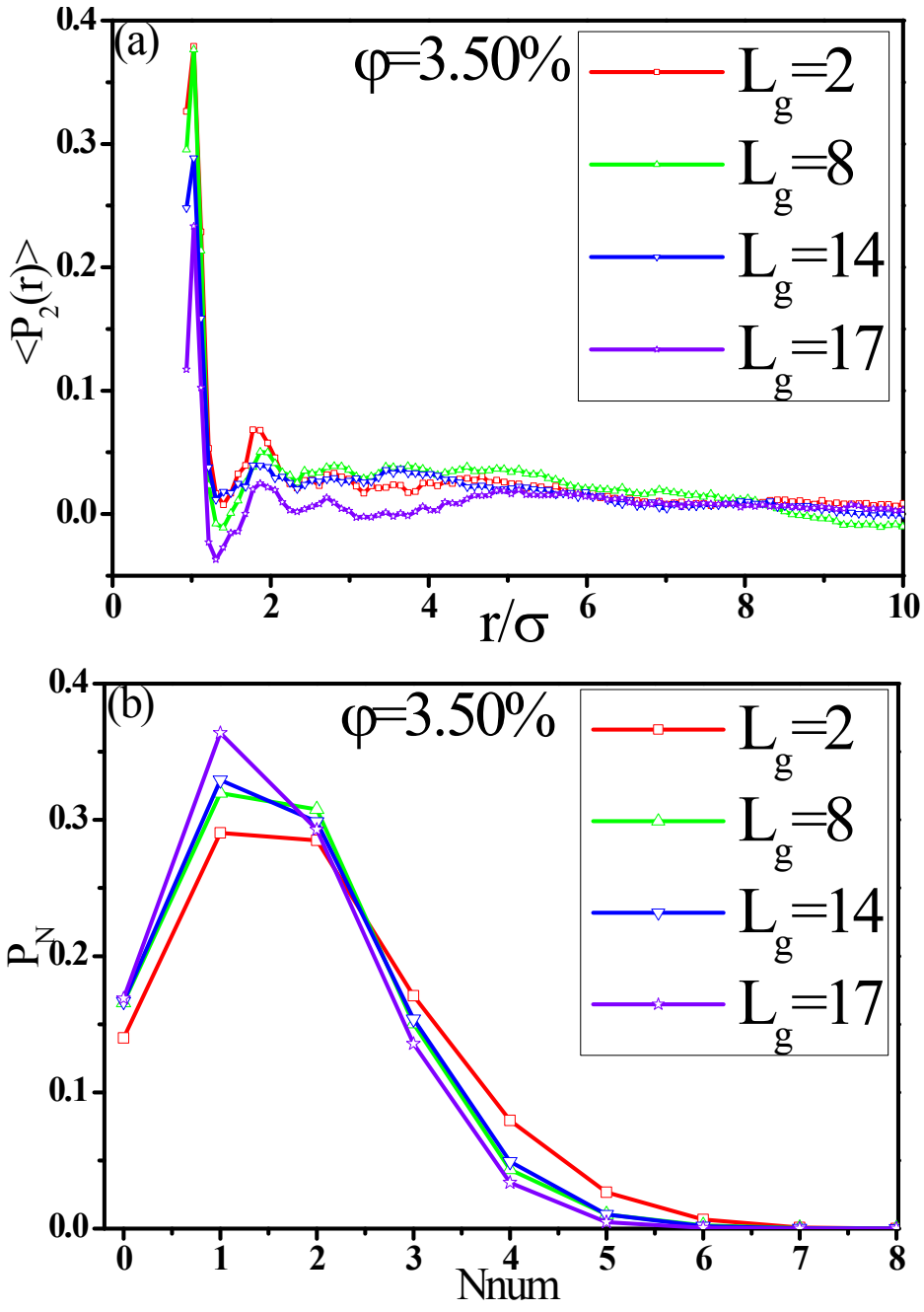

Fig. S4(a) The local order structure $< P_2(\mathrm{r}) >$ of the nanorod (NR) aggregation and (b) the probability distribution (P_N) of the nearest neighbor NRs surrounding one NR at a separation closer than 1.5σ (Nnum) for different length of grafted chains (L_g). (T^*=1.0, χ=0.0)

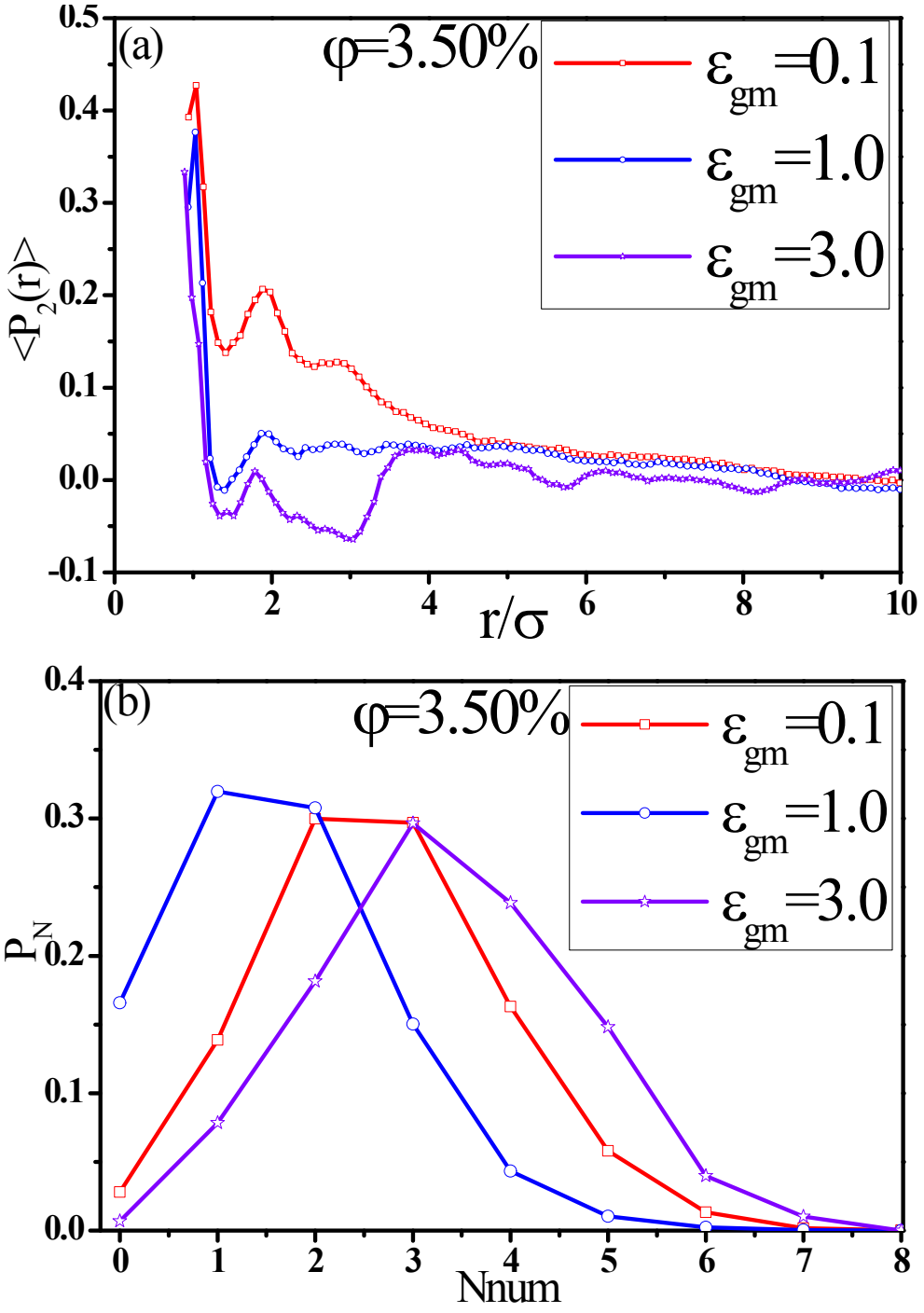

Fig. S5(a) The local order structure $< P_2(\mathrm{r}) >$ of the nanorod (NR) aggregation and (b) the probability distribution (P_N) of the nearest neighbor NRs surrounding one NR at a separation closer than 1.5σ (Nnum) at different interactions (ε_{gm}) between grafted chains and free chains. (T^* =1.0, χ=0.0)

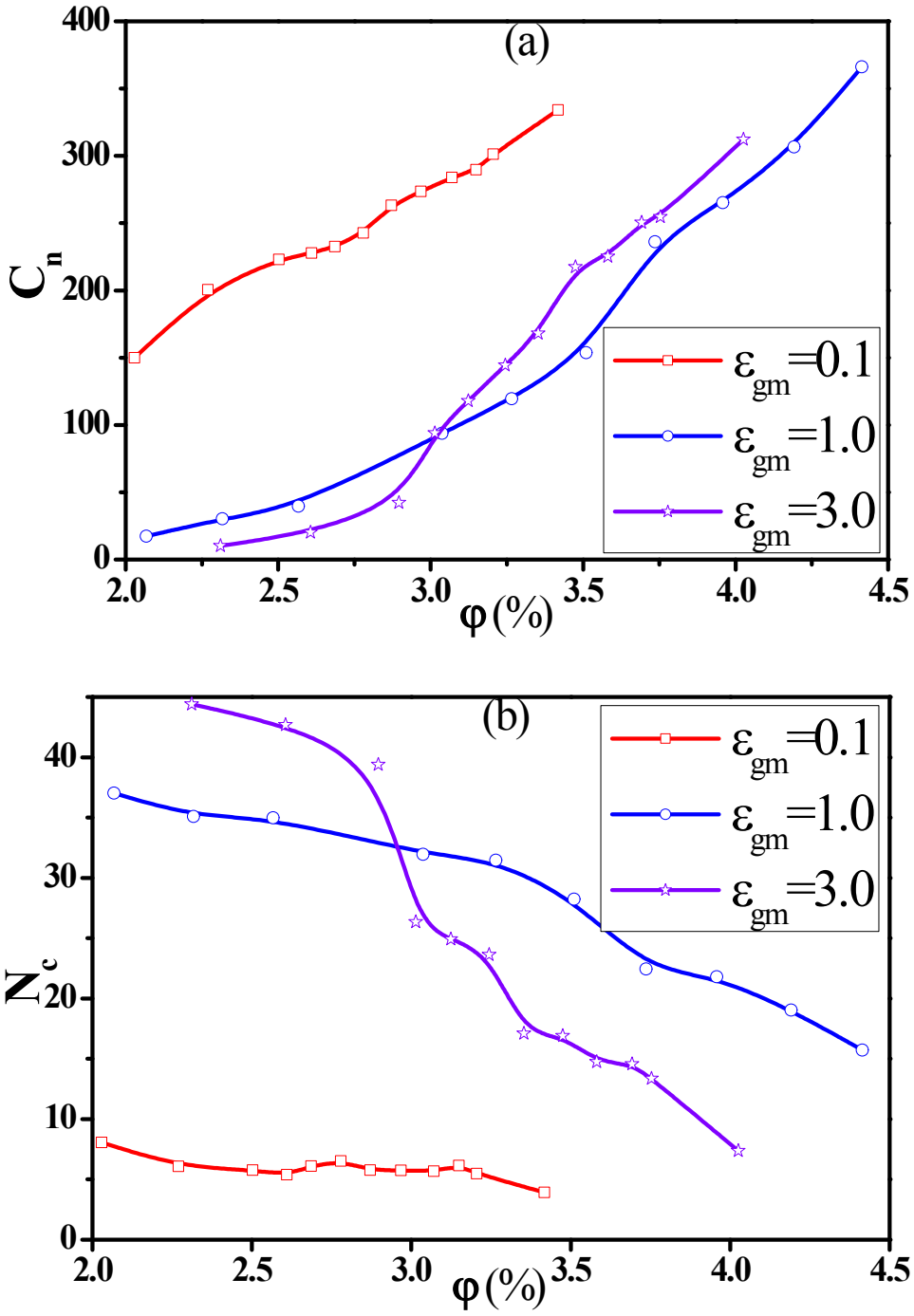

Fig. S6 Change of (a) the main cluster size C_n and (b) the total number of clusters N_c as a function of the nanorod volume fraction φ for different interactions (ε_{gm}) between grafted chains and free chains. (T^*=1.0, χ=0.0)

Table S1 Nonbonded interaction parameters used in this work.

Interaction types	ε_{ij} [a] (ε)	r_{cutoff} [b] (σ)
PB[c]-PB[c]	**1.0**	$2\times2^{1/6}$
GB[d]-GB[d]	**1.0**	$2\times2^{1/6}$
NR[e]-NR[e]	**1.0**	**2.5**
PB[c]-GB[d]	**0.1, 1.0, 3.0**	$2\times2^{1/6}$
PB[c]-NR[e]	**1.0**	**2.5**
GB[d]-NR[e]	**1.0**	**2.5**

[a] ε_{ij} the energy parameters between interacting sites i and j.

[b] r_{cutoff} is the cut-off distance.

[c]PB is the free bead.

[d]GB is the bead of grafted chains.

[e]NR is the nanorod.

References

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