

Supporting Information

Controlling the electrical conductive network formation of polymer nanocomposites via polymer functionalization

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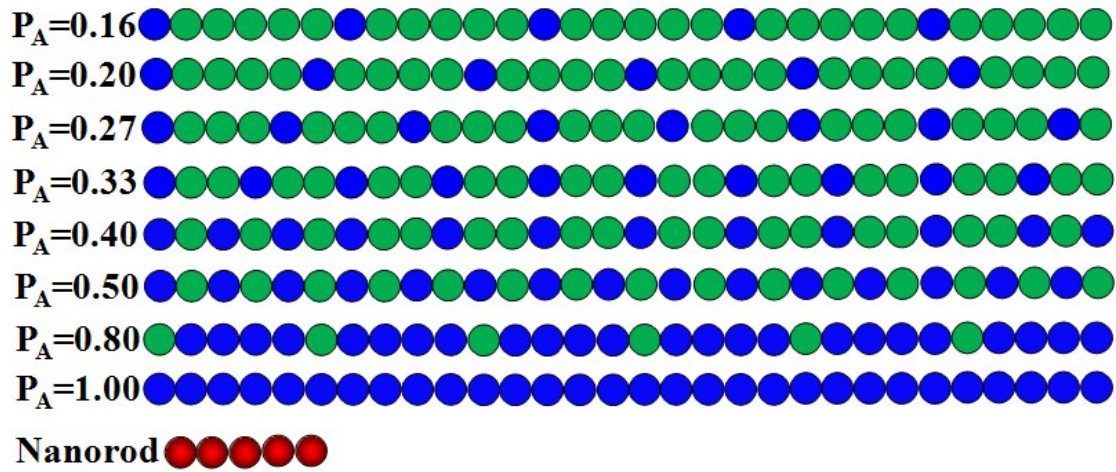


Fig. S1 The distribution of A and B monomers in each chain at different random functionalization degrees P_A . The blue beads denote the A monomers, the green beads denote the B monomers and the red beads denote the nanorod.

NR aggregation structure in the matrix

Figure S1 shows the random distribution of A monomers in each chain. In this section, the chain functionalization degree P_A varies from 0.16 to 1.0. Each system contains of 2100 NRs, which is corresponding to the volume fraction of NRs about 4.98%. The NR dispersion state in the matrix depends on the chain functionalization degree. First, similar to the works,^{1, 2} the inter-nanorod radial distribution function (RDF) is used to characterize the NR dispersion state, as shown in Fig. S2(a). The peak at $r = 1\sigma$ reflects the direct contact aggregation structure of the NR. At low functionalization degree $P_A = 0.16$, the peak at $r = 1\sigma$ is very high, which indicates the relatively bad dispersion of the NR. With the increase of the P_A , both peaks at $r = 1\sigma$ and $r = 2\sigma$ gradually decrease. At $P_A \geq 0.8$, the peak at $r = 1\sigma$ disappears, indicating the absence of the direct contact aggregation structure of the NR. The NRs intend to form the aggregate sandwiched by one polymer layer, which reflects

relatively uniform dispersion. To intuitively observe the NR dispersion state, the snapshots for different functionalization degrees are shown in Fig. S2(b). At $P_A \leq 0.5$, there are some peaks between $r = 1\sigma$ and $r = 2\sigma$. This is because several NRs are adsorbed by one A monomer at the same time, which is shown in Fig. S2(b). Depending on the polymer-NR interaction, the NRs exhibit the contact aggregation, dispersion, bridging, and telebridging behavior by employing the integral equation theory.³ In our systems, at $P_A \geq 0.8$, the NRs mainly form the bridging and telebridging structures. At $P_A \leq 0.5$, the NRs mainly form the contact aggregation and bridging structures. In summary, the NR dispersion state gradually changes from local aggregation to relatively uniform distribution with the increase of the P_A .

Meanwhile, from Fig. S2(b), we observe the local order of the NR aggregation at $P_A \leq 0.2$. As the increase of the P_A , the NRs disperse into the matrix with random orientation. To better characterize it, we calculate the local order of the NR aggregation as a function of the distance between any two NRs, defined as the second Legendre polynomial ($\langle P_2(\mathbf{r}) \rangle$), given by

$$\langle P_2(\mathbf{r}) \rangle = (3 \langle \cos^2 \theta \rangle - 1) / 2 \quad (1)$$

where θ denotes the angle between the two end-to-end vectors of a pair of NRs. Averaged over a set of NR pairs, this value is -0.5 for perpendicular alignment, 1.0 for parallel alignment, and 0.0 for random alignment. From Fig. S3(a), evaluation of local order of the NR aggregation as a function of their distance reveals very strong orientational correlations, which persists over relatively large distances at $P_A \leq 0.2$; however, at $P_A > 0.2$, there is a very weak level of orientational correlations indicated

by low value $\langle P_2(r) \rangle$ at $r < 3\sigma$, which reflects the random distribution of the NR. Then we calculate the number of the nearest neighbor NRs surrounding one NR at a separation closer than 1.3σ in Fig. S2(a), denoted by N_{num} . The probability distribution (P_N) of the N_{num} is obtained for systems with different functionalization degrees in Fig. S3(b). At $P_A \leq 0.2$, there are three obvious peaks of the probability distribution P_N , which are located at N_{num} equal to 1, 2 and 3 respectively. To better understand the N_{num} , from the illustration in Fig. S3(b), the N_{num} is 1, 2, and 3 for the yellow NR, green NR and red NR respectively. Above results actually reflect the local order of the NR aggregation at $P_A \leq 0.2$. At $P_A \leq 0.2$, the P_N at $N_{\text{num}}=0$ is 0, which indicates the absence of the single NR structure in the matrix. However, when the P_A increases from 0.16 to 1.0, the P_N at $N_{\text{num}} \geq 2$ decreases, while it increases at $N_{\text{num}}=0$. This indicates more single NR structure in the matrix. Especially, only the isolated single NR structure exists at $P_A = 1.0$.

Next, we calculate the probability distribution (P_S) of the aggregation size (defined as the number of NRs within the same aggregation). Here any two NRs are considered to belong to the same aggregation if their distance is less than 1.3σ . For the single NR structure, the aggregation size is equal to 1.0. Figure S4(a) presents the change of the probability distribution P_S of the aggregation size with the P_A . The relationship between the aggregation size and the serial number (SN) is shown in Table S1. We find that the P_S at $\text{SN} \geq 3$ gradually decreases, while it increases at $\text{SN}=1$ accompanied by the increase of the P_A . Furthermore, we calculate the average size C_{aver} of all the aggregations in our systems, defined as

$$\langle C_{aver} \rangle = \frac{\sum S^2 * P_S}{\sum S * P_S} \quad (2)$$

where S is the size of an aggregation and P_S is the probability that the aggregation in size S occurs. Figure S4(b) shows the average size C_{aver} at different functionalization degrees. It is interesting to find that the C_{aver} first increases and then decreases with the P_A . This result is attributed to different NR aggregation structures at different functionalization degrees. At $P_A \leq 0.2$, there is not enough A monomers which have strong attraction with the NR. Thus, one A monomer adsorbs some NRs at the same time, which leads to the local order of the aggregation in Fig. S3(a). Very few A monomers are left to connect the isolated aggregations together, which is reflected by the low average aggregation size C_{aver} . As a result, it mainly forms some isolated NR aggregates with local order (I) in Fig. S4(c). When the P_A increases to 0.4, these isolated NR aggregates are gradually broken up. Along with it, the peak of the probability distribution P_N changes from $N_{num}=2$ to 1 in Fig. S3(b). Additional A monomers can link the isolated NR aggregations together. As a result, at $P_A=0.4$, most NRs are connected each other, leading to the largest average aggregation size C_{aver} denoted by the structure II in Fig. S4(c). Meanwhile, the single NR structure begins to appear in the matrix at $P_A=0.4$. With further increasing P_A to 1.0, all NRs disperse uniformly in the matrix and are not connected each other, namely the single NR structure. Thus, the average aggregation size C_{aver} is equal to 1, which is denoted by the single NR structure (III) in Fig. S4(c). To better illustrate it, we calculate the ratio of the number of A monomers within the distance 1.3σ around the NRs to the number of total A monomers in the systems, which is shown in Fig. S5. We find that

this ratio gradually decreases with the increase of the P_A . This means there is not enough A monomers at low P_A , which further confirms above explanation.

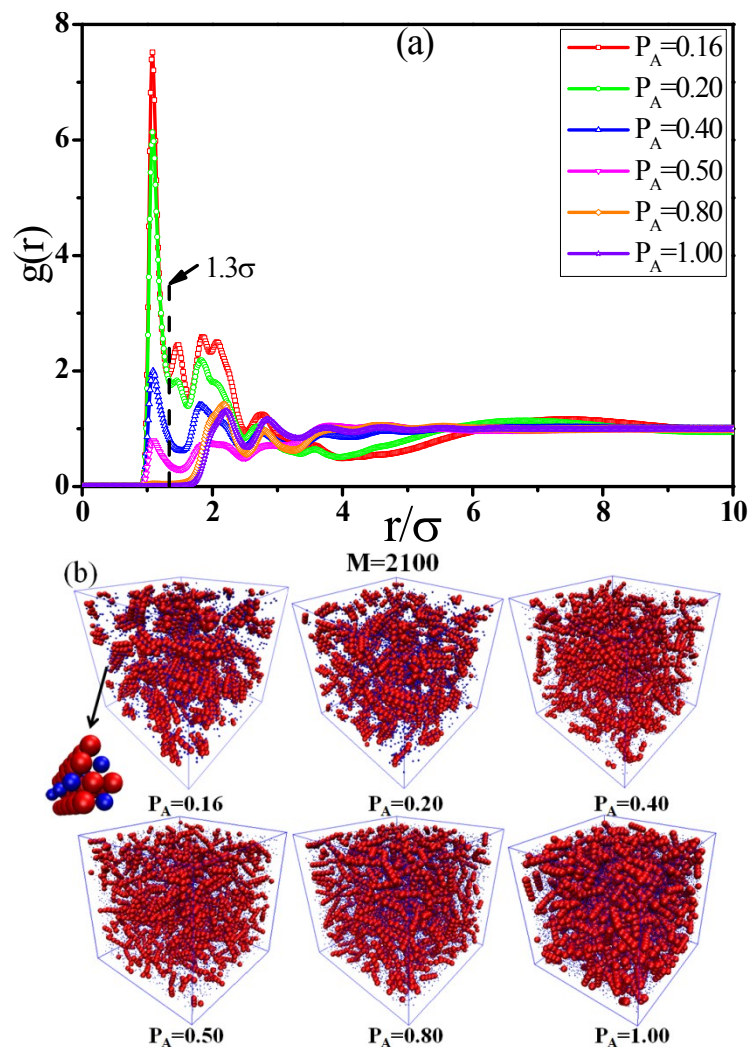


Fig. S2(a) RDF of nanorods and (b) snapshots for the systems with different chain functionalization degrees P_A . The red spheres denote the nanorods, the small blue spheres denote A monomers, and for clarity B monomers are not presented.

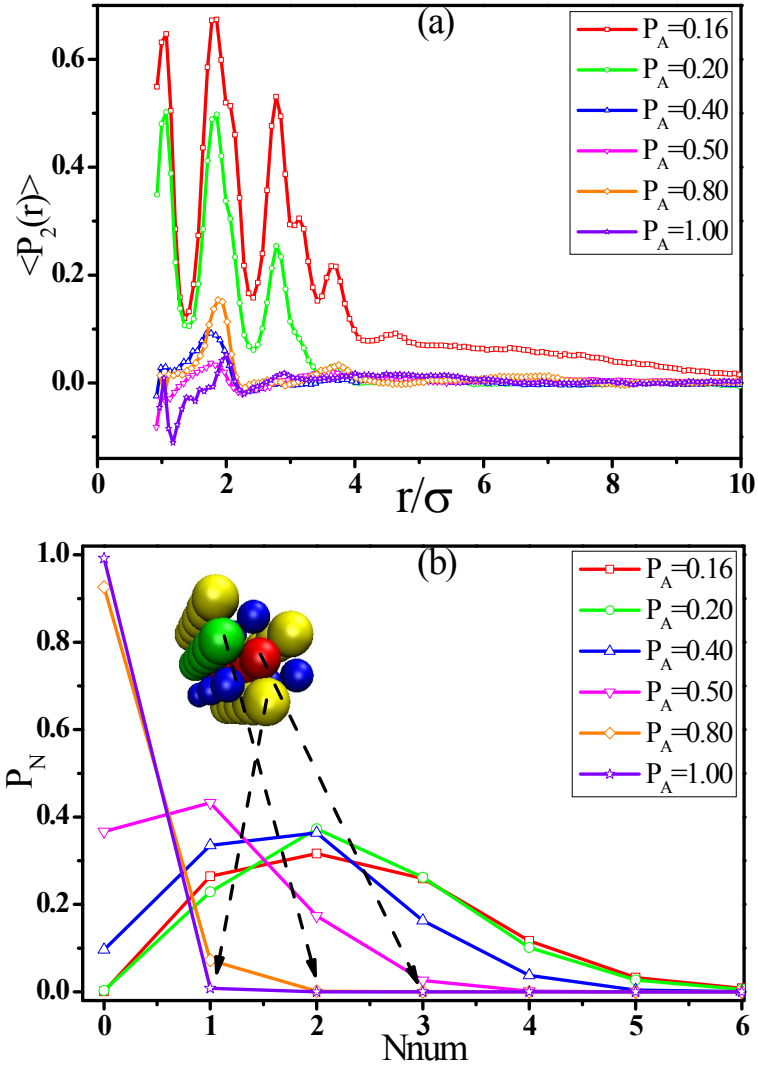


Fig. S3(a) The local order structure $\langle P_2(r) \rangle$ of the nanorod aggregation and (b) the probability distribution (P_N) of the nearest neighbor nanorods surrounding one nanorod at a separation closer than 1.3σ (N_{num}) at different functionalization degrees P_A . The red, green and yellow spheres denote the nanorods, the blue spheres denote some A monomers which are adsorbed by the nanorods.

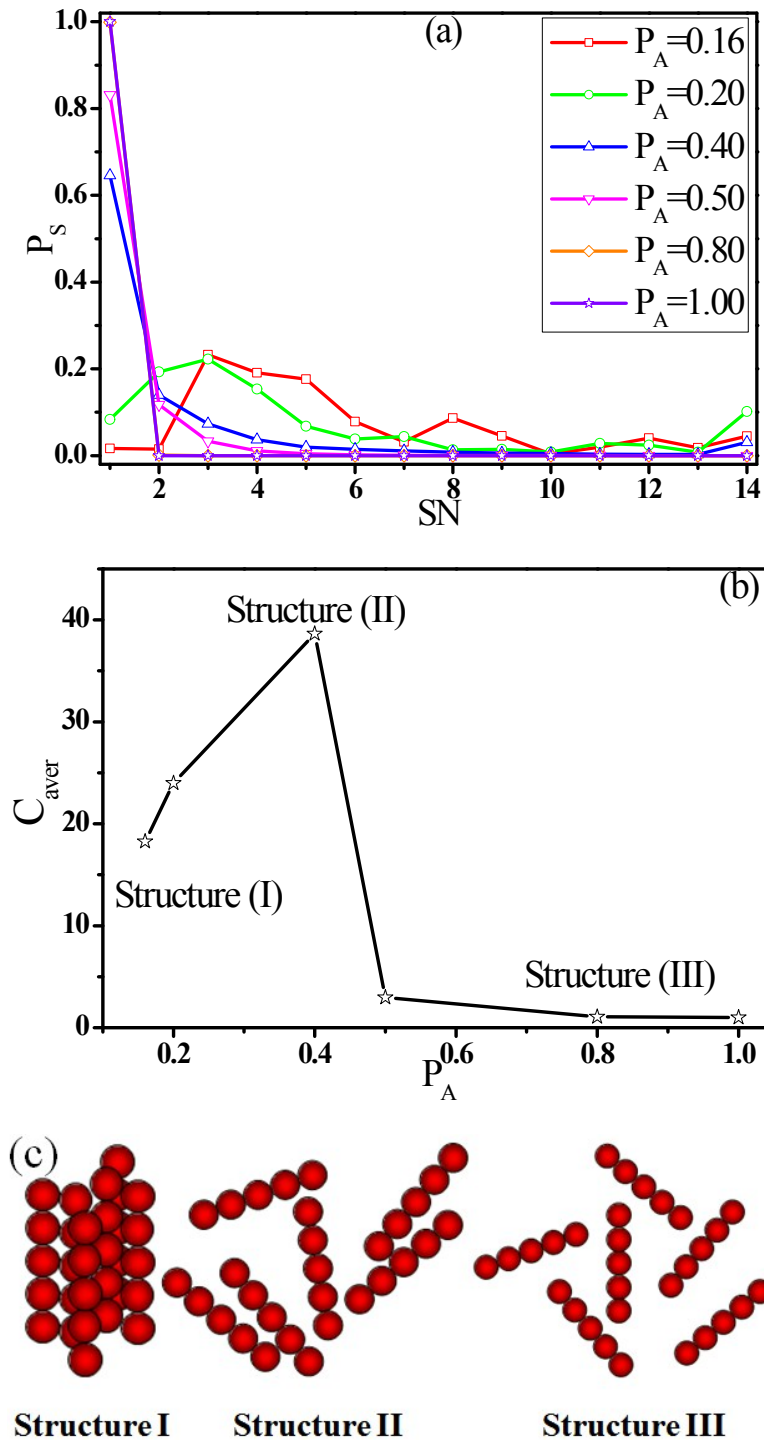


Fig. S4(a) The probability distribution (P_S) of the nanorod aggregation size as a function of the serial number (SN) and (b) the average aggregation size C_{aver} for different functionalization degrees P_A . (c) Three kinds of the nanorod aggregation structures I, II and III. The red spheres denote the nanorods.

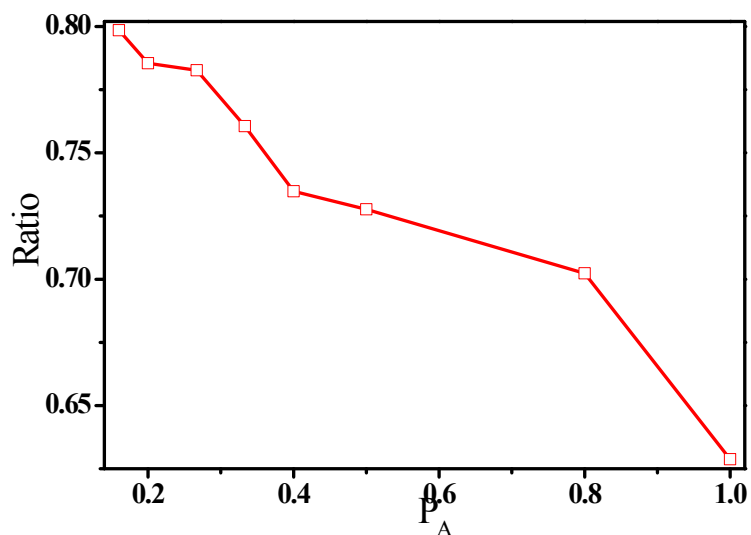


Fig. S5 Ratio of the number of A monomers within the distance 1.3σ around the nanorods to the number of total A monomers for the systems with different functionalization degrees P_A .

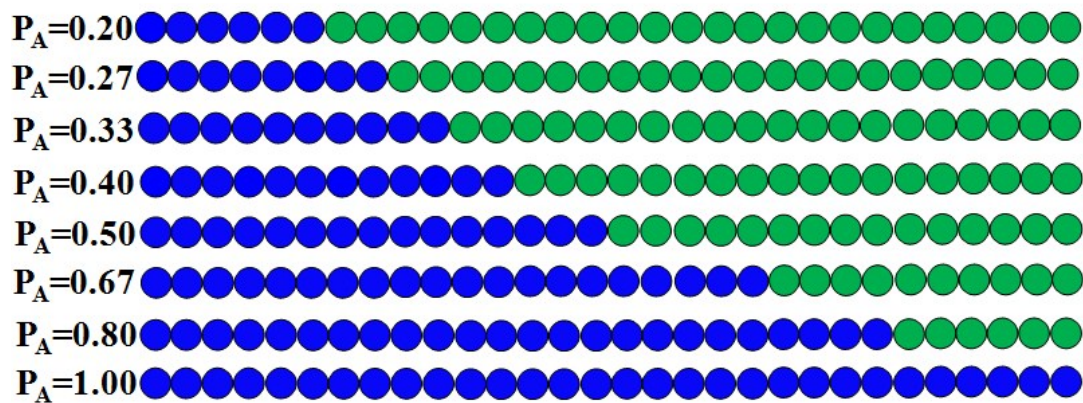


Fig. S6 The distribution of A and B monomers in each chain at different diblock functionalization degrees P_A . The blue beads denote the A monomers, the green beads denote the B monomers.

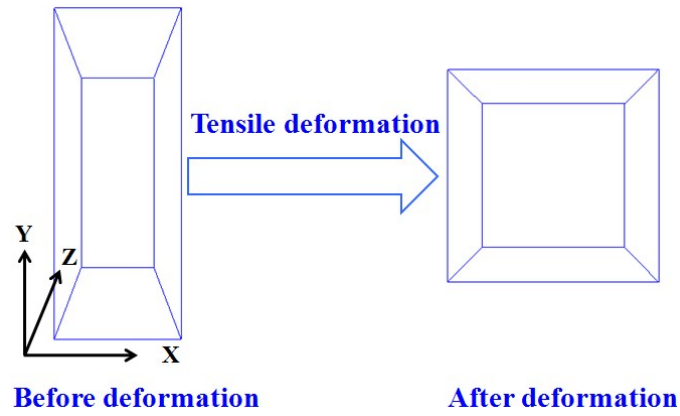
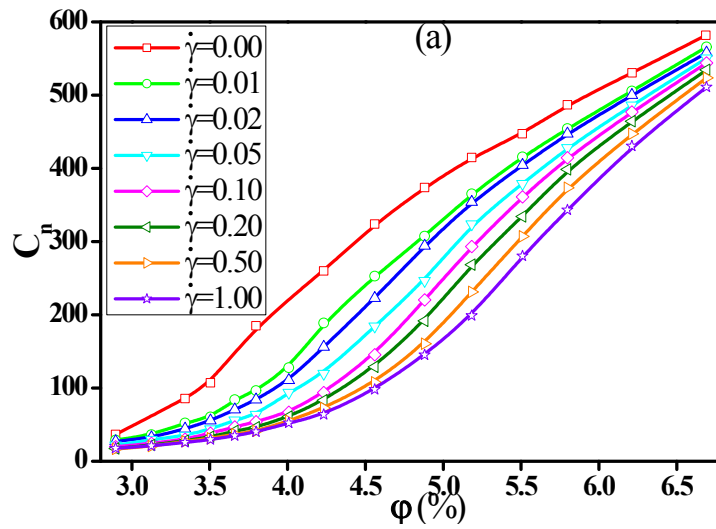


Fig. S7 The simulation box before and after deformation. The cell parameters of box before deformation are L_{x_0} , L_{y_0} , and L_{z_0} . The cell parameters of box after deformation are L_{x_1} , L_{y_1} , and L_{z_1} . There are some conditions, which should be met: (1) $L_{y_0}=L_{z_0}$, $L_{x_1}=L_{y_1}=L_{z_1}$; (2) $L_{x_0} \cdot L_{y_0} \cdot L_{z_0} = L_{x_1} \cdot L_{y_1} \cdot L_{z_1}$; (3) $L_{x_1} = (1 + \alpha) \cdot L_{x_0}$;



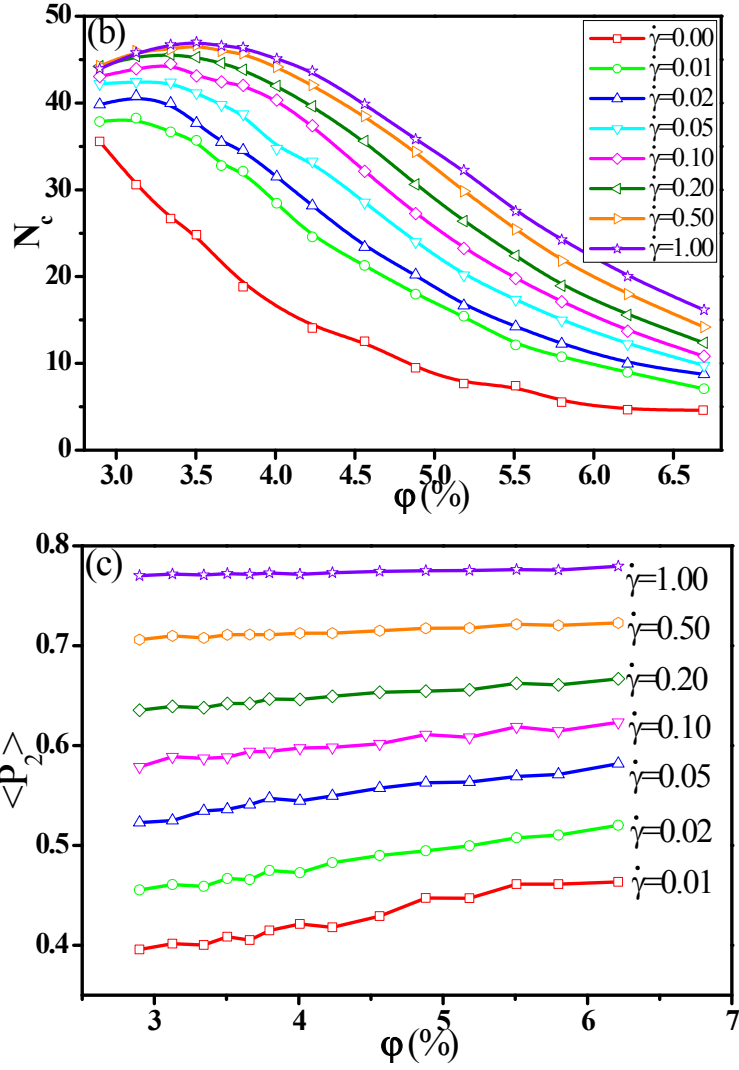


Fig. S8(a) The maximum cluster size C_n , (b) the total number of clusters N_c and (c) the nanorod orientation $\langle P_2 \rangle$ as a function of the nanorod volume fraction ϕ for different shear rates $\dot{\gamma}$. ($T^* = 1.0$, $P_A = 0.4$)

Table S1 Relationship between the aggregation size and the serial number.

The serial number	The aggregation size
1	1 or 2
2	3 or 4
3	5 or 6
4	7 or 8
5	9 or 10
6	11 or 12
7	13 or 14
8	15 or 16
9	17 or 18

10	19 or 20
11	21 or 22
12	23 or 24
13	25 or 26
14	≥ 27

1. Y. Gao, J. Liu, J. Shen, L. Zhang and D. Cao, *Polymer*, 2014, **55**, 1273-1281.
2. G. N. Toepperwein, N. C. Karayiannis, R. A. Riggleman, M. Kröger and J. J. de Pablo, *Macromolecules*, 2011, **44**, 1034-1045.
3. U. K. Sankar and M. Tripathy, *Macromolecules*, 2015, **48**, 432-442.