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半刚性高分子链螺旋结构诱导纳米棒的有序结构*

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在自然界中, 螺旋结构广泛存在. 在熵的驱动下, 高分子链能在某些特殊情形下形成螺旋结构. 采用分子动力学方法研究了高分子链诱导纳米棒的自组装行为, 发现纳米棒/高分子链体系的构象与纳米棒的数量、高分子链的刚性等密切相关. 当纳米棒与高分子链之间存在适度吸附能时, 纳米棒能够形成三种完全不同的构象, 特别是在半刚性高分子链诱导下纳米棒能够形成线型排列. 研究结果对新型材料制备具有一定指导意义.

关键词: 熵, 半刚性高分子链, 纳米棒, 分子动力学

PACS: 82.35.Lr, 82.35.Np, 82.20.Wt

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1 引言

纳米粒子的自组装是制备新型材料的很重要的一种方法. 高分子系统中的纳米粒子(如纳米球、纳米棒、纳米管等)的自组装行为已经受到越来越多的关注. 相对于球形纳米粒子而言, 非球形纳米粒子的研究更具挑战性^[1-4]. 最近, 人们发现在熵驱动下, 吸附在纳米管周围或者被限制在球内的半刚性高分子链会形成有序的螺旋结构^[5-11]. 螺旋结构一旦形成, 几个螺旋结构的轴就会趋向于构成一条直线, 因此, 本来分离的几条纳米棒就有可能自组装成有序结构. 本文采用分子动力学模拟方法研究了纳米棒/半刚性高分子链混合体系的构象, 发现不同刚性的高分子链会诱导纳米棒形成不同的结构. 研究结果可提供一种制备高质量新型材料的方法.

2 算法模型

在本文的模型中, 高分子链的总能量为

$$U_{\text{total}}(r, \theta) = -\frac{KR_0^2}{2} \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right]$$

$$+ b(1 + \cos \theta) + 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right], \quad (1)$$

第一项有限伸展非线性弹性势仅用于限制两相邻粒子间的键长为 $r (r < R_0)$, 其中 $K = 30\varepsilon/\sigma^2$, $R_0 = 1.5\sigma$; 第二项表示弯曲势能, 通过调节 b 值大小来控制高分子链的刚性, 其中 $\cos \theta$ 表示相邻两个键之间夹角的余弦值; 最后一项是Lennard-Jones势, 它表示粒子之间非共价键的相互作用, 可用于防止粒子重叠, 其中能量单位 $\varepsilon = 1.0k_B T$, 这里 r 表示两个非相邻粒子之间的距离. 截断半径为 $r < 2^{1/6}\sigma$, 这里 σ 是高分子链单体的直径.

体系中纳米棒由5个直径为 σ_r 的粒子组成($N_n = 5$), 纳米棒各粒子间的相互作用也用(1)式表示, 其中参数改为 $R'_0 = 1.5\sigma_r$, $b' = 10^4\varepsilon$, $\sigma' = 4\sigma$. 采用很大的弯曲势能($b' = 10^4\varepsilon$)能够保证纳米棒的性质. 一般纳米棒的粒子大小远大于高分子链单体的大小, 因此选择 $\sigma' = 4\sigma$.

另外, 采用Morse势来描述半刚性高分子链与纳米棒分子之间的相互作用,

$$U_{\text{Morse}}(r) = D_0 \left[e^{-2\alpha(r-r_{\text{mb}})} - 2e^{-\alpha(r-r_{\text{mb}})} \right], \quad (2)$$

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式中, 各个参数分别取为 $\alpha = 1.25/\sigma$, $r_{mb} = (\sigma + \sigma')/2$, $r_{cut} = 10\sigma$. r_{cut} 表示截断半径, D_0 表示吸附能的强弱. 起初链长 $N = 1000$ 的高分子链和纳米棒随机地放在大小为 $(500\sigma)^3$ 的盒子中. 采用 lammmps 软件 [12], 体系处于 NVT 系综, 体系温度设为 $T^* = 1.2\varepsilon/k_B$, 为了获得稳定的构象, 每个体系至少运算 $t = 8 \times 10^6\tau_0$, 其中时间步长 $\Delta t = 0.01\tau_0$.

3 模拟结果与数据分析

3.1 纳米棒的有序结构

图 1(a) 给出了不同高分子链的刚性和不同链与纳米棒之间的吸附能下纳米棒/高分子链共混体系的不同构象. 当吸附力很小时 ($D_0 < 1.0k_B T$), 高分子链与纳米棒的相互作用很小, 纳米棒几乎是自由的, 此时纳米棒的相结构与气态相类似. 而当吸附能增大到适当值 (与高分子链的刚性有关) 时, 会形成三种完全不同的构象 (图 1(b)): 当 b 很小时, 高分子链可以看成是柔性高分子链, 此时纳米棒的构象可以看成是边与边 (side-to-side) 相临的平行有序构象, 而高分子链则是无序地围绕着纳米棒; b 增大到一定时 (如 $b = 80k_B T$), 纳米棒就会出现头对头 (end-to-end) 相接的平行结构, 同时高分子链则有序地缠绕在棒上; 当继续增大 b , 纳米棒和高分子链都会慢慢地变得无序, 纳米棒则是分散的. 先前关于柔性高分子链本体/纳米粒子共混体系的研究表明 [13], 当柔性高分子链与纳米棒之间存在较大吸附能时, 体系会形成特殊的相分离构象. 图 1(b) 的现象可以理解为: 当 b 很小时, 在熵和吸附能的作用下, 纳米棒集聚形成边与边相临的有序结构, 高分子链吸附在纳米棒的周围; 当 b 适中时, 对于半刚性高分子链, 由于取向熵和高分子链的共同作用, 纳米棒集聚形成头对头相接的有序结构, 同时半刚性高分子链围绕着纳米棒形成有序螺旋结构; 而 b 很大时, 由于刚性高分子链不易弯曲, 导致纳米棒随机地吸附在刚性高分子链上, 不会形成有序结构. 以上的结果表明该体系中高分子链的构象与纳米棒的构象是密切相关的. 事实上, 当半刚性高分子链吸附在硬表面 (如纳米管 [4-11]) 时, 在熵驱动下就会形成螺旋结构, 半刚性高分子链的螺旋结构能够诱导纳米棒形成头对头排列的平行结构.

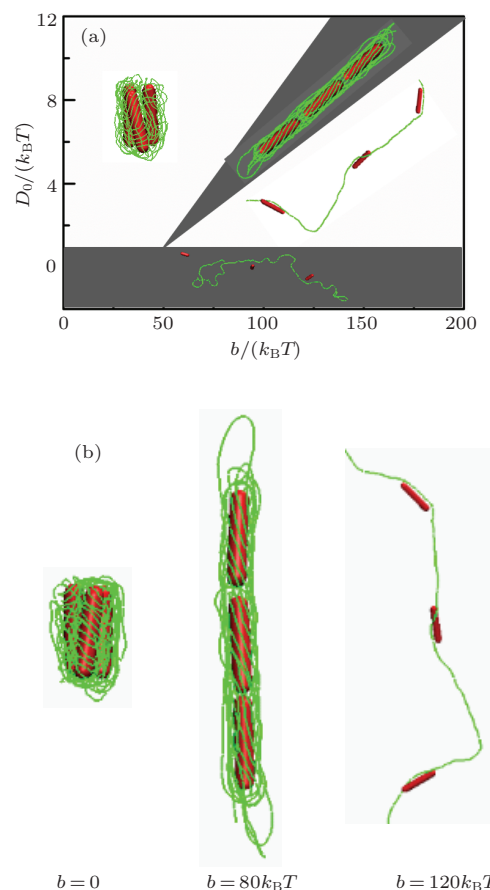


图 1 (网刊彩色) (a) 纳米棒/高分子链体系的构象与高分子链刚性 b 、链与纳米棒之间的吸附能 D_0 的关系; (b) 不同链刚性 b 时纳米棒的有序结构, 这里高分子链与纳米棒之间的吸附能 $D_0 = 5k_B T$, 棒的数目 $N_r = 3$

Fig. 1. (color online) (a) Relationship of phase diagram of NR/polymer nanocomposites to the stiffness (bending energy b) of polymer chain and the binding energy D_0 between polymer chains and NRs; (b) snapshots of different ordered structures for various bending energy b , here $D_0 = 5k_B T$ and $N_r = 3$.

为了更直观地描述纳米棒的排列构象, 引入空间分布密度函数, 结果如图 2 所示. r_{cm} 表示纳米棒质心与纳米棒质心之间的距离, 而 $P(r_{cm})$ 表示质心间距在 $[r_{cm} - \Delta r_{cm}/2, r_{cm} + \Delta r_{cm}/2]$ 内找到纳米棒的概率. 对于柔性高分子链 (b 很小情况), 图 2 中显示在 $r_{cm} \approx 5.5\sigma$ 出现一个很大的峰值. 很明显, 只有纳米棒是边与边相接的平行排列才会出现这样的概率分布. 对于半刚性高分子链的情况 (图 2 中的红色线), 其空间分布存在两个峰, 分别出现在 $r_{cm} = 16.5\sigma$ 和 $r_{cm} = 33\sigma$ 附近, 而与这两个峰值相对应的是头对头相接的平行结构, 这是因为纳米棒的棒长是 16σ . 对于刚性高分子链情况 (b 很大), 高分子链没有产生螺旋结构, 纳米棒则随机地吸附在刚性高分子链上, 因此 $P(r_{cm})$ 的分布是均匀的.

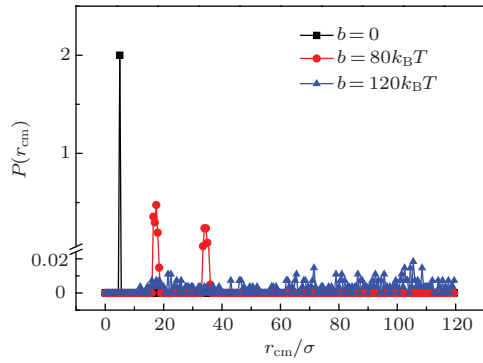


图2 (网刊彩色) 不同刚性下纳米棒质心的空间分布概率 ($D_0 = 5k_B T$)

Fig. 2. (color online) Spatial distribution of the centers of NRs for three bending energies at $D_0 = 5k_B T$.

前面提到纳米棒头对头相接的平行结构与半刚性高分子链的螺旋结构密切相关. 为了验证这种说法的正确性, 首先研究了半刚性高分子链螺旋结构的局部情况. 用半刚性高分子链在 ϕ - z 平面上的投影来显示高分子链吸附在纳米棒上的情况, 其中 ϕ - z 平面的定义如图 3(a) 所示, z 方向就是纳米棒所在的方向, 而 ϕ 方向指 x - y 平面内与 x 轴成角度 ϕ 的方向, ϕ - z 平面就是 z 方向和 ϕ 方向形成的平面. 图 3(b) 给出了高分子链在该平面内的投影, 投影图中能够看到一系列的平行线, 很明显这是高分子链均匀围绕纳米棒形成螺旋结构的结果. 图 3(b) 中的内插图显示了平均螺旋数 P_h 随 b 值的变化情况, 对于比较小的 b , P_h 值增加得比较慢; 当 $b \geq 40k_B T$ 时, P_h 突然大幅增加, 在 $b = 80k_B T$ 时达到最大值 $P_h^{\max} = 78\%$, 然后随着 b 值的继续增大, P_h 迅速减小至零. 因此, 纳米棒头对头的平行排列构象与吸附在纳米棒上的半刚性高分子链的螺旋结构密切相关.

图4 给出了在 $b = 80k_B T$ 和 $D_0 = 5k_B T$ 情形下纳米棒形成头对头平行排列构象的动态过程图.

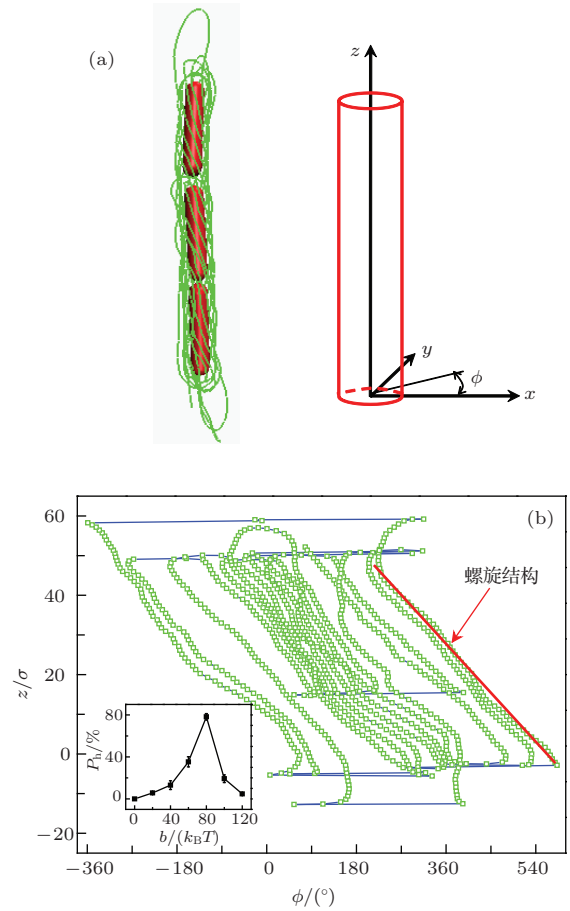


图3 (网刊彩色) (a) z 轴与方向 ϕ 的定义; (b) 高分子链某构象在 ϕ - z 平面上的投影, 内插图为不同刚性高分子链的螺旋百分比

Fig. 3. (color online) (a) Definitions of the axis z and the direction angle ϕ ; (b) projection of polymer monomers in the ϕ - z plane. The inset shows the average helix contents P_h for different bending energies at $D_0 = 5k_B T$.

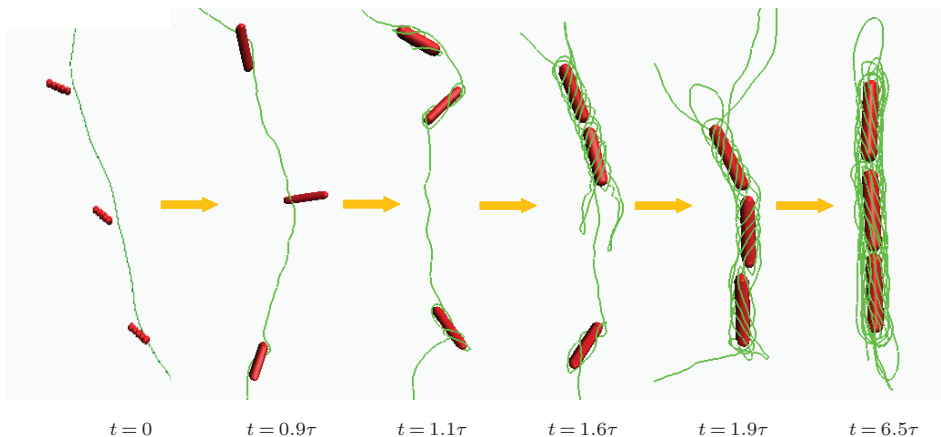


图4 不同模拟时间下纳米棒/高分子链的构象, 这里 $\tau = 10^6 \tau_0$, $b = 80k_B T$, $D_0 = 5k_B T$, $N_r = 3$

Fig. 4. Dynamical evolution of NR/polymer nanocomposites at $b = 80k_B T$ and $D_0 = 5k_B T$.

初始时刻, 纳米棒和高分子链还没吸附在一起, 它们都是随机分布的; 到了 $t = 1.1\tau$ ($\tau = 10^6\tau_0$) 时, 链吸附在了棒上, 且每根纳米棒上都产生了2到3个螺旋结构; 随着粒子运动的继续进行, 纳米棒慢慢聚合在一起, 吸附在棒上的螺旋数量也不断的增加; 最后, 三根棒全都聚合在一起形成了头对头平行排列的结构. 这些都是半刚性高分子链和纳米棒在熵的驱动下相互作用的结果.

3.2 半刚性高分子链熵力诱导纳米棒的取向

图5是纳米棒和高分子链共混体系在熵和吸引力的诱导下形成特殊构象的过程示意图. 开始时, 纳米棒和高分子链是分离的, 在吸引能的作用下, 纳米棒与高分子链慢慢吸附在一起; 随后在熵的作用下(高分子链周围的排斥体积(插图阴影部分)随着螺旋的形成会不断产生重叠, 从而导致总的排斥体积减小, 这样熵就会增加^[7]), 半刚性高分子链开始形成螺旋围绕在棒上^[4-11], 每根棒上的螺旋数一般都是3个; 之后, 随着螺旋数目慢慢增多, 纳米棒与纳米棒慢慢吸附在一起形成头对头平行排列的稳定结构; 这种结构形成后又反过来影响高分子链, 使其形成更多的螺旋.

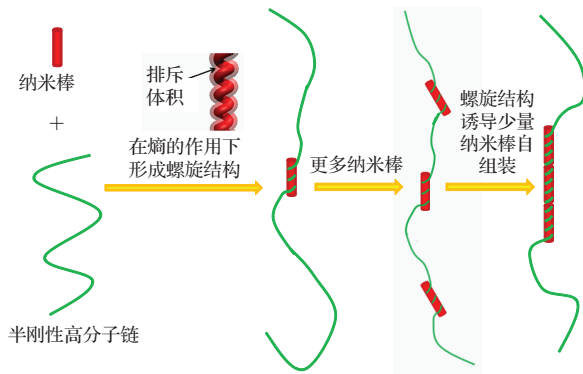


图5 (网刊彩色) 熵驱动下纳米棒形直线排列的原理图^[7]
 Fig. 5. (color online) A schematic illustration of the possible mechanism in which the formation of end-to-end parallel aggregation of NRs is driven by the helix of semiflexible polymer chain^[7].

最后分别模拟了在 $b = 80k_B T$ 时, 半刚性高分子链与不同纳米棒数目 $N_r = 5, 7, 9$ 和不同纳米棒长度 $N_n = 3, 7$ 时的自组装行为, 结果如图6所示. 很明显, 这些体系都能形成头对头平行排列的构象, 只是程度逐渐变差, 主要原因是对于一定长度的半刚性高分子链, 其形成螺旋的能力是一定的,

总的螺距也是一定的. 一旦纳米棒直线排列的长度大于半刚性高分子链形成螺旋的螺距, 纳米棒直线排列的程度就会变弱. 以上结果表明, 利用半刚性高分子链的特性来诱导纳米棒形成头对头的平行排列结构是可行的.

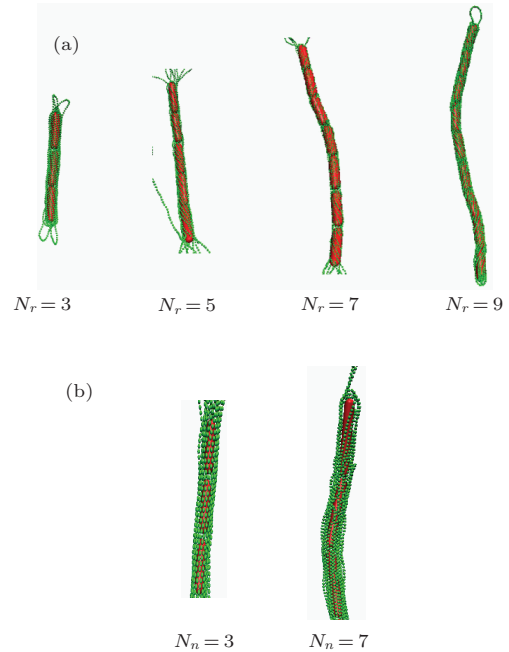


图6 (网刊彩色) $b = 80k_B T$ 和 $D_0 = 5k_B T$ 情况下, (a) 不同纳米棒数目时的自组装结构; (b) 不同纳米棒长度时的自组装结构

Fig. 6. (color online) Self-assembly structures of NR/polymer nanocomposites with (a) various numbers and (b) various lengths of NRs at $b = 80k_B T$ and $D_0 = 5k_B T$.

4 结 论

采用分子动力学方法模拟研究了纳米棒和高分子链共混体系的自组装行为. 当纳米棒和高分子链之间具有适当的吸附能时, 体系通过自组装会形成三种完全不同的构象: 柔性高分子链时纳米棒的边与边相接的平行构象; 半刚性高分子链时纳米棒头对头平行排列的构象; 刚性高分子链时纳米棒随机排列的构象. 在这个体系中, 纳米棒的自组装结构可以通过改变高分子链的刚性来实现, 这个特性为我们提供了一种新的合成新型材料方法.

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Ordered structures of nanorods induced by the helixes of semiflexible polymer chains*

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Abstract

Self-assembly of nanoparticles, such as nanospheres, nanorods (NRs), and nanotubes, in polymer systems is one of the most prominent and promising candidates for the development of novel materials with high mechanical, optical, and electrical performances. A most concerned topic on the nanoparticle/polymer composites is the spatial arrangement and distribution of nanoparticles in the nanocomposites, which is controlled by the competition between the entropic packing constraints related to the incompatibility between species with different sizes and geometries, and the enthalpic consequences of a variety of polymer-nanoparticle interactions. The studies on the nonspherical nanoparticles, such as NRs, are of more challenging than on spherical nanoparticles, because both positional and orientational ordering of anisotropic nanoinclusion have an important influence on the morphology of nanocomposition, while those studies are necessary for applications of nanoscopic anisotropic objects in photovoltaic and filled emission devices. When low-volume fractions of NRs are immersed in a binary, phase-separating blend, the rods can self-assemble into needle-like, percolating networks and this special structure can enhance the macroscopic electrical conductivity and mechanical property of the material. When an electric field is applied, the phase separations of ligand-functionalized NRs in a polymer matrix and densely packed hexagonal arrays of NRs are produced. In this paper, by employing the coarse-grained model and molecular dynamics simulation, we explore the structures of nanocomposites in which a small number of NRs bind with semiflexible polymer chain.

The morphology of NRs/polymer mixture is greatly affected by the bending energy b of semiflexible polymer and the binding energy D_0 between NRs and semiflexible polymer. If the binding energy D_0 is less than $1.1k_B T$, the NRs are almost free and a gas-like phase is observed. For a suitably large value of D_0 , three completely different morphologies of NRs/polymer mixtures are identified, namely, the side-to-side parallel aggregation of NRs, the end-to-end parallel aggregation of NRs, and the dispersion of NRs. For the flexible polymer chain (i.e., small bending energy b), the side-to-side parallel aggregation structure of NRs and the disordered conformation of adsorbed polymer chain are observed. In general, a typical equilibrium conformation of free flexible polymer chain is random coil, the binding energy between NRs and polymer can lead to the collapse of a random coil for flexible polymer chain, and the NRs aggregate in the manner of the side-to-side parallel to each other because the enthalpy is maximized through sharing the more polymer monomers between neighbor NRs. That is to say, the local aggregation of NRs can be found because the orientational entropy can make the aggregated NRs arrange in the side-to-side parallel manner. In the rigid polymer chain limit (very

large bending energy), the rigid polymer chain is stretched and the NRs are well dispersed. As the rigid polymer holds a long persistence length, the NRs can move freely along the stretched polymer chain, and the dispersed conformation of NRs is formed. For the semiflexible polymer chain with a moderate bending energy, the NRs are aggregated in the end-to-end parallel arrangement. Meanwhile, the polymer monomers wrap around those NRs in a well-defined helical structure. The above discussion indicates that the morphologies of NRs are closely related to the conformations of polymer chains. In fact, when a semiflexible polymer chain binds with a large rigid surface, such as nanotube, the helical structure will be formed and it is driven by entropy. The formation of helical structures for a semiflexible polymer chain can induce NRs to form an end-to-end parallel aggregation. The formation of end-to-end parallel arrangement of NR aggregation is driven by the helical structure of semiflexible polymer chain. For the moderate binding energy, the entropy can drive the semiflexible polymer chain to form local helical structure around the NRs. When more NRs are added to the semiflexible polymer chain/NR mixtures, more local helical structures around NRs are formed. Because the movements of NRs binding with the semiflexible chain are nearly free and an end-to-end parallel arrangement of NRs can form more helical structures than the dispersed NRs, the self-assembly of NRs into an end-to-end parallel structure is expected. That is to say, the formation of end-to-end parallel aggregation of NRs is induced by the helix of semiflexible polymers because it can gain more entropies. The self-assembly of a small number of NRs can be well controlled by varying the stiffness of adsorbed polymer chain. This investigation may provide a new pathway to develop “smart” medium to manipulate the aggregation behavior of a few NRs and to construct novel materials with high performance.

Keywords: entropy, semiflexible polymer chain, nanorods, molecular dynamics

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