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Molecular dynamics simulation on adsorption of pyrene-polyethylene onto ultrathin single-walled carbon nanotube

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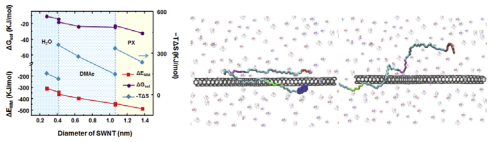
HIGHLIGHTS

- Conformational Entropy, besides binding energy of SWNT-polymer adsorption processes are calculated and the results give quantitatively insight on the effect of solvent polarity.
- We focus on the ultrathin SWNT with diameter less than 1nm, which has more highlight performance than normal SWNT.
- The roles of aromatic tail of polymer in different solvents are different, not only for the adsorption dynamics process, but also for the final adsorption conformation.

GRAPHICAL ABSTRACT



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ABSTRACT

The mechanism of the adsorption of pyrene-polyethylene (Py-PE) onto ultrathin single-walled carbon nanotube (SWNT) was studied by using all-atom molecular dynamics (MD) simulations. We found that solvent polarity and pyrene group are two critical factors in the Py-PE decoration on ultrathin SWNT. Combined MD simulations with free energy calculations, our results indicate that larger solvent polarity can decrease the contribution of conformation entropy, but contributes little to the interaction energy, moreover, larger SWNT diameter can decrease the contribution of conformation entropy but lead to the increasing of the interaction energy. In polar organic solvent (N, N-Dimethylacetamide), the pyrene group plays a key role in the adsorption of Py-PE onto ultrathin SWNT, not only facilitates the spontaneous adsorption of Py-PE onto ultrathin SWNT, but also helps to form compact structure between themselves in the final adsorption states. While in aqueous solution, pyrene group no longer works as an anchor, but still affects a lot to the final adsorption conformation. Our present work provides detailed theoretical clue to understand the noncovalent interaction between aromatic segment appended polymer and ultrathin SWNT, and helps to explore the potential application of ultrathin SWNT in the fields of hybrid material, biomedical and electronic materials.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have already become an ideal and promising candidate for nanofunctional applications and reinforcements of resulting "matrix materials/SWNTs" composites on

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Table 1
Simulation systems.

System	Initial volume (nm^3)	Final volume (nm^3)	Solvent number	Solvent density (g/cm^3)
(3, 3)/PE_{45}/DMA_C	$20 \times 10 \times 10$	$16.37 \times 8.18 \times 8.18$	7000	0.9238
(3, 3)/Py-PE_{45}/DMA_C	$20 \times 10 \times 10$	$16.37 \times 8.18 \times 8.18$	7000	0.9238
(5, 5)/Py-PE_{45}/DMA_C	$20 \times 10 \times 10$	$16.39 \times 8.19 \times 8.19$	7000	0.9202
(8, 8)/Py-PE_{45}/DMA_C	$20 \times 10 \times 10$	$16.40 \times 8.20 \times 8.20$	7000	0.9174
(8, 8)/PE_{45}/p-xylene	$20 \times 10 \times 10$	$18.30 \times 9.15 \times 9.15$	7000	0.8045
(8, 8)/Py-PE_{45}/p-xylene	$20 \times 10 \times 10$	$18.30 \times 9.15 \times 9.15$	7000	0.8045
(10, 10)/Py-PE_{45}/p-xylene	$20 \times 10 \times 10$	$18.30 \times 9.15 \times 9.15$	7000	0.8045
(2, 2)/PE_{45}/H_2O	$20 \times 10 \times 10$	$20.19 \times 10.09 \times 10.09$	66,223	0.9630
(2, 2)/Py-PE_{45}/H_2O	$20 \times 10 \times 10$	$20.19 \times 10.09 \times 10.09$	66,207	0.9628
(2, 2)/Py-PE_{10}/H_2O	$20 \times 10 \times 10$	$20.19 \times 10.09 \times 10.09$	66,294	0.9641
(3, 3)/Py-PE_{45}/H_2O	$20 \times 10 \times 10$	$20.19 \times 10.09 \times 10.09$	66,169	0.9622

account of their unique remarkable electrical, thermal, and mechanical properties. [1–3] In particular, ultrathin SWNTs with a smaller diameter and a higher curvature demonstrate much superior properties, such as higher elastic bending modulus, [4] excellent thermal stability, [5] superconducting property, [6,7] and acting as a promising nanoreactor [8,9] and nanocontainer [10] for catalysts. Nevertheless, SWNTs always tend to aggregate in most solvents, originating from the interaction between themselves, which has hindered the real-life applications of SWNTs to a considerable extent, especially for ultrathin SWNTs.

Noncovalent decoration is regarded as an ideal method to modify SWNTs to improve their properties with the aid of the physical interaction between SWNTs and compounds, such as polymers, small molecules and biomacromolecules. [11,12] This decoration can consummately get rid of the aggregation without changing the hybridization form and charge distribution of SWNTs carbon atoms. However, the efficiency of noncovalent modification will be compromised as the size decreasing of SWNTs due to the weaker physical interaction between compounds and ultrathin SWNTs. [13,14] Considering that polymers could serve as an excellent wrapping material for the noncovalent functionalization of SWNTs as a result of their π-π stacking and Van der Waals interactions between the polymers and SWNTs, [16–18] many researchers recently suggested to improve the properties of the SWNTs through noncovalent functionalization with polymers, aiming to preserve the structural integrity of SWNTs but remarkably improve their solubility. [15] In our previous study, various supramolecular conformations of polymer/SWNTs have been obtained by absorption of different polymers, like PE, polyethylene oxide (PEO), to SWNTs in supercritical CO_2, and of copolymer PE-*b*-PEO in different solvent environments. [19,20] Xin et al. also found that poly(propylene oxide)-*b*-polyethylene oxide (PPO-*b*-PEO) with branched structure gets a much better ability to disperse CNTs. [21] At the same time, a lot of simulation researches give us interesting information which is not possible to be obtained experimentally. [22–29] Edita Sarukhanyan et al. [22] clarified the noncovalent coating mechanism of SWNTs by several polyethers, and those results suggest a preferential binding to the SWNT surface of more hydrophobic molecules. Gurevitch and Srebnik, [23] Tallury and Pasquinelli [24,25] reported that the adsorption conformation of polymeric chains of different stiffness on SWNT. Maria Sammalkorpi et al. [26] investigated the effects of the polymer length and the size of SWNT in diameter on the adsorption conformation. However, there is seldom report about the adsorption of polymer molecules onto the ultrathin SWNT surface, which probably because it is difficult for polymer to bind ultrathin SWNT with a smaller size.

In this work, we focus on two factors which could have significant impact on the adsorption of polymer onto ultrathin SWNT. Firstly, choose a proper solvent. The style of solvent has been demonstrated to possess complex sensitive effects on the self-assembly of polymer and SWNTs, and play a key role in stable dispersion or solubilization of SWNTs in polymer solution at high concentrations. [14,20] Secondly, introduce aromatic segment into the polymer molecule. Experimental studies reveal that, through noncovalent interaction of the sidewall of SWNTs, aromatic molecules-appended polymer can not only improve the self-assembly of polymer/SWNTs remarkably by means of specific π-π stacking interactions, [30,31] but also induce gelling processes at concentrations lower than their typical gelling point in supramolecular gels and accelerate the velocity of crystallization in the polymer/SWNTs system. [32–34] In this paper, the adsorption of a pyrene molecules-appended Polyethylene (Py-PE) molecule onto the ultrathin SWNT in different solvents (p-xylene, N, N-Dimethylacetamide and H_2O) was studied using all atoms molecular dynamics simulation. The effects of solvent polarity and the function of pyrene group on their adsorption process and final adsorption conformation have been comprehensively investigated.

2. Simuluation method

2.1. Simulation system

Polymer Py-PE_{45} (with 45 repeat monomers), PE_{45} (without pyrene terminal) and Py-PE_{10} were introduced into simulation system in this work. Three kinds of solvent p-xylene, N, N-Dimethylacetamide (DMAc), and H_2O with different polarity were chosen. The solvation parameter of PE, p-xylene, DMAc and H_2O is 8.0, 8.2, 11.2 and 23.1, respectively, p-xylene with close polarity is the excellent solvent for Py-PE_{45}, while DMAc and H_2O are poor solvents for Py-PE_{45}. Ultrathin SWNTs (2, 2), (3, 3) and (8, 8) with a length of 8.2 nm are discussed in the following study. The simulation results of SWNT (10, 10), (15, 15) and (20, 20) with large size are not showed. The simulated systems sizes are all set to $20 \times 10 \times 10$ nm^3 initially. The simulation system parameter was list in Table 1.

2.2. Simulation method

All the simulations were carried out using the GROMACS 5.0.2 software package. [35,36] Given the periodic boundary conditions, a single SWNT is modeled as an infinite rigid tube fixed in the central area of the box. Each carbon atom of SWNT is represented using an uncharged Lennard–Jones (LJ) spherical particle with $\sigma = 0.34$ nm and $\varepsilon = 0.3601$ kJ/mol. [37,38] For the polymer molecules, the fully atomistic Optimized Potentials for Liquid Simulations-All Atom (OPLS-AA) force field [39–41] is used, which has been extensively used to simulate CNTs/polymer systems. [42,43] The water molecules was modeled by SPC/E model, [44] which has been previously used in the simulation of the solvation behavior around pyrene derivative [45] and polymer/carbon materials systems [22,46] in aqueous solution. All the parameters for the other