

Polypyrrole Induced By Carbon Nanotube To Form Multiple-Strand Helix

Wendi Gong

Linyi University

Danhui Zhang (✉ njustzdh@126.com)

Linyi University

Ruquan Liang

Linyi University

Dengbo Zhang

Linyi University

Shiming Liang

Linyi University

Anmin Liu

Dalian University of Technology

Research Article

Keywords: polypyrrole, carbon nanotube, helix nanostructure, molecular dynamics,

Posted Date: November 1st, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1021802/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

In this manuscript, a molecular dynamics simulation is used to study the formation of multiple-strand helix through polypyrrole induced by carbon nanotube. The results exhibit that the multiple polypyrrole chains arranged in parallel can self-assemble to helix. The formation mechanism is also illustrated in detail. The formation process may experience two stages which are insertion and torsion. Both the van der Waals potential well and the π - π stacking interaction among the multiple polypyrrole and carbon nanotube play a major role in the self-assembly process. Furthermore, a lot of factors such as the chain number of polypyrrole, the length of polymer and the simulation temperature influence the final configuration of composite. This theory research can provide valuable theoretical support for design and manufacture hybrid structures in the fields of advanced composite materials and functional devices.

1. Introduction

Pyrrole is a five-membered heterocyclic compound containing a nitrogen heteroatom.[1, 2] Its structure is shown in Fig. 1(a) and its molecular formula is C_4H_5N . In industrial production, pyrrole is mainly produced by the reaction of 1,4-dicarbonyl compounds and ammonia.[3, 4] Polypyrrole which has a lot of pyrrole monomers (Its structure is shown in Fig. 1(b)) has a special molecular structure and excellent physical and chemical properties, which make it have broad application prospects in metal protection,[5, 6] energy,[7, 8] optoelectronic devices,[9, 10] electromagnetic shielding and stealth technology. [11–14]

Carbon nanotube(CNT), also known as bucky tube, is a one-dimensional quantum material owning hollow cylindrical structures made of networks of carbon atoms.[15, 16] due to its special structure, it has many significant properties such as thermal conductivity, electrical properties and mechanical strength, which excite potential applications in nanosized electronic and mechanical devices, especially for the fabrication of CNTs composites.[17–19] At present, the research of polypyrrole/carbon nanotube composite materials mainly focuses on the synthesis and performance of composite materials.[20] For example, Niloufar Behzadpour and his coworkers scrutinized synthesis and characterization of a polypyrrole-coated multi-walled carbon nanotubes composite which is used in sonodynamic therapy.[21] Luo team[22] reported a polypyrrole (PPy)-coated carbon nanotube/cotton hybrid fabric, fabricated by a highly facile and scalable knitting and chemical polymerization process, which owns high performance flexible supercapacitors, flexible electrodes with good electrochemical performance, high stability and superior mechanical property. Hamouma et al. [23] prepared the low-cost, conductive Pap@CNT-NH₂@PPy composites through sonochemical polymerization of pyrrole in the presence of oxidizing agent and tosylate co-dopant (TS) which decorated on the cellulosic paper strips. The various characteristics of modified paper electrodes were examined by XPS, Raman, SEM, cyclic voltammetry and electrochemical impedance spectroscopy. However, from the theoretical point of view, there are almost no reports on the interaction of polypyrrole/carbon nanotube composites.

In this manuscript, we used a molecular dynamics simulation to study the formation of multiple-strand helix through polypyrrole induced by carbon nanotube. The formation mechanism is illustrated in detail.

The formation process may experience two stages which are insertion and torsion. Both the van der Waals potential well and the π - π stacking interaction among the multiple polypyrrole and carbon nanotube play a major role in the self-assemble process. Furthermore, a lot of factors such as the chain number of polypyrrole, the length of polymer, the diameter of carbon nanotube and the simulation temperature influence the final configuration of composite. Although there have been reports about the formation of helical structures by polymers in carbon nanotubes or boron nitride nanotubes, the reaction process and reaction mechanism experienced by different reactions are different.[24, 25] This study can provide valuable theoretical support for design and manufacture hybrid structures in the fields of advanced composite materials and functional devices.

2. Simulation Method

In this work, all calculations were carried out by molecular dynamics (MD) simulation, and the atomic interaction was described by the force field of condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) [26, 27]. COMPASS is an ab initio force field that has been parametrized and validated using condensed-phase properties in addition to various ab initio calculations and experimental data, with a functional form that includes covalent terms as well as long-range, non-bond (van der Waals (vdW)) interactions and electrostatic forces. It aims to achieve high accuracy in prediction of the properties of very complex mixtures [28, 29].

All the simulations are done in the constant temperature and constant volume canonical ensemble (NVT). The equations of motions were integrated using Verlet algorithm with integration time step of 1 fs and the temperature is controlled by a Nosé-Hoover thermostat.[30] The simulation system was equilibrated for 1000 ps to stabilize the interaction. After this stage, the total intermolecular interaction energy was recorded for 1000 ps with an interval of 2 ps. Finally, averages were computed to get rid of the fluctuation during the simulation.

3. Results And Discussion

3.1 Trajectory Visualization

The molecular dynamic (MD) snapshots of the helix formation process through three polypyrrole chains and CNT are shown in Fig. 2. Each polypyrrole chain owns 60 repeat units with the length of 234.8 Å. Initially, three polypyrrole chains are parallel with each other and all of them are inserted into the one end of CNT. As the simulation time starts, due to the π - π interactions existing among the three polypyrrole chains, three polypyrrole chains fluctuate like a worm crawling. At the same time, three polypyrrole chains slide into the CNT from this end to other which is exhibited in the first 24 ps. With the time goes on, a part of the three polypyrrole chains penetrate the CNT, and the all polymer chains are twisted simultaneously. As the kinetic time continues to grow, the polymer chains twist more and more significantly, and are confined inside the carbon nanotube which lastly forms a perfect triple helix configuration. Completely the whole process needs about 90 ps. Throughout the entire process, it includes two parts: penetration

and twist. The configuration changes of this process are mainly attributed to the van der Waals potential well and the π - π stacking interaction among the three polypyrrole chains and CNT.

Figure 3(a) exhibits the time evolution of total potential energy (E_p) and Van der Waals energy (E_{vdW}) for polypyrrole/carbon nanotube system. In Fig. 3(a), the curves of the total potential energy and Van der Waals energy for polypyrrole/carbon nanotube system are almost the same. Both curves show a downward trend at the first 90 ps, and then remain unchanged which means that the interaction of this system only needs 90 to reach the equilibrium. There are two inflection points in this part of curve, which can be divided into three different regions. Region I(0 ps-24 ps), two curves exhibit a great reducing trend which belongs to “penetration” process. Region II (25 ps- 90ps), the energy goes on reducing which is attributed to twist process. However, when the simulation time exceeds 90 ps (area III), the energy keeps almost the same with little fluctuation which means that the system reaches the equilibrium. These curves point out three key points: one is this whole process undergoes two stages; the second is 90 ps is a long enough for the system to reach well-equilibrated; the third is the van der Waals potential well and the π - π stacking interaction are the main driving force.

The interaction energy of polypyrrole/carbon nanotube system is shown in Fig. 3(b). To explore the origin of this difference, the interaction energy among three polypyrrole chains and CNT was calculated using the following equation:

$$E_{Interaction} = E_{total} - E_{polypyrrole} - E_{CNT} \quad (1)$$

In this equation, $E_{Interaction}$ is the interaction energy of the polypyrrole/carbon nanotube system, E_{total} is the total energy of the composite, $E_{polypyrrole}$ is the energy of individual polymer molecules and E_{CNT} is the energy of individual CNT.[24, 31]

In Figure 3(b), the curve of interaction energy can be divided into three stages similar to the reverse shape of Fig. 3(a). In stage I, the interaction energy is about -1325.8 Kcal/mol. In this process, in addition to the interactions among three polymer chains, there are also increasing interactions between polymers and carbon nanotubes. In stage II, the interaction energy among the polymer molecule and CNT still keeps increasing which gets to -2155.8 Kcal/mol. However, when the simulation time reaches 90 ps (stage III), the interaction energy remains unchanged. The conclusion is that the interaction energy among the polymer molecule and CNT is about -2155.8 Kcal/mol.

The concentration profile can give the information about the geometric parameters of the polypyrrole/CNT composite system. The 3D periodic structures can be computed through the profile of atom density within evenly spaced slices parallel to the bc, ca and ab planes. Figure 4 exhibits the concentration profiles of the final structure of the f polypyrrole/CNT composite system in the X and Y direction. [30] In Fig. 4(a), the curve of polypyrrole is surrounded by the CNT, which means that the polymer self-curls into the inside of CNT. However, the carbon nanotubes have undergone slight deformation and are no longer a perfect cylindrical structure. According to the peaks detail exhibited in Fig. 4(a), the distance between polypyrrole chain and CNT is 1.1-1.5 Å, this value is corresponded with the

stacking distance of the offset face-to-face π - π stacking interaction, which suggests that the main driving force is the π - π stacking interaction.[32] In Figure 4(b), the length of CNT is about 73.8 Å, which is corresponded with the theory value of 73.79 Å. Furthermore, a little part of helix locates outside of CNT. The total length of the helix is about 86.7 Å. According to the cure of polymer in Fig. 4(b), the helix has gone through three turns.

3.2 The different number of polymer chain number

In this part, we investigate that how the chain number of polymer influences the interaction of polypyrrole/CNT composite systems. Initially, we set all the CNT with same diameter (33.90 Å) and length (73.79 Å) and the polypyrrole chain has 60 monomers with the length of 234.8 Å. All the different polypyrrole/CNT composite system just change the number of polymer chain from one, two, three, four to five. The initial and final configurations of composite and pure polymer chain are shown in Fig. 5(a). When just one polymer chain existing in this system, the whole chain curves to irregular configuration and enters into the inside of CNT. As the chain number of polymer goes on increasing from two to four, all the chains simultaneously curls to perfect helix structures. However, when the number of polymer chain exceeds five, the polymers do not have enough space to twist and only fluctuate in a wave form. The interaction energy for these different polypyrrole/CNT systems are shown in Fig. 5(b). As the number of polymer chains increases, the interaction energy between polymer and carbon nanotubes gradually increases. These are attributed to more and more van der Waals potential well and the π - π stacking interaction existing in these systems. However, when the chain number is five, the interaction energy is decreasing, this reason is that the main interaction force is between the polymers, and the force between the polymer and the carbon nanotubes is relatively small.

3.3 The length of polymer chain

The length of polymer chain also influences the final configuration of polypyrrole/CNT system. At the first time, all the CNT are set with same diameter (33.90 Å) and length (73.79 Å). The length of polypyrrole chain changes from 78.3 Å, 146.6 Å, 234.8 Å to 293.2 Å. The initial and final configurations of different polypyrrole/CNT systems are shown in Fig. 6(a). When the length of polymer is too short, the CNT have enough space to accommodate all the curled polymer chains. These can be seen in the Fig. 6(a) from I to III. However, when the length of polymer is long enough, the intense interaction exists between the polymers which make the inserted polymer far away from the CNT and lead the polymer do not enter into the CNT. The final configuration is displayed in Fig. 6(a)(IV). The interaction energy for these systems are also shown in Fig. 6(b). The longer the polymer, the stronger the interaction energy existing in these systems. If the polymer is too long, the interaction energy goes down. This is corresponded with configuration change which are shown in Fig. 6(a).

3.4 The different simulation temperature

How the simulation temperature influences the final configurations of polypyrrole/CNT system? In this part, all the CNTs and polypyrrole are set with the same parameters. Only the simulation temperature is different, which is set as 100K, 200K, 300K, 400K, 500K, respectively. The final configurations of different polypyrrole/CNT systems and pure polypyrrole chains are exhibited in Fig. 7(a). The final configurations are almost the same when the simulation temperature changes from 100K, 200 K, 300 K to 400 K. The higher the temperature, the more and more, more and more perfect multi-helical polymers are confined in carbon nanotubes. However, when the temperature is 500 K, the polymer also twists but locates outside the surface of CNT. The interaction energy for these different polypyrrole/CNT systems are also shown in Fig. 7 (b). The energy difference for these systems is very small, which is corresponded with the final configurations.

4 Conclusions

In summary, we use a molecular dynamics simulation to study the formation of multiple-strand helix through polypyrrole induced by carbon nanotube. The results exhibit that the multiple polypyrrole chains arranged in parallel can self-assemble to helix. The formation process experiences two stages which are insertion and torsion. Both the van der Waals potential well and the π - π stacking interaction among the multiple polypyrrole and carbon nanotube play a major role in the self-assemble process. Furthermore, a lot of factors such as the chain number of polypyrrole, the length of polymer and the simulation temperature influence the final configuration of composite. The theory results can provide valuable theoretical support for design and manufacture hybrid structures in the fields of advanced composite materials and functional devices.

Declarations

Acknowledgment

This investigation was supported by the National Natural Science Foundation of China(No.51976087 and 12002142) and Natural Science Foundation of Shandong Province(No.ZR2020MF025 and ZR202102230860).

Conflict of Interest

The authors declare that they have no conflict of interest.

References

1. A.R. Davies, D.J. Kemp, T.G. Wright, *Journal of Molecular Spectroscopy*. **376**, 111410 (2021)
2. R.H.E. Schirmacher, D. Rösch, F. Thomas, *Tetrahedron*. **83**, 131985 (2021)
3. H. Lee, B.H. Kim, *Tetrahedron*. **69**(32), 6698 (2013)
4. H.S.P. Rao, S. Jothilingam, *Tetrahedron Lett*. **42**(37), 6595 (2001)
5. R. Babaei-Sati, J.B. Parsa, M. Vakili-Azghandi, *Synthetic metals*. 247, 183(2018)

6. S. Javadian, Z. Ahmadpour, A. Yousefi, Progress in Organic Coatings. **147**, 105678 (2020)
7. S. Dey, A.K. Kar, Materials Science in Semiconductor Processing. **103**, 104644 (2019)
8. R. Malik, S. Lata, R.S. Malik, Journal of energy storage **27**, 101162 (2019)
9. S. Dey, A.K. Kar, Materials Science in Semiconductor Processing. **103**, 104644 (2019)
10. S. Kasisomayajula, N. Jadhav, V.J. Gelling, Prog. Org. Coat. **154**, 106190 (2021)
11. I. Ebrahimi, M.P. Gashti, J. Phys. Chem. Solids **118**, 80 (2018)
12. I. Ebrahimi, M.P. Gashti, Materials Research Bulletin. **83**, 96 (2016)
13. C.C. Wan, J. Li, Carbohydr. Polym. **161**, 158 (2017)
14. N. Gill, V. Gupta, M. Tomar, A.L. Sharma, O.P. Pandey, D.P. Singh, Composites Science and Technology. **192**, 108113 (2020)
15. J. Xie, Q.Z. Xue, H.J. Chen, D. Xia, C. Lv, M. Ma, J. Phys. Chem. C **114**, 2100 (2010)
16. D. Xia, Q.Z. Xue, K.Y. Yan, C. Lv, Appl. Surf. Sci. **258**, 1964 (2012)
17. Q. Wang, Phys. Lett. A **375**, 624 (2011)
18. Y.Y. Jiang, H. Li, Y.F. Li, H. Yu, M.K. Liew, Y. He, X. Liu, ACS Nano **5**(3), 2126 (2011)
19. F.W. Sun, H. Li, Carbon. **49**, 1408 (2011)
20. K.C. Zhang, X.F. Chen, X.B. Gao, L. Chen, S.Z. Ma, C.Y. Xie, X.G. Zhang, W. Lu, Synthetic Metals. 260, 116282(2020)
21. N. A. Behzadpour, N. Ranjbar, N. Azarpira, Sattarahmady, Ultrasound in Medicine & Biology. 46(9), (2020)2322
22. X.G. Y.X. Luo, W. Liang, Z.X. Weng, Y. Hu, J.J. Zhang, L.J. Yang, M.F. Yang, Zhu, Energy Storage Materials. 33, 11(2020)
23. O. Hamouma, N. Kaur, D. Oukil, A. Mahajan, **M. M.Chehimi**, Synth. Met. **258**, 116223(2019)
24. C. Lv, Q. Xue, M. Shan, N. Jing, C. Ling, X. Zhou, Z. Jiao, W. Xing, Z. Yan, Nanoscale. **5**, 4191 (2013)
25. D.H. Zhang, R.Q. Liang, H.B. Yang, Y.M. Song, J.H. Shi, D.B. Zhang, L. Yang, A.M. Liu, Chemical Physics. 544, 111135(2021)
26. H. Sun, J. Phys. Chem. B. 102, 733(1998)
27. D.H. Zhang, H.B. Yang, Z.K. Liu, A.M. Liu, G.F. Ji, Molecular Simulation. 44(3), 200(2018)
28. Q. Wang, Nano Lett. **9**, 245 (2009)
29. H. Li, J.M. Knaup, E. Kaxiras, J.J. Vlassak, Acta. Mater. **59**, 44 (2011)
30. D.H. Zhang, H.B. Yang, Z.K. Liu, A.M. Liu, J. Alloy. Compd. **765**, 140 (2018)
31. S.W. Bunte, H. Sun, J. Phys. Chem. B. **04**, 2477 (2000)
32. B. Yu, S. Fu, Z.Q. Wu, H.W. Bai, N.Y.Ning, Q. Fu, Computational Materials Science **58**, 7(2012)

Figures

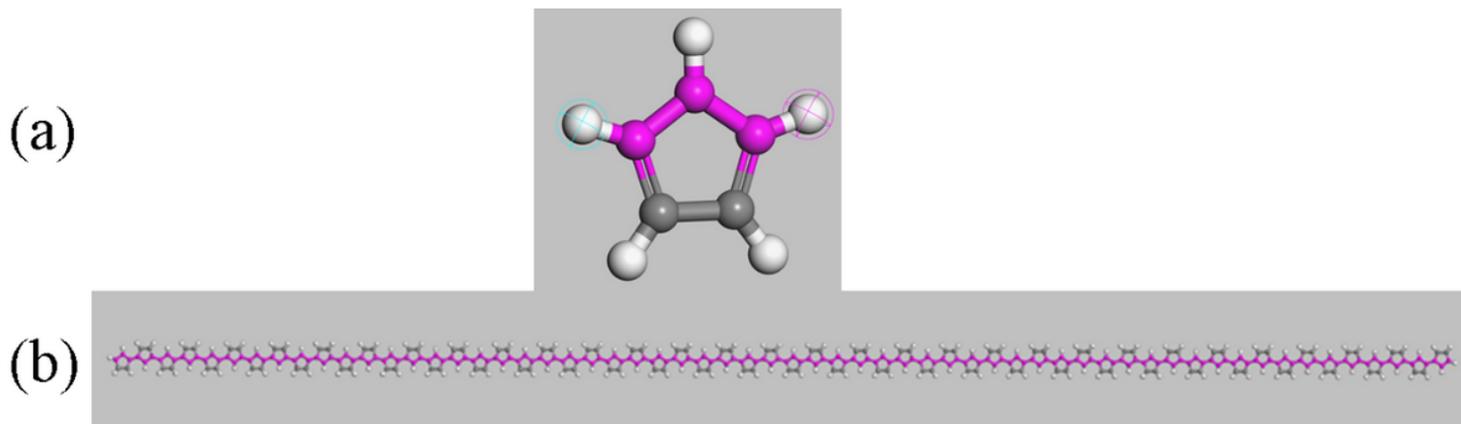


Figure 1

The structure of pyrrole(a) and polypyrrole(b)(containing 60 monomers).

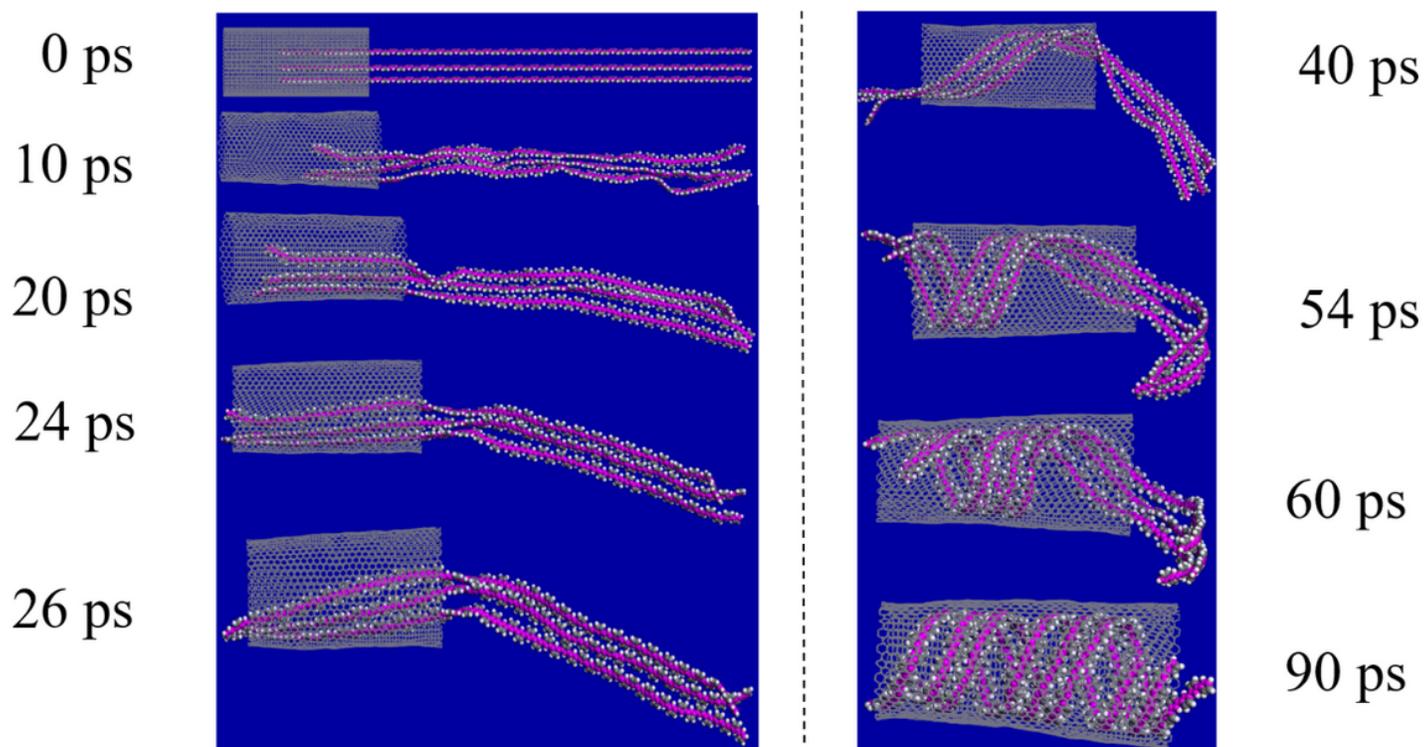


Figure 2

The molecular dynamic snapshots of the self-assemble process at different time.

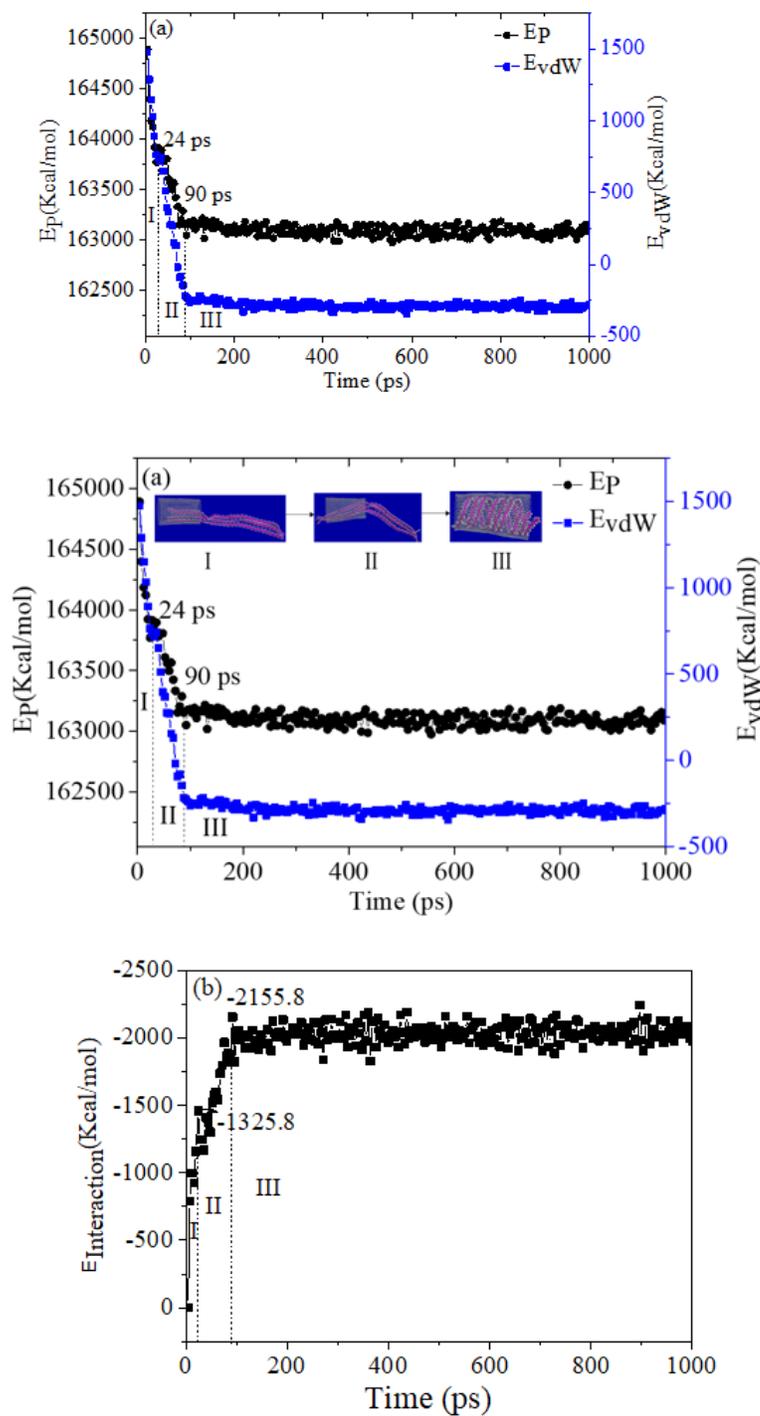


Figure 3

Time evolution of total potential energy (E_p) and Van der Waals energy (E_{vdW}) for polypyrrole/carbon nanotube system. (a) The interaction energy for the polypyrrole/carbon nanotube system with simulation time. (b)

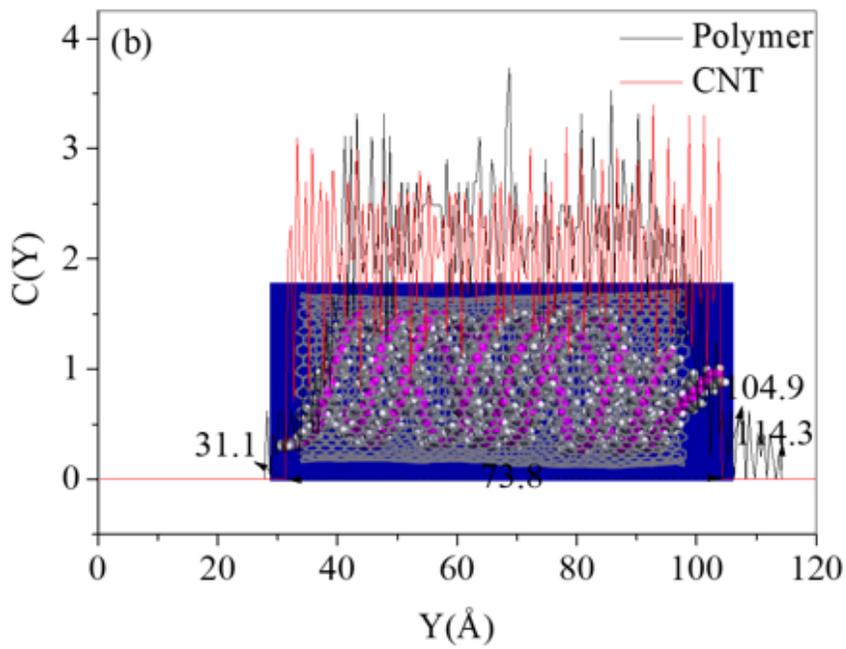
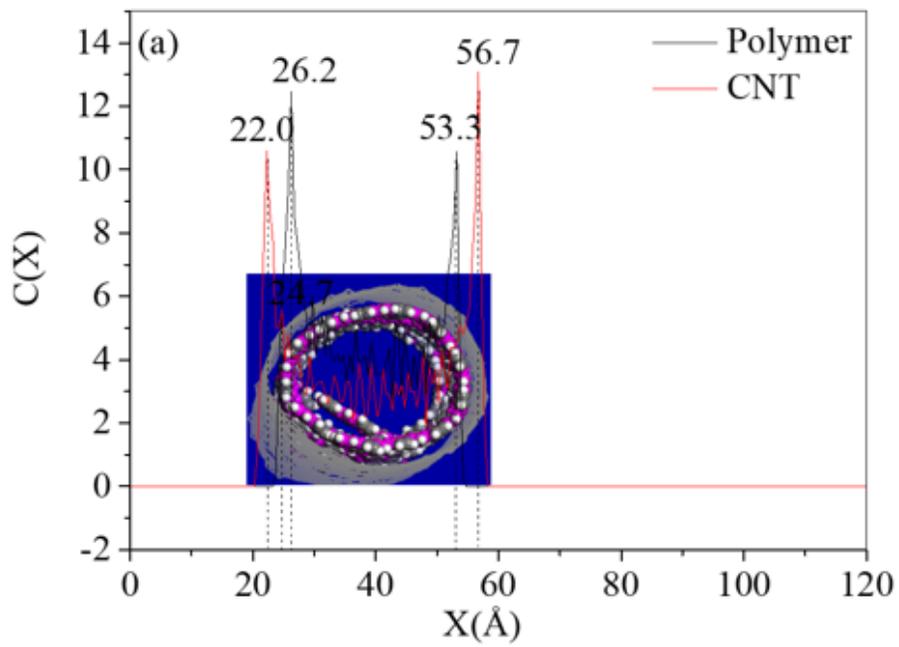


Figure 4

Concentration distribution profiles of the final structure including polypyrrole and carbon nanotube in the X(a) and Y(b) directions. The inset is the corresponding final structure.

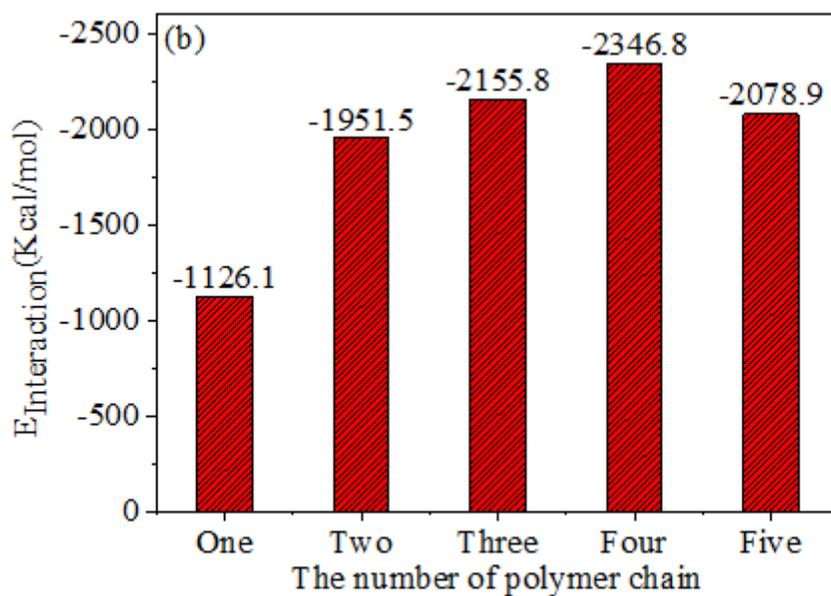
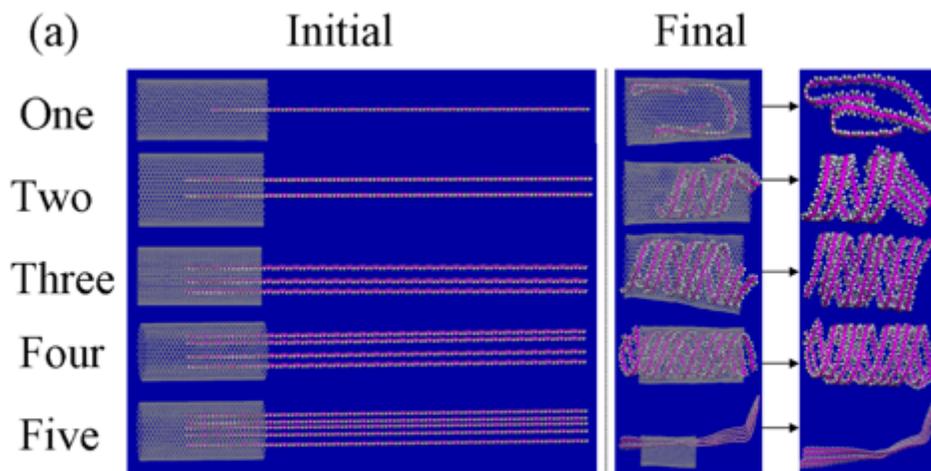


Figure 5

The initial and final configurations of different polypyrrole/CNT systems.(a) The interaction energy for these different polypyrrole/CNT systems.(b) (The chain number of polypyrrole changes from one, two, three, four to five.)

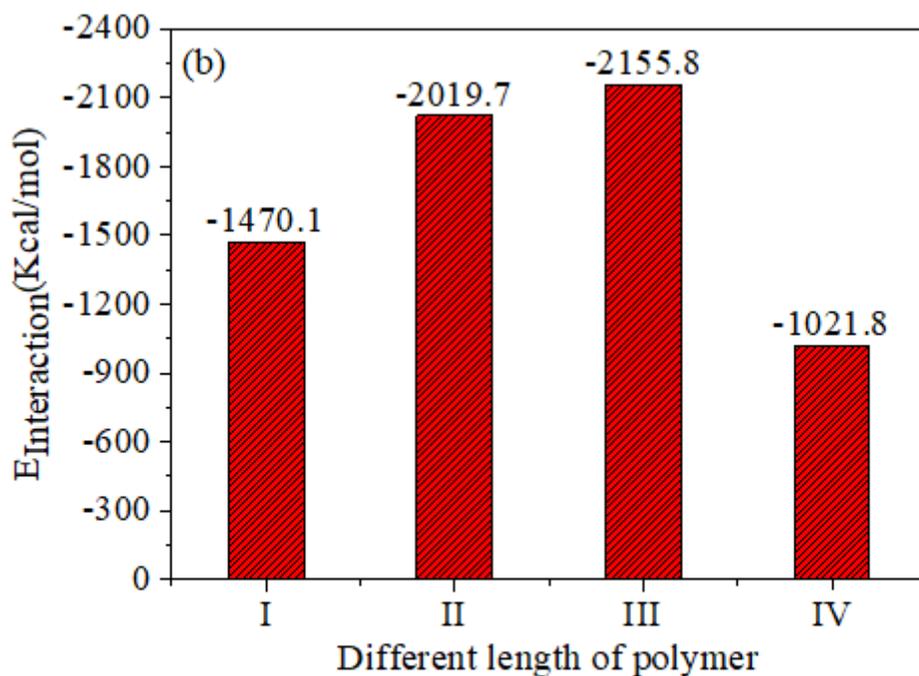
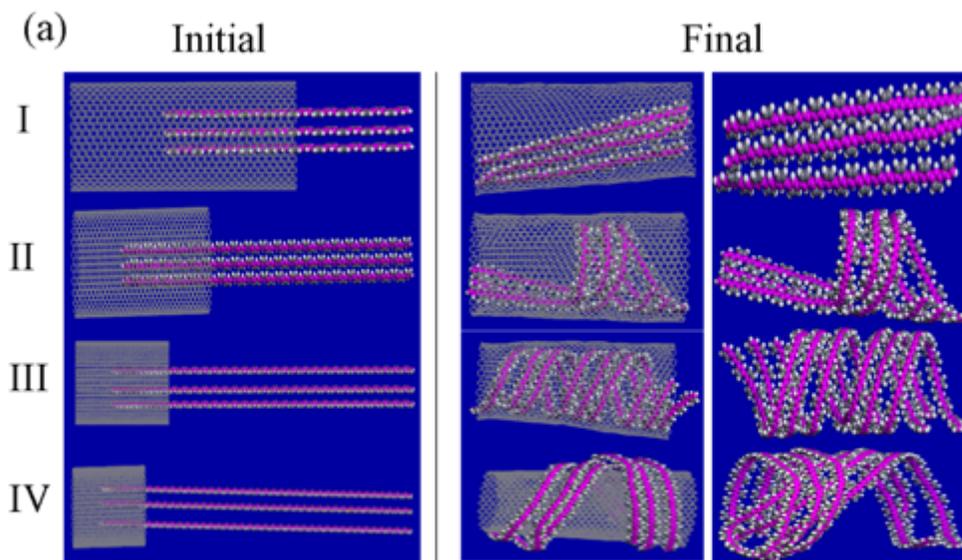


Figure 6

The initial and final configurations of different polypyrrole/CNT systems. (a) The interaction energy for these different polypyrrole/CNT systems. (b) (The length of polypyrrole changes from 78.3 Å(I), 146.6 Å(II), 234.8 Å(III) to 293.2 Å(IV).)

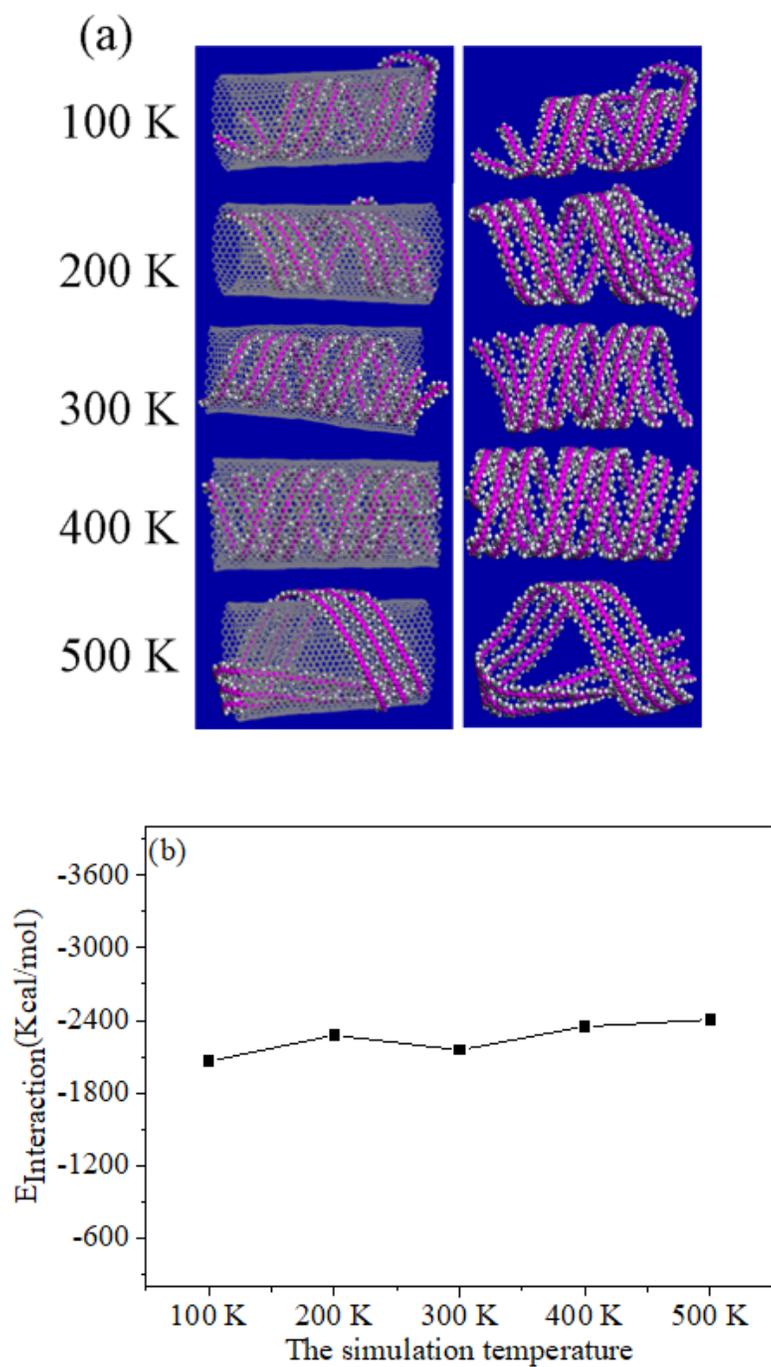


Figure 7

The final configurations of different polypyrrole/CNT systems and pure polypyrrole chains at different temperature. (a) The interaction energy for these different polypyrrole/CNT systems at different temperature. (b)