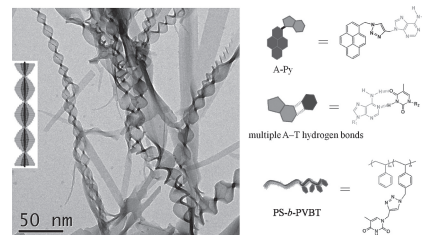


From Random Coil Polymers to Helical Structures Induced by Carbon Nanotubes and Supramolecular Interactions

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A simple method is reported for the preparation of double-helical structures through a series of achiral random and block copolymers poly(styrene-*co*-4-vinylbenzyl triazolylmethyl methylthymine) (PS-*co*-PVBT) with various T units on the side chains through click reactions of poly(styrene-*co*-4-vinylbenzyl azide) (PS-*co*-PVBN₃) with propargyl thymine (PT) and also the synthesis of the A-appended pyrene derivative (A-Py) through click chemistry. This double-helical structure is observed from achiral random-coil polystyrene (PS) main chains, stabilized through the combination of multiple A–T hydrogen bonds, and π – π stacking between pyrene units and single-walled carbon nanotubes (SWCNTs).



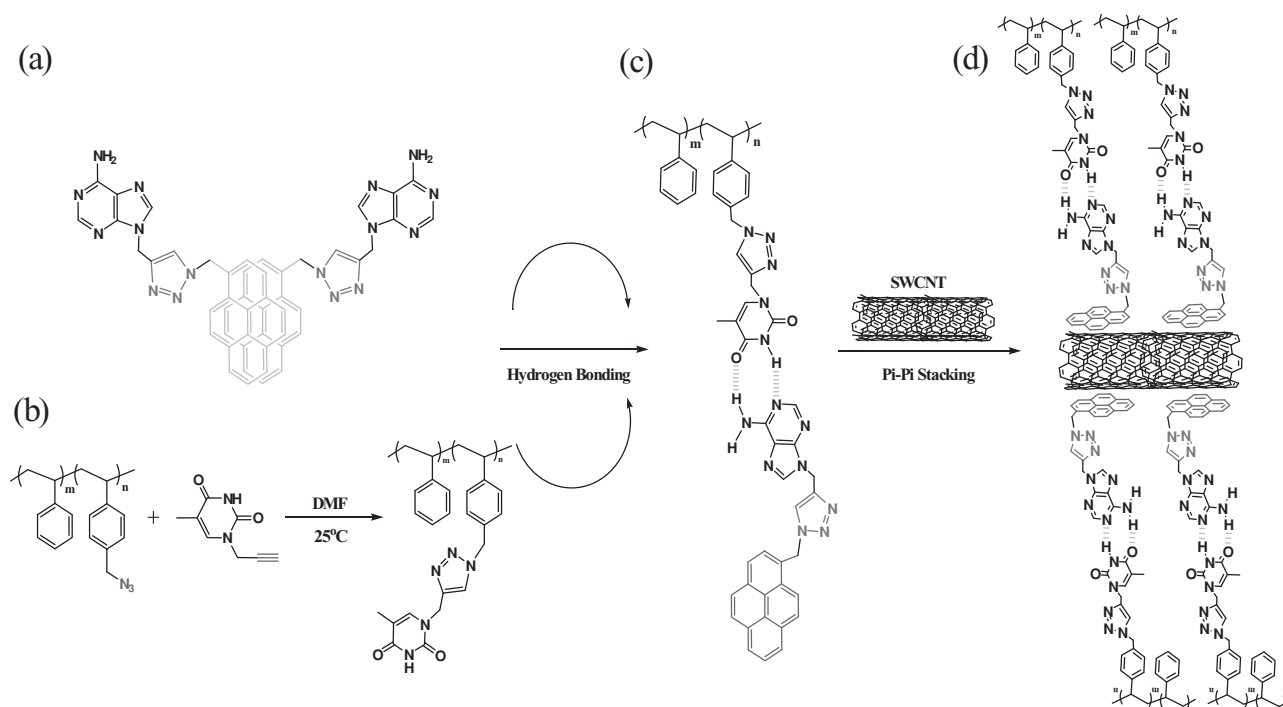
1. Introduction

Controlling the self-assembly of helical structures remains an interdisciplinary challenge, but it has been one of the recent highlights of supramolecular chemistry.^[1] Inspired by Nature's structures created in biological systems, there is growing interest in the design of synthetic molecules that can self-assemble into compact helical aggregates, analogous to the DNA double helix.^[2] Double-helical DNA structures are stabilized through Watson–Crick base pairing (hydrogen bonding) of their four nucleobases—adenine (A), thymine (T), guanine (G), and cytosine (C)—and through π -stacking of adjacent base pairs.^[3] The fabrication of artificial helical structures in synthetic self-assembling systems is usually achieved through amplified

supramolecular chirality using hydrogen bonding, π – π stacking, or metal–ligand coordination.^[4] In addition, control over the helical structure can be induced through transfer of chiral information from the molecular level to the supramolecular, and molecular recognition has been performed in both biomimetic and synthetic supramolecular systems.^[5] For example, Shimizu and co-workers^[6] blended a thymidylic acid-appended oligo(*p*-phenylenevinylene) with a complementary single-stranded 20-meric oligodeoxyadenylic acid to form a helical structure through binary self-assembly; blending with noncomplementary 20-meric oligothymidylic acid did not form such helical stacks. Similar results have been observed from the complementary oligonucleotide-templated self-assembly of the thymidine-appended bolaamphiphile with oligoadenylic acid, edged by a double-helical arrangement of A–T base pairs.^[7]

It remains, however, a challenging task to synthesize well-defined double-helical structures from achiral random coil polymers. Here, we report a simple method (Scheme 1) for the preparation of double-helical structures from achiral random-coil polystyrene (PS) main chains, stabilized through the combination of multiple A–T hydrogen bonds and π – π stacking between pyrene units and single-walled carbon nanotubes (SWCNTs).

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Scheme 1. Chemical structures of (a) the monomer A-Py, (b) the copolymer PS-co-PVBT, (c) the binary PS-co-PVBT/A-Py complex stabilized through multiple hydrogen bonding interactions, and (d) the ternary PS-co-PVBT/A-Py/SWCNT hybrid complex stabilized through multiple hydrogen bonds and π - π interactions.

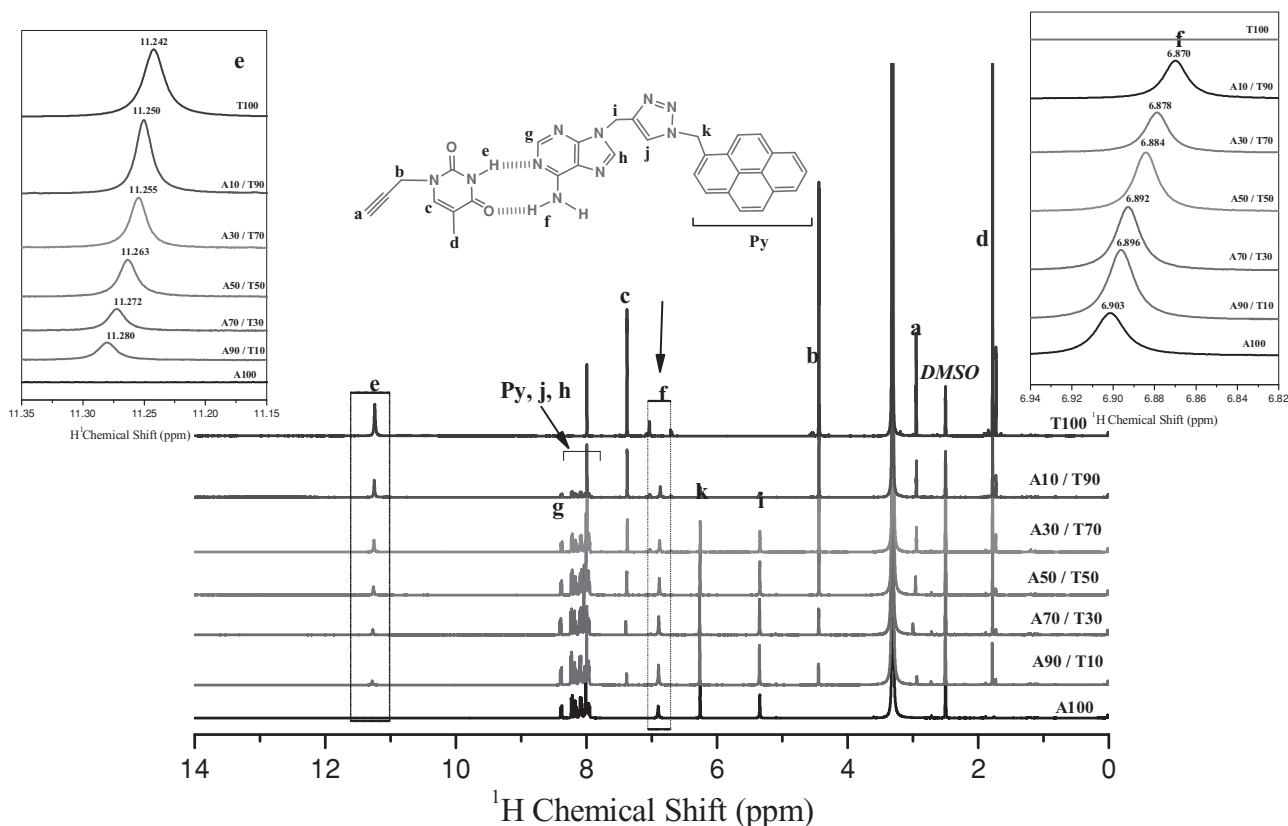
We synthesized the A-appended pyrene derivative (9-[[1-(pyren-1-ylmethyl)-1*H*-1,2,3-triazol-4-yl]methyl]-9*H*-purin-6-amine) (A-Py) through click chemistry from 9-(prop-2-ynyl)-9*H*-purin-6-amine and 1-(azidomethyl)pyrene (Scheme S1, Figures S1–S3, Supporting Information) and prepared a series of achiral random and block copolymers poly(styrene-co-4-vinylbenzyl triazolylmethyl methylthymine) (PS-co-PVBT) with various T units on the side chains through click reactions of poly(styrene-co-4-vinylbenzyl azide) (PS-co-PVBN₃) with propargyl thymine (PT; Figure 1, Figures S4–S10, Supporting Information).^[8] The helical structures were formed through ternary components of PS-co-PVBT/A-Py/CNT hybrid complex system.

2. Results and Discussion

Because PS-co-PVBT random copolymer is not dissolved in chloroform, the ¹H NMR spectra of PT (model compound of PVBT) with A-Py in *d*-chloroform/*d*-DMSO were shown in Figure 1. The addition of A-Py to PT solution led to downfield shift of the signal (N–H) of the T group, which initially appeared at 11.242–11.280 ppm (90 wt% A-Py). Similarly, the addition of PT to A-Py solution led to high-field of the signal (NH₂) of the A group, which appeared at 6.903–6.870 ppm, indicating that multiple intermolecular

hydrogen bonding occurred between the T and A groups. In our previous study,^[9] the inter-association equilibrium constant ($K_a = 534 \text{ M}^{-1}$) between T and A groups from two low-molecular-weight model compounds mixtures, 9-hexadecyladenine (AC-16) and 9-hexadecylthymine (TC-16), was calculated using the results of ¹H NMR spectroscopic titration in CDCl₃ at room temperature, on the basis of the method that had been developed by Benesi and Hildebrand.^[9] In this study, pure A-Py dissolves only in highly polar solvents, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), therefore, the chemical shift or inter-association equilibrium constant would be smaller than in CDCl₃ solution.

Figure 2a shows the fluorescence spectra in the bulk state of A-Py and PS-co-PVBT random copolymer at different molar ratios of A-Py after excitation at 343 nm. The spectrum of pure A-Py features a signal for the strong fluorescent excimer at 493 nm; its intensity decreased, but those of the fluorescent monomer at 377 and 397 nm increased, upon increasing the content of the PS-co-PVBT copolymer, because multiple hydrogen bonds were formed between the A and T units, coordinating the A-Py moieties to the polymer chains and, thereby, disrupting the π - π stacking of the Py units. CNTs are known to quench the emissions from Py units, as indicated in Figure 2b.^[10] This quenching effect was so efficient that is dictated the copolymer-hybrid system comprising PS-co-PVBT, A-Py,



■ Figure 1. ^1H NMR spectra ($\text{CDCl}_3/\text{DMSO} = 1/1$) of PT/A-Py mixtures featuring various A/T ratios at room temperature.

and CNTs, stabilized through a combination of multiple hydrogen bonding between the A and T units and π - π interactions between the Py and CNT moieties. Figure S9 (Supporting Information) displays macroscopic images of DMSO solutions containing various amounts of SWCNTs. Although the pure SWCNTs precipitated completely, the addition of A-Py into the polymer hybrid complex solution resulted in a clear brown solution, indicating that a soluble system is obtained as a result of noncovalent interactions (multiple hydrogen bonding and π - π stacking interactions) between the different components of the mixture.

We used scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to further investigate the self-assembly of the ternary components of PS-co-PVBT/A-Py/CNT hybrid complex in ethanol with $10^{-3} \text{ g mL}^{-1}$ by ultrasonic vibration machine for stirring. Figure 3a,b presents TEM images of a random copolymer of PS-co-PVBT/A-Py/CNT blend, featuring 62 mol% of T units in the PS-co-PVBT random copolymer and 3 wt% of CNT, where the residual T-to-A stoichiometry was 1:1. The TEM images reveal the formation of helical stacks from this ternary PS-co-PVBT/A-Py/CNT hybrid complex, with an average width of ≈ 50 – 60 nm , an average helical pitch

of $\approx 100 \text{ nm}$, and an average length of 2–3 μm . Pyrene units undergo favorable π - π interactions with CNTs, forcing their packing into a dense, parallel arrangement.^[5d] We suspect that such a packing arrangement resulted in the PS-co-PVBT/A-pyrene/CNT blends forming 1D, linear supramolecular polymers, the excimer emission of which was quenched abruptly (Figure 2b). Figure 3b reveals that 1D nanoribbons or nanofibers lacking helical structures were present, with some nanofibers existing at the ends of the helical structures. The latter structures presumably arose from loosely packed PS-co-PVBT/A-Py complexes not bound to CNTs, with a large degree of freedom of the polymer chains; this observation is consistent with Figure S10b (Supporting Information), which reveals that the binary PS-co-PVBT/A-Py aggregation complex formed only nanofiber structures with an average width of 50–60 nm. In contrast, the presence of the CNTs would enhance the hydrophobicity of the PS chains and strengthen the multiple hydrogen bonding interactions between the A and T units and the π - π stacking interactions between Py and CNT, thereby triggering the polymer chains to adopt more-planar conformations, due to the restricted rotational freedom of the Py units. Eventually, the planar polymer chains became closely

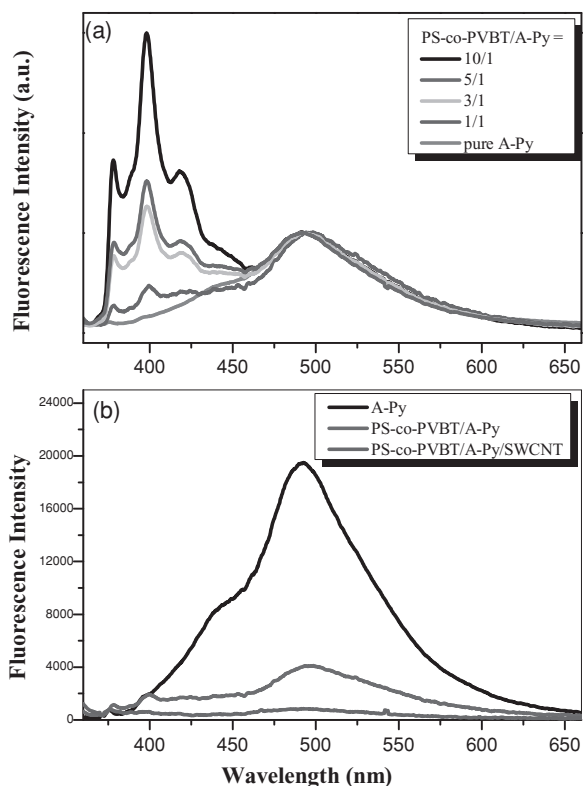


Figure 2. a) Nominal fluorescence spectra of PS-co-PVBT/A-Py blends of various molar ratios and b) fluorescence spectra of pure A-Py and the binary PS-co-PVBT/A-Py and ternary PS-co-PVBT/A-Py/CNT blends prepared with 62 mol% of T units relative to the PS-co-PVBT copolymer and 3 wt% of CNTs, recorded in solution.

packed, stacking together with mutual rotation in a preferred direction along the stacking axis (i.e., along the length of the CNTs) to form chiral supramolecular polymers. Accordingly, the helical pitch length increased generally upon increasing the CNT content (Figure S11, Supporting Information), again attributable to π - π stacking. As a result, the helical length could be controlled by varying the CNT length from several hundreds of nanometers to a few micrometers. In addition, the complementary A-T base pairs were aligned helically; in the absence of such complementary A-T interactions, the PS-co-PVBT/CNT hybrid formed only random nanofibers (Figure S9d, Supporting Information). Because the PS main chain is an achiral polymer, both single and double strands were found in Figure 3a,b, respectively, with no signals appearing in circular dichroism (CD) spectra.^[2] The single and double strands of the PS main chains with complementary A-T base pairs were stacked vertically around the CNTs along the same axis to give helical nanofibers. From wide-angle X-ray diffraction (WAXD; Figure S11, Supporting Information) and small-angle X-ray scattering (SAXS; Figure 3d) analyses, we obtained information about the molecular packing of the PS-co-PVBT/A-Py/CNT blends. The WAXD pattern was characterized by four sharp reflections peaks at 31.4, 23.5, 15.7, and 7.85 Å, with a peak ratio of 1:2:3:4, indicating an inter-planar layered structure with an interlayer distance of 31.4 Å, corresponding to the A-Py/CNT complex, which is similar with pure A-Py. The diffraction pattern

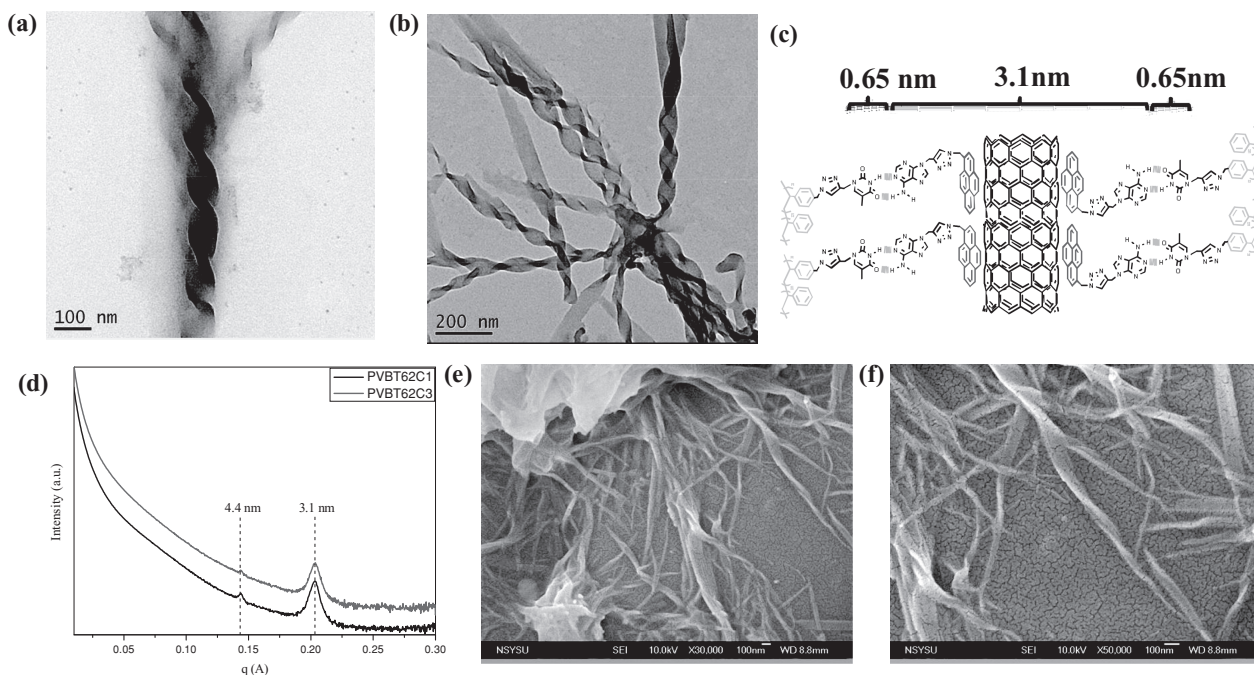


Figure 3. a,b) TEM images of PS-co-PVBT/A-Py/CNT prepared with 62 mol% of T units relative to the PS-co-PVBT copolymer and 3 wt% of CNTs. c) Possible structure for the ternary components of the PS-co-PVBT/A-Py/CNT blend. d) SAXS patterns of PS-co-PVBT/A-Py/CNT blends prepared with 62 mol% of T units relative to the PS-co-PVBT copolymer and 3 and 5 wt% of CNT, where the residual T-A stoichiometry was 1:1. e,f) SEM images of PS-co-PVBT/A-Py/CNT prepared with 62 mol% of T units relative to the PS-co-PVBT copolymer and 5 wt% of CNTs.

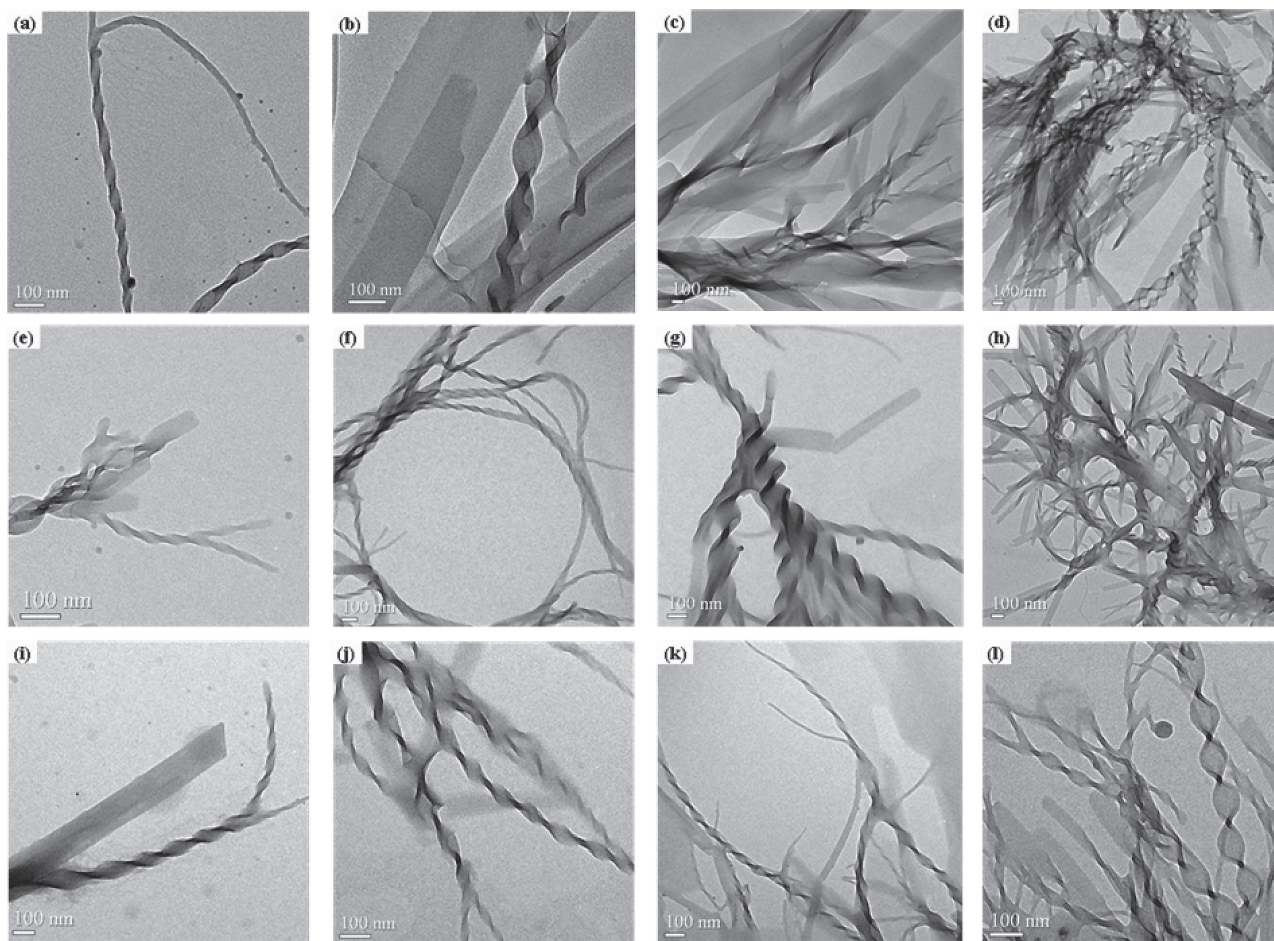


Figure 4. TEM images of ternary PS-*co*-PVBT/A-Py/CNT blends prepared with various contents of T units relative to the copolymer (residual T-A stoichiometry, 1:1). CNT contents: a–e) PS₃₈-*co*-PVBT₆₂/A-Py/CNT: a) 3, b,c) 5, and d,e) 10 wt%; f–h) PS₁₃-*co*-PVBT₈₇/A-Py/CNT: f) 3, g) 5, and h) 10 wt%; i–l) PVBT₁₀₀/A-Py/CNT: i,j) 3, k) 5, and l) 10 wt%.

in the SAXS image (Figure 3d) was characterized by two sharp reflection peaks at 3.14 and 4.4 nm, corresponding to the lengths of the A-Py/CNT and PS-*co*-PVBT/A-Py/CNT hybrid complexes, respectively (Figure 3c). Figure 3e,f presents SEM images of a PS-*co*-PVBT/A-Py/CNT blend, featuring 62 mol% of T units in the PS-*co*-PVBT copolymer and 5 wt% of CNTs. The SEM images again reveal the formation of helical stacks from this ternary PS-*co*-PVBT/A-Py/CNT hybrid complex.^[11]

Figure 4 presents TEM images of the ternary PS-*co*-PVBT/A-Py/CNT hybrid complexes prepared with various contents of T units relative to the PS-*co*-PVBT random copolymers and various amounts of CNTs. We observe that all of the ternary blends formed helical structures, with the helical pitch length increasing from ≈ 105 – 110 to ≈ 140 – 160 nm upon increasing both the content of T units relative to the PS-*co*-PVBT copolymer and the content of the CNTs (Figure S11, Supporting Information). Considering a π - π stacking distance of 0.35 nm, as revealed in Figure S12 (Supporting Information, $q = 1.79$), we assume

that ≈ 300 – 450 molecules of the repeating unit—the A-T binary pair—formed the helical pitch (105–160 nm) in the helical stack. However, the large gap between the dimensions of ternary random copolymers of PS-*co*-PVBT/A-Py/CNT hybrid complexes (diameter of ca. 5 nm according to Figure 3c) and helical structure (Figure 3a,b) visualized by TEM is due to the random copolymers used in Figure 3, which prepared through free radical copolymerization. They would have the polydisperse molecular weight, which is very difficult to have well-defined structures. As a result, the widths of these helical structures are much larger than the predicted in Figure 3c through multiple aggregations by random copolymers.

Block copolymers attract considerable attention because of their abilities to self-assemble in the bulk state or in solution to form a range of different morphologies and sizes.^[4] Here, the ternary block copolymers of PS-*b*-PVBT/A-Py/CNT hybrid complexes prepared with various degree polymerizations of T units in PS-*b*-PVBT block copolymers and various amounts of CNTs were

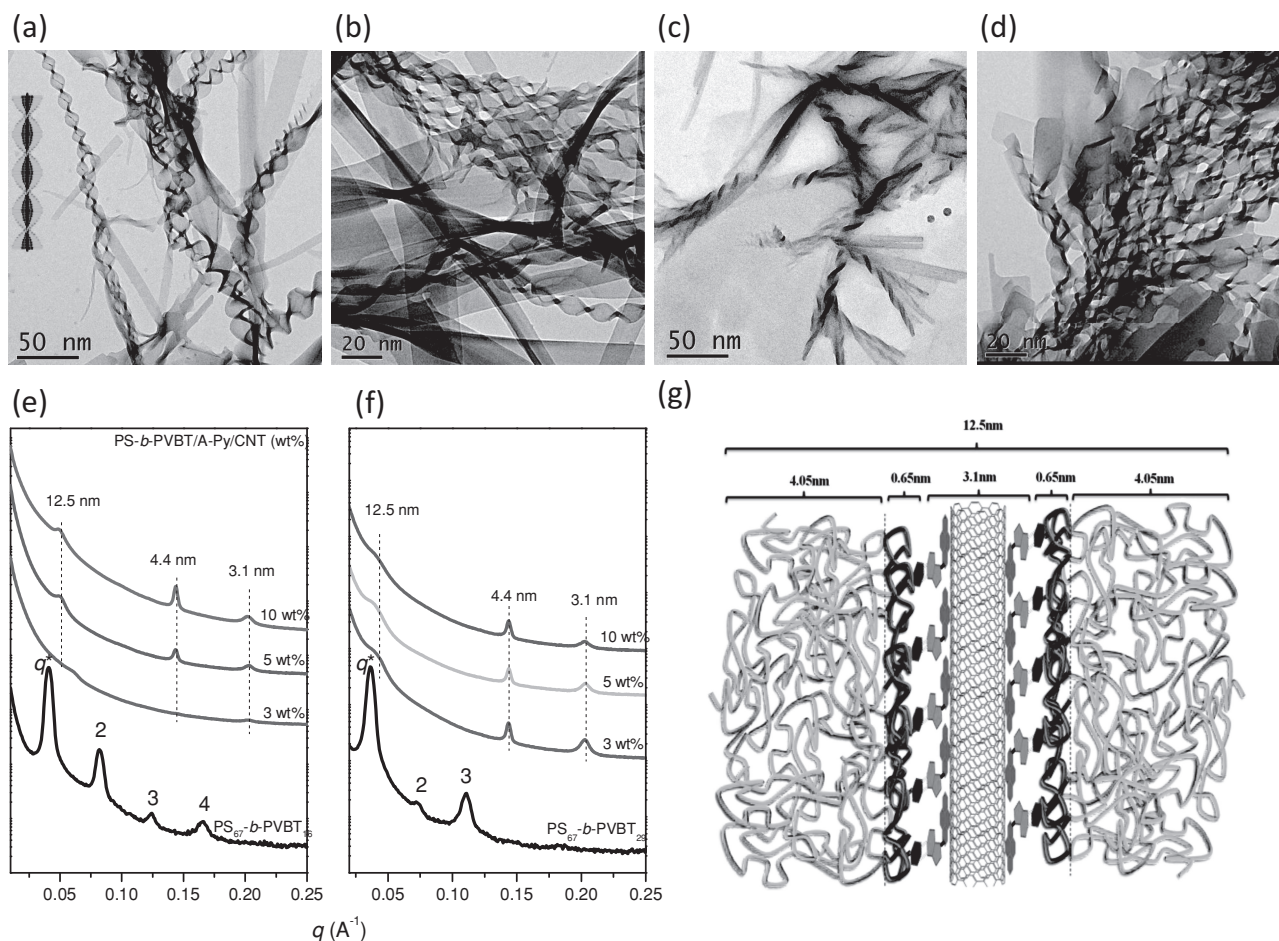


Figure 5. TEM images of PS_{67} - b - $PVBT_{16}$ /A-Py/CNT: a) 3 wt%, b) 5 wt%, and c) 10 wt% of CNTs, d) TEM image of PS_{67} - b - $PVBT_{29}$ /A-Py/CNT with 3 wt% CNT, e) SAXS patterns of PS_{67} - b - $PVBT_{16}$ /A-Py/CNT, f) SAXS patterns of PS_{67} - b - $PVBT_{29}$ /A-Py/CNT, and g) possible structure for the ternary components of block copolymers of PS- b -PVBT/A-Py/CNT hybrid complex.

shown in Figure 5. Figure 5a–d presents TEM images of block copolymers of PS- b -PVBT/A-Py/CNT hybrid complex, where the residual T-to-A stoichiometry was 1:1. The TEM images reveal the formation of helical stacks from this ternary hybrid complex with PS- b -PVBT block copolymers, with an average width of ≈ 10 – 15 nm, an average helical pitch of ≈ 10 – 15 nm, and an average length of 2–3 μm . We believe that the mechanism of helical formation in PS- b -PVBT block copolymers is similar with PS- co -PVBT random copolymers hybrid complex with A-Py/CNT. Clearly, the average width and helical pitch of block copolymers of PS- b -PVBT/A-Py/CNT hybrid complex is much smaller than the random copolymer of PS- co -PVBT/A-Py/CNT hybrid complex. The diffraction patterns in the SAXS image of block copolymers of PS- b -PVBT/A-Py/CNT hybrid complex were shown in Figure 5e,f. Both pure PS- b -PVBT block copolymers show the long-range-order lamellar structure, judging from the positions of the high-order scattering maxima at the scattering vectors q of multiple

integers relative to the position of the first-order scattering maximum ($q/q_m = 1, 2, 3,$ and 4). The corresponding TEM images of pure PS- b -PVBT block copolymers in bulk state were also shown in Figure S13 (Supporting Information), confirming the long-range order of the lamellar structure. The dry helical structures of block copolymers of PS- b -PVBT/A-Py/CNT hybrid complex were also found two sharp reflection peaks at 3.14 and 4.4 nm, corresponding to the lengths of the A-Py/CNT and PVBT/A-Py/CNT hybrid complexes, respectively (Figure 5g), which is similar with random copolymer of PS- co -PVBT/A-Py/CNT hybrid complex. However, the peak at 4.4 nm for block copolymers is much stronger and sharper than random copolymers, indicating much high-range-ordered structure of PVBT/A-Py/CNT hybrid complex in block copolymer. In addition, another lower angle diffraction at 12.5 nm for all block copolymers of PS- b -PVBT/A-Py/CNT hybrid complex is indicated the widths of the individual helical nanofibers, which did not observe such a dimension in the SAXS

spectrum of the helical nanofibers in random copolymers of PS-co-PVBT/A-Py/CNT hybrid complex. The observed spacing is close to the thickness (12.5 nm) expected for the repeated packing of a “{PS}-{PVBT}-{A-Py}-{CNT}-{A-Py}-{PVBT}-{PS}” bilayer structure, as estimated from (4.05 nm for PS + 4.4 nm for PVBT/A-Py/CNT/APy/PVBT + 4.05 nm for PS = 12.5 nm) as shown in Figure 5g. These findings support the notion that the helical structures were well-ordered aggregates. Considering a π - π stacking distance of 0.35 nm, we assume that ≈ 30 – 40 molecules of the repeating unit—the A–T binary pair—formed the helical pitch (10–15 nm) in the helical stack.

3. Conclusions

A series of achiral random and block copolymers of PS-co-PVBT with various T units on the side chains through click chemistry were successfully synthesized and then formed multiple hydrogen bonding interactions with A-Py. The pyrene units also formed π - π stacking between pyrene units and SWCNTs. This ternary component of PS-co-PVBT/A-Py/CNT hybrid complex induces the double-helical structure. In summary, spontaneous self-assembly of helical structures from achiral PS chains led to DNA-like polynucleotide chains stabilized through inter-nucleobase (A–T) multiple hydrogen bonding and π - π stacking between the pyrene and CNT moieties, which were fixed within the internal PS hydrophobic environment.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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