Functionalization of Multiwalled Carbon Nanotubes with Amphiphilic Poly(aspartic acid)

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A new method to functionalize multiwalled carbon nanotubes (MWNTs) with amphiphilic poly(aspartic acid) was investigated. The amphiphilic polymer (PASP-C16) was synthesized by thermal condensation and aminolysis by hexadecylamine, followed by hydrolysis of the remaining succinimide units in the polymer backbone. The functionalization of MWNTs was achieved by physical adsorption of the biopolymer onto the surfaces of MWNTs. Ultraviolet-visible (UV-vis) spectra showed that the functionalized MWNTs had a good aqueous dispersity and solubility. The interaction of PASP-C16 with MWNTs was investigated by analyzing X-ray diffraction (XRD) patterns, circular dichroism (CD), spectra and high-resolution transmission electron microscopy (HRTEM). From the XRD patterns, it can be known that the aggregate of PASP-C16 due to intermolecular interaction between hexadecyl chains has been reduced when the polymer interacting with MWNTs. CD spectra indicated that the interaction of hexadecyl chains of PASP-C16 with the wall of MWNTs is the major interaction between PASP-C16 and MWNTs, and MWNTs were covered by the poly(aspatic acid) backbone. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 772–777, 2011
Keywords: amphiphilic poly(aspartic acid), carbon nanotubes, interaction, functionalization

Introduction

Carbon nanotubes (CNTs) have extraordinary electrical, mechanical, and thermal properties and have the potential for a wide variety of applications.[1,2] The sidewall surface of a pristine CNTs is highly hydrophobic and bundles are formed mainly due to van der Waals interactions between the sidewalls of the individual tubes. Individually dispersed CNTs in biocompatible media are very important for many biomedical and nanomedicine applications, therefore, functionalization for aqueous solubility has been a major goal in carbon nanotube chemistry.[3] CNTs can be debundled into individual nanotubes in aqueous solutions via covalent or noncovalent functionalization.[2,4] Covalent functionalization entails damage to the CNTs, while noncovalent functionalization has the advantage of preserving the intrinsic electronic structure and properties.[5] Physical adsorption of polymers on CNT surfaces is an useful strategy and has been demonstrated to be effective in dispersing CNT and preparing CNT based composite materials, such as poly(ethylene oxide),[6] linear and hyperbranched glycopolymers,[7] metallopolymers,[8] aminopolymers,[9] poly(acrylic acid),[10] and amphiphilic block polyelectrolytes[11] have been used to functionalize carbon nanotubes.

Poly(aspartic acid) (PASP) is a water-soluble polymer, which has amide linkages like proteins. PASP is an attractive candidate for biomedical applications due to completely

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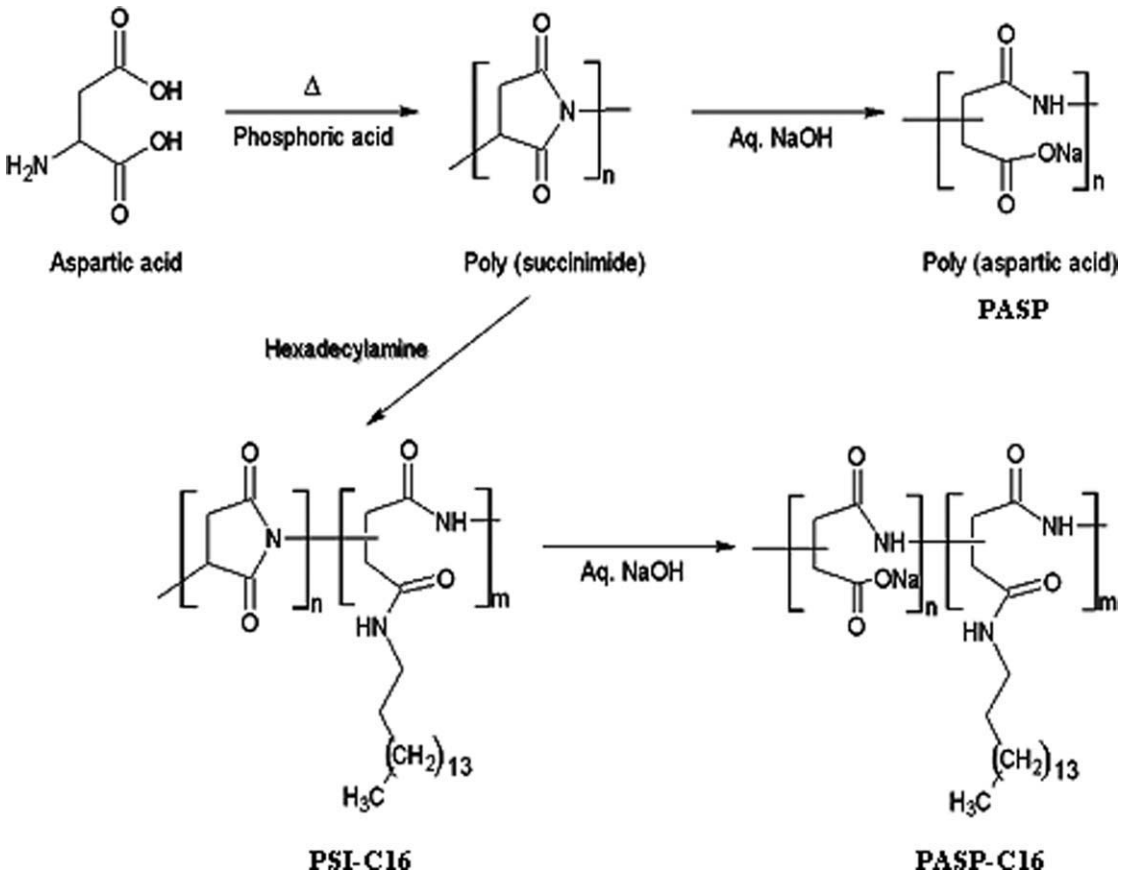

Figure 1. Synthesis of poly(succinimide) (PSI), PASP and PASP grafted with hexadecyl chain (PASP-C16).

biodegradable and acid-containing water-soluble properties.[12] Hydrophobically modified poly(aspartic acid) has been investigated for its potential medical application.[12–15] In this study, we report MWNT functionalization with an amphiphilic polymer. The polymer is synthesized by grafting hexadecyl chains to poly(aspartic acid) backbone. The interaction of amphiphilic poly(aspartic acid) (PASP-C16) with MWNTS will be studied through UV-vis spectra, XRD patterns and circular dichroism (CD) spectra.

Experimental

MWNT purification

MWNTs (98% purity, 20-30-nm dia., 1-5 μm length) were obtained from Nanotech Port Co., Ltd. (Shenzhen, China). The CNTs were refluxed in 2.6 M nitric acid at 70°C for 45–48 h to remove the exposed graphite particles. Then, the samples were centrifugated, filtered with 0.45 μm filter, washed with water until pH became neutral. Finally, the samples were dried in a vacuum oven at 80°C.

Synthesis of amphiphilic poly(aspartic acid)

The amphiphilic poly(aspartic acid) (PASP-C16) was synthesized according to following procedure.[12,13,15] L-aspartic acid (4 g) was suspended in flask in the presence of phosphoric acid (2 mL) and stirred at 190°C. After 2 h, the reaction mixture was precipitated in excess methanol and successively washed with water until the pH of the suspension became neutral. The precipitate was dissolved in DMF, and the mixture was incubated at 40°C for 2 h. The mixture was then filtered, and the filtrate was precipitated in excess methanol. The precipitate was dried at 80°C *in vacuo*. The structure of poly(succinimide) (PSI) was confirmed by 1H NMR analysis. ^{1}H NMR (DMSOd6): δ = 2.723 and 3.185 (-CH2-, 2H, s); 5.253 (-CH-, 1H, t).

The synthesized PSI (970 mg) was dissolved in DMF (10 mL). Hexadecylamine (723 mg) dissolved in DMF was added to the mixture rapidly. The reaction mixture was stirred at 70°C for 24 h. The reaction mixture was cooled to room-temperature. Insoluble product was filtered out. The clear solution was added dropwise to 1N NaOH solution to hydrolyze remaining succinimide unit of PSI. After stirring for 3 h in an ice water bath, the reaction mixture was precipitated in excess methanol twice. The precipitate was filtered and washed with methanol and then dried *in vacuo* at 60°C. The structures of PASP, PSI-C16, and PASP-C16 (as shown in Figure 1) were confirmed by ^{1}H NMR analysis. PASP: ^{1}H NMR (D_2O): δ = 2.73 and 2.68 and 2.65 and 2.52 (-CH_2-,2H, m); α = 4.45 (α-opening, 1H, s); δ = 4.63 (β-opening, 1H, s); PSI-C16:1H NMR (DMSO-d_6): α = 0.84 (-CH_3, 3H, t); α = 1.22 (-CH_2-, 3H, s); δ = 2.73 and 3.18 (-CH_2-, 2H, s); 5.26 and 4.49 (-CH-, 1H, t). PASP-C16:1H NMR (D_2O): δ = 0.81 (CH_3-, 3H, t); δ = 1.22 (-CH_2-,

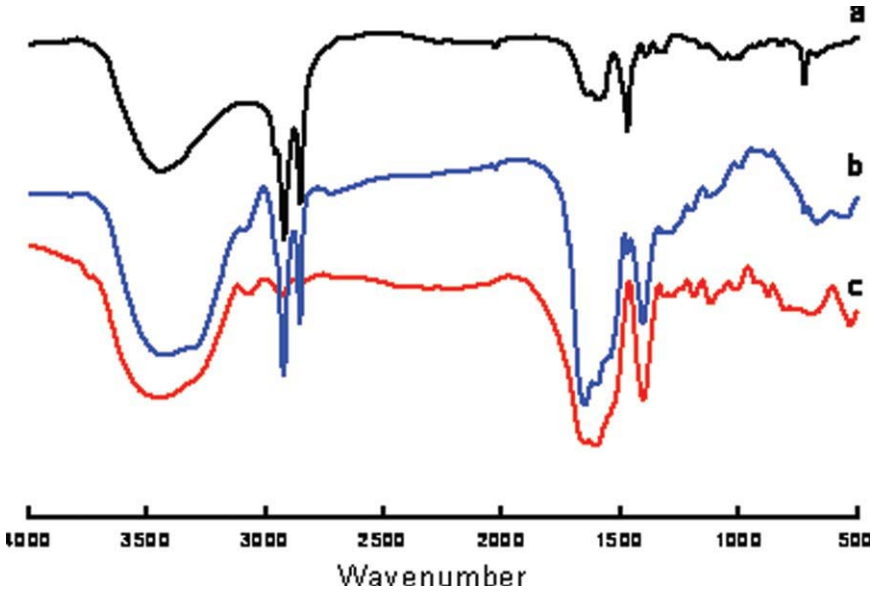

Figure 2. FT-IR spectra of hexadecylamine(a), PASP-C16 (b) and PASP(c).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

28H,s); $\delta = 2.71$ and 2.96 and 2.99 and 3.09 (-CH_2-, 2H, m); $\delta = 4.435$(α-opening, 1H, s); $\delta = 4.604$ (β-opening, 1H, s). The degree of substitution (DS) is the mole percent of the attached unit with alkyl group per total succinimide unit. The DS value of 23% was obtained by analyzing 1H NMR of PSI-C16.

Functionalization of MWNTs with PASP-C16

PASP-C16 was suspended in deionized water and mixed by vortexing. A clear solution was obtained under sonication for 20 min using a bath type sonifier at room temperature. Purified-MWNTs were added to deionized water and sonicated for half an hour, followed by addition of the PASP-C16 solution. The component ratio of the mixture was 1.0 mL of water: 0.5 mg of PASP-C16:0.2 mg of MWNTs. The mixture was sonicated for 1 h and followed by centrifugation at 12,000 rpm for 30 min, yielding well-suspended MWNTs in the supernatant. The supernatant was filtered through 0.45 μm membrane to remove unbound PASP-C16. The MWNTs attached with PASP-C16 were redispersed and suspended in water by sonication. The suspension was monitored by UV-vis spectroscopy using a Shimadzu spectrophotometer (model UV 2550) operated at a resolution of 1 nm. For HRTEM analysis, the suspension was deposited onto a 400-mesh Cu grid by dropping and drying.

Fourier transform infrared spectroscopy

The FTIR spectra of the sample were recorded on a Fourier transform infrared spectrometer 3100 (Varian, USA) at room-temperature. A sample, prepared for KBr determinations, consisted of 1 mg of substance (hexadecylamine, or PASP-C16, or PASP) mixed with 100 mg of spectroscopic grade KBr. A total of 512 scans at 2 cm^{-1} resolution were averaged to obtain each spectrum.

X-ray diffraction

For X-ray diffraction (XRD) measurement, the nanotube films were obtained similarly as described prevously. The nanotubes were dried to constant weight *in vacuo* at 50°C, the obtained solid was used for XRD measurement. XRD patterns of the sheet samples was recorded on a X-ray diffractometer (D/Max2500VB2+/PC, Rigaku, Japan) with area detector operating at a voltage of 40 kV and a current of 50 mA using Cu Kα radiation ($\lambda = 0.154$ nm). The scanning rate was 5 °/min, and the scanning scope of 2θ was from 5 to 90°C at room-temperature.

Circular dichroism

Circular dichroism (CD) spectroscopy was used to monitor the secondary structures of PASP and PASP-C16. The aqueous solutions of PASP (1.0 mg/mL) and PASP-C16 (1.0 mg/mL) under 50-min sonication were used for the CD measurement. For the system PASP-C16/MWNTs, the aqueous solution of PASP-C16 (1.0 mg/mL) was sonicated for 20 min, followed by addition of MWNTs. The final concentration of MWNTs was 0.10 mg/mL. Further sonication of the mixture for 30 min was carried out. The CD spectra (200–260 nm) were recorded on a Jasco J-810 CD instrument with a bandwidth of 0.5 nm and a scan speed of 500 nm/min. Cell length was 1.0 mm. For monitoring the secondary structure of the PASP-C16 attaching on MWNTs, the spectra were corrected by subtracting a blank spectrum of purified MWNTs. Each scan was repeated 10 times, the spectra were then averaged.

Results and Discussion

Synthesis of PASP-C16

Figure 2 shows the FTIR spectra for hexadecylamine, PASP-C16, and PASP, respectively. In line a, the peak at

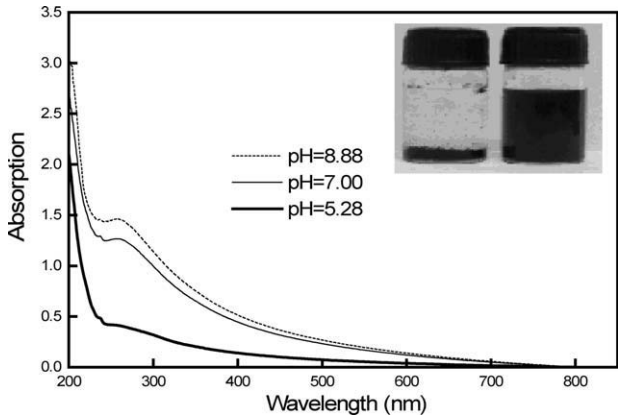

Figure 3. The UV-vis spectra of the aqueous solutions of functionalized MWNTs at pH 5.28, pH 7.0 and pH 8.88.

Insert: purified MWNTs (left) and functionalized MWNTs (right) in water at pH7.0.

3442.55 cm^{-1} is due to the N-H and O-H stretching vibration. N-H is from hexadecylamine. The peaks at 2918.14 cm^{-1} and 2850.01 cm^{-1} are due to the C-H stretching vibration of $-CH_2$. The peak at 1468.86 cm^{-1} is due to the C-H stretching vibration of $-CH_3$. In line c, the peak at 3446.58 cm^{-1} is due to the N-H and O-H stretching vibration. The spectrum exhibits a strong band at 1600 cm^{-1} assigned to the vibration of the carbonyl group (C = O). The results show that there are plenty of =CONH. The bands at about 1401.47 cm^{-1} exhibits bending vibration of $=CH_2$ and $\equiv$CH. The spectrum of PASP-C16 exhibits characteristic peaks of PASP at 1600 cm^{-1} and 1401.47 cm^{-1}, it also exhibits adsorption bands of the grafted hexadecyl chain at 2921.15 cm^{-1} and 2851.80 cm^{-1}. The FTIR analysis showed that the hexadecyl group was successfully grafted to the PASP backbone.

Solubilization of functionalized MWNTs in water

Poly(aspartic acid) is a water-soluble polymer.[12] Its derivative PASP-C16, which is composed of poly(aspartic acid) as the hydrophilic backbone and hexadecyl chain as the hydrophobic segment, has a good solubility in water as well. When MWNTs was added to the aqueous solution of PASP-C16 and the solution was well mixed under sonication, the hexadecyl chains of PASP-C16 interacted with the wall of MWNTs, and, thus, MWNTs were covered by the poly(aspartic acid) backbone. Such functionalized MWNTs can be dispersed well and have a good solubility in water, as shown by the insert in Figure 3.

The solubility of MWNTs in the aqueous solution of PASP-C16 was pH-dependent as shown in Figure 3. In the acidic solution, carboxyl groups of aspartic acid in the hydrophilic backbone were protonated, and the attractive interaction between protonated aspartic acid units in the PASP backbone made the functionalized MWNTs less soluble in water. In neutral and basic pH ranges, deprotonated aspartic acid units endow the PASP backbone with negative charge. The repulsive interaction between aspartic acid units in the PASP backbone facilitates the solubilization of the functionalized MWNTs in water.

X-ray diffraction

PASP-C16 with hexadecyl chains facilitates aggregate formation by association with hexadecyl chains in other polymers,[13,15] as schematically explained by Figure 4a. The

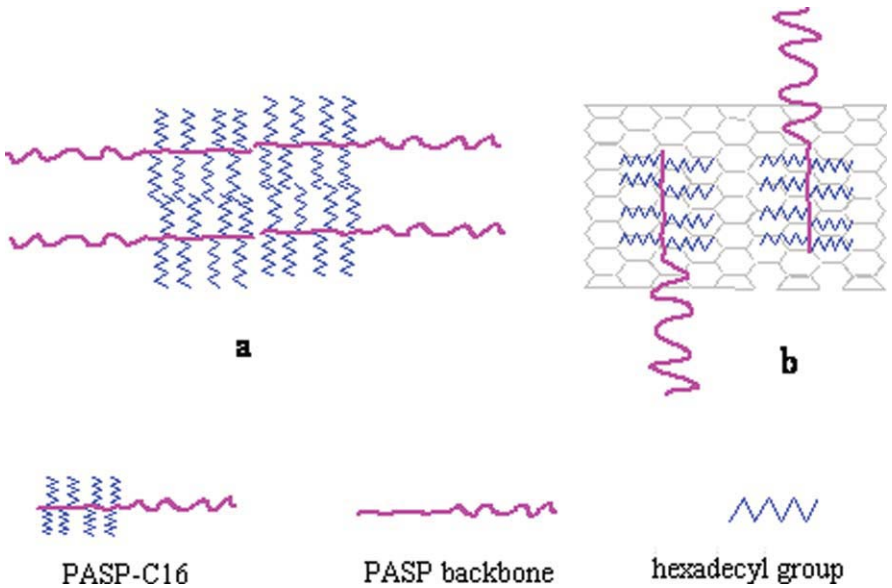

Figure 4. Schematic explanation of the interactions due to hexadecyl chains.

(a) Self -aggregation of PASP-C16 due to the interaction between hexadecyl chains, and (b) Interaction of PASP-C16 with the wall of MWNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

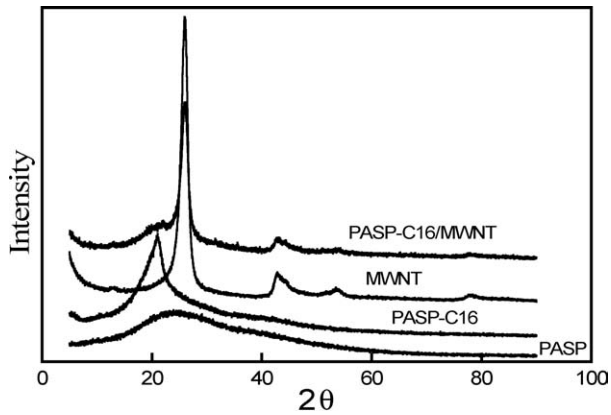

Figure 5. XRD patterns of PASP, PASP-C16, PASP-C16/MWNT and MWNT.

aggregates are relatively weak and easily dissociated under sonication. The sonication of PASP-C16 in water reduced the intensity of aggregates of the polymer by breaking hydrophobic domains formed due to the intermolecular interaction,[13] subsequent addition of MWNTs into the solution and further sonication facilitated the hexadecyl chains of PASP-C16 to interact with the wall of MWNTs, as schematically explained by Figure 4b.

The interaction of PASP-C16 with MWNTs was characterized with XRD patterns. Figure 5 presents the XRD patterns of the materials PASP, PASP-C16, PASP-C16/MWNT, and purified MWNTs isolated at pH 7.0. The diffraction pattern of MWNTs contains sharp, prominent signature peaks at 26 deg and 43 deg. For PASP, there is no sharp peak in the diffraction pattern, meaning that there are no regular crystalline planes to diffract X-rays. PASP-C16 presents a sharp peak at 21 deg in the diffraction pattern. From the XRD patterns of PASP and PASP-C16, we can deduce that

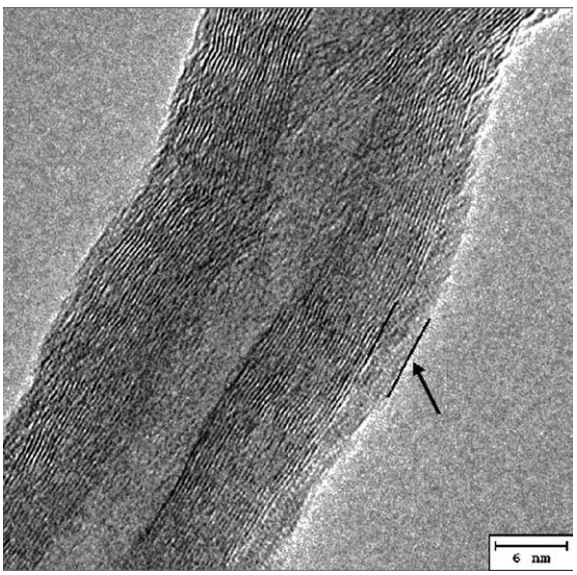

Figure 6. HRTEM image of MWNTs attached by PASP-C16.

The arrow indicating a thin layer of PASP-C16 formed on the wall of MWNT.

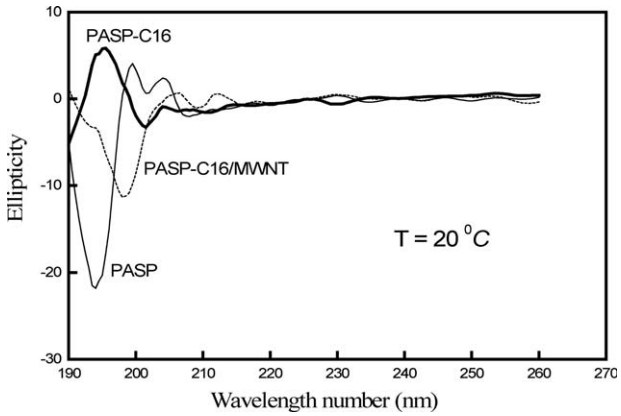

Figure 7. CD spectra of PASP-C16, PASP-C16/MWNT and PASP.

T = 20°C; pH = 7.0.

the hexadecyl chains, which were grafted to PASP, result in the formation of aggregates of PASP-C16 in aqueous solution, as schematically explained by Figure 4a. Because of this, the sharp peak at 21 degrees appears in the diffraction pattern of PASP-C16. While in the XRD pattern of PASP-C16/MWNTs, a broad peak appears near 21 degrees, which means that the aggregates of PASP-C16 were reduced. Once the hexadecyl chains interacted with the wall of MWNTs, the intermolecular interaction between the hexadecyl chains was decreased. As a result, the aggregate of PASP-C16 was reduced. The interaction of PASP-C16 with MWNTs was also confirmed by the HRTEM image as shown in Figure 6. As can be seen, a thin layer of PASP-C16 formed on the wall of MWNT as indicated by the arrow.

Circular dichroism

Secondary structure can be determined by CD spectroscopy in the "far-UV" spectral region (190–250 nm). At these wavelengths the chromophore is the peptide bond, and the signal arises when it is located in a regular, folded environment. Figures 7 to 9 show the CD spectra of PASP-C16, PASP-C16/MWNT, and PASP at neutral conditions and different temperatures. At 20°C, PASP presents one negative

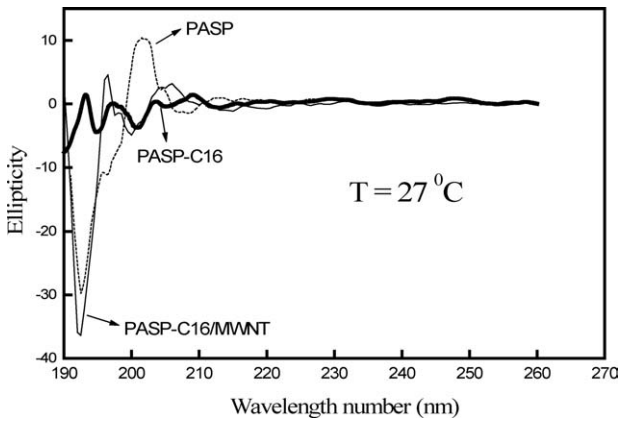

Figure 8. CD spectra of PASP-C16 PASP-C16/MWNT, and PASP T = 27°C; pH = 7.0.

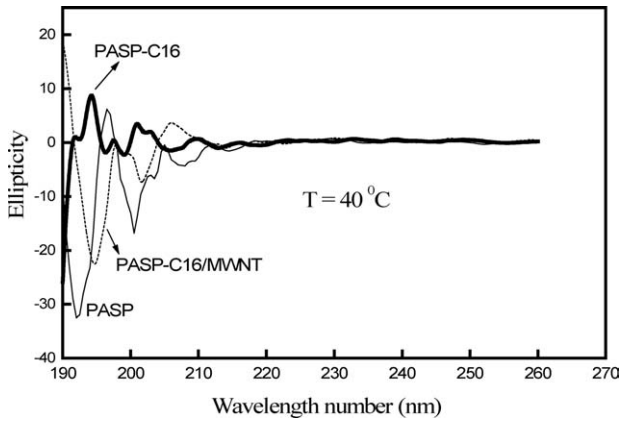

Figure 9. CD spectra of PASP-C16, PASP-C16/MWNT and PASP. T = 40 °C; pH = 7.0.

peak at 194 nm; PASP-C16/MWNT exhibits one negative peak at 198 nm. At 27°C, PASP: one negative peak at 192.5 nm; PASP-C16/MWNT: one negative peak at 192.5 nm; PASP-C16: two negative peaks at 194.5 nm and 201 nm with low intensity. At 40°C, PASP exhibits two negative peaks at 192 nm and 200.5 nm; PASP-C16/MWNT has two negative peaks at 194.5 nm and 201.5 nm.

In terms of the band position, PASP-C16 interacting with MWNTs presents a spectrum which is significantly distinct from that of free PASP-C16, while the spectrum of PASP-C16/MWNTs bears resemblance to that of PASP. From the results, we deduce that the hexadecyl chains of PASP-C16 interacted with the wall of MWNTs, and this attractive interaction reduced the aggregate formation due to intermolecular interaction between hexadecyl chains. MWNTs were covered by the poly(aspartic acid) backbone as schematically presented by Figure 4b.

Conclusions

Amphiphilic poly(aspartic acid) (PASP-C16) was synthesized and used to functionalize MWNTs by physical adsorption of the biopolymer on MWNT surfaces. UV-vis spectra showed that the functionalized MWNTs had a good aqueous dispersity and solubility. The interaction of PASP-C16 with MWNTs was investigated by analyzing XRD patterns, CD spectra and HRTEM. From the XRD patterns, we know that the aggregate of PASP-C16 due to intermolecular interaction between hexadecyl chains has been reduced when the polymer interacting with MWNTs. CD spectra indicated that the interaction of hexadecyl chains of PASP-C16 with the wall of MWNTs is the major interaction between PASP-C16 and MWNTs. PASP-C16 interacting with MWNTs presented CD spectra bearing resemblance to that of PASP, and, hence, it can be deduced that MWNTs were covered by the polyaspatic acid backbone.

Acknowledgments

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