

Architectural effect of poly(acrylic acid) and poly(amide imide) block copolymers on dispersion of carbon nanotubes in water

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ABSTRACT: The dispersion of carbon nanotubes (CNTs) in water by poly(acrylic acid) (PAA) and poly(amide imide) (PAI) block copolymers and homo-PAA is investigated. Poly(acrylic acid)-*block*-poly(amide imide) (PAA-*block*-PAI), poly(acrylic acid)-*block*-poly(amide imide)-*block*-poly(acrylic acid) (PAA-*block*-PAI-*block*-PAA), and heteroarm star block copolymer poly(acrylic acid)₂poly(amide imide) (PAA₂PAI) with similar molecular weights and PAA contents are used as the copolymers. The dispersion of CNTs is observed by dynamic light scattering and ultraviolet-visible spectroscopy. The presence of the hydrophobic sequence improves the dispersion. PAA₂PAI has the best dispersion ability, followed in order by PAA-*block*-PAI-*block*-PAA, PAA-*block*-PAI, and homo-PAA. In the dry state, aggregates of CNT are observed by transmission electron microscopy (TEM) in the mixture with PAA-*block*-PAI and homo-PAA. The adhesion of the copolymers to CNT is also observed by TEM and is due to the high affinity between hydrophobic PAI and CNT. In particular, PAA₂PAI and PAA-*block*-PAI-*block*-PAA well cover the CNTs. The presence of PAI and the PAA location are important for the dispersion of CNTs. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43461.

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INTRODUCTION

The dispersion of carbon nanotubes (CNTs) has been well investigated in many studies.^{1–3} CNT is a promising nanomaterial. Because of its good properties, such as thermal conductivity, electroconductivity, and mechanical strength, CNTs are applied in many materials and in medicine, electrodevices, vehicle materials, construction, and so on.^{4–9} As a nanomaterial, it is important to disperse the CNTs homogeneously in a matrix. However, CNTs are difficult to disperse, even in solvents and especially in water.^{10,11} Ultrasonication, surface-modified CNT, and dispersants such as surfactants and polymers have been used to improve the dispersion.^{2,12–15} Insufficient dispersion of CNT in water by poly(acrylic acid) (PAA) (acid to base) has been reported.^{15,16} To disperse CNTs in water, the dispersants are required to have not only dispersibility in water but also an affinity for CNTs.

Previously, we synthesized three different types of poly(acrylic acid)-poly(amide imide) (PAA-PAI) copolymers.¹⁷ They are three-arm poly(acrylic acid)₂poly(amide imide) (PAA₂PAI, 3arm), poly(acrylic acid)-*block*-poly(amide imide) (PAA-PAI, diblock), and poly(acrylic acid)-*block*-poly(amide imide)-*block*-poly(acrylic acid) (PAA-PAI-PAA, triblock). Their chemical structures are shown in Figure 1. The PAA sequence provides good dispersibility in water, and the PAI sequence is adhesive to

CNTs.^{18–20} It is possible to disperse CNTs in water by using these copolymers as dispersants. The polymer architecture is an important factor in the dispersion.^{21,22} The molecular weights and PAA contents of these copolymers are very close. Therefore, the architecture is the only different feature of these copolymers.

In this work, we investigated the effect of the architecture of PAI-PAA copolymers on the dispersion of CNTs in water. The architecture will influence the dispersion with three factors, which are expansion of the PAA sequence, dispersion of the PAA sequence on the CNT, and number of PAA sequences attached to a certain place on the CNT. They will correspond to the repulsive area, the dispersion of repulsive charge on the CNT, and the local concentration of repulsive charge on a certain place on the CNT, since ionized PAA sequences that are attached to a CNT repel each other. The most effective factor for the dispersion of CNTs will be clarified. In this work, the dispersion of CNTs in water by PAA-PAI copolymers was estimated by ultraviolet-visible spectroscopy (UV-vis), dynamic light scattering (DLS), and transmission electron microscopy (TEM) observations.

EXPERIMENTAL

Materials

PAA₂PAI, PAA-PAI, and PAA-PAI-PAA were synthesized from the same PAI sequence. Three copolymers were synthesized by

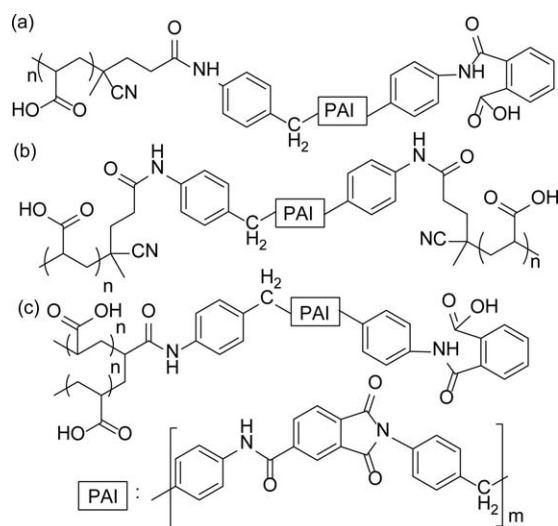


Figure 1. Chemical structure of (a) poly(acrylic acid)-*block*-poly(amide imide) (PAA-PAI); (b) poly(acrylic acid)-*block*-poly(amide imide)-*block*-poly(acrylic acid) (PAA-PAI-PAA); (c) poly(acrylic acid)₂poly(amide imide) (PAA₂PAI).

postpolymerization of acrylic acid after the chain ends of PAI were capped or modified with an azo initiator. The details of the procedure were described elsewhere.¹⁷ The chemical structures of the copolymers are shown in Figure 1. The characteristics of them and PAA are listed in Table I. Carbon nanotubes (TCI, Tokyo, Japan, C2154 multiwall, $\Phi = 20\text{--}40$ nm, length = $5\text{--}15$ μm), ruthenium oxide (IV) (RuO_4 , Strem Chemicals, Newburyport, Massachusetts), acetone (Kanto, Tokyo, Japan >99.0%), and methyl sulfoxide-*d*₆ for NMR (d-DMSO, Acros Organics, Geel, Belgium, 0.03% TMS, 99.9 atom % D), were used as received. Deionized water prepared with a disposable demineralizer (Kurita, Tokyo, Japan, DS N-075) was used.

Characterization

UV-vis Measurement. The turbidity of the CNT solution was measured by UV-vis spectroscopy with a UV-vis spectrophotometer (V-630, Jasco, Tokyo, Japan) for 7 h at 25 °C. The wavelength was set to 650.0 nm. After 0.2 g/L polymer aqueous was prepared, the same weight of CNT as polymer was added to the aqueous solution. Just before the measurement, the CNTs were well dispersed by an ultrasonic cleaner (AS-ONE, Osaka, Japan, Vs-F100) at 50 kHz for 10 min.

Dynamic Light Scattering. The DLS of polymer and polymer/CNT aqueous was performed with a DLS-8000PNA (Otsuka Electronics Co., Osaka, Japan, control unit: LS-81, pump controller: LS-82) at angles of 30°, 60°, and 90° at 25 °C. The wavelength of the laser was 632.8 nm. Water was used for the solvent. The polymer concentration was set to 1.0 g/L. The polymer/CNT aqueous solution was prepared as for the UV-vis measurement. The CNT (3.0 mg) was added to the polymer aqueous solution (3.0 mL, 1.0 g/L of polymer concentration), and the aqueous solution was ultrasonicated with an ultrasonic cleaner (AS-ONE, Vs-F100) at 50 kHz for 10 min at 25 °C. The measurement was conducted immediately after the ultrasonication. The non-negative least squares method was used for analysis.

Transmission Electron Microscopy. TEM studies were conducted using a Hitachi H-7100 operating at 75 kV equipped with a charged coupling device (CCD) camera (with an AMT Advantage ERL-A attached, Hitachi High Technologies). The sample aqueous solution was prepared as for the UV-vis measurement. The polymer concentration was set to 10 g/L. The aqueous solution was cast on the grids and dried gradually for a day. The PAI domains were stained with ruthenium (IV) oxide vapor and dried for a day. Then, a few drops of the aqueous solution were added to acetone. The solutions were cast on carbon-coated copper grids and dried immediately at room temperature.

RESULTS AND DISCUSSION

First, the CNTs were dispersed in a 1 wt % polymer aqueous solution by ultrasonication. The CNT concentration was 0.1 g/L. The solutions were kept for 1 day at room temperature. The CNT was dispersed in PAA-PAI copolymer aqueous, though it was completely precipitated in PAA aqueous. It is clear that the PAI sequence of PAA-PAI copolymers was important for the dispersion stability of CNT in water. CNTs were attached to hydrophobic PAI sequences, and the PAA sequences in the copolymers became driving forces in the dispersion.

To define the dispersion of CNT, a DLS measurement was carried out. After measurement for 100 scans, CNT completely precipitated in PAA aqueous. Therefore, the accumulation time was set to 30 scans. Figure 2 shows the plots of the peak tops from the DLS data. Since CNTs are not spherical, the measurement was conducted at 30°, 60°, and 90°. The peak tops in water and PAA aqueous showed a clear dependence on angle because of the anisotropy of CNT. In contrast, the peak tops in the copolymer solution showed close values. The aggregate with copolymers became more spherical than rod. This was because the copolymers covered the CNTs. The hydrophobic PAI sequence would be attached to the CNT, and the PAA extending into the water from the surface of the CNT would help the dispersion of CNTs in water.

UV-vis Measurement

To quantify the dispersion stability of CNT, the time dependence of absorbance of the CNT/polymer aqueous solutions was measured at 650 nm for 7 h. Figure 3 shows their absorbance curves. The high absorbance value indicates that the CNTs

Table I. Characteristics of the Polymers

| Polymer | PAA content (mol %) ^a | M_n^b |
|----------------------|----------------------------------|--------------------|
| PAA | 100 | 46.1×10^3 |
| PAA ₂ PAI | 72.8 | 5.84×10^3 |
| PAA-PAI | 77.8 | 6.46×10^3 |
| PAA-PAI-PAA | 71.7 | 5.74×10^3 |

^a Determined by ¹H-NMR.

^b M_n is the number-average molecular weight calculated by a combination of PAA content and the M_n of PAI (3.87×10^3), except for PAA. The number-average molecular weight of PAA was calculated from M_n of methylated PAA determined by gel permeation chromatography with poly(methyl acrylate) standards.

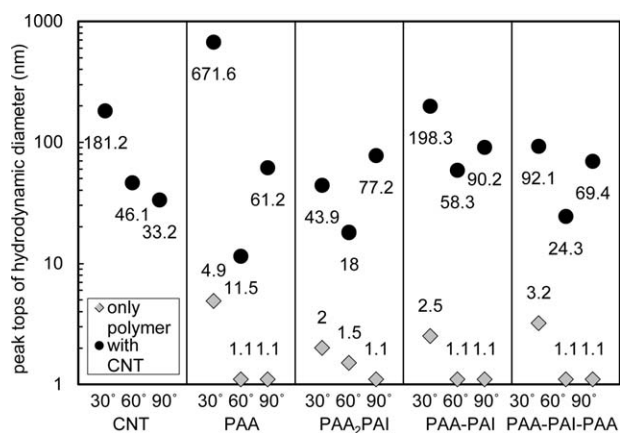


Figure 2. Peak tops of hydrodynamic diameters of CNT in water and polymer aqueous solutions.

dispersed well. The absorbance value of PAA aqueous was only 0.09 and did not change during measurement. CNTs precipitated immediately in PAA aqueous. It was impossible to disperse the CNTs by linear PAA. In contrast, all CNT/copolymer aqueous solutions showed good dispersion of CNTs, with absorbance values larger than 1.5. The initial absorbance values were 2.34 for PAA₂PAI, 1.70 for PAA-PAI-PAA, and 1.47 for PAA-PAI. The absorbance of copolymer aqueous was constant up to 90 s and then gradually decreased. The absorbance values at 1.0×10^4 s were 0.553 for PAA₂PAI, 0.398 for PAA-PAI-PAA, and 0.138 for PAA-PAI. The absorbance of PAA-PAI at 1.0×10^4 s agreed well with that of PAA aqueous (0.080), indicating PAA-PAI had the lowest dispersibility of CNTs among the three copolymers. PAA₂PAI showed the best dispersibility of CNTs, with the largest absorbance in the initial stage and at 1.0×10^4 s. PAA-PAI-PAA aqueous showed intermediate absorbance between PAA₂PAI and PAA-PAI in the initial stage, though the absorbance was close to that of PAA₂PAI at 1.0×10^4 s. Therefore, the order of dispersibility, best to worst, of CNT in water was PAA₂PAI, PAA-PAI-PAA, PAA-PAI, and PAA.

From these results, two points were found. One is the importance of hydrophobic sequence. Again, all PAA-PAI copolymers showed better dispersion of the CNTs than did PAA. Hydrophobic PAI is anticipated to have interactions with hydrophobic CNTs. In other words, CNTs would be attached to PAI in water. As a result, the CNTs were covered with copolymer. The PAA sequences of the copolymers worked as soluble sequences in water. The combination of two sequences was effective for the dispersion of CNTs in water. The other interesting point was the effect of molecular architecture. The three copolymers had almost the same compositions and molecular weights. This means the whole amounts of charge per molecule owing to the PAA sequences were the same. However, the local charge density of a molecule depends on the architecture. The density, length, and location of repulsive PAA were differently dependent on the architecture. Assuming that PAI attached to the surface of the CNT, the localization and expansion of PAA would be different. Thus, the dispersion of CNT strongly depended on the architecture of the copolymers.

Transmission Electron Microscopy (TEM)

Figure 4 shows TEM images of polymer/CNT mixtures. The top images show the polymer/CNT mixtures with no staining. The dark regions correspond to CNTs. To avoid the aggregation of the polymers, these aqueous solutions were diluted with an excess amount of acetone. Networks with small particles were formed with PAA₂PAI and PAA-PAI-PAA. The average diameter of the particle was less than 100 nm. The CNTs were well covered with these particles. The observed diameters agreed well with the hydrodynamic diameters of the aggregates detected by DLS. In the case of PAA-PAI, CNTs were attached with polymer and aggregated. These results correspond to the final stage of the UV measurement, which is the larger absorbances of PAA₂PAI and PAA-PAI-PAA than those of PAA-PAI and PAA. The formation of small particles with PAA-PAI and PAA-PAI-PAA maintained good dispersibility of CNTs for a long time.

Strictly, the size of aggregation of PAA-PAI was smaller than that of PAA. The diameter of the aggregates with PAA was larger than 500 nm. The large aggregates formed from PAA and CNT caused rapid precipitation of CNTs in water. The bottom images are the aggregates cast with water, and the PAI sequence was stained dark with RuO₄ to identify its location. It was found that the CNTs were well covered by the PAI sequence. The PAI sequence adhered to the CNTs. The PAA sequences were extended from the CNT surface and increased the dispersibility of CNTs.

The effect of architecture of polymers on dispersion of CNTs is interesting. The polymers attached to CNTs are expanded as follows (Figure 5). The hydrophobic PAI sequence attaches to the CNT. The ionized PAA sequences that are attached to the CNT repel each other. The PAA sequence of PAA-PAI extends the longest because the PAA length of PAA-PAI is twice that of PAA-PAI-PAA and PAA₂PAI. This will correspond to a large repulsive area. The PAA sequence of PAA-PAI-PAA is the most

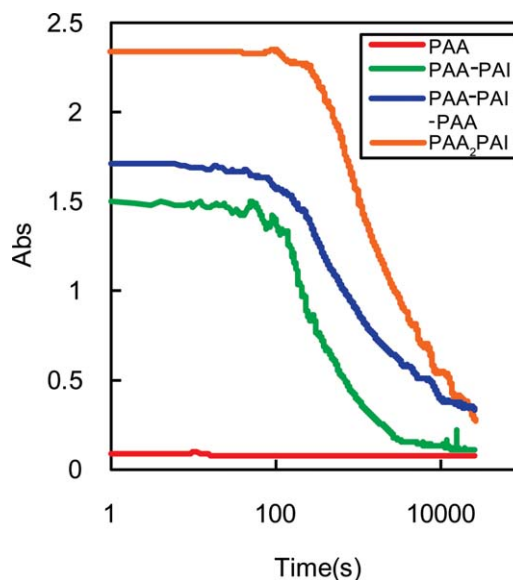


Figure 3. Absorbance curves of CNTs dispersed in polymer aqueous solutions at 650 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

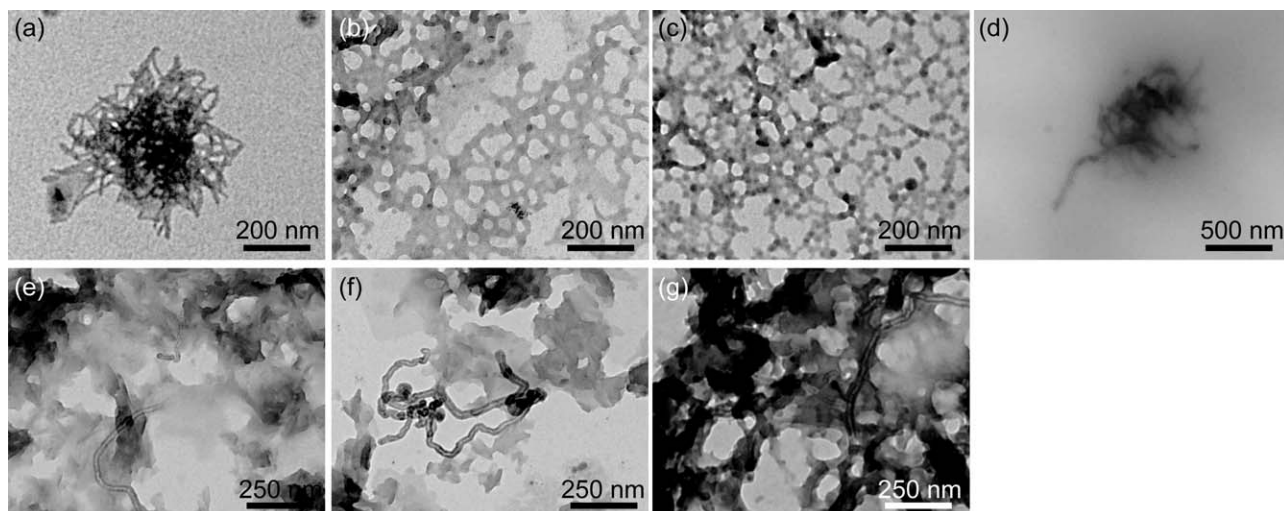


Figure 4. TEM images of CNT with (a) PAA-PAI without stain, (b) PAA-PAI-PAA without stain, (c) PAA₂PAI without stain, (d) PAA without stain, (e) PAA-PAI stained with RuO₄, (f) PAA-PAI-PAA stained with RuO₄, and (g) PAA₂PAI stained with RuO₄.

homogeneously dispersed on CNT because two PAA chains exist on both chain ends of PAI. This will correspond to a good dispersion of repulsive charge on the CNT. In the case of PAA₂PAI, two PAA chains are at a certain place on the CNT. The locally concentrated PAA chains induce strong repulsion in water. This will correspond to a high local concentration of charge on a certain place on the CNT. Again the order of good dispersibility of CNT estimated by UV-vis (Figure 3) was PAA₂PAI, PAA-PAI, and PAA-PAI-PAA. Therefore, the number of PAA sequences attached to a certain place on the CNT was the most effective factor in the dispersion of CNT. The dispersion of PAA sequences on the CNT was more effective for the extension of PAA

sequences for the dispersion of CNTs in aqueous solution. Thus the architectural control of copolymers can be applied in the dispersion of CNTs in water.

CONCLUSIONS

For the dispersion of CNTs in water, three copolymers composed of PAA sequences, PAA-PAI, PAA-PAI-PAA, and PAA₂PAI, and PAI with similar molecular weight and components and different molecular architecture, were compared with linear PAA. All copolymers better dispersed the CNTs in water than did linear PAA because the hydrophobic PAI sequence attached to the CNTs and the copolymers covered the CNTs. The molecular architecture of the copolymer greatly influenced the dispersion of the CNTs. The multiangle DLS results suggested the coverage of CNTs by copolymers. From the UV-vis measurement, the dispersion of CNTs by PAA₂PAI was the highest and kept for the longest time than other copolymers in water. PAA-PAI-PAA showed slightly better dispersion of CNT than PAA-PAI. From the TEM observations, PAA₂PAI and PAA-PAI-PAA covered the CNTs and formed networks with particles, while the CNTs were aggregated in PAA-PAI aqueous. The TEM observation with the PAI sequence stained dark revealed the hydrophobic PAI sequence attached to the CNT. Among the three copolymers, PAA₂PAI had the highest dispersibility owing to two PAA sequence chains on a certain place on the CNT. PAA-PAI-PAA had the highest dispersed PAA sequences on the surface of CNT, and PAA-PAI had the largest extension of PAA sequences. The number of PAA sequences attached on a certain place on the CNT is the most effective factor for the dispersion. The molecular architecture was the important factor in the molecular design of the dispersant.

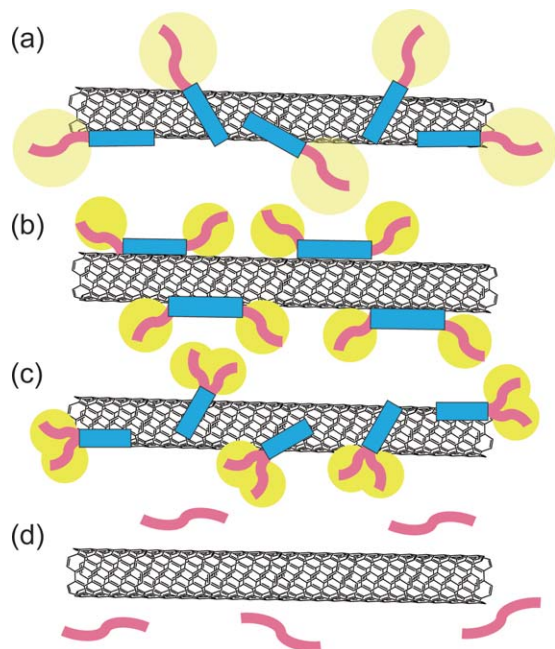


Figure 5. Polymers attached to CNTs: (a) PAA-PAI, (b) PAA-PAI-PAA, (c) PAA₂PAI, (d) PAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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