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Dispersion of single-walled carbon nanotubes in water by the use of novel fluorinated dendrimer-type copolymers

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Abstract New fluorinated dendrimer-type block copolymers were applied to the dispersion of single-walled carbon nanotubes (SW-CNTs) and single-walled carbon nanotubes containing carboxy groups [(SW-CNT)-COOH] in water. Fluorinated block copolymer could disperse SW-CNTs more effectively in water, compared to that of the corresponding ABA triblock-type fluoroalkyl end-capped dimethylacrylamide oligomer [R_F-$(DMAA)_n$-R_F]. Dynamic light-scattering (DLS) measurements and transmission electron microscopy (TEM) images show that SW-CNTs could be smoothly encapsulated into fluorinated copolymeric aggregates cores. Interestingly, it was demonstrated that SW-CNTs could be in part released from the fluorinated copolymeric aggregates/SW-CNTs composites or encapsulated into these composites with increasing the dispersion times. On the other hand, fluorinated block copolymer and R_F-$(DMAA)_n$-R_F oligomer were not able to disperse well (SW-CNT)-COOH in water; however, ABA triblock-type fluoroalkyl end-capped acrylic acid oligomer was able to disperse quite effectively (SW-CNT)-COOH in water.

Introduction

In recent years, there has been attractive interest in single-walled carbon nanotubes (SW-CNTs) due to exhibit unique physical and chemical properties such as a high flexibility, chemical stability, electrical conductivity, which result from the high ratio of length to diameter and π–π connections among adjacent carbons [1]. SW-CNTs have a variety of potential applications such as nanodevices, biochemistry, and reinforcing materials for polymer composites; however, they have a great deal of difficulties to obtain uniform dispersed distribution of SW-CNTs in aqueous and organic media, because SW-CNTs exhibit an extremely poor solubility in these media [2]. Hitherto, we have reported that ABA triblock-type fluoroalkyl end-capped oligomers could exhibit a wide variety of unique properties such as high solubility, surface active properties, biological activities, and nanometer size-controlled self-assembled molecular aggregates which cannot be achieved by the corresponding non-fluorinated and randomly fluoroalkylated ones [3]. Especially, these fluorinated oligomeric aggregates could provide suitable host moieties to interact with a variety of guest molecules such as organic dyes, low-molecular biocides, calcium carbonates, and fullerenes to afford stable fluorinated oligomeric aggregates/guest molecules nanocomposites [4]. In these fluorinated oligomeric aggregates/guest molecules nanocomposites, we have also succeeded in preparing fluorinated oligomeric aggregates/carbon nanotube composites possessing a dispersibility in water [5]. Therefore, the preparation of fluorinated oligomeric aggregates/carbon nanotubes composites possessing a higher dispersibility and stability in water is of particular interest from the developmental viewpoint of new fluorinated functional materials. Very recently, we have found that new fluoroalkyl end-capped dendrimer-type block copolymers can be prepared by the use of fluoroalkanoyl peroxide as a key intermediate [6]. It was also demonstrated that these fluorinated dendrimer-type block copolymers could form the new fluorinated molecular aggregates to have a higher dispersion ability for not only SW-CNTs and fullerenes but

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also magnetic nanoparticles in water, compared to that of the corresponding ABA triblock-type fluoroalkyl end-capped oligomers [6]. We now give a full account of the dispersion of SW-CNTs in water by the use of new fluorinated dendrimer-type block copolymer.

Experimental

NMR spectra and Fourier-transform infrared (FTIR) spectra were measured using JEOL JNM-400 (400 MHz) FT NMR SYSTEM (Tokyo, Japan) and Shimadzu FTIR-8400 FT-IR spectrophotometer (Kyoto, Japan), respectively. Molecular weights were measured using a Shodex DS-4 (pomp) and Shodex RI-71 (detector) gel permeation chromatography (GPC) calibrated with polystyrene standard using tetrahydrofuran (THF) as the eluent. Dynamic light-scattering (DLS) and static light-scattering (SLS) measurements were performed using Otsuka Electronics DLS-7000 HL (Tokyo, Japan). Ultraviolet-visible (UV-vis) spectra were measured using Shimadzu UV-1600 UV-vis spectrophotometer (Kyoto, Japan). Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-1210—electron microscopy (Tokyo, Japan).

Materials

SW-CNT [purity >50%: diameter: 1–2 nm, length: 0.5–100 μm; impurities: other nanotube, amorphous carbon, carbon-coated metal nanoparticles] and SW-CNT containing carboxy groups [(SW-CNT)-COOH: purity: 80–90%; the coverage of carboxy groups on the side wall of SW-CNT is 3–6 atomic %; diameter: 4–5 nm; length: 500–1,500 μm; impurities: other nanotube, amorphous carbon, carbon-coated metal nanoparticles (5–10%)] were purchased from Sigma-Aldrich Japan Corp. (Tokyo, Japan).

Dendrimer-type copolymer containing fluoroalkyl segments [R_F-(TRIV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F] was prepared according to our previuosly reported method [6]. ABA triblock-type fluoroalkyl end-capped oligomers were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding monomers according to our previously reported method [7].

Dispersion of SW-CNT in water by the use of R_F-(TRIV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F

To an aqueous solution of R_F-(TRIV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F; $R_F = CF(CF_3)OC_4F_9$; 4.0 g/dm^3: 2 mL] were added SW-CNTs (2.0 mg). The mixture was stirred with a magnetic stirring bar at 30 °C for 3 days. The aqueous solution thus obtained was centrifuged for 30 min (1000 rpm), and then the residual transparent black SW-CNTs solution was filtered through a 1.2-μm filter membrane to obtain a similar transparent solution. The relative amounts of dispersed SW-CNTs in water were estimated by the optical density at 500 nm (UV-vis. spectra) with the use of the molar absorption coefficient (ε) of SW-CNTs-*o*-dichlorobenzene solution reported by Smalley et al. [8] and the relative amounts of dispersed SW-CNTs were summarized in Fig. 1.

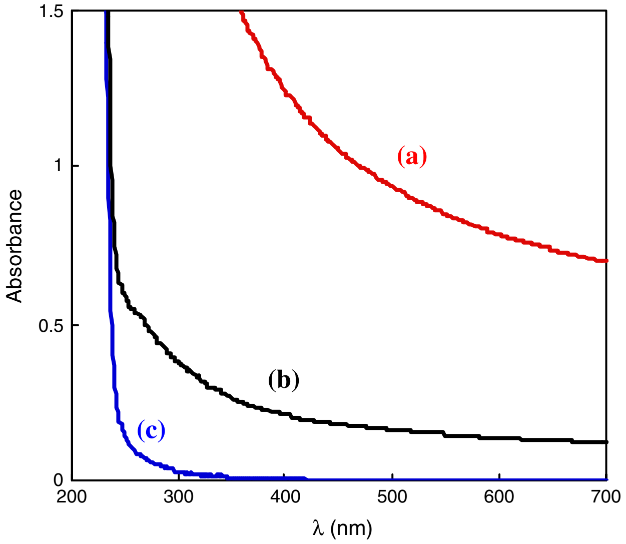
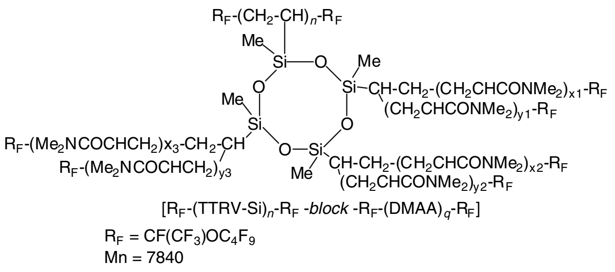


Fig. 1 UV-vis spectra of aqueous solutions of fluorinated polysoaps [$R_F = CF(CF_3)OC_4F_9$] in the presence of SW-CNTs. Concentration of fluorinated polysoaps: 4.0 g/dm^3 (2 mL); Stirring conditions: 30 °C/3 days; Used SW-CNT: 2 mg. (a) R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F in the presence of SW-CNTs. Dispersed SW-CNTs: 129 μg/mL, (b) R_F-(DMAA)$_n$-R_F in the presence of SW-CNTs. Dispersed SW-CNTs: 22 μg/mL, (c) R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F

The amounts of dispersed (SW-CNT)-COOH in water with ABA triblock-type fluorinated oligomer were also determined under similar conditions.

Results and discussion

Single-walled carbon nanotubes (2 mg) were added to an aqueous solution of dendrimer-type fluoroalkyl end-capped block copolymer [R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F; $R_F = CF(CF_3)OC_4F_9$; Mn = 7840, 4 g/dm^3: 2 mL] illustrated in Scheme 1. The mixture was stirred with a magnetic stirring bar at 30 °C for 3 days. The aqueous solution thus obtained was centrifuged, and then the residual SW-CNTs solution was filtered through a 1.2-μm filter membrane to obtain a transparent black solution. We have also studied on the dispersion of SW-CNTs in water by the use of the corresponding ABA triblock-type fluoroalkyl end-capped



Scheme 1 Fluorinated block copolymer

dimethylacrylamide oligomer [R_F-($CH_2CHCONMe_2$)$_n$-R_F [R_F-(DMAA)$_n$-R_F]: R_F = CF(CF_3)OC_4F_9; Mn = 6480, 4 g/dm^3: 2 mL] under similar conditions, for comparison. The relative amounts of dispersed SW-CNTs in water were estimated by the optical density at 500 nm with the use of the molar absorption coefficient (ε) of SW-CNTs-*o*-dichlorobenzene solutions reported by Smalley et al. [8]. The original R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F and R_F-(DMAA)$_n$-R_F have no absorbance around 500 nm, and the relative amounts of dispersed SW-CNTs were summarized in Fig. 1.

As shown in Fig. 1, R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F and R_F-(DMAA)$_n$-R_F oligomer were able to disperse SW-CNTs in water. This finding suggests that these fluorinated block copolymer and oligomer should provide the suitable host moieties to interact with SW-CNTs in water. The DLS measurements at 30 °C showed that the size (number−average diameter) of molecular assemblies formed in aqueous solutions of R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F could increase from 20 to 254 nm by dispersion of SW-CNTs. A similar tendency for the increase of the size (from 11 to 146 nm) was also observed in the dispersion of SW-CNTs in water with R_F-(DMAA)$_n$-R_F oligomer. More interestingly, R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F was able to disperse SW-CNTs quite effectively about six times compared to that of R_F-(DMAA)$_n$-R_F oligomer under similar conditions.

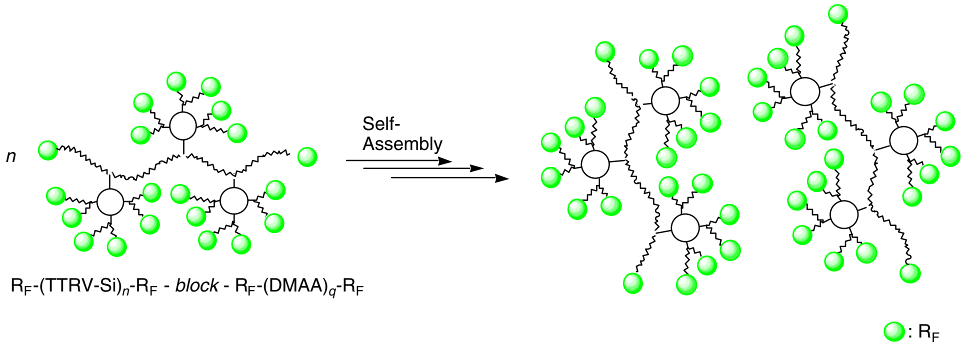
Table 1 Molecular weights of R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F and R_F-(DMAA)$_n$-R_F homooligomer determined by GPC and static light-scattering (SLS) measurements in water [R_F = CF(CF_3)OC_4F_9]

Polymer	GPC[Mn]	SLS (DLS)
R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F	7840	199800(26.1 ± 3.3 nm)
R_F-(DMAA)$_n$-R_F	6480	569500(10.8 ± 1.1 nm)

An extremely higher dispersibility of SW-CNTs thus obtained would be due to the architectures of self-assembly of fluorinated dendrimer-type block copolymers in aqueous solutions. It is well-known that fluoroalkyl end-capped dimethylacrylamide homooligomers [R_F-(DMAA)$_n$-R_F] can form the nanometer size-controlled self-assembled molecular aggregates imparted by the aggregation between end-capped fluoroalkyl segments in oligomers in aqueous and organic media [7(a), 9]. Therefore, it is suggested that our present fluorinated dendrimer-type block copolymers could also form the molecular aggregates resembling micelles derived from the aggregations of end-capped fluoroalkyl segments in block copolymers in aqueous solutions. We have measured the molecular weights of R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F copolymer in water by SLS measurements at 30 °C. These results were shown in Table 1.

As shown in Table 1, the molecular weights of R_F-(DMAA)$_n$-R_F homooligomeric aggregates determined by SLS and GPC measurements were 569500 and 6480, respectively. This finding indicates that fluorinated molecular aggregate formed by R_F-(DMAA)$_n$-R_F oligomer in aqueous solutions are considered to consist of around 88 fluorinated oligomeric molecules. Similarly, the molecular weight (199800) of R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F copolymer determined by SLS was higher than that (7840) by GPC. Thus, fluorinated dendrimer-type copolymer should form the self-assembled molecular aggregates, which consists of around 25 fluorinated block copolymeric molecules in aqueous solutions, and in particular, the aggregations of end-capped fluoroalkyl segments in block copolymers are strongly involved in establishing the molecular aggregates as shown in Fig 2.

Fig. 2 Schematic illustration for the self-assembly of R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F



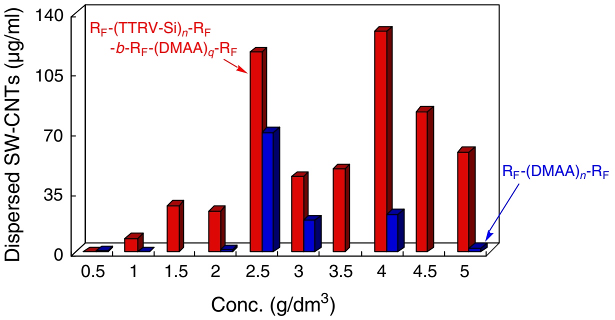


Fig. 3 Relationship between the amounts of dispersed SW-CNTs and concentration of fluorinated polysoaps [$R_F = CF(CF_3)OC_4F_9$] in water at 30 °C

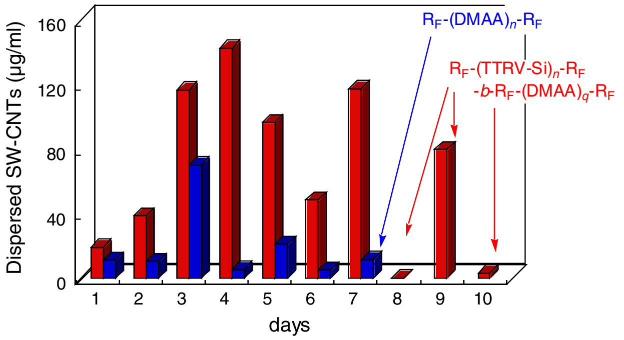


Fig. 5 Relationship between the amounts of dispersed SW-CNTs in water and dispersing time at 30 °C. Concentrationof fluorinated polysoaps [$R_F = CF(CF_3)OC_4F_9$]: 2.5 g/dm^3 (2 mL); Used SW-CNTs: 2 mg

Thus, such new fluorinated dendrimer-type block copolymers should open new development in the higher dispersion of SW-CNTs, which in general exhibit an extremely poor dispersibility in water, through the encapsulation of SW-CNTs into the fluorinated dendrimer-type copolymeric aggregates in aqueous solutions. Especially, fluorinated dendrimer-type block copolymers should form the more suitable aggregates cores for the encapsulation of SW-CNTs, compared to that of traditional ABA block-type fluorinated R_F-(DMAA)$_n$-R_F oligomer.

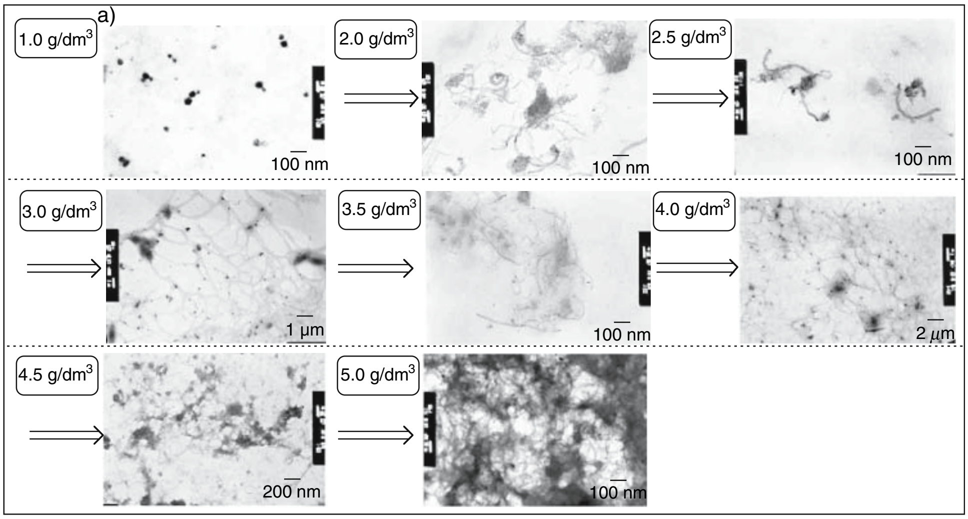
We studied in detail on the dispersion of SW-CNTs in water by the use of R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F copolymer and R_F-(DMAA)$_n$-R_F oligomer, and these results were shown in Fig. 3.

As shown in Fig. 3, R_F-(TTRV-Si)$_n$-R_F-*block*-R_F-(DMAA)$_q$-R_F copolymer was more effective in the dispersion of SW-CNTs in water, compared to that of R_F-(DMAA)$_n$-R_F oligomer. The amounts of dispersed SW-CNTs in water were increased with the increase of the concentration of block copolymer from 0.5 to 2.5 g/dm^3. However, unexpectedly, the amounts of dispersed SW-CNTs were found to decrease by the increase of the concentration of block copolymer from 2.5 to 3.0 g/dm^3. Similarly, unexpected results were obtained in the cases of the concentrations of the block copolymer from 3.5 to 4.0 g/dm^3 and from 4.0 to 5.0 g/dm^3. TEM images show that SW-CNTs could be smoothly encapsulated into dendrimer-type block copolymeric aggregate cores to afford the corresponding fluorinated aggregates/SW-CNTs composites in each concentration of block copolymer, especially above the concentration of 3.0 g/dm^3 (block copolymer) (see Fig. 4).

In addition, we studied on the relationship between the amounts of dispersed SW-CNTs in water and the dispersion time, and these results were shown in Fig. 5.

As shown in Fig. 5, the amounts of dispersed SW-CNTs in water by using block copolymer were found to become extremely higher than that of R_F-(DMAA)$_n$-R_F oligomer in each dispersion time. Especially, the amounts of dispersed SW-CNTs by using block copolymer increased with increasing the stirring times from 1 to 4 days; however, the amounts of dispersed SW-CNTs decreased with the increase of stirring times from 4 to 6 days. Such similar

Fig. 4 TEM images of R_F-(TTRV-Si)$_n$-R_F-block-R_F-(DMAA)$_q$-R_F/SW-CNTs composites in water. (a) Concentration of RF-(TTRV-Si)n-RF-block-RF-(DMAA) q-RF



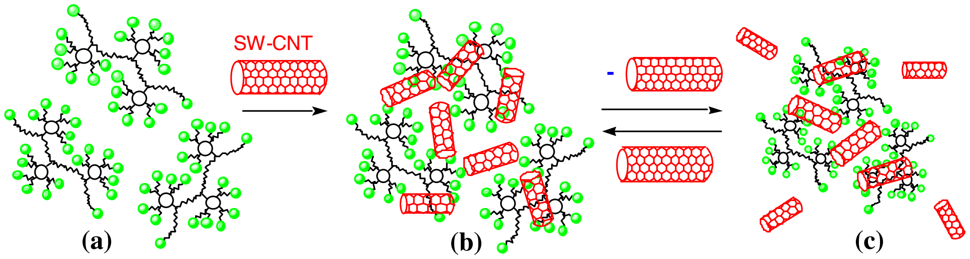


Fig. 6 Schematic illustration for the interaction of self-assembled dendrimer-type fluorinated copolymeric aggregates with SW-CNTs in aqueous solutions

results were observed in the cases of the increase of stirring times from 7 to 8 days, from 8 to 9 days, and from 9 to 10 days. These interesting findings in Figs. 3 and 5 are not clarified in detail at the present time; however, one though is as follows (see Fig. 6): that is, fluorinated dendrimer-type copolymeric aggregates could provide suitable host moieties to interact with SW-CNTs as guest molecules (Fig. 6a). SW-CNTs should be in part released (to Fig. 6c) from the fluorinated aggregates/SW-CNTs composites (Fig. 6b) or encapsulated (from Fig. 6c) into these composites with increasing the dispersion times. These release and encapsulation behaviors of SW-CNTs would be due to the flexible architectures formed by the aggregation of terminal fluoroalkyl segments in our present fluorinated dendrimer-type block copolymer.

(SW-CNT)-COOH possesses carboxy groups on the sidewall of SW-CNTs. Thus, it is strongly expected that self-assembled fluorinated oligomeric aggregates formed by ABA triblock-type fluoroalkyl end-capped acrylic acid oligomers [R_F-$(CH_2CHCOOH)_n$-R_F; R_F = fluoroalkyl groups [R_F-$(ACA)_n$-R_F)]] should interact more effectively with (SW-CNT)-COOH as a guest molecule through the intermolecular hydrogen bonding between the carboxy groups in both (SW-CNT)-COOH and R_F-$(ACA)_n$-R_F oligomers, compared to that of block copolymer or R_F-$(DMAA)_n$-R_F oligomer. In fact, we have studied on the dispersion of (SW-CNT)-COOH in water by the use of R_F-$(ACA)_n$-R_F oligomer, fluorinated block copolymer and R_F-$(DMAA)_n$-R_F oligomer, and these results were shown in Fig. 7.

As shown in Fig. 7, UV-vis. spectra of dispersed (SW-CNT)-COOH solutions in water show that the relative amounts of dispersed (SW-CNT)-COOH estimated by the optical density at 500 nm were found to increase effectively in the case of R_F-$(ACA)_n$-R_F oligomer [$R_F = CF(CF_3)OC_4F_9$; Mn = 2550].

Additionally, we summarized the amounts of dispersed (SW-CNT)-COOH and SW-CNTs in water by the use of R_F-$(ACA)_n$-R_F oligomer, fluorinated block copolymer, and R_F-$(DMAA)_n$-R_F oligomer including their composites size under similar conditions, and these results were shown in Table 2.

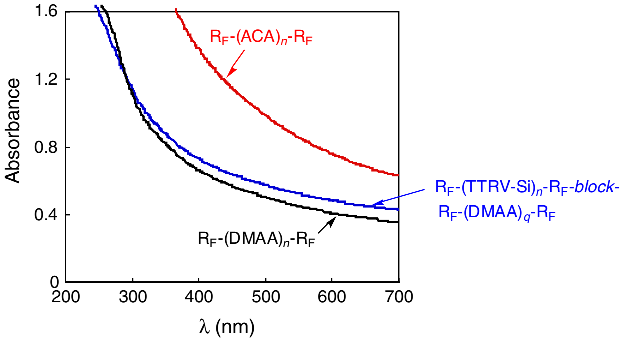


Fig. 7 UV-vis. spectra of aqueous solutions of fluorinated polysoaps in the presence of (SW-CNT)-COOH. Concentration of fluorinated polysoaps [$R_F = CF(CF_3)OC_4F_9$]: 2.5 g/dm^3 (2 mL); Stirring conditions: 30 °C / 3 days; Used (SW-CNT)-COOH: 2 mg

As shown in Table 2, the amounts of dispersed (SW-CNT)-COOH in water were estimated to be 136, 76, and 69 μg/ml, respectively, and the highest dispersibility was obtained by the use of R_F-$(ACA)_n$-R_F oligomer. On the other hand, fluorinated block copolymer was the most effective for the dispersion of SW-CNTs in water. DLS measurements show that the size of self-assembled molecular aggregates formed by R_F-$(ACA)_n$-R_F oligomer could increase effectively from 11 to 112 nm and 116 nm by the dispersion of (SW-CNT)-COOH and SW-CNTs in water, respectively, as well as fluorinated block copolymer and R_F-$(DMAA)_n$-R_F oligomer. TEM images also show that (SW-CNT)-COOH should be smoothly encapsulated as a guest molecule into fluorinated acrylic acid oligomeric aggregate cores (Fig. 8a). In contrast, (SW-CNT)-COOH could be tightly encapsulated into fluorinated block copolymeric aggregate cores (Fig. 8b), because dendrimer-type block copolymeric aggregate cores consist of fine networks in water.

In this way, it was verified that R_F-$(ACA)_n$-R_F oligomer was able to disperse (SW-CNT)-COOH quite effectively in water, although this oligomer failed to disperse SW-CNTs effectively in water. This finding indicates that intermolecular hydrogen bonding between the carboxy groups in both oligomer and SW-CNTs could afford the good dispersibility of (SW-CNT)-COOH in water. In order to clarify this dispersion characteristic with R_F-$(ACA)_n$-R_F oligomer, we have studied in detail on the dispersion of (SW-CNT)-COOH in water by the use of R_F-$(ACA)_n$-R_F. We also studied on the dispersion of (SW-CNT)-COOH in

Table 2 The amounts of dispersed (SW-CNT)-COOH and SW-CNTs in water using fluorinated polysoaps and size of fluorinated polysoaps/(SW-CNT)-COOH and /SW-CNTs composites in water determined by dynamic light-scattering measurements at 30 °C

Fluorinated polysoaps	Dispersed (SW-CNT)-COOH (μg/ml)	Dispersed SW-CNTs (μg/ml)	Composite size		Size of original fluorinated polysoap aggregates (nm)
			(SW-CNT)-COOH (nm)	SW-CNTs (nm)	
R_F-(ACA)$_n$-R_F	136	53	112.2 ± 26.2	115.5 ± 33.0	10.8 ± 1.1
R_F-(TTRV-Si)$_n$-R_F-*b*-R_F-(DMAA)$_q$-R_F	79	117	210.1 ± 36.7	271.4 ± 40.5	20.2 ± 4.8
R_F-(DMAA)$_n$-R_F	69	70	126.7 ± 28.8	116.1 ± 35.1	10.8 ± 1.1

Concentration of fluorinated polysoaps: 2.5 g/dm^3 (2 mL); R_F=CF(CF$_3$)OC$_4$F$_9$ S

Stirring conditions: 30 °C/3 days

Used (SW-CNT)-COOH or SW-CNT: 2 mg

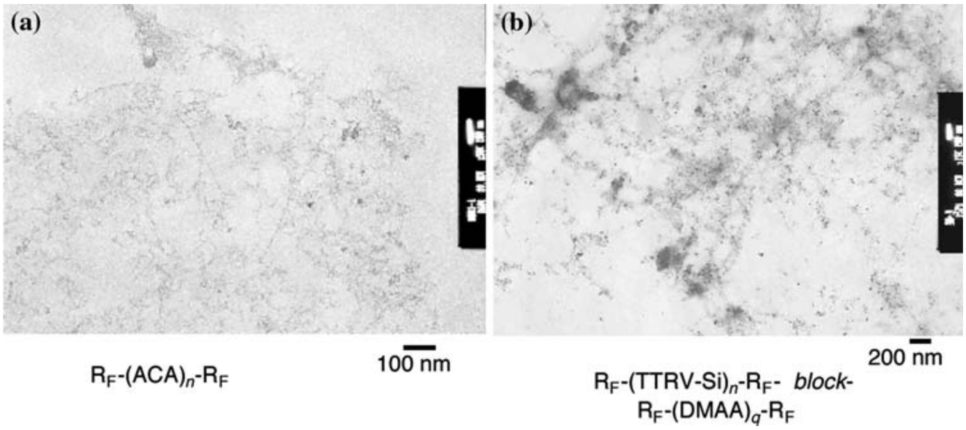


Fig. 8 TEM Images of dispersed fluorinated polysoap/(SW-CNT)-COOH composites. Concentration of fluorinated polysoaps [R_F = CF(CF$_3$)OC$_4$F$_9$]: 2.5 g/dm^3; Stirring conditions: 30 °C/3 days; Used (SW-CNT)-COOH: 2 mg

water by the use of fluorinated block copolymer under similar conditions, for comparison. These results were shown in Fig. 9.

As shown in Fig. 9, R_F-(ACA)$_n$-R_F oligomer was able to increase the amounts of dispersed (SW-CNT)-COOH with increasing the stirring times from 1 h to 1 day, and almost constant values (ca. 135 μg/ml) were obtained above 1 day. This dispersion characteristic behavior in R_F-(ACA)$_n$-R_F oligomer is quite different from that of fluorinated block copolymer, indicating that the dispersion of (SW-CNT)-COOH with R_F-(ACA)$_n$-R_F oligomer would be depend on the intermolecular hydrogen bonding interaction. Thus, the release of (SW-CNT)-COOH from the fluorinated nanocomposites illustrated in Fig. 6 [from (b) to (c)] could not be occurred due to the hydrogen bonding interactions related to carboxy groups.

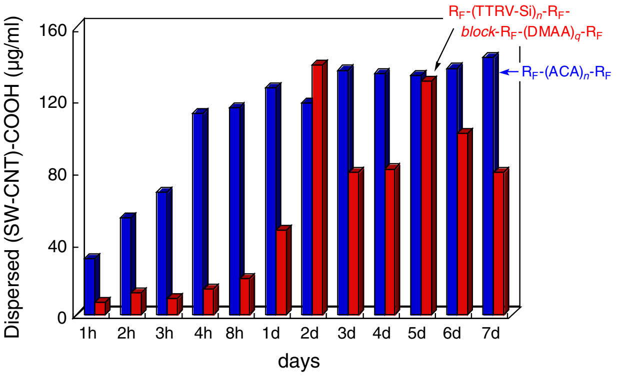


Fig. 9 Relationship between the amounts of dispersed (SW-CNT)-COOH in water and the dispersing times at 30 °C. Concentration of fluorinated polysoaps [R_F = CF(CF$_3$)OC$_4$F$_9$]: 2.5 g/dm^3 (2 mL); Used SW-CNT-COOH: 2 mg

In conclusion, dendrimer-type fluoroalkyl end-capped block copolymer was able to disperse SW-CNTs quite effectively in water. On the other hand, the corresponding ABA triblock-type R_F-(DMAA)$_n$-R_F oligomer was not able to disperse SW-CNTs in water, effectively. DLS measurements and TEM images of fluorinated block copolymer showed that SW-CNTs could be smoothly encapsulated into fluorinated block copolymeric aggregate cores as guest molecules to increase their aggregate core size. On the other hand, dendrimer-type fluorinated block copolymer was not effective for the dispersion of (SW-CNT)-COOH in water; however, (SW-CNT)-COOH could be more effectively dispersed into water by the use of R_F-(ACA)$_n$-R_F oligomer.

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