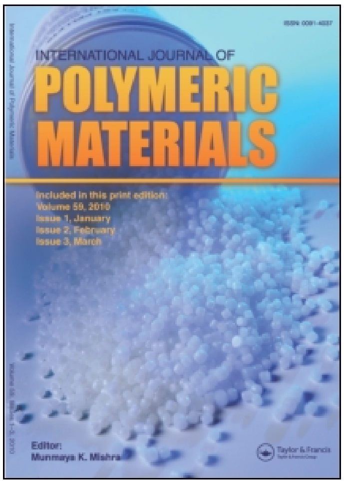

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DISSOLUTION OF CARBON NANOTUBES IN WATER AND ORGANIC MEDIA WITH A VARIETY OF FLUOROALKYL END-CAPPED OLIGOMERS

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SHORT COMMUNICATION

DISSOLUTION OF CARBON NANOTUBES IN WATER AND ORGANIC MEDIA WITH A VARIETY OF FLUOROALKYL END-CAPPED OLIGOMERS

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Dissolution of single-wall carbon nanotube (SW-CNT) in water and organic media was studied by the use of fluoroalkyl end-capped acrylic acid oligomers [R_F*–(ACA)*$_n$*–*R_F*], N,N-dimethylacrylamide oligomers [*R_F*–(DMAA)*$_n$*–*R_F*], acryloylmorpholine oligomers [*R_F*–(ACMO)*$_n$*–*R_F*], and N-(1,1-dimethyl-3-oxobutyl) acrylamide oligomers [*R_F*–(DOBAA)*$_n$*–*R_F*]. Among these fluorinated oligomers, it was demonstrated that* R_F*–(ACMO)*$_n$*–*R_F*;* R_F*=CF(CF*$_3$*)OC*$_6$*F*$_{13}$*] oligomer is more effective for the dissolution of SW-CNT in both aqueous and organic media. Additionally, it*

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was demonstrated that R_F–(DOBAA)$_n$–R_F oligomer is a convenient tool for the arrangement of SW-CNT on PMMA surface.

Keywords: dissolution, carbon nanotube, fluorinated oligomer, water and organic media, surface arrangement

Applications of carbon nanotubes [CNTs] in various fields have been limited by their insolubility in water and most common organic solvents, although it is well known that carbon nanotubes exhibit extraordinary mechanical and electronic properties [1,2]. From this point of view, there have been some reports on the dissolution of CNTs in aqueous and organic media by the covalent modification of CNTs [3]. However, the covalent modification has the disadvantage that it might impair their physical properties. Thus, a supramolecular approach to the dissolution of carbon nanotubes in aqueous and organic media, namely the noncovalent functionalization of CNTs by the use of polymeric surfactants is very interesting. There have been some reports on the dissolution of CNTs in aqueous and organic media by the use of polymeric surfactants. For example, Connell et al. reported that single-walled carbon-nanotubes (SW-CNTs) have been reversibly dissolved in water by wrapping them with polyvinylpyrrolidone (PVP) [4]. Poly(metaphenylenevinylene) [PmPV] was wrapped SW-CNTs by π–π interactions between SW-CNTs and the fully conjugated PmPV backbone to afford the SW-CNTs suspension solutions of PmPV in chloroform [5]. However, the exploration of the compounds that could exhibit a good solubility of CNTs in both aqueous and organic media have been very limited so far, although these compounds have been the subject of considerable research of both fundamental and applied nature. Hitherto, the synthesis and applications of a variety of novel fluoroalkyl end-capped oligomers has been studied by using fluoroalkanoyl peroxide as a key intermediate, and recently these fluorinated oligomers were demonstrated to form self-assembled molecular aggregates with the aggregation of end-capped fluoroalkyl groups in aqueous and organic media to interact with numerous guest molecules [6]. In the course of the authors' study on the dissolution of CNTs in various solvents, they obtained the surprising finding that fluoroalkyl end-capped oligomers, especially fluoroalkyl end-capped acryloylmorpholine oligomers, can exhibit a good solubility of SW-CNT into not only water but also organic solvents such as toluene, xylene, and chloroform. To the best of their knowledge, thus finding is the first example of the dissolution of SW-CNT in both aqueous and organic media.

A typical procedure for the dissolution of SW-CNT in organic media by the use of a variety of fluoroalkyl end-capped oligomers [7] is as follows: To a toluene solution of fluoroalkyl end-capped *N*-1,1-dimethyl-3-oxobutylacrylamide oligomer [R_F–$(DOBAA)_n$–R_F, R_F=$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$; Mn = 17200, $4\,g/dm^3$: 3 ml] was added SW-CNT (2 mg). The mixture was stirred with a magnetic stirring bar at room temperature for 3 days. The toluene solution thus obtained was centrifuged for 30 min, and then the residual transparent pale yellow SW- CNT solution was filtered through a 0.45 μm PTFE filter membrane to obtain a similarly transparent solution (see Figure 1).

UV-vis spectrum of a toluene solution of SW-CNT dissolved with R_F–$(DOBAA)_n$–R_F oligomer showed an absorption band around 340 nm as in Figure 2.

Recently, Sun et al. have reported the dissolution of SW-CNT in aniline through the formation of charge-transfer complex between aniline and SW-CNT [8]. In fact, the present authors have tried to dissolve SW-CNT (2 mg) in aniline (5 ml) under reflux conditions (185°C for 12 h) according to the method reported by Sun et al. [8]. The complete dissolution of SW-CNT in aniline was observed, and the UV-vis spectrum of this solution had an absorption band around 380 nm. The relative amounts of solubilized SW-CNT by fluoroalkyl end-capped DOBAA oligomer was estimated by the use of the molar absorption coefficient (ε) of SW-CNT-aniline solution and the solubilized SW-CNT was 44 μg/ml.

Similarly, the authors studied the solubility of SW-CNT in toluene and other organic solvents by some fluoroalkyl end-capped oligomers, and the results are shown in Table 1.

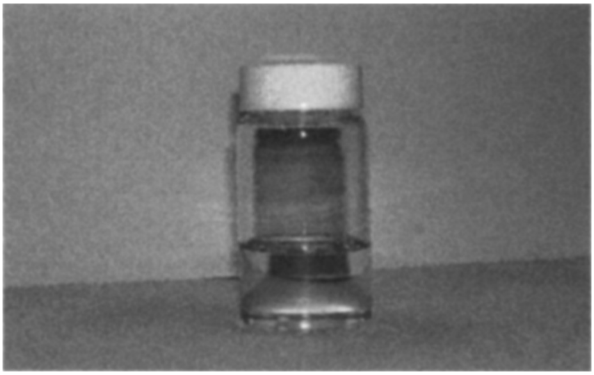


FIGURE 1 Transparent toluene solution of R_F–$(DOBAA)_n$–R_F [R_F=$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$]–SW-CNT.

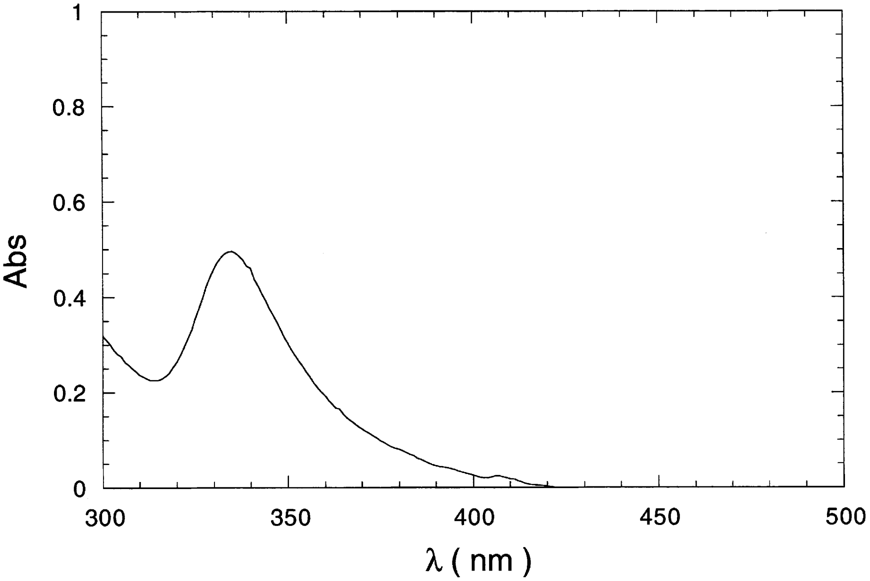
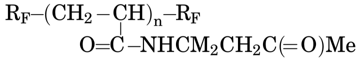
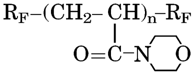
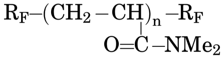


FIGURE 2 UV-vis spectra of toluene solution of R_F–$(DOBAA)_n$–R_F oligomer in the presence of SW-CNT. $R_F = CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$.

As shown in Table 1, fluoroalkyl [R_F=$CF(CF_3)OC_6F_{13}$] end-capped DOBAA oligomers were effective in dissolving SW-CNT not only in toluene but also in xylene and chloroform, compared with the case of the absence of oligomers. Perfluoro-1-methyl-2-oxaoctyl [R_F=$CF(CF_3)OC_6F_{13}$] end-capped acryloylmorpholine (ACMO) and dimethylacrylamide (DMAA) oligomers were also effective in dissolving SW-CNT in such organic media. However, the solubility of SW-CNT in organic media was slightly lowered by using longer perfluorooxaalkyl [R_F=$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] end-capped DOBAA oligomer.

Fluoroalkyl end-capped oligomers such as R_F–$(ACMO)_n$–R_F, R_F–$(DMAA)_n$–R_F, and fluoroalkyl end-capped acrylic acid oligomers [R_F–$(ACA)_n$–R_F] have been already reported to exhibit surfactant properties typical of the amphipathic compounds [9,10]. Thus, it is very interesting to explore the possibility of dissolving SW-CNT in aqueous solutions of these fluorinated oligomers. In fact, the authors have tested for the dissolution of SW-CNT in water by the use of a variety of fluoroalkyl end-capped oligomers under similar conditions as those in Table 1. The UV-vis spectrum of aqueous solution of SW-CNT dissolved with fluoroalkyl end-capped ACMO oligomer [R_F=$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] is shown in Figure 3. The

TABLE 1 Dissolution of SW-CNT into Organic Media with Fluoroalkyl End-Capped Oligomers

Oligomer	R_F	Solubilized CNT (μg/ml) Toluene	Solubilized CNT (μg/ml) Xylene	Solubilized CNT (μg/ml) Chloroform
 $R_F{-}(CH_2{-}\underset{O=C-NHCM_2CH_2C(=O)Me}{CH})_n{-}R_F$	$CF(CF_3)OC_6F_{13}$ [Mn = 14300]	43	70	11
$[R_F{-}(DOBAA)_n{-}R_F]$	$CF(CF_3)OCF_2CF(CF_3)O$ $CF_2CF(CF_3)OC_3F_7$ [Mn = 17200]	44	40	13
 $[R_F{-}(ACMO)_n{-}R_F]$	$CF(CF_3)OC_6F_{13}$ [Mn = 4360]	—4)	54	12
 $R_F{-}(CH_2{-}\underset{O=C-NMe_2}{CH})_n{-}R_F$ $[R_F{-}(DMAA)_n{-}R_F]$	$CF(CF_3)OC_6F_{13}$ [Mn = 2220]	56	53	6
No oligomer	—	0	3	1

1. Concentration of oligomer: 4 g/dm^3 in toluene and xylene (3 ml); 6 g/dm^3 in chloroform (3 ml).
2. Used SW-CNT: 2 mg.
3. Conditions: R.T./3 day.
4. This oligomer was not soluble in toluene.

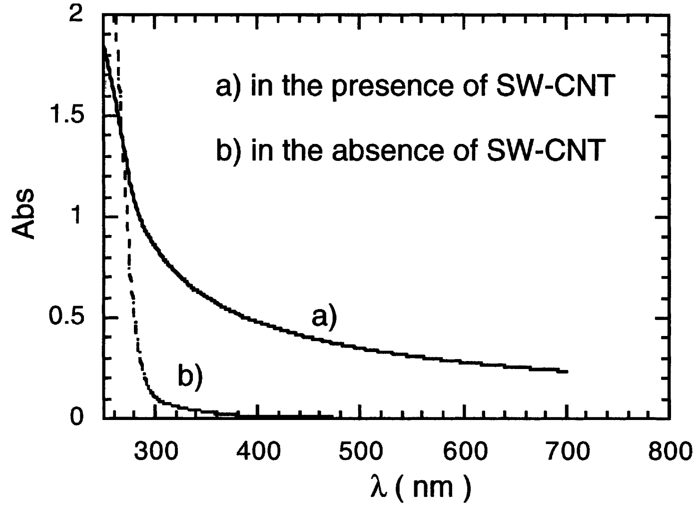


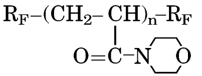
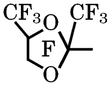
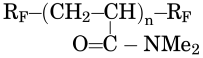
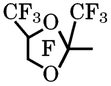
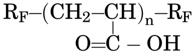
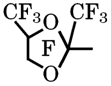
FIGURE 3 UV-vis spectra of aqueous solutions of R_F–$(ACMO)_n$–R_F oligomer [Mn = 1970] in the presence and the absence of SW-CNT. R_F=$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$.

absorption of the SW-CNT–oligomer well extends to ~700 nm, compared to that in the absence of SW-CNT or the case of dissolution of SW-CNT in organic media with fluorinated oligomer as in Figure 2. A similar UV-vis spectrum of SW-CNT was also reported in the dissolution of SW-CNT in 1,2-dichlorobenzene, and the optical density at 500 nm was used to determine the concentration of SW-CNT dissolved in other organic solvents [11]. The relative amounts of dissolved SW-CNT in water were similarly estimated by the optical density at 500 nm with the use of the molar absorption coefficient (ε) of SW-CNT-1,2-dichlorobenzene solution reported by Bahr et al. [11] and the relative amounts of dissolved SW-CNT are shown in Table 2.

As shown in Table 2, R_F–$(ACMO)_n$–R_F and R_F–$(DMAA)_n$–R_F oligomers, especially longer perfluorooxaalkyl [R_F=$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] end-capped ACMO and DMAA oligomers were more effective in dissolving SW-CNT in water to afford a transparent gray solution (see Figure 4) Oligomers containing cyclic perfluorooxaalkyl group, and the corresponding non-fluorinated oligomers were not able to dissolve SW-CNT at all under similar conditions.

Laser Diffraction Particle Size Analyzer (Shimadzu SALD-300V, Kyoto, Japan) measurements showed that the size of molecular assemblies formed in aqueous solutions of R_F–$(ACMO)_n$–R_F [R_F=CF

TABLE 2 Dissolution of SW-CNT into Water with Fluoroalkyl End-Capped Oligomers

Oligomer	R_F	Mn	Solubilized SW-CNT (μg/ml)
	$CF(CF_3)OC_6F_{13}$	4360	94
$[R_F-(ACMO)_n-R_F]$		2110	0
	$CF(CF_3)OC_3F_7$	2490	1
	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	1970	73
 $R_F-(CH_2-\underset{O=C-NMe_2}{CH})_n-R_F$	$CF(CF_3)OC_6F_{13}$	2200	65
$[R_F-(DMAA)_n-R_F]$		1730	0
	$CF(CF_3)OC_3F_7$	1740	1
	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	1950	35
 $R_F-(CH_2-\underset{O=C-OH}{CH})_n-R_F$	$CF(CF_3)OC_6F_{13}$	4140	46
$[R_F-(ACA)_n-R_F]$		3840	0
	$CF(CF_3)OC_3F_7$	2030	8
	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	2630	16
$-(ACMO)_n-$	Non-fluorinated	1090	0
$-(DMAA)_n-$		1670	0

Concentration of oligomer: 2 g/dm^3 (3 ml); Used SW-CNT: 2 mg; Conditions: R.T./3 day.

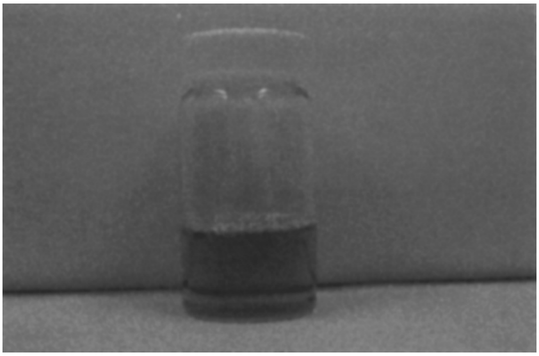


FIGURE 4 Transparent aqueous solution of R_F–$(ACMO)_n$–R_F [R_F=$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] SW-CNT.

$(CF_3)OCF_2CF(CF_3)OC_3F_7$] and that in aqueous solution of SW-CNT dissolved by this oligomer are 219 nm and 916 nm, respectively. The increase of the size of the molecular assemblies formed by the dissolution of SW-CNT in water indicates that SW-CNT could interact strongly with fluorinated oligomers. It was recently reported that SW-CNTs can be dissolved in water by wrapping them with linear polymers such as polyvinyl pyrrolidone (PVP) [4]. Thus, it is suggested that the present fluoroalkyl end-capped oligomers can dissolve SW-CNT in aqueous and organic media by oligomer wrapping similar to that of PVP.

In the authors' comprehensive studies on the synthesis and applications of fluoroalkyl end-capped oligomers, they have already found that the fluoroalkyl segments in these oligomers can be arranged regularly on the surface of common organic polymers such as polystyrene and poly(methyl methacrylate) (PMMA) [12]. Especially, these fluorinated oligomers can form self-assembled molecular aggregates in aqueous and organic media to interact with a variety of guest molecules [6]. This suggests that SW-CNT should be arranged on the PMMA surface through the interaction of fluorinated DOBAA oligomers with SW-CNT. Previously, the fluorescence spectra of polymer-bound CNTs were studied in detail, and a strong luminescence was observed in these chemically modified CNTs [13]. In order to broaden the use of SW-CNTs, it is of considerable interest to apply the fluorinated molecular aggregates to the arrangement of SW-CNT on common polymeric materials such as PMMA. In fact, PMMA films (film thickness: 170 μm and 230 μm) were prepared by casting homogeneous toluene solutions (25 ml) containing SW-CNT (376 μg and 451 μg) and

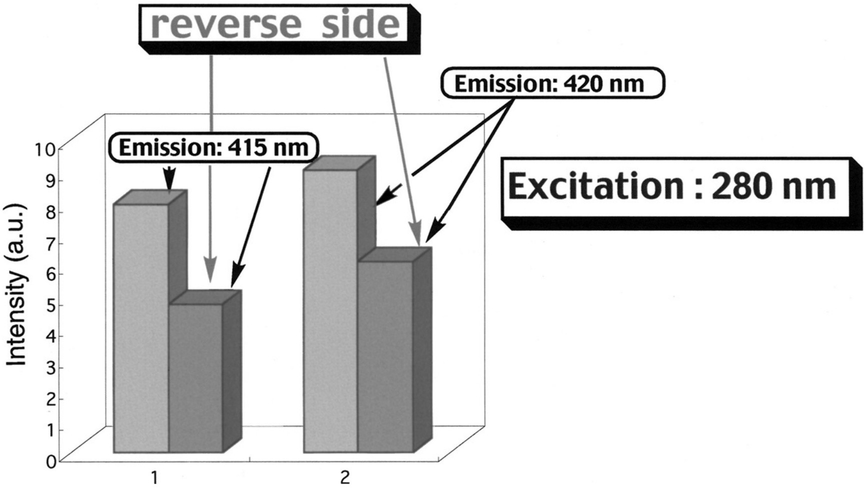


FIGURE 5 Relative fluorescent intensity of PMMA films treated with SW-CNT$-$R$_F$$-$(DOBAA)$_n$$-R_F$ oligomers [$R_F = CF(CF_3)O[CF_2CF(CF_3)O]_2C_3F_7$]. [No 1]: Content of SW- CNT: 376 μg; film thickness: 230 μm. [No 2]: Content of SW-CNT: 451 μg; film thickness: 170 μm.

R$_F$$-$(DOBAA)$_n$$-R_F$ oligomer [R_F=$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] [concentration of oligomer: 4 g/dm^3] on a glass plate. The authors have measured the fluorescence spectra of these modified cast films, and the results are shown in Figure 5.

When the cast film surface of PMMA treated with SW-CNT$-$R$_F$$-$(DOBAA)$_n$$-R_F$ is excited ($\lambda = 280$ nm), the surface of this film (the content of SW-CNT: 376 μg) exhibits a strong fluorescent intensity with a peak maximum at 415 nm. Additionally, as the content of SW-CNT (from 376 to 451 μg) becomes higher, the fluorescence intensity was found to increase, too. Of particular interest, the fluorescent intensity of the reverse side of each cast film surface treated with SW-CNT$-$R$_F$$-$(DOBAA)$_n$$-R_F$ decreased remarkably compared with that of the corresponding cast film surface. This finding indicates that R$_F$$-$(DOBAA)$_n$$-R_F$ oligomer could form self-assembled molecular aggregates in toluene to interact with SW-CNT as a guest molecule, and these fluorinated aggregates$-$SW-CNT complexes are able to arrange regularly above the PMMA surface during the cast film formation.

In conclusion, the authors succeeded in dissolving SW-CNT not only in water but also in common organic solvents such as toluene, xylene, and chloroform by the use of a variety of fluoroalkyl end-capped oligomers. In fact, SW-CNT was demonstrated to be arranged regularly on the surface of common polymeric material such as PMMA by the use of fluoroalkyl end-capped DOBAA oligomers. This interesting characteristic for the dissolution of SW-CNT with fluoroalkyl end-capped oligomers would open a new route to the purification of CNTs, applications in biological fields, and surface modifications in material sciences.

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