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ORIGINAL CONTRIBUTION

Synthesis and application of novel fluoroalkyl end-capped cooligomers having adamantane as a pendant group

Masaki Mugisawa · Keiichi Ohnishi · Hideo Sawada

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Abstract Fluoroalkyl end-capped cooligomers having adamantane as a pendant group [R_F-(Ad-HAc)$_x$–(Co-M)$_y$-R_F] were prepared by the reactions of fluoroalkanoyl peroxide with 3-hydroxy-1-adamantylacrylate (Ad-HAc) and comonomers (Co-M) such as acrylic acid (ACA), *N,N*-dimethylacrylamide (DMAA), and acryloylmorpholine (ACMO) under mild conditions. Thermogravimetric analyses (TGA) showed that thermal stability of R_F-(Ad-HAc)$_x$–(Co-M)$_y$-R_F was superior to that of the corresponding fluoroalkyl end-capped cooligomers having adamantane in the main chains [R_F-(Ad)$_x$–(Co-M)$_y$-R_F] and the fluoroalkyl end-capped homooligomers possessing no adamantyl segments [R_F-(M)$_n$-R_F]. It is interesting to note that fluoroalkyl end-capped Ad-Hac–DMAA cooligomer [R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F] was found to form the nanometer size-controlled cooligomeric aggregates which consist of around 16 fluorinated cooligomeric molecules in methanol/water mixed solvents. Furthermore, these fluorinated cooligomeric aggregate could occupy around 320 ADMDD [5-(2-adamantylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione] molecules as guest molecules per aggregate core, although ADMDD could not be encapsulated into the R_F-(Ad)$_x$–(Co-M)$_y$-R_F cooligomeric and R_F-(M)$_n$-R_F homooligomeric aggregate cores under similar conditions.

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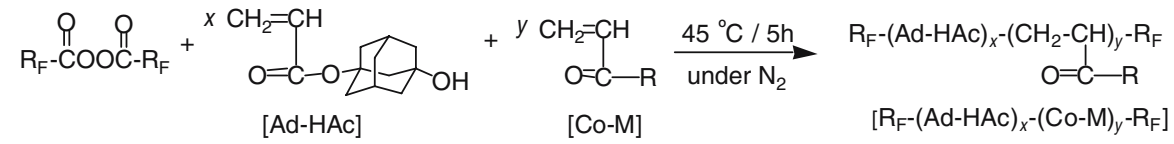
Introduction

Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a thermodynamically very stable and highly symmetric tricyclic hydrocarbon with three fused chair-form cyclohexane rings in a diamond lattice structure [1, 2]. Therefore, the introduction of adamantane units into organic polymers could afford the enormous changes in their physical and chemical properties compared to the original polymers [3–5]. In fact, there have hitherto been numerous reports on the synthesis and properties of polymers having an adamantyl moiety in their main and side chains [6–11]. On the other hand, it is well known that amphiphilic fluoroalkyl end-capped oligomers are attractive materials, because they exhibit various unique properties such as high solubility, surface active properties, biological activities, and nanometer size-controlled molecular aggregates which cannot be achieved by the corresponding nonfluorinated and randomly fluoroalkylated ones [12–18]. For example, self-assembled fluorinated molecular aggregates formed by fluoroalkyl end-capped acryloylmorpholine oligomers could interact with fullerene and single-walled carbon nanotube as guest molecules in aqueous media to afford a good solubility of fullerene and single-walled carbon nanotube in water [19–22]. Thus, the exploration of fluoroalkyl end-capped cooligomers having adamantane as a pendant group is in particular interest from the developmental viewpoints of new functional polymeric materials imparted by not only adamantyl groups but also end-capped fluoroalkyl segments. In this paper, we would like to report on the synthesis and application of fluoroalkyl



R = OH (ACA), NMe_2,(DMAA), N O [ACMO]

$R_F = CF(CF_3)OC_3F_7$

R_F in Peroxide (mmol)	Ad-HAc (mmol)	Comonomer (mmol)	Product Yield[a] (%)	R_F-(Ad-HAc)$_x$-(CH_2-CHCOR)$_y$-R_F Mn (Mw/Mn)	x : y[b]
$CF(CF_3)OC_3F_7$ (8.9)	(26.8)	ACA (44.7)	77	6700(2.42)	18 : 82
$CF(CF_3)OC_3F_7$ (8.9)	(26.8)	DMAA (44.7)	80	2130(2.61)	36 : 64
$CF(CF_3)OC_3F_7$ (8.9)	(26.8)	ACMO (44.7)	86	4880(3.04)	41 : 59

a) Yield based on the decarboxylated R_F-R_F unit in peroxide, Ad-HAc and comonomer

b) Cooligomerization ratio determined by ^{1}H NMR

Scheme 1 Reactions of fluoroalkanoyl peroxide with 3-hydroxy-1-adamantylacrylate and comonomer

end-capped cooligomers having adamantane as a pendant group, with emphasis on the formation of self-assemble fluorinated cooligomeric aggregates possessing adamantly segments including the interaction of these fluorinated cooligomeric aggregates with guest molecules.

Experimental

Measurements

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. 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. Dynamic light-scattering (DLS) and static light-scattering (SLS) measurements were measured using Otsuka Electronics DLS-7000 HL (Tokyo, Japan). Thermal analyses were recorded on RIGA-KUDENKI TG8101 D differential thermobalance (Tokyo, Japan). Ultraviolet–visible (UV–vis) spectra were measured using Shimadzu UV-1600 UV–vis spectrophotometer (Kyoto, Japan).

Table 1 Thermal stability (T_{dec})[a] of fluoroalkyl end-capped cooligomers having adamantane as a pendant groups [R_F = $CF(CF_3)OC_3F_7$]

Oligomer	x:y	Mn (Mw/Mn)	T_{dec}(°C)
R_F-(Ad-HAc)$_x$-(ACA)$_y$-R_F	18:82	6,697 (2.42)	205
R_F-(Ad)$_x$–(ACA)$_y$-R_F[b]	3:97	740 (3.83)	243
R_F-(ACA)$_n$-R_F	–	2,410 (1.27)	241
R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F	36:64	2,130 (2.61)	210
R_F-(Ad)$_x$–(DMAA)$_y$-R_F	1:99	750 (1.14)	148
R_F-(DMAA)$_n$-R_F	–	1,010 (1.12)	151
R_F-(Ad-HAc)$_x$–(ACMO)$_y$-R_F	41:59	4,877 (3.04)	265
R_F-(Ad)$_x$–(ACMO)$_y$-R_F	3:97	1,180 (1.47)	186
R_F-(ACMO)$_n$-R_F	–	1,660 (1.22)	177

[a] Defined by a 10% mass loss 10 °C/min heating rate

[b] R_F-(Ad)$_x$–(ACA)$_y$-R_F: R_F-(Ad)$_x$-(CH_2-CHCOOH)$_y$-R_F

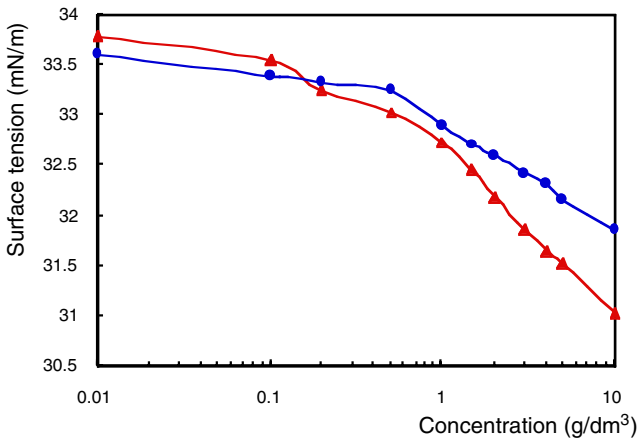


Fig. 1 Surface tension of R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F and R_F-(ACA)$_n$-R_F MeOH/H_2O(3/1: vol) mixed solutions at 30 °C. *Filled triangle* R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F; R_F=$CF(CF_3)OC_3F_7$ [x:y=18:82]; *filled circle* R_F-(ACA)$_n$-R_F; R_F=$CF(CF_3)OC_3F_7$

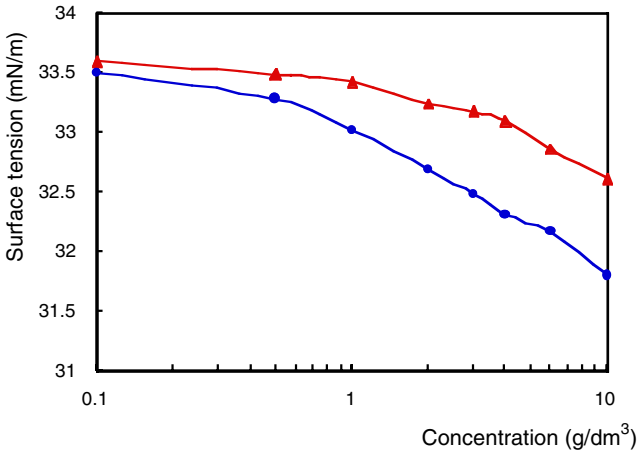


Fig. 2 Surface tension of R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F and R_F-(DMAA)$_n$-R_F MeOH/H_2O(3/1: vol) mixed solutions at 30 °C. *Filled triangle* R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F; R_F=$CF(CF_3)OC_3F_7$ (*x*:*y*= 36:64); *filled circle* R_F-(DMAA)$_n$-R_F; R_F=$CF(CF_3)OC_3F_7$

Materials

Acrylic acid (ACA), *N*,*N*-dimethylacrylamide (DMAA) and acryloylmorpholine (ACMO) were used as received from Toagosei (Tokyo, Japan) and Kohjin (Tokyo, Japan), respectively. 3-Hydroxy-1-adamantylacrylate (Ad-HAc) was used as received from Idemitsu Kosan (Tokyo, Japan). 5-(2-Adamantylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (ADMDD) was purchased from Sigma–Aldrich Japan (Tokyo, Japan).

General procedure for the synthesis of fluoroalkyl end-capped cooligomers having adamantane as a pendant group

Perfluoro-2-methyl-3-oxahexanoyl peroxide (8.9 mmol) in AK-225 (1:1 mixed solvents of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane: 60 g) was added to a mixture of 3-hydroxy-1-adamantylacrylate [Ad-HAc] (26.8 mmol), acrylic acid (ACA: 44.7 mmol), and AK-225 (200 g). The solution was stirred at 45 °C for 5 h under nitrogen. After the removal of solvent, the obtained crude products were washed well with AK-225, which exhibits a good solubility for Ad-HAc and ACA, to give an α, ω-bis(perfluoro-1-methyl-2-oxapentylated) Ad-HAc–ACA cooligomer [R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F] (11.0 g). This cooligomer exhibited the following spectra characteristics:

$$R_F-(Ad-HAc)_x-(ACA)_y-R_F: R_F= CF(CF_3)OC_3F_7:$$
$$IR(\nu/cm^{-1})3449(OH), 2924(CH),$$
$$1724\,[C(=O)], 1350(CF_3), 1242(CF_2);$$
$$^1H\,NMR(CD_3OD)\delta\,1.05 \sim 2.20(CH, CH_2),$$
$$2.20 \sim 2.55(CH).$$

The other products obtained (see Scheme 1) exhibited the following spectra characteristics.

$$R_F-(Ad-HAc)_x-(DMAA)_y-R_F: R_F= CF(CF_3)OC_3F_7:$$
$$IR(\nu/cm^{-1})3421(OH), 2924(CH),$$
$$1724[C(=O)(Ad-HAc)],$$
$$1628[C(=O)(DMAA)], 1308(CF_3), 1242(CF_2);$$
$$^1H\,NMR(CDCl_3)\delta\,1.00 \sim 2.20(CH, CH_2),$$
$$2.25 \sim 2.77(CH), 2.80 \sim 3.30(CH_3).$$

$$R_F-(Ad-HAc)_x-(ACMO)_y-R_F: R_F= CF(CF_3)OC_3F_7:$$
$$IR(\nu/cm^{-1})3425(OH), 2924(CH),$$
$$1724[C(=O)(Ad-HAc)], 1639[C(=O)(DMAA)],$$
$$1304(CF_3), 1238(CF_2);$$
$$^1H\,NMR(CDCl_3)\delta 1.00 \sim 2.20(CH, CH_2),$$
$$2.25 \sim 2.85(CH), 3.05 \sim 3.95(CH_3).$$

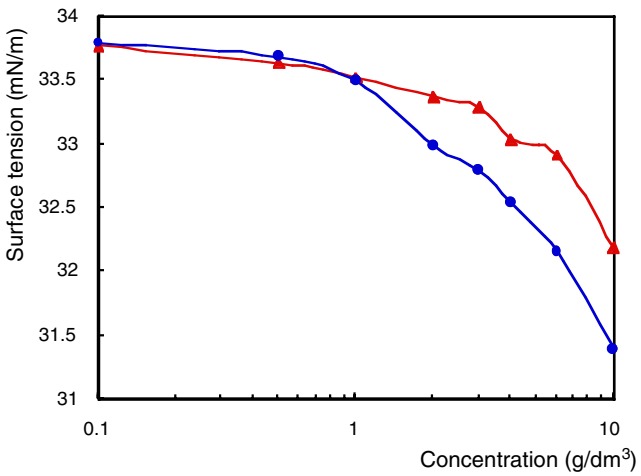


Fig. 3 Surface tension of R_F-(Ad-HAc)$_x$–(ACMO)$_y$-R_F and R_F-(ACMO)$_n$-R_F MeOH/H_2O(3/1: vol) mixed solutions at 30 °C. *Filled triangle* R_F-(Ad-HAc)$_x$–(ACMO)$_y$-R_F; R_F=$CF(CF_3)OC_3F_7$ (*x*:*y*= 41:59); *filled circle* R_F-(ACMO)$_n$-R_F; R_F=$CF(CF_3)OC_3F_7$

Dispersion of 5-(2-adamantylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione] (ADMDD) into methanol–water (3/1) mixed solvent by the use of R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F cooligomer

To a methanol–water (3/1) solution (5 ml) of 2 g/dm^3 R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F was added ADMDD (181 mmol). The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. The amounts of dispersed ADMDD in the supernatant solution were estimated by the use of UV–vis. spectra (λ_{max}= *257* nm).

Results and discussion

The reactions of fluoroalkanoyl peroxide with 3-hydroxy-1-adamantylacrylate (Ad-HAc) were carried out by the use of

Table 2 Size of fluorinated molecular aggregate in methanol solutions determined by dynamic light scattering measurements

Cooligomer	R_F	R_F-cooligomer aggregate (nm)
R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F		10.3±1.2
R_F-(Ad)$_x$–(ACA)$_y$-R_F	$CF(CF_3)OC_3F_7$	11.3±2.3
R_F-(ACA)$_n$-R_F		10.8±1.1
R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F		10.7±1.3
R_F-(Ad)$_x$–(DMAA)$_y$-R_F	$CF(CF_3)OC_3F_7$	12.4±5.0
R_F-(DMAA)$_n$-R_F		11.1±1.2
R_F-(Ad-HAc)$_x$–(ACMO)$_y$-R_F		10.7±1.6
R_F-(Ad)$_x$–(ACMO)$_y$-R_F	$CF(CF_3)OC_3F_7$	12.0±0.8
R_F-(ACMO)$_n$-R_F		10.7±1.1

acrylic acid (ACA), *N,N*-dimethylacrylamide (DMAA) and acryloylmorpholine (ACMO) as comonomers at 45 °C for 5 h under nitrogen. The process is outlined in Scheme 1.

Fluoroalkanoyl peroxide was found to react with Ad-HAc and comonomers under very mild conditions to afford fluoroalkyl end-capped cooligomers having adamantane as a pendant group [R_F-(Ad-HAc)$_x$–(Co-M)$_y$-R_F] in 77~86% isolated yields.

Adamantane is well-known to be thermodynamically very stable. Thus, the thermal stability of our present fluorinated cooligomers containing adamantyl segments is suggested to become higher, compared to those of the corresponding homooligomers having no adamantyl segments. We have studied on the thermal stability of these fluorinated cooligomers by the use of thermogravimetric analyses (TGA), in which the weight loss of these cooligomers were measured by raising the temperature around to 800 °C. In addition, we have studied on the thermal stability of the corresponding fluoroalkyl end-capped homooligomers having no adamantyl segments and fluoroalkyl end-capped cooligomers having adamantane in the main chains [23] under similar conditions, for comparison. The results were shown in Table 1.

As shown in Table 1, R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F, R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F, and R_F-(Ad-HAc)$_x$–(ACMO)$_y$-R_F lost 10% of their weights around 205, 210, and 265 °C, respectively under air atmosphere conditions. In contrast, thermal stability: T_{dec} (151~241 °C for the corresponding homooligomers and 148~243 °C for the fluorinated cooligomers having adamantane in the main chains: defined by a 10% mass loss at a 10 °C/min heating rate under air atmosphere conditions) of other fluorinated homooligomers and cooligomers having adamantane in the main chain were found to decrease compared to those of fluoroalkyl end-capped cooligomers having adamantane as a pendant group except for R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F cooligomer. This finding is due to the presence of adamantane segments in cooligomers and their higher molecular weights. A lower thermal stability of R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F cooligomer would be derived from the intramolecular hydrogen bonding interaction between carboxyl groups and hydroxyl groups in Ad-HAc in cooligomers. The thermal stability of fluoroalkyl end-capped cooligomers having adamantine in the main chains [R_F-(Ad)$_x$–(Co-M)$_y$-R_F] was not higher than that of the corresponding homooligomers and cooligomers having adamantine as a pendant group. This finding is due to the lower contents (1~3%) of adamantane segments in cooligomers.

R_F-(Ad-HAc)$_x$–(Co-M)$_y$-R_F, thus obtained, were easily soluble in methanol, ethanol, tetrahydrofuran (THF), chloroform, dimethyl sulfoxide, and *N,N*-dimethylforma-

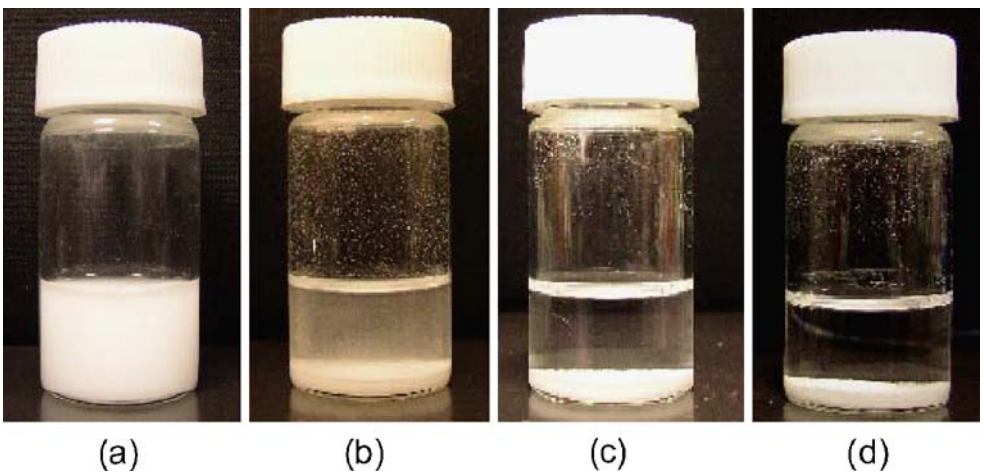


Fig. 4 Photographs of aqueous methanol solutions (MeOH/H_2O=3/1: vol) of 36.3 mmol/dm^3 5-(2-adamantylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (ADMDD) in the presence of fluoroalkyl end-capped oligomers after stirring for 1 day at room temperature (concentration of oligomer: 2 g/dm^3). **a** R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F; R_F=$CF(CF_3)OC_3F_7$; **b** R_F-(Ad)$_x$–(ACA)$_y$-R_F; R_F=$CF(CF_3)OC_3F_7$; **c** R_F-(ACA)$_n$-R_F; R_F=$CF(CF_3)OC_3F_7$; **d** 36.2 mmol/dm^3 ADMDD in the absence of oligomer

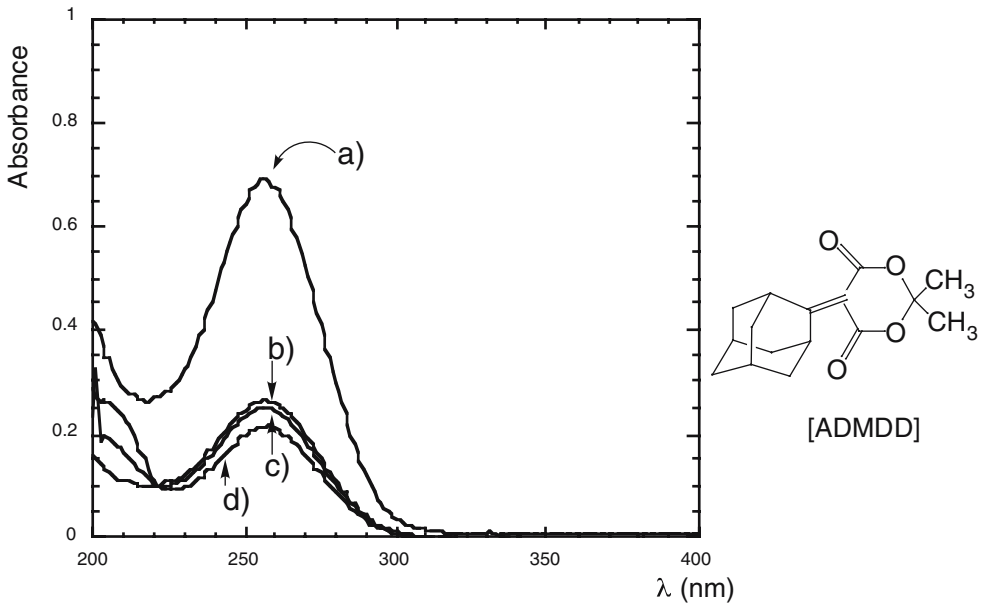


Fig. 5 UV–vis spectra of MeOH/H_2O (3/1: vol) mixed solutions of 36.2 mmol/dm^3 5-(2-adamantylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (ADMDD) in the presence of fluoroalkyl end-capped oligomers after stirring for 1 day at room temperature (concentration of oligomer: 2 g/dm^3). *a* R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F; R_F=CF(CF_3)OC_3F_7; *b* R_F-(Ad)$_x$–(ACA)$_y$-R_F; R_F=CF(CF_3)OC_3F_7; *c* R_F-(ACA)$_n$-R_F; R_F=CF(CF_3)OC_3F_7; *d* 36.2 mmol/dm^3 ADMDD in the absence of oligomer

mide. It is interesting to note that R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F cooligomer was found to exhibit an amphiphilic characteristic. The surface properties of these fluorinated cooligomers were evaluated by measuring surface tension of MeOH/H_2O (3/1 vol) mixed solutions of these fluorinated cooligomers using the drop weight method at 30 °C. We have also measured surface tension of the solutions containing the corresponding fluorinated homooligomers with no adamantyl segments, for comparison. These results were shown in Figs. 1, 2, and 3.

As shown in Figs. 1, 2, and 3, a decrease in the surface tension of MeOH/H_2O mixed solutions was observed for each homo- and cooligomer. R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F was able to reduce the surface tension of the mixed solvent, compared to the corresponding homooligomer (see Fig. 1). This would be due to the relatively lower content (~18%) of adamantane segments in cooligomer, and not only fluoroalkyl segments but also adamantyl segments in this cooligomer are likely to be arranged regularly above the mixed solvent surface because the parent adamanatane exhibit a poor solubility in this mixed solvent. On the other hand, other fluorinated hooligomers are more effective in reducing the surface tension, compared to the corresponding fluorinated Ad-HAc cooligomers (see Figs. 2 and 3). This finding is due to the higher contents (36 and 41%) of adamantyl segments in cooligomers, and these fluorinated cooligomers are not likely to be arranged regularly above the mixed MeOH/H_2O surface owing to the steric hindrance of adamantyl segments.

Previously, we reported that fluoroalkyl end-capped oligomers can form the self-assembled fluorinated oligomeric aggregates with the aggregations of terminal fluoroalkyl segments in aqueous and organic media. R_F-(Ad-HAc)$_x$–(Co-M)$_y$-R_F (4 g) are also expected to form the

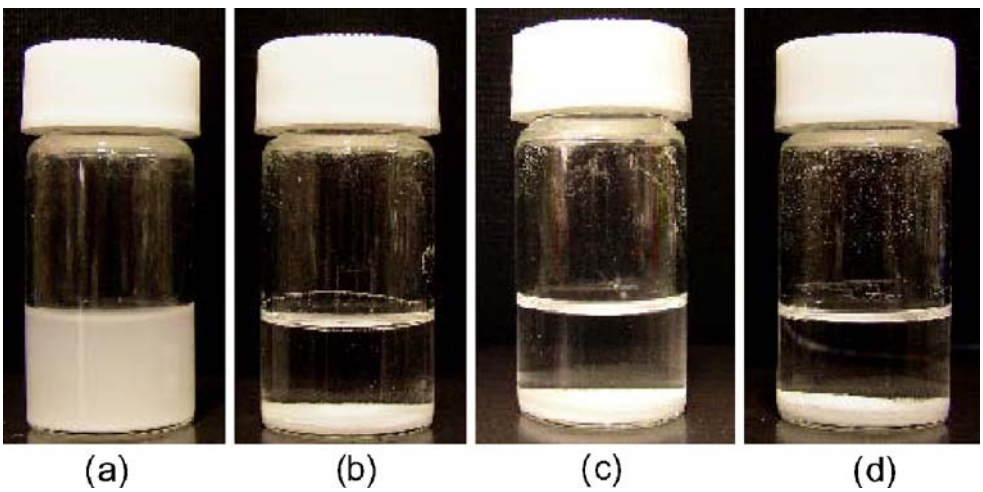


Fig. 6 Photographs of aqueous methanol solutions (MeOH/H_2O=3/1: vol) of 36.3 mmol/dm^3 5-(2-adamantylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (ADMDD) in the presence of fluoroalkyl end-capped oligomers after stirring for 1 day at room temperature (concentration of oligomer:2 g/dm^3). **a** R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F; R_F=CF(CF_3)OC_3F_7; **b** R_F-(DMAA)$_n$-R_F; R_F=CF(CF_3)OC_3F_7; **c** R_F-(AD)$_x$–(DMAA)$_y$-R_F; R_F=CF(CF_3)OC_3F_7; **d** 36.2 mmol/dm^3 ADMDD in the absence of oligomer

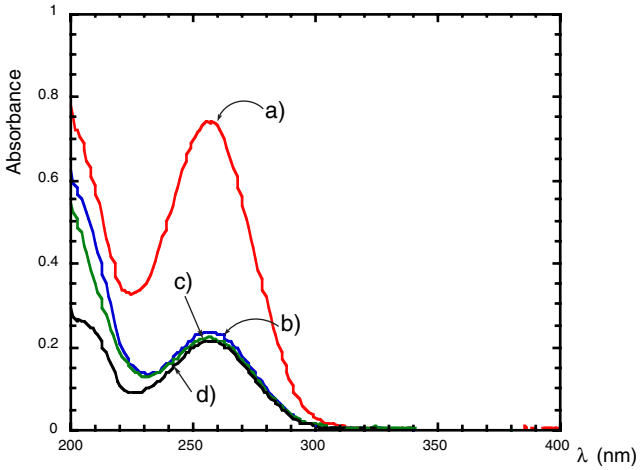


Fig. 7 UV–vis spectra of MeOH/H_2O (3/1: vol) mixed solutions of 36.3 mmol/dm^3 5-(2-adamantylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (ADMDD) in the presence of fluoroalkyl end-capped oligomers after stirring for 1 day at room temperature (concentration of oligomer:2 g/dm^3). *a* R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F; R_F=CF(CF$_3$)OC$_3$F$_7$; *b* R_F-(DMAA)$_n$-R_F; R_F=CF(CF$_3$)OC$_3$F$_7$; *c* R_F-(AD)$_x$–(DMAA)$_y$-R_F; R_F=CF(CF$_3$)OC$_3$F$_7$; *d* 36.2 mmol/dm^3 ADMDD in the absence of oligomer

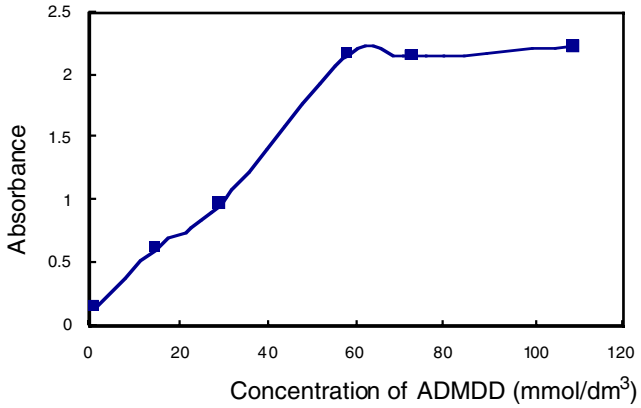
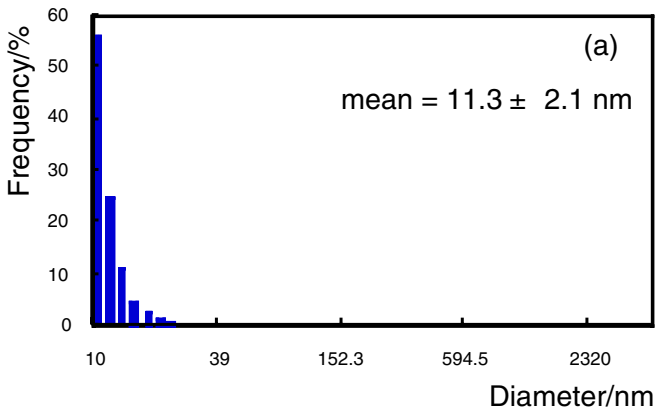


Fig. 9 Relationship between the absorbance (λ_{max}: 257 nm) and the concentrations of ADMDD in the presence of R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F; (2 g/dm^3) in MeOH/H_2O (3/1: vol) mixed solutions

nanometer size-controlled molecular aggregates. We have measured the size of fluorinated molecular aggregates formed by R_F-(Ad-HAc)$_x$–(Co-M)$_y$-R_F in methanol solutions by the dynamic light scattering (DLS) measurements, and the results were shown in Table 2.

As shown in Table 2, each size of fluorinated molecular aggregates formed by these cooligomers were of 10 nm level, and these obtained values were almost the same as those of the corresponding cooligomers containing adamantane units in the main chains [R_F-(Ad)$_x$–(Co-M)$_y$-R_F] and the homooligomers [R_F-(M)$_n$-R_F]. Our present fluorinated cooligomeric aggregates possess adamantyl segments as the recognition moieties in their aggregate cores. Therefore, these fluorinated aggregates are suggested to interact selectively with the guest molecules having adamantly segments. From this point of view, it is of particular interest to apply our present fluorinated cooligomeric aggregates into the encapsulation of low-molecular adamantane derivative [5-(2-adamantylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione: ADMDD] as a guest molecule. As shown in Fig. 4d, ADMDD exhibits an extremely poor dispersibility in methanol–water 3:1 mixed solvent. A similar poor dispersibility of ADMDD was observed in the presence of R_F-(ACA)$_n$-R_F homooligomer (see Fig. 4c). However, a slight increase of the dispersion of ADMDD into this mixed solvent was observed in the presence of R_F-(Ad)$_x$–(ACA)$_y$-R_F (see Figs. 4b and 5b). A remarkable increase of dispersion of ADMDD was observed by the use of R_F-(Ad-HAc)$_x$–(ACA)$_y$-R_F cooligomer, indicating that van der Waals interaction between ADMDD and adamantly segments in cooligomeric aggregate cores should be essential for the dispersion of ADMDD into this mixed solvent, and the amounts of dispersed ADMDD in this solvent was estimated to be



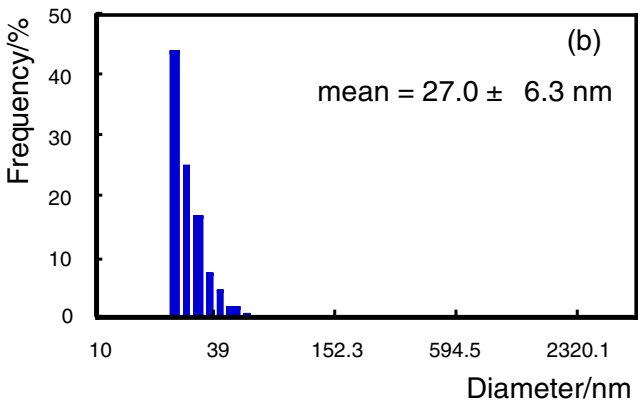


Fig. 8 Histogram of self-assembled molecular aggregates formed by R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F (R_F=CF(CF$_3$)OC$_3$F$_7$; Mn=2,130) cooligomer in MeOH/H_2O(3/1: vol) mixed solutions (**a**) and self-assembled molecular aggregates formed by R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F cooligomer-encapsulated ADMDD in MeOH/H_2O(3/1: vol) mixed solutions (**b**) by dynamic light scattering measurements

Table 3 Size of molecular aggregates formed by R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F (2 g/dm^3) in the presence of ADMDD in MeOH/H_2O (3/1: vol) mixed solutions determined by dynamic light scattering measurements

Concentration of ADMDD (mmol/dm^3)	Size of molecular aggregates (nm)
0	10.7±1.3
0.72	13.5±5.6
28.9	18.7±4.7
57.9	21.1±5.0
72.4	23.4±5.2
109	22.2±5.3

34% (based on the used ADMDD) by the use of UV–vis spectra measurements (λ_{max}=257 nm) shown in Figs. 4a and 5a. A similar dispersion behavior of ADMDD (the amount of dispersed ADMDD based on the used ADMDD: 36%; see Figs. 6a and 7a) in this mixed solvent was observed by using R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F as shown in Figs. 6 and 7; however, R_F-(Ad)$_x$–(DMAA)$_y$-R_F cooligomer failed to afford the similar dispersibility of ADMDD to that of R_F-(Ad)$_x$–(ACA)$_y$-R_F (see Figs. 6c and 7c). This would be due to the lower content (1%) of adamantane units in cooligomers than that (3%) of R_F-(Ad)$_x$–(ACA)$_y$-R_F.

In this way, R_F-(Ad-HAc)$_x$–(Co-M)$_y$–R_F were clarified to be effective for the dispersion of ADMDD in the MeOH/H_2O mixed solvent. This finding suggests that R_F-(Ad-HAc)$_x$–(Co-M)$_y$-R_F should provide the suitable host moieties to interact with ADMDD as a guest molecule in this solvent. DLS measurements at 30 °C showed that the size (number–average diameter) of molecular assemblies formed in the mixed solvent could increase from 11.3± 2.1 to 27.0±6.3 nm by dispersion of ADMDD as shown in Fig. 8. The significant increase of the aggregate size would be due to the encapsulation of ADMDD in the fluorinated aggregate cores through the van der Waals interaction of adamantly segments in the fluorinated aggregate cores with ADMDD.

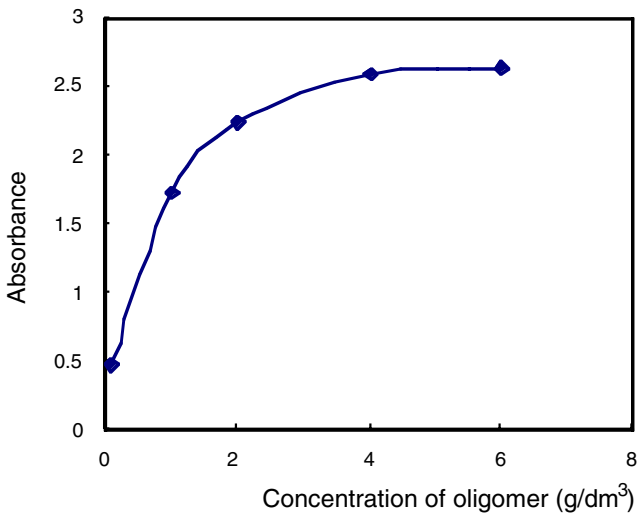


Fig. 10 Relationship between the absorbance (λ_{max}: 257 nm) of ADMDD (57.9 mmol/dm^3) and the concentrations of R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F in MeOH/H_2O (3/1: vol) mixed solutions

To calculate the maximum number of ADMDD that could occupy the fluorinated cooligomeric aggregate cores, experiments were conducted with varying molar ratios of ADMDD in the mixed solvent, and the results were shown in Fig. 9.

The absorbance of 257 nm related to ADMDD in the presence of 2 g/dm^3 R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F increased remarkably with increasing the concentration of ADMDD, and the almost constant values were obtained above 57.9 mmol/dm^3. Similarly, DLS measurements at 30 °C showed that the size of fluorinated cooligomeric aggregate–ADMDD composites increased with the increase of concentration of ADMDD, and the almost constant size (21~23 nm) was obtained above the 57.9 mmol/dm^3 (see Table 3). Furthermore, as shown in Fig. 10 and Table 4, the absorbance of 257 nm in the presence of 57.9 mmol/dm^3 ADMDAA was found to increase with increase of the concentration of cooligomer, and the almost constant absorbance values and the size (21~27 nm) of the composites were obtained above the concentrations of 2 g/dm^3 cooligomer. These experimental results show that 2 g/dm^3 (or one mole) of R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F could interact with 57.9 mmol/dm^3 (or ca. 20 mol) of ADMDD. Thus, it is suggested that the fluorinated cooligomeric aggregate could occupy around 320 ADMDD molecules per aggregate core; this fluorinated cooligomeric aggregate is considered to consist of around 16 fluorinated cooligomeric molecules because the molecular weight of the aggregates formed by R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F determined by the static light scattering measurements and the molecular weight of the fluorinated oligomer determined by GPC measurements are 34,380 and 2,130, respectively.

Table 4 Size of molecular aggregates formed by R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F in the presence of ADMDD (57.9 mmol/dm^3) in MeOH/H_2O (3/1: vol) mixed solutions determined by dynamic light scattering measurements

Concentration of cooligomer (g/dm^3)	Size of molecular aggregates (nm)
0.1	12.5±2.0
1	17.0±3.5
2	21.1±5.0
4	22.1±5.4
6	27.0±6.3

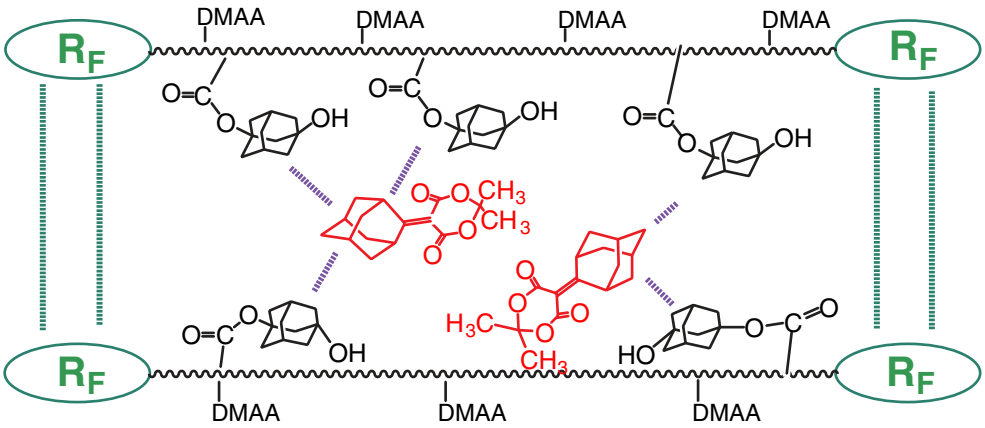


Fig. 11 Schematic illustrations for the recognition of ADMDD by the self-assembled R_F-(Ad-HAc)$_x$–(DMAA)$_y$-R_F aggregates

Thus, as shown in Fig. 11, the insides of fluorinated molecular aggregate cores consist of the solvophobic environment containing the adamantyl segments, and in addition, the host moieties in these cores could recognize selectively ADMDD as guest molecules through the van der Waals interaction between the adamanatane units. In particular, UV–vis spectra of ADMDD in the nanocomposite in Fig. 7 showed no absorption band change, compared to that of the parent ADMDD (λ_{max} 257 nm), indicating that carbonyl groups in ADMDD could not interact with the fluorinated cooligomeric aggregate cores.

In conclusion, we have succeeded in preparing fluoroalkyl end-capped cooligomers having adamantane as a pendant group by the reactions of fluoroalkanoyl peroxide with acrylate monomer containing adamantyl segments and radical polymerizable comonomers such as acrylic acid, *N*, *N*-dimethylacrylamide and acryloylmorpholine under very mild conditions. Fluoroalkyl end-capped cooligomers having adamantane as a pendant group thus obtained/exhibited a higher thermal stability than that of the corresponding homooligomers and fluoroalkyl end-capped cooligomers having adamantine in the main chains. In addition, these fluorinated cooligomers could form the nanometer size-controlled fluorinated molecular aggregates in methanol/water mixed solvent. It is interesting to note that ADMDD could be encapsulated more effectively as a guest molecule into the fluorinated cooligomeric aggregate cores than the corresponding fluoroalkyl end-capped homooligomeric aggregates and R_F-(Ad)$_x$–(Co-M)$_y$-R_F cooligomeric aggregates.

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