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SHORT COMMUNICATION

Hideo Sawada
Tamikazu Narumi
Atsushi Kajiwara
Katsuya Ueno
Kazuo Hamazaki

Preparation of novel fluoroalkyl end-capped oligomers/silica hybrid nanoparticles-encapsulation of a variety of guest molecules into fluorinated nanoparticles

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H. Sawada (✉) · T. Narumi
Department of Materials Science
and Technology, Faculty of Science
and Technology, Hirosaki University,
Bunkyo-cho, Hirosaki 036-8561, Japan
E-mail: hideosaw@cc.hirosaki-u.ac.jp
Tel.: +81-172-393578
Fax: +81-172-393541

A. Kajiwara
Nara University of Education,
Nara 630-8528, Japan

K. Ueno · K. Hamazaki
Asahi Glass Co., Ltd, Yurakucho,
Chiyoda-ku, Tokyo 100-8405, Japan

Abstract Fluoroalkyl end-capped oligomers reacted with tetraethoxysilane and silica/nanoparticles under alkaline conditions to afford fluoroalkyl end-capped oligomers/silica nanoparticles (mean diameters: 31–54 nm) with a good dispersibility and stability in organic media. Interestingly, the isolated fluorinated particle powders were found to afford nanometer size-controlled colloidal particles with a good redispersibility and stability in these media. In addition, fluoroalkyl end-capped oligomers/silica nanoparticles-encapsulated guest molecules such as stable organic radicals and ionic liquids were prepared under similar conditions. These fluorinated nanoparticles-encapsulated guest molecules were applied to a new type of surface-modification agent, and these particles were able to disperse well above the poly (methyl methacrylate) films.

Keywords Fluorinated nanoparticle · Redispersibility · Silica-nanoparticle · Stable organic radical · Ionic liquid · Encapsulation · Surface dispersion

Introduction

Recently, considerable effort has been devoted to the design and controlled fabrication of nanostructured materials with a variety of unique properties, which results from a function of nanoscale materials' size, composition, and structural order [1]. In particular, there have been comprehensive studies to fabricate core–shell colloidal materials with tailored structural, optical. and surface-active properties [2, 3]. From a developmental viewpoint of core–shell colloidal particles, polymer-coated particles offer interesting prospects of abroad applications in a variety of fields [2–10]. Hitherto, there has been increasing interest in the material sciences toward the development of partially fluoroalkylated polymeric compounds [11–15]. In these partially fluoroalkylated polymers, especially fluoralkyl end-capped oligomers are attractive functional materials because they exhibit various unique properties such as high solubility, surface-active properties, biological activities, and nanosize-controlled self-assembled molecular aggregates which cannot be achieved by the corresponding non-fluorinated and randomly fluoroalkylated ones [16–22]. Thus, it is of particular interest to prepare new fluoroalkyl end-capped oligomer-coated nanoparticles for new organofluorine materials chemistry. Now, we have found that fluoroalkyl end-capped oligomers react with tetraethoxysilane (TEOS) in the presence of silica nanoparticles under alkaline conditions produce fluorinated oligomeric nanoparticles, and these fluorinated nanoparticles exhibit a good dispersibility and stability in organic media. More interestingly, we have succeeded in encapsulation of a variety of guest molecules such as stable organic radicals and ionic liquids (Ilqs) into fluoroalkyl end-capped oligomeric nanoparticles. These results will be described herein.

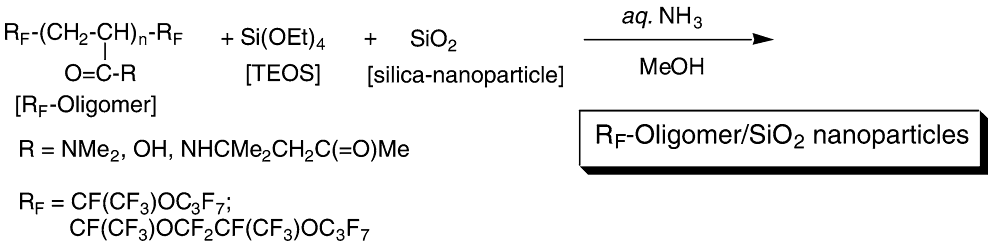
Table 1 Preparation of fluroalkyl end-capped oligomers [R_F-($CH_2CHC(=O)R)_n$-R_F]/silica nanoparticles

Run	R_F, R in oligomer R_F, R [Mn] (g)	TEOS (g)	30% SiO_2 nanoparticle (g, MeOH solution)	Yield[a] (%)
1	$R_F = CF(CF_3)OC_3F_7$ NMe_2 [4,820] (0.50)	0.47 (2.3 mmol)	3.33	79
2	OH [2,770] (0.50)	0.47	3.33	49
3	$NHCMe_2CH_2C(=O)Me$ [3,710] (0.50)	0.47	3.33	61
4	$R_F = CF(CF_3)OF_2CF(CF_3)OC_3F_7$ OH [2,630] 0.50	0.47	3.33	56

[a] Isolated yield based on oligomer (0.50 g), SiO_2[(2.3 mmol) (0.14 g)], and SiO_2 nanoparticle (1.00 g)

Experimental

Following is a typical experimental procedure for the preparation of fluorinated oligomeric nanoparticles. To a methanol solution (20 ml) of fluoroalkyl end-capped *N*,*N*-dimethylacrylamide oligomer [R_F-($CH_2CHC(=O)NMe_2)_n$-R_F[R_F-(DMAA)$_n$-R_F]; $R_F = CF(CF_3)OC_3F_7$; Mn = 4,820 (0.50 g)], which was prepared by the reaction of fluoroalkanoyl peroxide with the corresponding monomer according to our previously reported method [23], were added tetraethoxysilane (TEOS: 0.47 g), silica-nanoparticle methanol solution (30% wt.: 3.33 g; average particle size: 11 nm [Methanol Silica-sol (TR): Nissan Chemical Industrials Ltd, Tokyo, Japan], and 25% aqueous ammonia solution (0.50 ml). The mixture was stirred with a magnetic stirring bar at room temperature for 2 h. After the solvent was evaporated off, methanol (25 ml) was added to the obtained crude product. The methanol solution was stirred with magnetic stirring bar at room temperature for 2 days, and then was centrifuged for 30 min. The expected fluorinated nanoparticles were easily separated from the methanol solution. Fluorinated nanoparticle powders thus obtained were dried in vacuum at 50 °C for 2 days to produce purified particle powders (1.30 g). The purified fluorinated nanoparticle powders were added to fresh methanol, and were stirred with magnetic stirring bar at room temperature for 2 days to obtain fine colloidal nanoparticles with a good redispersibility and stability in methanol. Fluoroalkylated end-capped oligomers/silica nanoparticles-encapsulated guest molecules such as stable organic radicals and ILqs were prepared in the presence these guest molecules under similar conditions. We have conducted the elementary analyses of fluorine and nitrogen in these fluorinated nanoparticles in order to confirm the presence of fluorinated oligomers and ILqs in these nanoparticles, respectively. In addition, we have conducted the ESR analysis of fluorinated oligomers/silica nanoparticles-encapsulated stable radicals by the use of the mixture of 2,2,6,6-tetramethyl-1-piperidinyloxy free radical and 2,2,6,6-tetramethylpiperidine as an external standard method in order to measure the concentration of stable radicals in these nanoparticles.



Results and discussion

As shown in Scheme 1, a variety of well-dispersed fluorinated nanoparticles were obtained by using fluoroalkyl end-capped oligomers, and the results are listed in Table 1.

As shown in Scheme 1 and Table 1, not only R_F-(DMAA)$_n$-R_F oligomer but also fluoroalkyl end-capped acrylic acid oligomers: R_F-($CH_2CHCOOH)_n$-R_F [R_F-(ACA)$_n$-R_F] and fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl) acrylamide oligomer [R_F-(DOBAA)$_n$-R_F] reacted with TEOS in the presence of silicananoparticles to afford fluoroalkyl end-capped oligomers/silica hybrid nanoparticles in 49–79% isolated yields. We have measured the size of fluorinated oligomer–silica nanoparticles in methanol by dynamic light-scattering (DLS) measurements (DLS-6000 HL: Otsuka Electronics Co. Ltd, Japan) at 30 °C. The size of the parent fluorinated oligomeric aggregates was also measured under similar conditions for comparison. These results are shown in Table 2.

As shown in Table 2, the size (31–54 nm: number-average diameter) of fluorinated oligomers/silica hybrid nanoparticles was increased by the hybridiza-

Table 2 Size of fluroalkyl end-capped oligomers [R_F(R_F-$CH_2CHC(=O)R_n$-R_F)/silica nanoparticles in methanol solution determined by DLS measurements

Run	R_F, R in oligomer R_F, R	Size of dispersed particles (nm)	Size of redispersed particles (nm)
1	$R_F = CF(CF_3)OC_3F_7$ NMe_2	48.6 ± 10.1 [11.1 ± 1.2][a]	44.6 ± 6.5
2	OH	31.0 ± 8.4 [10.8 ± 1.1][a]	24.4 ± 2.4
3	$NHCMe_2CH_2C(=O)Me$	54.3 ± 8.8 [10.9 ± 1.6][a]	36.2 ± 3.3
4	$R_F = CF(CF_3)OF_2CF(CF_3)OC_3F_7$ OH	30.5 ± 5.8 [10.8 ± 1.1][a]	24.5 ± 2.5

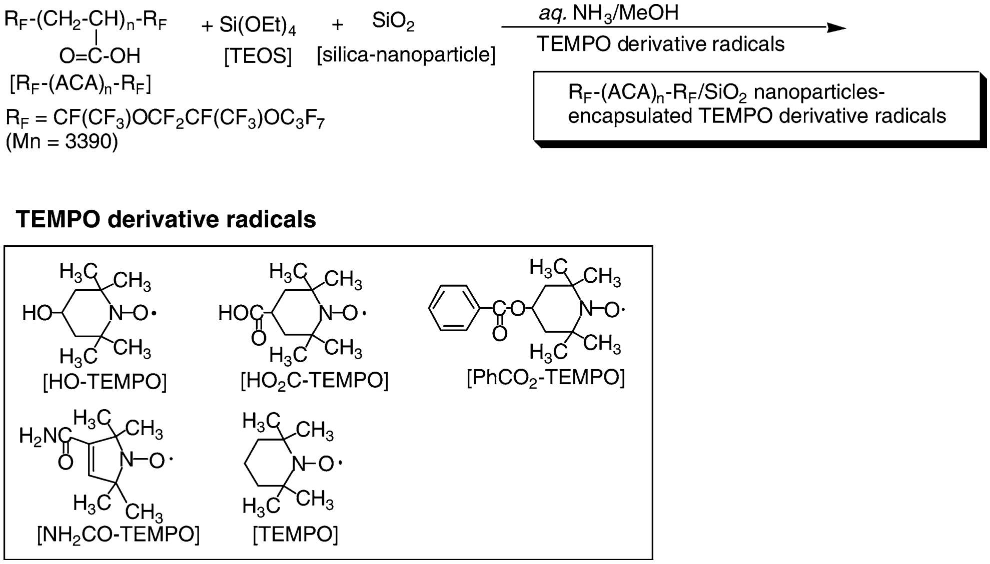
[a] Size of fluroalkyl end-capped oligomer aggregates

tions of fluoroalkyl end-capped oligomers, compared to that (11 nm) of the parent fluoroalkyl end-capped oligomeric aggregates. The increase of the size of naoparticles indicates that the hybridizations of fluoroalkyl end-capped oligomers with TEOS in the presence of silica nanoparticles could proceed smoothly to yield fine fluorinated nanoparticles with around 40-nm size levels. Especially, fluoroalkyl end-capped oligomers should be incorporated homogeneously into the silica gel including the hydrolyzate of TEOS, utilizing hydrogen-bonding interaction between the silanol groups and amido (or carboxy) groups of oligomers to afford the expected fluorinated oligomers/silca nanoparticles. We have measured SEM (scanning electron microscopy) photographs of methanol solution of fluoroalkyl end-capped *N*,*N*-dimethylacrylamide oligomer/silica nanoparticles [$R_F = CF(CF_3)OC_3F_7$], and the result is shown in Fig. 1.

The electron micrograph also shows the formation of fluorinated oligomer/silica nanoparticles with a mean diameter of 87 nm. The difference in the average sizes determined by DLS and SEM (DLS: ~45 nm and SEM: ~87 nm) could be due to the coagulation or agglomeration of the nanoparticles during sample preparation for SEM measurements.

Interestingly, a variety of isolated fluorinated nanoparticle powders were found to exhibit a superior redispersibility and stability in methanol. The size (24–45 nm) of the redispersed fluorinated particles did not change even after the redispersion of the parent fluorinated particle powders into methanol (see Table 2), and the size of each particle showed a monodispersed characteristic.

It is of particular interest to apply our present fluorinated nanoparticles to the encapsulation of guest molecules. Hitherto, stable organic radials such as aminoxyl radicals are of great interest due to their role in building blocks for molecular-based magnetic materials and their utility in a variety of fields including biological and synthetic chemistry [24]. Thus, the encapsulation of stable radicals into our present fluorinated nanoparticles is important from the viewpoint of development of new fluorinated functional materials.



As shown in Scheme 2, we have succeeded in encapsulating a variety of stable TEMPO-derivative radicals such as 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy, free radical (HO-TEMPO), 4-carboxy-2,2,6,6-tetramethylpiperidinyloxy, free radical (HO_2C-TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy benzoate, free radical ($PhCO_2$-TEMPO), 4-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolinyloxy, free radical (NH_2CO-TEMPO), and 2,2,6,6-tetramethylpiperidinyloxy, free radical (TEMPO) into fluorinated nanoparticles by the hybrid-

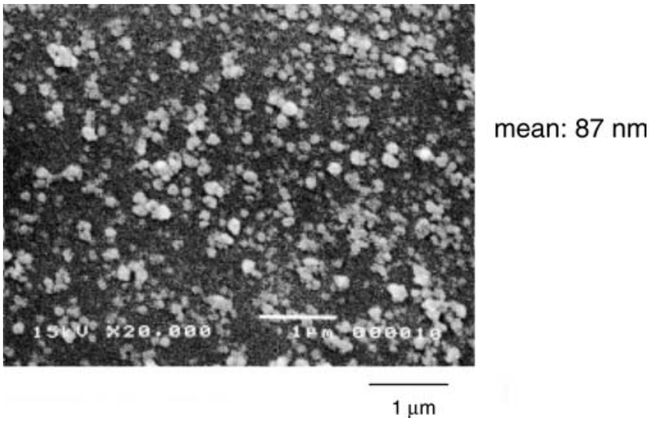


Fig. 1 SEM (scanning electron microscopy) images of methanol solution of R_F-(DMAA)$_n$-R_F–silica nanoparticles [$R_F = CF(CF_3)OC_3F_7$]

izations with the corresponding TEMPO-derivative radicals. The fluorinated nanoparticles-encapsulated TEMPO-derivative radicals thus obtained exhibited a similar good dispersibility and stability to that of the corresponding parent nanoparticles in 1,2-dichloroethane. In addition, the DLS study showed that the average diameter of fluorinated nanoparticles-encapsulated TEMPO radicals is 27–83 nm and these particles possess monodispersed characteristics.

The presence of fluoroalkyl end-capped oligomers and stable radicals in nanoparticles was confirmed by fluorine analysis and ESR study, respectively. The results are shown in Table 3.

Fig. 2 Photograph of R_F-(DMAA)$_n$-R_F[$R_F = CF(CF_3)OC_3F_7$] oligomer/silica nanoparticles-encapsulated [C_4mim][PF_6] dispersed in 1,2-dichloroethane (average particle size: 83 nm; concentration of oligomer/silica nanoparticles-encapsulated ILq: 2 g/dm^3)

Fluorine analysis showed that fluorinated oligomers could be tightly bound into the silica core matrix. In addition, it was demonstrated that TEMPO- derivative radicals were tightly encapsulated in fluorinated nanoparticles in each case. The amounts of encapsulated TEMPO-derivative radicals were increased by increasing the amounts of used radicals except for unsubstituted TEMPO radical.

Table 3 Contents of fluorine and TEMPO-derivatives radicals in R_F-(ACA)$_n$-R_F/SiO_2 nanoparticles-encapsulated TEMPO-derivative radicals [$R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] (the composition is based on the assumption of 100% conversion)

Used TEMPO-derivative radical (g)		Content of fluorine in particles (at%)	Content of TEMPO-derivative radical (%)
HO-TEMPO	0.1	2.24[a] [6.88][b]	0.06[c] [5.76][b]
	0.2	2.05 [6.51]	0.10 [10.9]
HO_2C-TEMPO	0.1	2.85 [5.34]	0.04 [5.76]
	0.2	2.54 [5.06]	0.14 [10.9]
$PhCO_2$-TEMPO	0.1	2.97 [5.34]	0.13 [5.76]
	0.2	3.36 [5.06]	0.40 [10.9]
NH_2CO_2-TEMPO	0.1	1.93 [6.88]	0.10 [5.76]
	0.2	2.10 [6.51]	0.22 [10.9]
TEMPO	0.1	1.99 [6.88]	0.12 [5.76]
	0.2	2.52 [6.51]	0.06 [10.9]

[a] Elementary analyses
[b] Theoretical values
[c] ESR technique

ILqs are attractive functional materials, because they are considered to be the suitable “green” solvents being the environmentally friendly alternatives to volatile organic compounds [25, 26]. Henceforth, we tried to encapsulate ILqs into fluorinated nanoparticles. In fact, not only TEMPO-derivative radicals but also ILqs (1-butyl-3-methylimidazolium hexafluorophosphate: [C_4mim][PF_6]) were encapsulated in fluorinated nanoparticles under the same conditions as those illustrated Scheme 2. The size of the obtained nanoparticles-encapsulated [C_4mim][PF_6] determined by DLS analyses was 25–83 nm. Furthermore, analysis of nitrogen in fluoroalkyl end-capped acrylic acid oligomer [$R_F = CF(CF_3)OC_3F_7$]/silica nanoparticles-encapsulated [C_4mim][PF_6] were performed in order to clarify the presence of ILq in nanoparticles. We have measured the contents of nitrogen related to [C_4mim][PF_6] in nanoparticles after the purification of the particles by washing them well with methanol followed by 1,2-dichloroethane (these solvents exhibit a good solubility toward [C_4mim][PF_6]). The contents of encapsulated [C_4mim][PF_6] in nanoparticles were increased by increasing the amounts of used [C_4mim][PF_6] as follows:

Used [C_4mim] [PF_6] (ml)	Nitrogen (at%) in the obtained particles	Particle size (nm)
0.3	1.18 (1.71)[a]	42
0.5	1.35 (2.38)[a]	31

[a] Theoretical value

In this way, it was verified that a variety of fluoroalkyl end-capped oligomers/silica nanoparticles-encapsulated guest molecules possess a good dispersibility and stability toward aqueous and organic media. Figure 2 shows the photograph of R_F-(DOBAA)$_n$-R_F[$R_F = CF(CF_3)OC_3F_7$] oligomer/silica nanoparticles-encapsulated [C_4mim][PF_6] dispersed in 1,2-dichloroethane, which is a transparent colorless solution. It is of particular to mention that when this transparent solution was centrifuged for 30 min at room temperature, we could easily isolate fluorinated nanoparticles as white-colored powders. Further, the isolated powders were easily redispersed in 1,2-dichloroethane as a a transparent colorless solution by continuous stirring with a magnetic stirring bar at room temperature for 1 day. Therefore, these transparent fluorinated nanoparticles-encapsulated guest molecules are expected to develop to the surface modification for common polymeric materials such as poly(methyl methacrylate).

The fluorinated oligomers/silica nanoparticles-encapsulated HO-TEMPO radicals and [C_4mim][PF_6] were tested for the surface activity as a new type of surface- modification agent. We have prepared the cast PMMA film (film thickness: 231–294 µm) treated with the fluorinated oligomers/silica nanoparticles-encapsulated HO-TEMPO radicals and [C_4mim][PF_6], and the contact angle of dodecane on the modified PMMA films showed a significantly large value (19–28°), which exhibits a good oleophobicity imparted by fluoroalkyl segments in nanoparticles on the PMMA surface. In contrast, the contact angles of dodecane on the reverse side were 0° in each film, indicating that our present fluorinated nanoparticles can be dispersed regularly above the polymer surface during the cast film formation. Thus, not only fluorinated nanoparticles but also encapsulated guest molecules should be well dispersed above the polymer surface.

In conclusion, it was demonstrated that fluoroalkyl end-capped oligomers were able to react with TEOS in the presence of silica nanoparticles under alkaline conditions to afford fluoroalkyl end-capped oligomers/silica nanoparticles with a good dispersibility and stability in organic media. Fluorinated nanoparticles-encapsulated guest molecules were also prepared under similar conditions. These fluorinated nanoparticles were applied to a new type of surface-modification agent and were well dispersed above the polymer surface. Therefore, these fluorinated nanoparticles-encapsulated guest molecules could open new development in fluorinated nanomaterials chemistry. Further studies are actively in progress.

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