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Preparation and Applications of Fluoroalkyl End-Capped Oligomeric Composites

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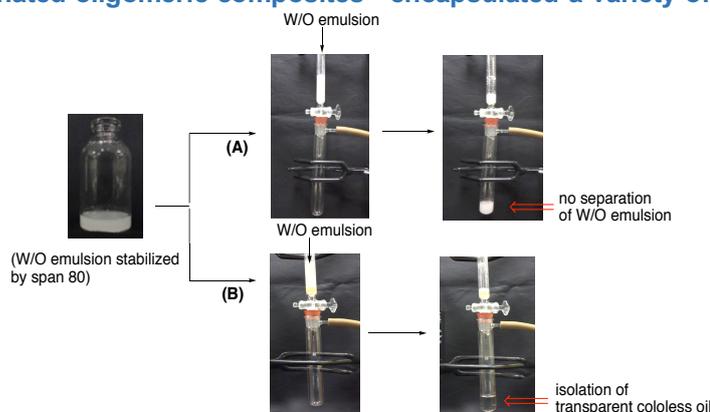
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Abstract - Fluoroalkyl end-capped oligomers can form the nanometer size-controlled self-assembled oligomeric aggregates through the aggregations of terminal fluoroalkyl segments in oligomers in aqueous and organic media. A variety of guest molecules such as inorganic fine particles, organic molecules and organic polymers can be effectively encapsulated into these fluorinated oligomeric aggregate cores to form the corresponding fluorinated oligomeric aggregates/guest molecules composites. In these fluorinated oligomeric composites, interestingly, fluoroalkyl end-capped oligomers/silica nanocomposites can give no weight loss behavior corresponding to the contents of oligomers in the composites even after calcination at 800°C. More interestingly, the fluorinated oligomeric composites - encapsulated a variety of guest molecules can exhibit superoleophobic/superhydrophobic (superamphiphobic), superoleophobic/superhydrophilic and superoleophilic/superhydrophobic characteristics on the modified surfaces by controlling the structures of these guest molecules, respectively. These fluorinated composites possessing such unique wettability have been also applied to the separation of oil and water.



Separation of the W/O emulsion by using the usual silica gel (A) and the fluorinated oligomeric nanocomposite powders possessing a superoleophilic/superhydrophobic characteristic (B) as the packing material, respectively, for the column chromatography

Keyword: Fluorinated Oligomer; Composite; No Weight Loss Behavior; Separation of Oil/Water

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Preparation and Applications of Fluoroalkyl End-Capped Oligomeric Composites

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1. Introduction

There has been a considerable interest in block copolymers possessing longer perfluoroalkyl groups which can exhibit low surface energy and self-assembled polymeric micellar aggregates in aqueous and organic media: these unique characteristics are not displayed by the corresponding random perfluoroalkylated and partially fluorinated polymers¹⁻¹⁰. In these fluorinated block copolymers, two fluoroalkyl end-capped ABA triblock-type oligomers [$R_F-(M)_n-R_F$; R_F = fluoroalkyl groups, M = radical polymerizable monomers], which can be synthesized by the radical oligomerization of the corresponding monomers initiated by fluoroalkanoyl peroxides [$R_F-C(=O)-OO-(O=C)-R_F$], are of particular attractive materials, because they exhibit a variety of unique properties such as high solubility, surface active properties, biological activities, and the nanometer size-controlled self-assembled molecular aggregates through the aggregation between the end-capped fluoroalkyl groups in oligomers¹¹⁻²⁶. These fluorinated molecular aggregates can interact with numerous guest molecules such as fullerene, carbon nanotube, organic dyes, and inorganic metal fine particles (silica, gold, silver, copper, palladium, zinc oxide, hydroxyapatite, magnetite, magnesium carbonate, magnesium oxide, talc, and calcium carbonate) as guest molecules to afford the corresponding fluorinated oligomeric aggregates/guest molecules nanocomposites²⁷⁻⁶⁹. These fluorinated

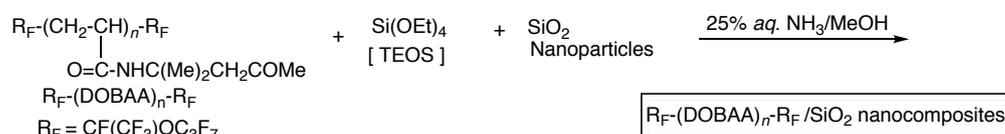
nanocomposites thus obtained can display not only the surface active characteristic imparted by end-capped fluoroalkyl groups in oligomers but also unique properties related to the encapsulated guest molecules into the composite cores²⁷⁻⁶⁹. In this review, we would like to demonstrate on the preparation of numerous fluoroalkyl end-capped oligomeric composites including their applications. The unique wettability of the modified surfaces treated with these fluorinated oligomeric composites will be also reviewed in this article.

2. Preparation of fluoroalkyl end-capped oligomers/silica nanocomposites possessing no weight loss characteristic even after calcination at 800 °C

As indicated above, fluoroalkyl end-capped oligomers can form the nanometer size-controlled self-assembled molecular aggregates imparted by the aggregations of end-capped fluoroalkyl segments to interact with a variety of guest molecules. However, the shape of these fluorinated molecular aggregates is easily exchangeable under a variety of conditions. Therefore, it is in particular interest to prepare new fluoroalkyl end-capped oligomeric aggregates – encapsulated a variety of guest molecules from the developmental viewpoints of new fluorinated functional materials. Fluoroalkyl end-capped oligomeric aggregates could interact with silica nanoparticles as guest molecules in their aggregate cores. The

fluoroalkyl end-capped oligomers/silica nanocomposites can be easily prepared by the sol-gel reactions of tetraethoxysilane (TEOS)

and silica nanoparticles in the presence of the corresponding oligomer under alkaline conditions as shown in Scheme 1^{31, 49}.



Scheme 1. Preparation of fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutylacrylamide) oligomer [R_F-(DOBAA)_n-R_F]/silica nanocomposites

Heretofore, it is well known that traditional fluoropolymers such as poly (tetrafluoroethylene) (PTFE) possess an excellent thermal resistance^{70, 71}. Hybridization of PTFE with silica gels is of particular interest from the developmental viewpoint of novel fluorinated functional polymeric materials. Chen et al. have been already prepared PTFE/SiO₂ hybrids; however parent PTFE in the silica gel hybrids decomposes completely around 700 °C⁷². On the other hand, the molecular weights of fluoroalkyl end-capped oligomers are in general within 10,000, and their thermal stability is extremely poor compared to that of usual perfluorinated polymers⁴⁹. In fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutylacrylamide)

oligomers [R_F-(DOBAA)_n-R_F]/silica nanocomposites [the contents of oligomer: 23 %], which were prepared under alkaline conditions (see Scheme 1), unexpectedly, weight loss behavior corresponding to the content of oligomer in the silica nanocomposites was not observed at all even after calcination at 800 °C, affording the same TGA curve to that of the original silica nanoparticles (see Figure 1)^{31, 53}. In contrast, R_F-(DOBAA)_n-R_F/silica nanocomposites prepared under acidic conditions showed a clear weight loss at 800 °C, a value quite similar to that of the elementary analyses of fluorine in the nanocomposites (see Figure 1)^{31, 53}.

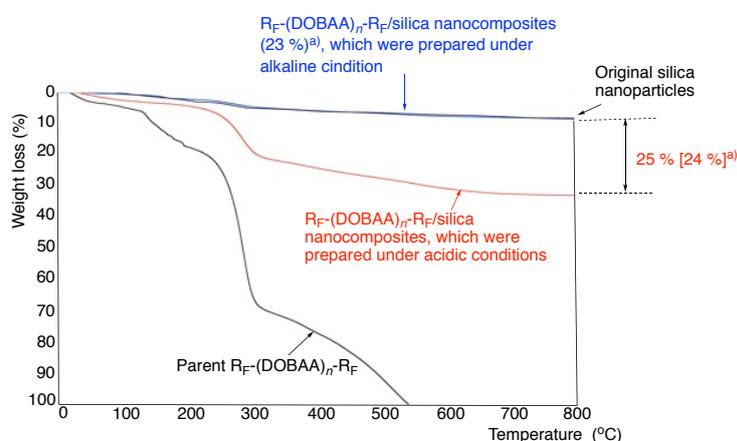
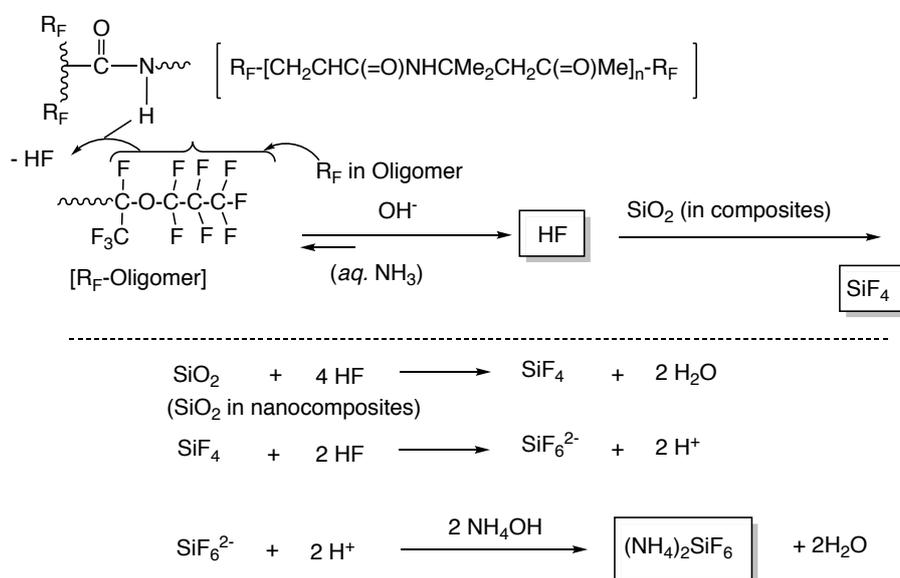


Figure 1. Thermogravimetric analyses of the parent R_F-(DOBAA)_n-R_F oligomer, R_F-(DOBAA)_n-R_F/silica nanocomposites, which were prepared under alkaline or acidic conditions, respectively. a) Oligomer content in composites determined by elementary analyses of fluorine

The nanocomposite reaction of R_F -(DOBAA) $_n$ - R_F oligomer with silica nanoparticles should proceed smoothly under alkaline conditions to afford not only the expected R_F -(DOBAA) $_n$ - R_F /silica

nanocomposite but also ammonium hexafluorosilicate as shown in the plausible reaction mechanism (see Scheme 2)⁵².



Scheme 2. Plausible reaction mechanism for the formation of ammonium hexafluorosilicate

The formation of ammonium hexafluorosilicate during the composite reactions can afford a nonflammable characteristic toward R_F -(DOBAA) $_n$ - R_F oligomer. That is, R_F -(DOBAA) $_n$ - R_F oligomer in nanocomposite should be encapsulated quite effectively into the nanometer size-controlled silica gel matrices through the molecular-level synergistic combination, which is due to not only the strong interaction between fluorine in oligomer and silicon in silica gel nanocomposite but also the effective interaction

between ammonium hexafluorosilicate and R_F -(DOBBA) $_n$ - R_F oligomer in silica gel matrices, to afford a nonflammable characteristic for oligomer⁵².

On the other hand, fluoroalkyl end-capped acrylic acid oligomer $[R_F$ -(ACA) $_n$ - R_F]/silica nanocomposites $[R_F$ -(CH₂CHCOOH) $_n$ - R_F /SiO₂], which were prepared under alkaline conditions, has been shown to exhibit a clear weight loss at 800 °C corresponding to the content of oligomer (see Figure 2)⁵⁴.

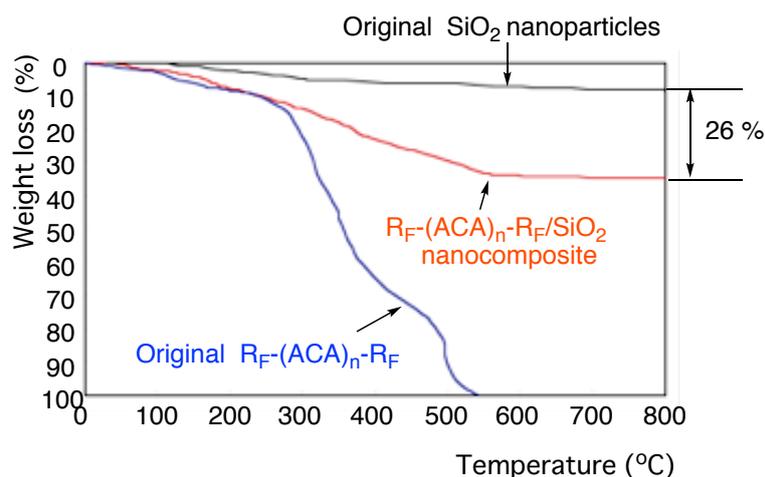


Figure 2. Thermogravimetric analyses of the parent $R_F-(ACA)_n-R_F$ oligomer and $R_F-(ACA)_n-R_F/silica$ nanocomposites, which were prepared under alkaline conditions

This weight loss behavior is due to no formation of ammonium hexafluorosilicate during the composite reactions, because fluoroalkyl end-capped acrylic acid oligomer possesses no higher acidic protons to form the ammonium hexafluorosilicate illustrated in Scheme 2. In fact, fluoroalkyl end-capped 2-methacryloyloxyethane sulfonic acid/silica nanocomposites

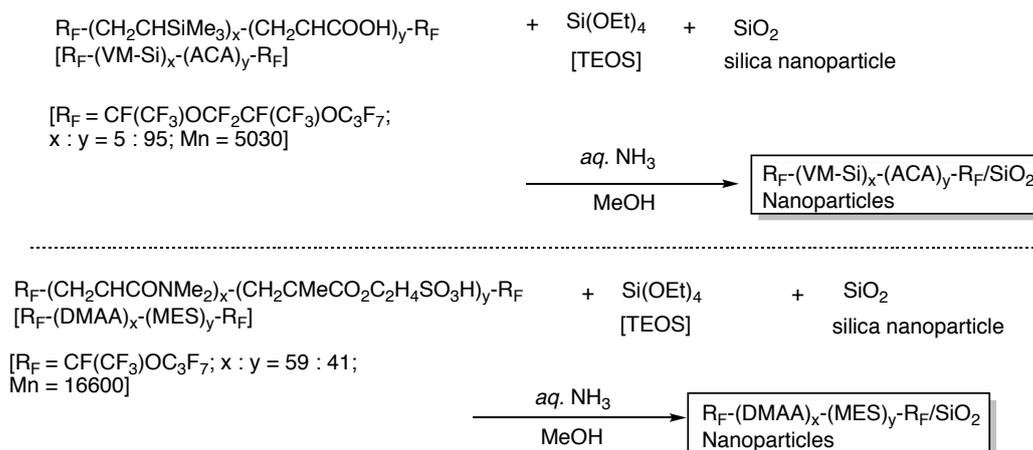
$[R_F-(CH_2CHMeCO_2CH_2CH_2SO_3H)_n-R_F/SiO_2]$, perfluoro-1,3-propanedisulfonic acid/silica $[HO_3SCH_2CH_2CH_2SO_3H/SiO_2]$ nanocomposites,

and fluoroalkyl end-capped oligomers containing carboxy groups possessing electron-withdrawing CF_3 units as neighboring groups

$[R_F-(CH_2-CMeCOOH)_x-(CH_2-CCF_3COOH)_y-R_F]$, of whose nanocomposites were prepared under alkaline conditions, respectively, can exhibit no weight loss behavior under the similar calcination conditions⁵².

In this way, fluoroalkyl end-capped oligomers containing amido protons or more acidic protons such as sulfo groups can exhibit a nonflammability, even after calcination at 800 °C, through the formation of ammonium hexafluorosilicate during nanocomposites reactions. In contrast, the lack of formation of ammonium hexafluoro-silicate during the usual composite reactions affords a flammable behavior for the $R_F-(DOBAA)_n-R_F$ oligomer or $R_F-(ACA)_n-R_F$ oligomer in silica nanocomposites⁵⁴.

Fluoroalkyl end-capped acrylic acid oligomer $[R_F-(ACA)_n-R_F]$ reacted with tetraethoxysilane (TEOS) and silica nanoparticles in the presence of low molecular weight aromatic compounds [**Ar-H**] such as cetylpyridinium chloride (CPC) and bisphenol AF under alkaline conditions to afford the $R_F-(ACA)_n-R_F/SiO_2$ nanocomposites-encapsulated **Ar-H** in excellent to moderate isolated yields (see Scheme 3)⁵¹.

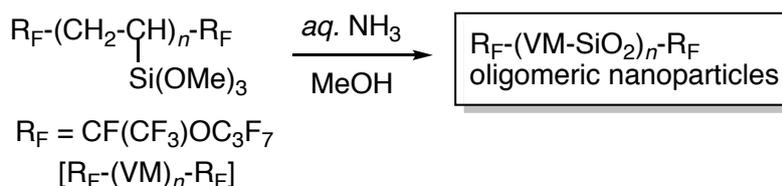


Scheme 5. Preparation of fluoroalkyl end-capped cooligomers/silica nanocomposites possessing an anti-HIV-1 activity.

$\text{R}_F\text{-(VM-Si)}_x\text{-(ACA)}_y\text{-R}_F\text{/SiO}_2$ nanocomposites were found to have a potent and selective anti-HIV-1 activity³². In contrast, $\text{R}_F\text{-(DMAA)}_x\text{-(MES)}_y\text{-R}_F\text{/SiO}_2$ nanocomposites were able to exhibit a potent and selective anti-SIV_{mac} (Simian Immunodeficiency Virus) activity³². Therefore, these fluorinated cooligomeric silica nanocomposites are expected to be widely applicable for not only antiviral polymeric drugs but also the fields of the materials science.

3. Preparation and surface wettability of fluoroalkyl end-capped vinyltrimethoxysilane oligomeric silica nanocomposites – encapsulated a variety of guest molecules

In numerous fluoroalkyl end-capped oligomers, fluoroalkyl end-capped vinyltrimethoxysilane oligomer [$\text{R}_F\text{-(CH}_2\text{CHSi(OMe)}_3)_n\text{-R}_F$; $\text{R}_F = \text{CF(CF}_3\text{)OC}_3\text{F}_7$, $n = 2, 3$: $\text{R}_F\text{-(VM)}_n\text{-R}_F$ oligomer] is of particular interest due to them exhibiting the higher surface activity and the good adhesion ability compared with those of the traditional monomeric fluoroalkylated silane coupling agents [$\text{R}_F\text{-CH}_2\text{CH}_2\text{Si(OMe)}_3$; $\text{R}_F =$ longer fluoroalkyl chains]⁷³. $\text{R}_F\text{-(VM)}_n\text{-R}_F$ oligomer can undergo the sol-gel reactions under alkaline conditions to afford the corresponding fluorinated oligomeric silica nanoparticles [$\text{R}_F\text{-(CH}_2\text{CHSiO}_2)_n\text{-R}_F$; $\text{R}_F = \text{CF(CF}_3\text{)OC}_3\text{F}_7$, $n = 2, 3$: $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F$ oligomer nanoparticles] in good isolated yields (see Scheme 6)⁷⁴.



Scheme 6. Preparation of $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F$ oligomeric nanocomposites

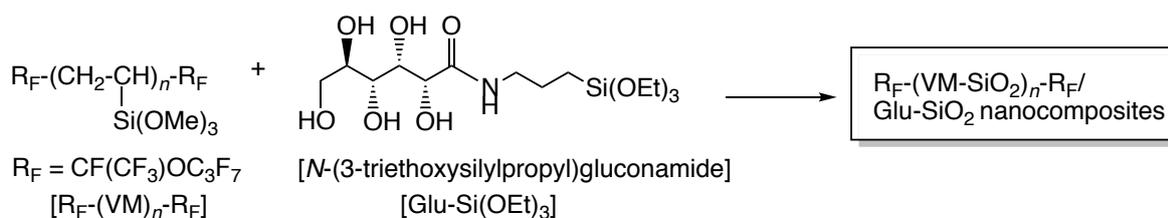
Especially, $R_F-(VM)_n-R_F$ oligomer also form the self-assembled molecular aggregates with the aggregation of the terminal fluoroalkyl segments, and a variety of organic and inorganic guest molecules can be effectively encapsulated into such oligomeric aggregates cores, and successively the sol-gel reactions under alkaline conditions derive the tightly encapsulated guest molecules into fluorinated oligomeric nanocomposite cores.

$R_F-(VM-SiO_2)_n-R_F$ oligomeric nanoparticles are applicable to the surface modification of glass to provide not only a good oleophobicity but also a completely superhydrophobic characteristic (a water contact angle: 180°) with a non-wetting property against water droplets⁷⁴. Furthermore, it was clarified that superoleophobic/superhydrophobic (superamphiphobic), superoleophobic/superhydrophilic and superoleophilic/superhydrophobic surfaces can be easily created by using $R_F-(VM)_n-R_F$ oligomer as a key material. In addition, such unique surfaces have been applied to the separation of

oil and water. These findings will be demonstrated in detail in the following section (3.1 ~ 3.4).

3-1. Creation of superoleophobic/superhydrophobic surface

The fabrication of superoleophobic surface is in general difficult due to the lower surface tension of oils than that of water. Thus, a superoleophobic surface can be realized by lowering the surface energy and enhancing the surface roughness^{75 ~ 81}. From this point of view, fluoroalkyl end-capped oligomeric silica nanocomposites containing gluconamide units [$R_F-(VM-SiO_2)_n-R_F/Glu-SiO_2$] have been prepared by the sol-gel reaction of the corresponding oligomer [$R_F-(CH_2-CHSi(OMe)_3)_n-R_F$ ($R_F-(VM)_n-R_F$)] in the presence of *N*-(3-triethoxysilylpropyl)gluconamide [$Glu-Si(OEt)_3$] under alkaline conditions (see Scheme 7)⁸².



Scheme 7. Preparation of $R_F-(VM-SiO_2)_n-R_F/Glu-SiO_2$ nanocomposites

These obtained nanocomposites were applied to the surface modification of glass to provide the unique wettability such as superoleophobic/superhydrophobic characteristics on the modified glass surface. Such superoleophobic/superhydrophobic characteristic was also observed on the modified PET (polyethylene

terephthalate) fabric swatch, which were prepared under similar conditions, and this modified PET fabric swatch was applied to the separation membrane for the separation of the mixture of fluorocarbon oil and hydrocarbon oil (see Figure 3)⁸².

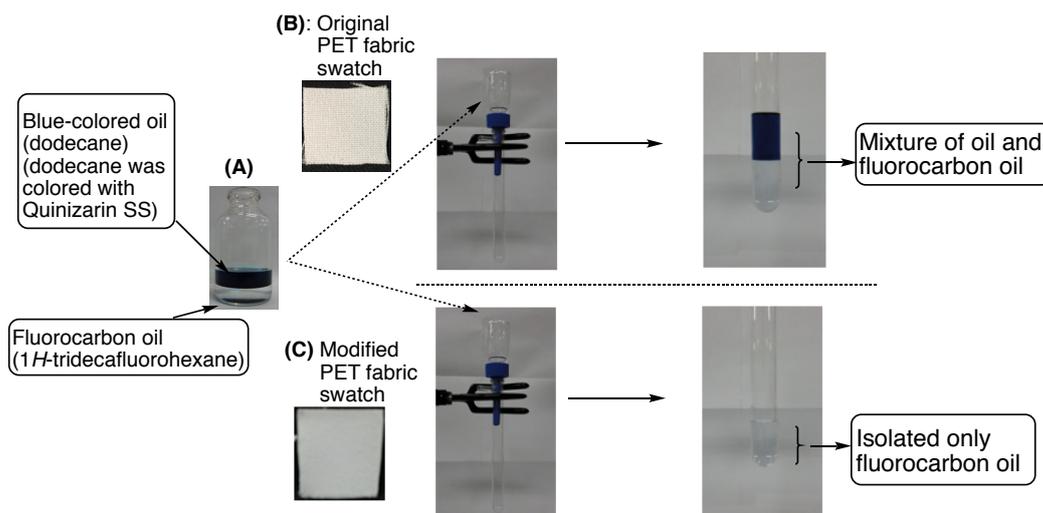
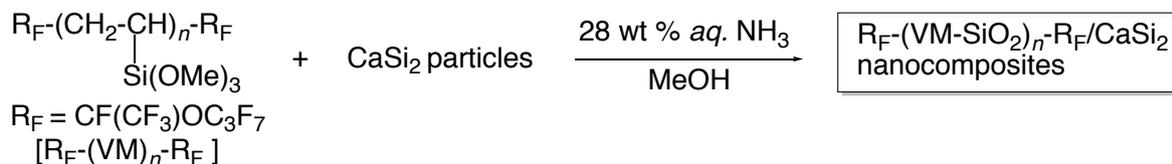


Figure 3. Separation of the mixture **(A)** of blue-colored hydrocarbon oil (dodecane) and fluorocarbon oil (1H tridecafluorohexane) by using the original PET fabric swatch **(B)** and the modified PET fabric swatch treated with the $R_F-(VM-SiO_2)_n-R_F/Glu-SiO_2$ nanocomposites **(C)** as the separation membrane, respectively

3-2. Creation of superoleophobic/superhydrophilic surface

Usually, inorganic and organic materials such as ceramics, polystyrene and poly (tetrafluoroethylene) can provide hydrophilic-oleophilic, hydrophobic – oleophilic and hydrophobic – oleophobic characteristics, respectively⁸³. Based on the surface free energy diagram of these materials, we have some difficulties to develop the materials possessing both hydrophilic and oleophobic characteristics⁸⁴. A highly oleophobic (superoleophobic) surface

is realized by lowering the surface energy and enhancing the surface roughness^{67, 75, 79, 85 – 87}. The fabrication of the superoleophobic surface is in general difficult due to the lower surface tension of oils than that of water. From this point of view, we have prepared the fluoroalkyl end-capped vinyltrimethoxysilane oligomer/calcium silicide nanocomposites $[R_F-(VM-SiO_2)_n-R_F/CaSi_2]$ by the sol-gel reactions of the corresponding oligomer in the presence of calcium silicide particles under alkaline conditions (see Scheme 8)⁶⁷.



Scheme 8. Preparation of $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites

The contact angles of dodecane on the modified glass surfaces treated with the $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites showed large values: 118° , of whose value can exhibit superoleophobic characteristic imparted by fluoroalkyl segments in the composites⁶⁷. On the other hand, interestingly, a steep time dependence of water contact angle was observed in the $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites. The water contact angles decreased smoothly from 129° to 0° over 5 min to give a superhydrophilicity on the modified surfaces⁶⁷. This finding suggests that at the interface with water, hydrophobic fluoroalkyl segments are replaced by the hydrophilic $CaSi_2$ particle surface, of whose parent particles can exhibit the water contact angle: 0° on the modified surface. It takes about only 5 min to replace the fluoroalkyl segments by the $CaSi_2$

units when the environment is changed from air to water.

The dodecane contact angle value on the parent polyester (PET) fabric swatch is 0° . However, the modified PET fabric swatch treated with the $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites was found to exhibit the dodecane and water contact angle values: 105° and 0° (the water contact angles decreased smoothly from 85° to 0° over 5 min.), respectively. This finding suggests that these modified surfaces can exhibit the superoleophobic and superhydrophilic characteristic. Thus, we tried to separate the mixture of oil (dodecane) and water (water was red-colored with Rhodamine B illustrated in Figure 4) by using the modified PET fabric swatch as the liquid-liquid separation membranes, and the result was shown in Figure 5⁶⁷.

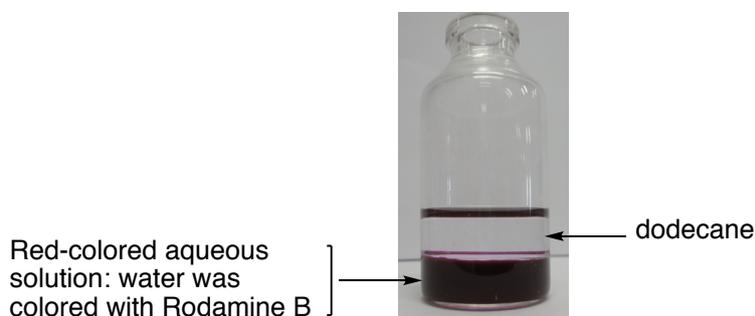


Figure 4. Photograph of the mixture of dodecane and red-colored aqueous solution

Figure 5 shows that the modified PET fabric swatch can be used for the effective separation of water and oil (dodecane), and only red-colored water has been removed under atmospheric pressure (see Figure 5-(B),

although we cannot use the parent PET fabric swatch as the water – dodecane separation membrane under the similar conditions (see Figure 5-(A))⁶⁷.

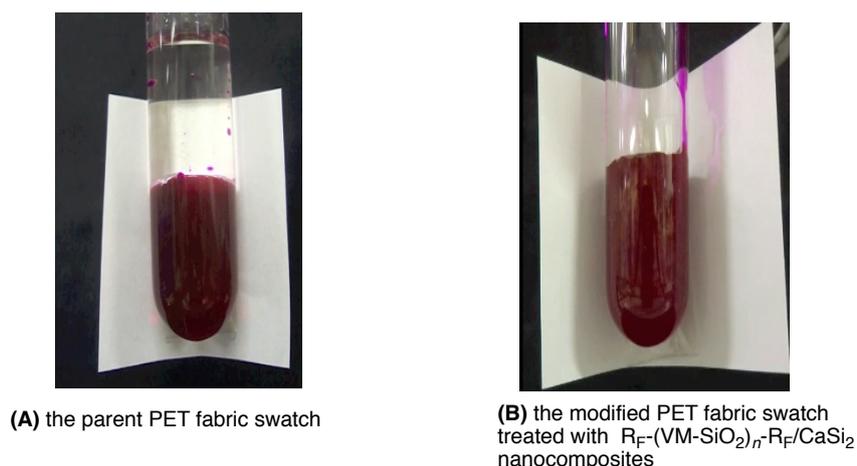
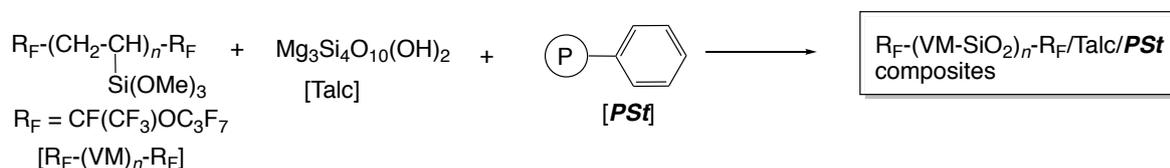


Figure 5. Separation of oil (dodecane)/water (red-colored aqueous solution) by using the parent PET fabric swatch (A) and the modified PET fabric swatch treated with the $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites (B) under atmospheric conditions

3-3. Creation of superoleophilic/superhydrophobic surface

Superhydrophobic surfaces, characterized by a water contact angle greater than 150° , have been comprehensively studied due to their possessing superior water repellency and self-cleaning property. In general, superoleophilic surfaces have a strong affinity of organic oils. Thus, the surfaces possessing a superoleophilic/superhydrophobic characteristic can simultaneously repels water and strongly

absorbs oils. Such interesting behavior has been applied to the oil-water separating membranes and self-cleaning surface^{87 ~ 90}. Fluoroalkyl end-capped vinyltrimethoxysilane oligomer [$R_F-(VM)_n-R_F$] has been developed to the creation of such unique wettability. In fact we have succeeded in the preparation of the $R_F-(VM-SiO_2)_n-R_F/talc/cross-linked$ polystyrene particles (**Pst**: average particle size: $92 \mu m$) into the $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposite cores as shown in Scheme 9⁹¹.



Scheme 9. Preparation of $R_F-(VM-SiO_2)_n-R_F/Talc/PSt$ composites

The $R_F-(VM-SiO_2)_n-R_F/Talc/Pst$ nanocomposites can show a superoleophilic/superhydrophobic characteristic on the modified surface, because the dodecane and water contact angles are 0 and 180° , respectively. Thus, we

tried to apply the $R_F-(VM-SiO_2)_n-R_F/talc/Pst$ nanocomposites to the packing material for the column chromatography⁹¹.

The surfactant (span 80)-stabilized water-in-oil

(W/O) emulsion was prepared under ultrasonic conditions for 5 min at room temperature. The R_F -(VM-SiO₂)_n-R_F/Talc/**PSt** nanocomposite powders (particle size: 21 μm) were applied to the separation of W/O emulsion. This nanocomposite was effective to separate the fresh W/O emulsion under reduced pressure to isolate the colorless oil (1,2-dichloroethane). We tried to study on the reusability of the

present composite particles as the packing material, and the colorless oil was quantitatively isolated under similar conditions even after using the W/O emulsion three times. In contrast, the silica gel (Wakogel^{TR} C-500HG: average particle size: 22 μm), which is well known as the packing material, was unable to separate the W/O emulsion under similar conditions (see Figure 6)⁹¹.

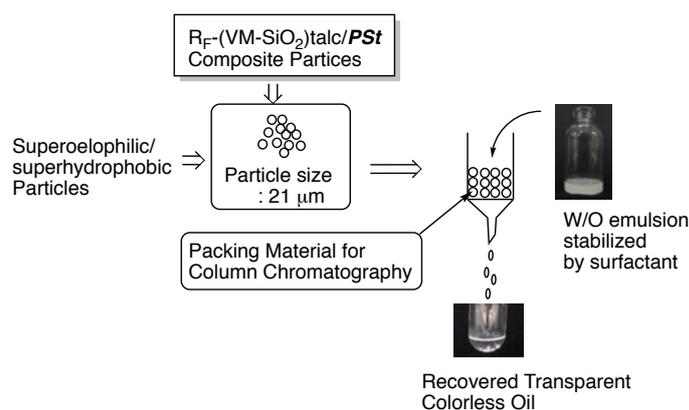
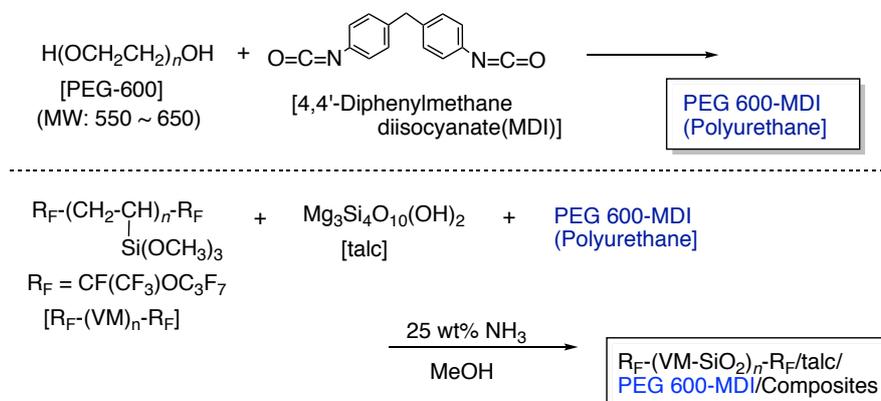


Figure 6. Schematic illustration of the isolation of the transparent colorless oil through the separation of W/O emulsion by the R_F -(VM-SiO₂)_n-R_F/talc/**PSt** composite powders as the packing material for the column chromatography

Similarly, fluoroalkyl end-capped vinyltrimethoxysilane oligomer [R_F -(VM)_n-R_F] has been also applied to the preparation of the corresponding fluorinated oligomeric silica/talc/

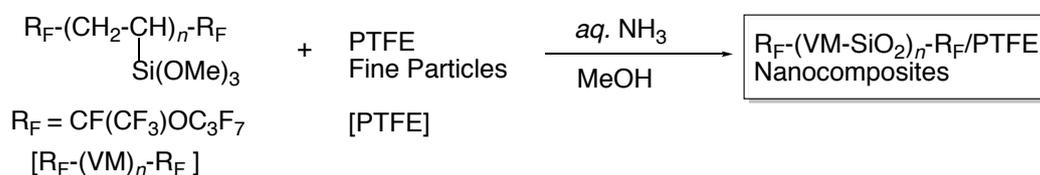
polyurethane composites [R_F -(VM-SiO₂)_n-R_F/talc/PEG600-MDI] as shown in Scheme 10⁹².



Scheme 10. Preparation of fluorinated oligomeric silica/talc/polyurethane composites [R_F -(VM-SiO₂)_n-R_F/talc/PEG600-MDI]

However, the modified surface treated with the composites was found to give not a superoleophilic/superhydrophobic but superoleophobic/superhydrophilic characteristic⁹². The composite powders were applied to the packing material for the separation of O/W (oil in water) emulsion, which was stabilized by SDS (sodium dodecyl sulfate)⁹². Especially, it was also demonstrated that this composite powder has a good reusability even after three cycle for the isolation of the transparent colorless water⁹².

From the developmental viewpoints of new fluorinated functional materials, it is of



Scheme 11. Preparation of R_F-(VM-SiO₂)_n-R_F/PTFE nanocomposites

Interestingly, the modified glass surface treated with the obtained nanocomposites was found to exhibit a superoleophilic/superhydrophobic characteristic, although the modified glass surface treated with the parent PTFE particles and the R_F-(VM)_n-R_F oligomeric silica nanoparticles [R_F-(VM-SiO₂)_n-R_F] can provide the usual oleophobic/hydrophobic and oleophobic/superhydrophobic properties, respectively⁹³. More interestingly, these fluorinated PTFE nanocomposites were applied to the packing material for the column chromatography to separate not only the mixture of water and oil but also water-in-oil (W/O) emulsions. The reusability of the present nanocomposite particles as the packing material is also studied, and the colorless oil was quantitatively isolated under similar conditions even after the use of the W/O emulsions three times⁹³.

particular interest to encapsulate not only cross-linked polystyrene particles (**PSt**) or polyurethane but also other polymeric guest molecules such as poly(tetrafluoroethylene) [PTFE] fine particles into the fluoroalkyl end-capped vinyltrimethoxysilane oligomeric silica nanoparticle cores. Fluoroalkyl end-capped vinyltrimethoxysilane oligomer can undergo the sol-gel reactions in the presence of PTFE fine particles under alkaline conditions to afford the corresponding fluorinated oligomeric silica/PTFE nanocomposites (see Scheme 11)⁹³.

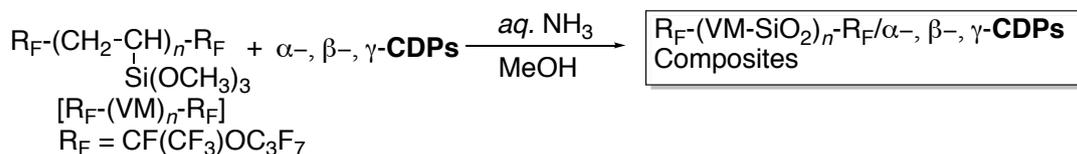
3-4. Application of the adsorption of low molecular weight compounds by the use of fluoroalkyl end-capped vinyltrimethoxysilane oligomeric composites possessing a superoleophilic/superhydrophobic characteristic

Cyclodextrins have been predominantly used for the stabilization, solubilization and formulation of drugs, in the food industrial and for the separation of the isomers and analogs in analytical chemistry⁹⁴. However, cyclodextrins possess a solubility toward water, limiting its reusability as the adsorbent for these compounds. Therefore, it is deeply desirable to develop the water-insoluble cyclodextrin polymers. In fact, there have been a variety of reports on the synthesis of the water-insoluble cyclodextrin polymers by the use of epichlorohydrin and diisocyanates as the crosslinking

agents, so far⁹⁵). These water-insoluble cyclodextrin polymers thus obtained have been applied to the adsorbents for the organic pollutants such as phenol, *p*-nitrophenol, benzoic acid, *p*-nitrobenzoic acid, 4-*t*-butylbenzoic acid, and bisphenol A⁹⁶).

We have recently found that R_F-(VM)_{*n*}-R_F oligomer can undergo the composite reactions in the presence of micrometer size-controlled macromolecular particles such as α-, β- and γ-cyclodextrins polymers (α-, β-, γ-**CDPs**) under alkaline conditions to afford the corresponding R_F-(VM-SiO₂)_{*n*}-R_F/**CDPs** composites (see Scheme 12)⁹⁷). Interestingly, these obtained composites can provide a superoleophilic/superhydrophobic characteristic on the modified surface, and these composites particle powders are also applicable to the packing material for the column chromatography to

separate not only the mixtures of oil and water but also the water-in-oil (W/O) emulsions⁹⁷). More interestingly, these composites were found to have an effective adsorption ability of low molecular weight aromatic compounds such as bisphenol A and bisphenol F in their aqueous solutions, and the highest adsorption ability was observed in the R_F-(VM-SiO₂)_{*n*}-R_F/β-**CDP** composites⁹⁷). The adsorption ability of the present composites toward such aromatic compounds was superior to that of the original β-**CDP** under similar conditions⁹⁷). In addition, it was demonstrated that a variety of volatile organic compounds such as benzene, toluene and xylenes can be more effectively adsorbed by using the R_F-(VM-SiO₂)_{*n*}-R_F/**CDPs** composites, compared to that of the original **CDPs**⁹⁷).



Scheme 12. Preparation of R_F-(VM-SiO₂)_{*n*}-R_F/α-, β-, γ-**CDPs** nanocomposites

4. Conclusion

Fluoroalkyl end-capped oligomers can undergo the sol-gel reaction in the presence of tetraethoxysilane and silica nanoparticles under alkaline conditions to afford the corresponding fluorinated oligomers/silica nanocomposites. In these fluorinated nanocomposites, fluoroalkyl end-capped oligomers possessing carboxy groups/silica nanocomposites can exhibit a potent and selective anti-HIV-1 activity, and fluoroalkyl end-capped oligomers possessing amide protons or sulfo groups/silica nanocomposites were found to exhibit no weight loss

behavior corresponding to the contents of the oligomer in the silica composite cores even after calcination at 800 °C. Similarly, fluoroalkyl end-capped vinyltrimethoxysilane oligomer was applied to the preparation of the corresponding fluorinated oligomeric silica nanocomposites through the sol-gel reaction under alkaline conditions. A variety of guest molecules have been effectively encapsulated into such fluorinated oligomeric composite cores to produce the fluorinated oligomeric silica/guest molecules composites. Interestingly, it was demonstrated that the surface wettability

treated with these composites can be easily controlled by changing the structure of these guest molecules. Therefore, these fluorinated composites illustrated in this work will have high potential for new fluorinated functional materials into a wide variety of fields.

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