

# Preparation and Applications of Novel Fluoroalkyl End-Capped Sulfonic Acid Oligomers–Silica Gel Polymer Hybrids

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**ABSTRACT:** Fluoroalkyl end-capped 2-methacryloxyethanesulfonic acid homo-oligomer [R<sub>F</sub>-(MES)<sub>n</sub>-R<sub>F</sub>] and 2-methacryloxyethanesulfonic acid-*N,N*-dimethylacrylamide co-oligomers [R<sub>F</sub>-(MES)<sub>x</sub>-(DMAA)<sub>y</sub>-R<sub>F</sub>] reacted with tetraethoxysilane (TEOS) under acidic conditions to afford R<sub>F</sub>-(MES)<sub>n</sub>-R<sub>F</sub> homo-oligomer-SiO<sub>2</sub> polymer hybrid and R<sub>F</sub>-(MES)<sub>x</sub>-(DMAA)<sub>y</sub>-R<sub>F</sub> co-oligomer-SiO<sub>2</sub> polymer hybrid, respectively. Thermogravimetric-mass spectra showed that the thermal stability of R<sub>F</sub>-(MES)<sub>n</sub>-R<sub>F</sub> homo-oligomer-SiO<sub>2</sub> polymer hybrid was superior to that of traditionally well-known perfluorinated ion exchange polymers such as Nafion 112 (TR). The sol solutions of the fluorinated co-oligomer-SiO<sub>2</sub> polymer hybrid were applied to the surface modification of glass to exhibit not only a strong oleophobicity imparted by fluorine but also a good hydrophilicity on the glass surface. On the other hand, R<sub>F</sub>-(MES)<sub>x</sub>-(DMAA)<sub>y</sub>-R<sub>F</sub> co-oligomer reacted with TEOS in the presence of a variety of silica nanoparticles (mean diameters: 11–95 nm) under alkaline conditions to afford fluoroalkyl

end-capped oligomers–silica nanoparticles (mean diameters: 32–173 nm) with a good dispersibility and stability in methanol. Similarly, a variety of fluorinated oligomers containing sulfo groups–silica nanoparticles were prepared by the homo- and co-oligomerizations of fluoroalkanoyl peroxides with 2-methacryloxyethane sulfonic acid (MES) and comonomers such as *N,N*-dimethylacrylamide (DMAA) and acryloylmorpholine (ACMO) in the presence of silica nanoparticles. Interestingly, these isolated fluorinated particle powders were found to afford nanometer size-controlled colloidal particles with a good redispersibility and stability in aqueous and organic media such as methanol. These fluorinated nanoparticles containing sulfo groups were also applied to an excellent heterogeneous catalyst for Bronsted acid-catalyzed transformations. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 110–117, 2007

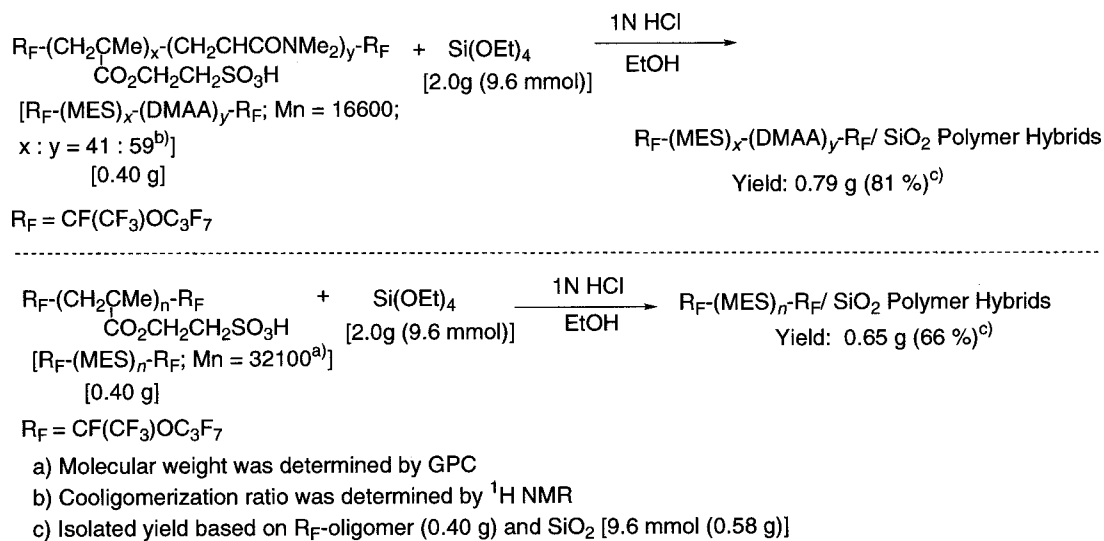
**Key words:** fluoropolymers; nanoparticles; silicas; thermal properties

## INTRODUCTION

Organic–inorganic hybrid materials constitute a class of material with properties of great technological interest.<sup>1</sup> In particular, considerable efforts have been devoted to the studies involving hybrids based on blends of silica and organic polymers dispersed at a molecular level for the aim of the development of high-performance thermal-resistant materials such as abrasives and coatings.<sup>2,3</sup> For example, polystyrene–SiO<sub>2</sub> nanocomposites have been prepared through miniemulsion polymerization by using sodium lauryl sulfate surfactant, hexadecane costabilizer in the presence of silica particles coated with methacryloxy(propyl)trimethoxysilane.<sup>4</sup> It was suggested that these organic polymers–SiO<sub>2</sub> hybrid particles are potentially

useful in the areas of coatings, electronics, catalysis, and diagnostics.<sup>4</sup> Very recently, perfluorinated sulfonic acids have been immobilized into mesoporous silica frameworks, and these mesoporous silica–perfluorosulfonic acid hybrids have also been shown to be excellent catalysts for Bronsted acid-catalyzed reactions.<sup>5</sup> Hitherto, there has been increasing interest in the material sciences toward the development of partially fluoroalkylated polymeric compounds, which exhibit various unique properties such as surface active properties and nanometer size-controlled self-assembled molecular aggregates, which cannot be achieved by the corresponding nonfluorinated and randomly fluoroalkylated ones.<sup>6–12</sup> Therefore, it is of particular interest to prepare novel fluoroalkyl end-capped oligomers containing sulfo groups–silica gel polymer hybrids from the developmental viewpoint of not only new organofluorine functional materials but also fluorinated hybrid catalytic systems. In this article, we would like to report on the preparation and applications of fluoroalkyl end-capped sulfonic

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Scheme 1

acid oligomers–silica gel polymer hybrids, with emphasis on the applications to the catalysts for Brnsted acid-catalyzed transformations.

## EXPERIMENTAL

### Measurements

Molecular weights were measured using a Shodex DS-4 (pump) and Shodex RI-71 (detector) gel permeation chromatography (GPC) calibrated with standard poly (ethylene glycol) using  $0.2 \text{ mol dm}^{-3}$   $\text{Na}_2\text{HPO}_4$  solution as the eluent. NMR spectra and gas chromatography were measured using a Varian Unity-plus 500 (500 MHz) spectrometer and Shimadzu GC-8A, respectively. Contact angles were measured by the use of the goniometer type contact angle meter (ERMA G-1-1000). Fourier transform infrared (FTIR) spectra and dynamic light-scattering (DLS) measurements were measured using a Shimadzu FTIR-8400 FT-IR spectrophotometer (Kyoto, Japan) and Otsuka Electronics Co., Ltd. (DLS-7000 HL; Tokyo, Japan), respectively. Thermal analyses were recorded on a Rigaku Denki TG8101 D differential thermobalance. Thermogravimetric–mass spectra (TG–MASS) analyses were measured by using Rigaku Thermo Plus TGS 120.

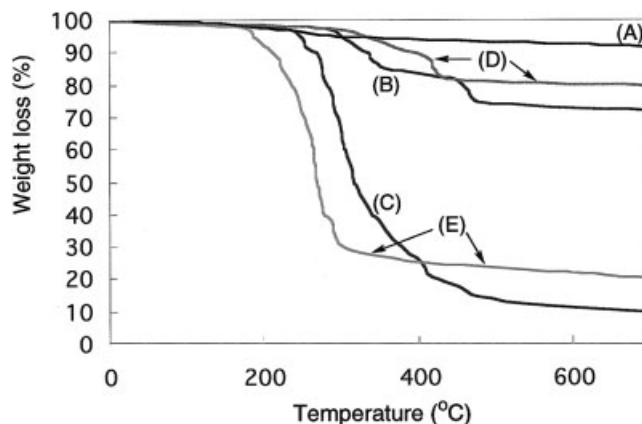
### Materials

2-Methacryloxyethanesulfonic acid (MES), *N,N*-dimethylacrylamide (DMAA), and acryloylmorpholine (ACMO) were used as received from NOF Corporation (Tokyo, Japan) and Kohjin Co., Ltd. (Tokyo, Japan), respectively. Nafion-112 was purchased from Sigma Aldrich Japan Co. (Tokyo, Japan). Tetraethoxysilane, tetraallyltin, and benzaldehyde were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Fluoro-

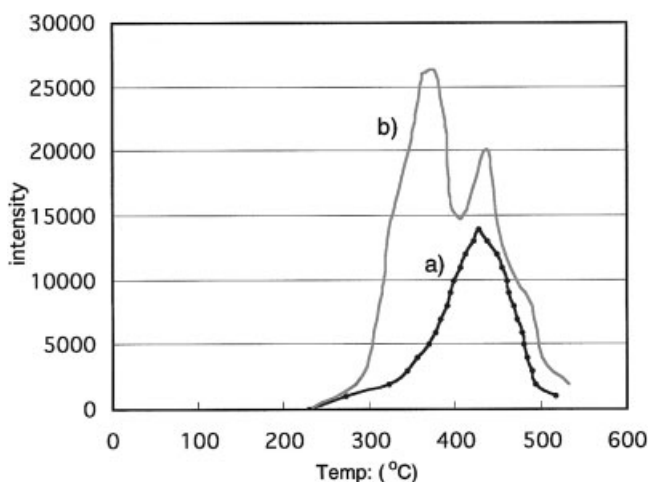
alkyl end-capped 2-methacryloxyethane sulfonic acid homo-oligomer [ $\text{R}_F\text{-(MES)}_n\text{-R}_F$ ] and 2-methacryloxyethane sulfonic acid–*N,N*-dimethylacrylamide co-oligomer [ $\text{R}_F\text{-(MES)}_x\text{(DMAA)}_y\text{-R}_F$ ] were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding monomers according to our previously reported methods.<sup>13</sup>

### Preparation of fluoroalkyl end-capped oligomers–silica gel polymer hybrids

In an ethanol solution, 5 mL of  $\text{R}_F\text{-(MES)}_x\text{(DMAA)}_y\text{-R}_F$  [ $\text{R}_F = \text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ;  $x : y = 41 : 59$ ;  $\text{Mn} = 16,600$  (0.40 g)] were dissolved in tetraethoxysilane (TEOS; 2.0 g) and aqueous 1N HCl (1.0 g). The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. After the removal of the solvent, a transparent homogeneous hybrid was obtained. This glassy



**Figure 1** Thermogravimetric analyses of (A)  $\text{SiO}_2$ , (B)  $\text{R}_F\text{-(MES)}_n\text{-R}_F\text{-SiO}_2$  polymer hybrid, (C)  $\text{R}_F\text{-(MES)}_n\text{-R}_F$  homo-oligomer, (D)  $\text{R}_F\text{-(MES)}_x\text{(DMAA)}_y\text{-R}_F\text{-SiO}_2$  polymer, and (E)  $\text{R}_F\text{-(MES)}_x\text{(DMAA)}_y\text{-R}_F$  co-oligomer.



**Figure 2** TGA-MASS analyses for the extrusion of  $\text{SO}_2$  in the pyrolysis of (a)  $\text{R}_F\text{-(MES)}_n\text{-R}_F\text{-SiO}_2$  polymer hybrids and (b) Nafion 112.

silica gel was purified by Soxhlet extraction with mixed solvents of water and ethanol [4 : 1 (v/v)] to afford the expected fluorinated polymer hybrid (0.79 g).

#### Contact angle measurements

The glass plates ( $10 \times 10 \text{ mm}^2$  pieces) were dipped into the sol ethanol solutions of  $\text{R}_F\text{-(MES)}_x\text{-(DMAA)}_y\text{-R}_F\text{-silica gel}$  polymer hybrid at room temperature and left for 5 min. They were lifted from the solution at a constant rate of 0.5 mm/min and subjected to heat treatment for 30 min at  $50^\circ\text{C}$ . After the heat treatment, the contact angles of water and dodecane for these glass plates were measured.

#### Preparation of fluoroalkyl end-capped MES-DMAA co-oligomer-silica nanoparticles

To a methanol solution (20 mL) of fluoroalkyl end-capped MES-DMAA co-oligomer [ $\text{R}_F\text{-(MES)}_x\text{-(DMAA)}_y\text{-R}_F$ ;  $\text{R}_F = \text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$  (0.20 g)] were added TEOS (0.9 mmol), silica nanoparticle methanol solution (30% (wt.): 1.33 g; average particle size: 11 nm [Methanol Silica-sol (TR): Nissan Chemical Industrials Ltd., Tokyo, Japan], and 25% aqueous ammonia solution (0.20 mL). The mixture was stirred with a magnetic stirring bar at room temperature for 2 h. After the solvent was evaporated off, to the obtained crude products was

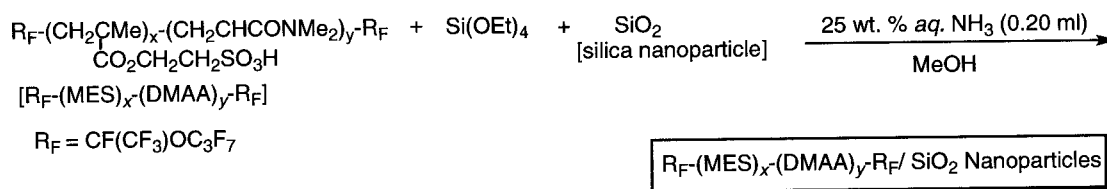
added methanol (25 mL). The methanol solution was stirred with magnetic stirring bar at room temperature for 2 days, then centrifuged for 30 min. The expected fluorinated nanoparticles were easily separated from the methanol solution. Fluorinated nanoparticle powders thus obtained were dried *in vacuo* at  $50^\circ\text{C}$  for 2 days to afford purified particle powders (0.31 g). The purified fluorinated nanoparticle powders were added to fresh methanol and were stirring with magnetic stirring bar at room temperature for 1 day to afford fluorinated fine colloidal nanoparticles with a good re-dispersibility and stability in methanol.

#### Reactions of fluoroalkanoyl peroxide with MES in the presence of silica nanoparticles

Perfluoro-2-methyl-3-oxahexanoyl peroxide (3.1 mmol) in 1 : 1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane (120 g) was added to MES (13.6 mmol) and silica nanoparticle aqueous solution (20 wt. %: 2.50 g; average particle size: 12 nm; Nissan Chemical Industrials Ltd.). The heterogeneous solution was stirred at  $45^\circ\text{C}$  for 5 h under nitrogen. After the solvent was evaporated off, to the obtained crude products was added methanol (25 mL). The methanol solution was stirred with magnetic stirring bar at room temperature for 1 day, then centrifuged for 30 min. The expected fluorinated nanoparticles were easily separated from the methanol solution. These fluorinated nanoparticles were also dispersed into methanol, then centrifuged for 30 min. Fluorinated nanoparticle powders thus obtained were dried *in vacuo* at  $50^\circ\text{C}$  for 2 days to afford purified particle powders (0.35 g).

#### Reactions of tetraallyltin with benzaldehyde in the presence of fluorinated co-oligomeric silica nanoparticles

To a mixture of  $\text{R}_F\text{-(MES)}_x\text{-(DMAA)}_y\text{-R}_F\text{-SiO}_2$  nanoparticles (particle size: 409 nm; 50 mg) and benzaldehyde (0.1 mmol) in tetrahydrofuran (0.5 mL) was added tetraallyltin (0.1 mmol) in tetrahydrofuran (0.5 mL) at room temperature. The mixture was stirred for 24 h at this temperature, then centrifuged for 30 min. The tetrahydrofuran layer was analyzed by the use of gas chromatography to afford the corresponding



Scheme 2

TABLE I  
Preparation of  $R_F-(MES)_x-(DMAA)_y-R_F$ -Silica Nanoparticles

$R_F-(MES)_x-(DMAA)_y-R_F$	TEOS (g)	30% SiO <sub>2</sub> nanoparticle MeOH solution (g, size of particle)	$R_F-(MES)_x-(DMAA)_y-R_F$ -SiO <sub>2</sub> nanoparticles Yield <sup>a</sup> (%)
0.20 g	0.19 g (0.9 mmol)	1.33 g, 11 nm	48
0.20 g	0.19 g (0.9 mmol)	1.33 g, 45 nm	44
0.20 g	0.19 g (0.9 mmol)	1.33 g, 95 nm	39

<sup>a</sup> Isolated yield based on oligomer (0.20 g), SiO<sub>2</sub> [(0.9 mmol) (0.05 g)], and SiO<sub>2</sub> nanoparticle (0.40g).

homoallylic alcohol (97%). In this reaction,  $R_F-(MES)_x-(DMAA)_y-R_F$ -SiO<sub>2</sub> nanoparticle catalyst could be easily recovered and reused. These results are shown in Scheme 4.

## RESULTS AND DISCUSSION

In an ethanol solution of fluoroalkyl end-capped MES-DMAA co-oligomer  $R_F-(MES)_x-(DMAA)_y-R_F$  [ $R_F = CF(CF_3)OC_3F_7$ ] were added TEOS and aqueous 1N HCl. The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. After the removal of the solvent, a transparent homogeneous hybrid was obtained. This glassy silica gel was purified by Soxhlet extraction with mixed solvents of water and methanol to afford the expected fluoroalkyl end-capped MES-DMAA co-oligomer-SiO<sub>2</sub> polymer hybrid in 81% isolated yield. Similarly, we have succeeded in preparing fluoroalkyl end-capped MES homo-oligomer-SiO<sub>2</sub> polymer hybrid in 66% isolated yields after the purification of the crude products with the Soxhlet extraction. These results are shown in Scheme 1.

It is well known that the incorporation of organic commodity polymers into a silica glass causes phase separation and the composite glass becomes turbid. However, our present fluoroalkyl end-capped MES-DMAA co-oligomers and MES homo-oligomer-silica gel polymer hybrids are transparent and have no phase separation. Furthermore, the carbonyl stretching band of  $R_F-(MES)_x-(DMAA)_y-R_F$  co-oligomer was shifted from 1,728 to 1,717 cm<sup>-1</sup> by the hybridization. A similar lower-wavelength-number region shift of the carbonyl stretching band from 1,724 to 1,717 cm<sup>-1</sup> was also observed in fluoroalkyl end-capped MES homo-oligomer. These findings suggest that molecular-level combination, which is due to not only the interaction between the carbonyl groups in oligomers and residual silanol groups through the intermolecular hydrogen bonding but also the esterification between the sulfo groups and the residual silanol groups, has been accomplished.

Thermal stability of fluoroalkyl end-capped MES homo- and co-oligomers-silica gel polymer hybrids was studied by the use of thermogravimetric analyses (TGAs), in which the weight loss of these hybrids were

measured by raising the temperature around to 700°C, and the results are shown in Figure 1.

As shown in Figure 1,  $R_F-(MES)_n-R_F$  oligomers-SiO<sub>2</sub> polymer hybrids and  $R_F-(MES)_x-(DMAA)_y-R_F$  co-oligomer-SiO<sub>2</sub> polymer hybrid lost 10% of their weights around 332°C and 393°C under nitrogen, respectively. In contrast, thermal stability of the parent fluorinated oligomers was found to decrease significantly compared to the corresponding fluorinated polymer hybrids. The content of fluorinated oligomers in the fluorinated hybrids was estimated by the use of TGAs for the weight loss of the fluorinated hybrids (Fig. 1B and D), in comparison with those of the parent oligomers (Fig. 1C and E) and silica gel (Fig. 1A). The contents of oligomers in the hybrids were as follows:  $R_F-(MES)_x-(DMAA)_y-R_F$ , 12%;  $R_F-(MES)_n-R_F$ , 19%.

Furthermore, thermal stability of fluorinated MES homo-oligomer-silica gel polymer hybrid was also studied by using TG-MASS analyses. Thermal stability of Nafion 112 was also studied under similar conditions for comparison. These results are shown in Figure 2.

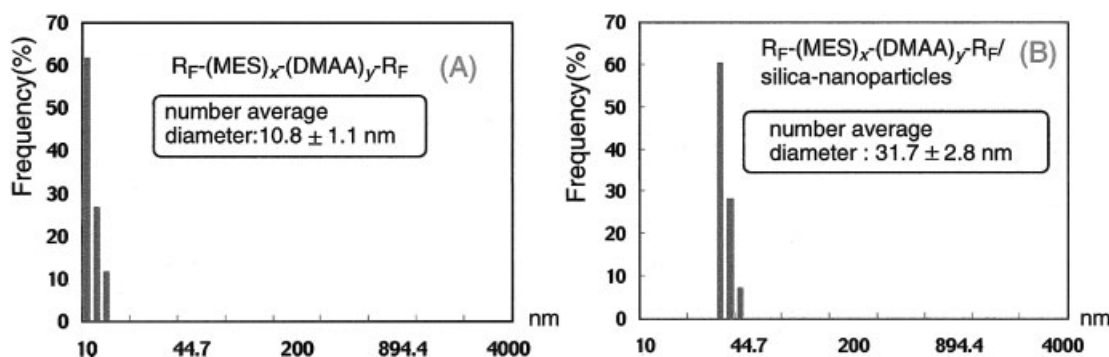
As shown in Figure 2, the maximum temperatures for the extrusion of SO<sub>2</sub> in the pyrolysis of  $R_F-(MES)_n-R_F$ -SiO<sub>2</sub> polymer hybrid and Nafion 112 (TR) are 430°C and 360°C, respectively. This indicates that thermal stability of  $R_F-(MES)_n-R_F$ -SiO<sub>2</sub> polymer hybrid is superior to that of traditionally well-known perfluorinated ion exchange polymer (Nafion 112). Thus, it is suggested that fluorinated MES homo- and co-oligomers could be tightly incorporated into the siloxane net-

TABLE II  
Size of  $R_F-(MES)_x-(DMAA)_y-R_F$ -Silica Nanoparticles in Methanol Solution Determined by Dynamic Light-Scattering Measurements

Size of used parent silica nanoparticles <sup>a</sup>	Size of dispersed particles (nm)	Size of redispersed particles (nm)
11 nm	31.7 ± 2.8 [10.8 ± 1.1] <sup>b</sup>	39.3 ± 4.9
45 nm	67.9 ± 10.1	94.4 ± 21.3
95 nm	173.2 ± 32.1	160.9 ± 26.2

<sup>a</sup> See Table I.

<sup>b</sup> Size of  $R_F-(MES)_x-(DMAA)_y-R_F$  co-oligomeric aggregates.



**Figure 3** Histograms of number-average diameter of fluorinated aggregates formed by (A)  $R_F-(MES)_x-(DMAA)_y-R_F$  and (B)  $R_F-(MES)_x-(DMAA)_y-R_F$ -silica nanoparticles in methanol solutions determined by dynamic light-scattering measurements.

works, which are obtained after the hydrolysis and subsequent condensation of TEOS under acidic conditions to afford the corresponding fluorinated co-oligomer-silica gel polymer hybrids.

It is of great interest to apply the sol solution, which is obtained by the reaction of  $R_F-(MES)_x-(DMAA)_y-R_F$  with TEOS in ethanol under acidic conditions for 4 h at room temperature, to the surface modifications of the glass. In fact, this fluorinated oligomer-silica gel polymer hybrid was tested for surface activity as a new type of surface modification agents. The contact angles for dodecane on the modified glass with fluorinated oligomer-silica gel polymer hybrid showed a significantly large value ( $51^\circ$ ) compared to that ( $0^\circ$ ) of the glass treated with the corresponding nonfluorinated MES-DMAA co-oligomer-silica gel polymer hybrid. In this modified glass, time dependence of contact angle of dodecane was not observed. Interestingly, a steep time dependence of contact angle of water was observed in this fluorinated co-oligomer-silica gel polymer hybrid as shown in the following: time: 0 min, 5 min, and 10 min; contact angle of water (degree):  $9$  ( $49^a$ ),  $0$  ( $45^a$ ), and  $0$  ( $43^a$ ), where  $a$  is the value for the corresponding nonfluorinated co-oligomer- $\text{SiO}_2$  polymer hybrids.

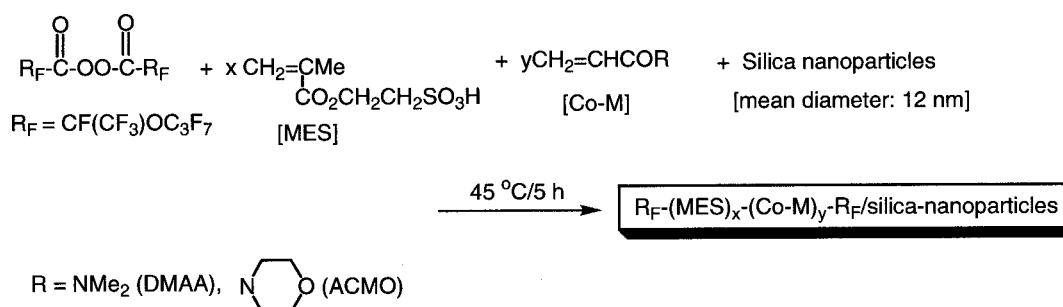
The contact angles were found to decrease significantly from  $9^\circ$  to  $0^\circ$  over 5 min, although the corresponding nonfluorinated  $(MES)_x-(DMAA)_y$  co-oligomer-silica gel polymer hybrid failed to exhibit a good

hydrophilic character. This finding suggests that at the interface with water, hydrophobic fluoroalkyl segments in fluorinated oligomers are easily replaced by the strongly hydrophilic sulfo and amido segments in fluorinated oligomers, and these hydrophilic segments should be arranged more regularly at the water interface.

As mentioned above, it was demonstrated that the hydrolysis of TEOS under acidic conditions in the presence of fluorinated oligomers afforded the fluorinated oligomers-silica gel polymer hybrids. However, these fluorinated hybrids exhibited no dispersibility and stability in aqueous and organic media, and fluorinated fine particles could not be prepared under these conditions. Therefore, we tried to prepare fluorinated fine nanoparticles by the use of silica nanoparticles as core units in fine particles. These results are shown in Scheme 2.

As shown in Scheme 2, well-dispersed fluorinated nanoparticles were obtained by the reactions of  $R_F-(MES)_x-(DMAA)_y-R_F$  with TEOS under alkaline conditions in the presence of a variety of silica nanoparticles, and the results are listed in Tables I and II.

As shown in Table I,  $R_F-(MES)_x-(DMAA)_y-R_F$  reacted with TEOS in the presence of silica nanoparticles to afford fluoroalkyl end-capped co-oligomers-silica nanoparticles in 39–48% isolated yields. We have measured the size of fluorinated co-oligomer-silica nanoparticles in methanol by DLS measurements at



**Scheme 3**

**TABLE III**  
**Preparation of Fluoroalkyl End-capped Sulfonic Acid Homo- and Co-oligomers/silica Nanoparticles by the use of Fluoroalkanoyl Peroxide**

$(R_F\text{COO})_2$ (mmol)	MES (mmol)	Co-M (mmol)	SiO <sub>2</sub> nanoparticle (g)	Oligomers/silica nanoparticles and yield <sup>a</sup> (%)
3.1	13.6	—	0.50	R <sub>F</sub> -(MES) <sub>n</sub> -R <sub>F</sub> -silica nanoparticles 7
2.7	13.6	DMAA (13.8)	0.50	R <sub>F</sub> -(MES) <sub>x</sub> -(DMAA) <sub>y</sub> -R <sub>F</sub> -silica nanoparticles 6
2.9	13.7	ACMO (13.6)	0.50	R <sub>F</sub> -(MES) <sub>x</sub> -(ACMO) <sub>y</sub> -R <sub>F</sub> -silica nanoparticles 8

<sup>a</sup> Isolated yield based on the decarboxylated peroxide unit (R<sub>F</sub>-R<sub>F</sub>), MES, Co-M, and SiO<sub>2</sub> nanoparticle (0.50 g).

30°C. The size of the parent fluorinated oligomeric aggregates was also measured under similar conditions for comparison. Figure 3 shows that the number-average diameter of fluorinated molecular aggregates formed by R<sub>F</sub>-(MES)<sub>x</sub>-(DMAA)<sub>y</sub>-R<sub>F</sub> is 10.8 ± 1.1 nm, and the size (number-average diameter) of fluorinated R<sub>F</sub>-(MES)<sub>x</sub>-(DMAA)<sub>y</sub>-R<sub>F</sub> co-oligomer-SiO<sub>2</sub> nanoparticles, which was prepared by the use of the silica nanoparticles (mean diameter: 11 nm), was increased from 10.8 nm to 31.7 ± 2.8 nm. A similar result was obtained in the other fluorinated co-oligomers-silica nanoparticles, and the size (68 and 173 nm) of these fluorinated oligomer nanoparticles was increased by the hybridizations of fluoroalkyl end-capped MES-DMAA co-oligomers compared to that of the parent fluoroalkyl end-capped MES-DMAA co-oligomeric aggregates (Table II). In particular, the size of the obtained fluorinated nanoparticles was found to increase with the increase of the size of the used silica nanoparticles (11, 45, and 95 nm). Fluoroalkyl end-capped MES-DMAA co-oligomers should be incorporated homogeneously into the silica gel, including the hydrolyzate of TEOS, utilizing hydrogen-bonding interaction between the silanol groups and carbonyl (or sulfo, amido) groups of co-oligomers to afford the expected fluorinated oligomers-silica nanoparticles. The increase of the size of fluorinated co-oligomer-SiO<sub>2</sub> nanoparticles indicates that the hybridizations of

fluoroalkyl end-capped co-oligomers with TEOS in the presence of silica nanoparticles could proceed smoothly to afford fine fluorinated nanoparticles with around 30–170 nm size levels. Of particular interest, the isolated fluorinated nanoparticle powders in Table II were found to exhibit a superior redispersibility and stability in methanol. The size (39–161 nm) of the redispersed fluorinated particles did not change even after the redispersion of the parent fluorinated particle powders into methanol (Table II), and the size of each particle showed a monodispersed characteristic. This finding would be due to the electrostatic repulsion between fluoroalkyl segments in fluorinated nanoparticles comprised of silica cores and fluoroalkyl end-capped oligomer coronas.

Furthermore, we have succeeded in preparing fluorinated nanoparticles by the homo- and co-oligomerizations of fluoroalkanoyl peroxides with MES and comonomers such as DMAA and acryloylmorpholine (ACMO) in the presence of silica nanoparticles (mean diameter: 12 nm), and the results are shown in Scheme 3 and Table III.

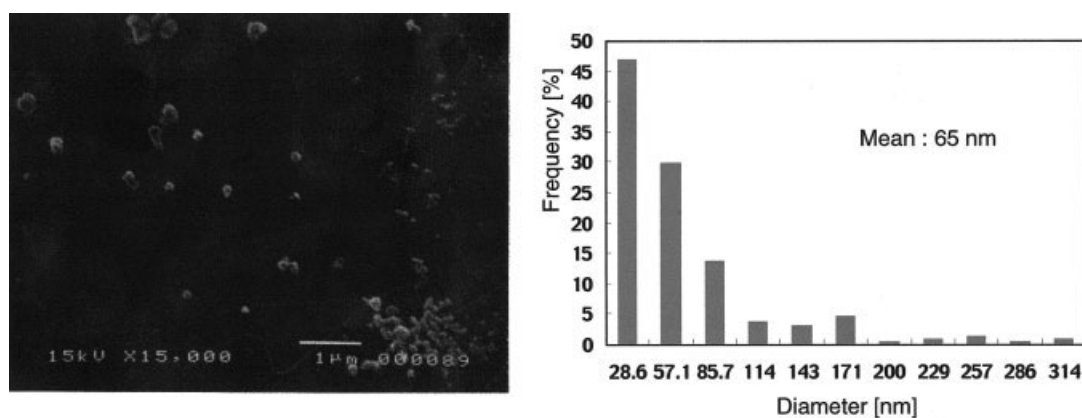
As shown in Scheme 3 and Table III, fluoroalkanoyl peroxide reacted with MES and comonomers in the presence of silica nanoparticles to afford fluoroalkyl end-capped MES homo- and co-oligomers-silica nanoparticles in 6–8% isolated yields under very mild conditions. The size of fluorinated oligomer-silica nano-

**TABLE IV**  
**Size of Fluoroalkyl End-Capped Sulfonic Acid Homo- and Co-oligomers-Silica Nanoparticles Prepared by the Use of Fluoroalkanoyl Peroxide in Methanol and Aqueous Solutions Determined by Dynamic Light-Scattering Measurements**

Oligomer/silica nanoparticles	Size of dispersed particles (nm)	Size of redispersed particles (nm)
R <sub>F</sub> -(MES) <sub>n</sub> -R <sub>F</sub> -silica nanoparticles <sup>a</sup>	32.6 ± 3.3	35.4 ± 2.2
R <sub>F</sub> -(MES) <sub>x</sub> -(DMAA) <sub>y</sub> -R <sub>F</sub> -silica nanoparticles <sup>a</sup>	408.9 ± 46.8	425.7 ± 43.4
R <sub>F</sub> -(MES) <sub>x</sub> -(ACMO) <sub>y</sub> -R <sub>F</sub> -silica nanoparticles <sup>b</sup>	36.5 ± 3.3	55.7 ± 5.7

<sup>a</sup> Methanol solution.

<sup>b</sup> Aqueous solution.



**Figure 4** SEM image of aqueous solution of  $R_F-(MES)_x-(ACMO)_y-R_F$ -silica nanoparticles.

particles thus obtained in methanol (or water) was measured by the use of DLS measurements under similar conditions as those of Table II. The size of the isolated fluorinated nanoparticle powders was 33–409 nm (Table IV).

These fluorinated nanoparticles showed a superior redispersibility and stability in methanol or water, and the size (35–426 nm) of the redispersed fluorinated particles did not change to possess a monodispersed characteristic even after the redispersion of the parent fluorinated particle powders into methanol or water (Table IV).

We have measured scanning electron microscopy (SEM) photographs of aqueous solution of fluoroalkyl end-capped MES-ACMO co-oligomer-silica in Table IV, and the result is shown in Figure 4.

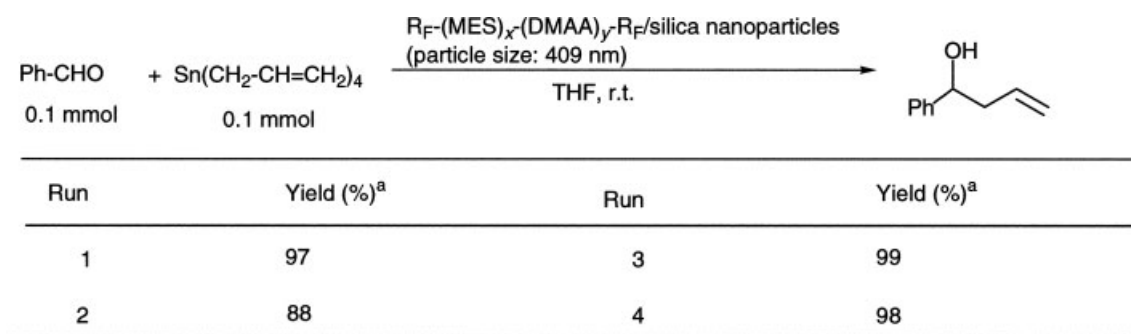
The electron micrograph also shows the formation of fluorinated oligomer-silica nanoparticles with a mean diameter of 65 nm. The difference in the average sizes determined by DLS and SEM (DLS:  $\sim 37$  nm; SEM:  $\sim 65$  nm) would be due to the coagulation or agglomeration of the nanoparticles during sample preparation for SEM measurements.

There has been an area of growing importance for the development of environmentally friendly catalysts

for organic transformation, and especially the use of polymer-supported catalysts offers some advantages such as simplification of product workup, separation, and isolation as well as reuse of the catalyst.<sup>14–18</sup> From this point of view, it is of particular interest to apply our present fluorinated sulfonic acid oligomers-SiO<sub>2</sub> nanoparticles to the heterogeneous Brnsted catalysts. In fact, we have tested fluoroalkyl end-capped MES-DMAA co-oligomer-SiO<sub>2</sub> silica nanoparticles in the catalyst for allylation reaction of tetraallyltin with benzaldehyde; these results are shown in Scheme 4.

As shown in Scheme 4, fluorinated oligomeric silica nanoparticles containing sulfo groups (particle size: 409 nm) were found to be effective in allylation to afford the expected products in good yields. It is noted that this fluorinated oligomeric nanoparticles could be easily recovered and reused. The catalyst was recovered quantitatively by simple centrifugation and could be reused. The catalytic activity of the recovered fluorinated silica nanoparticles did not decrease even after four uses (Scheme 4). Therefore, this novel fluorinated catalyst has high potential for the application to other useful synthetic reactions.

In conclusion, it was demonstrated that fluoroalkyl end-capped sulfonic acid homo- and co-oligomers-



<sup>a</sup> Yield is based on the PhCHO consumption.

**Scheme 4**

SiO<sub>2</sub> polymer hybrids were prepared by the reactions of TEOS and the corresponding fluorinated homo- and co-oligomers under acidic conditions. Fluorinated sulfonic acid homo-oligomer–SiO<sub>2</sub> polymer hybrid thus obtained was demonstrated to possess a higher thermal stability compared to that of Nafion 112 (TR). We have succeeded in the surface modifications of glass by the use of the sol solutions of the fluorinated sulfonic acid co-oligomer–SiO<sub>2</sub> polymer hybrid to exhibit not only a strong oleophobicity imparted by fluorine but also a good hydrophilicity on the surface. R<sub>F</sub>–(MES)<sub>x</sub>–(DMAA)<sub>y</sub>–R<sub>F</sub> co-oligomer reacted with TEOS and silica nanoparticles under alkaline conditions to afford fluoroalkyl end-capped oligomers–silica nanoparticles. In particular, it was demonstrated that a longer-size fluorinated silica nanoparticle could be prepared by the use of a longer-size silica nanoparticle as a starting material. Furthermore, a variety of fluoroalkyl end-capped sulfonic acid homo- and co-oligomers–silica nanoparticles were prepared by the oligomerizations of fluoroalkanoyl peroxides with MES and comonomers such as DMAA and ACOMO in the presence of silica nanoparticles. These fluorinated sulfonic acid oligomeric nanoparticles thus obtained exhibited a good redispersibility and stability in water and methanol. Fluorinated oligomeric nanoparticles were also applied to the excellent reusable catalyst for Brnsted acid-catalyzed allylations of aldehyde of tetraallyltin. There-

fore, these fluorinated sulfonic acid oligomers–SiO<sub>2</sub> polymer hybrids could open new development in fluorinated materials chemistry.

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