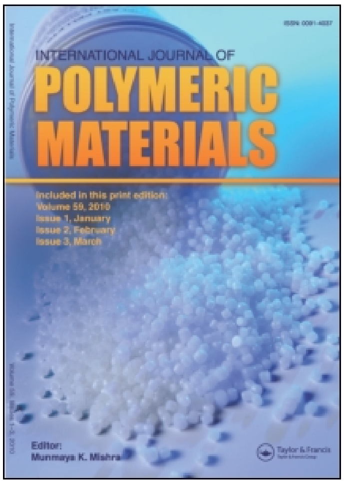

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Synthesis and Applications of Novel Fluoroalkyl End-capped Oligomers/Silica Gel Polymer Hybrids

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SYNTHESIS AND APPLICATIONS OF NOVEL FLUOROALKYL END-CAPPED OLIGOMERS/SILICA GEL POLYMER HYBRIDS

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Fluoroalkyl end-capped N,N-dimethylacrylamide and acryloylmorpholine oligomers were polymerized with hydrolysis and condensation of tetraethoxysilane (TEOS) to afford homogeneous fluoroalkyl end-capped oligomers and silica gel polymer hybrids, respectively. In particular, the sol solutions of fluorinated oligomers/TEOS polymer hybrids were applied to surface modifications of glass with not only a strong oleophobicity but also good hydrophilicity.

Keywords: fluorinated oligomer, silica gel, polymer hybrid, surface modification, oleophobicity, hydrophilicity, fluoroalkyl, oligomers, polymers

Recently, there has been a great interest in composite materials of inorganic materials and organic polymers from the viewpoint of the development of high-performance, highly functional polymeric

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materials [1]. These materials in general could show improved properties superior to those of the parent materials [2]. Alkoxysilanes are a convenient tool for the preparations of organic/inorganic hybrid materials by the sol-gel reactions. In fact, there have been hitherto many reports on the organic polymers/silica gel hybrids that are dispersed at the molecular level by utilizing the sol-gel reactions with alkoxysilanes in the presence of organic polymers [3]. Fluorinated polymers are a useful class of materials due to their unique balance of properties such as low surface free energy, low coefficient of friction, and solvent and chemical resistance, which cannot be achieved by the corresponding non-fluorinated polymer [4]. It is very interesting to prepare fluorinated polymer/inorganic polymer hybrids from the viewpoint of the development of new fluorinated functional materials. However, the preparation and the development of these fluorinated polymer hybrids have been limited except for the reports on the synthesis of poly(methacrylic acid)/tetraethoxysilane (TEOS)/2-perfluorooctylethyltriethoxysilane polymer hybrids [5], and poly(vinylidene fluoride) [6], fluorinated polyimides [7], telechelic perfluoropolyethers-containing triblock copolymers [8], and Nafion^{TR} resin [9]/silica composites. In the authors' comprehensive studies of fluorinated polymers, they have reported that fluoroalkyl end-capped oligomers exhibit a variety of unique properties such as high solubility, surface active properties, antibacterial activity, anti-HIV-1 activity, and the formation of self-assembled molecular aggregates, which cannot be achieved by the corresponding randomly fluoroalkylated polymers and fluoroalkylated block polymers [10]. Therefore, it is of particular interest to develop novel fluoroalkyl end-caped oligomer/silica gel polymer hybrids possessing a variety of unique properties imparted by fluorine such as surface active properties and biological activity. This communication, reports on the synthesis and applications of novel fluoroalkyl end-capped oligomer/silica gel polymer hybrids.

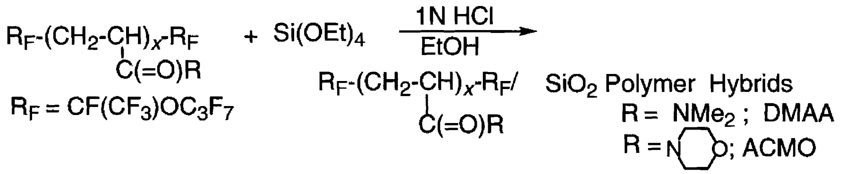
Fluoroalkyl end-capped *N,N*-dimethylacrylamide oligomer [R_F–$(DMAA)_n$–R_F] and acryloylmorpholine oligomer [R_F–$(ACMO)_n$–R_F] were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding DMAA and ACMO monomers according to the authors' previously reported method [11]. In an ethanol solution (5 ml) of R_F–$(DMAA)_n$–R_F [$R_F = CF(CF_3)OC_3F_7$: Mn = 2020 (Mw/Mn = 1.12) (0.4 g)] were added TEOS (2.0 g) and aqueous 1 N HCl (1.0 g). The mixture was stirred with a magnetic stirring bar at room temperature for 2 days. After the removal of the solvent, a transparent homogeneous hybrid was obtained. This glassy silica gel was purified by Soxhlet extraction with chloroform to afford the expected fluorinated polymer hybrid (1.17 g). Similarly, by using R_F–$(ACMO)_n$–R_F oligomer

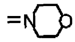
[Mn = 12500 (Mw/Mn = 1.26)], fluorinated ACMO oligomer/SiO_2 polymer hybrid (0.73 g) was obtained. Scheme 1 illustrates the preparation of fluorinated oligomers/silica gel polymer hybrids.

It is well known that the incorporation of organic commodity polymers into a silica gel causes phase separation and the composite gel becomes turbid. In contrast, the present fluorinated oligomers/silica gel polymer hybrids are transparent, and have no phase separation. Elementary analyses of fluorine in the polymer hybrids have been performed in order to clarify the presence of the fluorinated oligomers in the hybrids, and the results are listed in Table 1.

As shown in Table 1, the content of fluorine in the product hybrid after Soxhlet extraction was detected by elementary analysis, which was not significantly lower than the theoretical value. This indicates that fluorinated oligomers are tightly bound into the silica matrix because the original fluorinated oligomer has excellent solubility in chloroform. Furthermore, the carbonyl stretching band of R_F–$(DMAA)_n$–R_F oligomer was shifted from 1632 to 1624 cm^{-1} by the hybridization. These findings suggest that molecular-level combination, which is due to the interaction between the amide groups in oligomers and residual silanol groups through intermolecular hydrogen bonding, has been accomplished.

Additionally, the contents of fluorinated oligomers in the obtained hybrids were estimated by the use of thermogravimetric analyses



Run	R_F-$[CH_2$-$CHC(=O)R]_x$-R_F (g)	$Si(OEt)_4$ (g)	1N-HCl (g)	Product Yield (g)
	R= NMe_2 [Mn (Mw/Mn): 2020 (1.12)]			
1	0.4	2.0	1.0	1.17
2	0.8	2.0	2.0	0.21
3	1.2	2.0	3.0	0.16
	R =  [Mn (Mw/Mn): 12500 (1.26)]			
4	0.4	2.0	1.0	0.73

SCHEME 1

TABLE 1 Elementary Analyses for Fluorine in R_F–Oligomers/SiO_2 Polymer Hybrids

R_F–Oligomer [R_F = $CF(CF_3)OC_3F_7$] [Fluorine Atom (%)]		R_F–Oligomer/SiO_2 Polymer Hybrid [Fluorine Atom (%)]	
R_F–$(DMAA)_x$–R_F	Found	Found	Theoretical
1[a]	24.56	6.70	10.02
R_F–$(ACMO)_x$–R_F			
4[a]	21.26	6.03	8.68

[a]Different from those in Scheme 1.

(TGA), in which the weight loss of these hybrids was measured by raising the temperature to around 800°C; the results are shown in Figure 1.

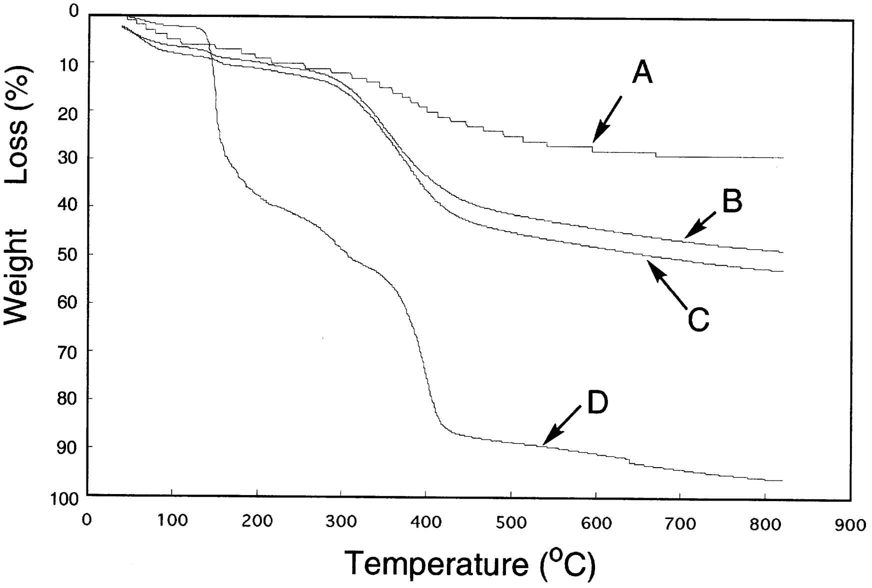


FIGURE 1 Thermogravimetric analyses of R_F–$(CH_2CHCONMe_2)_x$–R_F and R_F–$(CH_2CHCONMe_2)_x$–R_F/SiO_2 Polymer Hybrids. **A**: 1[a] R_F–$(CH_2CHCONCHCONMe_2)_x$–R_F/SiO_2 Polymer Hybrid [oligomer/TEOS = 0.4/2.0(m/m)]. **B**: 2[a] R_F–$(CH_2CHCONMe_2)_x$–R_F/SiO_2 Polymer Hybrid [oligomer/TEOS = 0.8/2.0 (m/m)]. **C**: 3[a] R_F–$(CH_2CHCONMe_2)_x$–R_F/SiO_2 Polymer Hybrid [oligomer/TEOS = 1.2/2.0(m/m)]. **D**: R_F–$(CH_2CHCONMe_2)_x$–R_F. [a]Different from those in Scheme 1.

As shown in Figure 1, fluorinated DMAA oligomer hybrids lost 20% of their weight around 350°C under nitrogen, whereas the original fluorinated DMAA oligomer lost the same weight around 150°C. The weight loss of fluorinated hybrids by TGA was found to decrease with a decrease of the feed ratio of $R_F-(DMAA)_n-R_F$. This finding suggests that fluoroalkyl end-capped oligomers could be incorporated homogeneously into the silica gel by utilizing hydrogen bonding interaction between the silanol groups and amide segments of fluorinated oligomers.

Interestingly, it was demonstrated that the sol solution, which is obtained by the reaction of TEOS and $R_F-(DMAA)_n-R_F$ [$R_F = CF(CF_3)OC_3F_7$] in ethanol under acidic conditions of 4 h at room temperature, can be applied to surface modifications of glass. Contact angle measurements of dodecane and water on the modified glass surface with these fluorinated sol solutions exhibited not only strong oleophobicity[1] imparted by fluorine, but also a good hydrophilicity.[2] This finding suggests that at the interface with water, hydrophobic fluoroalkyl segments in fluorinated oligomers are easily replaced by the a strongly hydrophilic dimethyamino carbonyl segments [$-C(=O)NMe_2$] in fluorinated oligomers, and the dimethylamino carbonyl segments should preferentially be arranged at the water interface. It takes about 30 min to replace the fluoroalkyl segments by dimethylamino carbonyl segments when the environment is changed from air to water. Of particular interest, it was clarified that this modified glass possesses similar oleophobic and hydrophilic properties even after dipping this glass in a chloroform solution for 1 day at room temperature, although the modified glass surface with the original R_F-(DMAA)$_n$-R_F oligomer did not exhibit a similar good oleophobicity. This may result from the strong interaction of the silanol groups of the glass surface with fluorinated oligomer/SiO_2 polymer hybrids.

In this way, it was verified that fluoroalkyl end-capped DMAA and ACMO oliogomers are convenient preoligomers for the preparation of new fluorinated oligomers/silica gel polymer hybrids by sol-gel reactions, by the use of TEOS under very mild conditions. Especially, the fluorinated sol solutions are useful as a novel surface modification agent of a variety of common materials, such as glass, to exhibit strong

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[1] Contact angle of dodecane on the modified glass is 42°, although the corresponding non-treated one is 0°.

[2] A steep time dependence of contact angle of water was observed, and the contact angles of water on the modified glass decreased extremely from about 42° to 0° over 30 min.

oleophobicity imparted by fluorine. Further studies are actively in progress.

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