

# Fluoroalkyl End-Capped Oligomer Possessing a Nonflammable Characteristic in Silica Gel Matrices Even at 800°C Under Atmospheric Conditions

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**ABSTRACT:** We succeeded in observing the similar solid-state NMR spectra (<sup>1</sup>H-magic-angle spinning NMR spectra) of fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer [R<sub>F</sub>-(DOBAA)<sub>*n*</sub>-R<sub>F</sub>]/silica gel nanocomposite before and even after calcinations at 800°C. This finding suggests that R<sub>F</sub>-(DOBAA)<sub>*n*</sub>-R<sub>F</sub> oligomer in R<sub>F</sub>-(DOBAA)<sub>*n*</sub>-R<sub>F</sub>/silica gel nanocomposite can afford a nonflammable characteristic to exhibit no weight loss behavior even at 800°C under atmospheric conditions. In addition, we had good oleo- and hydrophobic characteristics on the modified glass surface treated with R<sub>F</sub>-(DOBAA)<sub>*n*</sub>-R<sub>F</sub>/silica

gel nanocomposite even after calcination at 800°C as well as those before calcinations. Especially, R<sub>F</sub>-(DOBAA)<sub>*n*</sub>-R<sub>F</sub>/silica gel nanocomposite-encapsulated cetylpyridinium chloride (CPC) possessing no weight loss characteristic even at 800°C exhibited a clear UV-vis absorption band around 260 nm related to the presence of CPC before and even after calcinations at 800°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3482–3487, 2009

**Key words:** fluorinated oligomer; silica nanocomposites; nonflammable characteristic; MAS NMR spectra

## INTRODUCTION

The bond-strengthening effect of fluorine for C—C and C—F bonds in highly fluorinated compounds when compared with that of the corresponding nonfluorinated ones [i.e., CF<sub>3</sub>—CF<sub>3</sub> bond energy = 98.7 (413) kcal (kJ)/mol vs. 88.8 (372) kcal (kJ)/mol for CH<sub>3</sub>—CH<sub>3</sub>, and CF<sub>3</sub>—F bond energy = 130.5 (546) kcal (kJ)/mol vs. 108.3 (453) kcal (kJ)/mol for CH<sub>3</sub>—F] gives rise to the extraordinary thermal and oxidative stability that generally characterizes these compounds.<sup>1</sup> This property can afford fluorinated polymers, such as poly(tetrafluoroethylene) and poly(vinylidene fluoride), with high thermal and oxidative stability, and excellent resistance to most chemicals.<sup>2,3</sup> Therefore, from the developmental viewpoints of novel high-performance thermally resistant materials, hybridizations of these fluorinated polymers with metal alkoxides are of particular interest, and in fact, some studies on the hybridization

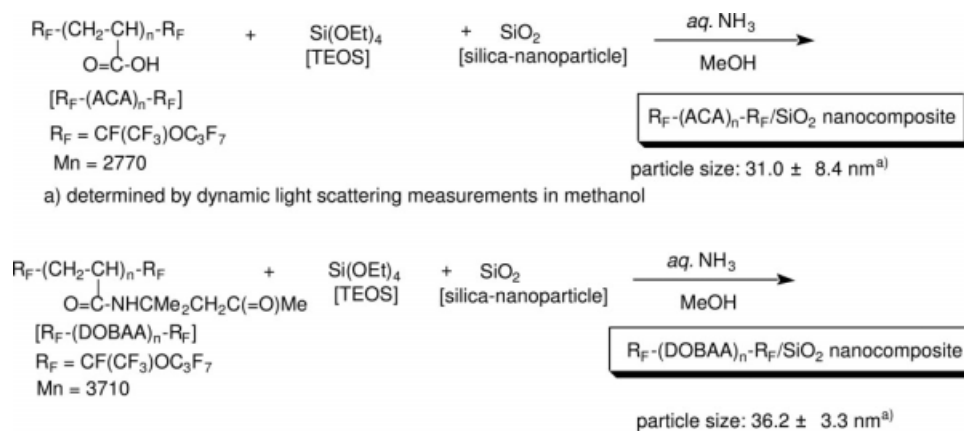
of fluorinated polymers with alkoxy silanes have been hitherto reported.<sup>4–7</sup> However, the thermal stability of these hybrids is generally inferior to that of the original silica gels.<sup>4–7</sup> From this point of view, the exploration of new fluorinated functional materials possessing the extraordinary thermal and oxidative stability as well as metal alkoxides such as silica gel is deeply desirable, and these materials should have high potential for the practical applications to a wide variety of fields.

Hitherto, it is well known that 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 self-assembled molecular aggregates, which cannot be achieved by the corresponding nonfluorinated and randomly fluoroalkylated ones.<sup>8–23</sup> Therefore, it is in particular interest to study the hybridization of these fluoroalkyl end-capped oligomers with silica gel. In fact, we previously reported that fluoroalkyl end-capped acrylic acid oligomer [R<sub>F</sub>-(ACA)<sub>*n*</sub>-R<sub>F</sub>]/silica gel nanocomposite, which was prepared by reaction of the corresponding oligomer with tetraethoxysilane (TEOS) and silica gel nanoparticles under alkaline conditions (see Scheme 1),<sup>24</sup> exhibited a clear weight loss at 800°C, which corresponds to the content (22%) of

Additional Supporting Information may be found in the online version of this article.

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**Scheme 1** Preparation of fluoroalkyl end-capped oligomers/silica gel nanocomposites.

$\text{R}_F\text{-(ACA)}_n\text{-R}_F$  oligomer determined by elementary analyses of fluorine.<sup>25</sup> On the other hand, we reported that  $\text{R}_F\text{-(DOBAA)}_n\text{-R}_F$ /silica gel nanocomposite (see Scheme 1) exhibited no weight loss behavior even at 800°C under atmospheric conditions, although the content of  $\text{R}_F\text{-(DOBAA)}_n\text{-R}_F$  oligomer in this nanocomposite was estimated to be 23% by elementary analyses of fluorine.<sup>25</sup> It was previously suggested that this would be due to the complete encapsulation of evolved gaseous products such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  during the pyrolysis of the composite into nanometer size-controlled silica gel matrices.<sup>25</sup>

In this study, we show that partially fluoroalkylated oligomers such as fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer [ $\text{R}_F\text{-(DOBAA)}_n\text{-R}_F$ ] in  $\text{R}_F\text{-(DOBAA)}_n\text{-R}_F$ /silica gel nanocomposite can afford a nonflammable characteristic to exhibit no weight loss behavior even at 800°C under atmospheric conditions.

## EXPERIMENTAL

### Measurements

<sup>1</sup>H-magic-angle spinning (MAS) NMR spectra were measured at room temperature using JEOL JNM-ECA600 with 4.0-mm CP/MAS probe. Fourier transform infrared (FTIR) spectra were measured using Shimadzu FTIR-8400 spectrophotometer (Kyoto, Japan). Ultraviolet-visible (UV-vis) spectra were measured using Shimadzu UV-1600 UV-vis spectrophotometer (Kyoto, Japan). Molecular weights of fluorinated oligomers were measured using a Shodex DS-4 (pump) and Shodex RI-71 (detector) gel permeation chromatography (Tokyo, Japan), calibrated with polystyrene standard using tetrahydrofuran (THF) as the eluent. Thermal analyses were recorded by raising the temperature around 800°C (the heating rate: 10°C/min) under atmospheric conditions by the use of Bruker axs TG-DTA2000SA differential thermobalance (Kanagawa, Japan). Dynamic light-

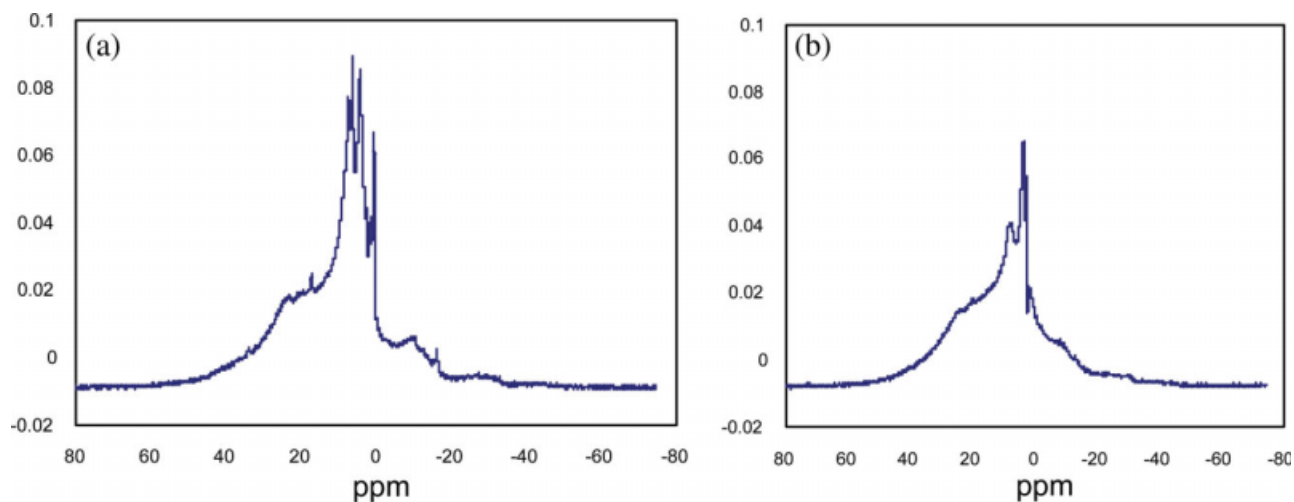
scattering (DLS) measurements were performed using Otsuka Electronics DLS-7000 HL (Tokyo, Japan). The contact angles were measured by the use of Kyowa Interface Science Drop Master 300 (Saitama, Japan).

### Preparation of fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer/silica gel nanocomposite

To a methanol solution (20 mL) of fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer [ $\text{R}_F\text{-[CH}_2\text{CHC(=O)NHCMe}_2\text{CH}_2\text{C(=O)Me}]_n\text{-R}_F$  [ $\text{R}_F\text{-(DOBAA)}_n\text{-R}_F$ ];  $\text{R}_F = \text{CF(CF}_3\text{)OC}_3\text{F}_7$ ;  $M_n = 3710$  (0.50 g)], which was prepared by the reaction of fluoroalkanoyl peroxide with the corresponding monomer according to our previously reported method,<sup>26</sup> 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, Tokyo, Japan)], and 25% aqueous ammonia solution (0.50 mL) were added. 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 products. The methanol solution was stirred with magnetic stirring bar at room temperature for 2 days, and then centrifuged for 30 min. The expected fluorinated nanocomposite was easily separated from the methanol solution. Fluorinated nanocomposite powders thus obtained were dried *in vacuo* at 50°C for 2 days to afford purified particle powders (1.00 g). Fluoroalkyl end-capped acrylic acid oligomer/silica nanocomposite was also prepared under similar conditions.

### Treatment of $\text{R}_F\text{-(DOBAA)}_n\text{-R}_F$ /silica gel nanocomposite with aqueous hydrogen fluoride

$\text{R}_F\text{-(DOBAA)}_n\text{-R}_F$ /silica gel nanocomposite (10 mg) was put on a teflon-made watch dish, and then



**Figure 1**  $^1\text{H}$ -MAS NMR spectra of  $\text{R}_F\text{-(DOBAA)}_n\text{-R}_F/\text{SiO}_2$  nanocomposites before (a) and after (b) calcination at  $800^\circ\text{C}$ . [Color figure can be viewed in the online issue which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

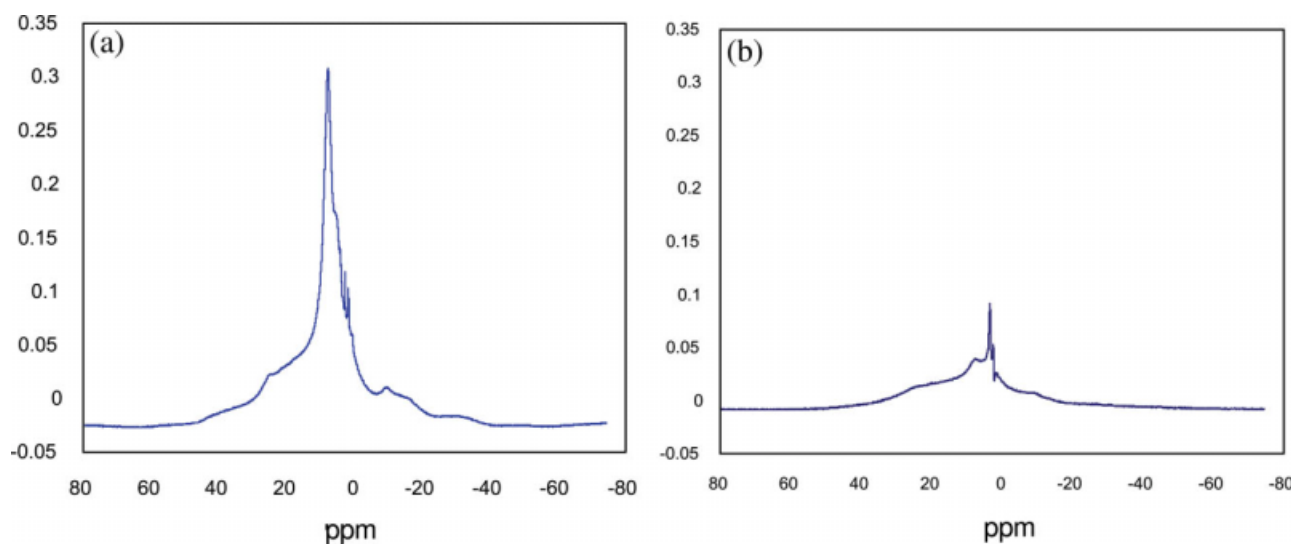
aqueous 47% hydrogen fluoride (2 mL) was slowly dropped on this dish. The reaction mixture was heated at  $150^\circ\text{C}$  to evaporate the solvent. The product thus obtained was analyzed by the use of FTIR measurements.

## RESULTS AND DISCUSSIONS

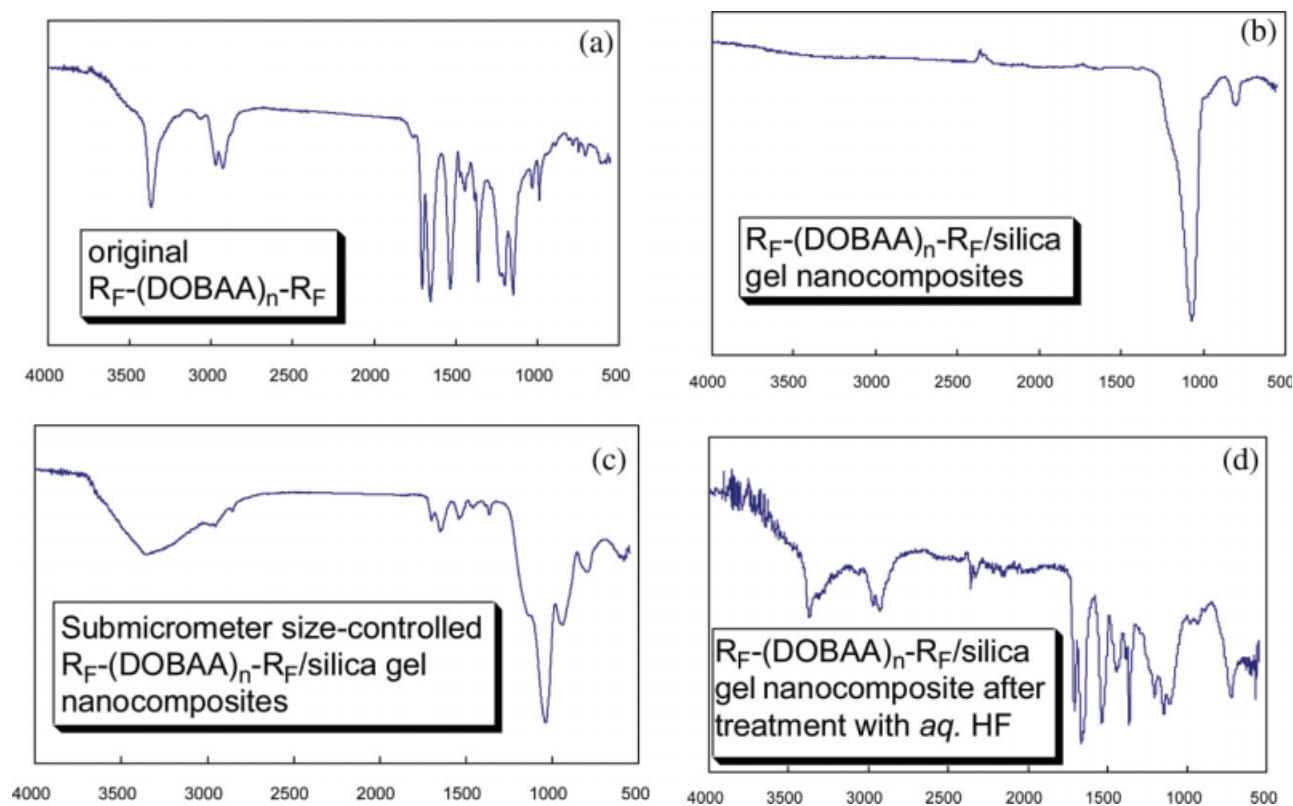
For  $^1\text{H}$ -MAS NMR spectra of  $\text{R}_F\text{-(DOBAA)}_n\text{-R}_F/\text{silica}$  nanocomposite [average particle size determined by DLS measurements : 36 nm; content of oligomer in the composite: 23% (determined by elementary analyses of fluorine)] possessing no weight loss characteristic even at  $800^\circ\text{C}$  (see Supporting Information Fig. 1), we have observed relatively sharp peaks around 50–20 ppm (ppm relative to  $\text{CFCl}_3$ ) before calcination,

as shown in Figure 1(a). In addition, unexpectedly, we have succeeded in observing (Fig. 1) similar sharp peaks in the nanocomposite after calcinations at  $800^\circ\text{C}$  with those before calcinations, and the peak area of the nanocomposites after calcination has decreased by only 19% when compared with that before calcinations [see Fig. 1(b)]. On the other hand,  $^1\text{H}$ -MAS NMR spectra of  $\text{R}_F\text{-(ACA)}_n\text{-R}_F/\text{silica}$  nanocomposite possessing a clear weight loss at  $800^\circ\text{C}$  (see Supporting Information Fig. 2), in which the content of oligomer is 22% (determined by elementary analyses of fluorine), showed an extreme decrease of the peak areas for this nanocomposite by 90% after calcination at  $800^\circ\text{C}$  [see Fig. 2(a,b)].

A carboxyl band in the parent  $\text{R}_F\text{-(ACA)}_n\text{-R}_F$  oligomer was observed around  $1716\text{ cm}^{-1}$ , and the



**Figure 2**  $^1\text{H}$ -MAS NMR spectra of  $\text{R}_F\text{-(ACA)}_n\text{-R}_F/\text{silica}$  gel nanocomposites before (a) and after (b) calcination at  $800^\circ\text{C}$ . [Color figure can be viewed in the online issue which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



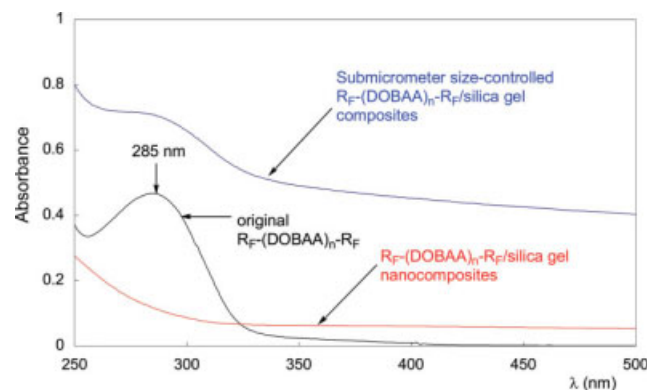
**Figure 3** FTIR spectra of (a) parent  $R_F-(DOBAA)_n-R_F$  oligomer, (b)  $R_F-(DOBAA)_n-R_F/silica$  gel nanocomposite, (c) submicrometer size-controlled  $R_F-(DOBAA)_n-R_F/silica$  gel composite, and (d)  $R_F-(DOBAA)_n-R_F/silica$  gel nanocomposite after the treatment with aqueous HF. [Color figure can be viewed in the online issue which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

same carboxyl band was also observed in  $R_F-(ACA)_n-R_F/silica$  nanocomposites possessing a clear weight loss behavior at 800°C by the use of FTIR spectra measurements.<sup>26</sup> FTIR spectra at room temperature of  $R_F-(DOBAA)_n-R_F/silica$  gel nanocomposite possessing no weight loss characteristic showed the complete disappearance of carbonyl bands (1709, 1655, and 1543  $cm^{-1}$ ) related to  $R_F-(DOBAA)_n-R_F$  oligomer in  $R_F-(DOBAA)_n-R_F/silica$  gel nanocomposite [see Fig. 3(a,b)]; although these carbonyl bands were clearly observed in  $R_F-(DOBAA)_n-R_F$  oligomer in submicrometer size-controlled  $R_F-(DOBAA)_n-R_F/silica$  gel nanocomposite [see Fig. 3(c)].<sup>27</sup> However, interestingly, we have succeeded in observing the same FTIR spectra of  $R_F-(DOBAA)_n-R_F$  oligomer as with those of the original  $R_F-(DOBAA)_n-R_F$  oligomer by the treatment of this  $R_F-(DOBAA)_n-R_F/silica$  gel nanocomposite with aqueous hydrogen fluoride [see Fig. 3(d)].

UV-vis spectra of 1,2-dichloroethane solution of original  $R_F-(DOBAA)_n-R_F$  oligomer show carbonyl absorption band around 285 nm, and the same absorption band was observed in well-dispersed 1,2-dichloroethane solution containing submicrometer size-controlled  $R_F-(DOBAA)_n-R_F/silica$  gel composite

possessing a clear weight loss behavior at 800°C (see Fig. 4).

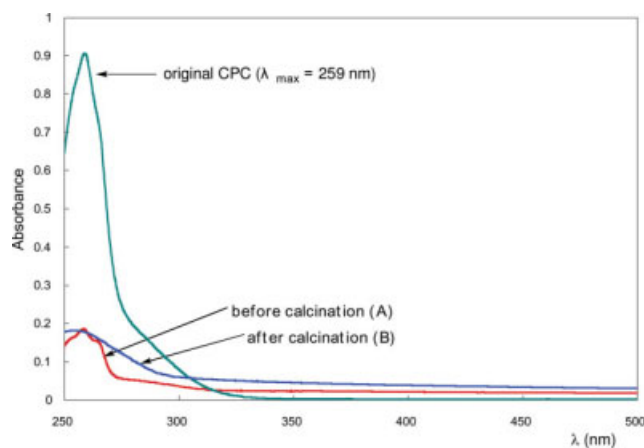
However, we failed to detect such absorption band in  $R_F-(DOBAA)_n-R_F/silica$  nanocomposite possessing no weight loss characteristic under similar



**Figure 4** UV-vis spectra of  $R_F-(DOBAA)_n-R_F/silica$  nanocomposite (5  $g/dm^3$ ), submicrometer size-controlled  $R_F-(DOBAA)_n-R_F/silica$  gel composites in 1,2-dichloroethane (5  $g/dm^3$ ), and  $R_F-(DOBAA)_n-R_F$  in 1,2-dichloroethane (2  $g/dm^3$ ). [Color figure can be viewed in the online issue which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

conditions as well as those of FTIR spectra measurements as in Figure 3; although this  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica nanocomposite afforded a well-dispersed transparent colorless 1,2-dichloroethane solution. These findings suggest that  $R_F$ -(DOBAA) $_n$ - $R_F$  oligomer in nanocomposite should be encapsulated quite effectively into the nanometer size-controlled silica gel matrices through the molecular-level synergistical combination, which is due to the intermolecular hydrogen bonding interaction between the amido and carbonyl groups in  $R_F$ -(DOBAA) $_n$ - $R_F$  oligomer and residual silanol groups in silica gel matrices. Such effective interactions should enable  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite to afford the complete disappearance of carbonyl band in  $R_F$ -(DOBAA) $_n$ - $R_F$  oligomer in FTIR spectra and UV-vis spectra measurements, respectively. Thus, the surface of encapsulated  $R_F$ -(DOBAA) $_n$ - $R_F$  oligomer into silica gel nanomatrices could possess an extraordinarily high oxidation resistance to exhibit a nonflammable characteristic during the calcination process at 800°C.

Our present  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel composite possessing no weight loss characteristic at 800°C is nanometer size-controlled fine nanoparticles. Average particle size [37.1 nm  $\pm$  4.8 nm (determined by DLS)] of this composite after calcination at 800°C was almost the same as that (36.2 nm  $\pm$  3.3 nm) before calcination, and the appearance of white-colored composite powder did not change at all before and even after calcinations at 800°C. These  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposites before and after calcinations at 800°C have a good dispersibility not only in water but also in common organic solvents such as THF, methanol, and 1,2-dichloroethane including fluorinated aliphatic solvents (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) to afford a transparent colorless solution. Thus, it is of particular interest to develop our  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite to the surface modification for glass. We have prepared the modified glasses by casting the  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite solutions (1 g/dm<sup>3</sup> in 1,2-dichloroethane), and then the contact angles of dodecane and water on the modified glasses were measured. The contact angles of dodecane and water on the modified glass surface treated with  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite before calcination are 23° and 66°, respectively. These values are similar to those (dodecane: 29°; water: 76°) of the modified glass surface treated with the parent  $R_F$ -(DOBAA) $_n$ - $R_F$  oligomer, and these values are higher than those of the original nontreated glass (dodecane: 0°; water: 42°). On the other hand, interestingly,  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite after calcination at 800°C was found to show similar large values (dodecane: 27°; water: 87°) on the modi-



**Figure 5** UV-vis spectra of  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite-encapsulated CPC before (a) and after (b) calcination in 1,2-dichloroethane and original CPC in 1,2-dichloroethane. Concentrations:  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite-encapsulated CPC in 1,2-dichloroethane (1 g/dm<sup>3</sup>); original CPC in 1,2-dichloroethane (67 mg/dm<sup>3</sup>). [Color figure can be viewed in the online issue which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

fied glass surface as with those before calcination. These higher contact angle values on the modified glass surfaces suggest that fluorinated oligomer should be tightly encapsulated into the silica gel nanomatrices even after calcination at 800°C.

We have succeeded in observing a clear absorption band related to the presence of cetylpyridinium chloride (CPC) in  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite-encapsulated CPC (average particle size: 36 nm), which was prepared by the reaction of the corresponding oligomer with TEOS, silica gel nanoparticles, and CPC under alkaline conditions (see Supporting Information Scheme 1). The ratio of introduced CPC into nanocomposite based on the used CPC was estimated to be 12% by the use of UV-vis spectra. Of particular interest, we have succeeded in observing the same clear absorption band around 260 nm as that of the original CPC even after calcination at 800°C (see Fig. 5), and this calcinated fluorinated silica nanocomposite-encapsulated CPC was found to exhibit no weight loss behavior at 800°C equal to original silica nanoparticles and the corresponding  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite (see Supporting Information Fig. 3), indicating that CPC should be effectively encapsulated as a guest molecule into the  $R_F$ -(DOBAA) $_n$ - $R_F$ /silica gel nanocomposite matrices to exhibit a nonflammable characteristic during the calcination process at 800°C through an extraordinarily high oxidation resistance above the encapsulated CPC surface.

In conclusion, these experiments demonstrate that silica nanocomposite reaction with fluoroalkyl end-capped DOBAA oligomer can afford not only a

nonflammable characteristic for the parent fluorinated oligomer but also the novel nanocavity possessing an extraordinarily high oxidation resistance, which exhibits no weight loss characteristic during the calcination process at 800°C under atmospheric conditions. This novel nanocavity can change an encapsulated flammable guest molecule to the nonflammable one through the simple encapsulation technique. Thus, this unique technology can open new development for oxidation-resistant functional materials in a wide variety of fields.

## References

1. Dolbier, W. R. *J Fluorine Chem* 2005, 126, 157.
2. Scheirs, J., Ed. *Modern Fluoropolymers*; Wiley: Chichester, 1997.
3. Ameduri, B.; Boutevin, B. *Well-Architected Fluoropolymers: Synthesis, Properties and Applications*; Elsevier: Amsterdam, 2004.
4. Harmer, M. K.; Farneth, W. E.; Sun, Q. *J Am Chem Soc* 1996, 118, 7708.
5. Cho, J.-W.; Sul, K.-I. *Fibers Polym* 2001, 2, 135.
6. Yano, S.; Okubo, N.; Takahashi, K. *Macromol Symp* 1996, 108, 270.
7. Fabbri, P.; Messori, M.; Montecchi, M.; Nannarone, S.; Pasquali, L.; Pilati, F.; Tonelli, C.; Toselli, M. *Polymer* 2006, 47, 1055.
8. Johns, K.; Stead, G. F. *J Fluorine Chem* 2000, 104, 5.
9. Ameduri, B.; Boutevin, B. *J Fluorine Chem* 2000, 104, 53.
10. Berret, J.-F.; Calvet, D.; Collet, A.; Viguier, M. *Curr Opin Colloid Interface Sci* 2003, 8, 296.
11. Kujawa, P.; Goh, C.C. E.; Calvet, D.; Winnik, D. F. M. *Macromolecules* 2001, 34, 6387.
12. Imae, T. *Curr Opin Colloid Interface Sci* 2003, 8, 307.
13. Andruzzi, L.; Chiellini, E.; Galli, G.; Li, X.; Kang, S. H.; Ober, C. K. *J Mater Chem* 2002, 12, 1684.
14. Imae, T.; Tabuchi, H.; Funayama, K.; Sato, A.; Nakamura, T.; Amaya, N. *Colloids Surf A* 2000, 167, 73.
15. Jankova, K.; Hvilsted, S. *J Fluorine Chem* 2005, 126, 241.
16. Lebreton, P.; Ameduri, B.; Boutevin, B.; Corpart, J.-M. *Macromol Chem Phys* 2002, 203, 522.
17. Sawada, H. *Chem Rev* 1996, 96, 1779.
18. Sawada, H.; Kawase, T. *Kobunshi Ronbunshu* 2001, 58, 147.
19. Sawada, H.; Kawase, T. *Kobunshi Ronbunshu* 2001, 58, 255.
20. Sawada, H. *J Fluorine Chem* 2000, 105, 219.
21. Sawada, H. *Prog Polym Sci* 2007, 32, 509.
22. Sawada, H. *Polym J* 2007, 39, 637.
23. Sawada, H. *J Fluorine Chem* 2003, 121, 111.
24. Sawada, H.; Narumi, T.; Kajiwara, A.; Ueno, K.; Hamazaki, K. *Colloid Polym Sci* 2006, 284, 551.
25. Sawada, H.; Narumi, T.; Kodama, S.; Kamijo, M.; Ebara, R.; Sugiya, M.; Iwasaki, Y. *Colloid Polym Sci* 2007, 285, 977.
26. Sawada, H.; Yoshino, Y.; Kurachi, M.; Kawase, T.; Takishita, K.; Tanedani, T. *Polymer* 2000, 41, 397.
27. Sawada, H.; Tashima, T.; Kodama, S. *Polym Adv Technol* 2008, 19, 739.