J Mater Sci (2007) 42:7147–7153
DOI 10.1007/s10853-007-1549-2

Preparation and antibacterial activity of novel fluoroalkyl end-capped oligomers/silica nanocomposites-encapsulated low molecular biocides

Hideo Sawada · Hiroshi Kakehi · Masashi Koizumi · Yoshihiro Katoh · Masashi Miura

Received: 26 October 2006 / Accepted: 24 January 2007 / Published online: 10 May 2007

Abstract Fluoroalkyl end-capped N-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer [R_F-(DOBAA)$_n$-R_F] reacted with tetraethoxysilane (TEOS) and silica nanoparticles in the presence of low-molecular weight biocides such as hibitane, hinokitiol, and hinokioil under alkaline conditions to afford R_F-(DOBAA)$_n$-R_F/silica nanocomposites-encapsulated these biocides in excellent to moderate isolated yields. Fluoroalkyl end-capped *N*,*N*-dimethylacrylamide oligomer [R_F-(DMAA)$_n$-R_F] and acrylic acid oligomer [R_F-(ACA)$_n$-R_F]/silica nanocomposites-encapsulated hibitane were obtained under similar conditions. Dynamic light scattering measurements showed that the size of these fluorinated nanocomposites-encapsulated biocides thus obtained is nanometer size-controlled. Additionally, these fluorinated nanocomposites were shown to have a good dispersibility and stability in methanol and water. Of particular interest, these fluorinated nanocomposites-encapsulated biocides were found to have a good antibacterial activity against *Staphylococcus aureus*, and these nanocomposites were applied to the surface modification of traditional organic polymers such as poly(methyl methacrylate).

H. Sawada (✉) · H. Kakehi · M. Koizumi
Department of Frontier Materials Chemistry, Faculty of Science and Technology, Hirosaki University, Bunkyo-cho, Hirosaki 036-8561, Japan
e-mail: hideosaw@cc.hirosaki-u.ac.jp

H. Kakehi · Y. Katoh · M. Miura
R & D Center, INAX Corporation, Tokoname, Aichi 479-8588, Japan

Introduction

Partially fluorinated, in particular, fluoroalkyl end-capped oligomers are attractive materials, because they exhibit various unique properties such as high solubility, surface active properties, and nanometer size-controlled self-assembled molecular aggregates which cannot be achieved by the corresponding non-fluorinated and randomly fluoroalkylated polymers [1]. For example, self-assembled fluorinated molecular aggregates formed by fluoroalkyl end-capped acryloylmorpholine oligomers could interact with fullerene and carbon nanotube as guest molecules in aqueous media to afford a good solubility of fullerene and carbon nanotube in water [2, 3]. Nanometer size controlled self-assemblies formed by the aggregation of end-capped fluoroalkyl segments in oligomers could also provide suitable host moieties to interact with low-molecular weight biocides such as hibitane as a guest molecule [4]. The modified polymer surface treated with these fluorinated aggregates—biocide nanocomposites could exhibit a surface antibacterial activity with the oleophobicity imparted by fluorine [4]. The shape of these fluorinated molecular aggregates is in general easily exchangeable under a variety of conditions, and the encapsulated guest molecules should have an easily releasing characteristic from the aggregates cores to their outsides under these conditions [4]. In fact, we have some difficulties for exhibiting unique characteristics imparted by guest molecules in the nanocomposites for a long time on their modified polymer surface [2–4]. Therefore, it is in particular interest to prepare new fluoroalkyl end-capped oligomeric nanoparticles-encapsulated a variety of low molecular biocides in which their structures are fixed from the developmental viewpoints of new fluorinated functional materials possessing a good antibacterial activity. In this paper, we would like to

report on the synthesis and antibacterial activity of novel fluoroalkyl end-capped oligomers/silica nanocomposites-encapsulated a variety of low molecular biocides such as hibitane, hinokitiol and hinkioil. These results will be described herein.

Experimental

Measurements

Molecular weights were measured using a Shodex DS-4 (pomp) and Shodex RI-71 (Detector) gel permeation chromatography (GPC) calibrated with polystyrene standard using tetrahydrofuran (THF) as the eluent. NMR spectra were measured using a JEOL JNM-400 (400 MHz) FT NMR SYSTEM (Tokyo, Japan). Dynamic light scattering (DLS) were measured using Otsuka Electronics DLS-7000 HL (Tokyo, Japan). Ultraviolet–visible (UV–vis.) spectra were measured using a Shimadzu UV-1600 UV–vis. spectrophotometer (Kyoto, Japan). Contact angles were measured by the use of the goniometer type contact angle meter (ERMA G-1-1000).

Materials

N,N-Dimethylacrylamide (DMAA) was used as received from Kohjin Co., Ltd (Tokyo, Japan). *N*-(1,1-Dimethyl-3-oxobutyl)acrylamide (DOBAA) and hinokioil were used as received from Kyowa Hakko Kogyou Co., Ltd. (Tokyo, Japan) and Yushiseihin Co., Ltd. (Osaka, Japan), respectively. Tetraethoxysilane and hibitane were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan), respectively. Hinokitiol was purchased from Wako Pure Chemical Industrials, Ltd. (Osaka, Japan). R_F-$(DOBAA)_n$-R_F, R_F-$(ACA)_n$-R_F and R_F-$(DMAA)_n$-R_F were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding monomers according to our previously reported methods [5].

General procedure for the preparation of fluoroalkyl end-capped oligomers/silica nanoparticles-encapsulated hibitane

To a homogeneous methanol solution (40 mL) of [R_F-$(DOBAA)_n$-R_F]; [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$; Mn = 6,720 (80 mg)] including hibitane (16 mg) were added tetraethoxysilane (TEOS: 80 mg), silica nanoparticle methanol solution [30% (wt.): 267 mg; average particle size: 11 nm [Methanol Silica-sol (TR): Nissan Chemical Industrials Ltd., Tokyo, Japan]], and 25% aqueous ammonia solution (6 mL). The mixture was stirred with a magnetic stirring bar at room temperature for 4 h. After the solvent was evaporated off, to the obtained crude products was added methanol (40 mL). The methanol solution was stirred with magnetic stirring bar at room temperature for 2 day, and then was centrifuged for 30 min. The expected fluorinated nanoparticles-encapsulated hibitane were easily separated from the methanol solution. Fluorinated nanoparticle powders thus obtained were dried in vacuo at 50 °C for 2 day to afford purified particle powders (123 mg). The purified fluorinated nanoparticle powders were added to fresh methanol, and were stirring with magnetic stirring bar at room temperature for 2 day to afford fluorinated fine colloidal nanoparticles with a good redispersibility and stability in methanol and water. R_F-$(DOBAA)_n$-R_F/silica nanoparticles-encapsulated low molecular biocides such as hinokitiol and hinokioil were prepared in the presence of these biocides under similar conditions.

Similarly, R_F-$(DOBAA)_n$-R_F oligomer/ and other fluoroalkyl end-capped oligomers/silica nanoparticles-encapsulated hibitane were prepared by the hybridizations of the corresponding oligomers with TEOS and silica nanoparticles in the presence of hibitane in methanol under acidic and alkaline conditions, respectively.

Contact angle measurements

The contact angles for glasses were measured with the use of the goniometer-type contact angle meter (Erma G-1-1000), according to our previously reported method [6]. The PMMA films were prepared by casting the mixture of 1,2-dichloroethane solution (12.5 ml) of PMMA (1.00 g) and the dispersed 1,2-dichloroethane solutions (12.5 ml) containing fluoroalkyl end-capped oligomer/silica nanocomposites-encapsulated biocides (67 mg; the content of fluorinated oligomer: 1% based on PMMA) on a glass plate. The solvents were evaporated at room temperature, and the films formed peeled off and dried at room temperature for 24 hr under vacuum to afford the modified PMMA films. The contact angles of dodecane for the surface and reverse sides of these films were measured, respectively.

Antibacterial assessment

The antibacterial activity of the fluorinated composites was evaluated against *S. aureus* by viable cell counting method as described previously [7].

Results and discussion

Hibitane [chlorhexidine dihydrochloride {1,1′-hexamethylenebis[(5-(4-chlorophenyl)biguanide) dihydrochloride] is a derivative of guanidine and this compound is one of the potent low-molecular weight biocides [8]. First, we tried to prepare fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer [R_F-(DOBAA)$_n$-R_F]/silica nanocomposites-encapsulated hibitane by the reaction of the corresponding oligomer with tetraethoxysilane (TEOS) and silica nanoparticles in the presence of hibitane, and the results were shown in Scheme 1 and Table 1.

As shown in Scheme 1 and Table 1, hybridizations of R_F-(DOBAA)$_n$-R_F with TEOS and silica nanoparticles in the presence of hibitane were found to proceed smoothly under alkaline or acidic conditions to afford R_F-(DOBAA)$_n$-R_F/silica nanocomposites-encapsulated hibitane in 20–70% isolated yields. The higher isolated product yields were obtained under alkaline conditions. The contents of encapsulated hibitane in the fluorinated composites were estimated to be 41–59% by the use of UV–vis. spectra (hibitane: λ_{max} = 260 nm). We have measured the size of R_F-(DOBAA)$_n$-R_F/silica nanocomposites-encapsulated hibitane in methanol solutions by dynamic light-scattering (DLS) measurements at 30 °C. The size of the parent R_F-(DOBAA)$_n$-R_F/silica nanocomposites was also measured under similar conditions for comparison. These results were also shown in Table 1.

As shown in Table 1, the size (~821 nm: number-average diameter) of R_F-(DOBAA)$_n$-R_F/silica nanocomposites-encapsulated hibitane, which were prepared under alkaline conditions, was increased by the encapsulation of hibitane into the nanocomposites, compared to that (67 nm) of the parent R_F-(DOBAA)$_n$-R_F/silica nanocomposites. This finding indicates that the encapsulation of hibiane into R_F-(DOBAA)$_n$-R_F/silica nanocomposites should be proceeded effectively under alkaline conditions. The size of R_F-(DOBAA)$_n$-R_F/silica nanocomposites, which were prepared under acidic conditions, was also nanometer size-controlled (22–453 nm levels). However, the size of R_F-(DOBAA)$_n$-R_F/silica composite, which was prepared in the absence of silica nanoparticle, was found to increase remarkably to 617 nm, indicating that the hybridization of R_F-(DOBAA)$_n$-R_F with TEOS in the presence of silica nanoparticles should be proceeded smoothly to afford the core (silica nanoparticle)/corona (fluorinated oligomers)-type nanoparticles. In addition, a variety of these R_F-(DOBAA)$_n$-R_F/silica nanocomposites-encapsulated hibitane in Table 1 were found to exhibit a good dispersibility and stability in water and methanol.

Not only R_F-(DOBAA)$_n$-R_F oligomer but also fluoroalkyl end-capped *N*,*N*-dimethylacrylamide oligomer {R_F-($CH_2CHCONMe_2$)$_n$-R_F [R_F-(DMAA)$_n$-R_F]} and fluoroalkyl end-capped acrylic acid oligomer {R_F-($CH_2CHCOOH$)$_n$-R_F [R_F-(ACA)$_n$-R_F]} could react with TEOS and silica nanoparticles in the presence of hibitane under alkaline conditions to afford the corresponding fluorinated oligomers/silica nanocomposites-encapsulated hibitane, and these results were shown in Scheme 1 and Table 2.

As shown in Scheme 1 and Table 2, the encapsulations of hibitane into R_F-(DMAA)$_n$-R_F/silica nanocomposites and R_F-(ACA)$_n$-R_F/silica nanocomposites were found to proceed smoothly under the same conditions as in Table 1 to afford the corresponding fluorinated oligomers/silica nanocomposites-encapsulated hibitane from 49 to 95% isolated yields. Furthermore, DLS measurements showed that the size of the fluorinated nanocomposites-encapsulated hibitane thus obtained were 173–637 nm levels. In particular interest, these fluorinated nanocomposites had a good dispersibility and stability in water and methanol.

In a variety of low-molecular weight biocides, not only hibitane but also hinokitiol and hinokioil have been hitherto well-known as the most potent antibacterial agents. Hinokitiol and hinokioil are natural biocides, and in particular, hinokioil possess the wooden perfume with a good antibacterial characteristic. Therefore, it is in particular interest to synthesis novel fluoroalkyl end-capped oligomers/silica nanoparticles-encapsulated hinokitiol and hinokioil from the developmental viewpoints of new fluorinated functional materials. In fact, we tried to synthesize fluoroalkyl end-capped oligomers/silica nanocomposites-encapsulated hinokitiol and hinokioil. These results were shown in Scheme 1 and Table 3.

The expected nanocompsoites-encapsulated hinokitiol and hinokioil were not obtained at all under acidic condi-

Scheme 1

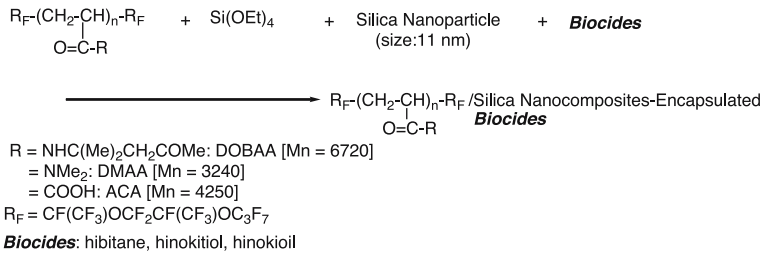

Table 1 Reactions of R_F-(DOBAA)$_n$-R_F with TEOS and silica nanoparticles (size: 11 nm) in the presence of hibitane

Run	Oligomer (mg)	TEOS (mg)	MeOH (mL)	25% aq. NH_3 (mL)	Hibitance (mg)	Silica nanoparticle (mg)	Reaction time	Yield (%)[a]	Particle size[b] (nm)	Contents of hibitane (%)[c]
1	80	80	40	12	–	80	4 h	29	66.5 ± 3.2	–
2	80	80	40	6	16	80	4 h	26	58.1 ± 4.0	54
3	80	80	40	12	16	80	1 day	65	730.7 ± 127.6	51
4	80	80	40	6	8	80	1 day	70	272.8 ± 55.2	53
5	80	80	40	6	32	80	1 day	57	821.3 ± 176.0	50
				1 N HCl (g)						
6	200	1,000	16	0.75	20	–	1 day	20	617.2 ± 126.7	53
7	200	1,000	16	0.75	20	0.2	1 day	36	453.1 ± 93.4	53
8	200	1,000	16	0.75	20	0.4	1 day	44	34.0 ± 4.1	48
9	200	1,000	16	0.75	20	0.8	1 day	48	22.7 ± 3.0	47
10	200	1,000	16	0.75	–	0.8	1 day	50	78.2 ± 11.4	–
11	200	1,000	16	0.75	8	0.8	1 day	54	95.7 ± 23.3	59
12	200	1,000	16	0.75	16	0.8	1 day	43	126.2 ± 24.8	41
13	200	1,000	16	0.75	32	0.8	1 day	53	244.3 ± 81.1	47

[a] The yields are based on oligomer, TEOS, silica nanoparticle and hibitane

[b] Average particle size in MeOH was determined by dynamic light scattering measurements

[c] Contents of hibitane in nanoparticles determined by UV–vis. spectra based on the used hibitane

Table 2 Reaction of R_F-(ACA)$_n$-R_F[R_F-(DMAA)$_n$-R_F] with TEOS and silica nanoparticles (size: 11 nm) in the presence of hibitane

Run	Oligomer (mg)	TEOS (mg)	MeOH (mL)	25% aq. NH_3 (mL)	Hibitance (mg)	Silica nanoparticle (mg)	Reaction time	Yield (%)[a]	Particle size[b] (nm)	Contents of hibitane (%)[c]
R_F-(ACA)$_n$-R_F										
1	80	80	40	12	–	80	4 h	49	85.7 ± 18.2	–
2	80	80	40	6	16	80	4 h	62	103.4 ± 20.8	90
3	80	80	40	12	16	80	1 day	95	637.1 ± 97.2	86
R_F-(DMAA)$_n$-R_F										
4	80	80	40	12	–	80	4 h	78	263.4 ± 40.6	–
5	80	80	40	6	16	80	4 h	67	173.1 ± 49.5	70
6	80	80	40	12	16	80	1 day	95	521.8 ± 83.1	57
7	80	80	40	12	16	80	1 day	95	521.8 ± 83.1	71

[a] The yields are based on oligomer, TEOS, silica nanparticle and hibitane

[b] Average particle size in MeOH was determined by dynamic light scattering measurements

[c] Contents of hibitane in nanoparticles determined by UV–vis. spectra based on the used hibitane

tions; however, we have succeeded in preparing R_F-(DOBAA)$_n$-R_F/silica nanocomposites-encapsulating hinokitiol and hinokioil from 24 to 52% isolated yields as shown in Scheme 1 and Table 3. DLS measurements showed that the size of these fluorinated nanocomposites thus obtained were nanometer size-controlled (86–563 nm), and these nanoparticles have a good dispersibility and stability in methanol and water. Interestingly, the size of fluorinated nanocomposites-encapsulated hinokitiol was found to increase from 86 to 117 nm with the increase of the used hinokitiol (from 0.12 to 0.24 mmol: Runs 1 and 2 in Table 3), and was also increased from 117 to 563 nm with the increase of the reaction time (from 4 h to 1 day: Runs 2 and 5 in Table 3). These findings indicate that R_F-(DOBAA)$_n$-R_F oligomer should be incorporated homogeneously into the silica gel including the hydrolysis of TEOS, utilizing hydrogen bonding interaction between the silanol groups and amido groups of oligomers in the presence of hinokitiol or hinokioil to afford the fluorinated oligomers/silica nanocomposites-encapsulated biocides in which their size becomes larger. Especially, fluorinated oligomers/silica nanocomposites-encapsulated hinokioil have been found to possess the wooden perfume related to the presence of hinokioil for a few months.

Table 3 Reactions of R_F-(DOBAA)$_n$-R_F with TEOS and silica nanoparticles (size:11 nm) in the presence of hinokitiol and hinokioil

Run	Oligomer (mg)	TEOS (mg)	25% aq. NH_3 (mL)	Hinokitiol (mg)	Silica nanoparticle (mg)	Reaction time	Yield (%)[a]	Particle size[b] (nm)	Contents of hibitane (%)[c]
1	80	80	12	0.12	80	4 h	52	86.1 ± 12.1	51
2	80	80	12	0.24	80	4 h	51	116.8 ± 24.6	37
3	80	80	12	0.48	80	4 h	46	120.3 ± 23.1	28
4	80	80	12	0.60	80	4 h	30	166.1 ± 30.1	21
5	80	80	12	0.24	80	1 day	38	562.7 ± 103.5	48
6	80	80	12	0.12	80	1 day	46	294.2 ± 50.0	63
				Hinokioil					
7	80	80	12	200 mg	80	4 h	48	117.6 ± 31.4	20[d]
8	80	80	6	200 mg	80	4 h	32	93.4 ± 18.7	31[d]
9	80	80	12	400 mg	80	4 h	24	173.4 ± 23.2	15[d]

[a] The yields are based on oligomer, TEOS, silica nanoparticle and hinokitiol (or hinokioil)

[b] Average particle size in MeOH was determined by dynamic light scattering measurement

[c] Contents of hinokitiol (or hinokioil) in nanoparticles determined by UV–vis. spectra based on the used hinokitiol (or hinokioil)

[d] Content of hinokioil (%)

Our new fluorinated oligomers/silica nanocomposites-encapsulated hibitane, hinokitiol and hinokioil are expected to exhibit an antibacterial activity related to the presence of these low-molecular weight biocides in the composites. Therefore, it is very interesting to test these fluorinated nanocomposites for their antibacterial activity. In fact, we investigated the antibacterial activity of these fluorinated nanocomposites against *Staphylococcus aureus* by the vial cell counting method. About 10^6 cells per mL of *S. aureus* were exposed to 500 μg/ml of the nanocomposites in saline, and Table 4 shows the colony-forming units (cfu) versus exposure of these nanocomposites against *S. aureus*.

As shown in Table 4, fluorinated nanocomposite-encapsulated no biocide was not able to exhibit an antibacterial activity at all; however, fluorinated nanocom-

Table 4 Antibacterial activity of fluoroalkyl end-capped oligomer/silica nanocomposites-encapsulated hibitane, hinokitiol, and hinokioil against *S. aureus*

	Oligomer	Contents of biocide in composites (%)[a]	*S. aureus* (cfu)[b]
Control	–	Hibitane	3.2×10^6
	R_F-(DOBAA)$_n$-R_F	0	3.0×10^7
	R_F-(DOBAA)$_n$-R_F	0.7	2.9×10^3
	R_F-(DOBAA)$_n$-R_F	1.2	20
	R_F-(DOBAA)$_n$-R_F	2.1	10
	R_F-(DMAA)$_n$-R_F	5.8	<10
	R_F-(DMAA)$_n$-R_F	8.2	<10
	R_F-(DMAA)$_n$-R_F	14.8	<10
Control	–	Hinokitiol	4.8×10^6
	R_F-(DOBAA)$_n$-R_F	11.0	1.0×10^2
	R_F-(DOBAA)$_n$-R_F	13.6	<10
	R_F-(DOBAA)$_n$-R_F	22.0	<10
	R_F-(DOBAA)$_n$-R_F	25.2	<10
	R_F-(DOBAA)$_n$-R_F	28.8	<10
Control	–	Hinokioil	7.2×10^6
	R_F-(DOBAA)$_n$-R_F	23.3	<10

[a] Contents of biocide based on the obtained nanocomposites (wt.%)

[b] Cfu indicates colony forming unit

[c] Concentration of nanocomposites: 500 μg/mL

Table 5 Contact angles of dodecane on modified PMMA films treated with fluoroalkyl end-capped oligomers/silica nanocomposites-encapsulated hibitane, hinokitiol, and hinokioil[a]

Composite	Contact angle (°)		
	Surface side	Reverse side	Film thickness (μm)
R_F-(DOBAA)$_n$-R_F/Silica nanocomposites-encapsulated hibitane (particle size: 23 nm)	37	9	248
R_F-(DOBAA)$_n$-R_F/Silica nanocomposites-encapsulated hibitane (particle size: 173 nm)	28	1	194
R_F-(DOBAA)$_n$-R_F/Silica nanocomposites-encapsulated hibitane (particle size: 86 nm)	33	3	177
R_F-(DOBAA)$_n$-R_F/Silica nanocomposites-encapsulated hibitane (particle size: 117 nm)	27	0	209
R_F-(DOBAA)$_n$-R_F/Silica nanocomposites-encapsulated hibitane (particle size: 118 nm)	19	0	181
R_F-(DOBAA)$_n$-R_F/Silica nanocomposites-encapsulated hibitane (particle size: 93 nm)	25	2	195
Non-treated PMMA film	0	0	

[a] The contents of fluoroalkyl end-capped oligomers in the modified PMMA films is 1 wt.%

posites-encapsulated hibitane, hinokitiol and hinokioil were found to exhibit a good antibacterial activity against *S. aureus*, and these nanocomposites are capable of killing the bacterial cells from 10^6 to below 10 cfu (colony forming unit). Of particular interest, the contents of hibitane in nanocomposites become higher from 0.7 to 14.8%, antibacterial activity was found to increase with the increase of the contents of hibitane, and almost the same antibacterial activity (below 10 cfu) was obtained above the concentration of 5.8%. A similar result was obtained in the case of fluorinated nanocomposites-encapsulated hinokitiol and hinokioil, and an extremely higher antibacterial activity (below 10 cfu) was obtained above the contents of 13.6% hinokitiol in composites and at the content of 23.3% hinokioil in composite, respectively. The compounds, which are capable of killing bacterial cells from 10^6 to 10^3 cfu, are in general considered to possess antibacterial activity. Therefore, our present fluorinated nanocomposites are an attractive functional material possessing a potent antibacterial activity.From these findings, it is in particular interest to apply our present fluorinated nanocomposites-encapsulated these low molecular biocides to the surface modification of traditional organic polymers such as poly(methyl methacrylate) [PMMA]. We have prepared the modified PMMA films treated with fluorinated nanocomposites-encapsulated hibitane, hinokitiol and hinokioil by the use of cast film formation methods. These results were shown in Table 5.As shown in Table 5, the contact angles of dodecane on the modified PMMA film surface treated with these fluorinated composites showed significantly large values (19–37°), respectively, which exhibit a good oleophobicity imparted by fluoroalkyl segments in nanocomposites on the PMMA surface. In contrast, the contact angles of dodecane on the reverse sides were extremely decreased (9–0°), indicating that our present fluorinated nanocomposites can be dispersed regularly on the polymer surface during the cast film formation. Thus, not only fluorinated oligomers but also encapsulated low-molecular weight biocides should be well dispersed above the polymer surface.In conclusion, we have succeeded in preparing fluoroalkyl end-capped oligomers/silica nanocomposites-encapsulated low-molecular weight biocides such as hibitane, hinokitiol, and hinokioil by the hybridizations of the corresponding oligomers with TEOS and silica nanoparticles in the presence of these biocides. These fluorinated nanocomposites-encapsulated biocides are nanometer size-controlled particles, and these nanocomposites were found to exhibit a good antibacterial activity against *S. aureus*. Interestingly, these fluorinated nanocomposites were applied to the surface modification of traditional organic polymers such as PMMA to exhibit a surface active characteristic imparted by fluoroalkyl segments in nanocomposites on their surface. Thus, not only fluorinated oligomers but also the encapsulated biocides should be arranged on the modified PMMA films. Therefore, these fluorinated nanocomposites-encapsulated biocides have high potential for new fluorinated functional materials possessing the antibacterial characteristic with the surface active property imparted by fluorine.

Acknowledgements Thanks are due to Kohjin Co. Ltd., Kyowa Hakko Kogyou Co., Ltd., and Yushiseihin Co., Ltd. for supply of DMAA, DOBAA, and hinokioil, respectively.

References

1. (a) Ameduri B, Boutevin B (2004) Well-architectured fluoropolymers: synthesis, properties and applications, Elsevier, Amsterdam, p 231; (b) Cochin D, Hendlinger P, Laschewsky A, (1995) Colloid Polym Sci 273:1138; (c) Park IJ, Lee S-B, Choi CK, Kim K-J (1996) J Colloid Interface Sci 181:284; (d) Morita M, Kubo M, Matsumoto M (1996) Colloid Surf A 109:183; (e) Park IJ, Lee S-B, Choi CK (1994) J Appl Polym Sci 54:1449; (f) Imae T, Tabuchi H, Funayama K, Sato A, Nakamura T, Amaya N (2000) Colloid Surf A: Physicochem Eng Asp 167:73; (g) Imae T (2003) Curr Opin Colloid Interface Sci 8:307; (h) Johns K, Stead G (2000) J Fluorine Chem 104:5; (i) Ameduri B, Boutevin B (2000) J Fluorine Chem 104:53; (j) Sawada H (1996) Chem Rev 1996 96:1779; (k) Sawada H, Kawase T (2001) Kobunshi Ronbunshu

58:147; (l) Sawada H, Kawase T (2001) Kobunshi Ronbunshu 58:255; (m) Sawada H (2000) J Fluorine Chem 105:219; (n) Sawada H, Matsumoto T, Nakayama M (1992) Yuki Gosei Kagaku Kyokaishi 50:592; (o) Sawada H (2000) J Fluorine Chem 101:315; (p) Sawada H (2003) J Fluorine Chem 121:111

2. (a) Sawada H, Iidzuka J, Maekawa T, Takahashi R, Kawase T, Oharu K, Nakagawa H, Ohira K (2003) J Colloid Interface Sci 263:1; (b) Sawada H, Iidzuka J, Kawase T, Oharu K, Nakagawa H (2003) Eur Polym J 39:1991
3. (a) Sawada H, Shindo K, Ueno K, Hamazaki K (2005) Polym Adv Technol 16:764; (b) Sawada H, Shindo K,Iidzuka J, Ueno K, Hamazaki K (2005) Eur Polym J 41:2232
4. Sawada H, Yanagida K, Takahashi R, Nishikawa Y, Kawase T, Oharu K, Nakagawa H, Ohira K, Wada K (2002) Polym J 34:855
5. (a) Sawada H, Yoshino Y, Kurach M, Kawase T, Takishita K, Tanedani T (2000) Polymer 41:397; (b) Sawada H, Yoshino Y, Ikematsu Y, Kawase T (2000) Eur Polym J 36:231; (c) Sawada H, Kawase T, Ikematsu Y, Yoshii Y, Oue M, Hayakawa Y (1996) J Chem Soc Chem Commun 179; (d) Sawada H, Gong Y-F, Minoshima Y, Matsumoto T, Nakayama M, Kosugi M, Migita T (1992) J Chem Soc Chem Commun 537
6. Sawada H, Gong Y-F, Matsumoto T, Nakayama M, Kosugi M, Migita T (1991) J Jpn Oil Chem Soc 40:730
7. (a) Sawada H, Katayama K, Oue M, Kawase T, Hayakawa Y, Baba M, Tomita T, Mitani M (1996) J Jpn Oil Chem Soc 45:161; (b) Sawada H, Wake A, Maekawa T, Kawase T, Hayakawa Y, Tomita T, Baba M (1997) J Fluorine Chem 83:125; (c) Sawada H, Tanba K, Tomita T, Kawase T, Baba M, Ide T (1997) J Fluorine Chem 84:141
8. Babbs M (1956) J Pharm Pharmacol 8:110