Colloid Polym Sci (2008) 286:965–973
DOI 10.1007/s00396-008-1856-4

ORIGINAL CONTRIBUTION

Preparation and applications of novel fluoroalkyl end-capped 2-acrylamido-2-methylpropanesulfonic acid oligomer/clay nanocomposites

Hideo Sawada · Airi Takebayashi · Kazuo Sasazawa · Masaki Mugisawa · Keigo Takahashi · Mitsugu Uejima · Toshihide Murakami

Received: 23 December 2007 / Revised: 5 February 2008 / Accepted: 19 February 2008 / Published online: 2 April 2008

Abstract New fluoroalkyl end-capped 2-acrylamido-2-methylpropanesulfonic acid oligomers/clay composites were prepared by reaction of fluoroalkanoyl peroxide with the corresponding monomer in the presence of clay in aqueous solutions. These obtained fluorinated composites were nanometer size-controlled and were found to exhibit a good dispersibility in water and polar organic solvents such as methanol. The contents of clay in these nanocomposites were estimated to be 3~19% by the thermogravimetric analysis measurements. X-ray diffraction spectra showed the successful intercalation of fluorinated oligomers into the interlayer spaces of clay. These fluorinated clay nanocomposites were applied to the surface modification of poly(vinyl alcohol). In addition, these fluorinated nanocomposites were found to interact with methylene blue effectively to afford the fluorinated oligomers/clay/methylene blue nanocomposites.

Keywords Fluorinated oligomer · Betaine-type · Clay · Nanocomposite · Dispersibility · Surface modification · X-ray diffraction · Methylene blue

H. Sawada (✉) · A. Takebayashi · M. Mugisawa · K. Takahashi
Department of Frontier Materials Chemistry,
Graduate School of Science and Technology, Hirosaki University,
Bunkyo-cho,
Hirosaki 036-8561, Japan
e-mail: hideosaw@cc.hirosaki-u.ac.jp

K. Sasazawa
Central R & D Laboratories, Taiyo Yuden Co., Ltd.,
8-1 Sakae-cho,
Takasaki, Gunma 370-8522, Japan

M. Uejima · T. Murakami
Zeon Corporation,
Kawasaki-Shi,
Kanagawa 210-9507, Japan

Introduction

Recently, considerable interest in organic/clay nanocomposites has been increasing at an unprecedented level in a wide variety of fields because the molecular level combination of organic and inorganic compounds in a nanocomposite not only can improve the existing material properties but also can develop new functionalities such as acting as gas barriers, their gas selectivity, the interesting thermal, mechanical, and optical properties that set them apart from those of the parent materials [1–4]. The clay in the polymer/clay composites can be dispersed well at the nanometer scale through insertion of polymer chains into the silicate interlayers of the modified clay treated with quaternary cationic surfactants by the replacing the metals in the clay interlayers [1–4]. The interaction of this modified clay with numerous radical polymerizable monomers such as methyl methacrylate and styrene followed by free radical polymerization has been widely studied to afford a variety of polymer/clay nanocomposites [5, 6]. Thus, an organic modification of clays is required to enhance their compatibility with polymeric materials. Naturally abundant silicate clays are hydrophilic in nature and lack the affinity for hydrophobic polymer. It is well-known that the layered silicates are generally modified to become organophilic by intercalating organic surfactants such as alkylammonium and phosphonium salts [7–10]. Therefore, a considerable interest should be focused on the modifications of clays through the enlarged basal spacing in the layered clays by the use of novel intercalating agents from the view of development of new organic–inorganic nanocomposites. However, the organic modification of the clays has been very limited to the cationic organic surfactants, and organic polymers such as poly(propylene oxide)-amido acid have been directly used to intercalate non-treated parent clay to afford the corresponding polymer/clay nanocomposites [11]. Fluorinated polymer/clay nanocomposites have attracted much interest because fluorinated polymers exhibit numerous unique characteristic such as excellent chemical and thermal stability, low surface energy, and low refractive index and dielectric constant, which cannot be achieved by the corresponding non-fluorinated polymers [12]. In these fluorinated polymers, partially fluorinated, in particular 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 non-fluorinated, randomly or block-type fluoroalkylated polymers, and low-molecular weight fluorinated surfactants [13, 14]. From the developmental viewpoints of novel polymer-layered silicate nanocomposites possessing a variety of unique characteristics, it is very interesting to synthesize new fluorinated polymers–clay nanocomposites by the use of a variety of fluoroalkyl end-capped oligomers as key intermediates. In fact, we have already found that nonionic-type amphiphilic fluoroalkyl end-capped acryloylmorpholine and *N*,*N*-dimethylacrylamide oligomers are able to widen the clay basal spacing to afford the corresponding fluoroalkylated oligomers–clay nanocomposites possessing good dispersibility and stability in aqueous and organic media [15]. In these fluoroalkyl end-capped oligomers, fluoroalkyl end-capped oligomers containing betaine-type segments are of particular interest, because these fluorinated oligomers possess both anionic and cationic segments, which should interact effectively with the silicate interlayers of the non-treated hydrophilic clay. Thus, in this paper, we would like to demonstrate on the preparation and application of fluoroalkyl end-capped 2-acrylamido-2-methylpropanesulfonic acid oligomers/clay nanocomposites, with emphasis on the preparation of fluorinated oligomers/clay nanocomposites-encapsulated organic dyes such as methylene blue.

Experimental

Measurements

Dynamic light-scattering measurements were measured using Otsuka Electronics DLS-7000 HL (Tokyo, Japan). Ultraviolet–visible spectra were measured using Shimadzu UV-1600 UV–vis spectrophotometer (Kyoto, Japan). X-ray diffraction measurements were performed by the use of RIGAKU RINT 2500 (Tokyo, Japan). The contact angles were measured by the use of Kyowa Interface Science Drop Master 300 (Saitama, Japan).

Materials

2-Acrylamido-2-methylpropanesulfonic acid, lucigenin, methylene blue, acridine hydrochloride, and acriflavine hydrochloride were purchased from Tokyo Kasei Kogyou Co. (Tokyo, Japan). Sumecton SA (TR) (a synthetic inorganic polymer with a saponite structure (average particle size 55 nm; a cation exchange capacity value: 100 mequiv. per 100 g), which was supplied by Kunimine Ind. Co., Japan.

Preparation of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites

Perfluoro-2-methyl-3-oxahexanoyl peroxide [16] (9 mmol) in a 1:1 mixture (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane (370 g) was added to an aqueous solution (7 ml) containing Sumecton SA (0.23 g) and 2-acrylamido-2-methylpropanesulfonic acid (30 mmol). The heterogeneous mixture was stirred vigorously at 45 °C for 5 h under nitrogen. After evaporation of the solvent, the crude product obtained was reprecipitated from methanol-tetrahydrofuran to give the expected R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA composites (5.50 g).

A typical procedure for gelation test

A procedure for studying the gel-formation ability was based on a method reported by Hanabusa et al. [17] Briefly, weighted fluoroalkylated end-capped 2-acrylamido-2-methylpropanesulfonic acid oligomer/Sumecton SA composites were mixed with water in a tube. The mixture was treated under ultrasonic conditions until the solid was dissolved. The resulting solution was kept at 30 °C for 1 h, and then the gelation was checked out visually. When it was formed, the gel was stable and the tube could be inverted without changing the shape of the gel.

Surface modification of poly(vinyl alcohol) with R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites

The modified poly(vinyl alcohol) film was prepared by casting the mixtures of aqueous solutions (10 ml) of poly (vinyl alcohol) (0.98 g) and the transparent aqueous solution (2.1 ml) containing 10 g/dm^3 R_F–(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites on glass plates. The solvent was evaporated at room temperature, and the film formed peeled off and dried at 50 °C for 72 h under vacuum to afford the modified poly (vinyl alcohol) film. The contact angles for dodecane of both the surface and the reverse sides of this film were measured at room temperature by the use of the contact angle measurements.

Preparation of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA/methylene blue nanocomposites

To an aqueous solution (3 ml) of 8 g/dm^3 R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites was added an aqueous solution (3 ml) of methylene blue (25 μmol/dm^3). The mixture was stirred with a magnetic stirring bar at room temperature for 1 h to afford R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA/methylene blue nanocomposites. The formation of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA/methylene blue nanocomposites in the aqueous solution was confirmed by the use of UV–vis spectra. Other R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA/dyes composites were prepared under similar conditions, and the formation of these composites was spectrophotometrically confirmed.

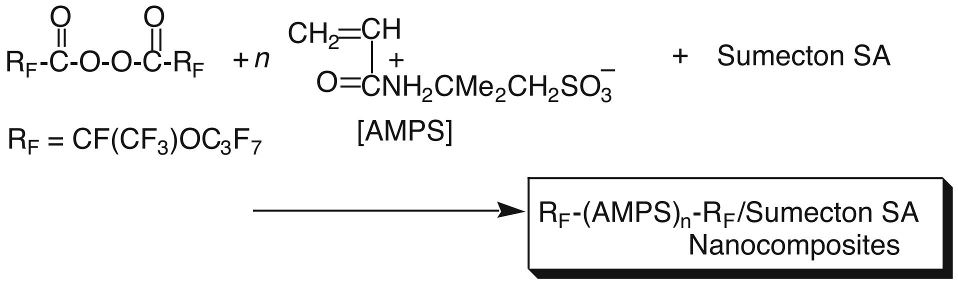
Results and discussion

The reactions of fluoroalkanoyl peroxide with 2-acrylamido-2-methylsulfonic acid and Sumecton SA were carried out in heterogeneous solvent systems [AK-225 (1: 1 mixed solvents of 1,1-dichloro-2,2,3,3,3-pentafluoropropane-1,3-dichloro-1,2,2,3,3-pentafluoropropane) and water] by stirring vigorously at 45 °C for 5 h under nitrogen. The process is outlined in Scheme 1.

Fluoroalkanoyl peroxide was found to react with 2-acrylamido-2-methylpropanesulfonic acid and Sumecton SA under mild conditions to afford fluoroalkyl end-capped 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA composites in 36~51% isolated yields as shown in Scheme 1.

To clarify the presence of Sumecton SA in these composites, the contents of Sumecton SA in the composites in Scheme 1 were estimated by the use of thermogravimetric analysis, in which the weight loss of the composites was measured by raising the temperature to around 800 °C. The thermal stability of each fluorinated oligomer/Sumecton SA composite was found to decrease significantly compared to that of the parent Sumecton SA. In contrast, the thermal stability of these composites was found to increase compared to that of the parent R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomer. (see Fig. 1).

The contents of Sumecton SA in these composites were estimated to be 3 ~ 19%, in comparison with the parent Sumecton SA, and these results were also shown in Fig. 1. Interestingly, the contents of Sumecton SA in R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA composites are markedly dependent on the feed ratios of Sumecton SA and 2-acrylamido-2-methylpropanesulfonic acid used, increasing from 3 to 19% with greater Sumecton SA ratios in Sumecton SA/2-acrylamido-2-methylpropanesulfonic acid, indicating that the compositization of Sumecton



Run	$(R_FCOO)_2$ (mmol)	AMPS (mmol)	Sumecton SA (g)	R_F-(AMPS)$_n$-R_F/Sumecton SA Nanocomposites Yield (%)$^{a)}$
1	9	30	0.23	47
2	9	30	0.45	39
3	9	30	0.90	36
4	9	30	1.35	51

Scheme 1 Reactions of fluoroalkanoyl peroxide with 2-acrylamido-2-methylsulfonic acid and Sumecton SA. ^{a}Isolated yields were based on the decarboxylated peroxide units (R_F–R_F), 2-acrylamido-2-methylpropanesulfonic acid, and Sumecton SA [R_F = CF(CF$_3$)OC$_3$F$_7$]

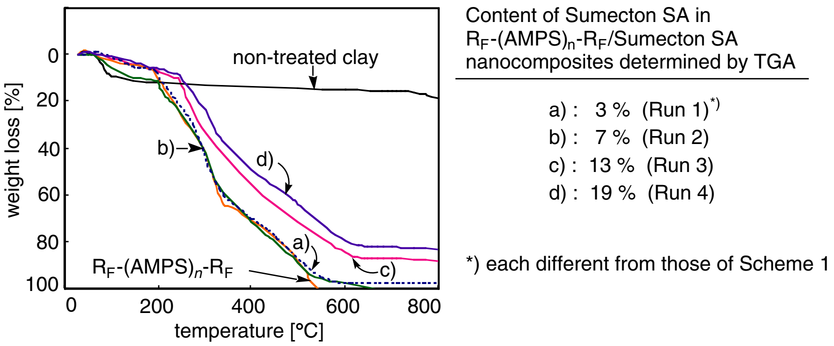


Fig. 1 Thermogravimetric analyses of non-treated Sumecton SA and R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F and R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$-R_F/Sumecton SA nanocomposites

SA with R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$-R_F oligomers could be smoothly proceeded to afford the corresponding fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomer/Sumecton SA composites under mild conditions as shown in Scheme 1.

Previously, we reported that R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomers can form gels in water and organic media due to the synergistic interaction between the aggregations of end-capped fluoroalkyl groups and ionic interactions of the betaine-type segments. [18] Thus, it is in particular interest to test our present R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA composites for the dispersibility in water and traditional organic solvents. In fact, we tried to study on the dispersibility of these composites, and the results were shown in Table 1.

As shown in Table 1, R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA composites, in which the content of Sumecton SA in composites is 3%, were found to form gels in water and polar organic solvents as well as the parent R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomer. The minimum concentration for gelation ($C_{\min}$) in water for R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomer at 30 °C are given in Table 2, for comparison. R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA composites (content of Sumecton SA: 3%) exhibited lower gelling ability (higher $C_{\min}$ value) compared to that of the parent R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$-R_F oligomer ($C_{\min}$: 68 g/dm^3). This finding suggests that the main driving force for gelation is governed by the synergistic interaction with the aggregation of fluoroalkyl segments and ionic interaction of betaine-type segments, and ionic interaction between the betaine-type segments should be in part decreased due to the intercalation of betaine-type segments in oligomers into the layered silicate. Thus, the R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomer composites with higher contents of Sumecton SA could afford not gel formation but a good dispersibility in water and polar organic media such as methanol, ethanol, dimethyl sulfoxide and *N*,*N*-dimethylformamide.

In this way, it was clarified that our present R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA composites exhibits a good dispersibility in a variety of solvents. The expected intercalated fluoroalkyl end-capped 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA composites should be derived from the ionic interaction between the R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomer and layered silicates. We have measured the size of self-assembled fluorinated molecular aggregates, which were formed by the aggregations of end-capped fluoroalkyl segments in R_F-(2-acrylamido-2-methyl-

Table 1 Dispersibility of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites

Composite (content of Sumecton SA)$^{(1)}$	SOLVENT$^{(2)}$								
	H_2O	MeOH	EtOH	THF	PhMe	AK-225	DMSO	DMF	$(CH_2Cl)_2$
R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F (0 %)	G$^{(3)}$	G	G	×$^{(4)}$	×	×	G	G	×
3%	G	G	G	×	×	×	G	G	×
7%	○$^{(5)}$	○	○	×	×	×	○	○	×
13%	○	×	×	×	×	×	×	×	×
19%	○	×	×	×	×	×	×	×	×

THF tetrahydrofuran, *DMSO* dimethyl sulfoxide, *DMF* *N*,*N*-dimethylformamide

(1) Determined by *TGA* Thermogravimetric analysis

(2) AK-225: 1:1 mixed solvent of $Cl_2CHCF_2CF_3$ and $CClF_2CF_2CHClF$

(3) G : Gel;

(4) ×: Insoluble

(5) ○: well-dispersed solution

Table 2 Size of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites in aqueous solutions determined by dynamic light scattering measurements and critical gel concentration (C_{min}) of these nanocomposites in water at 30 °C

Content of Sumecton SA in composite[1] (%)	Size of particle (nm)	C_{min} (g/dm^3) (gelator/water)
0 [R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F only]	44.1±6.2	68
3	83.9±9.0	217
7	185.4±17.4	No gelation (dispersed)
13	423.5±41.4	No gelation (dispersed)
19	267.5±28.0	No gelation (dispersed)
100 (Sumecton SA only)	54.5±8.2	–

[1] Determined by thermogravimetric analysis

propanesulfonic acid)$_n$–R_F oligomers, and fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA composites in water by dynamic light-scattering measurements at 30 °C, respectively. The size of parent Sumecton SA was also measured under similar conditions for comparison, and these results were shown in Table 2.

As shown in Table 2, the number-average diameters of fluorinated molecular aggregates formed by fluoroalkyl end-capped 2-acrylamido-2-methylpropanesulfonic acid oligomer and the parent Sumecton SA in water are 44.1±6.1 nm and 54.5±8.2 nm, respectively. The size of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomeric aggregates/Sumecton SA composites (84 ~ 426 nm) was found to increase effectively, compared to that of the corresponding fluorinated molecular aggregates or the parent Sumecton SA. This indicates that fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers could interact with Sumecton SA to form the fluorinated molecular aggregates/Sumecton SA nanocomposites through the intercalation of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers into Sumecton SA interlayers. Thus, these fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA nanocomposites should exhibit a good dispersibility against water and polar organic media such as methanol.

To clarify the possibility of the intercalation of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers into Sumecton SA, the basal spacing of the fluorinated oligomeric aggregates/Sumecton SA nanocomposite powders were analyzed by an X-ray powder diffractometer of the parent Sumecton SA and fluorinated oligomeric aggregates/Sumecton SA nanocomposites (see Fig. 2). The parent Sumecton SA contains the basal reflection that is characteristic of the unintercalated repeat distance at d=1.3 nm (2θ=3.8°). The basal spacing of the intercalated fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomeric aggregates/Sumecton SA nanocomposites were determined to be 7.3 ~ 8.5 nm. The diffraction peaks of the fluorinated aggregates–Sumecton SA nanocomposites were shifted to lower angles around 2θ= 1.0 ~ 1.2° compared to that (2θ=3.8°) of the pristine Sumecton SA. The basal spacing increasing from 1.3 to 7.3 ~ 8.5 nm, indicating not only encapsulation of Sumecton SA into the fluorinated oligomeric aggregates cores, but also the successful intercalation of fluoroalkyl end-capped 2-acrylamido-2-methylpropanesulfonic acid oligomers into the interlayer spaces of Sumecton SA. Hitherto, it is well-known that quaternary cationic salts are capable of replacing the metal ions in the silicate interlayers, thus widening the silicate basal spacing, and the modified smectite clays become hydrophobic and are suitable for applications such as nanocomposite uses [7–10]. Therefore, we believe that this finding is the first example for the application of betaine-type fluorinated polymeric surfactants to the convenient intercalating agents

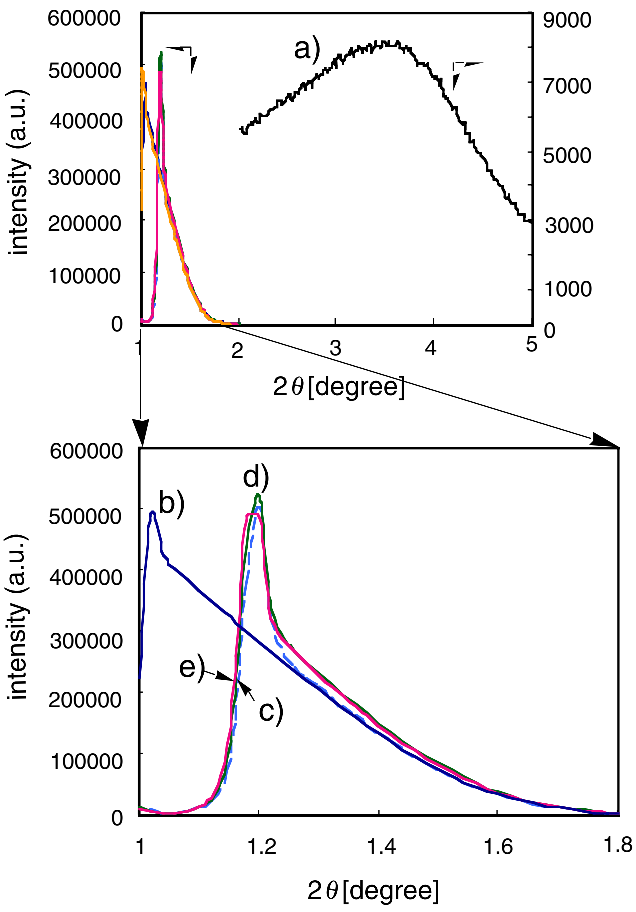


Fig. 2 X-ray diffraction of (**a**) non-treated Sumecton SA (d=1.3 nm), R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$-R_F/Sumecton SA nanocomposites [(**b**) d=8.5 nm, content of Sumecton SA : 3%, (**c**) d= 7.3 nm, content of Sumecton SA : 7%, (**d**) d=7.4 nm,content of Sumecton SA : 13%, (**e**) d=7.4 nm, content of Sumecton SA: 19%]

Table 3 Contact angles of dodecane on poly(vinyl alcohol) films treated with R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites

R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites (content of Sumecton SA in composite; %)	Contact angle (degree)		Thickness of film (mm)
	Dodecane	Reverse side dodecane	
7	39	5	140
13	39	13	65
19	33	5	129

for the achievement of an enlarged basal spacing of the clay layers.

Our present fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomeric aggregates/Sumecton SA nanocomposites were clarified to exhibit a good dispersibility not only in water but also in polar organic media. Previously, we reported that fluoroalkyl end-capped oligomers could be arranged regularly above the poly(methyl methacrylate) (PMMA) surface to exhibit a strong oleophobicity imparted by fluoroalkyl groups [19]. Therefore, it is of particular interest to develop our present fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA nanocomposites to the surface modification of traditional organic polymers such as PMMA and poly(vinyl alcohol). The modified poly(vinyl alcohol) film was prepared by casting the well-dispersed aqueous solutions (22 ml) containing poly(vinyl alcohol) (980 mg) and R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites (20 mg) on a glass plate. We have measured the contact angles of dodecane on the surface and reverse sides of this modified poly(vinyl alcohol) films (film thickness: 65 ~ 140 µm) and the results are shown in Table 3.

As shown in Table 3, contact angles of dodecane on the surface sides and reverse sides are 33° ~ 39° and 5° ~ 13°, respectively, although the contact angle values of dodecane on the non-treated poly(vinyl alcohol) film are 0°. A higher value for the contact angle on the surface side suggests that R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomer in the nanocomposites could be arranged above the polymer surface to exhibit a markedly strong oleophobicity imparted by fluoroalkyl segments on the surface, resulting in the surface arrangements of Sumecton SA in the fluorinated oligomers/Sumecton SA nanocomposites.

Hitherto, there has been numerous studies on the interactions of clay mineral with not only cationic surfactants but also cationic dyes such as methylene blue from the applicable viewpoints of photofunctional materials [20]. For example, Neumann et al. reported on the influence of the layer charge and clay particle size on the interactions between methylene blue and clays in aqueous solutions [21]. Therefore, it is in particular interest to study on the interactions between a variety of organic dyes and our present fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/clay nanocomposites from the developmental viewpoints of new fluorinated photofunctional materials. In fact, we have studied on the interaction of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA nanocomposites with a variety of organic dyes such as lucigenin, acridine hydrochloride, acriflavine hydrochloride, and methylene blue. Fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA nanocomposites could not interact effectively with these organic dyes except for methylene blue; however, these nanocomposites were found to exhibit a unique interaction with methylene blue. These results were shown in Figs. 3–5.

As shown in Fig. 3, UV–vis spectra of an aqueous solution of methylene blue in the presence of Sumecton SA showed a slightly blue-shifted absorption band at 658 nm with an enhanced absorption peak around 610 nm, which was characterized as that of methylene blue dimer [(methylene blue)$_2$] [22], compared to that of the original

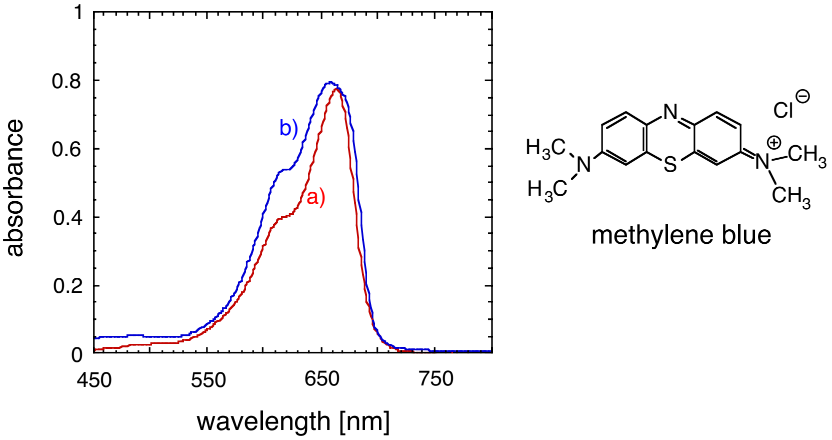


Fig. 3 UV–vis spectra of aqueous solutions of 12.5 μmol/dm^3 methylene blue in the presence of Sumecton SA. **a**) 12.5 μ mol/dm^3 methylene blue in the absence of clay, **b**) 4 g/dm^3 Sumecton SA—12.5 μmol/dm^3 methylene blue

methylene blue (λ_{max}=665 nm). A similar result in Fig. 3 has been already reported by Jacobs et al. [22]

On the other hand, it is interesting that methylene blue was found to afford the red-shifted absorption peak around 747 nm, which was characterized as protonated methylene blue (MbH^{2+}) [22], with an effectively enhanced (methylene blue)$_2$ absorption peak at 610 nm in the presence of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomer (see Fig. 4). Fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomer/Sumecton SA nanocomposites (see Fig. 5) could also exhibit a similar enhanced (methylene blue)$_2$ absorption band to that of Fig. 4; however, these composites could not afford an absorption band related to MbH^{2+} band. The formation of the MbH^{2+} is due to the direct interaction of acidic fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers with methylene blue, and the enhanced absorption peak around 610 nm related to the formation of (methylene blue)$_2$ would be dependent upon it that methylene blue should be effectively encapsulated into fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomeric aggregate cores and fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA composite cores. Previously, Newmann et al. reported that the methylene blue molecules readily adsorb on the clay particles, especially on the external surface to afford methylene blue aggregates [[methylene blue trimer: (methylene blue)$_3$], (methylene blue)$_2$], and dye molecules can also migrate from the external surfaces to the interlamellar to lead MbH^{2+}, when methylene blue is added to a clay aqueous suspension. [21]

To clarify these results in detail, we have measured the size of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA/methylene blue nanocomposites (content of Sumecton SA in composites: 19%) in Fig. 5 with the original Sumecton SA/methylene blue nanocomposites by the use of DLS measurements. These results are as follows:

R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA/methylene blue nanocomposites:	123.0±11.1 nm
Sumecton SA/methylene blue nanocomposites	91.8±17.0 nm
R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites	267.5±28.0 nm (see Table 2)

The size of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA/methylene blue nanocomposites in water was found to decrease effectively by the interactions of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA nanocomposites with methylene blue. In contrast, the size of these nanocomposites increased compared to that of Sumecton SA/methylene blue nanocomposites (92 nm), indicating that methylene blue should be effectively encapsulated as guest molecule into

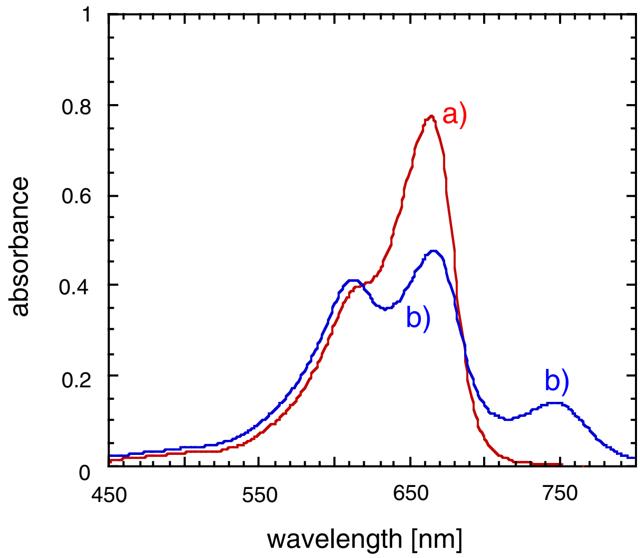


Fig. 4 UV–vis spectra of aqueous solutions of 12.5 μmol/dm^3 methylene blue in the presence of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F [R_F=CF(CF$_3$)OC$_3$F$_7$] after stirring for 1 day at room temperature. **a**) 12.5 μmol/dm^3 methylene blue in the absence of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F **b**) 4 g/dm^3 R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$-R_F—12.5 μmol/dm^3 methylene blue

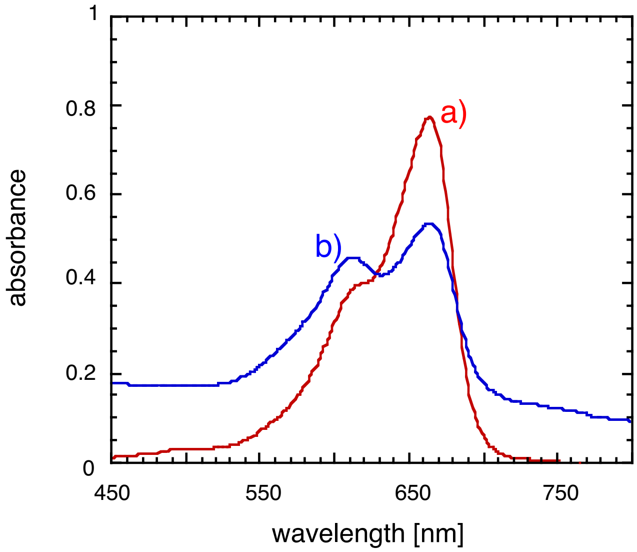


Fig. 5 UV–vis spectra of aqueous solutions of 12.5 μmol/dm^3 methylene blue in the presence of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposite (content of Sumecton SA: 19%) [R_F=CF(CF$_3$)OC$_3$F$_7$] after stirring for 1 day at room temperature. **a**) 12.5 μmol/dm^3 methylene blue in the absence of nanocomposites, **b**) 4 g/dm^3 nanocomposites—12.5 μmol/dm^3 methylene blue

fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomer/Sumecton SA composite cores.

In addition, we have studied on the relationship between the concentration of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers and methylene blue absorbances at 747 nm (MbH^{2+}), 665 nm (original methylene blue), 612 nm [(methylene blue)$_2$] and 570 nm [(methylene blue)$_3$] in the fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomer/methylene blue nanocomposites under the concentration of methylene blue: 12.5 μmol/dm^3. We have also studied on the relationship between the concentration of fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA nanocomposites and methylene blue absorbances (665 nm, 612 nm and 570 nm). These results are shown in Figs. 6 and 7.

As shown in Fig. 6, the absorbance (747 nm) related to the MbH^{2+} was found to increase with the increase of the concentrations of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomers from 10^{-4} to 5 g/dm^{-3}. In the concentrations of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomers from 10^{-3} to 0.02 g/dm^{-3}, the absorbances 570 and 612 nm for (methylene blue)$_3$ and (methylene blue)$_2$, respectively, were found to increase compared to that (665 nm) of the original methylene blue, and the absorbance for (methylene blue)$_3$ became higher compared to that of (methylene blue)$_2$ in each concentration. In particular, as shown in Fig. 8, the higher absorption band due to the (methylene blue)$_3$ is also evident from the difference in color of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/methylene blue nanocomposite aqueous solutions (concentration of composites: 0.02 g/dm^3; purple color; Fig. 8c) and the parent methylene blue (blue color; Fig. 8a). On the other hand, in the concentrations of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomers: 0.1 ~ 5 g/dm^3, the absorbance due to (methylene blue)$_2$ became higher than that of (methylene blue)$_3$, and these composites afforded the similar transparent blue-colored solutions (Fig. 8b) to those of the parent methylene blue. A favorable formation of (methylene blue)$_3$ would be due to the weak network architectures derived from the lower concentrations of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomers.

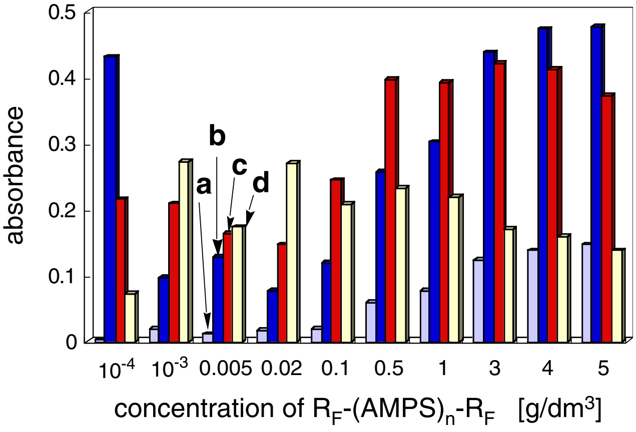


Fig. 6 Relationship between the concentration of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F and absorbance of methylene blue (12.5 μmol/dm^3) in the presence of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F in aqueous solutions after stirring for 1 day at room temperature. **a**) Absorbance of λ=747 nm, **b**) absorbance of λ=665 nm, **c**) absorbance of λ=612 nm, **d**) absorbance of λ=570 nm

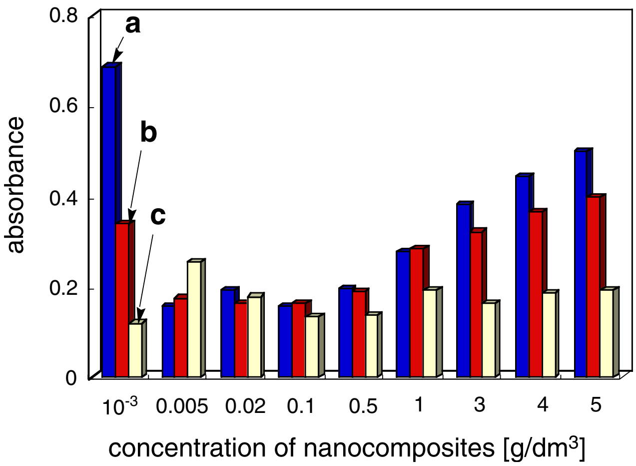


Fig. 7 Relationship between the concentration of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites (content of Sumecton SA: 19%) and absorbance of methylene blue (12.5 μmol/dm^3) in the presence of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/ Sumecton SA nanocomposites in aqueous solutions after stirring for 1 day at room temperature. **a**) Absorbance of λ= 665 nm, **b**) absorbance of λ=612 nm, **c**) absorbance of λ=570 nm

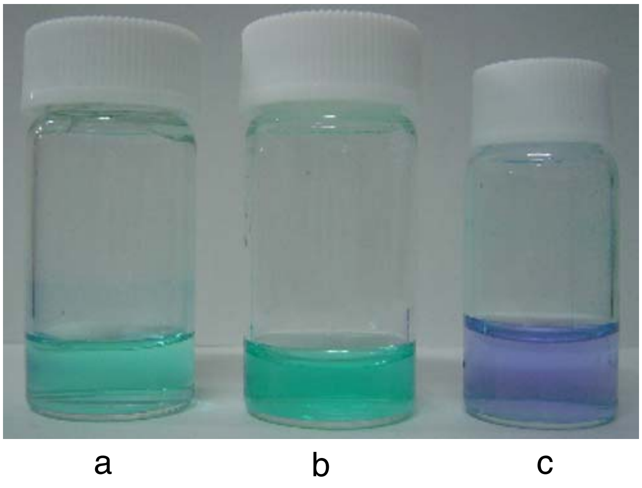


Fig. 8 Photograph of aqueous solutions of 12.5 μmol/dm^3 methylene blue in the presence of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$-R_F [RF =$CF(CF_3)OC_3F_7$] after stirring for 1 day at room temperature. **a**) 12.5 μmol/dm^3 methylene blue in the absence of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$-R_F, **b**) R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$-R_F (4 g/dm^3)-methylene blue, **c**) R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$-R_F (0.02 g/dm^3)-methylene blue

In contrast, the favorable formation of (methylene blue)$_2$ would be due to the relatively fixed network architectures derived from the higher concentrations of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomers. The higher absorbance (665 nm) of the original methylene blue at 10^{-4} g/dm^3 would be due to the weak interaction of methylene blue and R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F oligomeric aggregates in aqueous solutions.

On the other hand, in the case of R_F-(2-acrylamido-2-methylpropanesulfonic acid)$_n$–R_F/Sumecton SA nanocomposites, the absorption band due to MbH^{2+} could not be observed at all in each concentration of the composite. This indicates that fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers could be tightly interacted with Sumecton SA through the ionic interaction between the betaine-type segments in oligomers and the ionic sites on the interlayer of the Sumecton SA to afford the colloidal stable fluorinated 2-acrylamido-2-methylpropanesulfonic acid oligomers/Sumecton SA nanocomposites (see Fig. 7). In the lower concentration of the composites (10^{-3} g/dm^3), the absorption band for the original methylene blue was predominantly observed; however, the absorption bands at 612 nm: (methylene blue)$_3$ and 517 nm: (methylene blue)$_2$ were observed with the formation of methylene blue monomer (665 nm) in the concentration of the composites: 10^{-3} to 5 g/dm^3. In particular, the composites in which concentrations are from 0.005 to 0.02 g/dm^3 afforded not transparent blue-colored but purple-colored aqueous solutions due to the relatively higher absorption band for (methylene blue)$_3$, as well as that of Fig. 8c).

In conclusion, we have succeeded in preparing new fluoroalkyl end-capped betaine-type oligomers/clay nanocomposites by the reaction of fluoroalkanoyl peroxide with the corresponding betaine-type monomer in the presence of clay in aqueous solutions. These nanocomposites thus obtained were found to exhibit a good dispersibility in water and methanol, and were applied to the surface modification of poly(vinyl alcohol) to exhibit a good oleophobicity imparted by fluorine on the surface. These fluorinated oligomers/clay nanocomposites could interact with methylene blue effectively to afford fluorinated oligomers/clay/methylene blue-monomer, methylene blue-dimer and methylene blue-trimer nanocomposites, although the corresponding fluorinated betaine-type oligomers afforded the corresponding oligomers/methylene blue-monomer, methylene blue-dimer, methylene blue-trimer, and protonated methylene blue nanocomposites. Therefore, these fluorinated oligomers/clay nanocomposites have high potential for new fluorinated functional materials through their unique properties not only imparted by fluorine but also clay minerals including organic dyes such as methylene blue.

References

1. Utracki LA, Sepehr M, Boccaleri E (2007) Polym Adv Technol 18:1–37
2. Okada A, Usuki A (2006) Macromol Mater Eng 291:1449–1476
3. Nguyen QT, Baird DG (2006) Adv Polym Technol 25:270–285
4. Giannelis EP (1996) Adv Mater 8:29–35
5. Tseng CR, Wu J-Y, Lee H-Y, Chang FC (2002) J Appl Polym Sci 85:1370–1377
6. Weimer MW, Chen H, Gliannelis EP, Sogah DY (1999) J Am Chem Soc 121:1615–1616
7. Lin J-J, Cheng I-J, Wang R, Lee R-J (2001) Macromolecules 34:8832–8834
8. Bottino FA, Fabbri E, Fragala IL, Malandrino G, Orestano A, Pilati F, Pollicino A (2003) Macromol Rapid Commun 24:1079–1084
9. Albrecht M, Ehrler S, Muhlebach A (2003) Macromol Rapid Commun 24:382–387
10. Salahuddin N, Akelah A (2002) Polym Adv Technol 13:339–345
11. Lin J-J, Chang Y-C, Cheng I-J (2004) Macromol Rapid Commun 25:508–512
12. Ameduri B, Boutevin B (2004) Well-Architectured Fluoropolymers: Synthesis, Properties and Applications. Elsevier, Amsterdam
13. Sawada H (2007) Polym J 39:637–650
14. Sawada H (2007) Prog Polym Sci 32:509–533
15. Sawada H, Takebayashi A, Uejima M, Murakami T (2006) Polym Adv Technol 17:479–483
16. This peroxide was prepared by the reaction of the corresponding acyl fluoride with hydrogen peroxide in the presence of aqueous sodium hydroxide according to our previously reported method; see H. Sawada and M. Nakayama, J Fluorine Chem 51:117–129 (1991).
17. Hanbusa K, Karaki K, Kimura M, Shirai H (1997) J Colloid Interface Sci 195:86–93
18. Sawada H, Katayama S, Ariyoshi Y, Kawase T, Hayakawa Y, Tomita T, Baba M (1998) J Mater Chem 8:1517–1524
19. Sawada H, Yanagida K, Inaba Y, Sugiya M, Kawase T, Tomita T (2001) Eur Polym J 37:1433–1439
20. Ogawa M, Kuroda K (1995) Chem Rev 95:399–438
21. Neumann MG, Gessner F, Schmitt CC, Sartori R (2002) J Colloid Interface Sci 255:254–259
22. Jacobs KY, Schoonheydt RA (1999) J Colloid Interface Sci 220:103–111