

Solubilization of Phthalocyanines into Methanol with Fluoroalkyl End-Capped *N*-(1,1-Dimethyl-3-oxobutyl)- and *N,N*-Dimethyl-Acrylamide Oligomers

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ABSTRACT: Self-assembled molecular aggregates of fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)- and *N,N*-dimethyl-acrylamide oligomers in methanol were found to interact with phthalocyanines as guest molecules to exhibit good solubility. On the other hand, the corresponding non-fluorinated oligomers were not effective in solubilizing phthalocyanines under similar conditions. In these oligomers, fluorinated *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers were more effective in solubilizing phthalocyanines in methanol. Self-assemblies formed by fluorinated oligomer-phthalocyanine complexes are applied to the surface modifications of polystyrene (PS), and the modified PS

surface exhibited not only a strong oleophobicity imparted by fluorine but also good hydrophilicity. Thus, these fluorinated molecular aggregate-phthalocyanine systems are suggested to have high potential for new fluorinated functional materials through their excellent properties imparted by fluorine and phthalocyanines. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 521–525, 2004

Key words: fluorinated oligomers; phthalocyanines; self-assembly of fluorinated oligomer; solubility; surface modification

INTRODUCTION

Phthalocyanines are well-known functional dyes and can be utilized as functional colorants and electronic materials in the field of material science.¹ However, most unsubstituted phthalocyanines have only very limited solubility in virtually all solvents; thereby, the applications of these materials to such fields have hitherto been very limited. From this point of view, the development of phthalocyanines highly soluble in common organic solvents has been hitherto desired. The solubility of phthalocyanines can be improved in general by introducing substituents in the periphery that increase the distance between the planar macrocycle rings carrying the π -electrons and make the solvation easier.² We have been studying the synthesis and properties of a variety of fluoroalkyl end-capped oligomers by the use of fluoroalkanoyl peroxide as a key intermediate.^{3,4} Very recently, we have found that

these fluorinated oligomers were able to reduce the surface tensions of water and organic media as effectively as the low-molecular fluorinated surfactants, and these oligomers can form the self-assembled molecular aggregates with the aggregation of end-capped fluoroalkyl segments in aqueous and organic media.⁵ Of particular interest, it was demonstrated that fluorinated molecular aggregates formed by fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers could recognize selectively hydrophilic amino and *N,N*-dimethylamino compounds as a guest molecule.⁶ It should be expected that this interesting finding is applicable not only to the improvement in the solubility of phthalocyanines but also to the development of the phthalocyanines possessing the unique properties imparted by fluorine. In view of the development of such phthalocyanines, we studied the solubilization of phthalocyanines into methanol with fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers and *N,N*-dimethylacrylamide oligomers. These results will be described herein.

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RESULTS AND DISCUSSION

In general, methanol exhibits poor solubility toward the popular organic polymers such as polystyrene,

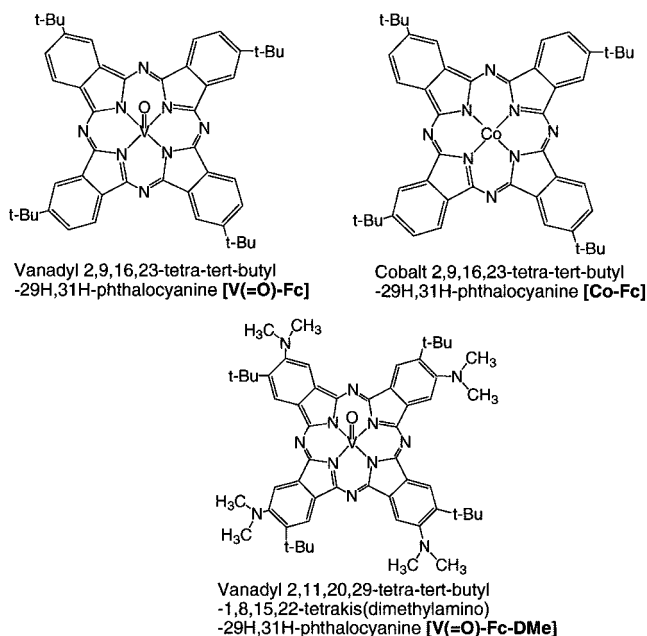


Figure 1 Structures and abbreviations of phthalocyanines.

poly(methyl methacrylate), and polycarbonate. Therefore, the phthalocyanines, which should exhibit good solubility into methanol by using fluoroalkyl end-capped oligomers, can be developed to the novel surface modifications of these organic polymers. In fact, we have tested a variety of phthalocyanines in Figure 1 with fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers [R_F -(DOBAA) $_n$ - R_F] and *N,N*-dimethylacrylamide oligomers [R_F -(DMAA) $_n$ - R_F] for solubility into methanol.

UV-Vis spectra of a methanol solution of Co-Fc solubilized with R_F -(DOBAA) $_n$ - R_F : $R_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ showed an absorption band at 670 nm as in Figure 2. The absorbance of Co-Fc at 670 nm was [Fig. 2] found to increase remarkably compared to that of the absence of fluorinated oligomers. The amount of solubilized Co-Fc was estimated by the use of the molar absorption coefficient (ϵ) of completely solubilized Co-Fc at 670 nm in the absence of oligomer. Additionally, the solubilization of other phthalocyanines into methanol by the use of various fluoroalkyl end-capped DOBAA oligomers were also studied under similar conditions, and these results are shown in Table I.

As shown in Table I, R_F -(DOBAA) $_n$ - R_F oligomers, especially longer fluoroalkyl groups [$R_F = \text{CF}(\text{CF}_3)\text{OC}_6\text{F}_{13}$, $\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$] containing DOBAA oligomers were more effective in solubilizing phthalocyanines into methanol. In contrast, the corresponding nonfluorinated DOBAA oligomer [$-(\text{DOBAA})_n-$] was not effective for the solubilization of phthalocyanines into methanol as well as in the case of the absence of oligomer. This finding sug-

gests that R_F -(DOBAA) $_n$ - R_F oligomers can form the self-assembled molecular aggregates in methanol, and these fluorinated aggregates would interact with phthalocyanines as a guest molecule to exhibit a good solubility. In fact, the dynamic light scattering measurements showed that the size of molecular assemblies in methanol solutions of R_F -(DOBAA) $_n$ - R_F [$R_F = \text{CF}(\text{CF}_3)\text{OC}_6\text{F}_{13}$] was found to increase by the solubilization of Co-Fc from 12 to 26 nm. The increase of the size of the molecular assemblies formed by the solubilization of Co-Fc into methanol indicates that Co-Fc's are encapsulated in the self-assemblies of R_F -(DOBAA) $_n$ - R_F .

Furthermore, we studied the solubilization of V(=O)-Fc-DME with R_F -(DOBAA) $_n$ - R_F : $R_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ in detail, and the results are shown in Figures 3 and 4.

As shown in Figure 3, the amounts of solubilized V(=O)-Fc-DME were found to increase with increasing the concentrations of oligomers, and the amounts of solubilized V(=O)-Fc-DME became almost constant ($\sim 3.5 \text{ g/dm}^3$) above a concentration of 8 g/dm^3 . In addition, the amounts of solubilized V(=O)-Fc-DME increased with increasing the amounts of V(=O)-Fc-DME at the concentration of 2 g/dm^3 of oligomer, and almost constant values ($\sim 2 \text{ g/dm}^3$) were obtained above a concentration of 6 mg (see Fig. 4).

We have also tested fluoroalkyl end-capped DMAA oligomers for solubility of Co-Fc in methanol under similar conditions; the results are shown in Table II.

As shown in Table II, it was clarified that R_F -(DMAA) $_n$ - R_F oligomers exhibit a similar solubility as that of R_F -(DOBAA) $_n$ - R_F oligomers in Table I, and the corresponding nonfluorinated DMAA oligomer [$-(\text{DMAA})_n-$] showed an extremely poor solubility of Co-Fc into methanol. The amounts of solubilized Co-Fc with R_F -(DMAA) $_n$ - R_F was slightly decreased com-

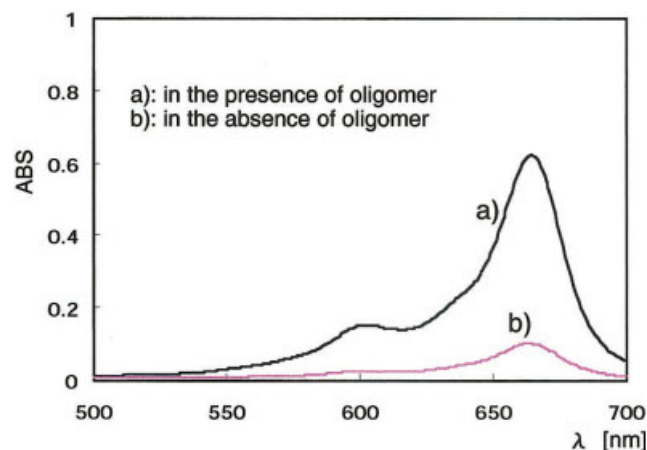


Figure 2 UV-Vis spectra of MeOH solution of Co-Fc in the presence and the absence of R_F -(DOBAA) $_n$ - R_F oligomer [$R_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$]. Concentration of R_F -(DOBAA) $_n$ - R_F : 2 g/dm^3 ; solubilized Co-Fc: 0.74 g/dm^3 .

TABLE I
Solubilization of Phthalocyanines into MeOH with $R_F-(DOBAA)_n-R_F$

R_F	Phthalocyanines	Solubilized phthalocyanines (mg)
$-\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)$ $\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ $M_n = 17,220 (M_w/M_n = 1.26)$	V(=O)-Fc	1.1
	Co-Fc	1.5
	V(=O)-Fc-DMe	4.1
$-\text{CF}(\text{CF}_3)\text{OC}_6\text{F}_{13}$ $M_n = 14,250 (M_w/M_n = 1.38)$	V(=O)-Fc	0.6
	Co-Fc	2.0
	V(=O)-Fc-DMe	5.6
$-\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ $M_n = 5710 (M_w/M_n = 2.74)$	V(=O)-Fc	0.6
	Co-Fc	1.7
	V(=O)-Fc-DMe	2.4
$-(DOBAA)_n-$ $M_n = 18,330 (M_w/M_n = 1.24)$	V(=O)-Fc	0.4
	Co-Fc	0.5
	V(=O)-Fc-DMe	2.0
No oligomer	V(=O)-Fc	0.4
	Co-Fc	0.2
	V(=O)-Fc-DMe	0.9

Used phthalocyanines: 10 mg.

pared to that of $R_F-(DOBAA)_n-R_F$. This would be dependent upon whether the self-assembled molecular aggregates formed by $R_F-(DMAA)_n-R_F$ oligomers are not likely to interact with Co-Fc as a guest molecule in comparison with those of $R_F-(DOBAA)_n-R_F$ oligomers.

In this way, fluoroalkyl end-capped DOBAA and DMAA oligomers are convenient tools for the solubilization of phthalocyanines into common organic solvents such as methanol. It was demonstrated that self-assemblies formed by fluoroalkyl end-capped oligomers in methanol especially could interact strongly with phthalocyanines. Previously, we reported that these fluoroalkyl end-capped oligomers can be ar-

ranged regularly above the common organic polymer surface such as polystyrene (PS) and poly(methyl methacrylate).⁷ This suggests that these phthalocyanine-fluorinated oligomer complexes are applicable to the surface modification of common organic polymers. Thus, Co-Fc- $R_F-(DOBAA)_n-R_F$ and Co-Fc- $R_F-(DMAA)_n-R_F$ complexes were tested for surface activity as a new type of surface modification agent.

As shown in Table III, contact angles for dodecane on the cast films of PS treated with Co-Fc- $R_F-(DOBAA)_n-R_F$ and Co-Fc- $R_F-(DMAA)_n-R_F$ complexes

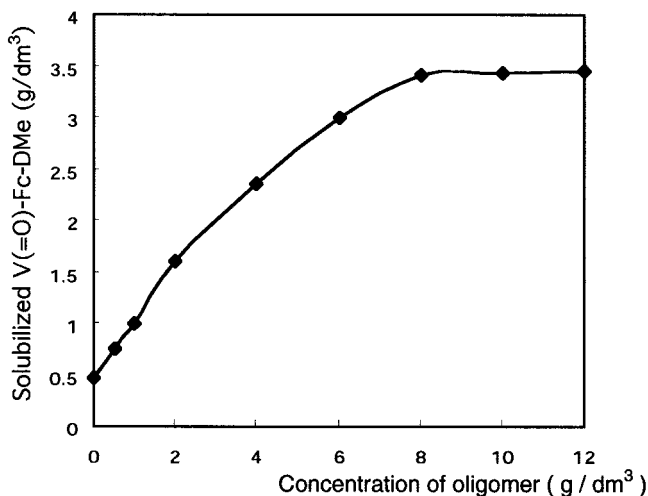


Figure 3 Relationship between the amount of solubilized V(=O)-Fc-DMe into MeOH and the concentration of fluorinated oligomer. Fluorinated oligomer: $R_F-(DOBAA)_n-R_F$ [$R_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$]. Oligomer solution: 2 mL; used: V(=O)-Fc-DMe: 10 mg; condition: RT/24 h.

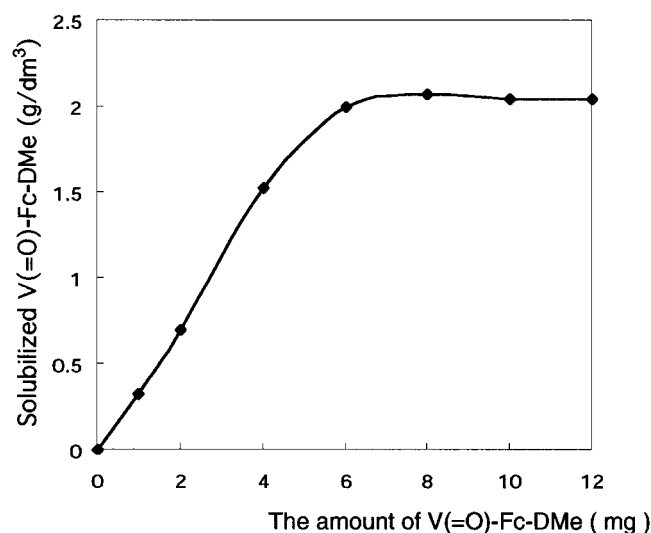


Figure 4 Relationship between the amount of solubilized V(=O)-Fc-DMe into MeOH and the amount of used V(=O)-Fc-DMe. Fluorinated oligomer: $R_F-(DOBAA)_n-R_F$ [$R_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$]. Oligomer concentration: 2 g/dm³; Oligomer solution: 2 mL; condition: RT/24 h.

TABLE II
Solubilization of Co-Fc into MeOH with
 $R_F-(DMAA)_n-R_F$

R_F	Solubilized phthalocyanines (mg)
$-\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ $M_n = 1950 (M_w/M_n = 1.03)$	1.3
$-\text{CF}(\text{CF}_3)\text{OC}_6\text{F}_{13}$ $M_n = 2220 (M_w/M_n = 1.49)$	1.6
$-\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ $M_n = 1740 (M_w/M_n = 1.04)$	1.4
$-(\text{DMAA})_n-$ $M_n = 1670 (M_w/M_n = 1.16)$	0.6
No oligomer	0.5

Used Co-Fc: 10 mg.

showed a significantly large value (26–53°) compared with that of nontreated PS (0°). In each case, time dependence of contact angle of dodecane was not observed. From these results, these complexes exhibit a markedly strong oleophobicity above the surface imparted by fluoroalkyl segments.

Of particular interest, a steep time dependence of contact angle of water was observed in Co-Fc-fluorinated oligomer complexes as shown in Table III. The contact angles of water were found to decrease extremely from 20–11° (83–68°) to 6–0° (52–33°) over 30 min with each complex. Such a time dependence of contact angle of water was not observed in the nontreated PS surface. Therefore, these complexes were clarified to exhibit a markedly strong hydrophilicity above their surface, although these complexes possess a hydrophobic fluoroalkyl segment. This finding suggests that, at the interface with water, hydrophobic fluoroalkyl segments are easily replaced by the strongly hydrophilic amide segments. The amide segments in complexes should be arranged more regularly at the water interface. It takes about 30 min to replace the fluoroalkyl segments by amide segments

when the environment is changed from air to water. Fluorinated DOBAA-Co-Fc complexes especially were not able to exhibit good hydrophilicity on the PS surface compared to that of $R_F-(DMAA)_n-R_F$ -Co-Fc complexes. This result would depend upon whether the hydrophilicity of DOBAA segments is weaker than that of the corresponding DMAA segments, because $R_F-(DOBAA)_n-R_F$ oligomers exhibit a poor solubility in water. From these findings, it is expected that not only fluoroalkyl segments but also Co-Fc units could arrange regularly above the PS surface during the cast film formation.

In conclusion, $R_F-(DOBAA)_n-R_F$ and $R_F-(DMAA)_n-R_F$ oligomers were applied to the dramatic improvement in the solubilization of phthalocyanines, which have very limited solubility in various solvents. In these fluorinated oligomers, $R_F-(DOBAA)_n-R_F$ oligomers were more effective in solubilizing phthalocyanines into methanol, although the corresponding nonfluorinated oligomers exhibit poor solubility in methanol. It was suggested that this good solubility is derived from the interaction of self-assembled fluorinated molecular aggregates with phthalocyanines. Furthermore, these fluorinated aggregate-phthalocyanine complexes were applied to the surface modification on the PS surface, and the modified PS surface exhibited not only a strong oleophobicity imparted by fluorine with a good hydrophilicity. Therefore, these fluorinated oligomer-phthalocyanine systems are applicable to new fluorinated optical functional materials.

EXPERIMENTAL

Measurements

UV-Visible spectra were obtained by using a Shimadzu UV-1600 spectrophotometer (Kyoto, Japan). Molecular weights of fluorinated oligomers were calculated by using a Shodex DS-4 (pump) (Tokyo, Ja-

TABLE III
Contact Angles of Dodecane and Water on PS Films Treated with Fluoroalkyl End-Capped
Oligomers—Co-Fc Complexes^a

R_F in oligomer no.	Contact angle (degree)							
	Dodecane	Water						
		0 min	5 min	10 min	15 min	20 min	25 min	30 min
$R_F-(DOBAA)_n-R_F$								
1 $R_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	46	68	62	57	53	45	39	33
2 $R_F = \text{CF}(\text{CF}_3)\text{OC}_6\text{F}_{13}$	47	76	73	69	64	61	57	51
3 $R_F = \text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	26	83	79	71	68	67	64	52
$R_F-(DMAA)_n-R_F$								
4 $R_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	53	11	8	5	3	2	1	0
5 $R_F = \text{CF}(\text{CF}_3)\text{OC}_6\text{F}_{13}$	51	14	13	9	7	5	4	4
6 $R_F = \text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	43	20	18	15	14	11	7	6
Non-treated PS	0	86						

^a Concentration of oligomer based on PS is 1% (m/m).

pan) and Shodex RI-71 (detector) GPC calibrated with standard PS by using THF as the eluant. Dynamic light scattering of fluorinated oligomer-phthalocyanine solutions were measured by using Wyatt DAWN DSP and NICOMP 380ZSL particle sizing systems (California). Contact angles were measured by the use of the goniometer-type contact angle meter (ERMA G-1-1000, Tokyo, Japan) according to our previously reported method.⁸

Materials

N-(1,1-Dimethyl-3-oxobutyl)acrylamide (DOBAA) and *N,N*-dimethylacrylamide (DMAA) were used as received from Kyowa Hakko Kogyo Co., Ltd. (Tokyo, Japan) and Kohjin Co., Ltd. (Tokyo, Japan), respectively. Fluoroalkyl end-capped DOBAA and DMAA oligomers were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding monomers according to our previously reported method.^{9,10}

Solubilization of phthalocyanines into methanol with R_F -(DOBAA) $_n$ - R_F and R_F -(DMAA) $_n$ - R_F

To a methanol solution of R_F -(DOBAA) $_n$ - R_F : [R_F = CF(CF₃)OCF₂CF(CF₃)OCF₂CF(CF₃)OC₃F₇; 2 g/dm³ (2 mL)] was added Co-Fc (10 mg). The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. The methanol solution thus obtained was centrifuged for 30 min, and then the residual Co-Fc was filtered through a 0.45- μ m polytetrafluoroethylene (PTFE) filter membrane to obtain a transparent solution. The amount of solubilized Co-Fc was estimated by UV-Vis spectra. The solubilization of other phthalocyanines in methanol with fluoroalkyl

end-capped oligomers was studied under similar conditions.

Surface modification of PS

The PS films were prepared by casting the mixture of 1,2-dichloroethane solution (12.5 g), PS (1.0 g), and the transparent 1,2-dichloroethane solution (20 g) containing fluorinated oligomer (20 mg) and phthalocyanines (10 mg) on a glass plate. The solvent was evaporated at room temperature, and the film formed peeled off and dried at 50°C for 24 h under vacuum.

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