

Reactions of Copper Ions With Amines in the Presence of Self-Assembled Fluorinated Oligomeric Aggregates

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ABSTRACT: Copper acetylacetonate reacted with *N,N*-diethylmethylamine and 4,4'-thiobis(6-*t*-butyl-*o*-cresol) in the presence of self-assembled fluorinated oligomeric aggregates formed by fluoroalkyl end-capped 2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate-*N,N*-dimethylacrylamide copolymer $[R_F-(BTRI)_x-(DMAA)_y-R_F]$; $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ to afford stable fluorinated aggregates-copper ions nanocomposites. These fluorinated oligomeric aggregates-copper ions nanocomposites thus obtained were applied to the dispersion of copper ions nano-

composites above the traditional organic polymeric materials such as poly(methyl methacrylate) (PMMA) surface. On the other hand, copper (II) chloride reacted with hydrazine hydrate in the presence of fluorinated oligomeric aggregates formed by fluoroalkyl end-capped *N,N*-dimethylacrylamide homooligomer to afford stable copper nanoparticles. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1328–1334, 2006

Key words: copper ion; fluoropolymer; dispersion; PMMA; molecular aggregate; XRD; XPS

INTRODUCTION

In recent years, considerable interest has been paid to the synthesis of metal nanoparticles because of their applications in a variety of fields such as optics, electronic, magnetic materials, catalysis, and biochemistry.^{1–3} Among a variety of kinds of metal nanoparticles, preparations of copper nanoparticles are relatively difficult because they are easily oxidized, although copper nanoparticles are very attractive materials from the high potential applicable viewpoints into a variety of practical fields. Therefore, the preparation of stable copper nanoparticles is very important, and in fact, many efforts have been directed towards the chemical synthesis of the stable copper nanoparticles so far.^{4–19} In our comprehensive studies on the preparations of stable colloidal metal particles by the use of fluorinated oligomeric surfactants, we have already reported that fluoroalkyl end-capped oligomers can form the self-assembled molecular aggregates with nanometer size levels in aqueous and organic media.^{20,21} This finding indicates that these flu-

orinated aggregates should provide a suitable host moiety to interact with copper particles as guest molecules. In particular, it is suggested that the stability of copper particles should be increased in these fluorinated oligomeric aggregate cores. In this paper, we would like to report on the formation of novel fluorinated aggregates-copper ions nanocomposites and stable copper nanoparticles by the use of fluorinated oligomeric aggregates formed by fluoroalkyl end-capped oligomers.

EXPERIMENTAL

Measurements

Molecular weights were measured using a Shodex DS-4 (pomp) and Shodex RI-71 (Detector) gel-permeation chromatography (GPC; Tokyo, Japan) calibrated with standard polystyrene, using THF as the eluent. UV-vis spectra of fluorinated oligomeric aggregates-copper ions (and copper) nanocomposites were obtained using a Shimadzu UV-1600 spectrophotometer (Kyoto, Japan). Dynamic light scattering of fluorinated assemblies and fluorinated assemblies-copper ions (and copper) nanocomposites was measured using an Otsuka Electronics DLS-6000 HL (Tokyo, Japan) at 30°C. Transmission electron microscopy was done at the Hitachi H-9000 microscope (Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements were performed by the

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use of ULVAC-PHI-Quantera SXM (Kanagawa, Japan), and Mac Science M18XHF-SRA, respectively. 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.²²

Materials

Cu(acac)₂, copper acetate, and copper (II) chloride were purchased from Wako Chemicals (Osaka, Japan). Diethylmethlamine, TBBC, 4-hydroxythiophenol, and 2,2'-thiodiethylbis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate] were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). R_F-(BTRI)_x-(DMAA)_y-R_F cooligomer and R_F-(DMAA)_n-R_F homooligomer were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding monomers, according to our previously reported method.^{23,24}

Preparation of fluorinated oligomeric aggregates-copper ions nanocomposites

To a 1,2-dichloroethane solution of R_F-(BTRI)_x-(DMAA)_y-R_F [R_F = CF(CF₃)OCF₂CF(CF₃)OC₃F₇; M_n = 4000, x : y = 7 : 93; 4 g/dm³ (2 mL)] was added 1,2-dichloroethane (4.5 mL) containing Cu(acac)₂ (0.01 mol/dm³) and TBBC (0.01 mol/dm³). The mixture was stirred with a magnetic stirring bar at room temperature for 0.5 h. Diethylmethlamine (0.5 mL) was mixed with this solution, and then the mixture was stirred for 1 day at room temperature to afford a transparent yellow solution. UV-vis spectra of the 1,2-dichloroethane solution thus obtained exhibited an absorption peak at around λ_{max} = 422 nm.

Preparation of fluorinated oligomeric aggregates-copper nanocomposites

To an aqueous solution of R_F-(DMAA)_n-R_F [R_F = CF(CF₃)OCF₂CF(CF₃)OC₃F₇; M_n = 3240, 4 g/dm³ (1 mL)] was added an aqueous CuCl₂ (1 mmol/dm³) solution (1 mL). The mixture was stirred with a magnetic stirring bar at 40°C for 0.5 h. An aqueous solution (0.5 mL) containing hydrazine hydrate (2 mol/dm³) was mixed with this solution, and then the mixture was stirred for 0.5 h at 40°C to afford a transparent dark-red solution. UV-vis spectra of the aqueous solution thus obtained exhibited a plasmon peak at around 602 nm.

Surface modification of PMMA film

The PMMA films were prepared by casting the mixture of 1,2-dichloroethane solution (12.5 mL) of PMMA (1.0 g) and the transparent yellow solution (1.2

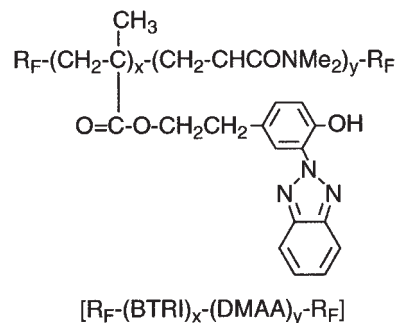


Chart 1

mL) containing fluorinated oligomer (8 mg), Cu(acac)₂ (0.01 mmol), TBBC (0.01 mmol), and diethylmethlamine (4.1 mmol) 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.

RESULTS AND DISCUSSION

To an 1,2-dichloroethane solution of fluoroalkyl end-capped *N,N*-dimethylacrylamide cooligomers containing benzotriazole segments [R_F-(BTRI)_x-(DMAA)_y-R_F (see Chart 1); R_F = CF(CF₃)OCF₂CF(CF₃)OC₃F₇; M_n = 4000, x : y = 7 : 93²³] was added 1,2-dichloroethane containing copper acetylacetonate [Cu(acac)₂], and 4,4'-thiobis(6-*t*-butyl-*o*-cresol) (TBBC). The mixture was stirred with a magnetic stirring bar at room temperature for 0.5 h at room temperature. An 1,2-dichloroethane solution containing diethylmethlamine was mixed with this solution, and then the mixture was stirred for 1 day at room temperature to obtain a transparent yellow solution. Figures 1 and 2 show that UV-vis spectra of the 1,2-dichloroethane solution thus obtained displayed a new absorption peak at around λ_{max} = 422 nm. On the other hand, a similar absorption peak (λ_{max} = 422 nm) was not observed at all when 4-hydroxythiophenol or 2,2'-thiodiethylbis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate] was used instead of TBBC, under similar conditions. Additionally, this absorption peak was observed only when TBBC, Cu(acac)₂, and diethylmethlamine were added into the 1,2-dichloroethane solution of R_F-(BTRI)_x-(DMAA)_y-R_F cooligomer, indicating that self-assembled fluorinated oligomeric aggregates formed by R_F-(BTRI)_x-(DMAA)_y-R_F cooligomer should interact with Cu(acac)₂ in the presence of TBBC and diethylmethlamine to afford fluorinated oligomeric aggregates-copper ions complexes, which would result from the reactions of Cu(acac)₂ with diethylmethlamine and TBBC in the presence of fluorinated aggregates. We have measured the size of fluorinated oligomeric aggregates in the presence of copper ions including, diethylmethlamine and TBBC, by the dy-

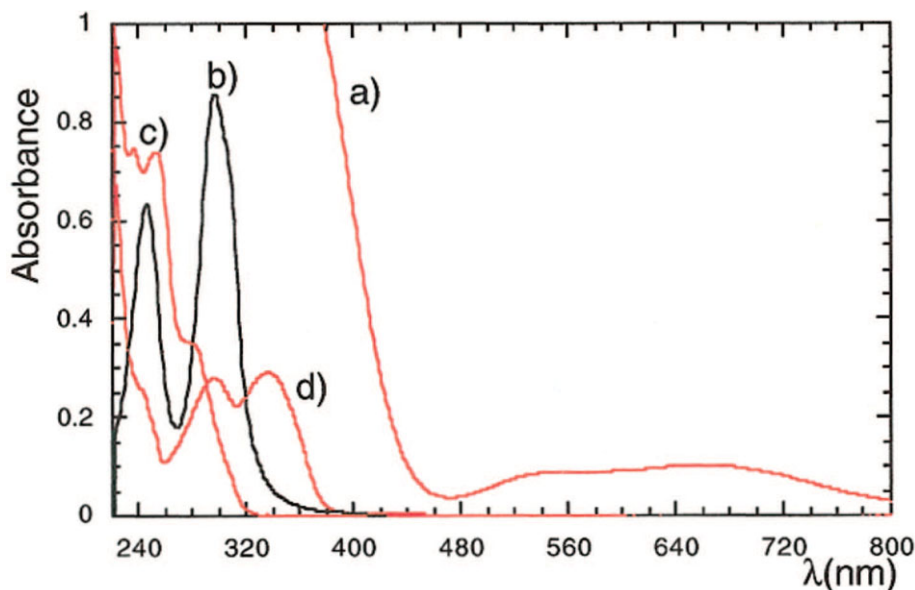


Figure 1 UV-vis spectra of $\text{Cu}(\text{acac})_2$, TBBC, and fluorinated cooligomer in $\text{CH}_2\text{ClCH}_2\text{Cl}$: (a) $\text{Cu}(\text{acac})_2$ [$89 \mu\text{mol}/\text{dm}^3$]; (b) $\text{Cu}(\text{acac})_2$ [$23 \mu\text{mol}/\text{dm}^3$]; (c) TBBC [$50 \mu\text{mol}/\text{dm}^3$]; (d) $\text{R}_F\text{-(BTRI)}_x\text{-(DMAA)}_y\text{-R}_F$ [$\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$; $0.25 \text{ g}/\text{dm}^3$]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nanometric light scattering (DLS) measurements at 30°C . The size of the fluorinated oligomeric aggregates in the absence of the copper ions, TBBC, and diethylmethylamine was also measured under similar conditions, for comparison.

Figure 3 shows that the number-average diameter of fluorinated oligomeric aggregates formed by $\text{R}_F\text{-(BTRI)}_x\text{-(DMAA)}_y\text{-R}_F$ cooligomer is $11.0 \pm 1.1 \text{ nm}$, and the size (number-average diameter) of fluorinated aggregates-copper ions complexes increased from 11.0 nm to $211.2 \pm 90.7 \text{ nm}$. This finding strongly suggests that nanometer size-controlled copper ions compos-

ites should be formed in the fluorinated oligomeric aggregate cores. In fact, transmission electron microscopy (TEM) image of freshly prepared sample by the use of fluorinated oligomeric aggregates under similar conditions is shown in Figure 4. Copper ions nanocomposites protected by fluorinated molecular aggregates essentially are well dispersed and possess an average diameter of 7.3 nm . The XRD of both the $\text{R}_F\text{-(BTRI)}_x\text{-(DMAA)}_y\text{-R}_F$ cooligomeric aggregates-copper ions nanocomposites in Figure 2 and the mixture of $\text{R}_F\text{-(BTRI)}_x\text{-(DMAA)}_y\text{-R}_F$ cooligomer, diethylmethylamine, and TBBC is shown in Figure 5, respectively.

The XRD analyses failed to afford characteristic peaks related to Cu nanoparticles ($2\theta = 44, 51, \text{ and } 74^\circ$)²⁵ or Cu_2O ($2\theta = 37 \text{ and } 62^\circ$),²⁵ indicating the formation of copper ions nanocomposites.

Figure 6 shows that the absorbance at 422 nm related to fluorinated oligomeric aggregates-copper ions nanocomposites was increased remarkably with increase in the molar ratio of diethylmethylamine-based $\text{Cu}(\text{acac})_2$, and the almost constant values were obtained above $20 \text{ mmol}/\text{mmol}$. Similarly, the size (number-average diameter) of fluorinated aggregates-copper ion nanocomposites determined by DLS increased with the increase (the increase of the absorbance related to 422 nm) in the yields of copper ions nanocomposites, and the almost constant size ($600\text{--}700 \text{ nm}$) was obtained above $100 \text{ mmol}/\text{mmol}$. These findings suggest that $\text{Cu}(\text{acac})_2$ could react smoothly with diethylmethylamine in the presence of TBBC and fluorinated oligomeric aggregates to afford copper ions-fluorinated aggregates nanocomposites. The in-

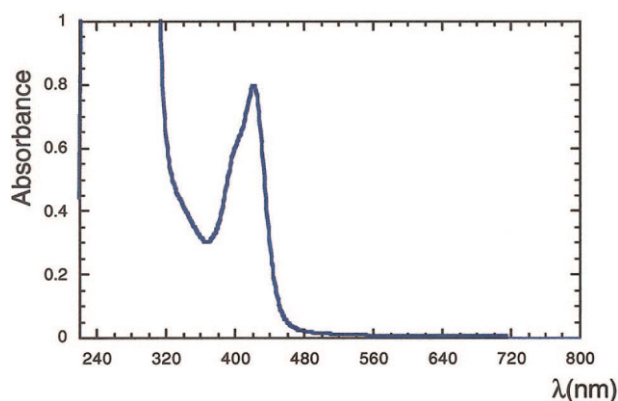


Figure 2 UV-vis spectra of $\text{CH}_2\text{ClCH}_2\text{Cl}$ solution (10.5 mL) containing $\text{Cu}(\text{acac})_2$, TBBC, and fluorinated cooligomer after the addition of Et_2NMe (4.1 mmol): $\text{Cu}(\text{acac})_2$ [$23 \mu\text{mol}/\text{dm}^3$]; TBBC [$50 \mu\text{mol}/\text{dm}^3$]; $\text{R}_F\text{-(BTRI)}_x\text{-(DMAA)}_y\text{-R}_F$; [$\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$; $0.25 \text{ g}/\text{dm}^3$]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

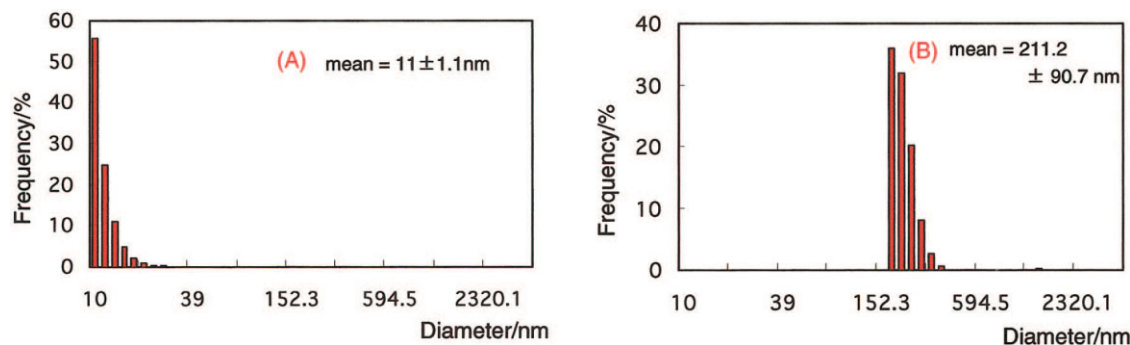


Figure 3 Particle size distributions of $R_F-(BTRI)_x-(DMAA)_y-R_F$ in CH_2ClCH_2Cl (A) and $Cu(acac)_2$, TBBC, Et_2NMe , and $R_F-(BTRI)_x-(DMAA)_y-R_F$ (B) determined by dynamic light scattering measurement. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

crease of the size of the fluorinated oligomeric assemblies in 1,2-dichloroethane indicates that copper ions nanocomposites should be encapsulated in the self-assemblies of fluoroalkyl end-capped cooligomers, and the size of fluorinated aggregates should be increased by the encapsulation of copper ion nanocomposites.

Previously, we reported that fluoroalkyl end-capped oligomers could be arranged regularly above the PMMA [poly(methyl methacrylate)] surface to exhibit a strong oleophobicity imparted by end-capped fluoroalkyl segments.²⁶ This suggests that copper ions nanocomposites should be dispersed above the PMMA surface through the interaction of self-assembled oligomeric aggregates formed by $R_F-(BTRI)_x-(DMAA)_y-R_F$ cooligomer with copper ions nanocomposites. From the developmental viewpoint of metal nanocomposites into the material sciences, it is of considerable interest to apply these fluorinated molecular aggregates into the dispersion of copper ions nano-

composites above the common polymeric materials such as PMMA. In fact, it is well known that spherical nanoparticles with ultrathin metal coatings are in demand due to their unusual optical properties.²⁷ Thus, the PMMA film (film thickness: 170 μm) was prepared by casting the homogeneous 1,2-dichloroethane PMMA solutions containing $R_F-(BTRI)_x-(DMAA)_y-R_F$ cooligomer-copper ion nanocomposites on a glass plate. We have measured the UV-vis spectra of the obtained film in which the surface colors in the yellow, and the result was shown in Figure 7.

As shown in Figure 7, the modified cast PMMA film exhibited a similar absorption peak at around 422 nm, the same as for the 1,2-dichloroethane solution system in Figure 2. This finding suggests that copper ions nanocomposites should be well dispersed without the agglomeration between the copper ions nanocomposites in the cast film. Furthermore, we have measured the contact angles for dodecane on the surface and the reverse sides of this film at room temperature, and the results are as follows:

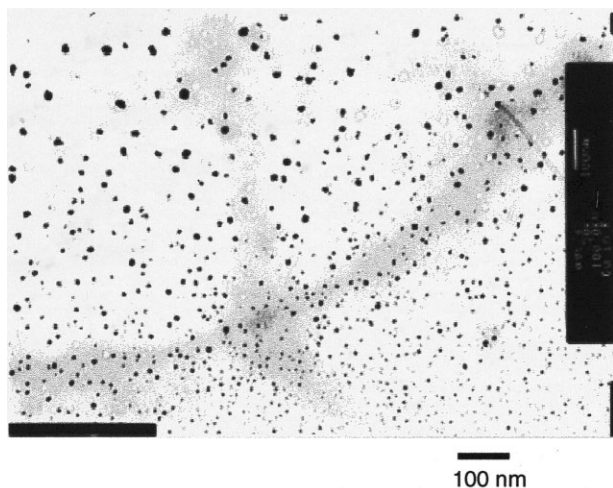


Figure 4 TEM image of freshly prepared fluorinated oligomeric aggregates-copper ions nanocomposites in CH_2ClCH_2Cl [$R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$].

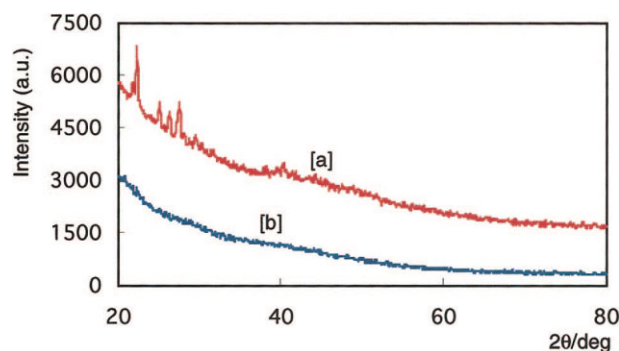


Figure 5 XRD pattern of CH_2ClCH_2Cl solution containing $Cu(acac)_2$, TBBC, Et_2NMe , and $R_F-(BTRI)_x-(DMAA)_y-R_F$ (a), and CH_2ClCH_2Cl solution containing TBBC, Et_2NMe , and $R_F-(BTRI)_x-(DMAA)_y-R_F$ (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

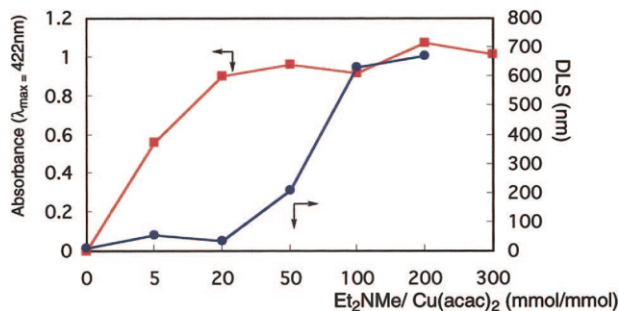


Figure 6 Relationship between the absorbance (or particle size) and molar ratio of Et₂NMe and Cu(acac)₂ in the preparation of fluorinated oligomeric aggregates–copper ions nanocomposites shown in Figure 2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

	Surface-side	Reverse-side
Contact angle (°).	48	0

We have obtained higher values for the contact angles of the surface side of this cast film compared to that of the reverse side. Contact angle measurements show that fluoralkyl end-capped cooligomer could exhibit a markedly strong oleophobicity imparted by end-capped fluoroalkyl segments above the surface.

To clarify the dispersion of copper ions nanocomposites on the PMMA surface, we have analyzed the PMMA film (film thickness: 170 μm) modified by fluorinated molecular aggregates–copper ion nanocomposites, using XPS technique, and the amounts of copper (Cu_{2p}) and fluorine (F_{1s}) at the surface were also estimated. These results were shown in Figure 8.

As shown in Figure 8, interestingly, the relative peak area of fluorine was found to decrease extremely with increase in the etching time (etching rate is about

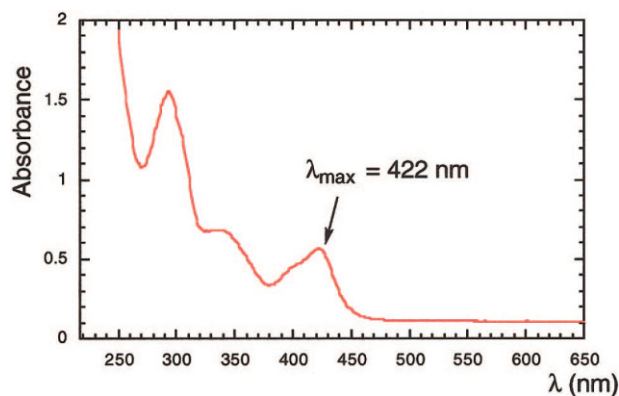


Figure 7 UV-vis spectra of the modified PMMA films treated with fluorinated oligomeric aggregates–copper ions nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

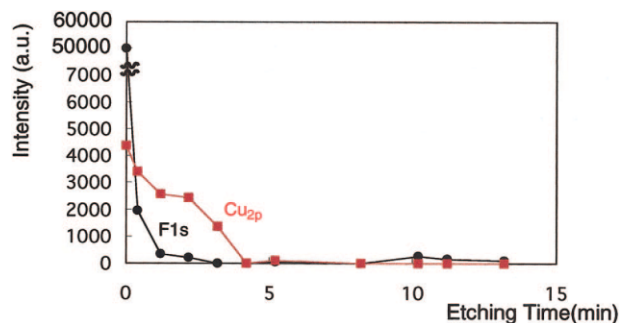
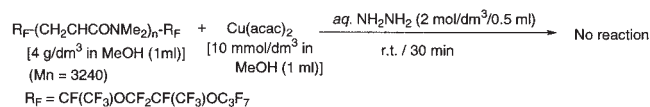
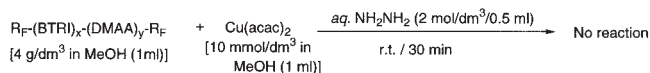


Figure 8 Depth profiles of fluorinated oligomeric aggregates–copper ions nanocomposites measured by XPS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

50 Å/min). A similar tendency was observed in the peaks of Cu_{2p}, and the relative peak area of this peak decreased with increase of the etching time. Thus, it was verified that copper ions nanocomposites should be well dispersed above the polymer surface as well as fluorinated oligomer.

It is well known that hydrazine is useful for the reduction of copper ions to afford metallic copper. For example, Tomalia et al. reported that copper acetates were reduced to zerovalent copper in poly(amidoamine) dendrimers thus providing a dendrimer–metal nanocomposites.²⁹ Similarly, Edward et al. demonstrated on the preparation of poly(vinyl-2-pyrrolidone)-protected copper organosol by the use of hydrazine hydrate in acetonitrile.²⁸ Therefore, it is of particular interest to study on the reduction of Cu(acac)₂ in the fluorinated molecular aggregates by the use of hydrazine hydrate. As shown in Scheme 1, we tried to react Cu(acac)₂ with hydrazine hydrate in methanol in the presence of R_F–(BTRI)_x–(DMAA)_y–R_F cooligomer and fluoroalkyl end-capped *N,N*-dimethylacrylamide homooligomer [R_F–(DMAA)_n–R_F]; however, the expected copper nanoparticles could not be obtained at all. Copper nanoparticles could not be also produced by the reductions of copper acetate with hydrazine hydrate in methanol under similar conditions. On the other hand, CuCl₂ failed to react with hydrazine hydrate in the presence of R_F–(BTRI)_x–(DMAA)_y–R_F coo-



Scheme 1

ligomer; however, interestingly, it was clarified that CuCl_2 could react smoothly with hydrazine hydrate in the presence of $\text{R}_F\text{-(DMAA)}_n\text{-R}_F$ homooligomer to afford dark-red colored fluorinated oligomeric aggregates–copper nanocomposites solutions as shown in Scheme 2.

UV–vis spectra of this solution displayed a plasmon absorption in the visible region ($\lambda_{\text{max}} = 602 \text{ nm}$; see Fig. 9). This finding suggests that fluorinated DMAA oligomers can form the self-assembled fluorinated oligomeric aggregates with the aggregations of the end-capped fluoroalkyl segments in aqueous media to interact with copper nanoparticles as guest molecules. On the other hand, $\text{R}_F\text{-(BTRI)}_x\text{-(DMAA)}_y\text{-R}_F$ cooligomer could not afford copper nanoparticles under similar conditions, indicating that benzotriazole segments in cooligomer should interact strongly with CuCl_2 , and the reduction of copper ions with hydrazine is not likely to be occurred. Furthermore, the size of fluorinated oligomeric aggregates in the presence of copper nanoparticles was determined by the DLS measurements. The size of the fluorinated molecular aggregates in the absence of copper nanoparticles was $10.8 \pm 1.1 \text{ nm}$, and the size (number-average diameter) of fluorinated aggregates–copper nanoparticles composites was increased from 10.8 nm in $393.8 \pm 87.3 \text{ nm}$. This finding strongly suggests that nanometer size-controlled copper nanoparticles should be capsulated in the fluorinated molecular aggregate cores. More interestingly, our present fluorinated oligomeric aggregates–copper nanocomposites were found to be relatively stable at room temperature.

In conclusion, we have succeeded in preparing new fluorinated aggregates–copper ions nanocomposites by the reactions of $\text{Cu}(\text{acac})_2$ with diethylmethylamine and TBBC in the presence of self-assembled fluorinated oligomeric aggregates formed by $\text{R}_F\text{-(BTRI)}_x\text{-(DMAA)}_y\text{-R}_F$ cooligomer at room temperature. These fluorinated aggregates–copper ions nanocomposites that are obtained are very stable and exhibited light absorption at around $\lambda_{\text{max}} = 422 \text{ nm}$. In addition, $\text{R}_F\text{-(BTRI)}_x\text{-DMAA}_y\text{-R}_F$ cooligomer was applied to the dispersion of copper ions nanocomposites above the poly(methyl methacrylate) film surface. Therefore, our present fluorinated copper nanocomposites are expected to have a high potential to apply into new fluorinated optical materials. On the other hand, CuCl_2 reacted with hydrazine hydrate in the presence of fluorinated oligomeric aggregates formed by $\text{R}_F\text{-}$

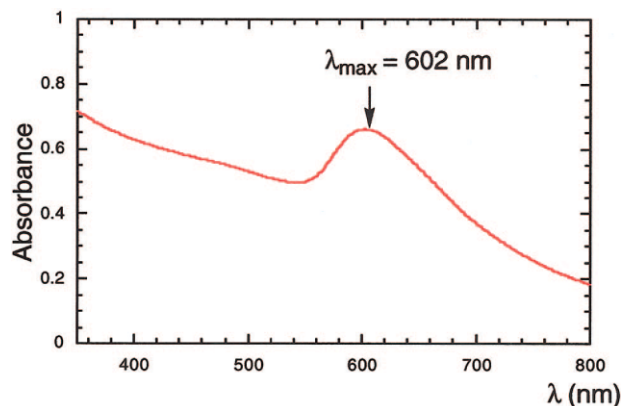
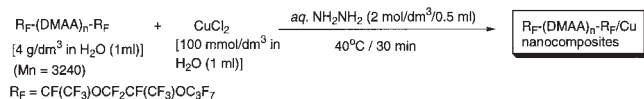


Figure 9 UV–vis spectra of aqueous solutions of copper nanoparticles protected by $\text{R}_F\text{-(DMAA)}_n\text{-R}_F$ oligomeric aggregates [$\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$\text{DMAA}_n\text{-R}_F$ homooligomer to afford fluorinated oligomeric aggregates–copper nanocomposites. These copper nanocomposites protected by these fluorinated oligomeric aggregates exhibited a plasmon absorption in the visible region ($\lambda_{\text{max}} = 602 \text{ nm}$), and are found to be stable at room temperature.

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Scheme 2

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