

Colloidal crystallization of C₆₀/polymer-grafted silica particles in organic solvent

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Received: 8 March 2015 / Revised: 27 March 2015 / Accepted: 10 April 2015 / Published online: 28 April 2015
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Abstract Synthesis of fullerene (C₆₀)-tethered polymer-grafted silica and colloidal crystallization of the particles was investigated. The particles were prepared by the reaction of C₆₀ with 4-azidobenzoyl groups introduced in poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate), followed by esterification of 2-hydroxyethyl methacrylate moieties with 4-azidobenzoyl chloride and grafting onto colloidal silica. The reaction afforded bindings of C₆₀ in the range from 0.44×10^4 to 1.71×10^4 molecules/particle. The C₆₀ amounts did not monotonously increase with 4-azidobenzoyl group on the particles, but decreased with mole fraction of methyl methacrylate in the copolymer. Colloidal crystallizations of the C₆₀-tethered silica particles were observed in acetonitrile with critical volume fractions in the range from 0.018 to 0.024. Inter-sphere distances in the colloidal crystals were consistent with calculated values on assumption of face-centered cubic-closed packing, and then it was suggested that the crystallization took place due to electrostatic repulsion between the particles.

Keywords Fullerene-tethered polymer · Polymer grafting · Colloidal silica · Colloidal crystallization

Electronic supplementary material The online version of this article (doi:10.1007/s00396-015-3601-0) contains supplementary material, which is available to authorized users.

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Introduction

Three-dimensional (3D) particle-arrayed structure, inter-sphere distance of which is comparable to visible light wave length, has been receiving much attention for the promising application to optical devices, such as wave guide, sensor, and so on [1–6]. So far, many approaches for fabrication of 3D particle arrays have been reported [1–22]. One of the attractive approaches is the fabrication employing colloidal crystals formed in solution due to easy tuning inter-sphere space by changing the volume fraction and exhibiting sharp and clear Bragg reflection. The fabrications have been mostly carried out by immobilization of colloidal crystals formed in aqueous solution in hydrogels [7, 10, 14–18]. However, in the practical application, it is quite difficult to utilize the hydrogels for optical devices because they contain much water. In this regard, we have successfully achieved colloidal crystallization of polymer-grafted silica in organic solvents [23–26] and then immobilization of the crystals in polymer matrix [19–22]. Colloidal crystallizations in organic solvents are favorable for fabrication of 3D particle-arrayed structure by immobilization in polymer matrixes because of being able to utilize various polymerization reactions.

Concerning colloidal crystallization in solution, in many cases, monodisperse colloidal silica, polystyrene, and poly(methyl methacrylate) are employed for colloidal particles because of giving stable crystallites. Among them, colloidal silica usually brings stable colloidal crystals in aqueous solution due to negatively high surface charge. However, fabrication of 3D particle-arrayed optical device from colloidal crystals of silica has major shortcomings stemming from original property of silica, comparatively low refractive index, and dielectric constant. In this respect, we have reported that introduction of ferrocenyl groups in polymer grafted onto silica

particles effectively increases refractive index of colloidal crystal system [27].

Meanwhile, fullerenes have been attractive and highlighted materials due to spherical π -conjugated molecule exhibiting characteristic properties, i.e., electron accepting or releasing abilities, high dielectric constant, high heat conductivity, thermal stability, high refractive index, radical trapping, UV absorption, and so on. Thus, C_{60} and C_{60} -based nanomaterials have been contributing to a variety of promising application to functional materials, such as high surface area particles and supports in catalysis [28], electron carriers in electronic devices [29], and semiconductors [30, 31]. Furthermore, Tu and coworkers have recently reported that grafting of C_{60} into polyesters elevates refractive index to give the maximum value of 1.79 [32]. Therefore, incorporation of C_{60} into colloidal crystals could lead not only to improvement of refractive index but also to challenging fabrication of new functional materials, exhibiting specific properties of C_{60} . In this study, preparation of C_{60} -tethered polymer-grafted silica (C_{60} /polymer/SiO₂) and colloidal crystallization of the composite particles in organic solvent was investigated.

Experimental

Materials

Colloidal silica aqueous sol, containing 20 wt% SiO₂ of 134 nm in diameter with a polydispersity 0.030, was kindly gifted by Nikki Catalysts & Chemical Co. Ltd., Kanagawa, Japan. Fullerene (C_{60}), Nanom purple ST, was purchased from Frontier Carbon Co. Ltd., Tokyo, Japan. Methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA), (3-mercaptopropyl)trimethoxysilane, 2,2'-azobis(isobutyronitrile) (AIBN), tetrahydrofuran (THF), *N,N,N*-triethylamine, diethyl ether, 1,2-dimethoxyethane (DME), acetonitrile, and toluene were obtained from Wako Chemicals Co. Ltd., Osaka, Japan. 4-Azidobenzoyl chloride was purchased from Kanto Chemicals Co. Ltd., Tokyo, Japan.

Measurements

Number average of molecular weight (M_n) of the synthesized polymers were determined by a gel permeation chromatography (GPC) on the columns, TSK gel G4000H₆, and G5000H₆, Tosoh Co. Ltd., Yamaguchi, Japan, at 35 °C using THF as an eluent at the flow rate of 0.8 mL/min calibrated with a polystyrene standard. ¹H NMR spectra for solution samples and ¹³C CP/MAS NMR spectra for solid state samples were recorded on a Bruker AVANCE 400 (400 MHz) and 300 (300 MHz) using a 7-mm rotor probe, Karlsruhe, Germany respectively. Amounts of grafted polymer and C_{60} were determined by a thermal-

gravimetric analysis on TG-50, Shimadzu Co. Ltd., Kyoto, Japan, during elevating temperature up to 800 °C at heating rate 10 °C/min. Particle size and its distribution were determined by a dynamic light scattering (DLS) on an Otsuka Electronics DLS-7000 spectrophotometer, equipped with a He-Ne laser (10 mW, 633 nm), Osaka, Japan. Reflection spectra of colloidal crystals were recorded on a multichannel spectrometer, Hamamatsu Photonics PMA-11, Shizuoka, Japan.

Synthesis of trimethoxysilyl-capped poly(MMA-*co*-HEMA)(1)

A typical run was as follows. A mixture of 12.0 mL (112 mmol) MMA, 0.68 mL (5.6 mmol) HEMA, 10 mg (0.07 mmol) (3-mercaptopropyl)trimethoxysilane, 16 mg (0.17 mmol) AIBN, and 20 mL dry THF was put into a 50-mL flask and stirred at 70 °C for 10 h in N₂ atmosphere. After evaporation of THF from the mixture and precipitation with diethyl ether, drying under reduced pressure gave 7.2 g copolymer **1**, of M_n 24,000 and MMA/HEMA mole ratio 14.7:1.0. The mole ratio was determined by the area ratio of resonance peak at 3.63 ppm assigned to methyl protons of MMA moiety to peaks at 3.87 and 4.15 ppm assigned to methylene protons of HEMA moiety on ¹H NMR spectrum (Fig. 2a). ¹H NMR (CDCl₃): 0.87, 1.05, 1.23 (m, CH₃), 1.76–2.15 (broad, CH₂, CH), 3.63 (s, OCH₃), 3.87 (broad, COOCH₂), and 4.15 ppm (broad, CH₂OH).

Synthesis of trimethoxysilyl-capped poly(methyl methacrylate-*co*-2-(4-azidobenzoyloxy)ethyl methacrylate) (2)

Into a 50-mL flask, 2.0 mL *N,N,N*-triethylamine, 3.0 g **1**, and 30 mL dry chloroform were put, and the mixture was cooled on an ice bath. Chloroform solution 2.0 mL containing 3 g (17 mmol) 4-azidobenzoyl chloride was added dropwise to the solution, followed by stirring for 6 h at room temperature. Filtration, evaporation of solvent, and precipitation with diethyl ether gave 2.45 g **2**. ¹H NMR (CDCl₃): 0.87, 1.05, 1.23 (m, CH₃), 1.76–2.15 (broad, CH₂, CH), 3.63 (s, OCH₃), 3.87 (broad, COOCH₂), 4.15 (broad, CH₂OH), 4.32 (broad, COOCH₂CH₂OC=OC₆H₄N₃), 4.55 (broad, CH₂OC=OC₆H₄N₃), 7.18 (broad, *o*-CH₂ (C=OC₆H₄N₃)), and 8.09 ppm (broad, *m*-CH₂ (C=OC₆H₄N₃)).

Preparation of poly(methyl methacrylate-*co*-2-(4-azidobenzoyloxy)ethyl methacrylate)-grafted silica (3)

Colloidal silica suspended in ethanol was prepared by solvent exchanging with azeotropic evaporation of water after

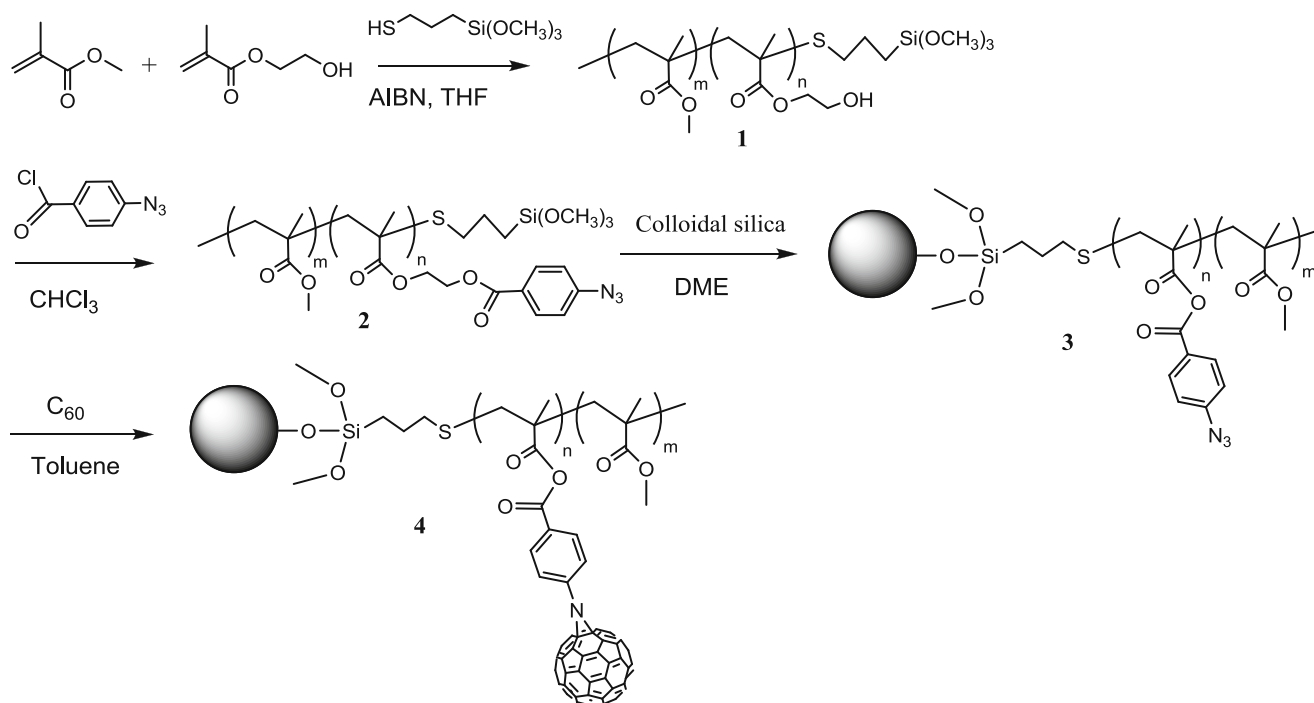
addition of ethanol to the original aqueous sol. A mixture of 0.5 g **2**, 50 mL colloidal silica ethanol suspension, containing 1.0 g SiO₂, and 50 mL DME was put into a 100-mL flask. After sonication for 30 m, the suspension was stirred at 90 °C for 5 h along with azeotropic removal of ethanol. Centrifugal washing with THF eight times and drying under reduced pressure gave 1.0 g **3**, with 47.8 mg/g grafted polymer. ¹³C CP/MAS NMR: 10.3–25.2 (broad, –CH₂–C(CH₃)(C=O)–), –CH₂–C(CH₃)(C=O)–, 44.5 (–CH₂–C(CH₃)(C=O)–), 40.8–62.0 (broad, O–CH₃, O–CH₂CH₂–O), and 177.8 ppm (C=O).

Reaction of C₆₀ with **3**

Into 20 mL toluene, 50 mg C₆₀ and 1.0 g **3** were put, and the mixture was stirred at 110 °C under a nitrogen atmosphere for 24 h. Centrifugal separation of resulting particles with toluene and drying under reduced pressure gave 0.88 g **4**. ¹³C CP/MAS NMR: 9.9–26.8 (broad, –CH₂–C(CH₃)(C=O)–), –CH₂–C(CH₃)(C=O)–, 44.6 (–CH₂–C(CH₃)(C=O)–), 39.1–70.3 (broad, O–CH₃, O–CH₂CH₂–O), 107.7–153.0 (broad, –C₆₀), and 177.3 ppm (C=O).

Determination of grafted polymer and C₆₀ on silica

Amounts of grafted polymer on **3** and **4** were determined by weight decrease (W_{polymer}) during elevation from 170 to 420 °C on a thermogravimetric analysis. The amount of C₆₀ tethered on **4** was also determined by weight loss ($W_{\text{C}_{60}}$),



Scheme 1 Synthesis of C₆₀/polymer-grafted silica, **4**

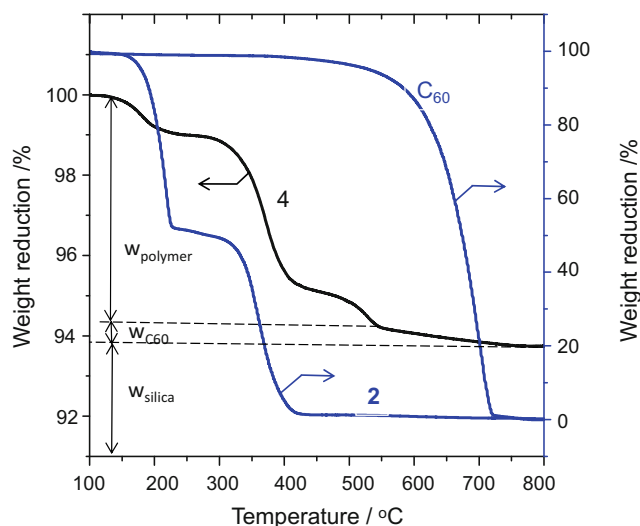


Fig. 1 Typical thermogravimetric thermograms of **2** with mole ratio of MMA/HEMA=1.9:1.0, **4-1** and C₆₀

corresponding to C₆₀ ignition, during elevation from 550 to 800 °C. Typical thermograms of **4**, along with those of poly(MMA-*co*-HEMA) **2** with mole ratio of MMA/HEMA=1.9/1.0 and C₆₀, are shown in Fig. 1.

Observation of colloidal crystallization and determination of inter-sphere distance

Colloidal crystallization of silica composite particles in organic solvent was observed by naked eyes and a digital camera. Inter-sphere distance (d_{cal}) in colloidal crystal was calculated

Table 1 Characterization of **1**, **2**, **3** and **4**

Polymer 1	4-N ₃ C ₆ H ₄ group in 2 , mmol/g		Grafted polymer on 3 , mg/g-SiO ₂		4-N ₃ C ₆ H ₄ group on 3 , μmol/g-SiO ₂		Particle 4		C ₆₀ on 4	
Mole ratio, m/nM _n /10 ³	11	0.59	3-1	62.7	34.1	10.2	1.71	mg/g-SiO ₂	μmol/g-SiO ₂	Number of C ₆₀ /10 ⁴ /unit particle
1.9:1.0	13	0.73	3-2	34.1	19.9	7.84	1.31	7.37	10.2	1.71
4.2:1.0	15	0.86	3-3	54.1	41.1	5.20	0.97	5.65	7.84	1.31
5.7:1.0	16	1.03	3-4	56.2	51.5	4.01	0.67	3.75	5.20	0.97
9.3:1.0	24	0.22	3-5	43.7	10.5	2.63	0.44	2.93	4.01	0.67
14.7:1.0								1.90	2.63	0.44

from the volume fraction on assumption of face centered cubic (fcc) closed packing by Eq. (1) [33]:

$$d_{\text{cal}} = 0.9047 \times r \div \phi^{1/3} \quad (1)$$

where ϕ is volume fraction of polymer-grafted silica, d_{cal} is neighboring inter-sphere distance, and r is diameter of the particle. The inter-sphere distance (d_{obs}) in the crystals was also determined according to Bragg formula by following the equation [34]:

$$d_{\text{obs}} = \sqrt{\frac{3}{8}} \frac{\lambda_p}{n} \quad (2)$$

where λ_p is the peak top wavelength on a reflection spectrum and n is average refractive index of the suspension system calculated by Eq. (3)

$$n = \phi \times n_{\text{silica}} + (1-\phi) \times n_{\text{sol}} \quad (3)$$

where n_{silica} and n_{sol} are refractive index of silica and solvent, respectively, and ϕ is volume fraction of silica. Equations (1), (2), and (3) are given in detail in [Online resource](#).

Results and discussion

Synthesis of C₆₀/polymer/SiO₂ (**4**)

In Scheme 1, the synthetic route of **4** was shown. Trimethoxysilyl-terminated poly(MMA-co-HEMA), **1**, was synthesized by a radical copolymerization of MMA and HEMA in the presence of (3-mercaptopropyl)trimethoxysilane of a chain transfer reagent using AIBN as a radical initiator. The polymers of $M_n=11,000$ – $24,000$ with mole ratios of MMA/HEMA in the range from 1.9:1.0 to 14.7:1.0 were obtained by changing feed ratio of the monomers (Table 1). The reaction of 4-azidobenzoyl chloride with **1** was carried out in the presence of *N,N,N*-triethylamine at 4 °C. In Fig. 2, ¹H NMR

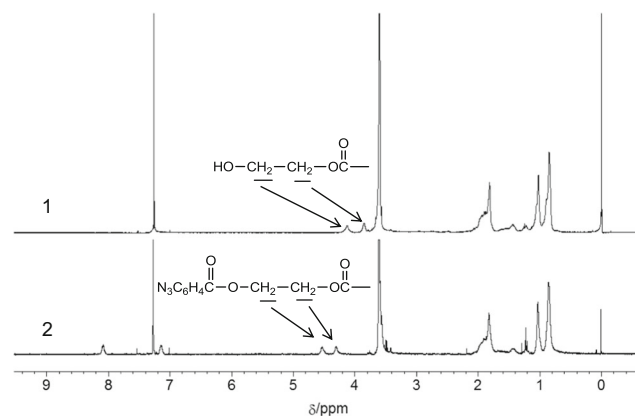


Fig. 2 Typical ¹H NMR spectra of **1** and **2** with mole ratio of MMA/HEMA=9.3:1.0

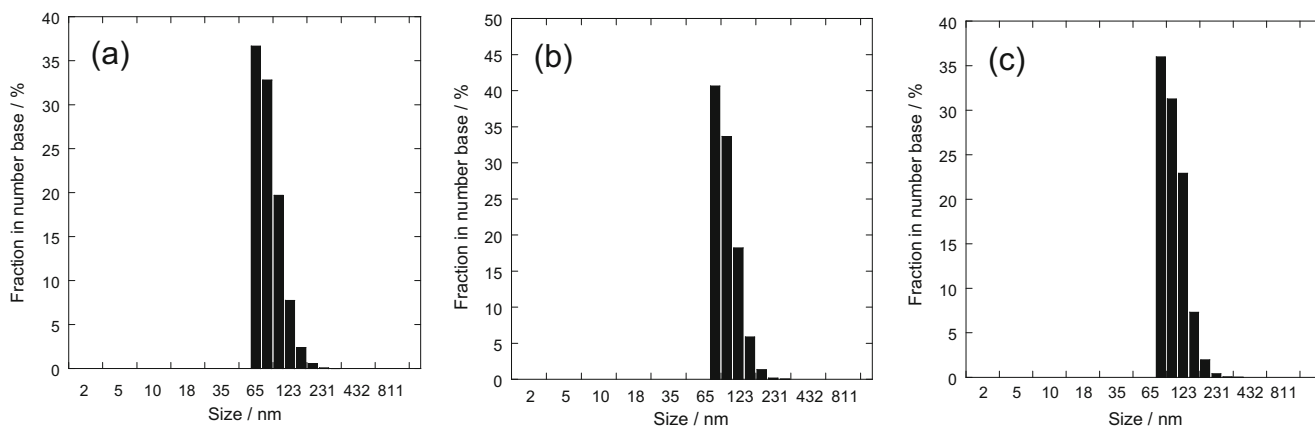


Fig. 3 Particle size distributions of original colloidal silica (a), 3-4 (b), and 4-4 (c) in THF

spectra of respective **1** and **2** were shown. The introduction of 4-azidobenzoyl group into HEMA moieties in **2** was confirmed by the appearance of resonance peaks at 4.32 and 4.55 ppm on ^1H NMR spectrum, assignable to protons in ethylene group of HEMA moiety, and at 7.18 and 8.09 ppm, assignable to protons in 4-azidobenzoyl group (Fig. 2). Amounts of 4-azidobenzoyl group were determined by area ratio of peaks at 7.18 and 9.08 ppm to peaks at 3.87 and 4.15 ppm, assignable to unreacted methylene groups of HEMA moiety. The amounts of 4-azidobenzoyl group unexpectedly increased with decreasing HEMA fraction in **1** (Table 1). Polymer chains of **1** with high MMA fraction were probably favorable to react with 4-azidobenzoyl chloride due to highly affinity with chloroform. The reaction of **2** with colloidal silica particles was conducted in DME at 90 °C for 5 h along with azeotropic removal of ethanol. Average particle sizes of **3** were in the range from 145 to 150 nm, summarized in Table 1, being 11–16 nm larger than that of the original silica. Particle sizes of **3** slightly became larger by polymer grafting, but distributions of particle size were still narrow, as shown in Fig. 3. Therefore, we confirmed that aggregation between the particles scarcely occurred during the reaction. A ^{13}C CP/MAS NMR spectrum of **3** distinctly indicated grafting of **2** on silica particles by the appearance of resonance peaks at 10.3–25.2, 44.5, 40.8–62.0, and 177.8 ppm assigned to CH_2 on polymer backbone and branched CH_3 , quaternary carbon, OCH_3 of MMA moieties, and $\text{OCH}_2\text{CH}_2\text{O}$ of HEMA in HEMA moieties and carbonyl respectively, as shown in Fig. 4. The grafting reactions resulted in bindings of 4-azidobenzoyloxy groups in the range from 10.5 to 51.5 mmol/g- SiO_2 on **3** (Table 1). Amounts of 4-azobenzoyl group on **3**, calculated from grafted polymer on **2**, decreased with increasing of MMA fraction in **1**. The reaction of C_{60} with **3** was carried out in toluene at 110 °C under a nitrogen atmosphere for 30 h to give bindings of C_{60} from 1.90 to 7.37 mg/g- SiO_2 , that is, from 2.63 to 10.2 $\mu\text{mol/g-SiO}_2$. The bindings of C_{60} on **4**

were confirmed by the appearance of resonance peaks at 107.7–153.0 ppm, assignable to carbon atoms in C_{60} , on a ^{13}C CP/MAS NMR spectrum in Fig. 4. Particle sizes of **4** were 157–167 nm, being ca. 15 nm larger than those of **3**, but those distributions were still narrow (Fig. 3c). Thus, it was observed that aggregation between particles of **3** scarcely took place during the reaction of **3** with C_{60} . Interestingly, amounts of tethered C_{60} decreased with mole ratio of MMA/HEMA in **1**, not simply with amounts of 4-azidobenzoyl group on **3**. Probably, polymer chains with 4-azidobenzoyl groups on **3**, prepared from high mole fraction of HEMA in **1**, might have high flexibility during the reaction of C_{60} with **3** in toluene. In other words, 4-azidobenzoyl group in grafted polymer composed of high mole fraction of MMA moiety on **3** could be less active for C_{60} bindings due to shrinking of polymer chains in toluene.

Colloidal crystallization

The authors have reported that poly(methyl methacrylate)-grafted silica particles formed colloidal crystals in polar solvents, such as CH_3CN , acetone, and *N,N*-dimethylformamide [23–25]. When spheres of **4** were dispersed in CH_3CN ,

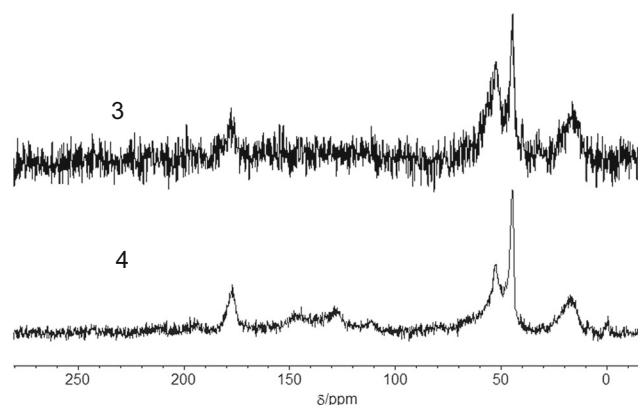


Fig. 4 ^{13}C CP/MAS NMR spectra of 3-4 and 4-4

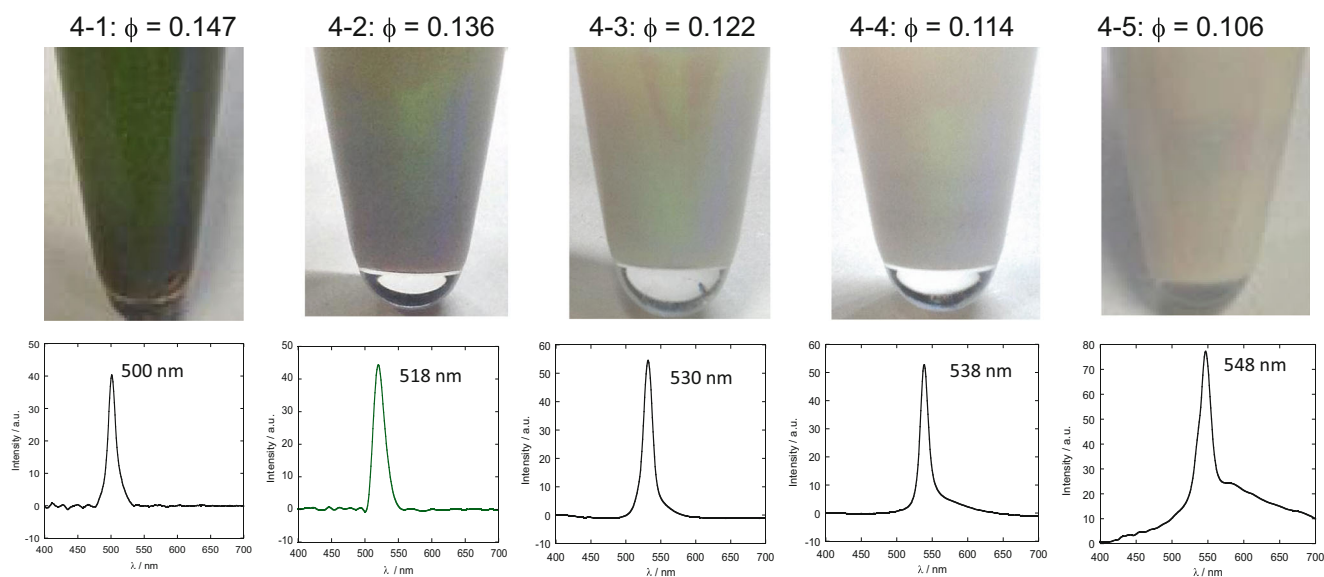


Fig. 5 Photographs and reflection spectra of colloidal crystals of **4** in CH_3CN

formation of colloidal crystals was observed. Typical photographs and reflection spectra of the crystals were shown in Fig. 5. Color of the crystals of **4** with much amount of tethered C_{60} was dark green, which gradually became pale green with decrease of the C_{60} amount, probably due to absorption of C_{60} at near ultraviolet light region. In Table 2, critical volume fractions of **4**, ϕ_o , being minimal volume fraction in the crystallization in CH_3CN were listed. Values of ϕ_o for colloidal crystallization in CH_3CN were in the range from 0.018 to 0.022, being mostly comparable in the crystallization of poly(MMA)-grafted silica [23, 24]. Values of ϕ_o in CH_3CN were independent on C_{60} amounts on silica. The reasons for the phenomenon were still unclear.

In Table 3, inter-sphere distances, d_{obs} and d_{cal} , in colloidal crystals of **4** in CH_3CN were summarized. The observed values of d_{obs} estimated by Eq. (2) were well coincident with d_{cal} , which were evaluated on postulation of fcc-closed packing from volume fraction of the particles by Eq. (1). Therefore, these results indicated that the colloidal crystallization took place based on electrostatic repulsion between the particles to form fcc-closed packing, as well as ones of colloidal silica in aqueous solution [34]. Colloidal crystallization of spherical particles in solution

predominantly holds stable fcc structure rather than bcc packing [34].

Conclusions

Fullerene(C_{60})-tethered polymer-grafted silica spheres were successfully synthesized via reaction of C_{60} with 4-azidobenzoyl group in poly(MMA-*co*-HEMA) grafted on silica. Bindings of C_{60} on poly(MMA-*co*-HEMA)-grafted silica were confirmed by appearance of characteristic resonance peaks at 107–153 ppm, assignable to carbon atoms of C_{60} , on a ^{13}C CP/MAS NMR spectrum. The reaction afforded bindings of C_{60} in the range from 2.63 to 10.2 $\mu\text{mol/g-SiO}_2$, corresponding to 0.44×10^4 to 1.71×10^4 molecules/particle, on the polymer-grafted silica. Colloidal crystallization of C_{60} /polymer/ SiO_2 particles was observed in CH_3CN , and critical volume fraction in the crystallization was in the range from 0.018 to 0.024. Inter-sphere distances in the colloidal crystals mostly agreed with calculated values on assumption of fcc-closed packing. Therefore, it was suggested that the crystallization occurred due to electrostatic repulsion between

Table 2 Critical volume fraction (ϕ_o) of C_{60} /polymer-grafted SiO_2 , **4**, in colloidal crystallization in acetonitrile

Particle	Size / nm	ϕ_o
4		
4-1	157	0.024
4-2	162	0.022
4-3	164	0.021
4-4	166	0.020
4-5	167	0.018

Table 3 Inter-particle distances in colloidal crystals of C_{60} /polymer-grafted silica in CH_3CN

Particle	Volume fraction (ϕ)	d_{cal}/nm	$\lambda_{\text{max}}/\text{nm}^{\text{a}}$	d_{obs}/nm
4-1	0.147	229	500	222
4-2	0.136	235	518	231
4-3	0.122	244	530	237
4-4	0.114	250	538	241
4-5	0.106	256	548	248

the particles as well as those of colloidal silica particles in aqueous solution.

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