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journal or publication title	Colloid and Polymer Science
volume	293
number	7
page range	2075-2081
year	2015-07
URL	http://hdl.handle.net/10228/00006504

doi: [info:doi/10.1007/s00396-015-3601-0](https://doi.org/10.1007/s00396-015-3601-0)

Colloidal Crystallization of C₆₀/Polymer-Grafted Silica Particles in Organic Solvent

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Running title: Colloidal Crystallization of C₆₀/Polymer/Silica

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Abstract

Synthesis of fullerene (C_{60})-tethered polymer-grafted silica and colloidal crystallization of the particles were investigated. The particles were prepared by the reaction of C_{60} 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 C_{60} in the range from 0.44×10^4 to 1.71×10^4 molecules/particle. The C_{60} 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 C_{60} -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.

Key words: Fullerene-tethered polymer, Polymer-grafting, Colloidal silica, Colloidal crystallization,

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 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 attractive approaches is the fabrication employing colloidal crystals formed in solution, due to easy tuning inter-sphere space by changing the volume fraction and to 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 of containing 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, 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, and UV absorption 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], 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 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 were 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., Japan. 4-Azidobenzoyl chloride was purchased from Kanto Chemicals Co. Ltd., 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 C₆₀ 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, Osaka 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, Osaka, 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 7.2g 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. 2(a)). 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) ppm.

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 3g (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)), 8.09 (broad, *m*-CH₂ (C=OC₆H₄N₃)) ppm.

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), 177.8 (C=O) ppm.

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**. ^{13}C CP/MAS NMR: 9.9-26.8 (broad, $-\text{CH}_2-\text{C}(\text{CH}_3)(\text{C}=\text{O})-$), $-\text{CH}_2-\text{C}(\text{CH}_3)(\text{C}=\text{O})-$, 44.6 ($-\text{CH}_2-\text{C}(\text{CH}_3)(\text{C}=\text{O})-$), 39.1-70.3 (broad, $\text{O}-\text{CH}_3$, $\text{O}-\text{CH}_2\text{CH}_2-\text{O}$), 107.7-153.0 (broad, $-\text{C}_{60}$), 177.3 ($\text{C}=\text{O}$) ppm.

Determination of grafted polymer and C_{60} on silica

Amounts of grafted polymer on **3** and **4** were determined by weight decrease (W_{polymer}) during elevation from 170 °C to 420 °C on a thermogravimetric analysis. Amount of C_{60} tethered on **4** was also determined by weight loss ($W_{\text{C}_{60}}$), corresponding to C_{60} ignition, during elevation from 550°C 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 C_{60} 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 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 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, 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. Eqs. (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 Mn=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 spectra of respective **1** and **2** were shown. The introduction of 4-azidobenzoyl group into HEMA moieties in **2** was confirmed by 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 azeotropical removal of ethanol. Average particle sizes of **3** were in the range from 145 nm 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 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 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. 3(c)). 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 CH₃CN, acetone, and *N,N*-dimethylformamide [23-25]. When spheres of **4** were dispersed in CH₃CN, 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 C₆₀ was dark green, which gradually became pale green with decrease of the C₆₀ amount, probably due to absorption of C₆₀ at near ultraviolet light region. In Table 2, critical volume fractions of **4**, ϕ_o , being minimal volume fraction in the crystallization in CH₃CN were listed. Values of ϕ_o for colloidal crystallization in CH₃CN 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 CH₃CN were independent on C₆₀ 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 CH₃CN 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(C₆₀)-tethered polymer-grafted silica spheres were successfully synthesized *via* reaction of C₆₀ with 4-azidobenzoyl group in poly(MMA-*co*-HEMA) grafted on silica. Bindings of C₆₀ on poly(MMA-*co*-HEMA)-grafted silica was confirmed by appearance of characteristic resonance peaks at 107-153 ppm, assignable to carbon atoms of C₆₀, on a ¹³C

CP/MAS NMR spectrum. The reaction afforded bindings of C₆₀ in the range from 2.63 to 10.2 μmol/g-SiO₂, corresponding to 0.44×10^4 to 1.71×10^4 molecules/particle, on the polymer-grafted silica. Colloidal crystallization of C₆₀/polymer/SiO₂ particles was observed in CH₃CN, 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 the particles as well as those of colloidal silica particles in aqueous solution.

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Figure legends:

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

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

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

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

Figure 4. ¹³C CP/MAS NMR spectra of **3-4** and **4-4**.

Figure 5. Photographs and reflection spectra of colloidal crystals of **4** in CH₃CN.

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

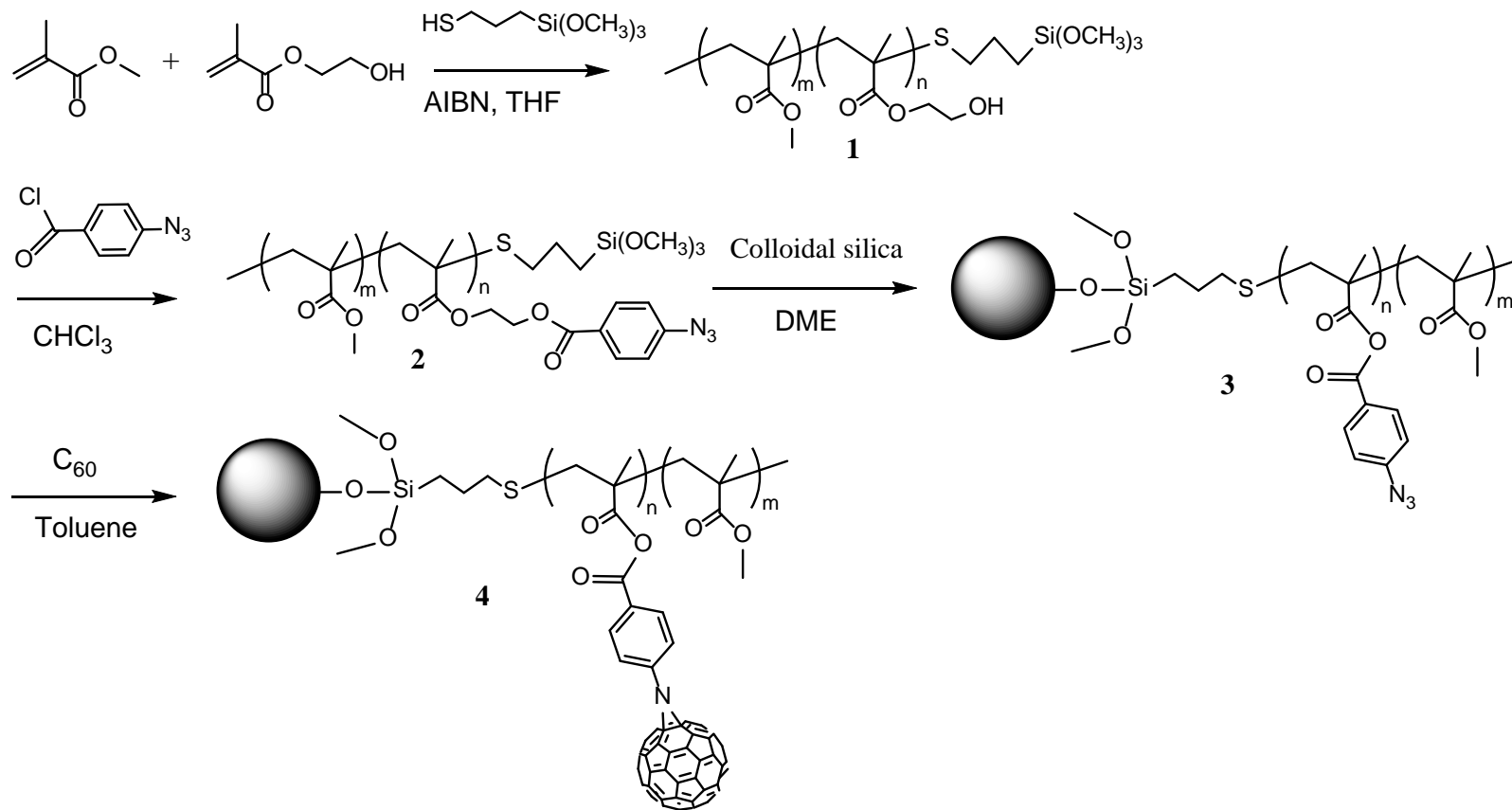
Polymer 1 Mole ratio m/n	$M_n/10^3$	4-N ₃ C ₆ H ₄ group in 2 / mmol/g	Par- ticle 3	Grafted polymer on 3 / mg/g-SiO ₂	4-N ₃ C ₆ H ₄ group on 3 /μmol/ g-SiO ₂	Par- ticle 4	C ₆₀ on 4		
							mg/g-SiO ₂	μmol/g-SiO ₂	Number of C ₆₀ /10 ⁴ /unit particle
1.9/1.0	11	0.59	3-1	62.7	34.1	4-1	7.37	10.2	1.71
4.2/1.0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

Table 2. Critical volume fraction (ϕ_o) of C₆₀/polymer-grafted SiO₂, **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 C₆₀/polymer-grafted silica in CH₃CN

Particle	Volume fraction (ϕ)	d_{ca}/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



Scheme 1. Synthesis of C_{60} /polymer/ SiO_2 , **4**.

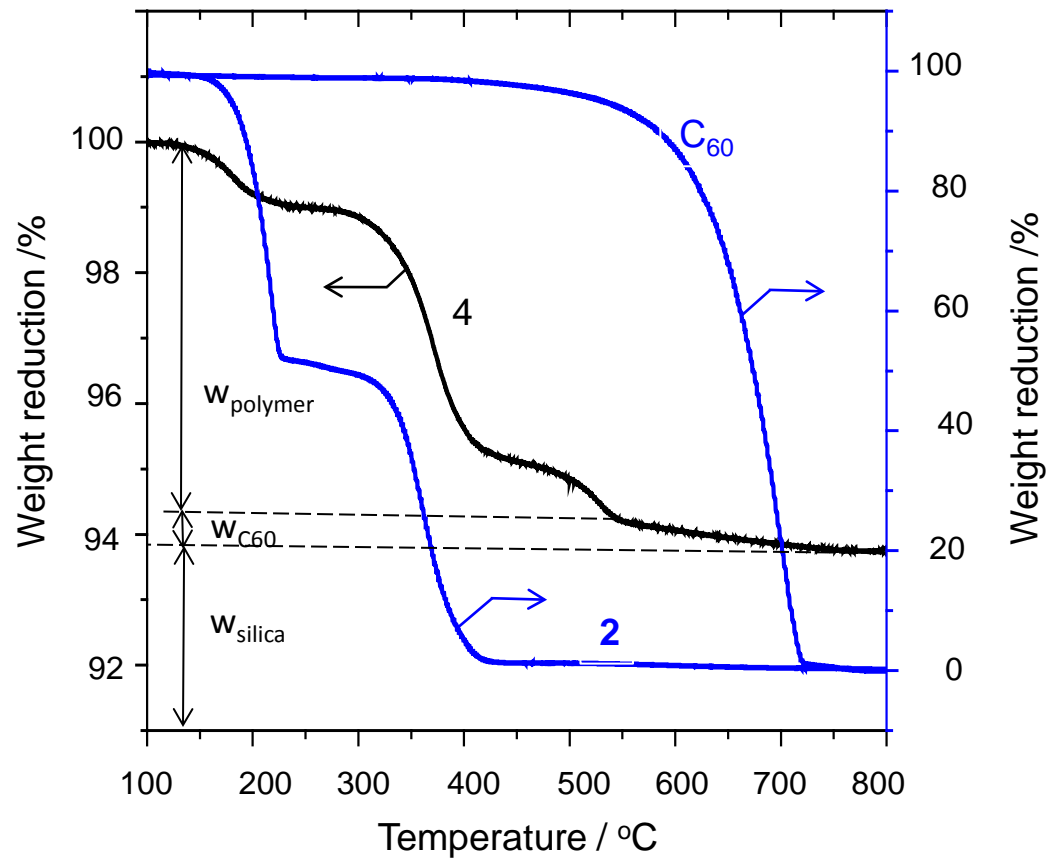


Figure 1. Typical thermogravimetric thermograms of **2** with mole ratio of MMA/HEMA=1.9/1.0, **4-1** and C₆₀.

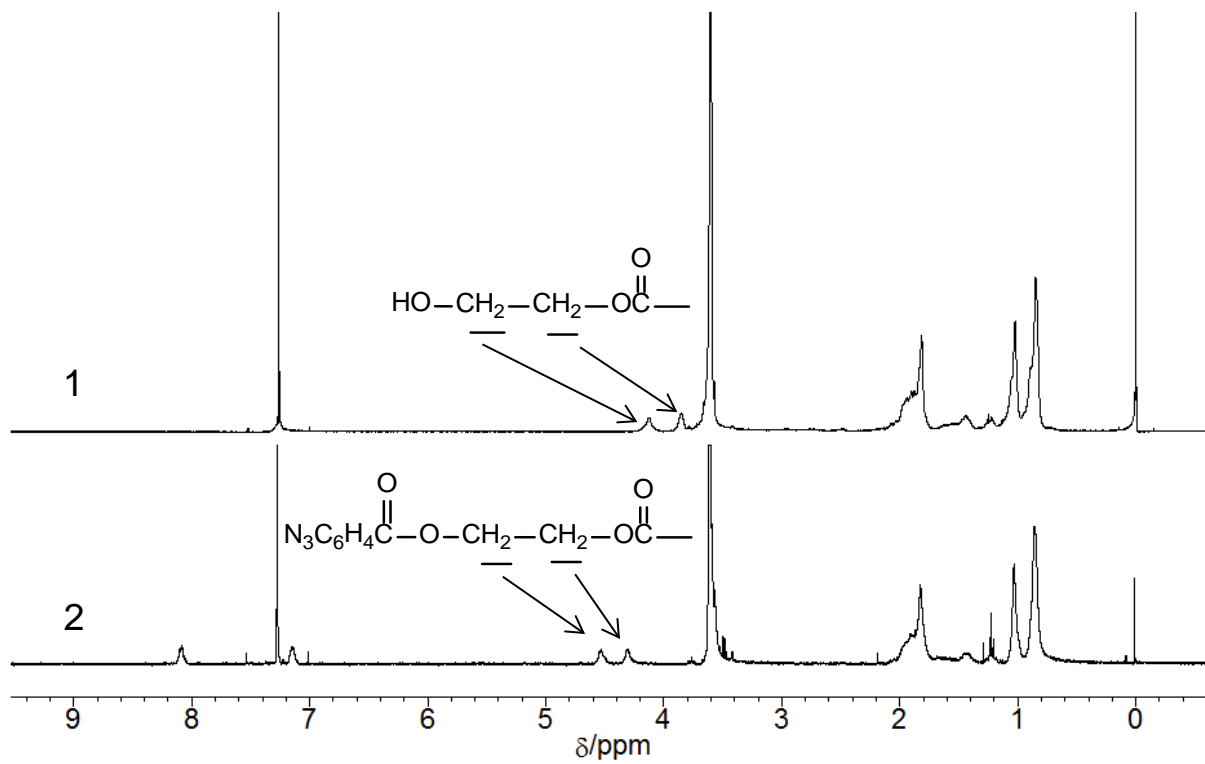


Figure 2. Typical ^1H NMR spectra of **1** and **2** with mole ratio of MMA/HEMA=9.3/1.0

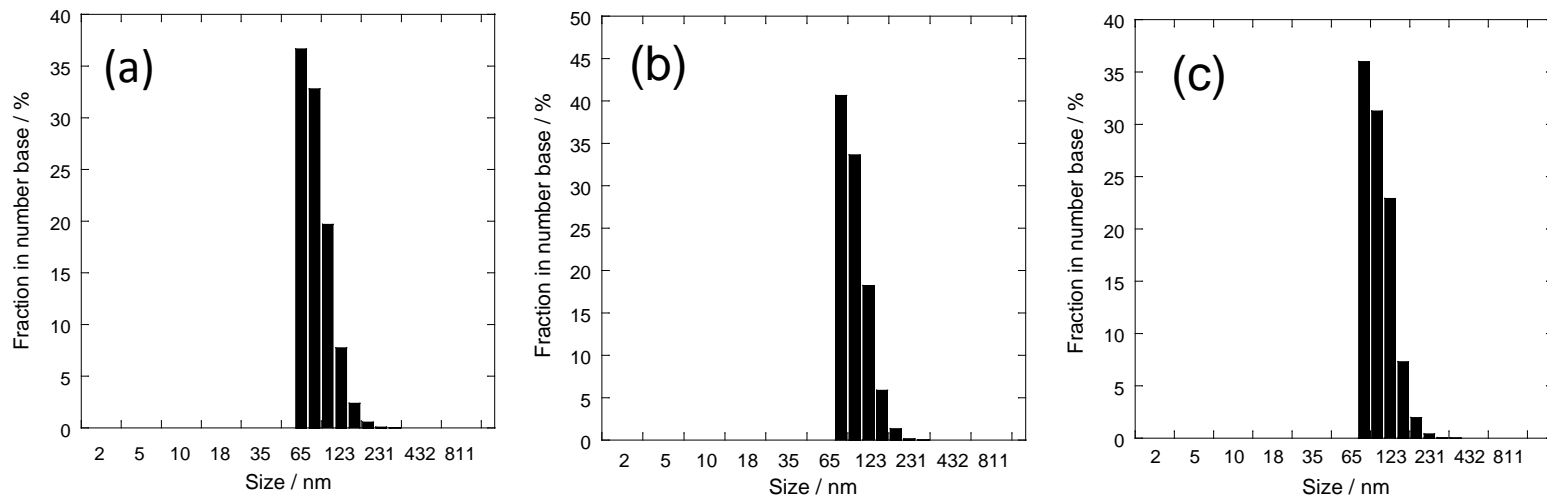


Figure 3. Particle size distribution of the original colloidal silica (a), **3-4**(b) and **4-4** (c).

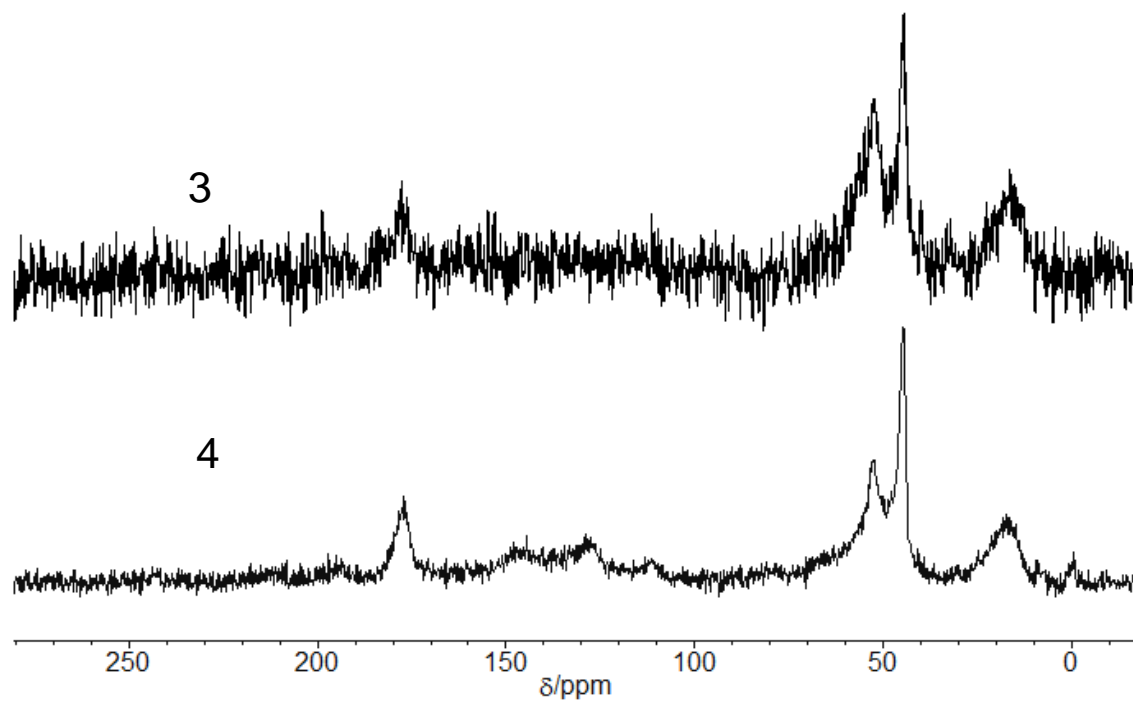


Figure 4. ^{13}C CP/MAS NMR spectra of **3-4** and **4-4**.

4-1: $\phi = 0.147$



4-2: $\phi = 0.136$



4-3: $\phi = 0.122$



4-4: $\phi = 0.114$



4-5: $\phi = 0.106$

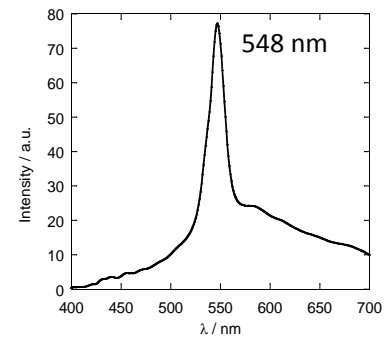
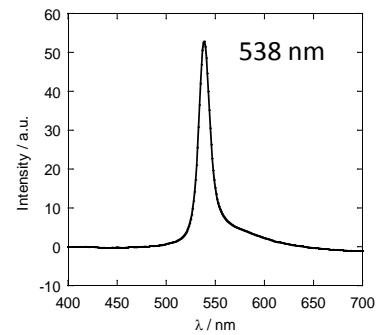
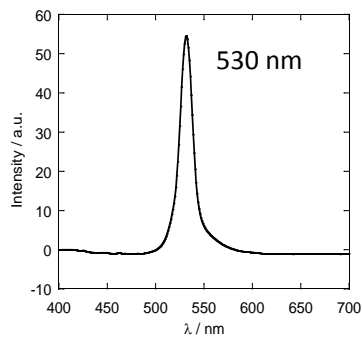
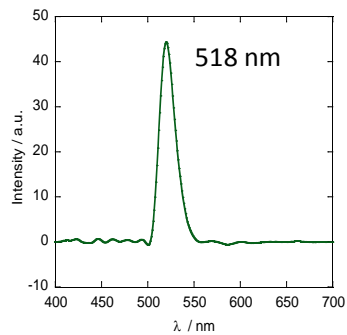
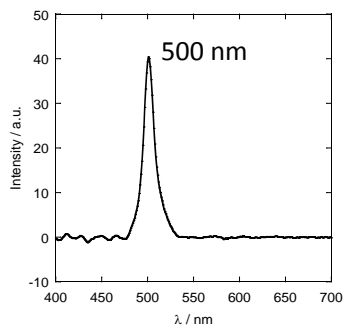


Figure 5. Photographs and reflection spectra of colloidal crystals of **4** in CH_3CN .