

**Synthesis of Novel Polymer-brush-afforded Hybrid
Particles for Well-organized Assemblies**

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Chapter 1

General Introduction

1-1. Assemblies of Monodisperse Fine Particles

The terms “fine particles” has a relatively broad concept and, in this thesis, is to designate monodisperse small particles of any shape which can hardly be individually distinguished by visual observation. Fine particles are attractive for a large variety of applications including catalysis, sensors, optoelectronic materials and environmental remediation.¹ However, a successful use of such small fine particles in a real and macroscopic world requires their macroscopic organization or orientation. The organization of nanometer-sized particles, both of organic and inorganic nature, is a topic of colloidal science which has been realized in colloidal crystals, and liquid crystals.^{2,3} These two kinds of assemblies promising for the applications of photonic materials and optoelectronic devices, which also will be introduced in detail below, have attracted many attentions over past several decades.⁴

1-1-1. Colloidal Crystals

Colloidal crystal, the most famous assembly of fine particles, which is a three-dimensionally periodic lattice assembled from monodisperse colloidal particles, analogous to a well-known crystal where repeating subunits are atoms or molecules.² The periodic arrays of spherical particles make similar arrays of interstitial voids, which act as a natural diffraction grating for lightwaves in photonic crystals, especially when the interstitial spacing is of the same order of magnitude as the incident lightwave. In natural world, a gem opal is a typical example, exhibiting the iridescence in color for the highly ordered structure of particles.⁵ Colloidal crystals have attracted much interest not only as photonic materials but also as a model system to investigate fundamentals in crystallization of condensed matter.^{6,7}

Driving forces for the formation of colloidal crystals are believed to be repulsive potentials

affecting between colloidal particles. Besides the well-known *hard* and *soft* colloidal crystals, *semisoft* colloidal crystals were newly fabricated by Ohno et al. with

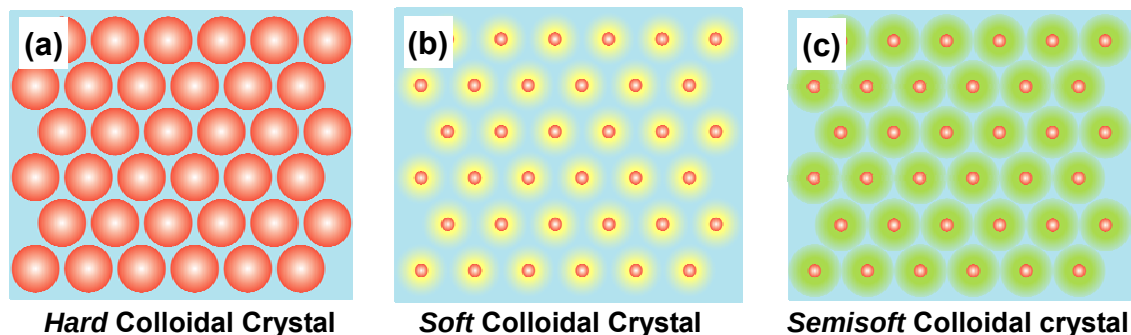


Figure 1-1. Schematic illustrations of colloidal crystals

concentrated-polymer-brush-afforded silica particles.^{6c-h,7,8,9} The steric and short-range interaction in nature is proved to be the *hard*-sphere potential for the crystallization of rigid uncharged particles (Figure 1-1a). The electrostatic potential, which is of long range depending on the ionic strength of the system, works between particles for forming *soft* colloidal crystals (Figure 1-1b). Different from two traditional colloidal crystals, in *semisoft* colloidal crystals, the driving force of crystallization is the excluded-volume interactions between polymer chains densely grafted on spherical particles. (Figure 1-1c)

1-1-2. Liquid Crystals

Researches about anisotropic liquid crystals have become intriguing subjects over past several decades for their applications in electrooptical devices, artificial intelligent materials,

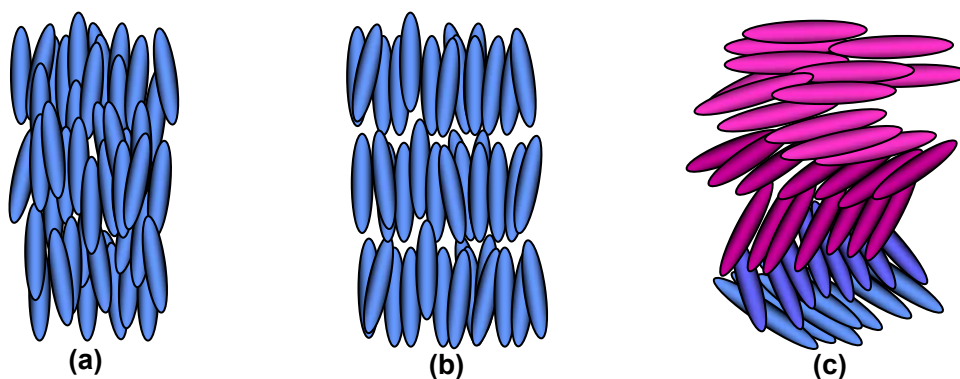


Figure 1-2. Schematic illustrations of liquid crystalline phases. (a) the alignment in nematic phase; (b) the alignment in smectic phase; (c) the ordering of chiral liquid crystal phase.

shape-memory materials and nano-scale machines.¹⁰⁻¹⁴ Liquid crystals are a state of matter that has properties between the liquid and the solid crystal.³ For instance, the liquid crystal may flow like a

liquid, but its rod-like mesogens may be oriented in a crystal-like order. Nematic, smectic and chiral liquid crystalline phases are mostly well-known ordering of liquid crystals (Figure 1-2). In colloidal science, oriented mesogens of liquid crystals refer to a kind of rigid rod-like material, which is oriented to a direction, giving liquid crystals a well known optic property of birefringence. The anisotropic liquid crystals have been well utilized for their unique physicochemical properties.¹⁰⁻¹⁴ Many kinds of materials have been utilized for the fabrication of liquid crystals. In the world of colloid, fabricating the liquid crystal with rigid nanorods has gathered many attentions over several decades. Zocher firstly discovered liquid crystals with nanometer-scale particles and since then many reports have appeared on liquid crystalline phases with embedded objects, such as charged V_2O_5 assemblies or tobacco mosaic viruses in water.¹⁵⁻¹⁷ However, these systems are restricted to solvent, concentration and surface properties of nanorods. To overcome these restrictions and obtain better understanding of these systems, the concept of “hairy” rods was introduced by functionalizing the surface of anisotropic particles, which was originally developed for rigid-chain polymer.¹⁸ For the rigid nanoparticles, the insoluble core is solubilized by polymeric surfactants, leading to an easy fabrication of liquid crystals.¹⁹⁻²¹ The group of Lekkerkerker firstly reported an isotropic-nematic phase transition in toluene by using polymeric surfactants functionalized rodlike particles and gibbsite platelets.^{22,23} Zentel et al. fabricated the lyotropic liquid crystalline phases with “hairy” nanorods and, furthermore, a polymeric matrix with liquid crystalline order embedded.^{21,24}

1-2. Core-shell Particles

Core-shell particles, i.e., particles consisting of a core of one chemical composition coated with a shell of another material, have tremendous properties surpassing those of mono-component particles.²⁵ The “hairy” rods introduced above sharing the same concept as core-shell particles. With the concept of core-shell particles, various assemblies of core-shell particles can be fabricated with different shapes of cores. In this thesis, spherical particles and rod-like particles are used as the core of core-shell particles for fabricating assemblies of colloidal crystal and liquid crystal, respectively.

The shells of core-shell particles cultivated on the surface of particles are polymer layers synthesized by the living radical polymerization (LRP).

1-2-1. Surface Modification on Fine Particles

The surface properties of fine particles play a crucial role in their overall function and performance. Several physical and/or chemical methods were utilized for surface-modifying fine particles by various organic compounds ranging from alkyl chains to macromolecules.²⁶ Amongst others, a polymeric architecture composed of polymer chains end-tethered to a solid surface has been attracting particular attention for the applicability in areas of science and technology, e.g., colloidal stabilization, adhesion, lubrication, tribology, and rheology.²⁷ Strategies have been developed for introducing polymer chains to the surface of fine particles using chemical (using covalent bonding) or physical (by physisorption) methodologies.²⁸ Physisorption involves the absorption of a block copolymer with a segment which sticks on the surface of the object. Such polymer chains are not stably attached especially under conditions where high shear forces are involved or a good solvent of the polymer is used. In order to achieve a stable interfacial compatibility between the two phases of particles and polymers, covalent grafting techniques are preferred. These techniques can be categorized into two methods. The first method called “grafting to” lies in the attachment of preformed polymers with reactive sites onto the surface of particles.²⁹ The other one called “grafting from” consists in the growth of polymer chains directly from the surface of particles and which will be introduced in details below.

1-2-2. Surface-Initiated Polymerization

The “grafting from” method, also called as surface-initiated polymerization, firstly developed by Prucker and R  he, which tailoring solid surface with high content of polymers with enhancing the graft density of polymers.³⁰ Their works established the fundamental strategies of this technique formed with two steps of process for surface-modification of materials. Bifunctional compounds are firstly used to introduce an initiator layer tethered on solid surfaces, and then, the polymerizations are carried out from these initiator sites. Comparing to the “grafting to” technique,

the addition of monomer polymerized to the grafted chains is not strongly hindered by the grafted polymer chains, indicating this promising technique to produce polymeric shell on solid surface with more thickness and graft density.

With the development of bifunctional initiators, various polymerization methods including free radical, ionic, and ring-opening metathesis mechanisms have been introduced into the family of surface-initiated polymerization.³⁰⁻³² In particular, the surface-initiated polymerization carried out with a living fashion gives not only a fine control of length and structure (linear, random, gradient or block copolymers, comb polymers, etc.) of graft polymers but also a dramatic increase of graft density. From the above, surface-initiated living radical polymerization (SI-LRP) is extraordinarily promising due to its versatility and good ability of surface-modification. Nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) polymerization are mostly used for surface-initiated polymerization for their versatility.³³⁻³⁵ Fukuda's group firstly succeeded in surface-grafting low-polydispersity poly(methyl methacrylate) (PMMA) with an exceptionally high graft density by surface-initiated ATRP.³⁶ This technique was applied to surfaces of fine particles of different materials such as gold, silica, iron oxide, cadmium sulfide, carbon, polymer, and so on.^{9a,37}

1-2-3. Polymer Brush

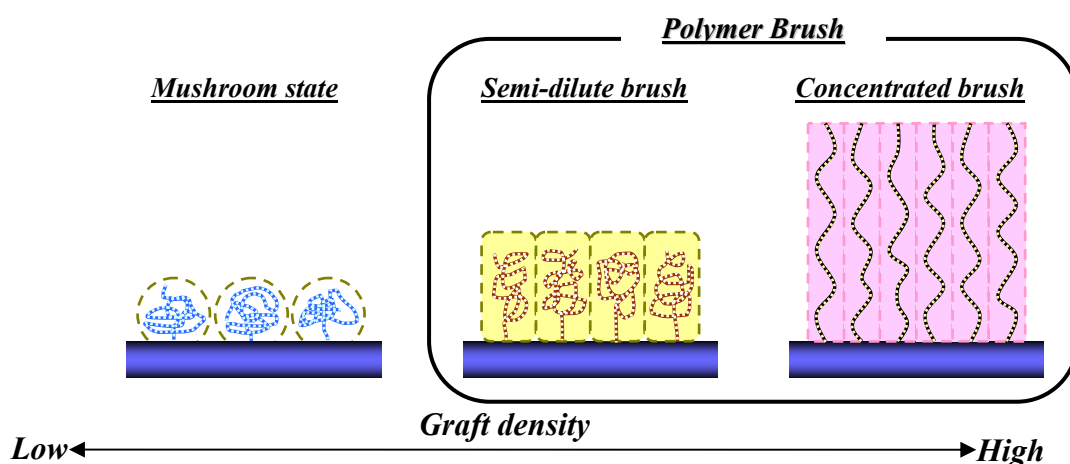


Figure 1-3. Schematic illustrations of tethered polymer chains

Among three kinds of conformational states of polymer chains on solid surface, polymer brush was categorized into two groups as the difference of graft density, i.e. semi-dilute and

concentrated polymer brushes. (Figure 1-3) Polymer brushes synthesized through SI-LRP have received significant attentions for their great effects on the surfaces of various materials. Different from the thin coatings of polymer on solid surface, the conformation of tethered polymer brushes is controllable according to the graft density. The concentrated polymer brush has been well utilized for synthesizing hybrid particles with good dispersibility in solvent. As above-mentioned, Ohno et al. successfully fabricated hybrid particles with a shell of concentrated polymer brush, and firstly fabricated a new kind of colloidal crystal, *semisoft* colloidal crystal of such particles.^{9a} The driving force of forming well-dispersible hybrid particles is proved to be the excluded-volume interactions between polymer chains.³⁸ The studies of Ohno et al. also revealed a fact that the effective surface density of the brush is not constant but varies with the varying radical distance from the sphere center. It is predictable that the decrease of effective surface density of polymer will lead to a shape change as the polymer brush layer tailed on the surface of rod-like core. Because of the great versatility and robustness of SI-LRP, Ohno et al. fabricated a hollow particle using a block polymer brush on silica surface, which also indicating that the polymer brush layer can be modified with functional groups for designing a nanoparticle.

1-3. Background and Purpose of This Thesis

In the view of the vast potential of *semisoft* colloidal materials, it is of great importance to develop their science and technology into higher possible achievements.

In the scope of this current situation, the author set up the first goal for this thesis to establish a strategy of synthesizing hybrid particles with the diameter of silica core less than 100 nm. This has never been done as SI-ATRP carried out on such small size of nanoparticles without any aggregates. And the author will achieve the goal and fabricate two- and three-dimensional order array of such hybrid particles.

The achievements of the first goal will broaden the applicability of SI-ATRP on much smaller sized silica particles. However, insofar as examined, the colloidal crystal was formed in

volatile organic solvent. The concentration and structure of colloidal crystal are hardly stable as the evaporation of solvent or the vibration from surrounding. To overcome these restrictions of colloidal crystal, the author set up the goals for this thesis to establish strategies of fabricating stable colloidal crystal for the *semisoft* colloidal crystal system. In this study, two methods will be introduced for overcoming the restrictions stem from the volatile organic solvent and fragile structure in the suspension system.

Considering the findings of polymer brushes as described in Section 1-2-3, polymer brushes formed on rod-like particles were targeted in this thesis and, as the anisotropic nature of nanorods; the author will also try to fabricate a liquid crystal and a film with oriented hybrid nanorods.

1-4. Outline of This Thesis

This thesis firstly developed hybrid particles synthesized by SI-ATRP with the diameters of silica core less than 100 nm and fabricated a two-dimensional ordered array and a *semisoft* colloidal crystal of these hybrid particles. Secondly, two kinds of colloidal crystals stabilized in structure and in concentration were fabricated for applications. Thirdly, besides the colloidal crystal, liquid crystals and films with anisotropic structure were fabricated with the hybrid nanorods synthesized by SI-ATRP on the surface of nanorods.

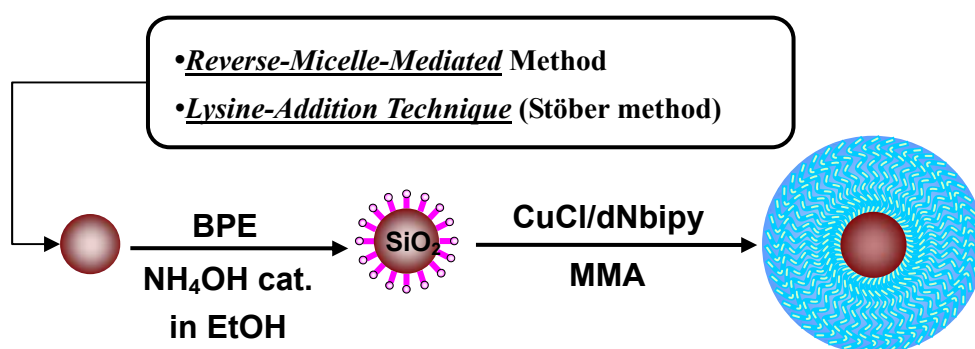


Figure 1-4. Schematic representation of the strategy for the synthesis of polymer-brush-grafted silica particle with core sizes less than 100nm.

In **Chapter 2**, as shown in Figure 1-4, two methods, the reverse-micelle technique and the lysine-addition technique, are used for the preparation of narrowly size-distributed silica

nanoparticles (SiNPs) of diameters less than 100 nm. These nanoparticles are surface-modified with a triethoxysilane derivative containing an ATRP-initiating group. The surface-initiated ATRP of methyl methacrylate (MMA) mediated by a copper complex is carried out with the initiator-fixed SiNPs in the presence of a “sacrificial” free initiator. These core-shell hybrid particles are characterized by transmission electron microscopic (TEM) observations with a particular attention paid to their dispersibility in solution. A *semisoft* colloidal crystal of such hybrid particles is fabricated and characterized by the confocal laser scanning microscopic (CLSM) observations.

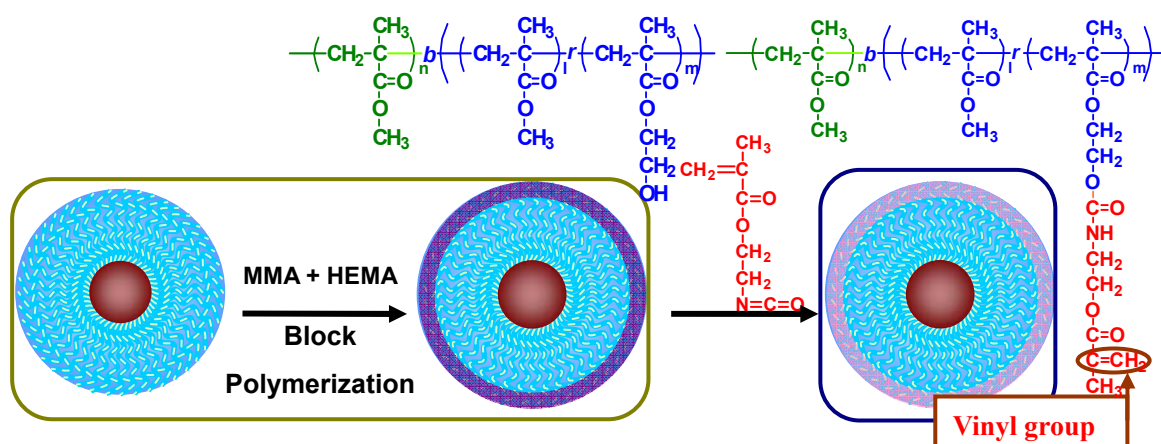


Figure 1-5. Schematic representation for the synthesis of SiP grafted with a block copolymer brush by SI-ATRP.

In **Chapter 3**, a *semisoft* colloidal crystal system with a stable structure is developed by synthesizing hybrid particles having functional groups in polymer brushes as schematized in Figure 1-5, which involves three steps to synthesize vinyl groups holding hybrid particles. The first step shares the similar process of synthesizing hybrid particle as mentioned in Chapter 2. With adding free copolymer having vinyl groups into the colloidal crystal suspension, thus obtained *semisoft* colloidal crystal is immobilized in a gel by a photo-radical polymerization.

In **Chapter 4**, non-volatile ionic liquids are innovatively applied as the solvent for *semisoft* colloidal crystals (Figure 1-6). Direct observation of the *semisoft* colloidal crystal is carried out by CLSM to characterize the crystalline structure. The *semisoft* colloidal crystal suspension is investigated to clarify the effect of graft-chain length on brush-layer thickness and Daoud-Cotton-type scaling theory is also applied to understanding the hydrodynamic thickness of

swollen brush. The properties of *semisoft* colloidal crystals in ionic liquids are discussed with comparing the similar system in organic solvents as previous reported.

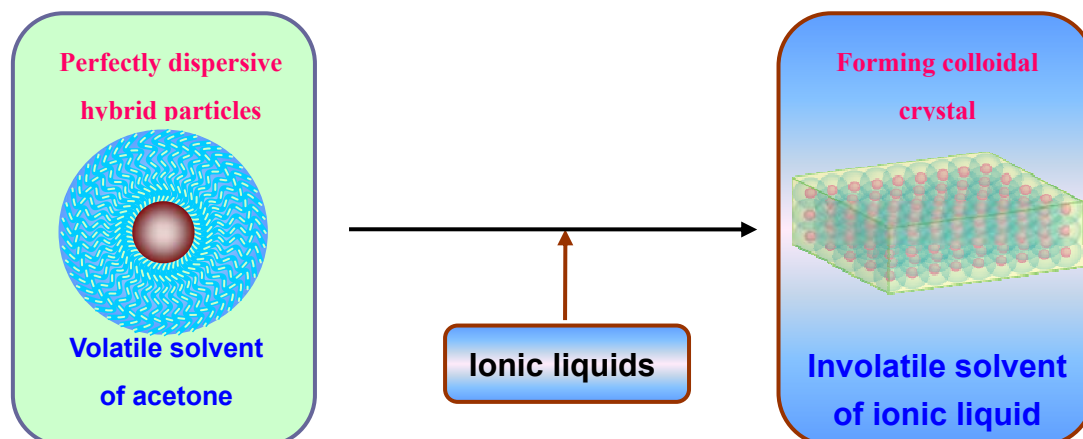


Figure 1-6. Schematic illustration of the fabrication of semisoft colloidal crystals in ionic liquids

In **Chapter 5**, anisotropic hybrid nanorods are designed to fabricate liquid crystalline assemblies (Figure 1-7). The α -Fe₂O₃ nanorod with an aspect ratio of 6 and a length axis of 600 nm is successfully made and a modified with PMMA polymer brush by SI-ATRP. Furthermore, a silica-coated α -Fe₂O₃ nanorod is also fabricated with the stöber method and surface-modified with a PMMA polymer brush layer. Hydrochloride acid is used to etch the iron oxide and fabricate a hollowed hybrid nanorod. Such an anisotropic hollowed hybrid nanorod is casted using an organic solvent and observed under polarized light for confirming liquid crystalline phases.

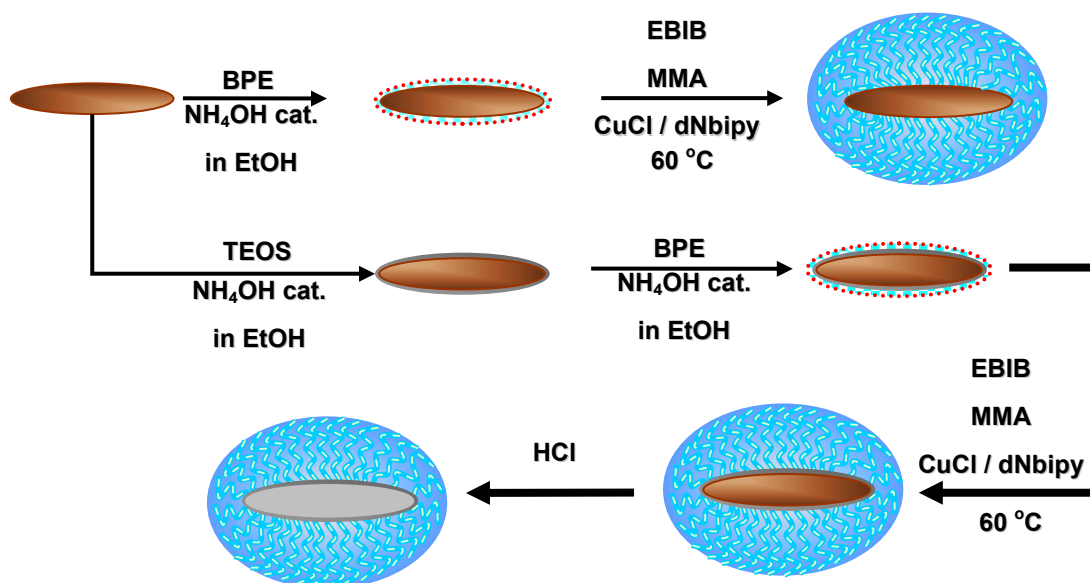


Figure 1-7. Schematic representation for the synthesis of polymer-coated hollowed nanorods by SI-ATRP

In **Chapter 6**, a β -FeOOH nanorod is modified with a PMMA polymer brush via SI-ATRP

(Figure 1-8). Using such a kind of hybrid nanorods, transparent films with liquid crystalline order embedded are fabricated without addition of polymer and oligomer matrix. Liquid crystalline texture is confirmed under the observation of polarized optical microscopy (POM). With adjusting the thickness of the polymer-brush layer by controlling the condition of SI-ATRP, the order like a colloidal crystal is also observed by the scanning electron microscopy.

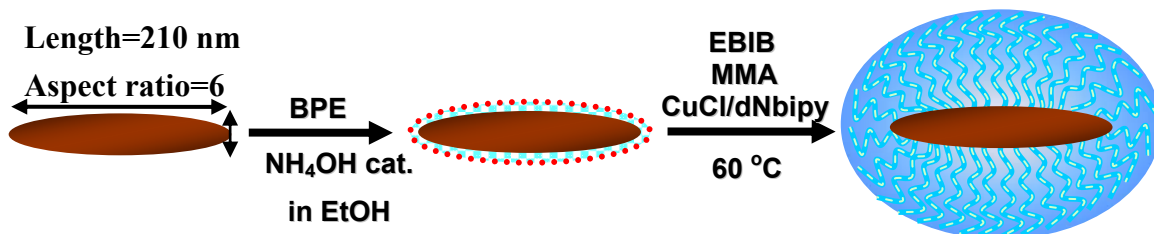


Figure 1-8. Schematic representation for the synthesis of polymer-coated β -FeOOH nanorods by SI-ATRP

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Chapter 2

Surface-Initiated Living Radical Polymerization from Narrowly Size-Distributed Silica Nanoparticles of Diameters less than 100 nm

2-1. Introduction

Surface-initiated living radical polymerization (SI-LRP) has attracted much attention over the past decade for its excellent control of the molecular weight and polydispersity of graft polymers, and its ability to afford an exceptionally high graft density.¹⁻⁴ Thanks to the robustness and versatility of living radical polymerization (LRP),⁵⁻¹⁰ this surface-modification technique has been applied to many types of substrates. Spherical fine particles have been surface-modified via SI-LRP in conjunction with various methods for initiator fixation, depending on the characteristics of the particle surfaces.¹¹⁻⁴⁵ Silica particles (SiPs) are among the most extensively studied particles for the application of SI-LRP because of the simplicity of initiator-fixation on their surfaces with organosilane compounds.¹¹⁻²⁹ The diameters of SiPs used so far for SI-LRP range from the nanometer to the micrometer scale.

The author's group has succeeded for the first time in preparing perfectly dispersive, monodisperse SiPs grafted with a polymer brush of high grafting density by surface-initiated atom transfer radical polymerization (SI-ATRP). Thanks to the good dispersibility and high uniformity of the hybrid particles, two- or three-dimensional ordered particle arrays were fabricated.^{46,47} However, strategies have never been developed for the synthesis of narrowly size-distributed silica nanoparticles (SiNPs), with core diameters less than 100 nm, and having polymer brushes, which keep their perfect dispersibility in solutions. Two reasons may be given for this: one is the difficulty in obtaining narrowly size-distributed SiNPs of diameter less than 100 nm. In fact, it is difficult to prepare such nanoparticles by the Stöber method,⁴⁸ the most common method for the synthesis of monodisperse SiPs. The second reason may be that such small nanoparticles tend to form

aggregates easily because of their large surface area. The aim of this work is to overcome the limitation on the size of silica particle available in this area of chemistry.

In this work, two methods for the preparation of monodisperse SiNPs were chosen: one is the reverse-micelle-mediated technique,^{49,50} in which reverse micelles act as templates for the formation of SiNPs with average diameters ranging from 30 nm to 70 nm. The other is the lysine-addition technique,⁵¹⁻⁵³ in which lysine controls the particle growth by adsorbing to the growing surface so as to produce nearly monodisperse SiNPs of around 10 nm in diameter. The author will describe how, by preventing particle aggregation throughout all the processes from initiator fixation to polymerization, SiNPs produced by these methods are decorated by polymer brushes with high surface densities, and retain good dispersibility in solvents. The author will also describe the formation of colloidal crystals using hybrid particles to demonstrate their high dispersibility and uniformity.

2-2. Experimental Section

2-2-1. Materials

Allyl alcohol (99%) was purchased from Wako Pure Chemicals, Osaka, Japan. 2-Bromoisobutyryl bromide (97%) and ethyl 2-bromoisobutyrate (2-(EiB)Br, 98%) were obtained from Tokyo Chemical Industry, Tokyo, Japan. 2,2'-Bipyridine (99 %) was used as received from Nacalai Tesque Inc., Osaka, Japan. 4,4'-Dinonyl-2,2'-bipyridine (dNbipy, 97 %) was purchased from Aldrich (St Louis, Mo, USA) and used without further purification. Copper(I) chloride (Cu(I)Cl, 99.9%) was purchased from Wako Pure Chemicals. Methyl methacrylate (MMA, 99%) was obtained from Nacalai Tesque Inc. and purified by flash chromatography over activated neutral alumina. A platinum catalyst (Karstedt's catalyst) solution (Pt-114, platinum content: 3 wt %) was obtained from Johnson Matthey Catalysts, Royston, UK. Triethoxysilane (99%) and tetraethoxysilane (99.9%) were obtained from Chisso Corp., Tokyo, Japan. Igepal[®] CO-520 was used as received from Aldrich. Ammonium hydroxide solution (28% NH₃), cyclohexane (99.5%),

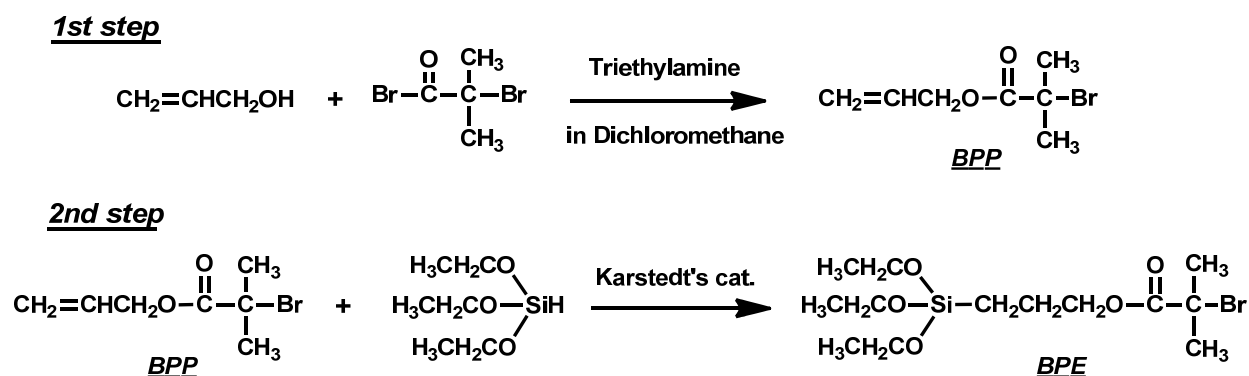
and *N,N*-dimethylformamide (DMF, 99.5%) were purchased from Wako Pure Chemicals. Water was purified by a Milli-Q system (Nihon Millipore Ltd., Tokyo, Japan) to a specific resistivity of ca. 18 MΩ-cm. All other reagents were used as received from commercial sources.

2-2-2. Measurements

Gel permeation chromatographic (GPC) analysis was carried out at 40 °C on a Shodex (Showa Denko K.K., Tokyo, Japan) GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-806L, exclusion limit = 2×10^7), and a differential refractometer (Shodex RI-101). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.8 mL/min. Poly(methyl methacrylate) (PMMA) standards were used to calibrate the GPC system. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a JOEL/AL300 spectrometer (JEOL, Tokyo, Japan). Elemental analyses were performed at the Laboratory of Elemental Analysis, Institute for Chemical Research, Kyoto University, Japan. The C and H contents were determined by combustion followed by differential thermal conductivity detection using a micro corder JM10 Elemental Analyzer (J-Science Lab Co., Ltd., Kyoto, Japan) and the Br contents were determined by combustion followed by ion chromatographic separation and electrical conductivity detection using a XS-100 Elemental Analyzer (Mitsubishi Chemical Analytech Co., Ltd., Kanagawa, Japan). Dynamic light scattering (DLS) measurements were performed in acetone solvent at 30 °C on a DLS-7000 photometer (Otsuka Electronics Co., Ltd., Osaka, Japan) with a He-Ne laser (wavelength 633 nm and power 10 mW) as a light source. The scattering light intensity was measured at a scattering angle of 90°. Data analysis was performed by the histogram method, including non-negative least-squares analysis. Transmission electron microscopy (TEM) observations were made on a JEOL transmission electron microscope (JEM-1010) operated at 100 kV. Thermal gravimetric analyses (TGA) were performed on a Shimadzu TGA-50 (Shimadzu, Kyoto, Japan) under a nitrogen atmosphere. Confocal laser scanning microscopic (CLSM) observations were made on an inverted type CLSM (LSM 5 PASCAL, Carl Zeiss, Germany) with a 488 nm wavelength Ar laser and ×63 objective (Plan

Apochromat, Carl Zeiss) in reflection mode. The distance of the focal plane from the inside surface of the coverslip was 50 μm .

2-2-3. Synthesis of the Fixed Initiator, (2-Bromo-2-methyl)propionyloxypropyl Triethoxysilane (BPE)



Scheme 2-1. Schematic representation of the synthesis of fixed initiator for atom transfer radical polymerization (ATRP), (2-bromo-2-methyl)propionyloxypropyl triethoxysilane (BPE).

BPE was synthesized via a two-step reaction (Scheme 2-1). First step: 2-bromoisobutyryl bromide (450 g, 1.96 mol) was added dropwise to a cold solution of allyl alcohol (170 g, 2.93 mol) in dry dichloromethane (2 L) with triethylamine (238 g, 2.35 mol) at 0 °C. The mixture was magnetically stirred for 3 h at 0 °C and then for another 10 h at room temperature. The system was evaporated to dryness under reduced pressure and the residue was diluted with THF (1 L). The system was passed through a filter paper, and the filtrate was evaporated to dryness under reduced pressure. The residue was diluted with chloroform (1 L), and washed twice with 1 N HCl aqueous solution (2 $\times$ 1 L), twice with saturated NaHCO₃ aqueous solution (2 $\times$ 1 L), and twice with water (2 $\times$ 1 L). Drying over Na₂SO₄, filtration, and removal of the solvent gave a brown oil, which was purified by distillation under reduced pressure to yield 1-(2-bromo-2-methyl)propionyloxy-2-propene (BPP) as a transparent liquid collected at ca. 1.5 mmHg and ca. 40 °C (308 g, 76%). ¹H NMR (CDCl₃): δ 1.95 (s, 6H, CCH₃), 4.68 (d, 2H, CH₂O), 5.26–5.42 (d, 2H, CH₂=CH), 5.94 (m, 1H, CH₂=CH). ¹³C NMR (CDCl₃): δ 30.8 (CCH₃), 55.6 (CBr), 66.4 (CH₂O), 118.5 (CH₂=CH), 131.4 (CH₂=CH), 171.3 (C=O). Anal. Calcd for C₇H₁₁O₂Br:

C, 40.60; H, 5.35; O, 15.45; Br, 38.59. Found: C, 40.67; H, 5.21; O, 14.65; Br, 38.38.

Second step: BPP (190 g, 918 mmol) was charged into a two-necked round-bottom flask equipped with a magnetic stirring bar and a rubber septum, and the system was deoxygenated by purging with argon. Triethoxysilane (350 g, 2.13 mol) that had been purged with argon beforehand was added into the flask in a glove box purged with argon, and subsequently Karstedt's catalyst solution (1 g) was added to the system using a syringe. The reaction mixture was magnetically stirred under an argon atmosphere for 24 h. The complete disappearance of BPP, and hence completion of the reaction, was confirmed by ^1H NMR spectroscopy. (If the reaction is not complete in 24 h, it should be continued by adding a suitable amount of the catalyst to the mixture.) The system was subjected to distillation under reduced pressure to yield the initiator BPE as a transparent liquid collected at ca. 1.5 mmHg and ca. 130 °C (230 g, 67%). ^1H NMR (CDCl_3): δ 0.69 (t, 2H, SiCH_2), 1.23 (t, 9H, $\text{CH}_3\text{CH}_2\text{OSi}$), 1.80 (m, 2H, CH_2), 1.93 (s, 6H, CCH_3), 3.83 (q, 6H, $\text{CH}_3\text{CH}_2\text{OSi}$), 4.15 (t, 2H, CH_2O). ^{13}C NMR (CDCl_3): δ 6.41 (SiCH_2), 18.3 ($\text{SiOCH}_2\text{CH}_3$), 22.0 (CH_2), 30.8 (CCH_3), 56.0 (CBr), 58.4 ($\text{SiOCH}_2\text{CH}_3$), 68.0 (CH_2O), 171.7 (C=O). Anal. Calcd for $\text{C}_{13}\text{H}_{27}\text{O}_5\text{BrSi}$: C, 42.05; H, 7.33; Br, 21.52. Found: C, 41.78; H, 7.44; Br, 21.61.

2-2-4. ATRP-Initiator Fixation on SiNPs Prepared by the Reverse-Micelle-Mediated Method

SiNP cores were prepared by the reverse-micelle-mediated technique developed by Osseo-Asare et al.^{49,50} In a typical run, a reverse microemulsion was prepared at room temperature by vigorously shaking a 2 L conical flask charged with a mixture of 28% NH_3 aqueous solution (4.48 g), Igepal[®] CO-520 (27.1 g), and cyclohexane (1 L). Tetraethoxysilane (5.21 g) diluted with cyclohexane (5 mL) was added to the microemulsion, and the system was gently shaken. The mixture was allowed to stand at room temperature for 4 days. To fix the initiator onto the surface of the produced SiNPs, a mixture of BPE (5.2 g) and cyclohexane (5 mL) was added to the microemulsion system, and the system was gently shaken and allowed to stand at room temperature for another 2 days. Cyclohexane was removed using a rotary evaporator. The residue was diluted with acetone (50 mL), and the solution was poured into hexane (750 mL) to yield a white

precipitate which was then collected by centrifugation (1000 rpm, 5 min). This reprecipitation cycle with acetone/hexane was repeated three times. The collected precipitate was then dissolved in ethanol (20 mL). The suspension was added under stirring to a mixture of 28% NH₃ aqueous solution (4.8 g) and ethanol (80 mL). After 1 h, a solution of BPE (0.5 g) and ethanol (5 mL) was added to the particle suspension, and the reaction was carried out for 20 h at ambient temperature. The reaction mixture was passed through a membrane filter (Millipore, MitexTM, pore size: 5 µm), and the filtrate was subjected to centrifugation (12,000 rpm, 20 min) to recover the surface-modified nanoparticles, which were subsequently washed three times by consecutive centrifugation and redispersion in ethanol. Finally, the suspension of the ATRP initiator-fixed SiNPs was solvent-exchanged to *N,N'*-dimethylformamide (DMF) by repeated redispersion/centrifugation to obtain a DMF stock suspension. Yield: 0.81 g of solid.

2-2-5. ATRP-Initiator Fixation on SiNPs Prepared by the Lysine-Addition Technique

SiNP cores were prepared according to the method developed independently by Yokoi et al.⁵¹ and Tsapatsis et al.^{52,53} Typically, *L*-lysine (0.15 g) was dissolved in a solution of water (139 g) and octane (7.31 g) at 60 °C. Tetraethoxysilane (10.4 g) was added to the mixture, and the system was stirred for 20 h at 60 °C and then allowed to stand for 20 h at 100 °C. The reaction mixture was subjected to dialysis against water, using a regenerated cellulose tube (Spectrum Laboratories Ltd., Spectra/Por[®]6, molecular cut off: 8000), for 1 week to remove unreacted compounds. Ethylene glycol (35 g) was added to the dialyzed solution, and the mixture was subjected to rotary evaporation at 55 °C to remove water from the mixture. For the ATRP-initiator fixation, the residue containing SiNPs (2.6 g) was diluted with ethanol (20 mL), and a mixture of triethylamine (7.8 g) and ethanol (230 mL), and then a mixture of BPE (7.8 g) and ethanol (10 mL), were added to the particle solution, in that order. The reaction mixture was stirred for 2 days at room temperature. The system was concentrated *in vacuo*, and the residue was diluted with acetone (50 mL) and then added to hexane (800 mL) to obtain a white precipitate of the surface-modified nanoparticles. This reprecipitation cycle with an acetone/hexane system was repeated three times to purify the

ATRP-initiator-fixed nanoparticles. Finally, the precipitate was dissolved in DMF, and the particle solution was concentrated *in vacuo* to remove volatile compounds, yielding a nanoparticle suspension in DMF to stock. Yield: 2.23 g of solid.

2-2-6. Surface-Initiated ATRP on SiNPs

Polymerization of MMA with the initiator-fixed SiNPs prepared by the reverse-micelle-mediated technique was carried out as follows: just before polymerization, the initiator-fixed SiNPs in DMF were solvent-exchanged to MMA to obtain a 1 wt% suspension in MMA. A Pyrex glass tube was charged with a predetermined amount of Cu(I)Cl (solid). A mixture of the initiator-fixed SiNP suspension in MMA containing a prescribed concentration of 2-(EiB)Br and dNbipy was quickly added to the Pyrex glass tube. The tube was equipped with a three-way stopcock, and the system was immediately degassed by three freeze–pump–thaw cycles and subsequently purged with argon. The mother reaction solution was divided nearly equally into a prescribed number of Pyrex glass tubes, each equipped with a three-way stopcock, in a glove box purged with argon. The divided solution was degassed by one freeze–pump–thaw cycle and sealed off under vacuum. The polymerization was carried out in a shaking oil bath (TAITEC Corp., Saitama, Japan, Personal H-10) thermostatted at 70 °C and, after a prescribed time t , quenched to room temperature. An aliquot of the solution was removed for NMR measurements to estimate monomer conversion, and for GPC measurements to determine the molecular weight and its distribution. The rest of the reaction mixture was diluted with acetone and centrifuged to collect the polymer-grafted SiNPs. The cycle of centrifugation and redispersion in acetone was repeated five times to obtain polymer-grafted SiNPs completely free of unbound (free) polymer. To determine the molecular weight of the graft polymer, PMMA chains were cleaved from the surface as follows: the polymer-grafted SiNPs (50 mg) and tetraoctylammonium bromide (50 mg), as a phase transfer catalyst, were dissolved in toluene (5 mL), to which a 10% HF aqueous solution (5 mL) was added. The mixture was vigorously stirred for 3 h. The cleaved polymer in the organic layer was subjected to GPC measurements.

In a typical run, the bulk polymerization of MMA was carried out at 70 °C for 4 h with the starting materials MMA (9.6 g, 96 mmol), 2-(EtB)Br (6.3 mg, 0.032 mmol), Cu(I)Cl (31 mg, 0.32 mmol), dNbipy (271 mg, 0.66 mmol), and initiator-fixed SiNPs of average diameter 55 nm (100 mg; the amount of initiator molecules fixed on the SiNP = 7.6 μ mol). This gave a monomer conversion of 61%, a free polymer with M_n = 128,000 and M_w/M_n = 1.18, and a graft polymer with M_n = 122,000 and M_w/M_n = 1.19, where M_n and M_w are the number- and weight-average molecular weights, respectively, and M_w/M_n is the polydispersity index. The polymer-grafted SiNPs were purified by repeated cycles of centrifugation (12,000 rpm for 60 min) and redispersion in acetone (3 $\times$ 200 mL) and in THF (3 $\times$ 200 mL).

Polymerization of MMA with the initiator-fixed SiNPs prepared by the lysine-addition technique was carried out as follows. A Pyrex glass tube was charged with a predetermined amount of Cu(I)Cl (solid). A mixture of the initiator-fixed SiNP suspension in DMF, MMA, 2-(EtB)Br, and dNbipy was quickly added to the Pyrex glass tube. The polymerization and the characterization of the resultant polymers were carried out in a similar way to that used for the polymerization with SiNPs prepared by the reverse-micelle method, as described above.

In a typical run, the solution polymerization of MMA in DMF was carried out at 70 °C for 3 h with the starting materials MMA (8.9 g, 89 mmol), DMF (0.95 g), 2-(EtB)Br (28.8 mg, 0.148 mmol), Cu(I)Cl (14.6 mg, 0.15 mmol), dNbipy (121 mg, 0.30 mmol), and initiator-fixed SiNPs of average diameter 15 nm (50 mg; the amount of initiator molecules fixed on the SiNPs = 7.0 μ mol), which gave a monomer conversion of 72% and a free polymer with M_n = 38,400 and M_w/M_n = 1.17, and a graft polymer with M_n = 35,300 and M_w/M_n = 1.15. The polymer-grafted SiNPs were purified by five cycles of centrifugation (20,000 rpm for 120 min) and redispersion in acetone (3 $\times$ 40 mL) and in THF (3 $\times$ 40 mL).

2-3. Results and Discussion

2-3-1. Synthesis of ATRP Initiator-Fixed SiNPs

The SiNP cores were prepared by the two methods: the reverse-micelle-mediated technique and the lysine-addition technique. The reverse-micelle-mediated technique provides highly monodisperse SiNPs with diameters of relative standard deviation around 5%. The particle size can be controlled by the composition of the reaction medium during preparation. The particle size was tuned within the range 30–70 nm by varying the Igepal[®] CO-520 concentration. In this paper, a sample will be focused as one typical example, which has an average diameter of 55 nm as evaluated from its TEM image in Figure 2-1a. After formation of the SiNPs in the reverse micelles, a BPE solution was added to modify the particle surfaces with ATRP-initiating sites. To introduce a sufficient number of initiating sites, the modified SiNPs were further treated with BPE in ethanol in the presence of NH₃. In fact, without this additional step, the dispersibility of the nanoparticles in organic solvents was not good enough, and the subsequent surface grafting was unsatisfactory, yielding a low grafting density. To estimate the amount of initiator fixed on the SiNPs after the additional treatment, an elemental analysis was carried out and determined the bromine content to be 1.52 %, which, along with the known density (1.9 g/cm³) and the average diameter (55 nm) of the SiNPs, led to a surface density of about 2 initiator molecules/nm². The initiator-fixed SiNPs were highly dispersible in many organic solvents. A suspension in DMF formed no aggregates and could be stably stored in a refrigerator, without any change, for at least 1 year.

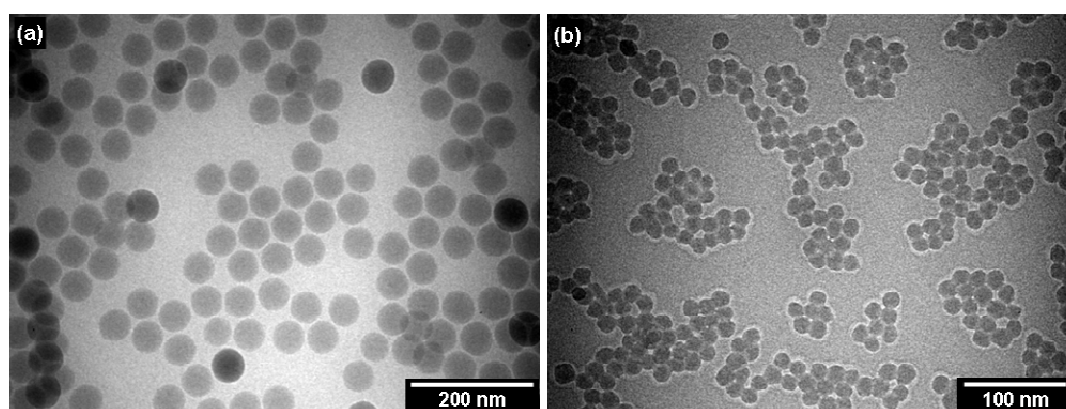


Figure 2-1. Transmission electron microscopic images of silica nanoparticles prepared by (a) the reverse-micelle-mediated technique and (b) the lysine-addition technique. The average diameters are (a) 55 nm and (b) 15 nm.

The synthesis of monodisperse SiNPs in the 10 nm range has until recently proven to be

difficult. Yokoi et al. and Tsapatsis et al. independently introduced the formation of such particles via hydrolysis of tetraethoxysilane in aqueous lysine solution.⁵¹⁻⁵³ This method was adopted for the preparation of silica cores in the present work. Although the method can control the particle size in the range 5–20 nm, depending on the reaction conditions,⁵¹⁻⁵³ The author used the reaction conditions described above for a typical example. Figure 2-1b shows a TEM image of the produced SiNPs. Although the shapes are not perfectly spherical, the size is nearly monodisperse, with an average diameter of 15 nm. BPE was used to decorate the surface of the resultant SiNPs with ATRP initiators. However, unlike the case for 55-nm SiNPs, described above, triethylamine was used as an alkaline catalyst instead of NH_3 because the addition of NH_3 induced aggregates of particles as soon as NH_3 was added to the system. Special care was also taken in the purification of the initiator-fixed SiNPs produced via the lysine-addition technique: if high-speed centrifugation is used to collect the SiNPs, they are difficult to redisperse homogeneously in solvents, even with the aid of ultrasonication. In practice, the initiator-fixed SiNPs were purified by reprecipitation with an acetone/hexane solvent system, and no aggregates were found after purification. Elemental analysis of the initiator-fixed SiNPs gave a bromine content of 5.60%, which led to a surface density of 2.4 initiator molecules/ nm^2 . This figure is comparable to those obtained for SiNPs prepared by the reverse-micelle-mediated technique described above, as well as with commercially available silica particles previously reported by us.⁴⁴ The dispersibility of initiator-fixed SiNPs with an average diameter of 15 nm in organic solvents is somewhat limited compared to other cases. For instance, the nanoparticles were perfectly dispersed in DMF, but not in toluene and anisole. This is the reason for using DMF as the stock solution.

2-3-2. Surface-Initiated ATRP of MMA from SiNPs

The initiator-fixed SiNPs were subsequently subjected to copper-mediated ATRP of MMA. According to our group's previous reports on SI-ATRP, the following two conditions are required to obtain a satisfactory result. First, the initiator-fixed SiNPs should never be dried before polymerization, to ensure their homogeneous dispersibility in the polymerization medium. Second,

a “sacrificial” or free initiator, 2-(EiB)Br in this study, must be added to the polymerization mixture. The role of the free initiator is to accumulate an appropriate amount of Cu(II) species via the termination of polymer radicals at an early stage of polymerization and thus to control the polymerization by the so-called persistent radical effect.⁴⁹⁻⁵⁰ Another role of the free initiator is to prevent interparticle coupling, causing gelation or particle aggregation, because free polymers produced by the free initiators will produce an entangled network structure through which the particle can hardly diffuse.

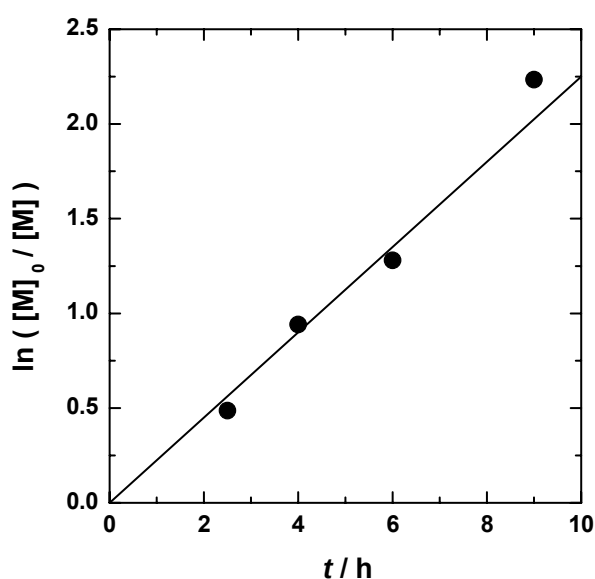


Figure 2-2. Plot of $\ln([M]_0/[M])$ vs t for the bulk polymerization of methyl methacrylate (MMA) at 70 °C with initiator-fixed silica nanoparticles of average diameter 55 nm (1 wt%): $[MMA]_0/[ethyl\ 2-bromoisobutylate]_0/[Cu(I)Cl]_0/[4,4'-dinonyl-2,2'-bipyridine]_0 = 3000/1/10/20$.

In the system with SiNPs prepared by the reverse-micelle-mediated technique, the suspension of the initiator-fixed SiNP in DMF was solvent-exchanged to the monomer to conduct bulk polymerization of MMA. Figure 2-2 shows the first-order kinetic plot of monomer concentration for the bulk polymerization of MMA with 2-(EiB)Br in the presence of BPE-functionalized SiNPs of average diameter 55 nm. The plot can be approximated by a straight line passing through the origin, thus giving first-order kinetics with respect to monomer conversion. The linear relationship reveals that the concentration of the propagating radical species is constant

throughout the course of polymerization. SiNPs purified after polymerization were treated with HF to cleave the graft polymer from the surface, and the cleaved polymer was subjected to GPC analysis. Figure 2-3 shows the evolution of M_n and M_w/M_n of the cleaved graft polymer and of the free polymer simultaneously produced from the free initiator 2-(EiB)Br. The dotted line shows the theoretical value of M_n ($M_{n,theo} = M_{MMA} \times C \times [MMA]_0 / ([2-(EiB)Br]_0 + [\text{initiation sites available on$

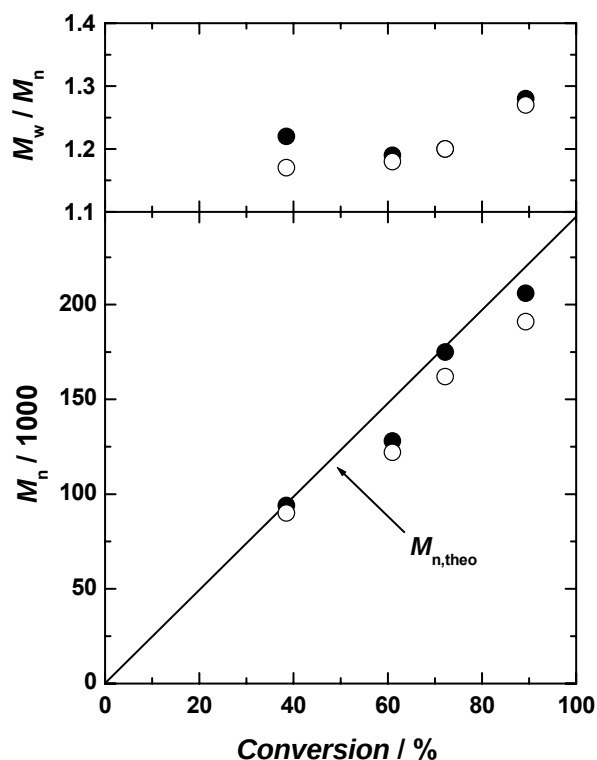


Figure 2-3. Evolution of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the graft (○) and free (●) polymers as a function of monomer conversion for the bulk polymerization of methyl methacrylate (MMA) at 70 °C with initiator-fixed silica nanoparticles of average diameter 55 nm (1 wt%): $[MMA]_0/[ethyl\ 2-bromoisobutylate]_0/[Cu(I)Cl]_0/[4,4'-dinonyl-2,2'-bipyridine]_0 = 3000/1/10/20$.

SiNP surface] $_0$)), where M_{MMA} is the molecular weight of MMA, C is the conversion, and $[MMA]_0$ and $[2-(EiB)Br]_0$ are the concentrations of MMA and 2-(EiB)Br in the feed, respectively. The initiation sites available on the SiNP surfaces were estimated from the polymer grafting density, as will be described below. It can be seen that the M_n values of the graft and free polymers are nearly the same, both increasing in proportion to monomer conversion. These M_n values agree well with $M_{n,theo}$. The M_w/M_n ratio remains fairly low, around 1.2 for most samples. All these results confirm

that the polymerization of MMA initiated from the SiNP surfaces proceeds in a living fashion, giving SiNPs with well-defined PMMA (PMMA-SiNP).

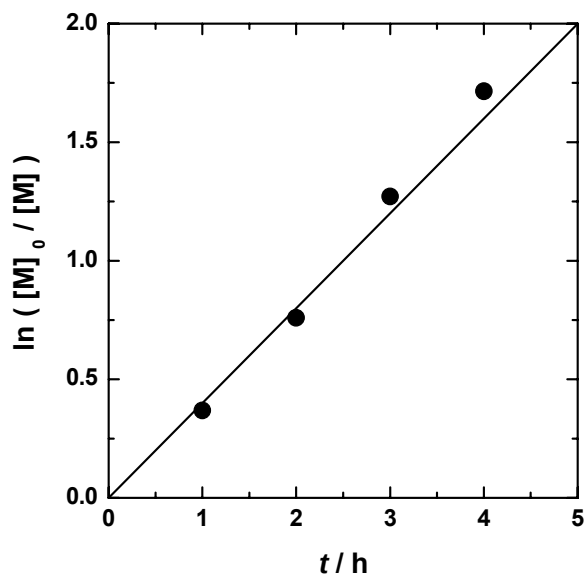


Figure 2-4. Plot of $\ln([M]_0/[M])$ vs t for solution polymerization of methyl methacrylate (MMA) in *N,N*-dimethylformamide (10 wt%) at 70 °C with initiator-fixed silica nanoparticles of average diameter 15 nm (0.5 wt%): $[MMA]_0/[ethyl\ 2-bromoisobutylate]_0/[Cu(I)Cl]_0/[4,4'-dinonyl-2,2'-bipyridine]_0 = 600/1/2/4$.

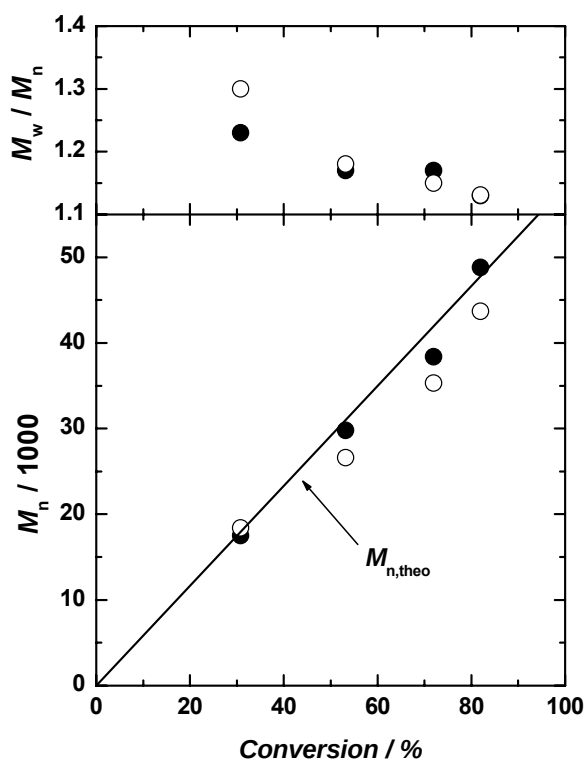


Figure 2-5. Evolution of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the graft (○) and free (●) polymers as a function of monomer conversion for solution polymerization of MMA in *N,N*-dimethylformamide (10 wt%) at 70 °C with initiator-fixed silica nanoparticles of average diameter 15 nm (0.5 wt%): $[MMA]_0/[ethyl\ 2-bromoisobutylate]_0/[Cu(I)Cl]_0/[4,4'-dinonyl-2,2'-bipyridine]_0 = 600/1/2/4$.

For the polymerization with the SiNPs prepared by the lysine-addition technique, a suspension of the BPE-functionalized SiNPs in DMF was used directly to prepare a solution for polymerization because the SiNPs, once centrifuged at high-speed rotation, were not redispersed homogeneously in solution. Solution polymerization of MMA in DMF (10 wt%) was carried out with the initiator-fixed nanoparticles in the presence of 2-(EiB)Br. Similar to the polymerization with the 55-nm SiNPs mentioned above, the polymerization proceeded in a living manner, showing a linear relationship for $\ln[M]_0/[M]$ vs t , as shown in Figure 2-4, and a proportional increase in M_n of the produced polymers as a function of monomer conversion, and relatively low M_w/M_n values, as shown in Figure 2-5.

2-3-3. Polymer Grafting Density

Thermogravimetric analyses of the PMMA-SiNP hybrids were carried out to estimate the mass (w) of polymer grafted on the SiNPs. The graft density (σ) was then calculated using Eq. (1):

$$\sigma = (w/M_n)A_v/(\pi d_c^2) \quad (1)$$

where d_c is the diameter of the SiNP core, and A_v is Avogadro's number. For the PMMA-SiNPs with a core diameter of 55 nm (see Figures 2 and 3 for the polymerization data for the SiNP core), the graft density is nearly constant independent of the polymerization time, and approximately equal to 0.8 chains/nm², as shown in Figure 6a. In the case of polymerization with SiNP cores of 15 nm (see Figures 2-4 and 2-5 for the polymerization data), as can be seen in Figure 2-6b, the graft density ranges from 0.4 to 0.5 chains/nm², which is somewhat smaller than in the case of polymerization with 55-nm SiNP cores. The reason for this is not at present clear, but it may possibly be due to some experimental error in determining the core diameters. More importantly, the graft densities obtained are high enough to demonstrate that the layer of polymer grafts is in the concentrated-brush regime.

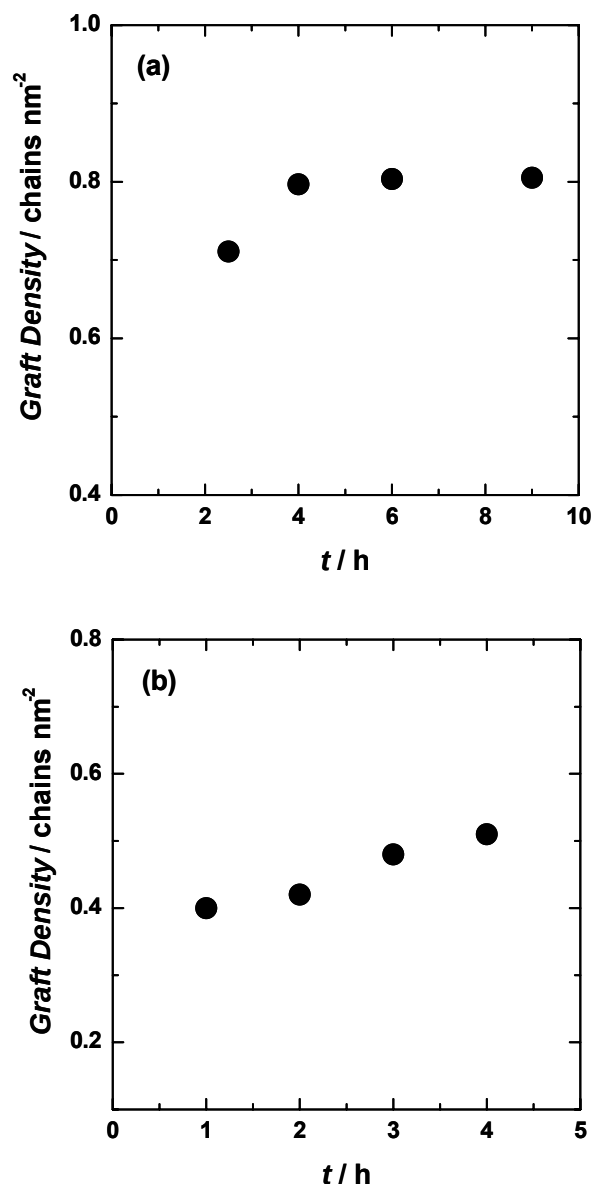


Figure 2-6. Time dependence of the graft density of poly(methyl methacrylate) grown from the surfaces of silica nanoparticles of average diameter (a) 55 nm and (b) 15 nm.

2-3-4. DLS Measurements of PMMA-SiNPs

The PMMA-SiNPs obtained here are well dispersed in most common solvents for PMMA. DLS measurements were conducted for a series of hybrid particles in dilute acetone solution. Figures 2-7a and 2-7b show the hydrodynamic diameters D_h for the hybrid particles with the core diameters of 55 nm and 15 nm, respectively, as a function of the M_w of the PMMA grafts. The diameters of the compact core-shell model and the fully stretched core-shell model are also shown in the figures. The former model consists of a SiNP core and a PMMA shell of bulk density, and the

latter consists of a SiNP core and a PMMA shell whose size is equal to that of the PMMA chains radially stretched in an all-trans conformation. In both cases, the D_h value increases with increasing M_w , being intermediate between the diameters of the two models.

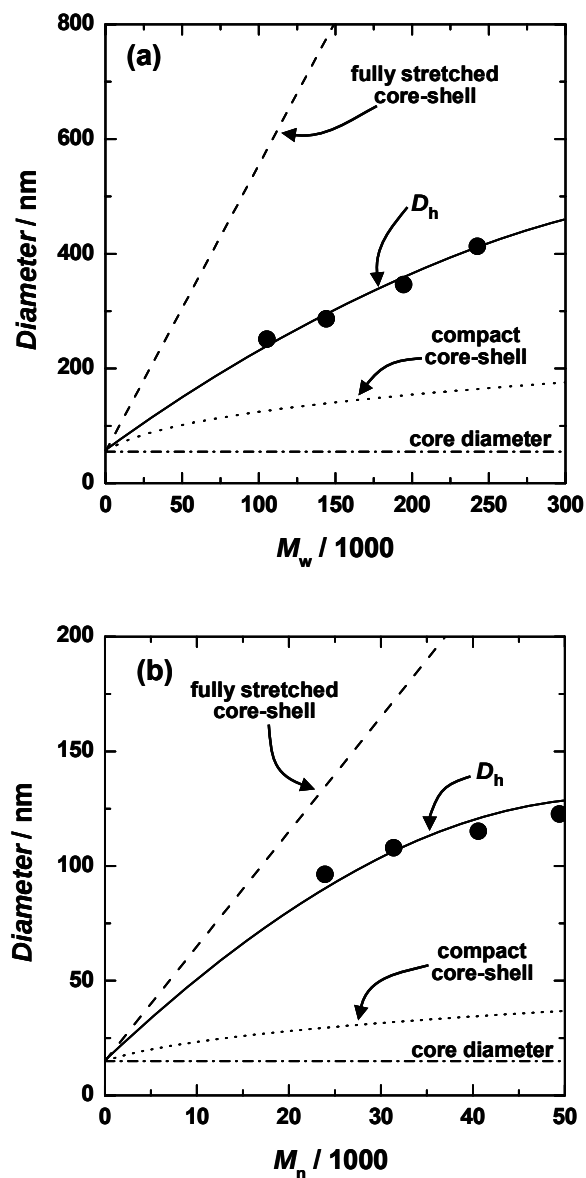


Figure 2-7. Plot of average hydrodynamic diameter D_h of silica nanoparticles grafted with poly(methyl methacrylate) (PMMA-SiNP) as a function of weight-average molecular weight M_w of the PMMA graft chains. The D_h values were determined by dynamic light scattering in dilute acetone suspension at 30 °C. The diameters of the SiNP cores are (a) 55 nm and (b) 15 nm. The broken and dotted lines represent the diameters of the fully stretched and compact core-shell models, respectively (see text).

2-3-5. Formation of Two Dimensional Ordered Arrays

PMMA-SiNPs monolayers were prepared following a previously reported procedure.⁴⁴

Briefly, a droplet of a concentrated suspension of PMMA-SiNPs in toluene was deposited onto the surface of purified water, giving a thin film at the air-water interface as the toluene evaporated. This thin film was transferred onto a TEM grid. Figure 2-8 shows the TEM images of transferred monolayers for PMMA-SiNPs with a core diameter of 55 nm and different molecular weights of PMMA grafts (M_n = a: 90,000, b: 191,000), and transferred monolayers with core diameters of 15 nm and different molecular weights of PMMA grafts (M_n = c: 17,500, d: 43,700). In all cases, the SiNP cores, visible as dark circles, are uniformly dispersed throughout the film; while the PMMA chains, which should form fringes surrounding the SiNP cores, are hardly seen because of their much lower electron density. The center-to-center distance between the nearest-neighbor particles increased with increasing molecular weight of graft chains. Interestingly, the hybrid particles with 55-nm cores are hexagonally close-packed in a monolayer. This is in contrast to the case for the hybrids of 15-nm SiNP cores, which do not form an ordered array, probably due to somewhat higher polydispersity in size and shape.

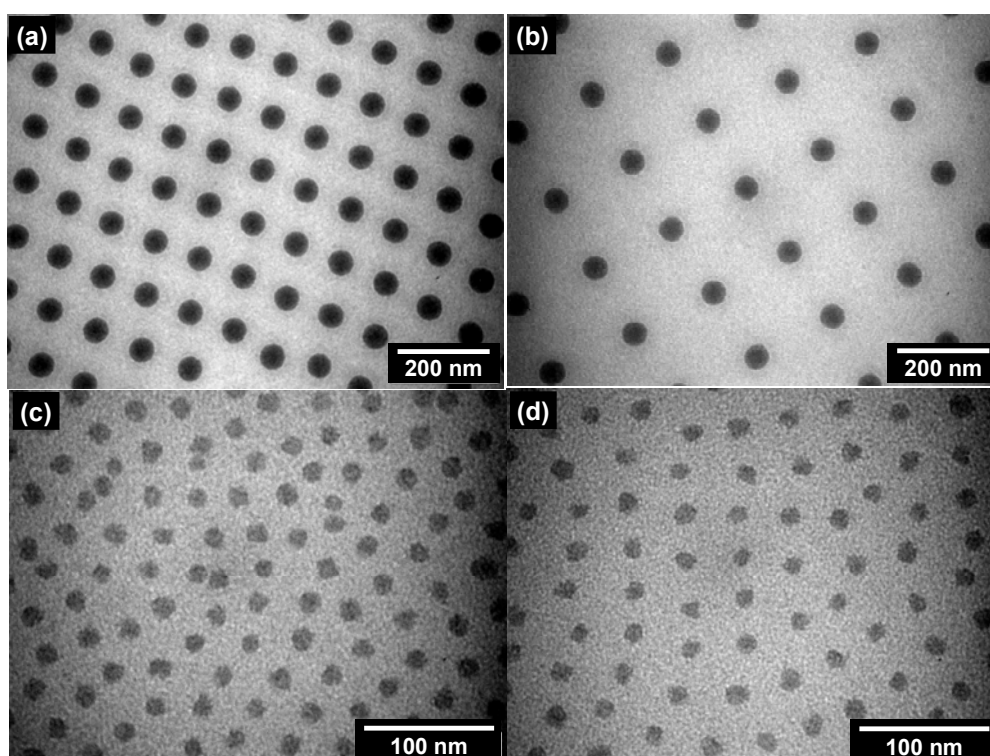


Figure 2-8. Transmission electron microscopic images of the transferred films of silica nanoparticles end-grafted with poly(methyl methacrylate) brushes (PMMA-SiNPs): the average diameters of the silica particle cores are (a and b) 55 and (c and d) 15 nm. Number-average molecular weights of the graft polymers are (a) 90,000, (b) 191,000, (c) 17,500, and (d) 43,700.

2-3-6. Formation of Colloidal Crystals

As described in Chapter 1, a colloidal crystal in a suspension of hybrid particles having a spherical silica core and a shell of well-defined PMMA concentrated brush was identified from conventional colloidal crystal. Following the same procedure, fabrication of a colloidal crystal was attempted using the PMMA-SiNPs prepared in the present work. Briefly, the PMMA-SiNP hybrid particles used here have a SiNP core of average diameter 55 nm and a shell of PMMA graft chains of $M_n = 122,000$ and $M_w/M_n = 1.19$, end-grafted on the SiNP surface with a surface density as high as 0.8 chains/nm². The hybrid particles were suspended in a mixture of chlorobenzene/1,2-dichloroethane of volume composition 66/34. The 6.14 vol% particle suspension was allowed to stand at ambient temperature. Tiny iridescent flecks were observed several minutes after the onset of the experiment, indicating the formation of Bragg-reflecting crystallites, and the formed crystallites filled the whole volume of the suspension, as shown in Figure 2-9.

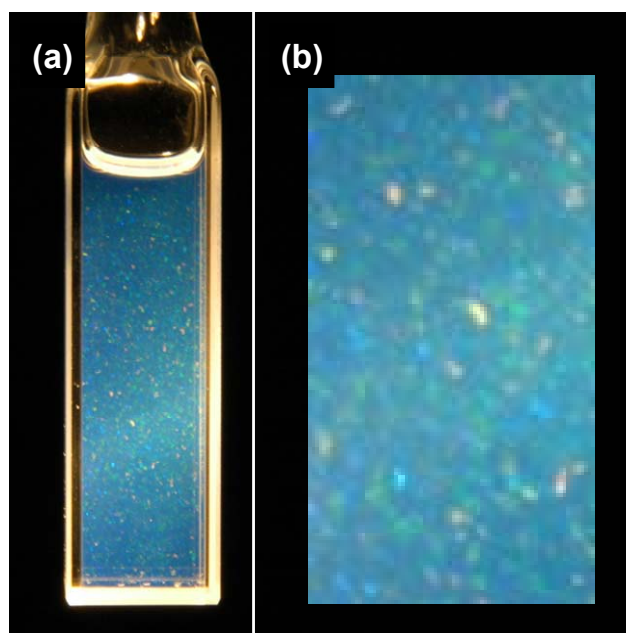


Figure 2-9. Photographs of a suspension of silica nanoparticles end-grafted with poly(methyl methacrylate) brushes (PMMA-SiNP) in a mixed solvent (chlorobenzene/1,2-dichloroethane, 66/34 volume ratio) illuminated from behind by white light. The number-average molecular weight of the PMMA graft is 122,000 and the average diameter of the SiNP core is 55 nm. The weight fraction of PMMA-SiNP was 6.14 vol%. (b) is a close-up of (a).

The PMMA-SiNP suspension was subjected to confocal laser scanning microscopic (CLSM) measurement to examine the crystal structure visually. Figure 2-10 shows a CLSM image

of a two-dimensional slice inside the sample. The SiNP cores of the hybrid particles are clearly visible as yellow dots forming a two-dimensional hexagonal array, while the PMMA brush layers are hardly visible because of their much lower reflectivity. The mean nearest-neighbor center-to-center distance D_{dis} between particles was found to be 350 nm (Figure 2-10). The distance can be estimated from the particle volume fraction ϕ in the crystal, according to the following relation, which is valid for closed-packed structures:

$$D_{\text{dis,cal}} = 2^{1/6}(V_p/\phi)^{1/3} \quad (2)$$

where V_p is the volume of a PMMA-SiNP particle in units of nm^3 . The $D_{\text{dis,cal}}$ value was calculated to be 320 nm, which is in good agreement with the experimentally observed D_{dis} value, and has a good correlation with the hydrodynamic diameter $D_h = 290$ nm of the hybrid particle determined in dilute suspension. This confirms the uniformity of the crystal as well as the consistency of the relevant experimental procedures.

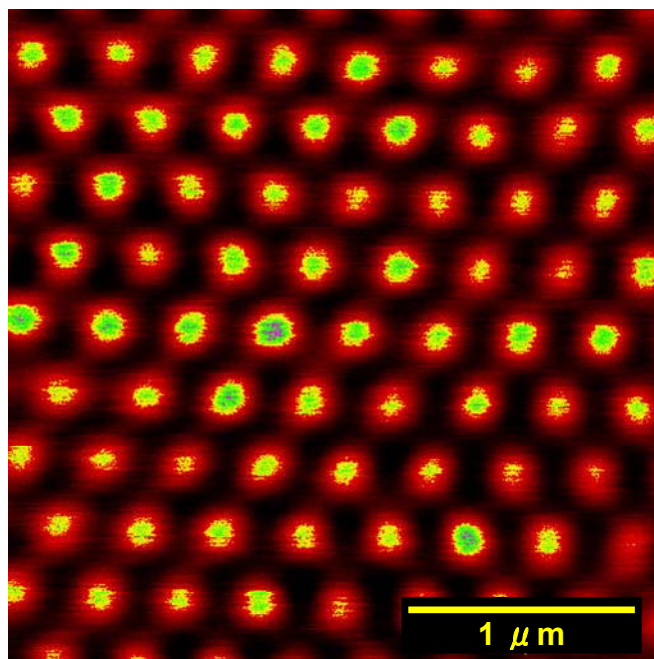


Figure 2-10. Confocal laser scanning microscopic image of colloidal crystals of silica nanoparticles end-grafted with poly(methyl methacrylate) brushes (PMMA-SiNP). Observations were performed using an Ar laser of wavelength 488 nm and $\times 63$ objective in reflection mode. The distance of the focal plane from the inside of the coverslip was 50 μm . The diameter of the SiNP cores is 55 nm. The number-average molecular weight of the PMMA graft is 122,000. The mean nearest-neighbor interparticle distance is 350 nm.

2-4. Conclusions

It was demonstrated that narrowly size-distributed SiNPs with average diameters less than 100 nm could be surface-decorated with ATRP initiation sites, while retaining their high dispersibility in solution. Surface-initiated ATRP of MMA using these functionalized SiNPs proceeded in a living fashion, yielding structurally controlled hybrid nanoparticles with a SiNP core and a shell of variable thickness composed of well-defined, concentrated PMMA brushes. Thanks to their exceptionally good dispersibility in solvents, these hybrid particles formed two- or three-dimensional ordered arrays with a high degree of structural order and wide controllability of the interparticle distances.

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Chapter 3

Immobilization of Semisoft Colloidal Crystals Formed by Polymer Brush-Afforded Hybrid Particles

3-1.Introduction

Colloidal crystals are three-dimensional periodic arrays of monodisperse colloidal particles, analogous to a conventional crystal where the repeating subunits are atoms or molecules.^{1,2} The driving forces for the formation of colloidal crystals are believed to be repulsive potentials working between colloidal particles. Two types of such potentials are known. One is the hard-sphere potential, which is steric and short-range in nature and induces the crystallization of rigid uncharged particles (hard colloidal crystal).³⁻⁸ The other is the electrostatic potential, which can be long-range depending on the ionic strength of the system and induces the crystallization of charged particles (soft colloidal crystal).⁹⁻¹² Recently, our group identified a colloidal crystal in a suspension of hybrid particles with a shell of well-defined poly(methyl methacrylate) (PMMA) chains densely grafted on spherical silica cores.^{13,14} The driving force of crystallization is the steric or excluded-volume interactions among the polymer chains densely grafted on the particle surface. This system is different from any previously observed colloidal crystals or similar ordered-assemblies formed by polymers of spherical architecture such as block copolymers and star-shaped polymers. This new colloidal crystal was named a semi-soft colloidal crystal.¹⁴⁻¹⁶

The three-dimensionally periodic structures of colloidal crystals can be used in many interesting applications such as optical filters, sensors, and structural color materials.¹⁷⁻⁴⁰ However, typical colloidal crystals formed in solution are fragile, and their structures are easily destroyed by mechanical vibration, evaporation of solvents, and impurities. Therefore, for broadening the applicability of colloidal crystals, it is important that they are immobilized in a way that retains their periodically ordered structure. Asher et al. immobilized colloidal crystals by first adding water-soluble monomers such as acrylamide to a colloidal crystal suspension in an aqueous system

and then in-situ photopolymerizing them to form a hydrogel entrapping the crystal lattice. They developed an optical sensor with the immobilized colloidal crystals, in which the interparticle distance was changed depending on the hydrogel volume in response to a chemical signal.¹⁸ Yamanaka et al. immobilized a soft type of colloidal crystals in a polyacrylamide hydrogel and demonstrated that its structural color was tunable by applying mechanical stress. The diffraction-peak wavelength shifted linearly and reversibly according to the compression force over a wide range of visible-light region.³⁸ Takeoka et al. also used a polyacrylamide gel to immobilize colloidal crystals and fabricated a smart membrane that exhibited a structural color controlled by the thickness and volume of the gel membrane.³⁹ Yoshinaga et al. reported a route to immobilize a colloidal crystal of polymer-grafted silica particles by a stepwise procedure comprising gelation by radical polymerization of 1,2-dimethacryloyloxyethane and methyl methacrylate in acetonitrile followed by the ring-opening radical polymerization of vinylidene-1,3-dioxolane.⁴⁰

The author herein report on the immobilization technique of semi-soft colloidal crystals formed by silica particles densely grafted with a polymer brush. Because the hybrid particles are synthesized by surface-initiated atom transfer radical polymerization (SI-ATRP), the brush layer can be easily modified via polymerization of the functional monomers by making use of the robustness and versatility of living radical polymerization.⁴¹⁻⁴⁵ For crystal immobilization, reactive groups are introduced into a limited part of the polymer-brush layer, and then the colloidal crystal formed by the reactive hybrid particles photo-reacts under UV light. The technique is useful for immobilizing semi-soft colloidal crystals, and the precise design of the hybrid particles is critical for maintaining the crystal structures before and after immobilization.

3-2. Experimental Section

3-2-1. Materials

4-Chloro-7-nitro-2,1,3-benzoxadiazole (NBD-Cl, >98%) and ethyl bromoisobutyrate (2-(EiB)Br, 98%) were obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. Copper(I)

chloride (Cu(I)Cl, 99.9%), 4,4'-dinonyl-2,2'-bipyridine (dNbipy, 97%), dibutyl(IV)dilaurate (DBTDL, 90%), hydroquinone monomethyl ether (MEHQ, 99%), anhydrous methyl ethyl ketone (MEK, 99%), Irgacure 907, methanol (MeOH, 99.5%), and tetraethyl orthosilicate (TEOS, 95%) were purchased from Wako Pure Chemical Industries, Ltd, Osaka, Japan, and were used without further purification. 3-Aminopropyltriethoxysilane (APTS, 98%), 1,2-dichloroethane (99.5%), chloroform (99%), *o*-dichlorobenzene (99%), methyl methacrylate (MMA, 99%), and hydroxyethyl methacrylate (HEMA, extra pure reagent) were obtained from Nacalai Tesque Inc., Osaka, Japan, and MMA was purified by flash chromatography over activated neutral alumina. Silica particle (SiP) (SEAHOSTER KE-E10, 20 wt% suspension of SiP in ethylene glycol) was obtained from Nippon Shokubai Co., Ltd., Osaka, Japan. The mean diameter of the SiP was 130 nm with a relative standard deviation of 10%, as measured by transmission electron microscopy. 2-Isocyanatoethyl methacrylate (MOI) was kindly donated by Showa Denko K.K., Co., Ltd., Tokyo, Japan. Methacryloxyethyl thiocarbamoyl rhodamine B (MTRhoB) was obtained from Polysciences, Inc., Warrington, USA. An ATRP-initiator-holding silane coupling agent, (2-bromo-2-methyl)propionyloxypropyl triethoxysilane (BPE), was synthesized by following a previous report and used to prepare initiator-coated SiPs.⁴⁶ All other reagents were used as received from commercial sources.

3-2-2. Measurements

Gel permeation chromatographic (GPC) analysis was carried out at 40 °C on a Shodex (Showa Denko K.K., Tokyo, Japan) GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-806L, exclusion limit = 2×10^7), and a differential refractometer (Shodex RI-101). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.8 mL/min. PMMA standards were used to calibrate the GPC system. ¹H NMR (300 MHz) measurement was made on a JOEL/AL300 spectrometer (JEOL, Tokyo, Japan). Confocal laser scanning microscopic (CLSM) observations were made on an inverted type microscope (LSM 5 PASCAL, Carl Zeiss, Germany) with a 488-nm Ar and a 543-nm

HeNe lasers and a $\times 63$ objective (Plan Apochromat, Carl Zeiss).

3-2-3. Preparation of P(MMA-*co*-HEMA)-*b*-PMMA-SiPs

SI-ATRP was employed to obtain SiPs grafted with a well-defined block copolymer of type P(MMA-*co*-HEMA)-*b*-PMMA. In the first step: A mixture of initiator-coated SiP suspension in MMA containing a prescribed concentration of 2-(EiB)Br and dNbipy was quickly added to a Pyrex glass tube charged with a predetermined amount of Cu(I)Cl (solid). Three freeze-pump-thaw cycles were carried out and the tube was sealed off under vacuum. The polymerization was carried out in a shaking oil bath (TAITEC Corp., Saitama, Japan, Personal H-10) thermostated at 60 °C and, after a prescribed time t , quenched to room temperature. An aliquot of the solution was taken out for NMR measurement to estimate monomer conversion and for GPC measurement to determine molecular weight and its distribution. The rest of the reaction mixture was diluted by acetone and centrifuged to collect polymer-grafted SiPs. The cycle of centrifugation and redispersion in organic solvents of acetone/THF/toluene was sequentially carried out, and each cycle was repeated three times to obtain PMMA-grafted SiPs (PMMA-SiPs) perfectly free of the unbound (free) polymer. In the second step, the SI-ATRP block copolymerization was carried out, in the similar way as the first step, in a monomer mixture of MMA and HEMA (mole ratio: [MMA]/[HEMA] = 95/5) in the presence of the macroinitiator PMMA-SiPs obtained in the first step to yield SiP coated with P(MMA-*co*-HEMA)-*b*-PMMA block copolymer.

In a typical run of the first step, the solution polymerization of MMA in anisole was carried out at 60 °C for 12 h with the starting materials of MMA (30 g, 300 mmol), anisole (28.1 g), 2-(EiB)Br (189 mg, 0.97 mmol), Cu(I)Cl (76.5 mg, 0.77 mmol), dNbipy (632 mg, 1.55 mmol), and initiator-coated SiPs (2 g). The polymerization gave a monomer conversion of 73 % and a free polymer with $M_n = 22,700$ and $M_w/M_n = 1.15$, and a graft polymer with $M_n = 23,000$ and $M_w/M_n = 1.17$. The polymer-grafted SiPs were purified by three cycles of centrifugation (12,000 rpm for 20 min) and redispersion in acetone (3×250 mL), THF (3×250 mL), and toluene (3×250 mL).

In a typical run of the second step, the bulk copolymerization was carried out at 60 °C for 3

h with the starting materials of MMA (21.1 g, 210 mmol), HEMA (1.44 g, 11.1 mmol), 2-(EiB)Br (86.5 mg, 0.44 mmol), Cu(I)Cl (87.7 mg, 0.89 mmol), dNbipy (724 mg, 1.77 mmol), and PMMA-grafted SiPs obtained from the first step as mentioned above (1.8 g). The polymerization gave a monomer conversion of 28 % and a free polymer with $M_n = 14,900$ and $M_w/M_n = 1.28$. The P(MMA-*co*-HEMA)-*b*-PMMA-SiPs were purified by three cycles of centrifugation (12,000 rpm for 20 min) and redispersion in acetone (3×250 mL), THF (3×250 mL), and toluene (3×250 mL). The characteristics of hybrid particles synthesized in this work are summarized in Table 3-1.

3-2-4. Preparation of Free P(MMA-*co*-HEMA) by ATRP

A free (ungrafted) statistical copolymer of type P(MMA-*co*-HEMA) was synthesized by ATRP. The bulk copolymerization was carried out in a shaking oil bath thermostated at 60 °C for 12 h with the starting materials of MMA (18.7 g, 187 mmol) and HEMA (1.28 g, 9.83 mmol), 2-(EiB)Br (12.8 mg, 0.066 mmol), Cu(I)Cl (19.5 mg, 0.020 mmol), dNbipy (161 mg, 0.039 mmol), which gave a monomer conversion of 37 % and a free copolymer with molecular weight of $M_n = 112,000$ and $M_w/M_n = 1.19$. The copolymer was purified by three cycles of reprecipitation in methanol (3×800 mL) and resolving in acetone (3×200 mL) after the measurement of GPC and NMR. The copolymer was dried *in vacuo* to remove volatile compounds for 3 h. Yield: 6.9 g.

3-2-5. Introduction of Vinyl Group to Hydroxyl Group of HEMA Unit

MOI (molar ratio of [MOI]/[hydroxyl groups of HEMA units] = 20) was added into the mixture of P(MMA-*co*-HEMA)-*b*-PMMA-SiPs (10 wt% with respect to MEK), DBTL (molar ratio of [DBTL]/[MOI] = 2.5×10^{-3}), MEHQ (1 wt% with respect to hybrid particles), and MEK. The mixture was stirred magnetically at 45 °C for 6 h, and then for 1 h at room temperature. The reaction was stopped by adding a solvent mixture of methanol (MeOH) and MEK. The free P(MMA-*co*-HEMA) was also modified in the similar manner.

In a typical run, the reaction was carried out at 45 °C for 6 h with the starting materials of hybrid particles P1 shown in Table 3-1 (1.74 g, 44 wt% of polymer content and 0.013 mmol of hydroxyl groups), MOI (0.41 g, 2.62 mmol), MEK (18 g), MEHQ (7.7 mg, 0.060 mmol), DBTL

(4.14 mg, 0.007 mmol). The reaction was stopped with a mixture of MeOH (0.41 g) and MEK (18 g). The particles were purified by three cycles of centrifugation (12,000 rpm for 20 min) and redispersion in acetone (3×250 mL), and redispersed in toluene to stock.

3-2-6. Fabrication and Immobilization of *Semisoft* Colloidal Crystals

Hybrid particles grafted with vinyl-group-carrying polymer brush were dispersed in a mixed solvent in the presence of a prescribed amount of vinyl-group-carrying free polymer. Knowing the weight fraction of polymer in the hybrid particles and literature values of refractive index (n) and density (ρ) of polymer and SiP in the bulk, the overall (average) n and ρ of hybrid particles used here were calculated and summarized in Table 3-1. The mixed solvents used for the preparation of particle suspensions were adjusted in composition so as to show the n and ρ values almost equal to those of hybrid particles assuming the additive rule for them.

A Pyrex glass cell connected with a glass tube for sealing was used for the formation and immobilization of colloidal crystal. A solution of photo-radical initiator, Irgacure 907, in 1,2-dichloroethane was poured into the cell, and subsequently, the organic solvent was removed *in vacuo*. A suspension of semi-soft colloidal crystal was placed in the Pyrex glass cell with the dried Irgacure 907 (0.1 wt% with respect to the suspension), and the cells was sealed off. The suspension was mixed by a vortex mixer MS 3 basic (IKA[®] Japan. K. K., Osaka, Japan), and allowed to stand at ambient temperature for the formation of colloidal crystal. The entire operations were carried out in the dark to prevent the onset of photo-reaction before the formation of colloidal crystal. The resultant colloidal crystal was exposed to UV irradiation (>300 nm, UV light, MAX-301, Asahi Spectra Co., Ltd., Tokyo, Japan) for 3 h.

3-2-7. Synthesis of Fluorescence-Labeled Silica Particles

The Stöber method was used to synthesize fluorescence-labeled SiPs. APTS (0.14 g, 0.632 mmol) was added, in a glove box purged with dry argon, into a solution of NBD-Cl (0.12 g, 0.601 mmol) dissolved in anhydrous ethanol (15 mL), and the mixture was magnetically stirred for 24 h. A part of the resultant solution (3.28 g) was subsequently mixed with a solution of TEOS (14.7 g) in

ethanol (30 mL) and the mixture was added dropwise at the speed of 7.0 mL/min into a mixture of ethanol (150 mL) and an ammonia solution (28% NH₃ aqueous solution, 36.4 g). The reaction was carried out at room temperature for 3 h with the stirring speed of 100 rpm. The resultant fluorescence-labeled SiPs were collected by centrifugation (8000 rpm for 10 min) and redispersed in ethanol followed by centrifugation. This cycle was repeated three times to obtain a suspension of fluorescence-labeled SiPs in ethanol.

3-2-8. Fixation of ATRP-Initiator BPE on Fluorescence-labeled Silica Particles.

A mixture of ammonia solution (28% NH₃ aqueous solution, 31.3 g) and ethanol (400 mL) was added dropwise into a suspension of fluorescence-labeled silica particles (4.25 g) in ethanol (60 mL) under magnetically stirring, and the system was stirred for 1 h at ambient temperature. BPE (2.5 g, 7.65 mmol) dissolved in ethanol (40 mL) was added dropwise into the system, and the reaction mixture was continuously stirred for another 18 h at ambient temperature. Thus surface-modified silica particles were cleaned by consecutive centrifugation and redispersion in ethanol. Finally, the suspension of the initiator-coated fluorescence-labeled silica particles in ethanol was subjected to the solvent-exchange treatment to obtain an anisole suspension to stock.

3-2-9. Synthesis of Fluorescence-labeled Silica Particles Grafted with Block Copolymer Brush by SI-ATRP.

In a typical run of the first step, the bulk polymerization of MMA was carried out at 70 °C for 24 h with the starting materials of MMA (19.8 g, 197 mmol), 2-(EiB)Br (4.81 mg, 0.003 mmol), Cu(I)Cl (12.2 mg, 0.012 mmol), dNbipy (101 mg, 0.25 mmol), and the initiator-fixed, fluorescence-labeled silica particles (0.4 g). The polymerization gave a monomer conversion of 38 % and a PMMA graft polymer with $M_n = 301,300$ and $M_w/M_n = 1.19$. The resultant hybrid particles were purified by three cycles of centrifugation (8,000 rpm for 10 min) and redispersion in acetone (3 × 250 mL), THF (3 × 250 mL) and in toluene (3 × 250 mL).

In a typical run of the second step, the solution polymerization was carried out at 60 °C for 3 h with the starting materials of MMA (5.62 g, 56.1 mmol), HEMA (0.384 g, 2.95 mmol), 2-(EiB)Br

(23.0 mg, 0.012 mmol), Cu(I)Cl (23.4 mg, 0.24 mmol), dNbipy (193 mg, 0.47 mmol), anisole (11.4 g), and PMMA-grafted SiPs synthesized in the first step (0.45 g). The polymerization gave a monomer conversion of 44 % and a free polymer with $M_n = 22,000$ and $M_w/M_n = 1.15$. The fluorescence-labeled hybrid particles were purified by three cycles of centrifugation (8,000 rpm for 10 min) and redispersion in acetone (3×250 mL), THF (3×250 mL) and in toluene (3×250 mL).

3-2-10. Synthesis of Fluorescence-Labeled Free Copolymer

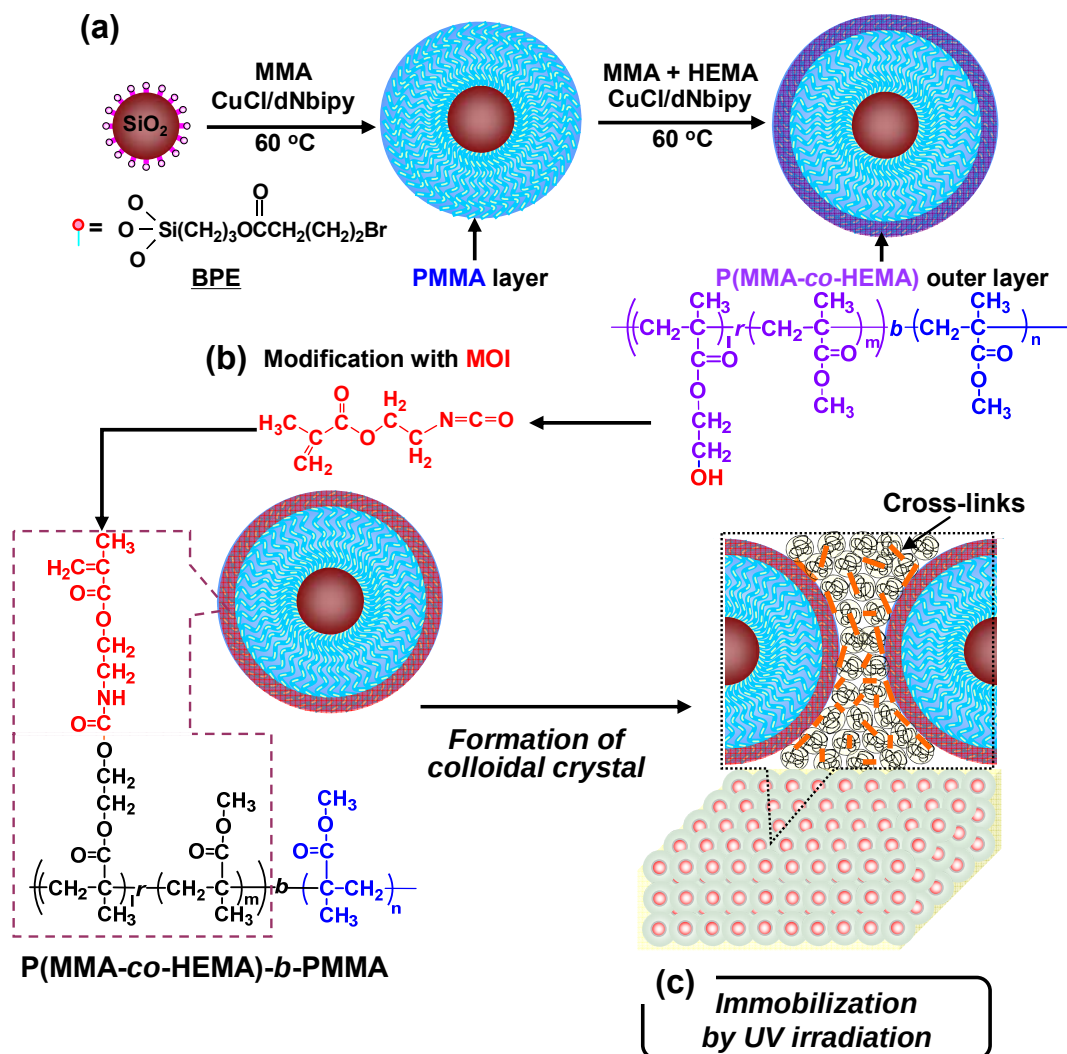
The atom transfer radical copolymerization was carried out in bulk at 60 °C for 12 h with the starting materials of MMA (18.7 g, 186 mmol), HEMA (1.28 g, 9.82 mmol), rhodamine-labeled monomer MTRhoB (44.7 mg, 0.007 mmol), 2-(EtB)Br (12.77 mg, 0.0065 mmol), Cu(I)Cl (97.22 mg, 0.98 mmol), dNbipy (803 mg, 1.96 mmol). The polymerization gave a monomer conversion of 67 % and a free fluorescence-labeled polymer with $M_n = 200,700$ and $M_w/M_n = 1.26$. The free polymer was purified by reprecipitation with acetone/methanol system for three cycles to obtain a fluorescence-labeled copolymer. Yield: 13.3 g. The copolymer was further modified with MOI to produce a vinyl-group-carrying copolymer, as described above.

3-3. Results and Discussion

3-3-1. Strategy for Immobilization of Colloidal Crystals.

The author set up the strategy for the immobilization of colloidal crystals consists of three steps as shown in Scheme 1. First, the hybrid particles grafted with a polymer brush that bears several hydroxyl groups near the free end of the polymer chains are synthesized, and subsequently, reactive vinyl groups are introduced into the hydroxyl groups. Second, the reactive hybrid particles are employed for the formation of colloidal crystals. Third, the resultant colloidal crystals are photo-irradiated by a UV light to form cross-linkages among the vinyl groups, leading to the immobilization of colloidal crystals. One of the important points of this strategy is the design of the polymer brush. Namely, the reactive sites of vinyl groups should only be placed in a limited part of the polymer brush. This can minimize the volume contraction of the system that can be caused by

the cross-link reaction that leads to the gelation or immobilization of the colloidal suspension. The use of a mild photo-reaction condition should also be stressed. These efforts are believed to be necessary to maintain the crystal structure before and after immobilization.



Scheme 3-1. Schematic representation of stepwise immobilization. (a) SiP grafted with well-defined PMMA is used as macroinitiator for block copolymerization, BPE: (2-bromo-2-methyl)propionyloxypropyl triethoxysilane. (b) MOI is used to modify hybrid particle with displacing hydroxyl groups of HEMA units with vinyl groups. (c) Immobilize *semisoft* colloidal crystal with the aid of free copolymer in suspension.

3-3-2. Synthesis of Vinyl-Group-Carrying Hybrid Particles.

Hybrid particles grafted with a block copolymer brush of polymer type P(MMA-co-HEMA)-b-PMMA were synthesized by surface-initiated block copolymerization using MMA and a mixture of MMA and HEMA to prepare the first and second blocks, respectively, as

described in the Experimental Section. The characteristics of thus obtained hybrid particles are given in Table 3-1. Table 3-1 shows that well-defined, low-polydispersity block polymers comprising PMMA of varying lengths in the first block and P(MMA-*co*-HEMA) of nearly the same length in the second block were successfully grafted on a SiP core with a diameter of 130 nm.

Table 1. Characteristics of Silica Particles Grafted with Block Copolymer Brush.

Sample code	1st block		2nd block		ρ^c (g/mL)	n^d
	PMMA		P(MMA- <i>co</i> -HEMA)			
	M_n^a	M_w/M_n^b	M_n^a	M_w/M_n^b		
P1	23 000	1.17	14 900	1.28	1.56	1.46
P2	121 000	1.21	14 000	1.24	1.28	1.48
P3	248 000	1.13	14 900	1.12	1.26	1.49

^a Number-average molecular weight of free polymers simultaneously produced in the polymerization. ^b Polydispersity index of free polymers simultaneously produced in the polymerization. ^c Calculated value of the overall (average) bulk density of the hybrid particles.

^d Calculated value of the overall (average) refractive index of the hybrid particles.

The P(MMA-*co*-HEMA) blocks of the hybrid particles were subsequently modified with MOI to introduce vinyl groups into the hydroxyl groups of the HEMA units. The content of the vinyl groups introduced was too low to be precisely determined even when all the hydroxyl groups were modified. Therefore, the author carried out a model experiment using a free (ungrafted) copolymer of type P(MMA-*co*-HEMA) containing 5 mol% of HEMA units with M_n and $M_w/M_n = 112,000$ and 1.19, respectively. Figure 3-1 shows the ^1H NMR spectroscopy of the purified copolymer before and after reaction with MOI. The assignment of the observed peaks is given in the figure. The molar fraction of HEMA units in the copolymer was estimated to be ca. 5 mol% based on the integral ratios of the corresponding peaks in Figure 1a; the value is approximately the same as the molar ratio of HEMA to total monomers in the feed for polymerization suggesting the formation of statistically random copolymer. In Figure 1b, the two peaks **g'** at 5.60 and 6.15 ppm are ascribed to the protons of the vinyl groups introduced into the HEMA units. Based on the

relative integral of these peaks **g'** against unchanged **a'** and **b'**, the molar fraction of the vinyl groups in the copolymer was calculated to ca. 4.6 mol%. This means that almost all the hydroxyl groups in the copolymer was calculated to ca. 4.6 mol%. This means that almost all the hydroxyl groups of the HEMA units reacted with MOI to obtain the vinyl groups. It can be reasonably assumed that the hydroxyl groups of the graft copolymers have the same reactivity as those of the free polymer, and hence that almost all the hydroxyl groups of P(MMA-*co*-HEMA)-*b*-PMMA-SiPs react with MOI, successfully producing hybrid particles with vinyl groups near the free end of the polymer brush.

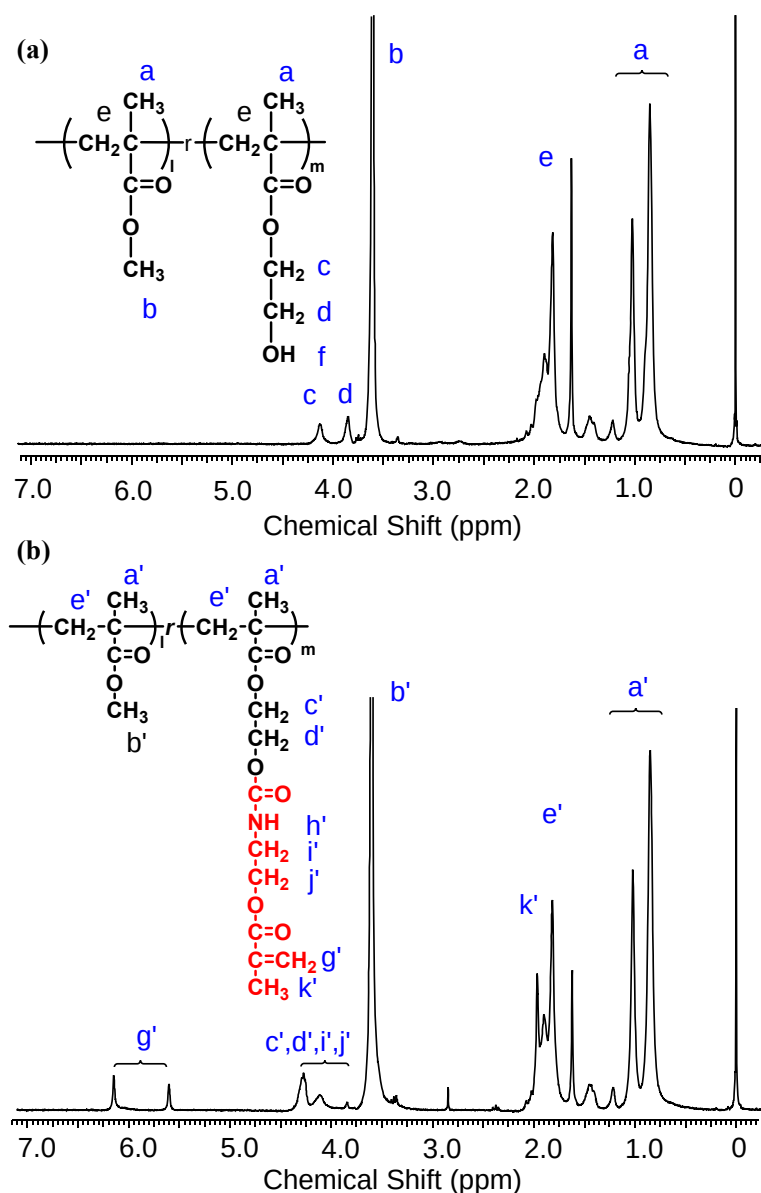


Figure 3-1. ^1H NMR spectrum of free copolymer P(MMA-*co*-HEMA) and free vinyl groups-holding copolymer. The solvent was CDCl_3 . a. ^1H NMR spectra of free copolymer P(MMA-*co*-HEMA). b. ^1H NMR spectra of free copolymer P(MMA-*co*-HEMA) after modification by MOI.

3-3-2. Immobilization of *Semisoft* Colloidal Crystal

The author prepared a colloidal crystal of vinyl-group-carrying hybrid particles using a n - and ρ -matched mixture of solvents containing a photo-radical initiator. However, the attempt to immobilize it by UV irradiation did not work satisfactorily. After UV light irradiation, the viscosity of the colloidal crystal suspension increased, and some parts of the suspension formed a gel, which was easily destroyed with gentle shaking of the system. This indicates that the cross-linking network is more or less formed among the hybrid particles, but that its density was too low to achieve sufficient mechanical strength.

To overcome the difficulty, a free (ungrafted) copolymer with vinyl groups, which has the M_n of 112,000 and the molar fraction of the vinyl group of ca. 5 mol%, was added to promote the cross-linking. In order to mainly locate the network at the interstitial space among the hexagonally assembled hybrid particles with solvent, the molecular weight of the copolymer was high enough to prevent its deep entry into the polymer brush layer of hybrid particles owing to the size-exclusion effect of the polymer brush as well as low enough to present the macroscopically exclusion (phase separation) from the colloidal crystal.

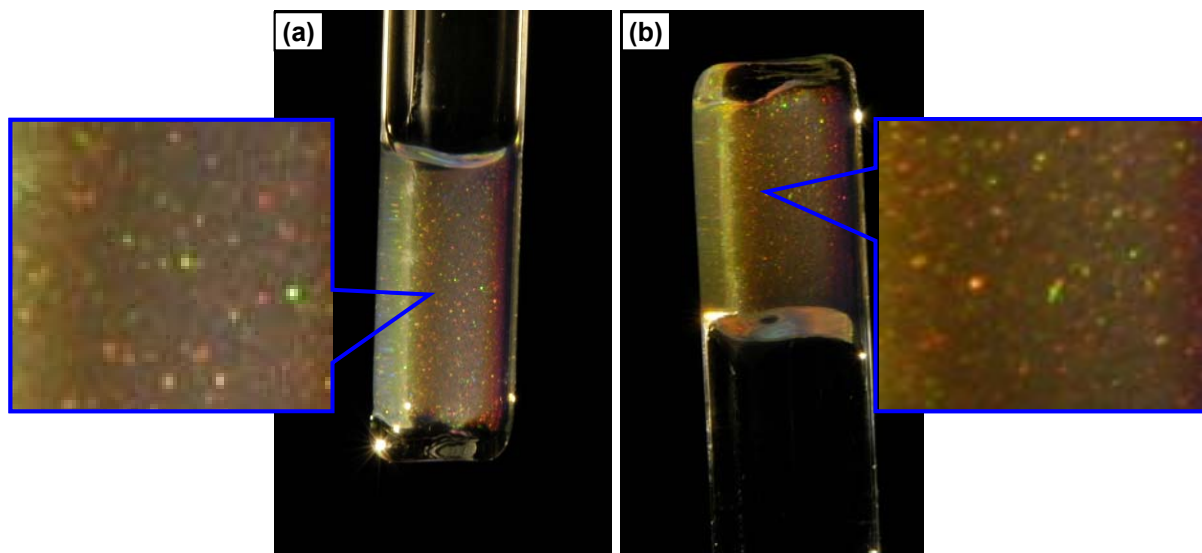


Figure 3-2. Photographs of *semisoft* colloidal crystals in Pyrex cell illuminated from behind by white light. (a) and (b) represent the semi-soft colloidal crystal before and after UV irradiation, respectively, to immobilize it. Each inset is the close-up.

To examine the effect of free-copolymer addition, a suspension of vinyl-group-carrying hybrid particles, P2v, which are P2 particles (see Table 3-1) modified with MOI, was prepared by dispersing the particles in a mixture of 1,2-dichloromethane/chlorobenzene with a volume composition of 53/47. One weight percent of the vinyl-group-carrying free copolymer and 0.1 wt% of the photo-radical initiator were added beforehand. As shown in Figure 2a, when the suspension of 9.45 vol% particle volume fraction was allowed to stand at ambient temperature, tiny iridescent flecks were observed in the entire volume of the suspension several minutes after the onset of the experiment, indicating the formation of Bragg-reflecting crystallites. The suspension containing the crystallites was subsequently subjected to UV irradiation to initiate a photo-radical reaction. Figure 2b shows that the photo-irradiated suspension did not flow even in an upside-down glass cell, and the tiny iridescent crystallites were still observed after UV irradiation. This result indicates the gelation of the system, i.e., the immobilization of the colloidal crystal. To tentatively demonstrate the mechanical strength of the crystal, thus immobilized colloidal crystal was taken out of a glass cell and placed in toluene but not destroyed even when the sample was shaken by hand.

The immobilization of semi-soft colloidal crystals for the suspensions of hybrid particles of MOI-modified P1 and P3 (Table 3-1) was also attempted using a similar technique. A colloidal crystal formed with a suspension of the MOI-modified P1 particles with particle volume fraction of 23.5 vol% in the absence of the free polymers, but it did not form in the presence of 1 wt% of the free copolymer. When the free polymer concentration was decreased to 0.3 wt%, a colloidal crystal formed with the same volume fraction of the particle. This may be due to the effect that the depletion force exerted between the hybrid particles by the addition of free copolymer. The effect probably makes it difficult for the P1 hybrid particles with a relatively short polymer chain to assemble into a crystal because of the attraction between the particles arising from the depletion force. Even though the concentration of the free copolymer was relatively low, 0.3 wt%, the colloidal crystal suspension prepared by the MOI-modified P1 particles still became a gel after UV irradiation. In the case of the MOI-modified P3 particles, a colloidal crystal was obtained with a

particle volume fraction of 7.13 vol%, even in the presence of 1 wt% of the free copolymer. However, the colloidal crystal could not be completely immobilized after UV irradiation. Increasing the free copolymer concentration to 1.8 wt% led to a sufficiently immobilized colloidal crystal. The polymer concentration near the free surface of the polymer brush layer on the particle was lower in the hybrid particles with a relatively long graft chain than in the hybrid particles with a relatively short polymer chain because of particle curvature. Therefore, an increased free polymer concentration should be needed to effectively achieve the cross-linking reaction for crystal immobilization.

The content of the vinyl groups in the second block of the polymer brush layer is also important for colloidal crystal immobilization. It has been attempted to immobilize the colloidal crystals prepared by hybrid particles, which have graft polymers of the M_n similar to that of the MOI-modified P2 particles but have vinyl groups in 1 and 20 mol% in the second block of graft polymers. The reactions for immobilization were carried out under similar conditions as described above, i.e., in the presence of 1 wt% of vinyl-group-carrying copolymers and 0.1 wt% of photo-radical initiator. However, these two systems failed to give a satisfactory result. The colloidal crystal prepared by the hybrid particles with 1 mol% of the vinyl group in the second block was not sufficiently immobilized, resulting in a mechanically weak gel. In the case of hybrid particles with 20 mol% of the vinyl group in the second block, the colloidal suspension was completely immobilized after UV irradiation, but a layer composed of only solvent was observed at the top of the formed gel. This indicated that syneresis occurred when the colloidal crystal formed a gel and exuded some of the solvent. These results suggest that the optimization of the vinyl group content is one of the crucial factors for achieving the immobilization of semi-soft colloidal crystals.

3-3-3. CLSM Observations

The structural analysis of colloidal crystals was carried out by in situ CLSM measurement before and after immobilization. For the analysis, a suspension of hybrid particles with an appropriate concentration for crystal formation was placed in a glass cell (0.8 cm in diameter and

1.5 cm in height), which had a bottom consisted of a coverslip and a top sealed by gluing a slide glass, and the suspension was observed by CLSM once the Bragg-reflecting crystallites formed. Figures 3-3a, b, and c show the CLSM images of the two-dimensional crystalline planes of the samples prepared by MOI-modified P1, P2, and P3 particles, respectively. The SiP cores of the hybrid particles are clearly visible in all the images as yellow circles forming a two-dimensional hexagonal array, while the polymer brush layers that should be surrounding the SiP cores are hardly visible because of their low reflectivity. The high degree of SiP core positional order and the strong dependence of the interparticle distance on the chain length of the copolymer grafts are particularly noteworthy. Figure 3-3a has poor resolution because of a smaller interparticle distance. The similar result as Figure 3-3a was proved in the image of the sample with MOI-modified P1 particles was taken under higher magnification. The mean nearest-neighbor center-to-center distances (D) in the images in Figures 3-3a–c were measured to be 280, 530, and 710 nm, respectively. In all the samples, the measured D values were larger than the diameter of the “compact core-shell model”, which consists of a SiP core and polymer shell of the bulk, and were as large as ~50% of the diameter of the “fully stretched core-shell model”, which consists of a SiP core and polymer shell with a size equal to that of the polymer chains radially stretched in *all-trans* conformation. Those colloidal crystals were irradiated by UV light to immobilize them. Figures 3-3d, e, and f show the CLSM images of the immobilized colloidal crystals prepared by MOI-modified P1, P2, and P3 particles, respectively. In all the samples, there was almost no change in the D values of the hexagonally close-packed ordered structures before and after immobilization. These results strongly support the conclusion that the semi-soft colloidal crystals were successfully immobilized without disturbing their ordered structures.

To verify the validity of the strategy for the immobilization of colloidal crystals, the author attempted to carry out a CLSM measurement in fluorescence mode on an immobilized colloidal crystal prepared using fluorescence dye (NBD)-labeled SiPs grafted with a polymer brush in the

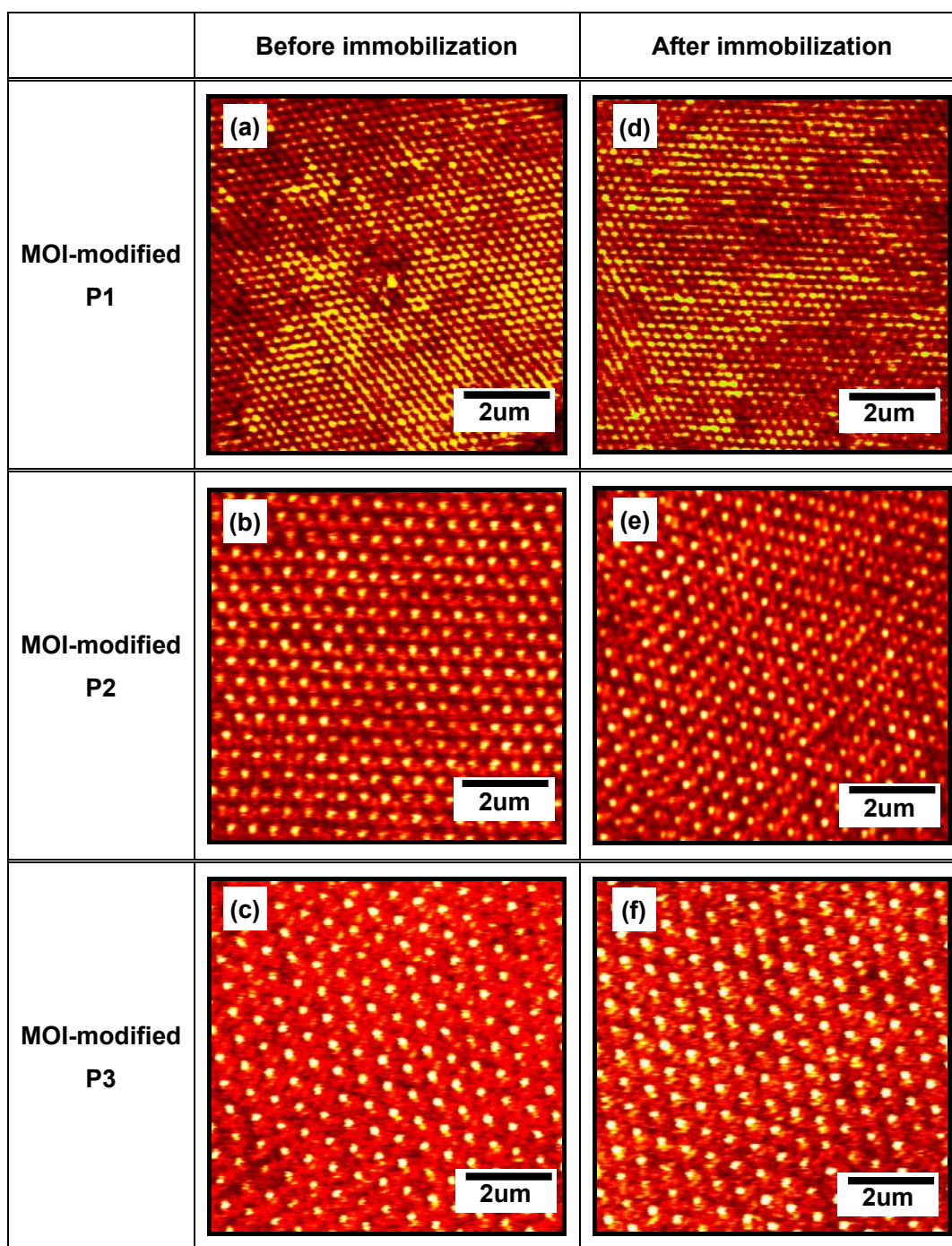


Figure 3-3. Confocal laser scanning microscopic images of colloidal crystals before and after immobilization. (a), (b), and (c) show the two-dimensional crystalline planes of colloidal crystals prepared by MOI-modified P1, P2, and P3 particles, respectively. (d), (e), and (f) show the images of the immobilized colloidal crystals prepared by MOI-modified P1, P2 and P3 particles, respectively. Observations were performed using an Ar laser of 458 nm wavelength and a $\times 63$ objective in reflection mode. The distance of the focal plane from the inside of the coverslip was $\sim 20 \mu\text{m}$. The diameter of the SiP core is 130 nm. The mean nearest-neighbor center-to-center distances in the images of a, b, and c are 280, 530, and 710 nm, respectively.

presence of a fluorescence dye (rhodamine)-labeled, vinyl-group-carrying copolymer. For the experiment, BPE-modified, NBD-labeled SiPs with an average diameter of 680 nm were subjected

to SI-ATRP to synthesize hybrid particles grafted with a block copolymer of type P(MMA-*co*-HEMA)-*b*-PMMA. In the block polymerization process, the M_n and M_w/M_n of the PMMA free polymer obtained in the first polymerization were 301,300 and 1.19, respectively, and those of the P(MMA-*co*-HEMA) free polymer produced in the second polymerization were 22,000 and 1.15, respectively. A rhodamine-labeled, vinyl-group-carrying free copolymer was also synthesized, as described in the Experimental Section, and its M_n and M_w/M_n were 200,700 and 1.26, respectively, and the content of the vinyl group was 5 mol%. A colloidal crystal was prepared using the NBD-labeled hybrid particles of 22 vol% in the presence of 1 wt% of the rhodamine-labeled copolymer in a mixed solvent of 1,2-dichloroethane/chloroform/*o*-dichlorobenzene (57/14/29 volume ratio); it was then immobilized in a similar way as the one described above. The sample was observed by CLSM in fluorescence mode by sequential lateral scanning using Ar (488 nm) and He-Ne lasers (543 nm).

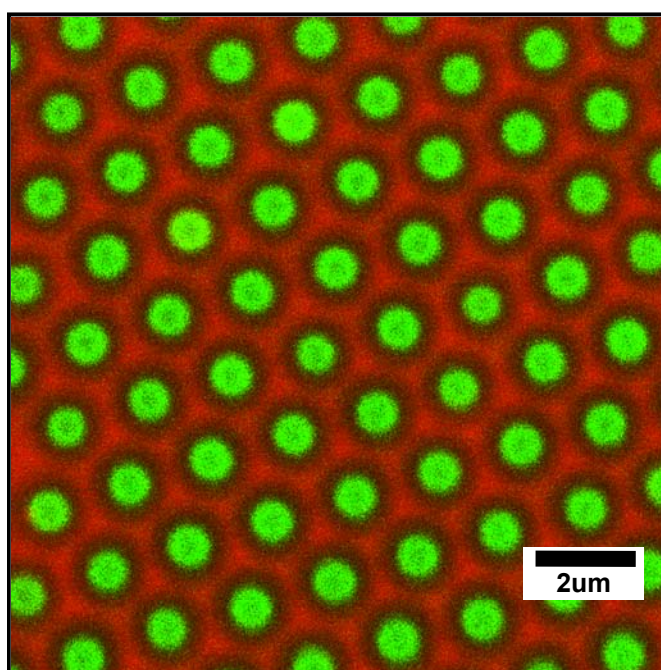


Figure 3-4. A confocal laser scanning microscopic image of immobilized colloidal crystals formed by NBD-labeled hybrid particles in the presence of rhodamine-labeled free copolymer. The image was constructed by merging two images obtained by sequentially laterally scanning the crystal using an argon-ion laser (488 nm) and a helium-neon laser (543 nm) with a $\times 63$ objective in fluorescence mode. Average diameter of the SiP core was 680 nm.

Figure 3-4 shows the merged image obtained by the CLSM measurement for the immobilized colloidal crystal using two different lasers. The red and green colors were assigned to the fluorescence emitted by rhodamine molecules of the free copolymer and NBD molecules of the SiP core, respectively. The hexagonally ordered structure of the SiP cores indicated the successful immobilization of the colloidal crystal. It is also noteworthy that the red colors only exist in the interstitial space among the hybrid particles composed of the green SiP core and black (non-labeled) polymer brush layer. This strongly suggests that the vinyl-group-carrying free copolymer is present in the interstitial space among the hybrid particles without completely mixing the polymer brush layer owing to the size-exclusion effect of the polymer brush. It also aids crystal immobilization by forming cross-linkages among the free copolymer molecules and, to some extent, between the copolymers and the vinyl-group-containing second block of the polymer brush on the SiP core. This phenomenon forms a part of novel strategy for immobilizing the semi-soft colloidal crystals.

3-4. Conclusions

Semi-soft colloidal crystals prepared by polymer-brush-afforded silica particles were successfully immobilized with almost no change in the crystal structure before and after the immobilization. The key for the immobilization is believed to be the precision design of the polymer brush structure with vinyl-group-carrying blocks of appropriate chain length and the addition of vinyl group-carrying free copolymer with appropriate vinyl group content and molecular weight. The CLSM measurement with a fluorescence-labeled system proved the validity of novel strategy for crystal immobilization with the above-mentioned molecular design. The success of immobilization will further broaden the applicability of semi-soft colloidal crystals by also considering the versatility and controllability of LRP, which can allow for the construction of a range of colloidal crystals with various functionalities.

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Chapter 4

Fabrication of Semisoft Colloidal Crystals in Ionic Liquid

4-1. Introduction

As mentioned in Chapter 3, the three-dimensional periodic structure of colloidal crystal imitates that of natural opal, inducing Bragg-diffraction effects of visible light, which presents interesting applications in photonic material, optical filter, sensor, non-bleachable color material etc. However, colloidal crystals are mainly formed in liquid media with a fragile structure which is easily affected by the evaporation of solvent and vibration. To broaden the applicability of colloidal crystals, it is important to precisely control the concentration of colloidal crystal. Namely, the non-volatile solvent is expected for the formation of a concentration-stable colloidal crystal. Ionic liquid has attracted much attention for their special properties such as non-volatility, excellent thermal stability, non flammability, etc. Because of such unique properties, ionic liquid has been well utilized as solvent, catalyst and so on.¹⁻¹⁰ Watanabe et al. developed colloidal glass arrays using an ionic liquid as the solvent.¹¹ For the semisoft colloidal crystal, the interparticle potential is exerted by the steric or excluded-volume interaction between the highly extended concentrated polymer brushes, and thus the lattice and other parameters of the colloidal crystals are widely and easily controlled by manipulating the properties of core, brush, and solvent.

In this work, the author tries to fabricate a *semisoft* colloidal crystal in an ionic liquid with similar hybrid particles, as described in previous chapters, with a silica core (diameter 130 nm) and a shell of concentrated poly(methyl methacrylate) brushes. The difference between colloidal crystals formed in an ionic liquid and an organic solvent is also discussed. At last, the author also tries to immobilize the colloidal crystal in an ionic liquid by the technique developed in Chapter 3.

4-2. Experimental Section

4-2-1. Materials

Ethyl bromoisobutyrate (2-(EiB)Br, 98%) were obtained from Tokyo Chemical Industry, Tokyo, Japan. 4,4'-Dinonyl-2,2'-bipyridine (dNbipy, 97%), copper(I) chloride (Cu(I)Cl, 99.9%), dibutyl(IV) dilaurate (DBTDL, 90%), hydroquinone monomethyl ether (MEHQ, 99%), anhydrous methyl ethyl ketone (MEK, 99%), Irgacure 907, methanol (MeOH, 99.5%) were purchased from Wako Pure Chemicals, Osaka, Japan. Methyl methacrylate (MMA, 99%) and hydroxyethyl methacrylate (HEMA, extra pure reagent), 1,2-dichloroethane (99.5%), chlorobenzene (99%), and *o*-dichlorobenzene (99%) were obtained from Nacalai Tesque Inc., Osaka, Japan, and MMA was purified by flash chromatography over activated neutral alumina. Silica particle SiP (SEAHOSTER KE-E10, 20 wt% suspension of SiP in ethylene glycol) was obtained from Nippon Shokubai Co., Ltd., Osaka, Japan. The mean diameter of the SiP was 130 nm with a relative standard deviation of 10%, as measure by transmission electron microscopy. 2-Isocyanatoethyl methacrylate (MOI) was kindly donated by Showa Denko K.K., Co., Ltd., Tokyo, Japan. The hybrid particles (PMMA-SiP) were synthesized by surface-initiated atom transfer radical polymerization of MMA, as mentioned in Chapters 3. The characteristics of PMMA-SiPs used in this work are summarized in Table 4-1.

N,N-Diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMI-TFSI), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄), 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (HMI-TFSI) and 1-hexyl-3-methylimidazolium tetrafluoroborate (HMI-BF₄) were bought from Toyo Gosei Co., Ltd., Osaka, Japan. All other reagents were used as received from commercial sources.

4-2-2. Selection of Ionic Liquid for PMMA-SiP Suspensions

The 0.05 g of unbound (free) polymer PMMA ($M_n = 36,000$ $M_w/M_n = 1.13$) synthesized by ATRP was added into mixtures of acetone (1 g) and different kinds of ionic liquids (0.15 g) in sample tubes. Subsequently, the tubes were put in oven thermostated at 60 °C for 6 hours. After acetone was evaporated off, the transparency of the samples was observed.

4-2-3. Preparation of PMMA-SiP Suspensions for Colloidal Crystal Formation

A stepwise process was adapted here for preparing PMMA-SiP suspension in an ionic liquid. Firstly, PMMA-SiPs were dispersed in mixed solvents matched both in refractive index n and density ρ . Typically, the sample P1 (see Table 4-1) was dispersed in a mixture of 1,2-dibromoethane/chloroform/*o*-dichlorobenzene of volume composition 3/86/11. Similarly, other samples were also prepared in solvent mixtures with different refractive index n and density ρ matching with those of hybrid particles. Secondly, the concentration of PMMA-SiP suspensions were estimated after colloidal crystals formed, and solvent mixtures were exchanged to an ionic liquid with the same volume fraction by an evaporation process. The volume fraction of each PMMA-SiP suspension was shown in Table 4-1.

Table 4-1. Characteristics of Silica Particles Grafted with Concentrated PMMA Brushes^a

Sample code	M_n^b	M_w/M_n^c	graft density (chains/nm ²)	n^d	ρ^e (g/mL)	volume fraction ^f (%)
P1	35,000	1.15	0.39	1.46	1.59	15.9
P2	32,500	1.13	0.40	1.46	1.58	16.7
P3	20,500	1.24	0.33	1.45	1.69	18.1
P4	6,600	1.27	0.32	1.44	1.82	33.0
P5	24,500	1.18	0.48	1.46	1.60	20.9
P6 ^g	---	---	---	1.46	1.56	23.5

^a The diameter of the silica particle core was 130 nm. ^b Weight-average molecular weight of PMMA grafts. ^c Polydispersity index (PDI) of PMMA grafts. ^d Refractive index and ^e density of PMMA-SiPs were calculated by knowing the weight fraction of PMMA in the hybrid particle and literature values of refractive index n and density ρ of PMMA and SiP in the bulk. ^f Volume fraction of *semisoft* colloidal crystal estimated from PMMA-SiP suspension in solvent mixture. ^g PMMA-SiP previously reported with a SiP core (diameter of 130 nm) and a shell of block copolymer with a first layer of PMMA ($M_n = 23,000$ $M_w/M_n = 1.17$) and second layer of P(MMA-*co*-HEMA) ($M_n = 14,900$ $M_w/M_n = 1.28$).

4-2-4. Immobilization of *Semisoft* Colloidal Crystal in Ionic Liquid

The hybrid particles of the sample P6 was subjected into an ionic liquid at the volume fraction of crystallization in the solvent mixture. (see Table 4-1) Subsequently, 0.3 wt% of vinyl-group-holding free polymer ($M_n = 200,000$, $M_w/M_n = 1.25$) was added in the suspension in an

ionic liquid. The system was allowed to stand at room temperature for 1 h for the formation of colloidal crystal. The suspension was poured into the NMR tube which had been previously subjected with Irgacure 907 as previous reported. The system was allowed to stand in dark for the formation of colloidal crystal and subsequently irradiated under UV light ($>300\text{nm}$) for 3 h.

4-2-5. CLSM Measurement of PMMA-SiP Suspensions

A PMMA-SiP suspension was put into a glass cell (0.8 cm in diameter and 1.5 cm in height) whose bottom was sealed with a coverslip. Observation was made on an inverted type CLSM (LSM 5 PASCAL, Carl Zeiss, Germany) with a 458nm-wavelength Ar laser and $\times 63$ objective (Plan Apochromat, Carl Zeiss) in reflection mode.

4-2-4. UV-VIS Spectroscopic Observations of PMMA-SiP Suspensions

A PMMA-SiP suspension in an ionic liquid was sandwiched between a pair of slide glasses with a silicon spacer (thickness: $100\ \mu\text{m}$). A square hole (length: 1 cm, width: 1 cm) in the center of silicon spacer was prepared for the suspension. The cell with the sandwich structure was fixed by two clips on two sides. After setup for 1 h, the suspension in the cell was measured by a UV-VIS spectrometer (UV-3600, Shimadzu, Japan) with the wavelength range from 350 nm to 800 nm.

4-3. Results and Discussion

4-3-1. A Proper Ionic Liquid for PMMA-SiP

As the excellent dispersibility of hybrid particles in good solvents for PMMA had been reported, the author utilized a free PMMA for evaluating the solubility of hybrid particles in ionic liquids. The solubility of PMMA in different ionic liquids was summarized in Table 4-2. BMI-TFSI shows a relatively low viscosity and a good solubility for PMMA as shown in Table 4-2. DEME-TFSI was previously reported by Nomura et al. to give a good solubility for PMMA.¹³ Thus, these two ionic liquids will be tried as the solvent for crystallization below.

Table 4-2. Information about Viscosity and Solubility of Ionic liquids.

cationic groups	1-ethyl-3-methylimidazolium salts (EMI)		1-butyl-3-methylimidazolium salts (BMI)		1-hexyl-3-methylimidazolium salts (HMI)	
anionic groups	BF ₄	(CF ₃ SO ₂) ₂ N	BF ₄	(CF ₃ SO ₂) ₂ N	BF ₄	(CF ₃ SO ₂) ₂ N
Viscosity (mPa·s 25 °C)	35	30	100	45	240	70
Solubility for PMMA	×	×	---	○	---	---

×means negative, ○means positive.

4-3-2. Preparation of PMMA-SiPs Suspensions for Colloidal Crystal Formation

Figure 4-1 shows the photograph of a P1 (see Table 4-1) suspension in the ionic liquid of BMI-TFSI illuminated from behind by the white light. The sample P1 has the number-average molecular weight M_n of the PMMA grafts of 35,000, $M_w/M_n = 1.15$, a surface density as high as

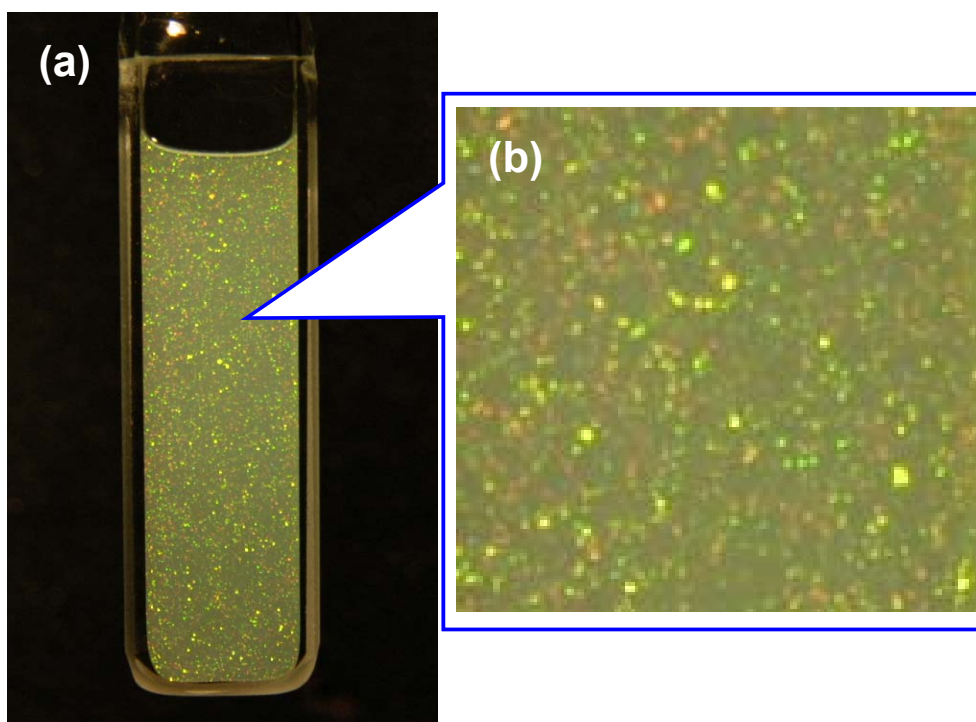


Figure 4-1. Photographs of P1 suspension in the solvent of Ionic liquid (BMI-TFSI) illuminated from behind by white light. The number-average molecular weight of the PMMA grafts is 35,000, and the diameter of the SiP core is 130nm. (a) is photograph of the suspension of colloidal crystal in the Pyrex cell. (b) Close-up of (a).

0.39 chains/nm². The P1 suspension with a volume fraction of 15.9 % was allowed to stand at ambient temperature. Tiny iridescent flecks were observed few hours after the onset of experiment,

indicating the formation of Bragg-reflecting crystallites. As shown in Figure 4-1, the formed crystallites of 0.1-1 mm in size are visible and filled the whole volume of the suspension with crystallites showing different colors depending on their orientations. All the samples showed in Table 4-1 successfully formed colloidal crystals in the suspension of both DEME-TFSI and BMI-TFSI.

4-3-3. CLSM Observations

The crystalline phase of the sample P1 was in-situ observed by CLSM. Figure 4-2 shows a CLSM image of a two-dimensional slice of the sample at the melting concentration. The SiP cores of the hybrid particles are visible as bright dots forming a two-dimensional hexagonal array, while the PMMA brush layers are hardly visible because of their much lower reflectivity. A high degree of positional order of the SiP cores and a constant interparticle distance were observed in the

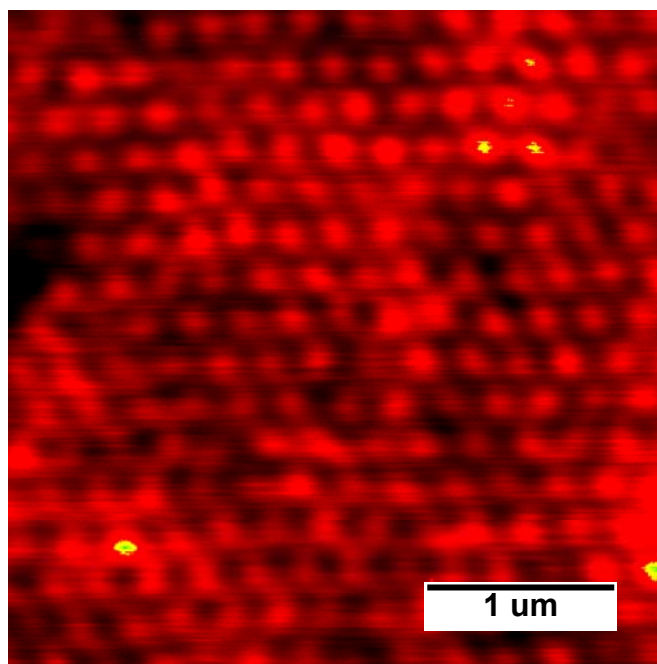


Figure 4-2. Confocal laser scanning microscopic image of colloidal crystal in P1 suspension. An observation was performed using an Ar laser of 488 nm wavelength and $\times 63$ objective in reflection mode. The diameter of SiP core is 130 nm. The number-average molecular weight of PMMA graft is 35,000, and the mean nearest-neighbor interparticle distances is 290 nm.

image. The mean nearest-neighbor center-to-center distance D_{dis} in Figure 4-2 was measured to be 290 nm. The distance D_{dis} can also be estimated from the melting concentration ϕ_m of the crystal, according to the relation reported by the previous research.¹² This value $D_{\text{dis,cal}}$ is 272 nm for P1,

which is in reasonable agreement with the CLSM value. The value of D_{dis} measured under CLSM is larger than the diameter of 260 nm for the “compact core-shell model”, which reported as our group’s previous work, and is as large as about 88% of the diameter of 331 nm (calculated from the M_n value of 35,000) for the “fully stretched core-shell model”. This means that the PMMA shell is not compact but largely extends in the radial direction in each crystallite. The result also revealed that the ionic liquid used as the solvent for the formation of the *semisoft* colloidal crystal has the similar effect solvent mixture for PMMA-SiP suspension previously reported by us. A low contrast of CLSM image shown in Figure 4-2 was reasonably ascribed to BMI-TFSI with a different refractive index as compared to PMMA-SiP as well as the interparticle distance not high enough for the resolution of the microscope.

4-3-4. UV-VIS Spectrometer

In this work, a UV-VIS spectrometer was utilized to confirm the colloidal crystalline phase formed in an ionic liquid. The samples P1 to P4 were put into cells and subjected to the UV-VIS spectroscopic measurement. Thus obtained spectra were shown in Figure 4-3. According to the Bragg’s law, the position of bandgap can be estimated from the interparticle distanced according to the following Eq. (1) and (2) for the closed-packed structure.¹⁶

$$(1) \quad d = \left(\frac{2}{3}\right)^{1/2} D$$

$$(2) \quad \lambda = 2nd \sin \theta$$

where n is the refractive index of whole system, λ is the wavelength, and θ is the angle between the incident and scattering planes. As shown in Figure 4-2, the sample P1 has the distance D_{dis} of 290 nm, the λ value was calculated to 700 nm, which showed a good agreement with the UV-VIS spectrum in Figure 4-3. This revealed the validity of D_{dis} locally measured in CLSM and proved that the colloidal crystal was homogeneously formed BMI-TFSI. In Figure 4-3, the peaks are shifted to a short wavelength with a decrease of molecular weight, indicating that the thickness of polymer layer determines the interparticle distance in colloidal crystal. Namely, SI-ATRP is also an effective

method to control the structure of colloidal crystal and the photonic band-gap as well.

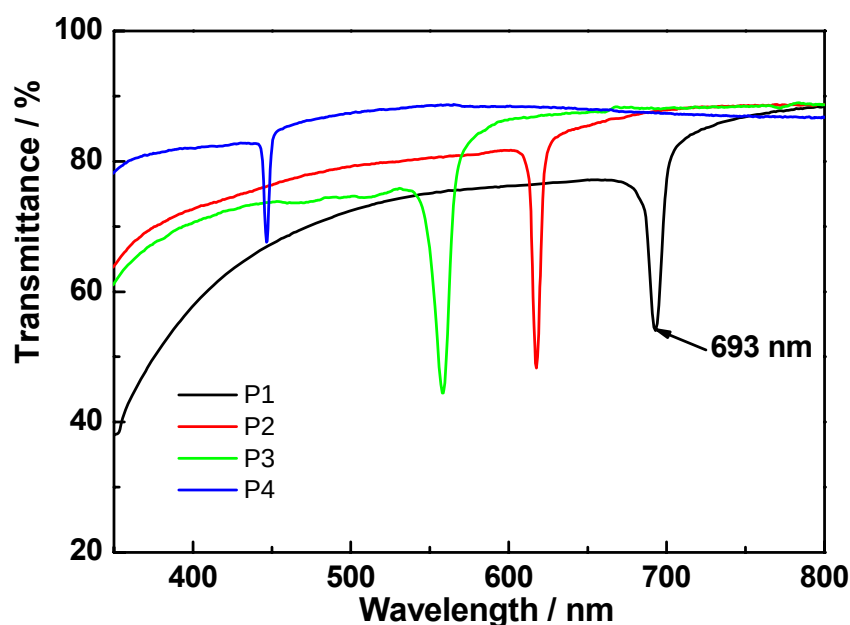


Figure 4-3. UV-VIS spectra of PMMA-SiP suspensions. Measurements were carried out from the wavelength of 800nm to 350nm. The black line shows the spectrum of suspension of P1 with number-average molecular weight of the graft polymer of 35,000. The red line shows the spectrum of suspension of P2 with number-average molecular weight of the graft polymer of 32,500. The green line shows the spectrum of suspension of P3 with number-average molecular weight of the graft polymer of 20,500. The blue line shows the spectrum of suspension of P4 with number-average molecular weight of the graft polymer of 6,600.

4-3-5. Phase Diagram

Suspensions of the sample P5 ($M_n=24,500$, $M_w/M_n = 1.18$) in ionic liquid of BMI-TFSI with different volume fractions ($\phi = 0.229-0.251$) were placed in Pyrex-glass cells ($10 \times 1 \times 40$ mm) allowed to stand in oil bath thermostated at 50 °C for 2 months without sealing the cell for the formation of colloidal crystal as the stability of concentration of PMMA-SiP suspension in non-volatile ionic liquid of BMI-TFSI. Figure 4-4 shows the photographs of the series of samples illuminated from behind by the white light. The number shown in Figure 4-4 represents the sample code (for the ϕ value, see the figure caption). In the sample 5 with the lowest concentration examined, the entire body of the suspension remained slightly turbid due to the Tyndall scattering. The sample 1 with the highest particle concentration exhibited heterogeneously iridescent colors within an hour after the sample setting, which hardly changed throughout the experimental period

of 2 months. In the samples 1-4 with intermediate concentrations, tiny iridescent flecks were observed soon after the onset of experiment, indicating the formation of Bragg-reflecting crystallites. In the sample 1, the formed crystallites filled the whole volume of the suspension without sedimentation even for 2 months. In the samples 2-4, as time elapsed, the crystallites precipitated under the effect of gravity, the similarly to the sedimentation of crystallites in solvent mixture. The boundary between the iridescent-colored sediment (crystalline phase) and the slightly turbid supernatant (fluid phase) became more and more clear, over two months, finally giving a

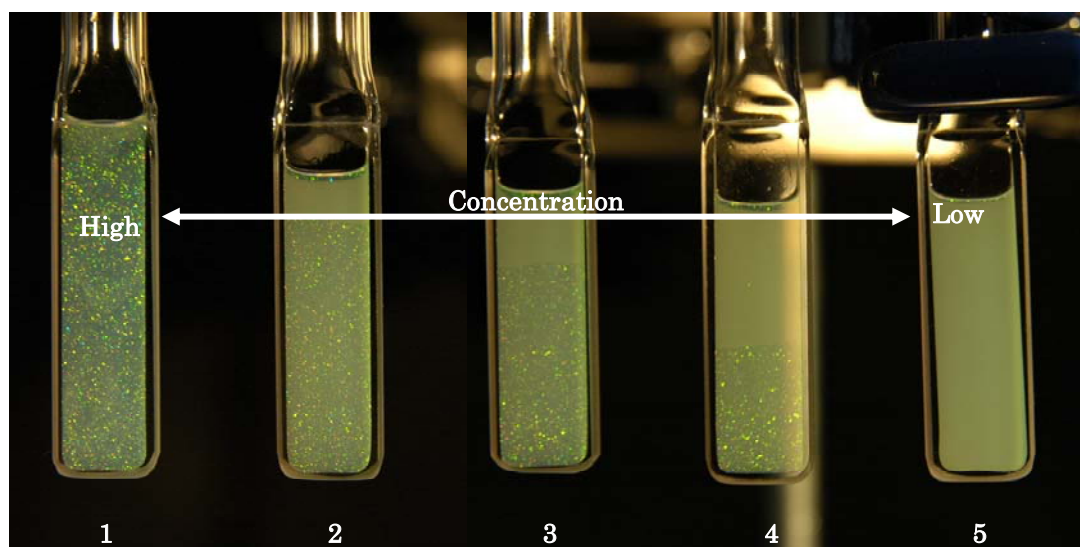


Figure 4-4. Photographs of the sample P5 suspensions in ionic liquid illuminated from behind by white light, 2 months after sample preparation. The number-average molecular weight of the PMMA grafts is 24,500, and the diameter of the SiP core is 130nm. (a) Samples with different PMMA-SiP volume fractions ϕ . The ϕ value decreases from 0.251 (leftmost) to 0.229 (rightmost). In samples 2-4, Bragg-diffracting crystalline and (random) fluid phases coexist, with the volume fraction of crystalline phase decreasing with decreasing ϕ .

sharp horizontal boundary line. This spontaneous phase separation can be interpreted by the idea of the Kirkwood-Alder transition.^{14,15} The sedimentation of the crystalline phase occurred because the average density of the hybrid particle was set slightly larger than that ($\rho_{\text{BMI-TFSI}}$: 1.44 g/mL) of the BMI-TFSI (see Table 4-1). Upon tumbling the cell, the iridescent colors of the samples 1–4 instantaneously disappeared, and upon standing, they readily appeared again in almost the same way as before. This result is very similar to the phase separation of the *semisoft* colloidal crystal in solvent mixture, indicating that BMI-TFSI is a solvent playing a similar role as solvent mixture for

the *semisoft* colloidal crystal with providing a non-volatile (concentration stable) system.

The phase diagram of the volume fraction of crystal as a function of the particle volume fraction of PMMA-SiP suspension in the ionic liquid was also discussed in this work, as shown in Figure 4-5. In the coexistent region of the fluid and crystalline phases, the plot shows a linear relationship similarly to the colloidal crystals in solvent mixture. By extrapolating it to 0% and 100% in volume fraction of crystal, the author determined the freezing and melting volume

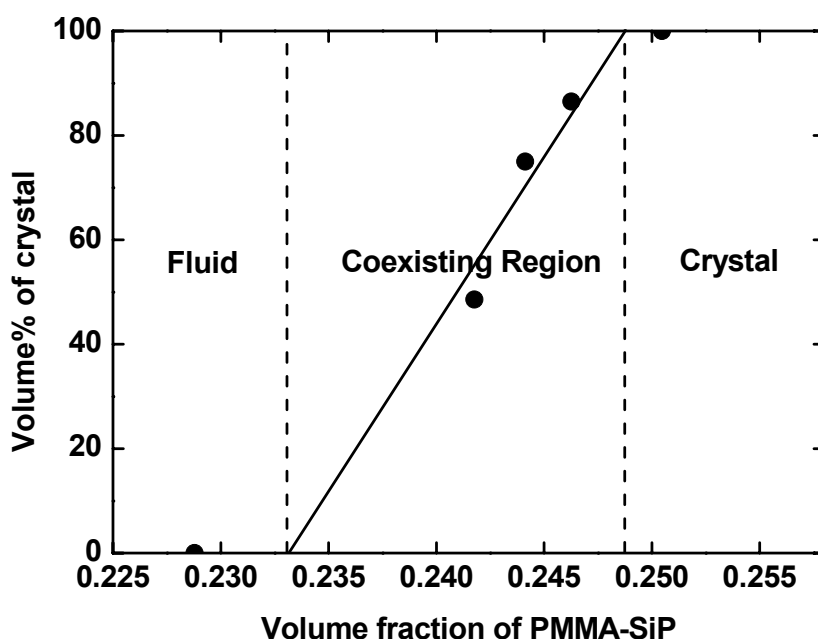


Figure 4-5. Phase diagram showing the volume fraction of crystal as a function of the particle volume fraction of the sample P5 suspension (data from Figure 4-4). By extrapolating the linear line observed for the coexisting region to 0% and 100% crystal, the freezing (ϕ_f) and melting (ϕ_m) volume fractions of the crystal were determined to be 0.233 and 0.249, respectively.

fractions, ϕ_f and ϕ_m , to be 0.233 and 0.249, respectively. It should be noted that as the reference, the ϕ_f and ϕ_m values are 0.494 and 0.545 for hard colloidal crystal system, respectively, and on the order of 0.01, which increases with increasing ionic strength for soft colloidal crystal systems.^{14, 17, 18} The crystals formed in ionic liquids showed a similar result as the *semisoft* colloidal crystal as previously reported,¹² also suggesting the formation of the *semisoft* colloidal crystal

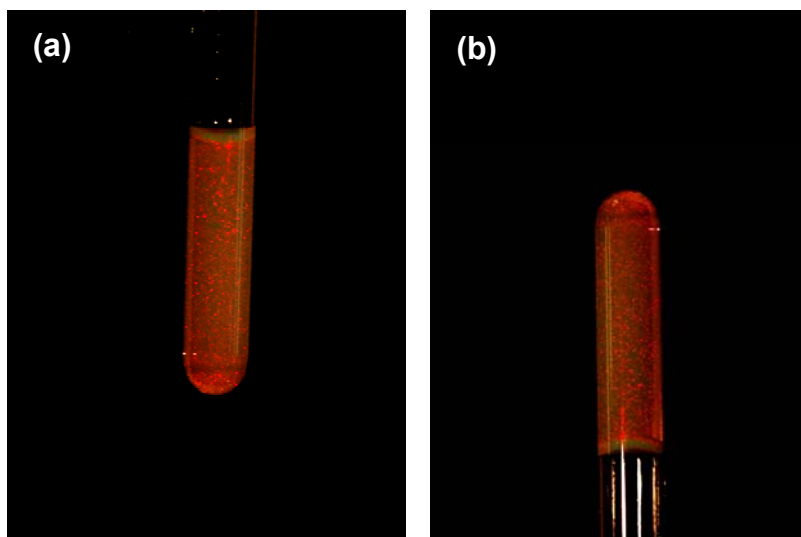


Figure 4-6. Photographs of *semisoft* colloidal crystals in DEME-TFSI in NMR tube illuminated from behind by white light. a. The picture of *semisoft* colloidal crystal before UV irradiation. b. The picture of *semisoft* colloidal crystal after UV irradiation in which tube was upturned. Tiny iridescent flecks were observed in the tube of colloidal crystals.

4-3-6. Immobilized *Semisoft* Colloidal Crystal in Ionic Liquid

The sample P6 had been successfully immobilized in solvent mixture as reported Chapter 3. The volume fraction of suspension of P6 was adjusted to 23.5% in DEME-TFSI and allowed to stand at ambient temperature in the presence of 0.3 wt% of vinyl-group-carrying copolymer. As shown in Figure 4-6a, tiny iridescent flecks were observed several minutes after the onset of the experiment, indicating the formation of Bragg-reflecting crystallites, and the formed crystallites filled the whole volume of the suspension. Figure 4-6b shows a picture of the immobilized colloidal crystal in NMR tube. The suspension was turned into a solidlike material well fixed even when the tube was upturned, while microcrystalline phases showing iridescent colors were still observed. The same result was also obtained as using BMI-TFSI for the immobilization of colloidal crystal.

4-4. Conclusions

Monodisperse SiP grafted with a concentrated-PMMA-brush layer and suspended in ionic liquids, i.e., BMI-TFSI and DEME-TFSI, forming a colloidal crystal in a certain concentration range. It was confirmed that the driving force of crystallization in this system is also a long-range repulsive (noninterpenetrating) interaction between the highly swollen concentrated polymer brush

layers similarly to that of the previously known *semisoft* colloidal crystal. With exchanging the solvent of the *semisoft* colloidal crystals with ionic liquids, the main advantage over the previously reported crystal is the applicability to keep the ordered structure without sealing. The colloidal crystals in ionic liquid are flowable and applicable for any shapes of spacers. Furthermore, thanks to the controllability of polymer brushes grafted, the colloidal crystal was successfully immobilized with irradiation of UV light. Thus, the author made the gel of the *semisoft* colloidal crystal with any shapes, broadening its applicability for photonic materials.

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Chapter 5

Fabrication of Liquid Crystal with Polymer-brush-afforded Iron Oxide Rods

5-1. Introduction

As mentioned in previous Chapters, surface-initiated LRP gathered much attention in this decade for its ability to precisely control the molecular weight and polydispersity of graft polymers and to afford an exceptionally high graft density with robustness and versatility of LRP retained. This technique has been rapidly applied on many surfaces of materials, such as flat substrates,¹⁻⁹ particles,¹⁰⁻¹⁹ porous structures,²⁰⁻²¹ other inorganic materials with different shape²²⁻²⁷ and organic polymer materials²⁸⁻³³. Strategies have been well developed to tailor the surface of rigid spherical particle with polymers by surface-initiated LRP.^{10,12,13} SI-ATRP has been well developed by Tsujii's group, grafting well-defined polymer brushes on monodisperse silica particle cores of diameters ranging from micrometer- to nanometer-scale. The perfect dispersibility of these hybrid particles allowed us to construct, a *semisoft* colloidal crystal, a new type of colloidal crystals in which the driving force of crystallization is the excluded-volume interactions between polymer chains densely grafted on spherical particles. The formation of the *semisoft* colloidal crystal has greatly broadened the applicability of SiPs as realizing a directly use of nanoparticles in macroscopic world. In fact, for the successful use of nanometer-scale objects in real, macroscopic assemblies such as a colloidal crystal and a liquid crystal of them are required. Therefore, after the success for fabricating *semisoft* colloidal crystals with spherical hybrid particles, the assembly of liquid crystal also attracted much interest for their additional benefit of allowing the orientation of nanometer-scale objects. Furthermore, the great capability of SI-ATRP for surface modification on different materials has encouraged us to synthesize hybrid nanometer-scale rods by SI-ATRP for the formation of liquid crystalline phases (LC phases).

The formation of LC phases is experimentally and theoretically well investigated for

rigid-rod objects such as V_2O_5 ribbons, tobacco mosaic viruses, and metal oxide nanorods.²⁵⁻²⁸ However, these systems are restricted to the concentration and solvent condition. To overcome such restrictions, the surface modification by polymers is one of the most effective methods. Polymeric surfactants have been well utilized since Lekkerkerker et al. reported the formation of LC phases employing an amine-functionalized polyisobutylene to sterically stabilize boehmite rod-like particles.²⁹ Zentel et al. functionalized semiconducting nanorods like TiO_2 , ZnO , SnO_2 and $CdTe$ with dopamine-functionalized diblock copolymers on surface and fabricated LC phases in organic solvent.³⁹ Abécassis et al. formed LC phases in aqueous suspension with $GdPO_4$ rodlike nanoparticles (nanorods) with a bisphosphonate-PEG-functionalized surface.⁴⁰ Müller et al. fabricated a bottle brush with stimuli responsibility by LRP, which was utilized as a template for synthesizing an organo-silica hybrid nanowire for lyotropic liquid crystalline phases (LC phases) in aqueous solution.⁴¹ In all of the previous reports, polymers grafted on nanorods simply played a role as surfactants for stabilizing nanorods in solvents or polymers while a dominant effect on the formation of LC phases. In this work, using SI-ATRP to supply a surface with densely grafted polymers, LC phases are attempted to be designed by the effect from graft polymers similarly to the story of fabricating a *semisoft* colloidal crystal.

In this work, rigid nanorods of $\alpha\text{-Fe}_2\text{O}_3$ ($\alpha\text{-Fe}_2\text{O}_3$ nanorods, average length of 600 nm and aspect ratio (length/width) of 6) were chosen and subjected to the SI-ATRP of MMA. The author will describe how $\alpha\text{-Fe}_2\text{O}_3$ nanorods are decorated by the ATRP initiator and subsequently by polymer brushes with high surface densities and retain good dispersibility in solvents. The author will also describe the fabrication of hollow hybrid nanorods using $\alpha\text{-Fe}_2\text{O}_3$ nanorods as a model. The formation of LC phases will be investigated by observing the suspensions of hollow hybrid nanorods by polarized-light microscopy. At last, a polymer brush afforded on hybrid nanorods will be discussed on its role for the formation of LC phases.

5-2. Experimental Section

5-2-1. Materials

Ethyl bromoisobutyrate (2-(EiB)Br, 98%) were obtained from Tokyo Chemical Industry, Tokyo, Japan. 4,4'-Dinonyl-2,2'-bipyridine (dNbipy, 97%), copper(I) chloride (Cu(I)Cl, 99.9%), iron(III) chloride hexahydrate (FeCl₃·6H₂O, 99.0%) and potassium dihydrogenphosphate (KH₂PO₄, 99.5%) were purchased from Wako Pure Chemicals. Methyl methacrylate (MMA, 99%), PVP-K30 ((C₆H₉NO)_n molecular weight av. 40,000) were obtained from Nacalai Tesque Inc., Osaka, Japan, and MMA was purified by flash chromatography over activated neutral alumina. Tetraethoxysilane (TEOS, 99.9%) were obtained from Chisso Corp., Tokyo, Japan. (2-Bromo-2-methyl)propionyloxypropyl triethoxysilane (BPE) was synthesized following the process in Chapter 2. Water was purified by a Milli-Q system (Nihon Millipore Ltd., Tokyo, Japan) to a specific resistivity of ca. 18MΩ-cm. All other reagents were used as received from commercial sources.

5-2-2. Measurements

Gel permeation chromatographic (GPC) analysis was carried out at 40 °C on a Shodex (Showa Denko K.K., Tokyo, Japan) GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-806L, exclusion limit = 2×10^7), and a differential refractometer (Shodex RI-101). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.8 mL/min. Poly(methyl methacrylate) (PMMA) standards were used to calibrate the GPC system. ¹H-NMR (300MHz) spectra were obtained on a JEOL/AL300 spectrometer. Thermal gravimetric analyses (TGA) were performed on a Shimadzu TGA-50 (Shimadzu, Kyoto, Japan) under a nitrogen atmosphere. Polarized-light microscopic observations were carried out on a digital microscope (VHX-200, KEYENCE, Osaka, Japan) with crossed polarizers. Transmission electron microscopic (TEM) observations were made on a JEOL transmission electron microscope (JEM-2100) operated at 200 kV. Scanning electron microscopic (SEM) observations were performed using a scanning electron microscope S-3400N (HITACHI,

Japan) at an accelerating voltage of 5 kV.

5-2-3. Synthesis of α -Fe₂O₃ Nanorods

A mixture of FeCl₃·6H₂O (27 g, 0.1 mol) and KH₂PO₄ (0.3 g, 2.25 mmol) in 5 L purified water was added in a round bottom flask and subsequently sealed off. The reaction was carried out in a heating mantle thermostatted at 115 °C and, after a continuously magnetic stir for 9 days, quenched to room temperature. The reaction mixture was passed through a filter paper (FILTER PAPER, ADVANTEC. No. 2: 300 mm per circle), and the filtrate was subjected to centrifugation (KUBOTA 7780, angle rotor AG-1k4, 3,000 rpm, 20 min) to recover the resultant nanorods, which were subsequently washed three times by consecutive centrifugation and redispersion in ethanol. Subsequently, the suspension of resultant nanorods in ethanol was centrifuged at a low speed of 300 rpm for 10min, and the supernatant fluid was recovered and centrifuged again at a higher speed of 2,000 rpm for 20 min. The supernatant fluid containing small size of nanorods was discarded, and the deposit was resuspended in ethanol to stock.

5-2-4. Synthesis of Silica Coated α -Fe₂O₃ Nanorods

A mixture of PVP-K30 (5 g) in ethanol (700 g) was added in a two-neck round-bottom flask equipped with a stir bar. The suspension of α -Fe₂O₃ nanorods (5 g) dispersed in ethanol (60 g) and subsequently an ammonia aqueous solution (70 g) were added sequentially under a vigorous stirring. The mixture of TEOS (3 g) in ethanol (50 g) was consecutively added into the reaction mixture in 1 h under a constant sonication. The reaction was allowed to proceed at room temperature for 1 h under sonication and another 1 h with a constant stirring. Finally, the resultant nanorods were recovered by centrifugation (6,000 rpm, 20 min) and subsequently washed three times by consecutive centrifugation and redispersion in ethanol to obtain a suspension for further usage.

5-2-5. Fixation of ATRP-Initiator on Nanorods

The α -Fe₂O₃ nanorods and the silica-coated α -Fe₂O₃ nanorods were surface-modified in a mixture of ethanol/water/ammonia with a triethoxysilane derivative (BPE) containing an

ATRP-initiating group, as previously reported.¹ Briefly, a mixture of ammonia solution (28 % NH₃ aqueous solution, 24 g) was added dropwise to the suspension of nanorods (4 g) in ethanol (400 g) under magnetically stirring. The system was allowed to stand at room temperature with a magnetic stirred for 1 h. Subsequently, BPE (2.5 g) dissolved in ethanol (97 g) was added dropwise into the system, and the reaction mixture was continuously stirred for 48 h at room temperature. Thus, surface-modified nanorods were recovered by centrifugation and consecutive washed by ethanol for three times, and solvent-exchange to DMF by repeated redispersion/centrifugation to obtain a DMF suspension for further usage.

5-2-6. Surface-Initiated ATRP on Nanorods

The suspension of the initiator-coated nanorods (α -Fe₂O₃ nanorods or the silica coated α -Fe₂O₃ nanorods) in DMF was solvent-exchanged to MMA with the aid of centrifugation. The mixture of the initiator-fixed nanorods suspension in MMA containing a prescribed concentration of 2-(EiB)Br and dNbipy was quickly added to a prepared Pyrex glass tube charged with a predetermined amount of Cu(I)Cl(solid). Three freeze-pump-thaw cycles were carried out and the tube was sealed off under vacuum. The polymerization was carried out in a shaking oil bath (TAITEC Corp., Saitama, Japan, Personal H-10) thermostated at 60 °C and, after a prescribed time t , quenched to room temperature. An aliquot of the solution was taken out for the NMR measurement to estimate the monomer conversion and for the GPC measurement to determine the molecular weight and its distribution. The rest of the reaction mixture was diluted by acetone and centrifuged to collect polymer-grafted nanorods (PMMA-rods). The cycle of centrifugation and redispersion in good solvent was repeated more than three times to obtain polymer-grafted nanorods perfectly free of the unbound (free) polymer. The resultant PMMA-rods purified after the polymerization was treated with HF to cleave the graft polymer from the surface, and the molecular weight of graft polymers was determined by GPC.

In a typical run, the bulk polymerization of MMA was carried out at 60 °C for 12 h with the starting materials of MMA (9.7 g, 97 mmol), 2-(EiB)Br (9.6 mg, 0.049 mmol), Cu(I)Cl (19 mg,

0.19 mmol), dNbipy (159 mg, 0.39 mmol), and initiator-coated α -Fe₂O₃ rods (100 mg). This gave a monomer conversion of 72%, a free polymer with $M_n = 145,000$ and $M_w/M_n = 1.15$, and a graft polymer with $M_n = 130,000$ and $M_w/M_n = 1.27$, where M_n and M_w are the number- and weight-average molecular weights, respectively, and M_w/M_n is the polydispersity index. The polymer-grafted α -Fe₂O₃ rods were purified by repeated cycles of centrifugation (8,000 rpm for 20 min) and redispersion in acetone (3×200 mL), toluene (3×200 mL) and in THF (3×200 mL). Resultant PMMA-rods were redispersed in toluene to obtain a toluene suspension to stock in fridge.

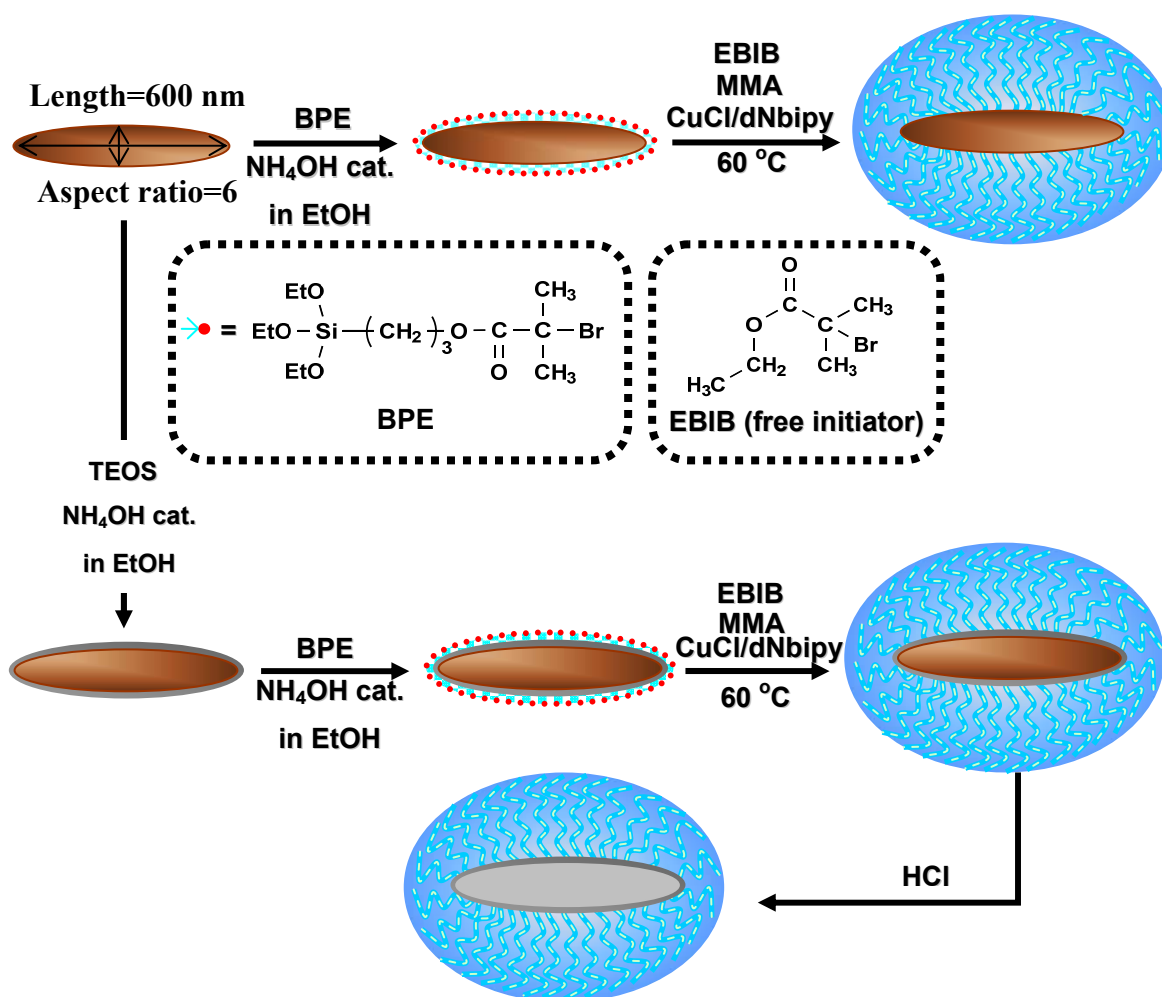
5-2-7. The Preparation of Hollow PMMA-rods

The PMMA-rods with a silica-coated α -Fe₂O₃ core-rod were solvent-exchanged to acetone to obtain a 0.75 wt% suspension in acetone (40.31 g). A 37% HCl aqueous solution (21.47 g) was added dropwise to the suspension with vigorously stirring for 3 h. The hollow PMMA-rods were recovered and purified by continuously centrifugation (8,000 rpm, 20 min) and redispersion in acetone (3×200 mL). Subsequently, hollow PMMA-rods were solvent-exchanged to toluene by centrifugation (8,000 rpm, 20 min) and redispersed in toluene by a shaker for 12 h. Finally, with a cycle of centrifugation and redispersion in toluene, a hollow PMMA-rods suspension in toluene was obtained.

5-3. Results and Discussion

5-3-1. Synthesis of Nanorods

The α -Fe₂O₃ nanorods used in this work were spindle-type colloidal hematite particles of narrow size distribution, which were synthesized by forced hydrolysis of ferric chloride solution at the temperature of 110 °C.³² After the purification, the α -Fe₂O₃ nanorod with an aspect ratio of 6 and a long axis of 600 nm was obtained. With the help of centrifugation, the density of the α -Fe₂O₃ nanorod was estimated to be 4 g/mL. On the other hand, the silica-coated α -Fe₂O₃ nanorod was obtained with an aspect ratio of 5.3 and a long axis of 630 nm as measured with TEM. The density of this nanorod was estimated to be 3.1 g/mL by the aid of centrifugation as mentioned.



Scheme 5-1. Schematic representation for the synthesis of polymer-coated α -Fe₂O₃ nanorods and polymer-coated hollowed nanorods (PMMA-rods) by immobilization of (2-bromo-2-methyl)propionyloxypropyl triethoxysilane (BPE) followed by SI-ATRP.

5-3-2. Synthesis of Initiator-Coated Nanorods

The ATRP-initiator BPE was fixed onto the α -Fe₂O₃ nanorod surface in ethanol solution with NH₃ added as an alkaline catalyst. Since BPE should have the similar chemical properties as (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane (BHE) for their similar chemical structure, the NH₃ concentration should be a key parameter in the reaction as for the system with BHE. The author optimized the final NH₃ concentration to be 1M in this work, which is the also a similar condition for the initiator BHE fixed onto silica particles. The condition also proved applicable for the surface of the silica-coated α -Fe₂O₃ nanorods, as expected for the similar silica surface. TGA was utilized to estimate the amount of initiator fixed on α -Fe₂O₃ nanorod and the silica coated

α -Fe₂O₃ nanorod. Both of them show a weight loss of about 2 wt%, indicating a surface density of about 3 initiator molecules/nm². The suspension of the initiator-coated nanorods in DMF formed no aggregation and could be stably stored in fridge without any change more than 1 year.

5-3-3. SI-ATRP on Nanorods

The initiator-fixed nanorods were subsequently used for the copper-mediated ATRP of MMA in bulk (Scheme 5-1). In practice, the polymerizations were carried out as almost the same as the process the Tsujii's group did on silica particles, in which the "sacrificial" free initiator of 2-(EiB)Br was also used for a easy control of the reaction. The polymerization proceeded on the surface of the silica-coated core-rod similarly as before. Here, the author will discuss the polymerization carried out on the surface of α -Fe₂O₃ nanorods. Figure 5-1 shows the first-order kinetic plot of monomer concentration for the polymerization of MMA in bulk with the BPE-coated α -Fe₂O₃ nanorod. The linear relationship observed in Figure 5-1 is similar to the polymerizations reported by Agarwal et al,⁴³ indicating that the concentration of the propagating radical species is constant throughout the course of polymerization. The PMMA-rods purified after the

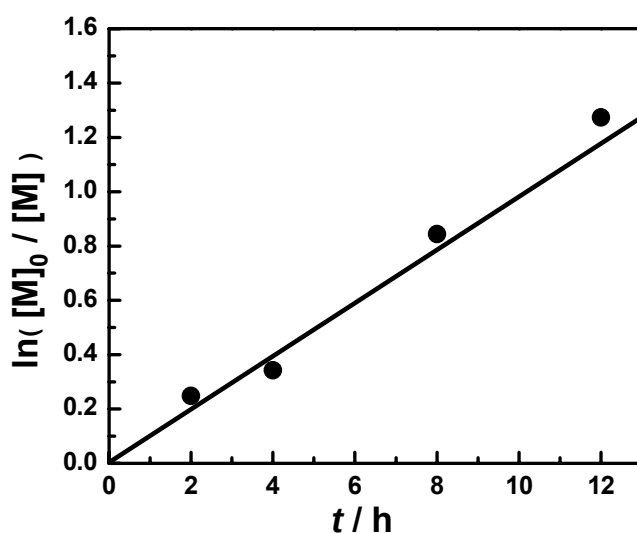


Figure 5-1. Plot of $\ln([M]_0/[M])$ vs t for the polymerization of methyl methacrylate (MMA) in bulk at 60 °C with initiator-coated α -Fe₂O₃ nanorods (1 wt%): $[MMA]_0/[ethyl\ 2-bromoisobutylate]_0/[Cu(I)Cl]_0/[4,4'-dinonyl-2,2'-bipyridine]_0 = 2000/1/4/8$.

polymerization were treated with HF to cleave the grafted polymer from the α -Fe₂O₃ nanorod

surface, and the recovered graft polymer was subjected to GPC. Figure 5-2 shows the evolution of the number-average molecular weight M_n and the polydispersity index M_w/M_n of the free and graft polymers simultaneously produced. Obviously, the M_n s of the grafted and free polymers showed good agreement with each other, both increasing in proportion to monomer conversion along the dotted line theoretically predicted as $M_{n, \text{calcd}}$. A low polydispersity M_w/M_n for most samples were also confirmed. All these results indicate that the polymerization of MMA initiated from the $\alpha\text{-Fe}_2\text{O}_3$ nanorod surface, similarly to the previous report, proceeded in a living fashion, giving the $\alpha\text{-Fe}_2\text{O}_3$ nanorods coated with a shell of well defined PMMA densely end-tethered.

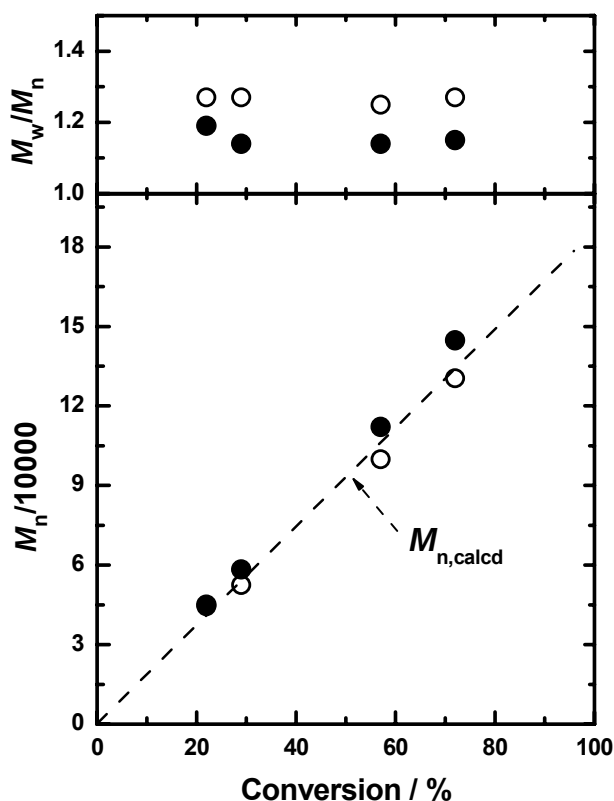


Figure 5-2. Evolution of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the graft (○) and free (●) polymers as a function of monomer conversion for the polymerization of methyl methacrylate (MMA) in bulk at 60 °C with initiator-coated $\alpha\text{-Fe}_2\text{O}_3$ nanorods (0.5 wt%): $[\text{MMA}]_0/[\text{ethyl 2-bromoisobutylate}]_0/[\text{Cu(I)Cl}]_0/[\text{4,4'-dinonyl-2,2'-bipyridine}]_0 = 2000/1/4/8$.

5-3-4. Determination of Graft Density of PMMA-Rods

In order to estimate the graft density (σ), the $\alpha\text{-Fe}_2\text{O}_3$ nanorod was well assumed to be a

prolate spheroid, as was revealed by the TEM image. TGA analysis of PMMA-rods was carried out to estimate the mass (w) of PMMA grafts on each α -Fe₂O₃ nanorod. The graft density was then calculated using Eq. (1):

$$\sigma = (w / M_n) A_v / 2\pi b^2 (1 + \frac{a}{be} \sin^{-1} e) \quad (1)$$

$$e^2 = 1 - b^2 / a^2 \quad (2)$$

where $2a$, $2b$, and e are the lengths of the semi-major and semi-minor axes and the eccentricity of the assumed spheroid, respectively, A_v is Avogadro's number. Eq. (2) shows the calculation of e from a and b . TEM observation determined the long and short axes of the nanorod to be 600 nm and 100 nm, respectively, as taken as the $2a$ and $2b$ values. TGA analysis determined the w value. As can be seen from Figure 5-3, the graft density is nearly constant independent of time and approximately equal to be as high as 0.7 chains/nm².

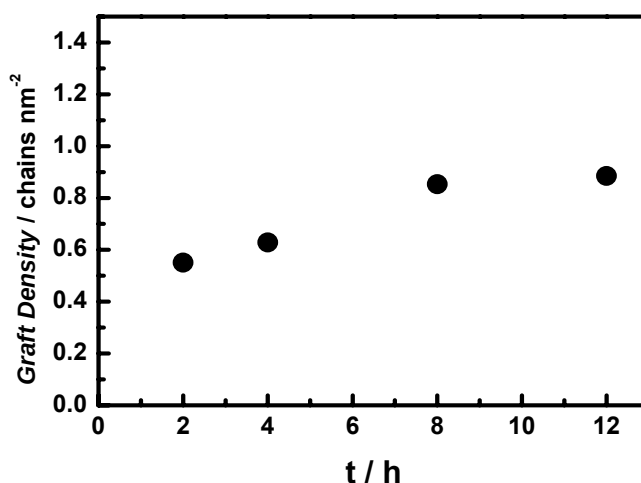


Figure 5-3. Time dependence of the graft density of poly(methyl methacrylate) grown on α -Fe₂O₃ nanorods surface.

5-3-5. Formation of PMMA-Rods Films

Two kinds of PMMA-rods film were made: one is the monolayer film prepared at the air-water interface following the procedure mentioned in Chapter 2; the other is the film prepared by casting a droplet of PMMA-rods suspension in toluene on the surface of slide glass. Figure 5-4a,b shows the TEM images of the thin films of the PMMA-rods with different molecular weights

of graft polymers, indicating that the cores of PMMA-rods observed as dark spindles were well dispersed throughout the thin film, while PMMA chains were hardly seen for their much lower electron density. More interestingly, the core-rods were more or less aligned with a constant spacing, suggesting homogeneous PMMA layer surrounded. The increase in spacing of PMMA layer with increasing molecular weight of graft chain was also confirmed in these images.

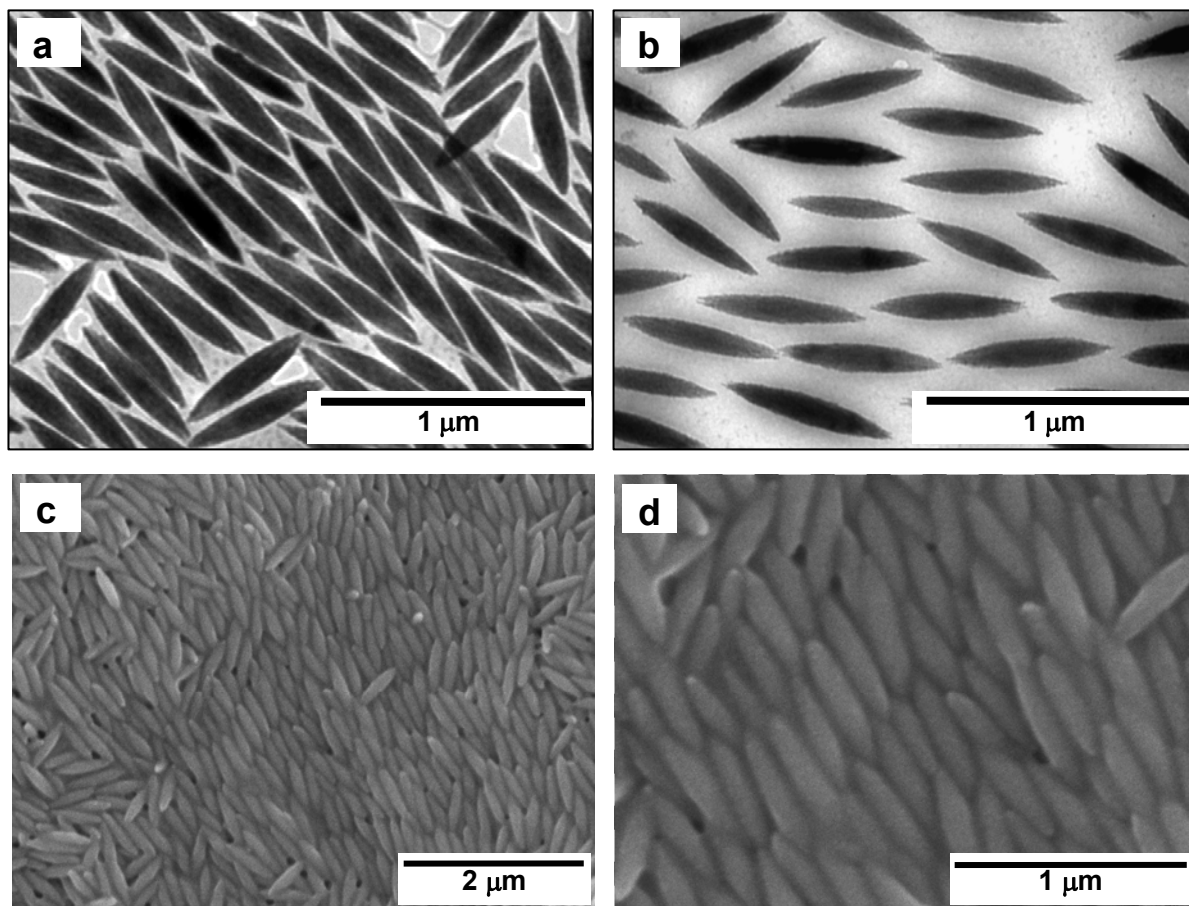


Figure 5-4. (a,b) Transmission electron microscopic (TEM) and (c,d) scanning electron microscopic (SEM) images of the films of α -Fe₂O₃ nanorods coated with poly(methyl methacrylate) brushes (PMMA-nanorods): the molecular weight of graft polymer on each nanorods is (a) 44,000, (b) 130,000, and (c, d) 44,000. (d) is the close up of (c).

The orientation of PMMA-rods was reasonably ascribed to anisotropy in shape as well as good dispersibility. The similar results were also observed under TEM for the PMMA-rods with a silica-coated core-rod. Orientational ordering (nematic ordering like in the liquid crystalline phase) was also confirmed in a cast-film formed on a slide glass as shown in Figure 5-4c,d (the SEM images). These results indicate the possibility of forming liquid crystalline phases in a good solvent

for PMMA.

5-3-6. Fabrication of Hollow PMMA-Rods

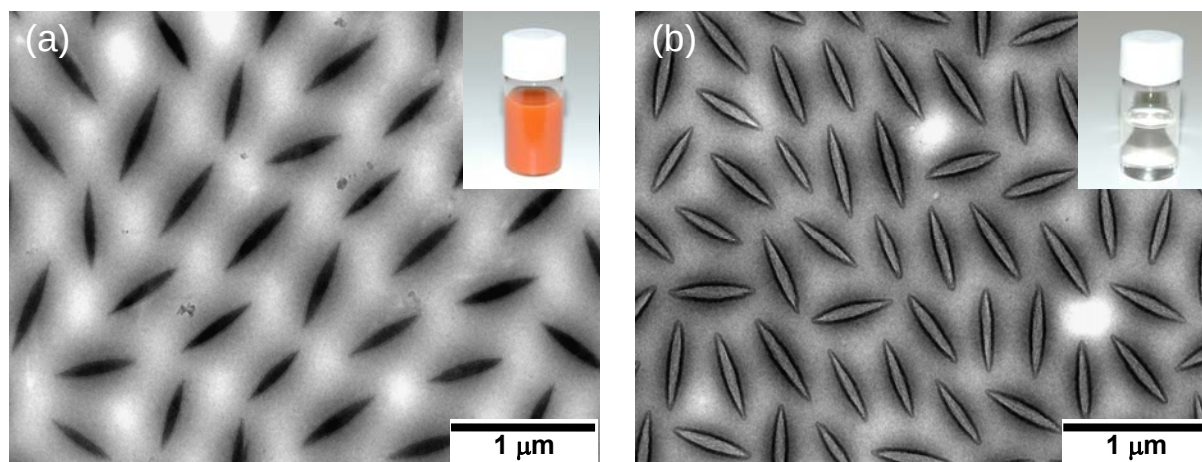


Figure 5-5. TEM images of monolayer films of PMMA-rods with the silica-coated core-rods prepared at water-air interface. (a) TEM image of PMMA-rods before HCl etching. (b) TEM image of hollow PMMA-rods after HCl etching. Insets are pictures of their suspension.

As shown in Scheme 5-1a, hollow PMMA-rod was fabricated by dissolving the α -Fe₂O₃ core from the PMMA-rods with the silica-coated core. This provided us a big advantage in transparency to observe the texture of liquid crystalline phases under polarized-light microscopy. The stöber method was successfully utilized to coat individual α -Fe₂O₃ nanorods with homogeneous silica shell of a thickness of 15 nm. After the PMMA layer was grafted from the surface of the silica shell, the α -Fe₂O₃ core were successfully etched by hydrochloride acid, giving a transparent suspension as shown in the inset of Figure 5-5b. The monolayer film of the PMMA-rods before and after etching was prepared at the air-water interface and observed by TEM (Figure 5-5c,d), revealing successful hollowing with its spindle shape unchanged.

5-3-7. Fabrication of Liquid Crystalline Phases

With increasing molecular weight, the effective graft density at the outmost surface will decrease through the crossover in graft density from the concentrated to semi-diluted polymer-brush regimes, which was already discussed for the spherical particles by Ohno et al. In addition to this, the aspect ratio of the PMMA-rods should decrease, affecting their liquid crystallinity. The author's

concern here is to design a hollow PMMA-rod with a short polymer chain and a high aspect ratio.

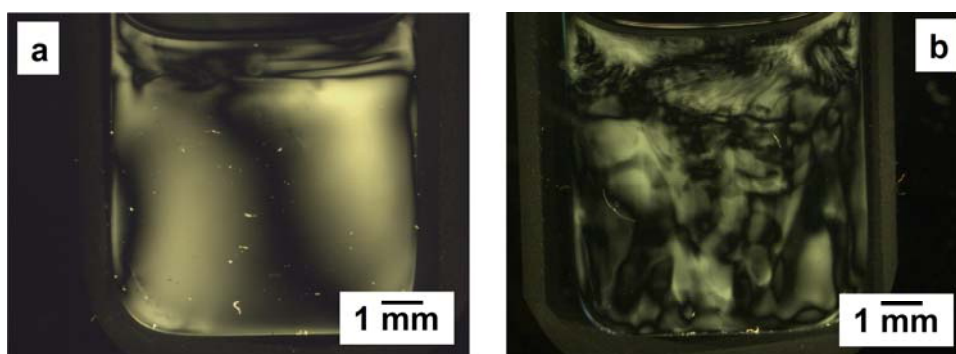


Figure 5-6. Cross-polarization images of the suspension of the hollow PMMA-rod with the graft polymer of $M_n=14,000$ in toluene observed by an optical microscope immediately (a) and (b) 12 h after injecting the suspension into the cell.

Thanks to the great controllability of SI-ATRP, the author successfully synthesized the hollow PMMA-rod with a good dispersibility in solvents and almost the same aspect ratio as silica-coated core-rods, when the graft polymer has $M_n = 14,000$. A suspension of this hollow PMMA-rod with a concentration of 25.4 wt% was prepared, poured into a Pyrex cell, and sealed off for keeping the concentration of the suspension. Figure 5-6 shows the images of the suspension observed by a polarized-light microscope. Weak birefringence was initially observed just after injecting the suspension into the cell, as shown in Figure 5-6b. The birefringence became stronger with time, indicating the formation of a liquid crystalline phase. Finally as shown in Figure 5-6b, a texture was well developed. The phenomenon is similar to the case of previously reported liquid-crystal system of mineral colloids, in which the liquid crystalline phase was induced by purely repulsive forces.³⁸ In this case, the strong excluded-volume repulsion force specific to the concentrated polymer brush on the surface of hybrid rods plays a major role as the driving force for the formation of liquid crystalline phases.

In the case of a suspension of rod, that is a lyotropic system, the phase transition should occur depending on the concentration as well as the aspect ratio of rods. In this work, the hollow PMMA-rod suspensions with various concentrations in toluene were prepared, poured into Pyrex cells, and sealed off. Figure 5-7 shows the images of these samples observed by polarized-light

microscopy after standing at room temperature for 2 h. Birefringent textures indicating the formation of liquid crystalline phases were observed in suspensions at concentrations of 27.3 wt% to 22.4 wt%, but not at concentrations below 19.9 wt%. The critical concentration between the isotropic and anisotropic phases was about 20 wt% in this case. It would be interesting to discuss the critical concentration between the isotropic and anisotropic phases as a function of the length of graft chain and hence the aspect ratio. Further details are under investigation.

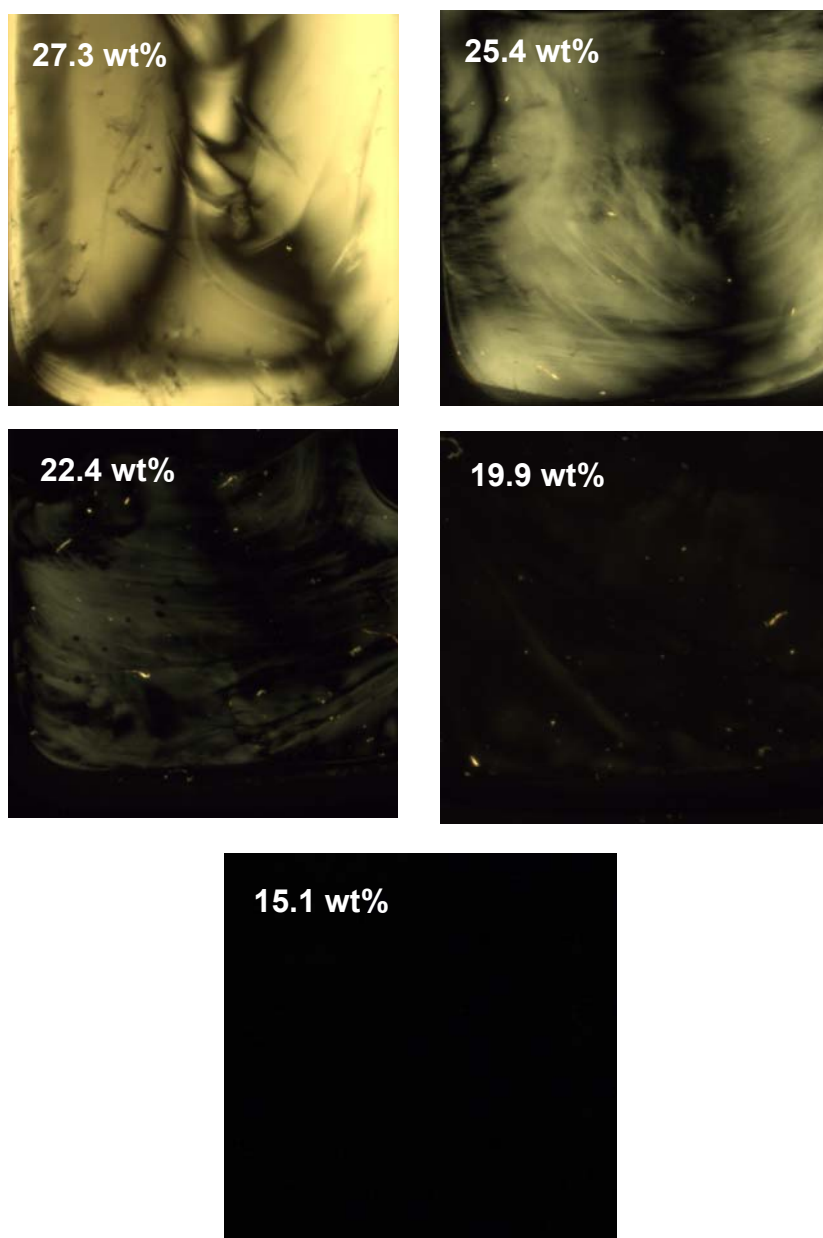


Figure 5-7. Cross-polarization images of suspensions of the hollow PMMA-rod with the graft polymer of $M_n = 14,000$ in toluene viewed by an optical microscope. The concentrations of suspension are from 27.3 to 15.1 wt%.

As mentioned in Figure 5-4a,b, the thickness of polymer graft surrounded core-rods depends on the molecular weight of polymer chain. For a spindle-type particle, a homogeneous growth of polymer grafted as a shell layer leads to a decrease in aspect ratio. This is off course the case in a lyotropic system. It should be noted that the hollow PMMA-rod with the PMMA chain of $M_n = 120,000$ gave no liquid crystalline phase even at a concentrated suspension with the concentration of 18.8 wt%, as shown in Figure 5-8 giving little birefringence.



Figure 5-8. Cross-polarization image of suspension of the hollow PMMA-rods with the graft polymer of $M_n = 120,000$ viewed by an optical microscope.

5-4. Conclusion

It was demonstrated that $\alpha\text{-Fe}_2\text{O}_3$ nanorods could be surface-decorated with ATRP initiation sites, with retaining their high dispersibility in solution. SI-ATRP of MMA using these functionalized $\alpha\text{-Fe}_2\text{O}_3$ nanorods preceded in a living fashion, yielding structurally well controlled PMMA-rods with a $\alpha\text{-Fe}_2\text{O}_3$ nanorod core and a PMMA-graft shell of variable thicknesses and high graft density. These PMMA-rods showed exceptionally good dispersibility in solvents and an orientational order in their thin films. Hollow PMMA-rods were successfully obtained through the HCl-etching process from hybrid nanorods with a silica-coated $\alpha\text{-Fe}_2\text{O}_3$ core. The lyotropic liquid crystalline phases were confirmed by the of polarized-light microscopic observation for the hollow

PMMA-rods with PMMA of sufficiently low molecular weights.

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Chapter 6

Fabrication of Thin Films with Highly Oriented Structure with Polymer-brush-afforded Iron Oxide Nanorods

6-1. Introduction

Particle assemblies consisting of one-, two-, and three-dimensional ordered arrays have attracted considerable attentions owing to their potential for use in various applications, including in optical and electronic devices and biological and chemical sensors.¹⁻⁶ Various types of particles having different sizes, shapes, and components have been employed for constructing these ordered assemblies. In addition, numerous techniques have been used for modifying the surfaces of the constituent particles to ensure that the assemblies can be constructed effectively.⁷⁻²⁹ Among the various surface-modification methods developed so far, surface-initiated living radical polymerization (SI-LRP) is one of the most powerful ones, because of the inherent robustness and versatility of LRP techniques. We had developed a method for modifying silica particles by surface-initiated atom transfer radical polymerization (ATRP) and had synthesized hybrid nanoparticles consisting of a monodisperse silica particle as the core and a well-defined, concentrated polymer brush; the diameters of the particles had ranged from the nanometer scale to the micrometer scale.^{30,31} The fact that these hybrid particles were perfectly dispersible allowed us to fabricate two- and three-dimensional ordered arrays of the particles at air-water interfaces and in suspensions, respectively.³¹⁻³⁵ In this study, in order to expand the versatility of the chemistry of surface-grafting polymers via LRP, the author investigated the feasibility of using SI-ATRP in the case of rod-type particles.

Lekkerkerker et al. employed an amine-functionalized polyisobutylene to sterically stabilize boehmite rod-like particles and reported that the resulting hybrid rods formed a liquid crystal in toluene.³⁶ Ji et al. reported the fabrication of gold nanorods grafted with a poly(*N*-isopropylacrylamide) brush using SI-ATRP. They envisaged that these nanorod hybrids

would find use in smart *in vivo* drug delivery systems, because the hybrids were sensitive to both temperature and near-infrared radiation.³⁷ Boyes et al. reported the surface modification of gold nanorods via the postpolymerization immobilization of polymers prepared by reversible-fragmentation chain transfer (RAFT) polymerization. The polymers had a thiol group at the chain end; the thiol group was produced by using a reducing agent to convert the end group of the RAFT chain-transfer agent on the polymer just after the completion of the polymerization process.³⁸ Zentel et al. employed poly(methyl methacrylate-*b*-dopamineacrylamide), which was also synthesized by RAFT, to modify the surfaces of TiO₂ rods by exploiting the anchoring ability of the dopamine units. The surface-functionalized hybrid rods formed a liquid crystal in a solvent.³⁹ They also fabricated a thin film of these hybrid rods in a poly(ethylene glycol) matrix through the dip-coating method and confirmed that the film exhibited birefringence during polarized optical microscopy.⁴⁰

Of the various rod-type particles synthesized so far, the author chose β -FeOOH rods to use as the substrate for SI-ATRP process in this study, because the method for synthesizing β -FeOOH rods with a narrow size distributed is well established, and metal oxide surfaces are suitable for introducing initiation sites for polymerization. Zocher et al. observed an iridescent layer at the bottom of a flask containing a suspension of β -FeOOH rod; this suggested the rods had formed some type of an ordered structure.⁴¹ Maeda et al. synthesized β -FeOOH rods with aspect ratios of 3.6–7.0, and were able to fabricate highly oriented structures of the rods in aqueous suspensions.⁴² The ability of β -FeOOH rods to form ordered structures is particularly attractive as it allows for the fabrication of well-organized assemblies of polymer-brush-afforded hybrid particles.

In this chapter, the author report the surface modification of β -FeOOH rods by the grafting of a high-density poly(methyl methacrylate) (PMMA) brush using SI-ATRP. Special attention was paid throughout all the processes, from initiator fixation process to polymerization process, to ensure that the rod-like particles did not form aggregates. We prepared thin films of the polymer-brush-afforded β -FeOOH rods using the dip-coating method. Finally, an oriented structure

of the hybrid rods in the thin film was also fabricated.

6-2. Experimental Section

6-2-1. Materials

Ethyl 2-bromoisobutyrate (2-(EiB)Br, 98%) were obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. 4,4'-Dinonyl-2,2'-bipyridine (dNbipy, 97%), copper(I) chloride (Cu(I)Cl, 99.9%), and iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 99.0\%$) were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Methyl methacrylate (MMA, 99%) was obtained from Nacalai Tesque Inc., Osaka, Japan, and purified by flash chromatography over activated neutral alumina. An ATRP-initiator-holding silane coupling agent, (2-bromo-2-methyl)propionyloxypentyl triethoxysilane (BPE), was synthesized following the Chapter 2. Water was purified by a Milli-Q system (Nihon Millipore Ltd., Tokyo, Japan) to a specific resistivity of ca. $18\text{M}\Omega\cdot\text{cm}$. $\beta\text{-FeOOH}$ rods were synthesized from aqueous FeCl_3 solution (40 mM, 20 L) by slow hydrolysis for six month at room temperature, according to the method of Zocher and Heller.^{41,43} The mean length (L) and width (W) of the resultant $\beta\text{-FeOOH}$ rods were 210 and 35 nm, respectively, as measured by transmission electron microscopy (TEM). All other reagents were used as received from commercial sources.

6-2-2. Measurements

Gel permeation chromatographic (GPC) analysis was carried out at 40°C on a Shodex GPC-101 high-speed liquid chromatography system (Showa Denko K.K., Tokyo, Japan) equipped with a guard column (Shodex GPC KF-G), two 30 cm mixed columns (Shodex GPC KF-806L, exclusion limit = 2×10^7), and a differential refractometer (Shodex RI-101). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.8 mL/min. Poly(methyl methacrylate) (PMMA) standards were used to calibrate the GPC system. $^1\text{H-NMR}$ (300MHz) spectra were obtained on a JEOL/AL300 spectrometer (JEOL, Tokyo, Japan). Thermal gravimetric analyses (TGA) were performed on a Shimadzu TGA-50 (Shimadzu, Kyoto, Japan) under a nitrogen atmosphere. Polarized optical microscopic (POM) observations were carried out by an optical microscope BX51

(OLYMPUS, Tokyo, Japan). Transmission electron microscopic (TEM) observation was made on a JEOL transmission electron microscope (JEM-2100) operated at 200 kV. Scanning electron microscope (FE-SEM) observation was performed using a field-emission scanning electron microscope JSM-6700F (JEOL) at an accelerating voltage of 1.5 kV.

6-2-3. Fixation of ATRP-Initiator BPE on β -FeOOH rods

A mixture of ammonia solution (28% NH_3 aqueous solution, 6 g) and ethanol (33 g) was added dropwise into the suspension of β -FeOOH rods (5 g) in ethanol (400 g) under magnetically stirring, and the system was stirred for 1 h at room temperature. BPE (2.5 g) dissolved in ethanol (67 g) was added dropwise into the system, and the reaction mixture was continuously stirred for 5 days at room temperature. The modified β -FeOOH rods were collected by centrifugation and subsequently washed three times by consecutive centrifugation and redispersion in ethanol. Finally, the suspension of initiator-coated β -FeOOH rods in ethanol was solvent-exchanged to anisole by repeated redispersion/centrifugation to obtain an anisole suspension to stock.

6-2-4. Surface-Initiated ATRP on β -FeOOH Rods

Just before polymerization, the initiator-coated β -FeOOH rods in anisole were solvent-exchanged to MMA. A mixture of initiator-coated β -FeOOH rods in MMA containing a prescribed concentration of 2-(*EiB*)Br and dNbipy was quickly added to the Pyrex glass tube charged with a predetermined amount of Cu(I)Cl (solid). Three freeze-pump-thaw circles were carried out and the tube was sealed off under vacuum. The polymerization was carried out in a shaking oil bath (TAITEC Corp., Saitama, Japan, Personal H-10) thermostated at 60 °C and, after a prescribed time t , quenched to room temperature. An aliquot of the solution was taken out for NMR measurement to estimate monomer conversion and for GPC measurement to determine molecular weight and its distribution. The rest of the reaction mixture was diluted by acetone and centrifuged to collect PMMA-grafted β -FeOOH rods (PMMA-FeRs). The cycle of centrifugation and redispersion in organic solvents of acetone/THF/toluene was sequentially carried out, and each cycle was repeated three times to obtain PMMA-FeRs perfectly free of the unbound (free) polymer.

The purified PMMA-FeRs were treated with HF to cleave the graft polymer from the β -FeOOH rods surface as reported previously, and the molecular weight of graft polymer was determined by GPC.

In a typical run, the bulk polymerization of MMA was carried out at 60 °C for 12 h with the starting materials of MMA (9.8 g, 98 mmol), 2-(EtB)Br (9.6 mg, 0.049 mmol), Cu(I)Cl (19 mg, 0.20 mmol), dNbipy (166 mg, 0.40 mmol), and initiator-coated β -FeOOH rods (50 mg). This gave a monomer conversion of 79 %, a free polymer with $M_n = 165,000$ and $M_w/M_n = 1.27$, and a graft polymer with $M_n = 203,000$ and $M_w/M_n = 1.15$, where M_n and M_w are the number- and weight-average molecular weights, respectively, and M_w/M_n is the polydispersity index. The polymer-grafted β -FeOOH rods were purified by repeated cycles of centrifugation (12,000 rpm for 20 min) and redispersion in acetone (3×200 mL), toluene (3×200 mL) and in THF (3×200 mL). The PMMA-FeRs were dispersed in toluene to obtain a toluene suspension to stock in refrigerator.

6-2-5. Dip-Coating with PMMA-Rods

A glass slide (size: 28×10 mm, thickness: 0.8–1.0 mm) was washed twice with water and once with ethanol using a bath sonicator. It was then rinsed with ethanol and dried at 60 °C.⁴⁴ A programmable dip-coater (SDI Company Ltd., Kyoto, Japan, Nano Dip Coater ND-0407-S1) was used to fabricate thin films of the PMMA-FeRs. The cleaned slide was immersed in a suspension of the PMMA-FeRs (6 wt%) in toluene (1 mL) contained in a Pyrex cell (size: 22×15×4 mm) and then withdrawn from the suspension at a controlled speed of 0.1–10 $\mu\text{m/s}$. The entire setup was placed on a vibration isolator and covered with a windshield box.

6-3. Results and Discussion

6-3-1. Synthesis of ATRP Initiator-Coated β -FeOOH Rods

Using a previously reported method, the author prepared narrowly size-distributed β -FeOOH rods from a dilute aqueous solution of FeCl_3 ; the long- and short-axis lengths of the rods were 210 and 35 nm, respectively. The reaction conditions for introducing the ATRP-initiating sites

on the surfaces of the β -FeOOH rods were similar to the ones which had been previously used for modifying the surfaces of silica particles. The starting materials for the reaction were the β -FeOOH rods (5 g), ethanol (500 g), a 28% aqueous NH_3 solution (24 g), and BPE (2.5 g). However, this attempt to synthesize ATRP initiator-coated β -FeOOH rods was unsuccessful and resulted in visually noticeable aggregates of the β -FeOOH rods soon after the addition of the aqueous NH_3 solution. Even though most of these aggregates disappeared as the reaction proceeded, an extremely tiny amount of the aggregates did remain in the system. This point will be discussed further later in the chapter.

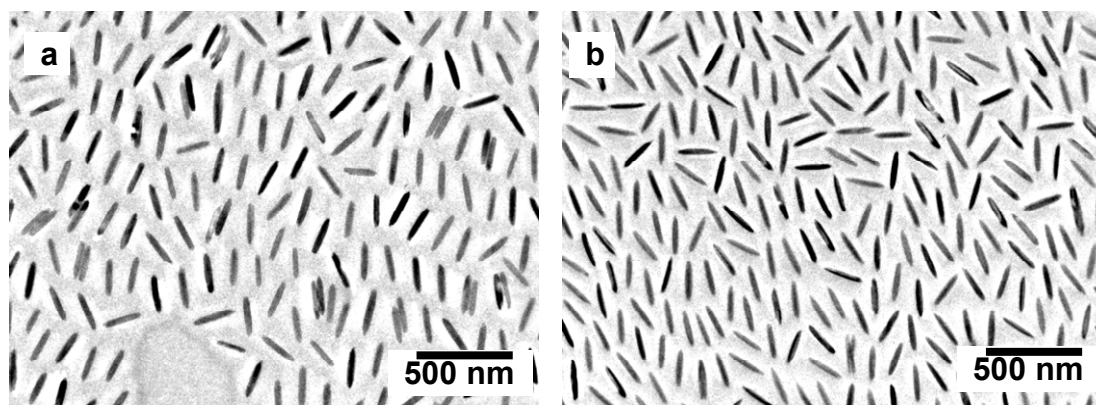
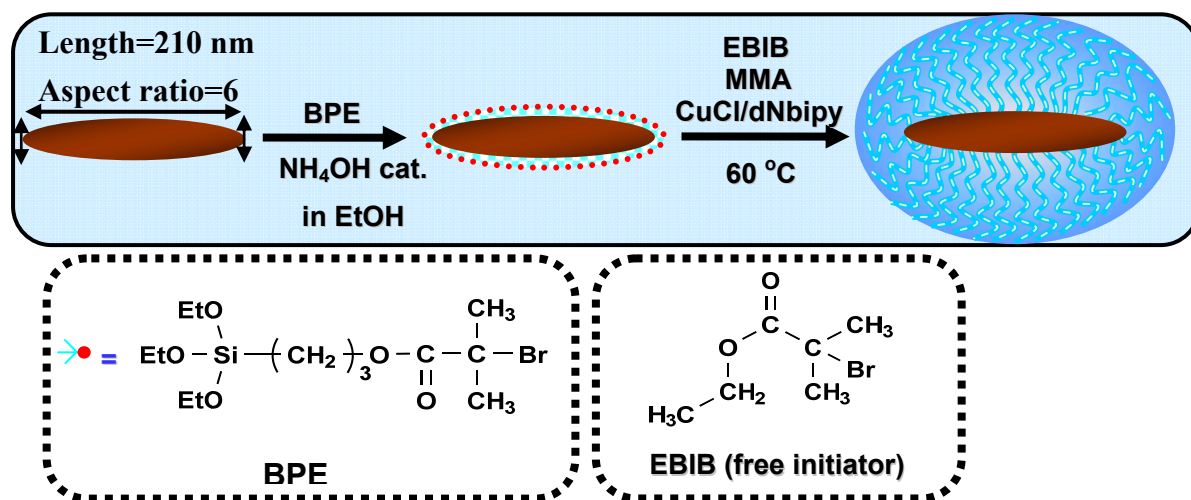


Figure 6-1. Transmission electron microscopic images of the films of β -FeOOH rods coated with poly(methyl methacrylate) brushes (PMMA-rods): a PMMA-rods with the initiator-coated β -FeOOH rods made by the condition with 24 g of ammonia solution. b PMMA-rods with initiator-coated β -FeOOH rods made by the condition with 6 g of ammonia solution added.

To overcome this issue, the author decreased the concentration of the NH_3 solution by a quarter. It was expected that the use of a low-concentration NH_3 solution would decrease the ionic strength of the system and consequently retard particle aggregation, resulting in perfectly dispersible ATRP-initiator-coated β -FeOOH rods. A low-concentration NH_3 solution also decreases the reaction rate; however, prolonging the reaction time to 5 days ensured that a sufficient number of initiation sites were introduced on the β -FeOOH rods. An elemental analysis of the initiator-coated β -FeOOH rods indicated a bromine content of 0.85%, which, along with the known density (1.98 g/cm^3) and the surface area of the spheroidal particles, suggested a surface density of

approximately 0.9 initiator molecules/nm². The resulting suspension of the initiator-coated β -FeOOH rods in anisole could be stably stored in a refrigerator for at least 6 months.

6-3-2. Surface-Initiated ATRP of MMA on β -FeOOH Rods



Scheme 6-1. Schematic representation for the synthesis of polymer-coated β -FeOOH rods by SI-ATRP

The initiator-coated β -FeOOH rods were subsequently used for the copper-mediated ATRP of MMA in bulk (Scheme 6-1). Figure 6-2a shows the first-order kinetic plot of monomer concentration for the polymerization of MMA in bulk with the BPE-coated β -FeOOH rods. The plot is concave upward with increasing polymerization time, as shown in Figure 6-2, which may come from the large increase of system viscosity due to the higher molecular weight of polymer-grafted nanorods, viz., a gel effect. Figure 6-2b shows the evolution of the number-average molecular weight M_n and the polydispersity index M_w/M_n of (cleaved) graft polymers and of free polymers simultaneously produced from the free initiator. The M_n s of the graft and free polymers showed good agreement with each other, both increasing in proportion of monomer conversion, in line with the theoretical predictions of $M_{n,calcd}$. The M_w/M_n ratio remains lower than 1.2 for most samples. All these results indicate that the polymerization of MMA initiated from the β -FeOOH-rod surface proceeds in a living fashion, giving β -FeOOH rods coated with a shell of well-defined PMMA.

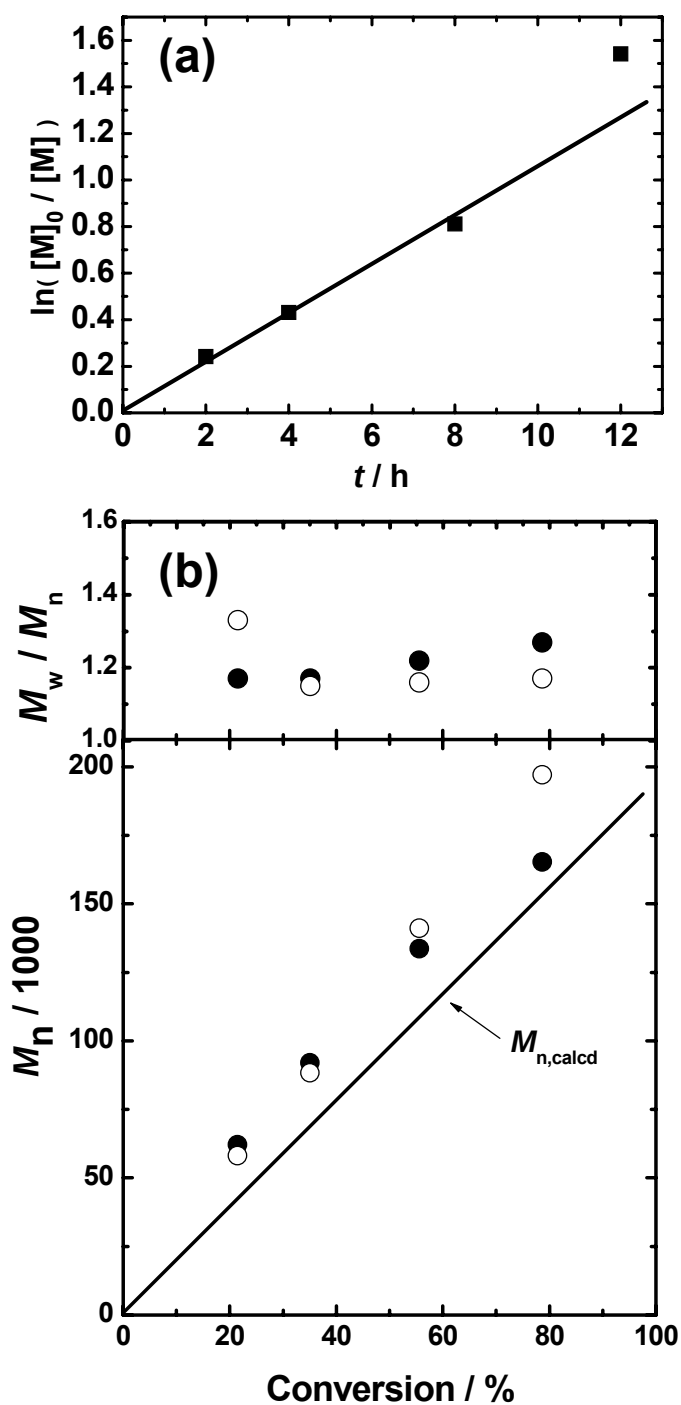


Figure 6-2. (a) Plot of $\ln([M]_0/[M])$ vs t , (b) values of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the graft (○) and free (●) polymers as a function of monomer conversion; the polymerization of methyl methacrylate (MMA) without a solvent at 60 °C with initiator-coated β -FeOOH rods (0.5 wt%): $[MMA]_0/[ethyl\ 2-bromoisobutylate]_0/[Cu(I)Cl]_0/[4,4'-dinonyl-2,2'-bipyridine]_0 = 2200/1/4/8$.

6-3-3. Determination of Graft Density of PMMA-rods

The calculation of graft density of PMMA-rods is similar to Eq(1) and Eq(2) shown in Chapter 5. As the density of lab-made β -FeOOH rod is needed for the calculation of w of each hybrid nanorod, the author centrifuged (1000 rpm for 10 min) PMMA-rods with the molecular weight of graft polymer of M_n 197,000 in solvent mixtures of various densities ranged from 1.2 to 1.8 g/mL. Sedimentation showed up as the density of solvent changed from 1.3 to 1.25 g/mL indicates the density of PMMA-rods approximately of 1.3 g/mL. With the known density of PMMA (1.2 g/mL) and the result from TGA analysis with an 87% of PMMA content, the density

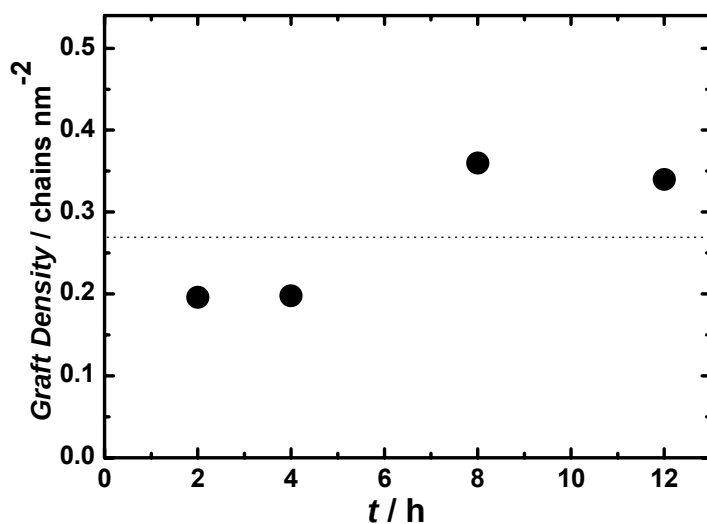


Figure 6-3. Time dependence of the graft density of poly(methyl methacrylate) grown on β -FeOOH rods surface.

of β -FeOOH rods was calculated to be 1.98 g/mL. Therefore, as the similar core rods were used for the polymerization, graft densities of PMMA grown on them (cf. Figure 6-2) were calculated as shown in Figure 6-3. The graft density is nearly constant independent of the polymerization time, and approximately equal to 0.27 chains/nm², which is somewhat smaller than those previously attained on silica particles. The reason for this is not at present clear, but it may possibly be due to some experimental error in determining the polymer content by TGA analysis. More importantly, the graft densities obtained are high enough to demonstrate that the layer of polymer grafts is in the concentrated-brush regime.

6-3-4. TEM Observation of PMMA-rods

A drop of PMMA-rod suspension in toluene was put on the surface of pure water, and formed a monolayer film at the air-water interface after the toluene evaporated off. Figure 6-4 shows the TEM images of the transferred films of PMMA-rods (cf. Figure 6-2). The high dispersibility of these PMMA-rods was confirmed in Figure 6-4 as they well dispersed throughout the films. A similar correlation between interparticle distance and M_n value of PMMA-graft chain as the system of PMMA-coated silica particles was also revealed. That is, the interparticle distance increased as M_n value of PMMA-graft chain increased. Furthermore, the orienting nature of PMMA-rods was also observed, indicating the potential application of fabricating thin films of highly oriented hybrid rods.

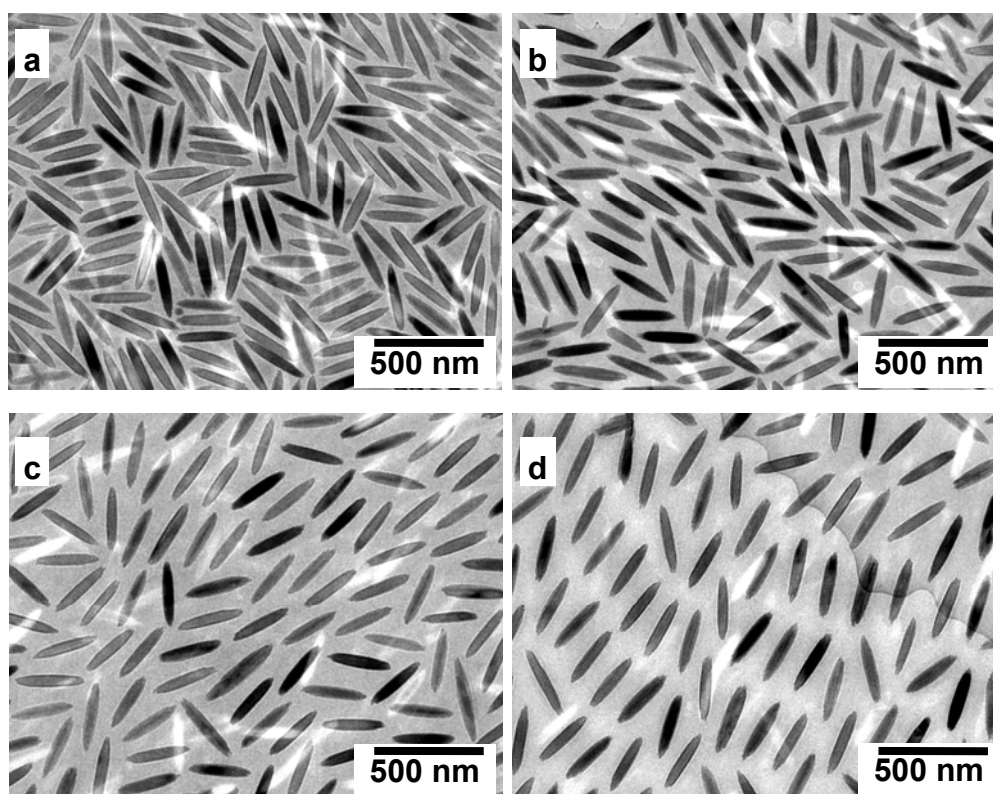


Figure 6-4. Transmission electron microscopic images of the films of β -FeOOH rods coated with poly(methyl methacrylate) brushes (PMMA-rods): the number-average molecular weight of PMMA grafts are: a 58,000, b 88,000, c 140,000 and d 197,000.

6-3-5. Fabrication of Thin Film by Dip-coating Method

PMMA-rods with different M_n values of PMMA grafts were deposited on a slide glass by dip-coating with a withdrawal speed of 2 $\mu\text{m/s}$. The thicknesses of the films were from 500 to 600 nm. Slightly turbid samples observed in Figure 6-5a,b indicating a light scattering stem from the

cracks in structure may appear in the aggregates of the two PMMA-rods of lower M_n values of graft

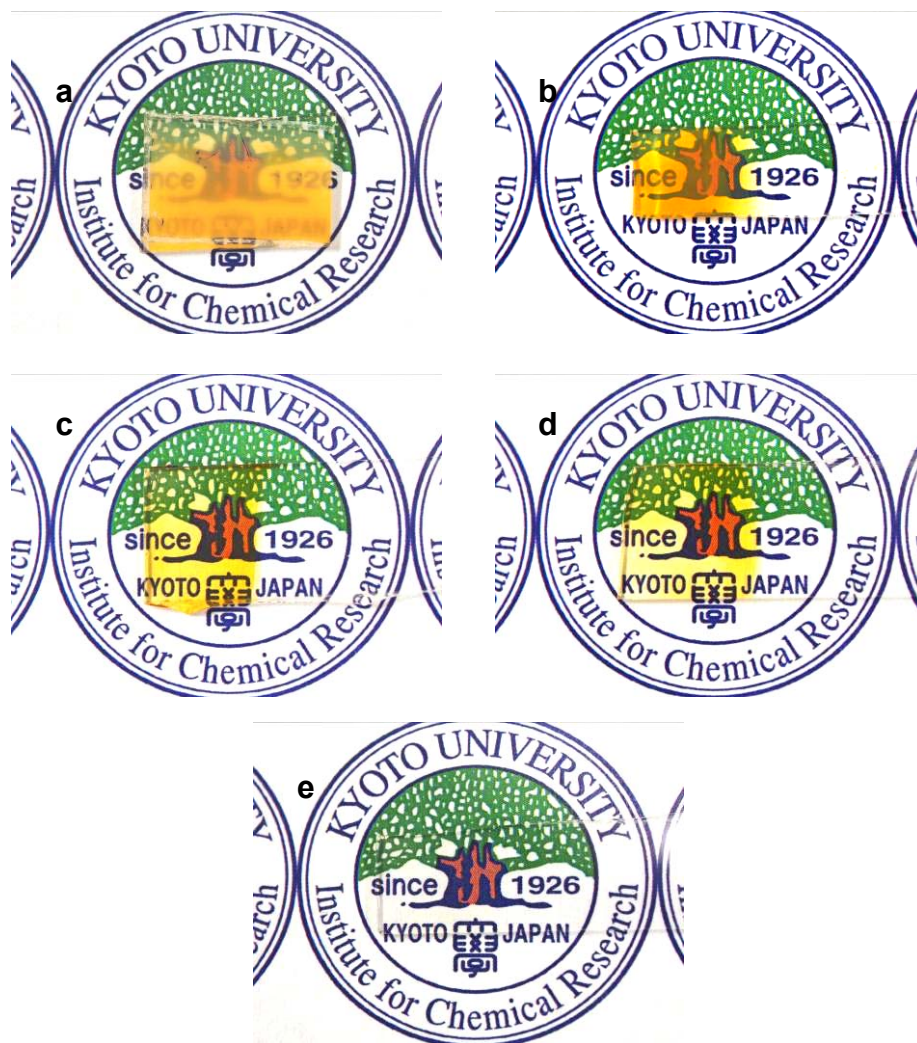


Figure 6-5. The photographs of PMMA-rod thin films dip-coated on slide glass. The number average molecular weight of PMMA grafts are: a 5,000, b 16,000, c 58,000, d 197,000 and e 700,000. The thickness of c,d,e films are 521 nm, 554 nm and 622 nm.

polymer. Meanwhile, transparent samples were observed in Figure 6-5c,d and e, accompanied with a decrease of the yellow color of β -FeOOH rods as the molecular weight of polymer brush increases. The change in color of these films is probably due to the increase of volume fraction of PMMA as the M_n value of graft polymer increases. Namely, to fill the same space on the surface of glass slide, PMMA-rod with higher M_n value of grafts fill with lower amount of them in the same space which leads to a lower amount of core in samples with a decrease of color. The transparency of the films may be benefited from two main reasons: a compacted arrangement in structure as PMMA-rods highly stack without any cracks; and the higher content of PMMA in these samples providing a

good enough space for light pass through samples. The results suggest a further confirmation of the success in fabricating thin films of PMMA-rods with higher values of graft polymer. The SEM observation was utilized to the confirmation as described below.

6-3-6. Effect of Polymer-chain Length of PMMA-Rods on Structure of Films

Figure 6-6 shows FE-SEM images revealing the correlation between the structures of films and the molecular weight of graft chains on PMMA-rods. In Figure 6-6a,b, cracks were observed in the samples, being responsible for slight turbid in Figure 6-5a,b which confirmed PMMA-rods with

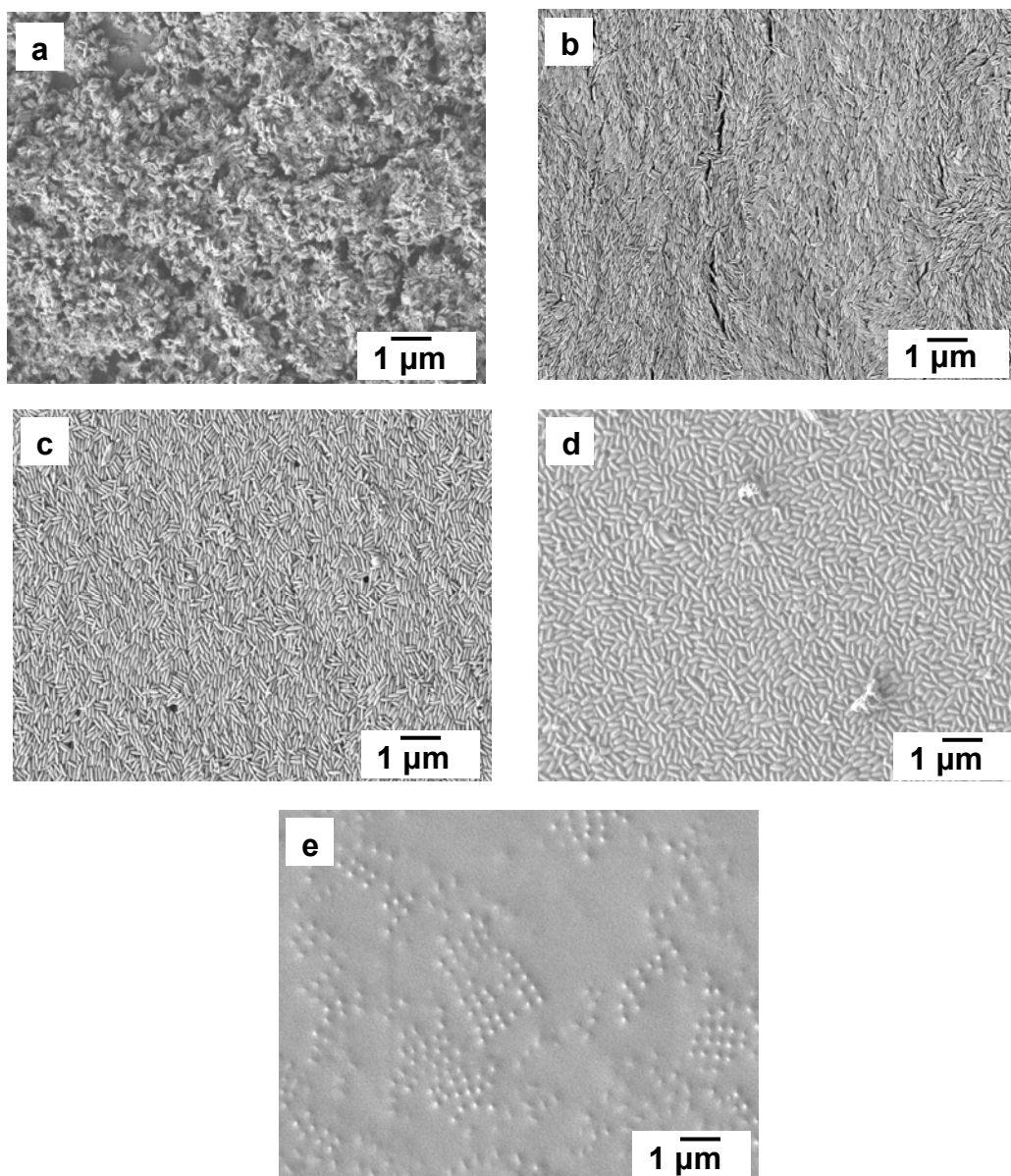
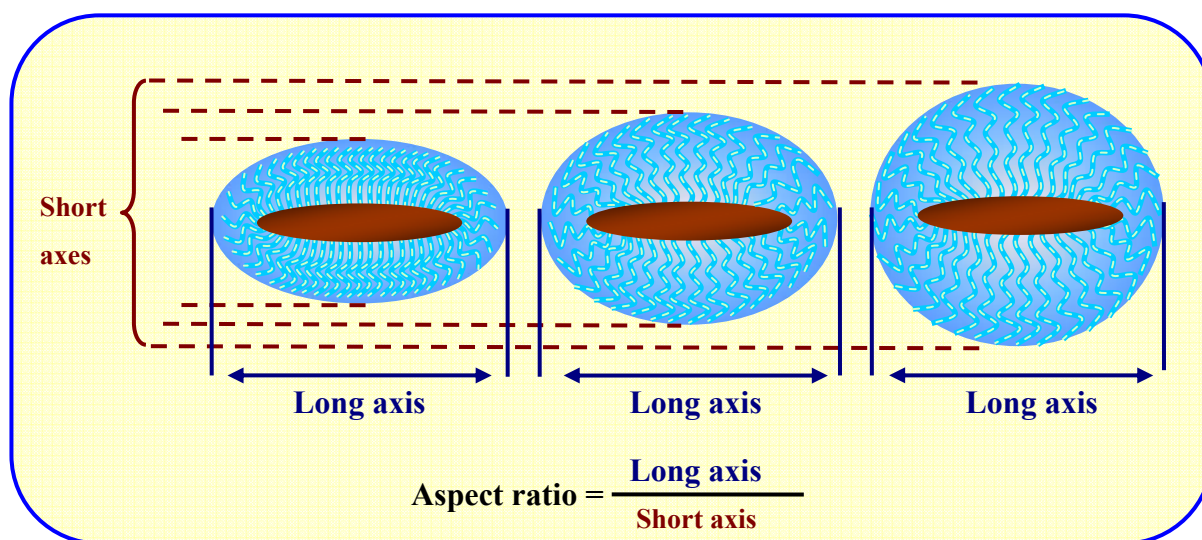


Figure 6-6. Field emission scanning electron microscopic (FE-SEM) images of PMMA-rod thin film dip-coated on slide glass. The withdrawal speed of dip-coating was 2 $\mu\text{m/s}$. The number average molecular weight of PMMA grafts are: a 5,000, b 16,000, c 58,000, d 197,000 and e 700,000. The thicknesses of c,d,e films are 521 nm, 554 nm and 622 nm.

the graft polymer chain of the number-average molecular weights 5,000 and 16,000 formed the defect ordering of PMMA-rods. Meanwhile, in Figure 6-6c,d,e, closely packed PMMA-rods in the films without any cracks were observed even though some tiny defects of air bubbles were captured in Figure 6-6c. The results confirm that PMMA-rods with longer graft polymer on the surface can form the thin films with the compacted arrangement in structure. This is probably due to the difference in conformation of polymer chain on the outmost surface of PMMA-rods depending on molecular weight of grafts. Similar to the case of spherical particles grafted with PMMA chains, polymer chains exhibit a crossover in conformation from the concentrated to semidilute brush regimes along the chain contour as the M_n value increases. This also means the effective graft density and hence the concentrated-brush effects would decrease as the radial distance from the core surface increases. The same phenomenon may occur for the β -FeOOH rods also having a curved surface. Therefore, the mutual interpenetrations during solvent evaporation occurred for the PMMA-rods with relatively longer graft chains. The reasons for the failure of forming thin films of PMMA-rods with lower M_n values may be the strong steric-repulsion effect remaining on the surface as well as the absolutely low content of polymer on the glass slides.

The correlation between orientation of PMMA-rods and molecular weight of graft chain was also discussed by the aid of SEM observation, as the results shown in Figure 6-6c,d and e. An orientation of most rods parallel to the withdraw direction of dip-coating was observed for the sample of $M_n = 58,000$ as shown in Figure 6-6c. Meanwhile, the sample of $M_n = 197,000$ shows a nearly isotropic order as seen in Figure 6-6d. White dots observed in Figure 6-6e should be the pointed end of β -FeOOH rods, indicating the PMMA-rods of $M_n = 700,000$ oriented perpendicular to the film surface and forming clusters on the glass. Variational arrangements of various PMMA-rods of different M_n values of polymer chain were apparently observed. Scheme 6-2 illustrates the reason for this by a contour change of hybrid rods as the length of graft chains increases. The aspect ratio decreases with increasing the chain length of grafts because the surface curvature at the pointed ends of β -FeOOH nanorod is higher than that at the central part. It is

predicable that PMMA-rods will loss their anisotropic nature and that the effective graft density at the outmost surface will decrease more dramatically especially along the long axis direction, giving change in inter-particle interactions along the long and short axes. This presumably explain the reason why the film of PMMA-rods with $M_n = 58,000$ shows the most anisotropic arrangement in this work.



Scheme 6-2. Illustration of the shape change of PMMA-rods depending on length of polymer chain.

6-3-7. Effect of Dip-Coating Speed on Ordering of Rods

Besides the length of graft chains, the withdrawal speed of dip-coating is also an important factor for the formation of oriented structures in the film. In this work, the author tried to optimize the speed for dip-coating the PMMA-rod of $M_n = 197,000$ which showed a nearly isotropic order in the films observed in Figure 6-6d. The withdrawal speed was varied from 0.1 to 10 $\mu\text{m/s}$, while the concentration of PMMA-rods suspension in toluene was kept at a weight ratio of 6%. The withdrawal direction of dip-coating is in a horizontal direction in the SEM images shown in Figure 6-7. The thicknesses of films are ranging from 243 nm to 1700 nm. Similar to that was noticed in Figure 6-6d, the PMMA-rods were arranged almost randomly in the films prepared at withdrawal speeds greater than 2 $\mu\text{m/s}$. On the other hand, as the speed drops to 1 $\mu\text{m/s}$, the PMMA-rod in the film showed a relatively well orientation perpendicular to the withdrawal direction. The degree of

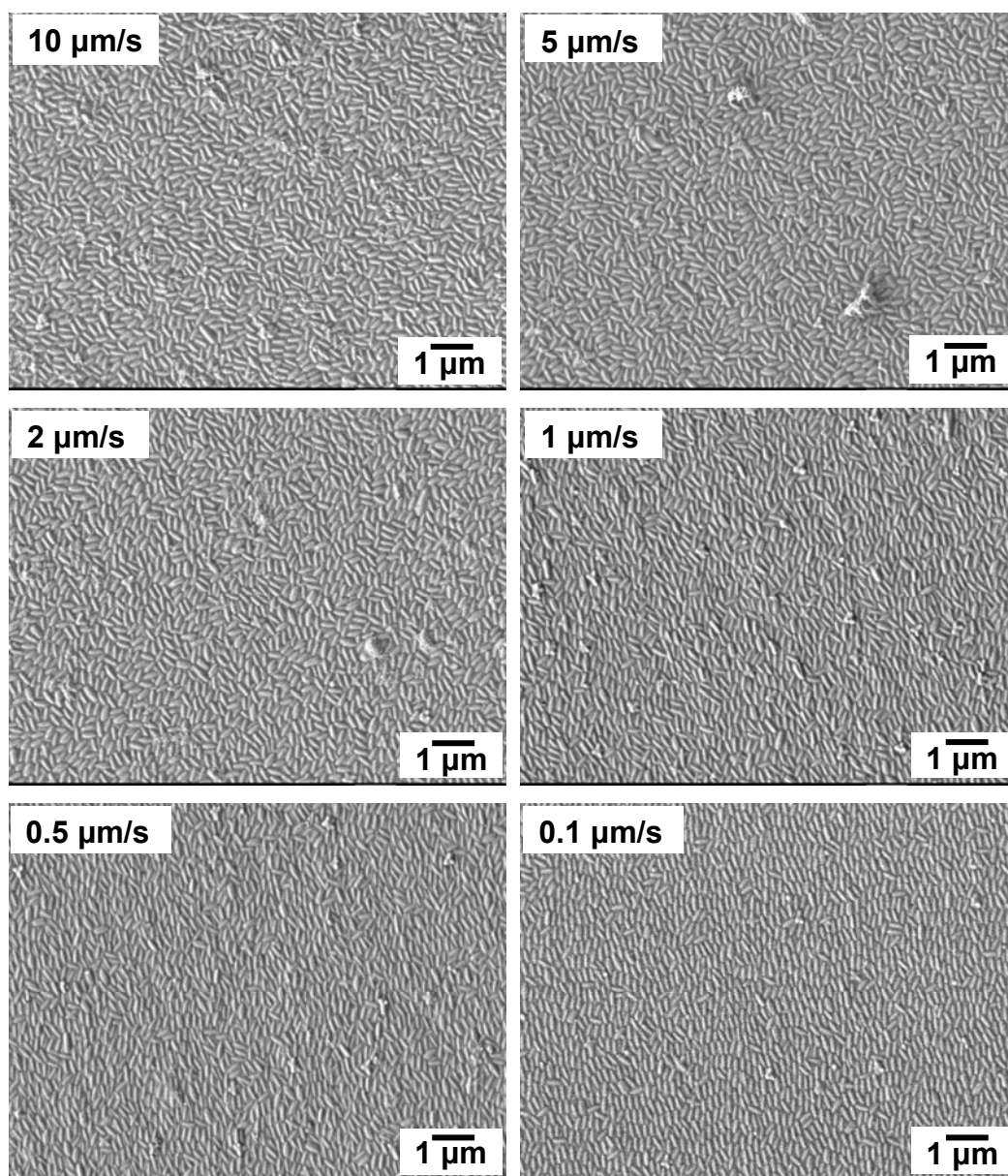


Figure 6-7. Field emission scanning electron microscopic (FE-SEM) images of films of PMMA-rods with the number-average molecular weight of 197,000. Speed of dip-coating process is varied from 0.1 to 10 $\mu\text{m/s}$, while the concentration PMMA-rods suspension in toluene was kept at weight fraction of 6%. The thicknesses of films are ranging from 243 nm to 1700 nm as decreasing the speed of dip-coating.

ordering were more improved with further decreasing speed, particularly in the film made at a speed of 0.1 $\mu\text{m/s}$. The shear-flow effect induced by withdrawing should be reduced with decreasing speed. Therefore, this may be ascribed to the dissipative and/or interfacial effects at the interface (among the solvent, the glass slide, and air) forming the meniscus. It is predictable that PMMA-rod with lower M_n value as 58,000, which has more in anisotropic nature, could also form the highly oriented order in a film.

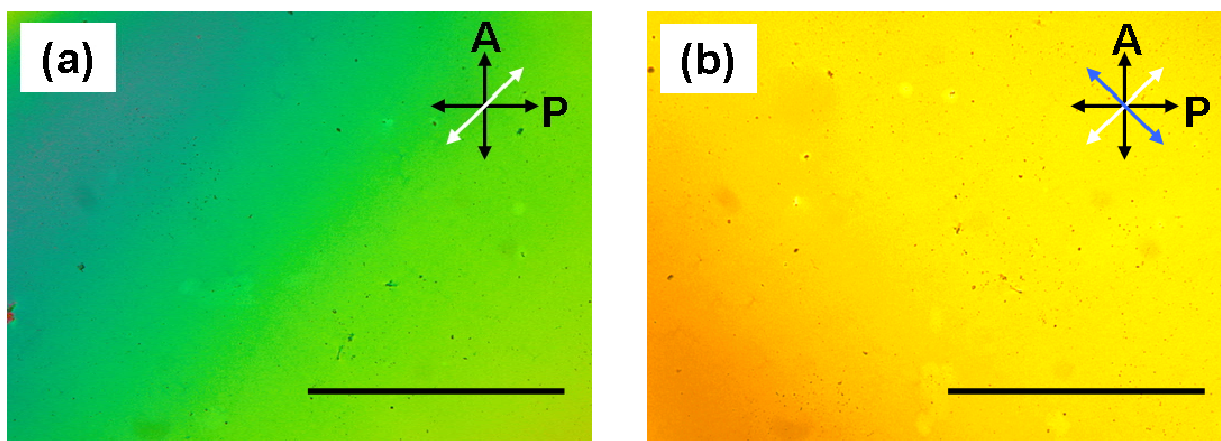


Figure 6-8. Polarized optical microscopic images of a thin films prepared by dip-coating β -FeOOH rods end-grafted with poly(methyl methacrylate) brushes on glass slides. Number-average molecular weight of the PMMA grafts was 197,000. The withdrawal speed during the dip-coating process was 0.1 $\mu\text{m/s}$. The sample was observed between two-crossed polarizers in horizontal (Polarizer indicated by P) and vertical directions (Analyzer indicated by A) with a phase compensator (U-TP530 530 nm retardation plate. the optical axis is indicated with the white arrow). (a) and (b) show R4 rods aligned parallel and perpendicular to the direction of the compensator, respectively. The scale bars indicate 50 μm .

Macroscopic orientation of the thin film was observed by POM. Figure 6-8 shows a POM image of the thin film formed by the R4 rods at a withdrawal speed of 0.1 $\mu\text{m/s}$. The observed birefringence strongly suggested the existence of an optically anisotropic structure in the film, that is, the presence of an oriented structure of the hybrid rods, as was noticed in the FE-SEM image in Figure 6-7. It should be noted that the transparency of the film allowed for this type of microscopy-based characterization. Any orientation defect (e.g. Schlieren texture) is not observed in the POM image, which indicate that the highly oriented structure of R4 rods formed homogeneously in a large area (at least in $22 \times 16 \mu\text{m}^2$ area), as shown in Figure 6-8. The POM picture reveals that highly oriented homogeneous structure of the rods can be fabricate in macroscopic scale by the dip-coating method.

6-4. Conclusion

Perfectly dispersive ATRP-initiator-coated β -FeOOH rods were successfully synthesized by optimizing the reaction condition for the fixation of the initiator-holding silane-coupling agent,

BPE, on their surface. The SI-ATRP of MMA with the initiator-coated β -FeOOH rods proceeded in a living manner, producing PMMA-rods consisting of well-defined PMMA brushes. Owing to the excellent dispersibility of the PMMA-rods, thin films of the rods could be fabricated successfully by the dip-coating method. By tuning the dip-coating conditions, the author was able to control the degree of orientation of the PMMA-rods in the films. This technique should be applicable to other particles as well, owing to the robustness and versatility of the SI-ATRP process, and should lead to the fabrication of particle-assembled systems with unique functionalities.

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Summary

In **Chapter 1**, the background and purposes of this thesis were described along with the outline of this thesis.

In **Chapter 2**, surface-initiated atom transfer radical polymerizations (SI-ATRP) from narrowly size-distributed silica nanoparticles (SiNPs) of diameters less than 100 nm were investigated. Two methods were used for the preparation of the SiNP cores: one was the reverse-micelle technique, which gave monodisperse SiNPs of an average diameter of 55 nm, and the other was the lysine-addition technique, which gave nearly monodisperse SiNPs of an average diameter of 15 nm. These nanoparticles were surface-modified with a triethoxysilane derivative containing an ATRP-initiating group. The surface-initiated ATRP of methyl methacrylate (MMA) mediated by a copper complex was carried out with the initiator-fixed SiNPs in the presence of a “sacrificial” free initiator. Well-defined poly(methyl methacrylate) (PMMA) brushes of a designed molecular weight were successfully grafted with surface densities as high as 0.4–0.8 chains/nm². These core-shell hybrid particles were highly dispersible, without any aggregation, in various solvents for PMMA. Because of exceptionally high uniformity and perfect dispersibility, these hybrid particles formed two- and three-dimensional ordered arrays at the air-water interface and in suspension, respectively.

In **Chapter 3**, a route for immobilizing the *semisoft* colloidal crystals was developed. A block-copolymer, poly(methyl methacrylate-*r*-hydroxyethyl methacrylate)-*b*-poly(methyl methacrylate) (P(MMA-*r*-HEMA)-*b*-PMMA), was grafted on a monodisperse SiP of an average diameter 130 nm via the SI-ATRP, and then by the reaction of the hydroxyl group of HEMA unit of the block copolymer with 2-isocyanatoethyl methacrylate (MOI), a vinyl group was introduced as a cross-linker. The key to success for immobilization was to introduce the cross-linker near the outermost surface in the shell of hybrid particles and to add an appropriate amount of free polymer containing the cross-linker to the *semisoft* colloidal crystals. Finally, well-defined *semisoft* colloidal crystals were formed in such a system and successfully immobilized with keeping their periodic structure by photo-irradiation, i.e., the photo-radical polymerization of the vinyl group in the

presence of a photo-initiator.

In **Chapter 4**, PMMA-afforded hybrid particles were well dispersed in ionic liquids, BMI-TFSI and DEME-TFSI, as non-volatile solvents, successfully forming a *semisoft* colloidal crystal in suspension at the prescribed concentrations. The system was off course stable without sealing, since the concentration of hybrid particle was constant, which is not the case with usual organic solvents. As expected, the photonic property could be controlled by changing the chain length of graft polymer and hence the interparticle distance. According to the technique described in Chapter 3, the *semisoft* colloidal crystals were immobilized in ionic liquids.

In **Chapter 5**, a hematite (α -Fe₂O₃) nanorod with an aspect ratio of 6 and a major axis of 600 nm and its silica-coated one were surface-modified with a triethoxysilane derivative containing an ATRP-initiating group and subjected to the SI-ATRP of methyl methacrylate (MMA) mediated by a copper complex in the presence of a “sacrificial” (free) initiator. Well-defined PMMA brushes of the prescribed molecular weights were successfully grafted with a surface density as high as 0.7 chains/nm². These core-shell hybrid nanorods were highly dispersible, without any aggregation, in various solvents for PMMA. For the sample with the silica-coated one, the α -Fe₂O₃ core was successfully etched, without any damage on PMMA brushes by the treatment with aqueous hydrochloride acid, giving a hollow type of polymer-brush-afforded rods. Because of perfect dispersity and anisotropic geometry, orientational ordering depending on the concentration of hybrid rods as well as the length of polymer brushes was observed. Especially, a lyotropic liquid crystalline phase was confirmed by the polarizing microscopic observation for the polymer-brush-afforded hollow rod.

In **Chapter 6**, a akaganéite (β -FeOOH) rod with a aspect ratio of 6 and an average length of 210 nm was targeted because a smaller-size rod had been expected to have better mobility in suspension as well as in bulk. SI-ATRP was successfully utilized to tailor the surface of this nanorod with well-defined PMMA brushes. These hybrid nanorods (PMMA-rods) were highly dispersible, without any aggregation, in various solvents for PMMA. Suspensions of PMMA-rods

with M_n of graft chain higher than 58,000 were deposited on a slide glass by the dip-coating process, giving thin films. The field-emission scanning electronic microscopic (FE-SEM) observation revealed orientational ordering, the degree of which was controlled by the length of PMMA chains as well as the condition of dip-coating. It should be noted that in the film made of the sample with a relatively longer graft chain ($M_n = 197,000$) at a dip-coating speed as slow as 0.1 $\mu\text{m/s}$, the hybrid nanorod was highly homogeneously oriented, as was revealed by the FE-SEM as well as the polarized microscopy.

List of Publications

Chapter 2.

- (1) Surface-Initiated Living Radical Polymerization from Narrowly Size-Distributed Silica Nanoparticles of Diameters less than 100 nm

Ohno, K.; Akashi, T.; **Huang, Y.**; Tsujii, Y. *Macromolecules* **2010**, 43, 8805–8812

Chapter 3.

- (2) Immobilization of *Semisoft* Colloidal Crystals Formed by Polymer Brush-Afforded Hybrid Particles

Huang, Y.; Morinaga, T.; Tai, Y.; Tsujii, Y.; Ohno, K. *Langmuir*. **2014**, in press.

Chapter 4.

- (3) Fabrication of *Semisoft* Colloidal Crystals in Ionic Liquid

Huang, Y.; Tsujii, Y.; Ohno, K. to be submitted.

Chapter 5.

- (4) Controlled Synthesis of Polymer-Brush-Afforded Iron-Oxide Nanorods and their Formation of Lyotropic Liquid Crystal

Huang, Y.; Sasano, T.; Tsujii, Y.; Ohno, K. to be submitted.

Chapter 6.

- (5) Fabrication of Thin Films of Polymer-brush-afforded Iron-Oxide Rods with a Controllable Structure

Huang, Y.; Ishige, R.; Tsujii, Y.; Ohno, K. Submitted to *Langmuir*.

Other Associated Publications.

- (6) Drying dissipative structures of spindle-shaped hematite particles coated with polymer brush
Ohno, K.; **Huang, Y.**; Okubo, T. *Colloid. Polym. Sci.* 2014, Ahead of Print.
- (7) Colloidal crystallization of spindle-shaped hematite particles coated with polymer brush in deionized aqueous suspension
Ohno, K.; **Huang, Y.**; Tsuchida, A.; Okubo, T. *Colloid. Polym. Sci.* 2013, Ahead of Print.
- (8) Surface-Initiated Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization from Fine Particles Functionalized with Trithiocarbonates
Ohno, K.; Ma, Y.; **Huang, Y.**; Mori, C.; Yahata, Y.; Tsujii, Y.; Maschmeyer, T.; Moraes, J.; Perrier, S. *Macromolecules* **2011**, 44, 8944–8953.
- (9) Rheological Behavior of Modified Starch-Alumina Oxide Suspensions
Huang, Y.; Chen, L.; Ye, J.; Li, X.; Zhang, X.; Ju, C. *Key Engineering Materials* **2008**. Vols. 368-372, 679-682.
- (10) Controlling Porosity and Pore Size Distribution of Alumina Ceramics in Consolidation Forming Process Using Modified Starches
Chen, L.; Peng, X.; **Huang, Y.**; Li, L.; Li, X. *Key Engineering Materials* **2008**. Vols. 368-372, 697-700.

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