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Colloidal crystallization of colloidal silica modified with ferrocenyl group-contained polymers in organic solvents

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Abstract

Surface modification of colloidal silica with ferrocenyl-grafted polymer and colloidal crystallization of the particles in organic solvent were studied. Poly(methyl methacrylate-*co*-vinylferrocene)-grafted silica never formed colloidal crystals in polar solvent, such as actone, acetonitrile, ethanol and *N*,*N*-dimethylformamide (DMF), while poly(methyl methacrylate-*co*-ferrocenyl acrylate)-grafted silica gave colloidal crystallization in DMF. The particles prepared by grafting of poly(*N*,*N*-dimethylacrylamide-*co*-vinylferrocene), with vinylferrocene (Vfc) mole fraction of 1/13 and 1/23, were observed to give the crystallization in ethanol and DMF over particle volume fraction of 0.058. Further, silica modified with copolymer of Vfc and *N*-vinyl-2-pyrrolidone, *N*-vinylcarbazole or *N*-isopropylacrylamide formed colloidal crystals in ethanol and DMF. Especially, poly(*N*-isopropylacrylamide-*co*-Vfc)-grafted silica, which was composed of the highest mole fraction of vinylferrocene, 1/3, afforded colloidal crystallization in ethanol over particle volume fraction of 0.053. Relatively high polar vinylferrocene copolymer grafting of silica resulted in colloidal polymerization in organic solvents.

Keywords: Colloidal crystals; Ferrocenyl group; Polymer grafting; Colloidal silica

1. Introduction

Recently, fabrication of 3D-particle arrayed structure is receiving great attention for application to photonic crystals or sensors, pioneered by Asher and co-workers [1,2], because inter-particle spaces are corresponding to visible light wavelength, which are convenient for practical devices. So far, there are many papers regarding fabrication of 3D-particle ordering materials derived from colloidal crystals [2–11]. Approaches to the fabrication by using colloidal crystals are classified by two categories; solidification of deposited and closed packed particles array [8,12–14] and of colloidal crystals formed in suspension through electrostatic repulsion between the particles [9,10,15–17], called hard and soft type crystals, respectively. Former one has an advantage for easy making large size of single crystal, but a disadvantage for exhibiting wide Bragg reflection peak due to direct reflecting particle size distribution. On the other hand, colloidal crystallization in soft system is a phenomenon in which monodisperse colloidal particles ordering in 3D-structure through electrostatic repulsion between particles in suspension, which has first reported in 1960s [18–21]. Since Bragg reflection peak of soft colloidal crystals is usually sharp and clear, challenging of photonic crystal fabrication from the crystals formed in suspension was carried out by solidification of colloidal crystals in hydrogels [2–11]. Furthermore, in soft system, it is relatively easy to control inter-space distance, which is expected to be fairly favorable for valid application for photonic devices, by changing volume fraction of particles in crystallization, in spite of polycrystalline formation.

Concerning colloidal crystallization in soft system, in many cases, monodiesperse colloidal silica, polystyrene or poly(methyl methacrylate) latexes are employed for colloidal particles, because of giving stable crystallites. Among them, colloidal silica usually afford stable colloidal crystals in aqueous solution due to negatively high surface charge. We have previously reported that monodisperse polymer-grafted silica forms the colloidal crystals in organic solvent, which is a polar and good solvent for the grafted polymer [22,23].

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We have also successively immobilized the colloidal crystals from polymer-grafted silica by radical polymerization into poly(methyl methacrylate) gels [16,17]. However, fabrication of photonic crystals from soft colloidal crystals of silica has major shortcomings stemming from original properties of silica, comparatively low refractive index and dielectric constant. In this respect, Ashrit and co-workers have fabricated photonic crystal of WO$_3$ by use of inverse colloidal crystals of polystyrene latex [24]. Also, Foulger and co-workers have investigated photonic properties of rhodamine B-incorporated colloidal crystals of poly(methyl methacrylate) [25]. In general, incorporation of heavy atoms to polymer leads to increasing refractive index and dielectric constant. In this study, the modification of colloidal silica with copolymer of vinylferrocene (Vfc) and vinyl monomer and colloidal crystallization in organic solvent were investigated.

2. Experimental

2.1. Materials

Colloidal silica, of 135 nm in diameter, was kindly gifted by Catalysts & Chemicals Co. Ltd., Japan. Methyl metharylate (MMA), Vfc, *N*-vinyl-2-pyrrolidone (VP), *N*,*N*-dimethylacrylamide (DMAAm), *N*-vinylcarbazole (VC) and *N*-isopropylacrylamide (NIPAAm) were purchased from Wako Pure Chemicals Co., Japan. Ferrocenymethanol was obtained from Tokyo Chemical Ind. Co., Japan.

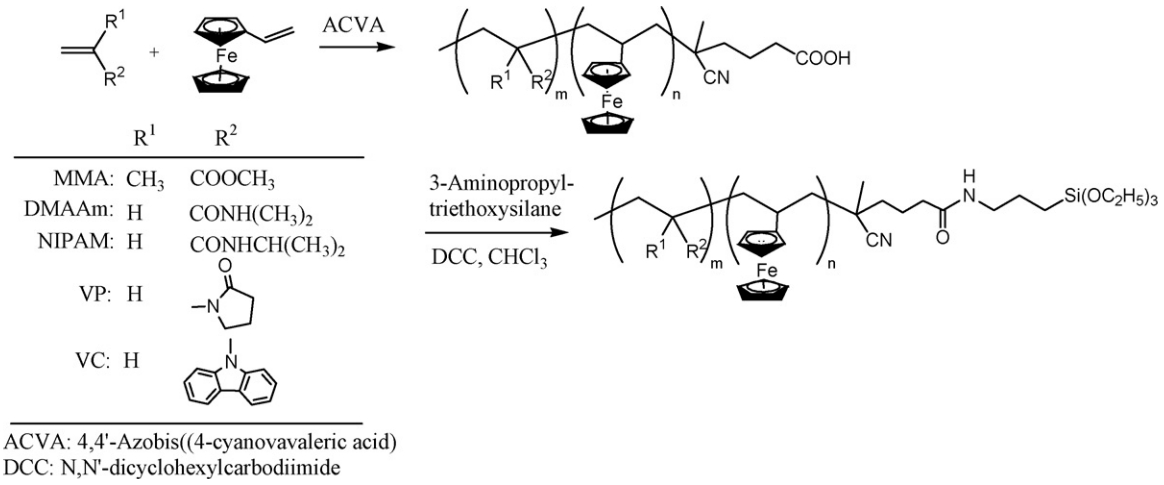
2.2. Measurements

Amounts of grafted polymer on silica were determined by thermogravimetrical weight reduce during elevating temperature from 200 to 800 °C after keeping at 200 °C for 30 min on TG-50 (Shimadzu, Kyoto, Japan). Number-average molecular weight polymer (M_n) was determined by gel permeation chromatography using THF eluent on TSK gel-3000H by calibration with polystyrene standard. The synthesized polymers were characterized by ^{1}H NMR spectroscopy on AVANCE 400 (Bruker, Germany). The reflection spectra were measured at 90° position from a cell surface by a multichannel spectral analyzer, PMA-11 (Hamamatsu Photonics Co., Hamamatsu, Japan), using a 150 W halogen lamp.

2.3. Synthesis of vinylferrocene copolymer silane

A typical run, shown in Scheme 1, is as follows. A mixture of 0.045 g vinylferrocene, 0.45 g MMA and 2.5 mg 4,4′-azobis(4-cyanovaleric acid) was put into a 25 cm^3 flask and was heated at 75 °C under nitrogen atmosphere for 8 h. The polymerization mixture was dissolved in 5 cm^3 tetrahydrofuran (THF) and then poly(MMA-*co*-Vfc) was precipitated by addition of 200 cm^3 diethyl ether; 0.30 g in yield. Resulting copolymer (0.30 g) and 10 mg *N*,*N*′-dicyclohexylcarbodiimide were dissolved in 20 cm^3 chloroform and the mixture was stirred at 0 °C for 1 h. After addition of 0.01 cm^3 3-aminopropyltriethoxysilane, the mixture was stirred at 4 °C for 4 h. After filtration to remove urea byproduct, evaporation of chloroform gave triethyoxysilyl-capped copolymer, poly(MMA-*co*-Vfc)-Si(OEt)$_3$ of 0.27 g. ^{1}H NMR (δ (CDCl$_3$)) for poly(MMA-*co*-Vfc)-Si(OEt)$_3$; 0.6 (Si–CH_2CH$_2$), 1.0 (SiOCH$_2$CH_3), 3.2 (NH–CH_2), 3.6–3.7 (O–CH_3), 3.8 (Si–O–CH_2CH$_3$), 4.0–4.2 (ferrocenyl) ppm. Mole fractions of vinylferrocenyl group in copolymer were determined by ^{1}H NMR spectroscopy.

Other triethyoxysilyl-capped copolymers, poly(DMAAm-*co*-Vfc)-Si(OEt)$_3$, poly(VP-*co*-Vfc)-Si(OEt)$_3$, poly(NIPAAm-*co*-Vfc)-Si(OEt)$_3$ and poly(VC-*co*-Vfc)-Si(OEt)$_3$ were synthesized by the same manner as described above. ^{1}H NMR (δ (CDCl$_3$)) for poly(DMAAm-*co*-Vfc)-Si(OEt)$_3$: 0.6 (Si–CH_2 CH$_2$), 1.0 (SiOCH$_2$CH_3), 2.7–3.2 (N(CH_3)$_3$), 3.2 (NH–CH_2), 3.8 (Si–O–CH_2CH$_3$), 4.0–4.2 (ferrocenyl) ppm; for poly(VP-*co*-Vfc)-Si(OEt)$_3$: 0.6 (Si–CH_2CH$_2$), 1.0 (SiOCH$_2$CH_3), 2.2 (N(C=O)CH$_2$), 3.2 (NH–CH_2), 3.8 (Si–O–CH_2CH$_3$), 4.0–4.2 (ferrocenyl) ppm; for poly(NIPAAm-*co*-VCfc)-Si(OEt)$_3$: 0.6 (Si–CH_2CH$_2$), 1.0–1.2 (SiOCH$_2$CH_3, NH–CH(CH_3)$_2$), 3.2 (NH–CH_2), 3.8 (NH–CH(CH$_3$)$_2$), 4.0–4.2 (ferrocenyl) ppm; for poly(VC-*co*-Vfc)-Si(OEt)$_3$: 0.6 (Si–CH_2CH$_2$), 1.0 (SiOCH$_2$CH_3), 3.2 (NH–CH_2), 3.8 (Si–O–CH_2CH$_3$), 4.0–4.2 (ferrocenyl), 6.0–8.0 (carbazolyl) ppm.



Scheme 1. Synthesis of vinylferrocene copolymer silane.