Thermally Responded Self-Aggregation of Ultrafine Particles Prepared by Modification of Monodisperse Colloidal Silica with Iron(II)-Bipyridyl Branched Polymer

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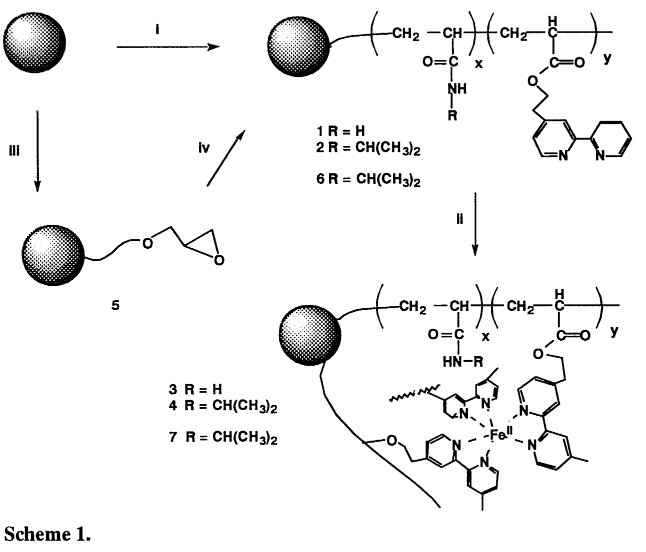
Monodisperse colloidal silica particles modified by Fe(II)-bipyridyl complex-branched, *N*-isopropylacrylamide-contained polymer showed self-aggregation via the ligand exchange among the particles in response to temperature elevation from 15 °C to 35 °C.

Fabrication of physical and chemical properties on ultrafine particles is promising to lead to new developments in materials chemistry.[1-3] The ultafine particles in a very narrow size distribution, i.e. monodispersion, are recently supplied in a state of suspension in aqueous or alcoholic solution. An arbitrary control of surface polarity and/or potential of colloidal particles by chemical modification could give a new functionality. If the aggregation or agglutination of the particles could be thermodynamically or kinetically controlled via the interaction among the particles, it would be possible to lead to a self-assembling system triggered by a temperature change.

The metal ions such as iron(II), cobalt(II), ruthenium(III), and copper(II) are known to have large stability constants with bipyridyl derivatives. In some metal-bipyridyl complex-anchored polymers, intramolecular coordination was changed to the entropically favorable intermolecular coordinations by the rapid ligand exchange reaction between the polymeric ligands.[4] Thus, the particle aggregation or agglutination could be successfully controlled through the intermolecular ligand exchange among the particles by thermodynamic stability of the complex on the surface. In this paper, the temperature response in self-aggregation of the polymer-modified colloidal silica particles, prepared by the procedure shown in Scheme 1, via the ligand exchange reaction of Fe(II)-bipyridyl complex between the particles was described.



Scheme 1.
i) P(AAm-Bpy)-Si(OMe)$_3$ or P(NIPAM-Bpy)-Si(OMe)$_3$, dil. NH$_4$OH, DME, 80 °C, 12h. ii) aq. Fe(SO$_4$), 25 °C, 12 h. iii) (3-Glycidyloxypropyl)trimethoxysilane, DME, 80 °C, 12 h. iv) aq. Ce(NO$_3$)$_4$, NIPAM, Bpy-monomer, 25 °C, 3h.

Colloidal silica, of 120 nm in diameter, suspended in ethanol (SiO$_2$, 23 wt%) was employed. The trimethoxysilyl-terminated copolymer coupling agents (P(AAm-Bpy)-Si(OME)$_3$ or (P(NIPAM-Bpy)-Si(OME)$_3$) of 2-{4-(4'-methyl-2,2'-bipyridyl)}ethyl acrylate (Bpy),[5] and acrylamide (AAm) or *N*-isopropylacrylamide (NIPAM) were prepared by AIBN initiator in the presence of (3-mercaptopropyl)trimethoxysilane in benzene at 75 °C.[6] The molecular weight and composition of each monomer in each polymeric coupler were shown in Table 1. The fraction of Bpy monomer in P(AAm-Bpy)-Si(OMe)$_3$ and P(NIPAM-Bpy)-Si(OMe)$_3$ was of less than 0.10, in spite of increasing of Bpy monomer in the polymerization. Probably, steric bulkiness of Bpy monomer prevents the increase of the fraction. Composites **1** and **2** were prepared by the reaction of the polymeric couplers with colloidal silica under refluxing the suspension containing the silica (1.15 g) and the coupler in 15 cm^3 DME in the presence of 0.1 cm^3 diluted aqueous ammonia (5 vol%).[7] Successive coordination of Fe(II) to composite **1** and **2** was conducted by immersing of the particles in 5 cm^3 FeSO$_4$ (7.54 x 10^{-1} mmol dm^{-3}) at 25 °C for 12 h. The bound polymers on composites **3** and **4** were lower than 50 mg g^{-1}, which was determined by weight loss during temperature elevation from 100 °C to 800 °C by a thermogravimetric analysis. Coordinations of Fe(II) on the composites were of less than 5 x 10^{-1} μmol g^{-1}, respectively.[8]

The composite **3** and **4** were dispersible in aqueous solution at 15°C, and suspensions of both composite particles showed monodispersion. The absorbance, i.e. turbidity, of these aqueous suspensions (0.1 wt%) at 500 nm was constant at 15°C over 24 h. On elevating temperature from 15°C to 35°C, the absorption of the suspension of composite **4** slightly and gradually decreased, as shown in Figure 1. The absorbance decrease with time indicated gradual and partial aggregation of the composite **4**. A dynamic light scattering analysis of the suspension also showed the formation of large particles in the range of 1.2 μm to 1.4 μm at 35°C. In this case, the aggregated particles was reversibly dispersed in aqueous solution on lowering temperature to 15°C. However, the absorbances of the suspension of the composite **3** at 15°C were unchanged after the temperature elevation to 35°C. These results indicated that NIPAM moiety played an important role in the aggregation of the composite **2** caused by temperature elevation. Further, it was also observed that the PNIPAM-modified particles did not clearly show the absorbance decrease on

Table 1. Characteristics of polymeric coupling agent and composite **3** and **4**

Coupler	10^{-3} x M_n	y/(x + y)	Composite **3** or **4** Bound polym. mg g^{-1}	Composite **3** or **4** Coord. Fe^{2+} μmol g^{-1}
P(AAm-Bpy)-Si(OMe)$_3$	6	0.08	28.6	0.47
P(NIPAM-Bpy)-Si(OMe)$_3$	4	0.10	11.4	<10^{-2}
	9	0.03	46.5	<10^{-2}

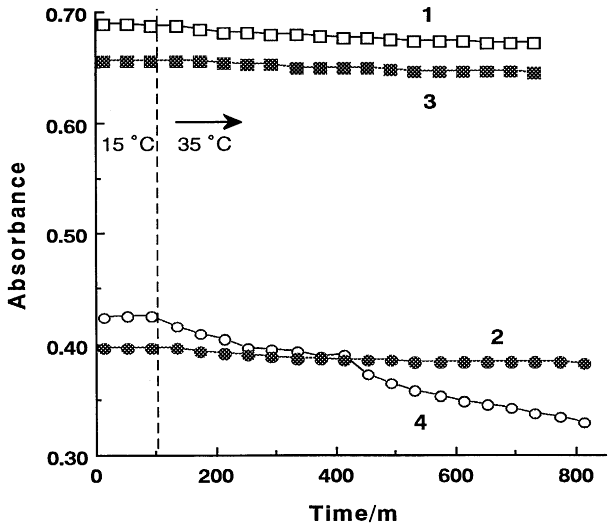


Figure 1. Absorbance changes of the suspension (0.1 wt%) of composite **1**, **2**, **3** and **4** at 500 nm with time.

elevating temperature to 35 °C.[9] Poly(*N*-isopropylacrylamide) (PNIPAM) in aqueous solution is known to have the lower critical solution temperature at 34 °C, and then the polymer was desolvated to lose coordinated water molecules and to shrink over 34 °C. Therefore, this phenomenon of composite **4** probably can be explained as follows. At 15°C the PNIPAM component of the copolymer bound to the silica surface is hydrophilic and then at 35°C the polyamide become hydrophobic to shrink in the aqueous solution. Successively, the elevation of temperature from 15°C to 35°C makes the Fe(II)-Bpy complexes come to the surface of the polymer layer on the composite and promotes the particle-aggregation via the ligand exchange to form thermodynamically favorable Fe(II)-Bpy complex among the particles.

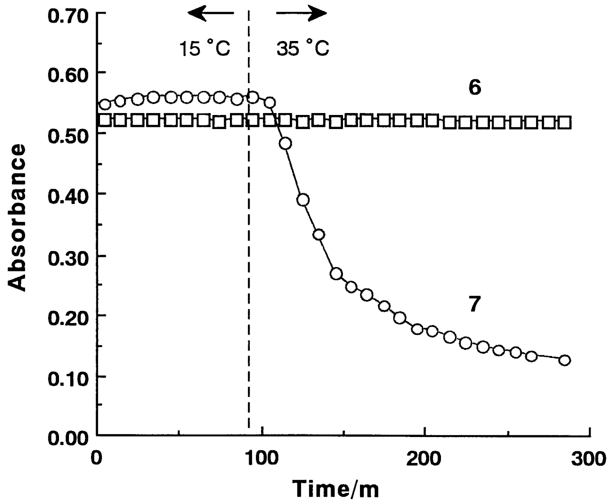


Figure 2. Absorbance changes of the suspension (0.1 wt%) of composite **6** and **7** at 500 nm with time.

Although the composite **4** showed the temperature response in the self-aggregation, the extent of the aggregation was low, because of low Fe(II)-Bpy complex concentration on the particle surface. Hence, we have conducted the graft-copolymerization of NIPAM and Bpy-monomer onto the composite **5**, which was prepared by the reaction of (3-glycidyloxypropyl)trimethoxy-silane with colloidal silica by the same manner as that of composite **1** or **2**, employing the redox radical polymerization with Ce(IV) nitrate in order to increase the Bpy moiety in the grafted polymer on the particle surface. The copolymerization of 0.3 g NIPAM and 0.08 g Bpy-monomer employing 0.1 cm^3 Ce(NO$_3$)$_3$ solution (1 mmol dm^{-3}) in H$_2$O/MeOH (5/5 cm^3) cosolvent at a room temperature for 3 h gave the composite **6** grafted the copolymer of 72.0 mg g^{-1}. The Coordination of Fe(II) on the polymer-grafted particles afforded the Fe(II)-Bpy complex concentration of 2.2 x 10^{-5} mol g^{-1} and the fractions (y/(x+y)) of Bpy monomer in the copolymer were 0.13.[10] Hence, the radical copolymerization resulted in the increasing of the Bpy fraction and Fe(II) coordination. The suspension of the Fe(II)-coordinated composite (**7**) particles showed quick and sharp decrease of the absorbance, from 0.55 to 0.15, at 500 nm in 180 min after the temperature change from 15°C to 35°C, as shown in Figure 2. This result indicated that the particle-aggregation took place to make large masses enough to precipitate after the temperature elevation. Unfortunatelly, the precipitate possibly consisted of randomly aggregated particles, or nonclose-packed particles, because the brilliance due to Rayleigh scattering was not observed in the aggregation phase. On the contrary, however, lowering temperature from 35°C to 15°C never made the aggregated particles disperse in the aqueous solution even under ultrasonic irradiation. Presumably, the entropy increase based on expanding of the surface polymer through hydration of NIPAM moiety at 15°C is not high enough to promote the reverse ligand exchange reaction, i.e. conversion to the intramolecular coordination. On conclusion, it is necessary for the composite particles to have a critical surface concentration of NIPAM moiety and Fe(II)-Bpy complex on the particles for thermally responded self-aggregation.

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References and notes

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8 Coordinated Fe(II) was estimated by the subtraction of Fe(II) amount in the supernatant by a centrifugal separation from dosed Fe(II) amount. The Fe(II) concentration in the solution was determined by the spectrophotometrical absorbance of Fe(II)-tris(bipyridyl) complex at 522 nm (ε=8000).
9 The PNIPAM-modified compsite particles was preprared by the same method as that of composite 4 in the absence of Bpy monomer.
10 The Bpy fraction in the grafted copolymer was estimated on the assumption that the Fe(II)-tridentate bipyridyl complex was formed.