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pH- and Temperature-induced Crystallization of Aqueous Dispersions of Positively Charged Poly(styrene-*co*-2-vinylpyridine) Particles

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We report that aqueous dispersions of cationic poly(styrene-*co*-2-vinylpyridine) particles exhibit pH- and temperature-induced crystallization. Thus far, these crystallization methods have been examined only for negatively charged colloids. The present findings will be useful for the fabrication of positively charged colloidal crystalline materials.

Charged colloidal particles dispersed in an aqueous medium form colloidal crystal structures when the electrostatic interaction between the particles is sufficiently strong. In the crystal state, the particles are regularly arranged in 3D arrays with body-centered cubic (BCC) or face-centered cubic (FCC) lattice symmetry.[1] Thus far, the crystallization of charged colloids has been a model for studying phase transitions in general.[2] In addition, colloidal crystals have been expected to be useful as novel optical materials such as photonic crystals.[3] To date, various ingenious crystallization methods have been reported for fabricating high-quality colloidal crystals.

Aqueous dispersions of charged colloidal silica and polystyrene (PS) particles have frequently been used as charged colloid samples. Both of them have anionic dissociable groups on their surfaces. The silica particles have weakly acidic silanol (Si–OH) groups, while the PS particles usually have strong acid groups that result from an anionic polymerization initiator and/or copolymerized acidic monomers. Therefore, most studies on charged colloidal crystallization have been performed using negatively charged colloids.

On the other hand, positively charged particles have been receiving increasing attention because of their ability to adsorb anionic polymers, e.g., DNA. Zhu et al. have reported the synthesis and crystallization of an aqueous dispersion of cationic poly[styrene-*co*-(vinylbenzyl)trimethylammonium chloride] particles.[4] Therefore, it is worthwhile to study methods of fabricating positively charged colloidal crystals.

It has been reported that negatively charged colloidal silica exhibits pH-induced crystallization[5] upon the addition of bases such as sodium hydroxide (NaOH) and pyridine (Py). This is because of an increase in the degree of dissociation of the silanol groups with increasing pH, through which the charge numbers Z of the silica particles become large enough for them to crystallize. In addition, we note that the degree of dissociation of Py significantly varies with changing temperature T. Therefore, silica colloids in the presence of Py exhibit pH-induced crystallization with increasing T.[6] In this letter, we examine pH- and temperature-induced crystallization of positively charged colloids.

We synthesized positively charged particles using surfactant-free emulsion polymerization as follows. Styrene (monomer), 2-vinylpyridine (2VP) (comonomer), and divinylbenzene (DVB) (crosslinker) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and they were used after washing with 1 M aqueous NaOH to remove polymerization inhibitor. Styrene (20 mL), 2VP (1.4 mmol), and DVB (1 mL) were dissolved in a mixture of water (210 mL) and methanol (5 mL) in a three-necked flask. The solution was then stirred for 30 min at 300 rpm while being purged by argon gas to remove dissolved oxygen. Then, 2,2′-azobis(2-aminopropane) dihydrochloride (AIBA, cationic initiator, 0.37 mmol) was added to the reaction solution, and the solution was further stirred at 80 °C under an argon atmosphere. After 7 h, poly(styrene-*co*-2-vinylpyridine) copolymer (hereafter designated as p(St-*co*-2VP)) particles were obtained. They were purified by dialysis and ultrafiltration, as described earlier.[7] The diameter of the particles was determined to be 193 nm by applying dynamic laser scattering (FDLS-3000 system, Otsuka Electronics Co., Ltd., Osaka, Japan).

The ζ potential of the particles determined by microscopic electrophoresis (ZC-3000U, Microtec Co., Ltd., Chiba, Japan) was +25.0 mV. That is, the p(St-*co*-2VP) particles obtained here were confirmed to bear positive charges. These charges should have originated from pyridyl groups associated with the 2VP and ammonium groups from AIBA, both of which are weak bases. Figure 1 shows the electrical conductivity (κ) titration curve for the p(St-*co*-2VP) dispersion (the particle volume concentration, $\phi = 0.018$, 15 mL) obtained using hydrochloric acid (HCl). In the absence of HCl, the purified p(St-*co*-2VP) particles had OH^- ions as counterions. The Z value determined from the κ value, estimated from the molar conductivity of the OH^- ions (198.3 S cm mol^{-1}), was 669. As the molar concentration of HCl ([HCl]) increased, the κ value also increased. This is attributable to enhanced dissociation of the pyridyl and ammonium groups due to partial neutralization with HCl. That is, the Z value increased with the HCl concentration.

As seen in Figure 1, the neutralization point is at a HCl concentration of about 90 μM. It should be noted that the

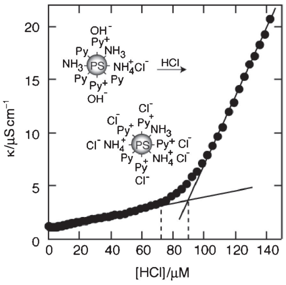

Figure 1. Electrical conductivity titration curve of an aqueous dispersion of p(St-*co*-2VP) particles with HCl. The inset shows a schematic illustration of neutralization of the surface charge of p(St-*co*-2VP) by addition of HCl.

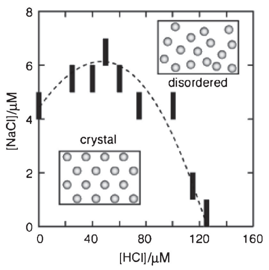

Figure 2. Crystallization phase diagram of the p(St-*co*-2VP) colloid defined by the concentrations of HCl and NaCl ($\phi = 0.018$, $T = 25$ °C).

titration curve began to deviate from a linear relation at a HCl concentration of approximately 70 μM. This indicates that H^+ and Cl^- ions were present in excess in the aqueous medium at a HCl concentration greater than 70 μM.

Based on the titration curve, we examined the pH-induced crystallization of the p(St-*co*-2VP) colloids. Figure 2 shows the phase diagram defined by the HCl and NaCl concentrations. The observed phase boundaries are shown by rectangular symbols. The regions with a NaCl concentration lower and higher than that at the phase boundary are the crystal and disordered (noncrystal) regions, respectively. As the HCl concentration increased, the crystal region widened because of the increase in Z. Further addition of HCl ([HCl] > about 60 μM), however, prevents the crystallization. This is attributable to an increase in the ionic strength of the medium resulting from the excess H^+ and Cl^- ions present (Figure 1). For HCl concentrations greater than about 130 μM, the crystallization was not observed. Thus, we could control the crystallization of the p(St-*co*-2PV) particles by changing the HCl concentration.

We then examined temperature-induced crystallization. Recently, we reported that aqueous dispersions of negatively charged PS particles having high charge crystallize upon cooling, while low-charged PS colloids crystallize *upon heating*.[8] These behaviors were explainable in terms of a decrease in the permittivity of water, which increases the electrostatic interparticle interactions, and an increase in the thermal motion of the particles.[8] In these experiments, the Z values did not vary greatly with T. The Z of p(St-*co*-2PV) particles determined from the electrical conductivity was considerably large ($Z = 699$ at $T = 25$ °C) and increased slightly with increasing T (linear fit: $Z(T) = 562.7 + 3.6T$), presumably because of enhanced dissociation of the pyridyl groups upon heating. The large value of Z favors crystallization at low T, while an increase in Z should instead lead to crystallization upon heating. The crystallization of the p(St-*co*-2PV) colloids should be governed by these conflicting effects.

Figure 3 shows reflectance spectra of the p(St-*co*-2VP) colloid ($\phi = 0.018$, [NaCl] = 2 μM) at various values of T. The sharp Bragg peaks due to the crystal structures were observed below $T = 45$ °C, and they disappeared upon heating to $T = 50$ °C or higher. Thus, the colloids exhibited crystallization upon cooling. This indicates that augmented thermal motion at high T had the most significant effect on the phase transition of the present colloids. The crystallization behavior was thermoreversible, that is, the melted colloid froze to form a crystal structure upon cooling below the melting temperature.

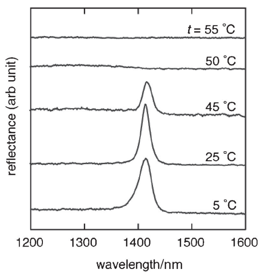

Figure 3. Temperature dependence of reflection spectra of the p(St-*co*-2VP) colloid ($\phi = 0.02$, [NaCl] = 2 μM).

We note that the Bragg wavelength λ_B calculated by assuming for diffractions from (110) planes of BCC lattice is given by

$$\lambda_B = 2\sqrt{2}n_r\sqrt[3]{\frac{\pi}{3\phi}}a_p$$

where n_r is the refractive index of the colloids and a_p is the particle radius. The λ_B value calculated by assuming $n_r = \phi n_s + (1 - \phi)n_w$ (n_s and n_w are the refractive indexes of PS and water, respectively) was 1412 nm, which shows close agreement with the observations (≈1410 nm). The calculated Bragg wavelength for FCC (111) plane was 1452 nm. Thus we assumed that the crystal had the BCC structure.

In the present study, we demonstrated pH- and temperature-induced crystallizations of positively charged colloids. For negatively charged colloids, we have already obtained centimeter-sized crystals by unidirectional crystallization under pH[9a] and temperature gradients.[9b] The present findings will be useful for the fabrication of positively charged colloidal crystalline materials.

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