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Oscillating Microgels

Self-Flocculating/Self-Dispersing Oscillation of Microgels**

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Stimulus-sensitive hydrogels undergo swelling/deswelling transitions as a result of a change in temperature,[1] pH,[2] ionic strength,[3] solvent composition,[4] light,[5] presence of biomolecules,[6,7] and so on. One of the most widely studied stimulus-sensitive hydrogels is composed of poly(*N*-isopropylacrylamide), pNIPAm, which is a thermosensitive polymer with a lower critical solution temperature (LCST) of about 31 °C in pure water.[8,9] Hydrogels of PNIPAm have a volume phase-transition temperature (VPTT) around the LCST of pNIPAm, and various functional groups have been added by copolymerization to make the hydrogel multiresponsive. Compared to macro- or bulk gels, microgels additionally have the properties of colloidal dispersions.[10,11] Thus, many interesting applications such as drug carriers,[12,13] microreactors,[14–16] emulsifiers,[17,18] photonic crystals,[19–22] and microlenses[7,23] have already been reported. Although these microgel systems are usually called smart or intelligent due to their sensitivity to stimuli, their properties change only when on/off switching of external stimuli occurs.

Herein we report on self-oscillating microgels, that is, they swell/deswell periodically without any external stimulus. We designed (4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine)ruthenium(II) bis(hexafluorophosphate), denoted $Ru(bpy)_3$ monomer, for the preparation of pNIPAm copolymer microgels (Figure 1). The $Ru(bpy)_3$ moiety was selected as a catalyst for the Belousov–Zhabotinsky (BZ) reaction, which generates rhythmical redox changes from the oxidized Ru^{III} state to the reduced Ru^{II} state[24] (see the Supporting Information). Compared to microgels in the reduced Ru^{II} state, those in the oxidized Ru^{III} state have a higher VPTT because the polymers composing the microgels become more hydrophilic than those in the reduced Ru^{II} state, which was confirmed by our previous experiments with the bulk hydrogel[25] and the linear polymer chain.[26] This means that the chemical oscillation of the $Ru(bpy)_3$ moiety can be converted to strong mechanical (swelling/deswelling) oscillation at a constant temperature.

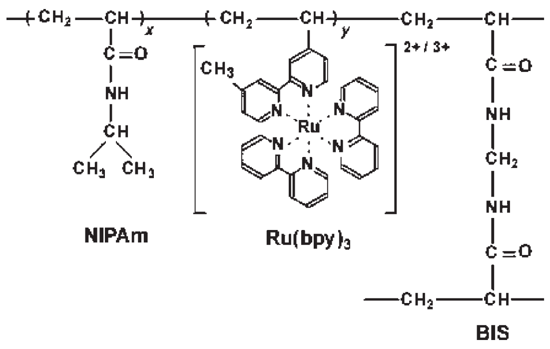

Figure 1. Chemical structure of the microgel.

To obtain the microgels, NIPAm, $Ru(bpy)_3$ monomer, and *N*,*N*′-methylenebisacrylamide (BIS) cross-linker were copolymerized by surfactant-free aqueous precipitation polymerization[11] at 70 °C. Before the self-oscillation study, we checked the temperature dependence of the hydrodynamic diameter of the obtained microgels as dispersions in NaCl solutions of three different concentrations (Figure 2), because the BZ reaction only occurs at high salt concentrations (greater than 0.1 M).[25b] Note that the $Ru(bpy)_3$ moieties were fixed in the reduced Ru^{II} state here. At low NaCl concentration (10 mM), the microgels were colloidally stable both below and above the VPTT (15–55 °C). On the other hand, at higher NaCl concentrations (100 and 500 mM), the microgels flocculated above the VPTT, where the microgels were in the deswollen state, because interparticle electrostatic repulsion is greatly reduced.[27] However, in contrast to hard particles

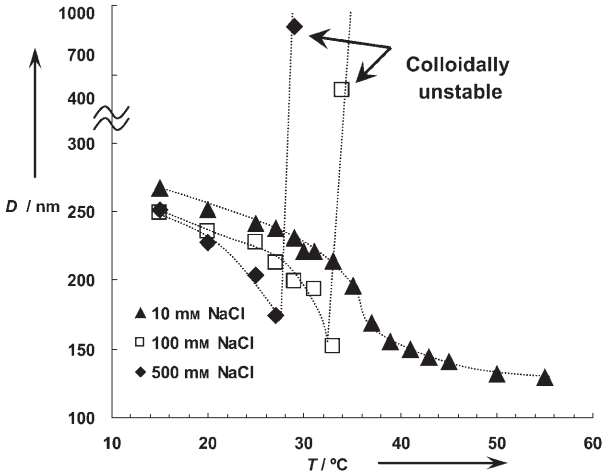

Figure 2. Deswelling curves for 0.005-wt % microgel dispersions in NaCl solutions of three different concentrations, as measured by dynamic light scattering. The microgels were flocculated at 34 °C in 100 mM NaCl solution and at 29 °C in 500 mM NaCl solution.

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such as polystyrene and silica particles, the flocculated microgels could be redispersed when cooled quickly below the VPTT.

We also checked hydrodynamic diameters as a function of temperature for the reduced Ru^{II} and oxidized Ru^{III} states at high salt concentrations (Figure 3). In both cases, the microgels flocculated when heated above the VPTT because the interparticle electrostatic repulsion is extremely low at high salt concentration (ca. 0.3 M). The microgels in the oxidized Ru^{III} state flocculated at slightly higher temperature (34 °C) than those in the reduced Ru^{II} state (32 °C). This temperature shift is due to increased hydrophilicity of the polymer because of higher charge density on the copolymer chains.[25] As a result, microgels in the oxidized Ru^{III} state have larger hydrodynamic diameters at any temperature, because pNIPAm-based microgels show continuous changes in diameter below the VPTT.[10] These deviations in hydrodynamic diameter and different colloidal stabilities at the same temperature could result in self-oscillation of the microgels.

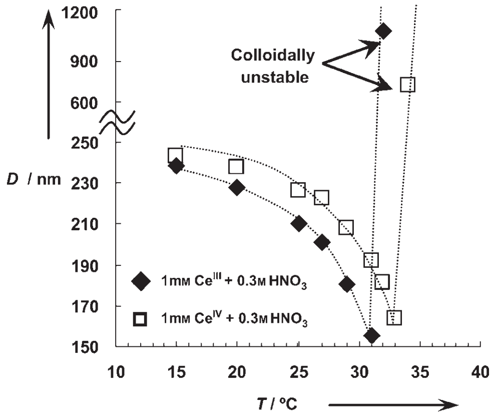

Figure 3. Deswelling curves for the microgels under the different conditions, as measured by dynamic light scattering: the reduced state Ru^{II} in 1 mM Ce^{III} and 0.3 M HNO_3 solution, and the oxidized state Ru^{III} in 1 mM Ce^{IV} and 0.3 M HNO_3 solution. The dispersion concentration was 0.005 wt % in both cases.

Next, we carried out the BZ reaction using the microgels. Malonic acid (MA), sodium bromate ($NaBrO_3$), and nitric acid (HNO_3) were used as substrates for the BZ reaction at a fixed concentration. Figure 4 shows the oscillation profiles of transmittance for the microgel dispersions. To observe transmittance changes originating from periodic swelling/deswelling of the microgels, an isosbestic point (570 nm) of the Ru^{II} and Ru^{III} states was chosen for the measurement (see the Supporting Information). In all experiments, self-oscillations were observed after an induction period, which is a typical phenomenon of the BZ reaction. First, temperature dependence of the oscillation was checked (Figure 4a). At low temperatures (20–26.5 °C), on raising the temperature, the amplitude of the oscillation became larger. The increase in amplitude is due to increased deviation of the hydrodynamic diameter between the Ru^{II} and Ru^{III} states, as shown in Figure 3.

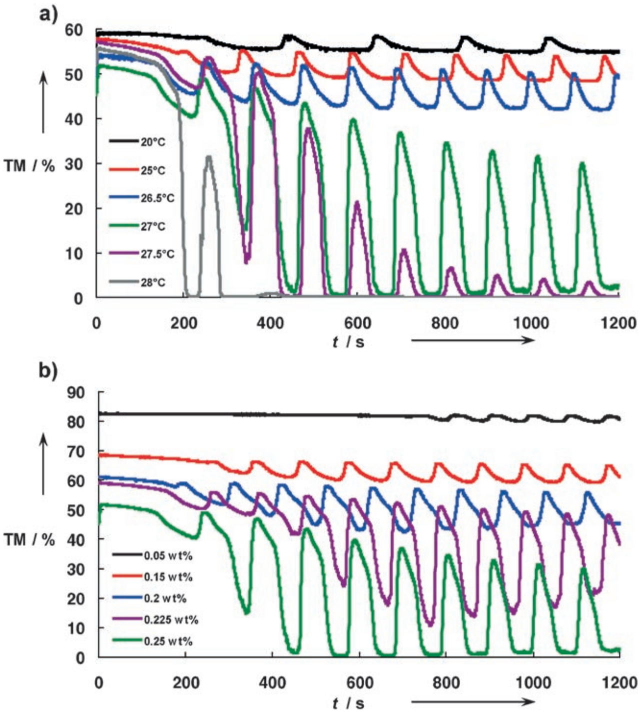

Figure 4. Self-oscillating profiles of optical transmittance (TM) for the microgel dispersions. The microgels were dispersed in aqueous solutions containing MA (62.5 mM), $NaBrO_3$ (84 mM), and HNO_3 (0.3 M). Microgel concentration was 0.25 wt %. a) Profiles measured at different temperatures. b) Profiles measured at different microgel dispersion concentrations at 27 °C.

Furthermore, a remarkable change in waveform was observed between 26.5 and 27 °C. Then the amplitude of the oscillations dramatically decreased at 27.5 °C, and finally the periodic transmittance changes could no longer be observed at 28 °C. Taking the results obtained in Figure 3 into consideration, the sudden change in oscillation waveform should be related to the difference in colloidal stability between the Ru^{II} and Ru^{III} states. Here, the microgels should be flocculated due to lack of electrostatic repulsion at a high salt concentration when the microgels were deswollen. The temperature at which the colloidal stability changes in Figure 3 is different from that of the remarkable change in waveform, because colloidal stability increases with decreasing ionic strength and dispersion concentration.[27] In this system, because precise adjustment of ionic strength is very difficult,[28] we checked the influence of dispersion concentration on the oscillations at 27 °C, where the remarkable change in waveform was observed in Figure 4a. As can be seen clearly in Figure 4b, the waveform of the oscillation is related to the dispersion concentration: The remarkable change in waveform was only observed at higher dispersion concentrations (greater than 0.225 wt %).

Figure 5 shows an explanation for the two different oscillations around the VPTT for two representative waveforms observed in Figure 4a. The BZ reaction is understood in terms of the Field–Körös–Noyes (FKN) mechanism,[29] according to which it can be divided into three main processes: consumption of Br^- ions (process A), autocatalytic

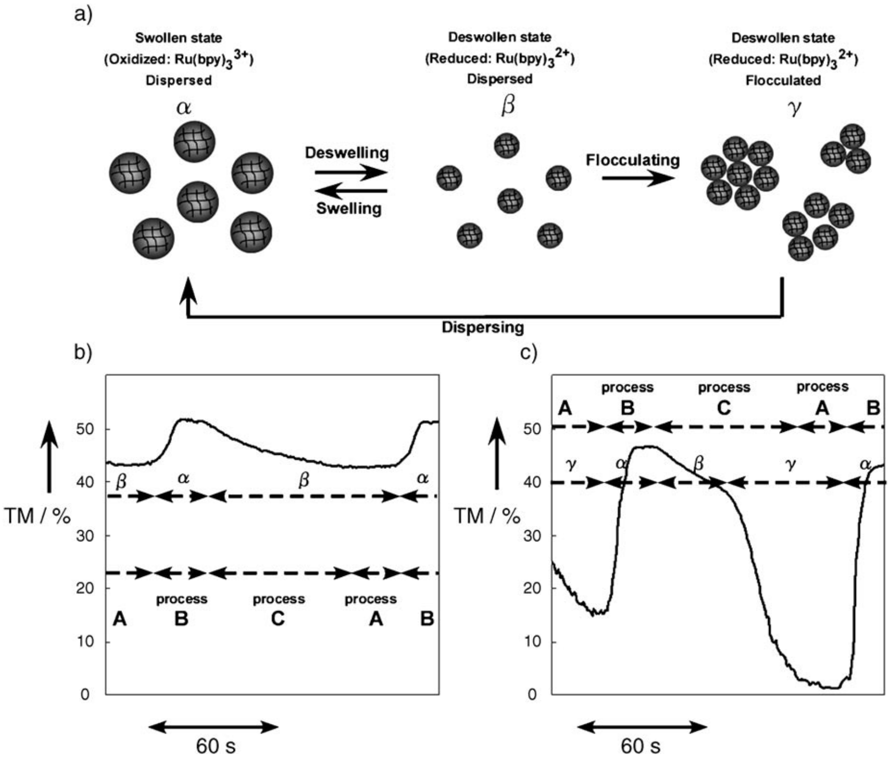

Figure 5. a) Self-oscillation of microgels around the phase-transition temperature. The states of the microgels (α–γ) correspond to those shown in (b) and (c). b) Waveform observed at 26.5 °C in Figure 4 a. c) Waveform observed at 27 °C in Figure 4 a. Division of processes A, B, and C in the waveform is based on a typical simulation of the Field–Körös–Noyes (FKN) model of the BZ reaction.[25b]

formation of $HBrO_2$ (process B), and formation of Br^- ions (process C). Roughly speaking, the $Ru(bpy)_3$ complexes are oxidized in process B, which corresponds to state α of the microgels, as shown in Figure 5 a. After process B, process C (reduction of the $Ru(bpy)_3$ complexes) starts, which corresponds to the region in which transmittance gradually decreases. In this region, the microgels gradually deswell to form the β state, as shown in Figure 5 a. In particular, a remarkable decrease in transmittance was observed during process C (Figure 5 c) when the microgels in the reduced Ru^{II} state were not colloidally stable. In this region, the microgels are flocculated (γ state).

After process C, process A, during which the $Ru(bpy)_3$ complex is in a steady state of reduced Ru^{II}, starts. During process A, the microgel flocs became larger. After process A, process B, which leads to the oxidized Ru^{III} state, starts again. In the system shown in Figure 5 c, the microgel aggregates became colloidally stable because they did not reside in a deep potential minimum,[27] which can be confirmed by recovery of the transmittance from 0 to about 40 %.

We also checked the oscillation period P_{osc} below and above the VPTT. Here the oscillation frequency F_{osc} ($F_{osc} = 1/P_{osc}$) was used for analysis. In general, the oscillation frequency of the BZ reaction tends to increase as the temperature increases, in accordance with the Arrhenius equation.[30] In this study, this tendency was observed below the VPTT (ca. 26.5 °C), as confirmed by a linear plot (Figure 6). On the other hand, the oscillation frequency decreases above the VPTT (27–28 °C), and the corresponding plots deviated from the Arrhenius equation. These deviations may be related to the difficulty of the reactants' diffusing into the microgel aggregates, because each microgel should be highly deswollen when the microgels flocculate (i.e., in the γ state shown in Figure 5).

In conclusion, we have synthesized self-oscillating microgels by introducing the catalyst for the BZ reaction into a cross-linked copolymer microgel. In this microgel system, the chemical energy of the BZ reaction is converted into periodic swelling/deswelling oscillations, which are detected by changes in optical transmittance. The amplitude of oscillation can be easily controlled by adjusting the temperature and the dispersion concentration. In particular, self-flocculating/self-dispersing oscillation of the microgels was observed around the phase-transition temperature, with a remarkable change in optical transmittance. We believe that the self-oscillating property makes microgels more attractive for future developments such as microgel assembly, drug/gene-controlled release, and optical and rheological applications.

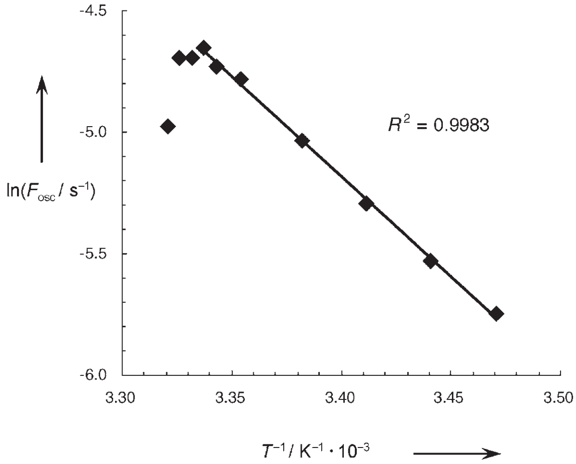

Figure 6. Arrhenius plot of the self-oscillation frequency F_{osc}.

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