Characterization of Autonomously Oscillating Viscosity Induced by Swelling/Deswelling Oscillation of the Microgels

Hajime Taniguchi,[†] **Daisuke Suzuki,**[*,‡] **and Ryo Yoshida**[*,†,§]

Department of Materials Engineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, International Young Researchers Empowerment Center, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan, and PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama, Japan

We report on autonomously oscillating viscosity in microgel dispersions induced by swelling/deswelling oscillations of the microgels. The microgels are composed of poly(*N*-isopropylacrylamide) in which ruthenium tris(2,2′-bipyridine), (Ru(bpy)$_3$), a catalyst for the Belousov−Zhabotinsky (BZ) reaction, is covalently bonded to the polymer chain. At first, we measured hydrodynamic diameters of the microgels under the oxidized and reduced ruthenium states by dynamic light scattering. Then, measurements of viscosity in microgel dispersions under various microgel concentrations, ionic strengths, and temperatures were investigated. Next, the BZ reaction was carried out to measure the autonomously oscillating viscosity in the dispersions. In this study, the effect of the concentration of microgels, the concentration of the substrates for the BZ reaction, and the amount of Ru(bpy)$_3$ immobilized in microgels were investigated to authenticate how swelling/deswelling oscillations of the microgels were linked to the viscosity oscillations.

Introduction

Microgels are spherical, cross-linked polymeric networks swollen by a good solvent. Recently, microgels composed of stimulus-responsive polymers have attracted much attention due to their possible applications, including drug delivery,[1] microreactors,[2−4] chemical/biological separations,[5] emulsifiers,[6,7] photonic crystals,[8−11] and microlenses.[12] Physicochemical properties of these stimulus-responsive microgels are affected by temperature, pH, ionic strength, presence of biomolecules, and applied external fields.[13] One of the most widely studied stimulus-responsive microgels is composed of poly(*N*-isopropylacrylamide), pNIPAm, which is a temperature-responsive polymer with a lower critical solution temperature (LCST) of 31 °C in pure water.[13,14] PNIPAm-based microgels have a volume phase transition temperature (VPTT) around the LCST of pNIPAm, and various functional groups have been incorporated by copolymerization or modification after polymerization in order to make the microgel multiresponsive.

Our group continued the study of self-oscillating gels.[15] In contrast to the simple stimulus-responsive gels as abovementioned, self-oscillating gels undergo a periodical swelling/deswelling oscillation without any external stimulus. The gels contain the chemical network of the Belousov−Zhabotinsky (BZ) reaction;[16] ruthenium tris(2,2′-bipyridine), Ru(bpy)$_3$, which is a catalyst for the BZ reaction, was immobilized into crosslinked pNIPAm hydrogels. The BZ reaction generates autonomous and rhythmical redox oscillations from the oxidized Ru^{III} state to the reduced Ru^{II} state. Thus, self-oscillating gels show volume oscillations synchronized with the redox oscillations of the ruthenium catalyst when the gels are immersed in an aqueous acidic solution containing the substrates for the BZ reaction (e.g.,

malonic acid and sodium bromate). Up to now, we have achieved the development of autonomously walking actuators[15e] and the detection of macroscopic peristaltic motion of the gels.[15f] Recently, we reported on autonomously oscillating microgels which disperse in aqueous medium.[17] We found that the microgels show not only swelling/deswelling oscillation as the bulk gel does but also dispersing/flocculating oscillation[17a] of microgels, which is a result of autonomous and periodical change of interparticle interactions. We believe that the microgels could be useful as artificial oscillators, rheological modifiers, light-modulating liquid, and so on. In this paper, we investigate rheological properties of self-oscillating microgel dispersions.

Rheological properties of colloidal dispersions are widely investigated, since they play important roles in many fields such as pharmaceutical formulations, paints, printing industries, cosmetics, and food. In general, the effective volume fraction of the dispersed phase is the factor that mainly determines the viscosity of the microgel dispersion; viscosity in microgel dispersion increases as the effective volume fraction of microgel increases. The dispersions of thermosensitive pNIPAm microgel can control their viscosity dramatically because they can change their hydrodynamic diameters, that is, their effective volume fraction.[18] If the viscosity of the dispersions can be controlled periodically and autonomously, such dispersions may be used as microactuators, in future microfluidics devices; they do not require external fields such as electro- or magneto-rheological fluids do.

Very recently, we have achieved autonomously oscillating viscosity in a microgel dispersion using autonomously oscillating microgels.[19] In the previous study, we found out that viscosity oscillation occurs in two different manners, exhibiting a simple pulsatile waveform or a complex waveform with two peaks per period. It was suggested that the difference in waveform is due to the difference in oscillating manner of the microgels: swelling/deswelling or dispersing/flocculating oscillation. Then, we

* Author to whom correspondence should be addressed. E-mail: d_suzuki@shinshu-u.ac.jp (D.S.); ryo@cross.t.u-tokyo.ac.jp (R.Y.).
† The University of Tokyo.
‡ Shinshu University.
§ Japan Science and Technology Agency.

demonstrated the different types of viscosity oscillations; however, many subjects still remained for precise control of the oscillating behavior. In particular, considering application to functional rheological fluids, it is important to establish concepts and methods for controlling amplitude in viscosity oscillation by design of microgel network. For this purpose, we need to clarify how the two types of microgel oscillations are linked to the oscillating viscosity.

In this paper, we focused on the autonomously oscillating viscosity in microgel dispersions induced by the swelling/deswelling oscillation of the microgels and investigated it in more detail. Herein, we prepared two kinds of microgels showing different oscillating amplitudes by changing the feed ratio of the chemical reagents during the polymerization. Using the microgels, the viscosity measurement was carried out with a coaxial-cylinder rotational viscometer. First, we checked the effect of ionic strength and then concentrations of microgels on viscosity in the dispersions as a function of temperature. Next, the BZ reaction was carried out to measure autonomously oscillating viscosity in the dispersions. In this study, the effects of the concentration of microgels, the concentration of the substrates for the BZ reaction, and the amount of Ru(bpy)$_3$ immobilized in microgels were discussed.

Experimental Details

Materials. Unless stated otherwise, all reagents were purchased from Wako Pure Chemical Industries, Ltd. *N*-Isopropylacrylamide (NIPAm, Sigma-Aldrich) was recrystallized from hexanes and dried in vacuo prior to use. The cross-linker *N,N′*-methylenebisacrylamide (BIS, Kanto Chemical Co., Inc.) and the initiator azobis-amidinopropane dihydrochloride (V-50) were used as received. Ruthenium(II)(4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine)bis(hexafluorophosphate) [Ru(bpy)$_3$ monomer] was synthesized according to a previous work.[20] Malonic acid (MA), sodium bromate (NaBrO$_3$, Kanto Chemical Co., Inc.), nitric acid (HNO$_3$, Kanto Chemical Co., Inc.), cerium(IV) sulfate tetrahydrate [Ce(SO$_4$)$_2$·4H$_2$O], cerium(III) sulfate *n*-hydrate (*n* = 5) [Ce$_2$(SO$_4$)$_3$·5H$_2$O], and sodium chloride (NaCl) were all used as received. Water for all reactions, solution preparation, and polymer purification was first distilled and then ion-exchanged.

Synthesis of the Microgels. The Ru(bpy)$_3$ copolymerized pNIPAm microgels were synthesized via surfactant-free aqueous radical precipitation polymerization as previously reported.[17] A mixture of NIPAm, Ru(bpy)$_3$, BIS, and water (195 mL) was poured into a 200 mL three-neck, round-bottom flask equipped with a stirrer, a condenser, and a nitrogen gas inlet. The comonomer ratio, (NIPAm:Ru(bpy)$_3$:BIS) was (95:1:4) or (96:2:2) in this study. The microgels were denoted as NRu1(4) and NRu2(2), respectively; in the sample code, N and Ru stand for NIPAm and Ru(bpy)$_3$, respectively, while the number following each letter represents the mole percentage of Ru(bpy)$_3$ fed during polymerization. After the number, the mole percentage of BIS fed in polymerization is shown in brackets. The initial total monomer concentration was 150 mM for NRu1(4) microgels and 75 mM for NRu2(2) microgels, respectively. Note that NRu2(2) microgels were synthesized in 30 mM NaCl solution in order to suppress the electrostatic repulsion of Ru(bpy)$_3{}^{2+}$. Under a stream of nitrogen to purge oxygen and with constant stirring, the solution was heated in an oil bath to 70 °C. After stabilizing the solution for 30 min, the V-50 initiator (1.08 g) dissolved in 5 mL of water was added to the flask to start the polymerization, which then continued for 4 h. After polymerization, the dispersion was cooled to room temperature. The

obtained microgels were purified by daily changes of water by means of dialysis for a week and by centrifugation/redispersion with water four times using a relative centrifugal force (RCF) of 50000g.

Characterization of the Microgels. Microgel sizes and polydispersity indices (PDI) were determined by dynamic light scattering (DLS, Malvern, Zetasizer3000HS$_A$). PDI values were calculated from the cumulants analysis as defined in ISO13321. Diluted microgels were analyzed in a quartz cuvette (microgel concentration: 0.01 wt %). The samples were allowed to equilibrate at the desired temperature for 10 min before data collection. Scattered light was collected at 90°. In order to maintain the reduced Ru^{II} and oxidized Ru^{III} states, 1 mM Ce^{III} and 0.3 M HNO$_3$ solution and 1 mM Ce^{IV} and 0.3 M HNO$_3$ solution were used, respectively. The amount of introduced Ru(bpy)$_3$ into the microgels was calculated on the basis of UV−vis measurements (Shimadzu UV-2500PC). The absorbance at 460 nm, which is a wavelength of the maximum absorbance for [Ru(bpy)$_3$]$^{2+}$, of the microgels dispersed in pure water was determined to calculate the introduced Ru(bpy)$_3$ monomer into the microgels.

Measurement of Viscosity in Microgel Dispersions. The viscosity measurements of microgel dispersions were performed with a coaxial-cylinder rotational viscometer (Brook Field, LVDV II+ viscometer) equipped with a thermo-controller. All measurements of viscosity in the microgel dispersions were taken at a constant shear rate of 132 s^{-1}. Before the autonomously oscillation study, the measurements of viscosity in the microgel dispersions were performed at different ionic and microgel concentrations, and as a function of temperature. In these experiments, temperature was raised at a rate of 0.5 °C/min. For the autonomously oscillation study, the microgels were dispersed in aqueous solution containing the reactants of the BZ reaction: MA, NaBrO$_3$, and HNO$_3$. The microgel dispersions were poured into a cylinder, and were kept at a constant temperature for 10 min while rotating using a spindle (SC-32) to measure the viscosity in the microgel dispersions. Under a constant temperature and stirring conditions, change of viscosity in the microgel dispersions as a function of time was monitored.

Results and Discussion

Synthesis and Characterization of the Microgels. The chemical structure of the microgel is shown in Figure 1. In this study, we prepared two different types of microgels by changing the feed ratio of the reagents during the polymerization to obtain microgels showing different amplitudes of volume oscillation. We have discussed NRu1(4) microgel before.[17b] Herein, NRu2(2) microgel was synthesized for the first time. To synthesize it, the comonomer ratio was changed, and the monomer concentration was reduced to 75 mM so that the hydrophobic Ru(bpy)$_3$ monomer could dissolve in pure water. In addition, the polymerization was carried out in a 30 mM NaCl solution in order to suppress electrostatic repulsion from Ru(bpy)$_3{}^{2+}$ and make several hundred nanometer sized particles. We controlled the size of the microgel because a smaller sized microgel (less than 100 nm) is difficult to handle (e.g., purification by centrifugation). We reported previously that Ru(bpy)$_3$ monomer plays the role of the stabilizer of the precursor particles in precipitation polymerization, and the size of the microgel becomes smaller.[17b] In this study, Ru(bpy)$_3$ was introduced in the microgel ∼50% for both NRu1(4) and NRu2(2) microgels. PDI indices were below 0.05 for all batches of the microgels under all conditions. Figure 2 shows the temperature dependence of the hydrodynamic diameters of NRu1(4) (a) and NRu2(2)
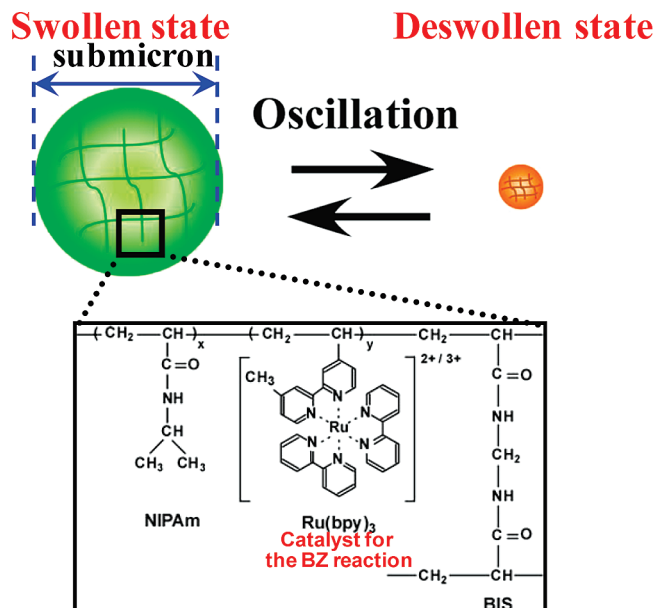
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Figure 1. Chemical structure of the autonomously oscillating microgel.
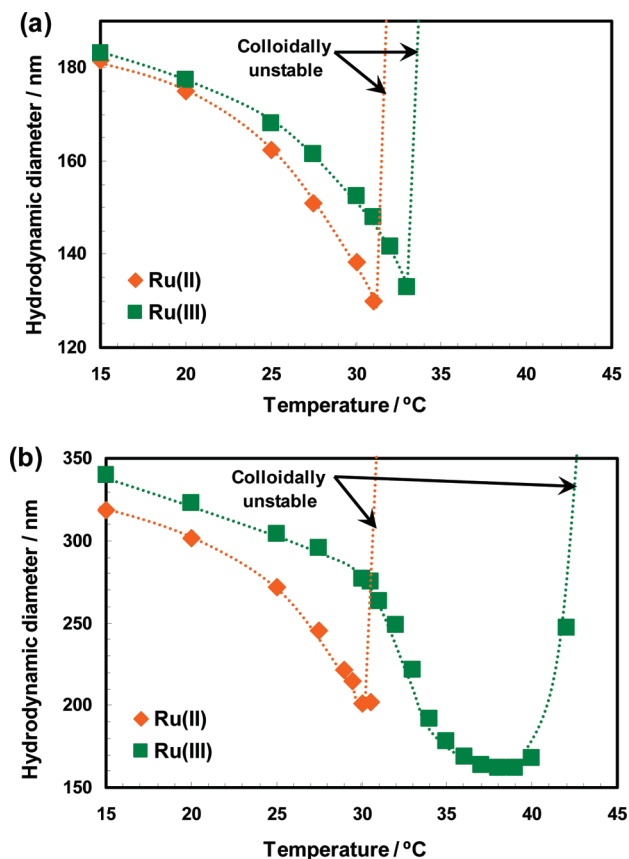

Figure 2. Deswelling curves for the Ru(bpy)$_3$ copolymerized pNIPAm microgels under the different conditions, as measured by dynamic light scattering: the reduced state Ru^{II} in 1 mM Ce^{III} and 0.3 M HNO$_3$ solution (orange diamonds) and the oxidized state Ru^{III} in 1 mM Ce^{IV} and 0.3 M HNO$_3$ solution (green squares). Samples are (a) NRu1(4) and (b) NRu2(2) microgels. The dispersion concentration was 0.01 wt % in both cases.

microgels (b) measured by DLS. Note that they are measured in both the reduced Ru^{II} and oxidized Ru^{III} states, and each solution contains 0.3 M HNO$_3$ because the BZ reaction only occurs at high salt concentrations (more than 0.3 M). As can

be seen from Figure 2, the microgels were flocculated above their volume phase transition temperatures (VPTTs). In this study, we regarded the temperature as critical flocculating temperatures (CFTs). In general, pNIPAm microgels in pure water are colloidally stable both below and above the VPTT. In particular, pNIPAm microgels above the VPTT are colloidally stable due to electrostatic repulsion from the residues of the initiator even though steric hindrance is not so effective. Herein, the microgels were flocculated because interparticle electrostatic repulsion is extremely reduced due to high salt conditions. For NRu1(4) microgels (Figure 2a), CFTs are at 32 °C for the Ru^{II} state and at 34 °C for the Ru^{III} state. This CFT shift between the Ru^{II} and Ru^{III} states is due to increased hydrophilicity of the polymer because of a higher charge density on the copolymer chains even though the microgels are under high salt conditions. As a result, the diameters in the oxidized Ru^{III} states were bigger than those in the reduced Ru^{II} states at the same temperature. This corresponds to our previous results.[17b] Compared to NRu1(4) microgels, Figure 2b shows that CFTs of NRu2(2) microgels are at 32 °C for the Ru^{II} state and at 40 °C for the Ru^{III} state. This increased shift compared to that of NRu1(4) is attributed to the increased number of immobilized Ru(bpy)$_3$ in NRu2(2) microgels. As a result, this phenomenon led to increases in size deviation between the Ru^{II} and Ru^{III} states at the same temperatures. From the DLS data shown in Figure 2, we can assume that the maximum volume changes in oscillation are theoretically 1.5 times (at 31 °C) for NRu1(4) microgels and 2.6 times (at 31 °C) for NRu2(2) microgels, respectively. However, we cannot simply apply these assumptions to the volume oscillations because conditions of the BZ reaction are very complex once the reaction occurs (i.e., the overall BZ reaction consists of more than 80 chemical reactions, and thus the ionic strength of the solution is not constant).

Before the measurement of autonomously oscillating viscosity in microgel dispersions, we checked the effect of ionic strength on the viscosity in the dispersions as a function of temperature. Figure 3 shows viscosity in NRu1(4) microgel dispersions (1.2 wt %) in NaCl solutions of different concentrations. At the same temperature (e.g., at 20 °C), viscosity in the dispersion greatly decreased with increasing salt concentrations. This result is due to smaller microgels, and thus lower effective volume fractions of the microgels, caused by weaker electrostatic repulsion of Ru(bpy)$_3^{2+}$ at higher salt concentrations. In addition, the viscosity in the dispersions decreased as the temperature increased, which corresponds to both a decrease of solvent viscosity and a decrease of hydrodynamic diameters, that is, the effective volume fractions of the microgels as shown in Figure 2a. In particular, the viscosity in the dispersions in 100 and 400 mM NaCl solution increased at 31 and 25 °C, respectively (shown by arrows in Figure 3b). This phenomenon is linked to the flocculation of the microgels; the solvent might be trapped in the early stages of flocculation, and the effective volume fraction of the microgel might increase when increases in viscosity are detected. Next, we also checked the effect of the concentration of the microgels on viscosity in the dispersions as a function of temperature (Figure 4). Herein, ionic strength is fixed at 400 mM using NaCl, which is close to that of the BZ reaction. The viscosity in the dispersion increased as the concentration of the microgels increased at the same temperature (e.g., 25 °C) even though the ionic strength was high. In addition, increases in viscosity in the dispersion were observed around the VPTTs (31 °C for 0.25 wt %, 29 °C for 1 wt %, 27 °C for 3 wt %, 27 °C for 5 wt %, and 27 °C for 7 wt %). This change is also due to the flocculation of the microgels, as shown
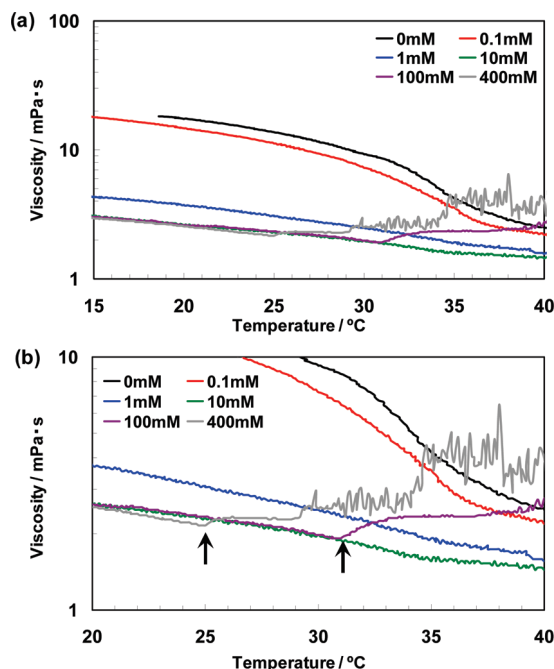
(a)

(b)

Figure 3. Temperature dependence of viscosity in 1.2 wt % microgel dispersions at different ionic strengths. The dispersion was heated at a rate of 0.5 °C/min. All data were taken at a constant shear rate of 132 s^{-1}. Figure 4b is a close-up of Figure 4a. The arrows point to the critical flocculation temperatures of the microgels in Figure 4b.
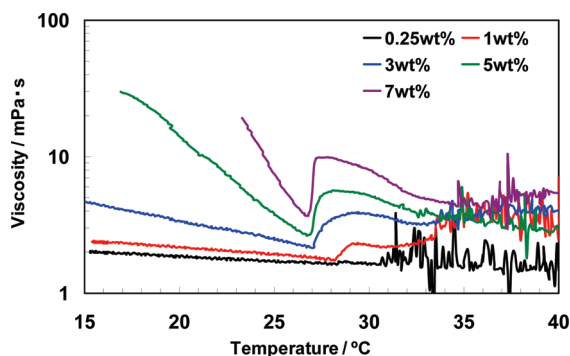

Figure 4. Temperature dependence of viscosity in microgel dispersions at different microgel concentrations. The dispersion was heated at a rate of 0.5 °C/min. The ionic strength was 400 mM in all cases. All data were taken at a constant shear rate of 132 s^{-1}.

in Figure 3b. After the increases, decreases and then fluctuations in viscosity were observed. This is because aggregates became larger as a function of time: after the measurements, there were precipitations at the bottom of the cylinder at all concentrations of the microgel.

Characterization of Autonomously Oscillating Viscosity in Microgel Dispersions. The BZ reaction was carried out using the NRu microgels. Herein, MA, NaBrO$_3$, and HNO$_3$ were used as substrates for the BZ reaction. Note that all experiments were carried out at a constant temperature of 15 °C so that the swelling/deswelling oscillation of the microgels could be investigated. We have already found that the different type of oscillation, that is, dispersing/flocculating oscillation of the microgels, occurs around the VPTT of the microgels.[17,19] The oscillating viscosity was observed after an induction period of several hundred seconds. Figure 5 shows the oscillating viscosity in the dispersions using NRu1(4) microgels. In these experiments, the dispersions contained 62.5 mM MA, 84 mM NaBrO$_3$, and 300 mM HNO$_3$. In addition, a constant shear rate of

132 s^{-1} was selected so that the result could be clear (i.e., the BZ reaction is affected by stirring). Autonomously oscillating viscosity was not observed when concentrations of the microgel were below 1.5 wt % (Figure 5b). Compared to a control experiment without MA, as shown in Figure 5a, the oscillation shown in Figure 5b should exist but in this case at very low amplitude. Although oscillating viscosities were not observed at low concentrations of the microgel, the oscillating profiles by optical transmittance were detected at almost the same conditions as previously reported.[17b] Taking the previous data into consideration, we conclude that oscillating viscosity might not be detected at low concentrations of the microgels in this experiment even though volume oscillation of the microgel occurred; the difference of viscosity in microgel dispersions between the oxidized, swelling state and reduced, deswelling state might be too small to detect in this experiment. With increasing concentrations of the microgel, the amplitude of the oscillation increased (0.24 mPa·s for 3 wt % (Figure 5c) and 2.74 mPa·s for 5 wt % (Figure 5d)). Herein, the averaged value of the amplitude between the first and fifth oscillation was regarded as the amplitude of the oscillation. In general, the effective volume fraction of the dispersed phase is the factor that mainly determines the viscosity in a microgel dispersion; the viscosity in a microgel dispersion increases as the effective volume fraction of the microgel increases. In this system, the effective volume fraction of the microgels increased when Ru(bpy)$_3$ was in the oxidized Ru^{III} state, while the effective volume fraction of the microgels decreased when Ru(bpy)$_3$ was in the reduced Ru^{II} state. In these two cases, as shown in Figure 5c and d, there is little difference in oscillation period (370 s for 3 wt % and 350 s for 5 wt %). However, the amplitude of the oscillation at 5 wt % was ∼10 times bigger than that at 3 wt %. The degree of change in volume oscillation of microgels should not be different as much at all microgel concentrations because the concentration of the substrates for the BZ reaction was the same in all cases. Thus, the reason for the bigger amplitude of the 5 wt % case may be linked to interparticle interactions: the averaged distance among microgels was closer than that for the 3 wt % case, resulting in a larger difference of interparticle interaction between the expanded and contracted states.

As can be seen from Figure 5c and d, the amplitude of the oscillation attenuated remarkably. This may be mainly due to the consumption of the substrates for the BZ reaction, which was not observed in our previous study using low concentrations of the microgels (0.25 wt %) and using the same concentrations of the substrates for the BZ reaction.[17b] Next, we measured the autonomously oscillating viscosity in the dispersions by adjusting the concentrations of the substrates for the BZ reaction. We found that the oscillating viscosity became stable when microgels were dispersed in aqueous solutions containing a higher concentration of the BZ reactants (Figure 6): 100 mM MA, 150 mM NaBrO$_3$, and 500 mM HNO$_3$. Moreover, the oscillating viscosity in NRu2(2) microgel dispersions was also measured using the same conditions as NRu1(4) microgels (black line for NRu1(4) microgels and red line for NRu2(2) microgels, Figure 6). In both cases, constant oscillating behavior continued for more than 6000 s. In these two cases shown in Figure 6, there is little difference in oscillating period (194 s for NRu1(4) microgels and 201 s for NRu2(2) microgels). Compared to the case for low concentrations of BZ reactants, as shown in Figure 5, the period became shorter at higher concentrations of the BZ reactants, which agrees well with our previous data.[17c] However, the amplitude of the oscillation for NRu2(2) microgels

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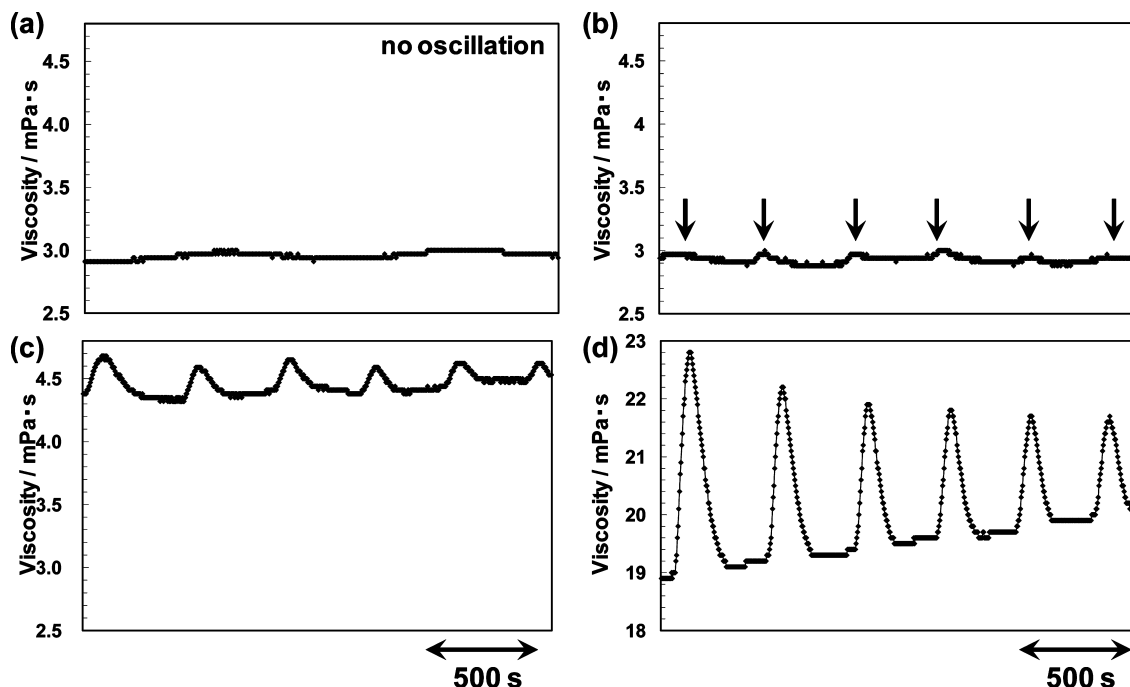*J. Phys. Chem. B, Vol. 114, No. 7, 2010* **2409**

Figure 5. Autonomously oscillating profiles of viscosity in NRu1(4) microgel dispersions at 15 °C. (a) Control experiment; microgels were dispersed in aqueous solutions containing $NaBrO_3$ (84 mM) and HNO_3 (300 mM), which did not allow the BZ reaction to occur. (b–d) All samples were dispersed in aqueous solutions containing MA (62.5 mM), $NaBrO_3$ (84 mM), and HNO_3 (300 mM). Microgel concentrations were (b) 1.5 wt %, (c) 3.0 wt %, and (d) 5.0 wt %. All data were taken at a constant shear rate of 132 s^{-1}.
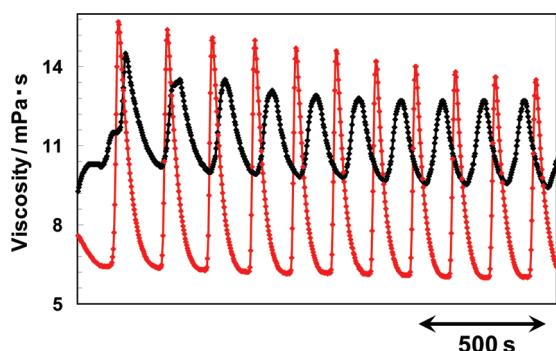

Figure 6. Autonomously oscillating profiles of viscosity in the microgel dispersions measured at 15 °C. Samples were NRu1(4) (black line) and NRu2(2) microgels (red line). The microgels were dispersed in aqueous solutions containing MA (100 mM), $NaBrO_3$ (150 mM), and HNO_3 (500 mM). The microgel concentration was 5.0 wt % in both cases. Both data were taken at a constant shear rate of 132 s^{-1}.

was ~2 times greater than that for NRu1(4) microgels (8.8 and 3.6 mPa·s, respectively). Considering the size differences at the same temperature between the Ru^{II} and Ru^{III} states, as shown in Figure 2, this result is due to the higher degree of amplitude of the swelling/deswelling oscillation of NRu2(2) microgels as compared with that of NRu1(4) microgels.

Conclusion

Autonomously oscillating viscosity in microgel dispersions induced by swelling/deswelling oscillation of the microgels was investigated with a coaxial-cylinder rotational viscometer. In order to characterize the viscosity oscillation, two types of microgels were synthesized by changing the feed ratio of Ru(bpy)₃ and BIS cross-linker. The viscosity of the microgel dispersions at high salt concentrations could be controlled by changing the concentrations of the microgels. In this study, autonomously oscillating viscosity was only measured when the concentration of the microgels was high (more than 1.5 wt %).

The amplitude of the oscillation became bigger with increasing concentrations of the microgels. By adjusting the concentration of the substrates for the BZ reaction, we could achieve the constant oscillation for 6000 s. Moreover, with increasing Ru(bpy)₃ and decreasing the BIS cross-linker, microgels showed a high degree of swelling/deswelling oscillation, resulting in bigger amplitudes of autonomously oscillating viscosity. This finding may be useful for future applications such as microfluidic devices.

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