J|A|C|S COMMUNICATIONS

Autonomously Oscillating Viscosity in Microgel Dispersions

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Rheological properties of colloidal dispersions are widely studied because such dispersions are important in many applications, such as paints, cosmetics, food, and pharmaceutical formulations. In this field, polymer colloids are attractive because they can be synthesized in uniform sizes and surface properties. Also, the sizes and properties can be controlled and reproduced as a result of contributions by many researchers over a long period of time.[1] In particular, over the past decade or so, there has been increasing interest in aqueous stimuli-responsive microgels because of their multiple functions that may be applied in various applications, including drug delivery,[2] photonic crystals,[3] chemical/biological separation,[4] templating for inorganic nanoparticle synthesis,[5] emulsifiers,[6] and rheological modifiers.[7]

In contrast to simple stimuli-sensitive microgels such as temperature- and pH-sensitive ones, very recently we reported *self-oscillating* microgels.[8] Our microgels show an autonomous *swelling/deswelling* oscillation that is synchronized with the redox oscillation of the Belousov−Zhabotinsky (BZ) reaction.[9] The microgels are copolymerized with the tris(2,2′-bipyridine)ruthenium monomer, denoted Ru(bpy)$_3$, which is the catalyst for the BZ reaction. Thus, the volume of the microgel oscillates in aqueous solution containing the substrates for the BZ reaction. In addition, an autonomous *flocculation/redispersion* oscillation near the volume phase transition temperature of the microgels was discovered.[10] In general, the viscosity is related to the effective volume fraction of the microgels and the status of dispersion (flocculated or not). Thus, these two types of autonomous oscillation of the microgels should affect the viscosity in the dispersion. If autonomously oscillating viscosity of the dispersion is realized, this technology could be applied in many applications, as have electro- and magnetorheological (ER and MR) fluids. In particular, the dispersion with autonomously oscillating viscosity may be used as a micropump, which could realize next-generation microfluidics devices.

In this communication, we demonstrate a new rheological property of colloidal dispersions using self-oscillating microgels, which were synthesized by surfactant-free aqueous precipitation polymerization as in our previous report.[8] The chemical structure of the microgel is shown in SI Figure 1 in the Supporting Information. Our previous study revealed that the microgels obtained by this approach are very monodispersed.[8] In this case, dynamic light scattering (DLS) measurements gave a hydrodynamic diameter of ∼200 nm for the obtained microgel in a dilute dispersion (at 25 °C in 1 mM NaCl solution). Before the self-oscillating study, we checked the temperature dependence of the hydrodynamic diameters of the reduced Ru(II) and oxidized Ru(III) states by DLS. From these data, we can estimate the degree of volume change in the oscillation. In this case, the diameters were measured to be several tens of nanometers at all temperatures (see SI Figure 2).

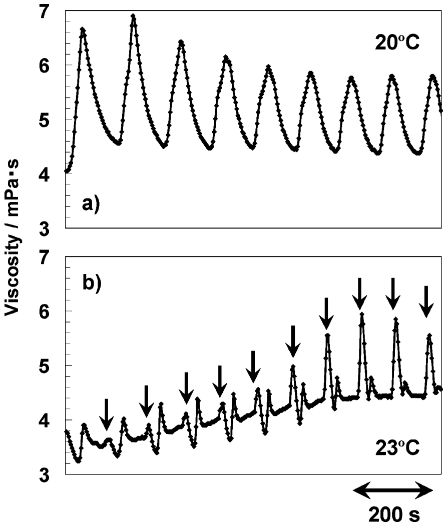

Figure 1. Self-oscillating profiles of viscosity in the microgel dispersions. The microgels were dispersed in aqueous solution containing MA (100 mM), NaBrO$_3$ (150 mM), and HNO$_3$ (0.5 M). The microgel concentration was 5 wt %. All of the data were taken at a constant shear rate of 132 s^{-1}. The viscosity was measured at various temperatures: (a) 20 and (b) 23 °C. Characteristic peaks that emerged at 23 °C are indicated by the arrows in (b).

Next, we carried out the BZ reaction using the microgel dispersions. Malonic acid (MA), sodium bromate (NaBrO$_3$), and HNO$_3$ were used as substrates for the BZ reaction at a fixed concentration. Figure 1 shows self-oscillating profiles of viscosity in microgel dispersions measured at different temperatures. Because one of the components of the microgel, poly(*N*-isopropylacrylamide) (pNIPAm),[11] shows a temperature-sensitive property, the diameter of the microgel decreased as the temperature increased up to the critical flocculation temperature (CFT) (see SI Figure 2). In this case, concentrations of microgel (5 wt %) and substrates for the BZ reaction were fixed.[12] Thus, the effective volume fraction of the microgels should decrease with increasing temperature up to the CFT. At 20 °C (Figure 1a), autonomously oscillating viscosity was observed. The waveform of the oscillation is similar to that detected by optical transmittance as reported previously.[8] With increasing temperature, oscillating profiles with the same waveform but decreased amplitude were observed up to 22 °C (see SI Figure 3a). The decrease in amplitude is attributed to the decrease in effective volume fraction of the microgels at higher temperatures.[13] Next, the waveform suddenly changed at 23 °C to include two peaks per period (Figure 1b). Finally, oscillation was no longer

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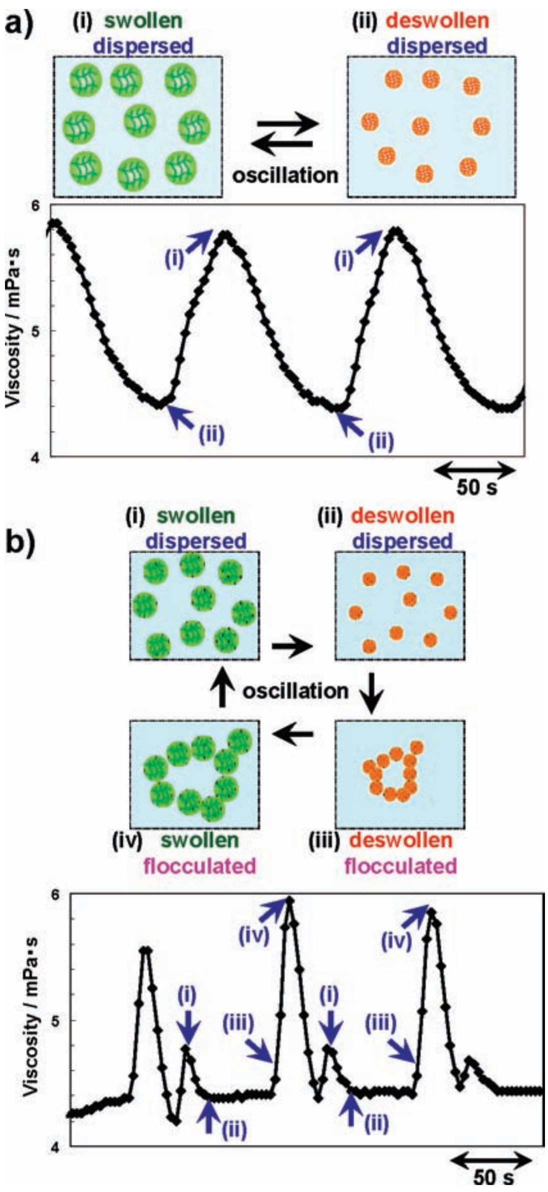

Figure 2. Two different types of oscillating waveforms observed at 20 and 23 °C in Figure 1a,b, respectively. The numbers in each oscillating profile refer to the corresponding cartoons.

observed at higher temperatures (25 °C), which should be due to flocculation of the microgels (see SI Figure 3b).

In order to clarify the difference between the two types of oscillations, representative waveforms observed in Figure 1 were compared in Figure 2. At 20 °C (Figure 2a), the waveform is the same as that usually shown by the BZ reaction.[14] Thus, the viscosity in the dispersion is oscillating because of the autonomous *swelling/deswelling* oscillation of the microgels; the viscosity is high when the microgels are in the swollen state, (i), and low when they are in the deswollen state, (ii). In contrast, the waveform in Figure 2b has never been previously observed for the BZ reaction. Thus, the viscosity in the dispersion at 23 °C must be oscillating because of the autonomous *dispersion/flocculation* oscillation of the microgels. In this case, the smaller peak is attributed to simple volume oscillation of each microgel, (i)−(ii).[15] The observed dramatic change in amplitude is due to flocculation of the microgels, (iii), wherein the flocs become larger.[16] The flocculation continues until colloidal stability is recovered by swelling, (iv). After that, the viscosity in the dispersion decreases by redispersion of the aggregates, which may be redispersed completely when the viscosity indicates a minimum value. The swelling/deswelling oscillation of the microgels then starts again. Further evidence for autonomous *dispersion/flocculation* oscillation is that the amplitude of the peaks indicated by the arrows in Figure 1b gradually increases, which is a typical phenomenon for this oscillation, as observed previously by optical transmittance (see SI Figure 4).[10]

In conclusion, we have achieved autonomously oscillating viscosity in microgel dispersions using self-oscillating microgels. Although we need more detailed characterization to clarify the phenomenon, our preliminary data reveal that the oscillating rhythm and amplitude of the viscosity in the microgel dispersion can be controlled by two types of oscillation of the microgels. This new technology may be useful in the development of materials such as micropump-equipped microfluidic devices.

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Supporting Information Available: Experimental details, chemical structure of the microgel, hydrodynamic diameters by DLS, and oscillating profile of viscosity at high temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Saunders, B. R.; Vincent, B. *Adv. Colloid Interface Sci.* **1999**, *80*, 1. (b) Pelton, R. *Adv. Colloid Interface Sci.* **2000**, *85*, 1. (c) Kawaguchi, H. *Prog. Polym. Sci.* **2000**, *25*, 1171. (d) Nayak, S.; Lyon, L. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 7686.
(2) (a) Hsiue, G.-H.; Hsu, S.-H.; Yang, C.-C.; Lee, S.-H.; Yang, I. K. *Biomaterials* **2002**, *22*, 457. (b) Nayak, S.; Lee, H.; Chmielewski, J.; Lyon, L. A. *J. Am. Chem. Soc.* **2004**, *126*, 10258.
(3) (a) Weissman, J. M.; Sunkara, H. B.; Tse, A. S.; Asher, S. A. *Science* **1996**, *274*, 959. (b) Lyon, L. A.; Debord, J. D.; Debord, S. B.; Jones, C. D.; McGrath, J. G.; Serpe, M. J. *J. Phys. Chem. B* **2004**, *108*, 19099. (c) Suzuki, D.; McGrath, J. G.; Kawaguchi, H.; Lyon, L. A. *J. Phys. Chem. C* **2007**, *111*, 5667.
(4) (a) Morris, G. E.; Vincent, B.; Snowden, M. J. *J. Colloid Interface Sci.* **1997**, *190*, 198. (b) Kawaguchi, H.; Kisara, K.; Takahashi, T.; Achiha, K.; Yasui, M.; Fujimoto, K. *Macromol. Symp.* **2000**, *151*, 591.
(5) (a) Zhang, J.; Xu, S.; Kumacheva, E. *J. Am. Chem. Soc.* **2004**, *126*, 7908. (b) Suzuki, D.; Kawaguchi, H. *Langmuir* **2005**, *21*, 8175. (c) Suzuki, D.; Kawaguchi, H. *Langmuir* **2005**, *21*, 12016. (d) Suzuki, D.; Kawaguchi, H. *Langmuir* **2006**, *22*, 3818. (e) Lu, Y.; Mei, Y.; Ballauff, M.; Drechsler, M. *J. Phys. Chem. B* **2006**, *110*, 3930.
(6) (a) Fujii, S.; Read, E. S.; Binks, B. P.; Armes, S. P. *Adv. Mater.* **2005**, *17*, 1014. (b) Suzuki, D.; Tsuji, S.; Kawaguchi, H. *J. Am. Chem. Soc.* **2007**, *129*, 8088.
(7) Ole Kiminta, D. M.; Luckham, P. F.; Lenon, S. *Polymer* **1995**, *36*, 4827.
(8) (a) Suzuki, D.; Yoshida, R. *Macromolecules* **2008**, *41*, 5830. (b) Suzuki, D.; Yoshida, R. *J. Phys. Chem. B* **2008**, *112*, 12618.
(9) Zaikin, A. N.; Zhabotin, A. M. *Nature* **1970**, *225*, 535.
(10) Suzuki, D.; Sakai, T.; Yoshida, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 917.
(11) (a) Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1968**, *A2*, 1441. (b) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(12) In this study, the viscosity of a 5 wt % microgel dispersion is not very high because they are dispersed in a solution with a high salt concentration.
(13) Senff, H.; Richtering, W. *J. Chem. Phys.* **1999**, *111*, 1705.
(14) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.
(15) The effective volume fraction of the microgels decreased with increasing temperature, so the amplitude originating from the swelling/deswelling oscillation became smaller than that measured at 20 °C (1.9 mPa s at 20 °C and 0.4 mPa s at 23 °C).
(16) Rasmusson, M.; Routh, A.; Vincent, B. *Langmuir* **2004**, *20*, 3536.

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