ORIGINAL ARTICLE

Self-oscillating core/shell microgels: effect of a crosslinked nanoshell on autonomous oscillation of the core

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We reported the effects of crosslinked nanoshells covering self-oscillating microgels on their oscillatory behaviors. We carried out seeded precipitation polymerization of *N*-substituted acrylamide derivatives using preformed, self-oscillating microgels as cores. The core/shell microgels obtained were characterized by dynamic light scattering. Oscillating behaviors were characterized by changes in optical transmittance. In addition, the characteristics (that is, induction period, oscillating period and waveform) of the oscillation of the core/shell microgels were compared with that of the parent core microgel to clarify the effect of the addition of a nanoshell on the autonomous oscillating behaviors of microgels.

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INTRODUCTION

Soft polymer microgels, which have a network structure that swells in an aqueous solution, have attracted a lot of attention in material science because of their stimulus-sensitive properties. The microgels undergo a volume phase transition as a result of a change in temperature,¹ pH,² ionic strength,³ light⁴ and so on. In many cases, microgels are composed of poly(*N*-isopropylacrylamide) (pNIPAm), which is a typical thermosensitive polymer with a lower critical solution temperature of around 31 °C.^{5,6}

PNIPAm-based microgels can be functionalized by constructing nanocomposites with inorganic nanoparticles^{7–10} for application in more complex biotechnologies and nanotechnologies (for example, drug delivery,^{11,12} chemical/biological separation^{13,14} and photonic crystals^{15–18}). In addition, we reported that microgels can show self-oscillation,^{19–22} coupled with the Belousov-Zhabotinsky (BZ) reaction,²³ which is an autonomous and periodic chemical reaction. We found that self-oscillating microgels show not only autonomous swelling/deswelling oscillation but also autonomous flocculating/dispersing oscillation near the volume phase transition temperature (VPTT) of the microgels.¹⁹ In addition, it became clear that volume oscillation is controlled by crosslinked network structures (that is, the BZ reaction of crosslinked microgels shows a longer duration of refractory state and a shorter duration of resting state than that of the bulk solution of the BZ reaction).^{20,21}

In this study, we investigated the effects of a crosslinked nanoshell covering self-oscillating microgels on their oscillatory behavior (Figure 1). One of the problems of self-oscillating microgels was their flocculation above their VPTT,¹⁹ which made their use difficult in specific applications. It could be assumed that the introduction of the nanoshell made self-oscillating microgels colloidally stable even above their VPTT when the nanoshell showed steric hindrance. In addition, core/shell structured microgels can exhibit multiple responsiveness and core- or shell-specific functionalities. Herein, we carried out seeded precipitation polymerization^{16,24–28} of *N*-substituted acrylamide derivatives using self-oscillating microgels as cores. The microgels obtained were characterized by dynamic light scattering. Their self-oscillating behaviors were then detected by changes in optical transmittance. Here the characteristics (that is, induction period, oscillating period and waveform) of the self-oscillation of the core/shell microgels are compared with that of the parent core microgel to clarify the effect of nanoshell addition on the autonomous oscillatory behavior of microgels.

EXPERIMENTAL PROCEDURE

Materials

Unless stated otherwise, all reagents were purchased from Wako Pure Chemical Industries (Osaka, Japan). *N*-isopropylacrylamide (NIPAm, Sigma-Aldrich, Tokyo, Japan) was recrystallized from hexanes and dried *in vacuo* before use.

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Figure 1 (a) Autonomous swelling/deswelling oscillation of microgels. (b) Chemical structures of core and core/shell microgels. A full color version of this figure is available at the *Polymer Journal* journal online.

N-isopropylmethacrylamide (NIPAm, Sigma-Aldrich) was used as received. The crosslinker *N,N'*-methylenebis(acrylamide) (BIS, Kanto Chemical, Tokyo, Japan) 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) [$\text{Ru}(\text{bpy})_3$ monomer] was synthesized according to the previous work.^{29,30} Malonic acid, sodium bromate (NaBrO_3 , Kanto Chemical), nitric acid (HNO_3 , Kanto Chemical), cerium(IV) sulfate tetrahydrate [$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$], cerium(III) sulfate *n*-hydrate ($n=5$) [$\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$] and sodium chloride (NaCl) were all used as received. Water for all reactions, as well as for solution preparation and polymer purification, was first distilled and then ion exchanged.

Synthesis of core microgel

The core microgels of $\text{Ru}(\text{bpy})_3$ copolymerized pNIPAm were synthesized by surfactant-free aqueous radical precipitation polymerization as previously reported.^{19–22} A mixture of NIPAm (97 mol%, 3.292 g), $\text{Ru}(\text{bpy})_3$ (1 mol%, 0.270 g), BIS (2 mol%, 0.092 g) and water (195 ml) was poured into a 300 ml three-neck, round-bottom flask equipped with a stirrer, a condenser and a nitrogen gas inlet. Under a stream of nitrogen to purge oxygen and with constant stirring, the solution was heated in an oil bath to 70 °C. After the solution was stabilized for 1 h, the V-50 initiator (0.108 g) was dissolved in 5 ml of water and added to the flask to start polymerization, which then continued for 6 h. After polymerization, the dispersion was cooled to room temperature. The microgels were purified by centrifugation/redispersion with water four times using a relative centrifugal force of 52 490 g and by daily changes of water by means of dialysis for 1 week.

Synthesis of core/shell microgel

For shell synthesis, core microgels (0.4 g) were dispersed in a 5 mM NaCl solution (175 ml) and placed in a 300-ml three-neck, round-bottom flask

equipped with a stirrer, a condenser and a nitrogen gas inlet. Under a stream of nitrogen to purge oxygen and with constant stirring, the solution was heated to 70 °C. After 50 min, a 20 ml solution of NIPAm (98 mol%, 0.888 g) and BIS (2 mol%, 0.024 g) or NIPMAm (98 mol%, 0.998 g) and BIS (2 mol%, 0.024 g) was added to the flask. After 10 min, polymerization was initiated by injecting 5 ml of V-50 (0.108 g) solution. The reaction was maintained at 70 °C for 4 h. The core/shell microgels were purified by centrifugation/redispersion with water four times using a relative centrifugal force of 52 490 g and by daily changes of water by means of dialysis for 1 week.

Characterization

The size and polydispersity indices of microgels were determined by dynamic light scattering (Zetasizer 3000HSA, Malvern Instruments, Kobe, Japan). Polydispersity index values were calculated from the cumulant analysis as defined in ISO13321. Diluted microgel dispersions were analyzed in a quartz cuvette (microgel concentration: 0.005 wt %). The samples were allowed to equilibrate at the desired temperature for 10 min before data collection. Scattered light was collected at 90°. NaCl was then used to adjust each solution to 1 mM total ion concentration. Moreover, to maintain the reduced Ru^{II} and oxidized Ru^{III} states, a solution of 1 mM Ce^{III} and 0.3 M HNO_3 , as well as a solution of 1 mM Ce^{IV} and 0.3 M HNO_3 , were used, respectively. The amount of $\text{Ru}(\text{bpy})_3$ introduced into the microgels was calculated on the basis of ultraviolet visible measurements (Shimadzu UV-2500PC, Shimadzu, Kyoto, Japan). Absorbance at 460 nm, which is the wavelength of the maximum absorbance for $[\text{Ru}(\text{bpy})_3]^{2+}$, of the microgels dispersed in pure water was determined to calculate the amount of $\text{Ru}(\text{bpy})_3$ monomer introduced into the microgels.

Optical transmittance data of self-oscillation were collected on a Shimadzu UV-2500PC spectrophotometer. Microgels were dispersed in an aqueous solution containing the reactants of the BZ reaction: malonic acid (62.5 mM), NaBrO_3 (84 mM) and HNO_3 (0.3 M). Under constant temperature and stirring

conditions, the time course of transmission was monitored. The $\text{Ru}(\text{bpy})_3$ complex has different absorption spectra in the reduced Ru^{II} state and in the oxidized Ru^{III} state as an inherent property. The solution exhibited absorption maximum at ~ 460 nm in the reduced state, as well as at ~ 420 nm in the oxidized state, and has an isosbestic point at 570 nm. In this study, the 570 nm wavelength was selected to detect the swelling/deswelling signals of the microgels, whereas the 460 nm wavelength was used to detect the redox change of $\text{Ru}(\text{bpy})_3$ for the bulk solution of the BZ reaction as a control.

RESULTS AND DISCUSSION

Preparation and characterization of self-oscillating core/shell microgels

The synthesis of core microgels was carried out using NIPAm and $\text{Ru}(\text{bpy})_3$ monomers and the crosslinker by surfactant-free aqueous precipitation polymerization as previously reported.^{19–22} Using microgels as cores, seeded precipitation polymerization of NIPAm or NIPMAm was carried out. Figure 2 shows the temperature dependence of the hydrodynamic diameters for all microgels synthesized in this study. As shown in Figure 2a, comparing core and both core/shell microgels, increases in size both below and above VPTTs were observed for core/shell microgels. This result indicates that pNIPAm and pNIPMAm shells were indeed added to the core. In this study, the pNIPAm shell is thicker than the pNIPMAm shell, which is probably because of the difference in reactivity with the crosslinker; pNIPMAm might not be crosslinked effectively when they are added to the core microgels. Importantly, each dispersion of the microgels was determined to be monodispersed (calculated polydispersity indice values from DLS measurements were below 0.05 for all batches of microgels at all temperatures). Thereafter, we checked the temperature dependence of the hydrodynamic diameters in a 0.3 M NaCl solution (Figure 2b) because the BZ reaction only occurs at high salt concentrations (> 0.3 M). In contrast to the microgels dispersed in NaCl solutions of lower concentration (0.01 M), as shown in Figure 2a, all microgels flocculated above VPTTs in a 0.3 M NaCl solution, as shown in Figure 2b. Under this condition, the core microgels flocculated at 32 °C (=critical flocculation temperature, CFT), whereas the core/pNIPAm and the core/pNIPMAm shell microgels flocculated at 31 and 39 °C, respectively. These changes in CFT are one of the proofs of shell addition. In general, pNIPAm-based microgels lose colloidal stability above the VPTT when they are dispersed in a salt solution of high concentration because colloidal stability is highly influenced by surface structures. The CFTs obtained here are slightly different than the lower critical solution temperatures of pNIPAm and pNIPMAm in pure water (31 and 44 °C, respectively). This difference may be related to differences in salt concentrations and to the lowered VPTT of the shell due to the deswelling of the core.²⁸

Next, we checked the changes in hydrodynamic diameters between the reduced Ru^{II} and the oxidized Ru^{III} states. Figure 3 shows the temperature dependence of the hydrodynamic diameters in the reduced Ru^{II} and oxidized Ru^{III} states as measured by DLS. Here, each solution contains 0.3 M HNO_3 because the BZ reaction only occurs at high salt concentrations. For core microgels, size deviations between the Ru^{II} and Ru^{III} states at the same temperatures are clearly seen from 15 to 31 °C (Figure 3a). In addition, CFTs of the reduced Ru^{II} and oxidized Ru^{III} states (32 and 34 °C, respectively) differed because of the change in colloidal stability. After shell addition, size deviations between the Ru^{II} and Ru^{III} states at the same temperatures became smaller than that of the core microgel. This effect is due to core compression as a result of seeded precipitation polymerization: thus, the swelling ability of the core becomes smaller.^{24–28} In this study, the pNIPAm shell is thicker than the pNIPMAm shell. It has

Figure 2 Temperature dependence of the hydrodynamic diameters of core (black diamond), core/pNIPAm shell (blue triangle) and core/pNIPMAm shell (red square) microgels as measured by DLS. Ionic strengths were 0.001 (a) and 0.3 (b). The dispersion concentration was 0.005 wt % in both cases. A full color version of this figure is available at the *Polymer Journal* journal online.

been thoroughly proven that the addition of thicker shells greatly restricts core swelling.³¹ Thus, the core/pNIPMAm shell microgel clearly showed size deviations at the same temperatures, whereas the core/pNIPAm shell microgel did not show quite as much. Most importantly, CFTs of the core/pNIPMAm shell microgel in both the Ru^{II} and Ru^{III} states became higher (38 and 39 °C, respectively) than that of the parent core microgels. However, the core/pNIPAm shell microgel did not show higher CFTs than the parent core microgel. These results suggest that the combination of chemical structures between the core and the shell is important to design the desired core/shell microgels. In contrast to our expectations, these CFTs of the core/shell microgels in the Ru^{II} and Ru^{III} states did not correspond to each other (38 and 39 °C for the core/pNIPMAm shell microgel and 31 and 32 °C for the core/pNIPAm shell microgel, respectively). This fact suggests that the contraction of the core and/or electrostatic repulsion from the core may influence the colloidal stability of the core/shell microgels.

Effect of nanoshell addition on oscillatory behavior

To clarify the effect of the addition of a nanoshell on oscillatory behavior, we carried out the BZ reaction using core and core/shell microgels. In this investigation, malonic acid (62.5 mM), NaBrO_3

Figure 3 Temperature dependence of the hydrodynamic diameters of core (a), core/pNIPAm shell (b) and core/pNIPMAm shell (c) microgels under the reduced state Ru^{II} in 1 mM Ce^{III} and 0.3 M HNO₃ solution (orange diamond), as well as the oxidized state Ru^{III} in 1 mM Ce^{IV} and 0.3 M HNO₃ solution (green square) as measured by DLS. The dispersion concentration was 0.005 wt % in all cases. I to III shown in Figure 3c correspond to those in Figure 5. A full color version of this figure is available at the *Polymer Journal* journal online.

(84 mM) and HNO₃ (0.3 M) were used as substrates for the BZ reaction at fixed concentrations for all experiments. Figure 4 shows the temperature dependence of self-oscillating profiles of optical transmittance for core and core/shell microgel dispersions. For all

Figure 4 Self-oscillating profiles of optical transmittance for core (a), core/pNIPAm shell (b) and core/pNIPMAm shell (c) microgels. The microgels (80 μM of Ru(bpy)₃) were dispersed in aqueous solutions containing malonic acid (62.5 mM), NaBrO₃ (84 mM) and HNO₃ (0.3 M). The profiles were measured at different temperatures. In this study, a wavelength of 570 nm was selected. A full color version of this figure is available at the *Polymer Journal* journal online.

profiles, the oscillations were observed after an induction period, which is a typical characteristic of the BZ reaction. Note that we conducted these investigations by changing the temperature, whereas the other conditions were fixed (that is, initial concentrations of substrates, stirring and microgel concentrations) to compare the characteristics with each other, that is, the induction period, oscillating period and oscillating waveform. Figure 4a shows the oscillation profiles of transmittance for core microgel dispersions as a function of temperature. At low temperatures (15–25 °C), the amplitude of the oscillation became slightly greater with increasing temperatures (for example, 1.1% at 15 °C and 1.8% at 25 °C). The increase in amplitude is mainly due to the increased deviation of the hydrodynamic

diameters between the Ru^{II} and Ru^{III} states, as shown in Figure 3a. Next, a remarkable change in waveform and amplitude was observed at 27 °C. The amplitude then attenuated at 27.5 °C. The periodic transmittance changes could no longer be observed at higher temperatures because of the flocculation of microgels. We had observed these phenomena previously; the dramatic change in oscillating waveform and amplitude is related to the difference in colloidal stability between the Ru^{II} and Ru^{III} states. The difference led to the autonomous flocculating/dispersing oscillation of the microgels.¹⁹ On the other hand, such a dramatic change in amplitude was not observed for the core/shell microgels, as shown in Figures 4b and c. For the core/pNIPAm microgels shown in Figure 4b, the amplitudes of oscillation were not very different between 15 and 27 °C, which should be because of small deviations in size between the Ru^{II} and Ru^{III} states at all temperatures (0.7% at 15 °C, 0.8% at 20 °C, 0.8% at 25 °C, 0.8% at 26.5 °C and 0.7% at 27 °C). The periodic transmittance changes could no longer be observed at higher temperatures because of the flocculation of microgels. For the core/pNIPMAm microgels shown in Figure 4c, the oscillatory behavior as a function of temperature was different from that of core/pNIPAm microgels. The amplitudes of oscillation became slightly greater with increasing temperature from 15 to 29 °C (1.2% at 15 °C, 1.3% at 20 °C, 1.9% at 25 °C, 2.7% at 27.5 °C, 2.7% at 29 °C) and then became slightly smaller from 30 to 33 °C (1.7% at 30 °C and 1.5% at 33 °C). The increase in amplitude at low temperatures is mainly due to the increased deviation of the hydrodynamic diameters between the Ru^{II} and Ru^{III} states, as shown in Figure 3c, which is the same reason for the behavior of the core microgels. However, the decrease in amplitude is a new phenomenon, which should be related to smaller deviations in size between the Ru^{II} and Ru^{III} states at higher temperatures, as shown in Figure 3c. After that, an increased amplitude with a decreased total transmittance was observed at 34 °C, which may be due to autonomous dispersing/flocculating oscillation of microgels.¹⁹ A possible oscillating mechanism of the core/pNIPMAm microgels is illustrated in Figure 5. At low temperatures (region I, Figures 3c and 5), the amplitude of the swelling/deswelling oscillation increases with temperature because of increases in size deviation, as can be seen in Figure 3c. The amplitude then decreases with rising temperature because the core is largely deswollen; thus, the size deviations between the Ru^{II} and Ru^{III} states measured by DLS become almost the same (region II, Figures 3c and 5). Thereafter, the oscillatory amplitude increases, but the total transmittance decreases because of the autonomous dispersing/flocculating oscillation (region III, Figures 3c and 5).¹⁹ In this region III, the core part should be completely deswollen. Thus, the

autonomous dispersing/flocculating oscillation of the core/pNIPMAm shell microgels indicates that the charge density originating from the core may contribute to the colloidal stability of the microgels.

We next compared the oscillations of the microgels with the bulk solution of the BZ reaction in terms of the induction period. It should be noted that we did not use the core/pNIPAm microgels further because the core/shell microgels did not show desirable properties. Figure 6 shows the temperature dependence of the induction periods of the microgel oscillations and the bulk solution of the BZ reaction. It is to be noted that the induction periods for the microgels could not be measured above the CFTs of the microgels because of flocculation. The induction period for both core and core/pNIPMAm shell microgels became longer than that of the bulk solution of the BZ reaction in this temperature range. Moreover, the induction period for core/pNIPMAm microgels became longer than that of core microgels at all temperatures. In particular, the induction period for core/pNIPMAm microgels increased with temperatures above 27.5 °C. The most accepted hypothesis to explain the induction period of the BZ reaction is that a crucial concentration of the organic brominated species, mainly bromomalonic acid, must be reached before oscillation begins.³² Thus, the results in Figure 6 can be understood by the effect

Figure 6 Effect of temperature on the duration of the induction period for the bulk solution of the BZ reaction as a control (black triangle), as well as for core (red diamond) and the core/pNIPMAm shell (blue square) microgels. The microgels (80 μM $\text{Ru}(\text{bpy})_3$) were dispersed in aqueous solutions containing malonic acid (62.5 mM), NaBrO_3 (84 mM) and HNO_3 (0.3 M). A full color version of this figure is available at the *Polymer Journal* journal online.

Figure 5 Different oscillating modes for core/shell microgels. I–III shown here correspond to those in Figure 3c. A full color version of this figure is available at the *Polymer Journal* journal online.

Figure 7 Arrhenius dependence of oscillating frequency (F_{osc}) using core (red diamond) and core/pNIPMAm shell (blue square) microgels. Microgels (80 μm Ru(bpy)₃) were dispersed in aqueous solutions containing malonic acid (62.5 mM), NaBrO₃ (84 mM) and HNO₃ (0.3 M). Control experiments of the BZ reaction without microgels were investigated (black triangle) in the same aqueous solution. A full color version of this figure is available at the *Polymer Journal* journal online.

of Ru(bpy)₃ immobilization in the microgels, which is similar to the hydrogel-immobilized enzyme reaction.³³ In the microgel systems described in this study, the rate of bromomalonic acid production is lower than that of the bulk solution of the BZ reaction because of the lower diffusion constant of substrates and intermediates in the microgels. In addition, the diffusion constant of the substrates and intermediates in the core/shell microgels is lower than that in the parent core microgels. In particular, the diffusion constant should be very low when the core/pNIPMAm shell is highly deswollen (that is, above 27.5 °C). This result is one of the proofs of the addition of shells to the parent core.

We then compared the oscillations of microgels with the bulk solution of the BZ reaction in terms of the oscillation period, P_{osc} . In this study, the average value of the period between the second and the sixth oscillation was regarded as the oscillation period. Because our measurements of oscillations were completed after a small percentage of the initial quantity of the substrates was consumed, the concentration of the substrate at a specific measuring time may be approximated as its initial concentration. Here, the frequency of the oscillation, F_{osc} ($F_{\text{osc}} = 1/P_{\text{osc}}$), was used for analysis. As shown in Figure 7, the frequency of the bulk solution for the BZ reaction increased with temperature, in accordance with the Arrhenius equation.³⁴ For core microgels, the Arrhenius equation could be fitted in the case in which the temperature was below the VPTT, as shown in Figure 7. However, the frequency decreased near the VPTT of the microgels because of the autonomous dispersing/flocculating oscillation, and the corresponding plots deviated from the Arrhenius equation, which agrees with our previous data.²⁰ For core/pNIPMAm shell microgels, the Arrhenius equation could be fitted when the temperature was above the VPTT of the parent core microgels (up to 29 °C). Above 29 °C, the plots deviate slightly from the Arrhenius equation before the flocculation of microgels. These deviations both for the core and core/pNIPMAm shell microgels may be related to the lowered diffusibility of the substrates and intermediates in the microgels; the diffusion constant should be lower in highly deswollen aggregates of the core microgels, whereas the constant should be lower without aggregation of the core/pNIPMAm shell microgels, that

is, the simple deswelling of the core/shell microgels. In addition, the frequency for the core/pNIPMAm shell microgels became higher than that for the parent core between 15 and 25 °C. We have already reported that the frequency increased as the crosslinked density of the microgels increased when they are in the swollen state.²⁰ Thus, in this study, higher frequencies for core/pNIPMAm shell microgels may be because of greater difficulties in mass transportation in the core/shell microgel than in the parent core. In conclusion, the structure of the microgel has an important role in controlling the oscillation frequency.

Next, to understand the effect of the addition of the nanoshell to parent core microgels on the oscillation period in more detail, we compared the representative waveforms observed for the core microgels and the core/pNIPMAm shell microgels (Figure 8). Before comparing these waveforms, we will provide the outline of the Field-Körös-Noyes mechanism.^{35,36} According to this scheme, the overall BZ reaction may be divided into the following three main processes: the consumption of the bromide ion (process A), the autocatalytic reaction of the bromous acid with oxidation of the catalyst (process B) and the organic reaction with reduction of the catalyst (process C).

Following the Field-Körös-Noyes mechanism, we divided the waveforms into processes A, B and C, as shown in Figure 8. Table 1 summarizes the oscillating periods P_{osc} , the durations of processes A–C, as well as the A/P_{osc} , B/P_{osc} and C/P_{osc} values for the bulk solution, the core microgels and the core/pNIPMAm shell microgels. At the same temperatures, the B/P_{osc} and C/P_{osc} values for the microgel systems became larger than those for the bulk solution. Moreover, these values for the core/pNIPMAm shell microgels became larger than those of the parent core microgels at the same temperatures. We have already reported that the change in oscillating rhythm between the bulk solution and microgels can also be understood from the effect of Ru(bpy)₃ immobilization in the microgels because processes B and C contain a catalytic reaction; the rate of an immobilized catalytic reaction is lower than that of the same amount of a soluble catalyst.²⁰ In this study, we found that shell addition affected the rhythm of oscillation further because of greater difficulties in mass transportation in core/pNIPMAm shell microgels than in the parent core. In contrast, the A/P_{osc} values for microgels became smaller than those for the bulk solution at the same temperatures. The values for core/pNIPMAm shell microgels also became smaller than that for the parent core at the same temperatures. The smaller A/P_{osc} values of microgels may be related to their larger C/P_{osc} values; the lowered rate of process C may affect process A.²¹ As a result, we found that changes in the oscillation period between core and core/pNIPMAm shell microgels were due to a similar effect on the dependence of the crosslinking density as previously reported; that is, mass transportation in microgels has an important role in determining the oscillatory behavior.

CONCLUSIONS

We synthesized self-oscillating core/shell microgels by precipitation polymerization. Compared with parent core microgels, the flocculation temperature for core/pNIPMAm shell microgels increased, resulting in a new oscillating mode, which is supported by changes in the

Figure 8 Typical oscillating waveforms in the bulk solution of the BZ reaction (a–d) and in core/pNIPMAm shell microgels (e–h). Microgels (80 μm Ru(bpy)₃) were dispersed in aqueous solutions containing malonic acid (62.5 mM), NaBrO₃ (84 mM) and HNO₃ (0.3 M). The profiles were measured at different temperatures: 15 °C (a, e), 20 °C (b, f), 25 °C (c, g) and 30 °C (d, h). Control experiments of the BZ reaction without microgels were investigated in the same aqueous solution containing 80 μm Ru(bpy)₃. A full color version of this figure is available at the *Polymer Journal* journal online.

Table 1 A/P_{osc} , B/P_{osc} and C/P_{osc} values for the bulk solution of the BZ reaction, the core and the core/pNIPMAm shell microgel systems

Sample	Temp., °C	P_{osc} , s	A, s	B, s	C, s	A/P_{osc}	B/P_{osc}	C/P_{osc}
Bulk solution	15	357	183	18	155	0.51	0.05	0.43
Bulk solution	20	197	111	17	69	0.56	0.09	0.35
Bulk solution	25	120	70	14	37	0.58	0.11	0.31
Bulk solution	30	77	41	11	26	0.53	0.13	0.34
Core/pNIPMAm shell	15	248	78	16	154	0.31	0.06	0.62
Core/pNIPMAm shell	20	152	27	19	106	0.18	0.13	0.70
Core/pNIPMAm shell	25	96	11	16	69	0.11	0.17	0.72
Core/pNIPMAm shell	30	71	9	13	49	0.13	0.18	0.69
Core	15	273	103	18	152	0.38	0.07	0.56
Core	20	177	45	15	117	0.25	0.08	0.66
Core	25	103	27	13	63	0.26	0.13	0.61

induction period, the amplitude of oscillation, the oscillating period and the oscillating waveforms. We believe that this material will enable us to create new technologies including microactuators for use in microfluidic devices.

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