Magnetically Activated Swelling for Thermosensitive Gel Composed of Interpenetrating Polymer Network Constructed with Poly(acrylamide) and Poly(acrylic acid)

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The volume change of the thermosensitive gel composed of an interpenetrating polymer network (IPN) was controlled magnetically. Thermally triggered swelling of the IPN gel containing poly(acrylamide) and poly(acrylic acid) resulted from heating inside the gels due to the magnetic hysteresis loss of the ferromagnetic powder immobilized. The 16% γ-Fe_2O_3-loaded IPN gel swelled 1.5 times as large as the initial volume within 1 h under the alternating magnetic field (effective value 830 Oe, maximum value 1,170 Oe, 2.08 kHz). The IPN gel deswelled after cooling. The cycle process of swelling-deswelling was repeated by the on-and-off control of the magnetic field.

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Keen interests are paid for a variety of functional gel. There are many reports concerning the thermosensitive polymer gel which has a lower critical solution temperature (LCST).[1-5] In recent years, authors reported the gel of the magneto-responsive poly(*N*-isopropylacrylamide), (NIPAAm), supplemented by ferromagnetic powder; the volume phase transition of the gel was observed under exposure of the alternating magnetic field.[6] γ-Fe_2O_3 powder immobilized in the gel generated heat due to the magnetic hysteresis loss, and made the gel temperature increase above the LCST of the polymer. Accordingly, the gel deswelled spontaneously in the presence of the magnetic field. This intelligent gel could be utilized as chemomechanical system[7] or carriers of enzymes.[8,9]

As compared with the LCST gels, there have been reported only a few thermally-swelling gels concerning the properties of an upper critical solution temperature (UCST). Ogata et al. reported the thermally triggered swelling of the interpenetrating polymer networks (IPN), and investigated the swelling properties of the IPN gels as drug carriers.[10-12] These IPN hydrogels are composed of poly(acrylamide) and poly(acrylic acid), abbreviated to polyAAm and polyAA, respectively. At the deswelling state of the gel, intermolecular complexes are formed between amide groups of polyAAm and carboxylic acid groups of polyAA via hydrogen bonds. The UCST, at which the hydrogen bonds between polymers are scissored up by heating, is observed as the critical temperature where the gel to expand. Cleavage of the hydrogen bonds between polymer chains can cause the gel swelling due to the hydration of polymers after heating above the UCST.[10]

Some kinds of hydrogels containing magnetic powder were studied to make the functional gels exhibiting the magnetic properties. Ferric oxide powder was immobilized in poly(vinyl methyl ether) gel to prepare the fast-responsive gel by Hirasa et al.[13,14] Sakai et al. used the ferrite powder as tiny vibrators in the gel under exposure of the alternating magnetic field.[15] According to Huang et al., the ferric oxide powder was effective to increase the heat transfer rate in the gel.[14] They used the ferric oxide powder as heat transmitter. On the other hand, γ-Fe_2O_3 powder was served as heat generator in our previous report.[6]

In this paper, we describe the new type of magnetically activated gel, which expands under exposure of the alternating magnetic field. The magnetic heating method was applied to the γ-Fe_2O_3-loaded IPN gel. The temperature of the gel increases, when the ferromagnetic powder immobilized in the gel generates heat in the presence of alternating magnetic field. Heating polymers in the gel makes the cleavage of hydrogen bonds between amide group of polyAAm and carboxylic acid groups of polyAA. Following the dissociation of the polymer complex, the polymer molecules associate with surrounding water molecules to swell the IPN gel. After turning the magnetic field off, the temperature decreases and the IPN gel deswells. This gel is possible to be applied for the construction of the magnetically triggered absorbent system for the targeted molecules, molecular separation, etc.

The purpose of our research is to characterize the magneto-responsive IPN gel and to control the repetition process between the swelling and the deswelling magnetically.

Experimental

Materials γ-Fe_2O_3 powder was gratefully received from TDK Electronics Co. All other chemicals were of guaranteed grade or the best commercially available.

Synthesis of IPN gel IPN gels were prepared by a method of sequential IPN synthesis. γ-Fe_2O_3-loaded polyAAm gel was crosslinked by *N*, *N*'-methylenebisacrylamide (MBA) as an initial polymer-network for the IPN, and then the polymer-network of polyAA was synthesized within the polyAAm gel. Feed composition for the initial and the secondary polymer-networks of the IPN was shown in Table 1. Abbreviation of polyAAm(0.2)-polyAA(0.1) means that the former is the initial polymer-networks of polyAAm crosslinked by 0.2 mol% MBA and the latter is the secondary polymer-networks of polyAA

Table 1 Feed composition for the initial and the secondary gels of the IPN constructed with polyAAm and polyAA

	Initial gel component[a]			Second gel component[a]	
	γ –Fe_2O_3	AAm	MBA	AA	MBA
	g	mmol	mmol	mmol	mmol
polyAAm (0.1) – polyAA (0.1)	0	20	0.020	20	0.020
polyAAm (0.1) – polyAA (0.2)	0	20	0.020	20	0.040
polyAAm (0.2) – polyAA (0.1)	0	20	0.040	20	0.020
γ –Fe_2O_3 (8) –polyAAm (0.1) – polyAA (0.1)	0.82	20	0.020	20	0.020
γ –Fe_2O_3 (16) –polyAAm (0.1) – polyAA (0.1)	1.80	20	0.020	20	0.020
γ –Fe_2O_3 (8) –polyAAm (0.2) – polyAA (0.2)	0.82	20	0.040	20	0.040
γ –Fe_2O_3 (16) –polyAAm (0.2) – polyAA (0.2)	1.80	20	0.040	20	0.040

a) Eight ml each of water was mixed with the components for the initial and the secondary gels, respectively.

crosslinked by 0.1 mol% MBA, respectively. The content of γ-Fe_2O_3 (0, 8, 16%) was determined as the weight ratio just after the polymerization of the polyAAm gel.

The desired amount of AAm and MBA was dissolved in water, and then needle-like γ-Fe_2O_3 powder (0.5-0.8 μm length) was suspended in the solution. Nitrogen gas was bubbled into the mixture to remove dissolved oxygen. Polymerization was carried out within silicone tubes (ϕ 2mm) in order to prepare cylindrical gel by addition of aqueous solution of ammonium peroxodisulfate (APS) and *N*, *N*, *N*', *N*'-tetramethylethylene-diamine. The silicone tubes were roatated during the polymerization to avoid the sedimentation of the γ-Fe_2O_3 powder in the mixture. The cylindrical gel prepared was washed with water and allowed to stand at the room temperature for 48 h, and then dried *in vacuo* at room temperature for 7 h. The dried gel rod was re-swollen within a glass tube (ϕ 2mm) using the pre-gel solution of AA gel containing APS at 5°C for 48 h. The fully absorbed gel within the glass tube was heated at 60°C for 24 h to synthesize the polymer-network of AA. The IPN gel rod synthesized was pulled out of the tube and washed, and was equilibrated in water at 22 °C before the following experiments. Similarly, various polyAA-polyAAm gels were prepared by the sequential method.

Swelling-deswelling profiles After the equilibration at 22°C, the temperature of the gel rod was jumped up to 40°C. The length of the gel rod (L) was measured with time, and $(L/L_o)^3$ was calculated as the swelling ratio, where L_o is the initial length of the gel rod at 22°C. The swelling-deswelling profiles were measured in the case of the temperature-jump between 22 and 40°C.

Magnetic heating An alternating magnetic field (magnetic strength: effective value 830 Oe, maximum value 1,170 Oe, 2.08 kHz) was generated by a bipolar power supply (BWS40-15, Takasago) with a function generator (FG-203, Kenwood) using the apparatus as shown in Fig. 1. Ten of gel rods (50 mm long) were packed into the glass column (ϕ 12mm) filled with water, and the column was set between the gap (19 mm) of the electromagnet in order to expose the alternating magnetic field. A york of the electromagnet was cooled by cold water to remove the heat generated at the york.

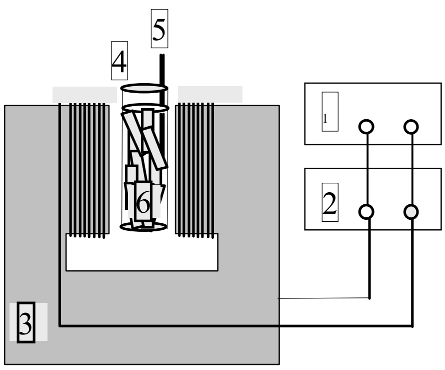

Fig. 1 Apparatus of the magnetic heating for the IPN gels. 1 Function generator; 2 Electronic power supply; 3 Electromagnet; 4 Glass column; 5 Thermocouple; 6 IPN gel rods.

Measurement of the gel magnetization The M-H curve (the magnetization vs. the magnetic strength) of the gel containing γ-Fe_2O_3 powder was measured with a vibrating sample magnetometer (VSM) (BHW-55, Riken Denshi Co.) in the air at the room temperature just after the separation of the gel from water. It took about 10 min to measure the M-H curve. The gel volume was kept constant during the measurement, because there was no water to absorb for expanding the gel volume. The content of the magnetic powder in the gel was determined by a thermogravimetric analyzer (TG/DTA6200, Seiko Instruments).

Results and Discussion

Swelling-deswelling profiles of IPN gels Two kinds of IPN gels, polyAAm-polyAA and polyAA-polyAAm, were synthesized by the sequential method. Both IPN gels without the ferromagnetic powder were transparent in the range between 22 and 40°C. Figure 2 shows the representative profiles for the volume change of polyAA(0.1)-polyAAm(0.2) and polyAA(0.2) -polyAAm(0.1) in the case of the temperature-jump between 22 and 40°C. The gel swelled for 24 h at 40°C, and then deswelled for 24 h at 22°C in response to the temperature-jump. The similar profiles were obtained concerning the reversibility of

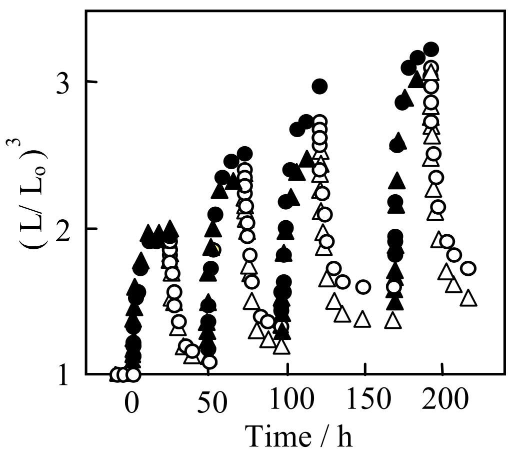

Fig. 2 Reappearance of the swelling and deswelling of the IPN gels constructed with polyAA and polyAAm. Closed symbols; 40°C, Open symbols; 22°C. ○: polyAA(0.2)-polyAAm(0.1), △: polyAA(0.1)-polyAAm(0.2).

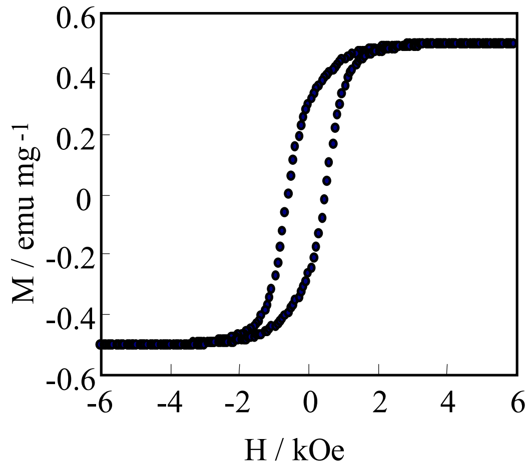

Fig. 3 Magnetization curve of the gel containing 16% γ-Fe_2O_3 powder.

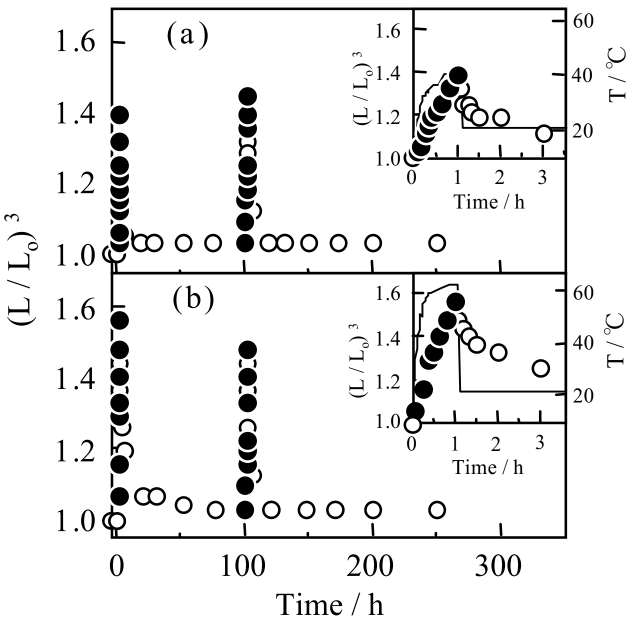

Fig. 4 Magnetically activated swelling of γ-Fe_2O_3-loaded IPN gels constructed with polyAAm and polyAA. $(L/L_o)^3$ as swelling ratio: in the presence (●) and absence (○) of the alternating magnetic field (effective value: 830 Oe, maximum value 1,170 Oe, 2.08 kHz). After turning the magnetic field off, the gels were cooled at 22°C. Solid line in the inserted figure: temperature. (a) 8% γ-Fe_2O_3-polyAAm(0.2)-polyAA(0.2), (b) 16% γ-Fe_2O_3-polyAAm(0.2)-polyAA(0.2).

swelling-deswelling for polyAAm(0.1)-polyAA(0.2) and polyAAm(0.1)-polyAA(0.2) (data not shown). However, the baseline at 22°C increased gradually with time in the repetition of swelling-deswelling process as shown in Fig. 2. It seems that it will take more time to restore the original volume in deswelling process at 22°C than in swelling at 40°C. The velocity of swelling at 40°C is higher than that of deswelling at 22°C. Swelling and deswelling are connected with hydration and dehydration to polymer chains in the gel. Therefore, it is reasonable that the water content is accumulated in the repetition of swelling-deswelling process. PolyAAm-polyAA can perform the swelling-deswelling profiles between 40 and 22°C as well as polyAA-polyAAm. This result suggests that the sequence of a series of polymerization in the IPN preparation may not make

Table 2 Initial rates of the volume increase (V_s) and the temperature increase (V_t)

	10^3V_s	V_t
	min^{-1}	$K\ min^{-1}$
γ-Fe_2O_3(8)-polyAAm(0.1)-polyAA(0.1)[a]	10	1.7
γ-Fe_2O_3(16)-polyAAm(0.1)-polyAA(0.1)[a]	9.5	3.5
γ-Fe_2O_3(8)-polyAAm(0.2)-polyAA(0.2)[a]	7.2	1.7
γ-Fe_2O_3(16)-polyAAm(0.2)-polyAA(0.2)[a]	9.7	3.6
polyAAm(0.1)-polyAA(0.1)[b]	44	–
polyAAm(0.1)-polyAA(0.1)[c]	24	–

a) The gel at 22°C was exposed in the alternating magnetic field (830 Oe, 2.08 kHz).
b) The gel temperature jumped from 22 to 50°C in water bath.
c) The gel temperature jumped from 22 to 40°C in water bath.

serious difference on the IPN polymer-network for the temperature-dependence of the volume change (data not shown).

M-H curve The curve of the magnetization (M) against the magnetic strength (H) was measured using the gel containing 16 % γ-Fe_2O_3, 14% polymer, and 70% water (Fig. 3). From Fig. 3, the coercive force, the residual magnetization, and the saturation magnetization were obtained to be 0.48 kOe, 0.27 emu/mg-gel, and 0.51 emu/mg-gel, respectively.

The alternating magnetic field applied to the IPN gel using the electromagnet of Fig. 1 was 1.17 kOe at maximum value. This value was much larger than the coercive force of the ferromagnetic powder. Consequently, the heat was generated effectively inside the 16 % γ-Fe_2O_3-loaded IPN gel due to the magnetic hysteresis loss, which is equivalent to the area surrounded by a loop of M-H curve.

Magnetically activated swelling of the IPN gels The magnetic heating was used for the volume change of the gel rod containing 8 or 16% γ-Fe_2O_3 (Fig. 4). The magnetic field was turned off after 1 h exposing and the gel rods were cooled down by water of 22°C. The temperature profile in the inserted figures in Figs. 4a and 4b shows that the heat was generated from the inside of the gel rods in the column, and the temperature of the IPN gels containing 8 or 16% γ-Fe_2O_3 increased from 22 to 43 or 61°C within 1 h. It is reasonable that the column temperature for the 16% γ-Fe_2O_3 is much higher than that for the 8% γ-Fe_2O_3. Because the heat generation in principle is in proportion to the amount of the magnetic powder in the gel as described in our previous paper.[6] However, it is plausible that the final temperature leveled off at around 61°C after the 1-h-exposure of the alternating magnetic field on the 16% gel rods as considered the heat loss due to emission.

The inserted figures in Figs. 4a and 4b showed that $(L/L_o)^3$ increased linearly with time in the presence of the alternating magnetic field, and decreased gradually after turning the magnetic field off. The magnetically activated swelling can be repeated twice for 8% γ-Fe_2O_3-polyAAm(0.2)-polyAA(0.2) and 16% γ-Fe_2O_3- polyAAm(0.2) -polyAA(0.2). The swelling ratios of $(L/L_o)^3$ gave maxima at around 1.4 - 1.5 and 1.5 - 1.6 after 1-h-heating, respectively. In the case of the 8% γ-Fe_2O_3-polyAAm(0.1)-polyAA(0.1) or 16% γ-Fe_2O_3-polyAAm(0.1)-polyAA(0.1), the swelling-deswelling profiles were also reappeared (data not shown).

The initial swelling rates (V_s) are calculated from the slopes of straight lines of $(L/L_o)^3$ against time in the inserted figures in Fig. 4. The initial rates of the temperature increase (V_t) are also determined from the plots of the temperature vs. time in the same figures. The V_s and V_t obtained are summarized in Table 2. The V_t's of 8% and 16% γ-Fe_2O_3-loaded gels are 1.7 and 3.5 - 3.6 $K\ min^{-1}$, respectively. The heating rate is confirmed to be in proportion to the γ-Fe_2O_3 content as heat generator. The V_s's for the magnetic heating were 0.72 - 1.0 $\times$ 10^{-2} min^{-1} as shown in Table 2. The V_s's were not dependent on the γ-Fe_2O_3 content during the magnetic heating. On the other hand, the V_s's in the case of the temperature-jump in water bath were 2.4 - 4.4 $\times$ 10^{-2} min^{-1} (not containing γ-Fe_2O_3). The higher the temperature-jump is, the higher the V_s increases. The V_s's of the temperature-jump method were larger than those of the magnetic heating method. These results indicate that the presence of γ-Fe_2O_3 in the gel may disturb to swell the gel.

In our previous reports, the 16% γ-Fe_2O_3-loaded polyNIPAAm gel, which exhibits the LCST properties after the immobilization of γ-Fe_2O_3, deswelled magnetically under the same condition (the effective value of the magnetic strength: 830 Oe, 2.08 kHz).[6] The V_s and V_t for the polyNIPAAm gel were around 6.6 $\times$ 10^{-2} min^{-1} and 11 K min^{-1}, respectively. The V_s and V_t of LCST gel were higher than those of UCST gel. This is because the LCST gel was heated in the process of excluding the water squeezed out of the gel under deswelling, while the UCST gel was heated for the swelling to absorb the surrounding water into the gel under exposure of the magnetic field.

In other words, the presence of water surrounding the UCST gel rods is indispensable for swelling during the exposure of the magnetic field. This result indicates that the heat generated magnetically must be consumed to increase the temperature of both gel and water in the column. Consequently, slow swelling is observed due to the low V_t's (1.7-3.5 K min^{-1}) for the IPN gels. However, the content increase of the ferromagnetic powder in the gel or the frequency increase of the alternating magnetic field made the heating rate higher significantly. In addition, the radiation from the apparatus was supposed to be one of the important factor to make the V_t lower. It suggests that V_t may increases significantly with improving the apparatus for the magnetic heating.

In conclusion, the magnetically activated swelling of gel was performed by using the magnetic heating due to the magnetic hysteresis loss of γ-Fe_2O_3 powder immobilized within the IPN gel. As shown in Fig. 4, the volume change of the gel can be repeated by the on-and-off of the alternating magnetic field. Therefore, this intelligent gel will be utilized in a variety of systems such as magnetically triggered separation for the targeted molecules, magnetically controlled bioreactor for the immobilized enzyme or microorganism, and the absorbent device for the molecular recognition.

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