ADVANCED MATERIALS

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# Fabrication of Temperature-Responsive Bending Hydrogels with a Nanostructured Gradient**

By *Taka-aki Asoh, Michiya Matsusaki, Tatsuo Kaneko,* and *Mitsuru Akashi**

Stimuli-responsive gels have attracted much attention as soft actuators due to their ability to change their volume or shape in response to an environmental trigger. The bending of these gels in response to signals is important for artificial muscles and switching devices.[1,2] Poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels are well-known thermo-responsive materials which upon being heated show a volume phase transition at a temperature corresponding to the lower critical solution temperature (LCST).[3] Many researchers investigated the isotropic kinetics of the swelling/deswelling process of PNIPAAm gels because of the comparatively slow deswelling process.[4,5] On the other hand, PNIPAAm-based hydrogels which bend in response to a temperature change has been reported as well. Hu et al. described partially interpenetrated polymer networks composed of PNIPAAm and poly(acrylamide) hydrogels, so-called "bi-gels",[6] which bend into circles in response to an increasing temperature. These "bi-gels" grasp or release an object simply by adjustment of the water temperature. However, their complicated configuration requires multistage processing and the contact surface of two gels may develop cracks during repetitive movements. And whilst composition-gradient copolymer gels, prepared from hydrophilic and hydrophobic substrates, are described in the literature,[7] they are difficult to control in terms of their curvature and bending speed. Therefore, the design of novel bending gels composed of thermo-responsive polymers has attracted much attention; and is particularly important for the development of high-performance, intelligent soft actuators that can function in water.

Herein, we report a novel strategy for the preparation of thermo-responsive bending gradient gels. PNIPAAm gels with two types of nanostructured gradients, consisting of either silica nanoparticles or nanopores, showed uniquely different bending properties depending on their deswelling characteristics. These gradient gels were simply fabricated through electrophoresis and subsequent photo-polymerization (Fig. 1). Osada et al. reported electrically driven systems comprising polymer gels and electrodes that were actuated to bend and stretch repeatedly in response to alternating voltages, whereby the mechanical motion of these gels is in fact driven by the direction of the electric field.[2] In contrast to this work, we designed nanostructured gradient gels which possess an inherent bending character for which the bending direction and curvature do not depend on the direction of an external stimulus, e.g., an electric field, but more so on the nanostructure of the gels.

PNIPAAm-silica composite hydrogels with a silica concentration gradient (silica-gradient gels) were prepared by electrophoresis of a silica suspension in a monomer solution in the presence of a cross-linker and photo-initiator. It is well known that silica particles have a negative charge in water and therefore move to the anode during electrophoresis.[8] We hypothesized that the thereby emerging gradient of the silica concentration can be fixed by photo-polymerization of the monomer and PNIPAAm hydrogels with a silica-concentration gradient can be obtained. An indium tin oxide (ITO) transparent electrode was used as the working electrode and a platinum (Pt) plate was used as the counter electrode. A pre-gel solution consisting of NIPAAm *N*,*N*′-methylenebis(acrylamide), 2,2-diethoxyacetophenone, and silica particles was injected between the ITO and Pt electrodes (1 mm spacing), and electrophoresis was carried out in a two- electrode electrolytic cell. Then, silica-gradient gels were prepared via photo-polymerization, with UV irradiation being applied from the ITO electrode side for 1 h at 4 °C. The gradient of the silica-concentration between cathode and anode in the obtained gels was confirmed by labeling the silica particles with a cationic dye post-polymerization.[9] Composite hydrogels were immersed into a 1 mM rhodamine 6G (R6G) solution for a few minutes at ambient temperature, and then rinsed with pure water. Figures 2a and 2b show hydrogels containing the labeled silica particles which were prepared with and without a voltage applied, respectively. Microscopic observation of the hydrogels clearly showed a gradient in intensity of R6G staining that confirmed the presence of a silica-gradient inside the hydrogel (Figs. 2b, 2c). Moreover, we determined the quantity of concentrated or diluted silica inside the hydrogels as a function of electrophoresis time and applied voltage using Fourier transform infrared spectroscopy (FT-IR) attenuated total reflection (ATR) measurements. IR spectra of lyophilized gradient hydrogels were measured from the ITO (anode) as well as the Pt (cathode) side. The $\nu_{Si\text{-}O}$ band was generally stronger at the ITO surface side compared to the Pt surface

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[*] Prof. Dr.M. Akashi, T. Asoh, Dr.M. Matsusaki, Dr.T. Kaneko
Department of Applied Chemistry, Graduate School of Engineering, Osaka University
2-1 Yamada-oka, Suita 565-0871 (Japan)
E-mail: akashi@chem.eng.osaka-u.ac.jp

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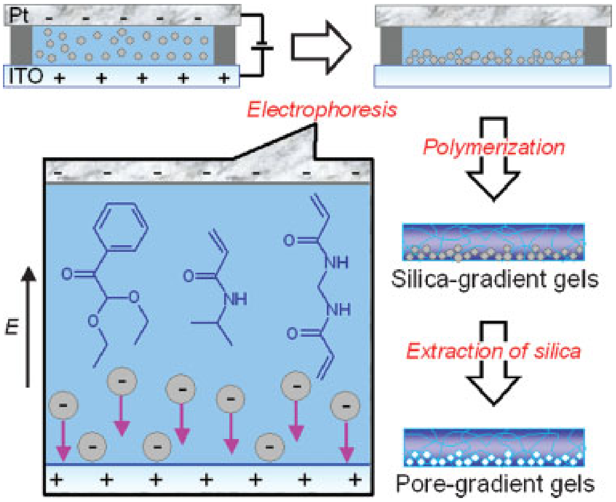

**Figure 1.** Schematic illustration of the synthesis of the two types of nanogradient gels via electrophoresis and subsequent photo-polymerization, and in the case of nanoporous gels silica-extraction.

side (Fig. 2d). Calculated silica concentrations are summarized in Table S1 (see supporting information). During electrophoresis the silica particles were diluted from the Pt side but concentrated at the ITO side. In order to characterize gradient properties quantitatively, we introduced a gradient constant, $g$, which was calculated using the following equation (Eq. 1)

$$g = (C_{ITO} - C_{Pt}) \cdot l^{-1} \qquad (1)$$

with $l$ being the thickness of the gels, and $C_{ITO}$ and $C_{Pt}$ the silica concentrations of the ITO and Pt sides of the gel, respectively. Increasing the duration of electrophoresis and/or the impressed voltage resulted in an increase of $g$ value, which clearly supported our hypothesis that the formation and control of a gradient concentration of silica particles in the PNIPAAm hydrogels via electrophoresis is possible. Interestingly, silica-gradient gels prepared via the electrophoresis route bent in an arc in response to temperature, whereas hydrogels without the electrophoresis treatment showed isotropic deswelling (Fig. 3a-d). In our experiments, the deswelling properties of silica-gradient gels depended on the concentration of silica particles inside the hydrogels. In the case of PNIPAAm hydrogels with a high silica concentration deswelling of the gels was inhibited by the silica particles (Fig. S1). In response to rising temperatures conventional PNIPAAm gels without silica deswelled to

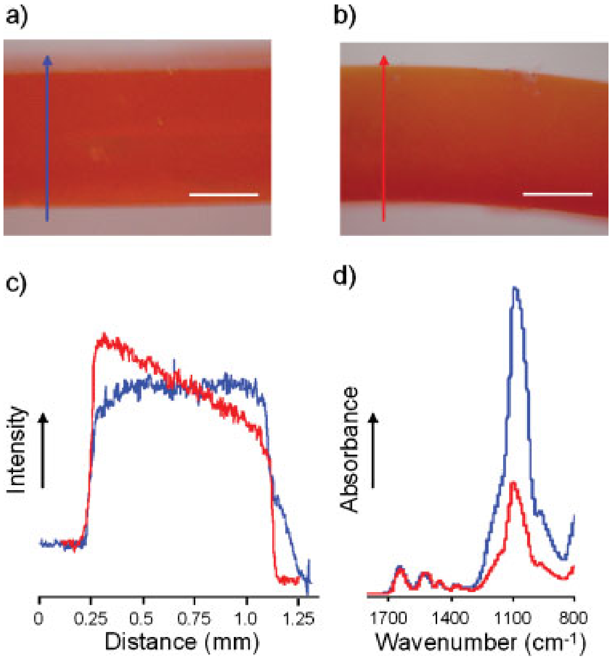

**Figure 2.** a-b) Microscopic images of hydrogels containing R6G labeled silica particles (at 20 °C) produced without and with electrophoresis, respectively (impressed voltage and electrophoresis time were, in that order, 2.0 V mm$^{-1}$ and 30 min). c) R6G intensity across the width of the same gels (blue = without, red = with electrophoresis). d) FT-IR/ATR spectra of a silica-gradient gel (2.0 V mm$^{-1}$, 7 min) were measured from the anode (blue) and cathode (red) side. All scale bars are 500 μm.

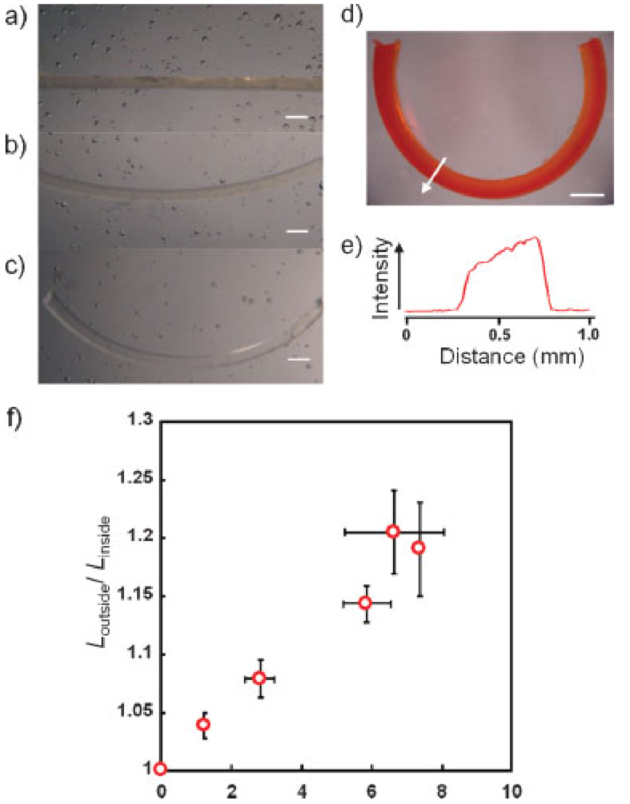

**Figure 3.** Microscopic images of silica-containing hydrogels at 40 °C, which were prepared using various voltage and electrophoresis times. a) 0 V mm$^{-1}$; b) 1.5 V mm$^{-1}$ and 7 min; c) 2 V mm$^{-1}$ and 7 min, respectively. d) Microscopic image of a R6G labeled silica-gradient hydrogel at 40 °C which was prepared using the same conditions as in Figure 2b). e) R6G intensity along the white line across the gel shown in Figure 3d). f) Relationship between $L_{outside}/L_{inside}$ ratio and gradient constant $g$ ($n = 3$). All scale bars are 1 mm.

about 50% of the volume at their swollen state at 20 °C, while composite hydrogels containing 10 v/v% silica particles deswelled to 77%, with lower amounts of silica particles not showing as significant effects. The difference in deswelling ratio between the two sides of the silica-gradient gels (*i.e.*, silica concentrated and diluted sides) is most likely the driving force behind the bending of the gels. After flexion of the silica-gradient gels the side with the higher amount of silica faces outwards, while the other side, containing a lower amount of silica, faces inwards (Fig. 3d,e). Furthermore, the deswelling speed of PNIPAAm hydrogels is enhanced by the presence of silica particles in low concentrations. Thus, fast bending of the silica-gradient gels was observed in response to temperature change. Increasing the voltage and/or the electrophoresis time resulted in an increase in curvature of the gels. Curvatures of bending gradient gels were estimated by measurement of the outside (convex, $L_{outside}$) and inside (concave, $L_{inside}$) lengths of the gels. A gel is flat (Fig. 3a) when the $L_{outside}/L_{inside}$ ratio equals 1 and a greater ratio means a larger curvature of the gel. The relationship between $L_{outside}/L_{inside}$ ratio and $g$ value is shown in Fig. 3f. The curvature of a silica-gradient gel in response to a temperature change depended on the corresponding gradient constant of the gel, with larger curvatures being observed for larger $g$ values. This result indicates that the silica-concentration gradients within the gels are the driving force for their flexion, and that the curvatures of the gradient gels are easily controlled by adjusting the silica gradient.

Previously we reported the rapid and controlled deswelling of porous PNIPAAm hydrogels prepared in the presence of silica particles with subsequent hydrofluoric acid treatment.[5] In that case, the porosity was easily controlled by changing the concentration and/or size of the silica particles; and the deswelling rate increased with an increasing pore content. If the silica particles can be removed from the silica-gradient gels using the same method, then novel pore-gradient gels, which show bending properties due to variations in porosity dependent deswelling speed, may be obtained. Porous PNIPAAm hydrogels with a gradient in porosity (pore-gradient gels) were derived from a silica-gradient gel structure when the silica was extracted out of the hydrogels through immersion in aqueous 23 wt% HF solution for 24 h (Fig. 4a). Extraction of the silica particles was confirmed using FT-IR/ATR.[5] The $\nu_{Si\text{-}O}$ vibration band of silica particles (1100 cm$^{-1}$) disappeared after treatment with HF. Deswelling properties of silica- and pore-gradient gels are summarized in Figure 4. We confirmed the rapid bending of these gradient gels with a temperature change from 20 to 40 °C in water. Figures 4b and 4c show the deswelling behavior of silica- and pore-gradient gels at 40 °C, respectively. Pore-gradient gels rapidly decrease in volume and bend dramatically forming an arc in the opposite direction of the silica-gradient gels during the process of deswelling (Figs. 4c and S2). As a matter of fact porous isotropic PNIPAAm hydrogels can undergo faster shrinkage in response to changing temperatures than conventional PNIPAAm hydrogels without any pores. Thus, the bending of the gels may have occurred due to differences in deswelling speed between the two sides, because one side shows faster deswelling than the other. This means for the design of bending gels that a difference in shrinkage rate at each surface would cause the anisotropic gels to bend. Further investigation of the deformation rates of pore-gradient gels is now in progress.

In conclusion, we prepared two types of nanostructured gradient gels that showed bending behavior in response to a temperature change. The present gradient gels were easily fabricated via electrophoresis and photo-polymerization, and where applicable subsequent silica extraction. The gradient ratio was easily controlled by changing the electrophoresis conditions. Differences in the physical properties between both sides of the gradient gels are the driving force behind the bending of the gels. We believe our novel, nanostructured gradient design of stimuli-responsive gels will further advance the development of functional gels for intelligent soft-actuator systems.

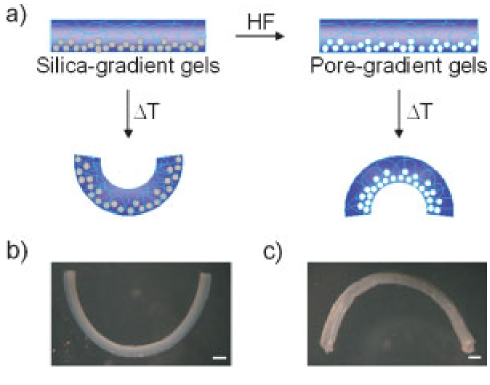

**Figure 4.** a) Schematic illustration of the synthesis of silica- and pore-gradient gels. b-c) Microscopic images of silica- and pore-gradient gels, respectively, after 40 s incubation at 40 °C. All scale bars are 1 mm.

## *Experimental*

*Materials*: *N*-isopropylacrylamide (NIPAAm) was kindly donated by Kohjin (Japan), and was used after recrystallization from *n*-hexane. *N,N′*-methylenebis(acrylamide) (MBAAm) was purchased from Nacalai Tesque (Japan). 2,2-diethoxyacetophenone and Rhodamine 6G were purchased from Wako (Japan) and used without further purification. Aqueous 23 wt% hydrofluoric acid (HF) solution was prepared via two-fold dilution of a 46 wt% HF solution which was purchased from Wako (Japan). Silica particles (mean diameter: 10 nm) were kindly donated by Nissan Chemical Ind. Ltd. (Japan) and were used as received.

*Preparation of gradient gels*: Pre-gel aqueous mixtures of the monomer NIPAAm (0.7 M), the cross-linker MBAAm (5 mol% of monomer), the photoinitiator 2,2-diethoxyacetophenone (1 mol% of monomer), and the silica particles (5 v/v%) were injected between ITO/Pt electrodes with 1 mm spacing. Afterwards, electrophoresis was carried out in two- electrode electrolytic cells before the silica-gradient gels were prepared by UV irradiation for 1 h at 4 °C. For the preparation of pore-gradient gels the silica was subsequently extracted through immersion of as-prepared composite gels in aqueous 23 wt% HF solution for 24 h at ambient temperature.

*Measurement methods*: After polymerization, the silica particles inside the hydrogels were labeled with a cationic dye, i.e., composite hydrogels were immersed in a 1 mM R6G solution for a few minutes at ambient temperature and then rinsed with pure water. Strong ionic binding of the cationic R6G to the anionic surface of the silica particles in water provided a convenient labeling procedure to observe the fabrication of the silica-concentration gradient inside the hydrogels. Shapes of hydrogels were observed using a Stemi DV4 microscope (Carl Zeiss, Germany) connected to a Cyber-shot DSC-F505V digital camera (Sony, Japan). Fourier-Transformed infrared (FT-IR) attenuated total reflection (ATR) spectra were collected on a Perkin Elmer Spectrum One FT-IR spectrometer at ambient temperature between 4000 and 400 cm$^{-1}$. Interferograms were co-added 16 times and Fourier transformed at a resolution of 4 cm$^{-1}$. FT-IR/ATR spectra of lyophilized hydrogels were measured from the ITO (anode) side as well as the Pt (cathode) side.

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