Photonic Hydrogels with Poly(ethylene glycol) Derivative Colloidal Spheres as Building Blocks

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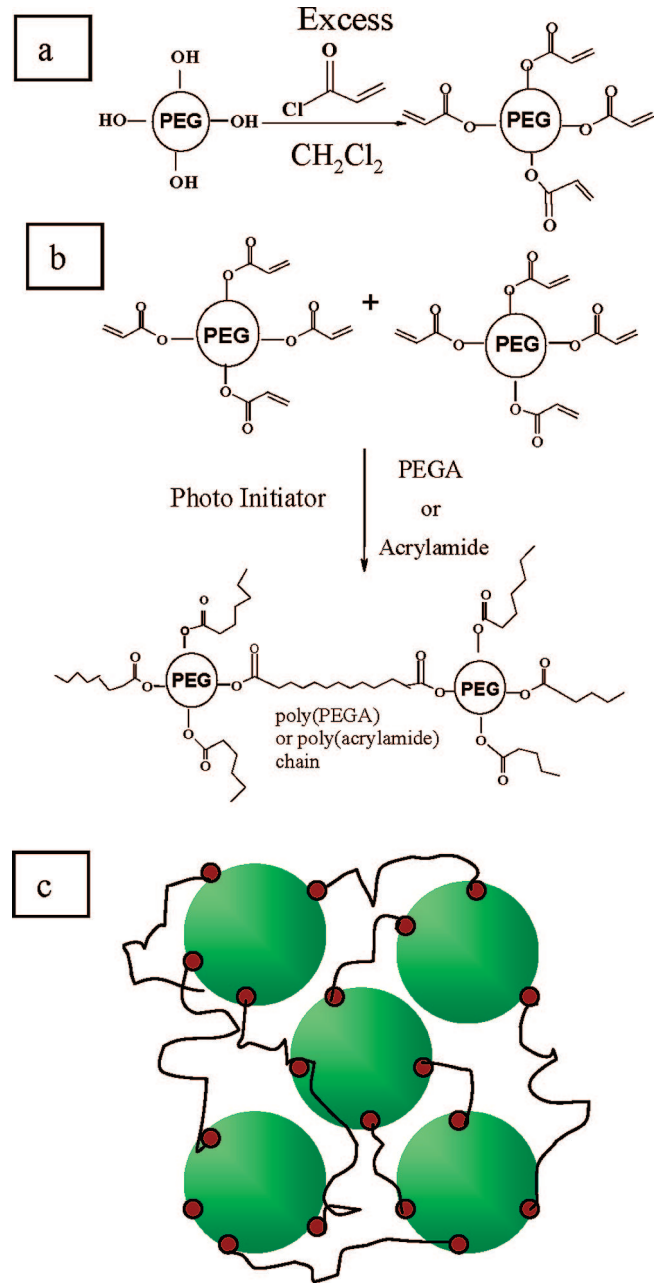
Photonic materials and devices that manipulate photons in visible and near-infrared spectra are the focus of research in diverse fields ranging from nanomaterials technology to optical computing.[1] Creating photonic hydrogels is part of this major thrust because they can not only control or detect photons by their ordered structures but also change propagation of photons in response to external stimuli.[2] The photonic hydrogel has been made by polymerizing a poly-*N*-isopropylacryalmide (PNIPAM) gel around a mesoscopically crystalline colloidal array of polystyrene (PS) colloids.[2] Inverse crystalline hydrogels have been obtained by using silica or PS colloidal arrays as templates.[3−5] A PNIPAM microgels array has been either entrapped by another gel matrix[6] or interconnected by cross-linkers.[7] Here we show that the microgels based on poly(ethylene glycol) (PEG) derivative polymers have been successfully used as building blocks for preparation of photonic hydrogels. These hydrophilic particles not only have thermal responsive behavior like PNIPAM particles but also can self-assemble into crystalline structures like PS, silica, or PNIPAM particles. Hydrogels are well-known for their hydrophilic and environmentally responsive properties.[8−11] Constructing photonic hydrogels with nontoxic, anti-immunogenic, thermally responsive PEG derivative polymers[12,13] could open a door for new applications.

Our approach is illustrated in Scheme 1. PEG derivative microgels are prepared and then attached with vinyl groups. After these particles self-assemble into an ordered array, they are used to connect neighboring polymer chains to stabilize the crystalline structure. Particles as cross-linkers can significantly enhance the mechanical properties of the gel.[14,15]

PEG derivative microgels were prepared by copolymerization of poly(ethylene glycol)ethyl ether methacrylate ($PEGETH_2MA$), poly(ethylene glycol) methyl ether methacrylate (PEGMEMA), and poly(ethylene glycol) acrylate (PEGA) using the free radical polymerization method.[13] The first two components have different values of the low critical solution temperature (LCST) due to their different molecular weights.[12] The combination of these two components made the LCST of the sample near the physiological temperature. The last component provided a functional group that will be used for the attachment of vinyl group after the microgel is prepared. Ethylene glycol dimethacrylate as cross-linker, dodecyl sulfate sodium as surfactant, and ammonium persulfate as initiator were mixed with monomer solution. The polymerization was carried out at 70 °C under a nitrogen atmosphere for 12 h. To attach vinyl groups, PEG derivative microgels were dried and redispersed in CH_2Cl_2. 1 g of acryloyl chloride and trace amount of triethylamine were slowly added into microgels solution. The reaction was carried out under dark at room temperature in an anhydrous environment for 24 h.

Scheme 1. (a) PEG Derivative Microgels Were Attached with Vinyl Groups; (b) Vinyl PEG Derivative Particles as Cross-Linkers To Connect PEGA or Polyacrylamide Polymer Chains Together under UV Irradiation; (c) Resultant Hydrogel Consists of a PEG Particle Crystalline Array That Diffracts Light and PEGA Polymer Chains That Stabilize the Particle Array[a]



[a] Green spheres represent PEG derivative particles, brown spheres vinyl group, and curved lined polymer chains.

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The PEG derivative microgels were characterized using an AFM microscope (Veeco/Digital Instruments Nanoscope III AFM). The sample was prepared by casting 4−5 drops of dispersion onto a glass slide. After it was naturally dried, the AFM images were taken, operating in tapping mode with a driving frequency 270 kHz. The average diameter of the particles was about 142 nm, which was smaller than the diameter (about 320 nm) in solution because the particles were dried. The inset of the bottom panel shows the fast Fourier transformation (FFT) of the bottom image. The 6-fold symmetry of the FFT clearly shows that the particles self-assemble into a crystalline structure with the (111) plane in parallel with the glass surface. The temperature-dependent average hydrodynamic radius (R_h) of these microgels with vinyl groups in water was characterized with dynamic light scattering measurements.

The hydrogel films with a PEG colloidal crystal array were synthesized using the following procedures. First, vinyl group attached PEG derivative microgels (see Scheme 1a) were mixed with an aqueous solution of either PEGA monomer or acrylamide monomer, including UV photoinitiator. The solution was then injected into a cell consisting of two clean quartz disks separated by a 125 μm Para-film. The colloidal crystalline structure was formed by slowly changing temperature from 29 to 4 °C in 24 h. This structure was then stabilized by long wavelength (365 nm) UV irradiation triggered free radical polymerization at 0 °C for 30 min.

Figure 2a shows a thermally reversible color change of the hydrogel thin film composed of PEG microgels cross-linked PEG acrylate (PEGA) polymer chains. The origin of the color comes from light diffraction from the long-range order of the PEG analogue microgels, similar to PNIPAM microgels.[16,17] Upon the increase of the temperature, the volume of the microgels decreases. Since the particles as cross-linkers are covalently connected to surrounding PEGA polymer chains, the shrinkage of the particles can take nontemperature-sensitive PEGA chains to move with them. As a result, the interparticle distance decreases with the temperature. This is the first crystalline hydrogel film that consists of all biocompatible materials including both the thermally responsive PEG derivative colloids and surrounding PEGA hydrogel matrix. PEG derivative microgels can be used as building blocks for a variety of other polymers. As a demonstration, we prepared a film composed of PEG microgels connecting polyacrylamide polymer chains as shown in Figure 2b.

The color change of the hydrogel film as a function of temperature has been quantitatively investigated using UV−vis spectroscopy. Figure 2c shows UV−vis spectra from a film composed of PEG derivative microgels and polyacrylamide chains. The sharp peak in the spectrum comes from the Bragg diffraction from periodic arrays of the microgels. The wavelength of the Bragg peak decreases from about 652 to 565 nm upon the increase of the temperature from 20 to 42 °C, in excellent agreement with visual inspection of the color change. The temperature-dependent wavelength of the Bragg peak is plotted in Figure 2d for both PEG microgel−PEGA polymer chains film and PEG microgel−polyacrylamide chains film.

The kinetics of the color change of hydorgel films has been investigated because it plays an important role for sensors and actuators applications. Figure 3a shows the UV−vis spectra from the film composed of PEG microgels and polyacrylamide chains when the temperature was increased from 21 to 55 °C. The wavelength of the Bragg peak is plotted against time in Figure 3b. It is known that the shrinking or swelling time (τ) of a gel is dependent on the square of the smallest linear dimension (a)

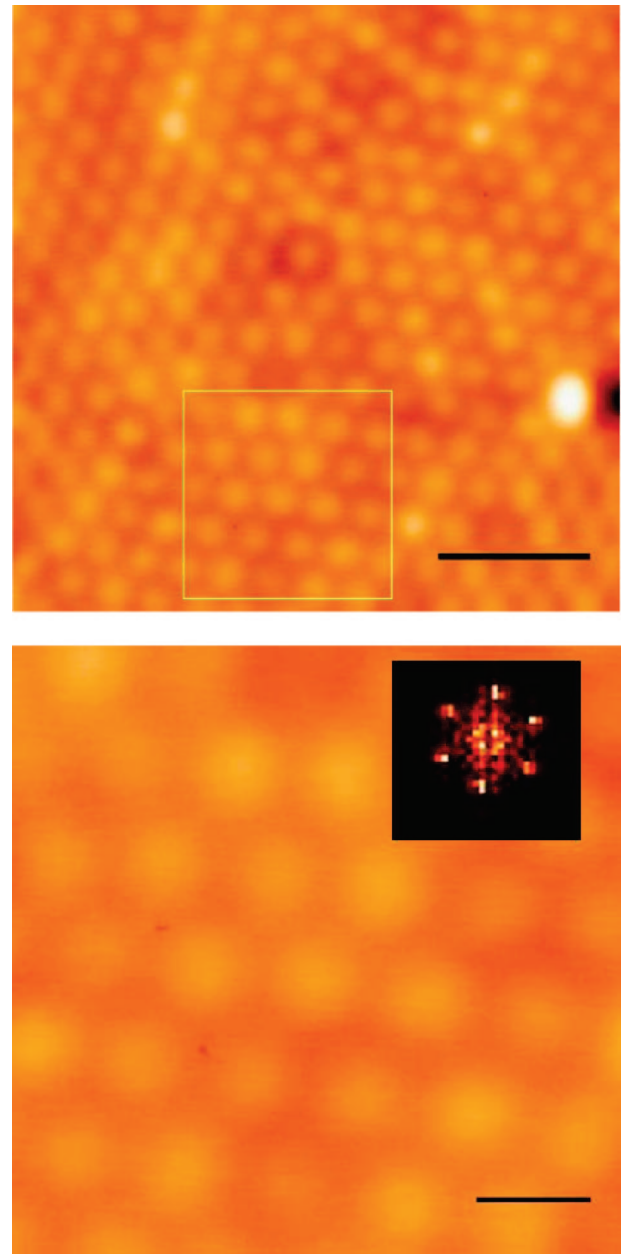

Figure 1. AFM images of PEG derivative microgels. The scale bars in the top and bottom panel are 500 and 150 nm, respectively. The bottom image is the enlargement of a boxed area in the top image. The inset of the bottom panel is the fast Fourier Transformation of the structure.

as described by $\tau = a^2/(\pi^2 D)$, where $D = (K + (4/3)\mu)/f$ is the collective diffusion constant of the gel network, and K, μ, and f are bulk molulus, shear modulus, and friction coefficient, respectively.[18] For a bulk gel, its size is large so that swells slowly. Since both the diameter of the microgels (about 320 nm) and the thickness of the final composite microgel/hydrogel film (about 140 μm) are small, the size and the color change should be fast in response to an external stimulus. Furthermore, because of the unique structure of particles as cross-linkers, the long chains between particles may act as free linear polymer chains that have less friction for water molecules.[19]

Using PEG derivative particles as both a colloidal ordered array and cross-linkers can provide not only crystal structures that diffract light but also enhance the mechanical properties of the resultant hydrogels. Two thin cylindrical gels have been made: one was PEG derivative particles as both a crystalline

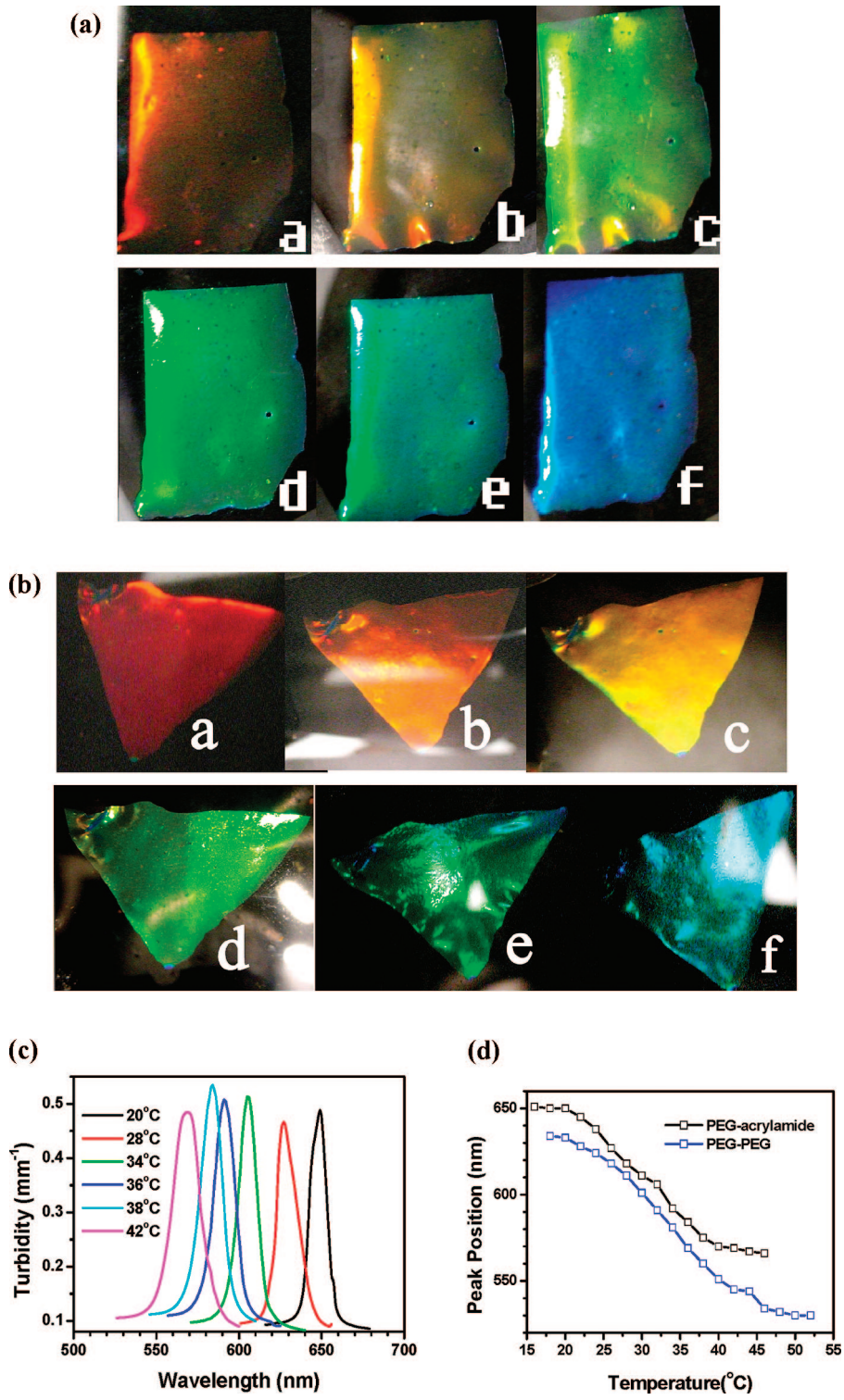

Figure 2. (a) A hydrogel thin film that PEG derivative microgels were used as cross-linkers to connect PEGA chains. Gel color changes with temperatures at (a) 22, (b) 24, (c) 30, (d) 34, (e) 40, and (f) 50 °C. (b) A hydrogel thin film that PEG derivative microgels were used as cross-linkers to connect polyacylamide chains. Gel color changes with temperature at (a) 22, (b) 27, (c) 29, (d) 33, (e) 41, and (f) 53 °C. (c) UV−vis spectra for a hydrogel thin film consisting of PEG derivative microgels and polyacylamide chains. (d) The relationship between the wavelength of Bragg peak and the temperature of the hydrogel thin films composed with either PEG derivative microgels and PEG chains (blue line and squares) or PEG derivative microgels and polyacrylamide chains (black line and squares).

array and cross-linkers that connect polyacrylamide chains, and the other was PEG derivative particles as a crystalline array surrounded by a polyacrylamide matrix using a small molecule *N,N′*-methyelenebis(acrylamide) (BIS) as a cross-linker. Figure 4 compares elongation measurements of these two samples that both exhibit iridescent colors, indicating the arrangement of PEG particles has a long-range order. The sample with PEG particles as cross-linkers can be stretched much longer than that of the sample with BIS as cross-linker. The tensile stress−tensile strain curves of the crystalline hydrogels with microgels as cross-linker and with BIS as cross-linker are compared in Figure 4f. The crystalline hydrogel with BIS as cross-linker broke as the strain reaching about 21%, compared with more than 80% for the gel with microgels as cross-linkers. From the tensile stress−strain

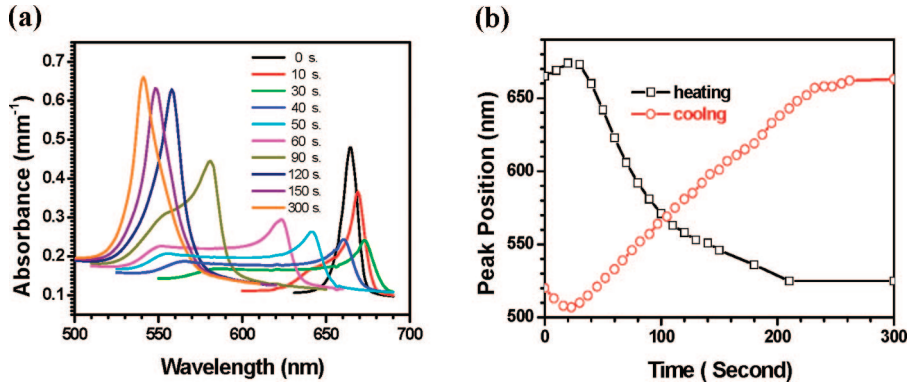

Figure 3. (a) Change of the UV−vis spectra as the temperature was increased from 21 to 55 °C for the hydrogel thin film composed with PEG derivative microgels and polyacrylamide chains. (b) The wavelength of the Bragg peak in (a) is plotted as a function of time.

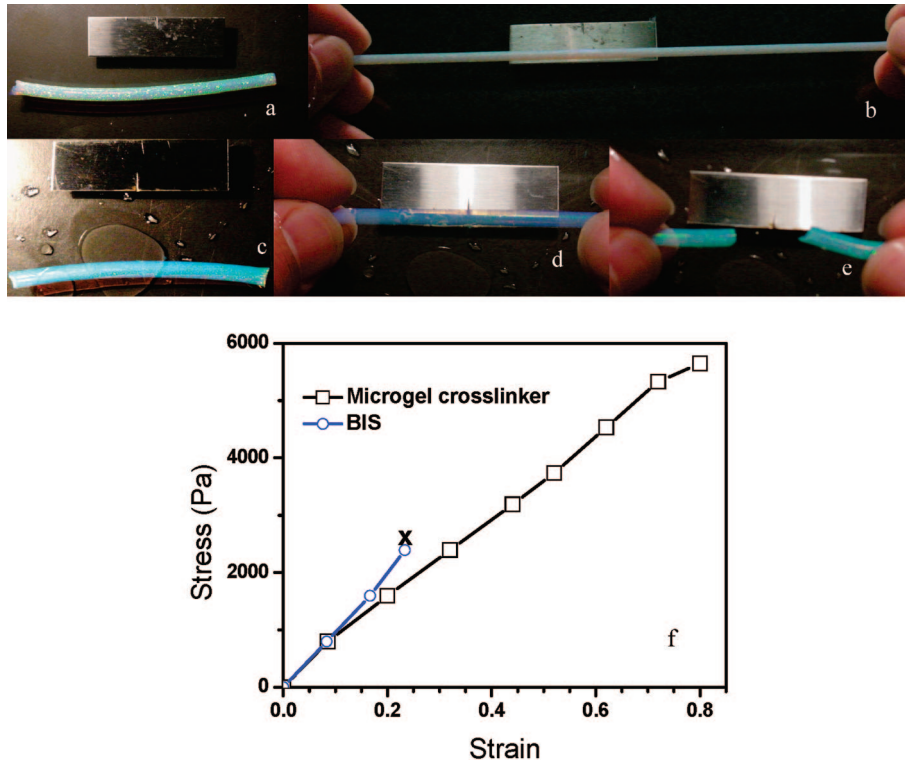

Figure 4. (a) Crystalline hydrogel composed with PEG derivative microgels and polyacrylamide chains with particles as cross-linker. (b) The gel in (a) was stretched to about 90% without rupture. (c) Crystalline hydrogel composed with PEG derivative microgels and polyacryamide chains with BIS as cross-linker. (d) Gel in (c) was stretched. (e) Gel in (c) is broken as the elongation reaches about 20%. The scale bar in pictures is 4.5 cm. (f) Tensile stress−tensile strain curves of the crystalline hydrogels with microgels as cross-linker (black squares) and with BIS as cross-linker (blue circles). x represents the place that the gel was broken.

curve, Young's modulii of the crystalline hydrogel with microgels as cross-linkers and with BIS as cross-linker were determined to be about 7.1×10^3 and 1.0×10^4 Pa, respectively. This suggests that the hydrogel with BIS is more stiff than the one with microgels as cross-linkers. The larger elongation of the particle cross-linkered gel over conventional small molecular cross-linkered gel is because the polymer chain lengths between the cross-linker points are proportional to the interparticle distance and are long and flexible, similar to previous reports using inorganic clay as a cross-linker to connect polymer chains.[19]

In summary, the monodisperse PEG derivative microgels have been synthesized and attached with vinyl groups. These particles act as both a crystalline array and cross-linkers that connect neighboring polymer chains to stabilize the crystal structure. The self-assembled particle array can diffract light, resulting in iridescent color, while particles as cross-linkers enhance the mechanical toughness. This innovative approach has led to the first thermally responsive, biocompatible photonic hydrogel film consisting of both PEG derivative colloids and PEGA polymer chains that connected by the colloids. The color of this photonic hydrogel film varies quickly and reversibly in response to the temperature change. The crystalline hydrogel with BIS as cross-linker broke as the strain reaching about 21%, compared with more than 80% for the gel with microgels as cross-linkers.

Experimental Section. *PEGETH$_2$MA-co-PEGMA-co-PEGA Microgel Preparation.* The copolymerization of poly(ethylene glycol)ethyl ether methacrylate (PEGETH$_2$MA, $M_n \sim 246$ g mol^{-1}), poly(ethylene glycol) methyl ether methacrylate (PEGMEMA, $M_n \sim 300$ g mol^{-1}), and poly(ethylene glycol) acrylate (PEGA, $M_n \sim 375$ g mol^{-1}) was carried out in a three-necked flask equipped with stirrer and a nitrogen feed. 5.63 g of PEGETH$_2$MA ($M_n \sim 246$ g mol^{-1}), 1.72 g of PEGMEMA

($M_n \sim 300$ g mol^{-1}), 1.07 g of PEGA ($M_n \sim 375$ g mol^{-1}), 0.064 g of SDS, and 4.6×10^{-4} mol of ethylene glycol dimethacrylate (EGDMA 97%) were dissolved in 400 mL of DI water. The solution was purged with nitrogen gas for 40 min at 70 °C. Ammonium persulfate (0.20 g), which was dissolved in 5 mL of water, was then added to initiate the emulsion copolymerization. The reaction lasted for 12 h under the nitrogen atmosphere. The reaction temperature was kept at 70 °C. Then the microgels were purified via a dialysis tube (MWCO13 000) against frequent changes of stirring water for 1 week at room temperature. The microgels were collected by ultracentrifugation.

Vinyl Thermoresponsive PEG Derivative Microgel Preparation. The collected PEGETH_2MA−PEGMEMA-*co*-PEGA microgel (10 g, 10 wt %) was dried by the freeze−dry method. Then the microgels were redispersed in 100 mL of CH_2Cl_2. 1 g of acryloyl chloride and trace amount triethylamine (compared with acryloyl chroride) were slowly added into microgels solution. The molar ratio between acrylate PEGA (OH group) to acryloyl chloride was 1 to 32. The reaction was carried out under dark at room temperature with an anhydrous environment for 24 h. The reaction in darkness was just precaution for protecting the vinyl group. The reaction was stopped by adding 300 mL of absolute ethyl alcohol. The vinyl-PEG based microgels were collected by ultracentrifugation. Then the vinyl microgels were dispersed in ethyl alcohol and put into a dialysis tube under dark for a week in absolute ethyl alcohol (1st day), 50 vol % ethyl alcohol (2nd day), 25 vol % ethyl alcohol (3rd day), and DI water (4th−7th days) at temperature 4 °C. The vinyl group was confirmed by IR spectra.

Vinyl PEG Derivative Microgel/PEG Acrylate (PEGA, $M_n \sim 375$ g mol^{-1}) Crystalline Gel Film Preparation. 0.45 g of PEG acrylate (20 wt %), 2 mg of UV initiator 2-hydroxy-1-[4-(2-hydroxyothoxy)phenyl]-2-methyl-1-propanone (CIBA) (0.2 wt %), and 0.55 g of vinyl PEG microgel (12 wt %) were mixed. Oxygen in the suspension was removed by the freeze−thaw method. The suspension was injected into a cell consisting of two clean quartz disks separated a 125 μm Parafilm film. The crystalline structures were formed by slowly changing temperature from 29 to 4 °C in 24 h. If this change was too rapid, there would be no crystallization. The crystalline structure was then stabilized by UV irradiation triggered free radical polymerization at 0 °C for 30 min. The gel was taken out from the cell and balanced with water for 3 days for further measurements.

Vinyl PEG Derivative Microgel/Acrylamide Crystalline Gel Film Preparation. The procedures and chemical compositions were the same as ones above, except that 0.45 g of 20 wt % PEG acrylate was replaced by 0.3 g of 20 wt % acrylamide. 0.5 g of 12 wt % of dispersion of vinyl PEG derivative microgels was used, and water was added to obtain the final weight of 1 g.

Vinyl PEG Derivative Microgel/Acrylamide Crystalline Cylindrical Gel Preparation. 0.6 g of acrylamide (20 wt %), 6 mg of CIBA (0.2 wt %), 1 g of vinyl PEG derivative microgel (12 wt %), and 0.4 g of DI water were mixed. Oxygen in the suspension was removed by the freeze−thaw method. The suspension was injected into a glass tube. The crystalline structures were formed by slowly changing temperature from 29 to 4 °C in 24 h. This structure was then stabilized by long wavelength (365 nm) UV irradiation triggered free radical polymerization at 0 °C for 30 min. After stabilized, the gel was taken out from the tube and balanced with water for 3 days for further measurements.

BIS Cross-Linked PEG Derivative Microgel/Acrylamide Crystalline Cylinder Gel Preparation. 0.6 g of acrylamide (20 wt %), 5 mg of BIS (2 mol % of acrylamide), 6 mg of CIBA (0.2 wt %), 1 g of PEG derivative microgel (12 wt %), and 0.4 g of DI water were mixed. The rest procedures were the same as the ones above.

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