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Hard-to-soft transition of transparent shape memory gels and the first observation of their critical temperature studied with scanning microscopic light scattering

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ABSTRACT

The novel transparent shape memory gels (SMGs) have been developed by simple bulk polymerization technique, while the previous SMGs are opaque and whitish ones. It has the ability to memorize an original shape that occurs during the gelation process. It is found that the SMGs are transparent both at room and at high temperature, mechanically elastic as well as thermoresponsive despite the high water contents. By virtue of the transparency of the SMGs, we observe the mesh size of the internal network structure in nanometer scales and the phase transition of the SMGs by dynamic light scattering. This is the first observation of SMGs by light scattering as far as we know. The SMGs show a critical slowing down around the critical temperature where they change the state of phase.

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1. Introduction

Gels are soft and wet materials and come as a new branch of material science in recent years. Several exclusive characteristics such as high water absorbent, soft, transparent and extremely low friction of gel make it an interesting material. Different kinds of gel materials have already been developed and reported in literatures [1–5]. From an engineering point of view, the mechanically high strength materials are suitable for medical, smart devices and other applications. Double-Network (DN) gels consisting of rigid and flexible polymer components show superior mechanical behavior despite the high water contents [6]. Gel containing with fluorescent particles can become a promising material in the nanotechnology fields [7]. Shape memory gel (SMG) [8–10] is one of the most interesting unique soft and wet materials since its creation, which bears shape recovery property [11].

As mentioned above, this gel can be possibly applied as bandages for broken bone [9], making optical lens as an eyeball [8] or developing smart button as an input device [10]. Several properties of the shape memory gel have already been discussed. However, the dynamical properties of the transparent SMG have not yet been reported in the literature as far as we are aware.

In this study, we have prepared a transparent shape memory gel in contrast to previous whitish ones. The transparency is not only important for the application of optical devices such as gel lens but also important for the analysis of internal structure using dynamic light scattering (DLS). Here, we report DLS results of the transparent SMG for the first time.

2. Experimental part

The transparent shape memory gel solution was prepared by the solvent free (SF) technique, in other words, simply by bulk polymerization [8–10]. In this process, the *N*, *N*-dimethyl acrylamide (DMAAm) was used as a monomer, which also worked as a solvent because the DMAAm is in liquid state at room temperature. Stearyl acrylate (SA) was the other monomer element having the crystalline characteristic. In the present study, the ratio of DMAAm and SA was 3:1 in molar ratio. The 0.05 mol% methylenebis acrylamide (MBAA) was used as a cross-linker. The 0.1 mol% benzophenone was also used as a UV initiator. The UV-polymerization process was done with black light (~360 nm, 20 W × 5 tubes) at 30 °C (303 K) temperature and was allowed for 20 h. Finally, the sample was swelled to an equilibrium state by dipping into pure water for several days. The chemical compositions used in this study are shown in Table 1.

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Table 1
The chemical compositions are used in the present study.

Chemical		Mole weight(g/mol)	Density (g/ml)	Ratio (mol/mol)	Unit	Weight (g)
Usual monomer	DMAAm	99.13	0.965	0.75	M	4.787
Crystalline monomer	SA	324.54	0.8	0.25	M	5.2125
Crosslinker	MBAA	154.17	1.235	0.05	mol%	0.0053
UV initiator	Benzophenone	182.22	1.11	0.1	mol%	0.0124

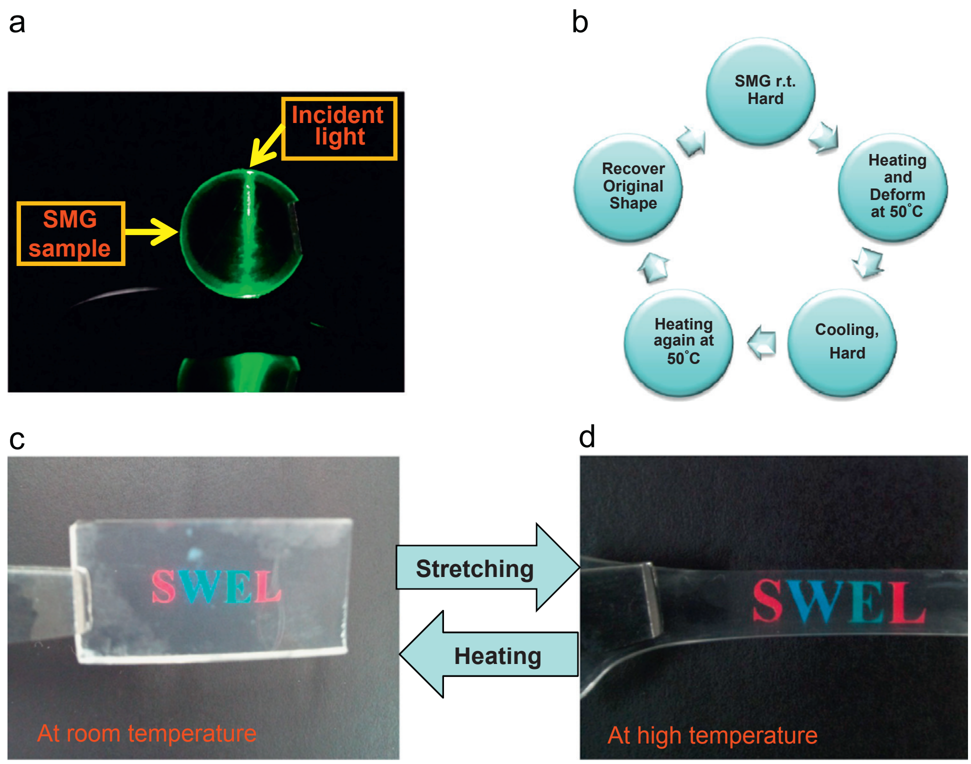

Fig. 1. Photographs of transparent shape memory gels. (a) Green laser (532 nm) light of 1 mm diameter propagates through the SMG. (b) Shape recovery cycle(SRC). (c) Visualization of transparency of SMG. (d) Visualization of transparency of SMG after stretching of sample (c).

The swollen gel sample was characterized by the Scanning Microscopic Light Scattering (SMILS) [12]. It is a typical DLS system [13] specially designed in our laboratory for analyzing the inner structure of gels by non-destructive and non-contact way. In the present study, Diode-Pumped Solid-State (DPSS) laser of 532 nm wavelength was used as a light source. The power of the laser was ~200 mW. The sample was kept in a cylindrical glass tube with a 10 mm outer diameter. The thickness and the length of the sample were 2 mm and greater than 10 mm, respectively. The measurement of each sample was carried out at three different angles (60°, 90° and 105°) and was measured at 31 different positions moving the sample holder vertically to obtain ensemble-averaged one.

The analysis of scattered light intensity fluctuations yields, the velocity of the Brownian motion and hence the size of particle can be determined using the well-known Stokes–Einstein relation [14].

$$D_{Coop} \cong \frac{k_B T}{3\pi\eta\xi} \quad (1)$$

Here, D_{Coop}: diffusion coefficient, k_B: Boltzmann constant, T: temperature, η: viscosity coefficient and ξ: mesh size.

3. Results and discussion

A photograph of transparent shape memory gel is shown in Fig. 1. A green laser light (532 nm) is used to investigate the propagation of light through the gel shown in Fig. 1(a). It is clearly shown from this figure that the gel is able to propagate the light leading this gel as an optical material while Fig. 1(b) shows the shape recovery cycle (SRC). It is found that the SMG shows transparency both at room and at high temperature. It is also observed that the gel becomes soft and possible to stretch by hand at high temperature, whereas the previous SMG [11] is brittle. Due to the above attractive properties, our SMG is a state-of-art material. Fig. 1(c) shows the well macroscopic visualization through the gel whereas Fig. 1(d) shows the visualization of SMG also after stretching of the same sample (Fig. 1(c)). The latest figure shows better transparency than previous ones even though it is stretched. The stearyl acrylamide (SA) is probably responsible for this behavior instead of DMAAm or MBAA [15]. During deformation, some stearyl side chains (SA) are separated from each other causing gel more transparent than previous. The gel can quickly recover its original shape and size only by heating above from the critical temperature. It implies that the network structure of the gel (due to crosslinkers) remembers their original shape during the gelation process.

The angle-dependent autocorrelation function $G_{en}^{(1)}(\tau)$ with respect to the relaxation time τ (s) at 40 °C is shown in Fig. 2(a). The angle-dependent distribution function $P_{en}(\tau_R)$ with respect to the relaxation time τ is shown in Fig. 2(b). From this figure, it is clear that the density probability $P_{en}(\tau_R)$ depends on the scattering

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