Shape Memory Gels Made by the Modulated Gel Technology

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ABSTRACT: Shape memory gels based on interpenetrating only part of one gel network with another gel network have been synthesized. These gels consist of two parts: a control element, which is responsive to a designated environmental stimulus, and a nonresponsive substrate element. By designing the pattern in the gelation process, a variety of shapes are obtained including "spiral," "square," "fish," "numbers," "alphabets," and "tube." The change between two different shapes can be controlled by external stimuli such as temperature and is reversible. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1173–1178, 1997

INTRODUCTION

Polymer gels have attracted much current interest because they respond adaptively to changes in their environment. Particularly, their volumes can be changed by three orders of magnitude in response to a variety of external stimuli such as solvent, temperature, pH, electric fields and light.[1] Therefore, gels have been explored to perform various functions including artificial muscles and organs, drug-delivery devices, chemical valves, and actuators.[1–4]

To improve the physical and chemical properties of gels, two or more polymer backbone components are often mixed to form a multicomponent material. Basic combinations of the components include random copolymerization,[5] grafting the end of one polymer with the backbone of another polymer network,[6,7] and interpenetrating polymer networks (IPN).[8] All these methods, however, produce macroscopically uniform media, which can only isotropically shrink or swell under uniformly environmental stimuli. It is apparent that advanced gel materials are needed in order to accomplish more complicated functions such as forming various shapes under external stimuli. This leads us to synthesize modulated polymer gels based on modulation of gel chemical nature in space.[9] Here we report recent progress for developing shape memory gels using the modulation technology.

EXPERIMENTAL

The bi-gel strip was synthesized by first making a *N*-isopropylacrylamide (NIPA) gel slab. Two glass slides with ~ 1.0 mm gap between them were immersed in 100 mL of an aqueous solution with 690 m*M* *N*-isopropylacrylamide, 8.6 m*M* methylenebisacrylamide (BIS), and 8 m*M* sodium acrylate. The polymerization of the solution was initiated by adding 240 μL of tetramethylethylenedia-

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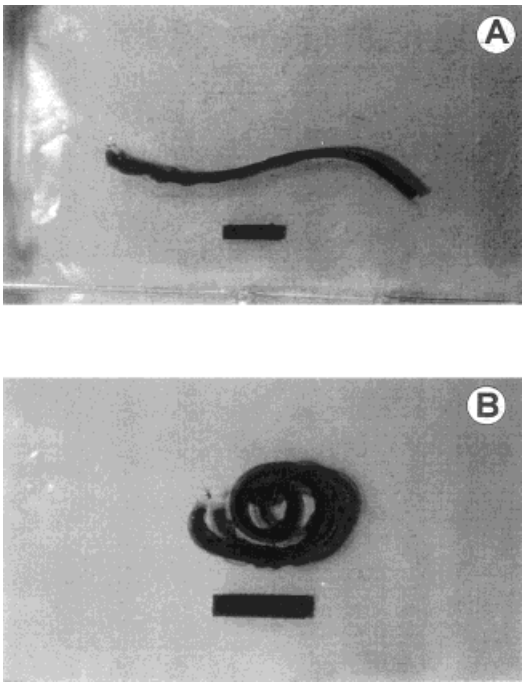

Figure 1 (a) A long bi-gel strip with one PAAM side modulated by NIPA gel. At room temperature, the bi-gel is in a straight shape. (b) When the sample temperature is raised to 39°C, the gel becomes a spiral.

mine (TEMED) and 40 mg ammonium persulfate (for experimental details, see ref. 6). In the second step, a polyacrylamide (PAAM) gel slab was made between two glass slides (approximately 2.0 to 3.0 mm apart) with the presence of the NIPA network ($\sim$ 1.2 mm) between them and in contact with one of the glass slides. Notice that the distance between the two glass slides is larger than that of the swollen NIPA network. A sufficiently long time was allowed for the acrylamide gel "ingredient" to diffuse into the NIPA network before the polymerization was initiated. This ensures the formation of the NIPA/PAAM interpenetrating networks. The acrylamide gel consisted of 700 m*M* acrylamide and 8.6 m*M* BIS. The end product is a gel slab 2.0 to 3.0 mm thick with layered network structure: A 0.8 to 1.8 mm thick PAAM network, and a 1.2 mm PAAM network interpenetrated by a NIPA network.

RESULTS AND DISCUSSION

Previously, we have shown that a bi-gel strip made by interpenetrating part of PAAM gel with NIPA gel can bend when the sample temperature is raised to 39°C.[9] This is due to the volume of the ionic NIPA gel (with 8 m*M* sodium acrylate) shrinks drastically at temperatures higher than 37°C, whereas the volume of the PAAM gel does not. As a result, when the bi-gel strip is heated uniformly, it gradually bends into an arc. The transition between the straight and the arc forms is reversible. The details of bending of bi-gels have been given in ref. 10.

The bending is not limited to a half circle as restricted for electric field induced gel bending. Large bending can be achieved by either increasing the sample length, or temperature. As shown

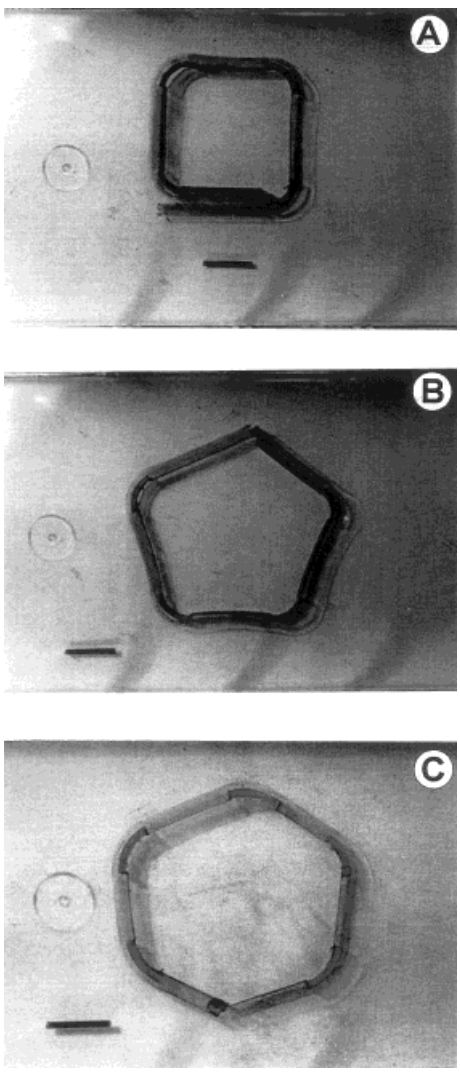

Figure 2 Modulating one side of the PAAM gel with NIPA gel at several different locations. The gels are in the straight shape at room temperature (a) square (41°C), (b) pentagon (39°C), and hexagon (39°C). The gel in (a) and (b) is the same one.

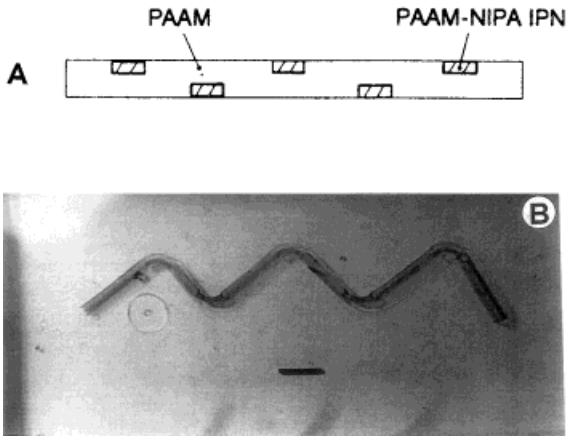

Figure 3 Both sides of a PAAM substrate are modulated alternatively at different locations by the NIPA gel. At 39°C, the gel forms a sinusoidal form.

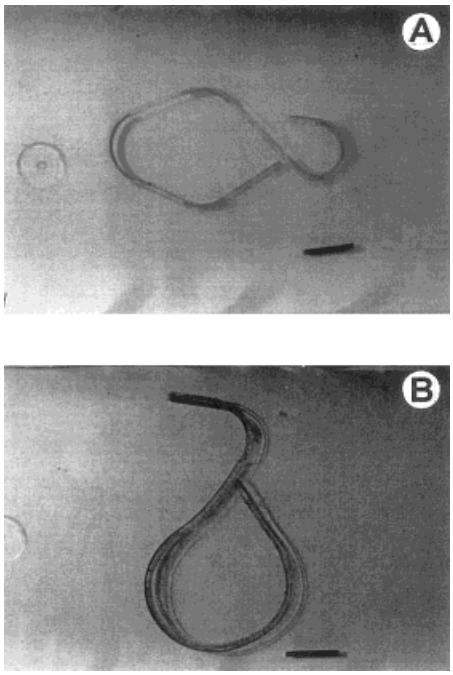

Figure 4 (A) A shape of "fish." At room temperature, the gel is straight. This gel changes its shape from a straight line to a shape of a "fish" at around 34°C. (B) A shape of "apple" at 34°C.

in Figure 1, a long bi-gel can bend from a straight strip at room temperature to a spiral at 39°C.

In general, a modulated gel consists of two parts: one is sensitive to a designated environmental stimulus, and the other is not. These two parts may be called the control element and the substrate element, respectively. The gel can only bend at the control element, or modulated sites. A small change of the control element can cause a large movement of the substrate element. This concept is demonstrated by modulating one side of the PAAM gel with NIPA gel at several different locations. Upon an increase of temperature, the "control elements"—NIPA modulated gel parts start to bend, causing the movement the "substrate element"—the PAAM gel parts. As a result, gels changes their shapes from a straight line at room temperature to a square (four control elements) [Fig. 2(A), 41°C], a pentagon (four control elements) [Fig. 2(B), 39°C], and a hexagon (five control elements) [Fig. 2(C), 39°C]. On the other hand, if both sides of a PAAM substrate are

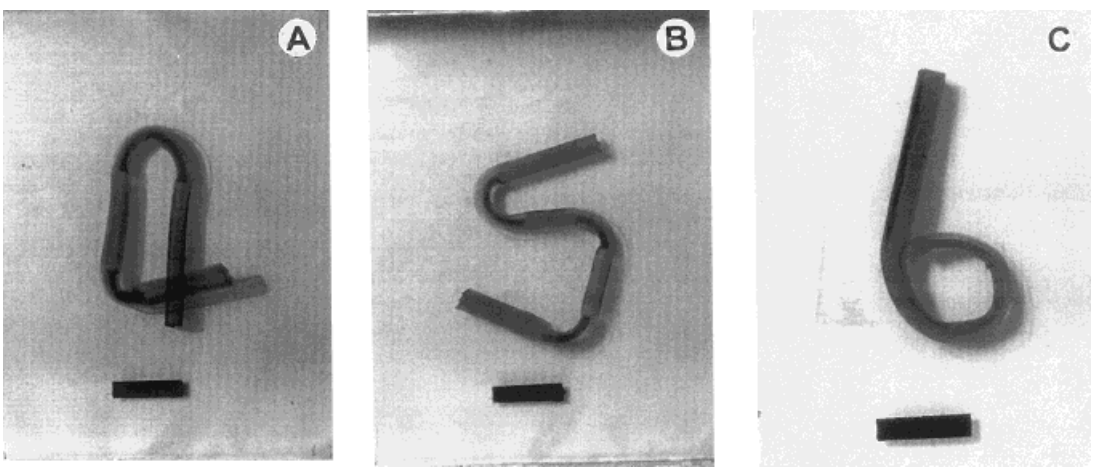

Figure 5 Shape memory gels change their room temperature straight-line shape to numerical numbers: (a) "4" at 39°C, (b) "5" at 39°C, and (c) "6" at 36°C.

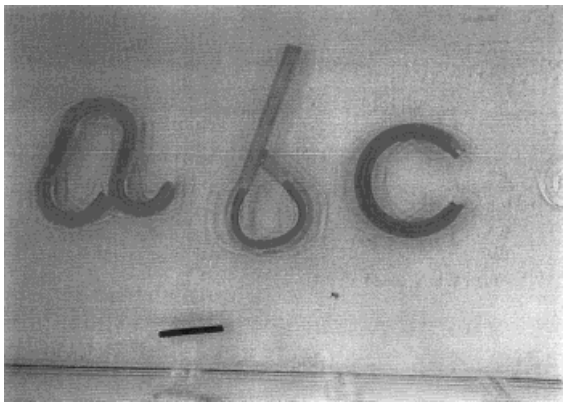

Figure 6 Three modulated gels change their shapes from straight lines at room temperature to "a," "b," and "c" at the same temperature (39°C).

modulated alternatively at different locations by the NIPA gel, one can obtain a "sinusoidal wave" as shown in Figure 3.

The shapes obtained are not limited to a regular geometric shape. A variety of other shapes at various temperatures can be obtained by designing the modulation pattern of the system during the gelation process. Figure 4(A) shows that a gel changes its shape from a straight line to a shape of a "fish" at around 34°C. Similarly, we have obtained a shape of an "apple" as shown in Figure 4(B). This method is also extended to make numerical numbers from 0 to 9. Figure 5 shows three typical numbers of "4," "5," and "6" corresponding to 38, 39, and 39°C, respectively. At room temperature, they all return to number "1."

Furthermore, several alphabets of "a," "b," and "c" have been made as shown in Figure 6. It is noted that these three initially straight gels at room temperature change to "a," "b," and "c" at a same temperature (38°C). This is quite a challenging task because the degree of gel bending depends on many factors such as degree of interpenetrating polymer networks, thickness of control element and substrate, and the gelation conditions. Currently, we have to rely on experience to make such samples, which exhibit designed shapes at a same temperature. This could be improved by systematically study of relations among the bending and other factors such as the gelation conditions.

All shapes shown above have their room-temperature shape of a straight line. Actually, the room-temperature shape could be designed to different forms as well. As demonstrated in Figure 7, the "leaves" of a "flower" are stretched at room temperature, and become curved at about 39°C.

The shapes discussed so far are limited in a

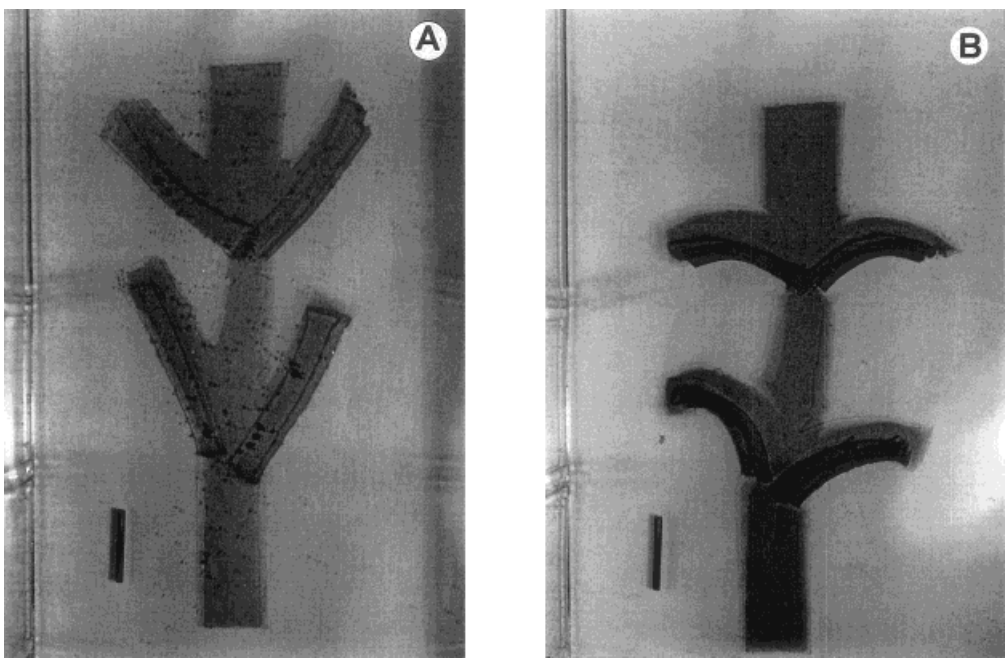

Figure 7 A shape of a "flower." (A) At room temperature, leaves of the flower are straight. (B) At 38°C, the leaves of the flowers become curved.

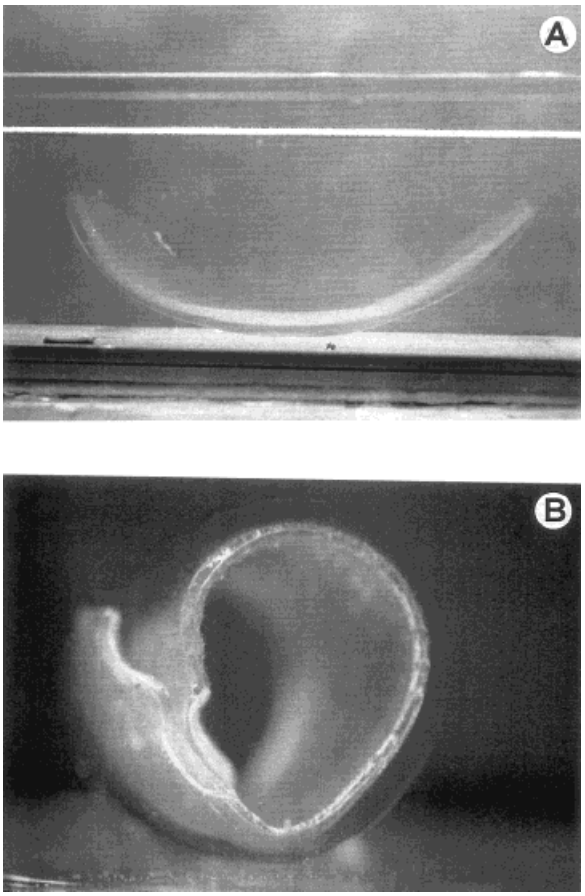

Figure 8 (A) At room temperature, a bi-gel layer of NIPA-PAAM forms a slightly curved plate. (B) At 39°C, the bi-gel layer forms a tubing-like shape.

two dimension. Shapes of three dimensions can be also made. For example, a slightly curved bi-gel layer with one side of PAAM-NIPA interpenetrating networks and one side of pure PAAM at room temperature forms a tube-like shape at 39°C as shown in Figure 8. The diameter of the tube can be adjusted by changing the ionic concentration of the NIPA component as well as the thickness of the bi-gel layer.

The shape memory effect demonstrated here is different from that reported by Osada et al.[11] In their experiment, the cylindrical gel is soft at $T > T_c$ (about 50°C) and can be deformed to a certain shape (a coil shape for example). At $T < T_c$, the gel becomes "frozen" and can keep the shape (the coil). As the sample temperature is raised above T_c, the sample becomes soft and restores its original cylindrical shape. The gel can only remember the shape that is formed by an operator at a high temperature. The memory will be erased once the gel is warmed above T_c. Therefore, it is a "one way" memory effect. In our case, the shapes at different temperatures essentially are determined in the gelation process and are reversible under the thermal cycles. The gel can memorize its shapes at all temperatures. Another approach for making a shape memory gel is to chemically crosslink a polymer network that is under external stretching or compression. An anisotropic effect has been observed for such gels. But this effect is too small to make significant shape change.[12]

Compared with well-established shape memory materials such as shape memory alloys (SMA), and shape memory polymers (SMP), shape memory gels (SMG) have some advantageous properties, such as very large deformation, and available to many external stimuli. The major controlling environment for SMA and SMP is limited to temperature, while SMG respond to a variety of variables such as temperature, pH, salt solution, acetone concentration, electric field, light, etc.

CONCLUSION

We have shown here that many different shapes can be obtained using the modulation technology. The transition between different shapes are controlled by the external stimuli and are reversible. The shape memory gels may be used as the display devices, bone joints, and artificial organs such as intravascular vessels.

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