

Temperature-Sensitive Switch from Composite Poly(*N*-isopropylacrylamide) Sponge Gels

LIANG LIANG, XIANGDONG FENG,* PAUL F. C. MARTIN, LONI M. PEURUNG

Pacific Northwest National Laboratory, 902 Battelle Boulevard, P. O. Box 999, Mail Stop K6-24, Richland, Washington 99352

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ABSTRACT: Thermally sensitive polymers change their properties with a change in environmental temperature in a predictable and pronounced way. These changes can be expected in drug delivery systems, solute separation, enzyme immobilization, energy-transducer processes, and photosensitive materials. We have demonstrated a thermal-sensitive switch module, which is capable of converting thermal into mechanical energy. We employed this module in the control of liquid transfer. The thermally sensitive switch was prepared by crosslinking poly(*N*-isopropylacrylamide) (PNIPAAm) gel inside the pores of a sponge to generate the composite PNIPAAm/sponge gel. This gel, contained in a polypropylene tube, was inserted into a thermoelectric module equipped with a fine temperature controller. As the water flux through the composite gel changes from 0 to $6.6 \times 10^2 \text{ L m}^{-2} \text{ h}$, with a temperature change from 23 to 40°C, we can reversibly turn on and off the thermally sensitive switch. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1735–1739, 2000

Key words: temperature-sensitive polymers; crosslinking polymer gels; poly(*N*-isopropylacrylamide); polymer sensors

INTRODUCTION

Smart polymers, which change their properties with a change in environmental stimuli, have been extensively studied in recent years. These polymers are significant in the control process of auto-feedback delivery systems and self-regulating systems. Smart polymers can be fine-tuned for a wide variety of applications, such as drug delivery,¹ biocatalysis,² size-selective separation,^{3,4} energy transduction,⁵ and analysis.⁶ Temperature-sensitive polymers are important smart polymers because temperature change is easy to control. Among thermally sensitive polymers, poly(*N*-isopropylacrylamide) (PNIPAAm) has been of great interest because aqueous solutions of

PNIPAAm undergo fast reversible changes around its lower critical solution temperature of 32°C.⁷ Crosslinked PNIPAAm gels extend the application field of PNIPAAm because the volume-phase transition leads to dramatic changes in the physical properties of the PNIPAAm gels. Meanwhile, the mechanical properties of PNIPAAm gel are improved by the generation of crosslinked networks. PNIPAAm and its copolymer gels were suggested to serve as (1) actuator,⁸ (2) temperature-modulated bioconjugator to control enzyme activity,^{9,10} (3) separation module to extract water from the solution of macromolecules,¹¹ (4) reversible surface,¹² (5) biomimetic materials,¹³ (6) temperature-sensitive surfactant,¹⁴ and (7) drug-delivery systems.^{15,16,17}

In this study, we demonstrated one novel temperature-sensitive switch prepared by the composite-crosslinked PNIPAAm sponge gels. The characteristics of the temperature-sensitive switch from the composite PNIPAAm sponge gel

Correspondence to: L. Liang (E-mail: liang.liang@pnl.gov).
*Present address: Ferro Corp., 7500 Pleasant Valley Rd., Independence, OH 44131.

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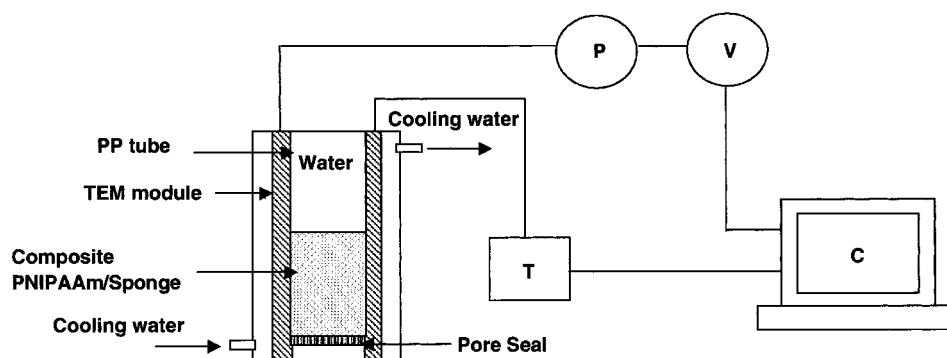


Figure 1 Schematic of equipment for evaluating the temperature-sensitive switch characteristics of composite PNIPAAm/sponge gels. C: Computer; P: power amplifier; T: temperature adjustment; V: voltage amplifier; TEM: thermoelectric module.

shows a potential application in the control of liquid transfer by a change in environmental temperature.

EXPERIMENTAL

Materials

PNIPAAm (97%, Aldrich, Milwaukee, WI) was recrystallized in hexane. Potassium persulfate ($K_2S_2O_8$; 99%, Aldrich) was recrystallized from ethanol. *N,N'*-methylenebisacrylamide (BisAAM; 99%, Aldrich) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA; 99%, Aldrich) were used without further purification. Ultrapure water with a conductivity of 18 S cm^{-1} was used in all of the experiments. A polypropylene (PP) tube (Fisher Sci., Pittsburgh, PA) with a volume of 50 mL and a diameter of 21 mm was used to contain the composite PNIPAAm sponge gel. Sponge of polyurethane (Polymer Technology Inc., Newark, DE) with a density of 0.03 g/cm^3 and a mean pore size of $300 \mu\text{m}$ was used as the supporting material for the composite PNIPAAm sponge gel.

Preparation of Composite PNIPAAm Sponge Gel

The sponge was cut to a diameter of 21 mm and a thickness of 40 mm and inserted inside the PP tube. 1 gram of NIPAAm, 0.017 g of BisAAM, and 0.032 g of $K_2S_2O_8$ were dissolved with 20 mL of water. The solution was stirred with a magnetic stirrer for 1 h and poured into the PP tube. The solution was purged by nitrogen gas for 0.5 h to remove air dissolved in solution. Then, the tube was evacuated first and filled with nitrogen gas. This process was repeated three times. Finally, the upper space of the tube was filled with nitro-

gen gas. To start polymerization, 0.2 mL of TMEDA was injected into the tube by syringe. The polymerization was kept at room temperature. After 0.5 h, the crosslinked PNIPAAm gel was generated inside the pores of the sponge. To remove the unreacted chemicals, the tube was immersed in water for 24 h, and the water was changed once every 8 h. A crosslinked PNIPAAm gel without the sponge was prepared by the same procedure.

Measurement of Volume Change of Polymer Gel

Polymer disks with a diameter of 21 mm and a thickness of 9 mm were immersed in water at a fixed temperature at least 4 h for equilibrium. The polymer disks were removed from water, and the change in size was measured with caliper. The change in polymer volume were defined as V_t/V_0 , where V_t is the volume of a polymer disk in water at different temperatures and V_0 is the volume of a dried polymer sample.

Measurement of Water Flux

The equipment shown in Figure 1 can be used to measure the water flux through the composite gels. The tube filled with the composite PNIPAAm sponge gel was inserted in one thermoelectric module (TEM). The TEM is a semiconductor-based electronic component that functions as a small heat pump. By applying a low-voltage DC power source to a TEM, heat is moved through the module from one side to the other. One module face, therefore, is cooled while the opposite face is simultaneously heated. This process can be reversed with a change in polarity of the applied DC voltage. The temperature of the tube can be controlled precisely.

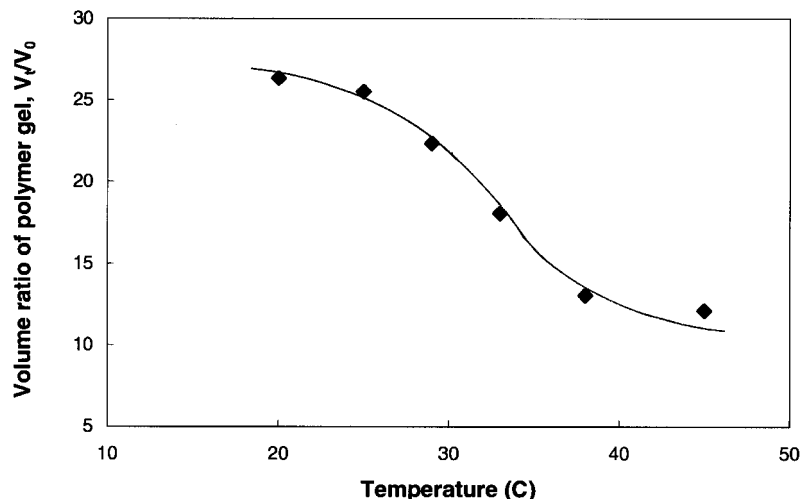


Figure 2 Effect of temperature on ratio of volume change of polymer gels. PNIPAAm/BisAAm = 80 (molar ratio).

The whole process was monitored by a computer. The upper side of tube was filled with water, and the flux of water was measured by collecting permeated water over 20 min. The mean value of three measurements was given in Figures 2, 3 and 4. The switch function of the composite PNIPAAm sponge gel was evaluated by the flux of water through the tube at different temperatures.

RESULTS AND DISCUSSION

Figure 2 shows the volume change of polymer disks as a function of temperature. The PNIPAAm gel shows a negative thermosensitivity as expected.¹⁸ An increase in temperature decreases the amount of water absorbed by the gel. Therefore, the volume changes of polymer disk decreases. Conversely, the PNIPAAm gel swells by

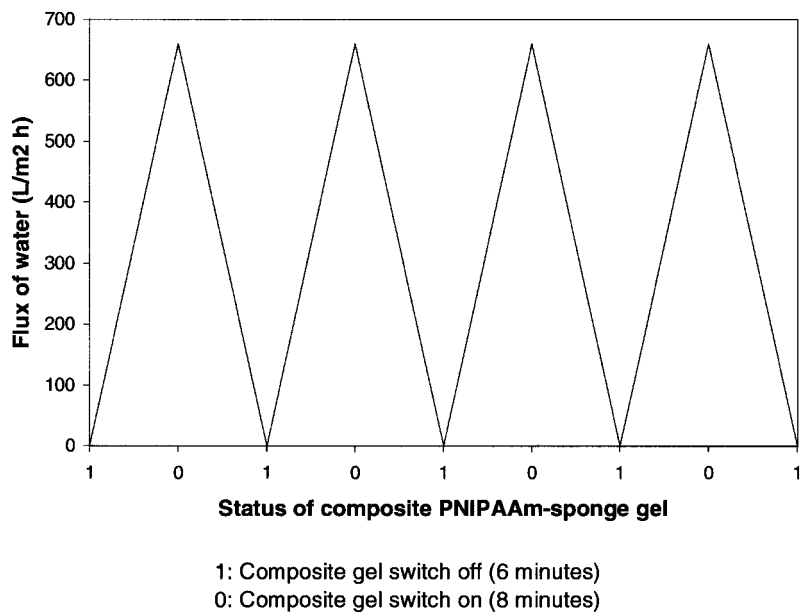


Figure 3 Temperature-sensitive switch characteristics of composite PNIPAAm/sponge gel. PNIPAAm/BisAAm = 80 (molar ratio); sponge size: diameter, 21 mm, thickness, 40 mm; mean porous size: 300 μm .

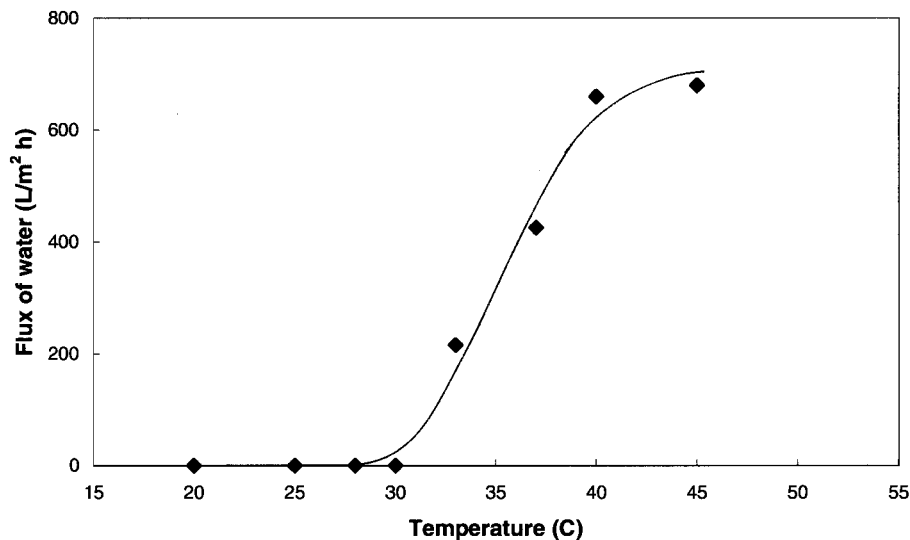


Figure 4 Flux of water and temperature. Composite PNIPAAm/sponge gel: PNIPAAm/BisAAm = 80 (molar ratio); sponge size: diameter, 21 mm, thickness, 40 mm; mean porous size: 300 μm .

decreasing the temperature and the volume change of the polymer disk increases. These properties can be attributed to the reversible formation and cleavage of the hydrogen bonds between the NH and C=O groups of PNIPAAm chains and the surrounding water molecules with changing temperature.¹⁹ We believe that the pentagonal water structure is generated among water molecules adjacent to the hydrophobic molecular groups of PNIPAAm. Because the pentagonal structure is stable at low temperatures and unstable at high temperatures,²⁰ the reversible swelling–unswelling process can be observed with the variation of temperature.

Figure 3 shows the characteristics of composite PNIPAAm sponge gel as the temperature-sensitive switch. At room temperature, the gel swelled and filled the whole space of the sponge pores. The flux of water through the tube became zero. The flux of water increased to 660 $\text{L m}^{-2} \text{h}^{-1}$ as the composite gel heated to 40°C. It takes about 6 min to switch off the flux of water, compared with 8 min to switch on the maximum flux of water. This process is reversible, and the experimental results can be repeated. It is clear that the composite PNIPAAm sponge gel demonstrates intelligent switch characteristics and can be expected to be used as the switch element in the process of liquid transfer. Another advantage of the intelligent switch from the composite PNIPAAm sponge gel is the energy savings, because the response switch only depends on small changes in environmental temperature.

Figure 4 shows the effect of temperature on the flux of water. The sigmoid pattern was observed

as predicated. The rapid increase of water flux around 35°C is attributed to the abrupt shrinkage of PNIPAAm gel, which filled the inside of the porous channels of the sponge. It is clear that the flux of water can be controlled depending on the change of environmental temperature. Because the flux of water depends on the variation in the porous spaces of the sponge, it can be expected that the pore size and the dimension of the sponge as well as the crosslinking density of PNIPAAm gel have significant effects on the flux of water.

The mechanism of the temperature-sensitive switch from the composite PNIPAAm sponge gel is further schematically described by Figure 5. At room temperature, the PNIPAAm gel was swollen and filled the whole space of the porous channels of the sponge. The swelling gel blocked the transfer of water. As the temperature increased, the PNIPAAm gel began to shrink and the spaces appeared between the gel and the porous channels of the sponge. Water transferred through the tube along these spaces.

We are further evaluating the relationship between the structure of composite gels and their temperature-sensitive switch characteristics.

CONCLUSION

Composite-crosslinked PNIPAAm sponge gels can be employed as the temperature-sensitive switch to control the transfer of water. The sponge improved the mechanical strength of PNIPAAm

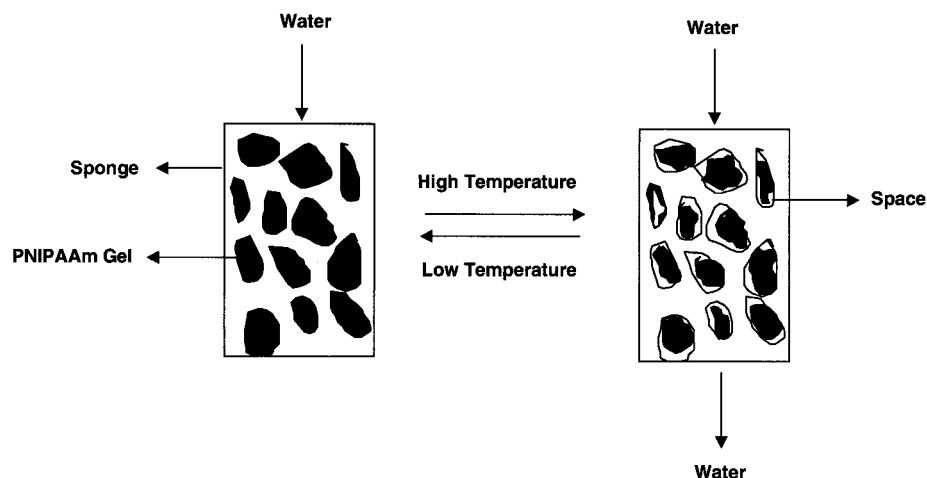


Figure 5 Schematic of temperature-sensitive switch principle.

gels. Because the crosslinking density of PNIPAAm gel plays an important role in controlling the release rate of water and the pore size and its distribution in the sponge will affect the morphology of PNIPAAm gel,²¹ it is reasonable to speculate that the switch properties of composite gel will depend on the crosslinking density of polymer gel and morphology of sponge. As the composite gel shows advantages in energy savings and flexible and intelligent characteristics, it can be expected that the composite gels could be used in the controlling processes of liquid transfer.

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REFERENCES

- Hoffman, A. S. in *Polymer Gel*; DeRossi, D.; Kajiwara, K.; Osada, Y.; Yamauchi, A., Eds., Plenum: New York, 1989; pp 289–297.
- Sun, Y.; Yu, K.; Jin, X. H.; Zhou, X. Z. *Biotech Bioeng* 1995, 47, 20–25.
- Iwata, H.; Oodate, M.; Uyama, Y.; Amemiya, H.; Ikada, Y. *J Membr Sci* 1991, 55, 119–130.
- Feil, H.; Bae, Y. H.; Feijen, J.; Kim, S. W. *J Membr Sci* 1991, 64, 283–294.
- Okuzaki, H.; Hori, H. *Nature* 1992, 355, 242–244.
- Kokufata, E.; Zhang, Y. Q.; Tanaka, T. *Nature* 1991, 351, 302–303.
- Schild, H. G. *Prog Polym Sci* 1992, 17, 163–249.
- Snowden, M.; Murray, M.; Chowdry, B. Z. *Chem Ind (London)* 1996, 15, 531–534.
- Dong, L. C.; Hoffman, A. S. *J Cont Rel* 1986, 6, 297–305.
- Shiroya, T.; Yasui, M.; Fujimoto, K.; Kawaguchi, H. *Colloids Surf, B* 1995, 4, 275–285.
- Freitas, R. S. F.; Cussler, E. L. *Chem Eng Sci* 1987, 42, 97–103.
- Liang, L.; Feng, X. D.; Liu, J.; Rieke, P. C.; Fryxell, G. E. *Macromolecules* 1998, 31, 7845–7850.
- Hirasa, O.; Ito, S.; Yamauchi, A.; Fujishige, S.; Ichijo, H. in *Polymer Gel*; DeRossi, D.; Kajiwara, K.; Osada, Y.; Yamauchi, A., Eds., Plenum: New York, 1989; pp 247–256.
- Lim, Y. H.; Kim, D.; Lee, D. S. *J Appl Polym Sci* 1997, 64, 2647–2655.
- Matsukata, M.; Hirata, M.; Gong, J. P.; Osada, Y.; Sakurai, Y.; Okano, T. *Colloid Polym Sci* 1998, 276, 11–18.
- Siegel, R.A.; Pitt, K.G. *J Controlled Release* 1995, 33, 173–188.
- Yoshida, R.; Okuyama, Y.; Saka, K.; Okano, T.; Sakura, Y. *J Membr Sci* 1994, 89, 267–277.
- Heskins, M.; Guillet, J. E.; James, E. *J Macromol Sci Chem*. 1968, 42, 1441–1455.
- Kaneko, Y.; Nakamura, S.; Sakai, K.; Aoyayi, T.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Macromolecules* 1998, 31, 6099–6105.
- McMurry, J. *Organic Chemistry*, 4th ed.; Brooks/Cole Publishing: New York, 1996; Chapter 4.
- Liang, L.; Feng, X. D.; Liu, J.; Rieke, P. C. *J Appl Polym Sci* 1999, 72, 1–11.