Volume Phase Transition in Poly(*N*-isopropylacrylamide) Gels in Seawater at High Pressures

Eiji Kato

Faculty of Maritime Sciences, Kobe University, 1-1, 5, Fukae-Minami, Higashinada, Kobe 658-0022, Japan

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ABSTRACT: The swelling behavior of poly(*N*-isopropylacrylamide) (PNIPA) gels in seawater at high pressures up to ~40 MPa is examined in terms of human activity at deep sea. The neutral gel in seawater undergoes a continuous volume transition at 26°C at atmospheric pressure. Addition of the ionic group (sodium acrylate) does not have much effect on the swelling properties of the gels in seawater except that the transition temperature is somewhat increased. At high constant pressures up to ~40 MPa, the gels undergo a continuous volume transition at 26–28°C as the temperature varies. Normally, the gel takes a swollen state at deep sea. The ratio of the volume change associated with the transition is more than 10, which is 3 times larger than that obtained by changing the pressure at a constant temperature. The results suggest a possibility that the phase transition of PNIPA gels is utilized for producing mechanochemical energy at deep sea. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1069–1072, 2005

Key words: hydrogels; swelling; transitions; seawater; high pressure

INTRODUCTION

Recently, the scope of human activity has been extended to the deep sea. In that isolated circumstance, an energy source is an important problem to maintain the activity. Therefore, new energy systems that are derived from new functional materials are desired. The mechanochemical system associated with the volume phase transition in polymer gels is known as the system in which chemical energy directly transfers to mechanical energy.[1,2] From this point of view, one can suggest that the system becomes one of the candidates for solving such problems.

It is well known that many polymer gels undergo a gel–gel transition (volume phase transition) from a shrunken state to a swollen state in response to infinitesimal changes in temperature, pH, solvent composition, and hydrostatic pressure.[3–7] The volume phase transition has attracted much attention because of its technological importance for applications to actuators[1,2] and drag delivery systems[8] as well as its scientific interest. Up to now, many investigations have been carried out to examine the volume phase transition in gels from the static and dynamic points of view.[9–12] However, these investigations have been performed only at atmospheric pressure. As far as I know, an investigation in seawater at high pressure has not been carried out.

It was previously reported that hydrogels such as poly(*N*-isopropylacrylaamide) (PNIPA) gels in pure water and acrylamide gels in acetone–water mixtures underwent a volume phase transition by a change in hydrostatic pressure (pressure-induced volume phase transition).[6,7] However, whether the gels in seawater undergo a phase transition at a pressure of ~10MPa, corresponding to ~1000 m in depth, where we are concerned with human activity, is unknown.

This article reports the swelling curves of PNIPA gels in seawater as functions of temperature and pressure, and the swelling properties of the gels in the deep-sea region is examined. The results are discussed from the point of view of the mechanochemical application of the gels at deep sea.

EXPERIMENTAL

Sample preparation

PNIPA gels were prepared by a free-radical copolymerization in water at 20°C. The NIPA monomer (main constituent), sodium acrylate (SA; ionic group), and *N*,*N*′-methylenebisacrylamide (8.6 m*M*; crosslinker) were dissolved in distilled water by bubbling with nitrogen gas. Three types of gels having different concentrations of the ionic group were prepared: one is a neutral gel in which the concentration of SA is zero, and the others are ionized gels in which the ratios of the concentration of NIPA to SA are 50:1 and

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Correspondence to: E. Kato (e-kato@maritime.kobe-u.ac.jp).

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22:1 (molar ratio). The sum of their concentrations was fixed at 700 m*M*. Ammonium persulfate (20 mg) and *N,N,N′N′*-tetramethylethylenediamine (120 μL) were added to the solution of 50 mL as an initiator and an accelerator for gelation, respectively. The solution was transferred to a glass beaker that contained glass tubes with a 1.63-mm inner diameter. Gelation was completed after several hours at 20°C. The gels were taken out of the tubes and immersed in distilled water to removed residual substances. The obtained cylindrical gels were cut into approximately 5-mm lengths and dried. Consequently, they were immersed in seawater.

High pressure measurement

The main optical high pressure apparatus in the present measurements was the same one used in the previous experiment, except that another small glass cylinder with a small piston was set in the cylinder of the apparatus. A sample gel was put in this small glass cylinder filled with seawater, and the cylinder was closed by inserting the piston. The cylinder was set on the bottom of the cylinder of the main pressure apparatus filling with water. Then, the water was compressed through a piston. The pressure of the water was measured by a Heise Bourdon's gage. The temperature was controlled to an accuracy of within ±0.1°C by circulating the temperature-regulating water around the cell. The diameter of the gel was measured with a microscope through a sapphire glass window. The equilibrium swelling ratio (V/V_0) was calculated from the relation $V/V_0 = (d/d_0)^3$, where V is the volume of the gel and V_0 and d_0 are the volume and diameter when the gel was prepared, respectively.

RESULTS AND DISCUSSION

Swelling ratio at atmospheric pressure

The swelling ratios of the neutral and ionized PNIPA gels immersed in seawater at atmospheric pressure are plotted as a function of temperature in Figure 1. The data of the gels immersed in pure water are also plotted for comparison. The solid symbols represent the data of the gels in seawater and the open symbols the data of the gels in pure water. As shown in Figure 1, the gels undergo volume transitions from a swollen state to a shrunken state at particular temperatures (transition temperature), depending on the concentration of the ionic group of SA as the temperature increases. The transition temperatures of both gels in seawater and pure water increase as the concentration of SA increases. The transition temperatures of the gels in seawater are lower than those of the gels in pure water, which for the neutral gel is approximately 7°C. It is also seen that the volume phase transition in the gels in pure water becomes more discontinuous and the degree of a change in volume associated with the phase transition becomes larger with increasing concentration of SA. On the contrary, the transition in the gels in seawater becomes more gradual and the degree of the volume change scarcely varies with the concentration of SA. The value of the degree is approximately 10, which is nearly equal to that for the neutral gel in pure water. The addition of the ionic group (SA) does not produce a drastic change in the swelling properties of PNIPA gels in seawater like the gels in pure water. This may be due to the fact that the ionic group of SA is scarcely dissociated in seawater, because such a drastic change in the swelling properties is caused by an increase in the number of counterions in the gel.

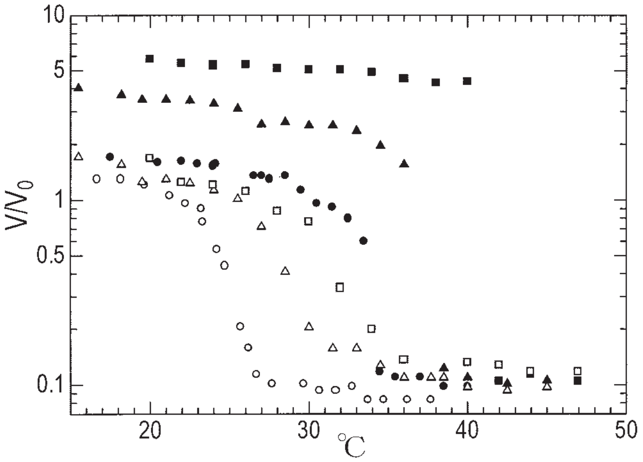

Figure 1 The swelling ratios of the neutral and ionized PNIPA gels in (○, △, □) seawater and (●, ▲, ■) pure water as a function of temperature. (○, ●) neutral gel, (△, ▲) ionized gel (50:1), and (□, ■) ionized gel (22:1).

Swelling ratios of PNIPA gels in seawater and aqueous solution of NaCl

Figure 2 shows the swelling ratios of PNIPA gels in seawater and an aqueous solution of NaCl (30 g/kg), representing the salt concentration in seawater. It is seen that all (neutral and ionized) gels undergo a volume transition. The transition temperature of the gel in seawater is somewhat lower than that of the gel in the aqueous solution, although the transitions in all gels, in addition to the neutral gel in the aqueous solution of NaCl, are continuous ones. As the concentration of SA is increased the transition becomes more gradual.

The swelling curves of PNIPA gels immersed in aqueous solutions of various salts was measured by Suzuki.[13] It was reported that the addition of the salts reduces the transition temperature of the gel and changes the phase transition to a more discontinuous

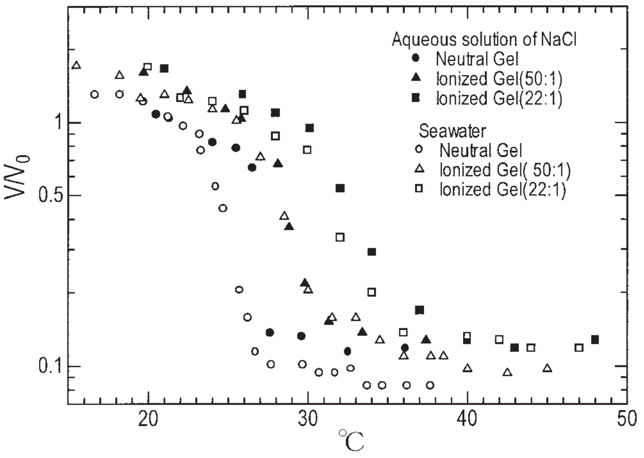

Figure 2 The swelling ratios of the neutral and ionized PNIPA gels in seawater and the aqueous solution of NaCl as a function of temperature.

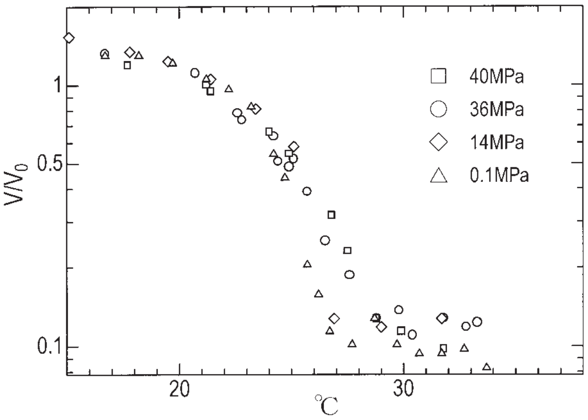

Figure 3 The swelling ratio of the neutral PNIPA gel in seawater as a function of temperature at various constant temperatures at 0.1, 14, 36, and 40 MPa.

one. For the present neutral PNIPA gel in the aqueous solution, Figure 2 shows that the transition is discontinuous and the transition temperature is about 7°C lower than that of the gel in pure water. This result confirms the above salt effect. However, when the SA concentration increases the transition becomes continuous, contrary to the case of the gels in pure water.

Seawater contains many kinds of salts with divalent ions besides NaCl. It is known that divalent ions have a more serious effect on the volume phase transition properties than monovalent ions. As the valency number of an ion in the aqueous solution increases, the swelling ratio of a gel decreases.[14] Thus, one can suppose that such divalent ions in seawater are responsible for the difference between the swelling behaviors of the gels in seawater and the aqueous solution of NaCl. However, it is found that, qualitatively, the swelling behavior of PNIPA gels in seawater is similar to that of the gel in the aqueous solution of NaCl.

Swelling ratio of NIPA gel in seawater at constant pressure

The swelling ratio of the neutral PNIPA gel in seawater at various constant pressures (0.1, 3.0, 14, 36, and 40 MPa) was measured as a function of temperature. The pressures correspond to the depths of seawater up to ~4000 m. The obtained data are plotted in Figure 3. Note that the gel undergoes a continuous volume transition from the swollen state to the shrunken state at 26–28°C at any seawater pressure as the temperature increases. Although there is not a large difference between the swelling curves measured at atmospheric pressure and a high pressure of 40 MPa, as the pressure increases the swelling curve seems to become a little more continuous. From these results one finds that the pressure of seawater (viz., the depth of the sea) scarcely exerted influence on the swelling behaviors of PNIPA gels. The ratio of the volumes associated with the transition is larger than 10 and the ratio is scarcely influenced by the pressure. As is known, the sea temperature at high depth is lower than these transition temperatures. Therefore, the gel at great depths of seawater normally takes the swollen state.

Swelling ratio of neutral pnipa gel in seawater at constant temperature

The swelling ratios of the neutral PNIPA gel in seawater at 19 and 26°C are plotted as a function of the hydrostatic pressure in Figure 4. The swelling behavior differs with the temperature at atmospheric pressure. It depends on whether the gel shrinks or swells at atmospheric pressure. As the pressure is increased, the gel at 26.5°C, which is just above the transition

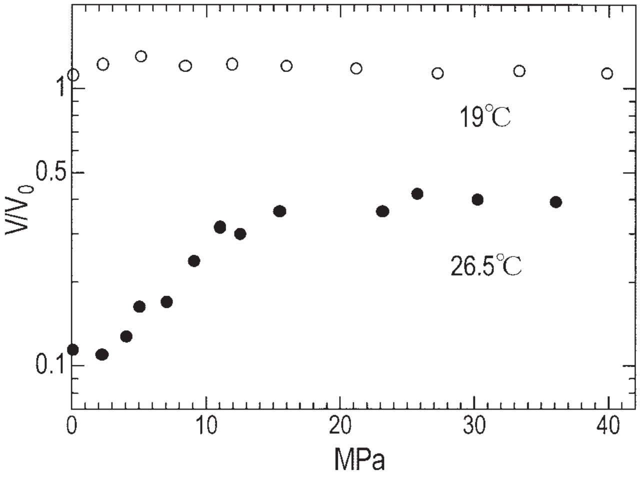

Figure 4 The swelling ratio of the neutral PNIPA gel in seawater as a function of pressure at constant temperatures of 19 and 26°C.

temperature, gradually swells and its volume ratio approaches a constant value of ~0.4 above 20 MPa. The ratio of the volumes for the shrunken and swollen states is as small as 4. This interesting behavior that the gel swells with pressure has also been found for PNIPA gels in pure water.[6] In that case, the hydrophobic hydration of PNIPA chains, that is, the swelling of the gel, under pressure P decreases the free energy of the gel by $\Delta V \times P$, where ΔV represents a decrease in volume associated with the hydration. In the present case, the solvent is not pure water, but it contains many kinds of salts. Although the structure of seawater may be much different than that of pure water, the gel in seawater also swells with pressure as well as the gel in pure water. The volume difference between the shrunken and swollen states induced by the pressure at a constant temperature of 26.5°C is as small as one-third of that by the temperature at a constant pressure. Meanwhile, when the gel swells at atmospheric pressure at 19°C, the volume scarcely changes with pressure. The gel is always in a swollen state in the measured pressure region. Because the temperature at deep sea is very low (~4°C), it also means that the gel normally swells at deep sea.

CONCLUSION

The swelling behaviors of PNIPA gels in seawater at high pressures up to ~40 MPa, corresponding to ~4000 m in depth, where human activity extends, were examined. The gels undergo continuous volume transitions in seawater as well as in pure water. The transition temperatures are lower than the gels in pure water; for the neutral gel at atmospheric pressure it is approximately 7°C. The addition of an ionic group (SA) does not have much effect on the swelling behavior of the PNIPA gel in seawater, contrary to the case of the gels in pure water. At high constant pressures up to ~40 MPa, the gels undergo a continuous volume transition at 26–28°C as the temperature varies. Normally, the gel is in a swollen state at deep sea. The ratio of the volume change associated with the transition is more than 10, which is 3 times larger than that obtained by changing the pressure at a constant temperature. The obtained results suggest a possibility that the volume transition of PNIPA gels can be utilized for producing mechanochemical energy at deep sea.

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