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The swelling behaviour of poly(*N*-n-propylacrylamide) hydrogel

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Hydrogel of poly(*N*-n-propylacrylamide) was prepared and its swelling dependence on temperature and pressure was investigated. Dramatic volume change of the gel with pressure and temperature was observed.

(Keywords: hydrogel; poly(*N*-n-propylacrylamide); swelling)

Introduction

Recently, much research has been conducted on environment-sensitive hydrogel owing to its potential engineering applications and scientific importance. A dramatic and sometimes discontinuous volume change can be induced by continuous and small variation of the surrounding conditions such as temperature[1]. The violent change of swelling with temperature occurs when the gel is near its critical point, which is analogous to the lower critical solution temperature of the corresponding polymer solution.

Poly(*N*-isopropylacrylamide) (PNIPA) temperature-sensitive gel is well known and has been extensively studied[1-3]. More recently, PNIPA gel was found to be sensitive to pressure as well[4], and the phenomenon was explained in the light of the free volume change of the system with pressure[5]. In this communication, we report the swelling characteristics of a relative of PNIPA gel, poly(*N*-n-propylacrylamide) (PNNPA) gel, upon changes of temperature and pressure. The PNNPA gel was also found to be sensitive to both temperature and pressure.

Experimental

The monomers of *N*-n-propylacrylamide and *N*-isopropylacrylamide were synthesized by a procedure similar to those described in refs 2 and 6. Propylacrylamide (or isopropylacrylamide) was prepared by reaction of n-propylamine (or isopropylamine) with acryloyl chloride in benzene at low temperature, with terephthalic phenol as polymerization inhibitor. The monomer was then purified by distillation at reduced pressure. Gel beads were prepared by reverse suspension polymerization at 4°C, with paraffin oil as dispersing medium and octylphenylether as stabilizer. The crosslinking agent was *N*,*N*′-methylenebisacrylamide and the initiator consisted of ammonium persulfate and *N*,*N*,*N*,*N*-tetramethylethylenediamine. The crosslinking agent took 2.4% (w/w) of the total amount of monomers and the overall monomer concentration in the pre-gel solution was 8% (w/w).

In the swelling measurement, a sample of gel beads in a pressure-resistant cell was immersed in a water bath (*Figure 1*). A thermoregulator was employed to control the temperature of the water bath and the cell. The pressure inside the cell was loaded and released through a piston system. The diameter of the gel bead was read with a calibrated microscope through the silica glass window on the cell. The equilibrium volume and swelling degree of the gel, Q_e, defined as the ratio of gel volumes at equilibrium and in the dry state, were then calculated according to the measured diameter.

Results and discussion

Like PNIPA and some other acrylamide derivative polymer gels, the PNNPA gel swells at low temperature and deswells at elevated temperature. However, the critical temperature is lower and the degree of swelling is smaller compared to the PNIPA gel of the same overall monomer concentration and crosslinking concentration (*Figure 2*). This indicates that the hydrophilicity of the PNIPA network is stronger than that of the PNNPA network, which leads the PNNPA gel to absorb less water at low temperature. For the same reason, hydrogen-bond deformation[7] inside the PNNPA gel takes place more easily and becomes so significant at lower temperature that the shrinkage of PNNPA gel occurs while the PNIPA gel is still in a swollen state.

Curves of the equilibrium degree of swelling of the PNNPA gel *versus* temperature and pressure are shown in *Figures 3* and *4*, respectively. The degree of swelling increases to different extents with increase of pressure, which is consistent with the prediction by Marchetti *et al.*[5]. It is observed that the PNNPA gel is sensitive to pressure as well. As for the PNIPA gel, the pressure sensitivity exists only within a very narrow range around the critical temperature, which suggests that the temperature sensitivity of the PNNPA gel is a precondition of its pressure sensitivity. This can be seen more clearly through a pressure–temperature–swelling degree (*P*–*T*–*Q*) three-dimensional phase diagram (*Figure 5*).

The *T*–*Q* planes and *P*–*Q* planes are equivalent to *Figures 3* and *4*, respectively. The top and bottom *P*–*Q* planes intersect with the chair-shaped surface, and the

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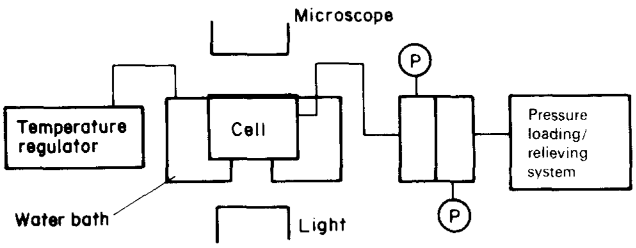

Figure 1 Schematic diagram of experimental set-up

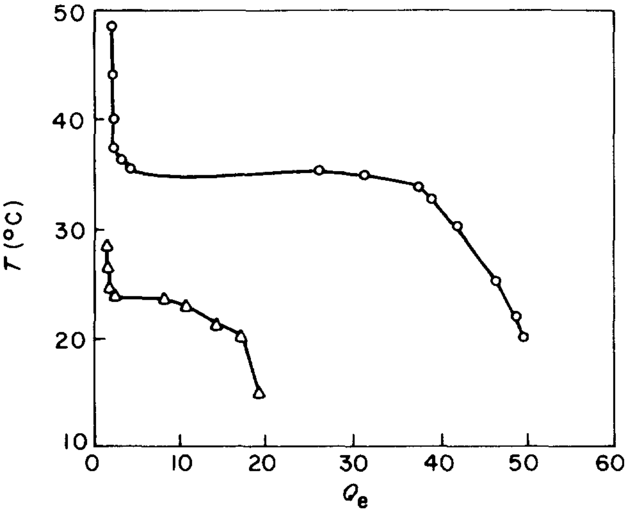

Figure 2 Comparison of the swelling curves of PNIPA (○) and PNNPA (△) gels

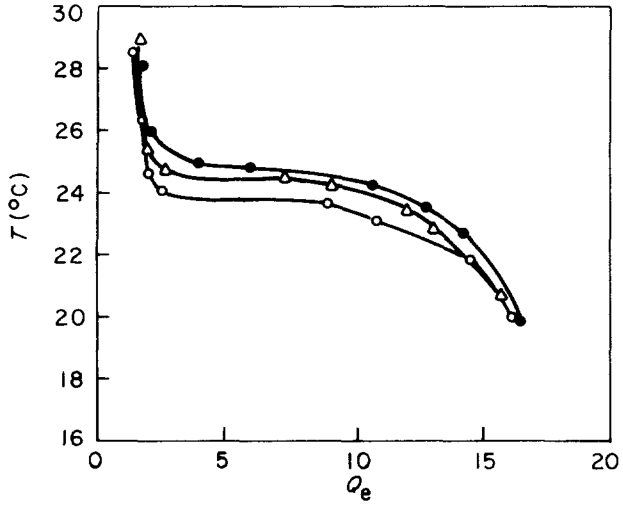

Figure 3 Equilibrium degree of swelling *versus* temperature under pressures of 1 (○), 60 (△) and 100 atm (●) for PNNPA gel (1 atm = 1.013 × 10^5 Pa)

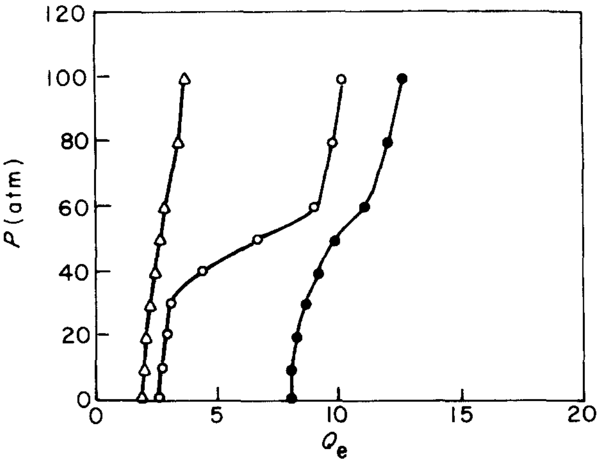

Figure 4 Equilibrium degree of swelling *versus* pressure under temperatures of 24.6 (△), 24.2 (○) and 23.0°C (●) for PNNPA gel (1 atm = 1.013 × 10^5 Pa)

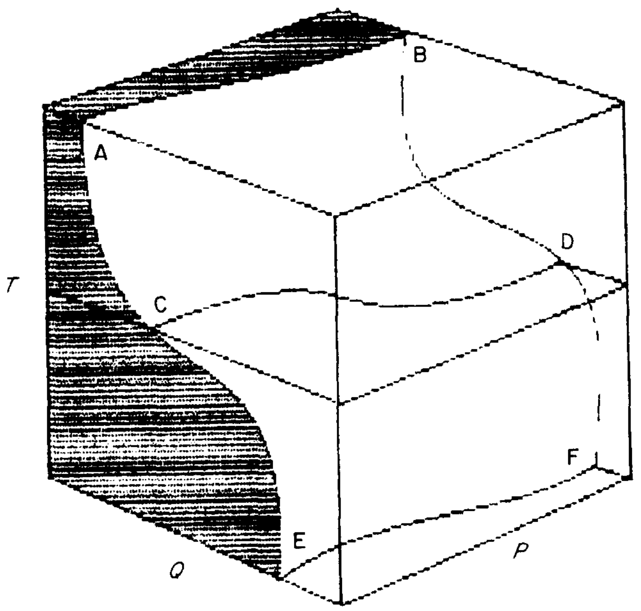

Figure 5 Schematic *P–T–Q* phase diagram of PNNPA gel

intersections form two curves, AB and EF, which correspond to the left- and right-hand curves in *Figure 4*, respectively. The middle *P–Q* plane, with the corresponding temperature just a little higher than the critical temperature under normal pressure, intersects with the chair-shaped surface and forms a curve, CD, which shows the pressure sensitivity and corresponds to the middle curve in *Figure 4*. It is now easy to realize that the pressure sensitivity of the PNNPA gel is a consequence of the increase of its critical temperature with pressure and its temperature sensitivity. Higher temperature is needed to break the structured water inside the gel, causing it to deswell or collapse at high pressure, since the shrinkage of the gel will result in a net increase in the volume as well as the entropy of the system[8], and the volume increase will be easily resisted under high pressure. However, the pressure effect on the volume increase, although significant, is very small. This leads to a slow variation of critical temperature with pressure, so that the pressure sensitivity can only be observed at the vicinity of the critical temperature.

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