In-Situ Interferometry Studies of the Drying and Swelling Kinetics of an Ultrathin Poly(N-isopropylacrylamide) Gel Film below and above Its Volume Phase Transition Temperature

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ABSTRACT: The temperature influence on the drying and swelling kinetics of ultrathin poly(N-isopropylacrylamide) gel film were studied by in-situ interferometry. The drying rate is greatly dependent on temperature. When T ≈ 31 °C, the original gel film was swollen and contained more than 99% of water before drying. Our results showed that the initial drying rate was constant. However, it became faster and faster toward the end of the drying. On the other hand, when T ≥ 32 °C, the gel film was in the collapsed state, but still contained ~70% of water, before drying. Three distinct drying processes were observed, namely, a very fast initial shrinking, a slow transition period, and a normal drying process similar to that of the gel film when T ≈ 31 °C. As for the swelling process, it can be better described by the first-order kinetics developed by Li and Tanaka. The cooperative diffusion coefficient and the ratio of the shear modulus to the longitudinal modulus were determined from a least-squares fitting of the swelling experimental data according to the swelling equation for a large disk. A critical slowing down of the gel swelling for the thin film was observed in the range of 33–35 °C.

Introduction

Hydrogels, which can undergo a volume phase transition, have been extensively studied in recent years. A typical example is poly(N-isopropylacrylamide) (PNIPAM) gel, which has a sharp volume phase transition around the lower critical solution temperature (LCST) of linear PNIPAM chains; i.e., PNIPAM gel swells when T < LCST, but collapses when T > LCST.¹ The volume change can be as large as ~10² times. Due to this special thermosensitivity, the PNIPAM gel might be utilized in various applications such as controlled drug delivery,²,³ molecular separation,⁴ and artificial muscle.⁵ Most of the past studies were focused on the swelling equilibrium. However, a better understanding of the swelling/shrinking kinetics of the PNIPAM gel is vitally important for its potential applications.

Few past studies have dealt with the swelling and shrinking kinetics of the PNIPAM gel in water.⁶–¹² Tanaka et al.⁶,⁷ studied the swelling and shrinking kinetics of spherical-shaped PNIPAM gels by monitoring the changes in shape, size, and transient pattern with a microscope. They have shown that the motion of a polymer gel network during the swelling or shrinking process could be described by a collective diffusion equation. For a spherical gel of radius R, the swelling or shrinking rate was proportional to R⁻². The collective diffusion coefficient (Dc) diminished at the critical point of the volume phase transition. They also observed that the swelling and shrinking kinetics were much different. There were two distinct processes in the swelling: a fast initial process followed by a slower first-order process. On the other hand, a plateau was observed in the shrinking process, which was attributed to the dense surface layer formed during the initial shrinking. Hoffman et al.⁸,⁹ and Kim et al.¹⁰,¹¹ characterized the shrinking kinetics of bulk disk PNIPAM gels by a conventional weighing method. They also found that the bulk gel did not collapse homogeneously, i.e., the formation of a dense surface layer and water pocket retarded the shrinking kinetics.

To eliminate the inhomogeneous swelling and shrinking existing in a bulk gel and to simplify the kinetic process, in this study we have studied an ultrathin PNIPAM gel film (~60 µm) by in-situ interferometry. The cooperative diffusion coefficient and the ratio of the shear modulus to the longitudinal modulus were determined on the basis of the following theory developed by Li and Tanaka.¹²

Theoretical Background

Swelling and Shrinking Kinetics. The swelling phenomena and its kinetics have been long studied. The swelling kinetics of a spherical gel was recently formulated by Tanaka and Fillmore on the basis of a cooperative diffusion theory,¹³ wherein the shear modulus was considered to be negligible in comparison with the osmotic compressive modulus. By including a nonnegligible shear modulus, Peters and Candau¹⁴ developed a general model to characterize the swelling kinetics of spherical, cylindrical, and disklike polymer gels. Later, Li and Tanaka¹² proposed a two-process mechanism after realizing that neither gel swelling nor shrinking can be considered to be a pure diffusion process. They predicted that the shear modulus (Ṁshear) is related to the net osmotic modulus (Ṁos) and the osmotic bulk modulus (K̇bulk) by¹²

\[
\frac{R}{Ṁos} = \frac{Ṁshear}{K̇bulk + 4/3 Ṁshear} \tag{1}
\]

According to Li and Tanaka, the swelling or shrinking follows

\[
\frac{Ẇn - W}{Ẇn} = \sum_{n=1}^{∞} B_n \exp(-t/τ_n) \tag{2}
\]

where W and Wn are the solvent uptake at time t and infinite time (i.e., at equilibrium), respectively; [(Ẇn - W)/Ẇn], the relative swelling capacity at time t; Bn, a complicated function of R; and τn, the relaxation time related to the nth mode. When τn > 1 or τn > τ0 (n ≥ 2) or B1 > 0 (n ≥ 2), all high-order terms (n ≥ 2) in eq 2 can be dropped. In this case, the swelling and shrinking follows a first-order kinetics, i.e.,

\[
\ln\left(\frac{Ẇn - W}{Ẇn}\right) = \ln B_1 - t/τ_1 \tag{3}
\]

where B1 is related to R by¹²
The PNIPAM microgel particles were made by suspension polymerization. NIPAM (15.90 g), N,N'-methylenebis(acrylamide) (BIS) (0.2835 g), and sodium dodecyl sulfate (SDS) (0.1130 g) were added to 500 mL of deionized water. The solution was heated to 70 °C and stirred at 200 rpm for 40 min with a nitrogen purge to remove oxygen. Finally, 0.6480 g of potassium persulfate (KPS) dissolved in 40 mL of deionized water was added to start the reaction. The solution was stirred at 1000 rpm for 4 h. N-isopropylacrylamide (courtesy of Kohjin Ltd., J. Japan) was recrystallized three times in a benzene/hexane mixture; BIS as a cross-linker was recrystallized from methanol. KPS (from Aldrich, analytical grade) as an initiator and SDS (from BDH, 99%) as a dispersant were used without further purification. In order to remove SDS, the obtained PNIPAM microgel solution was purified by successive centrifugation (15 300 rpm for 2.5 h), decantations, and dispersions in deionized water. The purified microgel solution was further concentrated to 7.5 wt% by centrifugation and decantation. The thin PNIPAM film with a thickness of 60 µm was prepared from these microgels by a high-precision quadruple film applicator. On a macroscale, the film is inhomogeneous. However, the diameter of our light beam is ∼1.5 mm and the cross-section of the light beam covers more than 10^7 particles. On the other hand, the film is much thicker than the wavelength of the light. A rough estimation shows that the light “sees” about 10^7 particles even in the expanded state. Therefore, the microscale inhomogeneities have been well averaged.

**In-Situ Interferometry.** As shown in Figure 1, the thin PNIPAM film was supported by a temperature-regulated optical glass plate. The top of the gel film was covered by either dry air in the drying process or by water in the swelling process. A very small fraction of the light from a Nd-YAG solid-state laser (ADLAS DPY 425 II, λ0 = 532 nm) was used as the light source. In the present setup, 15, 16 θ is very close to 0, and thus so are θ' and θ''. Therefore, cos(θ'') ∼ 1 in eq 7. The reflected light beams (I₀,1 and I₀,2) are interfered at a photodiode (Hamamatsu S2386-18K) to produce a voltage signal (V). V was recorded through an analog-to-digital data acquisition system including an A/D converter (National Instruments, DAQCard-700) and a notebook computer (NEC UltraLite Versa 486SL/33).

**Experimental Section**

**Sample Preparation.** PNIPAM gel is very sticky so that it is rather difficult to directly make an ultrathin gel film. Instead, we made a gel film from narrowly distributed spherical microgel particles with an average diameter of ∼0.4 µm. The PNIPAM microgel particles were made by suspension polymerization. NIPAM (15.90 g), N,N'-methylenebis(acrylamide) (BIS) (0.2835 g), and sodium dodecyl sulfate (SDS) (0.1130 g) were added to 500 mL of deionized water. The solution was heated to 70 °C and stirred at 200 rpm for 40 min with a nitrogen purge to remove oxygen. Finally, 0.6480 g of potassium persulfate (KPS) dissolved in 40 mL of deionized water was added to start the reaction. The solution was stirred at 1000 rpm for 4 h. N-isopropylacrylamide (courtesy of Kohjin Ltd., J. Japan) was recrystallized three times in a benzene/hexane mixture; BIS as a cross-linker was recrystallized from methanol. KPS (from Aldrich, analytical grade) as an initiator and SDS (from BDH, 99%) as a dispersant were used without further purification. In order to remove SDS, the obtained PNIPAM microgel solution was purified by successive centrifugation (15 300 rpm for 2.5 h), decantations, and dispersions in deionized water. The purified microgel solution was further concentrated to 7.5 wt% by centrifugation and decantation. The thin PNIPAM film with a thickness of 60 µm was prepared from these microgels by a high-precision quadruple film applicator. On a macroscale, the film is inhomogeneous. However, the diameter of our light beam is ∼1.5 mm and the cross-section of the light beam covers more than 10^7 particles. On the other hand, the film is much thicker than the wavelength of the light. A rough estimation shows that the light “sees” about 10^7 particles even in the expanded state. Therefore, the microscale inhomogeneities have been well averaged.

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**Results and Discussion**

Figure 2 shows one part of the typical observed signal in the swelling process for the thin PNIPAM gel film at 21 °C. The increase of the time interval between two neighboring minima (maxima) indicates a gradual slowing down of the swelling rate. This is expected because the elastic force inside the gel increases with swelling, while at the same time the osmotic pressure decreases. When these two forces are balanced, the gel reaches its swelling equilibrium. After correcting for the refractive index change, the signal profile in Figure 2 was transferred into the gel film thickness change (∆z) versus time (t). It should be noted that in the swelling the refractive index of the gel film (n'' in eq 7) is a function of time. For a completely dried PNIPAM film, n'' ∼ 1.5, while for a fully swollen PNIPAM gel, n'' ∼ 1.36. The total change of n'' is about 10%. Therefore, even if we use the average value of 1.43, the error introduced is
we have the maximum swelling proportional to the swelling of the PNIPAM gel film at 21 °C. For \( t \) from \( \Delta z \) continuous line is a least-squares fitting of \( \ln(\Delta z) \) to \( D(t) \). Tanaka's theory,12 a higher \( B \) smaller than \( B_n \). The higher \( B \) smaller than \( B_n \) is closer to 1, which indicates that \( \tau_1 \) and \( \tau_2 \) were determined from a least-squares fitting on the basis of eq 3. The value of \( \tau_2 \) is much faster than the center swelling. This is why for bulk gels all previous swelling curves showed a very fast initial swelling process followed by a much slower first-order process. In contrast, for an ultrathin gel film, the penetration of water is nearly instantaneous. There is hardly a difference between the gel surface and the gel–glass interface. This might explain why all data points follow the first-order fitting and \( B_1 \) is higher. Table 1 shows that around the volume phase transition temperature (33 °C), \( R \) has two distinct values, namely, \( R \sim 0.67 \) for \( T < 33 \) °C and \( R \sim 0.58 \) for \( T > 33 \) °C. According to its definition, \( R = (K_{bulk}/M_{shear}) + 4/3 \). When \( T \) increases from below 33 °C to above, water changes from a good solvent for the gel network to a poor one. In comparison with a swollen gel network, both \( K_{bulk} \) and \( M_{shear} \) of the collapsed gel will increase. The lower \( R \) for the collapsed state means that \( K_{bulk}/M_{shear} \) is relatively larger; namely, \( K_{bulk} \) increases faster than \( M_{shear} \). Our observed \( T \)-dependence of \( R \) is consistent with the experimental results of Hirotsu obtained from a bulk PNIPAM gel wherein they directly measured osmotic bulk modulus \( K_{bulk} \) and shear modulus \( M_{shear} \).17 For PVAC gels in i-PrOH, Zrinyi et al.17 also found that \( R \) depends on solvent quality. \( R \) decreases when a solvent becomes poor at low temperature.

Table 1. Summary of the Experimental Values of \( B_1, \tau_1, R, \) and \( D_c \) for the Ultrathin PNIPAM Gel Film (60 \( \mu m \)) at Different Swelling Temperatures (\( T \))

<table>
<thead>
<tr>
<th>( T/°C )</th>
<th>( B_1 )</th>
<th>( \tau_1/10^5 s )</th>
<th>( R )</th>
<th>( D_c/(cm^2/s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.0</td>
<td>0.95</td>
<td>0.53</td>
<td>0.69</td>
<td>3.6 \times 10^{-7}</td>
</tr>
<tr>
<td>25.0</td>
<td>0.93</td>
<td>0.81</td>
<td>0.67</td>
<td>1.5 \times 10^{-7}</td>
</tr>
<tr>
<td>30.0</td>
<td>0.93</td>
<td>0.91</td>
<td>0.67</td>
<td>1.1 \times 10^{-7}</td>
</tr>
<tr>
<td>32.0</td>
<td>0.93</td>
<td>0.93</td>
<td>0.67</td>
<td>7.7 \times 10^{-8}</td>
</tr>
<tr>
<td>33.0</td>
<td>0.88</td>
<td>1.26</td>
<td>0.61</td>
<td>1.7 \times 10^{-8}</td>
</tr>
<tr>
<td>34.0</td>
<td>0.86</td>
<td>1.38</td>
<td>0.57</td>
<td>6.3 \times 10^{-9}</td>
</tr>
<tr>
<td>35.0</td>
<td>0.87</td>
<td>1.64</td>
<td>0.59</td>
<td>5.1 \times 10^{-9}</td>
</tr>
</tbody>
</table>

Figure 3. Typical plot of the film thickness change (\( \Delta z \)) versus time (\( t \)) during the swelling process at 21 °C, which is calculated on the basis of eq 7 from the signal profile shown in Figure 2.

Figure 4. Typical plot of \( \ln(\Delta z - \Delta z_o)/\Delta z_o \) versus \( t \), where "o" are the experimental data and the continuous line represents a least-squares fitting on the basis of eq 3. Less than 5%. Practically, we measured the values of \( n^\ast \) at several different swelling stages to obtain an approximate calibration curve, namely, a plot of \( n^\ast \) versus the degree of the swelling. In this way, the error introduced by the uncertainty of \( n^\ast \) in the conversion of Figure 2 is no more than 1%.

Figure 3 shows a typical plot of \( \Delta z \) versus \( t \) for the swelling of the PNIPAM gel film at 21 °C. At \( t \to \infty \), we have the maximum swelling \( \Delta z_o \). On the basis of eq 7, \( B_1 \) and \( \tau_1 \) were determined from a least-squares fitting of \( \ln(\Delta z - \Delta z_o)/\Delta z_o \) versus \( t \), where we have utilized the fact that the solvent uptake (\( W \)) at time \( t \) is proportional to \( \Delta z \), or, in other words, \( \ln(W_o - W)/W_o \) = \( \ln(\Delta z_o - \Delta z_o)/\Delta z_o \) = \( \ln(B_1) - \tau_1 \). Figure 4 shows a typical plot of \( \ln(\Delta z_o - \Delta z)/\Delta z_o \) versus \( t \), where "o" are experimental data and the continuous line is a least-squares fitting of \( \ln(\Delta z_o - \Delta z)/\Delta z_o \) versus \( t \). It shows that the swelling of the thin PNIPAM gel film follows first-order kinetics. \( \tau_1 \) and \( B_1 \) were calculated from the slope and intercept of the fitting, respectively. \( R \) and \( D_c \) were further calculated from \( \tau_1 \) and \( B_1 \) on the basis of eqs 4–6. It should be noted that even the initial data follow the fitting line and \( B_1 \) is close to 1, which indicates \( B_n (n \geq 2) \) is much smaller than \( B_1 \) since \( \sum_{n=1}^{\infty} B_n = 1 \). According to Li and Tanaka's theory,12 a higher \( B_1 \) means a higher \( R \) (=\( M_{shear}/M_{flex} \)). Table 1 summarizes the values of \( B_1, \tau_1, R, \) and \( D_c \) calculated from \( \ln(\Delta z_o - \Delta z)/\Delta z_o \) versus \( t \) for the thin PNIPAM gel film swelling at different temperatures. When \( T \leq 32 °C \) or \( T \geq 34 °C \), \( B_1 \) and \( R \) are nearly independent of \( T \). The value of \( R \sim 0.67 \) is similar to that for the thin gelatin film,16 but significantly higher than those (~0.3–0.4) for macroscopic size gels.12,17 The higher \( R \) value might be related to the ultrathin thickness of the gel film. As we stated before,16 for a bulk gel, water gradually diffuses from the surface into the gel. The swelling takes place first at the surface and then in the center. The surface swelling is much faster than the center swelling. This is why for bulk gels all previous swelling curves showed a very fast initial swelling process followed by a much slower first-order process. In contrast, for an ultrathin gel film, the penetration of water is nearly instantaneous. There is hardly a difference between the gel surface and the gel–glass interface. This might explain why all data points follow the first-order fitting and \( B_1 \) is higher. Table 1 shows that around the volume phase transition temperature (~33 °C), \( R \) has two distinct values, namely, \( R \sim 0.67 \) for \( T < 33 \) °C and \( R \sim 0.58 \) for \( T > 33 \) °C. According to its definition, \( R = (K_{bulk}/M_{shear}) + 4/3 \). When \( T \) increases from below 33 °C to above, water changes from a good solvent for the gel network to a poor one. In comparison with a swollen gel network, both \( K_{bulk} \) and \( M_{shear} \) of the collapsed gel will increase. The lower \( R \) for the collapsed state means that \( K_{bulk}/M_{shear} \) is relatively larger; namely, \( K_{bulk} \) increases faster than \( M_{shear} \). Our observed \( T \)-dependence of \( R \) is consistent with the experimental results of Hirotsu obtained from a bulk PNIPAM gel wherein they directly measured osmotic bulk modulus \( K_{bulk} \) and shear modulus \( M_{shear} \).17 For PVAC gels in i-PrOH, Zrinyi et al.17 also found that \( R \) depends on solvent quality. \( R \) decreases when a solvent becomes poor at low temperature.
difference for solvent inside and outside the gel is nearly zero since there exists no solvent. Therefore, there is no extra hindering force outside to prevent the escape of solvent from the gel. The chemical potential difference for solvent inside and outside the gel is nearly a constant. This might explain why the initial decrease of $\Delta z$ is a linear function of $t$. Near the end of the drying, the polymer segment concentration inside the gel becomes higher and higher and the film undergoes a rubber-to-glass transition, so that the interaction between the segments becomes stronger and stronger. The stronger interaction between the segments will diminish the $\Delta z$ change at the initial stage is much different from that in a bulk sample.

Figure 6 shows how the PNIPAM gel film thickness change ($\Delta z$) varied with time ($t$) after $T$ jumped from 25.0 °C to a temperature higher than the volume phase transition temperature ($T_{pc}$). The lower values of $D_c$ observed in this study further confirm Tanaka and Li’s prediction that $D_c$ is related to the diffusion dimension (d), namely, for an ultrathin film, $d = 1$, while for spheres, $d = 3$.

Conclusions
The kinetics of the drying and swelling of ultrathin PNIPAM gel films can be studied by in-situ interferometry. In comparison with a conventional weighing or length-measuring method, our in-situ interferometry has several advantages: (1) the film thickness is much smaller than its size ($\sim 1 \times 1$ cm$^2$), so that the gel film can be considered as an infinitely large disk; (2) the film thickness change can be continuously and accurately recorded by a computer; (3) due to the ultrathin thickness, the difference between the gel surface and center is much smaller than that in a bulk sample; and (4) the experimental time required to reach the final swelling equilibrium is much shorter, i.e., minutes instead of hours or even days.

When the temperature is suddenly changed from 25 °C to a temperature higher than the volume phase transition temperature of PNIPAM gel, the drying involves a three-stage process, namely, a fast initial gel shrinking followed by a plateau and a normal drying process. The drying process is completely different from the gel shrinking process. Therefore, a quantitative theory is needed to describe the drying process. On the other hand, the swelling experimental results are satisfactorily represented by the swelling theory developed by Li and Tanaka. The ratio of the shear modulus ($M_{shear}$) over the bulk modulus ($K_{bulk}$) of the thin PNIPAM gel film shows two distinct values of $\sim 0.67$ and $\sim 0.58$, respectively, for temperature below and above the volume phase transition temperature ($\sim 33$ °C). The collective diffusion coefficient ($D_c$) diminishes at the critical phase transition temperature. The lower values of $D_c$ observed in this study further confirm Tanaka and Li’s prediction that $D_c$ is related to the diffusion dimension (d), namely, for an ultrathin film, $d = 1$, while for spheres, $d = 3$.

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