

STUDY ON THE GRAVIMETRIC MEASUREMENT OF THE SWELLING BEHAVIORS OF POLYMER FILMS

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Abstract. The present theories and experimental methods to evaluate the swelling behaviors by gravimetric measurement were experimentally tested for polyvinyl alcohol (PVA) films. It was found that the swelling behaviors and swelling kinetic parameters, such as diffusion exponent n , by gravimetric measurement may be greatly influenced by experimental procedures. In this paper, both the continuous (denoted as scheme A) and the separated (scheme B) experimental procedures of the gravimetric method to evaluate the swelling behaviors were presented and the difference between the two schemes were analyzed. The results suggest that the continuous diffusion of water molecules in films during gravimetric determination may be the key factor affecting the swelling behaviors. The advantages and disadvantages of the two schemes were discussed. It was concluded that an appropriate selection of experimental schemes is effective to extend the applicability range of gravimetric methodology and to increase the accuracy of gravimetric measurement.

1. INTRODUCTION

Polymer films based on biomaterials or other hydrophilic polymers are generally sensitive to water and environmental humidity because they are normally hygroscopic with plenty of hydrophilic groups on the macromolecule chains [1]. The knowledge of swelling behaviors of polymer films is of significant importance for various applications in biomolecular electronics and sensors, drug delivery systems, wound dressings, adsorption of chemical materials and contact lenses [2,3]. They have increasingly attracted the researchers' interests and many theoretical models have been developed with the development of materials sciences [4,5].

Swelling curve (swelling ratio vs. time) is usually used to characterize the swelling behaviors of films or hydrogels [5]. Some important parameters can be obtained from swelling curves, such as diffusion exponents and solvent diffusion coefficients in films. The swelling mechanisms can also be analyzed

based on swelling curves. Therefore, accurate experimental swelling data are particularly important for the development of synthesis and applications of films. To obtain the swelling curve of films, the gravimetric measurement has been extensively adopted because of its simplicity and easy implementation [4-6].

Most of the previous studies about the gravimetric measurements were focused on the swelling behaviors for different kinds of films [3-7]. The major experimental method can be simply summarized as follows: the analysis of the dynamic swelling characteristics of films is performed by accurately weighing the sample during the measurement, the swollen films are removed from the immersing solution at regular time intervals, and the film sample is weighed after removing the excess surface water. The sample was put into the solution again and the procedure was repeated until the swelling equilibrium was reached. Yin and coworkers measured

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the swelling ratios of sodium alginate-g-acrylic acid by the continuous method, and the swollen gels were withdrawn at regular time intervals and weighed after removal of surface water [6]. The most important feature of this kind of measurement is that only one sample is needed and used during the whole process and the experiment is continued after weighing. Therefore, it is called *continuous method*. On the other hand, there is a different procedure that requires a series of samples, in which each sample is immersed in solution for different time durations. The swelling ratios at different time can be obtained with separated identical samples, and the swelling method is usually used in the study of dimensional measurement [8]. So it is correspondingly called the *separated method*. Pornsak and coworkers studied the swelling behaviors of calcium polysaccharide gels by both gravimetric methods, but they failed to compare the differences between continuous and separated method [5]. As it's known, the two experimental procedures are always considered to be identical in the study of swelling properties of films.

In this work, the swelling behaviors of PVA films with continuous and separated methods were studied and the differences of swelling curves and calculated parameters by these two schemes were analyzed. To explain the differences between the two different schemes, a possible mechanism about the diffusion of solvent and experimental scheme was proposed. The influences of physical properties of films and experimental design on the experimental data were analyzed. It may be helpful for selecting suitable experimental schemes at different conditions. The purposes of this work were to improve the accuracy of the determination of swelling data, to extend the applicability range of gravimetric methodology, and to elucidate the relationship between experimental design and swelling behaviors of films.

2. EXPERIMENTAL

2.1. Materials and film production

The polymer films studied in this work were prepared using a commercial poly (vinyl alcohol) with a hydrolysis degree of 88% and an average polymerization degree of 1750 from Tianjin Kermel Co. Ltd., Tianjin, China. Glutaraldehyde (GTA) was used as a cross-linking agent. All the reagents were used as received without further purification.

PVA was dissolved in hot water (90 °C) while being stirred for 3 hours to obtain the film-forming solution containing 10 g PVA per 100 g of solution. The film-forming solution was then cooled to room

temperature. PVA films were obtained by casting the solution in glass trays (15×15 cm), followed by water evaporation at room temperature for 48 h. The thicknesses of the films were controlled by carefully controlling the dry matter / area of plate ratio.

Glutaraldehyde (GTA) cross-linked PVA films were prepared by the following in-situ cross-linking procedures: PVA films were immersed in a GTA (2% v/v) solution at 60 °C for 10 min, and then the cross-linked films were washed with double-distilled water and air dried at room temperature. There were sulfuric acid and sodium sulfate (Na_2SO_4) in the glutaraldehyde solution, here the sulfuric acid was used to catalyze the acetalization reaction, and sodium sulfate was used to inhibit the solubility of the PVA films during the in-situ cross-linking process.

2.2. Gravimetric determination

Analysis of the dynamic swelling behaviors of PVA films were performed in a PBS buffer solution. PBS solution was used as the solution medium in the swelling process in order to provide a constant pH, 7.2 ± 0.1 . The PBS solution contained NaCl (140 mM), KCl (3 M), Na_2HPO_4 (8.1 mM), and KH_2PO_4 (1.5 mM). After humidity regulation in a constant humidity (65% RH) and temperature (25 °C) chamber, the circular shaped PVA films, 12 mm in diameter, was used in all swelling experiments. The solution temperature was controlled at 25.0 ± 1.0 °C for all the swelling experiments.

The swelling experiments were as follows:

Experimental Scheme A (Continuous method): film was weighed before swelling and the weight was recorded as m_0 . The sample was then immersed in a 200 mL PBS solution. At the same time, a stop watch was initiated to record the swelling time (the time for the sample immersed in PBS solution) of the sample. After a definite swelling time t_r , the sample was removed from the solution and the surface water was quickly removed with a filter paper. The sample was weighed on an electronic balance (0.1 mg accuracy) and the weight was denoted as m_1 for the first immersion step. The sample was immersed in the solution for the second time, and the procedure was repeated until the equilibrium of swelling was reached. At time t , the weight of the sample was denoted as m_t . The swelling ratio at different swelling time can be calculated by Eq. (1).

Experimental Scheme B (Separated method): Different from the experimental scheme A, the swelling ratio can be determined with a series of samples. In this method, the pre-weighed films numbered from 1 to n were immersed in the PBS solution, removed

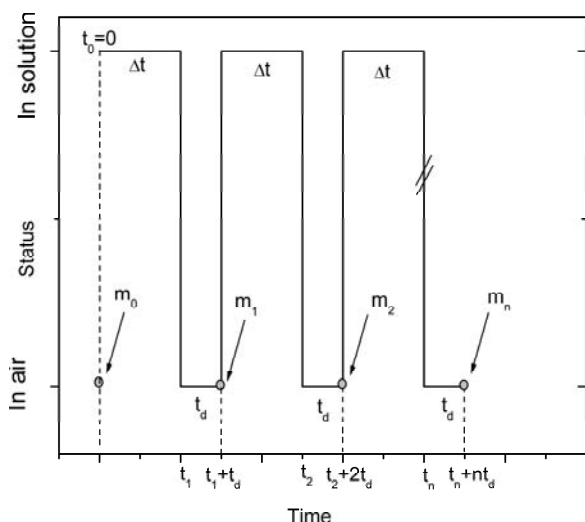


Fig. 1. Schematic diagram of experimental scheme A (continuous method).

out, and weighed at different swelling time t_1 , t_2 , t_3 ... t_n , respectively. For example, at time t_1 , sample 1 was removed out and weighed after the absorbing the surface water. The sample 1 was not used again. At time t_2 , sample 2 was removed out and weighed. The same procedure was repeated until the last sample n was weighed. Each sample has the same initial weight, m_0 . Although sometimes the same level may be kept, it is better to accurately record the weight of the samples.

Swelling behavior was described by the normalized swelling ratio (M_t) at time t . It can be obtained in grams of water per gram of dry sample using Eq. (1).

$$M_t = \frac{m_t - m_0}{m_0} \times 100\%, \quad (1)$$

where m_0 and m_t are weights of samples before swelling and after swelling time t , respectively. Swelling curves of films can be obtained by the plot of M_t vs. time. As mentioned above, m_0 in Eq. (1) may be different in separated method, and only the corresponding initial weight of the sample for determining the M_t can be used.

3. RESULTS AND DISCUSSION

3.1. Analysis of two different experimental schemes

The experimental process for the two different schemes related to gravimetric measurement was shown in Figs. 1 and 2. As has been known, there is a necessary step for absorbing the surface solution before weighing the samples. So the time inter-

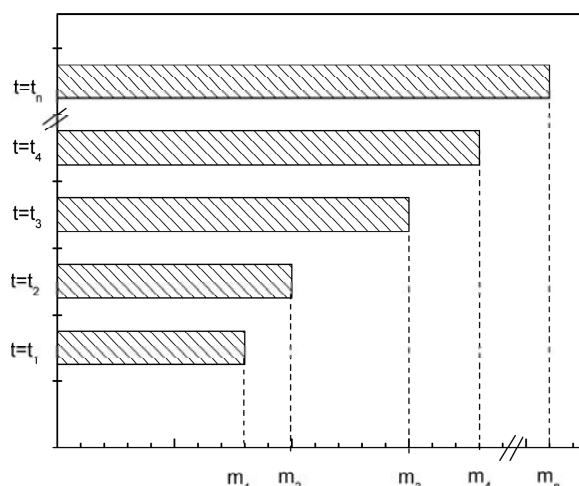


Fig. 2. Schematic diagram of experimental scheme B (separated method).

val for fetching out of the films from the solution is inevitable. In the study, a time interval of 30 seconds was set and it was called *dry time* (t_d). It is the time that the samples do not stay in solution.

As shown in Fig. 1, films are frequently moved out of solution during the whole experimental process. Δt is used to denote the immersion duration of film in solution between two weighing operations. To simplify the analysis, we supposed that the immersion duration Δt was the same during the whole measurement, though sometimes Δt might be changed a little according to the swelling properties at different swelling stages. So there were a series of original weight data corresponding to the data points on swelling curve at $t_1 = \Delta t$, $t_2 = 2\Delta t$, ..., and $t_n = n\Delta t$. However, the additional dry time (t_d) for weighing the samples was usually neglected. In order to fully understand the influence of the dry time on the results, the actual experimental procedure is discussed.

The initial weight (m_0) of the dry film is weighed at the time of $t_0 = 0$ as shown in Fig. 1. At the swelling time of t_1 , the film is taken out of the solution and weighed, noted as m_1 . The m_1 is the weight after the swelling duration t_1 ($t_1 = \Delta t$) on swelling curve, whereas the actual duration is $t_1 + t_d$ or $\Delta t + t_d$ as shown in Fig. 1. Similarly, at swelling time t_2 , we supposed $t_2 = 2t_1 = 2\Delta t$ was the total swelling time. So the actual time spent from the very beginning is not t_2 because of the additional time $2t_d$. Therefore, actually $t_2 + 2t_d$ or $2\Delta t + 2t_d$ has passed to obtain the weight of film after twice immersions. At swelling time t_n , $t_n + nt_d$ corresponds to m_n , the final weight of film. In Fig. 1, the black circles with

arrows marked as m_1 , m_2 , and m_n indicate the weights of samples at swelling time t_1 , t_2 and t_n .

If we suppose the dry time t_d is definite for all the repeated procedures, a series of swelling ratio M_t of swollen film at time t_1 , t_2 ... and t_n can be calculated by:

$$\begin{aligned} M_{t_1} &= (m_{t(t=t_1+t_d)} - m_0) \times 100\% / m_0, \\ M_{t_2} &= (m_{t(t=t_2+2t_d)} - m_0) \times 100\% / m_0, \\ &\dots \dots \\ M_{t_n} &= (m_{t(t=t_n+nt_d)} - m_0) \times 100\% / m_0. \end{aligned} \quad (2)$$

If the total duration of the measurement is $t_n + nt_d$, the additional time nt_d is corresponding to the total duration weight in air, which is the total dry time for the swelling measurement. Actually, the second, third and more parallel measurements may be performed to obtain more reliable swelling data. However, the total additional dry time nt_d may affect the swelling behaviors, compared to those without dry time. As has been mentioned above, the total swelling time for experimental scheme A to obtain a swelling curve is $t_n + nt_d$. So the proportion of dry time in scheme A (P_A) can be denoted as:

$$P_A = \frac{m_d}{t_n + nt_d} = \frac{t_d}{\Delta t + t_d} \quad (n = 1, 2, 3 \dots) \quad (3)$$

In scheme B, a series of samples were used. They were immersed in solution until the preset times were reached. Each separated sample corresponds to a single data point on the swelling curve.

Fig. 2 shows that every points on the swelling curve was by an independent sample. If the initial weight m_0 of each dry film is the same, after different period of swelling ($t = t_1, t_2, t_3, \dots, t_n$), the weights of each swollen film are m_1, m_2, m_3, \dots , and m_n . However, the weight determination of each sample also requires a surface water removing and weighing process. In other words, an additional dry time t_d is needed to obtain the weight of the sample. Therefore, the swelling ratio M_t of swollen film at time $t = t_1, t_2, t_3, \dots$, and t_n can be calculated as:

$$\begin{aligned} M_{t_1} &= (m_{t(t=t_1+t_d)} - m_0) \times 100\% / m_0, \\ M_{t_2} &= (m_{t(t=t_2+2t_d)} - m_0) \times 100\% / m_0, \\ &\dots \dots \\ M_{t_n} &= (m_{t(t=t_n+nt_d)} - m_0) \times 100\% / m_0. \end{aligned} \quad (4)$$

Each sample has only one chance to be swollen and weighed. Therefore, the proportion of dry

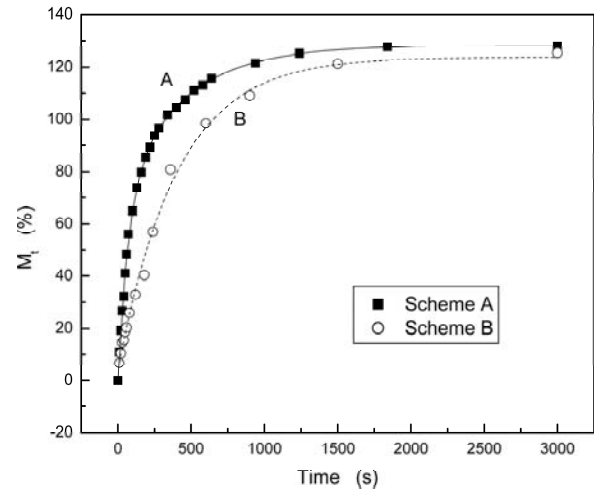


Fig. 3. Swelling curves (M_t vs. time) of PVA films measured by scheme A and B.

time in scheme B (P_B) is described by the following equation:

$$P_B = \frac{t_d}{t_n}, \quad (n = 1, 2, 3 \dots) \quad (5)$$

3.2. Influence of experimental schemes on the swelling behaviors

Fig. 3 shows the swelling curves of PVA films, 0.22 mm in diameter, by experimental scheme A and B, respectively. As has been mentioned above, a series of different time intervals Δt were used in the study, whereas the dry time is constant (30 s). The swelling ratios of the PVA films by schemes A and B are consistent at the initial stage of the swelling.

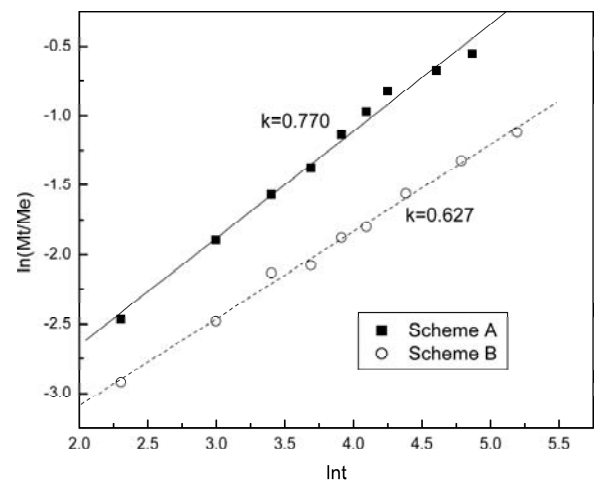


Fig. 4. Linear fitting of $\ln(M_t/M_0) \sim \ln t$ curves of PVA films measured by scheme A and B.

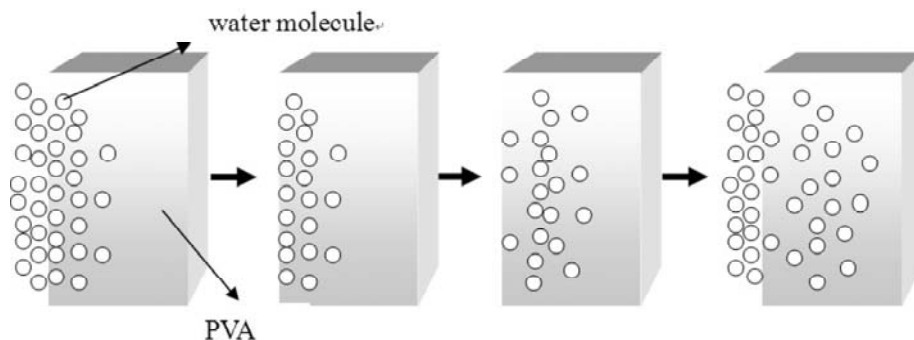


Fig. 5. Schematic diagram of the diffusion of water molecules in gravimetric measurement (scheme A).

With the increase of swelling time, the differences between the two curves become more and more obvious in the first few hours of experiment. When the swelling processes are approaching equilibrium, the swelling ratios of the two curves are approaching each other.

In order to clearly describe the differences of the two curves, the times needed for the swelling ratio to reach 60% of the equilibrium swelling ratio (denoted as $t_{60\%}$) were determined as shown in Fig. 3. The $t_{60\%}$ were 130 s and 334 s for swelling curves by scheme A and B, respectively. For the same kind of samples and at the same swelling condition (type of solution, temperature, etc.), measurement method should not affect the results of swelling experiment. In the study, however, the swelling curves obtained by the two methods are significantly different and the swelling ratios by scheme A is much larger than those by scheme B, especially at the intermediate swelling stage.

It is very important to obtain reliable swelling data in the study of films, which may help us to develop new film and to use suitable films for different kinds of purposes. In order to further understand the influence of experimental schemes on the swelling behaviors, experimental data can be treated [5-7] and the results are shown in Fig. 4. From the plots of $\ln(M/M_0)$ versus $\ln t$, the parameter n may be obtained by the slopes of the linear simulation, which can be used to describe the mechanism of diffusion process of films. The values of swelling parameter correspond to experimental schemes A and B is 0.77 and 0.63, respectively. This difference can not be explained with experimental errors.

3.3. A possible explanation for the experimental results

As discussed above, dry time may be the key factor affecting the swelling results by the two experimental schemes. From a macroscopic point of view,

swelling is a penetration process driven by pressure gradient or concentration gradient between the interior of the film and the external solution. Water transportation in the film can be supposed as following assumption: water transportation occurs mainly under the moisture concentration gradient between the surface layer of the film and the interior of the film [7]. Fig. 5 shows a schematic diagram about the influence of diffusion on the swelling behaviors. To simplify the problem, it is supposed that film sample is symmetrical in geometric shape and the model with only one surface contacting the solution was studied as shown in Fig. 5. Therefore, to explain the difference of swelling results between the two experimental schemes, the experimental procedure in scheme A may divided into four stages:

First, sample was immersed in water and the water molecules diffuse into the inner part immediately (Fig. 5a). Secondly, the sample was taken out of the water with only swelling water molecules existing in it (Fig. 5b). There are three such parts in the swelling gel as completely swollen gel, hydrating polymer layer, and dried polymer [7]. The moisture concentration gradient between different layers drives water molecules to diffuse from the surface parts of film to the inner dry parts until swelling equilibrium is reached. When polymer film is kept in solution, continuous supplement of water molecules constructs a successive process for the swelling of film. When the film is taken out of the solution during the dry time (t_d), though no free water from solution may fill up the surface vacancies with the progress of diffusion, the moisture concentration gradient still drives the water molecules in outer part to penetrate to the dryer inner part of film (Fig. 5c). Finally, after a period of t_d the film is put back into the solution, in which case, due to the diffusion of water during t_d the moisture concentration in the surface layer of film is reduced (Fig. 5d). Therefore, after staying in air, additional diffusion during t_d will

make the diffusion of water molecules from solution into the film much easier.

In scheme B, each samples are kept in solution throughout the swelling process until the predetermined time are reached, though at the initial stage of swelling, the influence of dry time is almost the same as that in scheme A. With the progress of the gravimetric measurement, the swelling results will be slightly affected by the additional diffusion of water molecules during dry time. Therefore, scheme A always yields a bigger swelling ratio, compared with that of scheme B. So the difference between the swelling curves in Fig. 3 is explained.

3.4. Influence of film properties on the swelling results by different schemes

To verify the possible explanation proposed above, the influence of film properties on the swelling results by different experimental schemes was investigated. In the present study, uncross-linked and GTA cross-linked PVA films were used. Fig. 6 shows swelling curves of cross-linked and uncross-linked PVA films by scheme A and B. The cross-linked film swells slower than the uncross-linked one, and the equilibrium swelling ratio becomes smaller after cross-linking treatment. At the same swelling time, the swelling ratios of both uncross-linked and cross-linked film by scheme A was significantly higher than those by scheme B. After cross-linking, at the same swelling time, the differences in swelling ratios between scheme A and B decrease obviously, which indicates that gel properties affect the swelling data by different schemes. In order to know the variation of experimental results, $t_{60\%}$ was studied and the results from Fig. 6 are 275 s and 370 s for cross-linked sample by experimental schemes A and B, respectively. The difference of $t_{60\%}$ before and after cross-linking is 204 s and 95 s. The decrease of $t_{60\%}$ after cross-linking treatment indicated that the swelling results by the experimental schemes A and B approached each other.

Uncross-linked film behaves rapidly and the cross-linked one behaves slowly in swelling process. In order to obtain more data on swelling curve to assure the accuracy of data simulation in the study of swelling kinetics, the swelling duration Δt in scheme A for cross-linked film can be increased due to the longer time of swelling before equilibrium is reached. Considering t_d is constant in all the swelling experiment, P_A decreases with the increase of Δt in Eq. (3), which means that the effect of the neglected swelling during t_d on the swelling behav-

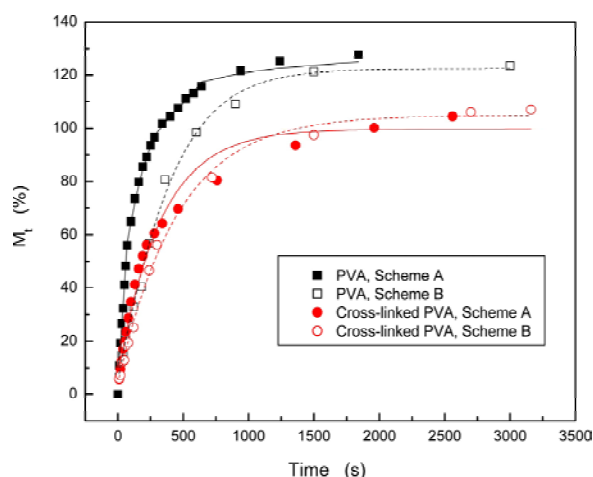


Fig. 6. Swelling curves of uncross-linked and GTA cross-linked PVA films by scheme A and B.

iors of film is reduced. Then, with the increase of water-resistance of films, the difference of swelling data by scheme A and B becomes unobvious. Therefore, it is concluded that scheme B is more applicable for the films swelling very quickly in moisture, while for slowly swelling samples such as highly cross-linked polymer networks, both scheme A and scheme B can be used to accurately determine the swelling behaviors. Scheme A is usually preferable because only one sample is needed for the study.

4. CONCLUSIONS

The difference between two experimental schemes of gravimetric measurement to studying the swelling behaviors of PVA films was studied. The effect of the additional diffusion process at dry time was investigated with the result that the usually neglected diffusion is the key factor affecting the results of swelling behaviors.

The accuracy of experimental data may be influenced by the properties of films. For the slowly swollen films, such as cross-linked PVA film, the difference of the swelling results by different experimental schemes is little. The difference is significant for easily swollen samples. More exact swelling results may be obtained by separated method. For slowly swollen film, continuous method is an effective and sample-saving method, while separated method is better to obtain more reliable swelling behaviors of rapidly swollen samples such as uncross-linked PVA film.

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