

Compression of poly(vinyl alcohol) gels by ultracentrifugal forces

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Received 9 May 2005; received in revised form 26 September 2005; accepted 10 October 2005

Available online 2 November 2005

Abstract

Compression due to ultracentrifugal forces was investigated for poly(vinyl alcohol) (PVA) gels. The concentration gradient profiles for the gels were obtained by experiment and were then compared with a theoretical prediction. By the application of the centrifugal forces, the concentration gradient near the bottom increases sharply whereas the gradient inside the gel remains almost constant in the region far from the bottom. Further application of the centrifugal forces enhances the peak near the bottom. These are well explained by the theory proposed in the previous paper [Urayama et al. *J Chem Phys* 2005;122:024906.]. The frictional coefficient f for the PVA gels, which originates from the friction between the polymer network and solvent molecules, is estimated to be $3.5 \times 10^{14} \text{ N s m}^{-4}$.

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Keywords: Poly(vinyl alcohol) gel; Ultracentrifuge; Frictional coefficient

1. Introduction

Control of the permeation of low molecular weight substances through a membrane is a key to the separation technique. Permeability as well as selectivity is strongly affected by the structure of membranes. To utilize a polymer gel as a membrane, studies on the frictional properties of the gel membranes becomes very important. However, there exist only a few studies on the frictional properties of the polymer gels. Tokita and Tanaka have examined the frictional properties of poly(*N*-isopropylacrylamide) gels showing the volume-phase transition [1]. They focused on the behavior near the transition point and found an anomaly on the frictional coefficient at the transition. The mode coupling theory was used to analyze the anomaly of the frictional coefficient [2]. We have also shown the frictional properties of poly(vinyl alcohol) (PVA) gels in one-dimensional as well as two-dimensional flow [3,4]. From the one-dimensional flow experiment the frictional coefficient was estimated for the PVA gel. A limited number of the studies on the friction is mainly due to the difficulty of experiment; of course, no commercial apparatus is available for the measurements. We

have shown in the previous paper that a ultracentrifuge is available to estimate the frictional coefficient of the ‘chemical’ gels, i.e. poly(acrylamide) gels whose cross-links are formed by covalent bonds [5]. The present study treats the PVA gels cross-linked by microcrystallites which are classified into the ‘physical’ gels. The compression behavior of the physical gels under ultracentrifugal forces have not been investigated before. In this paper, the frictional coefficient of PVA gels is estimated by an ultracentrifuge, and the data are analyzed in terms of the theory proposed in the previous paper [5].

2. Theoretical background

In the previous paper [5], a governing equation which determines the shrinking kinetics of polymer gels in an ultracentrifuge has been proposed. Let a sample cell of the ultracentrifuge be rectangular in shape and mounted on a rotor of the apparatus. When the rotor operates, a compressive force acts in the radial direction on a gel in the cell. We define r as the distance from the center of rotation, and r_2 as the position at the immobile bottom of the cell (i.e. the bottom of the gel). The position of the top of the gel, which corresponds to a moving boundary between the gel and pure solvent phases, is designated as r_1 . Here $r_1 < r_2$. When the friction between the gel and side walls is negligible, the equation of motion for a volume element in the gel is reduced to a one-dimensional problem [5].

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According to the theory [5], the volume element of the gel obeys the following equation.

$$\frac{\partial u(r,t)}{\partial t} = D \frac{\partial^2 u(r,t)}{\partial r^2} + \frac{\phi \Delta \rho \omega^2}{f} r \quad (1)$$

Here, $u(r,t)$ is the displacement in the radial direction of the volume element at distance r from the center of rotation and at time t . The quantities D and f are the diffusion constant and frictional coefficient, respectively. The volume fraction and the difference in density between the polymer network and solvent are respectively represented by ϕ and $\Delta \rho$, ω being the angular frequency. By combining the governing equation and appropriate initial and boundary conditions for the phenomenon occurring inside the ultracentrifuge, the displacement in the centrifugal direction can be written by [5]

$$u(r,t) = \sum_{n=1}^{\infty} A_n \exp\left(-\frac{(2n-1)^2 t}{\tau_L}\right) + u(r,\infty) \quad (2a)$$

with

$$A_n(r) = \frac{16a^2 \phi \Delta \rho \omega^2}{\pi^4 L} \left\{ \frac{(-1)^n \pi r_2}{(2n-1)^3} + \frac{2a}{(2n-1)^4} \right\} \times \cos\left\{ \frac{(2n-1)\pi(r-r_1)}{2a} \right\} \quad (2b)$$

where n is a positive integer and $a=r_2-r_1$. In the above equation, $\Delta \rho$ is given by $\Delta \rho = \rho_{\text{pva}} - \rho_{\text{sol}}$, L defined by $L = K + 4/3G$ with the bulk modulus K and the shear modulus G . The longest characteristic time τ_L is defined by

$$\tau_L = \frac{4a^2}{\pi^2 D} \quad (3)$$

Here, the diffusion constant D is given by $D = L/f$. In Eq. (2a), $u(r,\infty)$ stands for the displacement in the stationary state and is written by

$$u(r,\infty) = \frac{\phi \Delta \rho \omega^2}{6L} (r_2^3 + 3r_1^2 r - 3r_1^2 r_2 - r^3) \quad (4)$$

Eq. (4) indicates that the stationary state is achieved by the balance between the centrifugal force ($\sim \phi \Delta \rho \omega^2$) and the osmotic force ($\sim L$). The stationary position of the top of the gel is given by the displacement at $r=r_1$ in long time limit, namely $u(r_1,\infty)$.

3. Experimental

3.1. Materials

Poly(vinyl alcohol) (PVA) with the degree of polymerization of 1700 and the degree of saponification of 99.5 mol% was kindly supplied from Unitika, Japan. PVA was dissolved in a mixed solvent of water and dimethyl sulfoxide (DMSO) at 80 °C for 1 h. The ratio of water to DMSO was 1:4 by weight. Polymer concentration was fixed to be 3.2 wt%. After the complete dissolution of PVA, the solution was transferred to an optical cell of the ultracentrifuge and was gelled inside the cell

at −20 °C for 24 h. In analyzing the experimental data, the following values and methods were used. The density of PVA ρ_{pva} is $1.269 \times 10^3 \text{ kg m}^{-3}$ [6]. The density of the mixed solvent ρ_{sol} was measured at 25 °C to give $\rho_{\text{sol}} = 1.0943 \times 10^3 \text{ kg m}^{-3}$. The volume fraction of the polymer network ϕ was calculated by assuming additivity of volume for the polymer and the mixed solvent, leading to $\phi = 0.028$. From another experiment the fraction of the soluble PVA, not incorporated into the infinite network after gelation, in the system (the sol-fraction) was estimated to be 17 wt%. The relating high sol-fraction originates from the fact that the PVA concentration (3.2 wt%) is very close to the critical concentration for gelation. The gel with high concentration showed no finite displacement under the ultracentrifugal force owing to the large elastic modulus.

3.2. Ultracentrifugal measurement

The compressive behavior of the PVA gels were observed by using an ultracentrifuge (Beckman, Spinco Model E) at various rotational speeds (3.00×10^4 , 4.00×10^4 , 4.80×10^4 , 5.20×10^4 , 5.60×10^4 , and 6.00×10^4 rpm) at 25 °C. The cell has quartz windows and the walls of the cell are coated with poly(trifluorochloroethylene) to reduce friction between the gel and wall. The gel samples are rectangular in shape, and the cross-sectional area of the samples is $4 \text{ mm} \times 12 \text{ mm}$. The length in the moving direction ranges from 8 to 9 mm. The centrifugal force induces the change only in the moving direction and the sample dimension in the other direction are unchanged. The schlieren patterns were read on a contour projector (Nikon, L-16).

4. Results and discussion

Fig. 1 shows the schlieren patterns of the PVA gel at the centrifugal acceleration $\alpha (=r_1 \omega^2/g)$ of $2.53 \times 10^5 G$ (6.00×10^4 rpm). Here, g was the gravitational acceleration. At the shortest time ($t = 8.40 \times 10^2 \text{ s}$) only one vertical line is observed (Fig. 1(A)). This corresponds to the overlapped line of the air–solvent and solvent–gel interfaces. However, on the patterns at $t > 8.4 \times 10^2 \text{ s}$ (Fig. 1(B)–(D)) each of the air–solvent and the solvent–gel interfaces is clearly emerged as a divergence. The patterns inside the gel show no peak except for the region near the bottom, while a peak is observed on the patterns in the solvent region lying between the two divergent lines. The upturn near the bottom originates from the high condensation of the polymer network, and the peak in the solvent region is due to the sedimentation of free PVA chains existing the solvent phase. The sedimentation of the free chains and infinite networks obey different equations of motion, although their densities are comparable. For the sedimentation of the free chains, the elastic term in Eq. (1) is dropped off. The analysis of the sedimentation of free chains excluded from the gel is beyond the scope of the present paper.

At $t = 1.63 \times 10^4 \text{ s}$ the solvent–gel interface moves slightly and becomes distinguished from the air–solvent interface. At $t = 7.60 \times 10^4 \text{ s}$ the solvent–gel interface moves further

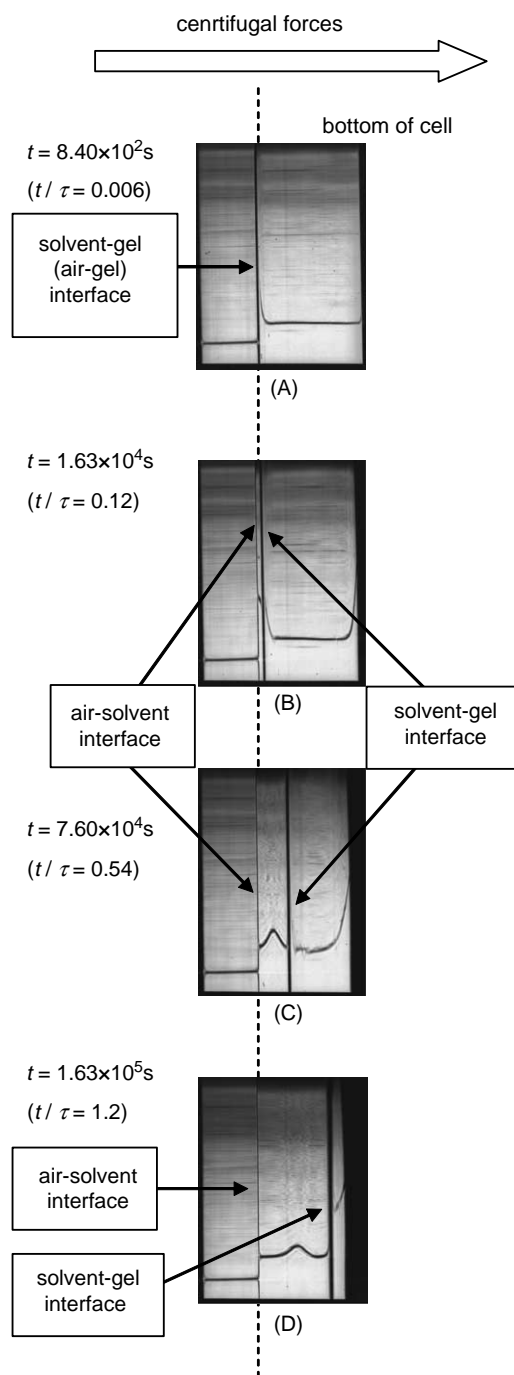


Fig. 1. Schlieren patterns in the course of centrifugation at the angular velocity (ω) of $5.73 \times 10^5 \text{ s}^{-1}$. (A) At $t = 8.40 \times 10^2 \text{ s}$, (B) at $t = 1.63 \times 10^4 \text{ s}$, (C) at $t = 7.60 \times 10^4 \text{ s}$, (D) at $t = 1.63 \times 10^5 \text{ s}$. Here, $\tau = 1.4 \times 10^5 \text{ s}$.

toward the bottom of the cell while the air–solvent interface remains at the initial position. The peak near the bottom appears to be larger. At long times (for example, $t = 1.63 \times 10^5 \text{ s}$), the solvent–gel interface becomes close to the bottom. The moving interface reaches the stationary state.

Fig. 2 shows the time dependence of the position of the solvent–gel interface for the same PVA gel in Fig. 1. At short times ($t < 7.8 \times 10^3 \text{ s}$), the displacement appears to be a little small probably because the rotation speed did not reach the steady rotation speed. In the middle region of t ($7.8 \times 10^3 \text{ s} <$

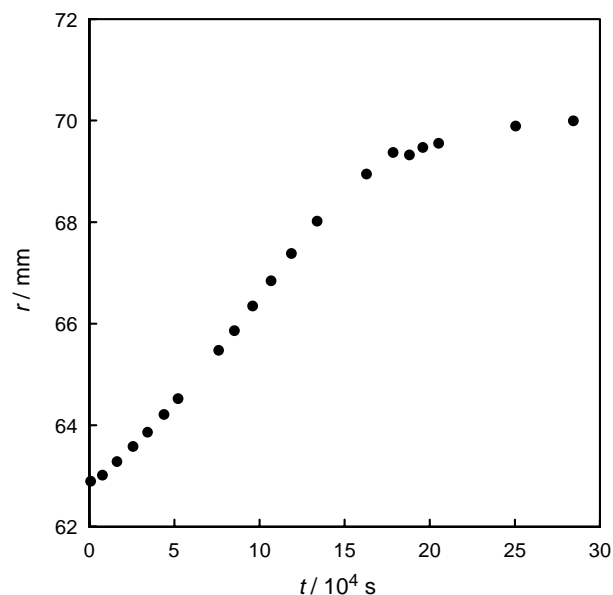


Fig. 2. Time (t) dependence of the position at the solvent–gel interface (r) for a PVA gel at the angular velocity (ω) of $5.73 \times 10^5 \text{ s}^{-1}$.

$t < 1.3 \times 10^5 \text{ s}$), the interface moves toward the bottom of the cell and the change in position is in proportion to time. In the late stage, the displacement becomes small with increasing time and finally the position of interface levels off to show a constant value ($r \cong 70 \text{ mm}$). The position at the cell bottom corresponds to r of 71.73 mm . This is very close to the saturated value of r (ca. 70 mm) observed from the experiment, suggesting that the gel sample becomes rather dense due to a stronger centrifugal force. From a simple calculation we found that the volume of the gel at $t = 2.8 \times 10^5 \text{ s}$ (longest time measured) corresponds to about 1/10 of the initial volume; still, the polymer concentration remains around 32 wt% since the concentration becomes 10 times higher than the initial one (3.2 wt%). The sample can be regarded as a polymer gel even in the collapsed state, ensuring that the estimation of the characteristic time is meaningful. The longest characteristic time in the course of compression (τ) was obtained as $1.4 \times 10^5 \text{ s}$.

The motion of the solvent–gel interface can be described in terms of $u(r_1, t)$. In the initial stage of the centrifugation ($t \ll \tau_L$), $u(r_1, t)$ is approximated by a linear term of t and is written as [5]

$$u(r_1, t) \cong \frac{\phi \Delta \rho r_1 \omega^2}{f} t \quad (5a)$$

or

$$v(r_1, t) \cong \frac{d}{dt} u(r_1, t) \cong \frac{\phi \Delta \rho r_1 \omega^2}{f} \quad (5b)$$

if the velocity is used. The velocity v is controlled by the balance between the centrifugal and frictional forces. The schlieren patterns correspond to the concentration gradient in the cell. Based on $u(r, t)$, the concentration of the polymer network normalized by the initial one c_0 is written by

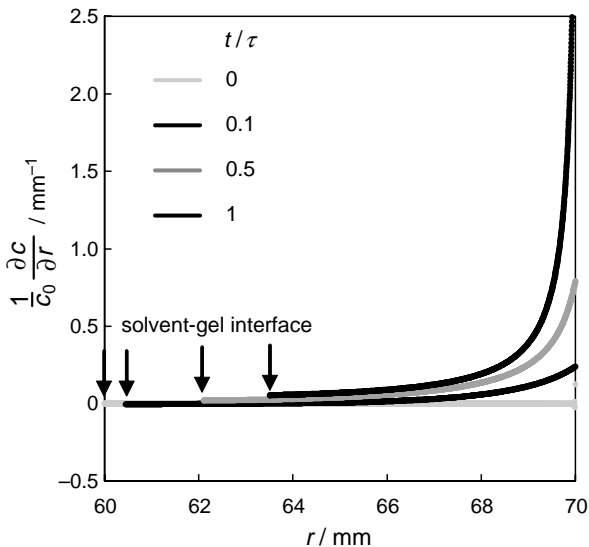


Fig. 3. A normalized concentration gradient, $(\partial c/\partial r)/c_0$ inside gel, plotted against distance from the center of rotation. (a) For $t/\tau=0$, (b) for $t/\tau=0.1$, (c) for $t/\tau=0.5$, (d) for $t/\tau=1$.

$$\frac{c(r,t)}{c_0} = \frac{1}{1 + \frac{\partial u(r,t)}{\partial r}} \quad (6)$$

Thus, the concentration gradient is written in the following form.

$$\frac{\partial}{\partial r} \frac{c(r,t)}{c_0} = \frac{-\frac{\partial^2 u(r,t)}{\partial r^2}}{\left(1 + \frac{\partial u(r,t)}{\partial r}\right)^2} \quad (7)$$

Fig. 3 shows the plots of the calculated concentration gradient against distance at various t . The gradient was calculated from Eq. (7) and the movement of the gel itself is taken into account for the data. This figure should be compared with the shlieren

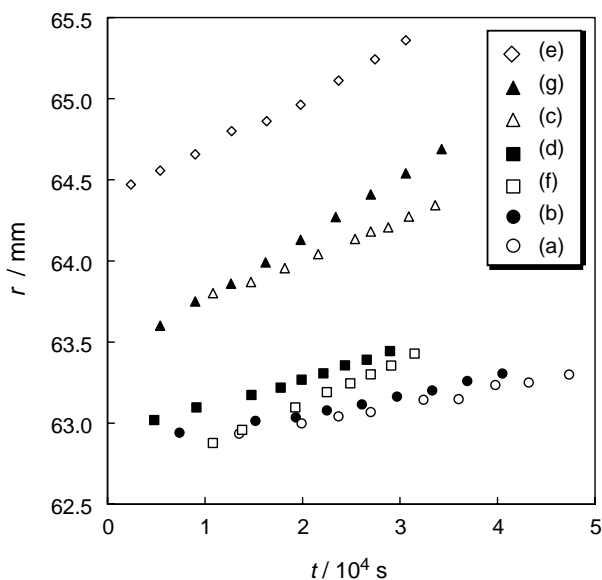


Fig. 4. Time (t) dependence of the position at the solvent–gel interface (r) for a PVA gel at the various angular velocities (ω). (a) $2.86 \times 10^5 \text{ s}^{-1}$, (b) $3.82 \times 10^5 \text{ s}^{-1}$, (c) $4.58 \times 10^5 \text{ s}^{-1}$, (d) $4.97 \times 10^5 \text{ s}^{-1}$, (e) $5.35 \times 10^5 \text{ s}^{-1}$, (f) $5.35 \times 10^5 \text{ s}^{-1}$, (g) $5.73 \times 10^5 \text{ s}^{-1}$.

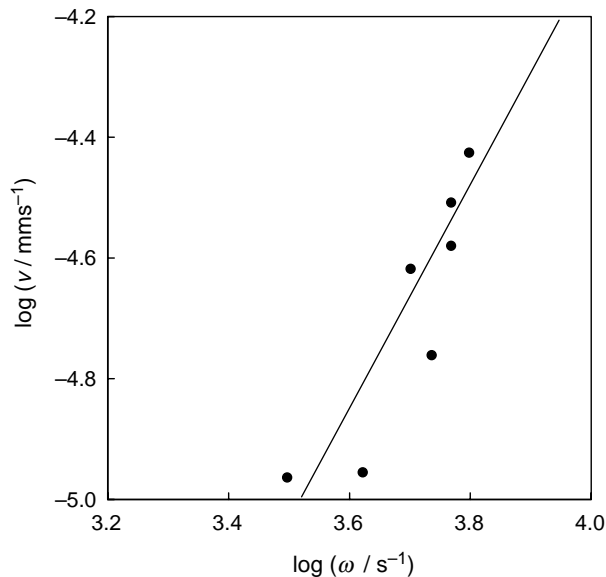


Fig. 5. Double-logarithmic plots of the velocity (v) against angular velocity (ω) for PVA gels. The line in the figure has the slope of 2.

patterns in Fig. 1. As t increases the upturn near the bottom becomes pronounced, as is the case of Fig. 1. In calculation, the parameters employed are as follows: $r_1=6 \times 10 \text{ mm}$, $r_2=7 \times 10 \text{ mm}$, $L=7.5 \times 10^4 \text{ Pa}$, $f=4 \times 10^{14} \text{ N s m}^{-4}$, $\phi=2 \times 10^{-2}$, $\Delta\rho=1.7 \times 10^2 \text{ kg m}^{-3}$. These values are very close with the values estimated from the experiment. The basic character of the shlieren patterns for the PVA gel is well reproduced on the calculated curves.

The plots of r vs. t for the PVA gels are shown in Fig. 4. The figure contains several groups of data differing in ω , but other parameters are almost the same for all runs (or samples). In the region of t shown in the figure, each set of the data falls on

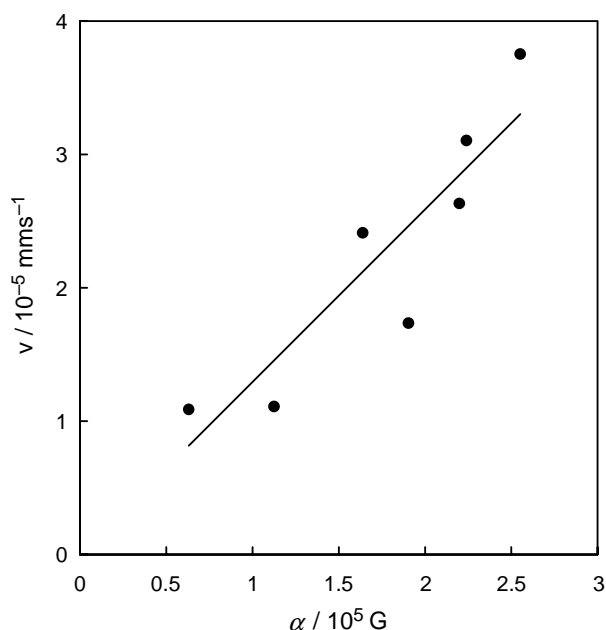


Fig. 6. Plots of the velocity (v) against centrifugal acceleration (α) for PVA gels. The line in the figure is determined by the method of least-squares.

a line. The slope of the line appear to increase with increasing ω . As stated previously, the slope is theoretically given by Eq. (5a): The slope becomes equal to $\phi\Delta\rho r_1\omega^2/f$. Fig. 5 shows the double-logarithmic plots of v against ω for the PVA gels. The line in the figure has the slope of 2 and the data points appear to be well represented by the line, suggesting that the relation $v \propto \omega^2$ expected by the theory holds. In Fig. 6 v is plotted against α . The velocity v is proportional to α . This linear relation allows us to estimate an average value of f from the slope of the line, $\phi\Delta\rho g/f$. The value lies about $3.5 \times 10^{14} \text{ N s m}^{-4}$.

5. Conclusion

The compressive behavior of the PVA gels under ultracentrifugal forces was investigated and the profiles of the concentration gradient of the gels obtained by experiment were compared with the theoretical prediction. When the centrifugal force is applied to the gel, the concentration gradient near the bottom of the cell increases sharply whereas the gradient remains almost constant in the region far from the bottom. Further application of the centrifugal forces enhances the peak near the bottom. These are well explained by

the theory. The ω -dependence of the position at the solvent–gel interface measured shows that the velocity of the interface is proportional to ω^2 , as is predicted by the theory. The frictional coefficient f of the PVA gels is estimated to be $3.5 \times 10^{14} \text{ N s m}^{-4}$.

Acknowledgements

This research was supported in part by the 21st century COE program ‘COE for a United Approach to New Materials Science’ from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References

- [1] Tokita M, Tanaka T. *J Chem Phys* 1991;95:4613.
- [2] Tanaka T, Ishiwata S, Ishimoto C. *Phys Rev Lett* 1977;38:771.
- [3] Takigawa T, Uchida K, Takahashi K, Masuda T. *J Chem Phys* 1999;111:2295.
- [4] Takigawa T, Uchida K, Takahashi K, Masuda T. *Biorheology* 1999;36:401.
- [5] Urayama K, Okada S, Nosaka S, Watanabe H, Takigawa T. *J Chem Phys* 2005;122:024906.
- [6] Sakurada I, Nukushina Y, Sone Y. *Kobunshi Kagaku* 1955;12:506.