

Swelling Effect of Semicrystalline Poly(vinyl Alcohol) in Hydrogen Peroxide

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SYNOPSIS

The effect of hydrogen peroxide on the physicochemical properties of semicrystalline poly(vinyl alcohol) (PVA) has been investigated. Significant and irreversible increases in equilibrium water swelling, dissolved oxygen permeability, and surface wettability have been observed in PVA samples treated with concentrated hydrogen peroxide. Based on the small amount of carbonyl content detected and the crystallinity reduction in hydrogen-peroxide-treated poly(vinyl alcohol) samples, a mechanism involving a combination of hydrogen-peroxide-induced oxidative chain scission and dissolution of crystalline regions in poly(vinyl alcohol) is proposed for the observed swelling kinetics and associated changes in polymer properties.

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a semicrystalline polymer of major industrial importance with diverse applications ranging from fiber and textile sizing^{1,2} to drug delivery systems^{3,4} and soft contact lenses.⁵⁻⁸ In almost every case, PVA crystallinity or crystalline weight fraction plays a significant role in determining the characteristics of the resulting polymer properties. Processing conditions such as drying and thermal annealing, particularly the latter, have been employed to impart different degrees of crystallinity in the PVA material. A direct consequence of increased PVA crystallinity is an increase in its modulus and tensile strength with a concomitant decrease in its water swelling.⁹

The oxidation and degradation of PVA in aqueous solutions by hydrogen peroxide (H_2O_2) have been studied by several investigators. Based on spectroscopic results obtained in dilute H_2O_2 solutions, Sakurada and Matuzawa¹⁰ reported marked degradation of PVA at 60°C, but not at 30°C without a catalyst. Similarly, Takayama¹¹ showed that, at neutral pH and 60°C, an increase in the amount of carbonyl groups was detected after treating a PVA

solution with dilute H_2O_2 . On the other hand, Bates and Shanks¹² demonstrated with viscometric data that oxidative scission of PVA at 25°C seemed to occur in the more concentrated 30% H_2O_2 . It was deduced by them that the oxidative cleavage initially occurred at the 1,2-glycol units followed by the further oxidation of the main chain. In the textile industry, dilute H_2O_2 solution has been applied to de-size PVA-sized fabrics. It was reported that PVA may be oxidatively degraded into lower molecular weight polymers by H_2O_2 under both neutral¹³ and alkaline^{14,15} conditions at elevated temperatures, thereby facilitating its removal.

Despite these interests on the oxidative degradation of PVA in dilute aqueous solutions by H_2O_2 , the effect of PVA crystallinity on the physicochemical changes induced by H_2O_2 on PVA in the solid state has not been studied. In this paper, we present results on the kinetics of swelling of semicrystalline PVA in concentrated H_2O_2 and the associated changes in PVA properties.

EXPERIMENTAL

Materials

Elvanol 71-30 (a fully hydrolyzed grade of PVA with M_w around 116,000, M_n around 39,500, and a dis-

persity of about 2.9 as determined by gel permeation chromatography) was obtained from DuPont. Hydrogen peroxide (30% w/w), sodium bisulfite, 2,4-dinitrophenylhydrazine, and other related analytical reagents were reagent grade and obtained from Aldrich Chemical Co. Heptane and *n*-octane (both 99%+) were obtained from MCB. Merckoquant peroxide test strips were obtained from Merck (Germany).

Methods

PVA films of dry thickness ranging from 0.11 to 0.15 mm were cast from 16–18% aqueous solutions of Elvanol 71-30 using a Gardner knife, and subsequently air-dried for 2 days at 23°C and 40% relative humidity. For the annealing process, PVA films were held between heated plates on a laboratory Carver press at a preset temperature for a specified duration. Circular discs of diameter approximately 6 mm were cut from the annealed PVA films, which were allowed to soak in deionized water for 2 days to achieve swelling equilibrium. The change in equilibrium water swelling of the PVA films was determined gravimetrically and the change in lateral dimension of the PVA discs was monitored on an optical comparator (Jena, Germany). To carry out the peroxide treatment, either dry or preswollen PVA discs were immersed in excess amounts of H₂O₂ solutions with a concentration range of 5–30% for a prescribed period of time. The termination of the peroxide reaction was accomplished by quenching peroxide-treated PVA samples in 0.5% sodium bisulfite solution for 3 h followed by equilibration in a large volume of deionized water. The absence of residual peroxide level (<1 ppm) was confirmed by the Merckoquant peroxide test strips.

Characterization

The densities of both dry and wet PVA films were determined by weighing the sample in air and in heptane at constant temperature on a microbalance. The octane and air underwater contact angles were determined using Hamilton's inverted surface technique.¹⁶ A Ramé-Hart goniometer with environmental chamber was used for the contact-angle measurement at 20 ± 0.2°C.

The crystallinities of dry PVA films were evaluated from their dry density according to the following equation:

$$\frac{1}{\rho} = w_x \left(\frac{1}{\rho_x} \right) + (1 - w_x) \left(\frac{1}{\rho_a} \right) \quad (1)$$

where w_x is the crystallinity or the crystalline weight fraction, ρ_x the density of the 100% crystalline PVA, ρ_a the density of 100% amorphous PVA, and ρ the density of sample. This is a widely accepted method with $\rho_a = 1.269$ and $\rho_x = 1.345$ as reported by Sakurada et al.¹⁷ The dissolved oxygen permeability (DK values) of swollen PVA films were measured with a YSI 5739 dissolved oxygen probe on a YSI 54 ARC dissolved oxygen meter at 34°C.

The 1,2-glycol content of Elvanol 71-30 was measured according to the titrimetric method of Harris and Pritchard,¹⁸ which involves the determination of periodate consumption in the oxidative cleavage of 1,2-glycol groups. The carbonyl contents of PVA samples treated with H₂O₂ were analyzed by the well-known reaction with 2,4-dinitrophenylhydrazine, followed by the separation of polymeric hydrazone and subsequently determined by UV analysis.^{19,20} The IR characterization was carried out on a Perkin-Elmer 467 infrared spectrophotometer and the intrinsic viscosities of PVA samples were measured on a Ubbelohde viscometer.

RESULTS AND DISCUSSION

Prior to studying the kinetics of swelling in concentrated H₂O₂, the effect of thermal annealing on the crystallinity and equilibrium water swelling of PVA film samples was examined experimentally. It is evident from Figure 1 that the PVA crystallinity increases almost linearly with annealing temperature. As a result of the crystallinity increase, a corresponding decrease in equilibrium water swelling is also observed (Fig. 2). The PVA samples were annealed at a specific temperature for up to 30 min. It was found that, above a minimum time required to

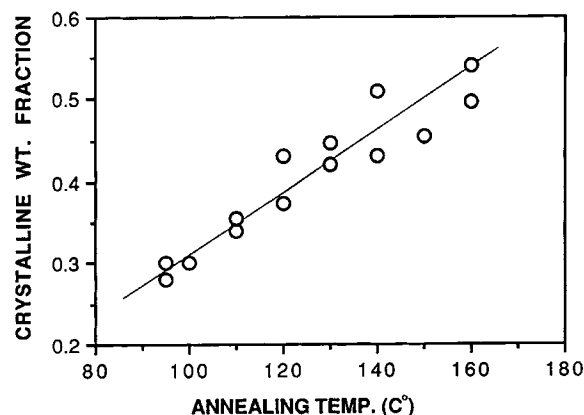


Figure 1 Effect of annealing temperature on PVA crystallinity.

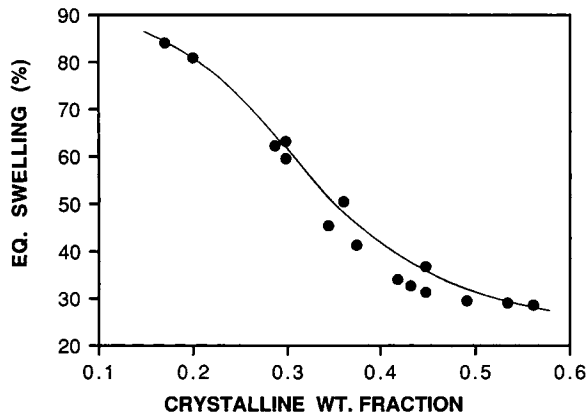


Figure 2 Equilibrium water swelling as a function of PVA crystallinity.

reach thermal equilibrium (generally less than 1 min), the annealing time no longer has any apparent effect on the resulting PVA crystallinity and equilibrium water swelling. Since the conditions of PVA film formation were identical in our experiment, it is reasonable that a direct correlation on crystallinity and equilibrium swelling as shown in Figure 2 is obtained. These results are consistent with those reported by Sakurada et al.^{21,22} and Nagai et al.²³

Figures 3 and 4 show the effect of H₂O₂ concentration and contact time on the swelling behavior of two annealed PVA films, one with a crystallinity level of 51.34% and the other 55.74%. At a H₂O₂ concentration of 30%, an initial sharp increase in the equilibrium water swelling is observed within the first hour followed by a near plateau, which may drift up slightly over a period of days. The magnitude of such an increase in equilibrium water swelling is reduced and the rate of swelling is slowed down at

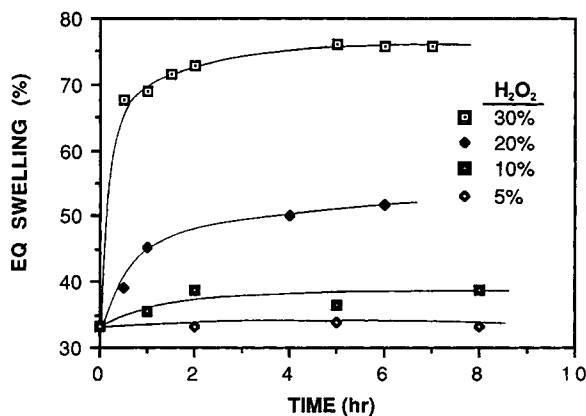


Figure 3 Effect of hydrogen peroxide concentration and contact time on the equilibrium water swelling of an annealed PVA with 51.34% crystallinity.

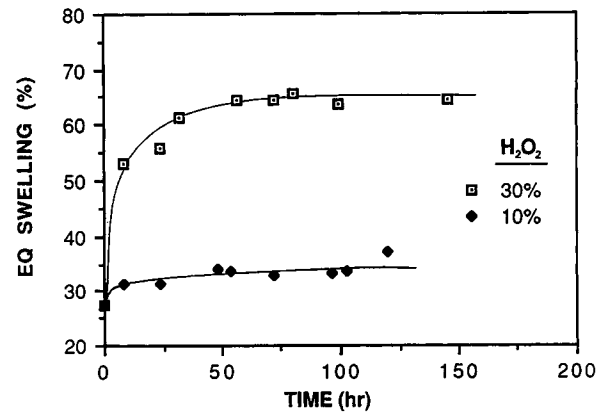


Figure 4 Effect of hydrogen peroxide concentration and contact time on the equilibrium water swelling of an annealed PVA with 55.74% crystallinity.

lower H₂O₂ concentrations. At an H₂O₂ concentration of 5% or lower, no appreciable change in water swelling is observed for up to a week. At a fixed H₂O₂ concentration, the apparent swelling plateau level is higher for PVA with initially lower crystallinity. The linear dimensional changes of these two PVA samples in 30% H₂O₂ are shown in Figure 5. Where the major part of the dimensional changes is seen to occur within the first half-hour of contact, again the swelling plateau level is higher for PVA with initially lower crystallinity. This is certainly consistent with the weight swelling results reported in Figures 3 and 4. When such a trend in swelling and dimensional changes is extrapolated to very low crystallinity levels, one would expect the swelling plateau to become even higher, which may eventually lead to polymer dissolution. Indeed, we observed that for an unannealed PVA film with a crystallinity below 20%, the swelling was increased to

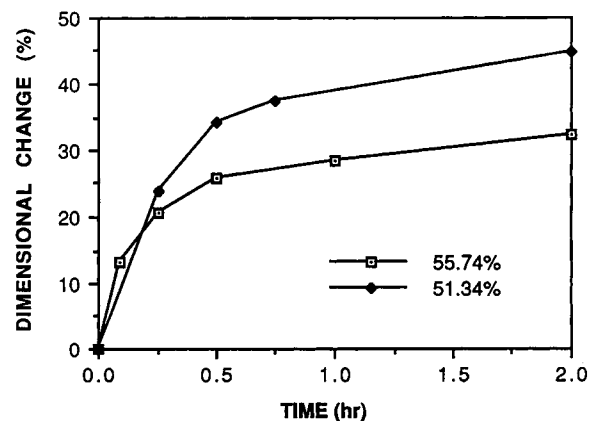


Figure 5 Effect of crystallinity on the linear dimensional changes of PVA in 30% hydrogen peroxide.

such an extent that the PVA film dissolved in 30% H_2O_2 within 30 min. In contrast, as shown in Figures 3 and 4, annealed PVA samples with high crystallinities can maintain the swelling plateau in 30% H_2O_2 for more than 5 days without dissolution. In lower concentrations of H_2O_2 , annealed PVA films generally remain intact indefinitely. It has to be mentioned that such hydrogen-peroxide-induced increases in swelling appear to be irreversible after the H_2O_2 treatment has been terminated and the PVA sample reequilibrated in water.

The irreversible swelling increase obtained by such hydrogen peroxide treatment is also reflected in changes in other properties of PVA. As summarized in Table I, the dissolved oxygen permeability (DK value) and the contact angles (both air-in-water and octane-in-water) for a PVA film with original crystallinity of 51.34% also show significant changes with increasing contact time in a 30% H_2O_2 . The dissolved oxygen permeability is seen to increase concomitantly with an increase in equilibrium water swelling of the PVA sample. Similarly, the contact angles, which are inversely related to the surface wettability,²⁴ decreases with increasing contact time in H_2O_2 . In other words, the wettability of these H_2O_2 -treated PVA samples increases with the contact time as a result of the increasing equilibrium water swelling.

Intuitively, one may attribute such irreversible increases in water swelling, dissolved oxygen permeability and surface wettability of PVA to the *in situ* partial oxidation of PVA by H_2O_2 . Such a process is known to induce chain scission at the 1,2-glycol units to generate carbonyl end groups,^{13,18} which should result in the breaking of intermolecular

hydrogen bonding within the swollen PVA and therefore an increase in water swelling. To determine the extent of such oxidative chain scission, PVA samples described in Table I were analyzed for carbonyl contents utilizing a well-established method based on 2,4-dinitrophenylhydrazine.^{19,20} Infrared measurements have also been investigated for this purpose, however the characteristic carbonyl band at 1705 cm^{-1} was too weak to be of any quantitative value. It has to be noted that any possible further H_2O_2 oxidation of the aldehydes, produced by the cleavage of 1,2-glycol units, to carboxylic acids may affect the amount of chain scission estimated from the carbonyl content determination, since 2,4-dinitrophenylhydrazine is known to be not reactive towards carboxylic acids.¹⁹ To examine this possibility, the dimensional changes of a 30% H_2O_2 -treated PVA disc under different pH conditions were studied. The presence of carboxylic acid groups in a hydrophilic polymer should result in a higher swelling at neutral and alkaline pHs and a lower swelling under acidic pHs. However, as shown in Table II, no detectable differences in swelling and dimensional changes have been observed on an H_2O_2 -treated PVA disc at pH 7.4 and pH 2.8; only a slight osmotic deswelling is noticed in both cases. Such a lack of pH sensitivity in swelling supports the possibility that the *in situ* partial oxidation of semicrystalline PVA by H_2O_2 produces primarily carbonyl end groups under the present experimental conditions.

As shown in the last column of Table I, it is clear that the carbonyl content increases with increasing H_2O_2 contact time. The observed value of the carbonyl content due to chain scission is of the order

Table I Characteristics of Poly(vinyl Alcohol) Films Treated in 30% Hydrogen Peroxide^a

Contact Time (h)	Eq. Water Swelling (%)	DK ^b	Contact Angle ^c (deg)		Carbonyl Content (mol %) ^d
			Φ_a	Φ_o	
0	31.87	5.98	40	43	0.0019
0.5	67.76	18.98	28	31	—
1.0	69.04	—	30	35	—
2.0	72.71	21.59	25	27	0.0120
5.0	76.19	19.27	22	28	0.0177
6.0	75.83	19.48	22	26	—
7.0	75.88	—	21	23	0.0202

^a Original crystallinity of PVA: 51.34%.

^b Dissolved oxygen permeability at 34°C with unit [$10^{-10}(\text{cm}^3 \text{ (STP) cm/cm}^2 \text{ s cm Hg)}$].

^c Φ_a = air-in-water contact angle; Φ_o = octane-in-water contact angle.

^d With respect to per mole of vinyl alcohol unit.

Table II Effect of pH on the Dimensional Changes of a 30% H₂O₂-Treated Poly(vinyl Alcohol) Disc^a

Condition	DI Water (pH ~ 6)	pH 7.4, Phosphate Buffer	pH 2.8, Simulated Gastric Fluid
Equilibrium Diameter (mm)	8.60	8.55	8.55

^a Original PVA crystallinity: 51.34%. PVA film thickness: 0.1531 mm. 30% H₂O₂-treated for 2 days.

of 10–100 $\mu\text{mol/mol}$ vinyl alcohol unit. Since the 1,2-glycol content of Elvanol 71-30 utilized in this study is determined to be about 1.88 mol % from our measurements, the maximum carbonyl content of 0.0202 mol % in the H₂O₂-treated PVA sample of the present study only amounts to about 0.5% of the total 1,2-glycol units available (one 1,2-glycol unit produces two carbonyl groups). This is equivalent to about one scission every 12 PVA chains based on M_n of 39,500. The magnitude of the carbonyl content determined here seems to be reasonable compared with the 0.22 mol % chain scission reported by Bates and Shanks¹² for an oxidative reaction of aqueous PVA solution with 30% H₂O₂ at 25°C. In our case, the steric factor, diffusional resistance, and crystallinity in the solid PVA gel may have contributed to the lower levels of carbonyl content derived from oxidative chain scission. Nevertheless, the initial sharp increase in water swelling followed by a slow plateau observed in H₂O₂-treated PVA samples agrees qualitatively with the kinetics of oxidative chain scission in PVA solutions by H₂O₂ as reported by Bates and Shanks, where an initial rapid chain cleavage followed by further oxidation of the main chain at a slower rate has been observed.

One may question whether or not a small amount of carbonyl formation due to chain scission, such as those reported in Table I, is sufficient to give rise to an observed equilibrium water swelling more than double that of the untreated control. To elucidate this aspect, we measured dry densities and calculated crystallinities of annealed PVA samples of Table I before and after the H₂O₂ treatment. As seen from

results in Table III, it is obvious that the PVA crystallinity is substantially reduced by the treatment with 30% H₂O₂, which results in more than double the sample swelling. The drying of the peroxide-treated sample was carried out slowly under room conditions. If any additional crystallinity is introduced by this drying process, it would only overestimate the true crystallinity. Thus, it is reasonable to suggest that the observed changes in PVA swelling and linear dimensions may also be a result of the dissolution of PVA crystalline regions by H₂O₂. Such a dissolution mechanism may be facilitated by the process of oxidative chain scission and, possibly, further oxidation of the main chain. Since crystalline regions serve as physical crosslinks, partial dissolution of these regions would increase the chain-to-chain distance and therefore the water swelling. In the extreme cases, such as PVA samples with crystallinity below 20%, when all the crystalline regions are dissolved, erosion and eventual dissolution of the PVA sample would result.

One interesting problem remained to be resolved is whether such dissolution mechanism yielding lower PVA crystallinity is reversible. Preliminary results comparing equilibrium water swellings of the PVA control (annealed at 150°C), 30% H₂O₂-treated PVA, and 30% H₂O₂-treated and reannealed PVA show that the reannealing process reduces the water swelling of the H₂O₂-treated PVA sample, suggesting the recovery of crystallinity by reannealing. However, the reannealing process does not reduce the water swelling of the H₂O₂-treated PVA to that of the annealed control (about 10% higher

Table III Effect of Hydrogen Peroxide Treatment on Poly(vinyl Alcohol) Crystallinity

Sample	Eq. Water Swelling (%)	Dry Density ^a	Calculated Crystallinity (%)
Control, annealed at 150°C for 30 min	31.87	1.305 ± 0.005	51.34
30% H ₂ O ₂ -treated for 4 h ^b	71.29	1.283 ± 0.005	19.40

^a Averaged over four measurements.

^b Sample air-dried under room condition.

for the former). This aspect is consistent with the process of oxidative chain scission of PVA by H_2O_2 , since a smaller PVA molecular weight (or degree of polymerization) is known to result in higher equilibrium water swelling at a given annealing temperature.²¹ Such a limited chain scission mechanism is further supported by results from intrinsic viscosity measurements, which reveal a 5–7% reduction in molecular weight in 30% H_2O_2 -treated PVA films. Thus, based on evidence gathered so far, the observed changes in PVA swelling and related properties are directly attributable to the dissolution of PVA crystalline regions by H_2O_2 and the facilitation of it by the oxidative chain scission and further oxidation of the main chain. Since these two processes occur concomitantly, it may be difficult to separate their respective contributions. However, one can reasonably be certain that, at higher concentrations, H_2O_2 is both a better solvent and a better oxidant for PVA, thus resulting in significant differences in the observed effects at different H_2O_2 concentrations.

CONCLUSION

The hydrogen peroxide treatment of annealed PVA films has been investigated. Significant and irreversible increases in equilibrium water swelling, dissolved oxygen permeability, and surface wettability have been observed in PVA samples treated with concentrated H_2O_2 . The majority of the changes occur during the early stage (0.5–1 h) of the contact with H_2O_2 . The rate and extent of such changes declines with decreasing H_2O_2 concentration. Below 5% H_2O_2 concentration, no appreciable change in PVA swelling has been observed. At a fixed H_2O_2 concentration, the equilibrium water swelling of the treated PVA is higher in samples with lower original crystallinity. In PVA samples of crystallinities below 20%, such significant increase in swelling led to the observed sample dissolution in 30% H_2O_2 within 30 min. A small amount of carbonyl content was detected on PVA samples treated with H_2O_2 , suggesting limited oxidative chain scission. Density measurements on annealed PVA samples show a substantial reduction of crystallinity on samples treated with 30% H_2O_2 . These results suggest that a combination of oxidative chain scission and dissolution of crystalline regions may be responsible for the observed kinetics of swelling and associated changes in PVA properties. A potential application of this

hydrogen peroxide process is for the recovery of water swelling, dissolved oxygen permeability, and surface wettability in thermally molded PVA soft contact lenses.

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REFERENCES

1. I. Sakurada, *Poly(vinyl Alcohol) Fibers*, Dekker, New York, 1985.
2. C. R. Blumenstein, *Text. Ind.*, **130**(7), 63 (1966).
3. R. W. Kormeyer and N. A. Peppas, *J. Membr. Sci.*, **9**, 211 (1981).
4. P. Colombo, C. Caramella, U. Conte, A. Gazzaniga, and A. LaManna, *Proc. Int. Symp. Contr. Rel. Bioac. Mater.*, **11**, 130 (1984).
5. N. A. Peppas and W. H. M. Yang, *Cont. Intraoc. Lens Med. J.*, **7**, 300 (1981).
6. P. I. Lee, U.S. Pat. 4,559,186 (1985).
7. P. I. Lee, U.S. Pat. 4,619,793 (1986).
8. M. Goldenberg, U.S. Pat. 4,598,122 (1986).
9. C. A. Finch, Ed., *Poly(vinyl Alcohol). Properties and Applications*, Wiley, New York, 1973.
10. I. Sakurada and S. Matuzawa, *Kobunshi Kagaku*, **16**, 565 (1959).
11. G. Takayama, *Kobunshi Kagaku*, **17**, 698 (1960).
12. J. S. Bates and R. A. Shanks, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 1867 (1979).
13. L. Kravetz, *Text. Chem. Colour.*, **5**, 29 (1973).
14. S. R. Khanna, *Text. Chem. Colour.*, **6**, 132 (1974).
15. A. Hebeish, I. I. Abdel-Gawad, I. K. Basily, and S. Elbazza, *J. Appl. Polym. Sci.*, **30**, 2321 (1985).
16. W. C. Hamilton, *J. Colloid Interface Sci.*, **40**, 219 (1972).
17. I. Sakurada, Y. Nukushina, and Y. Sone, *Kobunshi Kagaku*, **12**, 510 (1955).
18. H. E. Harris and J. G. Pritchard, *J. Polym. Sci. A*, **2**, 3673 (1964).
19. D. R. Burfield and K. S. Law, *Polymer*, **20**, 620 (1979).
20. H. Katsuke, T. Yoshida, C. Tanegashima, and S. Tanaka, *Anal. Biochem.*, **43**, 349 (1971).
21. I. Sakurada, Y. Nukushina, and Y. Sone, *Kobunshi Kagaku*, **12**, 506 (1955).
22. I. Sakurada, Y. Nukushina, and Y. Sone, *Kobunshi Kagaku*, **12**, 514 (1955).
23. E. Nagai, S. Mima, S. Kuribayashi, and N. Sagane, *Kobunshi Kagaku*, **12**, 199 (1955).
24. C. Jho, *J. Colloid Interface Sci.*, **94**, 589 (1983).

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