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Short Communication

## Gel permeation chromatographic properties of poly(vinyl alcohol) gel particles prepared by freezing and thawing

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### Abstract

The gel permeation chromatographic properties of poly(vinyl alcohol) gel particles prepared by a freezing-and-thawing procedure were investigated. From the calibration graph established with poly(ethylene glycol) and poly(ethylene oxide) samples, it was found that the value of the excluded molecular mass increased from 2500 (original) to 6000 (fifteen repeated cycles of freezing and thawing). In addition, the treated gels showed a favourable pressure-resisting property.

### 1. Introduction

We have been investigating the preparation of macroporous gel particles of poly(vinyl alcohol) [1]. These particles are obtained by the saponification of particles of poly(vinyl acetate) formed in the polymerization of vinyl acetate in a suspension process. The poly(vinyl alcohol) gel particles have been used as a column packing for aqueous separations. However, the gels have a disadvantage with regard to pressure-resistant properties because of their poor mechanical strength. We considered that a poly(vinyl alcohol) gel might have a potential high enough to realize excellent mechanical stability, because a poly(vinyl alcohol) aqueous solution more than 5 wt.-% was found to become strong hydrogel following a freezing-and-thawing procedure [2–4].

We report here that the freezing-and-thawing procedure is suitable for improving the performance of poly(vinyl alcohol) gel particles for use as a column packing for gel permeation chromatography in aqueous media.

### 2. Experimental

Vinyl acetate was freed from inhibitor by washing with a 5% aqueous solution of sodium hydrogensulfite and distilled water. Suspension polymerization of vinyl acetate was conducted in the presence of benzoyl peroxide as an initiator in a 300-ml round-bottomed flask equipped with an agitator and a reflux condenser. After the reaction product had been processed, the dry gel particles of poly(vinyl acetate) [degree of polymerization (DP) = 1000] was classified with a testing sieve. The classifier settings were chosen to give a particle size distribution with particle diameters in the range 200–250  $\mu\text{m}$ . The sapon-

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ification from poly(vinyl acetate) to poly(vinyl alcohol) was carried out at 30°C for 1 month by immersing the gel particles in a solution containing sodium hydroxide and methanol in an aqueous saturated sodium sulfate solution [5]. The completion of saponification was confirmed by IR measurement. The gel particles of poly(vinyl alcohol) obtained above have enough mechanical stability in water below 70°C without treatment for cross-linking. Observations by optical microscopy suggested that the diameter of a dry particle increased by a factor of  $\leq 1.38$  on swelling with water.

The gel particles of poly(vinyl alcohol) swollen in water were subjected to repeated freezing and thawing. The temperature range was between  $-30$  and  $20^\circ\text{C}$ . This was realized simply by placing the swollen gel particles in and removing them from a freezer at 3-h intervals; in this way the temperature was lowered from  $20$  to  $-30^\circ\text{C}$  in 1 h, kept at that temperature for 3 h, then raised from  $-30$  to  $20^\circ\text{C}$  and kept at  $20^\circ\text{C}$  for 3 h. The slurry of the gel particles was packed into a  $150 \times 4$  mm I.D. stainless-steel column at a pressure of about 5 MPa.

High-performance gel permeation chromatographic (HP-GPC) separations were performed with a Shimadzu LC6-AD instrument employing distilled water as eluent. Solutions ( $40 \mu\text{l}$ ) of individual solutes were injected with an off-column syringe-septum arrangement. Detection of solutes was performed with a Shimadzu Model RID-6A Refracto Monitor (cell volume =  $10 \mu\text{l}$ , aqueous reference). The samples of poly(ethylene oxide) (PEO) were narrow-distribution standards supplied by Showa Science (Tokyo Japan). The samples of poly(ethylene glycol) (PEG) are designated with a number indicating the molecular mass provided by the suppliers (Kanto Chemicals, Tokyo, Japan). The calibration graph was established at a flow rate of  $0.4$  ml/min with a PEG concentration of  $2.0\%$  (w/v) and a PEO concentration of  $1.0\%$  (w/v).

X-ray experiments were carried out using a Rigaku wide-angle X-ray diffractometer with nickel-filtered copper  $K\alpha_1$  radiation. Its power setting was at  $35$  kV and  $20$  mA.

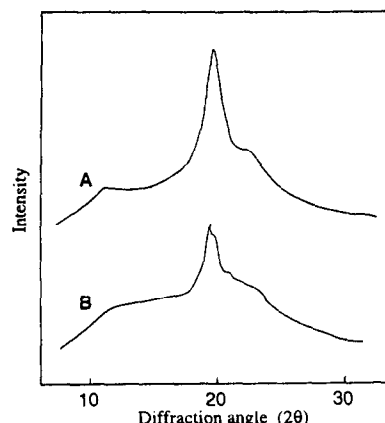


Fig. 1. X-ray diffraction patterns of poly(vinyl alcohol) gel particles. A, Original; B, after fifteen repeated cycles of freezing and thawing.

### 3. Results and discussion

Fig. 1 shows plots of X-ray diffraction intensity versus  $2\theta$  for particles subjected to the freezing-and-thawing treatment. The original sample shows clear (101) reflections in the angle regions  $2\theta = 19.40$ – $19.60^\circ$ . The main peak position in the X-ray pattern of the gel particles freezing and thawing on treatment by does not change. However, the intensity and sharpness of the profiles decrease compared with the original sample. In contrast, the halo portions in the angle range  $2\theta = 10$ – $15^\circ$  increase. This may be due to an increase in disordered domains.

The calibration graphs established with PEG and PEO samples are shown in Fig. 2. The value of the excluded molecular mass ( $M_{lim}$ ) increased from  $2500$  (original) to  $6000$  with increasing number of repeated cycles of freezing and thawing ( $N$ ). Above ten repeated cycles this value becomes independent of  $N$ . This result suggests that the fine structure of the gel particles prepared by the freezing-and-thawing procedure changes to a structure having larger pores because of the higher excluded molecular mass of the treated particles. In general, the cross-linking point in the network structure of gels is the crystalline relations which consist of aggregates of extended molecular chains associated by

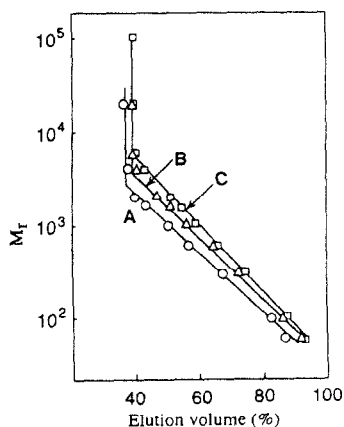


Fig. 2. Molecular mass calibration graphs for GPC column containing poly(vinyl alcohol) gel particles. A, Original; B, after five repeated cycles of freezing and thawing; C, after fifteen repeated cycles of freezing and thawing.

many hydrogen bonds [6]. Considering the results of X-ray scattering, in this case the development of a network structure having larger pores is not caused by an increase of crystalline regions, but probably by water interacting with amorphous chains between the cross-linking points.

HP-GPC is desirable in aqueous systems. In this case, the pressure resistance is an important property. Fig. 3 shows the relationship between the flow-rate and the pressure drop, compared with the behaviour observed for untreated poly(vinyl alcohol) gels. The straight line in Fig. 3 indicates that the gel particles prepared by the freezing-and-thawing procedure form rigid and stable packing materials for high-speed chromatography. When the gel particles are repeatedly treated by freezing and thawing, the hydrogen

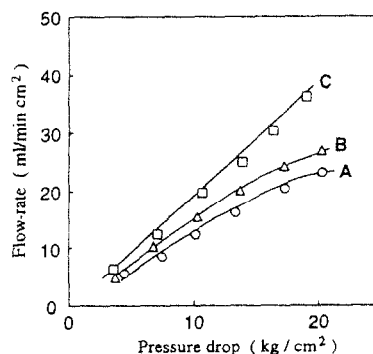


Fig. 3. Relationship between the flow-rate and pressure drop for poly(vinyl alcohol) gel particles. A, Original; B, after five repeated cycles of freezing and thawing; C, after fifteen repeated cycles of freezing and thawing.

bonds between chain molecules and water become stronger. This results in an increase in the rigidity of the particles. From the above results it is clear that the freezing-and-thawing treatment is useful for improving the performance of poly(vinyl alcohol) particles as packing materials.

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