

## Characterization and Physical Properties of Low Molecular Weight Poly(vinyl acetate) and Poly(vinyl alcohol)

Toshiaki SATO and Takuji OKAYA

Central Research Laboratories, Kuraray Co., Ltd.,  
2045-1 Sakazu, Kurashiki 710, Japan

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**ABSTRACT:** Low molecular weight poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) (PVA) having a 2-hydroxyethylthio group at one end were synthesized using 2-mercaptoethanol as a chain transfer agent. The dependence of physical properties of PVAc and PVA on the degree of polymerization was investigated. It became clear that vapor pressure osmometry was useful as well as  $^1\text{H}$  NMR analysis to determine the number average degree of polymerization of the low molecular weight PVAc and PVA. The glass transition temperature of the PVAc decreased below 150 as the number average degree of polymerization ( $\bar{P}_n$ ), and the melting temperature and degree of crystallinity of the PVA had no or little change above around 100 of  $\bar{P}_n$ , but changed below 100, especially at less than 50. The effect of chemical structure of the end groups on the swelling was also studied.

**KEY WORDS** Low Molecular Weight / Poly(vinyl acetate) / Poly(vinyl alcohol) / Chain Transfer / End Group / Vapor Pressure Osmometry / Degree of Polymerization / Glass Transition Temperature / Crystallinity / Melting Temperature / Swelling /

Some studies on poly(vinyl alcohol) (PVA) have been carried out with respect to the dependence of physical properties on degree of polymerization. Sone and Sakurada<sup>1</sup> and Imai<sup>2</sup> reported the dependence of degree of crystallinity on degree of polymerization, and Sakurada *et al.*<sup>3</sup> reported the relationships between the degree of swelling and heat-treatment temperature or degree of polymerization. However, in these studies low molecular weight PVAs, especially below 100 degrees of polymerization, were not dealt with and no attention was paid to the chemical structures of end groups of the PVAs.

From a kinetic investigation on the free radical polymerization of vinyl acetate in the presence of chain transfer agent, we propose a new method to synthesize PVAc and PVA, whose degrees of polymerization, distributions and end groups can be controlled.<sup>4</sup> According to the method, one can obtain the PVAc or

PVA having a sharp distribution of polymerization degree ( $\bar{P}_w/\bar{P}_n \sim 2$ ) and a specified end group at one end especially low molecular weight polymers having less than 100 degrees of polymerization, which were difficult to synthesize by the conventional method.

In this study, we report a series of low molecular weight PVAc and PVAs having a 2-hydroxyethylthio group at one end, and examine the degree of polymerization of these polymers. Secondly, we study the physical properties of PVAc and PVA with respect to dependence on the degree of polymerization, because the 2-hydroxyethylthio end group is thought to have little influence on molecular weight measurements and physical properties.

## EXPERIMENTAL

### Chemicals

VAc monomer produced in Kuraray Compa-

ny was used without further purification. Analytical grade of methanol (MeOH), 2-mercaptoethanol (2-ME), 1-dodecanethiol, 3-mercaptopropionic acid and 2,2'-azobisisobutyronitrile (AIBN) was used without purification.

### Polymerization

The polymerization of VAc was carried out in methanol solution at 60°C with uniformly continuous addition of 2-ME during the course of polymerization, and a series of PVAc having a 2-hydroxyethylthio group at one end with  $\bar{P}_w/\bar{P}_n \sim 2$ , confirmed by NMR measurement and GPC analysis, were obtained.<sup>4</sup> Five PVAc having various degrees of polymerization (LP-1 ~ LP-5) were prepared.

### Hydrolysis and Acetylation

PVAs having a 2-hydroxyethylthio group at one end (HOCH<sub>2</sub>CH<sub>2</sub>S-PVA) were obtained by the usual methanolysis of PVAc catalyzed with sodium hydroxide at 40°C.

PVA was acetylated into PVAc in a mixture of pyridine and acetic anhydride (1:5 by volume) at 120°C in a test tube degassed and sealed under vacuum.

PVAc as polymerized and PVAc obtained from the acetylation of the PVA are abbreviated as I-PVAc and R-PVAc, respectively.

The degrees of hydrolysis (DH) of all PVAs having a 2-hydroxyethylthio group at one end are more than 99.9 mol%.

### Measurements

The viscosity average degree of polymerization was calculated from intrinsic viscosities measured in acetone at 30°C for PVAc and in water at 30°C for PVA, using eq 1<sup>5</sup> for PVAc and eq 2<sup>6</sup> for PVA.

$$[\eta] = 7.94 \times 10^{-3} \bar{P}_v^{0.62} \quad (1)$$

$$[\eta] = 7.50 \times 10^{-3} \bar{P}_v^{0.64} \quad (2)$$

NMR spectra were measured in CDCl<sub>3</sub> for PVAc and in DMSO-*d*<sub>6</sub> for PVAs on JEOL 505, from which the number average degree of

polymerization was determined as described elsewhere.<sup>4</sup>

Vapor pressure osmometry was performed on PVAc and PVA with CORONA molecular weight apparatus model-117. The calibration constant of the instrument was obtained by using standard substances of known molecular weights, such as benzil and glucose.

The glass transition temperature of I-PVAc was obtained on a Perkin-Elmer DSC-2C. All samples weighed 7–20 mg, were cooled to –30°C, and run at constant heating rate, 10°C min<sup>-1</sup>, under N<sub>2</sub> atmosphere. The glass transition temperature was taken as the temperature at which half the heat capacity change during the glass transition occurred.

PVA films were prepared by casting 5% aqueous solutions on a poly(ethylene terephthalate) film, and evaporating water at room temperature for 120 hours, and drying at 40°C under vacuum. Heat treatment was carried out at 40°C and 160°C for 10 minutes.

Melting temperature and heat of fusion of PVA films heat-treated at 160°C were obtained from a Rigaku differential scanning calorimeter under N<sub>2</sub> atmosphere. The heating rate was 10°C min<sup>-1</sup> in all measurements. The temperatures of the onset of melting, the peak maximum and end of melting were defined as the point of intersection of the extrapolated crystalline baseline with the extrapolated steepest slope of endothermic peak, peak temperature of endothermic peak and point of intersection of the extrapolated melt baseline with the extrapolated steepest slope of exothermic peak, respectively.

The X-ray diffraction studies were conducted on PVA films prepared and heat-treated described above with Ni-filtered and graphite-monochromated Cu-K<sub>α</sub> radiation using a Rigaku SG-7 diffractometer. Relative crystallinity was determined using the method of Kawai *et al.*<sup>7</sup>

The PVA films were immersed in water at 30°C for 24 hours. After removing excess water by blotting on filter paper, the swollen films

were weighed. The films were dried and reweighed. The degree of swelling (DS) is given by the following equation.

$$DS = \frac{(\text{Weight of swollen film}) - (\text{Weight of dried film after swelling})}{(\text{Weight of dried film after swelling})} \quad (3)$$

## RESULTS AND DISCUSSION

### Degree of Polymerization

The average degrees of polymerization are shown in Table I for PVAc and PVA synthesized by utilizing 2-ME as a chain transfer agent. The viscosity average degrees of polymerization measured on I-PVAc ( $\bar{P}_{AC}$ ) were in good agreement with those measured on R-PVAc ( $\bar{P}_{RAC}$ ), which makes clear that control of the degree of polymerization by chain transfer reactions with 2-ME does work well, and I-PVAc as well as R-PVA has no long branches hydrolyzable in the course of alkaline hydrolysis. However, as shown in Table I, the viscosity average degrees of polymerization of the PVA ( $\bar{P}_A$ ) were much larger than those of the PVAc ( $\bar{P}_{AC}$  and  $\bar{P}_{RAC}$ ), especially in low molecular weight region. On such low molecular weight polymers, the intrinsic viscosity-degree of polymerization equations, established on conventional polymers of higher degrees of polymerization, seems to be not applicable to determine the degree of polymerization for both PVAc and PVA.

Then we measured the number average degree of polymerization on PVAc and PVA in such as low molecular weight region by the vapor pressure osmometry (VPO). The measurements were performed both on PVAc in benzene at 40°C and PVA in water at 60°C. Plots of  $\Delta V/C$  against concentration gave good straight lines for all I-PVAc and PVA samples, as shown in Figure 1 for PVAs. We can obtain the number average degree of polymerization by extrapolation to zero concentration according to eq 1 and 5,

**Table I.** Degrees of polymerization of PVAc and PVAs having a 2-hydroxyethylthio group at one end

Sample no.	$\bar{P}_{AC}$	$\bar{P}_{RAC}$	$\bar{P}_A$	$\bar{P}_n$ (PVA, NMR)
LP-1	28	26	66	30
LP-2	44	48	113	44
LP-3	88	96	191	80
LP-4	197	202	353	124
LP-5	300	317	532	164

**Table II.** Number average degrees of polymerization of PVAc and PVAs measured by vapor pressure osmometry

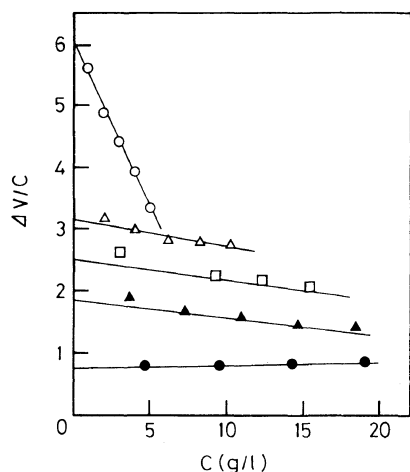
Sample no.	$\bar{P}_n$ (I-PVAc, VPO)	$\bar{P}_n$ (PVA, VPO)
LP-1	20	26
LP-2	46	47
LP-3	76	61
LP-4	137	88
LP-5	221	196

$$\frac{\Delta V}{C} = K \left( \frac{1}{M} + A_{2,v} \cdot C + A_{3,v} \cdot C^2 + \dots \right) \quad (4)$$

$$M = K \left/ \lim_{c \rightarrow 0} \frac{\Delta V}{C} \right. \quad (5)$$

where  $\Delta V$ ,  $C$ ,  $K$ ,  $M$ ,  $A_{2,v}$  and  $A_{3,v}$  represent voltage difference, concentration, apparatus constant, molecular weight, second virial coefficient and third virial coefficient, respectively.

The results are summarized in Table II. The number average degree of polymerization of I-PVAc ( $\bar{P}_n$ (I-PVAc, VPO)) coincided well with that of PVA ( $\bar{P}_n$ (PVA, VPO)), which agreed closely with the  $\bar{P}_n$  value obtained by NMR measurement ( $\bar{P}_n$ (PVA, NMR)) shown in Table I. The apparent second virial coefficients of the PVAs obtained from the slope of the straight lines in Figure 1 were negative except for LP-5, which had the highest degree of polymerization, and the absolute values became larger in decreasing molecular weight. VPO seems to be useful to measure the degree of polymerization for low molecular weight



**Figure 1.** Plots of  $\Delta V/C$  against  $C$  of VPO measurements on  $\text{HOCH}_2\text{CH}_2\text{S-PVAs}$  having various degrees of polymerization. ( $\circ$ )  $\bar{P}_n=26$ , ( $\triangle$ )  $\bar{P}_n=47$ , ( $\square$ )  $\bar{P}_n=61$ , ( $\blacktriangle$ )  $\bar{P}_n=88$ , and ( $\bullet$ )  $\bar{P}_n=196$ .

PVAs as well as low molecular weight PVAcS.

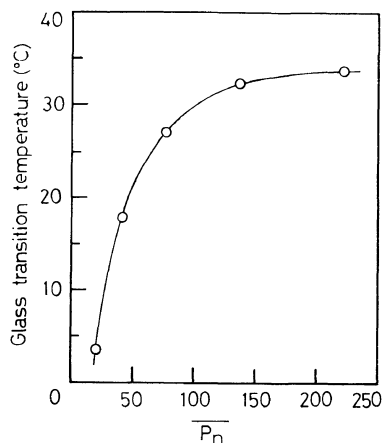
Then the number average degree of polymerization obtained by VPO measurement or NMR measurement is used in the following discussion.

#### Physical Properties

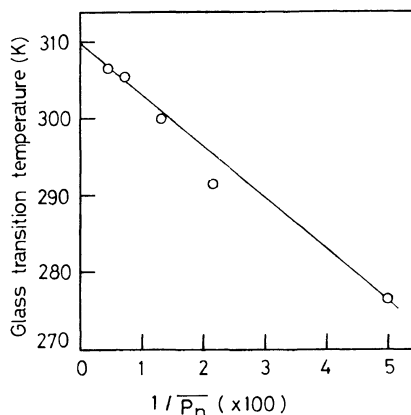
The dependence of glass transition temperature of I-PVAc on the degree of polymerization (DP) is shown in Figure 2. The glass transition temperature had little changed above around 150 of  $\bar{P}_n$ , but dropped sharply below 100, especially lower than 50. The relationship between glass transition temperature and degree of polymerization in fractionated polymer is well-established<sup>8</sup> as,

$$T_g = T_{g0} - \frac{K}{\bar{P}_n} \quad (6)$$

where  $T_g$  and  $T_{g0}$  are the glass transition temperatures of the polymers whose DPs are  $\bar{P}_n$  and infinity, respectively, and  $K$  is constant. A plot of  $T_g$  against the reciprocal of  $\bar{P}_n$  is shown in Figure 3. Although I-PVAc polymers were unfractionated, the plot gave a good straight line, from which  $T_{g0}$  and  $K$  were



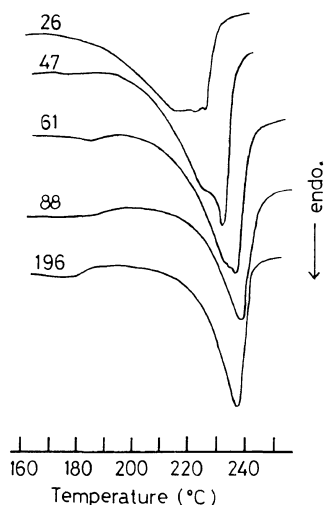
**Figure 2.** Variation of glass transition temperature of PVAc having a 2-hydroxyethylthio group at one end with the number average degree of polymerization.



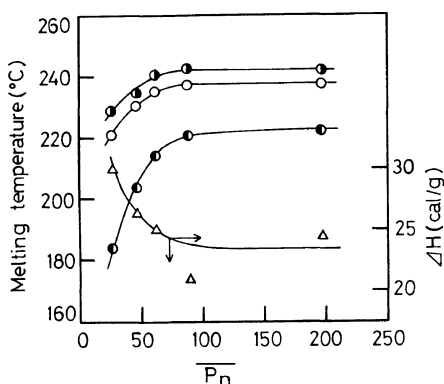
**Figure 3.** Plot of glass transition temperature against the reciprocal of the number average degree of polymerization of PVAc having a 2-hydroxyethylthio group at one end.

calculated as 310K (37°C) and 662, respectively.  $T_g$  of PVAc have been reported to be 31.4°C ( $\bar{P}_n=1930$ ) and 23.6°C ( $\bar{P}_n=46$ ) using the refractometric technique.<sup>9</sup> Our results indicate a little larger dependence on molecular weight, which may be caused by difference of molecular weight distribution of PVAc samples used in  $T_g$  measurement.

In Figure 4 are shown DSC traces of  $\text{HOCH}_2\text{CH}_2\text{S-PVAs}$  having various  $\bar{P}_n$ . The endothermic peak of melting broadened with



**Figure 4.** DSC traces of HOCH<sub>2</sub>CH<sub>2</sub>S-PVAs having various degrees of polymerization. Numerals in figure represent number average degrees of polymerization.



**Figure 5.** Dependence of the melting temperature and heat of fusion of HOCH<sub>2</sub>CH<sub>2</sub>S-PVAs on the number average degree of polymerization. (●)  $T_{mi}$ ; (○)  $T_{mp}$ ; (●)  $T_{me}$ ; (△)  $\Delta H$ .

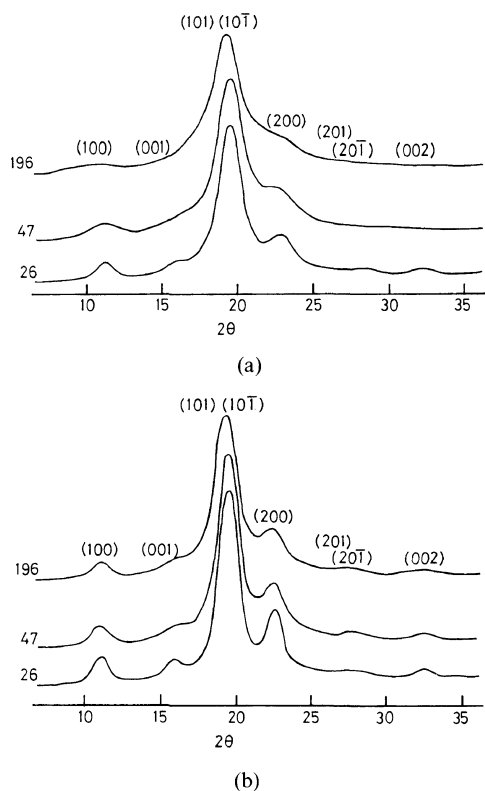
a decrease in  $\bar{P}_n$ . Figure 5 shows the dependences of melting temperature and heat of fusion ( $\Delta H$ ), on  $\bar{P}_n$ , where  $T_{mi}$ ,  $T_{mp}$ , and  $T_{me}$  are temperatures of the onset of melting, main peak maximum and the end of melting, respectively. These temperatures had little change above around 100 of  $\bar{P}_n$ , but decreased below 100, and  $T_{mi}$  particularly showed a large decrease below 100 of  $\bar{P}_n$ . The dependence of melting temperature of the PVA on  $\bar{P}_n$  seems

**Table III.** Calorimetric crystallinity of PVAs having various degrees of polymerization

Sample no.	$\bar{P}_n$ (PVA, VPO)	$\Delta H/\Delta H_u$
LP-1	26	0.805
LP-2	47	0.732
LP-3	61	0.668
LP-4	88	0.566
LP-5	196	0.641
PVA-105A	—	0.592
PVA-HCA	—	0.395

small compared with that of polyethylene whose melting temperature drops sharply below around 700 of  $\bar{P}_n$ .<sup>10</sup>  $\Delta H$  increased below 100 of  $\bar{P}_n$ , although it had little change above around 100, as noted also for melting temperatures. Table III shows the relationship between  $\Delta H/\Delta H_u$  and  $\bar{P}_n$ , where  $\Delta H_u$  represents the heat of fusion per chain repeating unit, and 1640 cal mol<sup>-1</sup> reported by Tubbs<sup>11</sup> is taken as  $\Delta H_u$ . PVA-105A and PVA-HCA are conventional fully hydrolyzed PVAs (DH > 99.9 mole%) whose degrees of polymerization ( $\bar{P}_A$ ) are 550 and 1750, respectively.  $\Delta H/\Delta H_u$ , which indicates the ease of crystallization, increased with decrease in  $\bar{P}_n$ , especially at less than 50. This suggests that low molecular weight PVAs crystallize easily and their degree of crystallinity is higher than that of high molecular weight PVAs.

In order to investigate in more detail the relation between the degree of crystallinity ( $\chi_c$ ) and degree of polymerization, we carried out X-ray diffraction measurement. In Figure 6 are shown the diffraction patterns in the range of  $2\theta$  from 5° to 35° for three HOCH<sub>2</sub>CH<sub>2</sub>S-PVAs having different  $\bar{P}_n$  heat treated at 40°C and 160°C. The crystallinity of PVA increased with decrease in  $\bar{P}_n$  and increased with increase in heat treatment temperature. As shown in Table IV and Figure 7,  $\chi_c$  increased slightly with decrease in  $\bar{P}_n$  above around 50, but increased rapidly at less than 50 irrespective of heat treatment temperature. This is in good agreement well with that observed in DSC



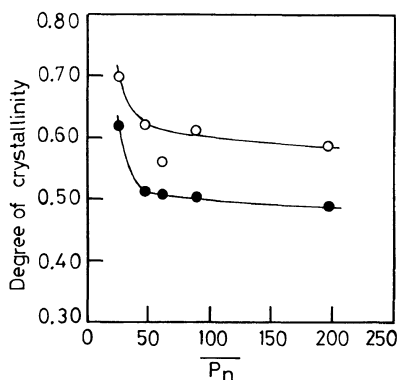
**Figure 6.** X-Ray diffraction patterns of PVA films having various degrees of polymerization heat treated at 40°C (a) and 160°C (b). Numerals represent the number average degrees of polymerization.

measurements.

The dependence of  $\chi_c$  on DP has been studied for PVAs and other polymers. Sone and Sakurada<sup>1</sup> measured the specific gravity of PVAs having from 3600 to 140 of  $\bar{P}_A$ , and reported that  $\chi_c$  of the PVA films heat treated between 40°C and 160°C increased with decrease in  $\bar{P}_A$  at less than 500. However, they recognized no increase of  $\chi_c$  by X-ray diffraction measurement. Imai<sup>2</sup> also reported almost the same, that is, increase in  $\chi_c$  with lowering  $\bar{P}_A$  in the range from 500 to 300, by measuring absorbance change of crystalline-sensitive band in IR spectra and specific gravity. An increase of  $\chi_c$  with lowering DP has also been recognized for various polymers, including polyethylene, poly(ethylene

**Table IV.** Degrees of X-ray crystallinity of PVAs having various degrees of polymerization

Sample no.	$\bar{P}_n$ (PVA, VPO)	Degree of crystallinity	
		HT at 40°C	HT at 160°C
LP-1	26	0.623	0.701
LP-2	47	0.514	0.623
LP-3	61	0.508	0.562
LP-4	88	0.504	0.615
LP-5	196	0.487	0.587
PVA-105A	—	0.480	0.578
PVA-HCA	—	0.414	0.537



**Figure 7.** Dependence of degree of crystallinity of PVAs on number average degree of polymerization. (○) heat treated at 160°C (●) heat treated at 40°C.

telephthalate), and *trans*-poly(2-methylbutadiene).<sup>12</sup> The results in this work coincide with those of Sakurada *et al.* and Imai, but the distinct increase of  $\chi_c$  was first observed by X-ray diffraction measurements on PVAs having such extremely low  $\bar{P}_n$  on which no investigation has been reported so far. With lowering DP of HOCH<sub>2</sub>CH<sub>2</sub>S-PVA, the size of crystallite probably becomes smaller due to increase in the number of 2-hydroxyethylthio end groups, which function to decrease  $\chi_c$ . Therefore, that lower  $\bar{P}_n$  HOCH<sub>2</sub>CH<sub>2</sub>S-PVAs, such as LP-1 ( $\bar{P}_n=26$ ) and LP-2 ( $\bar{P}_n=47$ ), have higher  $\chi_c$  may be caused by increase in the numbers of the crystallite.

The degrees of swelling in water for

HOCH<sub>2</sub>CH<sub>2</sub>S-PVA films are summarized in Table V. We could not prepare the film of LP-1 due to its lower degree of polymerization, and measurement on LP-2 film heat treated at 40°C could not be performed because the swelling film was not strong enough. DS showed minimum at around 200 of  $\bar{P}_n$  for films heat treated at 40°C and around 100 for films heat treated at 160°C.

The swelling behavior of PVA films in water is thought to be really complicated, depending on the the number of end groups, chemical structure of the end groups, degree of hydrolysis, degree of crystallinity, heat treatment temperature and conditions of film formation. Among these factors, increases in the degree of hydrolysis and degree of crystallinity and decrease in the number of end group seem to function to decrease the degree

of swelling. With lowering  $\bar{P}_n$  of HOCH<sub>2</sub>CH<sub>2</sub>S-PVA, both the number of 2-hydroxyethylthio end group and degree of crystallinity increase. These facts have the opposite effects each other, and the degree of swelling of HOCH<sub>2</sub>CH<sub>2</sub>S-PVA films shows minimum at some degree of polymerization. The results seem to be in contrast to those reported by Sakurada *et al.*,<sup>3</sup> which showed that DS increased monotonously with decrease in  $\bar{P}_A$  at low temperature of heat treatment below 120°C, but the reason is not clear.

We deal with the influence of the chemical structures of end groups because it has hardly been investigated so far and the low molecular weight PVA having a sharp distribution of polymerization degree ( $\bar{P}_w/\bar{P}_n \sim 2$ ) and specified end group at one end have been synthesized. Two other end groups modified PVAs, a PVA having a carboxyethylthio group at one end (HOOCCH<sub>2</sub>CH<sub>2</sub>S-PVA) and PVA having a *n*-dodecylthio group at one end (*n*-C<sub>12</sub>H<sub>25</sub>S-PVA) were prepared. They were synthesized by polymerizing VAc using 3-mercaptopropionic acid and 1-dodecanethiol as chain transfer agents instead of 2-ME, followed by hydrolysis and treatment with ion-exchange resin in the case of HOOCCH<sub>2</sub>CH<sub>2</sub>S-PVA. As shown in Table VI, an DS of HOOCCH<sub>2</sub>CH<sub>2</sub>S-PVA, especially heat treated at low temperature was much larger than that of HOCH<sub>2</sub>CH<sub>2</sub>S-PVA, and neutralization of the carboxyl group affected strongly DS. *n*-C<sub>12</sub>H<sub>25</sub>S-PVA had as

**Table V.** Degrees of swelling of PVAs having various degrees of polymerization heat treated at 40°C and 160°C

Sample no.	$\bar{P}_n$ (PVA, VPO)	Degree of swelling	
		HT at 40°C	HT at 160°C
LP-1	26	—	—
LP-2	47	—	0.70
LP-3	61	2.39	0.13
LP-4	88	1.46	0.33
LP-5	196	1.46	0.37
PVA-105A	—	1.83	0.39
PVA-HCA	—	1.42	0.51

**Table VI.** Variations in the degree of swelling of PVAs having a carboxyethylthio group and a *n*-dodecylthio group at one end

PVA	$\bar{P}_{Ac}$	DN	Degree of swelling	
			HT at 40°C	HT at 160°C
HOOCCH <sub>2</sub> CH <sub>2</sub> S-PVA	94	0	4.70	0.25
		0.5	16	0.41
		1.0	Soluble	0.38
<i>n</i> -C <sub>12</sub> H <sub>25</sub> S-PVA	112	—	1.56	0.18
HOCH <sub>2</sub> CH <sub>2</sub> S-PVA	88	—	1.46	0.33

small a value as HOCH<sub>2</sub>CH<sub>2</sub>S-PVA had. The above results indicate that the effect of chemical structure of end group on the swelling should be considered in the case of a hydrophilic group such as the carboxylate anion end group. It is well-known that carboxylate end groups, introduced by chain transfer reactions to VAc monomer and polymer, necessarily exist in PVA.

### CONCLUSION

The degrees of polymerization of low molecular weight PVAc and PVA were measured by vapor pressure osmometry. It was useful as well as <sup>1</sup>H NMR analysis to determine the number average degree of polymerization of low molecular weight PVA.

The dependence of physical properties on the degree of polymerization was investigated, including glass transition temperature for PVAc having a 2-hydroxyethylthio group at one end, and melting temperature, crystalline properties and swelling in water for PVA having a 2-hydroxyethylthio group at one end. The glass transition temperature of PVAc decreased sharply below 150 of  $\bar{P}_n$ . The melting temperature of PVA had no or little change above around 100 of  $\bar{P}_n$ , but changed below 100, especially at less than 50. The degree of crystallinity increased with decrease in  $\bar{P}_n$ ,

especially at less than 50. The degree of swelling showed minimum at around 200 of  $\bar{P}_n$  for the film heat treated at 40°C and around 100 for the film heat treated at 160°C. The effects of chemical structure of the end groups on the swelling were observed in the case of a hydrophilic group such as a carboxylate anion end group.

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