

Physical and Surface Properties of Aqueous Solutions of Polyvinyl Alcohols Having an *n*-Alkylthio End Group

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SYNOPSIS

The polyvinyl alcohols (PVAs) having a *n*-alkylthio end group of 10 through 16 carbon atoms were found to associate in the dilute aqueous solutions through hydrophobic interaction. From the apparent number-average molecular weight with vapor pressure osmometer, the PVAs having an *n*-dodecylthio and an *n*-hexadecylthio group at one end were calculated to associate by about five and three molecules, respectively. The aqueous solutions of the PVA having an *n*-dodecylthio group at one end showed much higher viscosity compared with the PVA having a hydroxyethylthio group at one end (HOCH₂CH₂S-PVA) in low concentration regions of below 10 wt % due to the association of the *n*-dodecyl end group. Surface tensions of the aqueous solutions of the PVAs having an *n*-alkylthio group at one end (*n*-C_{*n*}H_{2*n*+1}S-PVA) showed almost the same value, which was slightly smaller than that of HOCH₂CH₂S-PVA, at 4 and 6 of carbon atoms, lowered with an increase in the number of carbon atoms above 8, showed minimum at 12 and then increased at 16 and 18. In the emulsion polymerization of vinyl acetate, *n*-C_{*n*}H_{2*n*+1}S-PVAs of 10 through 18 carbon atoms acted effectively as a protective colloid.

INTRODUCTION

Some studies have been carried out with respect to polyvinyl alcohols (PVAs) having an *n*-alkyl end group. The PVAs were obtained from vinyl acetate (VAc) polymerization in the presence of cetyl bromide,¹ lauryl alcohol,² lauryl mercaptan,³ alcohols,⁴ and alkyl halides,⁵ and the solution and surface properties of the aqueous solutions of the PVAs were reported.^{6,7} However, in these studies no characterization of the PVAs was performed.

Okaya and Imai⁸ reported the existence of some kind of association in the dilute aqueous solutions of the PVAs having an alkyl end group obtained from the VAc polymerization in the presence of higher alcohols.

In the previous study,⁹ we have performed the theoretical investigation on the polymerization of VAc in the presence of thiol as a chain transfer agent and confirmed the structure of the derived polyvinyl alcohol, which had a moiety of thiol at one end.

In this work we prepared a series of PVAs having an *n*-alkylthio group of 3 through 18 carbon atoms at one end using *n*-alkyl thiols, and studied the solution and surface properties of the aqueous solutions of the PVAs with respect to the characterization.

EXPERIMENTAL

Polymers and Polymerization

VAc monomer produced by the Kuraray Company was used without further purification. Analytical grade methanol (MeOH), *n*-alkyl thiols of 3 through 18 carbon atoms, 2,2'-azobisisobutyronitrile (AIBN), and potassium persulfate were used without purification.

As described previously the chain transfer constant of thiols were much larger than the unity,⁹ and VAc was polymerized to PVAc having a moiety of thiol at one end by uniformly continuous addition of a thiol during polymerization to keep constant the thiol concentration. The PVA having a moiety of thiol at one end was obtained by usual metha-

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nolysis of the PVAc catalyzed by sodium hydroxide at 40°C.

The emulsion polymerization of VAc using the PVA as a protective colloid was carried out as follows: 70 g of water and 2.5 g of the PVA were dissolved with stirring at 95°C for at least 1 h. After being cooled to 60°C in nitrogen atmosphere, 50 g of VAc monomer and 20 g of water containing 0.25 g of potassium persulfate were added. The polymerization was carried out at 60°C for 3.0 h, withdrawing samples several times at appropriate intervals with a syringe and a hypodermic needle to determine conversion.

Measurements

The intrinsic viscosities were measured in acetone at 30°C for PVAc and in water at 30°C for PVA. Since the PVAc's synthesized with continuous addition of a thiol were found to have little or no branches caused by the chain transfer reactions to the polymer,¹⁰ the measurements for PVAc were carried out on the PVAc as polymerized.

The degrees of hydrolysis (DH) of all the PVAs employed in this work are more than 99.9 mol % unless otherwise mentioned, except for partially hydrolyzed HOCH₂CH₂S-PVA and PVA-205 whose DH are both 88 mol %.

The vapor pressure osmometry was performed on the PVAs with CORONA molecular weight apparatus model-117. The calibration constant of the instrument was obtained by using glucose as a standard substance of known molecular weight. The measurement was carried out at 60°C on the PVA aqueous solutions prepared by dissolving the PVA at 95°C for at least 1 h. The number-average molecular weight was obtained by extrapolations to zero concentration according to Eqs. (1) and (2).

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

$$M = \lim_{c \rightarrow 0} K \frac{\Delta V}{C} \quad (2)$$

Viscosities of the aqueous solutions of the PVAs were measured at 30°C on the solutions prepared by dissolving the PVAs at 95°C for at least 6 h and standing at 30°C for 30 min using Tokyo Keiki type-E viscometer.

Surface tensions were measured at 25°C by the du Nouy ring method using the Shimadzu surface tension meter. The measurement was carried out on the PVA aqueous solutions prepared by dissolving

the PVAs at 95°C for at least 1 h and standing at 25°C for 24 h.

RESULTS AND DISCUSSION

Aqueous Solution Properties of the End-Group Modified PVAs

Table I lists the intrinsic viscosities of a series of PVAs ($[\eta]_A$) having a *n*-alkylthio group at one end (*n*-C_{*n*}H_{2*n*+1}S-PVA) as well as those of the PVAc's ($[\eta]_{AC}$) corresponding to the PVAs, and the plots of $[\eta]_A$ against $[\eta]_{AC}$ are shown in Figure 1. The $[\eta]_{AC}$ of all the samples were very close with each other, which indicates all the PVAs in Table I have almost the same molecular weight. The $[\eta]_A$ of *n*-C₈H₁₇S-PVA could not be measured because of liability of the aqueous solution.

As shown in Figure 1, the plots of $[\eta]_A$ against $[\eta]_{AC}$ gave a good straight line for HOCH₂CH₂S-PVA, *n*-C₃H₇S-PVA, *n*-C₄H₉S-PVA, *n*-C₆H₁₃S-PVA, and *n*-C₁₈H₃₇S-PVA; however the plots for *n*-C₁₀H₂₁S-PVA, *n*-C₁₂H₂₅S-PVA, and *n*-C₁₆H₃₃S-PVA are located above the straight line. It suggests that the PVAs having an *n*-alkyl end group of 10 through 16 carbon atoms may associate in the aqueous solutions due to the end group.

Okaya and Imai⁸ investigated the dilute aqueous solution properties of the PVAs having an alkyl group at one end that were derived from the solution

Table I Values of the Intrinsic Viscosity of the PVA Having a Thioether Group at One End

RS-PVA	$[\eta]$ (dl/g)	
	$[\eta]_A$	$[\eta]_{AC}$
HOCH ₂ CH ₂ S-PVA	0.110	0.0629
HOCH ₂ CH ₂ S-PVA	0.155	0.0829
HOCH ₂ CH ₂ S-PVA	0.216	0.127
<i>n</i> -C ₃ H ₇ S-PVA	0.222	0.152
<i>n</i> -C ₄ H ₉ S-PVA	0.200	0.119
<i>n</i> -C ₆ H ₁₃ S-PVA	0.216	0.132
<i>n</i> -C ₈ H ₁₇ S-PVA	—	0.137
<i>n</i> -C ₁₀ H ₂₁ S-PVA	0.267	0.147
<i>n</i> -C ₁₂ H ₂₅ S-PVA	—	0.0478
<i>n</i> -C ₁₂ H ₂₅ S-PVA	—	0.0834
<i>n</i> -C ₁₂ H ₂₅ S-PVA	0.248	0.126
<i>n</i> -C ₁₂ H ₂₅ S-PVA	0.371	0.208
<i>n</i> -C ₁₂ H ₂₅ S-PVA	0.506	0.409
<i>n</i> -C ₁₆ H ₃₃ S-PVA	0.287	0.146
<i>n</i> -C ₁₈ H ₃₇ S-PVA	0.219	0.145

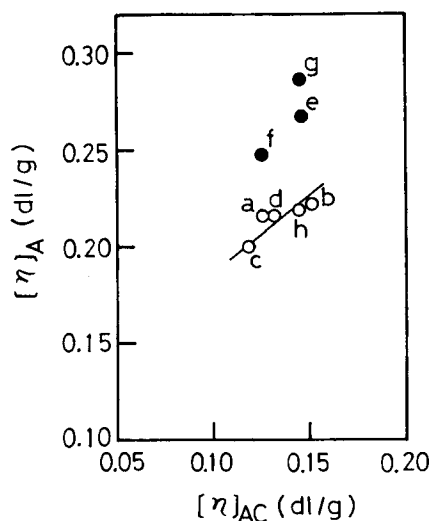


Figure 1 The plots of $[\eta]_A$ against $[\eta]_{AC}$ for the PVAs having a thioether group at one end. (a) $\text{HOCH}_2\text{CH}_2\text{S-PVA}$, (b) $n\text{-C}_3\text{H}_7\text{S-PVA}$, (c) $n\text{-C}_4\text{H}_9\text{S-PVA}$, (d) $n\text{-C}_6\text{H}_{13}\text{S-PVA}$, (e) $n\text{-C}_{10}\text{H}_{21}\text{S-PVA}$, (f) $n\text{-C}_{12}\text{H}_{25}\text{S-PVA}$, (g) $n\text{-C}_{16}\text{H}_{33}\text{S-PVA}$, (h) $n\text{-C}_{18}\text{H}_{37}\text{S-PVA}$.

polymerization of VAc in higher alcohols. From the abnormalities in the Huggins constants obtained by the Schulz-Blaschke equation in place of the Huggins equation as well as in the viscosity average degree of polymerization of the PVA in water compared with dimethyl sulfoxide and that of PVAc, they concluded that there exists the association of the PVA in water through the hydrophobic interaction between the alkyl groups in the PVAs having cetyl alcohol and stearyl alcohol moieties at one end, whereas there exists no abnormality in the PVAs derived from the solution polymerization in lower alcohols than myristyl alcohol. However, the degree of polymerization investigated were so high that they could not show the direct evidence of the association.

In order to investigate into the association, we attempted to measure the apparent molecular weights of $n\text{-C}_n\text{H}_{2n+1}\text{S-PVA}$ in water with vapor pressure osmometer. The plots of $\Delta V/C$ against C measured at 60°C are shown in Figure 2. The plots for $\text{HOCH}_2\text{CH}_2\text{S-PVA}$ and $n\text{-C}_8\text{H}_{17}\text{S-PVA}$ gave good straight lines, whereas the values of $\Delta V/C$ increased rapidly in low concentration regions for $n\text{-C}_{12}\text{H}_{25}\text{S-PVA}$ and $n\text{-C}_{16}\text{H}_{33}\text{S-PVA}$. The deviation from the straight line of the plots in low concentration region does not always prove the existence of association.¹¹ In this case, however, the values of $\Delta V/C$ of the PVAs showing deviations are much greater than those of the PVAs showing no deviation in high concentration region, where the linear relationship exists between $\Delta V/C$ and C , though both

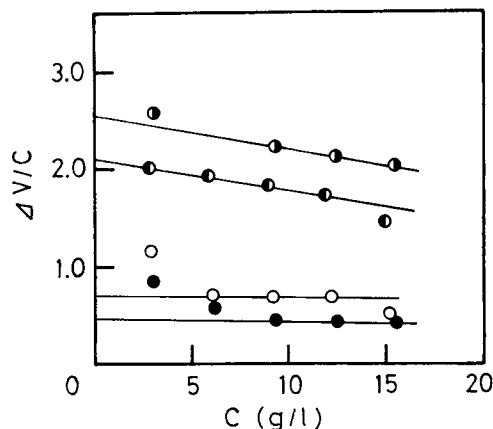


Figure 2 The plots of $\Delta V/C$ against C for the PVAs having a thioether group at one end: (●) $\text{HOCH}_2\text{CH}_2\text{S-PVA}$ ($[\eta]_{AC} = 0.127$ dl/g, $\text{DH} > 99.9$ mol %); (●) $n\text{-C}_8\text{H}_{17}\text{S-PVA}$ ($[\eta]_{AC} = 0.137$ dl/g, $\text{DH} > 99.9$ mol %); (○) $n\text{-C}_{12}\text{H}_{25}\text{S-PVA}$ ($[\eta]_{AC} = 0.126$ dl/g, $\text{DH} > 99.9$ mol %); (●) $n\text{-C}_{16}\text{H}_{33}\text{S-PVA}$ ($[\eta]_{AC} = 0.146$ dl/g, $\text{DH} > 99.9$ mol %).

of the PVAs have almost the same $[\eta]_{AC}$ as the PVAs showing no deviations. The results clearly indicate that some kind of association takes place in the aqueous solutions of $n\text{-C}_{12}\text{H}_{25}\text{S-PVA}$ and $n\text{-C}_{16}\text{H}_{33}\text{S-PVA}$, in fact the scattered light was observed in the aqueous solutions. Table II shows the apparent number-average molecular weights of the PVAs obtained by extrapolations to zero concentration in the range of the linear relationship between $\Delta V/C$ and C , and the number of association calculated by dividing the apparent molecular weight of $n\text{-C}_n\text{H}_{2n+1}\text{S-PVA}$ by molecular weight of $\text{HOCH}_2\text{CH}_2\text{S-PVA}$. From the number-average values, $n\text{-C}_{12}\text{H}_{25}\text{S-PVA}$ and $n\text{-C}_{16}\text{H}_{33}\text{S-PVA}$ are calculated to associate by about 5 and 3 molecules in the aqueous solutions, respectively, whereas the association scarcely occurs in $n\text{-C}_8\text{H}_{17}\text{S-PVA}$.

Viscosity behavior of the PVAs in concentrated aqueous solutions are shown in Figure 3. The plots

Table II Apparent Number-Average Molecular Weights of the PVA Measured in Water at 60°C by Vapor Pressure Osmometry

RS-PVA	$[\eta]_A$ (dl/g)	$(\bar{P}_n)_{\text{app}}$	NA ^a
$\text{HOCH}_2\text{CH}_2\text{S-PVA}$	0.216	2760	—
$n\text{-C}_8\text{H}_{17}\text{S-PVA}$	—	3400	1.2
$n\text{-C}_{12}\text{H}_{25}\text{S-PVA}$	0.248	13840	5.0
$n\text{-C}_{16}\text{H}_{33}\text{S-PVA}$	0.287	9890	3.6

^a Calculated from dividing $(\bar{P}_n)_{\text{app}}$ by \bar{P}_n of $\text{HOCH}_2\text{CH}_2\text{S-PVA}$.

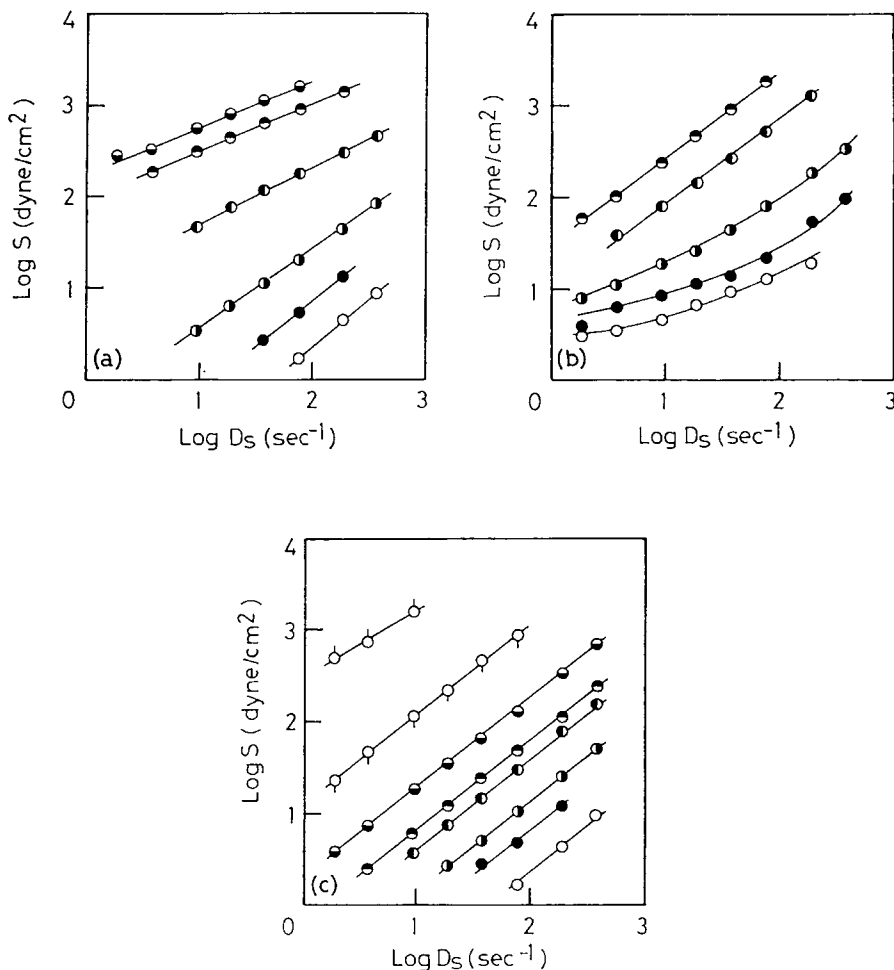


Figure 3 The plots of log (stress) against log (rate of shear) for the aqueous solutions of the PVAs having a thioether group at one end: (○) 5 wt %, (●) 10 wt %, (◐) 15 wt %, (◑) 20 wt %, (◒) 25 wt %, (◓) 30 wt %, (◔) 40 wt %, (◕) 50 wt %; (a) HOCH₂CH₂S-PVA ($[\eta]_{AC} = 0.127$ dl/g, DH > 99.9 mol %); (b) *n*-C₁₂H₂₅S-PVA ($[\eta]_{AC} = 0.126$ dl/g, DH > 99.9 mol %); (c) HOCH₂CH₂S-PVA ($[\eta]_{AC} = 0.127$ dl/g, DH = 88 mol %).

of stress against rate of shear according to Eq. (3) gave straight lines in the range of shear rate from 1.92 to 384 s⁻¹ for HOCH₂CH₂S-PVA and partially hydrolyzed HOCH₂CH₂S-PVA, however, the data of *n*-C₁₂H₂₅S-PVA in the low concentration below 15 wt % did not follow the linear relationship,

$$\log S = m \log D_s + \log \eta' \quad (3)$$

where S , D_s , and η' denote stress, rate of shear, and constant that represents viscosity coefficient in case $m = 1$, and m is a parameter representing a flow behavior.

The values of m obtained from the slope of straight lines in Figure 3 were found to be very close to 1, which means Newtonian viscosity, in the cases

of PVA-105A, PVA-205, partially hydrolyzed HOCH₂CH₂S-PVA up to 40 wt % of concentration, and HOCH₂CH₂S-PVA below 10 wt %. On the contrary the values of m were less than 1, which means structural viscosity, for HOCH₂CH₂S-PVA more than 15 wt % of concentration, partially hydrolyzed HOCH₂CH₂S-PVA at 50 wt % solution and *n*-C₁₂H₂₅S-PVA more than 20 wt %. The solution of *n*-C₁₂H₂₅S-PVA less than 15 wt % showed complicated features and did not follow Eq. (3). Figure 4 shows the relationships between concentration and viscosity calculated by S/D_s at 3.84 and 192 s⁻¹ of rates of shear for HOCH₂CH₂S-PVA and *n*-C₁₂H₂₅S-PVA in water at 30°C. The plot of logarithmic viscosity against concentration gave linearity for partially hydrolyzed PVA up to 40 wt %

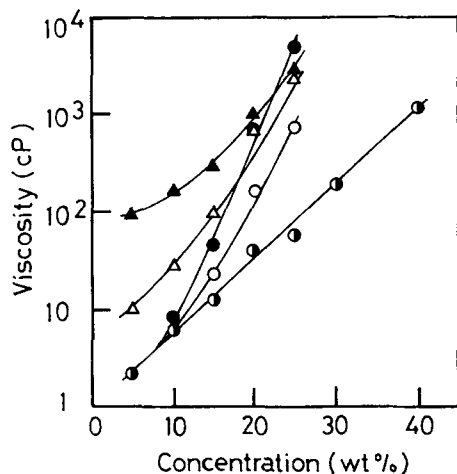


Figure 4 The relationships between concentration and viscosity for the PVAs having a thioether group at one end: (●) HOCH₂CH₂S-PVA ($[\eta]_{AC} = 0.127$ dl/g, DH > 99.9 mol %), $D_s = 3.84$ s⁻¹; (○) HOCH₂CH₂S-PVA ($[\eta]_{AC} = 0.127$ dl/g, DH > 99.9 mol %), $D_s = 192$ s⁻¹; (▲) *n*-C₁₂H₂₅S-PVA ($[\eta]_{AC} = 0.126$ dl/g, DH > 99.9 mol %), $D_s = 3.84$ s⁻¹; (△) *n*-C₁₂H₂₅S-PVA ($[\eta]_{AC} = 0.126$ dl/g, DH > 99.9 mol %), $D_s = 192$ s⁻¹; (●) HOCH₂CH₂S-PVA ($[\eta]_{AC} = 0.127$ dl/g, DH > 88 mol %), $D_s = 3.84$ and 192 s⁻¹.

showing Newtonian viscosity; however, for HOCH₂CH₂S-PVA the plot gave linearity only below 10 wt % and showed the upward deviation that increased sharply with concentration more than 10 wt % showing structural viscosity. In the aqueous solutions of the fully hydrolyzed PVA, the lower molecular weight PVA has stronger interaction through hydrogen bonding between vinyl alcohol units compared with the higher one, which probably brought about the structural viscosity at low concentration of 10 wt % in HOCH₂CH₂S-PVA. On the contrary the aqueous solution of *n*-C₁₂H₂₅S-PVA showed very high viscosity and much larger dependence on rate of shear than partially and fully hydrolyzed HOCH₂CH₂S-PVA especially in low concentration below 10 wt %, however, the viscosity became close to the viscosity of HOCH₂CH₂S-PVA with an increase in the concentration. This abnormality in the low concentrations was probably caused by the association through hydrophobic interaction between the *n*-dodecyl group at one end described above. The interaction seems to influence the viscosity distinctly only in semiconcentrated solutions, in which the interaction through hydrogen bonding is small and seems to be breakable against the shear stress.

Figure 5 shows the molecular weight dependence on concentration–viscosity relationships in water for

a series of HOCH₂CH₂S-PVAs whose degree of hydrolysis are around 88 mol %, which was adopted to avoid a viscosity increase due to the association through hydrogen bonding described earlier. The polymers used are listed in Table I. The plots of log (viscosity) against concentration gave straight lines up to about 40 wt % for all the samples and the viscosities in aqueous solutions increased with an increase in molecular weight.

Surface Properties of the Aqueous Solutions of the End-Group Modified PVA

Figure 6 shows the surface tensions of the aqueous solutions of the PVAs listed in Table I against logarithmic concentration for HOCH₂CH₂S-PVA and a series of *n*-C_{*n*}H_{2*n*+1}S-PVAs. The surface tensions of all the PVA solutions decreased with a decrease in concentration, depending on the number of carbon atoms of the *n*-alkylthio end group. The plots of the surface tensions at concentrations of 0.001, 0.01, and 0.1 g/100 mL against the number of carbon atoms are shown in Figure 7. The aqueous solutions of *n*-C_{*n*}H_{2*n*+1}S-PVAs of 4 through 6 carbon atoms gave almost the same surface tension, which is slightly smaller than that of HOCH₂CH₂S-PVA, in all range of concentration. The surface tensions, however, decreased with an increase in the number

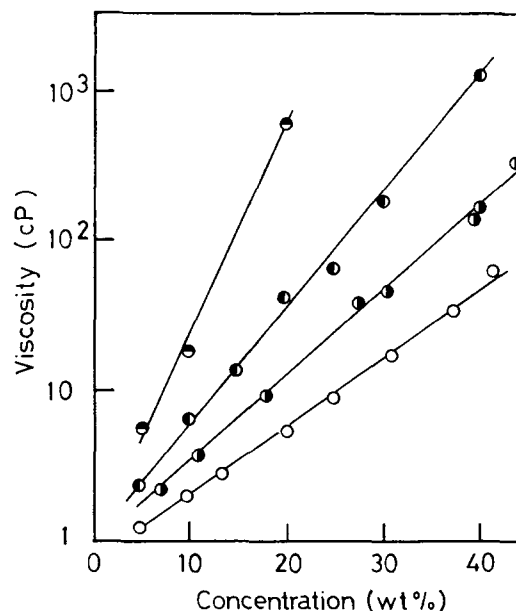


Figure 5 The relationships between concentration and viscosity for the aqueous solutions of 88 mol % hydrolyzed HOCH₂CH₂S-PVA having various molecular weight: (○) $[\eta]_{AC} = 0.0629$ dl/g, (●) $[\eta]_{AC} = 0.0829$ dl/g, (●) $[\eta]_{AC} = 0.127$ dl/g, (●) PVA-205.

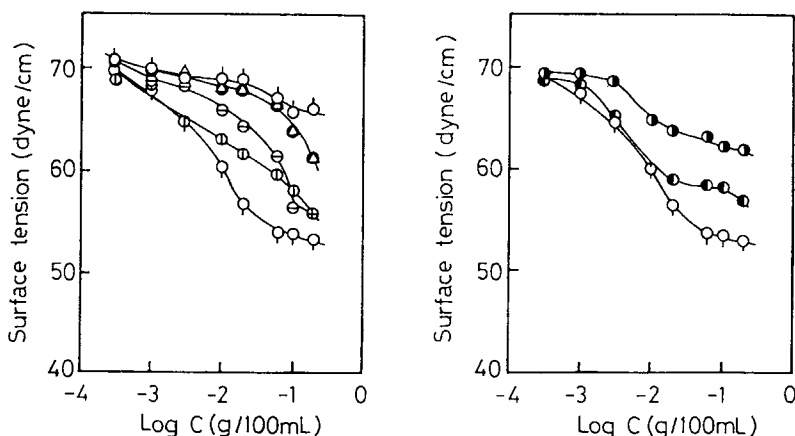


Figure 6 The relationships between concentration and surface tension for HOCH₂CH₂S-PVA and *n*-C_{*n*}H_{2*n*+1}S-PVA of 4 through 18 carbon atoms: (○) HOCH₂CH₂S-PVA, (●) *n*-C₄H₉S-PVA, (△) *n*-C₆H₁₃S-PVA, (⊖) *n*-C₈H₁₇S-PVA, (⊕) *n*-C₁₀H₂₁S-PVA, (○) *n*-C₁₂H₂₅S-PVA, (●) *n*-C₁₆H₃₃S-PVA, (●) *n*-C₁₈H₃₇S-PVA.

of carbon atoms above 8, showed minimum at 12, and then increased. The facts indicate that adsorptions of *n*-C_{*n*}H_{2*n*+1}S-PVA at air-water interface occur easily in the range from 8 through 16 carbon atoms, especially at 12.

Figure 8 shows the variation of the surface tensions of *n*-C₁₂H₂₅S-PVA aqueous solutions, which showed the highest surface activity in a series of *n*-C_{*n*}H_{2*n*+1}S-PVAs, with molecular weight. The polymers used are listed in Table I. The surface tension decreased with an increase in molecular weight, that is, the amounts of adsorption at air-water interface

decreased with an increase in molecular weight. It is probably because of an increase in adsorption area per molecule, that is, adsorption area per *n*-dodecylthio group with increasing in molecular weight. An increase in adsorption area with molecular weight is reported for polyoxyethylene nonylphenol liquid film.¹²

In order to estimate the interfacial activity of HOCH₂CH₂S-PVA and a series of *n*-C_{*n*}H_{2*n*+1}S-PVAs, we carried out the emulsion polymerization of VAc using the PVAs as a protective colloid. The time-conversion curves are shown in Figure 9. When *n*-C_{*n*}H_{2*n*+1}S-PVAs of 10 through 18 carbon atoms

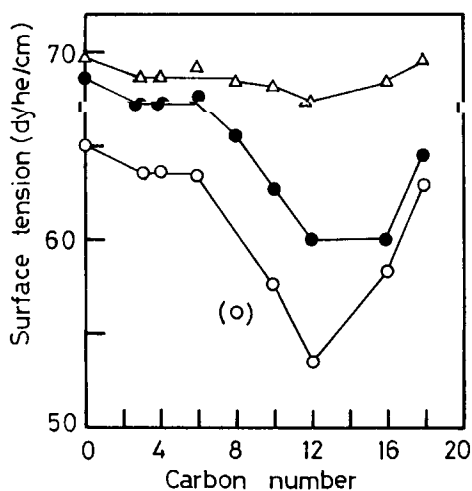


Figure 7 The relationships between the number of carbon atoms of *n*-alkylthio end group and surface tension for aqueous solutions of *n*-C_{*n*}H_{2*n*+1}S-PVA: (△) 0.001 g/dl, (●) 0.01 g/dl, (○) 0.1 g/dl.

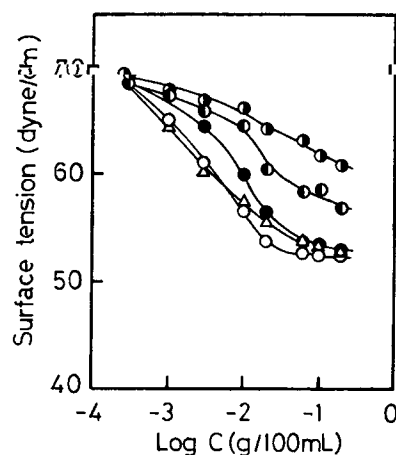


Figure 8 The dependence of molecular weight on surface tension for *n*-C₁₂H₂₅S-PVAs: (○) [η]_{AC} = 0.0478 dl/g, (△) [η]_A = 0.0834 dl/g, (●) [η]_A = 0.126 dl/g, (●) [η]_A = 0.208 dl/g, (●) [η]_A = 0.409 dl/g.

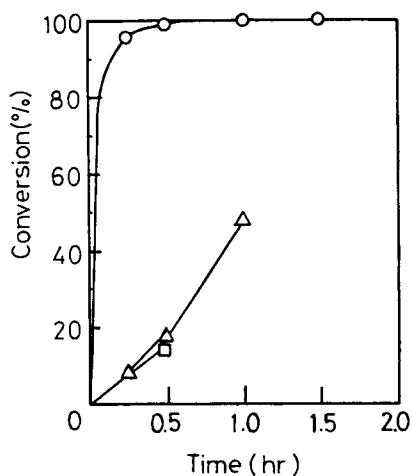


Figure 9 The time-conversion relationships for emulsion polymerization of VAc using the PVAs having a thioether group at one end: (□) HOCH₂CH₂S-PVA, (Δ) *n*-C_{*n*}H_{2*n*+1}S-PVAs of 3 through 6 carbon atoms, (O) *n*-C_{*n*}H_{2*n*+1}S-PVAs of 8 through 18 carbon atoms.

were utilized as a protective colloid, the emulsion polymerization proceeded very fast yielding stable and fine dispersed emulsions (the particle diameter $\sim 0.08 \mu\text{m}$). However, in the cases of HOCH₂CH₂S-PVA and *n*-C_{*n*}H_{2*n*+1}S-PVAs of below 6 carbon atoms, the rates of emulsion polymerization were slow (the particle diameter being extremely large), and the polymerization systems coagulated before the end of polymerization. In the case of *n*-C₈H₁₇S-PVA the polymerization was carried out as successfully as in *n*-C_{*n*}H_{2*n*+1}S-PVAs of above 10 carbon atoms, but the polymerization system coagulated just after finishing polymerization. These facts mean that *n*-C₈H₁₇S-PVA cannot be strongly adsorbed at the interface between polyvinyl acetate and water and so cannot stabilize the emulsion system, in spite of having almost the same ability of lowering the surface tension of the aqueous solution as *n*-C₁₈H₃₇S-PVA described above.

CONCLUSION

Some properties of aqueous solutions of a series of the PVAs having an *n*-alkylthio group of 3 through 18 carbon atoms at one end were investigated.

From the comparison of the intrinsic viscosities of the PVA with that of PVAc corresponding to the PVA, the association caused by *n*-alkyl end group was found to take place on *n*-alkyl groups of 10 through 16 carbon atoms. This is confirmed by measuring the apparent number-average molecular weight of the PVAs in water with vapor pressure osmometer.

The aqueous solutions of *n*-C_{*n*}H_{2*n*+1}S-PVA showed much higher viscosity compared with HOCH₂CH₂S-PVA in low concentration regions of below 10 wt % due to the association of an *n*-dodecyl end group.

Surface tensions of the aqueous solutions of *n*-C_{*n*}H_{2*n*+1}S-PVA showed almost the same value, which was slightly smaller than that of HOCH₂CH₂S-PVA, at 4 and 6 of carbon atoms, lowered with an increase in the number of carbon atoms above 8, showed minimum at 12 and then increased at 16 and 18. In the emulsion polymerization of VAc, *n*-C_{*n*}H_{2*n*+1}S-PVAs of 10 through 18 carbon atoms acted effectively as a protective colloid.

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