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SHORT COMMUNICATIONS

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Polymerization of vinyl acetate in fatty acids and properties of poly (vinyl alcohols) derived from the poly (vinyl acetates)

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Abstract Polymerization of vinyl acetate (VAc) in various fatty acids (carbon numbers 4–18) was carried out. Chain transfer constants to the acids were determined to be 20–35×10^{-4}, from which the constant to a methylene group was obtained to be 0.73×10^{-4}. Viscometry in aqueous solution of derived poly (vinyl alcohol) (PVA) showed the usual behavior in terms of Huggins' constant obtained by the Schulz–Blaschke's equation for PVAs derived from fatty acid systems lower than hexadecanoic acid. PVA derived from octadecanoic acid system showed abnormality, indicating association of alkyl groups. Contact angles on surfaces of PVAs cast from aqueous solutions were measured. While those of PVA derived from lower acid systems were 62°, those of PVAs derived from higher aids were higher and increased to 92° with increase in carbon number to octadecanoic acid. Alkyl groups in the PVAs were estimated to appear on the surfaces. Surface tension of aqueous solution of the PVA derived from octadecanoic acid showed high surface activity, and depended on pH of the solution, indicating the presence and cleavage of lactone ring at the combined portion between PVA and the acid.

Keywords Chain transfer reaction · Vinyl acetate · Fatty acid · Poly (vinyl alcohol) · Surface activity

Introduction

Half a century ago, Noma, Nishiura, and Sakurada studied the polymerization of vinyl acetate (VAc) in the presence of higher alkyl compounds such as alkyl halides [1, 2], higher alcohols [3, 4] and aldehydes [5, 6]. The poly (vinyl acetates) (PVAcs) obtained were of low degree of polymerization of approximately 100. Derived poly (vinyl alcohols) (PVAs) by hydrolyzing the PVAc showed surface-active nature, from which they supposed that alkyl groups were introduced to an end group of the PVA. Imai and Okaya [7] carried out the polymerization of VAc in the presence of various primary alcohols. They found that there were several abnormal properties depending on the lengths of alkyl groups that were introduced to an end group of derived PVAs, such as aqueous solution viscosities [8], surface tensions of aqueous solutions, and contact angles of film surfaces. Although detailed results were not reported, the important ones were summarized briefly [9]. Later Sato and Okaya prepared several PVAs with alkyl groups at one end by polymerizing VAc in the presence of regulated amounts of alkyl thiols [10, 11], and investigated their properties [12–15].

Since PVAc radical is very reactive in chain transfer reactions during the polymerization, especially in chain transfer to electron-deficient portion, fatty acids seem to be efficient reagents to introduce alkyl groups to an end group of PVA. Furthermore, carboxyl groups introduced to the combined portion between alkyl groups and PVA may be useful ones, since they are supposed to form lactone rings with an adjacent hydroxyl groups in PVA. The lactone rings may play an important role to give other functions to the PVA. In this paper, we will describe the polymerization of VAc in the presence of various fatty acids and some properties of derived PVAs from the PVAcs.

Experimental

Materials

Vinyl acetate was of polymerization grade supplied by Kuraray and used as received. Butanoic acid was of GR grade (Nacarai tesque), octanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, and octadecanoic acid were of GR grade (Wako Chemicals). These acids were used as received. Azo-bis-isobutyronitrile (AIBN, Nacarai tesque) was used as received. Commercial PVAs (PVA-105: degree of hydrolysis 98.5, degree of polymerization 500; PVA 420: 80, and 2000: Kuraray) were used after Soxhlet extraction with methanol.

Polymerization of VAc in fatty acid

In a 100 ml three-necked flask containing a magnetic stirrer tip equipped with a thermometer, argon inlet, and outlet tube, prescribed amounts of VAc and fatty acids were introduced and polymerized under argon atmosphere. Polymerization was carried out at 60 °C. A small portion of the reaction liquid was sampled out several times, and poured into large amounts of hexane containing hydroquinone. PVAc was purified three times by dissolving in acetone and precipitating into hexane. Conversion was determined gravimetrically. PVAc was dissolved in methanol, hydrolyzed by usual method with sodium hydroxide, and extracted with methanol with a Soxhlet apparatus.

Measurement

Viscosities of PVA were measured in water at 30 °C using an Ubelohde-type viscometer. Intrinsic viscosity $[\eta]$ and Huggins' constant (k') were determined using the following two equations:

Huggins' equation: $$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C \quad (1)$$

Schulz--Blaschke's equation: $$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]\eta_{sp} \quad (2)$$

Degree of polymerization ($\bar{P}_A$) was calculated by using the following equation [16].

$$[\eta] = 7.50 \times 10^{-1} \bar{P}_A^{0.62} \quad (\mathrm{ml/g})$$

Contact angle was measured using a contact angle meter (Kyowa Surface Science, Type CA-D) at room temperature by droping 1 μl of water on a surface of PVA film of 25 μm that was prepared by casting 5 wt% aqueous solution of PVA on a cleaned glass and drying in a desiccators equipped with phosphorous pentoxide.

Surface tension of PVA aqueous solution was measured with a Wilhelmy surface tension meter (Kyowa Surface Science) at 20 °C.

Results and discussions

Polymerization of VAc in fatty acids

Polymerization of VAc was carried out in butanoic acid, octanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, and octadecanoic acid. An example of time–conversion curve is shown in Fig. 1 for hexadecanoic acid polymerization system. Acceleration in rate of polymerization was observed in Fig. 1, and these were observed in all of the polymerizations depending on conversion and monomer concentration, although the data are not shown here. In the cases of higher fatty acids, the acceleration took place at low conversions. The systems were viscous even before polymerization,

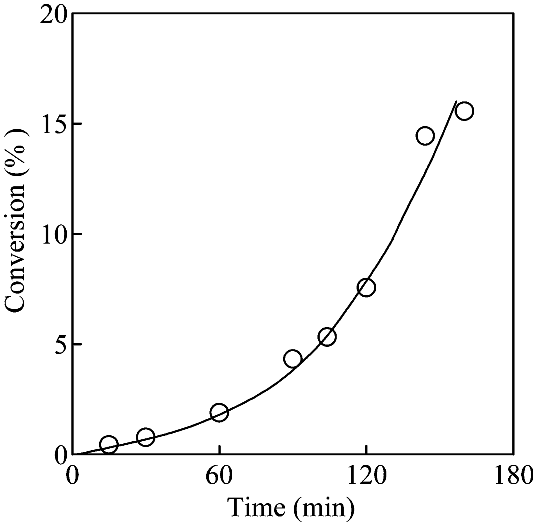


Fig. 1 Time–conversion curve of polymerization of VAc in hexadecanoic acid. VAc: 32.5 ml, hexadecanoic acid: 12.5 ml, AIBN: 0.030 g

and became more viscous with increase in conversions. This is arisen from the well-known gel-effect phenomenon due to the decrease in termination rate constant at high viscosity medium.

To determine chain transfer constant to solvent (fatty acid), the degree of polymerization at conversion 0 was estimated by extrapolating degree of polymerizations at various conversions to conversion 0. Table 1 lists the polymerization results in dodecanoic acid, and degrees of polymerization of derived PVA ($\bar{P}_{\mathrm{A}}$) together with the extrapolated ones ($\bar{P}_{\mathrm{A},0}$). Chain transfer constants to various fatty acids can be determined by Eq. 3, where C_{M}, C_{S}, and C_{P} are the chain transfer constants to monomer, solvent (fatty acid), and vinyl acetate unit in PVAc, respectively, where [S],

$$\frac{1}{\bar{P}_{\mathrm{A}}} = C_{\mathrm{M}} + C_{\mathrm{S}}\frac{[\mathrm{S}]}{[\mathrm{M}]} + C_{\mathrm{P}}\frac{[\mathrm{P}]}{[\mathrm{M}]} + \frac{(1+\lambda)k_t R_{\mathrm{p}}}{2k_{\mathrm{p}}^2[\mathrm{M}]^2} \tag{3}$$

[P], and [M] are the concentrations of solvent, PVAc expressed by monomer unit, and monomer, respectively, λ is the ratio of disproportionation termination in total termination reaction, k_{t}, and k_{p} denote the rate constants of termination and propagation reactions, respectively, and R_{p} denotes the rate of polymerization. In the polymerization of VAc at 60 °C, the fourth term on right-hand side containing rate of polymerization can be neglected when compared with the chain transfer terms, and the chain transfer to PVAc is removed at conversion 0. Hence Eq. 4 is obtained. Using $\bar{P}_{\mathrm{A},0}$ in Table 1 as $\bar{P}_{\mathrm{A}}$, we can obtain C_{s} from the slopes of straight lines shown in Fig. 2, where four sets of polymerization systems are plotted (carbon numbers in fatty acids: 4, 8, 16, and 18). The C_{M} value was taken as 2.0×10^{-4} as reported by Matsumoto and Maeda [17], and shown in Fig. 2 as a solid square.

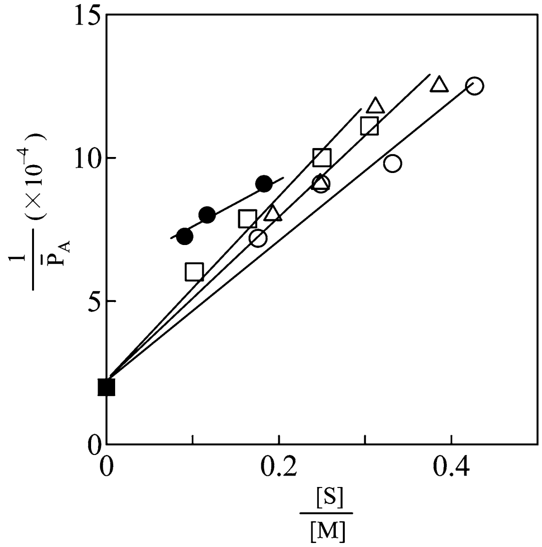


Fig. 2 Relationships between [S]/[M] and reciprocal $\bar{P}_{\mathrm{A}}$. Number of carbon atoms in fatty acid: *open circle* 4, *open triangle* 8, *open square* 16, *filled circle* 18, *filled square* from Ref. [17]

$$\frac{1}{\bar{P}_{\mathrm{A}}} = C_{\mathrm{M}} + C_{\mathrm{S}}\frac{[\mathrm{S}]}{[\mathrm{M}]} \tag{4}$$

In the case of hexadecanoic acid system, polymerization became inhomogeneous with increasing conversion. This means that precipitation took place because of decrease in VAc in a mixture of hexadecanoic acid and VAc, since PVAc is not soluble in higher fatty acids. Accordingly the values of $\bar{P}_{\mathrm{A}}$ are not reliable in this case, which is the reason of the deviation of the plots from straight line to some extent. In the case of octadecanoic acid system, the line differs remarkably from the others. This is caused by the inaccuracy of the intrinsic viscosity, which will be described later.

In Table 2, the chain transfer constants are listed to various fatty acids. They are rather large values to be $20–35\times10^{-4}$, with one exception, i.e., C_{S} to acetic acid being 0.17×10^{-4} [18]. This indicates the lower reactivity of hydrogen in methyl groups compared with one in

Table 1 Polymerization results in dodecanoic acid

VAc/dodecanoic acid (vol/vol)	Conversion (%)	($\bar{P}_{\mathrm{A}}$)	($\bar{P}_{\mathrm{A},0}$)
70/30	22.7	1,230	1,250
	32.3	1,200	
	43.6	1,170	
	53.9	1,110	
60/40	22.1	920	940
	34.6	870	
	47.0	830	
	63.7	810	
55/45	20.9	810	820
	35.4	800	
	50.5	760	
	73.5	710	
50/50	13.6	730	740
	21.9	710	
	41.4	660	
	49.7	590	

Table 2 Chain transfer constants to various fatty acid

Fatty acid	Chain transfer constant ($\times10^{-4}$)
Acetic acid	0.17[a]
Butanoic acid	26
Octanoic acid	28
Dodecanoic acid	32
Tetradecanoic acid	33
Hexadecanoic acid	34
Octadecanoic acid	21

[a] From Ref. [18]

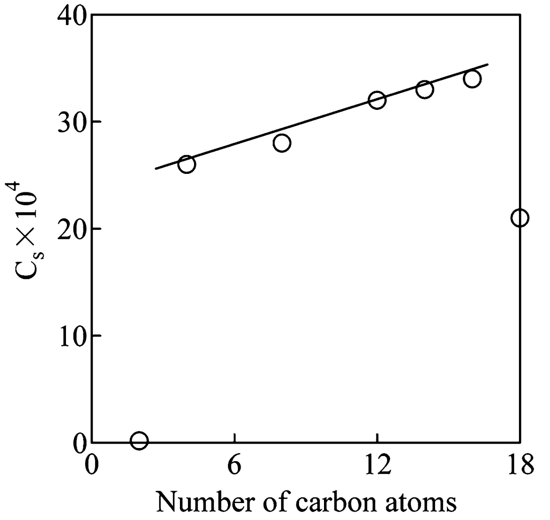


Fig. 3 Relationship between number of carbon atoms in fatty acid and C_S

methylene groups. Chain transfer to fatty acids takes place at α-hydrogen to carboxyl group, since the electron-deficient position is reactive against the PVAc radical with donor nature, and resulting radical is stabilized by conjugation with carbonyl group. However, chain transfer to other hydrogens may occur to some extent. Slight increase in C_S with increase in carbon numbers in the fatty acids, listed in Table 2, may be arisen from the chain transfer to methylene groups. Figure 3 shows the relationship between carbon numbers in the fatty acids and C_S. From the slope of the straight line, chain transfer constant to a methylene group was obtained to be 0.73×10^{-4}.

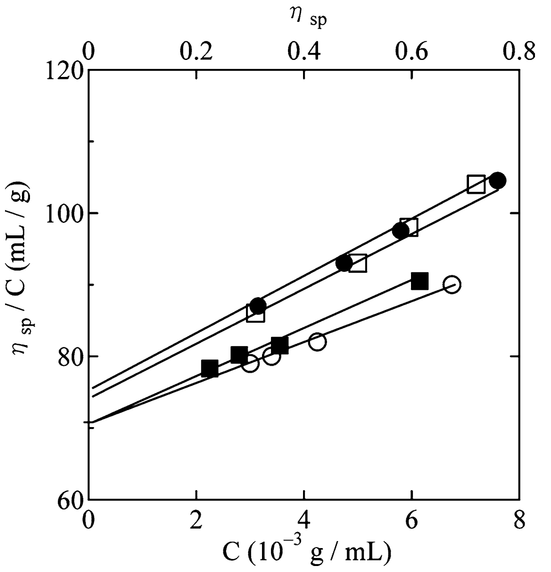


Fig. 4 Huggins' plots and Schulz–Blaschke's plots for viscometry of aqueous solutions of PVAs derived from hexadecanoic acid system. *PVA* polymerized at VAc/hexadecanoic acid being 32.5/12.5 ml; *open circle*, *filled circle*: conversion 18.0%; *open square*, *filled square*: conversion 24.4%; open mark: Huggins' plots; solid mark: Schulz–Blaschke's plots

Investigation of the behavior of PVA aqueous solutions

In the viscometry of aqueous solution of PVA, Huggins' constant k' in Eqs. 1 and 2 gives useful information of solution behavior of PVA in water [8]. According to Yamakawa [19], k' should be less than 0.5. Infact Huggins' constants, k'_H, obtained from Eq. 1, are much larger than 0.5, while those, k'_S, obtained from Eq. 2, are less than 0.5 for ordinary PVA [8]. Since Eq. 1 involves inevitable errors due to omitting the higher terms, Eq. 2 that is identical with Eq. 1 before omitting higher terms should be utilized [20]. In Fig. 4 some examples of k'_H and k'_S obtained in viscometry on PVA derived from hexadecanoic acid system are shown. From the slopes of Fig. 4, Huggins' constants can be calculated. Table 3 lists the intrinsic viscosities and Huggins' constants of PVAs derived from hexadecanoic acid system at various feed ratios of VAc to hexadecanoic acid. In Table 3, $[\eta]_H$ was smaller than $[\eta]_S$ to some extent, and k'_H was clearly larger than k'_S, which was similar tendency to the results of ordinary PVAs already reported [8].

To investigate the abnormality in aqueous solution behavior of PVAs derived from various fatty acid systems, Huggins' constants were plotted against intrinsic viscosities as shown in Fig. 5. There existed two groups in k'_S versus $[\eta]$: less than 0.5, and more than 0.5 groups. The former was for PVAs polymerized and derived in fatty acids lower than hexadecanoic acid. The relation of intrinsic viscosities and Huggins' constants coincides with that of ordinary PVAs [8] within experimental errors. The latter was for PVA derived from octadecanoic aid system. The values of k'_S were clearly larger than the others. This indicates that the PVA with octadecanoic acid moiety at an end group behaves differently in aqueous solution from the PVAs with lower acid moieties at an end group. This is arisen from the

Table 3 Intrinsic viscosities and Huggins' constants of aqueous solutions of PVA derived from hexadecanoic acid system

Vac/hexadecanoic acid (vol/vol)	Conversion (%)	$[\eta]_H$ (ml/g)	k'_H	$[\eta]_S$ (ml/g)	k'_S
75/25	5.4	67.4	0.68	68.9	0.45
	15.5	74.3	0.67	76.2	0.37
65/35	18.0	70.5	1.55	74.6	0.52
	24.4	73.5	0.66	70.2	0.47
55/45	14.1	62.1	0.73	63.6	0.53
	43.6	57.5	0.86	62.3	0.46
50/50	19.9	54.9	0.63	54.7	0.58
	23.3	51.7	1.07	57.2	0.48

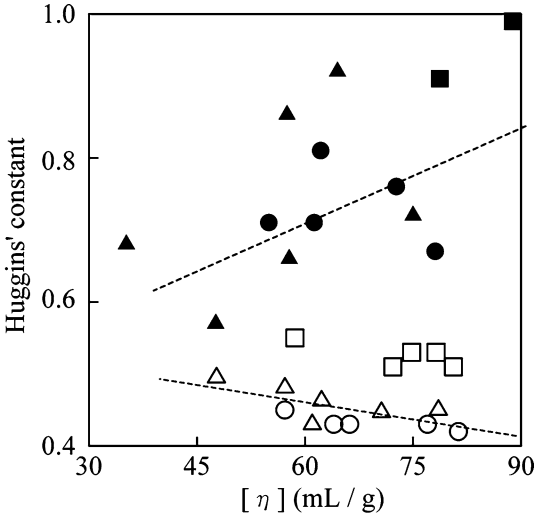


Fig. 5 Relationship between intrinsic viscosity and Huggins' constant of aqueous solution of PVAs with various end groups. Number of carbon atoms: *open circle*, *filled circle* 1–8; *open triangle*, *filled triangle* 12–16; *open square*, *filled square* 18; open mark: k'_S; solid mark: k'_H; dotted lines: for conventional PVA [8]

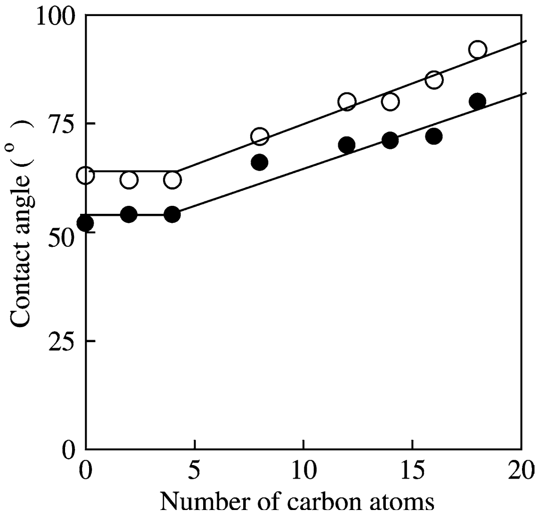


Fig. 6 Contact angles of films of PVA with various end groups *open circle*: as prepared, *filled circle*: heat treated at 160 °C

interaction of long alkyl end groups between molecules, resulting in association of the molecules [8, 12]. In this case the degrees of polymerization of PVA calculated from the intrinsic viscosities becomes larger and does not show the true values. This is the reason for the deviation of the PVA derived from octadecanoic acid system in Fig. 2.

Contact angles on surface of films of PVAs derived from fatty acid systems

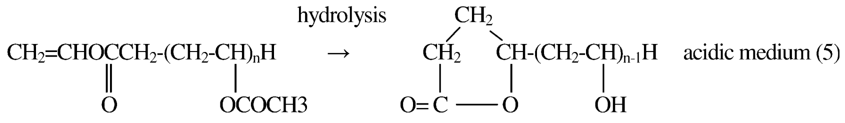
Contact angles of water were measured on the surfaces of films of PVAs derived from various fatty acid systems. The films were subjected to measurement as prepared and after heat-treatment at 160 °C for 10 min. Figure 6 shows the relationship between the contact angles and number of carbon atoms in fatty acids. Contact angles of PVAs derived from fatty acid systems lower than butanoic acid were 62° and 53° for the films as prepared and heat treated, respectively. They increased with increase in number of carbon atoms to 92° (as prepared) and 80° (heat treated) for the film of PVA derived from octadecanoic acid system. This indicates that alkyl groups in fatty acid moieties higher than octanoic acid bound to an end group of PVA are present selectively on the surfaces of the PVA films during the film formation, while those in fatty acid moieties lower than butanoic acid are not present on the surfaces of PVA films. In other words, the films of PVAs with the higher alkyl groups have water-repellent properties. It is interesting that contact angles of heat-treated films are lower than those as prepared. This may means that rearrangement of alkyl groups on the surfaces takes place with heat-treatment at 160 °C in accordance with motion of amorphous part of PVA, since glass-transition temperature of PVA is 80 °C.

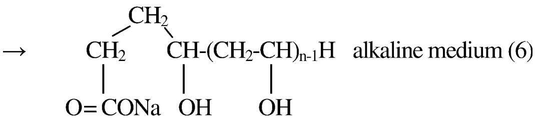
Surface tensions of aqueous solutions of PVAs derived from fatty acid systems

According to Amiya [21], there exist lactone-rings in PVA end groups when PVA is in acidic aqueous solution or prepared from the acidic medium. He measured ^{1}H NMR of PVA in D_2O that was derived from polymerization of α,β,β-trideuterated VAc. The lactone-rings are cleaved in alkaline condition to result in sodium carboxylate. These are shown as below.

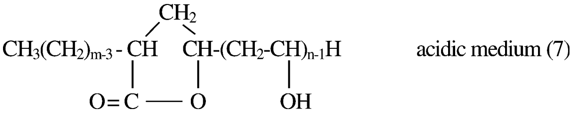
Since in the chain transfer reactions to fatty acids, hydrogen abstraction must occur at methylene group adjacent to carboxyl one, PVAs with a fatty acid moiety at an end group are expected to have the following structures, where *m* denotes carbon number in the acids, although these are not confirmed in this study.

Scheme 1

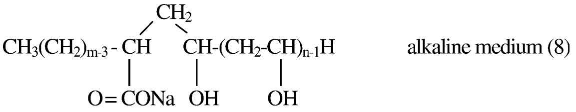




Scheme 2



Scheme 3



Scheme 4

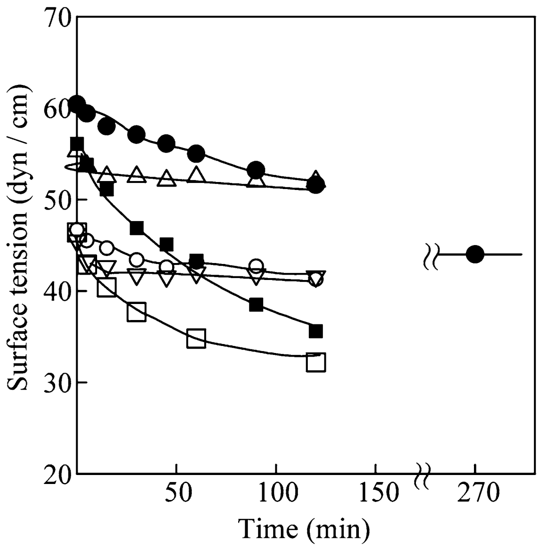


Fig. 7 Dependence of surface tensions of PVA aqueous solutions on standing time at acidic and alkaline media *open circle*, *filled circle*: derived from dodecanoic acid system; *open square*, *filled square*: derived from octadecanoic acid system; *open triangle*: PVA-105; *open inverted triangle*: PVA-420; open mark: at pH 6; solid mark: at pH 10

Accordingly pH of the medium must be taken into account when surface tensions of PVAs in aqueous solutions are measured. Surface tensions of aqueous solutions of PVAs derived from dodecanoic acid and octadecanoic acid systems were measured at various standing times. Figure 7 shows the results measured at 0.3 g/100 ml concentration. The PVA with octadecanoic acid moiety has high surface activity in aqueous solution, while with dodecanoic acid moiety has medium surface activity, compared with commercial two PVAs (PVA-105, and PVA-420). At pH 10, both of the PVA aqueous solutions showed lower surface tensions when compared to those at pH 6. This may be due to the change in the combined portions of PVA and fatty acid described above. In alkaline medium, hydrophilic nature at the portion seems to restrict the movement of alkyl chains to water surface. Long time was necessary for the surface tensions of PVAs with alkyl groups to become equilibrium, and it was remarkable at pH 10. This must be a characteristic of polymer surfactants.

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