



## RESULTS AND DISCUSSION

The properties of the acetalized PVAs are summarized in Table I. Acetalized group content was about 60–80 mol%. The glass transition temperatures ( $T_g$ ) decreased with increasing length of the methylene side chain, but the decomposition temperatures ( $T_d$ ) were almost the same.

Figure 2 shows the surface pressure-area curves of acetalized PVA on distilled water. The curves had shoulders which differed according to side chain length. The pressure at the shoulder increased and the slopes of the curves were higher with longer side chains. Thus, the monolayers of acetalized PVA were more stable when the length of methylene in the side chain was long rather than short. It was found from the results of compression-expansion recycle test that collapse occurred above the pressure in the plateau region as shown in Figure 2. Its plateau region might be due to conformational change. Limiting areas per repeat unit were determined as extrapolated areas at the zero pressure for the condensed region below the shoulder. In order to eliminate the influence of the different acetal group content, limiting areas per acetal unit were estimated assuming that limiting area of PVA is  $12\text{\AA}^2/\text{unit}$ .<sup>10</sup> The calculation method is as follows,

$$\text{Area per acetal unit} = [A - 12x(1-x)]/X$$

$A$  = Area per unit determined from Figure 2.

$X$  = Mole fraction of acetal group content.

Figure 3 shows the effect of side chain length on limiting area. It was found that the limiting area of acetalized PVA tended to a constant value with increasing length of the methylene side chain. This constant value of about  $32\text{\AA}^2/\text{acetal unit}$  is rather in reasonable agreement with the molecular model of acetalized PVA, assuming that the main chain lies flat on the water and the side chain is above the main chain.

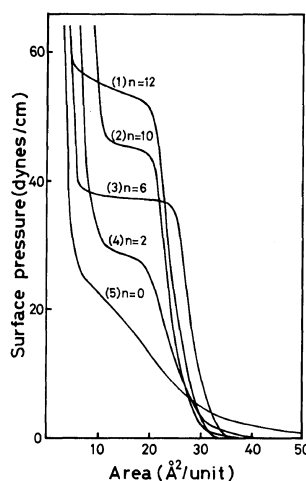
**Table I.** Properties of acetalized PVA

Polymer	$X/\text{mol}\%$ <sup>a</sup>	$T_g/^\circ\text{C}$ <sup>b</sup>	$T_d/^\circ\text{C}$ <sup>c</sup>
AA-PVA	61.00	116.0	340
BuA-PVA	71.90	60.0	317
OA-PVA	75.05	25.0	337
DDA-PVA	72.60	13.0	350
TeDA-PVA	76.40	4.8	347

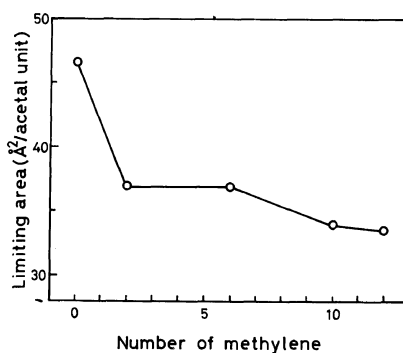
<sup>a</sup> Determined by elemental analysis.

<sup>b</sup> Measured by DSC.

<sup>c</sup> Measured by TG-DTA.



**Figure 2.** Surface pressure-area curves of acetalized PVA on distilled water. (1) TeDA-PVA; (2) DDA-PVA; (3) OA-PVA; (4) BuA-PVA; (5) AA-PVA; subphase temp,  $10.0\text{--}10.5^\circ\text{C}$ .



**Figure 3.** Effect of side chain length on limiting area.

The conditions for depositing acetalized PVA monolayers onto silicon and chromium substrates are shown in Table II. Silicon

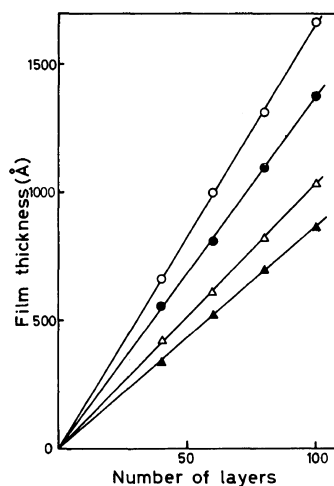
**Table II.** Deposition conditions of acetalized PVA

Polymer	Subphase temp/°C	Surface pressure /dyn cm <sup>-1</sup>	Deposition		
			Substrate	No. of layers	Ratio
AA-PVA	11.8	10	Si	—	—
BuA-PVA	11.0	25	Si	50	0.98
OA-PVA	10.5	30	Si	40	0.99
DDA-PVA	10.8	32	Si	50	0.98
TeDA-PVA	10.6	36	Si	40	1.00
OA-PVA	13.1	10	Cr	103	0.68
OA-PVA	13.5	20	Cr	70	0.87
OA-PVA	13.5	30	Cr	73	0.94
OA-PVA	9.5	20	Cr	7	0.50

was cleaned with hydrofluoric acid and chromium was cleaned with a mixture of hydrogen peroxide and sulfuric acid (1:3) in order to make hydrophobic and hydrophilic surfaces, respectively. With the exception of AA-PVA, monolayers of acetalized PVA were easily deposited onto hydrophobic and hydrophilic substrates. The resulting multilayers were Y type. Deposition ratios were influenced by subphase temperature and surface pressure.

Figure 4 shows the relationship between the number of layers and thickness of multilayers as measured by ellipsometry. It is clear from Figure 4 that each case gives a linear relationship, showing the thicknesses of multilayers to be proportional to the number of layers, and the thicknesses of multilayers to be higher with increasing length of the methylene side chain at a set number of layers. This was also found to be the case when a Talystep mechanical stylus was used.

In summary, monolayers of acetalized PVA having long alkyl side chains were stable on water and could be deposited onto various substrates. The obtained LB films of acetalized PVA having long alkyl side chains are well-ordered with the side chain directed normal to the main chain. More detailed characteristics of monolayers and multilayers of acetalized PVAs and their applications in electronics will be published in the near



**Figure 4.** Relationship between number of layers and thickness of multilayers.<sup>a</sup> (○) TeDA-PVA; (●) DDA-PVA; (△) OA-PVA; (▲) BuA-PVA.

<sup>a</sup> Measured by ellipsometry.

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## REFERENCES

1. V. Enkelmann and J. B. Lando, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1843 (1977).
2. G. L. Larkins, Jr., C. W. Burknart, E. D. Thompson, J. B. Lando, and E. Ortiz, *Thin Solid Films*, **99**, 277 (1983).
3. K. Fukuda, Y. Shibasaki, and H. Nakahara, *Thin Solid Film*, **99**, 87 (1983).
4. K. Fukuda and T. Shiozawa, *Thin Solid Films*, **68**, 55 (1980).
5. G. Lieser, B. Tieke, and H. Wegner, *Thin Solid Films*,

- 68, 77 (1980):
6. A. Barraud, C. Rosilio, and A. Ruauadel-Teixier, *Thin Solid Films*, **68**, 91 (1980).
  7. R. H. Tredgold and C. S. Winter, *Thin Solid Films*, **99**, 81 (1983).
  8. H. Noma and T. Koh, *Kobunshi Kagaku*, **4**, 123 (1943).
  9. H. Noma, T. Koh, and T. Tsuneta, *Kobunshi Kagaku*, **6**, 439 (1949).
  10. D. J. Crisp, *J. Colloid. Sci.*, **1**, 49 (1946).