The Stereoregularity-Fractionation of Polyvinyl Alcohol by Foaming

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It has been found that several properties of polyvinyl alcohol (PVA), probably related to its stereoregularity, vary with the polymerization conditions of the polyvinyl acetate from which PVA is derived[1]. Therefore, one method to obtain PVA differing in regularity is to control the conditions of the polymerization. As a complementary method, we have evolved a method for separating PVA into fractions differing in regularity. Besides being interesting for its own sake, such a fractionation procedure should give a method for determining the stereoregularity distribution of PVA. We found that PVA can be separated into fractions of different stereoregularity by foaming an aqueous solution of the polymer. Although it is well known that foams can serve to separate substances of different chemical structures[2], the foam method seems not yet to have been applied in the stereoregularity fractionation of polymers. The present report may, therefore, be the first communication about it.

Experimental

Three samples of PVA of differing stereoregularity were used. These samples are listed in Table I.

The fractionation procedure was as follows: a 1$\sim$2% aqueous solution of fully hydrolyzed PVA derived from polyvinyl acetate was placed in a 1$\sim$5 l. wide-mouthed bottle. The bottle was then shaken at a frequency of 100 cycl. per minute with an amplitude of 6.7 or 10.8 cm. on a horizontal shaker; a foam layer was thus created. After being shaken for a certain time, the solution was allowed to stand for more than 15 hr. In the course of this standing, part of the foam usually disintegrated and drained down, but the remaining layer was separated and the PVA contained in the foam was collected. The residual solution usually became cloudy, and a slight amount of gel precipitated at the bottom of the bottle. To obtain successive fractions, the cloudy solution was heated until it became a completely clear and uniform solution

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[1] Reference to literature appeared in *J. Polymer Sci.*, 55, 335 (1961).

[2] J. J. Bikermann, "Foams", Reinhold, New York (1953), p. 171; T. Sasaki, "Zikken Kagaku Koza", Vol. 7 Maruzen, Tokyo (1956), p. 215.

TABLE I. POLYMERIZATION CONDITIONS OF ORIGINAL POLYVINYL ACETATE FOR PVA SAMPLES

No.	Polymerization temp., °C	Polymerization medium		Initiator	Conversion %	PVA	
		Form	Concn. wt. %			$[\eta]$[a] dl./g.	Degree of polymerization
L-O-43	0	Methyl alcohol	40	Photosensitized with azobis compound	13	0.811	1510
W-6	60	Methyl alcohol	20	AIBN[b]	50	0.866	1680
DM32-2, 3	80	Dimethyl sulfoxide	50	AIBN[b]	63	0.878	1710

a) Measured in water at 30°C b) 2, 2′-Azobis-isobutyronitrile

TABLE II. D_{620} AND 1, 2-GLYCOL CONTENT OF PVA OBTAINED FROM THE FOAM LAYER

Fraction No.	Concn. of PVA g./l.	Amount of solution kg.	Capacity of bottle l.	Amplitude of shaking cm.	Shaking time day	PVA				
						Yield %	$[\eta]$ dl./g.	Degree of polymerization	D_{620}	1, 2-Glycol structure mol. %
S1-F1	19.8	2.5	5	6.7	1	5.3	0.895	1760	0.96	1.02
S4-F1	20.2	2.5	5	6.7	1	2.5	0.878	1710	0.73[a]	—
S5-F1	18.9	2.7	5	6.5	1	3.7	0.870	1690	0.83	—
S2-F1	20.1	2.5	5	6.7	3	15	0.927	1860	0.83	1.06
S3-F1	10.4	2.5	5	6.7	1	6.5	0.949	1930	0.91	1.04
S7-F1	10.2	1.0	2	10.8	1	11	1.00	2100	0.81	—
S8-F1	10.2	0.5	2	10.8	1	44	0.986	2050	0.48	—
S6-F1	9.8	0.5	1	10.8	1	14	0.952	1940	0.73	—
W-6[b]	—	—	—	—	—	—	0.866	1680	0.23	1.13

a) Standing time from cessation of shaking to separation of foam was only 2 hr.
b) Original unfractionated PVA

and then the procedure involving shaking, standing, separation and heating was repeated.

We have found that the color reaction of PVA with iodine-iodide in an aqueous solution can be used as a measure of the stereoregularity of PVA[3]. An absorption peak is produced at 620 mμ by the iodine-PVA complex when it is prepared under specified conditions, and the absorbance at this wavelength, D_{620}, is used as a quantitative index of the color reaction. According to some unpublished data of the authors and of K. Fujii, the color reaction does not occur for isotactic PVA, but since it appears to depend on the degree of syndiotacticity of PVA, the D_{620} value may be used as a parameter of the syndiotacticity for PVA samples having the same degree of polymerization. Strictly speaking, it is not certain whether the color reaction is due simply to the existence of the fraction of syndiotactic linkage or to their regular sequence length.

Results and Discussion

The D_{620} values of PVA contained in the foam layers are illustrated in Table II in comparison with that of the original PVA. The degree of the polymerization of the PVA contained in the foam layers is approximately the same as that of the original PVA, but the D_{620} value of the former is quite different from that of the original. In general, the values of the former exceed that of the latter.

Since the D_{620} value depends on the degree of polymerization, a difference in molecular weight distribution between the original PVA and the sample obtained from the foam layer could theoretically explain the observed color-test difference. However, the dependence of the D_{620} value upon the degree of polymerization is not strong enough to make this likely. For example, if the PVA sample is fractionated by a precipitation method from a solvent (water)-non-solvent (*n*-propyl alcohol)-mixture, the D_{620} values range from 0.08 for DP=639 up to only 0.31 for DP=3960. Even at this latter value, the sample lies well below the 0.5 to 1.0 range found in the foam layer in Table II.

The 1, 2-glycol content of the PVA from the foam layer is slightly less than that of the original, this also might be a cause of the different D_{620} value. However, since the difference in content of the 1, 2-glycol structure is quite small, the predominant cause of the different D_{620} value was considered to be the tacticity of the sample. From the results of Table II, it may be concluded that the stereoregularity, probably the syndiotacticity, of the PVA obtained from the foam layer is larger than that of the original PVA.

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3) K. Imai and M. Matsumoto, *J. Polymer Sci.*, 55, 355 (1961).

TABLE III. SUCCESSIVE FRACTIONATION OF PVA L-O-43 BY REGULARITY
(Capacity of bottle, 2 l.; amplitude of shaking, 10.8 cm.)

Fraction No.	Concn. of PVA g./l.	Amount of solution l.	Shaking time hr.	Foam volume l.	PVA			
					Yield %	$[\eta]$ dl./g.	Degree of polymerization	D_{620}
F1	9.54	1.0	2	1.7	2.7	8.46	1620	3.05
F2	—	1.0	4	1.4	5.3	8.84	1730	2.94
F3	—	1.0	8	1.3	10.9	9.06	1800	2.51
F4	—	0.9	24	1.5	34.3	9.57	1960	1.66
F5	—	—	24	0.6	7.1	8.92	1750	0.54
F6	—	0.8	24	0.5	2.2	8.25	1550	0.38
F7	4.55	0.8	50	0.4	2.1	7.48	1330	0.23
F8[a)]	11.0[a)]	0.3[a)]	24	0.1	1.3	7.14	1410	0.10
F9	—	—	—	—	34.1	5.94	928	0.02
F0[b)]	—	—	—	—	—	8.11	1510	1.11

a) Shaken with 1 l. bottle after concentration
b) Original unfractionated PVA, L-O-43

TABLE IV. SUCCESSIVE FRACTIONATION OF PVA W-6 BY REGULARITY
(Capacity of bottle, 5 l.; amplitude of shaking, 6.7 cm.)

Fraction No.	Concn. of PVA g./l.	Amount of solution l.	Shaking time day	Foam volume l.	PVA					
					Yield %	$[\eta]$ dl./g.	Degree of polymerization	D_{620}	Swelling degree	Solubility %
F1	18.88	2.7	1	3.5	3.67	0.870	1690	0.83	1.74	7.5
F2	18.64	2.5	1	3.1	5.21	0.858	1650	0.74	1.97	8.1
F3	—	2.4	1	3.5	6.25	0.899	1770	0.49	—	—
F4	—	2.3	1	3.5	6.19	0.908	1800	0.41	—	—
F5	16.16	2.2	1	3.5	6.97	0.938	1900	0.53	—	—
F6	—	2.2	1	3.3	6.35	0.938	1900	0.42	2.04	9.8
F7	—	2.1	1	3.4	5.50	0.941	1910	0.41	—	—
F8	—	1.9_5	1	2.8	3.80	0.929	1870	0.27	—	—
F9	—	1.9_5	1	2.0	5.44	0.949	1930	0.23	—	—
F10	12.60	1.9	1	2.5	3.86	0.939	1900	0.19	2.24	10.8
F11	—	1.8	1	3.0	3.33	0.955	1950	0.19	—	—
F12	—	1.7	1	3.0	2.41	0.923	1840	0.15	—	—
F13	—	1.7	1	3.0	4.02	0.921	1840	0.12	—	—
F14	—	1.6	1	2.5	3.01	0.926	1860	0.10	—	—
F15	11.14	1.5_5	2	1.1	8.64	0.882	1720	0.04	2.26	12.0
F16	—	1.5	2	0.8	5.94	0.850	1630	0.02	—	—
F17	—	1.3_5	2	0.6_5	2.89	0.835	1580	0.01	—	—
F18	—	1.1	2	0.6	1.37	0.809	1500	0.01	3.27	19.3
F19	—	1.1	2	0.4	0.78	0.784	1430	0.00	—	—
F20	6.80	1.1	1	0.4	0.75	0.809	1500	0.01	—	—
F21	—	1.0_5	2	0.3	0.52	0.728	1280	0.00	—	—
F22	—	0.9_5	2	0.3	1.00	0.733	1290	0.00	—	—
F23	6.10	0.9	—	—	12.08	0.570	870	0.00 (0.00)[a)]	3.37 (3.68)[a)]	27.4 (30.4)[a)]
F0[b)]	—	—	—	—	—	0.866	1680	0.23	2.2	—

a) For the sample performed a further treatment to decrease any residual acetyl group of PVA.
b) Original unfractionated PVA, W-6

TABLE V. SUCCESSIVE FRACTIONATION OF PVA DM32-2, 3 BY REGULARITY
(Capacity of bottle, 2 l.; amplitude of shaking, 10.8 cm.)

Fraction No.	Concn. of PVA g./l.	Amount of solution l.	Shaking time hr.	Foam volume l.	PVA			
					Yield %	[η] dl./g.	Degree of polymerization	D_{620}
F1	9.53	1.0	4.5	0.9	2.8	0.938	1900	0.07
F2	—	1.0	48	0.7	6.3	1.02	2150	0.03
F3	—	1.0	72	0.6	5.4	1.02	2160	0.03
F4	—	1.0	72	0.4_5	3.9	1.01	2120	0.02
F5	8.17	1.0	72	0.3	4.6	0.945	1920	0.01
F6	—	0.9	72	0.2	2.1	0.992	2070	0.00
F7	—	0.9	—	—	74.4	0.824	1550	0.00
F0[a]	—	—	—	—	—	0.878	1710	0.00

a) Original unfractionated PVA, DM32-2, 3

Tables III, IV and V show the results of three successive fractionations of PVA by foaming. From the properties and polymerization conditions, the stereoregularity order of the PVA used is as follows:

L-O-43 (Table III) > W-6 (Table IV) >
DM32-2, 3 (Table V)

Polyvinyl alcohol W-6 is an ordinary one and the same as the original PVA in Table II.

As may be seen in every table, the degree of the polymerization of PVA in each fraction is not constant, but increases slightly with an increase in the fraction number and then decreases again. On the other hand, as the fractionation progresses, the D_{620} value decreases and the swelling degree and solubility increase, suggesting that the sample is being separated according to regularity, i. e., syndiotacticity.

It is well-established that the lower the polymerization temperature of vinyl acetate, the more stereoregular the PVA obtained. Therefore, when PVA prepared by a low temperature polymerization is fractionated by the foam method, it is to be expected that the first fraction will furnish an extremely stereoregular PVA. Such a result is illustrated in Table III. The D_{620} value for PVA F1 in this table is 3.05, much larger than the 0.23 of an ordinary PVA W-6. This indicates that the F1 fraction is highly regular.

According to unpublished data collected by the present authors, the regularity of PVA is responsible for the foaminess of its aqueous solution; the foaminess of the solution increases with an increase in the regularity. This behavior seems to relate more closely to foam stability than to foaming capacity because the foam volume formed by a blowing method remains nearly constant, independent of the polymerization conditions of the parent ester polymer of PVA[4]. On the other hand, it is known that the aging of a concentrated aqueous solution of PVA depends upon such polymerization conditions as the temperature[5] and the solvent[4] used; it has also been observed that the regular polymer shows greater aging.

Furthermore, aqueous solutions of PVA have a tendency to gel at an air-water interface[6]. It is, therefore, believed that foam stabilization due to aging is a basic factor in the performance of fractionation according to regularity. When a blowing method is applied in the foam formation, PVA is not separated in regularity[4]. This is considered to be due to the fact that foam formation occurs more easily in the blowing method than in the shaking method, but foam rupture occurs more easily in the latter than in the former. To fractionate effectively, foaming alone is not sufficient; a proper breaking of the foam seems also to be required.

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