

Effect of 1,2-Glycol Structure and Stereoregularity of Poly(vinyl alcohol) on Poly(vinyl alcohol)—Iodine Reactions*

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ABSTRACT: The poly(vinyl alcohol)—iodine blue color reaction in dilute aqueous solution was investigated at 6–8°C and extinctions at the absorption maximum were measured as a function of the 1,2-glycol content and stereoregularity of poly(vinyl alcohol) (PVA). Increase in the 1,2-glycol content and in the isotacticity caused remarkable decrease in the color intensity. In particular, the reaction mixture was almost colorless when the 1,2-glycol content exceeded 5 mol% or the isotacticity was more than 70%. Wave length of the absorption maximum of the reaction mixture was not affected by the 1,2-glycol content (608 m μ), whereas the maximum was shifted to a shorter wave length with an increase of isotacticity. It is suggested that the 1,2-glycol structure simply decreases the content of the PVA—iodine complex. The sequence length of 1,3-glycol units required for the color reaction of atactic PVA was estimated to be about 120. The isotactic structure, on the other hand, may not only disturb the formation of the complexes, but may also affect their structure.

KEY WORDS Poly(vinyl alcohol)/1,2-Glycol Structure/Stereoregularity/PVA—Iodine Reaction/Iodine/Sequence Length/Color Reaction/

Various physical properties of poly(vinyl alcohol) (PVA) may be affected by molecular weight, 1,2-glycol structure, residual acetate group, branching, stereoregularity etc. PVA samples with different stereoregularities was prepared to study qualitatively the effect of stereoregularity on crystallinity, solubility in water and so on¹. It has also been ascertained that an increase in the 1,2-glycol content lowers the melting point of PVA and decreases crystallinity².

The blue color reaction of PVA with iodine proceeds in a similar manner to the amylose—iodine reaction. The intensity of the blue color was known to vary delicately with various kinds of PVA samples and this has been interpreted as being due to minor changes in the molecular structure of PVA. Among many structural variations, the effect of molecular weight has been

studied quantitatively³.

The present study was undertaken to elucidate the role of the 1,2-glycol structure and stereoregularity on the PVA—iodine reaction. During the course of our study Shibatani, *et al.*, reported the effect of these variables on the color intensity of the PVA-iodine reaction⁴. We have obtained further information on the position of the absorption maximum in addition to the intensity. The nature of the complex will be discussed on this basis.

EXPERIMENTAL

Preparation of Polymers

PVA samples with different 1,2-glycol contents were prepared by hydrolyzing copolymers of vinyl acetate and divinyl carbonate. Polymerization was carried out in methanol at 1°C using a monomer concentration of 2mol/l and triisobutylboron as a catalyst. The results of copolymerization are given in Table I and Figure 1, and the degree of polymerization and the 1,2-glycol content of the resultant PVA are given in Table II. Monomer reactivity ratios are found to be

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 Table I. Copolymerization of vinyl acetate (M_1) and divinyl carbonate (M_2)^a

Exptl no.	M_2 mole fraction in monomer ^b	Polymerization time, hr	Conversion, %	M_2 mole fraction in copolymer ^b
3	0.194	3	15.1	0.337
4	0.291	2.7	6.4	0.506
5	0.390	2.7	11.9	0.551
6	0.490	2.5	16.0	0.630
7	0.590	2.3	19.7	0.720
8	0.691	2.2	18.6	0.786
9	0.793	2	19.0	0.866
10	0.896	2	18.7	0.908

^a $[M_1]+[M_2]=2$ mol/l in methanol; Catalyst, triisobutylboron, 0.5 mmol, at 1°C.

^b One mole of divinyl carbonate was regarded as two equivalents.

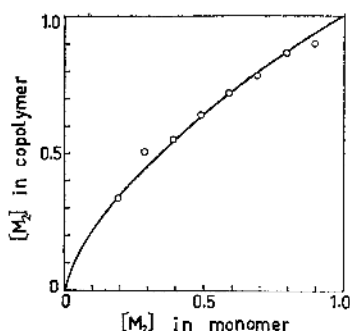


Figure 1. Copolymer composition curve for vinyl acetate (M_1) and divinyl carbonate (M_2): \circ , $[M_1]+[M_2]=2$ mole/l in methanol at 1°C; catalyst, $(i\text{-Bu})_3\text{B}$, 0.33 mol% of monomer. The curve is calculated for $r_1=0.41$, $r_2=1.55$.

$r_{\text{VAC}}=0.41$ and $r_{\text{DVC}}=1.55$, while in the presence of azobisisobutyronitrile as catalyst they are 0.77 and 1.33, respectively⁹.

PVA samples with 1,2,3-triol structure were prepared by hydrolyzing a copolymer of vinyl acetate and vinylene carbonate. Polymerization conditions were the same as in the vinyl acetate—divinyl carbonate copolymerization. The degree of polymerization and the 1,2,3-triol content of the PVA resulting are given in Table III.

PVA samples with different stereoregularities were prepared using various polymerization conditions and starting monomers. Polymerization conditions are summarized in Table IV. Stereoregularities and degrees of polymerization are

Table II. The effect of the 1,2-glycol structure on the PVA—iodine reaction

Sample no.	1,2-glycol mol%	DP	D_{916}/D_{849}	Extinction (D_{808}) ^a		
				I	II	III
1	1.41	623	0.35	3	1.88	—
2	1.87	631	0.40	2.8	1.41	—
3	2.73	518	0.34	1.08	0.50	—
4	3.17	—	—	—	—	—
5	4.09	342	0.29	0.26	—	0.83
6	4.69	335	0.29	0.11	—	0.47
7	5.09	310	0.26	0.048	—	0.19
8	5.67	332	0.29	0.026	—	0.14
9	5.17	—	0.27	0.013	—	0.037
10	6.66	290	—	0.009	—	0.017
Commercial	2.10	500	0.36	2.48	1.10	—

^a Reaction conditions: I, [PVA], 25 mmol/l; $[I_2]$, 1.25 mmol/l; [KI], 2.5 mmol/l; 20 hr, 6–8°C; II, [PVA], 14.5 mmol/l; $[I_2]$, 0.87 mmol/l; [KI], 1.75 mmol/l; 24 hr, 6–8°C; III, Two ml of an 0.5 mol/l aqueous boric acid solution was added to 7 ml of the reaction mixture of I and allowed to react for 24 hr at 6–8°C.

Table III. The effect of the 1,2,3-triol structure on the PVA—iodine reaction

Sample no.	1,2,3-triol mol%	DP	D_{916}/D_{840}	Extinction ^a (D_{697})
11	2.13	617	0.37	1.60
12	10.9	392	0.28	0.22
13	11.6	604	0.29	0.09
14	18.7	408	0.23	0.03

^a Reaction conditions: [PVA], 30 mmol/l; $[I_2]$, 1.25 mmol/l; [KI], 5 mmol/l; 20 hr, 6–8°C.

Table IV. Preparation of PVA samples with different stereoregularities

Sample no.	Monomer ^a	Catalyst	Solvent	Polymerization temp, °C	Yield, %
21	VOSi ^b	EtAlCl ₂ ^c	Toluene	–95	—
22	"	"	Toluene—CH ₂ Cl ₂ (8 : 2)	–78	86
23	"	"	" (6 : 4)	–78	58
24	"	"	" (4 : 6)	–78	53
25	"	"	" (5 : 5)	–78	100
26	"	"	" (3 : 7)	–78	59
27	"	"	CH ₂ Cl ₂	–78	100
28	"	"	"	–95	—
29	"	"	"	–78	—
30	"	"	"	–60	—
41	VAc	AIBN—UV ^d	Methanol	30–31	81.5
42	"	"	Hexane	30–31	87.7
43	"	"	Methanol	6–8	25.8

^a Monomer concentration was 20 vol%.

^b Vinyl trimethylsilyl ether.

^c Catalyst concentration was 0.0125 mol/l.

^d Photosensitized polymerization.

given in Tables V and VI.

Determination of 1,2-Glycol Content in PVA

1,2-Glycol content was determined by titrating the periodic acid consumption by PVA in accordance with the method used by Harris and Pritchard⁶. It was assumed that the -CH(OH)-CH(OH)-CH(OH)- structure, formed by the copolymerization of vinylene carbonate and vinyl acetate, would consume 2 mol of periodic acid, and thus the triol structure was regarded as one 1,2-glycol structure.

Determination of Tacticity

Triad tacticity was determined from NMR spectra of poly(vinyl acetate) derived from PVA samples using a JNM 4-100 spectrometer from the Japan Electron Optics Laboratory Co. Ltd.⁷ In some cases dyad tacticity was calculated from the absorbance ratio, D_{916}/D_{840} , of IR spectra of

PVA films according to the equation presented by us previously⁷.

The PVA—Iodine Color Reaction

An aqueous PVA solution was mixed with a KI-I₂ solution at 6–8°C and kept at this temperature for 20 hr. The mixture was then subjected to spectroscopic measurement at room temperature using a Hitachi spectrophotometer, EPS-3T.

RESULTS

Influence of the 1,2-Glycol Structure on the PVA—Iodine Reaction

Table II, Figures 2 and 3 show the influence of 1,2-glycol content on the PVA—iodine reaction. The 1,2-glycol structure significantly reduced the intensity of the blue color of the reaction mixture. It should especially be noted

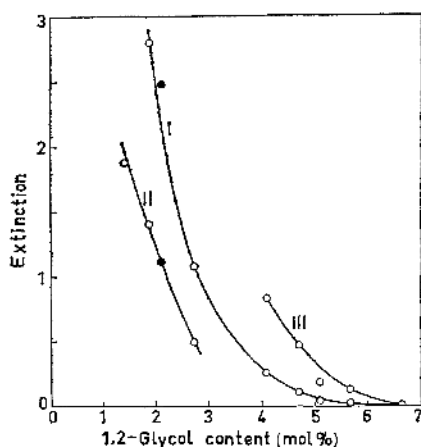


Figure 2. Effect of 1,2-glycol structure on PVA—iodine reaction: ○, samples from the vinyl acetate—divinyl carbonate copolymer; ●, commercial PVA. Reaction conditions for I, II, and III are listed in Table I.

that the position of the absorption maximum was unaltered ($608\text{ m}\mu$) and that in PVA in which 1,2-glycol content exceeded 5 mol% coloration did not develop. The absorption maximum shifted to $680\text{ m}\mu$ when boric acid was added.

Influence of Stereoregularity

Tables V and VI show the coloring abilities of PVA samples with various stereoregularities. The difference in stereoregularity markedly

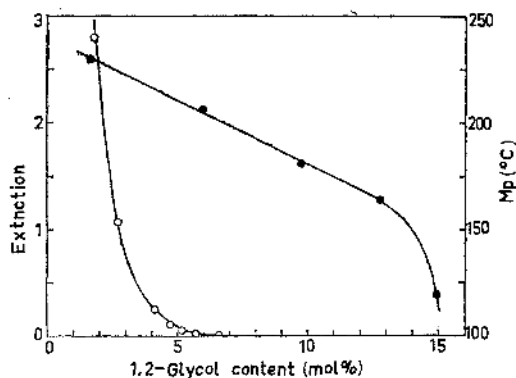


Figure 3. Effect of 1,2-glycol structure on PVA—iodine reaction (○) and on melting point of PVA (●).

affected the PVA—iodine reaction, and in particular the PVA samples with dyad syndiotacticity less than 30% did not have any visible absorption at all. The coloring ability in this case depended mainly on the increase of syndiotacticity.

It is characteristic that the PVA samples with approximately 40% syndiotacticity had their absorption maxima at a shorter wave length than PVA samples with higher syndiotacticity. Where syndiotacticity was higher than 44%, the absorption maximum remained practically constant, while increases in syndiotacticity caused increases in extinction.

Table V. The effect of stereoregularity on the PVA—iodine reaction

Sample no.	DP	Syndio-tacticity dyad, % ^c	Extinction ^a			
			I		II	
			λ_{max}	D_{max}	λ_{max}	D_{max}
21	2322	12	none	—	400—600 broad peak	0.33—0.34
22	1520	20	none	—	"	0.1—0.2
23	1485	29	none	—	—	—
24	678	39	562	0.27	—	—
25	1171	40	571	0.27	650	0.61
26	1010	44	620	0.31	—	—
27	858	55	(616) ^b	(1.06) ^b	654	2.21

^a Reaction conditions: I, [PVA], 14.0 mmol/l; $[I_2]$, 2.00 mmol/l; [KI], 3.00 mmol/l; 6—8°C, 20 hr; II, [PVA], 7.0 mmol/l; $[I_2]$, 0.33 mmol/l; [KI], 0.5 mmol/l; $[H_3BO_3]$, 100 mmol/l; 6—8°C, 20 hr.

^b $[I_2]$, 0.667 mmol/l; [KI], 1.00 mmol/l. Other conditions are the same as I.

^c Dyad tacticity was calculated from the absorbance ratio, D_{916}/D_{848} , of IR spectra of PVA films⁷.

Table VI. The effect of stereoregularity on the PVA—iodine reaction

Sample no.	DP	Stereoregularity, %					Extinction ^b	
		dyad ^a		triad			λ_{\max}	D_{\max}
		<i>i</i>	<i>s</i>	<i>I</i>	<i>H</i>	<i>S</i>		
28	2680	55	45	36	39	25	616	0.57
29	180	49	51	26	46	28	620	1.07
30	490	48	52	25	47	28	624	1.03
41	1995	53	47	28	49	23	617	0.71
42	2080	55	45	31	48	21	618	0.69
43	3127	53	47	29	48	23	620	0.81

^a Diad tacticity was calculated from the triad tacticity.

^b Reaction conditions: [PVA], 6.25 mmol/l; [I₂], 5.5 mmol/l; [KI], 16.7 mmol/l; 6–8°C, 20 hr.

DISCUSSION

Effect of the 1,2-Glycol Structure on the PVA—Iodine Reaction

The increase of 1,2-glycol content, as shown in Figure 2, strongly influences the PVA—iodine reaction. In particular, when the 1,2-glycol content exceeds 5 mol%, the reaction mixtures are colorless. The PVA samples are almost identical to one another in respect of stereoregularity and the degree of polymerization. Therefore the decrease in the intensity of visible absorption (coloring ability) depends solely on the increase in the 1,2-glycol content. Further, the fact that absorption maxima remain unchanged irrespective of the 1,2-glycol content suggests that the structures of the PVA—iodine complexes are identical to one another.

Table II shows that the IR absorbance ratios, D_{916}/D_{849} , decrease as the 1,2-glycol content decreases. The values of D_{916}/D_{849} , however, may not reflect the stereoregularity of PVA when PVA has a large 1,2-glycol content, as has been stated previously⁵. Polymerization conditions suggest these PVA samples are atactic.

We have previously reported that the 1,2-glycol structure is one of the important factors interfering with the crystallization of PVA. The influence of the 1,2-glycol structure in the present report differs from that on the crystallization. Figure 3 shows that the melting point of PVA is inversely proportional to the 1,2-glycol content when that content is less than 13 mol%⁵. On the other hand the PVA—iodine reaction is significantly affected by a much smaller 1,2-glycol

content. This tendency is specially noticeable at the reaction temperature of 20°C which was used by Shibatani, *et al.*⁴ The difference in these two properties suggests that the PVA—iodine reaction requires a longer 1,3-glycol sequence length than does the crystallization of PVA.

Let us assume that a sequence length n of 1,3-glycol units is required for the color reaction. If one assumes that the 1,2-glycol units are distributed statistically along the chain, the probability of the occurrence of sequence length x of 1,3-glycol units is obtained approximately by the formula,

$$P(x) = \left(\frac{a+1}{N}\right) \left(\frac{b-1}{N}\right)^x \quad (1)$$

where N is degree of polymerization, a and b are average numbers of 1,2- and 1,3-glycol units in polymer molecules, respectively, *i.e.*, $a+b=N$. Therefore the mole fraction of the 1,3-glycol units which are contained in sequences with more than n , $f(n)$, is obtained by the formula,

$$f(n) = 1 - \frac{\sum_{x=1}^n xP(x)dx}{\sum_{x=1}^{\infty} xP(x)dx} \quad (2)$$

Combination of eq 1 and eq 2 gives eq 3, which can be calculated assuming various n values.

$$f(n) = \left(\frac{b-1}{N}\right)^{n-1} \left(\frac{n-1/\ln\left(\frac{b-1}{N}\right)}{1-1/\ln\left(\frac{b-1}{N}\right)} \right) \quad (3)$$

Table VII shows the mole fraction of the 1,3-

Table VII. Mole fraction of the 1,3-glycol units contained in sequences of more than n^a

Sample no.	D_{\max}	$n=100$	$n=120$	$n=150$
1	—	0.552(2.92)	0.425(3.83)	0.305(5.87)
2	2.8(2.6)	0.378(2.11)	0.279(2.52)	0.174(3.35)
3	1.08(1.00)	0.179(1.00)	0.111(1.00)	0.052(1.00)
5	0.26(0.24)	0.046(0.25)	0.020(0.18)	0.0056(0.11)
6	0.11(0.10)	0.024(0.14)	0.0091(0.082)	0.0021(0.040)
7	0.048(0.045)	0.015(0.083)	0.0051(0.046)	0.00098(0.019)
8	0.026(0.024)	0.0073(0.041)	0.0023(0.021)	0.00035(0.007)
10	0.009(0.008)	0.0022(0.012)	0.0005(0.004)	0.00005(0.0009)

^a The values in parentheses are relative values taking no. 3 as standard.

glycol units with $n=100$, 120, and 150 in the PVAs with different 1,2-glycol contents. In order to facilitate a comparison between the observed extinction and the calculated value, sample no. 3 was taken as standard. In Figure 4, curves represent relations between the calculated relative amount of the 1,3-glycol units

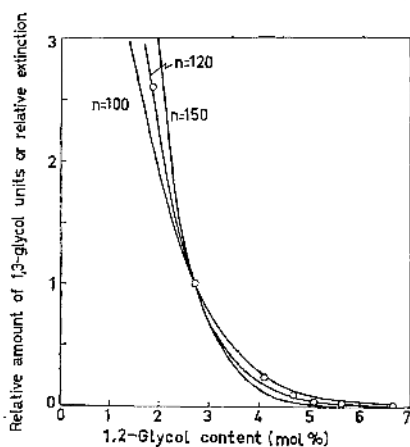


Figure 4. Relation between the calculated relative amounts of the 1,3-glycol units contained in sequences of more than n and the 1,2-glycol content. Curves represent the calculated values. Circles represent the observed relative extinctions versus 1,2-glycol content.

contained in sequences of more than n and the 1,2-glycol content. The relative coloring abilities (observed extinctions relative to that of sample no. 3) are plotted against the 1,2-glycol content. A close correlation is evident between the observed and calculated values when $n=120$. The conditions for the PVA-iodine reaction sup-

posedly require an extremely long 1,3-glycol sequence length of atactic configuration. The value of 120 in the 1,3-glycol sequence length obtained here does not directly relate to the PVA-iodine complex, because factors other than the 1,2-glycol structure may influence the PVA-iodine reaction. Thus an extremely long sequence length may be necessary in the case of atactic PVA. Indeed, syndiotactic PVA has a high coloring ability in spite of its low degree of polymerization⁴.

In order to check the effect of the vicinal arrangement of hydroxyl groups, a comparison between the influence of the 1,2,3-triol structure on the PVA-iodine reaction (black circles) and that of 1,2-glycol (white circles) was made in Figure 5. This figure indicates that the effect

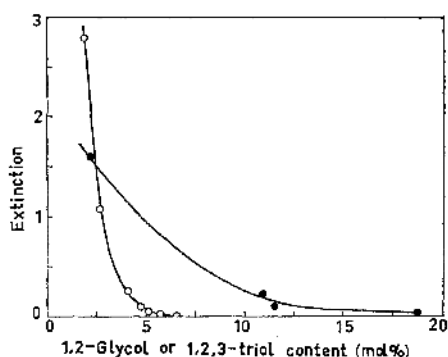


Figure 5. Effect of 1,2,3-triol structure on PVA-iodine reaction: ●, effect of 1,2,3-triol structure; [PVA], 25 mmol/l; $[I_2]$, 1.25 mmol/l; $[KI]$, 2.5 mmol/l; 6–8°C, 20 hr; ○, effect of 1,2-glycol structure; [PVA], 30 mmol/l (other conditions are the same as above).

of the 1,2-glycol structure inevitably results in the 1,4-glycol structure and both structures are probably not favorable to the color reaction, while the 1,2,3-triol structure does not give the 1,4-glycol structure. Thus it is not the vicinal arrangement of OH groups but the structural irregularity that influences the color reaction. Shibatani, *et al.*, have carried out a similar experiment and failed to obtain a difference between the 1,2-glycol and 1,2,3-triol structures⁴. It is conceivable that as compared with our experiment, the reaction temperature was high and thus the formation of the PVA—iodine complex was more difficult.

The Effect of the Stereoregularity on the PVA—Iodine Reaction

PVA samples (no. 21—30) derived from vinyl trimethylsilyl ether are known to contain negligibly small amounts of 1,2-glycol unit¹. The influence of stereoregularity on the PVA—iodine reaction is also remarkable. The results in Tables V and VI show that PVA with syndiotacticity larger than 50% show high coloring ability and that PVA samples with syndiotacticity less than 30% do not show the color reaction. It is characteristic of PVA samples with syndiotacticities of about 40% that increases in the isotactic structure results in the shift of the absorption maximum as well as a decrease in extinction. This fact is in contrast to the effect of the 1,2-glycol structure on the PVA—iodine reaction, and suggests that the effect of stereoregularity may be different qualitatively from that of the 1,2-glycol structure, *i.e.*, the isotactic structure may affect the structure of the PVA—iodine complex. The tendency of the isotactic PVA to form an intramolecular hydrogen bonding⁸ may reflect on the PVA—iodine reaction.

The similarity of the PVA—iodine reaction to the amylose—iodine reaction suggests that the blue color may be due to the interaction between polyiodine, I_n^{m-} , and oxygen atoms of surrounding PVA chains⁹⁻¹¹. The structure and the number of the site which stabilizes polyiodine may change the absorption maximum and the extinction. In the case of the amylose—iodine reaction, this structure is determined as a helix; in the case of the PVA—iodine reaction the situation is not clear, although a helical struc-

ture was suggested by Zwick¹⁰.

Imai and Matsumoto³ and Shibatani, *et al.*,⁴ have shown that the PVA—iodine reaction bears a close relation to the intermolecular interaction of PVA. Since an isotactic sequence interferes with the formation of the intermolecular hydrogen bonding, a blue shift in the absorption maximum with increasing isotacticity may be due to the fact that intramolecular hydrogen bonding reduces the interaction between polyiodine and oxygen atoms of PVA. The sequence length forming an intramolecular hydrogen bonding, however, is not sufficiently long to destroy the complex completely at these medium isotacticities.

The addition of boric acid generally promotes the PVA—iodine reaction and shifts the absorption maximum to a longer wave length (670—700 m μ). Boric acid may intensify the intermolecular interaction of PVA and consequently may promote the interaction between PVA and iodine. Without boric acid, the color reaction was not observed with Samples no. 21 and 22. The addition of boric acid to these developed the color, but the visible absorptions were too broad to determine the absorption maximum. It is interesting to note that a sample which is rich in isotactic structure (no. 21, 88% isotacticity) was colored more intensely than no. 22 (80% isotacticity). Sample no. 21 is less soluble in water than no. 22, which is the most soluble among various tacticities. Another type of intermolecular interaction other than hydrogen bonding was suggested¹. The intermolecular interaction is reinforced by boric acid, probably at the segments not having intramolecular hydrogen bondings, resulting in the formation of the PVA—iodine complex. The broad absorption spectrum also suggests that this interaction may not be as simple as the interaction in atactic or syndiotactic PVA.

The comparison between the influence of stereoregularity on the PVA—iodine reaction and that of the 1,2-glycol structure may be summarized as follows: the existence of the 1,2-glycol structure causes the interaction between PVA and iodine to be discontinued, but does not influence the structure of the PVA—iodine complex. The isotactic structure may modify the structure of the PVA—iodine complex so as

to weaken the interaction, finally entirely suppressing the complex formation at isotacticities higher than 70%.

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