

On the Poly(vinyl alcohol)–Iodine Complexes

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SYNOPSIS

The color development due to the complex formation of poly(vinyl alcohol) (PVA) with iodine increased with increasing syndiotacticity of PVA. Isotactic PVA showed no color development. The color development of syndiotacticity-rich PVA film decreased with increasing annealing temperature for films before complexization, whereas that of atactic (commercial) PVA increased with it. Lower temperatures, the elongation of complex film, and the presence of boric acid enhanced the absorbance at 600 nm due to I_5^- . The complexes are assumed to be made by incorporation of polyiodines into aggregates of syndiotactic sequences in PVA. The polarizability and electric conductivity of complex films are investigated. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl alcohol) (PVA)–iodine complexes have long been studied since the finding of blue color development of aqueous PVA solution with iodine by Staudinger et al.¹ The investigations on the complex before ca. 1970 have been summarized by Pritchard and Akntolar² and Haas.³ The facts revealed are that (1) the iodine molecules in PVA forms polyiodines of a period of 3.1 Å; (2) boric acid and the stereoregularity of PVA enhance the color development, whereas 1,2-glycol bonds reduce it; (3) the absorption maximum is observed at ca. 600–620 nm; and (4) the color development is enhanced through the introduction of acetal linkage. During 1971–1990, the following were reported: the finding of I_5^- using resonance Raman absorption;⁴ the finding of I_{10} , which is held by aggregated PVA molecules;⁵ the separation of I_5^- and $I_2 \cdot I_3^-$ (Ref. 6); and absence of dichroism in the complex in the visible range.⁷ Since aggregate⁸ and helix models⁹ were presented in 1965, both models have been supported.

This paper reports on the color development with iodine of PVA: first, on the importance of syndiotacticity using isotactic, syndiotactic, and atactic PVAs (*I*-PVA, *S*-PVA, *A*-PVA); second, on the complex formation under various conditions in

swollen *S*-PVA film compared with the case of *A*-PVA; and third, on the orientation of iodine molecules with drawing. In addition, the polarizability and electric conductivity of *S*-PVA-iodine complex films are reported.

EXPERIMENTAL

Materials

The PVAs used are shown in Table I. *I*-PVA-1 was prepared from poly(vinyl *tert*-butyl ether) polymerized cationically at -78°C .¹² *S*-PVA-1, *S*-PVA-2, and *S*-PVA-3 were prepared from poly(vinyl trifluoroacetates) polymerized radically at 60°C ,¹³ and *S*-PVA-4, from poly(vinyl trifluoroacetates) polymerized radically at 0°C .¹⁴ *A*-PVA-1 and *A*-PVA-2 are commercial PVAs, which were used after complete saponification and the purification by methanol extraction.

Formation and Measurements of Properties of PVA–Iodine Complexes

The content of syndiotactic diad, *s*-(diad) %, was determined from the infrared spectrum of film using the equation¹⁵

$$s\text{-(diad) \%} = 72.4(D_{916}/D_{849})^{0.43} \quad (1)$$

where *D* is the absorbance.

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Table I PVA Samples Used

Sample No.	Degree of Polymerization	s-(diad) (%)
I-PVA-1	390 ^a	15
A-PVA-1	1110 ^a	50
A-PVA-2	500 ^a	49
A-PVA-3	310 ^a	46
S-PVA-1	3350 ^b	55
S-PVA-2	2610 ^b	55
S-PVA-3	900 ^b	55
S-PVA-4	770 ^b	59

^a From intrinsic viscosity of PVA using $[\eta] = 7.50 \times 10^{-3} DP^{0.64}$ (water, 30°C).¹⁰

^b From intrinsic viscosity of acetylated PVA using $[\eta] = 8.91 \times 10^{-3} DP^{0.62}$ (benzene, 30°C).¹¹

Iodine of reagent grade and potassium iodide and boric acid of special grade were purchased from Wako Pure Chemical Industries Co. The formation of PVA-iodine complexes in the dissolved state in water was carried out in accordance with Imai-Matsumoto's method.¹⁶

The complex films were prepared by steeping PVA films in aqueous iodine/potassium iodide ($\frac{1}{2}$) solution in the absence or presence of boric acid. The films taken out from the solutions were rinsed with water to remove the solution adhered on the film surfaces.

Visible light absorption spectra of complex solutions and films were taken using a Shimadzu spectrometer UV-160. In the complex films, absorbances were measured by interposing the films between two glass plates.

The absorbances measured were divided by the thickness of film to reduce to values per 1 cm. The difference between the absorbance of the complex film and uncomplexed swollen film was regarded as the true absorbance.

Resonance Raman spectra of the complex films were taken using a Nippon Bunko NR-100 Laser Raman spectrophotometer, exciting with the light of Ar⁺ 514.5 nm.

The orientation of factors, F_1 , of polyiodines in elongated complex films was estimated using the equation¹⁷

$$F_1 = (D_{//} - D_{\perp}) / (D_{//} + 2D_{\perp}) \quad (2)$$

where $D_{//}$ and D_{\perp} are the absorbances for the lights with parallel and perpendicular electric vectors to the direction of elongation. The lights of wavelengths of 350 and 600 nm were chosen. An S-PVA-

iodine complex film prepared was used as a polarizer. The orientation factors, F_{cr} , of crystallites in films with no iodine were estimated with the equation shown above for the crystallization-sensitive band at 8.75 μm using a wire grid-type polarizer (JASCO PL-81).

The degrees of polarization, V , of a complex film were estimated using the equation

$$V(\%) = [(T_{//} - T_{\perp}) / (T_{//} + T_{\perp})]^{1/2} \times 100 \quad (3)$$

where $T_{//}$ and T_{\perp} are the transmittances of the film superimposed on each other parallel and perpendicular to the direction of the elongation of the film. In PVA, F_{cr} (< 0) decreases, whereas in polyiodines, F_1 (> 0) increases with increasing orientation.

The direct current conductivity, σ , of a complex film was determined by measuring the resistance, R , between the surface of the film under 2×10^{-4} Torr and 10 V after covering both surfaces with gold using the equation

$$\sigma = d / (R \cdot S) \quad (4)$$

where d is the thickness of film, and S , the area of the electrode.

Films of thickness 46 μm and size 2.5×0.5 cm were chiefly used. Films of thickness 25 μm and size 1.5×1.5 cm and of thickness 46 μm and size 2.5×2.5 cm were used for the polyiodine orientation and for the conductivity experiment.

RESULTS AND DISCUSSION

Tacticity Dependence of the Complex Formation in Solution

Table II shows the extent of color development due to the complex formation in solution for four kinds

Table II Absorbance (D) at ca. 600 nm of PVA-Iodine Complex in Solution and Tacticity of PVA ($[I_2] = 1 \times 10^{-3}$ [M], $I_2/KI = 1/4$, PVA: 0.25%)

Sample	s-(diad) (%)	$(D/DP) \times 10^3$	
		4.8°C	20°C
I-PVA-1	15	0.00	0.00
A-PVA-3	46	1.25 (591.0) ^a	0.00
A-PVA-2	49	1.75 (592.5)	0.00
S-PVA-4	59	10.60 (597.5)	9.86 (599.0)

^a Wavelength at λ_{max} .

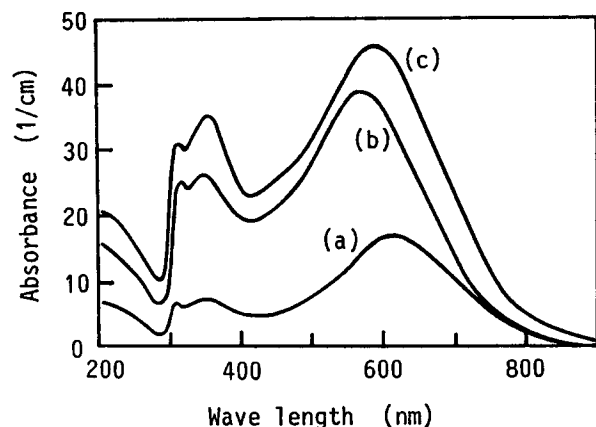


Figure 1 Absorption spectra of *S*-PVA-1-iodine complex prepared in the swollen state. Annealing temperature of film: (a) 120°C; (b) 80°C; (c) untreated. $[I_2] = 5.0 \times 10^{-4} [M]$, 30°C, 24 h.

of PVAs. The extents are shown in D/DP , where D is the absorbance and DP is the degree of polymerization. For *I*-PVA-1, no color development was observed even at 4.8°C. For *A*-PVA-2 and *A*-PVA-3, it was observed at 4.8°C though not at 20°C. For *S*-PVA-4, remarkable color development was observed even at 20°C. Clearly, syndiotacticity-rich PVA is favorable for the complex formation. The absorption maximum varied to longer wavelength with increasing syndiotacticity. This is discussed in the next section.

Complex Formation at Several Conditions for *S*-PVA in the Swollen State

Figure 1 shows the absorption spectra of the *S*-PVA-1- I_2 complex formed by steeping in I_2 -KI solution for the films annealed at different temperatures for 20 min. The absorption maxima (λ_{max}) at around 350 and 600 nm decreased with increasing annealing temperature. The former has been attributed to the complex with $I_2 - I_3^-$, and the latter, to I_5^- .^{4,6} Figure 2 shows the dependency of the absorbances at λ_{max} 's on the iodine concentration of the steeping solution and the annealing temperature for *S*-PVA-1 and *A*-PVA-1 films. The absorbances increased with increasing iodine concentration for both kinds of PVAs and decreased with increasing annealing temperature for *S*-PVA-1, whereas those increased up to the temperature of 120°C and decreased with annealing temperature beyond 120°C for *A*-PVA-1. The effects of annealing temperature means that the amorphous regions swellable to a fixed degree are necessary. At a fixed iodine concentration, the

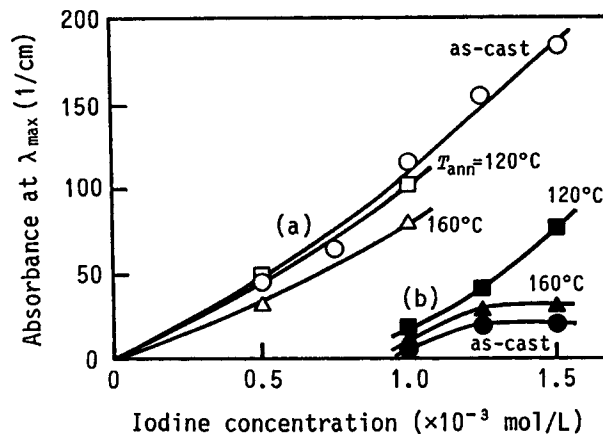


Figure 2 Effect of annealing temperature on complex formation (30°C, 24 h): (a) *S*-PVA-1; (b) *A*-PVA-1.

absorbances for *S*-PVA-1 are much larger than those for *A*-PVA-1. Figure 3 shows the resonance Raman spectra of the complexes for both kinds of PVAs. The absorbances of the *S*-PVA-1 complexes (b,c) are much larger than that of the *A*-PVA-1 complex (a). The absorption maxima at 160 and 108 cm^{-1}

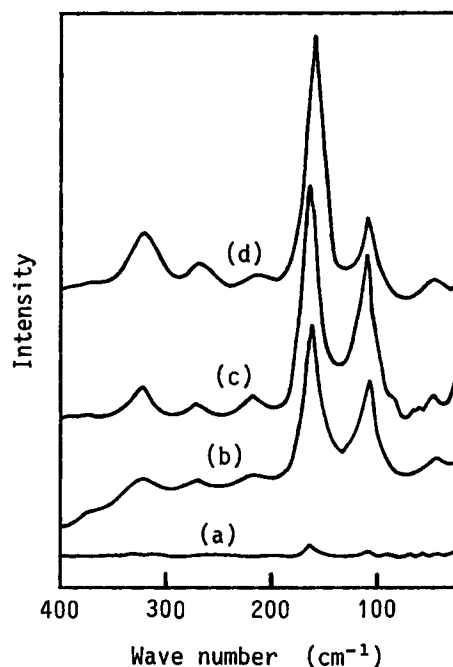


Figure 3 Resonance Raman spectra of PVA-iodine complexes: (a) *A*-PVA-1, annealed at 120°C, $[I_2] = 4.0 \times 10^{-3} [M]$, 100 mW; (b) *S*-PVA-1, annealed at 80°C, $[I_2] = 2.0 \times 10^{-3} [M]$, 20 mW; (c) *S*-PVA-1, as-cast, $[I_2] = 2.0 \times 10^{-3} [M]$, 20 mW; (d) *S*-PVA-1, as-cast, $[I_2] = 4.5 \times 10^{-6} [M]$, $[H_3BO_3] = 4.0 \times 10^{-1} [M]$, 20 mW.

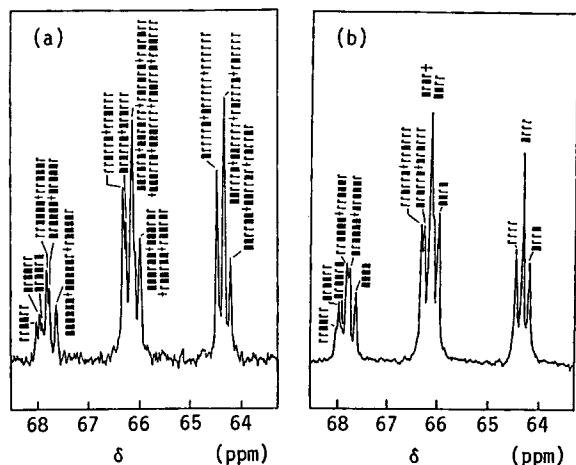


Figure 4 ¹³C-NMR spectrum of methine carbons in (a) S-PVA-1 and (b) A-PVA-1 in DMSO-d₆.

attributed to I₅⁻ and I₃⁻, respectively,⁴ are clearly seen for S-PVA-1, though the difference in syndiotactic diad content between both kinds of PVAs is small. Figure 4 shows the ¹³C-NMR spectra of both kinds of PVAs. The larger difference in pentad sequence is seen. This is considered to give the larger difference in complex formation.

The absorbance at 600 nm is plotted in Figure 5 as a function of iodine concentration for different reaction temperatures. The ratio of absorbance at 600 nm to that at 350 nm is plotted in Figure 6 as a function of iodine concentration for different re-

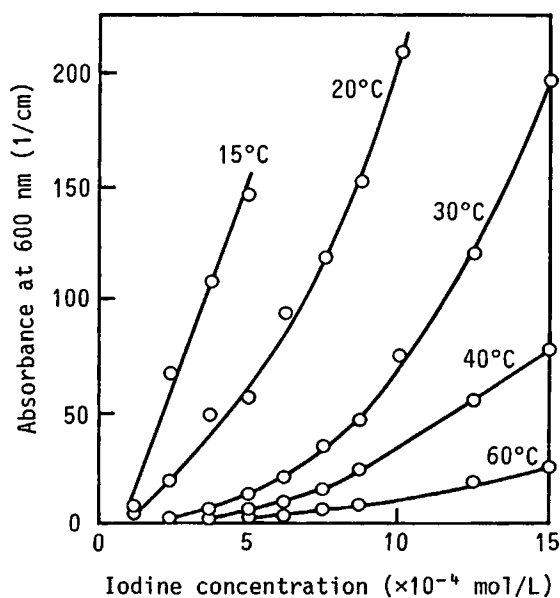


Figure 5 Effect of iodine concentration and temperature on complex formation for S-PVA-1 film.

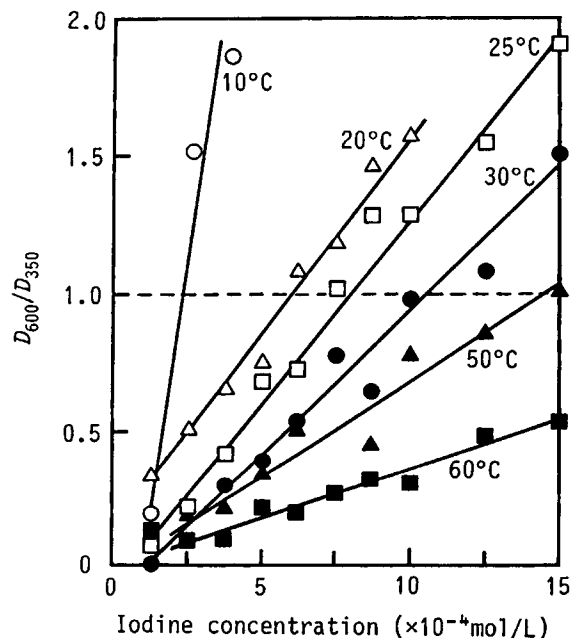


Figure 6 D_{600}/D_{350} of complex as a function of iodine concentration for S-PVA-1 film.

action temperatures. The absorbance and ratio increased with increasing iodine concentration and decreasing reaction temperature. This suggests that an equilibrium is established between I₃⁻ and I₅⁻:



The equilibrium shifts to the direction of the increase in I₅⁻ with decreasing temperature. Figure 7 shows the dependencies of the absorbances at 600 and 350 nm on boric acid concentration of steeping

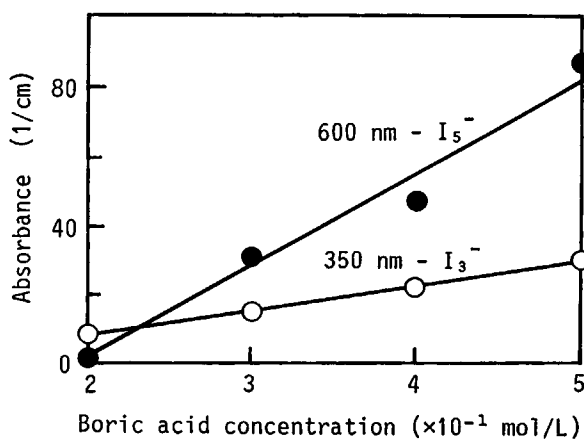


Figure 7 Effect of boric acid on complex formation for S-PVA-2 film. $[I_2] = 5.0 \times 10^{-5} [M]$, 30°C, 24 h.

Table III Turbidity of Solutions of PVA/H₃BO₃/H₂O System

Sample	PVA Concn (%)	H ₃ BO ₃ Concn (%)	Turbidity
S-PVA-3	0.91	0.36	Clear
	0.83	0.67	Clear
	0.77	0.92	Opaque (ppt) ^a
A-PVA-2	0.86	0.36	Clear
	0.78	0.67	Clear
	0.72	0.92	Clear
	0.63	1.30	Clear

^a Precipitates in solution.

solution. Boric acid accelerates the formation of I₅⁻. This is seen in the resonance Raman spectrum (d) shown in Figure 3.

Table III shows the turbidity of aqueous PVA solution containing boric acid. In the solution of the concentration of 0.92% of boric acid, the S-PVA-3 solution was opaque, whereas the A-PVA-2 solution was clear. Boric acid reacts with diols arranged isotactically,¹⁸ which are considered to cause the easy dissolution of A-PVA in water. Therefore, S-PVA molecules that have less isotactic diads than A-PVA aggregate easily after the reaction.

The aggregation of sequences in PVA molecules is considered to accelerate the production of I₅⁻, i.e., the complex. The increases in I₅⁻ at low temperature also seems to relate to the gelation of aqueous S-PVA solutions. Figure 8 shows the dependency of

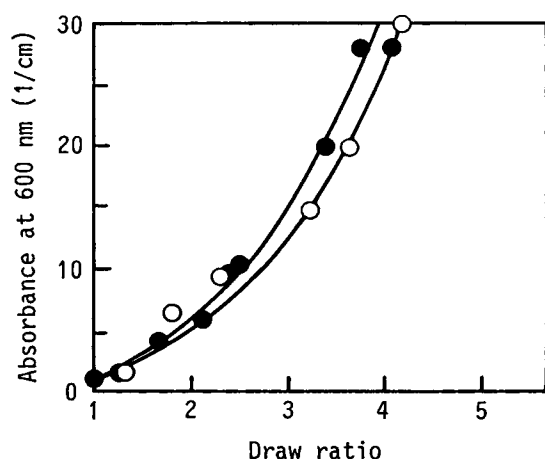


Figure 8 Effect of draw ratio on complex formation for S-PVA-2 films. Dipped in water [5 min: (●) 70°C; (○) 30°C] followed by stretching in I₂-H₃BO₃-H₂O at 30°C (after 1 min). [I₂] = 4.5 × 10⁻⁵ [M], [H₃BO₃] = 2.0 × 10⁻¹ [M]. Film size = 2.0 × 0.6 cm.

the absorbance at 600 nm of the complex prepared by steeping the S-PVA-2 film in water followed by drawing in the I₂-KI-H₃BO₃ solution. The draw ratio accelerates the formation of I₅⁻, i.e., the complex formation. This suggests that the extended sequences increases the amount of I₅⁻. These facts suggest that the complexes are formed by enveloping I₅⁻, presumably (I₅⁻)₂ (Ref. 5) with the aggregates of extended sequences in S-PVA molecules. Two models for the complex are shown in Figure 9. (a) is a simplified model and (b) is an adsorbed model in which iodine molecules adsorbed to the surface of the aggregates of syndiotactic sequences. In addition, the decrease in λ_{max} with annealing temperature of S-PVA films relates to the decrease in I₅⁻ and increase in I₃⁻, for which absorptions appeared at 620 and 510 nm, respectively.⁴

Orientation of Polyiodines and That of PVA Molecules

Figure 10 shows the orientation of polyiodines in the film drawn in water followed by steeping in an I₂-KI solution as a function of draw ratio. In this experiment, more concentrated I₂-KI solutions were used. The dependency of the orientation of crystallites on the draw ratio is also shown. The degree of orientation of the crystallites increased with increasing draw ratio, whereas that of polyiodines decreased through a maximum at the draw ratio of about 3 though the absorbances were constant irrespective of the draw ratio. These results are not

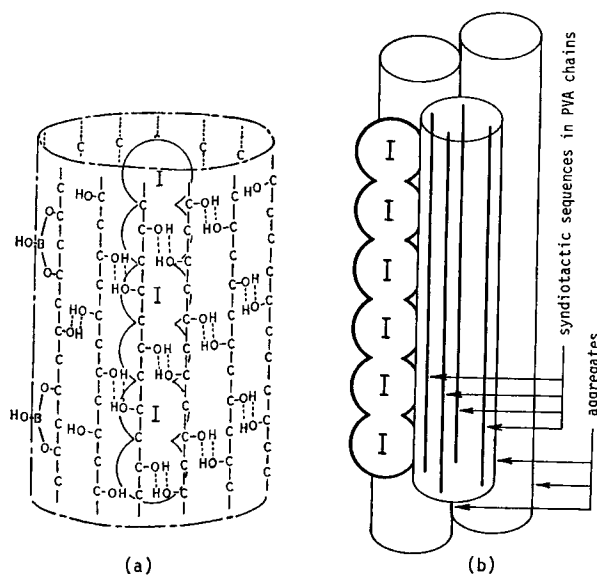


Figure 9 Models of PVA-iodine complex.

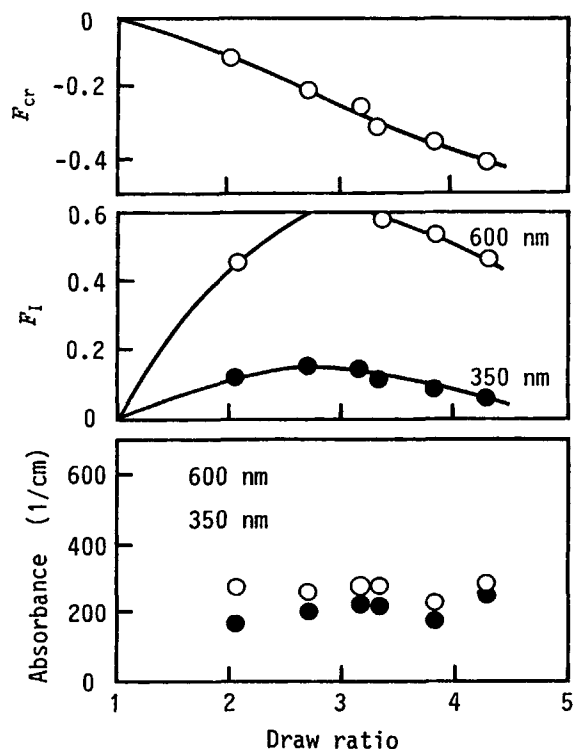


Figure 10 Orientation of polyiodines in complex *S*-PVA-1 film as a function of draw ratio. Steeping in water for 10 min at 30°C and then stretching followed by steeping for 30 min in I_2 —KI solution. $[I_2] = 2.0 \times 10^{-3}$ [M].

easy to explain. The authors considered the following: Loose aggregates of syndiotactic sequences developed in undrawn film absorb an amount of polyiodines that decreases with increasing draw ratio due to limited segmental mobility, whereas polyiodines arrange easily between extended syndiotactic sequences to lead to the increase in adsorbed polyiodines with drawing. The monotonous increase in absorbance of the complex film with drawing was described in the preceding section. In that case, the concentration of iodine of the steeping solution was so low that the amount of polyiodines adsorbed in the amorphous regions was small in the undrawn film and increased with drawing due to the aggregation of syndiotactic sequences. Besides, boric acid assisted the aggregation to lead to the increase in the amount of adsorbed polyiodines.

The independence on the draw ratio is due to the concurrence of two processes: The decrease in orientation factor beyond 3 of the draw ratio might be due to the damage of a small junction to make segments flexible. In this case, no increase in absorbance at 600 nm with draw ratio was found. For the films stepped in I_2 —KI solution followed by drawing in water, maximum absorbances and orientation

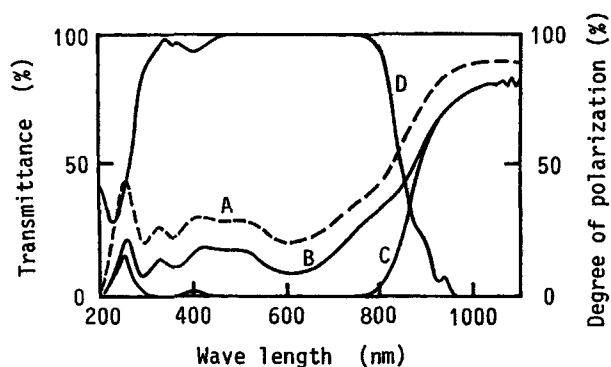


Figure 11 Behavior as a polarizer of *S*-PVA-1-iodine complex film (draw ratio 3.5). (A) Transmittance of a sheet of the film. (B, C) Transmittance of a layer of two sheets of the film. Parallel (B) and vertical (C) arrangement in direction of elongation. (D) Degree of polarization.

factors of polyiodines were found at the draw ratio of about 3.5. The complexes are considered to be damaged to eliminate iodine molecules in the complex films drawn beyond 3.5 of the draw ratio. Further investigation is necessary for the elucidation of these results.

Polarization of Light of Complex Films

Figure 11 shows the behavior as a polarizer of a complex film. The lights of wavelengths between 300 and 800 nm are polarized.

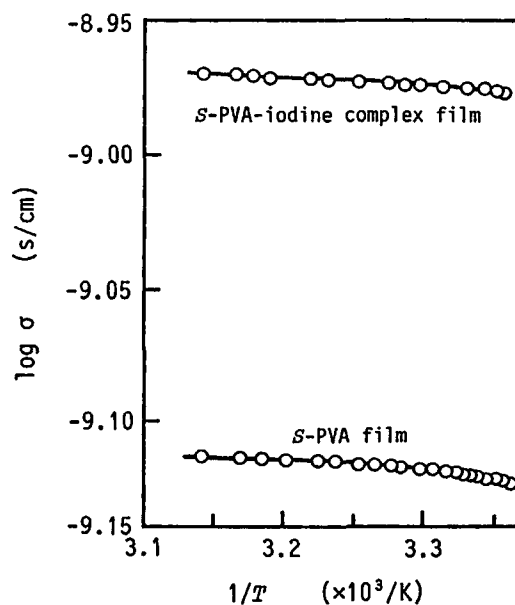


Figure 12 Temperature dependency of direct current conductivity for undrawn *S*-PVA films: (a) uncomplex film; (b) complex film. $[I_2] = 1.0 \times 10^{-1}$ [M], 30°C, 24 h.

Electric Conductivity of Complex Film

Figure 12 shows the dependency of direct current conductivity on the temperature of the complex film (iodine content = 27%) prepared from as-cast film. The conductivity at 25°C was 1.06×10^{-9} s/m, which is the lowest value as a semiconductor. No remarkable rise in conductivity as compared with pure PVA was found, though polyiodines are considered to serve as electron carriers. This might be due to the discrete arrangement of polyiodines and be overcome with the use of stretched films. Further study is necessary.

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