

Structure of Poly(vinyl alcohol)-Iodine Complex Formed in the Amorphous Phase of Poly(vinyl alcohol) Films

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SYNOPSIS

The effect of syndiotacticity of poly(vinyl alcohol) (PVA) both on the formation and thermal stability of the complex formed in the amorphous phase of PVA films is investigated, and then a model of the complex is presented. The amount of the complex formed in syndiotacticity-rich PVA is much larger than that formed in atactic PVA under a given iodine-soaking condition, and the former complex has a higher thermal stability in the soaking solution than the latter. The complex formed in the amorphous phase is proposed to have such a structure as that in which a linear polyiodine I_5^- or I_3^- with a 3.1 Å periodicity is enveloped by four PVA segments of syndiotactic configuration with extended conformation. In this model, these four PVA chains participating in a complex are supposed to be fixed by interchain hydrogen bonds. The observed X-ray meridional intensity curve of iodinated PVA film can be explained by a series of two I_5^- . © 1993 John Wiley & Sons, Inc.

INTRODUCTION

We have shown in previous papers¹⁻³ that when the iodine concentration of soaking solution is higher than about 1×10^{-2} mol/L, iodine intrudes into the crystal phase of PVA, as well as in the amorphous phase, to form a new "substitution type" crystal lattice: In the lattice, one of the chains paired with hydrogen bonds in the original PVA cell is replaced by a polyiodine chain. The spectrum of the heavily iodinated specimen shows an absorption maximum at about 480 nm (λ max), indicating that the complex formed in the crystal phase is constructed mainly with I_3^- polyiodines.

On the other hand, there have been many discussions about the structure of PVA chains in the complex formed in the amorphous phase of PVA. Zwick⁴ proposed a model of the complex in which a polyiodine chain is surrounded by helical PVA molecules, analogous to the amylose-iodine complex.^{5,6} It should be noted that Zwick's model was that constructed without any experimental evidence on the

spiral conformation of PVA chain: He supposed *a priori* the spiral conformation analogy to amylose in amylose-iodine complex. Inagaki et al.⁷ supported Zwick's structure due to the similarity in the Raman spectra of PVA-iodine and amylose-iodine complexes. On the other hand, Rundel et al.⁸ and Tebelev et al.⁹ suggested that a polyiodine chain might be surrounded by several extended PVA chains in the complex, although none of them showed any concrete figure for the structure of the complex.

This paper first reports the effect of syndiotacticity of PVA both on the formation and stability of the complex formed in the amorphous phase of PVA films, and then presents a model of the complex.

It should be noted that this sort of complex formed in the amorphous phase plays an important role in the birefringent PVA films used in liquid crystalline display systems.

EXPERIMENTAL

Atactic PVA (Wako Pure Chem. Co., DP = 2000) (*a*-PVA) was used after further saponification with sodium methoxide in Me-OH. Syndiotacticity-rich

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PVA (s-PVA) (s-diad = 0.62, s-triad = 0.363, DP = 1990, degree of saponification > 0.995) supplied by Kuraray was used as received. Films about 50 μm thick were cast from the 7 wt % (a-PVA) and 3 wt % (s-PVA) aqueous solutions.

The GR grade of iodine and potassium iodide (Wako Pure Chem. Co.) were used as received. Iodine-potassium iodide aqueous solutions with a mol ratio of 1 : 2 were prepared for soaking of PVA films. The iodine concentration in the solution varied from 1×10^{-3} to 4×10^{-3} mol/L. As cast PVA films prepared above were soaked in the soaking solutions at 45°C for 24 h, during which the equilibrium iodine sorption was reached.

The thermal stability of the complex was investigated by the following procedure: After the equilibrium complexation was reached in a solution of 2.5×10^{-3} mol/L iodine at 5°C, specimens were heated stepwise of 5°C with a heating rate of 1°C/min and kept at each temperature for 30 min, and were followed by photometry.

Visible ray spectra of iodinated PVA films were measured in a range of wavelength from 400 to 700 nm using a Hitachi U-2000 spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of PVA films iodinated in a 2×10^{-3} mol/L iodine solution at

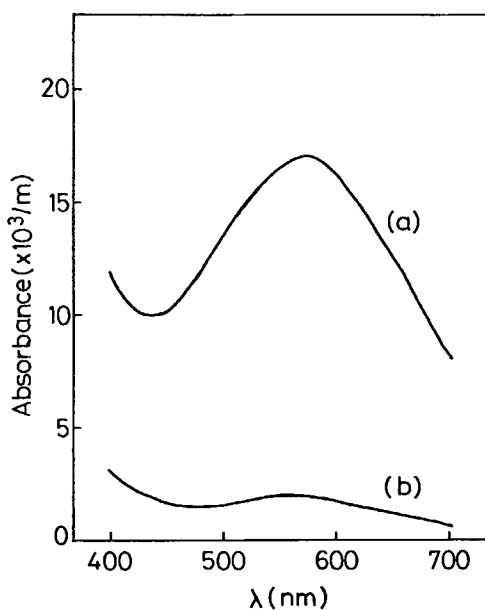


Figure 1 Absorption spectra of iodinated PVA films soaked in a 2×10^{-3} mol/L of iodine solution at 45°C: (a) s-PVA; (b) a-PVA.

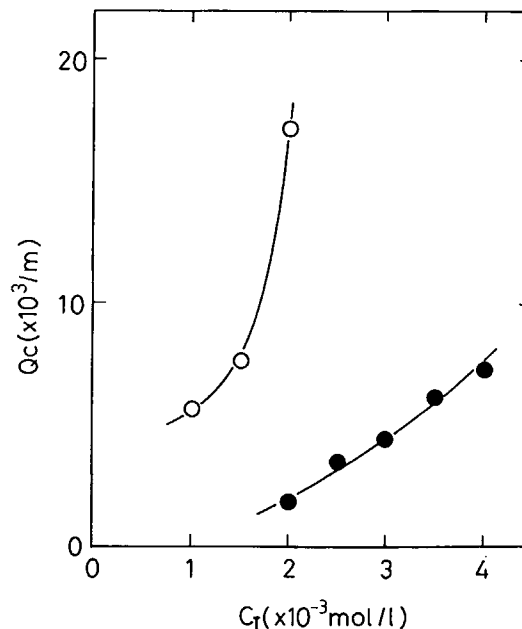


Figure 2 Relationship between the amount of complex Q_c and the iodine concentration C_I in soaking solutions: (○) s-PVA; (●) a-PVA.

45°C for 24 h. A broad absorption with a maximum at about 560 nm has already assigned to the PVA-iodine complex.¹⁰

In Figure 2 the absorbance at the absorption peak maximum (corresponding to wavelength λ_{max}) due to the PVA-iodine complex is plotted as a function of the iodine concentration in the soaking solutions. This absorbance at the λ_{max} is apparently proportional to the amount of complex formed: As the absorbance is normalized by the thickness of wet sample, it gives the relative amount of complex formed in a unit volume of sample at swollen state. Although the amounts of complex formed in both PVAs increase with increasing iodine concentration, that of s-PVA is much larger than that of a-PVA at any given iodine concentration.

Figure 3 shows the absorbance of the complex as a function of temperature, indicating that in both PVAs the amount of complex decreases linearly with increasing temperature above 20°C, while remaining almost constant below 20°C. Finally the complex disappears completely at about 60 and 85°C in the atactic and syndiotactic specimens, respectively. This fact shows that the complex formed in the syndiotacticity rich PVA has a higher thermal stability in the soaking solution than that formed in the atactic one. The results obtained for the syndiotacticity-rich PVA specimen—(1) the larger amount of complex formed under a given soaking condition

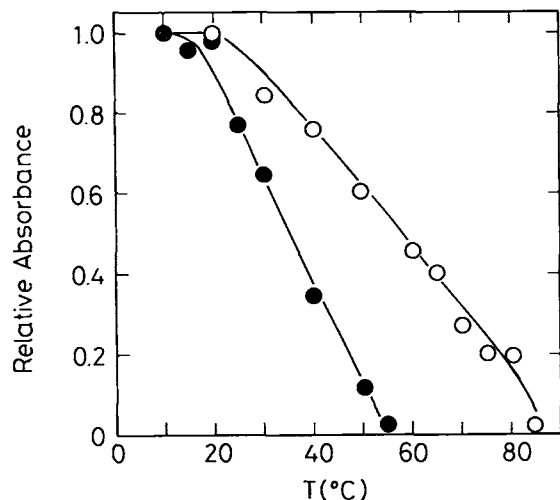


Figure 3 Change in the amount of PVA-iodine complex with heating the soaking solution: (○) s-PVA; (●) a-PVA.

(Fig. 2) and (2) the increased stability of the complex in the solution (Fig. 3)—strongly suggest that the segment of PVA participating in the complex formation must be that with the syndiotactic configuration. It should be, however, noted that this rule may not be strict but may have some exception similar to that in the crystallization of PVA: some atactic segments are supposed to participate in the crystallization, whereas every PVA crystal structure proposed so far is constructed only by syndiotactic segments.¹¹

For the structure of the PVA chain in the complex formed in the amorphous phase of PVA films, as mentioned in the Introduction of this paper, two models have been suggested, i.e., helical and aggregated models. Recently, Oishi and Miyasaka¹² found that the complexation is induced by extension of swollen PVA films even at iodine concentrations so dilute that no complexation takes place without extension. They concluded that the extended chain conformation enhances the complexation in the amorphous phase. We also confirmed that the extension-induced complexation using a highly drawn PVA film ($\lambda = 5$). These results imply that the PVA chains participating in the complex formed in the amorphous phase may take its extended chain conformation. These results are opposed to the Zwick's helical model. However, this opposition is not important, for his model is only the production of a priori assumption as mentioned above in introduction.

Oishi and Miyasaka¹² showed on the basis of FT-IR and NMR data that the complex formation increases the number of intramolecular hydrogen

bonds at the expense of interchain hydrogen bonds when the iodine concentration is higher than about 1×10^{-2} mol/L in the soaking solution where iodine intrudes into PVA crystals, forming cocrystals with PVA.¹ However, no evidence on the change in the states of hydrogen bonding with complexation when the iodine concentration is low, and the complexation takes place only in the amorphous phase of PVA has been obtained.¹³

As for the polyiodine participating in the complexation, we found two resonance Raman shifts at 109 and 161 cm^{-1} in comparatively lightly iodinated PVA samples,³ which have been assigned to I_3^- and I_5^- , respectively. This indicates that these two types of complex are formed in the amorphous phase of PVA, although the latter prevails over the former.

From these results, we reached a conclusion that the complex formed in the amorphous phase may have such structure as that in which a linear polyiodine I_5^- or I_3^- with a 3.1 Å periodicity is enveloped by four PVA segments of syndiotactic configuration with extended conformation as shown in Figure 4. Although most atactic segment should be excluded from the complex, some may be involved in the complexation as an exceptional case, causing faults in hydrogen bonding. This sort of faults makes the complex less thermally stable, which must be the

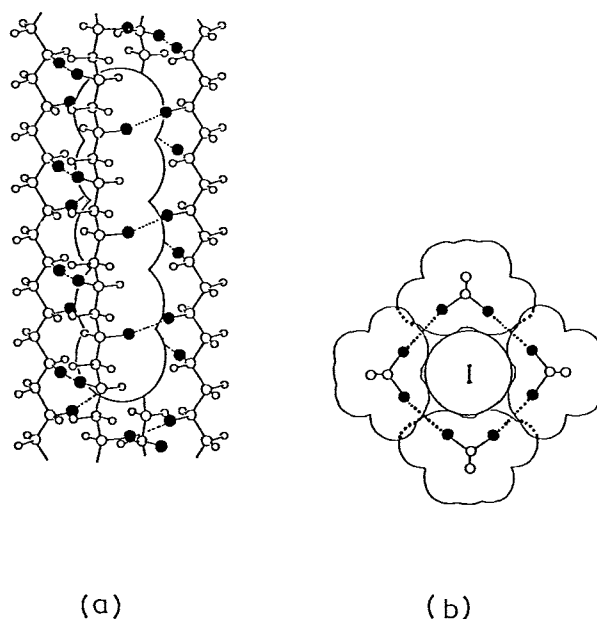


Figure 4 Proposed lattice match between I_5^- column and PVA chains in the complex. The intermolecular hydrogen bonds are shown by dashed lines. On the projection along the complex axis (b), solid lines outline van der Waals radius of each molecules: (○) hydrogen; (○) carbon; (●) OH group.

reason for the difference in the thermal stability shown in Figure 3. In this model, four PVA chains enveloping a polyiodine are fixed by interchain hydrogen bonding. An about 1.26 Å shift of the neighboring chain along the chain axis is required so that all the OH groups may participate in this mode of hydrogen bonding. The distance of interchain hydrogen bonds is 3.07 Å in this model.

To verify the model in Figure 4, the X-ray meridional intensity was calculated for the columnar Iodine arrays using the published distances between iodines in I_5^- species.¹⁴

Figure 5 shows the calculated meridional X-ray intensity curve for the I_5^- mode complex model. A main peak appears at $S = 0.165$ corresponding to the spacing of 3.03 ($S =$ scattering vector, the direction corresponding to the meridian parallel to the chain axis of PVA). The peaks in the intensity curve predicted by this model, however, do not satisfactorily explain the observed spacings. More importantly, the profile width of the peaks is much larger than experimentally observed values. This difference implies that the number of coherent iodine atoms causing the meridional reflections must be much larger than 5 in a complex.¹⁵ Thus we supposed that two I_5^- mode complex are arranged in series with a slightly larger distance (3.5 Å was assumed here) than that within each I_5^- (about 3.1 Å). The calculated meridional intensity curve for a pair of series arranged two I_5^- , i.e., $I_5^-I_5^-$ is shown in Figure 6 where comparatively good agreements are seen between observed and calculated ones in both the spacings and the width of profile. This seems to support the model of $I_5^-I_5^-$. As mentioned above, the distance between I_5^- species was assumed to be 3.5 Å.¹⁶ In general, the distance between ends of neighboring polyiodine chains is larger than the distance

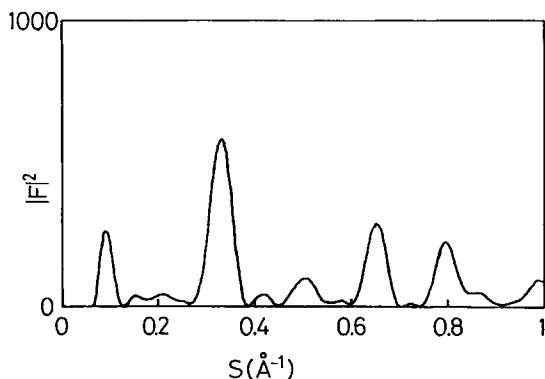


Figure 5 Calculated X-ray meridional intensity curve for the model having a I_5^- .

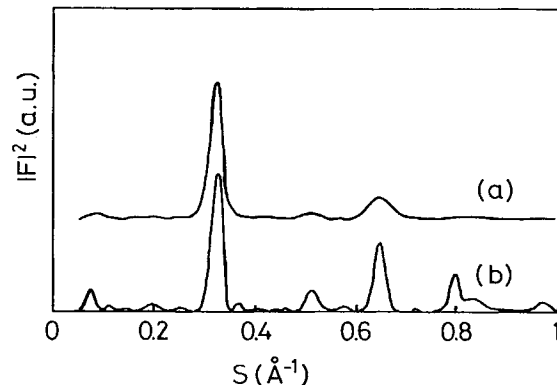


Figure 6 Calculated X-ray meridional intensity curve for the model having two I_5^- in comparison with observed intensity curve: (a) observed; (b) calculated.

between iodine atoms within a I_5^- .¹⁷ The $S = 0.8$ reflection, which appears in the observed curve but not in the calculated is mainly due to a half of periodicity of a PVA unit.

CONCLUSION

The amount of the complex formed in syndiotacticity-rich PVA is much larger than that formed in atactic PVA at a given iodine soaking condition, and the complex formed in a syndiotacticity rich PVA has a higher thermal stability in the soaking solution than that formed in atactic PVA.

A structure of the complex formed in the amorphous phase of PVA films in which a linear polyiodine I_5^- or I_3^- with a 3.1 Å periodicity is enveloped by four PVA chains of syndiotactic configuration with extended conformation is proposed. The four PVA chains participating in a complex are supposed to be fixed by interchain hydrogen bonds. The observed X-ray meridional intensity curve could be explained by a pair of series arranged two I_5^- , i.e., $I_5^-I_5^-$.

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Received December 9, 1991

Accepted July 7, 1992