Structure of Poly(vinyl alcohol)–Iodine Complex in Water Swollen Film

Yushi OISHI, Hiroshi YAMAMOTO, and Keizo MIYASAKA

Department of Textile and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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ABSTRACT: The structure of a poly(vinyl alcohol) (PVA)–iodine complex was investigated by a resonance Raman spectroscopy, wide angle X-ray diffraction, small angle X-ray scattering, NMR and IR spectroscopies. The Raman spectra of swollen PVA films exhibited fundamental scattering at 164, 108, and 42 cm^{-1} with Ar^+ ion and dye lasers as the excitation sources. The results of Raman spectra showed that only the I_5^- is formed in the complex, irrespective of the difference in the visible absorption spectra. The relative intensity of the peak at 65 ppm decreased with increasing amount of complex in the ^{13}C NMR spectra. The absorbance of the infrared spectrum in the region of $2900\text{--}3300\text{ cm}^{-1}$ decreased with increased iodine concentration of the soaking solution, while the absorbance in the region of $3300\text{--}3700\text{ cm}^{-1}$ increased. These results show that some changes in the state of hydrogen bondings are induced by complexation. The weight of the PVA film increased rapidly by iodine sorption at the first stage and then decreased. The changes of the long period and volume took place rapidly, being followed by much slower increase in Young's modulus. The ratio of the decrease in volume was much larger than that of the long period. It was assumed that the fast contraction in iodine-soaking was mainly due to the release of water out of membranes induced by iodine-sorption but not due to the complexation.

KEY WORDS Iodine–Poly(vinyl alcohol) Complex / Poly(vinyl alcohol) / Resonance Raman Spectroscopy / Wide Angle X-Ray Diffraction / Small Angle X-Ray Scattering / NMR / IR / Hydrogen Bond / Polyiodine /

The blue PVA-iodine complex has already been studied by many authors. X-ray diffraction studies¹ reveal that straight polyiodine chains of a $3.1\text{ \AA}$ periodicity lie parallel to the orientation direction of PVA. The number of iodine atoms in a polyiodine chain, however, depends on the researchers. Haisa *et al.*² proposed that the polyiodine chains are made of more than 15 iodine atoms on the basis of the width of an X-ray diffraction. Heyde *et al.*³ and Inagaki *et al.*⁴ found that the resonance Raman spectrum of the PVA–iodine complex formed in the solution was similar to that of the amylose–iodine complex, and assumed that I_3^- was formed in the PVA–iodine complex. Later however it was confirmed by Teitelbaum⁵ that I_5^- is still formed in the amylose–iodine complex.

In a previous paper,⁶ it was shown that under a given soaking condition, λ_{max} shifts continuously from 525 to 610 nm with increasing degree of hydration, DH and decreasing temperature. Kojima *et al.*⁷ observed that λ_{max} shifts continuously from 620 to 700 nm with extension of PVA films. Zwick⁸ reported that in a PVA solution, λ_{max} shifts continuously from 580 to 700 nm with increasing concentration of boric acid added to the iodine and PVA solution. It is believed that the red shift of λ_{max} is due to the increased number of iodine atoms in polyiodine chains. Only ambiguous explanations, however, have been given to this problem.

There have been many discussions about the structure of PVA chains in the complex. A helical model^{4,8} and an aggregation model^{9,10}

are proposed for the structure of the PVA-iodine complex. We observed an enhancement of the complexation by extension of a PVA film on soaking in a dilute iodine solution.¹¹ This seems to support the aggregation model for the PVA-iodine complex. Terao *et al.*¹² studied the state of hydrogen bonds and tacticity of PVA by high-resolution solid-state ¹³C NMR, implying the usefulness of the method for the study of the complex structure.

In this paper, the structure of the complex is studied in relation to the chain conformation of PVA and polyiodine chain, using a resonance Raman spectroscopy, wide angle X-ray diffraction, high-resolution solid-state ¹³C NMR and Fourier transform infrared spectroscopy FT-IR. The effect of the superstructure of PVA films on the complexation is also examined by small angle X-ray scattering.

EXPERIMENTAL

The preparation methods of PVA films and iodine aqueous solutions were the same as those described in a previous paper,⁶ PVA (DP=2000) was used after being saponified further with sodium methoxide in MeOH. Films 100 μ m thick were cast at room temperature from a 7 wt% aqueous PVA solution, followed by annealing to get different DHs of the specimens. The DH was defined as the volume fraction of water in a PVA film at the equilibrium swollen state. The concentration of iodine in the solution varied from 5×10^{-4} to 1×10^{-1} mol l⁻¹.

The Raman spectra were obtained by a Nippon Denshi 400D Raman spectrophotometer. The 514.5 nm line of an argon ion laser and 600.0 nm line of a rhodamine 6G dye laser were used as the excitation sources. To prevent damage to the samples due to irradiation of the laser beam, 50 milliwatts of power were used and the samples were rotated at 1500 rpm. For an oriented sample, the laser beam was defocused to reduce cross-sectional power density. Spectra were obtained at a

resolution of 5 cm⁻¹ and a 90° scattering geometry.

A stabilized generator (Rigaku Rotaflex RU-200) operating at 50 kV—180 mA was used as the X-ray source. Wide and small angle X-ray measurements were carried out by a transmission method using a Rigaku SG-7 and a Rigaku Model-1 goniometers, respectively. The SAXS intensity was desmeared using the following equation¹³

$$I(S) = -\frac{\exp(p^2 S^2)}{p\pi^{1/2}} \int_0^\infty \frac{N'[(S^2 + t^2)^{1/2}]}{(S^2 + t^2)^{1/2}} dt$$

where S is a scattering angle and $N(S) = I(S) \exp(-p^2 S^2)$.

Solid-state ¹³C NMR spectra were obtained by a Nippon Denshi GX-270 spectrometer operating at 67.9 MHz for ¹³C using the cross-polarization technique (CP) with high-power proton decoupling and magic-angle spinning (MAS). The contact time was 2.0 ms and a repetition period was 5.0 s. CP/MAS spectra were obtained at a spinning frequency of 3.5 kHz. ¹³C chemical shifts are shown in parts per million (ppm) relative to that of Me₄Si.

For measuring infrared spectra, films about 2—3 μ m thick were cast, followed by annealing at 170°C to get a low DH specimen. IR spectra were recorded on a JASCO FT/IR-3 spectrophotometer.

Strips 4 cm long and 5 mm wide cut from the films were soaked in an iodine concentration of 5×10^{-2} mol l⁻¹ and stretched at a rate of 2.3 mm min.⁻¹ The extension force was measured with a strain gauge, and then standardized by the cross-sectional area of the swollen films. Young's modulus was estimated from the slope.

RESULTS AND DISCUSSION

Swollen PVA films of DH=0.87 were soaked in iodine solutions of $1-4 \times 10^{-3}$ mol l⁻¹ for 24 hours to form the complex. The resonance Raman spectra of these wet specimens obtained with the 514.5 nm line of an Ar⁺ ion

Figure 1. The resonance Raman spectra (ν_0 514.5 nm) of swollen PVA films soaked at various concentrations of iodine solution: (a) 1×10^{-3} mol l $^{-1}$; (b) 2×10^{-3} mol l $^{-1}$; (c) 4×10^{-3} mol l $^{-1}$.

laser are shown in Figure 1. Their spectra exhibit strong scattering at 164 cm^{-1} and weaker ones at 108 and 42 cm^{-1} . In addition, the overtone bands at 108 and 164 cm^{-1} obviously appear at 213 and 322 cm^{-1} , respectively. The appearance of the combination band at 275 cm^{-1} may be evidence that the 164 and 108 cm^{-1} bands are due to fundamental transitions of the same iodine species. An intense transition at around 160 cm^{-1} has been found in compounds containing I_5^- species.^{14–16} The Raman active frequency of this transition varies depending on the I_5^- symmetry. For a symmetric and linear I_5^- ion, a strong band appears at 162 cm^{-1} ,¹⁴ while the frequency shifts to a higher value for distorted I_5^- species, formed by interactions between I_2 and I_3^- . The latter Type of I_2/I_3^- interactive units gives rise to vibrational transitions at

167 cm^{-1} in (benzophenone)₉ $(\text{KI})_2\text{I}_7\text{CH}\cdot\text{Cl}_3$,¹⁵ and at 175 cm^{-1} in the 2·perylene· 3I_2 complexes.¹⁴ On the other hand, the bent I_5^- ion in the $(\text{CH}_3)_4\text{N}^+\text{I}_5^-$ complex exhibits quite broad and split bands in the resonance Raman spectrum.¹⁴ In the PVA–iodine complex, a sharp and strong band is observed at 164 cm^{-1} , suggesting that the symmetric and linear I_5^- is formed. In the nylon 6–iodine complex, the band observed at 113 cm^{-1} was assigned to the I_3^- species because of the large change in the relative intensities of bands at 113 and 169 cm^{-1} with change in the sample history. In this case the ratio of the intensity at 108 cm^{-1} to that at 164 cm^{-1} , evaluated from the peak areas, remained almost unchanged with the iodine concentration. The resonance Raman spectrum of iodine containing PVA films seemed to depend on the degree of polymerization DP.⁴ In the case of PVA of DP=500, the strong Raman band at 106 cm^{-1} was found to appear and as many overtones could be observed as the sixth for the excitation by 488.0nm line of Ar^+ ion laser, while the scattering species was assigned to I_3^- , on the basis of the Raman data by Teitelbaum *et al.*⁵ However, in the case of PVA of DP=2000, the resonance Raman spectrum exhibited no band assignable to the I_3^- species. The difference between these Raman spectra may depend on the residual amount of acetyl groups.*

Anyway, PVA of DP=2000 was used in this study, and a combination band of the scatterings of 164 and 108 cm^{-1} was observed. Thus, we conclude that only the I_5^- species is formed in the PVA–iodine complex at this swollen system. Next, the reason for the red shift of λ_{max} with increasing DH was investigated. Generally, one may list the following three

* In the original manuscript we considered that the difference in the results of ref 4 and this work must be due only to differences in the degree of polymerization. One of the referees, however, kindly suggested that the difference might be also due to that in the residual amounts of acetyl groups, since in ref 4, the commercial sample was used without further saponification, while in this work, the sample was further saponified, and very small amounts of acetyl groups possibly have great influence on the complexation. His suggestion is considered to be reasonable enough to take into consideration.

possibilities for the problem: (I) the increase in the number of atoms in a polyiodine, (II) the increase in the fraction of the species with larger number of atoms, (III) some other changes in the structure of the complex than that in the number of iodine atoms, *i.e.*, the change in the surroundings of the polyiodine chain. The results on the resonance Raman spectra showed that the second possibility is not this case, although we adopted this explanation in our previous paper.⁶ Thus we should say that our explanation in ref 6 ought to be withdrawn.

Swollen PVA films of DH=0.87 and 0.47 soaked in an iodine solution of 1×10^{-3} mol l^{-1} for 24 hours, had $\lambda_{\max}$ at 614 and 532 nm in the visible absorption spectra, respectively. The resonance Raman spectra of these specimens obtained with the 514.5 nm line of the Ar^+ ion laser and the 600.0 nm line of a dye laser are shown in Figures 2 and 3, respectively. It should be noted that all these spectra are essentially identical, *i.e.*, these spectra are hardly affected by changes in DH of PVA films and by the wave length of excitation. This indicates that the scattering species are essentially identical even for specimens with different values of $\lambda_{\max}$. If the iodine in the PVA-iodine complex takes a form other than linear I_5^- , one would expect some differences in the spectra.

The change in the wavelength of excitation only causes a slight shift in the frequency of transition from 164 to 160 cm^{-1} and a sharpening of the peak at 160 cm^{-1} for both specimens, indicating that the scattering species are essentially identical for these specimens. Therefore, it is concluded that the shift changes in the surroundings of the I_5^- polyiodine chain.

The polarized Raman scattering of a specimen dried after being extended in a dilute iodine solution was measured to study the orientation of the polyiodine chain. Figure 4 shows the polarized resonance Raman spectra of an iodinated uniaxially oriented PVA

Figure 2. The resonance Raman spectra (ν_0 514.5 nm) of swollen PVA films on complexation of (a) DH=0.87; (b) DH=0.47.

Figure 3. The resonance Raman spectra (ν_0 600.0 nm) of swollen PVA films on complexation of (a) DH=0.87; (b) DH=0.47.

Figure 4. Polarized resonance Raman spectra of iodinated, uniaxially oriented PVA film. The polarizations with respect to the draw direction are shown in this figure.

film. Two major transitions at 108 and 164 cm^{-1} were observed. The scattering intensity in the polarization along the draw direction is much more intense than that in the polarization normal to the draw direction. This indicates that I_5^- species is highly oriented parallel to the draw direction.

The number of iodine atoms in a polyiodine chain was also estimated from the width of the X-ray diffraction meridional peak of the oriented specimen, which arises from the linear iodine lattice.¹ In this case, the meridional peak appeared at $2\theta = 28.8^\circ$, showing that the iodine atoms form a linear lattice of $3.1\text{ \AA}$ in the direction of molecular orientation. The Laue function for a linear lattice consisting of N atoms is given by

$$L^2(S) = (\sin N\pi S \cdot C / \sin \pi S \cdot C)^2$$

where S is the scattering vector, C is the lattice vector whose length is $3.1\text{ \AA}$ in this case. The width of the function was graphically estimated as a function of N to be compared with the experimentally estimated values. In the experimental estimation of this peak width, the instrumental broadening was corrected using silicon powder. The number of iodine atoms thus obtained is shown as a function of λ_{max} in Figure 5. The estimated number of iodine atoms at each λ_{max} gives about 9, which is certainly too large for I_5^- . It should be remarked that the width of the profile tends to increase slightly with increasing λ_{max} , and that the value of N estimated from the width increases between 9 and 10, as shown in Figure 5. Originally, N must be an integral number. However, it may be possible for N to be more than five if the I_5^- species can aggregate in the complex, having a phase correlation between (or among) them, although this possibility has not yet been checked. In the case of iodine-doped polyacetylene, the number of iodine atoms estimated by X-ray diffraction was also much larger than that expected from other reliable techniques, as in this case.¹⁷ The reason why such large values are estimated by

Figure 5. The number of iodine atoms as a function of λ_{max} of extended PVA film by a factor of 2.5 in the iodine solution of $3 \times 10^{-3}\text{ mol l}^{-1}$.

Figure 6. Exciting frequency (ν_0) dependence of the resonance Raman spectra of swollen PVA film on enhanced complexation by an addition of boric acid ($\text{I}_2\text{-2KI}$, $5 \times 10^{-4}\text{ mol l}^{-1}$; B(OH)_3 , $5 \times 10^{-1}\text{ mol l}^{-1}$): (a) 600.0 nm; (b) 514.5 nm.

X-ray diffraction method should be studied further.

The resonance Raman spectra of the PVA film soaked in an iodine solution added with boric acid, having λ_{max} at 650 nm obtained with the 514.5 nm and 600.0 nm lines of the Ar^+ ion and dye lasers are shown in Figure 6. There are no observable differences in their spectra. This also implies that the shift of λ_{max} caused by the addition of boric acid is due to the surroundings in the polyiodine chain.

A high-resolution solid state ^{13}C NMR by the combined techniques (CP/MAS) was also used to study the structure of PVA chains in the complex. The specimens were prepared by soaking PVA films in iodine solutions of 2×10^{-3} and $8 \times 10^{-2}\text{ mol l}^{-1}$, followed by drying in air. The CP/MAS spectra of these specimens and of an untreated PVA film are shown in Figure 7. The relative intensity of the

Figure 7. ^{13}C CP/MAS spectra of PVA films soaked in (a) water; (b) iodine solution of $2 \times 10^{-3} \text{ mol l}^{-1}$; (c) iodine solution of $8 \times 10^{-2} \text{ mol l}^{-1}$.

peak at 65 ppm decreases with increasing concentration of the iodine solution, *i.e.*, the increase in the amount of the complex. The decrease is considered to be attributable to the breakage of intermolecular hydrogen bonds.¹² This indicates that the PVA segments participating in the complexation, which is supposed to surround a polyiodine chain, lose their ability to form hydrogen bonds with the neighboring segments. This change in hydrogen bonding of PVA segments will be discussed further by IR spectrum.

It is well known that the broad band at 3340 cm^{-1} observed in the IR spectrum of PVA is assigned to the $\nu(\text{OH})$ mode,¹⁸ and that this absorption of frequency indicates the existence of an intermolecular type of hydrogen bonding. Then, we investigated the change in the structure of PVA on complexation by IR analysis. Figure 8(a) shows the infrared spectra for the region of $2800\text{--}3800 \text{ cm}^{-1}$ of PVA films soaked at various concentrations of iodine. The broad band at 3340 cm^{-1} observed in the spectra slightly shifts to a higher frequency with increasing iodine concentration. To clarify the change,

Figure 8. (a) The infrared spectra of iodine-sorbed PVA film: (—) untreated; (---) $6 \times 10^{-2} \text{ mol l}^{-1}$; (-----) $1 \times 10^{-1} \text{ mol l}^{-1}$. (b) The difference spectra of iodine-sorbed PVA film: (---) $2 \times 10^{-2} \text{ mol l}^{-1}$; (---) $6 \times 10^{-2} \text{ mol l}^{-1}$; (---) $8 \times 10^{-2} \text{ mol l}^{-1}$; (-----) $1 \times 10^{-1} \text{ mol l}^{-1}$.

the difference between the spectra of a PVA film which sorbed a given amount of iodine and of the pure PVA film is shown in Figure 8(b). A systematic change is observed in the region of $2800\text{--}3800 \text{ cm}^{-1}$ on the IR spectrum with increasing iodine concentration in the soaking solution. The absorbance in the region of $2900\text{--}3300 \text{ cm}^{-1}$ decreases with increasing iodine concentration, while the absorbance in the region of $3300\text{--}3700 \text{ cm}^{-1}$ increases. However, the magnitude of this change is small, as seen in Figure 8(a). It has been shown that certain dihydroxy compounds possess two OH stretching bands and that the higher and lower frequency bands are due to the intramolecular and the intermolecular hydrogen bonds¹⁹ respectively. These results indicate that the intermolecular hydrogen bonds are broken by complexation, resulting in the increase of the intramolecular hydrogen bond. This and the results on the resonance Raman seem to support an aggregation model in which the polyiodine is covered by a flux of some PVA chains.

Figure 9 shows small angle X-ray scattering profiles of swollen PVA films of $\text{DH}=0.60$ soaked in iodine solutions of 0 , 5×10^{-3} , $5 \times 10^{-2} \text{ mol l}^{-1}$. The scattering intensity in-

Figure 9. Change in small angle X-ray scattering profile of the swollen PVA film on complexation: (---) untreated; (-.-) $5 \times 10^{-3} \text{ mol l}^{-1}$; (—) $5 \times 10^{-2} \text{ mol l}^{-1}$.

Table I. Change in the long period of the swollen PVA film on complexation

Iodine concentration	Long period
mol l^{-1}	$\text{\AA}$
0	151
5×10^{-3}	139
5×10^{-2}	126

creases with increasing iodine concentration, which is considered due to the increase in the density difference between the PVA crystallite and iodine-sorbed amorphous PVA. The long period of each specimen observed in Figure 9 is shown in Table I. It decreases with increasing iodine concentration, and the ratio of the long period of the specimen soaked in the $5 \times 10^{-2} \text{ mol l}^{-1}$ solution to that of the unsoaked specimen was 0.83 in this specimen of $\text{DH}=0.60$.

Figure 10 shows changes of the volume, Young's modulus, long period and weight of the PVA film of $\text{DH}=0.70$ during soaking in the iodine solution of $5 \times 10^{-2} \text{ mol l}^{-1}$. The weight of the PVA film increased rapidly by iodine sorption during the first several minutes and then started to decrease. It is considered that this decrease in weight is due to the release of water. The changes of the long period and volume took place rapidly and ended in an hour, while the change of Young's modulus took place much slower and lasted for six or

Figure 10. The time dependency of volume, Young's modulus, long period and weight of the swollen PVA film during soaking in the iodine solution.

seven hours. Kojima *et al.*⁷ considered that the contraction of a film in an iodine solution was due to the additional formation of networks induced by PVA-iodine complexes. However, we would like to assume from the fast changes in the volume and the weight in an iodine solution that the contraction of the film is due to the release of water out of the membranes induced by iodine sorption. The ratios of the volume in the iodine solution to that in water was 0.90, while that of the long period was 0.62, indicating that the contraction of the long period is much larger than that of the volume. This implies that the contraction is induced in the amorphous chain networks formed by tie chains, both ends of which are fixed at the interfaces of the crystals stacked in series along the long period, and also suggests a high reliability of our proposal of the double network structure in a previous paper.⁷

CONCLUSION

The PVA-iodine complex at the swollen

state is formed so that the polyiodine chain (I_3^- species) may be surrounded by several extended PVA segments. The shift of $\lambda_{\max}$, caused by DH, the addition of boric acid and the extension of an iodine-sorbed PVA film, is due to the change in the surroundings of the polyiodine chain. Iodine sorption of PVA films leads to the release of water and contraction in the amorphous chain network, resulting in the contraction of the PVA film.

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