

Structure and Properties of Poly(vinyl alcohol)–Iodine Complex Formed in the Crystal Phase of Poly(vinyl alcohol) Films

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SYNOPSIS

The structure and optical properties of the complex formed in the crystal phase of PVA that is caused by soaking at very high iodine concentration are investigated. In the resonance Raman spectra of lightly and heavily iodinated specimens, two Raman shifts appeared at 109 and 161 cm^{-1} . The 109 cm^{-1} peak due to the I_3^- mode was much stronger than the 161 cm^{-1} peak in a heavily iodinated specimen, whereas the peak was comparable with the 161 cm^{-1} peak in a lightly iodinated specimen. The complex formed in the crystal phase is identified as the I_3^- mode complex. It has an averaged iodine–iodine distance of 3.2 Å, which is different from the 3.08 Å of the I_5^- mode complex formed in the amorphous phase. The effect of KI concentration in the soaking solution on the formation of the complex is also examined. The increased KI concentration in the soaking solutions at a fixed iodine concentration increases the amount of the complex formed in the crystal phase. The change in the hydrogen-bonding state in the crystal phase with the complex formation can be evidenced by IR and NMR. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It is well known^{1–3} that when PVA films are soaked in comparatively low concentrated iodine–KI solutions PVA forms a complex with iodine in the amorphous phase, resulting in a visible absorption with a maximum at about 600 nm depending on the soaking conditions. The iodine species consisting of the complex formed have been assigned to I_5^- or I_3^- on the basis of the Raman and visible absorption spectra.^{4–6}

Recently, we found that when the iodine concentration of the soaking solution is higher than about 1×10^{-2} mol/L, iodine penetrates into PVA crystals to form a cocrystal with PVA whose structure was proposed on the basis of X-ray equatorial diffraction.⁷ It was also found that a new absorption peak appears at about 470 nm in the sample in addition to the peak at about 600 nm due to the complex

formed in the amorphous phase and that the new 470 nm peak is due to the PVA–iodine complex formed in the crystal phase of PVA.⁸

In this article, the structure and optical properties of the complex formed in the crystal phase of PVA that is caused by soaking at very high iodine concentrations are investigated, using spectroscopic methods, wide-angle X-ray diffraction, and pulsed NMR. The effect of KI concentration in the soaking solution on the formation of the complex is also examined.

EXPERIMENTAL

The same PVA films and iodine–KI solutions as those used in a previous article⁸ were used. For measuring the infrared, visible ray, and Raman spectra, films about 2–3 μm thick were cast by the same method in the previous article, followed by annealing at 170°C to obtain low D.H. specimens. D.H., the degree of hydration, is defined as the volume fraction of water in a PVA film at the equilibrium swollen

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state. (The D.H. of PVA film greatly affects the complex formation.²)

IR spectra were measured using a JASCO FT/IR-3 spectrophotometer. 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. Resonance Raman spectra were measured using a Nippon Denshi 400D Raman spectrophotometer. The 514.5 and 488.0 lines of an argon ion laser were used as the excitation sources.

X-ray measurements were carried out with $\text{CuK}\alpha$ X-ray. The diffraction intensity was measured in a transmission mode using a Rigaku SG-7 diffractometer equipped with a graphite-monochromator and a scintillation counter. For X-ray measurements, thick and uniaxially drawn PVA films were used. Use of uniaxially drawn films was necessary to concentrate the diffraction from polyiodines in the complex on the meridian.

NMR measurements were carried out using a Nihon Bruker PC-20 spectrometer operated at 20 MHz in the diode mode. The spin-spin relaxation time T_2 was measured by the solid echo method. For each measurement, 1024 points were collected and averaged over a cumulative number of 100 and an attenuation of 10 and analyzed by an NEC PC-9801 computer. All the NMR measurements were carried out at 68°C, which is higher than T_g (65°C) of the PVA film used in this study, which was slightly depressed by the small amount of sorbed water.

RESULTS AND DISCUSSION

Figures 1 and 2 show the Raman spectra, excited with 514.5 and 488.0 nm lines of an Ar^+ ion laser, for two specimens soaked in solutions with low and high iodine concentrations. Two Raman shifts appear at 109 and 161 cm^{-1} in the spectra of both specimens, although their intensity ratios depend on the iodine concentration in soaking solutions. In Figure 1, the 109 cm^{-1} peak is stronger in the heavily iodinated specimen than is the 161 cm^{-1} peak, whereas both of them are comparable in the lightly iodinated specimen.

On the other hand, Figure 2 shows that the 109 cm^{-1} peak intensity is enhanced much more by 488.0 nm excitation compared with the 514.5 nm excitation. According to Teitelbaum et al.,⁹ the symmetric I_3^- species show a strong single Raman band due to a symmetric stretching vibration in the region of 108–118 cm^{-1} : The frequency varies depending on the structure of the I_3^- species. On the other hand, the I_5^- species shows an intense transition at around

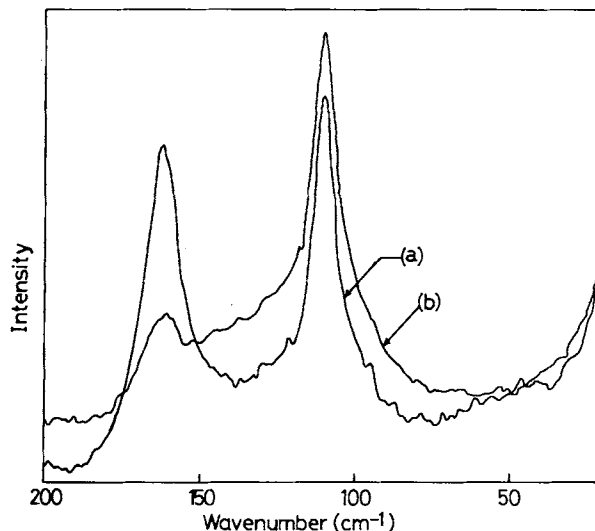


Figure 1 Resonance Raman spectra (ν_0 514.5 nm) of iodinated PVA films soaked at different concentrations of iodine solution: (a) 5×10^{-3} mol/L; (b) 1×10^{-1} mol/L.

160 cm^{-1} (Refs. 10–12): The frequency varies depending on the I_5^- symmetry. The changes in the intensity ratio of these two shifts with the changes in the iodine concentration in the soaking solution and in the exciting wavelength indicate that the ratio of amounts of the I_3^- complex to that of the I_5^- remarkably depends on the iodine concentration of the soaking solutions; at high iodine concentration, the amount of the I_3^- complex remarkably increases. From these results and the fact previously reported that iodine penetrates into PVA crystals to form a cocrystal at high iodine concentration soaking led us to speculate that the PVA–iodine complex formed in the crystals must be an I_3^- mode complex.

Figure 3 shows wide-angle X-ray meridional intensity curves due to polyiodines in the complex formed in PVA films soaked at various iodine concentrations. In the X-ray curve of the sample soaked at 5×10^{-2} mol/L, a shoulder appears at about $2\theta = 28^\circ$ in addition to the peak at $2\theta = 29^\circ$, indicating the formation of a new mode of polyiodine with about a 3.2 Å period. The curve of 1×10^{-1} mol/L shows the remarkable growth of the $2\theta = 28^\circ$ shoulder. The new peak appears only at a high enough iodine concentration soaking that iodine can penetrate into the PVA crystals. Thus, the new polyiodine giving rise to the 3.2 Å period must form in the PVA crystalline phase. It should be noted that most of the complexes forming in the PVA crystal are those of the I_3^- mode and that the I_3^- complex in the crystals is much less stable in the deiodination.⁸ Thus, the $2\theta = 29^\circ$ peak is attributed to the I_5^- mode

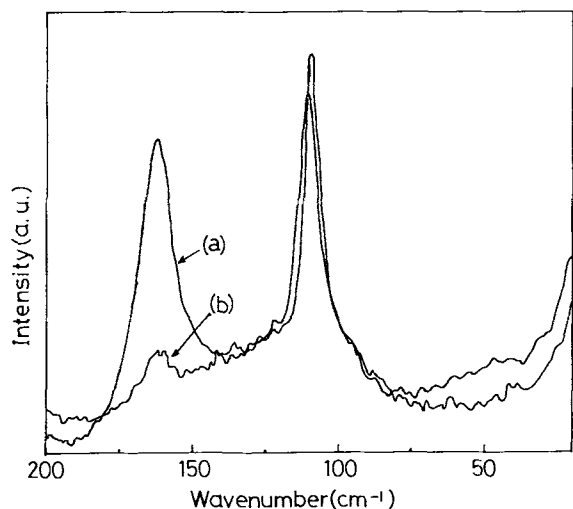


Figure 2 Exciting frequency (ν_0) dependence of the resonance Raman spectra of a iodinated PVA film soaked in a iodine solution (5×10^{-3} mol/L): (a) 514.5 nm; (b) 488.0 nm.

complex formed in the PVA amorphous phase, whereas the $2\theta = 29^\circ$ peak is attributed to the I_3^- mode, which is mainly formed in the PVA crystalline phase.[†]

Figure 4 shows the X-ray photographs of lightly and heavily iodinated $5\times$ drawn films. New meridional peaks appear at 4.8 \AA ($2\theta = 18.5^\circ$) and about 9.6 \AA ($2\theta = 9.2^\circ$) for the heavily iodinated sample, as indicated by arrows A and B, respectively. The 4.8 \AA spacing may be the second-order diffraction of the 9.6 \AA spacing. It should be noted that 9.6 \AA is very close to $9.4\text{--}9.7 \text{ \AA}$,¹⁴⁻¹⁶ which is the repeat distance of a polyiodine consisting of I_3^- ions. Herbstein et al.¹⁴ concluded from an analysis of triiodide of well-established structures that the repeat distance of the linear I_3^- chain varies between 9.59 and 9.89 \AA and suggested that a shorter repeat distance is due to kinking of successive I_3^- ions. Handa and Yajima assigned¹⁷ the Raman and absorption spectra of I_3^- ions in amylose with the bent dimeric I_3^- unit. These considerations led us to conclude that the 9.6 and 4.8 \AA meridional peaks observed in heavily iodinated specimens are assigned to the I_3^- arrays forming in the PVA crystals, although it is not certain whether the I_3^- arrays in the crystal phase are kinked.

[†] Murthy¹³ found that two kinds of polyiodine with spacings 3.08 and 3.2 \AA form in nylon 6 and that the polyiodine giving rise the 3.2 \AA spacing is less stable than is the other polyiodine, which is the same as that in the PVA case. However, he assigned both of the two polyiodines to the I_5^- mode on the basis of Raman spectroscopy, which is different from this PVA case, where each one is assigned to the I_5^- and I_3^- modes, respectively.

Figure 5 shows the effect of KI concentration in soaking solutions with a fixed iodine concentration on the absorption spectra of heavily iodinated specimens. The absorption peak at about 470 nm is intensified with increasing KI concentration at a fixed iodine concentration. On the other hand, it was confirmed that the effect of KI concentration on the absorption spectrum was almost negligible in lightly iodinated samples in which the PVA-iodine complex is formed only in the PVA amorphous phase. The increase in the KI concentration in the soaking solution must increase the concentration of I_3^- in the solution. Figure 5 indicates that the increased I_3^- concentration in the soaking solution increases the I_3^- mode polyiodine in the crystal phase.

This corresponds well to the change in the X-ray equatorial diffraction of iodinated PVA films soaked at the different KI concentrations shown in Figure 6. Figure 6 shows that the peak at $2\theta = 19.8^\circ$ becomes broader with the increase of KI concentration in the soaking solutions, implying the increased amount of iodine sorbed in the crystals.

In the PVA-iodine cocrystal proposed in a previous paper,⁷ polyiodine chains are intercalated between two PVA chains whose OH groups take a "face-to-face" position. Accordingly, the hydrogen bonding between PVA chains should be affected by the formation of the complex in PVA crystals.

Figure 7 shows the IR spectra in the region of $2800\text{--}3800 \text{ cm}^{-1}$ of iodinated PVA films soaked at various iodine concentrations. The broad band at 3340 cm^{-1} slightly shifts to a higher frequency side

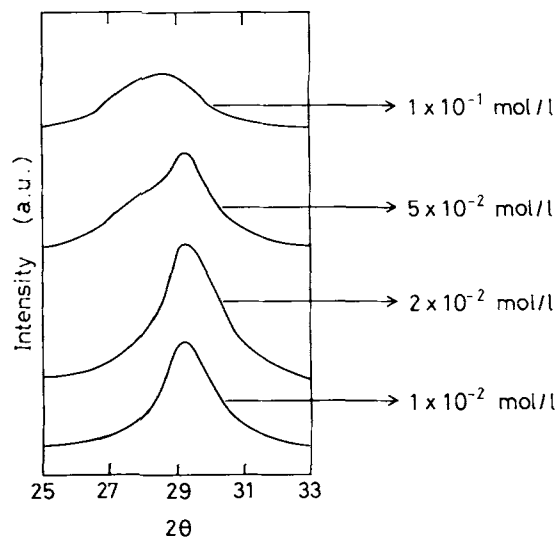


Figure 3 X-ray meridional intensity curves of iodinated PVA films soaked in the solution with various iodine concentrations.

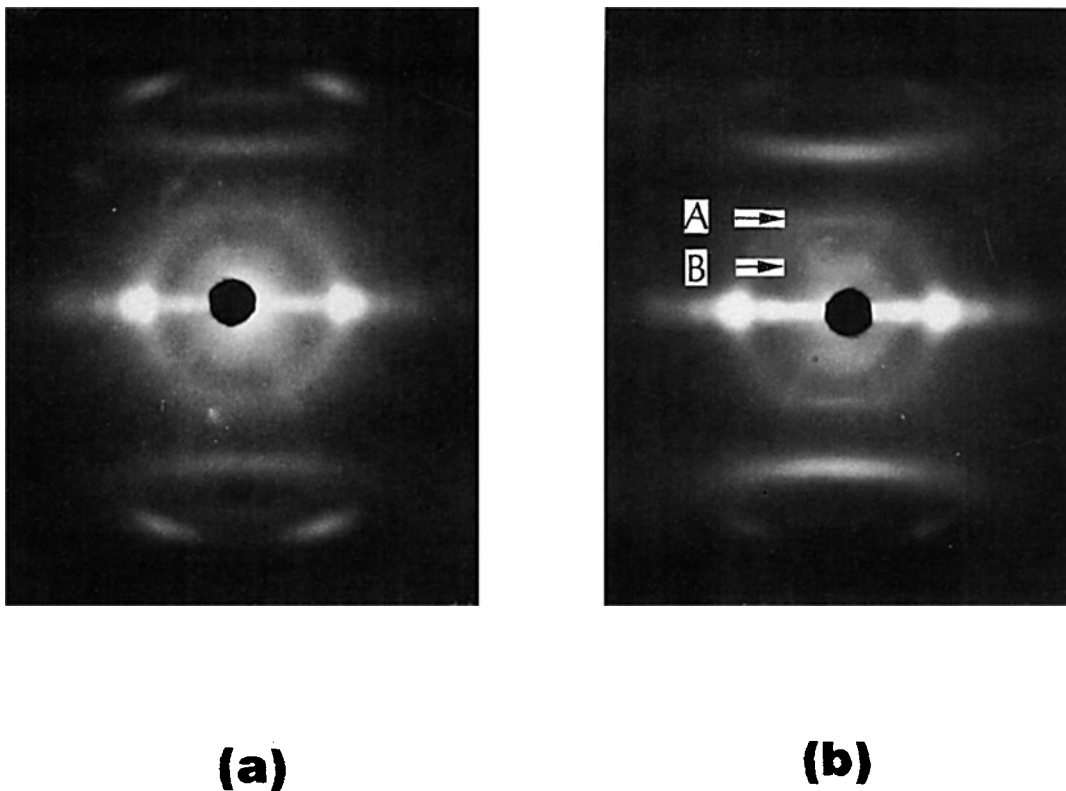


Figure 4 X-ray photographs of iodinated highly drawn PVA films ($\lambda = 5$) soaked in the solution with different iodine concentrations: (a) 1×10^{-2} mol/L; (b) 5×10^{-2} mol/L.

with increasing iodine concentration, accompanying a slight decrease in absorbance in the region of 2900–3300 cm^{-1} and increase in the 3300–3700 cm^{-1} region. It is well known that the high-frequency band is due to the free OH, whereas the low-frequency band is due to the bonded OH.^{18–21} Thus, Figure 7 indicates some breakage of the intermolecular hydrogen bonds is necessary to the complexation in the crystal phase.

A pulsed NMR also indicates the change of the hydrogen-bonding states of PVA chains on complexation. Figure 8 shows the semilog plots of the NMR free-induction decay (FID) of lightly and

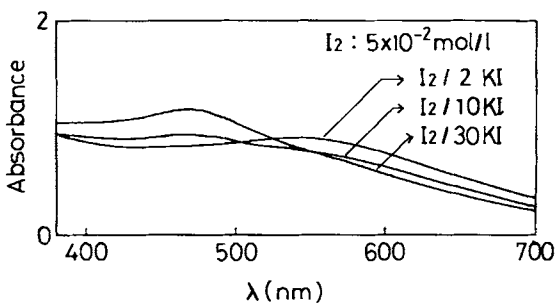


Figure 5 KI concentration dependence of the absorption spectra of heavily iodinated PVA films.

heavily iodinated PVA specimens. These FID curves are described with two components with each relaxation time related to the crystalline and amorphous

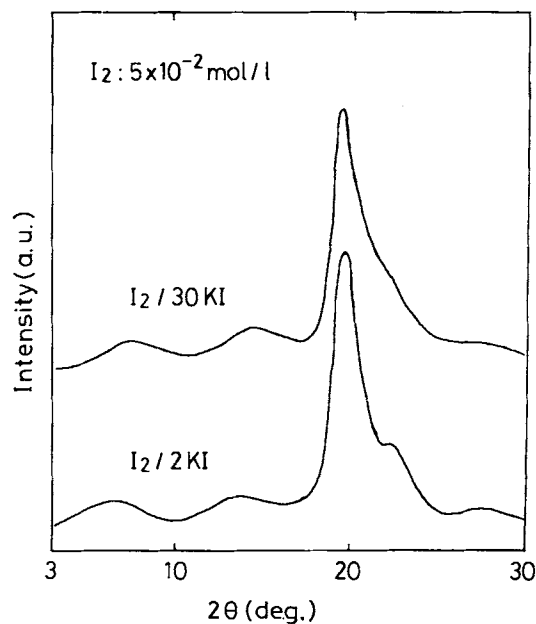


Figure 6 KI concentration dependence of the WAXD meridional intensity curves of heavily iodinated PVA films.

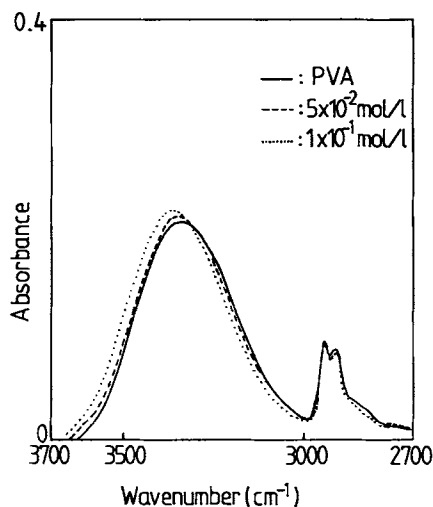


Figure 7 Infrared spectra of the iodinated PVA films soaked in the solution with various iodine concentrations: (a) untreated; (b) 5×10^{-2} mol/L; (c) 1×10^{-1} mol/L.

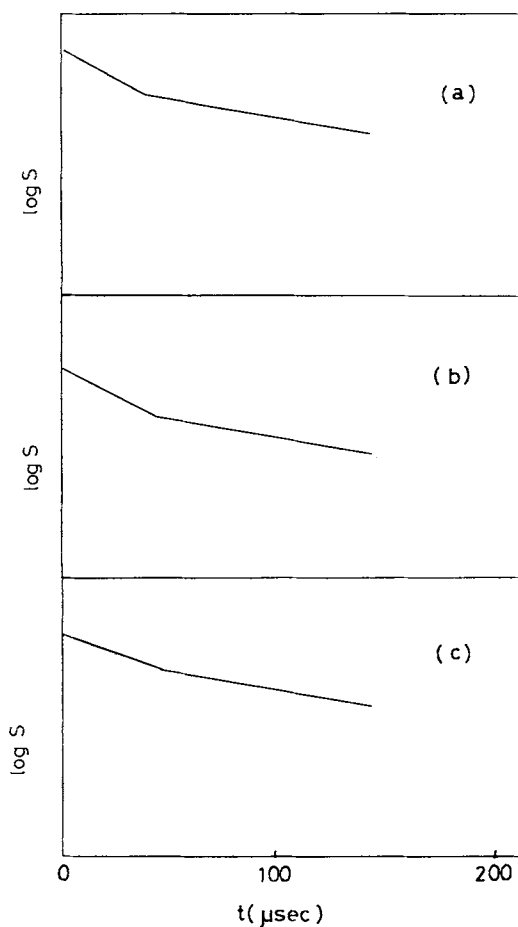


Figure 8 Semilog plots of the free induction decays (FID) of pulsed NMR for the iodinated PVA films soaked in the solution with various iodine concentrations: (a) untreated; (b) 5×10^{-3} mol/L; (c) 4×10^{-2} mol/L.

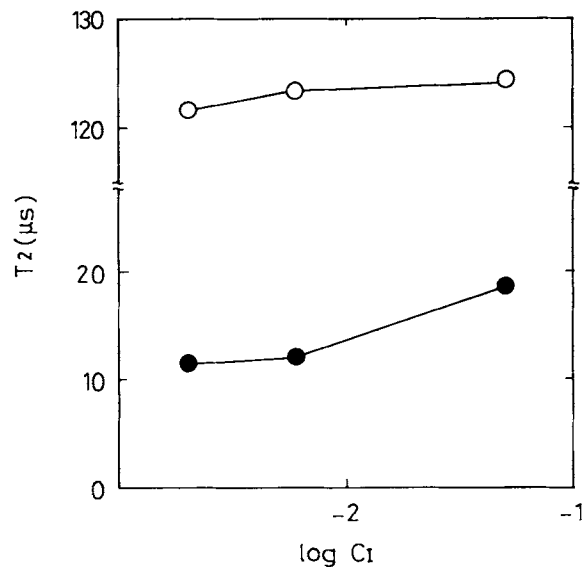


Figure 9 Changes of the T_2 relaxation times of the iodinated PVA films with increasing iodine sorptions.

phases of PVA.²² The two relaxation times, estimated from these FID curves by the method widely used for crystalline polymers,²³ are shown as a function of iodine sorption in Figure 9. For the lightly iodinated specimen, the relaxation times remain almost unchanged, except for the increase in T_2 , suggesting a slight increase in the mobility of the amorphous phase. For the heavily iodinated specimen, however, the mobility of the amorphous phase remains unchanged, whereas T_2 of the crystal phase increases, suggesting an increase in its mobility. These results are related to the changes of the hydrogen-bonding states in respective phases of PVA with increasing iodine sorption, in agreement with the above results.

CONCLUSIONS

1. In the resonance Raman spectra of lightly and heavily iodinated specimens, two Raman shifts appeared at 109 and 161 cm^{-1} . The 109 cm^{-1} peak due to the I_3^- mode was much stronger than the 161 cm^{-1} peak in a heavily iodinated specimen, whereas the peak was comparable with 161 cm^{-1} peak in a lightly iodinated specimen. This means that the complex formed in the crystal phase is identified as the I_3^- mode complex.
2. This I_3^- mode complex has an averaged iodine-iodine distance of 3.2 Å, which is larger than 3.08 Å of the I_5^- mode complex formed in the amorphous phase.

3. The increased KI concentration in soaking solutions at a fixed iodine concentration increases the amount of the complex formed in the crystal phase.
4. The change in the hydrogen-bonding state in the PVA crystal phase with the complex formation can be evidenced by IR and NMR.

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