Polymer Journal, Vol. 22, No. 7, pp 638—642 (1990)

SHORT COMMUNICATIONS

Poly(vinyl alcohol)–Iodine Complex in Poly(vinyl alcohol) Films Soaked at High Iodine Concentrations

Hiromi SAKURAMACHI, Yoon-So CHOI, and Keizo MIYASAKA

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

(Received December 7, 1989)

KEY WORDS Poly(vinyl alcohol)–Iodine Complex / Poly(vinyl alcohol) / Formalization / Visible Ray Absorption Spectrum / Poly(vinyl alcohol)–Iodine Crystal /

Poly(vinyl alcohol) (PVA) forms a complex with iodine in the amorphous region when PVA films are soaked in comparatively lower concentrated iodine–KI solutions.[1-13] Recently wide-angle X-ray diffraction patterns of iodinated PVA films showed that above 2×10^{-2} mol l^{-1} iodine concentrations in the soaking solution, iodine intrudes into PVA crystals and forms co-crystals with PVA.[14,15] This result stimulated our interest in the optical properties of highly iodinated samples. The amount of the complex formed in PVA films increases with increasing iodine–KI concentration of the soaking solution,[6] making visible ray absorption measurements difficult for iodinated PVA films at high iodine concentrations because of resulted large absorbance. This must be the reason why absorption spectra of highly iodinated PVA films have not yet been reported. To avoid this difficulty, however, we only had to use very thin PVA films. We are also interested in the effect of formalization of PVA on the complex formation. Formalization is considered to occur in the amorphous region[16] where the complex formation occurs as far as the iodine concentration is not so high as mentioned above. Thus formalization must affect the complex formation in the amorphous region.

This paper first reports absorption spectra of PVA films soaked at very high iodine concentrations where iodine atoms intrude into PVA crystals to form co-crystals, and then those of iodinated formalized PVA films to show the effect of formalization on the complex formation.

EXPERIMENTAL

Meterials and Films

PVA (Koso Chem. Co., DP = 2000, the degree of saponification = 0.99) was used after further saponification with sodium methoxide in methanol. Thin PVA films were cast in the following way: 7 wt% and 3 wt% PVA aqueous solutions were dropped on glass plates placed on a disk, and then the disk was rotated for one minute. These procedures resulted in dried films about 5 and 3 μm thick, respectively.

Annealing of PVA Films

These cast PVA films were annealed at 180°C for 10 min in vacuum. The degree of hydration D. H. defined as the volume fraction of water in water swollen PVA films was estimated at the equilibrium state at 20°C. (In our previous paper[6] it was reported that the structure of PVA films characterized by the D.

Table I.

Sample	D.H.	χ/%
Unannealed PVA film	0.90	49.8
Annealed PVA film	0.51	58.2

H. much affects their complex formation). Both as-cast and annealed films were used in this study. Table I shows the D. H. and crystallinity χ estimated by DSC.

Formalization

Some of annealed PVA films were formalized in a solution consisting of distilled water 50 cm^3, conc. sulfuric acid 5.5 cm^3, sodium sulfate anhydrous 10 g, and 37% formaldehyde solution 9.5 cm^3. The treatment was carried out at 60°C for 2 h, followed by washing with pure water and drying at 60°C for one hour. The reaction ratio (A) of products was determined by FTIR as follows:

$$A(\%) = (1 - D(\mathrm{OH})/D(\mathrm{OH}^0)) \times 100$$

where $D(\mathrm{OH}^0)$ and $D(\mathrm{OH})$ are the absorbance at 3340 cm^{-1} due to the OH stretching band measured before and after formalization.

Iodine-Soaking

Iodine and potassium iodine (Yanagishima Pharm. Co., GR grade) were used as received. Iodine–potassium iodide aqueous solutions with a mol ratio of 1 : 2 were prepared at iodine concentrations varied from 5×10^{-3} to 1×10^{-1} mol l^{-1}. PVA films were soaked in the soaking solutions at 20°C for 3 h which is long enough for absorption of iodine to reach the equilibrium.

Visible Ray Spectrum Measurements

Visible ray spectra of iodinated PVA films were measured in a range of wave length from 300 to 750 nm by a Hitachi-Perkin-Elmer 139 spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows absorption spectra of as-cast PVA films soaked at different iodine concentrations. Since both iodine–KI and KI solutions only show the absorption at 350 nm, it is clear that the 350 nm spectrum is not due to the complex. A broad absorption with a maximum at about 580 nm observed at an iodine concentration of 5×10^{-3} mol l^{-1} is due to a blue iodine–PVA complex. On the spectrum of 5×10^{-2} mol l^{-1} a new broad shoulder at about 470 nm appears in addition to the peak at 580 nm. This peak grows larger accompanying an observable color change of films from blue to red-violet with increasing iodine concentration. According to Choi a large amount of iodine penetrates into PVA crystals to form co-crystals with PVA above 2×10^{-2} mol l^{-1} iodine concentrations.[15] These results indicate that two different types of complex are formed when the iodine concentration of the soaking solution is high enough for iodine to penetrate into PVA crystals and form co-crystals with PVA.

Figure 2 shows absorption spectra of iodinated annealed PVA films soaked at different iodine concentrations. In this case the new broad absorption with a maximum at about 470 nm appears more clearly than that of as-cast PVA films. It should be remarked that the crystallinity is higher and the D. H. is lower in annealed films than in as-cast films, which corresponds to the fact that the 470 nm absorption is stronger in the former than in the latter.

In order to study stabilities of two absorptions at 580 and 470 nm, absorption spectra were measured in the course of iodine desorption. In this case PVA films were first soaked in a 1×10^{-1} mol l^{-1} solution and then dipped in pure water at 20°C. Figures 3 and 4 show changes of absorption spectra for as-cast and annealed PVA films soaked at a 1×10^{-1} mol l^{-1} iodine concentration with iodine desorption. In both as-cast and annealed

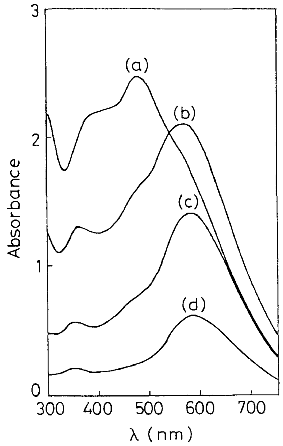

Figure 1. Absorption spectra of iodinated as-cast PVA-films soaked at different iodine concentrations. (a) $1 \times 10^{-1}\,\mathrm{mol\,l^{-1}}$; (b) $5 \times 10^{-2}\,\mathrm{mol\,l^{-1}}$; (c) $2 \times 10^{-2}\,\mathrm{mol\,l^{-1}}$; (d) $5 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ at 20°C.

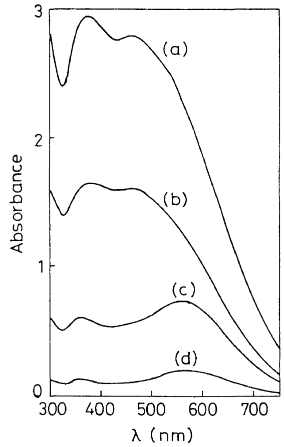

Figure 2. Absorption spectra of iodinated annealed PVA films soaked at different iodine concentrations. (a) $1 \times 10^{-1}\,\mathrm{mol\,l^{-1}}$; (b) $5 \times 10^{-2}\,\mathrm{mol\,l^{-1}}$; (c) $2 \times 10^{-2}\,\mathrm{mol\,l^{-1}}$; (d) $5 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ at 20°C.

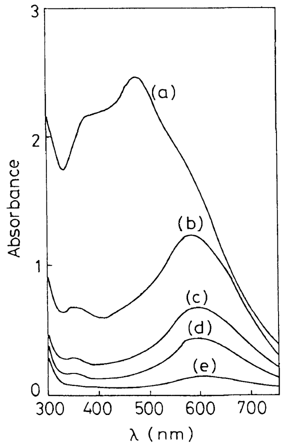

Figure 3. Changes of absorption spectra with iodine desorption for iodinated as-cast PVA films soaked at $1 \times 10^{-1}\,\mathrm{mol\,l^{-1}}$ iodine concentration. (a) 0 s; (b) 1 s; (c) 5 s; (d) 10 s; (e) 30 s.

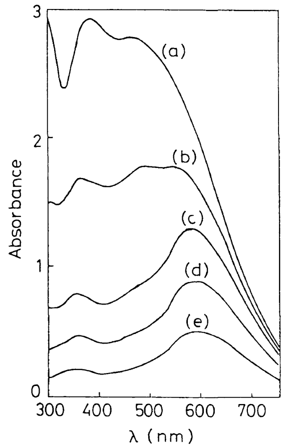

Figure 4. Changes of absorption spectra with iodine desorption for iodinated annealed PVA films soaked at $1 \times 10^{-1}\,\mathrm{mol\,l^{-1}}$ iodine concentration. (a) 0 s; (b) 1 s; (c) 5 s; (d) 10 s; (e) 30 s.

samples, absorption peaks at about 470 nm disappear more quickly than those at about 580 nm, indicating that the 470 nm complex is less stable than 580 nm one. As for Figures 3 and 4, one must be surprised to find that iodine desorption took place unbelievably quickly. This high rate of desorption may be related to the following points: (1) films were all very thin ($\sim 5\,\mu\mathrm{m}$), (2) iodine desorption must have continued for longer time than indicated in Figures 3 and 4 captions, *i.e.*, films were dipped in pure water for fixed times as indicated in captions, and then picked up out of water to be wiped, during which desorption must have continued. Thus we must not conclude that iodine desorption from the crystals took place in one second or so. The comparison of these figures shows that the 470 nm complex in

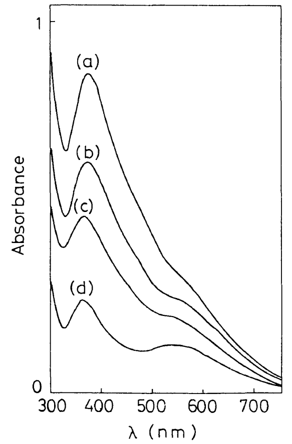

Figure 5. Absorption spectra of iodinated formalized PVA films soaked at different iodine concentrations. (a) 1×10^{-1} mol l^{-1}; (b) 5×10^{-2} mol l^{-1}; (c) 2×10^{-2} mol l^{-1}; (d) 5×10^{-3} mol l^{-1} at 20°C.

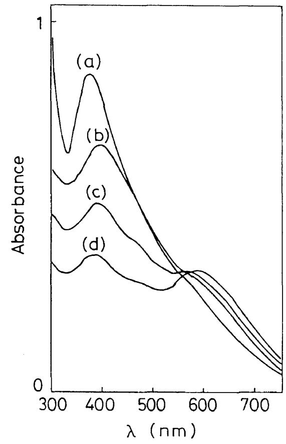

Figure 6. Changes of absorption spectra with iodine desorption for iodinated formalized PVA films soaked at 1×10^{-1} mol l^{-1} iodine concentration. (a) 0 s; (b) 5 s; (c) 10 s, (d) 30 s.

annealed films is stabler than that in as-cast ones. The annealed PVA film desorbed for one second clearly indicates the presence of two different types of complex. The facts that the 470 nm peak begins to appear remarkably at the iodine concentration where iodine begins to penetrate into PVA crystals, and that the complex in annealed PVA films is stabler against desorption than that in as-cast ones lead us to conclude that the new iodine–PVA complex with λ_{max} at about 470 nm is formed in the crystalline region of PVA films.

Now we will move to iodination of formalized PVA films. Figure 5 shows absorption spectra of iodinated formalized PVA films. An absorption peak at about 350 nm is so strong that the 470 nm peak is difficult to be distinguished, and therefore we cannot obtain any information about 470 nm peak due to the crystalline complex. The strong 350 nm peak, however, suggests that the amount of iodine absorbed in PVA films without participating with complex formation much increases with formalization. The color change of the complex from blue to red-violet was observed even at lower iodine concentrations in formalized specimens than in unformalized ones. Figure 6 shows changes of absorption spectra for formalized PVA films soaked at a 1×10^{-1} mol l^{-1} iodine concentration with iodine desorption. It should be noticed that the peak at about 580 nm which is due to the complex formed in the amorphous region still survives even after iodine desorption for 30 s indicating that the complex in formalized PVA films is stabler than that in non-formalized ones. The fact that the reaction ratio obtained from FTIR was 82% and the crystallinity was about 50% implies that formalization took place not only in the amorphous region but also partly in the crystalline region.

This is supported by Figure 7 showing changes of wide-angle X-ray diffraction intensity curves of PVA films with formalization. The peak at $2\theta = 19°$—$20°$ is assigned to a doublet of the (101) and $(10\bar{1})$ diffractions. Figure 7 indicates that formalization causes the peak to remarkably broaden and shift to a smaller angle, suggesting that formalization took place not only in the amorphous region but also in the crystalline region. The effect of formalization of PVA on visible ray absorption properties is being studied.

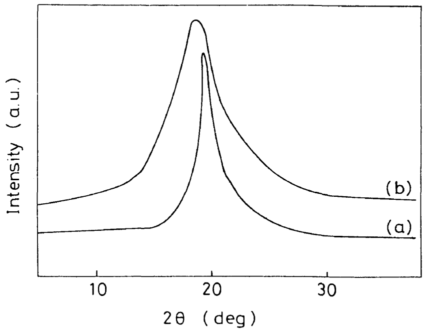

Figure 7. Change in the wide-angle X-ray intensity curves of an annealed PVA film with formalization. (a) before; (b) after formalization.

SUMMARY

1. When an iodine concentration of the soaking solution is higher than 2×10^{-2} mol l^{-1}, iodine forms co-crystals with PVA, and a new visible ray absorption peak appears at about 470 nm in addition to the peak at about 580 nm which appears usually at lower iodine concentrations. The new iodine–PVA complex at about 470 nm is concluded to be formed in the crystalline region of PVA films, while the conventional iodine–PVA complex at about 580 nm in this case is formed in the amorphous region.

2. This new 470 nm iodine–PVA complex disappears much more quickly with iodine desorption in pure water than 580 nm complex. The new 470 nm complex is stabler against desorption in annealed PVA films than in as-cast ones.

3. Formalization of PVA films affects the complex formation: (1) the amount of iodine absorbed in PVA films without participating in the complex formation seems to increase with formalization. (2) the stability of the complex formed in the amorphous region increases with formalization.

REFERENCES

1. W. O. Herrmann and W. Haehnel, *Ber. Dtsch. Chem. Ges.*, **60**, 1658 (1927).
2. H. Staudinger, K. Frey, and W. Starck, *Ber. Dtsch. Chem. Ges.*, **60**, 1782 (1927).
3. K. Imai and M. Matsumoto, *J. Polym. Sci.*, **55**, 335 (1961).
4. M. M. Zwick, *J. Appl. Polym. Sci.*, **9**, 2393 (1965).
5. M. M. Zwick, *J. Polym. Sci., A-1*, **4**, 1642 (1966).
6. Y. Oishi and K. Miyasaka, *Polym. J.*, **18**, 307 (1986).
7. M. Haisa and Y. Itami, *J. Phys. Chem.*, **61**, 817 (1957).
8. T. Yokota and Y. Kumura, *Makromol. Chem.*, **85**, 749 (1984).
9. T. Yokota and Y. Kimura, *Makromol. Chem.*, **186**, 549 (1985).
10. M. E. Heyde, L. Rimai, R. G. Kioponen, and D. Gill, *J. Am. Chem. Soc.*, **94**, 5222 (1972).
11. F. Inagaki, I. Harada, T. Shimanouchi, and M. Tasumi, *Bull. Chem. Soc. Jpn.*, **45**, 3384 (1972).
12. R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **102**, 3322 (1980).
13. S. Hayashi, T. Hirai, N. Hojo, H. Sugeta, and Y. Kyogoku, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 69 (1982).
14. V. K. Hess, R. Steinman, H. Kiessig, and J. Avisiers, Kolloid-Z., **153**, 128 (1957).
15. Y. S. Choi, Y. Oishi, and K. Miyasaka, *Polym. J.*, **22**, 601 (1990).
16. Kobunshi Gakkai ed, "Kobunshikagakujikkenho," Kagakudojin, Tokyo, 1986, p 61.