

Orientation of Polymer Chains in Films of Syndiotactic-Rich Poly(vinyl Alcohol)

KAZUO YAMAURA, KUNIKO TAKEYAMA, TETSUYA TANIGAMI, and SHUJI MATSUZAWA, *Faculty of Textile Science and Technology, Shinhsu University, Tokida 3-15-1, Ueda-city, Nagano-prefecture 386, Japan*

Synopsis

The infrared spectra of the films of syndiotactic-rich poly(vinyl alcohol) (*s*-PVA) prepared by the casting, frame, and bubble methods were obtained. The band at 705 cm^{-1} decreased with the increased inclination of the film plane to the direction of the irradiation of infrared rays and was related to the orientation of the molecules in the adsorbed phases of both sides of film.

INTRODUCTION

Films with a wide range of thickness of $60\text{ }\mu\text{m}$ to $260\text{ }\text{\AA}$ can be prepared from the aqueous solutions of syndiotactic-rich poly(vinyl alcohol) (*s*-PVA) by the casting, frame, and bubble methods.¹⁻⁴ The *s*-PVA molecules are adsorbed easily onto the air/solution interface.⁵ The adsorption was considered to play an important role in the formation of ultrathin films by the frame and bubble methods.^{1,4} For the ultrathin films of *s*-PVA, the authors have presented a soap membrane-like bilayer model in which a layer consisting of the hydrophobic regions (syndiotactic) are on the surface and hydrophilic regions (isotactic and atactic) are turned toward the interior.¹ However, the structure in the ultrathin *s*-PVA films has not been ascertained so far. It is of interest to determine the conformation of *s*-PVA molecules in films. This can be done by using infrared (IR) spectroscopy. In this article, the IR spectra of the films were taken by changing the angle between the light and film, and the differences examined.

EXPERIMENTAL

A *s*-PVA derived from vinyl trifluoroacetate (VTFA) was used. The bulk polymerization of VTFA was carried out at 60°C by using benzoyl peroxide as an initiator. Poly(vinyl trifluoroacetate) was converted to PVA by dissolving it in 2,2'-diaminodiethylamine. The degree of polymerization was 3980 and the content of syndiotactic diad was 55.1%.

All films were prepared from aqueous solutions as previously described.^{1,3,4} The polymer concentrations were 1.5 g/dL for the casting and the bubble methods and 0.6 g/dL for the frame method. The thickness of films obtained by the casting, frame, and bubble methods were $15\text{ }\mu\text{m}$, $2000\text{ }\text{\AA}$, and $700\text{ }\text{\AA}$, respectively. The preparation and thickness measurements of thin films obtained by the bubble and frame methods are described in our previous article.⁴

s-PVA films approximately 15 μm thick were cast from solution onto glass plates and air-dried for 24 h at about 20°C. The films used to record the IR spectra were taken from a pile of 8 sheets for the frame method and 20 sheets for the bubble method. IR spectra were taken using a JASCO A-302 infrared spectrophotometer (dispersive type).

RESULTS AND DISCUSSION

When the films were set perpendicularly to the direction of the irradiation of IR rays, the IR spectrum of the films prepared by the three methods resembled each other roughly except for the band at 1140 cm^{-1} . The band at 1140 cm^{-1} for the films prepared by the casting method was greater than that for the films prepared by the frame and bubble methods. Figure 1 shows the spectra obtained by inclining the film plane to the direction of the irradiation of IR rays for the films prepared by the bubble method by 90°, 75°, 60°, and 45°. The 705 and 770 cm^{-1} bands, which were not found for the films set in the normal direction, appeared distinctly when the angle was decreased from 75° to 45° for the former and at an inclination of 45° for the latter. This was almost the same for the films prepared by the frame method (Fig. 2), whereas for the films obtained by the casting method, the band at 705 cm^{-1} became a vague shoulder at an angle of 45° (Fig. 3). The band at 705 cm^{-1} increased with a decrease in thickness. If amount of polymer that is adsorbed onto the air/solution interface is assumed to be the same for the films prepared by the three methods, the fraction of the polymers in the middle phase between the adsorbed phases increases with an increase in film thickness. The band at 705

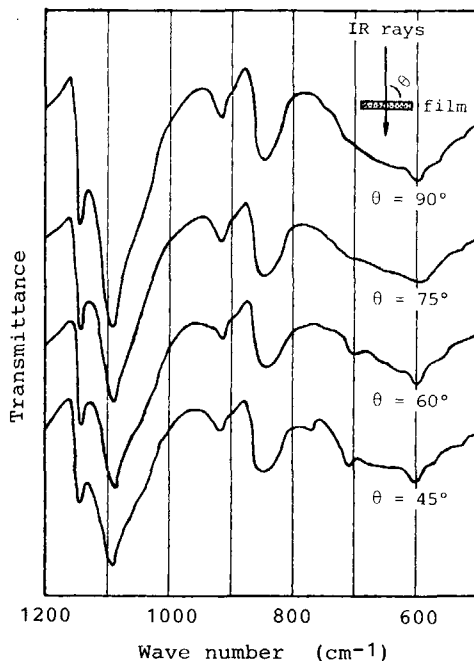


Fig. 1. IR spectra of *s*-PVA films obtained by the bubble method.

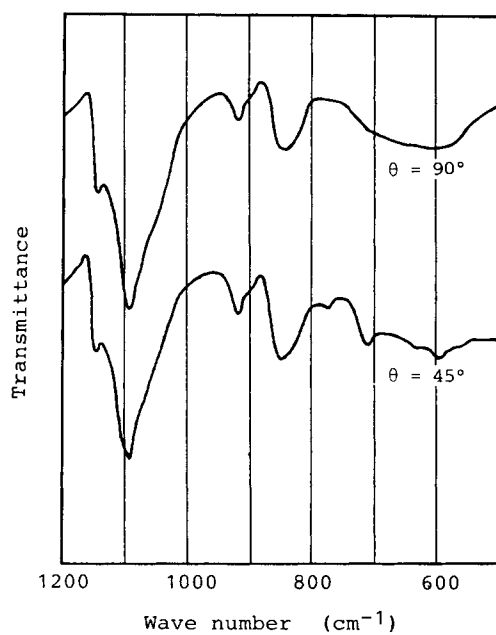


Fig. 2. IR spectra of *s*-PVA films obtained by the frame method.

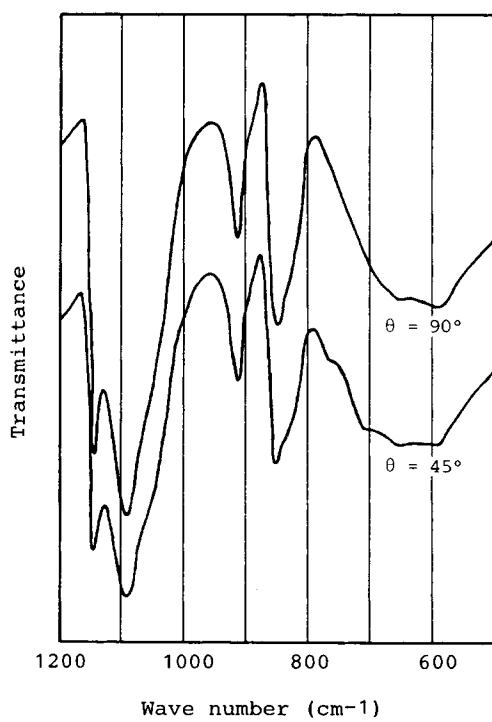


Fig. 3. IR spectra of *s*-PVA films obtained by the casting method.

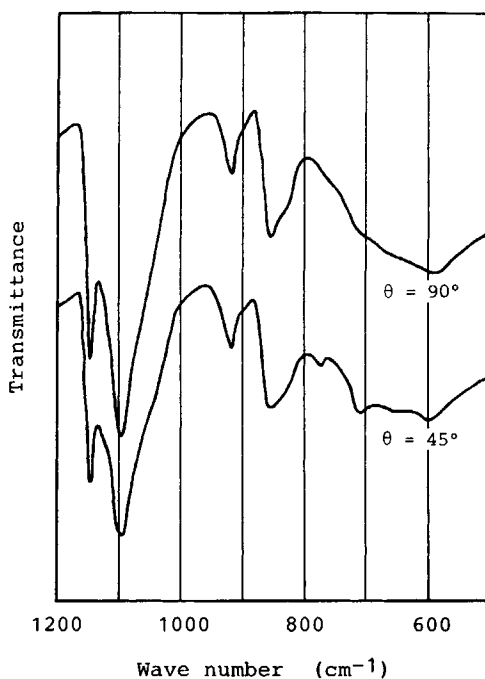


Fig. 4. IR spectra of *s*-PVA films, obtained by the casting method, drawn in steam three times its original length.

cm^{-1} is related to the ratio of the adsorbed molecules to the total molecules in film.

Figure 4 shows IR spectra of films prepared by the casting method followed by drawing in water to three times its original length. The band at 705 cm^{-1} for the drawn films appeared at an inclination of 45° . Figure 5 shows the IR spectra of films, prepared by the bubble method followed by drawing in steam to three times its original length. The bands at 705 and 770 cm^{-1} for the drawn films appeared even without the inclination of film (at 90°). Although the ductility of balloon films was lower than that of cast films, the Young's modulus of the former was higher than that of the latter.⁴ This means that the orientation of polymer chains in the direction of drawing for the former is higher than that of the latter and that the band at 705 cm^{-1} is due to the polymer segments oriented perpendicularly to the direction of incident light. Therefore, considerable amounts of the polymer segments at the surfaces of untreated films is assumed to be perpendicular to the film plane. However, even the untreated ultrathin films obtained by the bubble method showed no birefringence when observed under a polarizing microscope.

The normal IR spectrum of PVA films shows a broad absorption band at $700\text{--}500\text{ cm}^{-1}$ and an absorption band at 590 cm^{-1} , which is considered to be caused by twisting of —OH groups.⁶ However, the absorption bands at 770 and 705 cm^{-1} have not been assigned; although they may be caused by the orientation of the polymer backbone.

The authors wish to thank Prof. Dr. Y. Kondoh for generously lending the infrared spectrophotometer.

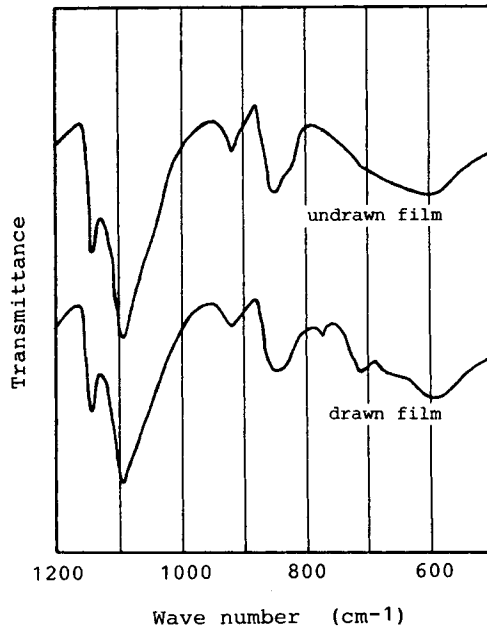


Fig. 5. IR spectra (at $\theta = 90^\circ$) of the undrawn and drawn s-PVA films obtained by the bubble method.

References

1. K. Yamaura, T. Tanigami, and S. Matsuzawa, *Polym. J.*, **15**, 848 (1983).
2. K. Yamaura and S. Matsuzawa, *J. Appl. Polym. Sci.*, **29**, 4009 (1984).
3. K. Yamaura, M. Tada, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **31**, 493 (1986).
4. K. Yamaura, K. Ikeda, M. Fujii, R. Yamada, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **34**, 989 (1987).
5. S. Matsuzawa, K. Yamaura, N. Yoshimoto, I. Horikawa, and M. Kuroiwa, *Colloid Polym. Sci.*, **258**, 131 (1980).
6. J. G. Pritchard, *Poly(vinyl Alcohol)—Basic Properties and Uses*, Gordon and Breach, London, 1970, pp. 31–35.

Received June 17, 1987

Accepted October 7, 1987