

# Preparation of Syndiotacticity-Rich High Molecular Weight Poly(vinyl alcohol)/Iodine Polarizing Film with High Water Resistance

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**ABSTRACT:** To enhance durability of poly(vinyl alcohol) (PVA)/iodine polarizing film under humid and warm atmospheres and to identify the effects of syndiotacticity on the polarizing efficiency (PE) and durability of PVA/iodine complex film, we prepared three high molecular weight (PVA)s with similar number-average degree of polymerization ( $P_n$ ) of 4000 and with different syndiotactic diad (s-diad) contents of 53, 56, and 59%, respectively. It was found that syndiotacticity of PVA had a significant influence on the durability of PVA/iodine complex film in warm and humidity conditions (relative humidity of 80% and temperature of 50°C). That is, both desorption of iodine in PVA/iodine film and transmittance of film

decreased with increasing syndiotacticity of PVA. In the case of PE, the values of over 99% were obtained at each optimum conditions. The change of PE (durability) of PVA/iodine complex films having  $P_n$  of 4000 and s-diad contents of 56 and 59%, respectively, in warm and humidity conditions was almost zero, whereas those of PVA/iodine film with s-diad content of 53% and with ( $P_n$ )s of 1700 and 4000 were about 60% and 50%, respectively, under same conditions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 917–922, 2010

**Key words:** durability; PVA/iodine polarizing film; syndiotacticity

## INTRODUCTION

Poly(vinyl alcohol) (PVA) is widely used as fibers, films, adhesives, and substitutes for asbestos because it has high tensile and impact strengths, high tensile modulus, high abrasion resistance, excellent alkali resistance, and oxygen barrier property that is superior to those of any known polymers.<sup>1–3</sup> PVA is classified into three types, isotactic, atactic, and syndiotactic, according to the stereoregularity of its hydroxyl groups. The physical properties of PVA are highly dependent on the degree of syndiotacticity.

It is well-known that PVA molecules forms a complex with iodine because polyiodide ions interrupt the intermolecular hydrogen bonds. The influencing factors on PVA/iodine complexation include the amount of 1,2-glycols<sup>4,5</sup> in the PVA chain, stereoregularity,<sup>6–8</sup> degree of polymerization<sup>6</sup> and so on. Imai and Matsumoto<sup>9</sup> discovered that the PVA-iodine interaction was sensitive to the molecular weight and the stereoregularity of the polymer

molecule. Yamaura et al.<sup>10</sup> have ascertained that PVA-iodine complex formation increased with increasing syndiotactic diad (s-diad) content of PVA using syndiotactic PVA (s-PVA) with s-diad content of 56–58% derived from poly(vinyl trifluoroacetate). Actually, an increase in the syndiotacticity of PVA has been reported to improve the physical properties such as heat resistance.<sup>11,12</sup>

The most important application of the complex is to use as polarizing films with a high quality of dichroism. Especially, PVA/iodine complex film is a second-to-none polarizing material for liquid crystal display. Commercial polarizing films are produced from atactic PVA (a-PVA). However, a-PVA/iodine complex films have a serious problem of iodine desorption under hot and humid conditions, which results mainly from the higher affinity of a-PVA molecules to water than to iodines. To overcome this defect by improving water resistance of PVA, PVA film was treated in boric acid solution to introduce crosslinking<sup>13,14</sup> or protecting films such as cellulose triacetate and polypropylene are used.

In this study, to precisely identify the effect of syndiotacticity of PVA on the durability and polarizing efficiency (PE) of high molecular weight (HMW) a-PVA and s-PVA/iodine complex films, we prepared one a-PVA and two (s-PVA)s with similar number-average degrees of polymerization ( $P_n$ )s of 4000 and with different s-diad contents, respectively.

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TABLE I  
The Molecular Parameters of PVA Specimens Used

No.	Source	$P_n$	DS (%)	S-diad content (%)
1	Solution polymerization	1700	99.9	53%
2	Bulk polymerization	4000	99.9	53%
3	Bulk copolymerization	4000	99.9	56%
4	Bulk copolymerization	4000	99.9	59%

The PVA with  $P_n$  of 4000 is of HMW grade. And, the change of PE (durability) of PVA/iodine complex film in heat and humidity conditions was checked.

## EXPERIMENTAL

### Materials

Vinyl pivalate (VPi) and vinyl acetate (VAc) purchased from Aldrich was washed with an aqueous solution of  $\text{NaHSO}_3$  and water and dried with anhydrous  $\text{CaCl}_2$ , followed by distillation in nitrogen atmosphere under reduced pressure. The initiator 2,2-azobis(2,4-dimethylvaleronitrile) (ADMVN) (Wako Co.) was recrystallized twice in methanol before use.<sup>15</sup> Other extra-pure grade reagents were used without further purification. Water used for all the procedures was deionized.

### Preparation of a- and s-PVAs

To prepare water soluble HMW s-PVA with s-diad content of 59%, bulk copolymerization of VPi and VAc [VPi/VAc = 3/7 (mol/mol)] using ADMVN concentration of  $3.4 \times 10^{-4}$  mol/mol of comonomer at polymerization temperature of 30°C with conversions of 25–35%, was performed, followed by saponification of copoly(VPi/VAc).<sup>16–18</sup> Also, to obtain HMW s-PVA with s-diad content of 56%, bulk copolymerization of VPi and VAc [VPi/VAc = 2/8 (mol/mol)] using ADMVN concentration of  $2.6 \times 10^{-4}$  mol/mol of comonomer at 30°C with conversions of 25–35%, was performed, followed by saponification of copoly(VPi/VAc).<sup>16–18</sup> To synthesize HMW a-PVA, bulk polymerization of VAc using ADMVN concentration of  $2.1 \times 10^{-4}$  mol/mol of VAc at 30°C, with conversions of 25–35%, was performed, followed saponification of PVAc.<sup>19</sup> To prepare the a-PVA with  $P_n$  of 1,700, VAc was solution polymerized in methanol using ADMVN concentration of  $2.3 \times 10^{-4}$  mol/mol of VAc at VAc/methanol of 4/6 (mol/mol) and polymerization temperature of 50°C with conversions of 30–40%, was performed, followed saponification of PVAc.<sup>19,20</sup> Table I shows the molecular parameters of HMW a- and s-PVAs used in this study.

### Preparations of PVA film and PVA/iodine film

PVA films, with a similar thickness of about 70  $\mu\text{m}$ , were prepared by casting PVA/water in a solution of 2.5 g/dL. The homogenized solution was poured into a stainless steel dish and dried under vacuum at 40°C for 3 days. Iodine ( $\text{I}_2$ )/potassium iodide (KI) aqueous solutions, with a molar ratio of 1/2, were prepared at iodine concentration of  $1.5 \times 10^{-2}$  mol/L. PVA film was soaked in  $\text{I}_2$ /KI aqueous solution at various temperatures for 15–60 sec. The PVA/iodine complex films obtained from the solutions were rinsed in cold water to remove the solution adhered to the film surfaces and dried in vacuum for 24 h.

### Wet drawing of film

The films were wet-drawn 3–5 times in boric acid (3 wt %) solution at 30–50°C. The stretched films were subsequently dried at 30°C for 24 h. The film having 70  $\mu\text{m}$  thickness, 20 mm width, and 5 cm length, was drawn at a speed of 10 mm/min. Figure 1 shows a schematic representation of the wet-drawing apparatus.

### Characterization

The molecular weight of PVPi was calculated using eq. (1)<sup>16</sup>:

$$[\eta] = 2.88 \times 10^{-5} [M_n]^{0.77} \quad (\text{in acetone at } 25^\circ\text{C}) \quad (1)$$

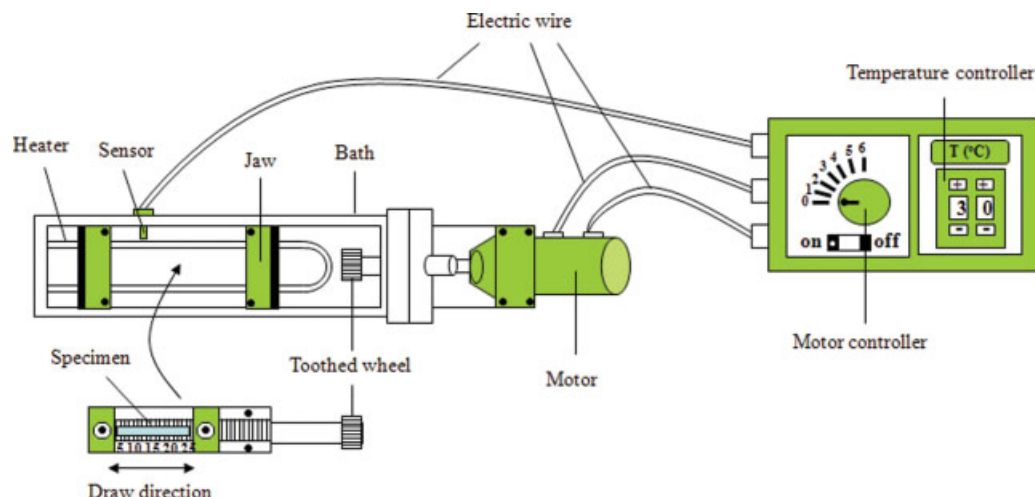
where  $M_n$  is the number-average molecular weight of PVPi.

The molecular weight of PVA was determined from that of PVAc produced by acetylating PVA using eq. (2)<sup>21</sup>:

$$[\eta] = 8.91 \times 10^{-3} [P_n]^{0.62} \quad (\text{in benzene at } 30^\circ\text{C}) \quad (2)$$

where  $P_n$  is the number-average degree of polymerization of PVAc. The s-diad content of the PVA was determined by 300 MHz  $^1\text{H-NMR}$ , using  $\text{DMSO-d}_6$  as the solvent, based on the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm.

The PE of PVA/iodine complex film was estimated using the eq. (3).



**Figure 1** Schematic representation of the wet-drawing apparatus used in this study. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$$PE (\%) = [(T_{\parallel} - T_{\perp}) / (T_{\parallel} + T_{\perp})]^{1/2} \times 100 \quad (3)$$

where  $T_{\parallel}$  and  $T_{\perp}$  are the transmittances of the film superimposed on each other parallel and perpendicular to the direction of the elongation of the film, respectively.

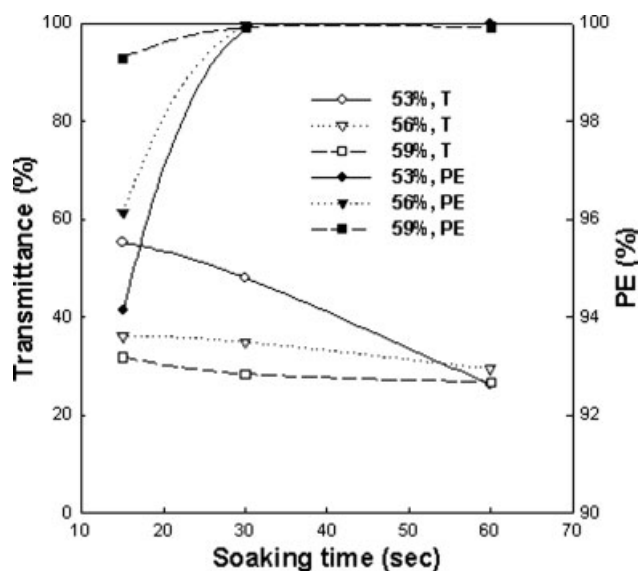
PVA/iodine polarizing film was kept in the constant temperature and humidity chamber (relative humidity of 80% and temperature of 50°C). And then, durability for heat and humidity of PVA/iodine polarizing film was evaluated from the change of PE.

## RESULTS AND DISCUSSION

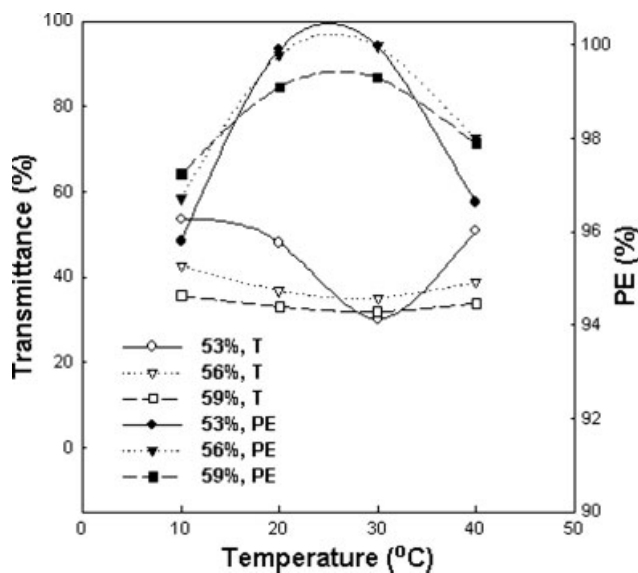
Generally, PVA has been well-known for forming blue-colored complexes with iodine. Also, PVA molecules associate with one another more easily because of increasing intermolecular hydrogen bonds with increasing content of long syndiotactic sequences, and iodine molecules enter into the aggregates formed to yield polyiodine. Therefore, we investigated the transmittance and PE of PVA/iodine complex films with different soaking time and temperature of the  $I_2/KI$  aqueous solution. In here, PVA resins are used depending on diverse syndiotacticity. The basic characteristics of PVA resins are presented in Table I. HMW PVA with various s-diad contents/iodine complex films were prepared by casting, dyeing and drawing. It has been known that water solubility of PVA film is increased with a decrease in the syndiotacticity of PVA. Thus, in this study, because of big solubility differences in water with tacticity, a-PVA with s-diad content of 53%/iodine complex film was prepared by soaking

in the  $I_2/KI$  aqueous solution at 20°C and HMW s-PVA with s-diad 56% and 59%/iodine complex films were prepared by soaking in  $I_2/KI$  aqueous solution at 30°C.

Effects of the soaking time in  $I_2/KI$  aqueous solution on the transmittance and PE of PVA with  $P_n$  of 4000 and different s-diad contents of 53, 56, and 59%/iodine films drawn by 4 times prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L at 20°C or 30°C are shown in Figure 2. These films are drawn in aqueous boric acid ( $H_3BO_3$ )



**Figure 2** Transmittance and PE of PVA with  $P_n$  of 4,000 and s-diad contents of 53, 56, and 59%/iodine complex films prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L at 20°C (a-PVA) and 30°C (s-PVA) and by drawing four times in boric acid solution of 3 wt % with soaking time in  $KI/I_2$  aqueous solution.



**Figure 3** Transmittance and PE of PVA with  $P_n$  of 4,000 and s-diad contents of 53, 56, and 59%/iodine complex films prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L and by drawing four times in boric acid solution of 3 wt % with soaking temperature.

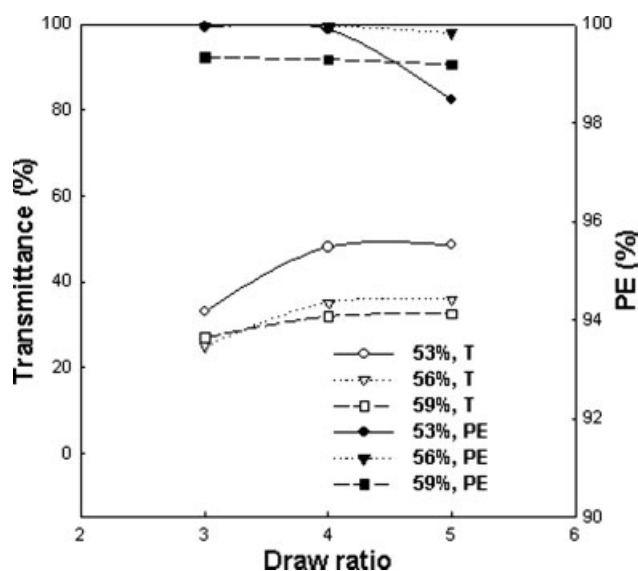
solution of 3 wt % after soaking in  $I_2/KI$  aqueous solution. As increasing soaking time, PE of HMW PVA with 53, 56, and 59%/iodine complex films was increased to high level of 99.9, 99.9 and 99.3%, respectively. However, transmittance of PVA/iodine complex films was decreased with increasing soaking time. In this work, optimum transmittance and PE values were obtained from PVA films with s-diad contents of 53, 56, and 59% soaked for 30 and 15 sec, respectively. According to these results, HMW s-PVAs with s-diad contents of 56% and 59% were combined with iodine easier than HMW a-PVA with s-diad content of 53%. In other words, we confirmed that PVA/iodine complex formation increased with increasing syndiotacticity.

Figure 3 shows the effect of soaking temperature of the  $I_2/KI$  aqueous solution on the transmittance and PE of PVA with  $P_n$  of 4000 and different s-diad contents of 53, 56, and 59%/iodine films with draw ratio of four prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L for 30 sec and 15 sec, respectively, at different temperatures of 10, 20, 30, and 40°C. In all cases, transmittance of PVA/iodine complex films was decreased with increasing temperature from 10 to 30°C, and then increased at 40°C. Also, PE of PVA/iodine complex films was increased with increasing temperature from 10 to 30°C, and then decreased at 40°C. From the results described above, it is supposed that PVA/iodine complex formation tend to increase with increasing temperature from 10 to 30°C, and to decrease at 40°C, owing to the sublimation of iodine at 40°C. In this work, optimum transmittance and PE values

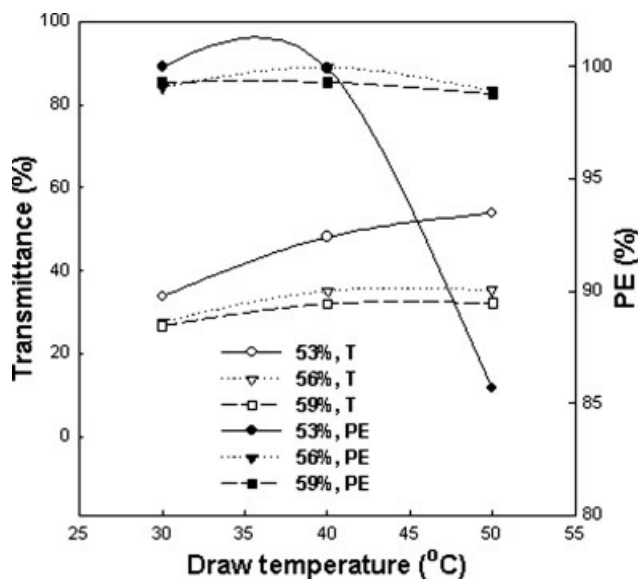
were obtained from PVA films with s-diad contents of 53 and 56, 59 soaked at 20°C and 30°C, respectively.

It is known that extension of PVA films enhances remarkably the PVA/iodine complex formation. Takamiya et al.<sup>7</sup> suggested that polyiodines were surrounded with the aggregates of extended sequences in s-PVA chains. Recently, Miyazaki et al.<sup>22</sup> investigated role of adsorbed iodine into PVA films drawn in  $I_2/KI$  solution. Figure 4 shows the effect of draw ratio on the transmittance and PE of PVA with  $P_n$  of 4000 and different s-diad contents of 53, 56, and 59%/iodine complex films drawn four times prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L for 30 sec and 15 sec, respectively. Transmittance of PVA/iodine complex films was increased with increasing draw ratio from 3 to 5. In case of draw ratio of four, optimum transmittance and PE values were obtained.

Figure 5 presents the effect of draw temperature on the transmittance and PE of PVA with  $P_n$  of 4000 and different s-diad contents of 53, 56, and 59%/iodine film with draw ratio of 4 prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L for 30 sec and 15 sec, respectively. With increasing draw temperature, the drawability of PVA/iodine complex films seemed to be increased. However, PE of PVA/iodine complex films was decreased at 50°C. In all cases, optimum transmittance and PE were obtained from draw temperature of 40°C. It was supposed that the reason for the increase of transmittance with increasing draw



**Figure 4** Transmittance and PE of PVA with  $P_n$  of 4000 and s-diad contents of 53, 56, and 59%/iodine complex films prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L at 20°C (a-PVA) and 30°C (s-PVA) and by drawing in boric acid solution of 3 wt % with draw ratio of film.

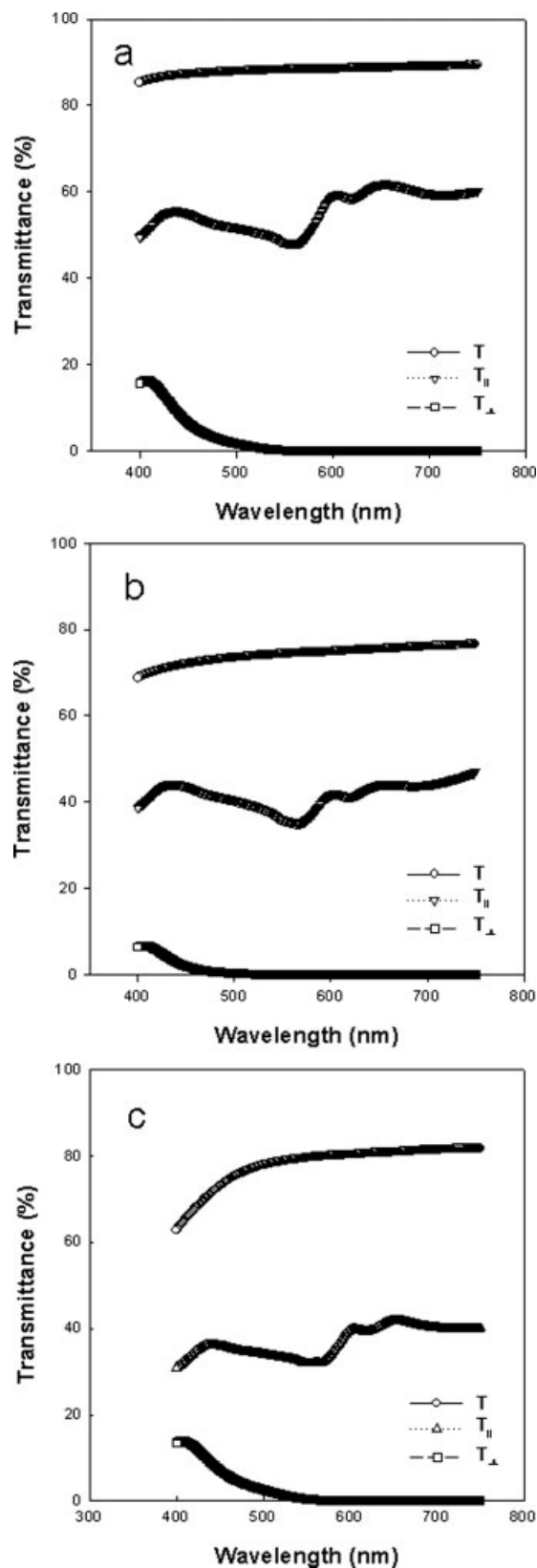


**Figure 5** Transmittance and PE of PVA with  $P_n$  of 4,000 and s-diad contents of 53, 56, and 59%/iodine complex films prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L at 20°C (a-PVA) and 30°C (s-PVA) and by drawing in boric acid solution of 3 wt % with different draw temperatures.

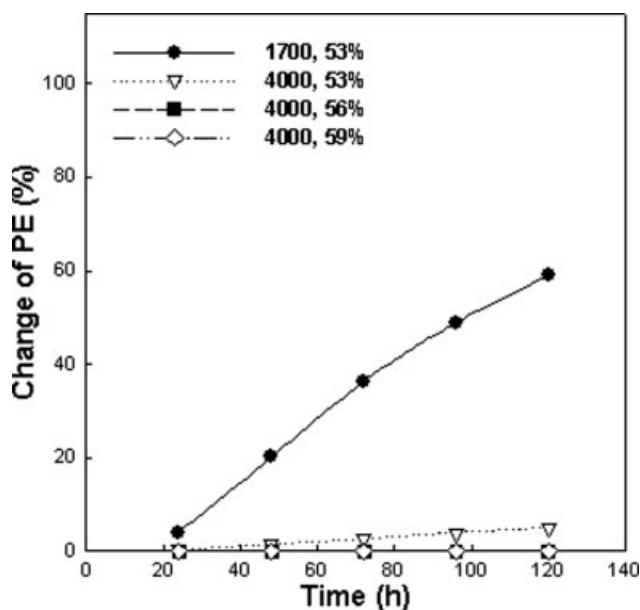
temperature was the sublimation of iodine from the PVA/Iodine film under the draw process at higher drawing temperature.

UV-visible spectra of PVA with  $P_n$  of 4000 and different s-diad contents of 53 (a), 56 (b) and 59% (c)/iodine complex films drawn by four times in boric solution (3 wt %) prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L for 30 sec (a), (b) and 15 sec (c) at 20°C (a) and 30°C (b), (c) are shown in Figure 6(a)–(c), respectively. Maximum transmittance and PE values of PVA with s-diad contents of 53 (a), 56 (b) and 59% (c)/iodine complex films are 48.0 (a), 35.1 (b), 31.9% (c), and 99.9 (a), 99.9 (b), 99.3% (c), respectively.

Commercial polarizing films produced from a-PVA have a serious problem of the sublimation of iodine under humid and warm atmospheres. Polyiodine molecules are easily deformed and released from PVA owing mainly to sublimation of iodine. For that reason, we prepared HMW s-PVA with 56% and 59%/iodine complex films which are expected to be promising materials having high heat and humidity resistance. Figure 7 shows the change of PE of PVA with  $P_n$  of 1700, 4000 and different s-diad contents of 53, 56, and 59%/iodine complex films under condition of relative humidity of 80% and temperature of 50°C. The change of PE of a-PVA with  $P_n$  of 1700, 4000 and s-diad content of 53%/iodine complex films was increased, particularly in a-PVA with  $P_n$  of 1700/iodine complex film. However, the change of PE of s-PVA with s-diad contents of 56 and 59%/iodine complex films was



**Figure 6** UV-visible spectra of PVA with  $P_n$  of 4,000 and different s-diad contents of 53 (a), 56 (b), and 59% (c)/iodine complex films drawn by four times in boric solution (3 wt %). The films were prepared by soaking in  $I_2/KI$  aqueous solution of  $1.5 \times 10^{-2}$  mol/L for 30 sec (a), (b) and 15 sec (c) at 20°C (a) and 30°C (b), (c), respectively.



**Figure 7** Change of PE of PVA with  $P_n$  of 1700, 4000 and with s-diad contents of 53, 56, and 59%/iodine complex films under condition of relative humidity of 80% and temperature of 50°C.

almost zero in the warm and humidity conditions, regardless of long treatment time.

### CONCLUSIONS

It is a very difficult job to prepare PVA/iodine polarizing film having high durability. To resolve problem of PVA/iodine polarizing film such as iodine sublimation, we used syndiotacticity -rich HMW PVA in the formulation of PVA/iodine polarizer. With increasing soaking time, PE was increased to a high level (over 99%), regardless of syndiotacticity and transmittance was decreased. On the other hand, it was found that, optimum soaking temperature of 30°C, which was revealing maximum PE and transmittance, was existed. The transmittance of film decreased with increasing syndiotacticity of PVA. The PE of over 90% was obtained at all syndiotacticities. The change of PE (durability) of PVA/iodine complex films having  $P_n$  of 4,000 and s-diad contents of 56 and 59%, respectively, in warm and humidity

conditions was almost zero. But, in the case of HMW a-PVA with s-diad content of 53%, the PE was decreased with an increase in the treatment time in the warm and humidity conditions. In the near future, we will report on the HMW s-PVA/dye complex film.

### References

- Sakurada, I. *Polyvinyl Alcohol Fibers*, Lewin, M., Ed. Marcel Dekker: New York, 1985.
- Masuda, M. *Polyvinyl Alcohol Developments*, Finch, C. A., Ed. Wiley: New York, 1991.
- Stammen, J. A.; Williams, S.; Ku, D. N.; Guldberg, R. E. *Biomaterials* 2001, 22, 799.
- Shibatani, K.; Nakamura, T.; Oyanagi, Y. *Koubunshi Kagaku* 1969, 26, 118.
- Kikukawa, K.; Nozakura, S.; Murahashi, S. *Polym J* 1971, 2, 212.
- Matsuzawa, S.; Yamaura, K.; Noguchi, H. *Makromol chem* 1974, 175, 31.
- Takamiya, H.; Tanahashi, Y.; Matsuyama, T.; Tanigami, T.; Yamaura, K.; Matsuzawa, S. *J Appl Polym Sci* 1993, 50, 1807.
- Noguchi, H.; Jyodai, H.; Matsuzawa, S. *J Polym Sci Part B: Polym Phys* 1997, 35, 1701.
- Imai, K.; Matsumoto, M. *J Polym Sci* 1961, 55, 335.
- Yamaura, K.; Matsuzawa, S.; Go, Y. *Koubunshi Kagaku* 1969, 26, 265.
- Lyoo, W. S.; Han, S. S.; Yoon, W. S.; Ji, B. C.; Lee, J.; Cho, W. W.; Choi, J. H.; Ha, W. S. *J Appl Polym Sci* 2000, 77, 123.
- Chio, J. H.; Lyoo, W. S.; Ghim, H. D.; Ko, S. W. *Colloid Polym Sci* 2000, 278, 1198.
- Zwick, M. M. *J Appl Polym Sci* 1965, 9, 2393.
- Saito, S.; Okutama, H.; Kishimoto, H.; Fujiyama, T. *Kolloid ZZ polym* 1995, 144, 41.
- Lyoo, W. S.; Kim, B. C.; Lee, C. J.; Ha, W. S. *Eur Polym J* 1997, 33, 785.
- Lyoo, W. S.; Blackwell, J.; Ghim, H. D. *Macromolecules* 1998, 31, 4253.
- Lyoo, W. S.; Yeum, J. H.; Ghim, H. D.; Kim, S. S.; Kim, J. H.; Lee, J. Y.; Lee, J. W. *J Appl Polym Sci* 2002, 88, 1482.
- Kwark, Y. J.; Lyoo, W. S.; Ha, W. S. *Polym J* 1996, 28, 851.
- Lyoo, W. S.; Lee, S. G.; Kim, J. P.; Han, S. S.; Lee, C. J. *Colloid Polym Sci* 1998, 276, 951.
- Lyoo, W. S.; Han, S. S.; Choi, J. H.; Ghim, H. D.; Yoo, S. W.; Lee, J.; Hong, S. I.; Ha, W. S. *J Appl Polym Sci* 2001, 80, 1003.
- Lyoo, W. S.; Ha, W. S. *J Polym Sci Part A: Polym Chem* 1997, 35, 55.
- Miyazaki, T.; Katayama, S.; Funai, E.; Tsuji, Y.; Sakurai, S. *Polymer* 2005, 46, 7436.