Role of Molecular Weight of Atactic Poly(vinyl alcohol) (PVA) in the Polarizing Efficiency of PVA/Azo Dye Complex Film with High Durability

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ABSTRACT: To precisely identify the effect of molecular weight of *atactic* poly(vinyl alcohol) (*a*-PVA) on the durability and polarizing efficiency (PE) of *a*-PVA/dye polarizing film, we prepared two (*a*-PVA)s with similar syndiotactic diad contents of 54.0%, degrees of saponification of 99.9%, and with different number-average degrees of polymerization [(P_n)s] of 1700 and 4000, respectively. Through a series of experiments, it was found that molecular weight of *a*-PVA had a significant influence on the durability of *a*-PVA/dye film in heat and humidity conditions (relative humidity of 80% and temperature of 90°C). That is, both desorption of dye in *a*-PVA/dye film and transmittance of film decreased with increasing molecular weight of PVA. The change of PE (durability) of *a*-PVA/dye film in heat and humidity conditions was limited to about below 5%. The change of PE of PVA/dye film having P_n of 4000 especially was limited to 1%, whereas that of *a*-PVA/iodine film with P_n of 4000, was almost 80% under the same condition. Also, transmittance of the drawn *a*-PVA/dye film was far higher than that of the undrawn one. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 967–974, 2005

Key words: molecular weight; durability; polarizing efficiency; *a*-PVA/dye film

INTRODUCTION

Poly(vinyl alcohol) (PVA), obtained by the saponification of poly(vinyl ester) like poly(vinyl acetate) (PVAc) is a linear semicrystalline polymer, which has been widely used as fibers for clothing, films, membranes, and biomaterials.[1–3] PVA fibers and films have high tensile and compressive strengths, high tensile modulus, and good abrasion resistance attributed to its high crystalline lattice modulus. To increase molecular weight, which is a fundamental factor affecting physical properties, improvement of polymerization methods for vinyl acetate (VAc)[4–11] is especially necessary.

Microhardness exists in the PVA crystalline phase because of inter- and intramolecular hydrogen bonding between adjacent hydroxyl groups, which gives rise to differences in the crystal structure. For this reason, on drawing PVA films and fibers, the full extension of molecular chains is prevented. Therefore,

to enhance the draw ratio and tensile properties of PVA film and fiber, gel drawing,[12] single-crystal mats drawing,[13] and high-temperature zone drawings of film[14] and fiber[15,16] have been actively studied. Generally, it is known that the zone-drawing technique has many advantages over hot drawing, such as lower probabilities of microcrystallite formation, of back folding of molecular chains, and of thermal degradation of the sample.[16,17]

Currently, high dichroic polarizers are desirable in many industrial applications such as thin-film transistor/liquid crystal displays, and high-precision optical devices. Conventional polarizers for these applications mostly use iodine as the dichroic chromophore because polyiodine molecules exhibit much higher dichroism than that of other dyes.[18,19] It is well known that PVA film is a second-to-none polarizing material for liquid crystal display. Actually, commercial polarizing films were prepared by *atactic* PVA (*a*-PVA). PVA/iodine polarizing film is usually laminated on both sides with a polymer film such as cellulose triacetate, acrylic, or urethane polymer for its protection.[20] However, PVA/iodine polarizing film is susceptible to heat and moisture attack. Therefore, at relatively high temperature and/or high humidity conditions, polyiodine molecules are easily deformed and released from the polymer. Recently, much effort has

been made to improve the durability of iodine polarizers, but polarizers prepared by dichroic dyes are better with respect to durability.[21,22] In particular, azo dye is widely used as a nonlinear optical chromophore, which is semifixed in a rigid matrix.

In recent years, much effort has been devoted to studies on the relationship between PVA film and dye. According to Van Gurp et al.,[23] the symmetry of the orientational distribution function of dye molecules in stretched a-PVA films was investigated using polarized fluorescence. They suggested that hydrogen bonding between the PVA chains, and between the dye molecules and the PVA chains, influence the symmetry of the distribution upon stretching. Kalontarov et al.[24] reported that the dye and the type of polymer bond affect the rate of photooxidation in a-PVA films. Also, Akiyama et al.[25] studied surface-selective modification of a-PVA films with azobenzenes. According to their work, the surface reaction is affected by the solvent, degree of saponification of PVA, structure of the acid chloride, and reaction period. Han and Hwang[22] suggested dependency of the optical anisotrophy of a-PVA/dye polarizer on the dye concentration using a new model. Ikada and Matsunaga[26] estimated the density of OH groups of a-PVA on a solid film by using the surface-selective carbamoylation with an isocyanate, followed by saponification to yield an amine, which was analyzed by a fluorescent probe technique.

However, there is little research published on the effect of molecular weight of PVA for PVA/dye polarizer with high polarizing efficiency (PE). In this work, to precisely identify the effect of molecular weight of a-PVA on the durability and polarizing efficiency of a-PVA/dye polarizing film, we prepared two (a-PVA)s with different number-average degrees of polymerization [(P_n)s] of 1700 and 4000, respectively. The a-PVA with P_n of 4000 is of high molecular weight grade. The PE and transmittance of a-PVA/dye film were investigated. Also, the drawing condition affecting the PE and transmittance of a-PVA/dye film was examined.

EXPERIMENTAL

Materials

VAc, purchased from Aldrich (Milwaukee, WI), was washed with an aqueous solution of $NaHSO_3$ and water and dried with anhydrous $CaCl_2$, followed by distillation in nitrogen atmosphere under a reduced pressure. The initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN; Wako Pure Chemicals, Tokyo, Japan) was recrystallized twice in methanol before use.[4] Azo dye (Direct Blue; M. Dohmen GmbH, Korschenbroich, Germany) was used for the dichroic dye. Other extrapure-grade reagents were used with-
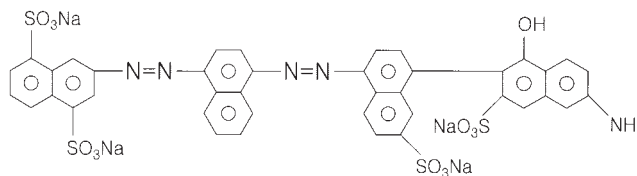

Figure 1 Chemical structure of the azo dye.

out further purification. Water used for all the procedures was deionized.

Preparation of a-PVA

For a-PVA with P_n of 4000, VAc was suspension polymerized at 30°C with ADMVN as an initiator using VAc/water of 0.5 L/L, agitation speed of 300 rpm, and suspending agent concentration of 1.5 g/dL of water.[7] To synthesize the a-PVA having P_n of 1700, VAc was solution polymerized in methanol at 40°C using an ADMVN concentration of 0.0002 mol/mol of VAc.[10]

Saponification of PVAc[7,10]

To a solution of 2 g of PVAc in 100 mL of methanol, 2.5 mL of 40% NaOH aqueous solution was added, and the mixture was stirred for 5 h at room temperature to yield PVA. The PVA produced was filtered and washed well with methanol.

Preparation of films

a-PVA films, having a thickness of about 70 μm, were prepared by casting (a-PVA)s with different (P_n)s of 1700 and 4000 in water at optimum polymer concentrations of 7.5 and 2.5 g/dL, respectively. The homogenized solution was poured into a stainless steel dish and dried under vacuum at 40°C for about 3 days. The azo dye (C.I. Direct Blue 71; Fig. 1) was used as a dichroic dye. PVA film was dipped into azo dye solution of various concentrations at the predetermined temperature for 30–150 s. The films, taken from the solutions, were rinsed with cold water to remove the solution adhering to the film surfaces and dried in a vacuum for 24 h. In contrast, a-PVA/iodine film, which was compared in durability with specimens of PVA/dye film, was prepared by dipping in aqueous iodine solution with iodine concentration of 0.1 mol/L.

Wet drawing of film

The films were wet-drawn three to five times in boric acid (2–4 wt %) solution at 40°C. The stretched films were subsequently dried at 30°C for 24 h. The film, having 70 μm thickness, 20 mm width, and 5 cm
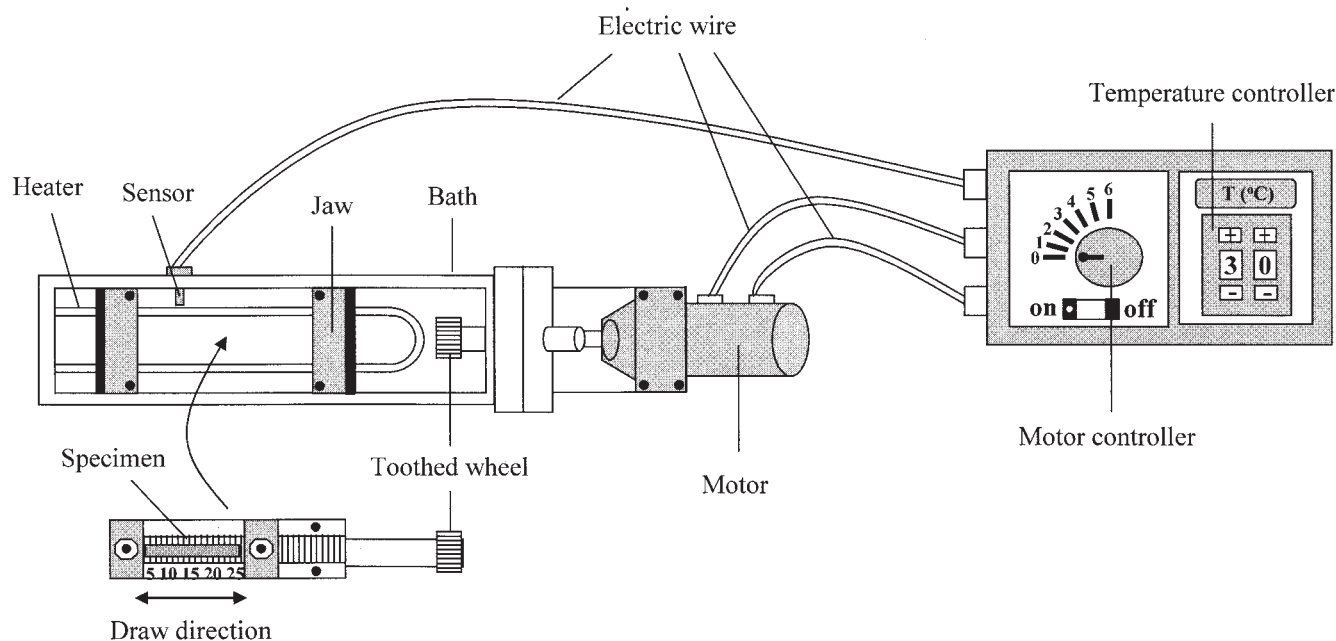
Figure 2   Schematic representation of wet-drawing apparatus.

length, was drawn at a speed of 10 mm/min. Figure 2 shows a schematic representation of the wet-drawing apparatus.

Determination of PE[27]

The PE of a-PVA/dye film was estimated using the following equation:

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

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.

Determination of durability

a-PVA/dye polarizing film was kept in a constant temperature and humidity chamber (relative humidity of 80% and temperature of 90°C). Durability for heat and humidity of dye polarizer was evaluated from the change of PE.

RESULTS AND DISCUSSION

Transmittance and PE of a-PVA/dye film

Generally, a dye polarizer suffers from a low degree of dichroism that makes it difficult to use for applications requiring high contrast imaging.[28] Therefore, an improvement of the dichroic ratio is the most significant task in the study of dye polarizers. In this work, using

a-PVA having different (P_n)s of 1700 and 4000/dye, complex films with high durability were prepared.

Effects of dye concentration on the transmittance and PE of a-PVA with different (P_n)s of 1700 and 4000/dye on film, drawn five times, prepared by soaking in aqueous dye solutions of 0.3 and 1.0 wt % at 30°C, are shown in Figure 3(a) and (b), respectively. These films were drawn in aqueous boric acid (H_3BO_3) solution of 3 wt % after soaking in aqueous dye solution. With increasing dipping time, PE was increased to a very high level (99.9%). Regardless of dye concentration, transmittance of a-PVA/dye film decreased with an increase in the dipping time. To obtain optimum transmittance and PE values above 40 and 99%, respectively, correct dipping time and dye concentration were necessary. In the case of dye concentration of 1.0 wt %, it was difficult to obtain the optimum transmittance and PE values. The transmittance of a-PVA/dye film dipped at dye concentration of 0.3 wt % indicated a higher level than that of a-PVA/dye film dipped at a concentration of 1.0 wt %. Also, the PE of a-PVA with larger molecular weight/dye film was higher at the same dipping time. This implies that PVA with longer chain and dye molecules are easily combined.

It is known that value of the pseudo-order parameter decreases with increasing dye concentration.[22] This fact suggests that the increase in the intermolecular forces among the dye molecules, through the increase in dye concentration, makes the orientation distribution of the dye molecules more dispersed, resulting in the more widely spread distribution of the
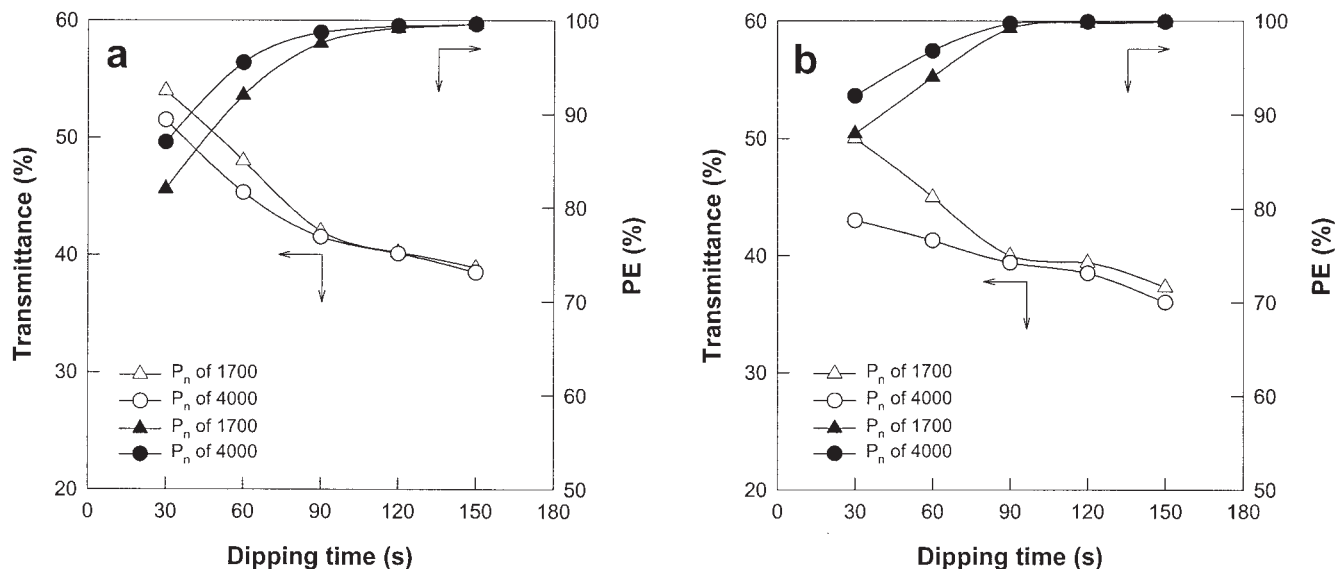
Figure 3 Transmittance and PE of a-PVAs with (P_n)s of 1700 and 4000/dye film prepared by soaking in aqueous dye solutions of 0.3 wt % (a) and 1 wt % (b) at 30°C and subsequent drawing (5 times) in aqueous boric acid solution (3 wt %) with dipping time.

PVA orientation. Figure 4 shows the effects of temperature of dye solution during soaking on the transmittance and PE of a-PVA with different (P_n)s of 1700 [Fig. 4(a)] and 4000/dye film [Fig. 4(b)] drawn five times, prepared by soaking in aqueous dye solution of 0.3 wt % at different temperatures of 20, 30, and 40°C. These films were drawn in aqueous boric acid solution of 3 wt % after soaking in aqueous dye solution. In all cases, transmittance of PVA/dye film was found to decrease with increasing temperature of the dye solu-

tion. This might be because, at higher temperature, many more dye molecules penetrated into the PVA film. In this work, optimum transmittance and PE values were obtained at 30°C. Effect of dyeing temperature, rather than dye concentration, on the transmittance and PE of PVA/dye film was clearer.

Effects of boric acid concentration on the transmittance and PE of a-PVA, with different (P_n)s of 1700 and 4000/dye, films drawn five times and prepared by soaking in aqueous dye solution of 0.3 wt % at 30°C
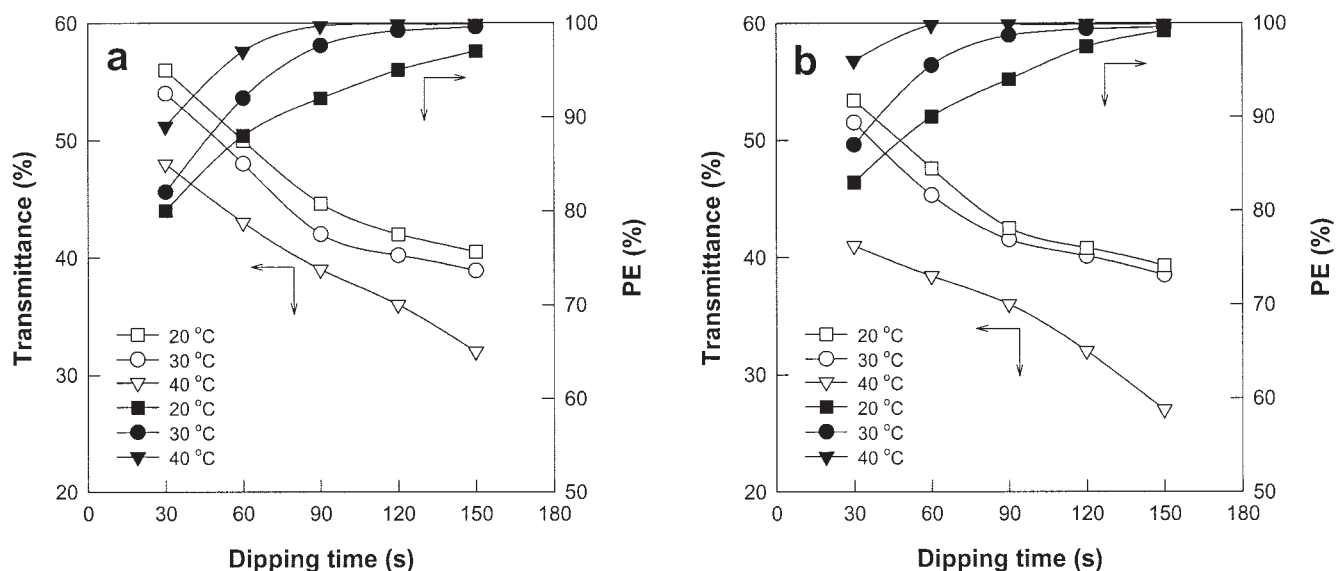

Figure 4 Transmittance and PE of a-PVAs with (P_n)s of (a) 1700 and (b) 4000/dye film prepared by soaking in aqueous dye solutions of 0.3 wt % at different temperatures of 20, 30, and 40°C and subsequent drawing (5 times) in aqueous boric acid solution (3 wt %) with dipping time.
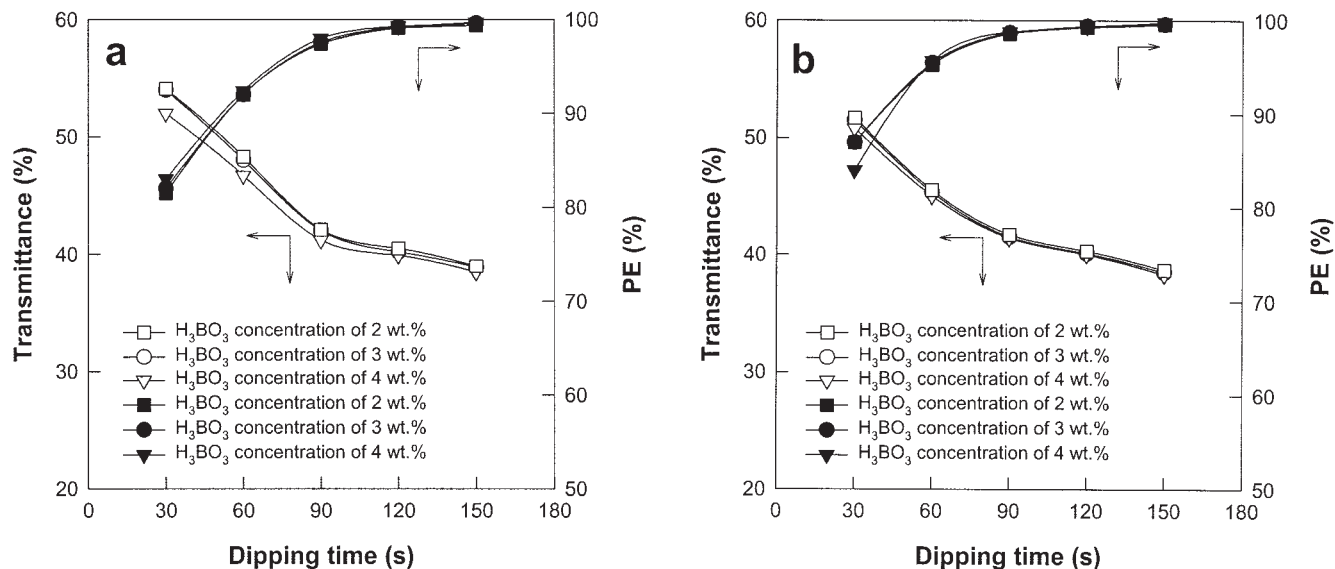
Figure 5 Transmittance and PE of *a*-PVAs with (P_n)s of (a) 1700 and (b) 4000/dye film prepared by soaking in aqueous dye solutions of 0.3 wt % at 30°C and subsequent drawing (5 times) in aqueous boric acid solution with different concentrations of 2, 3, and 4 wt % with dipping time.

are shown in Figure 5. In general, boric acid was used to promote the fastness of the PVA/dye film. Irrespective of molecular weight of PVA, with increasing boric acid concentration, transmittance was slightly decreased. In the case of boric acid concentration of 3 wt %, optimum transmittance and PE values were obtained. Figure 6 shows the effects of draw ratio on the transmittance and PE of *a*-PVA with different (P_n)s of 1700 [Fig. 6(a)] and 4000/dye film [Fig. 6(b)] prepared by soaking in aqueous dye solution of 0.3 wt % at

30°C. These films were drawn in aqueous boric acid solution of 3 wt % after soaking in aqueous dye solution. In accordance with expectations, it was found that the transmittance increased with increasing draw ratio. During drawing, the dichroic dyes orient, and consequently, anisotropic absorption of light in the visible wavelength range is generated. This results in the typical characteristics of a polarizer; that is, crossed polarizers hardly transmit light, whereas parallel polarizers are highly transparent. Dirix et al.[28]
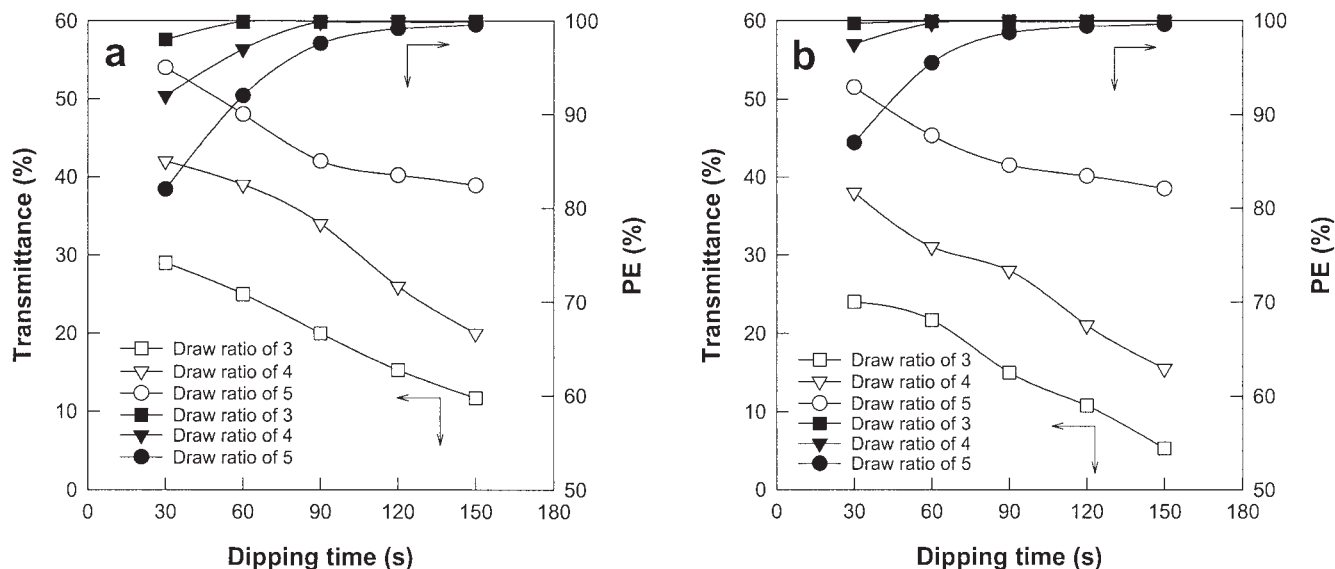
Figure 6 Transmittance and PE of *a*-PVAs with (P_n)s of (a) 1700 and (b) 4000/dye film prepared by soaking in aqueous dye solutions of 0.3 wt % at 30°C and subsequent drawing (3, 4, and 5 times) in aqueous boric acid solution (3 wt %) with dipping time.
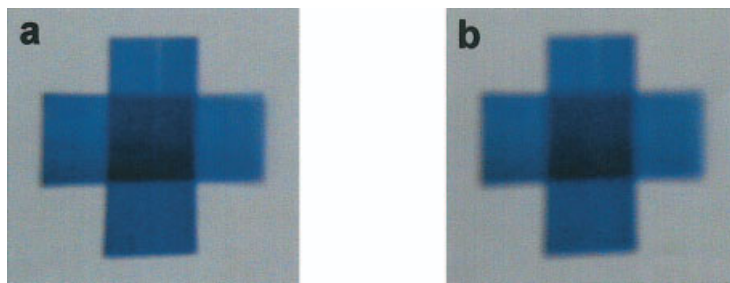
Figure 7 Photographs of *a*-PVAs with (P_n)s of (a) 1700 and (b) 4000/dye film prepared by soaking in aqueous dye solution of 0.3 wt % for 120 s at 30°C and subsequent drawing (5 times) in aqueous boric acid solution (3 wt %).

evaluated ultimate properties of polymer/dye polarizers using optical properties of oriented PVA and polypropylene/dye films. It is known that polymer/dye polarizer with infinite draw ratio has the ultimate optical properties as well as high temperature/humidity resistance. However, the maximum attainable draw ratio of PVA films is rather low because of intermolecular interactions (hydrogen bonds). As shown in Figure 6, with increasing draw ratio, the transmittance was substantially increased.

Photographs and UV–visible spectra of *a*-PVAs with P_n values of 1700 and 4000/dye film prepared by soaking in aqueous dye solution of 0.3 wt % for 120 s at 30°C and subsequent drawing (five times) in aqueous boric acid solution (3 wt %) are shown in Figures 7 and 8, respectively. Most applications of polarizers demand the combination of a high PE and transmittance. Maximum transmittance and PE values of *a*-

PVA, with P_n of 1700 and 4000/dye film, are 40.2 and 99.2% and 40.1 and 99.4% at 600 nm, respectively.

Durability of *a*-PVA/dye film

Generally, the dye molecules, that are absorbed in the PVA film have functional groups such as $-SO_3H$, $-NH_2$, and $-OH$, to be attached to the hydrophilic part of PVA.[20] Figure 9 presents the resistance to heat and humidity of PVA/dye polarizers. Also, *a*-PVA/iodine film, which was compared to specimens in durability, of PVA/dye film, was prepared by dipping in aqueous iodine solution with iodine concentration of 0.1 mol/L and drawing five times. In the case of durability for heat treatment (90°C), with increasing treatment time, the change in PE of PVA/iodine film was increased to 55%. Because of high sublimation characteristics of iodine, polyiodine molecules are easily de-
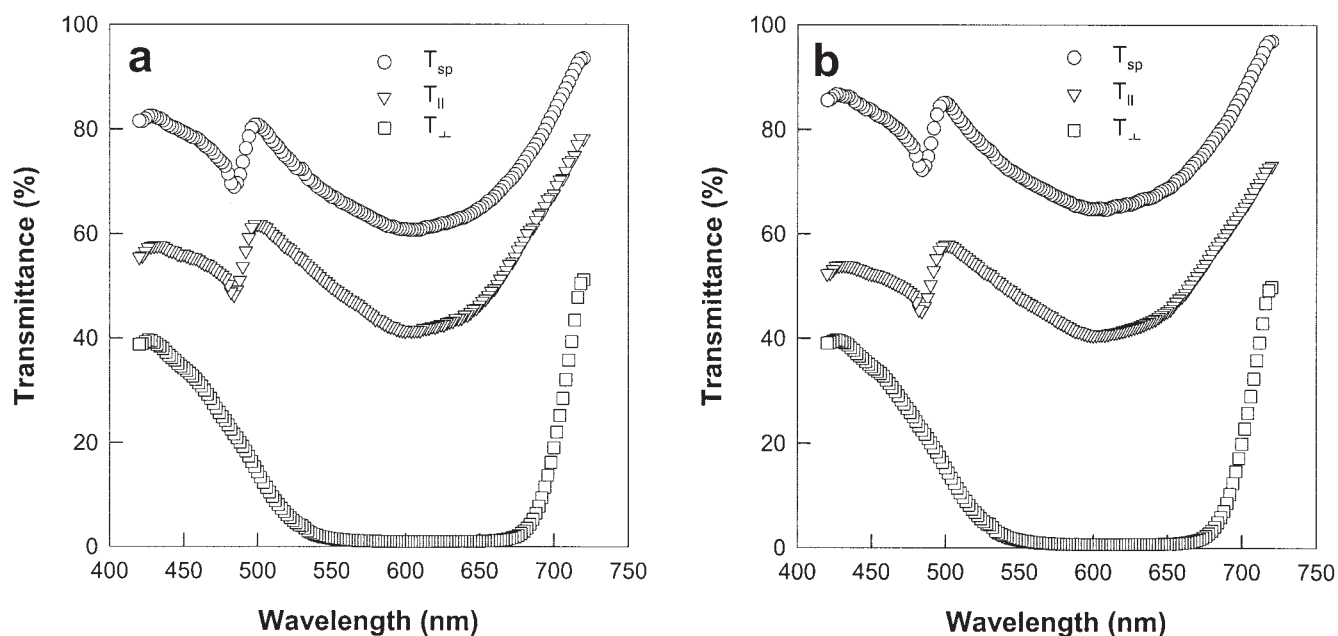

Figure 8 UV–visible spectra of *a*-PVAs with (P_n)s of (a) 1700 and (b) 4000/dye film prepared by soaking in aqueous dye solution of 0.3 wt % for 120 s at 30°C and subsequent drawing (5 times) in aqueous boric acid solution (3 wt %). (a, transmittance: 40.2%, PE: 99.2% at 600 nm; b, transmittance: 40.1%, PE: 99.4% at 600 nm).
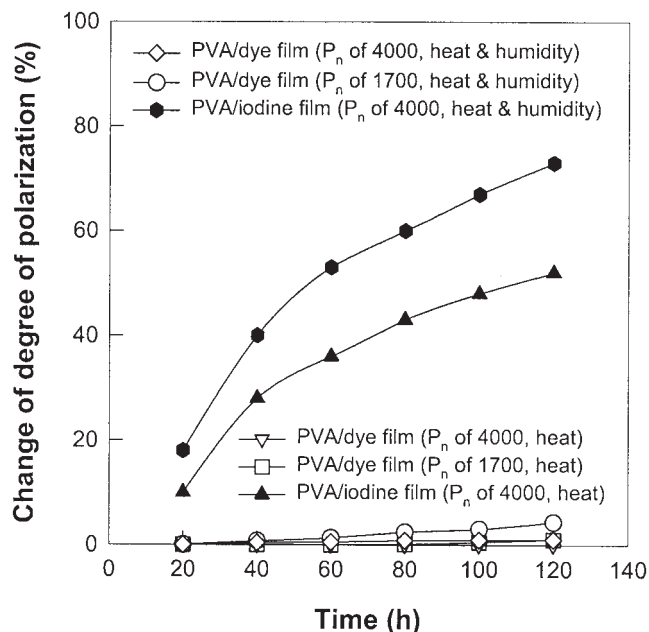
Figure 9 Change of PE of *a*-PVAs with (P_n)s of 1700 and 4000/dye polarizing film and *a*-PVA with P_n of 4000/iodine film under humidity and heat condition (relative humidity of 80% and temperature of 90°C) with time.

formed and released from the PVA. The change of PE of PVA/dye film is almost zero in Figure 9. Furthermore, in cases of heat and humidity conditions (relative humidity of 80% and temperature of 90°C), the change of PE of PVA/dye film is limited to below 5%. *a*-PVA with P_n of 1700/dye film surface suffered from some loss of flatness as a result of high temperature and humidity. In particular, the change of PE of PVA with P_n of 4000/dye film was about 1%, whereas the PE change of PVA/iodine film was very abrupt. It is observed that the heat and humidity resistance of *a*-PVA/dye polarizing film was much higher than that of *a*-PVA/iodine polarizing film. This can be explained by the fact that the interaction between polyiodine molecules and PVA chains is weakened by heat and humidity rather than by heat alone. From the durability test of *a*-PVA/dye film, it was clear that interaction between PVA chains and dye molecules was higher than that between PVA chains and polyiodine molecules, resulting in much higher durability than that of PVA/iodine film.

CONCLUSIONS

It is very difficult to obtain an *a*-PVA/iodine polarizer having high durability. To resolve defects in *a*-PVA/iodine polarizing film such as iodine sublimation, in this study, PVA samples with different molecular weights/dye polarizer were prepared. With increasing dipping time, PE increased to a very high level (99.9%) and transmittance was de-

creased. Regardless of dye concentration, transmittance of *a*-PVA/dye film decreased with an increase of dipping time. The transmittance of *a*-PVA/dye film dipped at a dye concentration of 0.3 wt % indicated a higher level than that of *a*-PVA/dye film dipped at a concentration of 1.0 wt %. Maximum transmittance and PE values of *a*-PVA with P_n of 1700 and 4000/dye film were prepared by soaking in aqueous dye solution of 0.3 wt % for 120 s at 30°C and subsequent drawing (five times) in aqueous boric acid solution (3 wt %) are 40.2 and 99.2% and 40.1 and 99.4% at 600 nm, respectively. With increasing treatment time, the change of PE of PVA/dye film is limited to below 5% at conditions of high heat and humidity (relative humidity of 80% and temperature of 90°C). It should be noted that, in the case of P_n of 4000, the PE change was limited to 1%. Durability to heat and humidity of *a*-PVA polarizing film was much higher than that of high molecular weight *a*-PVA/iodine polarizing film. Such a high molecular weight PVA/dye complex film is expected to be a promising polarizing film having high durability to moisture and heat. In the near future, we will report on the preparation of syndiotactic PVA/dye complex film.

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