Characterization of Poly(vinyl alcohol) Films with Various Molecular Parameters

Eun Mi Kim,[1] Man Ho Han,[1] Young Jae Lee,[1] Du Hyun Song,[1] Hyun Kyu Lee,[1] Oh Wook Kwon,[1] Dong Soo Shin,[1] Sung Soo Han,[1] Seok Kyun Noh,[2] Jae Kyun Shin,[3] Yeong-Soon Gal,[4] Won Seok Lyoo[1]

[1]*School of Textiles, Yeungnam University, Gyeongsan 712-749, Korea*
[2]*School of Chemical Engineering and Technology, Yeungnam University, Gyeongsan 712-749, Korea*
[3]*Tex-Tech Company, Limited, Pocheon, 487–890, Korea*
[4]*Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Hayang, 712–701, Korea*

ABSTRACT: The effects of three major molecular parameters of poly(vinyl alcohol)—the number-average degree of polymerization, degree of saponification, and syndiotactic dyad content—on the characteristics of poly(vinyl alcohol) films were investigated. Various poly(vinyl alcohol) films were prepared by a casting method. Then, the films were characterized with atomic force microscopy, differential scanning calorimetry, wide-angle X-ray diffraction, Fourier transform infrared spectroscopy, and Instron instrumentation. On the basis of atomic force microscopy images and calculated average roughness values, it was determined that the surface roughness of poly(vinyl alcohol) films increased with increasing molecular parameters. The crystallinities obtained with differential scanning calorimetry and wide-angle X-ray diffraction analyses were also enhanced with increasing molecular parameters, especially the degree of saponification. The tensile properties were improved with higher molecular parameters. This might be ascribed to the fact that the higher the molecular parameters were, the stronger the hydrogen bonding was. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3259–3267, 2007

Key words: degree of polymerization (DP); films; syndiotactic

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a semicrystalline polymer with hydroxyl groups that give rise to intermolecular and intramolecular hydrogen bonds. PVA fibers and films potentially have high tensile and impact strengths, high tensile moduli, high abrasion resistance, excellent alkali resistance, and oxygen barrier properties superior to those of any known polymers.[1–3] PVA is divided 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, which is determined primarily by the choice of the vinyl ester monomer. Efforts to enhance the syndiotacticity of PVA and its molecular weight have been centered on the polymerization of vinyl trifluoroacetate, vinyl trichloroacetate, and vinyl pivalate (VPi).[4–10] The effect of the degree of saponification (DS) is especially significant. The hydroxyl groups of PVA have a strong affinity for water, but strong hydrogen bonding between the intramolecular and intermolecular hydroxyl groups greatly inhibits its solubility in water. Consequently, fully hydrolyzed PVA (saponification $\leq$ 99 mol %) has poor solubility in cold water and must be heated to at least 80°C to dissolve completely. The residual acetate groups are essentially hydrophobic and weaken the hydrogen bonding of adjoining hydroxyl groups. Partially hydrolyzed PVA ($\sim$ 88 mol % hydrolyzed) is soluble in cold water. These polymers with high physical properties have been widely used as fibers for clothing and industry, as binders, as films, as membranes, as medicines, for drug delivery systems, and as cell-killing embolic materials.[1,3,5,11–19] In particular, PVA films are second-to-none polarizing materials for liquid-crystal displays. Actually, commercial polarized films are prepared with atactic poly(vinyl alcohol) (a-PVA).

A PVA/iodine complex film is a polarized film for high-quality liquid-crystal displays that require high transmissivity and excellent polarization properties. This polarized film uses iodine, which is highly dichromatic, to allow the transparent PVA film to absorb visible rays. Most polarized films used in liquid-crystal displays are iodine polarized films. However, this kind of film is susceptible to heat and moisture attack. Therefore, under relatively high temperature and/or high humidity conditions, poly-iodine molecules are easily deformed and released

TABLE I
Preparation Conditions of PVA

	a-PVA	s-PVA
Polymerization	VAc suspension polymerization	VPi/VAc bulk copolymerization (2/8 mol/mol feed ratio)
Initiator	ADMVN	ADMVN
Polymerization temperature	40°C	40°C
Saponification solvent	MeOH	MeOH
Alkali solution	NaOH	NaOH

TABLE II
Molecular Parameters of the PVA Resins

Number	Source	P_n	DS (%)	Concentration of s-dyads (%)
1	DC Chemical Co., Ltd.	1700	99.0	53
2	DC Chemical Co., Ltd.	2400	99.0	53
3	Suspension polymerization	4000	99.9	53
4	Suspension polymerization	4000	91.5	53
5	Suspension polymerization	4000	97.8	53
6	Bulk copolymerization	4000	99.9	59

from the polymer. Much effort has been made to improve the durability of iodine polarizers. To overcome this shortcoming through improvements in the water resistance of PVA, a PVA film is treated instantaneously in a boric acid solution to introduce crosslinking,[20,21] or protecting films such as cellulose triacetate and polypropylene are used. However, a study of the improvement of water resistance through the control of three major molecular parameters of PVA, such as the molecular weight, DS, and stereoregularity, has rarely been conducted.

Thus, in this study, to obtain more information on the characteristic changes in PVA films with various molecular parameters, such as the number-average degree of polymerization (P_n), DS, and syndiotactic dyad (s-dyad) content, and to establish basic data on the optimum molecular parameters for various polarized film applications, diverse analyses of PVA films were conducted.

EXPERIMENTAL

Materials

VPi and vinyl acetate (VAc), purchased from Shin-Etsu (Tokyo, Japan), were washed with an aqueous solution of $NaHSO_3$ and water and dried with anhydrous $CaCl_2$; this was followed by distillation in a nitrogen atmosphere under reduced pressure. The initiator 2,2-azobis(2,4-dimethylvaleronitrile) (ADMVN; Wako Co., Osaka, Japan) was recrystallized twice in methanol (MeOH) before use.[22] PVA with a number-average molecular weight of 127,000 and a DS value of 88% (Aldrich Co., St. Louis, MO) was used as a suspending agent. Other extrapure-grade reagents were used without further purification. The water used for all the procedures was deionized.

Preparation of the PVAs

PVAs with P_n = 1700 and DS = 99% or P_n = 2400 and DS = 99% were supplied by DC Chemical Co., Ltd. (Seoul, Korea). High-molecular-weight PVA with P_n = 4000 was prepared as follows. A suspending agent (0.5 g) was dissolved in 100 mL of water under a nitrogen atmosphere with constant stirring in a 250-mL reactor fitted with a condenser. The VAc monomer (50 mL) was polymerized in the suspension at 40°C with an ADMVN concentration of 5 × 10^{-5} mol/mol of VAc after degassing. a-PVAs with P_n = 4000 and different DS values were prepared through the saponification of poly(vinyl acetate) (PVAc), with the saponification times con-
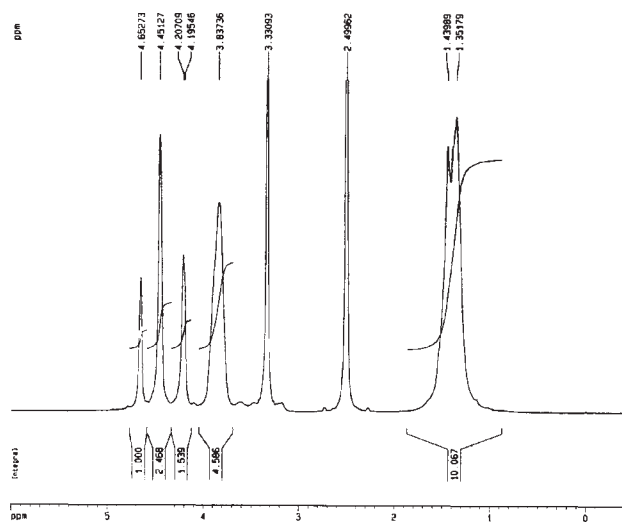

Figure 1 ^{1}H-NMR spectrum of PVA (P_n = 4000, DS = 99.9%, and s-dyad content = 59%) prepared by the complete saponification of copoly(vinyl pivalate/vinyl acetate) polymerized at 40°C.
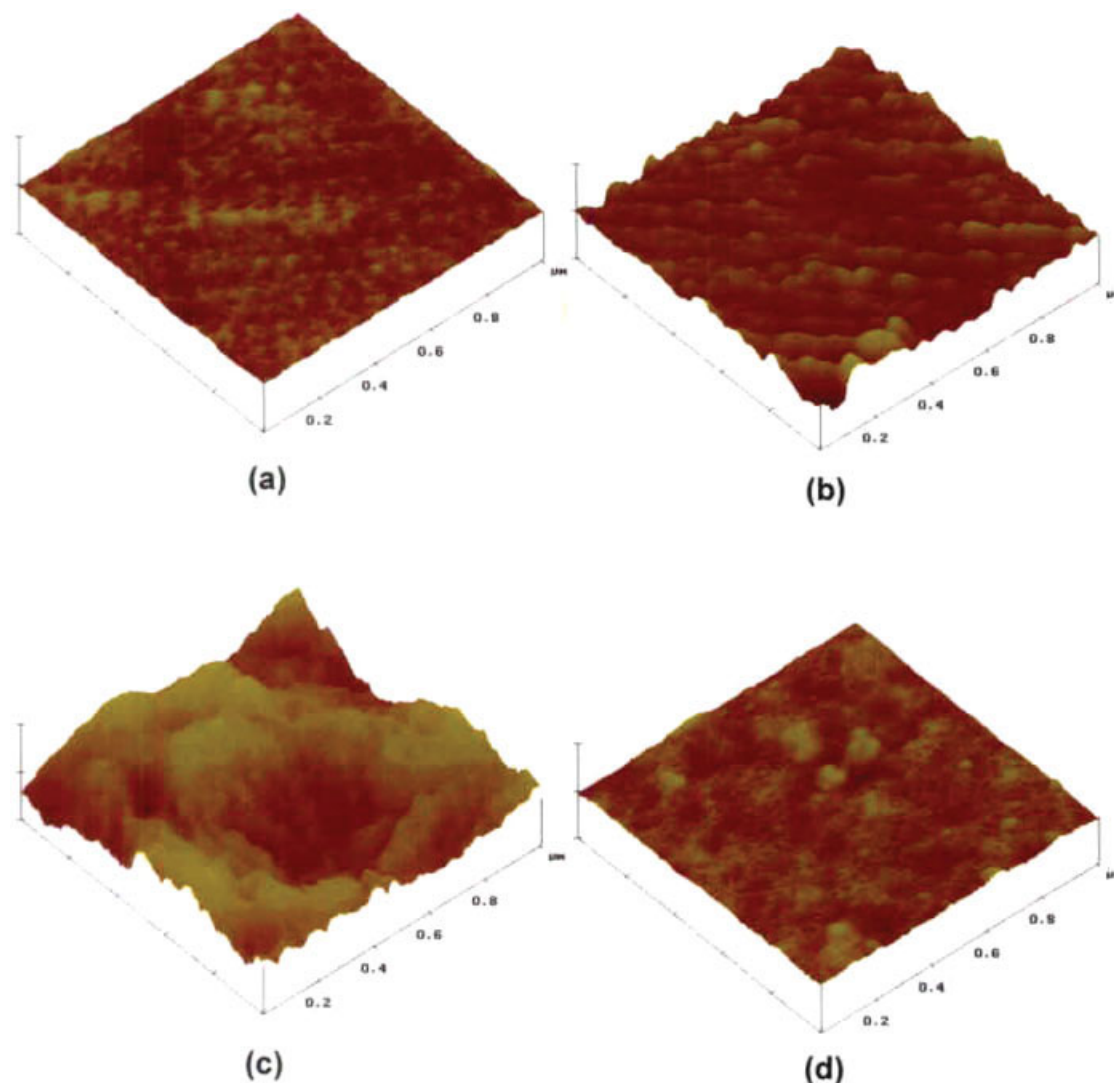
Figure 2 AFM images of PVA films with various P_n values, DS values, and s-dyad contents: (a) P_n = 1700, (b) P_n = 2400, (c) P_n = 4000, (d) DS = 91.5%, (e) DS = 97.8%, (f) DS = 99.9%, (g) s-dyad content = 53%, and (h) s-dyad content = 59%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

trolled.[16] For the preparation of syndiotactic poly(vinyl alcohol) (s-PVA), VPi and VAc in definite molar ratios were copolymerized in bulk at 40°C with ADMVN to produce poly(vinyl pivalate/vinyl acetate) copolymers having definite syndiotacticity. s-PVA with an s-dyad content of 59% was prepared by the saponification of copoly(vinyl pivalate/vinyl acetate)s.[6] The polymerization conditions are listed in detail in Table I.

Preparation of the PVA films

PVAs of various molecular parameters were dissolved in water at a polymer concentration of 2.5 g/dL. These solutions were poured into stainless steel dishes and dried under a vacuum at 40°C for 3 days to prepare PVA films with similar thicknesses of about 70 μm.

Characterization

The molecular weight of poly(vinyl pivalate) was calculated (in acetone at 25°C) as follows:[6]

$$[\eta] = 2.58 \times 10^{-5}[M_n]^{0.77} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity and M_n is the number-average molecular weight.

The molecular weight of PVA was determined (in benzene at 30°C) from that of PVAc produced by the acetylation of PVA:[4]

$$[\eta] = 8.91 \times 10^{-3}[P_n]^{0.62} \tag{2}$$

where P_n is the number-average degree of polymerization of PVAc. The s-dyad contents of PVAc were determined with 3000MHz ^{1}H-NMR, with dimethyl
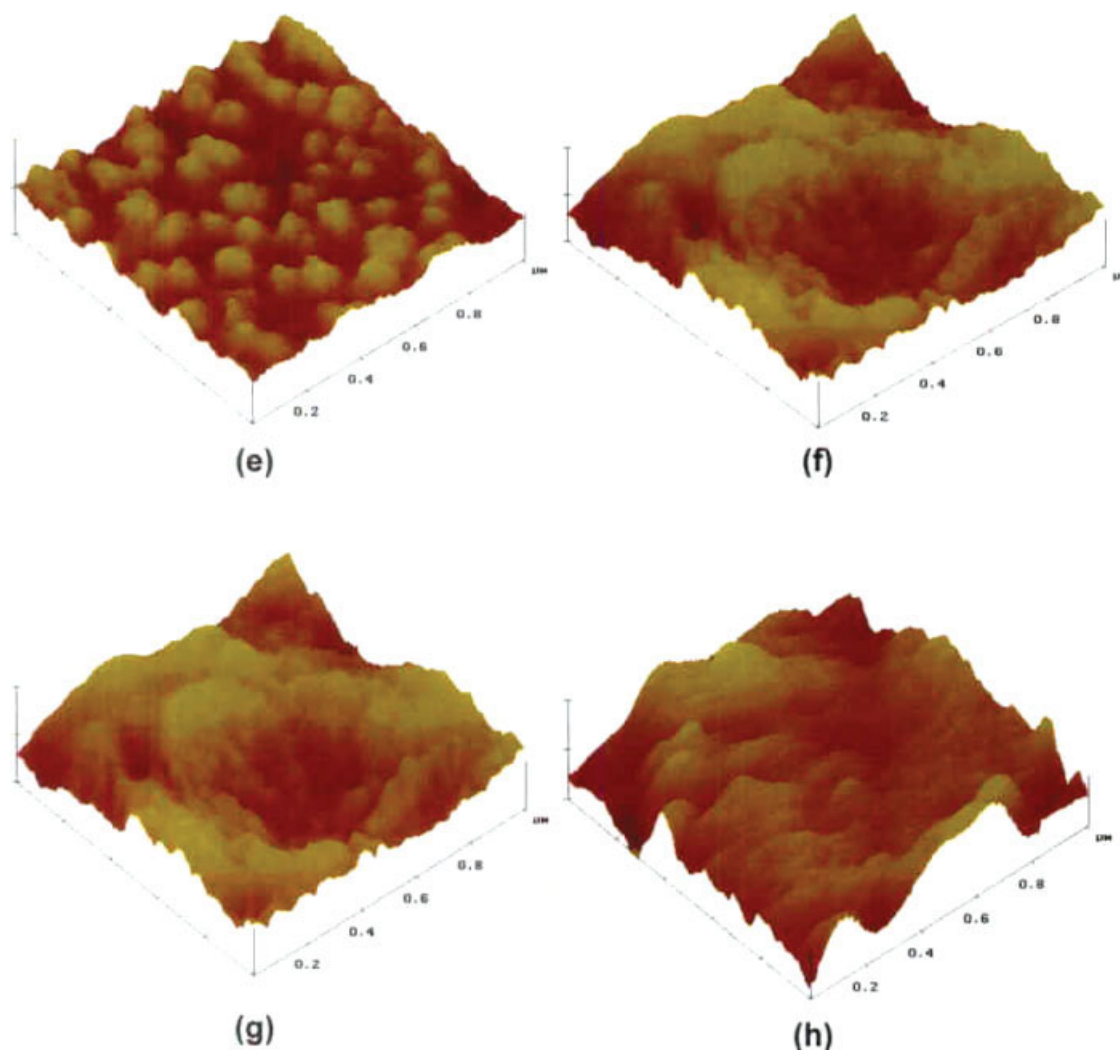
(e)

(f)

(g)

(h)

Figure 2 (*Continued*)

sulfoxide-d_6 as the solvent, on the basis of the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm.

Three-dimensional images of PVA film surfaces were obtained with a scanning probe microscope (Nano Scope IIIa, Digital Instrument, Stansted, Essex, England) equipped with a silicone tip at room temperature, 40% relative humidity, and a scanning rate of 0.5 Hz in a tapping atomic force microscopy (AFM) mode. The average roughness (R_a) was determined as the average derivation of the Z value (the height of the peak) within a given scan area. R_a is the area between the roughness profile (r) and its mean line or the integral of the absolute value of the roughness profile height over the evaluation length (L):[23]

$$R_a = \frac{1}{L} \int_0^L |r(x)| dx \qquad (3)$$

When it is evaluated from digital data, the integral is normally approximated with a trapezoidal formula:

$$R_a = \frac{1}{N} \sum_{n=1}^{N} |r_n| \qquad (4)$$

where N is an indefinite number, and r_n, is roughness profile.

The root-mean-square average roughness (R_q) of a surface is calculated from another integral of the roughness profile:

$$R_q = \sqrt{\frac{1}{L} \int_0^L r^2(x) dx} \qquad (5)$$

The digital equivalent normally used is

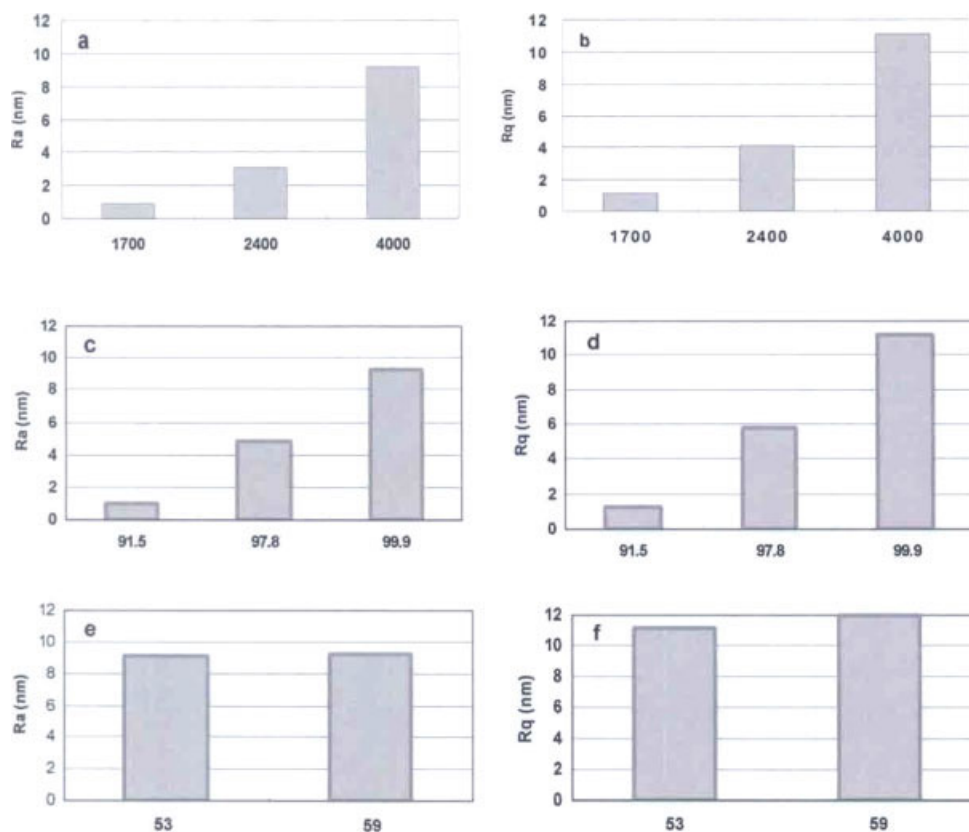$$R_q = \sqrt{\frac{1}{N} \sum_{n=1}^{N} r_n^2} \qquad (6)$$

Figure 3 R_a and R_q versus P_n, DS, and the s-dyad content: (a) R_a versus P_n, (b) R_q versus P_n, (c) R_a versus DS, (d) R_q versus DS, (e) R_a versus the s-dyad content, and (f) R_q versus the s-dyad content.

For a pure sine wave of any wavelength and amplitude, R_q is proportional to R_a; it is about 1.11 times larger. However, real profiles are not simple sine waves, and the approximation often fails miserably. Modern instruments either digitize the profile or do not report R_q. There is never any reason to make the approximation that is proportional to R_a. R_q has now been almost completely superseded by R_a in metal machining specifications. R_q still has value in optical applications, in which it is more directly related to the optical quality of a surface. PVA films (1×1 cm^2 scan size) were attached to sample changes in the chemical structure of the PVA film surfaces.

The crystal melting temperatures (T_m's) of the PVA films were obtained with differential scanning calorimetry (DSC; Q100, TA Instruments, New Castle, DE) with a sample weight of 10 mg and at a heating rate of 10°C/min from 20 to 250°C in a nitrogen atmosphere. The thermogravimetric analysis of the PVA films was conducted with thermogravimetry (Q500, TA Instruments) with a sample weight of 5 mg and at a heating rate of 10°C/min.

Wide-angle X-ray diffraction (WAXD) diffractograms were obtained with nickel-filtered Cu Kα radiation (18 kW, 40 kV, and 30 mA). The diffraction scans were collected at $2\theta = 5$–50°.

The Fourier transform infrared (FTIR) spectra of solution-cast PVA films were recorded on a Thermo Nicolet Avatar 370 FTIR spectrometer (Madison, WI) in the 4000–650-cm^{-1} range (64 scans and 8.0 resolution).

The stress–strain measurements were performed with a mechanical test machine (Ametek, Agawam, MA) to which a Hunter Spring Accu Fore II force gauge (0.01 N resolution) (Newark, DE) was attached. The reading was automatically recorded through a microprocessor as a function of time. A locally made device with a motor with a microswitch system was attached to the test machine to control the strain rate. The strain rate throughout the experiment was 0.04 cm/s. The samples used in the mechanical measurements were strips ($20 \times 2 \times 0.21$ mm^3) of PVA films.

RESULTS AND DISCUSSION

PVA resins are used according to diverse molecular parameters. The basic characteristics of PVA resins are presented in Table II. PVA films were prepared through the casting of PVAs with various P_n values, DS values, and s-dyad contents. Figure 1 shows the ^{1}H-NMR spectrum of PVA with a P_n value of 4000, a DS value of 99.9%, and an s-dyad content of 59% prepared by the complete saponification of copoly (vinyl pivalate/vinyl acetate) polymerized at 40°C.
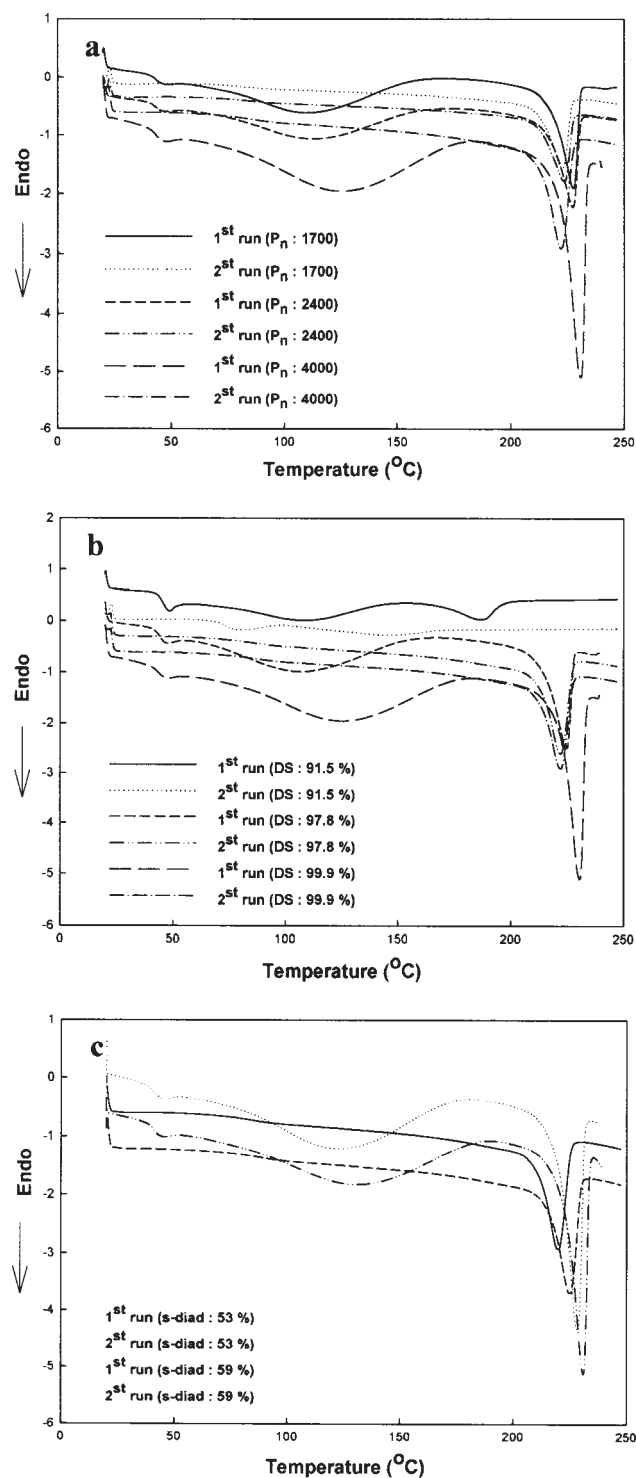
ent molecular parameters (P_n = 1700, 2400, or 4000; DS = 91.5, 97.8, or 99.9%; and s-dyad content = 53 or 59%) are shown in Figure 2. The surface roughness of the PVA films increased with increases in these three molecular parameters. The extent of the changes in the P_n values, DS values, and s-dyad contents could be measured quantitatively by the measurement of the R_a and R_q values in Figure 3. Figure 3 shows that the changes in the AFM parameters increased with increasing values of P_n, DS, and the

Figure 4 DSC thermograms of PVA films with (a) the P_n values, (b) the DS values, and (c) the s-dyad contents.

AFM can provide high-resolution, three-dimensional images of film surfaces without any sample pretreatment or damage to the polymer surface, especially if there is enough information on the film surface at the nanolevel in the height direction. Three-dimensional images of PVA films with differ-
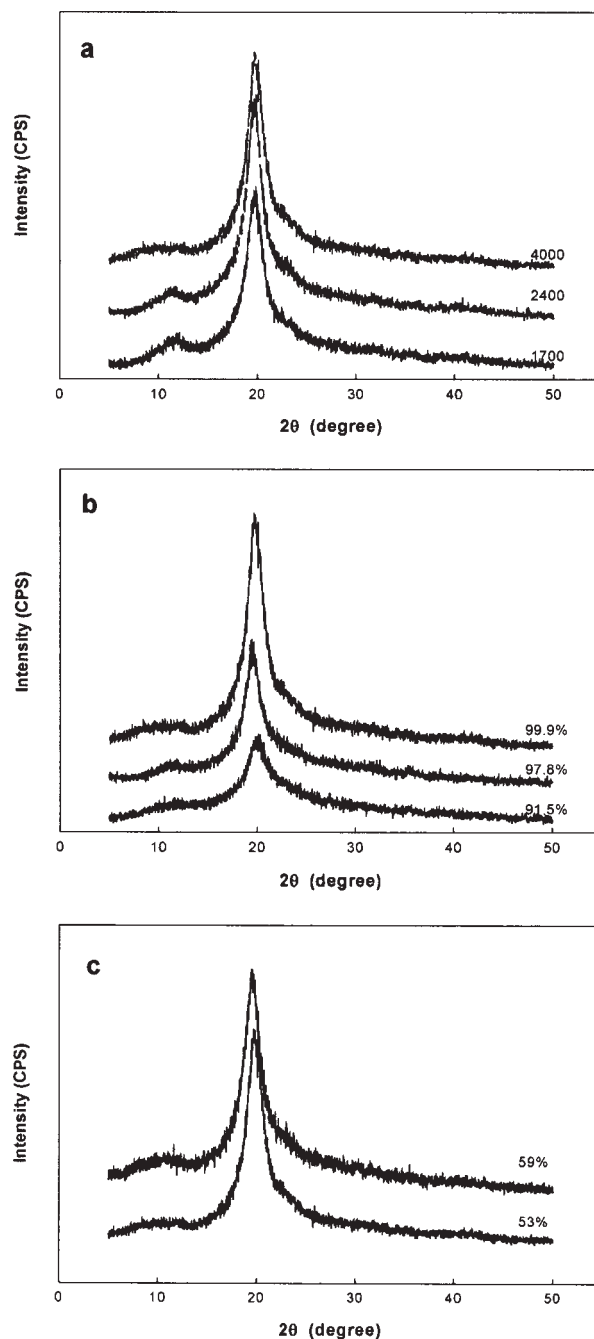
Figure 5 WAXD patterns of PVA films with (a) the P_n values, (b) the DS values, and (c) the s-dyad contents.

TABLE III
Assignments of the Bands in the IR Spectrum of PVA

ν (cm^{-1})	Intensity	Assignment
3340 ± 10	Very strong	ν(OH)
2942 ± 10	Strong	ν_S(CH$_2$)
2910 ± 10	Strong	ν_S(CH$_2$)
2840 ± 10	Sharp	(CH)
(1740)	Variable	C=O
(1710)	Variable	Residual CH$_3$CO
(1650)	Variable	Adsorbed water
(1595)	Variable	C=O
1446 ± 5	Strong	δ(CH$_2$)
1440 ± 5	Strong	
1420 ± 5	Strong	δ(OH) + ν(CH$_2$)$^{\#}$
1376 ± 5	Weak	δ(CH)$^{\#}$
1326 ± 5	Medium	δ(OH) + γ_W(CH)
1265	Variable	Residual CH$_3$CO
1235 ± 5	Weak	γ_W(CH)
1215 ± 5	Very weak	
1144 ± 5	Medium but varies	(C—O) of doubly hydrogen-bonded OH in crystalline regions
1096 ± 5	Strong	(C—O), unbonded, amorphous
1087 ± 5	Sharp	$\nu_+(\pi)$
1040 ± 5	Medium	
916 ± 5	Medium	γ_m(C—O), syndiotactic
890 ± 5	Very weak	
850 ± 5	Medium	γ_m(CH$_2$)
825 ± 5	Sharp	γ_s(CH$_2$)
640 ± 5	Medium broad	γ_w(OH)
610		γ_w(OH)
480		δ(OH)
410		γ_w(OH)

$^{\#}$Peak edge is very thin and not smooth or broad.

s-dyad content, and this agrees well with the data in Figure 2.

The T_m values from the first DSC runs of PVA films with P_n values of 1700, 2400, and 4000 were 227.6, 227.5, and 230.5°C, respectively [Fig. 4(a)]. However, the second run was different from the first run. The films with P_n values of 1700, 2400, and 4000 in the second run melted at 220.5, 221.4, and 219.9°C, respectively [Fig. 4(a)]. This is the reason for the degradation of the films after T_m. The endothermic enthalpy of a perfect PVA crystal was assumed to be 156 J/g.[24] In this study, the degree of crystallinity of PVA was calculated from the endothermic melting peak area. T_m of the PVA films in the first run definitely increased with increasing DS, as shown in Figure 4(b). That is, the films with DS values of 91.5, 97.8, and 99.9% melted at 187.3, 224.9, and 230.6°C, respectively. T_m in the second run also increased with increasing DS. The T_m values in the second run of films with DS values of 91.5, 97.8, and 99.9% were 142.1, 213.1, and 219.9°C, respectively. The degrees of crystallinity of the PVA films with DS values of 91.5, 97.8, and 99.9% were 17.3, 37.4,

and 46.6%, respectively. From this fact [Fig. 4(b)], it was determined that DS had a great influence on the thermal properties of the PVA films. T_m of the PVA films also increased with increasing s-dyad contents [Fig. 4(c)]. The T_m values in the first run of PVAs with s-dyad contents of 53 and 59% were 230.6 and 233.1°C, respectively. In the second run, PVAs with s-dyad contents of 53 and 59% melted at 219.9 and 225.0°C, respectively. The degree of crystallinity of
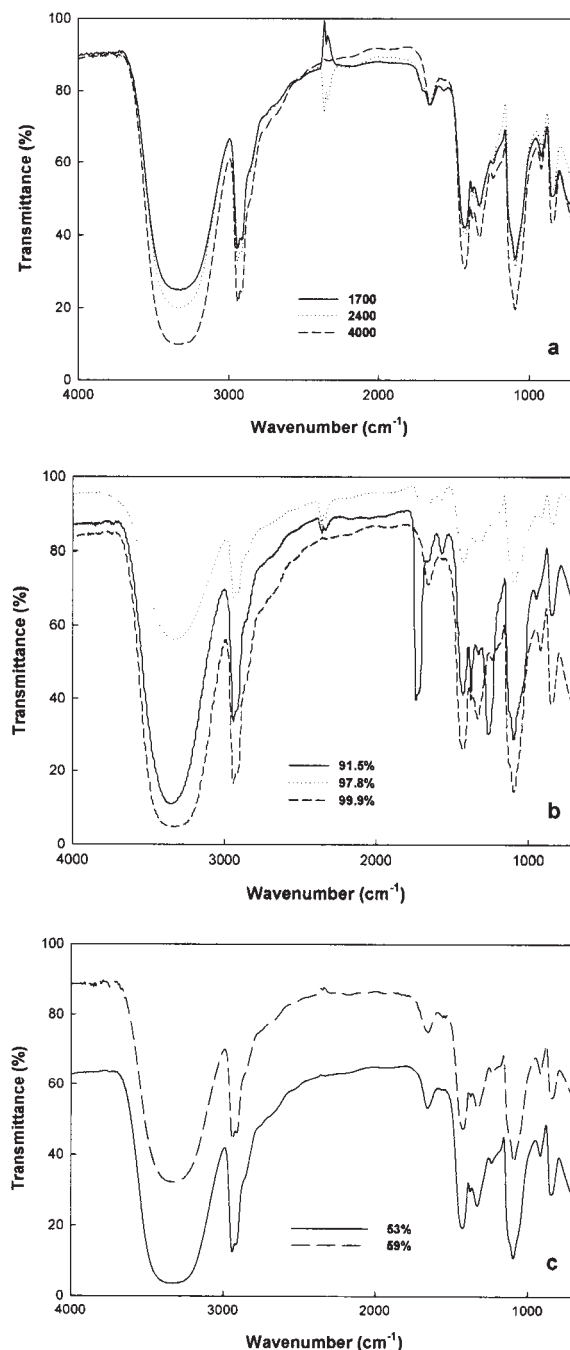

Figure 6 FTIR spectra of PVA films depending on (a) the P_n values, (b) the DS values, and (c) the s-dyad contents.
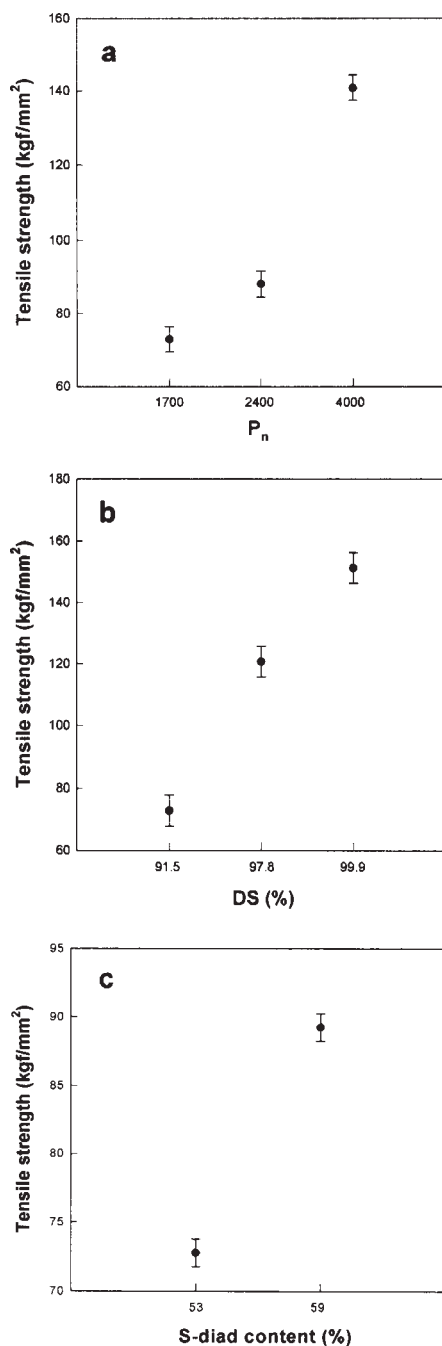
Figure 7 Tensile strengths of PVA films depending on (a) the P_n values, (b) the DS values, and (c) the s-dyad contents.

101 reflections. The X-ray diffraction peaks of all PVA films show sharp peaks at $2\theta = 20°$. This supports the idea that PVA is well crystallized and oriented despite a-PVA.[15]

Krimm et al.[26] and Tadokoro et al.[27] assigned all the bands that could be observed in the IR spectrum of PVA, as shown in Table III. In all the spectra, peaks at 2361 and 2330 cm^{-1} were due to atmospheric carbon dioxide. Peaks due to water in the films occurred at 1652 cm^{-1} and around 3240 cm^{-1}. The latter peak overlapped the peak due to the O—H stretching of hydroxyl groups. Peaks at 2940, 1331, 1091, and 847 cm^{-1} were attributed to C—H stretching, C—H bending, and C—O stretching of PVA, respectively. The broad and high absorption peak at 3230 cm^{-1} was estimated to arise from the O—H stretching frequencies of PVA and water hydroxyl groups. The band at 1708 cm^{-1} was attributed to the carbonyl-functional groups due to residual acetate groups remaining after the manufacture of PVA through the hydrolysis of PVAc or oxidation during manufacturing and processing.[28] Figure 6(a) presents the spectra of PVA films with various P_n values. The quantities of O—H stretching and C—H stretching peaks increased with an increase in P_n. The adsorbed water peak area at 1650 cm^{-1} also increased with P_n. Figure 6(b) shows the spectra of PVA films with various DS values, showing an outstanding residual CH_3CO peak at 1710 cm^{-1} for a DS value of 91.5%. The C=O peak at 1740 and 1595 cm^{-1} existed for DS values of 97.8 and 91.5%. Figure 6(c) presents the spectra of PVA films with the s-dyad contents. The intensity of the band at 916 cm^{-1} of an s-PVA film with an s-dyad content of 59% was stronger than that an s-PVA film with an s-dyad content of 53%.

Figure 7 shows that the tensile strength of the PVA films largely depended on the values of P_n, DS, and the s-dyad content of the PVA resins. The tensile strength increased with increases in the values of P_n, DS, and the s-dyad content.

CONCLUSIONS

PVA films from PVAs with various molecular parameters (P_n, DS, and s-dyad content), prepared through casting, were investigated with several analytical methods, including AFM, DSC, WAXD, FTIR, and Instron instrumentation. AFM is a well-established technique for probing surface topography and has been applied to polymer surfaces. In this case, it was applied in conjunction with vertical depth analysis, which gave an estimate of the surface roughness of PVA films with various P_n values, DS values, and s-dyad contents. According to the estimated

PVAs with s-dyad contents of 53 and 59% were 46.6 and 47.3%, respectively. The degree of crystallinity increased with increasing values of P_n, DS, and the s-dyad content.

The equatorial intensity curves of PVA films[15,18,25] with various P_n values, DS values, and s-dyad contents are shown in Figure 5(a–c), respectively. The peak around $2\theta = 20°$ shows $\theta/2\theta$ diffractometer scans along the equatorial direction through 101 and

results, the surface roughness of the PVA films increased with increases in the molecular parameters. The DSC thermogram data showed that the crystallinity, calculated with the enthalpy of fusion of PVA films (ΔH_f), remarkably increased with increasing DS. Increases in the molecular parameters of PVA films could prevent the volatility of iodide and dichromatic dyes because of increasing crystallinity in PVA polarized films. The crystallinity increase was identified with WAXD experiments. The hydroxyl groups affecting strong intermolecular hydrogen bonding were shown by peaks in FTIR spectra. Therefore, it can be concluded that with increasing values of P_n, DS, and the s-dyad content, the drawability of PVA films can be improved for an increasing polarizing effect. In the near future, we will report on the characterization of PVA/iodine complex films prepared with PVAs of various molecular parameters.

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