

Study on the Structure and Processibility of the Iodinated Poly(Vinyl Alcohol). I. Thermal Analyses of Iodinated Poly(Vinyl Alcohol) Films

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ABSTRACT: To get more information on the structure of iodinated poly(vinyl alcohol) (PVA), thermal analyses of unoriented and oriented PVA films were conducted. Unoriented and oriented PVA films iodinated with aqueous solutions at selected concentrations were carried out by thermogravimetry (TG) and differential scanning calorimetry (DSC). The TG curves for the iodinated film shows four or five weight-loss zones associated with degradation and evaporation of excess I₂ molecules and I₂ molecules from I₅⁻, partial OH side groups on PVA, and I₂ from I₃⁻, the remaining OH groups and the partial main chains, the remaining main chains, and a very small amount of residue from PVA. The char of KI salts remained. By investigating the TG results, it was identified that the amount of I₃⁻ ions

increased with increasing I₂/KI up to 65%, but above that weight gain, the rate of increase diminished and the amount of I₅⁻ ions from the I₃⁻ ions increased. The TG curve for the oriented film was very similar to that for the unoriented film except for its greater weight loss at zone I due to narrow space in amorphous region. The DSC thermogram of iodinated films indicated two peaks at 145°C and 160–170°C, corresponding to the melting of crystals and the degradations of OH groups and main chains, respectively. The maximum temperatures of peaks were much lower than that of the untreated one. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2407–2415, 2004

Key words: iodination; thermal properties; structure

INTRODUCTION

It is well known that polyiodide ions interrupt the intermolecular hydrogen bonds and make a complex with polymer chains not only in crystalline but also in amorphous regions of several polar polymers such as nylon 6, polyacrylonitrile, and poly(vinyl alcohol) (PVA). The PVA–iodine complex has long been investigated with various points of view since Staudinger et al.,¹ who found that the blue color was developed by iodination in an aqueous solution of PVA.

On the aspect of the iodine in PVA, West et al.² revealed that straight polyiodine chains of a 3.1 Å periodicity lie parallel to the orientation direction of PVA. Haisa and Itami³ proposed that the polyiodide chains were made of more than 15 iodine atoms. Heyde et al.⁴ and Hayashi et al.⁵ suggested that I₃⁻ or I₅⁻ was formed in the iodinated PVA. Recently, Choi et al.^{6–8} found that there were mainly I₃⁻ ions in the crystalline phase, whereas both the I₃⁻ and the I₅⁻ ions were mainly in the amorphous phase.

On the arrangement between the PVA and polyiodide chains, Rundle et al.⁹ and Tebelev et al.¹⁰ sug-

gested that a polyiodine chain might be surrounded by several extended PVA chains. However, Zwick¹¹ hypothesized after the structure of the iodine–amylose complex¹² that a linear polyiodine chain was included by helical PVA chains going around. Inagaki et al.¹³ supported Zwick's hypothesis with the similarity between the Raman spectra of iodine–PVA and iodine–amylose complexes.

On the formation of the PVA–iodine complex in not only amorphous but also crystalline phases, Hess et al.¹⁴ found new diffraction spots on X-ray diffraction of PVA fibers which absorbed iodine more than 12 wt % and concluded that iodine intruded in the crystal phase as well as in the amorphous phases at comparatively heavy iodine sorption. Choi et al.⁶ suggested that the iodine intruded into PVA crystals and formed cocrystal with PVA molecules in the case of 2×10^{-2} mol/L or more of I₂/KI in the soaking solution. Recently, Lyoo et al.^{15–20} reported on the effect of the syndiotactic PVA–iodine complex film.

On the other hand, there has been new attempts by Chuah and Poter²¹ and Lee and Porter²² to apply the iodination to an enhancement of processibility such as drawing of nylon 6, which has a limitation of processibility because of many intermolecular hydrogen bonds. The iodination is, therefore, capable of enhancing effectively the drawability of nylon 6 by the role of

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TABLE I
Intrinsic Characteristics of PVA

Degree of saponification (%)	Degree of polymerization	Tacticity				
		Triads			Diads	
		I	H	S	i	s
99.9 ↑	1750	20.8	49.8	29.4	45.7	54.3

reducing intermolecular attraction in crystalline as well as amorphous regions.

The PVA also has poor processibility mainly due to the presence of many intermolecular hydrogen bonds between adjacent OH groups in both the crystalline and the amorphous regions. Hence, we have planned this series of research with the ultimate object of improving the processibility of the PVA by the iodination as a reversible plasticization technique. To achieve this object, more information on the various conditions of the iodination and the resultant structure of the complex is required.

In the thesis, therefore, we have tried to get more data on the structure of PVA-iodine complex films possessing various quantities of iodine through thermal analyses. We have scarcely found any report on the thermal analyses for not only PVA-iodine complex but also on the pure PVA. An effect of the orientation of the PVA film on the iodination is also our concern; that is, thermogravimetry (TG) and differential scanning calorimetry (DSC) for the oriented and unoriented PVA films treated with aqueous I_2/KI solution with various concentrations were performed.

EXPERIMENTAL

Materials and film preparation

The PVA powder from Kuraray Co. in Japan was used to prepare films, the characteristics of which are shown in Table I. The degree of saponification and polymerization are reported by Kuraray Co. and the tacticity was evaluated from the H-NMR in dimethylsulfoxide by using a Bruker AC2000.

An unoriented film was prepared by the casting of an aqueous solution of 10 wt % PVA on a glass plate in air at 20°C and drawn to 4.7 times the original length at 110°C to be an oriented film. The crystallinity of the unoriented and oriented films determined by density gradient method were 21.3 and 37.0%, respectively, and the birefringence of the oriented film was 31.5×10^{-3} .

Iodination

The unoriented and oriented PVA films were iodinated with aqueous solutions of 0.1, 0.3, 0.5, 1.0, and 2.0 mol/L of I_2/KI (1 : 2) for 24 h at room temperature.

After removal from the solutions, the films were rinsed with water and air-dried at room temperature for over 1 week, which was the necessary time for the complete water evaporation and excess iodine sublimation. During the drying period, the weight of samples was checked daily to establish the complete water evaporation and excess iodine sublimation: The weight gain was determined from the weight difference of a dry film before and after soaking.

Measurements

TG and DSC were performed by a TA TGA 2950 and a TA DSC 2910, respectively. Both tests were conducted at heating rate of 20°C/min under an atmosphere of N_2 . In the case of DSC, the open stainless steel pans were used to allow the evaporation of iodine.

Infrared (IR) spectra were obtained with a MIDAC PRS-INT 189 FTIR spectrometer. The X-ray diffraction intensity was measured by using a Rigaku D/max-III-A with CuK_{α} radiation.

RESULTS AND DISCUSSION

Iodine absorption

Figure 1 shows the variations of the weight gain and molar ratio of I_2/KI to the PVA repeat unit by increasing the concentration of I_2/KI . The weight gains and molar ratios of the unoriented and oriented films increased rapidly with I_2/KI concentration to 1.0 and 0.5 mol/L, respectively; above these concentrations, the increasing tendencies leveled off. The maximum molar ratio was 0.1, which is an unexpectedly small value compared to the 0.53 in the case of nylon 6.

Assuming that only the I_3^- ions exist, it is basically impossible that every OH group holds an I_3^- ion because of the length of I_3^- ion (9.5 Å) greater than the distance between adjacent OH groups on a PVA molecule (2.18 Å). An I_3^- ion can occupy five OH groups, so even the arithmetic molar ratio cannot exceed 0.2. Consequently, the 0.1 of the maximum molar ratio is estimated to be reasonable in the respect that the maximum molar ratio was 0.53 in the case of nylon 6, although its arithmetical maximum molar ratio is 1.0.

The increasing rate and the maximum value of the weight gain of the oriented film were lower than those

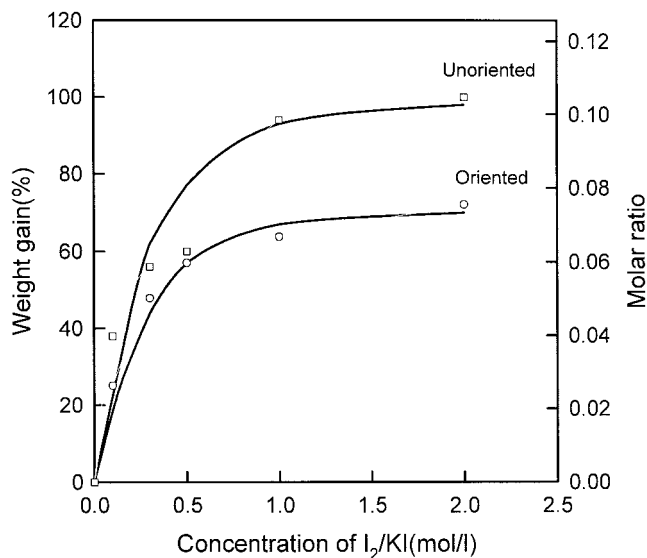


Figure 1 The changes on the weight gain and molar ratios of I_2/KI to the PVA repeat units for iodinated PVA films with the concentration of I_2/KI .

of the unoriented film. This may be a result of a difference of the overall intermolecular space volume between the oriented and unoriented films. In the iodinated film, there may be not only the polyiodide ions effective to form complex with PVA molecules but also ineffective iodine and potassium iodide molecules, which were recovered from the excess I_2/KI solution in the film during drying. The excess molecules may exist only in the amorphous region, whereas the polyiodide ions can exist even in the crystalline region. The oriented film therefore can contain lower amounts of the ineffective molecules because of the higher crystallinity and orientation than the unoriented film. This will be mentioned again in the discussion of the TG results.

TG analysis

Reports of the TG analysis for not only iodinated PVA complex but also pure PVA can scarcely be found. Therefore, the TG analysis for the pure PVA film had been investigated before the iodinated PVA films.

PVA film

The TG curve for untreated PVA film is shown in Figure 2. There are three or four distinguishable weight loss zones. The set-on temperature of zones II, III, and IV are 271, 399, and 540°C, respectively. Zone III can be divided at 469°C into two subzones of III-1 and III-2 by a difference of weight-loss rate. There was not any recognizable weight loss in zone I, but other zones should be investigated through an experimental method. An analysis of IR spectrum for the untreated

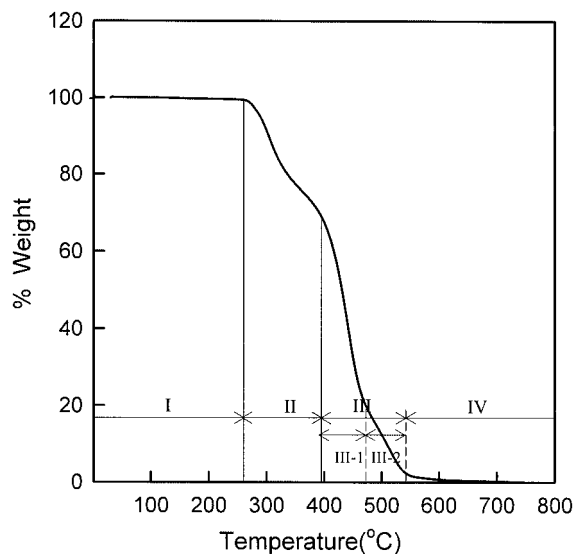


Figure 2 A zone classification of TG curve for the untreated PVA film.

film and the residue of each zone was performed to estimate the component lost in the corresponding zone.

Figure 3 shows the IR spectra for untreated PVA film, and residues of zone II and zone III-1. There are four bands related to the main chain at 2940 and 2909 cm^{-1} assigned to CH_2 symmetric stretching vibration, at 1435 cm^{-1} assigned to CH_2 bending vibration, and

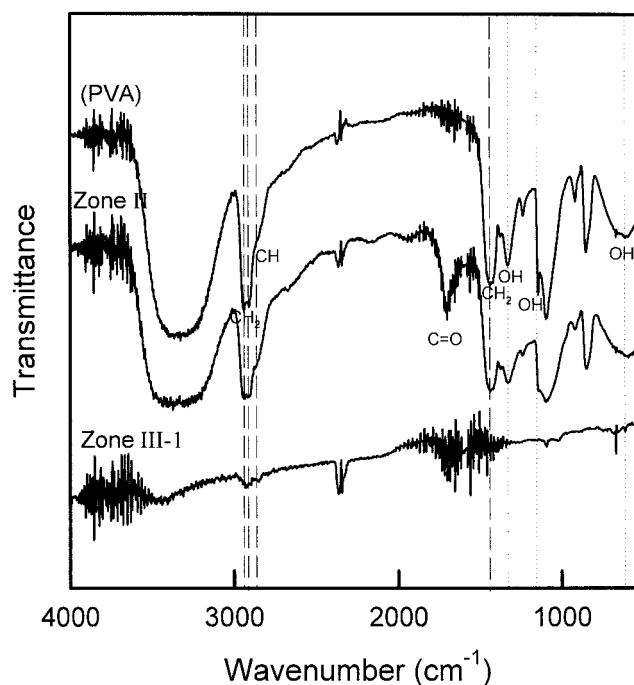


Figure 3 The IR spectra of the untreated PVA film and its remaining portions after zone II and zone III-1 on TG curve (—, main chain; ---, side group).

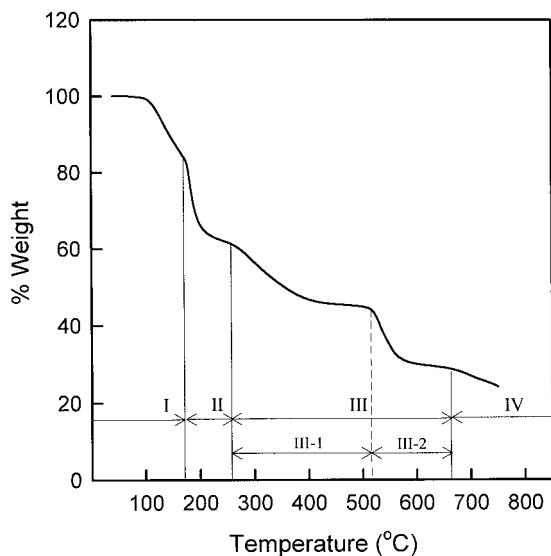


Figure 4 A zone classification of TG curve for the unoriented PVA film iodinated with 2.0 mol/L I_2/KI solution.

at 2840 cm^{-1} assigned to CH symmetric stretching vibration. Three bands are related to the side groups ($-\text{OH}$) at 1330 and 620 cm^{-1} assigned to OH bending vibration and at 1143 cm^{-1} assigned to OH symmetric stretching vibration in crystalline.²³

For the residue of zone II, the intensity of bands connected with OH groups decreased and did not disappear, and the new band at 1740 cm^{-1} likely assigned to ketone appeared. Ukida²⁴ and Yamaguchi and Amagasa^{25,26} reported that the ketone was formed after degradation of the OH groups in the case of isothermal heat treatment of PVA. Zone II must be associated with partial, not complete, degradation of OH groups. Such partial degradation of OH groups can be supported by the fact that the weight loss of zone II (35%) is less than the weight fraction of an OH group in a repeat unit of PVA (39%).

For the residue of zone III-1, the bands related to the OH groups disappeared perfectly but the bands related to the main chain remained a little, which suggests that zone III-1 must be associated with the degradation of the remaining OH groups and a part of main chains. Consequently, zone III-2 must be associated with the remaining main chains. Zone IV may be associated with the degradation of a very small amount of residue that evaporated gradually to 0% weight.

Iodinated films

A typical TG curve for unoriented film iodinated with 2.0 mol/L of I_2/KI is shown in Figure 4. Zone II and III appeared to lose much weight, the same as those of PVA film. However, there was a sudden weight loss in zone I from 100°C and a char in zone IV. The set-on

temperatures of zones II and III-1 were shifted greatly to a lower temperature than that of untreated PVA film, respectively, because of oxidization of I_2 molecular, which was evaporated just before each zone. We investigated the loss components for each zone of iodinated film through the IR spectrum.

The IR spectra for the residue of zone II and III-1 of iodinated film are shown in Figure 5. The spectrum was very similar to that of untreated PVA film; we know that the evaporated components of each zone for the iodinated film are the same as those of PVA. However, we cannot find any peaks associated with the iodine ion through the IR spectrum. Although there is a large residue after zone III-2, which degrades continuously through zone IV, the TG for the iodinated films was performed up to 750°C because of a limit of the machine.

As aforesaid, there may be several compositions related to I_2/KI in the iodinated film such as I_3^- , I_5^- , and K^+ ions and excess molecules of I_2 and KI, but no band assigned them on the IR spectra.

All the compositions related to I_2/KI may be converted into only two types of an evaporable I_2 molecule and a stable KI salt (bp: 1300°C) through heating on the TG. With increasing temperature, the I_2 molecules may be evaporated from the excess I_2 , I_5^- ions, and I_3^- ions accompanied by degradation of OH groups successively. The I_2 molecules are from the ions of I_5^- and I_3^- ions ($I_5^- \rightarrow I_3^- + I_2 \uparrow$, $I_3^- \rightarrow I^- + I_2 \uparrow$) as well as excess I_2 , and finally residual I^- ions ($I^- + K^+ \rightarrow KI$) and K^+ may reform to the KI salts. The excess and reformed KI salts must remain as char.

We have therefore been able to calculate the fraction of them in each zone as Table II. The percent weight

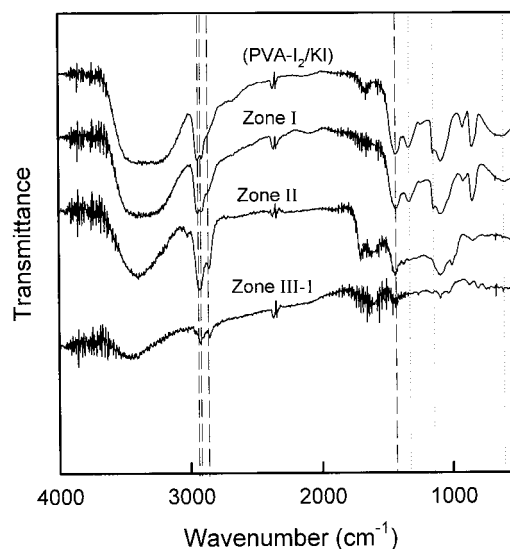


Figure 5 The IR spectra of the untreated PVA film iodinated with 2.0 mol/L I_2/KI solution and its remaining portions after zone I, II, and III-1 on TG curve (—, main chain; ---, side group).

TABLE II
% Weight Loss and Component Corresponding to Each Zone of TG Curve for Unoriented PVA Films Untreated and Iodinated with 2.0 mol/l I₂/KI Solution

Zone	I	II	III		IV
			III-1	III-2	
PVA					
% Weight loss[A]	0	36	61		3
Component	—	—OH	—OH Main chain	Main chain	—
PVA-I ₂ /KI					
% Weight loss[B]	18	24.5	30.5		28
[C] ([D])	0 (+18)	18 (+5.5)	30.5 (+0)		2 (+26)
Component	(+I ₂)	—OH(+I ₂)	—OH main chain	Main chain	(+KI)

[A]: Weight loss in Figure 2.

[B]: Weight loss in Figure 4.

$$[C] = [A] \times \frac{100}{200(\text{weight gain})}$$

$$[D] = [B] - [C].$$

losses of the PVA film [A] and I₂/KI film [B] were directly measured from Figures 2 and 4, respectively. Assuming that the percent weight loss of each zone for the PVA film should be applicable to the PVA in the PVA-I₂/KI film, another percent weight loss [C] was calculated by using the corresponding weight gain of 200%. In conclusion, the difference [D] in each zone between [B] and [C] must correspond to the weight fraction for the components related to I₂/KI such as evaporating I₂ (zone I, II) or the remainder of KI (zone IV).

The excess I₂ evaporating at the lowest temperature and the I₃⁻ ions degradable into I₂ (+I⁻) at the highest temperature must correspond to zone I and zone II, respectively, but it is impossible to estimate which zone is associated with the I₅⁻ ion degradable into I₂ (+I₃⁻) at the middle temperature.

Figure 6 shows the variation of the [D] values in Table II by increasing the weight gain. The [D] value increased with weight gain, but the increasing tendencies were changed all together at about 65%. As mentioned above, the I₂ molecules must be evaporated from three kinds of sources, but the weight loss related to its evaporation was able to distinguish into only two zones (I, II). The evaporation of I₂ in zone II was estimated to be associated with the I₃⁻ ions because of two factors such as the degradation of OH groups in this zone and [D] value of this zone, much less than zone I. For zone I and II, the [D] values were increased with the weight gain, but their tendencies were somewhat different from each other. The increasing tendencies of zone I became rapid and zone II leveled off at almost the same weight gains of 65%. These results suggest that zone II and I are associated with I₃⁻ ion and excess I₂ plus I₅⁻ ion, respectively: That is, above 65%, the amount of I₃⁻ ions combined with the OH group of PVA may indicate the upper limit, which is consistent with the line for zone II, and instead, the

amount of I₅⁻ ions converted from I₃⁻ ions may be increased. The amount of I₂ from this I₅⁻ ion must be added to the excess I₂ on the line for zone I to indicate rapid increase at above 65%. The KI salts in zone IV could be formed mainly by a combination of K⁺ and residual I⁻ ions from the degradation of I₃⁻, of which slope of the line must be similar to that of zone II.

Figure 7 shows the TG curve of unoriented films. With the concentration of I₂/KI, the tendency of the figure's shape gradually changes from untreated PVA to 2.0 mol/L of iodinated film. The weight loss of zone I is increased rapidly from 0.3 mol/L, but the variation of char is independent of the concentration of I₂/KI because of the much volatilization of excess I₂ of high concentration I₂/KI.

Figure 8 shows the TG curves of the unoriented and oriented films iodinated with 2.0 mol/L I₂/KI aqueous

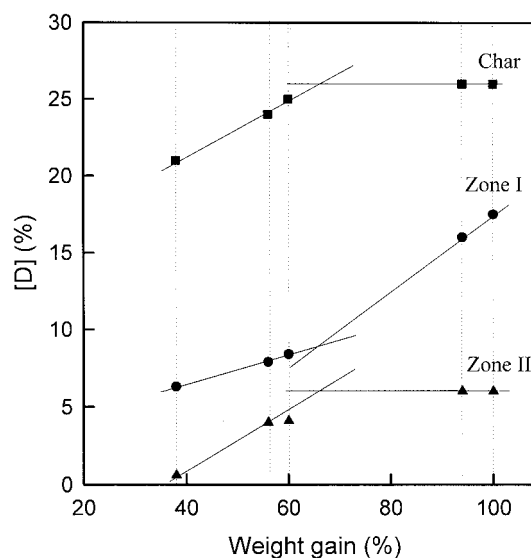


Figure 6 The changes on the [D] values in Table II with weight gain of iodinated films.

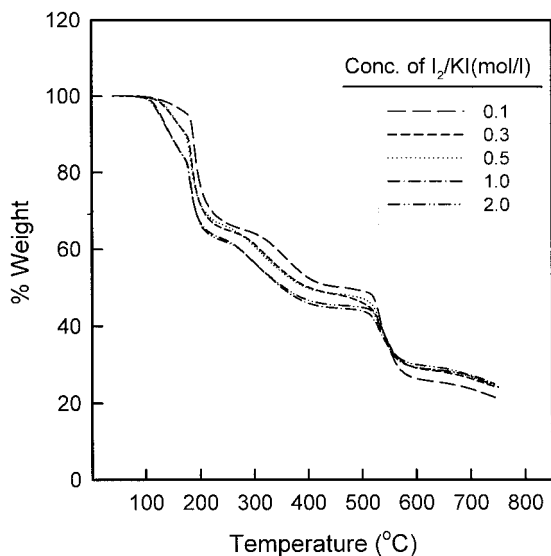


Figure 7 The TG curves of unoriented PVA films iodinated with various concentrations of I_2/KI solutions.

solution. The overall appearances of the curves are similar to each other, but the weight loss of zone I which may have a higher relation to the excess I_2 for the oriented film is smaller than that of the unoriented film. This must result from the finding that oriented film can contain lower amounts of the ineffective molecules because of the higher crystallinity and orientation than that of the unoriented film, which had been mentioned in the discussion on the iodine absorption of oriented film.

DSC analysis

The reports on the DSC analysis for the pure PVA have been found,²⁷⁻³⁰ which were focused on the behavior of melting of crystal mostly, but for iodinated PVA complex have been scarcely found. Therefore, we have investigated the behavior of the iodinated PVA complex as well as the pure PVA at higher temperatures to contradistinguish the TG results.

PVA film

Figure 9(a) shows the DSC thermogram of the untreated film. There are three kinds of endothermic peaks at around 230, 270, 370, and 470°C. The sharp peak at 230°C must correspond to the melting of crystal. Referring to the above-mentioned TG results, the components at 270, 370, and 470°C are estimated to be associated with the partial decomposition of OH side groups, the decomposition of the remaining side groups and the partial degradation of main chains, and the degradation of remaining main chains, respectively. To support this estimation, we performed additional experiments of DSC undergoing three succes-

sive steps of heating up to the maximum peak temperature of each peak followed by an isothermal abiding for 1 min, slow cooling to ambient, and then heating again to 550°C. The results are indicated in Figure 9(a, c). In general, a peak that makes a reappearance or not on the second heating step is associated with a reversible physical transition or a permanent chemical conversion, respectively.

In Figure 9(b) for the peak at 370°C, all the peaks which had appeared on the first heating step did not reappear except the peak at 470°C on the second (cooling) as well as the third (second heating) steps. This result confirms the fact that the peak at 370 and 470°C are associated with the degradation of main chains.

In Figure 9(c) for the peak at 270°C, there is an exothermic peak at 200°C on the cooling step, which is estimated as a crystallization peak and to be a source of the peak at 215°C associated with the melting of crystals on the second heating step. The peak at 270°C on the first heating step did not reappear, whereas the peak associated with the degradation of main chains reappeared on the second heating step. These results confirm the fact that the peak at 270°C on the first heating step is associated with a chemical degradation of side groups. The melting temperature of crystals (215°C) on the second heating step is lower than that (230°C) on the first heating step, which must be due to a decrease of intermolecular hydrogen bonds resulted from the removal of side groups for the first heating steps. This result also supports the finding that the peak at 270°C is associated with the degradation of side groups.

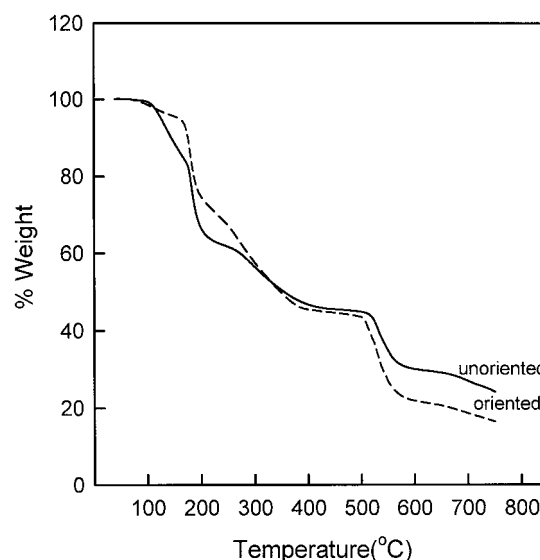
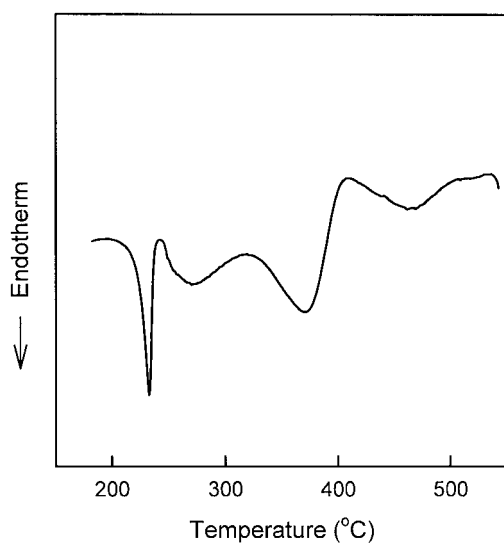
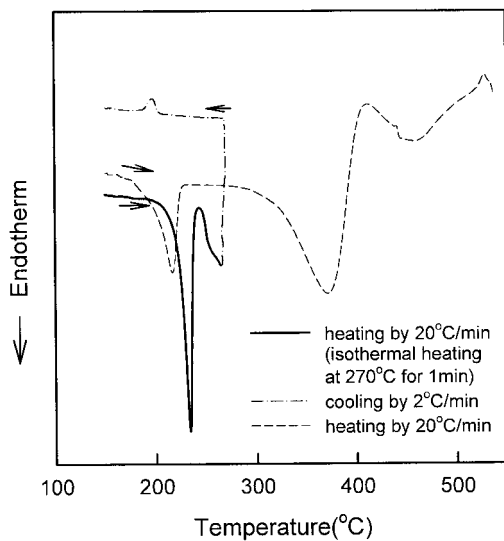


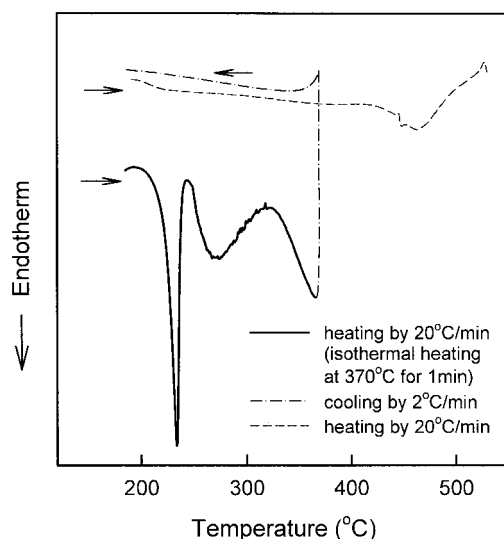
Figure 8 The TG curves for unoriented and oriented PVA films iodinated with 2.0 mol/L I_2/KI solutions.



(a)



(b)



(c)

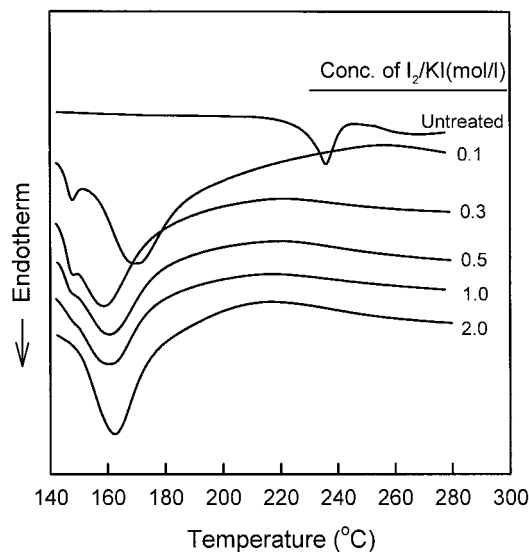


Figure 10 The DSC thermograms of unoriented PVA films iodinated with various concentrations of I_2/KI solutions.

Iodinated films

The DSC for the iodinated films was performed up to 350°C because of a serious unsteadiness of the baseline at the temperature range higher than 350°C . Figure 10 shows the DSC thermograms of unoriented films.

There are two obvious endothermic peaks at around 145 and $160\text{--}170^\circ\text{C}$. The sharp lower temperature peak must be associated with the melting of the PVA-iodine complex crystals, and the decreasing result of its temperature as compared with the pure PVA is a reasonable result from the disruption of the intermolecular hydrogen bonds by the polyiodide ions. Referring to the above-mentioned TG results, the broad higher temperature peak is estimated to be associated not only with the degradation of OH groups but also with the decomposition of polyiodide ions to I_2 molecules and their evaporation, such that the inclusion of the decomposition and evaporation of the polyiodide ions and I_2 molecules can also be supported by the increase of the relative intensity of the peak comparison with the melting peak.

In addition, there is a gentle endothermic slope beginning at 230°C , which looks similar to the initiation of a very broad peak. This must be associated with the degradation of main chains of PVA, of which the temperature decreased as compared with the pure PVA by the action of I_2 molecules, precedent-generated, as an oxidizer.

Figure 9 (a) The DSC thermogram of untreated PVA film. (b) The DSC thermograms of untreated PVA film (heating to 370°C → cooling to room temperature → heating to 550°C). (c) The DSC thermograms of untreated PVA film (heating to 270°C → cooling to room temperature → heating to 550°C).

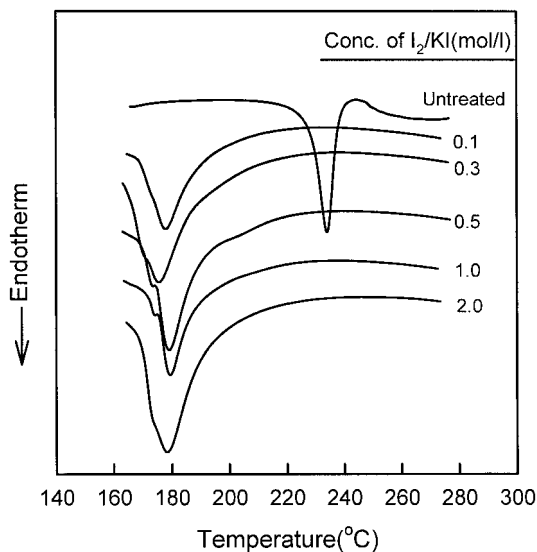


Figure 11 The DSC thermograms of oriented PVA films iodinated with various concentrations of I_2/KI solutions.

There are two considerable variations of increasing the concentration of I_2/KI and the weight gain: The intensity of the peak related to the melting and the temperature of the peak and slope initiation related to the decomposition and evaporation decreased in general.

Figure 11 shows the DSC thermograms of the oriented films. The overall appearance of the thermograms is similar to the case of the unoriented films. By comparing the case of the unoriented films, however, the melting peak temperature increased a little to 175°C , and consequently, those two peaks overlapped extremely and looked like one peak.

Additional increases of the temperature in the melting peak and the degradation peak must be resulted from the restraining effect of the high crystallinity, and orientation of the oriented film on the crystal melting was greater than on the degradation of OH groups and polyiodide ions. There is no considerable variation with increasing concentration of I_2/KI .

The X-ray diffraction scans were performed to support the discussion on the melting peaks on DSC thermograms, which are shown in Figures 12 and 13.

On the other hand, Choi and Miyasaka⁸ supposed the two types of intercalation and substitution model regarding crystal lattice for iodinated PVA film. The d -spacings of the intercalation type and the substitution type were 13.45 \AA (100) and 4.52 \AA (001) for a 14 wt % of I_2/KI , and 10 \AA (001), 6.03 \AA (101), 4.15 \AA (102), and 3.33 \AA (003) for a 100 wt % of I_2/KI , respectively.

Figure 12 shows the X-ray diffraction scans for the unoriented films. The intensity of main peak at $2\theta = 19.5^\circ$ (101) decreased with the weight gain compared with the untreated PVA because of the relax-

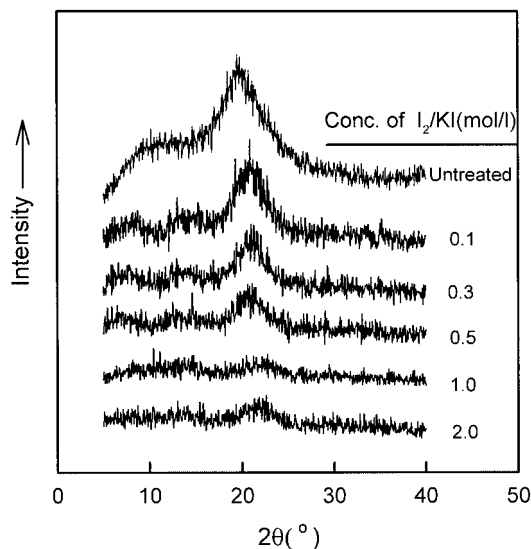


Figure 12 The X-ray diffraction scans of unoriented PVA films iodinated with various concentrations of I_2/KI solutions.

ation of crystal by the intrusion of iodide ions, which supported the DSC results that the intensity of the peak related to the melting and the temperature of the peak decreased in general. In the low concentration of I_2/KI for the 0.1, 0.3, and 0.5 mol/L, the diffraction peaks at $2\theta = 6.5, 13, 20.5^\circ$ appeared, which is similar to the intercalation model. In the high concentration of I_2/KI for the 1.0 and 2.0 mol/L, the diffraction peaks at $2\theta = 7.5, 14.5, 21.5, 28^\circ$ appeared, which is similar to the substitution model.

Figure 13 shows the X-ray diffraction scans for the oriented films. The overall appearance of the diffrac-

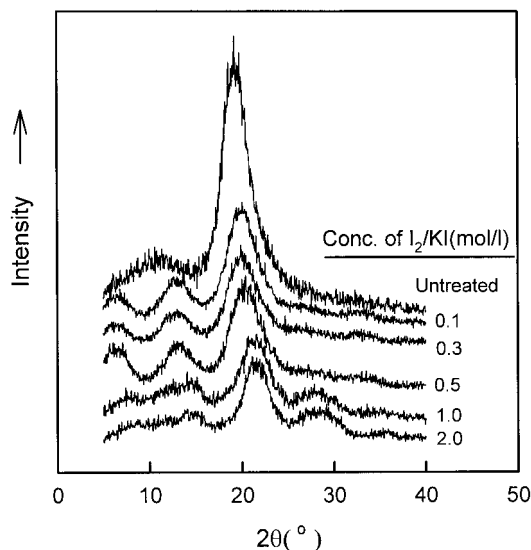


Figure 13 The X-ray diffraction scans of oriented PVA films iodinated with various concentrations of I_2/KI solutions.

tion scans is similar to but the intensity of the peak clearer than that of the unoriented films due to the high crystallinity and orientation of the oriented film.

CONCLUSION

Unoriented and oriented PVA films were iodinated with aqueous solutions of 0.1, 0.3, 0.5, 1.0, and 2.0 mol/L of I₂/KI. The thermal analyses for the untreated and iodinated PVA films were carried out by TG and DSC. Analyses of an IR spectrum and an X-ray diffraction were performed in aid of the TG and DSC, respectively.

The weight gains and molar ratios of the unoriented and oriented films increased rapidly with I₂/KI concentration up to 1.0 and 0.5 mol/L, respectively, and leveled off. With an increase in the concentration of I₂/KI, the weight gains of the unoriented films were generally higher than those of the oriented films.

The TG curve for the untreated PVA indicated three or four weight-loss zones, which may be associated with the evaporation of the components from the OH groups partially decomposed from main chains (zone II): the remaining OH groups and partial degradation of main chains (zone III-1), degradation of the remaining main chains (zone III-2), and a very small amount of residue (zone IV), respectively. For the iodinated films, evaporative components corresponding to each zone of weight loss may consist of not only the same ones as for the PVA film but also others related to the I₂/KI, such as excess I₂ molecules and I₂ molecules from I₅⁻ ions (zone I), and I₂ molecules I₃⁻ ions (zone II). The char (zone IV) may consist of KI salts. By the investigation of TG results, it was estimated that the amount of I₃⁻ ions increased with increasing I₂/KI to about 65%, but above that weight gain, the rate of increase diminished and the amount of I₅⁻ ions converted from the I₃⁻ ions increased. The TG curve for the oriented film was very similar to that for the unoriented film except for its greater weight loss at zone I due to narrow space in amorphous region.

The DSC thermogram of the untreated PVA film showed four endothermic peaks at 230, 270, 370, and 470°C, corresponding to the melting of crystals, the partial decomposition of side groups, the decomposition of the remaining side groups and the partial degradation of main chains, and the degradation of remaining main chains, respectively. However, the iodinated films indicated two peaks at 145 and 160–170°C, corresponding to the melting of crystals and

the degradations of OH groups and main chains, respectively. The maximum temperatures of peaks were much lower than the corresponding peaks of untreated films. The temperatures of peaks of oriented films were higher than those of the unoriented film, which may be a result of the higher crystallinity.

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