

Structure and Processability of Iodinated Poly(vinyl Alcohol). II. Drawability of Iodinated Films

Eun Joo Shin,¹ Yang Hun Lee,¹ Suk Chul Choi²

¹Division of Fashion and Textiles, Dong-A University, Pusan 604-714, South Korea

²Department of Clothing and Textiles, Pusan National University, Pusan 609-735, South Korea

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ABSTRACT: The drawability of poly(vinyl alcohol) (PVA) films iodinated with 0.1, 0.3, 0.5, 1.0, and 2.0 mol/L I₂/KI aqueous solutions was examined with a tensile tester and a hand-operated drawer at 30–150°C. The structure of the films drawn to a maximum draw ratio (MDR) and deiodinated was determined by X-ray diffractometry, differential scanning calorimetry, and birefringence. Generally, the improvement of the drawability for the PVA film via iodination was ascertained by the increased breaking strain and decreased yield stress on the stress–strain curves when increasing the I₂/KI concentration of the aqueous solutions used in the iodination. The MDR was generally increased with the concentration of I₂/KI and the draw temperature.

However, it diminished instead when close to the highest temperature and concentration of I₂/KI, which was likely due to molecular degradation by the action of iodine as an oxidizer. The variation of the structure of the films drawn and deiodinated seems to be dependent mainly upon the MDR rather than the concentration of I₂/KI. The greater the MDR was, the higher the degree of crystallinity, birefringence, and initial modulus were but the lower the melting temperature. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1209–1214, 2005

Key words: poly(vinyl alcohol); film; drawing; crystal structure

INTRODUCTION

Poly(vinyl alcohol) (PVA) has a very high potential for preparation of high strength and high modulus products because of its superior qualities of impact strength, crystalline modulus, and so on.^{1,2} PVA has many OH side groups causing strong intermolecular hydrogen bonds, which is beneficial for properties, providing a high melting point of 228–250°C; but it is a limitation for processability, such as drawability.³

Many reports^{4–6,11–17} on the iodination of PVA have been made. A considerable number of them, including the first part of this study,⁷ have maintained that iodine intrudes and ruptures the intermolecular hydrogen bonds in the crystalline and amorphous regions of PVA at comparatively heavy iodine sorption. This suggests the potentiality to enhance the drawability of PVA by iodination as the reversible plasticization concept.

Actually in the case of nylon 6, there has been some research on the enhancement of drawability by iodination. Chuah and Porter⁸ utilized iodination as a reversible plasticization to enhance the drawability of a nylon 6 film. The drawing of a nylon 6–iodine complex film was tried at above the α -relaxation temper-

ature and resulted in a maximum draw ratio (MDR) of 7.5 and a modulus after deiodination of 6.0 GPa. They concluded that iodine is the more effective plasticizer for enhancing the drawability because it can plasticize not only the amorphous but also the crystalline regions of nylon 6. Lee and Porter⁹ obtained an MDR of 48 by solid-state coextrusion of a nylon 6–iodine complex film at about the melting temperature.

Choi et al.'s¹⁰ report for PVA merely suggests the probability of a drawability enhancement by iodination through tensile tests for some iodinated PVA films, but there was no concrete study on it. Therefore, in this work we investigated the drawability of iodinated PVA films at various temperatures and the structure of the films drawn to the MDR and deiodinated was determined through dynamic mechanical thermal analysis (DMTA), tensile tests, X-ray diffractometry, differential scanning calorimetry (DSC), and birefringence.

EXPERIMENTAL

Material and film preparation

PVA powder (Kuraray Company) was used to prepare films. Its syndiotactic diad content as determined by ¹H-NMR (AC200NMR Spectroscopy, Bruker, Germany) and its number-average polymerization and degree of saponification as reported by Kuraray were 54.3, 1750, and >0.999, respectively. A film was pre-

Correspondence to: Y. H. Lee (leeyh@daunet.donga.ac.kr).

pared by casting an aqueous solution of 10 wt % PVA on a glass plate in air at 20°C. The material and film preparation procedure are the same as described in the first part of this study.⁷

Iodination

The film was iodinated with aqueous solutions of 0.1, 0.3, 0.5, 1.0, and 2.0 mol/L I₂/KI through a procedure identical to that described in Part I of this study.⁷

Drawing

The drawing tests were performed with a tensile tester (Autograph AGS-500D, Shimadzu) with a hot chamber at 30–90°C and with a hand-operated drawer at 90–150°C in silicon oil to prevent oxidation of the films. The width and length of the samples were 5 and 10 mm, respectively, and the drawing speed was 2 mm/min. The draw ratio was calculated from the change in distance between marks made on the undrawn film.

Deiodination

The iodinated films were deiodinated by dipping them in an aqueous solution of 7 wt % sodium thiosulfate and 5 wt % ethylene glycol at 20°C pending the complete removal of iodine.

Measurements

The DMTA for the undrawn films was performed with a Rheometric Scientific DMTA 3E under an atmosphere of N₂ at a heating rate of 4°C/min.

The X-ray diffractometry was performed using a Rigaku D/max-III-A with Cu-K_α radiation.

DSC was performed with a TA DSC 2910 under an atmosphere of N₂ at a heating rate of 20°C/min. Stainless steel open pans were used to allow the evaporation of iodine.

The birefringence was measured using a Leica polarizing microscope and Tilting compensator K.

RESULTS AND DISCUSSION

DMTA results for undrawn film

To examine the molecular mobility, which is the main factor affecting the drawability, the DMTA for the pure PVA film and the film iodinated with 2.0 mol/L I₂/KI solution was performed before drawing. Figure 1 shows the variation of the loss tan δ with increasing temperature for the untreated film and the film iodinated with 2.0 mol/L I₂/KI solution.

The peak of the α_a dispersion at 70°C for the untreated film is known to be assigned to the glass-

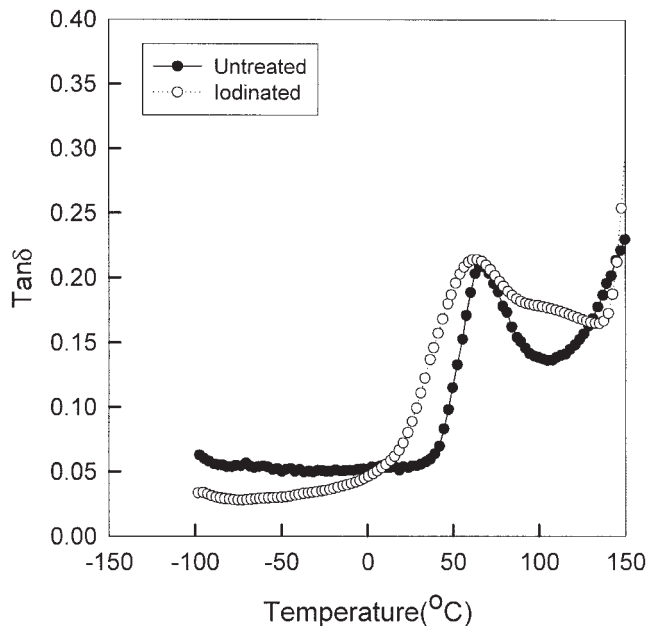


Figure 1 The curves of tan δ versus temperature for undrawn PVA films untreated and iodinated with 2.0 mol/L I₂/KI solution.

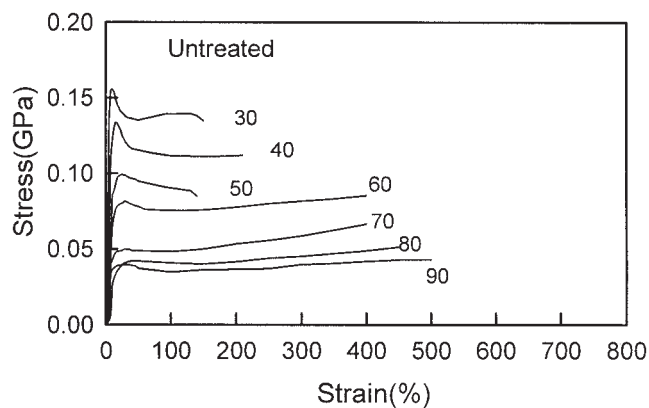
transition temperature (T_g) of PVA. The peak of the iodinated film was observed at 60°C, which was lower than that of the untreated film. Such a drop of the T_g by the iodination may have resulted from the rupture of intermolecular hydrogen bonds by iodine.

In addition, the intensity of the tan δ for the untreated film began to increase rapidly at around 120°C, which is estimated as the beginning of α-relaxation temperature ($T_α$) peak. It is known that PVA has a unique crystalline relaxation, referred to as the α-relaxation at $T_α$ (150°C), which is even lower than its melting point (230°C). Other flexible polymers with strong hydrogen bonds such as polyamide do not exhibit a crystalline relaxation. For the iodinated film, a very broad peak likely corresponding to the α-relaxation is observed at 100–130°C, which is lower than the $T_α$ of the untreated film. Such a drop of the $T_α$ by the iodination confirms that iodine ruptures the intermolecular hydrogen bonds in the crystalline region of PVA.

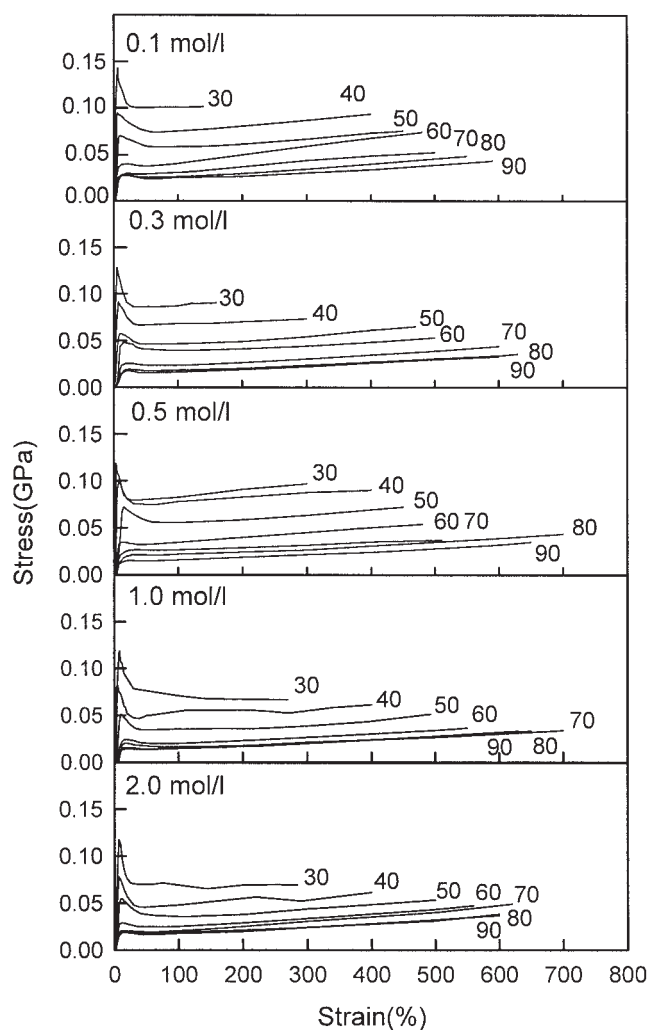
The rapid increase of the tan δ intensity from around 140°C must be associated with crystal melting, not the α-relaxation. This estimation can be supported by two factors: there is no reason for the iodination to enhance the $T_α$, and the temperature is similar to the melting point of the iodinated film (140°C) indicated in the first part of this study.⁷

Drawability

For the temperature range of 30–90°C, we obtained the stress-strain curves via a tensile tester. Figure



(a)



(b)

Figure 2 The stress-strain curves at various temperatures for (a) untreated film or (b) films iodinated with various concentrations of I_2/KI aqueous solutions.

2(a,b) shows the stress-strain curves at 30–90°C for the untreated film and the films iodinated with I_2/KI solutions, respectively.

In the untreated film in Figure 2(a) the yield stress and breaking strain at 30°C are 0.16 GPa and 130%, respectively. With increasing temperature, the yield stress decreased and the breaking strain increased generally. The yield stress and breaking strain at 90°C were 0.04 GPa and 500%, respectively.

For the iodinated films in Figure 2(b), in general, the yield and breaking stress were much lower and the breaking strain was much higher than those of the untreated film. This must be caused by the enhancement of the PVA molecular flexibility that is attributable to the rupture of intermolecular bonding by iodine.

The drawing tests at higher than 90°C could not be done by the tensile tester because of serious degradation of the PVA molecules. Therefore, it was tried in a hand-operated drawer in silicon oil; the MDR was determined, but the stress-strain curve could not obtained.

Figure 3 shows the change in the MDR when increasing the draw temperature. For the untreated film, the drawing of the film was practically impossible (MDR = 1.2–1.5) up to 50°C, but the MDR increased rapidly to 4 at 60°C and then increased steadily with increasing draw temperature.

For the iodinated films, generally the MDRs were higher than that of the untreated film and increased with the concentration of I_2/KI . However, in the case of 2.0 mol/L, the MDR at above 80°C was the lowest of all instead, which was likely due to the degradation of PVA molecules by a large quantity of iodine in the films. It is known that iodine acts as an oxidizer to accelerate degradation of polymer molecules.⁹ With

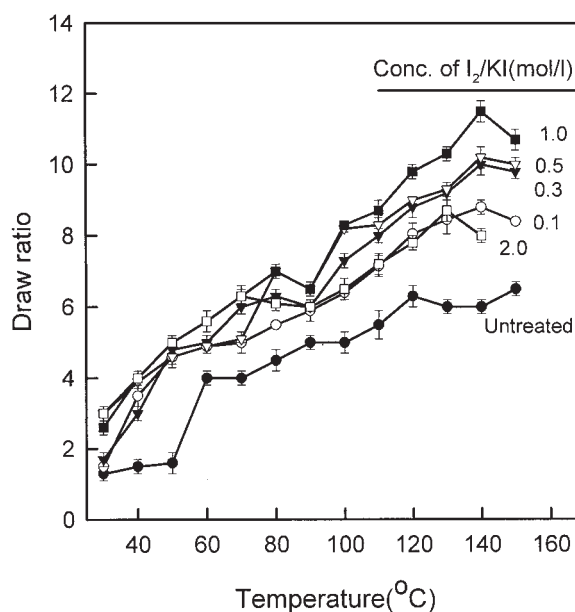


Figure 3 The change in the maximum draw ratio of iodinated PVA films with the draw temperature.

TABLE I
Maximum Draw Ratio of Films Iodinated with Aqueous Solution of Each Concentration of I₂/KI and Temperature at Which Obtained

| Concn of I ₂ /KI (mol/L) | Maximum draw ratio | Temperature (°C) |
|-------------------------------------|--------------------|------------------|
| Untreated | 6.5 (8.0) | 150 (180) |
| 0.1 | 8.0 | 140 |
| 0.3 | 9.0 | 140 |
| 0.5 | 10.0 | 140 |
| 1.0 | 11.0 | 140 |
| 2.0 | 8.3 | 130 |

increasing temperature, the MDR was generally increased. However, the MDRs were diminished instead. This was probably because of the molecular degradation by the action of iodine at temperatures close to the highest temperature in each temperature range of 30–90 and 100–150°C, which was related to the drawing apparatus of the tensile tester and hand-operated drawer, respectively. The beginning temperatures of the diminishing of MDRs achieved by the hand-operated drawer were higher than those by the tensile tester, because during the drawing by the hand-operated drawer the film was protected from the exclusive air by silicon oil. Furthermore, the degradation of PVA molecules by the action of iodine can be supported by another result: the beginning temperature of the diminishing of the MDR was decreased when increasing the concentration of I₂/KI, namely, the quantity of iodine in the films.

Table I shows the MDRs of the films iodinated with the aqueous solution of each concentration of I₂/KI and the temperature at which it was obtained. The MDRs of the iodinated films increased with the concentration of I₂/KI except at 2.0 mol/L of I₂/KI. According to the results of a separate test, the MDR of untreated PVA film was 8 at 180°C. It was then concluded that the drawability of the PVA film was improved; that is, the MDR was increased and/or its achievable temperature was decreased by the iodination.

Structure of drawn films after deiodination

If a drawing is carried out effectively, increasing the draw ratio enhances the orientation and the initial modulus proportionally, which is well known. It was confirmed that our drawing was effective by the results of a special experiment (Table II) in which the initial modulus of the drawn films iodinated with 1.0 mol/L I₂/KI solution after deiodination was increased with the draw ratio. Therefore, the structure, such as the crystallinity and orientation, and the initial modulus of the films drawn to the MDR as indicated in Table I were examined.

TABLE II
Draw Ratio and Initial Modulus of PVA Films Obtained Through Iodination with 1.0 mol/L I₂/KI Solution, Drawing, and Deiodination

| Draw ratio | Initial modulus (GPa) |
|------------|-----------------------|
| 0 | 1.7 |
| 4 | 2.7 |
| 6 | 3.8 |
| 8 | 4.9 |
| 11 | 10.7 |

Figure 4 shows the X-ray diffraction scans of the iodinated films drawn to the MDR. Generally, the diffraction peaks became clearer and their intensity was higher than that of the undrawn film.

The first part of this study⁷ for the undrawn iodinated films showed that the films iodinated with lower (0.1–0.5 mol/L) and higher (1.0–2.0 mol/L) concentration I₂/KI solutions had X-ray diffraction peaks at $2\theta = 6.5, 13,$ and 20.5° , characteristic of the intercalation model,¹⁰ and at $2\theta = 7.5, 14.5, 21.8,$ and 28° , characteristic of the substitution model,¹⁰ respectively. However, in this experiment for the drawn films only the film iodinated with 0.1 mol/L I₂/KI solution indicated the X-ray diffraction characteristic was likely associated with the intercalation model and the others with the substitution model. This shows that the drawing transformed the intercalation model into the substitution model for the films iodinated with 0.3 and 0.5 mol/L I₂/KI solutions.

Figure 5 shows the X-ray diffraction scans of the films drawn to the MDR and deiodinated. All the films

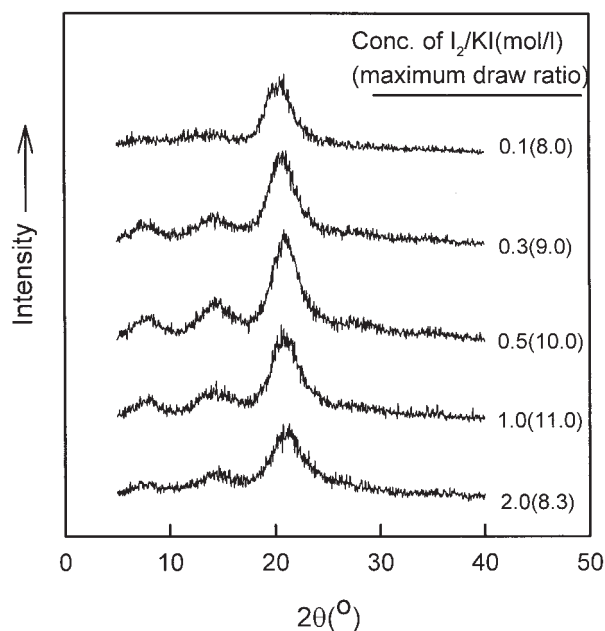


Figure 4 The X-ray diffraction scans of iodinated PVA films drawn to a maximum draw ratio.

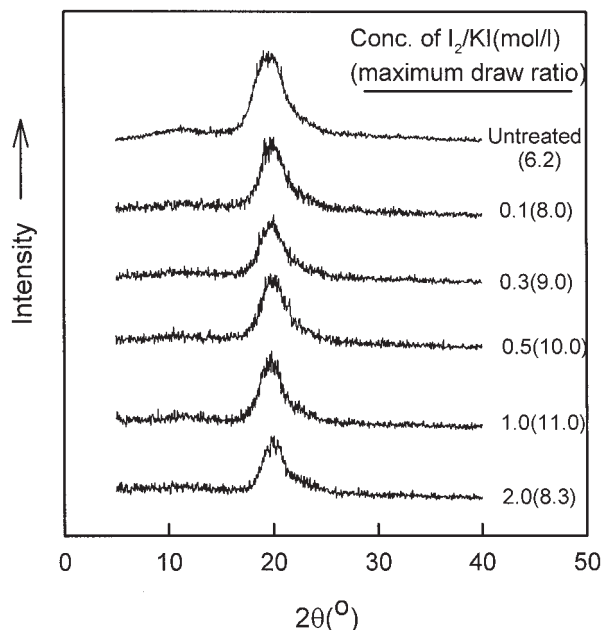


Figure 5 The X-ray diffraction scans of PVA films obtained by deiodination of iodinated PVA films drawn to the maximum draw ratio.

indicated the diffraction peaks as being characteristic of the original crystalline lattice of the PVA, which means that the proper crystalline structure of the PVA was restored through the deiodination, irrespective of the crystalline structure in the iodinated state.

Table III shows the DSC thermograms and thermal characteristics from them for the films drawn to the MDR and deiodinated, respectively. Generally, the greater the MDR was, the higher the heat of fusion (ΔH) and the degree of crystallinity were and the lower the melting temperature (T_m) was. Such a decrease of the T_m in spite of increasing the crystallinity may be caused by the fact that the extended chain crystals were mainly improved by the drawing. As is well known, the T_m of the extended chain crystal is lower than that of the folded chain crystal.

TABLE III
 ΔH , Degree of Crystallinity, and Melting Temperature from DSC Thermograms for Films Drawn to Maximum Draw Ratio and Deiodinated

| Concn of I ₂ /KI (mol/L) (max. draw ratio) | ΔH (J/g) | Degree of crystallinity (%) | T_m (°C) |
|---|------------------|-----------------------------|------------|
| Untreated (6.2) | 52.74 | 37.55 | 235.60 |
| 0.1 (8.0) | 58.83 | 37.94 | 231.44 |
| 0.3 (9.0) | 64.87 | 41.53 | 229.29 |
| 0.5 (10.0) | 75.56 | 47.73 | 230.43 |
| 1.0 (11.0) | 77.89 | 49.87 | 228.88 |
| 2.0 (8.3) | 63.29 | 40.52 | 225.56 |

TABLE IV
 Δn and Initial Modulus for Films Drawn to Maximum Draw Ratio and Deiodinated

| Concn of I ₂ /KI (mol/L) (max. draw ratio) | Δn ($\times 10^{-3}$) | Initial modulus (GPa) |
|---|---------------------------------|-----------------------|
| Untreated (6.2) | 33.6 | 5.5 |
| 0.1 (8.0) | 37.0 | 6.5 |
| 0.3 (9.0) | 37.2 | 6.6 |
| 0.5 (10.0) | 37.8 | 8.2 |
| 1.0 (11.0) | 38.8 | 10.7 |
| 2.0 (8.3) | 35.0 | 7.3 |

Table IV show the birefringence (Δn), and initial modulus of the films drawn to the MDR and deiodinated. The greater the MDR was, the greater the Δn and initial modulus were.

All the characteristics of the films indicated in Tables III and IV seem to be dependent mainly upon the MDR rather than the concentration of I₂/KI. This is supported by Figure 6, which indicates a generally proportional relationship between the characteristics and the MDR.

CONCLUSIONS

To investigate the drawability of iodinated PVA film, the films iodinated with aqueous solutions of I₂/KI with various concentrations were drawn at 30–150°C. The structure of the films drawn to the MDR and deiodinated was determined.

The improvement of the drawability for PVA film by iodination was ascertained by the increased breaking strain and the decreased yield stress on the stress-strain curves when increasing the I₂/KI concentration of the aqueous solutions used in the iodination. The

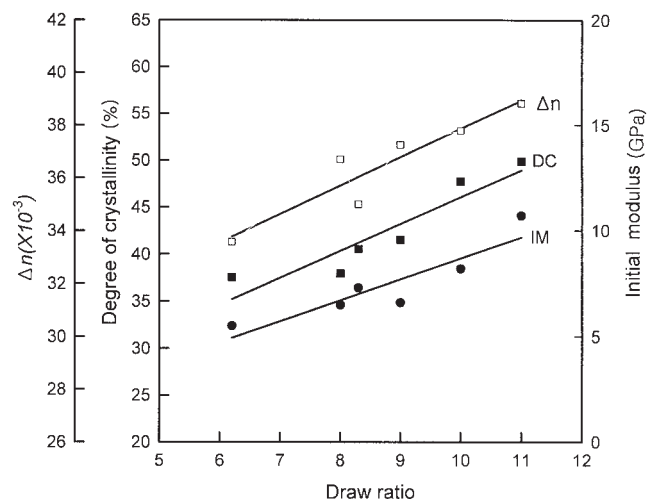


Figure 6 The degree of crystallinity, initial modulus, and Δn of PVA films obtained by deiodination of iodinated PVA films drawn to the maximum draw ratio.

MDR was generally increased with the draw temperature and concentration of I₂/KI, which was probably due to the molecular degradation by the action of iodine as an oxidizer. The improvement of drawability must be caused by the increase of the molecular mobility by iodine. This was supported by the results of the MDR that the thermal transition temperatures of the glass transition, crystalline relaxation, and crystalline melting of the iodinated film were lower than those of the pure film.

The variation of the structure of the films drawn and deiodinated seems to be dependent mainly upon the MDR rather than the concentration of I₂/KI. When increasing the MDR, the degree of crystallinity, birefringence, and initial modulus were increased but the melting temperature was decreased.

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