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Tensile drawing of ethylene/vinyl-alcohol copolymers: 4. Influence of iodine treatment

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Abstract

The effect of iodine treatment on the uniaxial tensile drawing of an ethylene/vinyl-alcohol copolymer containing 44 mol% of ethylene units is studied as a function of draw temperature and iodine concentration. Drawing, between 60 and 100°C, of films soaked in a 0.125 M iodine solution involves complexation of the amorphous phase as judged from X-ray diffraction. The monoclinic crystalline phase turns into the mesomorphic form. Drawing films soaked in a 0.5 M solution brings about complexation of the crystalline phase in addition to the amorphous phase. Miyasaka's model of substitution solid solution is assumed for the crystalline complex. It is suggested in addition that the mesomorphic form is a host structure for the complex. Drawing above 100°C involves segregation of molecular iodine accompanied by disruption of both the crystalline complex and the pure copolymer crystal. It is suggested that the polyiodides dissociate into molecular iodine which partly separates and crystallizes into pure domains and partly dissolves into the polymer crystals and breaks them down. Biaxial drawing of films soaked in 0.5 M solution has been carried out successfully at 90°C. Soaking into sodium thiosulfate solution removes iodine and regenerates a pure copolymer film in a biaxially oriented state. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ethylene/vinyl-alcohol copolymer; Polyiodine complex; X-ray diffraction

1. Introduction

Poly(vinyl alcohol) (PVOH) and ethylene/vinyl-alcohol copolymers (EVOH) are semicrystalline polymers with excellent gas-barrier properties. They can develop high plastic draw ratios upon uniaxial extension but display very poor ability for biaxial drawing because of a high propensity for fibrillation. This is a strong handicap for these materials, which have great potential for food packaging applications [1,2].

Following the gel-drawing technique established for processing polyethylene into high-strength fibres, uniaxial drawing of PVOH has been improved [3,4]. On the other hand, endeavours have been made to improve biaxial orientation by means of blending with incompatible polymers which exibit good aptitude for biaxial orientation [5]. Blending with compatible polymers capable of forming intermolecular hydrogen bonds with the hydroxyl groups of the vinyl alcohol units has also been a promising route towards improving biaxial drawability [6].

Water and electron donor compounds are known to bring about a plasticization effect in polymers having strong molecular interactions such as polyamides (PA), owing to the complexation phenomenon that reduces the intermolecular hydrogen bonding. Among the agents that can form molecular complexes with PA, iodine has received particular attention owing to its ability to bring about crystalline phase changes [7,8]. The structure of the crystalline complexes involving I_3^- and I_5^- polyiodines has been shown to disrupt the anisotropy of the original sheet-like structure [9,10]. Porter et al. [11,12] have shown that iodine treatment in 0.1–0.2 M solutions destroys the crystallinity of PA6, which becomes rubbery above 55°C. This phenomenon affords reduced yield stress and improved drawability. For higher concentrations true crystal complexation occurs, but this results in reduced drawability. PVOH complexation with iodine has also been extensively studied with special effort to characterize the nature and structure of the complexes [13–17]. Drawability is improved with increasing iodine concentration of the soaking solution in the range 5×10^{-4}–5×10^{-1} M.

It has been shown, for both PA6 and PVOH, that iodine complexation of the crystalline phase is more efficient for drawn specimens, irrespective of whether iodization is

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carried out after or prior to drawing [8,9,16,17]. Chain alignment seems to favour the association of the linear polyiodides parallel to the oriented chains, both in the amorphous phase and in the crystal.

The present study reports on the effect of iodine treatment on the mechanical and structural properties of a vinyl alcohol-rich EVOH copolymer, with the aim of improving the biaxial orientation process.

2. Experimental

The ethylene/vinyl-alcohol copolymer under investigation, Soarnol A from Nippon Gohsei, has an ethylene molar fraction of 0.44 and a crystal weight fraction of 0.60. Additional characteristics are reported in the first paper of this series [18]. The material was cast at 210°C from a T-die extruder into films about 200 μm thick and cooled on a chill roll at 90°C.

Film pieces were soaked for 24 h at room temperature in aqueous solutions of iodine and potassium iodide having a molar ratio $I_2/KI = 2$. Two iodine concentrations of 0.125 and 0.5 M were investigated. The films were subsequently allowed to dry freely in air at a relative humidity of about 50%, for 24 h.

The drawing experiments were performed on an Instron tensile testing machine equipped with an air-pulsed oven regulated at ± 1°C. Local draw ratios, $\lambda = l/l_0$, were directly measured on the samples from the spacing of ink marks printed 1.5 mm apart prior to drawing. The macroscopic draw ratio, $\Lambda = L/L_0$, is defined as the change of the sample gauge length. Dumbbell samples with gauge dimensions 24 mm × 5 mm were cut from the iodized films and drawn at a crosshead speed of 50 mm min^{-1} in the temperature range 60–130°C. The yield stress, σ_Y, is given by the ratio of the draw force to the actual cross-section of the sample at yield point. The maximum deviation of the data about the average σ_Y value at every draw temperature does not exceed 8%.

Two uniodized samples were drawn at 80°C and 130°C and annealed with fixed ends for 3 min at the draw temperature before unloading, in order to relax internal stresses without losing chain orientation. Both samples were subsequently soaked in a 0.5 M solution for comparison with the samples drawn after iodization.

Biaxial drawing experiments have been carried out on a Cellier tenter frame consisting of four pantographs each equipped with ten pneumatic grips. The two movable pantographs were driven by hydraulic jacks. Square specimens of 110 mm gauge width were stretched at 90°C at a constant jack speed of 600 mm min^{-1}.

The thermal properties were investigated by means of differential scanning calorimetry (DSC), using a Perkin–Elmer DSC-7-Delta apparatus. The heating rate was 10°C min^{-1} and the sample weight was in the range 5–10 mg. The melting of indium and zinc samples was used to calibrate temperature and heat flow scales at the same heating rate.

Wide-angle X-ray scattering (WAXS) patterns were recorded on flat films with the incident beam normal to the sample surface, using the Ni-filtered Cu–Kα radiation of a Philips tube operated at 40 kV and 20 mA. The two pinhole collimators of 0.5 mm diameter were 50 mm apart, the sample-to-film distance being 80 mm. Due to the high scattering power of iodine, X-ray recordings were four times longer for the iodized samples than for the uniodized ones.

Iodine removal treatment for regenerating the pure copolymer was carried out by soaking drawn samples in a 0.5 M sodium thiosulfate solution at 70°C for a few tens of seconds. In contrast to polyamides, room temperature treatment is inoperative over a period of several days.

3. Results and discussion

3.1. Yielding behaviour

Fig. 1 shows the yield stress, σ_Y, versus temperature for films soaked in 0.125 M and 0.5 M iodine solutions. For the case I_2–0.125 M, the σ_Y data are lower than those of the original film at 50% relative humidity, in the temperature range $20°C < T < T_g$, but the two sets of data fall on the same curve for $T > T_g$. This is not due to the sorbed water since the iodized film has also been held at 50% RH for 24 h before drawing. This effect is, however, similar to that observed in the case of water-saturated material [18]. It seems that iodine plays the same plasticizing effect as water in the amorphous phase, the main difference being that iodine remains deeply connected to the amorphous chains. The reason is that the I_3^- and I_5^- polyiodides that form in the I_2/KI solution have a very low vapour pressure

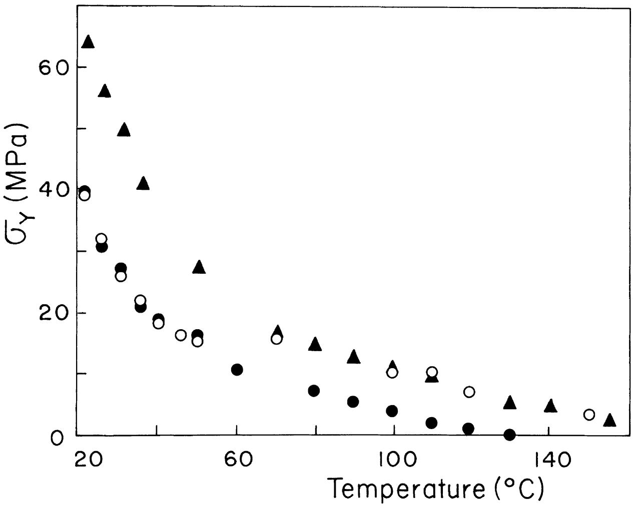


Fig. 1. Yield stress versus draw temperature for samples soaked in iodine solutions of concentration (○) 0.125 M and (●) 0.5 M compared to (▲) pure copolymer at 50% relative humidity.

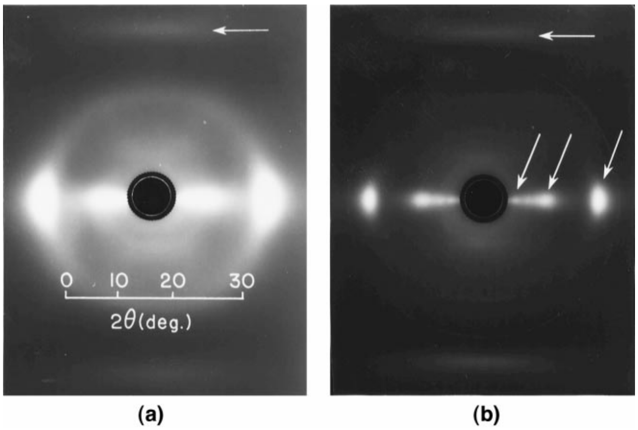
in conjunction with a strong affinity toward the hydroxyl groups that prevent them from escaping.

For the case I_2–0.5 M, σ_Y is depressed over the whole temperature domain studied. It is obvious that, as in the amorphous phase, yielding in the crystalline structure is also affected by iodine.

The WAXS pattern of the film soaked in the 0.5 M iodine solution shows no significant modification of the monoclinic crystalline phase prior to drawing. This indicates therefore that the reduced σ_Y, in the temperature range above T_g, is due to a structural change in the crystal that occurs during plastic deformation.

3.2. Structural behaviour

The copolymer film soaked in I_2–0.125 M displays the same deep brown colour as the I_2/KI solution because of direct sorption of molecular and ionic iodine species formed in the solution. The blue iridescence that appears upon drawing up to $\lambda \approx 6$ at 60°C suggests the build-up of the VOH–I_5^- complex species already characterized in oriented PVOH [16,17]. The WAXS pattern of Fig. 2(a) shows a meridian reflection at $2\theta \approx 29°$ that relates to complexation between some chains of the amorphous phase and the I_5^- polyiodides, according to Choi and Miyasaka [14,16]. Chain orientation compels an arrangement of the linear polyiodide parallel to the average chain axis and thus improves complexation. The corresponding spacing of 0.31 nm is just about the distance between the iodine atoms in an I_5^- polyiodide. The equatorial streak close to the centre of the pattern of Fig. 2(a), which does not exist in pure EVOH, confirms the presence of species highly aligned parallel to the draw direction and having a high scattering power, i.e. the I_5^- polyiodides. The radial broadness of this streak indicates that no periodic arrangement of the polyiodides occurs in the transverse direction due to the lack of crystallographic register between the oriented amorphous chains. The strong equatorial reflection at $2\theta \approx 20.5°$ relates to the strain-induced transformation of the crystalline phase from monoclinic to mesomorphic. Indeed, as previously reported for pure EVOH drawn below 110°C [19], the (110) and (200) reflections of the monoclinic crystal, which appear at about $2\theta = 20.0°$ and 21.5°, turn into a unique and strongly broadened reflection related to the mesomorphic state with roughly hexagonal symmetry.



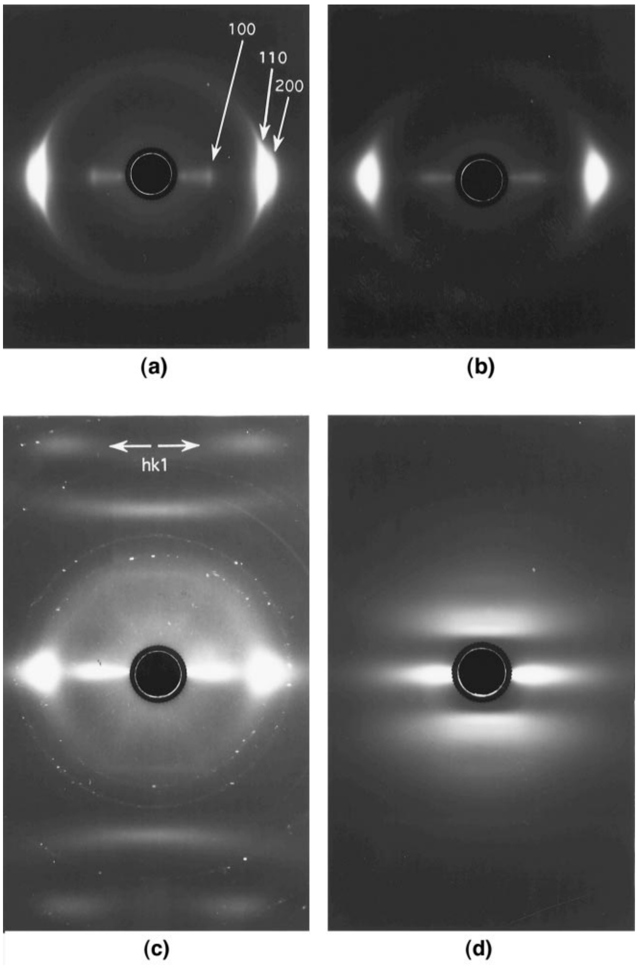
(a) (b)

Fig. 2. WAXS patterns of films soaked in two iodine solutions of different concentrations and drawn to $\lambda = 6$ at 60°C (same exposure time): (a) I_2–0.125 M and (b) I_2–0.5 M.

In the case of the copolymer film soaked in I_2–0.5 M and subsequently drawn at 60°C, the purple-red iridescence that develops in addition to the initial brown colour reveals the formation of the VOH–I_3^- complex species that mainly exist in the crystalline phase as judged from the studies of iodized PVOH reported by Miyasaka [16] and Takamiya et al. [17]. The equatorial scattering of the WAXS pattern of Fig. 2(b) relates to a large level of intrusion of polyiodides highly parallel to the draw direction. Moreover, the equatorial reflections that appear at $2\theta \approx 6.5°$ and 13° within this broad scattering are characteristic of the formation of the above-mentioned crystalline complex [16,17]. It is worth noting that the VOH–I_3^- crystalline complex is able to develop in drawn PVOH for iodine solutions of much lower concentration (0.02 M for instance), thanks to the greater amount of hydroxyl groups compared to the present copolymer. It is also to be noted that, after soaking an oriented PVOH film in a solution of concentration 0.4 M, the strong equatorial reflection characteristic of the pure PVOH crystal at about $2\theta = 20.5°$ is almost extinguished, indicating that nearly all the crystalline phase is intruded by the polyiodides and transformed into complex crystals [14,16].

The meridian reflection that appears at $2\theta \approx 28°$ in Fig. 2(b) is stronger than in the previous case of I_2–0.125 M (Fig. 2(a)), indicating an increased amount of complexed polyiodides owing to the larger iodine concentration. The slight shift by about 1° to lower Bragg angles is an indication that the predominent diffracting species is the crystalline VOH–I_3^- complex, after Choi and Miyasaka [15]. The main equatorial reflection at $2\theta \approx 21°$ is slightly shifted by about 0.5° to higher Bragg angles with respect to the case of I_2–0.125 M and to the pure copolymer. A similar effect has been reported for PVOH [13,16]. This reveals that the VOH–I_3^- complex disturbs the arrangement of the chains in the crystalline phase. One may thus suggest either a two-phase system of complex crystals of definite composition in thermodynamic equilibrium with a mesomorphic structure or a single-phase system consisting of a substitution solid solution of I_3^- polyiodides within the mesomorphic structure. The previously mentioned intensity decrease of the $2\theta \approx 21°$ equatorial reflection with increasing iodine concentration that has been observed for oriented PVOH [13,16], in parallel with the improvement of the two inner equatorial reflections at $2\theta \approx 6.5°$ and 13°, is evidence that the former reflection is originating from a remaining mesomorphic structure rather than from complex crystals. This supports the first proposal. The complex crystals may themselves be either a substitution or an intercalation solid solution. According to Miyasaka, in the case of PVOH, the substitution solid solution is more probable. Besides, the broadness of the characteristic reflections of the complex (see Fig. 23 in Ref. [16]) relates to a strongly disordered structure, which argues for a non-stoichiometric compound. The low thermal stability of the VOH–I_3^- crystalline complex indicates that complexation does not result from a large free energy gain with respect to the pure monoclinic crystal. In contrast, the fact that crystal complexation is particularly efficient via drawing iodized copolymer suggests that intrusion of the crystalline phase by the polyiodides proceeds through the strain-induced phase change mentioned above. Indeed, the mesomorphic form results from the disruption of the sheet-like structure of the initial monoclinic form which otherwise plays a diffusion-stopping part. In these circumstances, the mesomorphic phase behaves like a host structure for the complex. This is quite different from the case of binary systems such as polyethylene–urea [20] and poly(ethylene oxide)–(alkali metal thiocyanate) [21] which build up definite compounds of stoichiometric composition with well resolved WAXS patterns and higher thermal stability than the pure polymer component.

An additional piece of evidence for the determining role of the mesomorphic form in the crystalline complexation process comes from the study of iodine treatment of previously drawn copolymer samples. Drawing at 130°C up to $\lambda = 6$ preserves the stable monoclinic structure, whereas drawing at 80°C induces a mesomorphic state [19], as shown on the WAXS patterns of Fig. 3(a) and (b). After soaking in a 0.5 M iodine solution, the sample with the monoclinic structure does not display the characteristic reflections of the VOH–I_3^- crystalline complex as shown on the pattern of Fig. 3(c), in spite of the high molecular orientation. The three dotted Debye–Scherrer rings (at $2\theta \approx$ 21°, 25° and 36°) relate to the presence of I_2 and KI single crystals due to oversaturation of both compounds in the amorphous phase after drying. The appearance of reflexions belonging to the (hk1) first-order strata in the pattern of Fig. 3c supports the preservation of a crystalline order of pure EVOH nature [19]. In contrast, Fig. 3(d) shows a striking modification of organization in the sample having the mesomorphic structure prior to iodization: the characteristic equatorial reflection of the oriented mesomorphic structure [19] at $2\theta = 20.5$°C has thoroughly vanished together with the diffuse (hk1) reflections of the first-order strata [19]. In contrast, several meridian streaks have appeared. The main one, at $2\theta = 8.5°$, corresponds to a spacing of 1.0 nm, which is about the length of an I_3^- polyiodide. It has already been observed in the case of heavily iodized PVOH [15,16] and ascribed to a linear superlattice of I_3^- species in the crystalline phase. It is worth noting that a similar meridian diffraction with very close Bragg spacing has also been reported by Kawaguchi [10] in the case of iodized PA6, for which a one-dimensional superlattice arrangement of I_3^- polyiodides and molecular iodine has been proposed. The strong and very broad equatorial scattering of Fig. 3(d) without the discrete characteristic reflections of the crystalline complex at $2\theta \approx$ 6.5° and 13° (see Fig. 2(b)) is indicative of a great disorder in the lateral packing of EVOH chains and I_3^- polyiodides. In addition, the absence of the meridian reflection at $2\theta \approx 28°$ suggests that the polyiodides are in the kinked conformation rather than the linear one. These findings support Kawaguchi's conclusion that the superlattice is incommensurate with the crystalline complex, in the case of iodized PA6 [10].



(a) (b) (c) (d)

Fig. 3. WAXS patterns of samples drawn up to $\lambda = 6$ at (a) 130°C and (b) 80°C, then soaked in I_2–0.5 M solution after drawing at (c) 130°C and (d) 80°C.

The main pieces of information that come out from the above comparison of the two kinds of samples iodized after or prior to drawing, in relation to the draw temperature, are the following: (1) the sheet-like structure of the monoclinic form is a barrier to polyiodide intrusion in the crystalline phase; and (2) molecular orientation is not the determining factor for complexation. Consequently, it is strongly suggested that crystalline disordering with reduction of hydrogen bonding interactions is required for polyiodide intrusion and complexation of the crystal.

If chain orientation was the controlling parameter, complexation should readily occur in isotropic materials since

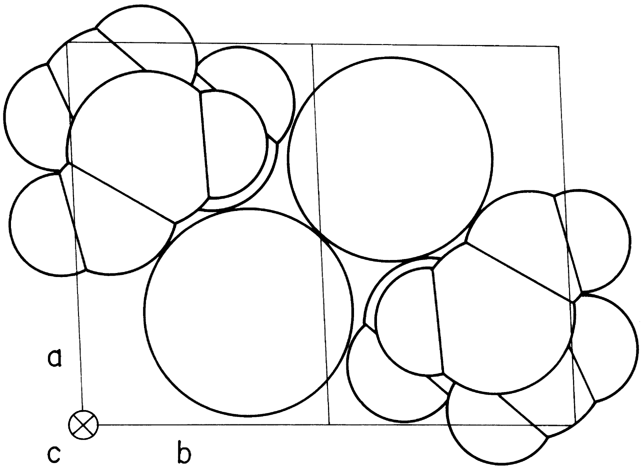


Fig. 4. Substitution model for the EVOH–polyiodide crystalline complex in projection on the basal plane of the monoclinic unit cell (reproduced from Ref. [13] with permission of the Society of Polymer Science of Japan).

the chains in the crystalline lamellae are perfectly aligned parallel to each other and the lamella thickness, which is about 10 nm [19], is large enough to accommodate linear I_3^- polyiodides in extended conformation.

The fact that phase change from monoclinic to mesomorphic is completed for $\lambda \geq 3$, as shown in the first paper of this series [18], seems contradictory to the observation of a strong influence of complexation on the deformation mechanisms at the yield point. An explanation is that every elementary event of plasticity, i.e. the dislocation-like defects in the crystals, locally distorts the sheet-like structure, thus allowing the occurrence of an elementary complexation event. The complexation process of the crystalline phase is expected to occur gradually by accumulation of such elementary events.

A molecular model of the substitution crystalline complex is sketched in Fig. 4 according to that proposed by Miyasaka et al. [13,16] for PVOH–I_3^-. It shows the disruption of the sheet-like structure of the original monoclinic crystal made of hydrogen-bonded chains along (100) planes [22,23] owing to the intrusion of the polyiodides within the sheets. This may account perfectly for the improved plasticity of the copolymer film soaked in I_2–0.5 M above the glass transition temperature, compared to the pure copolymer.

3.3. Thermal behaviour

Drawing of the iodized copolymer at temperatures above 80°C is accompanied by significant release of molecular iodine as judged from the characteristic smell and colour of the vapour filling the oven at the end of the experiment. Fig. 5 shows the DSC heating curve of a film soaked in I_2–0.5 M and drawn at 100°C up to $\lambda = 7.5$ compared to that of the same undrawn sample. The endotherm at about 110°C (Fig. 5(a)) may be ascribed to the crystalline complex that is induced by drawing. This assumption is borrowed from Lee and Porter [12] who reported true melting for the PA–I_3^- complex. The exotherm in the range 130–160°C may be the result of polyiodide destruction. The WAXS pattern of the drawn sample reported in Fig. 6(a) shows the three dotted Debye–Scherrer rings that are characteristic of very fine crystals of pure I_2 and KI. As already observed in Fig. 3(c), these do not exist in the case of drawing at 80°C. This is relevant to partial decomposition of the polyiodides at 100°C. In addition, the DSC heating curve of the undrawn iodized sample (Fig. 5(b)) displays a very broad exotherm at

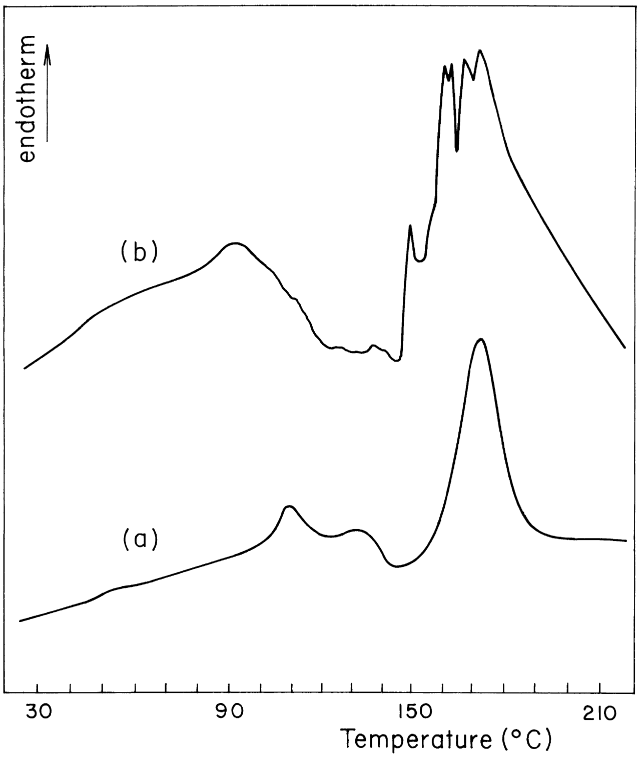


Fig. 5. DSC heating curves of samples soaked in I_2–0.5 M solution: (a) drawn to $\lambda = 7.5$ at 100°C and (b) undrawn.

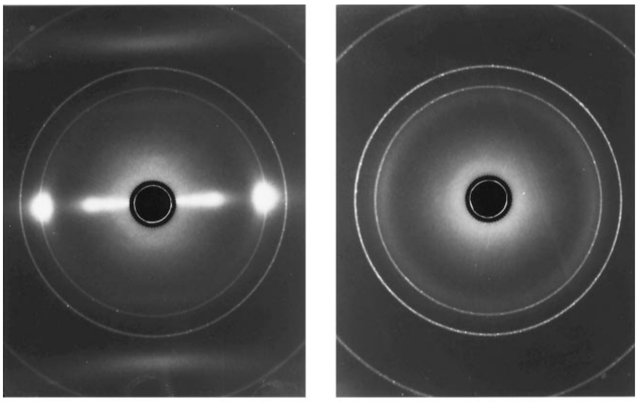

(a) (b)

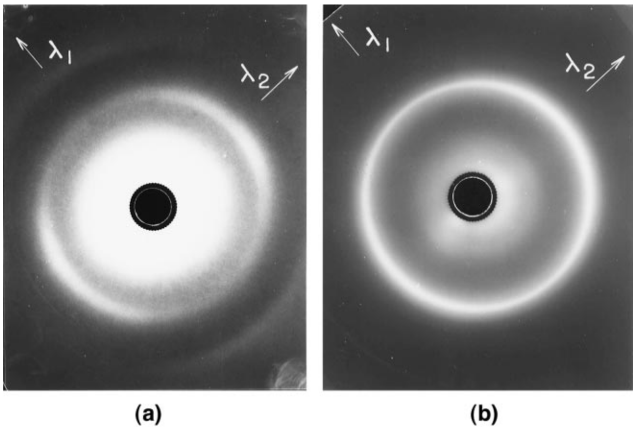
Fig. 6. WAXS patterns of samples soaked in I_2–0.5 M solution and drawn to $\lambda = 7.5$ at (a) 100°C and (b) 130°C.

100–160°C that is perfectly consistent with the recrystallization of iodine and potassium iodide from the decomposed polyiodides. The erratic endotherm that subsequently occurs in the range 160–190°C may therefore result from the vaporisation of iodine as its vapour pressure increases drastically. This suggests that the rather sharp endothermic peak that appears in the same temperature range for the drawn sample (Fig. 5(a)) also results from the vaporization of the molecular iodine previously segregated during the hot drawing step. Indeed, despite the proximity of this endotherm to the melting peak of pure copolymer [18], it cannot be attributed to this because of its slightly higher temperature. In addition, the WAXS pattern from an iodized sample drawn at 130°C (Fig. 6(b)) shows no evidence of any pure copolymer or complexed crystal content, favouring the absence of any melting peak in the DSC trace. The reason may be that segregated iodine that is freed in the crystal after polyiodide decomposition dissolves in it without being able to build up a definite crystalline compound.

It is to be noted that the preservation of the crystalline complex reflection for the draw temperature of 100°C (Fig. 6(a)) is an indication that either the uncomplexed polyiodides or the ones from the amorphous complex species mainly take part in the decomposition process. However, for drawing at 130°C, the crystalline complex is thoroughly destroyed (Fig. 6(b)). This is quite different from the behaviour of the PA–I_3^- crystalline complex, which is surprisingly thermally stable up to about 300°C [12].

3.4. Biaxial drawing

Fig. 7(a) shows the WAXS pattern of a copolymer film soaked in I_2–0.5 M and biaxially drawn at 90°C to $\lambda_1 \times \lambda_2 = 3 \times 2.5$. The slight anisotropy of the scattering is due to the unbalanced draw ratios. The broad diffraction at about $2\theta = 21°$ in the λ_2 direction (i.e. on the equator of the main draw axis λ_1) relates to the disordered copolymer structure oriented parallel to the main draw axis. The inner diffuse halo looking roughly isotropic is due to the scattering, normal to the axis of the I_3^- and I_5^- linear polyiodides, of the complexed and uncomplexed species. The characteristic reflections from the VOH–I_3^- crystalline complex are not resolved. The outer scattering at about $2\theta \approx 28$–$29°$ in the direction λ_1 (i.e. in the meridian position with respect to the main draw axis) is that arising from the iodine atom arrangement along the polyiodide axis, for both amorphous and crystalline complexes.



(a) (b)

Fig. 7. WAXS pattern of (a) a sample soaked in I_2–0.5 M solution and simultaneously biaxially oriented to $\lambda_1 \times \lambda_2 = 3 \times 2.5$ at 90°C, then (b) treated in a 0.5 M sodium thiosulfate solution.

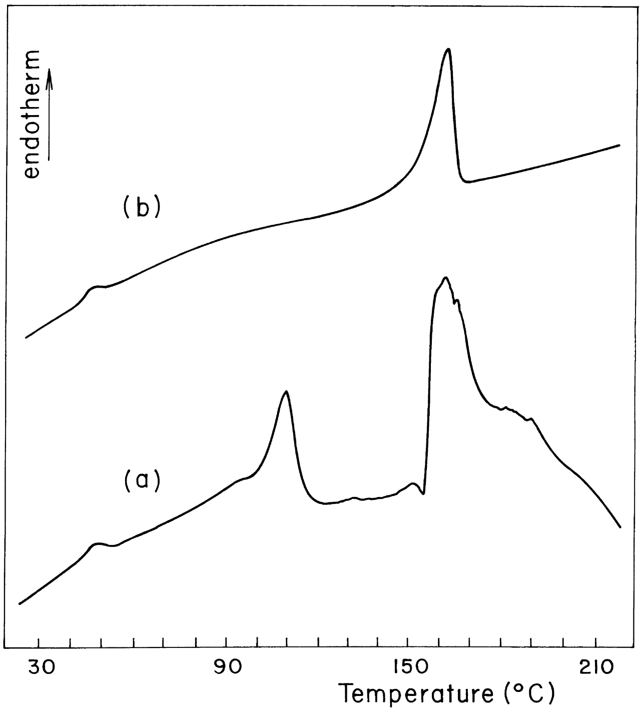


Fig. 8. DSC heating curves of the same sample as in Fig. 7: (a) soaked in I_2–0.5 M solution and simultaneously biaxially oriented to $\lambda_1 \times \lambda_2 = 3 \times 2.5$ at 90°C, then (b) treated in a 0.5 M sodium thiosulfate solution.

The same sample treated in a sodium thiosulfate solution at 70°C slightly shrinks to about $\lambda_1 \times \lambda_2 = 2.5 \times 2.2$ due to relaxation of the amorphous chains. However, the transparency of the sample gives evidence of complete iodine removal. The corresponding WAXS pattern of Fig. 7(b) shows the two main reflections of monoclinic EVOH, indicating recovery of the stable crystalline phase in the copolymer. These reflections are not as sharp as in the sample drawn at 130°C (Fig. 3(a)), due to either a strong disorder in the monoclinic crystals or a mesomorphous contribution. Despite the fact that the mesomorphic form is a host structure for the crystalline complex, it seems that iodine removal involves enough chain mobility to allow a good deal of crystal reorganization below the temperature of the α mechanical relaxation, which is about 110°C in the pure copolymer [18].

Fig. 8(a) shows the DSC curves of the same sample as in Fig. 7(a), i.e. a copolymer film soaked in I_2–0.5 M and biaxially drawn to $\lambda_1 \times \lambda_2 = 3 \times 2.5$. This curve is similar to that of Fig. 5(a) for the uniaxially drawn sample. First there occurs the endothermic peak at 110°C due to the melting of the crystalline complex, followed by an exotherm due to decomposition of the complex species with concomitant recrystallization of pure I_2 and KI. Finally, iodine vaporization takes place in the 160–200°C endotherm.

The DSC heating curve of the biaxially drawn sample treated with sodium thiosulfate at 70°C confirms recovery of the stable crystalline structure of the copolymer, as shown in Fig. 8(b). The unique sharp endotherm at 165°C is indeed indicative of the melting of pure monoclinic EVOH. The absence of an exotherm prior to the melting peak testifies to only a minor contribution of crystals in the mesomorphic form, if any.

There is thus clear evidence of a strain-induced complexation of both the crystalline and amorphous phases by polyiodides, which seems to be a determining factor in the achievement of biaxial drawing. In another connection, we have recently reported on the structural changes brought about during biaxial drawing of the uniodized copolymer [24]. The strain-induced monoclinic-to-mesomorphic modification that occurs in the crystalline phase at temperatures below the mechanical crystalline relaxation has been claimed to play a major part in the ability for biaxial orientation. So, considering the above conclusion that the mesomorphic form is a host structure for the crystalline complex, we suspect iodine intrusion in the crystal to be only an improving factor for the phase change but not the driving force for biaxial drawing efficiency.

4. Conclusion

It is well known that water helps polyiodine intrustion within the crystalline phase of PVOH owing to its swelling effect [16]. In parallel, water sorption considerably increases PVOH and EVOH permeability [25,26]. Thus, the much lower water solubility in EVOH compared to PVOH may be the reason for the lower complexing ability of EVOH at equivalent iodine solution concentration. However, we have shown that the strain-induced phase change of the crystalline phase from monoclinic to mesomorphic plays a determining role in the complexation process at temperatures below 100°C, thanks to its role of host structure for the polyiodides.

The above phase change and the accompanying destruction of the sheet-like structure due to randomization of the H-bonds about the chain axis provide improved ductility to EVOH copolymers and notably allow biaxial orientation [24]. Complexation is strongly suspected to contribute only a secondary part in the drawing behaviour of iodized copolymers by promoting the phase transformation process in the former stage of plastic deformation.

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