Morphology of uniaxial oriented films of poly(butylene terephthalate): 1. Orientation and structural transformation of crystals

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The crystalline morphology of oriented films of poly(butylene terephthalate) (PBTP) was characterized by wide-angle X-ray diffraction and scanning electron microscopy. The PBTP films were drawn to different draw ratios at various drawing temperatures. Transformation of the lamellar spherulites into a microfibrillar structure occurred in the necking region. The microfibrillar structure appeared at the end of the plateau region. Transformation to perfect microfibrillar structure and the subsequent drawing of this structure were observed in the strain hardening region. The orientation of crystals occurred above the yield point and continued rapidly with draw ratio, while the rate of orientation was decreased by drawing the microfibrillar structure. An optimal drawing temperature of about 423 K (which lies between the glass transition and melting temperatures) was found to provide the highest degree of crystalline orientation. In the glass transition region the strong movement of the non-crystalline chain segments influenced the orientation of crystals. The formation of the microfibrillar structure and the orientation of crystals were also disturbed at the drawing temperature near the melting point. Etching of PBTP films allowed the observation of the stacked lamellae oriented more or less perpendicular to the draw direction as well as the microfibrils existing between the stacked lamellae.

(Keywords: poly(butylene terephthalate); orientation; microfibrillar structure; X-ray diffraction; scanning electron microscopy)

INTRODUCTION

In semicrystalline polymers the crystals usually exist as spherulites consisting of lamellae. In general, according to Peterlin's model of plastic deformation of crystalline polymer solids[1–6], extension causes the spherulites and lamellae to gradually transform into a microfibrillar structure consisting of alternating crystalline and non-crystalline regions. A great number of taut tie molecules bridge the non-crystalline layer and connect the crystalline blocks in which folded chains and tie molecules exist[5,7]. This microfibrillar crystalline structure has been demonstrated in studies of oriented polyethylene and polypropylene[1–6,8].

Poly(butylene terephthalate) (PBTP) has been used primarily as an engineering thermoplastic and as a component in certain blends and block copolymers due to its attractive mechanical properties, rapid crystallization rate and good mouldability[9,10].

Many previous investigations[9,11–17] have dealt with the crystalline properties of PBTP. They have focused mainly on the determination of structures of the two crystalline modifications (α- and β-form) as well as the relationship of these modifications with the mechanical properties of PBTP. Generally, the β-form occurs under extension. In our laboratory we studied the oriented structures of both crystalline and non-crystalline regions of PBTP films drawn at various temperatures and draw ratios. In addition we concentrated on gas transport and sorption properties of these oriented films[18–21].

In this paper we describe the morphology and crystal structure of oriented PBTP films by means of both wide angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM) investigations.

EXPERIMENTAL

Materials

The as-received PBTP films used for preparation of all oriented samples were commercial products free of additives (Platilon KF, Atochem Deutschland, Bonn, Germany). The transparent film had a thickness of 0.15 mm. The density of this film was 1.284 g cm^{-3}, as determined by the density gradient column method using an aqueous calcium nitrate solution and factory calibrated density glass beads at 296 K. According to the literature concerning the density of amorphous[22] (1.256 g cm^{-3}) and crystalline[10] (1.396 g cm^{-3}, α-modification) PBTP the mass related crystallinity, X_{cw}^{D}, was 21.7%. A melting temperature of 498 K was obtained by differential thermal analysis using a Mettler TA 2000 thermoanalytic device in the temperature region 223 K–533 K. The scanning rate was 10 K min^{-1}. Al_2O_3 (14.5 mg) was used as reference. The glass transition temperature, T_g, was 319 K, as determined by a dynamic torsional pendulum device (Zwick Torsiomatic 5203) at

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a heating rate of 2 K min^{-1} and an oscillation frequency of 1 Hz.

Sample preparation

Samples were prepared by cutting rectangular strips from the as-received film. Samples were uniaxially drawn using a modified Instron 1026 tensile testing machine. The chamber was lined with insulation and contained heating elements coupled to a power regulator and temperature controller. The clamps were modified to take the film samples, which were closely held at both ends by the crosshead mechanism inside the chamber. The direction of extension was perpendicular to that of the original machine direction of the as-received film. The chamber was heated quickly to the desired drawing temperature and the sample was annealed at this temperature for 30 min, followed by drawing at a crosshead speed of 50 mm min^{-1}. The sample was immediately air-quenched to room temperature and stored under extension load at room temperature for 3 days to complete the stress relaxation. The oriented sample was then removed from the crosshead mechanism and stored for 3 more days. The draw ratio, λ, was determined from parallel ink lines along the transverse direction of the film. The draw ratios reported are actual and not nominal values since they were obtained by following additional ink lines in the central region of the undrawn specimen just before characterization. All samples used for physical characterization were taken from the central sections of the oriented films.

For the samples extended at 373 K the draw ratios were $\lambda = 1, 1.2, 2, 3$ and 4. Samples drawn to $\lambda = 4$ were prepared at drawing temperatures of 298, 323, 373, 423 and 473 K.

WAXD and SEM measurements

The WAXD photographs were taken by a Seifert Iso-Debyeflex 2002 device using filtered CuKα radiation. The exposure time was 20 h for all samples. The evaluation of diffraction intensity distribution for determining the orientation coefficient was made by using a Joyce Loeble microdensitometer type MK III C.

The SEM studies were carried out with a Cambridge Instruments Mark II device. In order to reveal the crystalline morphology, the oriented samples were etched for 15 min with chromosulphuric acid at 298 K before SEM study. The etching removes the non-crystalline sections without modifying the crystals significantly.

RESULTS AND DISCUSSION

Influence of draw ratio

The WAXD pattern (*Figure 1*) of the as-received PBTP film shows a diffuse halo indicating the non-crystalline phase and diffraction rings characterizing the crystalline phase. No orientation is found. The major part of the crystals exist in α-modification, while only a small part of the crystals is present in β-modification[21]. The SEM micrograph of this sample indicates that the crystals possess an isotropic spherulitic structure (*Figure 2*).

Figure 3 shows the WAXD patterns of the PBTP films drawn at 373 K to different draw ratios. The pattern for the sample annealed at 373 K but not drawn ($\lambda = 1$) exhibits much sharper and more intense crystalline reflections. These changes are indicative of both

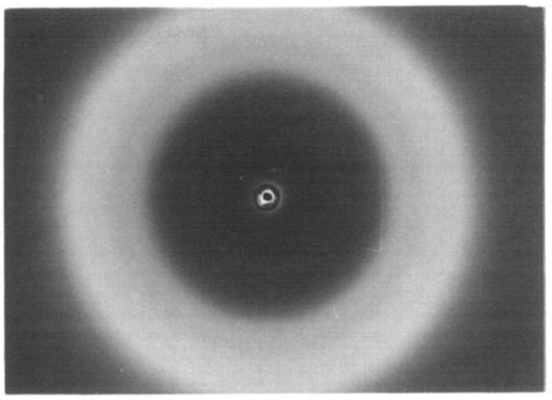

Figure 1 WAXD pattern of as-received PBTP film

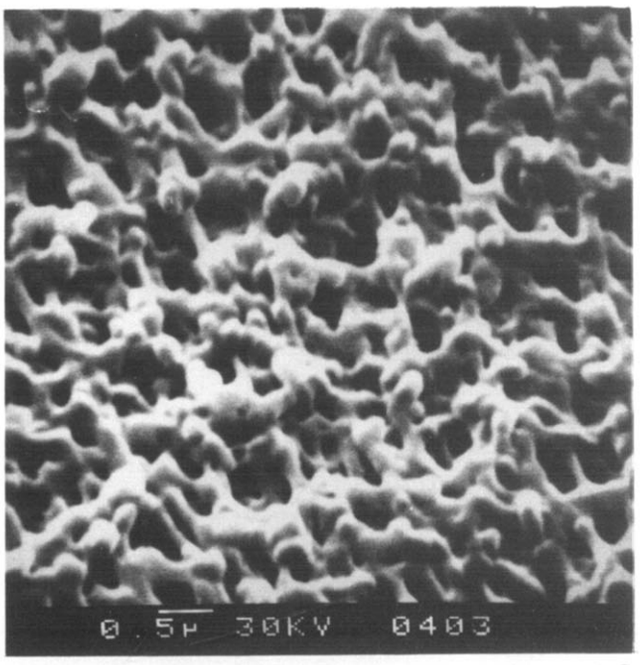

Figure 2 SEM micrograph of as-received PBTP film

increased crystallinity and increased crystallite size. On increasing the draw ratio to $\lambda = 1.2$ the crystals were still unoriented, as the pattern only shows diffraction rings. At $\lambda = 2$, reflection arcs with radial symmetry can be seen. With further drawing the length of the reflection arcs decreases which demonstrates that the degree of orientation of crystals increases on further increasing the draw ratio.

In order to obtain the orientation coefficient, the azimuthal intensity distribution of the reflections was measured photometrically. The orientation coefficients F for 1 0 0, 0 1 0 and 0 0 1 reflections were calculated by the corresponding determination and calculation methods[23]. F_c (0 0 1 reflection) characterizes the orientation of c-axis of 0 0 1 planes along the direction of uniaxial extension, while F_a (1 0 0 reflection) and F_b (0 1 0 reflection) represent the orientation of those axes perpendicular to the direction of extension. In *Figure 4* it can be seen that the orientation coefficients F_a, F_b and F_c do not change until $\lambda = 1.2$, and are equal to zero, indicating that the crystals are unoriented. With increasing draw ratio to $\lambda > 1.2$, F_c increases while F_a

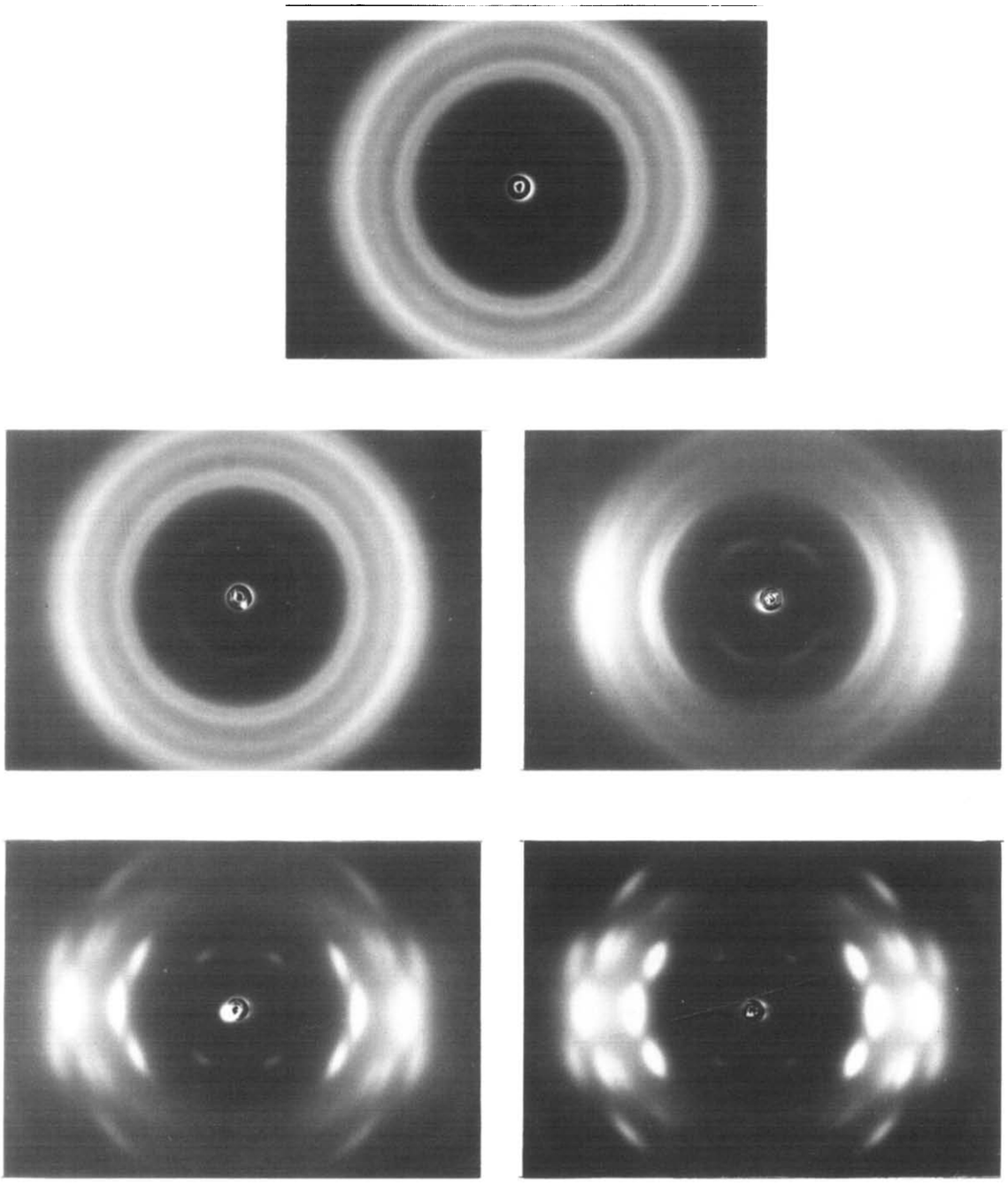

Figure 3 WAXD PBTP films drawn at 373 K to different draw ratios. Arrows indicate the direction of uniaxial extension

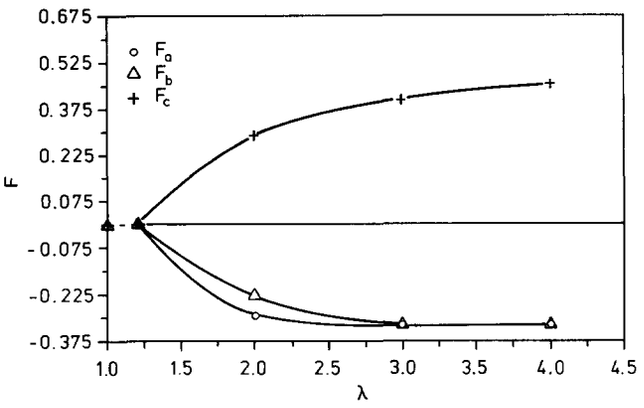

Figure 4 Orientation coefficients of PBTP films as a function of draw ratio. Drawing temperature 373 K

and F_b decrease. For small draw ratios the rate of orientation for the *a*-axis is greater than that for the *b*-axis. At $\lambda > 3$ the rates of orientation for axes *a* and *b* are the same. The greatest change of the orientation coefficients F_a, F_b and F_c appears to be between $\lambda = 1.2$ and 2.5. Above $\lambda = 3$ the rates of orientation for all three axes decrease gradually.

Figure 5 presents SEM micrographs of the samples drawn at 373 K to different draw ratios. The transformation of lamellar spherulites to microfibrillar structure occurs with increasing draw ratio: at $\lambda = 2$ very little microfibrillar structure is recognized, but at $\lambda = 3$ this structure appears to be perfectly formed and the transformation is complete. The SEM micrograph at $\lambda = 4$ (*Figure 5*) shows that the small shear displacement of the microfibrils takes place in the opposite direction

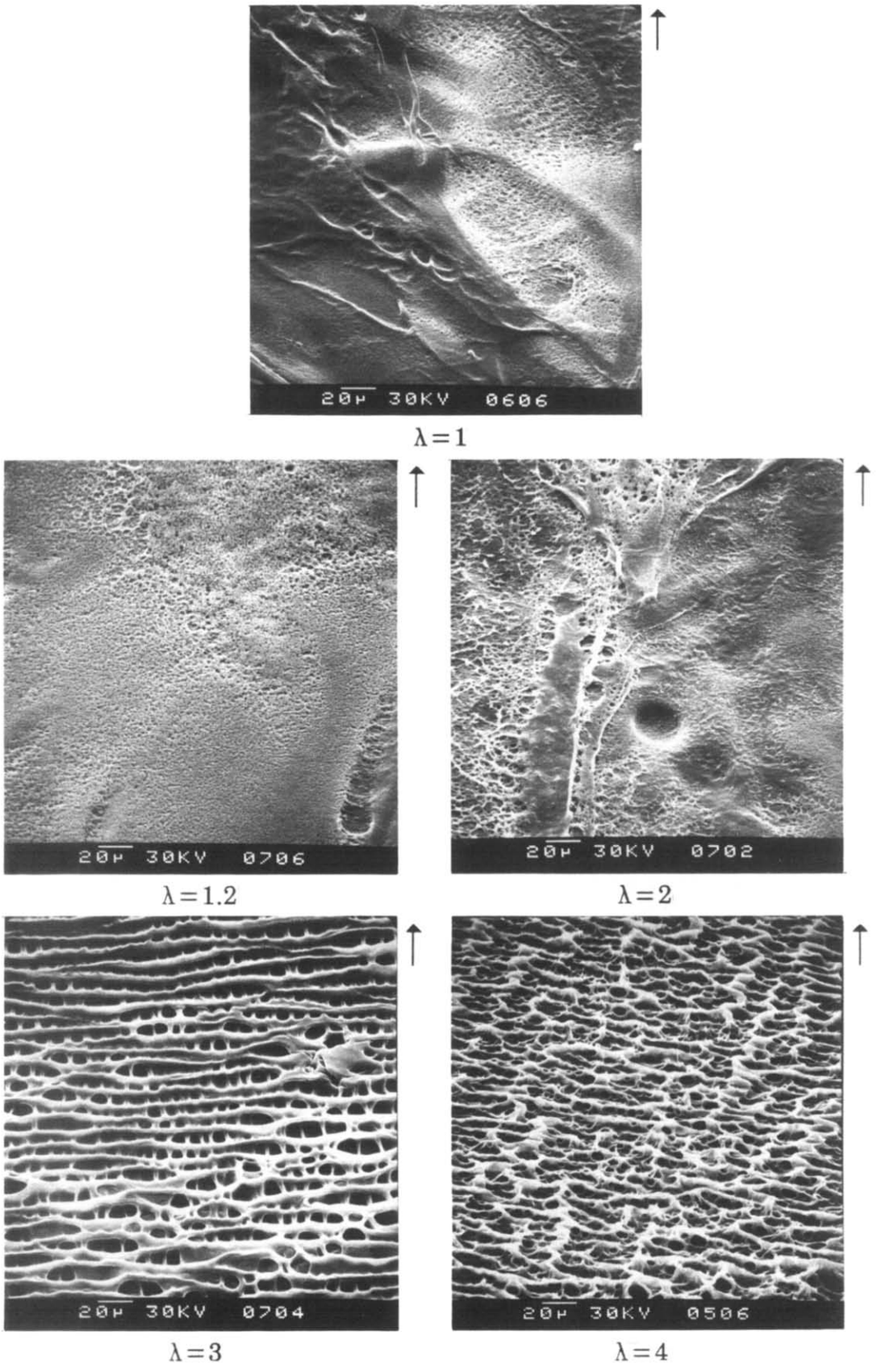

Figure 5 SEM micrographs of the PBTP films drawn at 373 K to different draw ratios

to the draw direction, which is in agreement with the description of Peterlin's model for drawing of microfibrillar structure[6].

As the samples were etched before SEM measurements, the crystalline part of the polymer can be observed. It is easily recognized that lamellae are oriented more or less perpendicular, or at a slightly oblique angle, to the draw direction. The appearance of lamellae after etching is a consequence of the almost complete removal of the non-crystalline layers between the crystalline blocks in

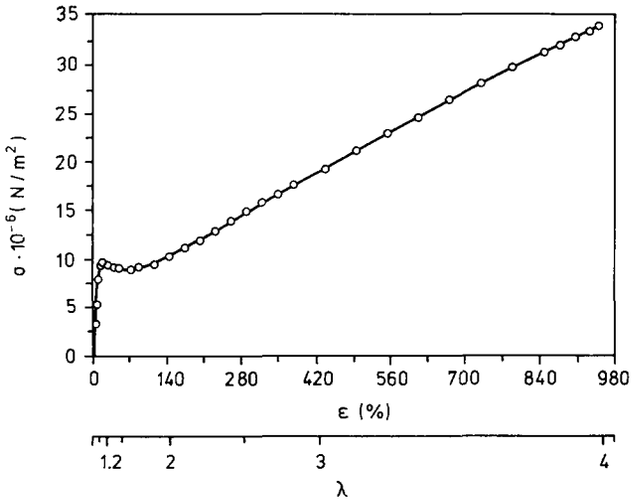

Figure 6 Stress (σ)–strain (ε) (and draw ratio λ) curve of PBTP films drawn at 373 K

the same microfibrils, so that the axial connection is almost completely lost[3,5]. The lateral connection of each block with crystalline blocks of adjacent microfibrils is much less impaired because the boundary contains hardly any non-crystalline material that could be etched away[5]. As a consequence, the stacked lamellae and the microfibrils are observed.

Figure 6 shows the stress (σ)–strain (ε) (and draw ratio λ) curve of the drawn samples. The strain was the nominal value. The curve shows a typical plastic deformation behaviour of crystalline polymers. However, the plateau region, i.e. the necking region, appears to be narrow. At $\lambda = 1.2$ the curve has already crossed the yield point. The plateau region ends at about $\lambda = 2$. Therefore, the transformation of lamellar spherulites into microfibrillar structure by chain tilting, slipping and the subsequent destruction of lamellae occurs in the necking region. Formation of completely perfect fibrils occurs in

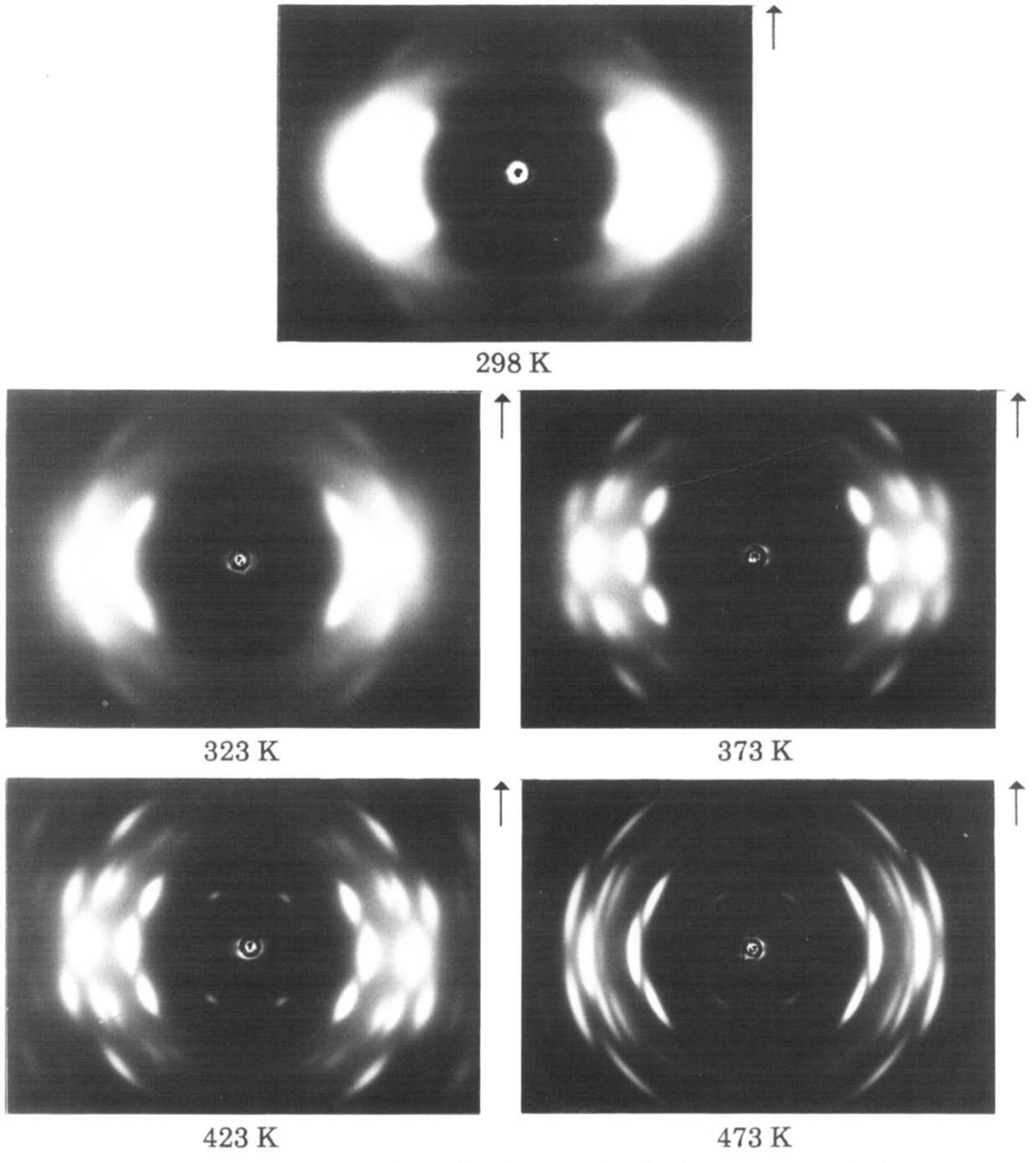

Figure 7 WAXD patterns of PBTP films drawn at various drawing temperatures to $\lambda = 4$

the so-called strain hardening region followed by drawing of the microfibrillar structure.

Influence of drawing temperature

WAXD photographs showing the influence of drawing temperature on crystalline orientation of the samples drawn to $\lambda = 4$ are shown in *Figure 7*. The reflection arcs are shorter as the drawing temperature is increased, therefore more crystalline reflections occur. This demonstrates that both crystalline orientation and crystallinity are increased. Compared with the WAXD pattern at 423 K, the length of the reflection arcs at 473 K

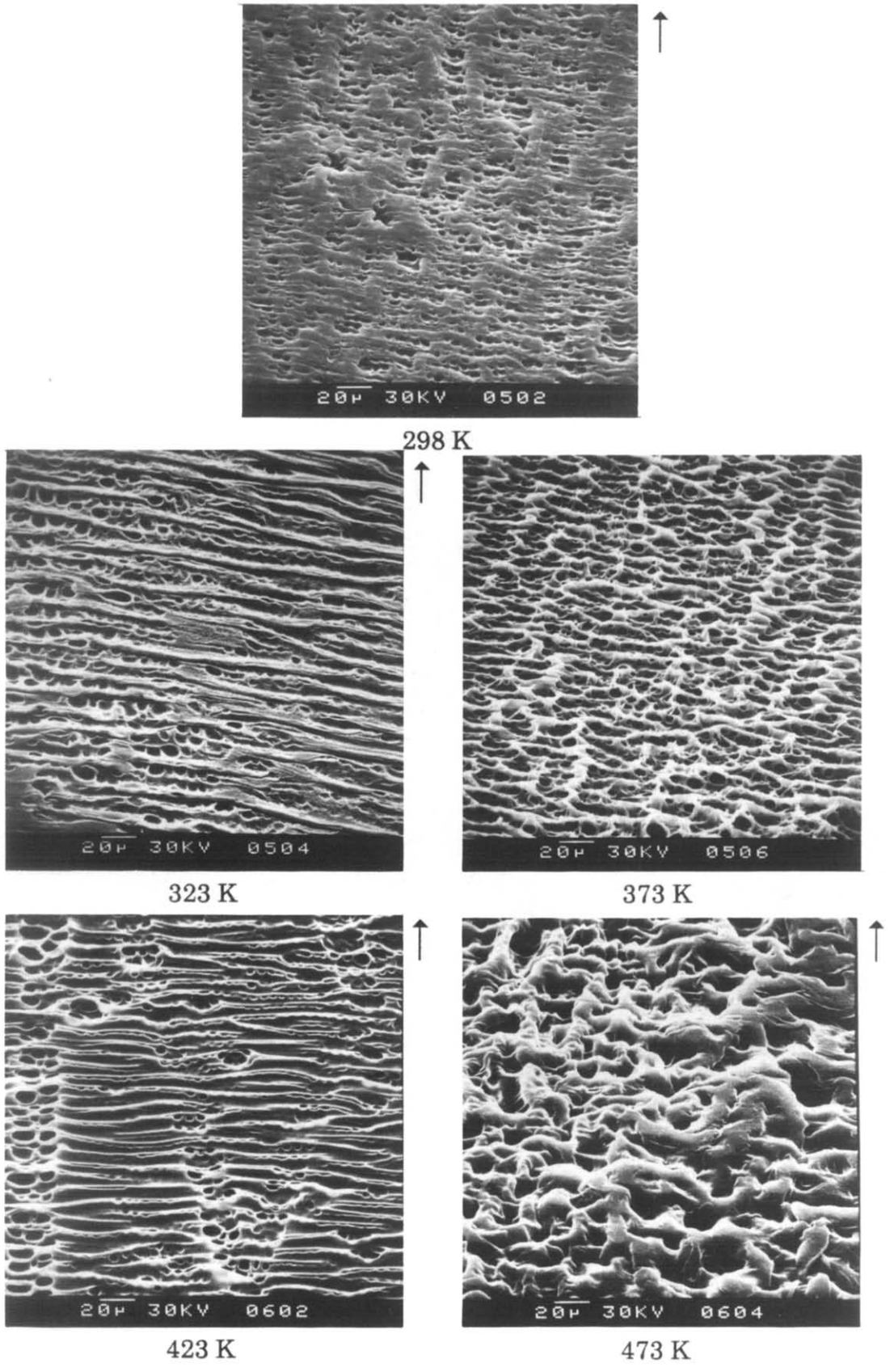

Figure 8 SEM micrographs of PBTP films drawn at various drawing temperatures to $\lambda = 4$

appears to increase again. The reflection along the double Bragg angle also seems to be narrow. This clearly indicates that at a drawing temperature of 473 K the orientation of crystals is decreased, while the crystallite size is increased. The reason is that strong crystallization takes place at 473 K which is the highest drawing temperature used in this study. So the orientation of crystals is disturbed. Therefore, an optimal drawing temperature should exist at which the degree of crystalline orientation takes a maximum value. From WAXD patterns this optimal temperature appears to be between 373 K and 423 K, as the length of the 0 0 1 reflection arcs at 298 K or 323 K are longer than at 373 K and 423 K. The calculated orientation coefficients F_c for 0 0 1 reflection are 0.45 at 373 K and 0.48 at 423 K. Consequently, the optimal drawing temperature for the highest orientation of crystals under the conditions of this study appears to be about 423 K.

From the overlapping reflections at 298 K as well as 323 K it is difficult to distinguish which is the better orientation, because the lengths of the reflection arcs are almost identical. The degree of overlap at 298 K is greater than that at 323 K. This could be attributed to the great movement of the non-crystalline chain segments in the glass transition region ($T_g = 319$ K), so that the orientation of crystals under extension at 323 K is probably disturbed.

As the samples are drawn to $\lambda = 4$ at various temperatures, all samples show the characteristics of microfibrillar structure in SEM micrographs (*Figure 8*). Because of lower crystallinity of the sample drawn at 298 K[21] the crystalline block of adjacent microfibrils contains non-crystalline material which cannot be removed completely under identical etching conditions. So some microfibrils appear less sharp and seem to be thicker in the lateral dimension. With increasing drawing temperature the microfibrillar structure becomes obvious.

As the strong crystallization at 473 K is an isotropic process, the microfibrillar structure is disturbed again. This agrees with the results of X-ray measurement. From the SEM micrograph of the sample drawn at 473 K the lamellar structure can hardly be distinguished. It is obvious from X-ray diffraction (*Figure 7*).

CONCLUSIONS

Transformation of the lamellar spherulites into microfibrillar structure for the drawn PBTP films occurs in the necking region. The formation of the microfibrillar structure appears to occur at the end of the plateau region of the stress–strain curve. Perfect microfibrillar structure is obtained in the strain hardening region. This structure was subsequently drawn. Crystal orientation occurs after passing the yield point, and develops rapidly with increasing draw ratio, until perfect microfibrillar structure is formed at $\lambda = 3$. However, when the microfibrillar structure is drawn, the rate of orientation decreases again.

The drawing temperature influences the oriented structure of PBTP. An optimal drawing temperature exists at which the maximum degree of crystalline orientation is attained. For this study the optimal drawing temperature was about 423 K, which is between the glass transition and the melting temperatures. The great mobility of the non-crystalline chain segments in the glass transition region disturbs the orientation of crystals. At the highest drawing temperature, which was about 25 K below the melting point (498 K), the formation of the microfibrillar structure is also disturbed and the degree of crystalline orientation is decreased.

As a consequence of etching the PBTP films, stacked lamellae are observed oriented more or less perpendicular to the draw direction as well as the microfibrils existing between the stacked lamellae.

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