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Uniaxial drawing behavior of syndiotactic polystyrene ☆

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Abstract

The drawing behavior of syndiotactic polystyrene (sPS) has been studied in the temperature range around its glass transition. Amorphous sheets have been prepared by quenching, and drawn at temperatures from 90–120°C. The development of orientation and crystallization has been examined using the optical birefringence method, standard thermal analysis, and X-ray diffraction. The effect of draw ratio, draw rate, and draw temperature on orientation and crystallinity were examined. Deformation dependent crystallization and orientation have been observed. Both orientation and crystallinity increase with increasing draw ratio and draw rate, but decrease with increasing draw temperature in the temperature range of 90–114°C. These results can be explained according to the competition between deformation and relaxation of molecular chains during drawing. Results show that crystallization of sPS is predominantly controlled by stress rather than by temperature during drawing in the temperature range of 90–114°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Syndiotactic polystyrene; Orientation; Drawing

1. Introduction

Syndiotactic polystyrene (sPS) has a number of properties, which are different from those of conventional styrenics, and are superior for many practical applications [1]. It has the highest melting point of any single-monomer polymerization product, high crystallization rate, and high chemical stability as well as excellent processability in most thermoplastic fabrication technologies. The sPS also provides excellent dimensional stability and low moisture absorption. It has gained increasing academic and industrial interest since successful development to synthesize sPS with a high degree of stereoregularity was first reported in 1986 [2]. However, it is known to have a high level of brittleness. Orientation gradually improves this behavior.

A variety of crystal structures have been reported for sPS. Its α form has an all-*trans* planar zigzag conformation and packs in a hexagonal structure. Its β form consists of an all-*trans* backbone conformation [3] or of the *trans*, *trans*, *gauche*, *gauche* (TTGG) skeletal conformation [4] but packs in an orthorhombic structure. The γ and δ forms, which can only be formed from solvent swelling of glass sPS, have a helix conformation and exist in the same monoclinic crystal structure. Besides these crystalline forms, a mesomorphic form occurs under certain conditions [5]. Local organization of this form may be in the form of disordered agglomerates of triplets of *trans*-planar chains. In a more recent study [6], the effect of compressed CO_2 on the phase transitions and polymorphism of sPS has also been reported.

Several spectroscopic studies including infrared (IR) [7], Raman [3,8,9], and solid-state NMR [10] have been used to study the crystalline structure of this polymer. The isothermal crystallization process [11,12] and crystallization induced by annealing [13] have also been studied. The sPS has been blended with atactic polystyrene (aPS) [14,15] and poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) [16], respectively. Both aPS and PPO were found miscible with sPS, and the polymorphic behavior was altered by blending with PPO [17,18]. When crystallization occurs from the quenched amorphous phase, only a disordered modification of the α form was obtained for pure sPS, while more perfect modifications of the α form and the thermodynamically more stable β form were obtained for blends of sPS/PPO.

The structure and morphology of injection-molded sPS were recently studied by X-ray diffraction, DSC, and optical and electron microscopy [19–21]. A skin-core structure was found and significant structure differences existed at the skin

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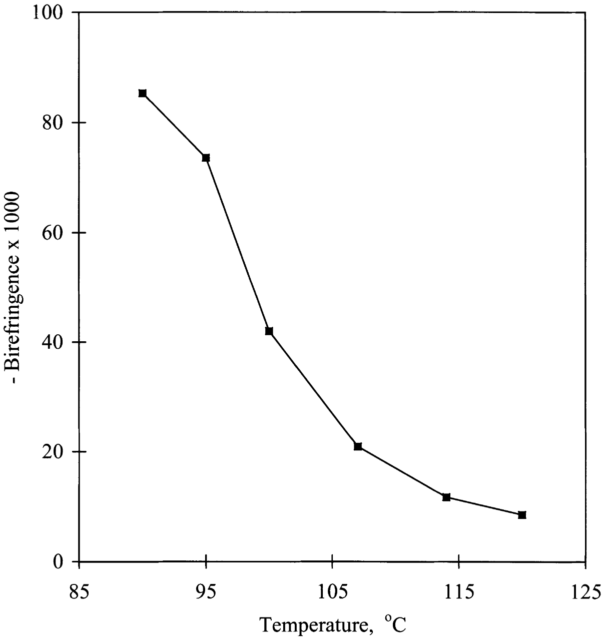

Fig. 1. Optical birefringence of sPS drawn at different temperatures to a draw ratio of 3.4.

of molded sPS samples. In one case [21], a shear crystalline structure was observed between the amorphous skin and the amorphous core for injection-molded sPS, but mechanical properties of the samples were mainly controlled by the degree of total crystallinity. The morphology of the injection-molded sPS was examined by small angle X-ray scattering (SAXS) [22]. Features indicating crystalline lamellae were very weak at room temperature, becoming increasingly intense above the glass transition temperature as a result of crystallization. Failure mechanisms and the effect of processing conditions on the fracture behavior have also been studied [23,24].

Relatively few studies have been reported on oriented sPS [25–30]. Orientation developed in the amorphous precursor apparently resulted in optical transparency. Dynamic mechanical properties of drawn sPS were also reported [27]. It was found that the glass transition temperature is affected by drawing, and particularly by draw temperature. Strain-induced orientation of the mesomorphic order was studied using dichroism of infrared spectra and WAXD for sPS films stretched at 110 and 130°C, respectively [28,29]. An oriented mesomorphic form gave rise to a clear IR dichroic effect, but without sharp oriented X-ray diffraction patterns. Some work relating optical properties to the development of orientation has also been published [30].

The present work investigates the effect of changing draw conditions on the microstructure of sPS, which develops during deformation of initially amorphous material. The drawing temperature of interest here is in the range around or just above T_g where the stress free crystallization rates are known to be quite slow.

2. Experimental

The sPS pellets used were supplied by the Dow Chemical Company. Their molecular characteristics as determined by GPC were $M_w = 212{,}072$ and $M_w/M_n = 2.06$. Sheet samples were prepared by compression molding. The sPS pellets were heated above melting point (ca. 300°C) for 7–10 min and then pressed in a mold to obtain sheets of 0.8 mm thickness, which were quenched in cold water. The sheets were optically transparent, and showed no crystalline diffraction maxima in the WAXD pattern.

The quenched sPS sheets were cut into 30×20 mm strips. Oriented specimens were prepared by uniaxial drawing. After preheating at draw temperature for 10 min, the strips were stretched in the Instron tensile machine. Except when otherwise stated, the draw rate used was 5 mm/min.

Thermal properties measurements were performed with a Perkin–Elmer DSC7 instrument. The temperature scale of the calorimeter was calibrated using indium as a standard, and nitrogen gas was used to prevent samples from oxidation. The heating rates used were 20 and 80°C/min in most cases. Based on the calculation by Wunderlich [31], under a heating rate of 100°C/min, the temperature difference between the center and the outside of a sample with a diameter of 0.8 mm is only ca. 0.65°C. Therefore, it is reasonable to perform the thermal analysis using a heating rate of 80°C/min for our film samples (most of them had a thickness of ca. 0.5 mm). In fact, a rapid heating rate, 80°C/min was found to minimize the re-crystallization, which occurs during the DSC scan [8,9]. The fractional crystallinity of samples was determined by calculating areas under melting and crystallization peaks, i.e.:

$$X_c = (\Delta H_m - \Delta H_c)/\Delta H_m^0, \qquad (1)$$

where ΔH_m is the heat absorbed during melting, ΔH_c the heat released during crystallization, and $\Delta H_m^0 = 53.2$ J/g the heat of fusion for 100% crystalline sPS [32].

A rapid measure of the relative orientation of the drawn samples was obtained using a technique developed for the on-line characterization of sheets during fabrication. It was based on measurements of the broad-spectrum optical properties. The oriented sPS strip was placed with the orientation direction perpendicular to the propagation direction of the incident white light beam. The specimen was positioned between two polarizers and the birefringence value calculated by fitting the measured transmitted intensity spectrum to theoretical predictions and the birefringence value calculated for a wavelength of 589.6 nm. The technical details of the technique can be found elsewhere [33,34].

Crystallographic information was obtained using line focused diffractometer traces (Philips diffractometer with a 0.2° (2θ) receiving slit using CuKα(radiation with PC-APD analysis software). The rotational axis of the diffractometer (one-dimensional) scan was oriented along the draw direction for most samples, so the trace was recorded in the equatorial plane (perpendicular to the draw direction). Some

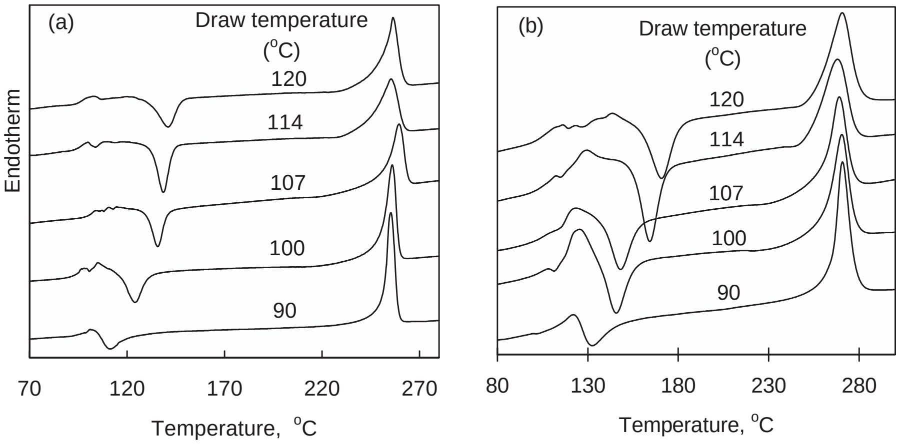

Fig. 2. DSC thermograms of sPS drawn at different temperatures to a draw ratio of 3.4. DSC heating rate: (a) 20°C/min; (b) 80°C/min.

samples were scanned at angles between 60–70° to the lateral or equatorial direction. All data have been corrected for background scatter. The degree of orientation was studied using flat plate transmission photographs to record the two-dimensional diffraction pattern.

3. Results and discussion

3.1. Draw temperature effect

The effect of draw temperature was studied in the first step. The initially amorphous sPS were drawn in the temperature range of $90 < T < 200$°C. The solid state thermal crystallization rate was found to increase rapidly at temperatures above 120°C, in agreement with preceding studies on crystallization kinetics [12]. In order to obtain optically transparent materials, most of the samples were drawn at temperatures from 90 to 120°C.

Dependence of birefringence on draw temperature for sPS drawn to the same draw ratio of 3.4 is presented in Fig. 1. It should be pointed out that sPS exhibits negative birefringence, i.e. $n_{\parallel} - n_{\perp} < 0$, for all the uni-axial oriented samples. In Fig. 1 we see that the birefringence value obviously decreases with increasing draw temperature, indicating that a total degree of molecular orientation in both crystalline and amorphous regions is lower for samples drawn at higher temperatures. This result can be understood according to temperature effect on molecular relaxation. The higher the temperature, more rapidly oriented molecular chains can relax during drawing. Consequently, the orientation degree will be lower if samples were drawn at higher temperatures.

DSC thermograms of sPS drawn at different temperatures, detected using heating rates of 20 and 80°C/min, respectively are shown in Fig. 2(a) and (b). We can directly see that position of the melting peak changes very little, and that of the cold crystallization peak moves to a higher temperature in Fig. 2(a) and (b). However, the cold crystallization peak is obviously affected by the glass transition in Fig. 2(b), which makes it difficult to precisely determine the peak area. In this case, the baseline was chosen by using the straight part of the line between crystallization and melting peaks.

The crystallinity and temperatures of melting (T_m), crystallization (T_{cc}), and glass transition (T_g), calculated from these DSC curves are respectively plotted in Figs. 3 and 4. In Fig. 3, the crystallinity measured either by a heating rate of 20 or 80°C changes in a similar way. The crystallinity drops with increasing draw temperature from 90 to 114°C, and increases as temperature is further increased to 120°C although birefringence continues to decrease somewhat up to 120°C (Fig. 1). The consistent decrease in both birefringence and crystallinity with increasing temperature from 90 to 114°C seemingly suggests that the orientation of the crystalline phase is the principal source for the sample's

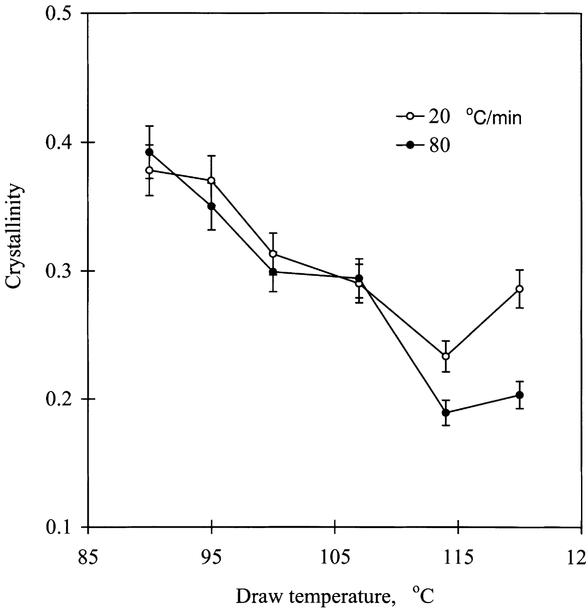

Fig. 3. Plots of crystallinity versus draw temperature for sPS drawn to a ratio of 3.4. DSC heating rate is indicated.

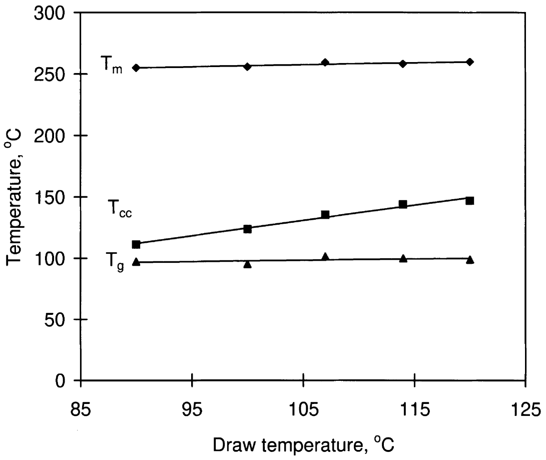

Fig. 4. Plots of melting (T_m), cold-crystallization (T_{cc}), and glass transition temperature (T_g) for sPS drawn at different temperatures to a draw ratio of 3.4. DSC heating rate: 20°C/min.

birefringence. In contrast, the increase in crystallinity (Fig. 3) for the sample drawn at 120°C implies that more crystalline materials are unoriented in this sample. The unoriented crystalline materials may result from thermally induced crystallization of relaxed molecules. The sample drawn at 120°C is less transparent than the others drawn at lower temperatures. To confirm the great effect of annealing-induced crystallization, we carried out the drawing at 130°C also and it was more difficult to obtain samples having a uniform draw ratio. Consequently an opaque sample with unequal draw ratio (necking) and a crystallinity of 0.57 was obtained. The transparency of sPS drawn at 130°C was too bad to get the birefringence measured. Another feature in Fig. 3 is that the DSC heating rate has greater effects on the samples drawn at 114 and 120°C, with lower crystallinity (<0.3) than the other samples with higher crystallinity. A similar effect can be seen in Fig. 8.

During DSC measurements on oriented materials, cold crystallization happens above T_g because the sample is far from fully crystallized. Crystallization is a process for the molecular chains to become ordered. Therefore, some amorphous chains, which have achieved a higher degree of order in the oriented sPS are able to crystallize more easily. With increasing draw temperature, the orientation of molecular chains decreases (Fig. 1), implying that possibly the amorphous chains, as well as the crystalline lamellae are more disordered. This is why the cold-crystallization temperature increases with the increase in draw temperature, as shown in Fig. 4. In a dynamic-mechanical study of drawn sPS [27], the glass transition was observed to be affected by draw temperature. But we do not see significant changes here in both glass transition and melting temperature.

The WAXD scans for both undrawn (isotropic, slow cooled) and drawn sPS specimens are shown in Fig. 5. Traces taken in different directions in the drawn sample show a similar loss of crystalline diffraction peaks upon drawing. All the three sPS samples drawn at 90, 107, and 120°C show only broad peaks, which have been interpreted in earlier works as an evidence for a "mesomorphic" structure [5,28]. It is also seen that the intensity of the two peaks (especially the peak at about 12°) decreases as draw temperature changes from 90 to 120°C. This result is in a qualitative agreement with the DSC results of Fig. 3, i.e. crystallinity or fraction of the mesomorphic phase decreases with the draw temperature.

In general, if a polymer crystallizes quiescently in a temperature range around T_g, we would expect the crystallinity to increase with temperature. However, a decrease in crystallinity was observed when sPS was

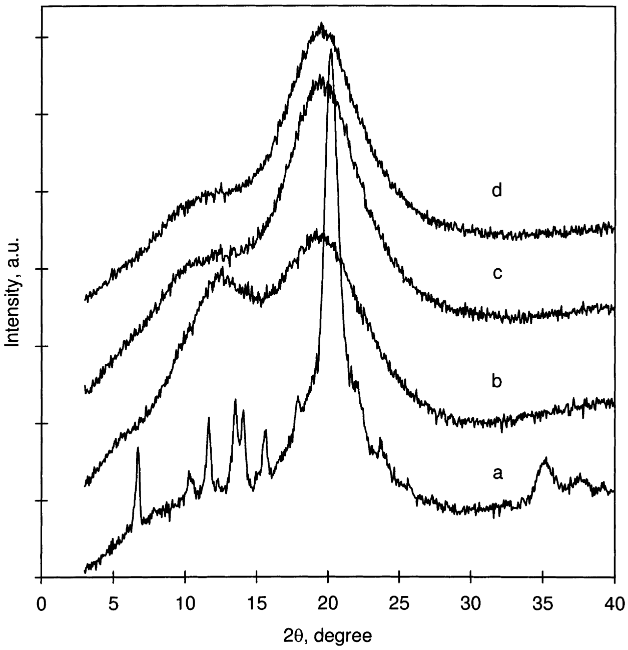

Fig. 5. X-ray diffractometer traces for: (a) undrawn (isotropic, slow cooled) sPS; and sPS drawn at (b) 90°C; (c) 107°C; (d) 120°C to a draw ratio of 3.4.

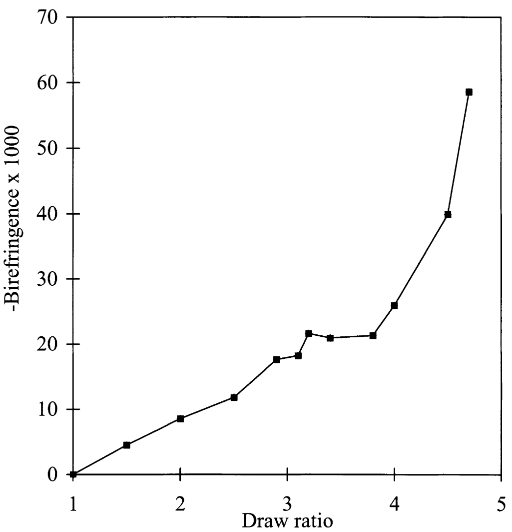

Fig. 6. Birefringence of sPS drawn at 107°C to different ratios.

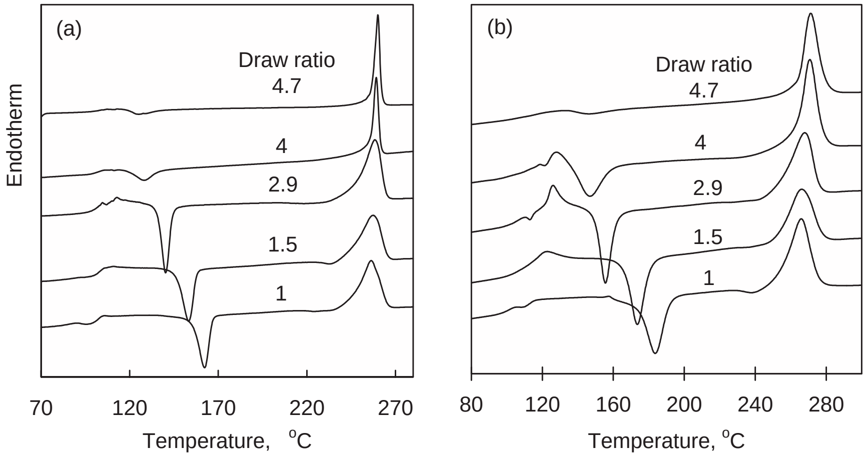

Fig. 7. DSC thermograms of sPS drawn at 107°C to different ratios. Draw ratio is indicated. DSC heating rate: (a) 20°C/min; (b) 80°C/min.

drawn at temperatures ranging from 90 to 114°C. This is because the crystallization occurring in the drawing process was mainly induced by tensile stress rather than by annealing. Molecular relaxation plays an important role in this process. Basically, crystallization and orientation development are determined by the competition of two contrary effects, drawing stress and relaxation of oriented chains. When the sample was drawn at a higher temperature using the same strain rate, more molecules are able to become relaxed. So the resultant material reaches a lower degree of orientation. The decrease in crystallinity with increasing draw temperature suggests that only the stretched molecular chains can crystallize. It may be difficult for the non-stretched or relaxed chains to crystallize due to their limited mobility at such low temperatures.

3.2. Draw ratio effect

In order to examine orientation development during drawing of sPS, birefringence has been measured for sPS drawn at 107°C to different draw ratios from 1.5 to 4.7, which is shown in Fig. 6. The birefringence value increases almost linearly with increasing draw ratio up to 4. With increasing draw ratio from 4 to 4.7, the increase in birefringence is more pronounced, indicating that molecular orientation can be more effectively achieved at a higher draw ratio.

DSC thermograms of sPS drawn at 107°C to different draw ratios, measured using heating rates of 20 and 80°C/min are compared in Fig. 7. With increasing draw ratio, the cold crystallization peak becomes smaller and moves to lower temperature, the melting peak becomes narrower and somehow moves to higher temperature. This simply reflects the fact that degrees of both crystallinity and orientation of the sample have been increased with the increase of draw ratio. It will be clearer to see the crystallinity calculated from these DSC thermograms, as shown in Fig. 8. With increasing draw ratio, the crystallinity measured either using a heating rate of 20 or 80°C/min increases. This increase is not pronounced when the draw ratio is less than 2.5, and it increases evidently as the draw ratio is higher than 3. We see also, similar to the result in Fig. 3, that the DSC heating rate effect on crystallinity is more significant for samples with lower crystallinity (<0.3).

Melting and cold-crystallization temperatures were plotted versus draw ratio in Fig. 9. As the draw ratio increases, melting temperature detected using both heating rates of 20 and 80°C/min increases and the cold-crystallization temperature decreases linearly. The increase in melting temperature probably indicates that the crystalline size was increased by drawing. The decrease in cold-crystallization temperature is, to some extent, related to development of the sample's orientation specifically in an amorphous region.

According to the DSC result in Fig. 8, the initially quenched sPS sheet has a crystallinity of 0.18 or 0.10 measured respectively using a heating rate of 20 or 80°C/min, although there is no indication of crystalline or mesomorphic structure in its WAXD pattern (see Fig. 11). Comparison of various methods including Raman spectroscopy for the determination of crystallinity of isotropic sPS

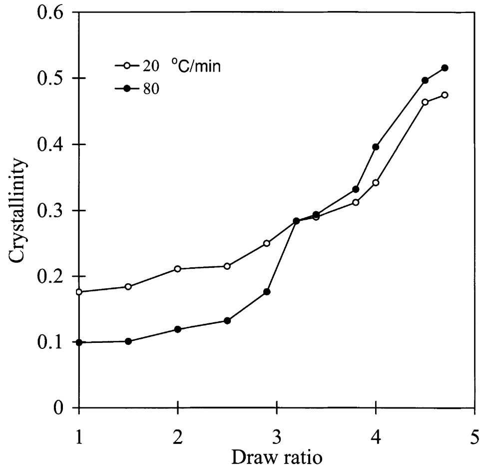

Fig. 8. Plots of crystallinity versus draw ratio for sPS drawn at 107°C. DSC heating rate is indicated.

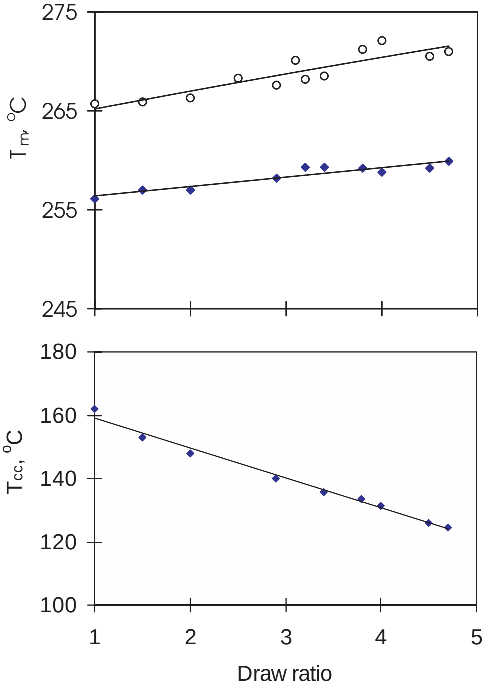

Fig. 9. Dependence of melting (T_m) and crystallization (T_{cc}) temperatures on draw ratio for sPS drawn at 107°C. DSC heating rate: (◆): 20°C/min; (○): 80°C/min.

gave similar results in literature [9]. From the above results, in Figs. 3 and 8, we know that the DSC crystallinity of sPS, especially for samples with low crystallinity, is heating rate dependent. To check how significant the DSC heating rate effect on crystallinity is, DSC experiments have been carried out using different heating rates from 2 to 80°C/min for the quenched sPS sheet, the result is shown in Fig. 10. The crystallinity decreases significantly with an increasing heating rate. When a low heating rate of 2°C/min was used, a high crystallinity of 0.32 was obtained. When a high heating rate of 80°C/min was used, a much lower crystallinity, 0.10, is obtained. Therefore, the quenched sPS sheet is most probably, as indicated by WAXD, completely amorphous.

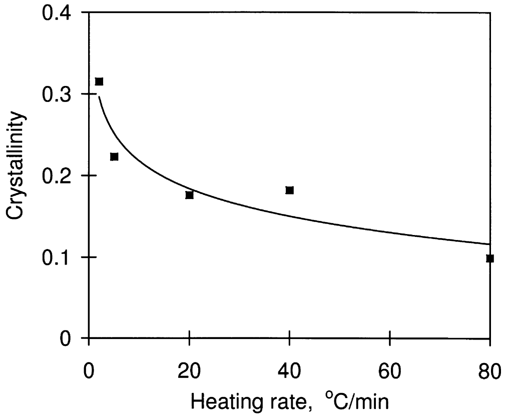

Fig. 10. Dependence of crystallinity on DSC heating rate for quenched sPS.

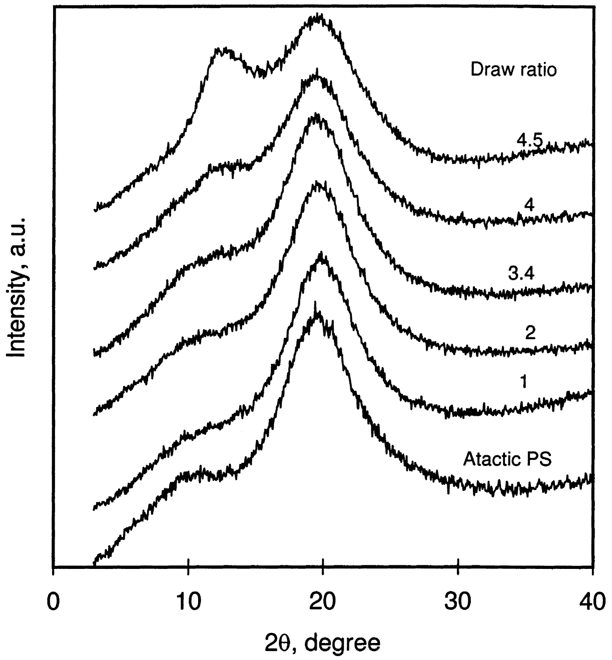

Fig. 11. X-ray diffractometer traces for isotropic atactic polystyrene, and sPS drawn at 107°C to different draw ratios.

The WAXD patterns for sPS drawn to different draw ratios are presented in Fig. 11. The WAXD curve of atactic polystyrene was also plotted in this figure. It is seen surprisingly that drawn sPS with draw ratios of 2 and 3.4 have similar patterns as quenched sPS and atactic polystyrene samples, without indications of any α, β crystalline or even mesomorphic form. This supports the speculation that oriented sPS with a draw ratio below 3 is almost fully amorphous as well as quenched. The lack of multiple sharp diffraction peaks seen for the isotropic slow cooled sPS (Fig. 5(a)) indicates that the crystallinity detected in the DSC scans must be in the form of crystals with a high defect density in which the unit cells are not perfectly periodically aligned.

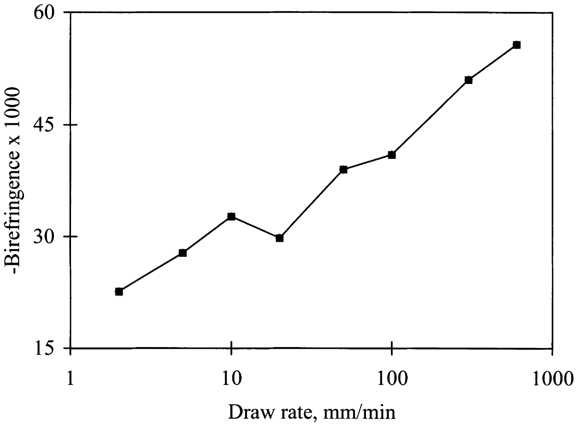

Fig. 12. Birefringence of sPS drawn at 107°C with different draw rates. Draw ratio of samples: 4×.

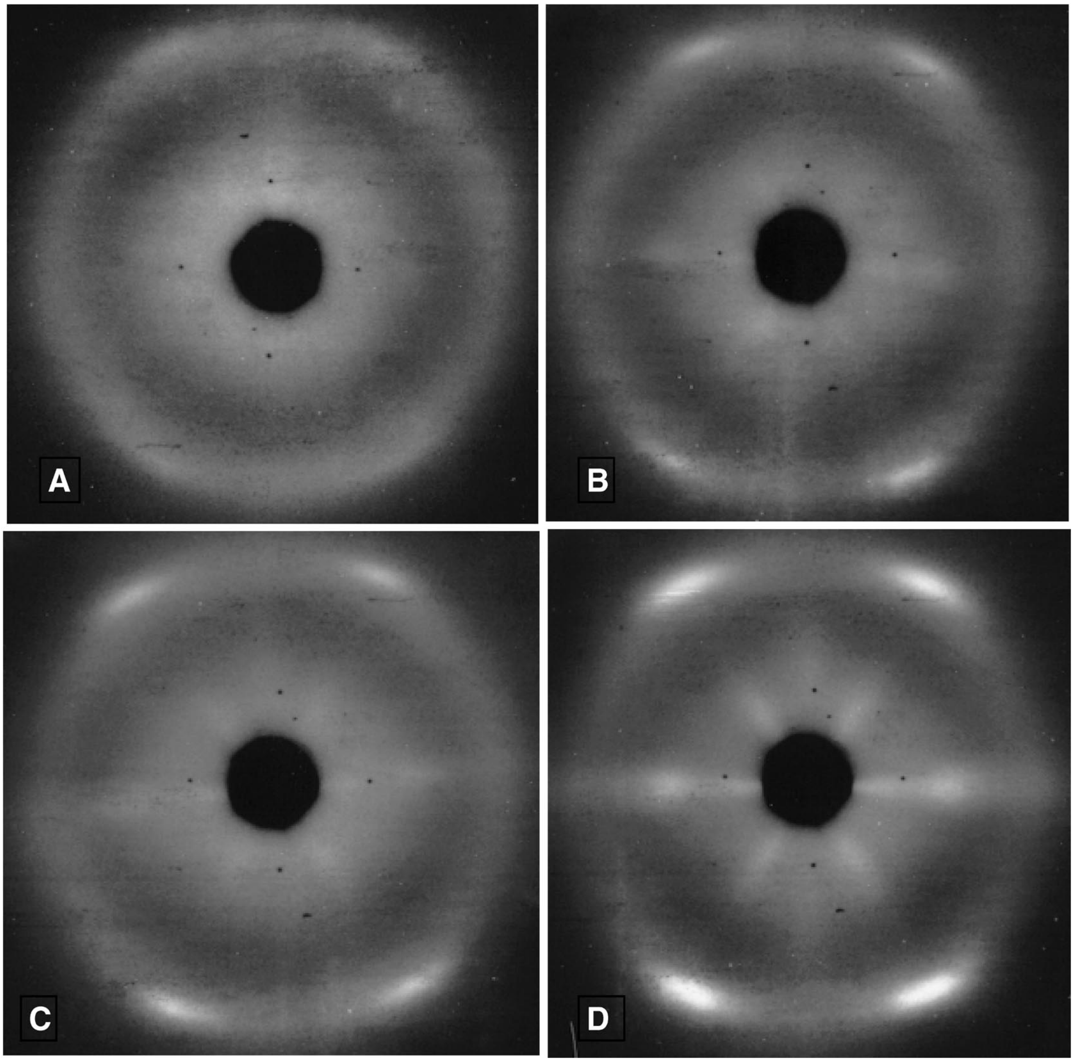

Fig. 13. Transmission wide angle X-ray diffraction patterns as a function of draw rate: (A) 2 mm/min; (B) 20 mm/min; (C) 50 mm/min; (D) 600 mm/min. The draw direction is vertical.

At 107°C or possibly below 120°C, quiescently annealing-induced crystallization is non-significant. Molecular chain packs in the mesomorphic form or crystallized only when a bunch of them were forced to be uni-directionally arranged by stretching. It looks as if the structure formation of the mesomorphic form requires a minimum draw ratio, ca. 2.5 × . Samples having a draw ratio below this value are approximately amorphous.

3.3. Draw rate effects

Dependence of birefringence on the draw rate for sPS drawn at 107°C is shown in Fig. 12. The birefringence value rises linearly from 23 to 56 with increase in the draw rate in the logarithmic scale from 2 to 600 mm/min, indicating a strong effect of the drawing rate on the sample's orientation. As the draw rate increases, the molecules have less time to relax as they crystallize, and so the degree of orientation increases. The transmission X-ray diffraction patterns are shown in Fig. 13 for different draw rates. The WAXD analysis shows that any crystalline ordering, at least connected with well-formed crystals can be considered absent for all the four samples. The outer ring of the pattern is seen to concentrate symmetrically about the draw direction as expected for molecular axis alignment parallel to the draw direction. A similar X-ray photograph was obtained for sPS drawn at 110° to a draw ratio of 5 by Vittoria et al. [28], and they suggested that this type of X-ray pattern results from the presence of very defective and small crystals, or more in general, of mesomorphic order.

The 2D wide-angle diffraction patterns in Fig. 13 show that there are only a small number of broad diffraction maxima, supporting the observations with the 1D-diffraction scans of Figs. 5, 11 and 17.

It is seen that the orientation measured using optical birefringence measurements is a manifestation of crystalline unit cell alignment. The degree of WAXD orientation is much stronger at the high rate of drawing. Similar

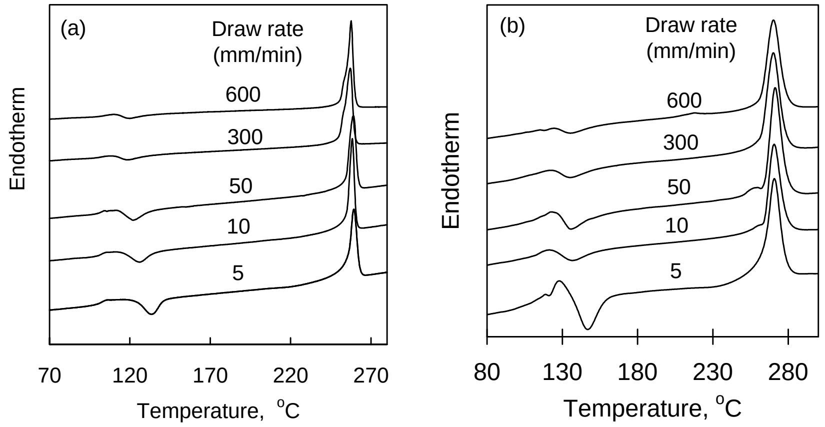

Fig. 14. DSC thermograms of sPS drawn at 107°C with different draw rates. Draw ratio of samples: 4 ×. DSC heating rate: (a) 20°C/min; (b) 80°C/min.

photographs indicate that the orientation effects are most likely due to unit cell crystallographic alignment, which is a necessary condition to obtain thermally stable microstructures.

DSC thermograms for sPS drawn using different draw rates are presented in Fig. 14. All the samples were drawn at 107°C to the same draw ratio of 4. It is seen that the drawing rate affects both area and positions of the crystallization peaks, but the melting peak position changes very little. Draw rate dependence of DSC calculated crystallinity is presented in Fig. 15. DSC crystallinity, measured using either a heating rate of 20 or 80°C, increases almost linearly with the logarithmic draw rate, being similar to the birefringence result in Fig. 12. The similarity in dependence of both birefringence and crystallinity on drawing conditions indicates that the molecular orientation in drawn sPS material results mainly from crystalline regions.

In addition to crystallinity, glass transition, crystallization and melting temperatures can be obtained from the DSC measurements. It was observed that both glass transition and melting temperatures do not show significant changes (not presented), but the crystallization temperature as presented in Fig. 16 decreases with increasing draw rate from 2 to 100 mm/min. The decrease in the crystallization temperature illustrates that crystallization happens more easily for the samples drawn using a higher draw rate because molecular chains in these samples have achieved a higher degree of order or orientation. Fig. 16 also shows that the cold crystallization temperature (T_{cc}) does not change when the draw rate is increased from 100 to 600 mm/min, although the birefringence continues to increase in Fig. 12. This is because T_{cc} is only related to the order or orientation of amorphous molecular chains and so it does not have to be related to the total orientation of the sample.

WAXD patterns for sPS drawn at 5, 50, and 600 mm/min are compared in Fig. 17. For the sample drawn at 600 mm/min (sample D in Fig. 13), two X-ray curves scanned at equatorial direction and at 60° to this direction are presented in this figure. All the X-ray patterns are similar but there is a difference in the relative intensity of the two broad peaks. Obviously, all the three samples have a mesomorphic structure and the fraction of mesomorphic phase (or crystallinity) increases with increasing draw rate. This is qualitatively consistent with the DSC results in Fig. 15.

Looking at the WAXD full 2D patterns (in Fig. 13), we see that besides equatorial direction strong spots occur at an angle of 60° to this direction as well. However, comparing the WAXD curves scanned at the equatorial direction and at 60° for the same sample drawn at 600 mm/min in Fig. 17, the overall shape of the patterns is the same, i.e. both show two broad peaks located at about 12 and 20°, respectively, and only the relative intensity of these peaks change. The wide peak at 12° gradually becomes clear with the increasing draw ratio of the sample, demonstrating a typical mesomorphic structure [5,28,29]. The evolution of the WAXD intensity also shows an increase of crystallinity with increasing draw ratio.

As mentioned above, the relaxation of molecular chains is very important during the drawing process. The effect of

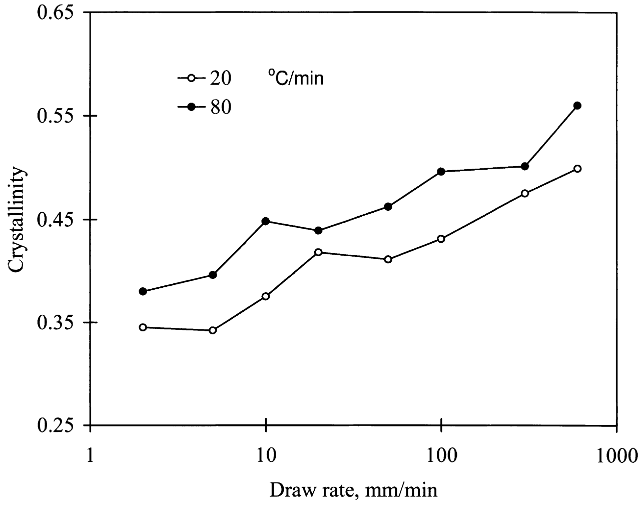

Fig. 15. Plots of crystallinity versus draw rate for sPS drawn at 107°C to a draw ratio of 4. DSC heating rate is indicated.

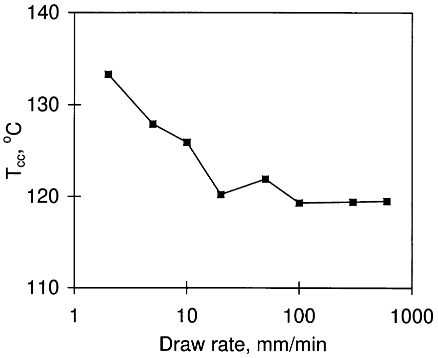

Fig. 16. Dependence of cold-crystallization temperature on draw rate for sPS drawn at 107°C to a draw ratio of 4. DSC heating rate: 20°C/min.

changing drawing rate on orientation and crystallinity results mainly from the interaction between drawing and relaxation of molecular chains. At a higher drawing rate, molecular chains have less time to relax. Therefore more molecular chains are able to retain their orientation and become crystallized.

When the sample of sPS is stretched, the molecular chains are forced to become oriented, and crystallization happens simultaneously. However, some chains with comparatively free ends may relax. The degree of this relaxation depends on draw temperature and draw rate. At a higher temperature or a lower draw rate, the molecular chains are able to relax easily or have sufficient time to become relaxed. By contrast, if the sample is drawn at a lower temperature or a higher rate, the chains' relaxation is more difficult due to their lower mobility or molecular chains have less time to relax, and then more molecular chains can keep their orientation and become crystallized in their oriented state. Therefore, the resultant sample will have a higher degree of orientation and higher crystallinity, as revealed in Figs. 1, 3, 12, 13 and 15.

4. Conclusion

Uniaxially drawn sPS has been produced from an amorphous sheet. The oriented sPS drawn at temperatures below 120°C has a mesomorphic ordered structure. In the draw temperature range from 90 to 114°C, decreasing temperature, increasing draw ratio or draw rate results in an increase of both orientation and crystallinity, but the sPS sample remains nearly amorphous if the draw ratio is lower than 2.5. The crystallization temperature detected by DSC is dependent upon draw conditions. The effect of draw temperature and draw rate can be explained according to the role of molecular chains' relaxation. In the temperature range studied, the crystallization or formation of the mesomorphic structure in the sPS sample is dominantly controlled by drawing stress rather than by temperature.

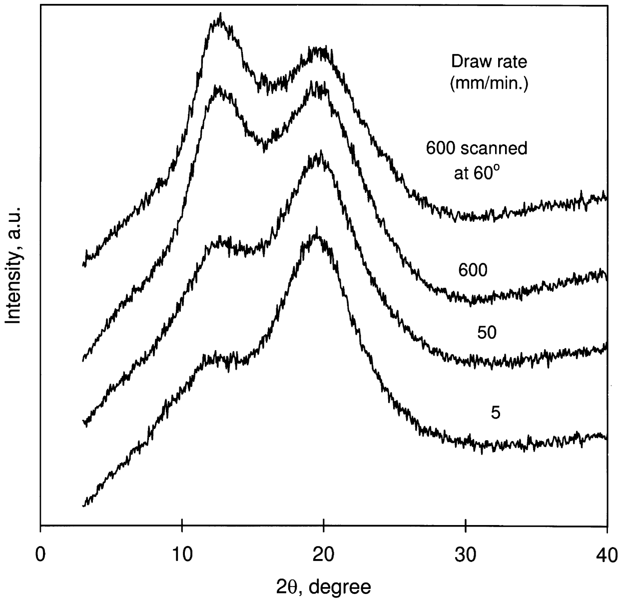

Fig. 17. X-ray diffractometer traces for sPS drawn at 107°C with different draw rates. Draw ratio of samples: 4×.

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