Brittle-to-Ductile Transition Based Upon Amorphous Orientation of Polystyrene Monofilaments

The primary purpose of this study is to investigate the effect of freezing of the oriented molten state on physical properties of oriented atactic polystyrene monofilaments. Molten polystyrenes are extruded directly into a bath (ethanol and water) or surrounding air maintained below the glass transition temperature (+50–−70°C) and wound at various velocities. Monofilaments of various degrees of orientation are obtained by changing the winding velocity, the distance between nozzle and the guiding roll directly under the nozzle, the distance between the nozzle and the surface of the cooling liquid, the molten polymer temperature, and so on.

There is the well-known study by Cleereman, Karam, and Williams[1] about the fabricating conditions of polystyrene monofilaments and physical properties of their monofilaments over a very wide range of various parameters. The most characteristic feature of their spinning method is that molten polystyrenes are extruded into a bath the temperature of which is controlled within the range above the glass transition temperature T_g, are stretched simultaneously in a bath with the same or lower temperature, and then quenched. Monofilaments of various degrees of orientation were obtained by changing the hot stretching ratio, temperature of stretching, rate of quench, and so on.

In our spinning method, however, the hot stretching process is omitted and the winding velocity is changed mainly to obtain monofilaments of various degrees of orientation.

Commercial polystyrenes, Styron 666 ($\overline{M}_w = 2.02 \times 10^5$, $\overline{M}_w/\overline{M}_n = 2.5$) and Styron 679 ($\overline{M}_w = 1.84 \times 10^5$, $\overline{M}_w/\overline{M}_n = 2.8$), were spun by using a screw-type extruder under various conditions, as presented in Table I.

Stress–strain curves were measured by a Tensilon UTM III instrument (Toyo-Baldwin Co., Ltd.) at a constant rate of 20 mm/min, a distance between jaws of 20 mm, room temperature of 20°C, and humidity below 65%.

The fibers extruded into ethanol were stored in other ethanol baths (−67°C) in order to keep their temperature below their cooling bath temperatures. After removal to surrounding air, the stress–strain curve of this fiber was measured under the condition that there is no ethanol on the surface and inside the fiber (the effect of ethanol on the stress–strain curve measurements is discussed later).

TABLE I
Various Spinning Conditions of Atactic Polystyrenes

Symbol[a]	Sample	Cooling bath	Temp. of cooling bath °C	Distance between nozzle and guiding roll, cm	Distance between nozzle and surface of cooling liquid, cm	Output rate, g/min	Molten polymer temp., °C
Δ	Styron 679		−67				
Δ/		ethanol	−25	23	7		
\Δ			+23			1	197
Δ̩		water	+50				
O			+23	81			
O		air	+10	471			211
O			+8			0.3	
×	Styron 666	ethanol	−72	23	7	1	255
×			+11				208

[a] The symbols in this table are used in Figures 1–5.

Journal of Applied Polymer Science, Vol. 22, 2707–2711 (1978)

0021-8995/78/0022-2707$01.00

The degree of birefringence was examined through a polarizing microscope (Olympus Co., Ltd.) with a Berek compensator and tricresyl phosphate to immerse the monofilaments. The measurements were carried out in daylight (whose optical center is at 550 mμ) and at room temperature.

The nominal tensile strength increases almost monotonically as drafts increase, where draft is defined by the ratio of winding velocity to linear output velocity at the nozzle; it is equal to the ratio of the cross section at the nozzle to that of the wound fiber under assumption of constant density. Elongation at break (nominal) is several percent at lower drafts, changes drastically to more than 100% at some draft, and decreases monotonically as drafts increase after that point. This point is designated as the brittle-to-ductile transition point. The regions of drafts lower and higher than that of this transition point are defined as brittle and ductile regions, respectively. This drastic increase in elongation at break of polystyrene monofilaments accompanies the necking phenomenon. Necking means that one or more constricted parts appear in the fiber and that, in the stress–strain curve, the plateau region is observed in the range of higher elongation than yield strain. The yield points are defined as the maximum in the stress–strain curve. Young's modulus increases monotonically as drafts increase. In the ductile region, the yield points have been observed clearly. Yield stress increases monotonically as drafts increase after this brittle-to-ductile transition point. Yield strain is constant or decreases rather slightly as drafts increase after that point.

The draft corresponding to this transition point depends on the spinning conditions. With increasing distance between the nozzle and the guiding roll directly under the nozzle, the draft for this point increases. With increasing molten polymer temperature, its draft increases. But the temperature of the cooling bath has no influence on the position of the brittle-to-ductile transition within the range from −70° to +50°C.

Ethanol is known as a stress crack agent for polystyrene. But there was no difference between the fibers spun by using ethanol for the cooling bath (+23°C) and those spun in surrounding air at the same temperature (+23°C). Therefore, ethanol used for cooling baths has no influence on the properties of fibers produced under our spinning conditions.

However, the following results should be noted. If there is no ethanol on the surface and inside the fiber, elongation becomes a few percent at lower drafts (in the brittle region). On the other hand, if the stress–strain curve of the fiber is measured just after it is removed from the ethanol bath and when there is ethanol on the surface and inside the fiber, elongation becomes drastically larger (a few hundred percent) at lower drafts (in the brittle region). Tensile strength, Young's modulus, and yield stress also become lower in this case. At higher drafts (in the ductile region), there are no differences between these two cases. This latter case corresponds to the soaking test at atmospheric pressure. Here, we are discussing the former case of stress–strain curve measurement.

As a parameter of molecular orientation, the degree of birefringence (Δn) is more interesting than draft. The degree of birefringence increases monotonically as draft increases. Figures 1 and 2 show tensile strength (nominal) and elongation at break (nominal) plotted for Δn. Elongation at break is several percent in the range of $|\Delta n| \lesssim |-2 \times 10^{-3}|$, but it increases drastically to ca. 160% in the vicinity of $\Delta n = -2 \times 10^{-3}$ and decreases monotonically with increase in degree of birefringence. In spite of the various conditions of our spinning method, the Δn dependence of the elongation at break is represented by a curve within the precision of measurement (see Fig. 2).

The Δn dependence of other mechanical properties such as tensile strength (nominal), Young's modulus, yield stress, yield strain, and so on, is represented by a similar curve. Tensile strength (nominal) of polystyrene monofilaments increases monotonically with increasing $|\Delta n|$ in the range of $|\Delta n| \lesssim |-2 \times 10^{-3}|$ and $|\Delta n| \gtrsim |-2 \times 10^{-3}|$, and in the vicinity of $\Delta n = -2 \times 10^{-3}$, a transition point is faintly recognized (see Fig. 1). But true tensile strength (corrected for area of filament) would show a distinct discontinuous transition point in the vicinity of $\Delta n = -2 \times 10^{-3}$ since the cross sections of these monofilaments drastically decrease at this transition point with increase in elongation at break. Young's modulus increases monotonically as $|\Delta n|$ increases. Drastic influence of this transition does not appear in the vicinity of $\Delta n = -2 \times 10^{-3}$ (see Fig. 3). Since yield points have not been found in the range of $|\Delta n| \lesssim |-2 \times 10^{-3}|$, yield stress and yield strain are significant in the range of $|\Delta n| \gtrsim |-2 \times 10^{-3}|$ (see Figs. 4 and 5). Yield stress increases monotonically as $|\Delta n|$ increases in the range of $|\Delta n| \gtrsim |-2 \times 10^{-3}|$. Yield strain is constant or decreases rather slightly as $|\Delta n|$ increases from ca. $|-2 \times 10^{-3}|$. In Figure 4, tensile strength is plotted simultaneously in the range of $|\Delta n| \lesssim |-2 \times 10^{-3}|$. In Figure 5, elongation at break is plotted in the range of $|\Delta n| \lesssim |-2 \times 10^{-3}|$. It is interesting that these curves intersect each other at the transition point $\Delta n \cong -2 \times 10^{-3}$.

From the above observation, it turns out that this brittle-to-ductile transition of atactic polystyrene monofilaments is based upon amorphous orientation and occurs in the vicinity of $\Delta n = -2 \times 10^{-3}$

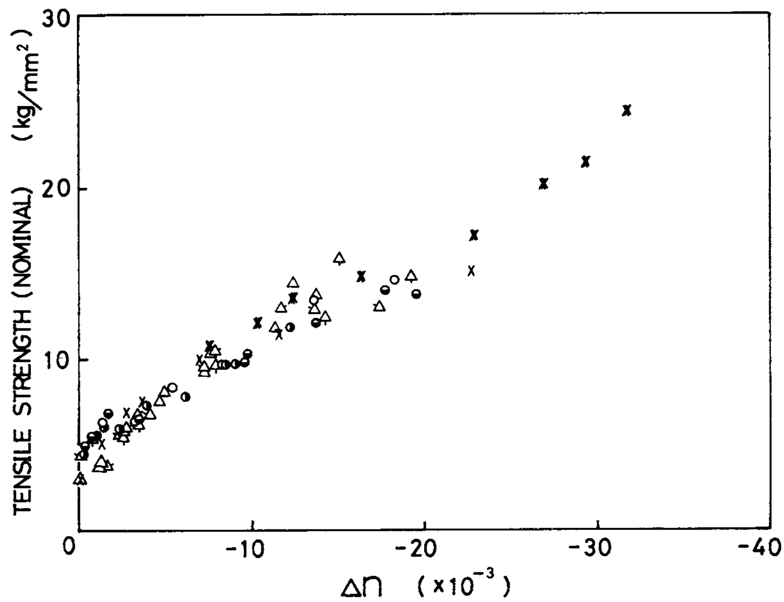

Fig. 1. Tensile strength (nominal) vs degree of birefringence (Δn) for oriented atactic polystyrene monofilaments under various spinning conditions. Symbols are shown in Table I.

at a stretching rate of 100%/min, temperature of 20°C, and relative humidity below 65%. But this transition has not been observed in the draft dependence of the degree of birefringence. This fact suggests that this transition is related more to the microscopic structure than to the range of light wavelengths.

The brittle-to-ductile transition of polystyrene monofilaments has been found in the investigation by Cleereman et al.[1] In their results, however, the position of this transition expressed by degree of birefringence depends strongly on the quenching and hot-stretching temperatures, and elongation at break of this point is several tens of percent lower than ours. Also, their monofilament sometimes had a milky appearance, which disappeared upon annealing the monofilament under low uniaxial tension.

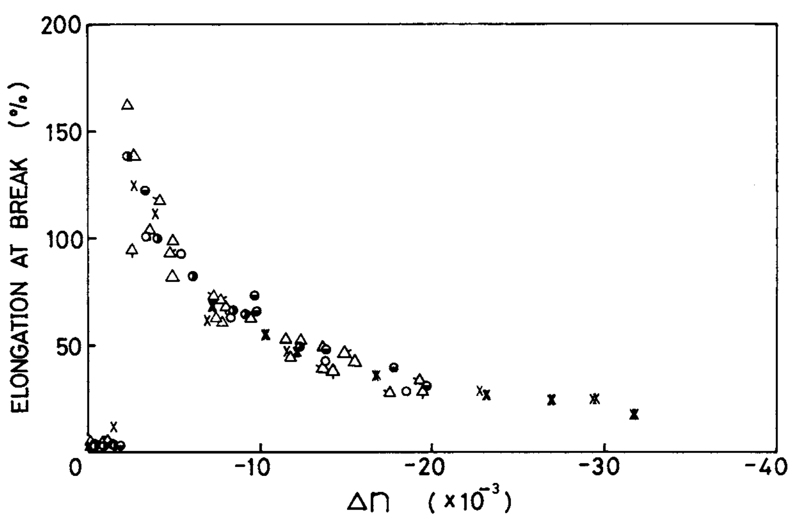

Fig. 2. Dependence of elongation at break (nominal) on degree of birefringence (Δn) of oriented atactic polystyrene monofilaments under various spinning conditions. Symbols are shown in Table I.

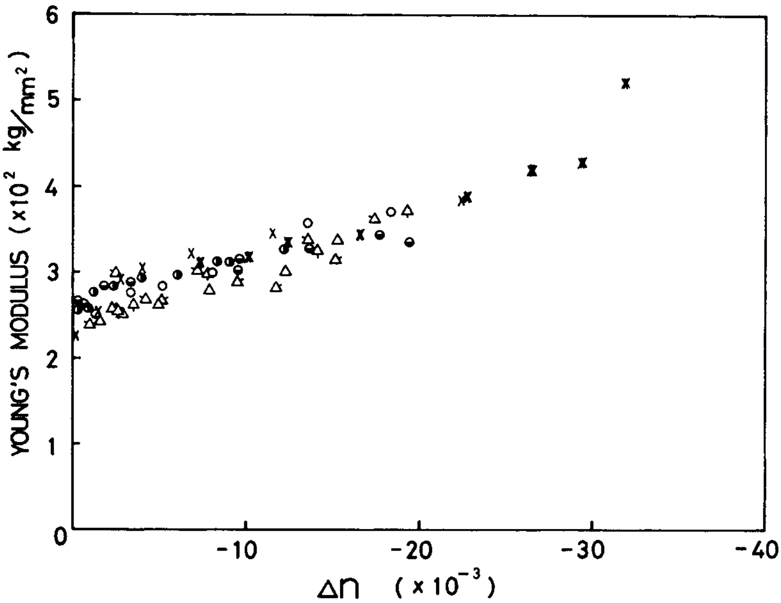

Fig. 3. Young's modulus vs degree of birefringence (Δn) for oriented atactic polystyrene monofilaments under various spinning conditions. Symbols are shown in Table I.

The range of our stress–strain curve measurement is narrower than that of Cleereman et al. Our spinning method is also different from their method. Accordingly, it should be noted that the fact that the brittle-to-ductile transition of polystyrene monofilament depends only on its birefringence is observed within limited conditions, and also that the transition point appears at $\Delta n \cong -2 \times 10^{-3}$ under the restricted conditions of a stretching rate of 100%/min, a stretching temperature of 20°C, relative humidity of below 65%, surrounding air, and so on. Our monofilament has no milky ap-

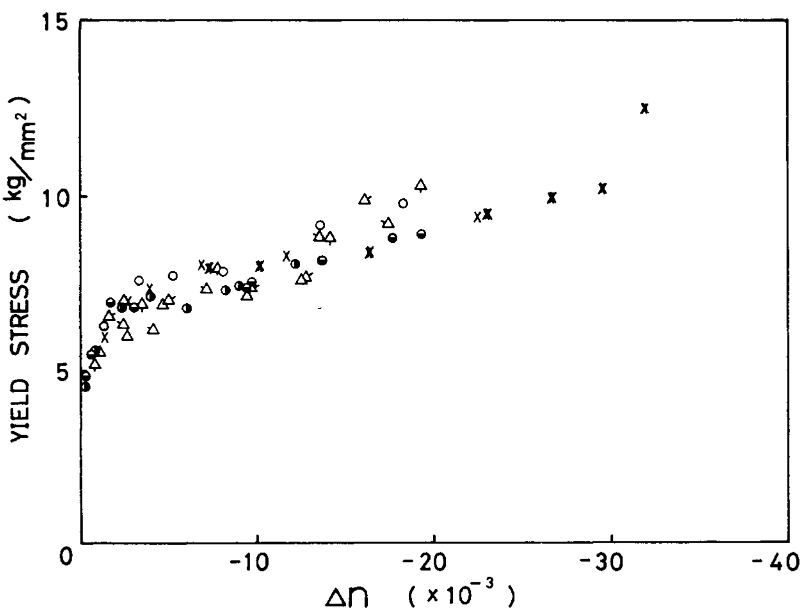

Fig. 4. Degree of birefringence (Δn) dependence of yield stress in ductile region and tensile strength in brittle region for oriented atactic polystyrene monofilaments. Symbols are shown in Table I.

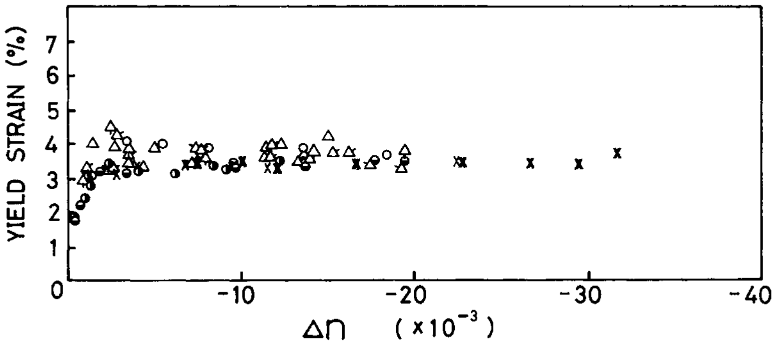

Fig. 5. Degree of birefringence (Δn) dependence of yield strain in ductile region and elongation at break in brittle region for oriented atactic polystyrene monofilaments. Symbols are shown in Table I.

pearance without any special annealing processes, and it is transparent under all spinning conditions.

These different results of polystyrene monofilaments are probably caused by the different processes of molecular orientation, which should be investigated in detail.

The authors are greatly indebted to T. Kurita for spinning of the polystyrene and also to Y. Maeda for the GPC curves of our samples. They also wish to thank the members of Polymer Physics Laboratory in this Research Institute for helpful discussions during the course of this work.

References

1. K. J. Cleereman, H. J. Karam, and J. L. Williams, *Mod. Plast.*, **30,** 119 (1953).

Y. TANABE

H. KANETSUNA

Research Institute for Polymers and Textiles
Kanagawa-ku, Yokohama 221, Japan

Received December 23, 1976
Revised July 7, 1977