

# Poly(ethylene-2,6-naphthalenedicarboxylate) Fiber for Industrial Applications

J. JAGER,\* J. A. JUIJN, C. J. M. VAN DEN HEUVEL, and R. A. HUIJTS†

Akzo Nobel Central Research, Location Arnhem, Velperweg 76, P.O. Box 9300, 6800 SB Arnhem, The Netherlands

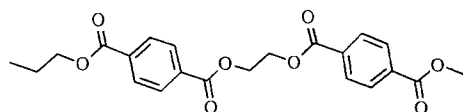
## SYNOPSIS

Poly(ethylene-2,6-naphthalenedicarboxylate)(PEN) has been prepared from commercial dimethyl-2,6-naphthalenedicarboxylate (DM-2,6-NDC) and ethylene glycol (EG) according to the well-known transesterification/polycondensation route. PEN fibers, intended for industrial yarn applications, were obtained by melt spinning and drawing high molecular weight PEN. The properties of these yarns were measured in detail and compared with those of PET industrial yarns. The development of molecular orientation in the spinline is more pronounced for PEN than for PET. Because the yield stress is lower, PEN yarns can more easily be drawn. Breaking tenacities of PEN yarns are comparable with those of PET yarns, but the modulus is much higher and the thermal shrinkage is lower. Therefore, PEN yarns have a better dimensional stability than PET yarns. In addition, it was demonstrated that the thermal resistance of PEN yarns is better. © 1995 John Wiley & Sons, Inc.

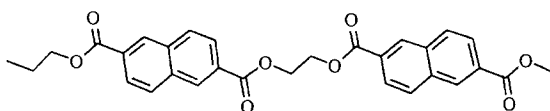
## INTRODUCTION

Poly(ethylene-2,6-naphthalenedicarboxylate) (PEN) is a new high-performance polyester that exhibits physical and chemical properties superior to those of poly(ethylene terephthalate) (PET). Structural formulae of both polymers are shown below.

PET



PEN



The naphthalene moiety in PEN provides stiffness to the linear polymer backbone, leading to improved thermal resistance, excellent mechanical properties, such as tensile properties and dimensional stability, and outstanding gas barrier characteristics. PEN has a DSC melting point that is about 10°C higher than that of PET (PEN: 265°C; PET: 255°C); the glass transition temperature is about 50°C higher than for PET (PEN: 125°C; PET: 75°C).<sup>1,2,3</sup> These properties make PEN an interesting material for investigating both the fiber spinning and drawing processes and the fiber properties.

PEN can be prepared from commercially available dimethyl-2,6-naphthalenedicarboxylate (DM-2,6-NDC) and ethylene glycol (EG) by means of an ester-interchange reaction to form a mixture of oligomers, followed by a polycondensation to obtain the PEN prepolymer. A separate solid-state post-condensation is required to achieve a high melt strength necessary for film extrusion or fiber spinning. The preparation of PEN was first described in 1948.<sup>4</sup> Later on, several other patents<sup>5-8</sup> were disclosed dealing with the preparation and applications of PEN. During these years, both the availability of the DM-2,6-NDC raw material and the price of the monomer were a major barrier for commercialization

\* To whom correspondence should be addressed.

† Present address: Akzo Nobel Coatings Research, P.O. Box 3, 2170 BA Sassenheim, The Netherlands.

of PEN. Recently, some chemical companies expressed their interest to scale up the preparation of the DM-2,6-NDC raw material.<sup>9,10</sup>

Like PET, PEN is a clear resin that can be used to produce films, containers, and industrial fibers. Detailed information on PEN films was recently given in the literature.<sup>11-14</sup> In the packaging resins area, PEN has excellent potential in hot-fillable and returnable refillable containers.

In this article, we present a detailed study on the preparation of PEN for industrial fiber applications. PEN fibers were prepared from high molecular weight PEN according to a melt-spinning process, followed by a fiber-drawing step. The properties of the resulting PEN yarns were measured and compared with those of PET industrial yarns. Thus, more insight into the characteristic features of PEN for industrial fiber applications was gained.

## EXPERIMENTAL

### Polymer Preparation

PEN polymer was produced on a standard 200 L polyester autoclave. A mixture of dimethyl-2,6-naphthalenedicarboxylate (DM-2,6-NDC, 48.0 kg) and ethylene glycol (EG, 32.0 kg) was transesterified by using manganese diacetate catalyst ( $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , 340 ppm) to give PEN oligomer. When the transesterification was finished at about 230°C, a phosphorous stabilizer (triethyl phosphonoacetate, 360 ppm) and an antimony trioxide polycondensation catalyst ( $\text{Sb}_2\text{O}_3$ , 250 ppm) were added. The oligomer was polymerized at 290°C by a standard procedure to a low-viscous PEN prepolymer with a relative solution viscosity of 1.540 (as measured on 1 g polymer in a solvent mixture of 60 g of phenol and 40 g of *o*-dichlorobenzene at 35°C). Postcondensation of the chips to high molecular weight PEN was carried out in the solid state by means of a tumble dryer for 14 h, under high vacuum, and at a granule temperature of 227°C. PEN chips with a relative solution viscosity of 1.915 were obtained. Chips were kept dry by storage in sealed bags.

In our study, a comparison is made with poly(ethylene terephthalate) (PET) having a relative solution viscosity of 1.850 (as measured on 1 g of polymer in 100 g of *m*-cresol at 25°C).

### Spinning

The spinning machine consisted of an electrically heated 30 mm extruder, adjusted at 310°C, which

fed the polymer melt at a pressure of 100 bar to a metering pump with a capacity of 2.25 cm<sup>3</sup> per revolution. The number of revolutions per minute (rpm) of this pump was adjusted to obtain the desired output. The spinning assembly was composed of a spin pack with 325 mesh gauzes (44 μm) as the finest filter medium, and a spinneret with 36 circular holes having a diameter of 400 μm and a l/d ratio of 1.6. The temperature of the metering pump and spinning assembly was maintained at 310°C. In one case, a 40 cm long tube, heated to a temperature of 354°C, was mounted directly under the spinneret. The yarn bundle was cooled with ambient air having a speed of 20–30 cm/s. A standard PET tire yarn finish was applied to the yarn. The winding speed was varied between 500 and 4000 m/min.

The PET chips were spun from a spinneret provided with 105 circular holes, each having a diameter of 500 μm, also with a l/d ratio of 1.6. The spinning temperature was 295°C; no hot tube was applied. In this case, the winding speed was varied between 500 and 5500 m/min. A more detailed survey of the spinning conditions is given in Table I.

### Drawing

Five PEN as-spun yarn bundles were assembled to give a drawn yarn with 180 filaments. Drawing was carried out in two stages. In the first stage, cold drawing, the yarn bundle was drawn on a hot metal pin (diameter 10 cm) wrapped once or twice. Proper adjustment of the drawing neck on the hot pin proved possible. To this end, the yarn was preheated to 115–120°C on a hot plate or on a hot roll, mounted closely before the draw pin. The optimum temperature of the draw pin was found to be 130–140°C. The draw ratio in the first stage was optimized by minimizing the number of broken filaments, as detected by a fluff counter. In the second stage, hot drawing, the yarn bundle was invariably drawn in hot steam at a temperature of 260°C in a 10 m long box. In this way, yarns with an elongation at break of 6–8% were produced. The winding speed during drawing was kept at 40–60 m/min.

In the case of PET, two yarn bundles were assembled to form a drawn yarn with 210 filaments. Drawing took place on a steamdrawing frame. Cold drawing was carried out on seven static pins at 75°C, whereas hot drawing took place in 250°C steam in a 10 m long box. Optimization of the draw ratio in the first stage was again carried out by detecting the minimum number of broken filaments. The total draw ratio was adjusted to impart to the drawn yarns an elongation at break of approximately 10%. The

**Table I Spinning and Drawing Conditions of PEN and PET**

	PEN	PET
Relative solution viscosity	1.915	1.850
Spinning:		
Spinning temperature (°C)	310	295
Number of spinneret holes	36	105
Hole diameter ( $\mu\text{m}$ )	400	500
Spinning speed (m/min)	500–4000	500–5500
Hot tube	in one case: 40 cm at 354°C, 700 m/min	none
Drawing:		
Number of filaments/bundle	180	210
Cold drawing:		
Preheating temperature (°C)	115–120	—
Pin temperature (°C)	130–140	75
Hot drawing:		
Steam temperature (°C)	260	250
Winding speed (m/min)	40–60	200
Yarn count (dtex)	900–1300	1100

yarns were wound at 200 m/min. Drawing conditions for PEN and PET are given in Table I also.

## Characterization

### *Tensile Measurements on PEN Yarns*

All measurements of thermal mechanical properties were performed on samples conditioned at 21°C and 65% relative air humidity. The linear density of the yarns was determined by weighing three lengths of 10 m of yarn and taking the average value. The filament count was measured with the aid of a vibroscope.

Load–elongation experiments were carried out on as-spun fibers in order to characterize the spinning speed influence. An Instron tensile tester with standard yarn grips was used. The gauge length of the yarn samples was 150 mm, the clamp speed amounted to 150 mm/min, and the pretension was 5 mN/tex. The data for each yarn are the average values of five repeated experiments. The as-spun yarn samples were not twisted. The apparent breaking tenacity, i.e., the maximum observed load divided by the initial linear density, the elongation at break, and the initial modulus were determined. The true tenacity was calculated according to the assumption of deformation at constant volume.<sup>15</sup>

Tensile experiments were carried out on as-spun PEN filaments at elevated temperatures in order to study the yield behavior of these fibers. The samples comprised yarns spun at 500 m/min up to 1000 m/min inclusive. Metal flat grips were used, the gauge

length was 40 mm, and the clamp speed amounted to 400 mm/min. The tensile tests were repeated five times on each type of filament at temperatures ranging from 90°C up to 160°C, with an increment of 10°C. A filament was clamped into the grips, and next the sample was more or less freely conditioned to the oven temperature. A pretension of 0.5 mN/tex was applied in order to calculate the stress–strain relations from the load–elongation curves. The yield stress was taken as the observed local maximum stress at an elongation of about 5%. The initial modulus was calculated from the slope of the first part of the stress–strain relation at an elongation of approximately 2%.

Load–elongation experiments were carried out on various drawn yarns in order to characterize their tensile properties. The yarns were twisted 90 turns per meter. Yarn grips were applied, a gauge length of 500 mm was used, the clamp speed was 500 mm/min, and a zero strain was defined by a pretension of 5 mN/tex. The data were averaged over five measurements for each type of yarn. Mechanical properties, such as breaking tenacity, elongation at break, and initial modulus, were obtained from the recorded load–elongation curves.

Tensile experiments were carried out at temperatures from room temperature up to 200°C in order to determine the thermal resistance of drawn PEN yarn relative to PET yarn. Three PEN yarns, spun at 700 m/min with and without a hot tube and at 4000 m/min, and two commercial PET yarns, Diolen 1125T and 2200T, were studied. An Instron dynamometer with oven was applied using standard grips. The gauge

length was 150 mm and the crosshead speed was 150 mm/min. The samples were more or less freely conditioned to the ambient temperature in the oven. Owing to this procedure some thermal shrinkage might have occurred. The load-elongation experiments were carried out five times on each yarn type.

### Dynamic Mechanical Analysis

Dynamic mechanical tests were carried out in the extension mode using a Qualimeter type Eplexor. The temperature dependence of the complex modulus of a representative drawn PEN yarn and a commercial PET yarn was measured over a range from  $-150$  to  $250^{\circ}\text{C}$ . The heating range was  $1^{\circ}\text{C}/\text{min}$ , the static strain was  $0.5\%$ , the dynamic strain was  $0.05\%$ , the frequency was  $60\text{ Hz}$ , and the hold force was  $5\text{ mN}/\text{tex}$ .

### Thermal Shrinkage

The yarn shrinkage in hot air (SHA) was measured on as-spun yarns. Skeins made at a tension of  $5\text{ mN}/\text{tex}$  with an initial length of about  $500\text{ mm}$  were given a tensionless heat treatment in hot air of  $190^{\circ}\text{C}$  for  $15\text{ min}$ . The shrinkage is equal to the relative decrease in skein length (averaged over three samples) after reconditioning. The hot air shrinkage (HAS) was measured on drawn yarns only. The hot air shrinkage is the relative decrease in length (approximately  $400\text{ mm}$ ) of the test specimen after  $4\text{ min}$  at a temperature of  $160^{\circ}\text{C}$  under a tension of  $5\text{ mN}/\text{tex}$ .

### X-Ray Diffraction

WAXS measurements were carried out in transmission on samples prepared by winding a smooth layer of yarn filaments around a metal frame. The vertical diffractometer (Philips) was equipped with a quartz monochromator, Soller slits, a divergence slit ( $1^{\circ}$ ), a scatter slit ( $0.2\text{ mm}$ ), a receiving slit ( $1^{\circ}$ ), and a sealed gas-filled detector PW1711/10. The X-ray source was a  $\text{CuK}\alpha$  tube with  $\lambda = 1.5418\text{ \AA}$ . The water-cooled PW1730/10 generator was operated at  $40\text{ kV} \times 40\text{ mA} = 1600\text{ W}$ . The diffractometer was coupled to a computer for collecting the data. The X-ray scans were fitted by means of Pearson functions.<sup>16,17</sup>

### Density

The density of the samples was determined at  $23^{\circ}\text{C}$  in a Davenport gradient column containing *n*-heptane and tetrachloromethane mixed in a ratio that

gradually decreased downwards. The density gradient was calibrated with floating balls of known density. The density measurements were carried out on three pieces of yarn that had been wetted and put into the column. After  $6\text{ h}$ , the density was calculated from their position in the column.

### Sonic Pulse Propagation

A piece of sample was clamped at one end, passed horizontally over a couple of pulleys, and loaded at the other end with  $2\text{ cN}/\text{tex}$ . Between the pulleys, two piezo-electric transducers were placed on the yarn for transmitting and receiving sonic pulses of  $60\text{ }\mu\text{s}$  long with a frequency of  $10\text{ kHz}$ . An oscilloscope was used to adjust the triggering of the pulses on a counter. The pulse propagation time through the yarn was measured in fivefold, with time intervals of  $15\text{ s}$  over a distance of  $120\text{ cm}$  and, subsequently, over a distance of  $40\text{ cm}$ . The difference in distance (being  $80\text{ cm}$ ) divided by the average difference in traveling time equals the sound velocity. The product of density and the squared velocity gives the sonic modulus of the yarn.

### Birefringence

Ten filaments, immersed in dibutyl phthalate, were positioned parallel between microscopic glasses and placed at an angle of  $45^{\circ}$  relative to the crossed polarizers of a microscope, which was equipped with a sodium lamp ( $\lambda = 0.5893\text{ }\mu\text{m}$ ) and a de Sénarmont compensator. At the ends of the filaments, which were cut on the bias, the overall difference of phase  $\phi$  was determined by measuring the number of fringes (including a partial fringe). For each filament, the birefringence was calculated by means of the formula  $\Delta n = (\phi/2\pi) * (\lambda/D)$ , where  $D$  is the diameter of the filament.

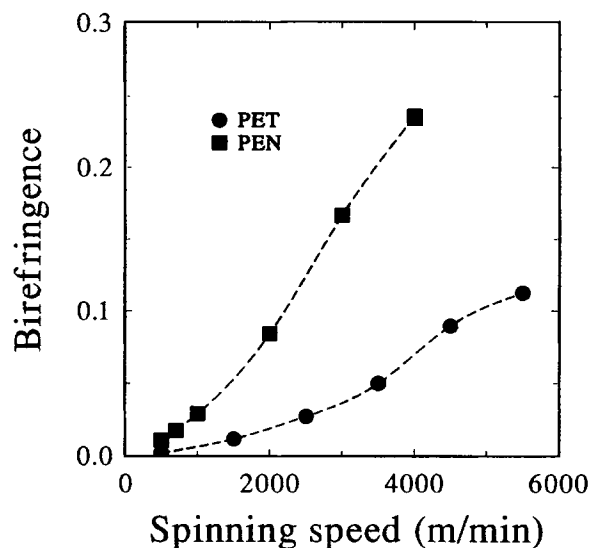
### Differential Scanning Calorimetry

Melting peaks of the yarns were determined with a Perkin-Elmer DSC-7 Differential Scanning Calorimeter by heating a cup containing the sample ( $3\text{--}4\text{ mg}$ ) at a heating rate of  $20^{\circ}\text{C}/\text{min}$ , and recording the heat flow difference between this cup and an empty reference cup.

## RESULTS AND DISCUSSIONS

### Spinning and Structural Aspects

The PEN chips could easily be spun at  $310^{\circ}\text{C}$ . The development of orientation with spinning speed was



**Figure 1** Birefringence of as-spun PEN and PET yarns as a function of spinning speed. Dashed lines are locally weighted regression fits.

followed by means of the birefringence of the as-spun yarns ( $\Delta n_{as}$ ). For PEN yarns, much higher values of the birefringence are measured than for PET yarns. These results are shown in Figure 1 and Table II.

For both polymers, an increase of the birefringence with the spinning speed is found, the increase being much stronger for PEN than for PET, how-

ever. At least partially, this difference must be attributed to the higher intrinsic birefringence of PEN, which is the result of the larger aromatic ring system. The values of the intrinsic birefringence of perfectly oriented crystalline and amorphous PEN are not yet known.<sup>18</sup> Therefore, the birefringence of a fully oriented yarn ( $\Delta n_o$ ), 0.487 for PEN and 0.244 for PET, was taken as the reference point. These scaling factors are obtained by correlating the birefringence with the absolute values of the orientational order parameters that are provided by polarized Raman scattering experiments for a range of PET and PEN fibers.<sup>19</sup> Values for the average orientation are given in Table II. Evidently, the orientation of PEN molecules, developed during spinning, is much higher than that of the PET molecules. Apparently, the slower relaxing PEN molecules<sup>20</sup> orient more effectively under the influence of spinline stress than the more flexible PET molecules do.

Just as for PET, the density of PEN increases with the average orientation (see Fig. 2). Unlike PET,<sup>21</sup> however, this was not attended with the formation of large crystals. Actually, the X-ray equator scans in Figure 3(a) show that, even at high spinning speeds, the present PEN samples do not contain large crystals [compared with the equatorial X-ray scan of drawn semicrystalline PEN yarn shown in Fig. 3(b)]. Possibly, the high-speed spun PEN yarns contain a substantial amount of crystallites, which

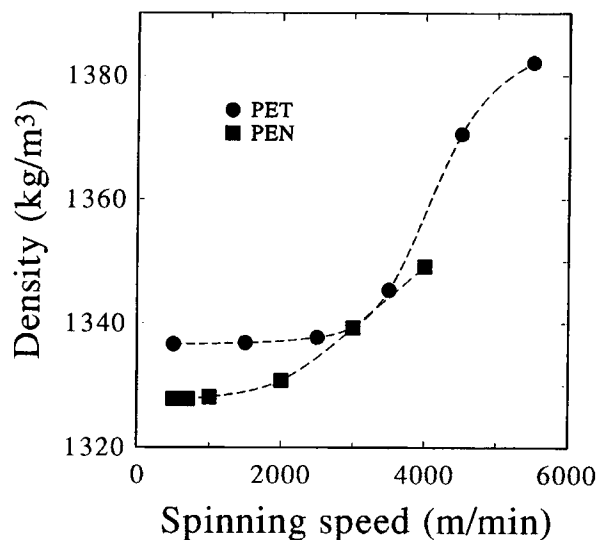
**Table II** Birefringence, Orientation, Density, and Thermal Shrinkage of PEN and PET Fibers Spun at Various Speeds

Spinning Speed (m/min)	Birefringence $\Delta n_{as}$	Orientation $\Delta n_{as}/\Delta n_o^a$	Density (kg/m <sup>3</sup> )	SHA <sup>b</sup> (%)
PEN:				
500	0.0107	0.022	1327.8	43.8
700	0.0172	0.035	1327.8	53.1
700 <sup>c</sup>	0.0074	0.015	1327.8	27.9
1000	0.0289	0.059	1328.1	60.9
2000	0.0842	0.173	1330.8	71.9
3000	0.1664	0.342	1339.2	69.4
4000	0.2357	0.484	1349.1	19.2
PET:				
500	0.0019	0.008	1336.6	
1500	0.0114	0.047	1336.8	
2500	0.0269	0.110	1337.7	
3500	0.0496	0.203	1345.3	
4500	0.0894	0.366	1370.5	
5500	0.1122	0.460	1382.1	

<sup>a</sup>  $\Delta n_{as}$  = birefringence of as-spun yarns,  $\Delta n_o$  = birefringence of fully oriented yarns. For PEN  $\Delta n_o$  = 0.487, for PET  $\Delta n_o$  = 0.244.

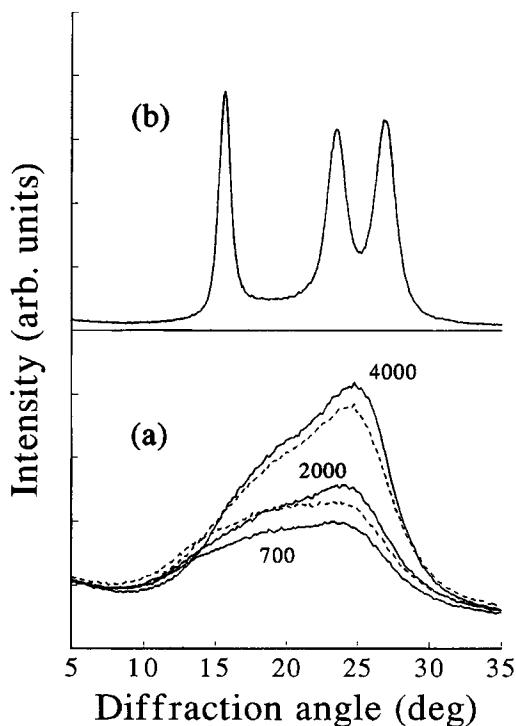
<sup>b</sup> SHA = shrinkage hot air.

<sup>c</sup> Hot tube applied.



**Figure 2** Density of as-spun PEN and PET yarns as a function of spinning speed. Dashed lines are locally weighted regression fits.

are too small to be detected by X-ray. Note that the melting point of a semicrystalline PEN yarn is much higher than that of the as-spun yarns (274°C vs. 265°C).



**Figure 3** (a) Equatorial X-ray diffractometer scans of as-spun PEN yarns as a function of spinning speed (700, 1000, 2000, 3000, and 4000 m/min from bottom to top). (b) Equatorial X-ray diffractometer scan of drawn semicrystalline PEN yarn.

**Table III** Drawing Data of As-Spun PEN and PET Fibers

Spinning Speed (m/min)	DR <sub>1</sub> <sup>a</sup>	DR <sub>total</sub> <sup>a</sup>	DR <sub>1</sub> /DR <sub>total</sub>
PEN:			
500	4.6	5.1	0.90
700	3.8	4.25	0.89
700 <sup>b</sup>	5.3	6.2	0.85
1000	3.3	3.6	0.92
4000	(1.2) <sup>c</sup>	1.3	(0.92) <sup>c</sup>
PET:			
500	4.02	5.70	0.71
1500	2.82	3.57	0.79
2500	2.15	2.55	0.84
3500	1.65	2.00	0.82
4500	1.30	1.72	0.76
5500	1.09	1.47	0.74

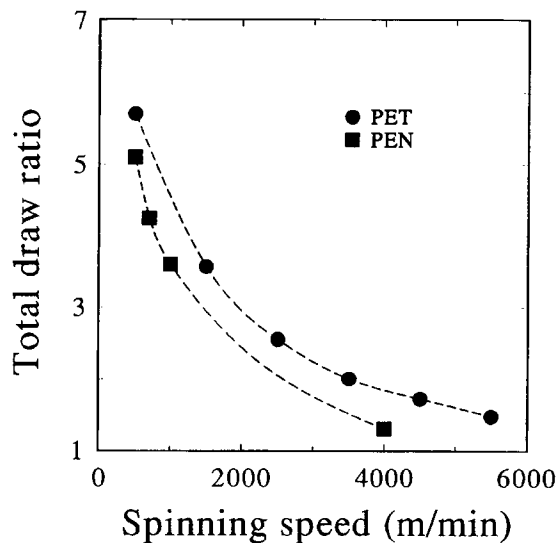
<sup>a</sup> DR<sub>1</sub> = cold draw ratio; DR<sub>total</sub> = total draw ratio.

<sup>b</sup> Hot tube applied.

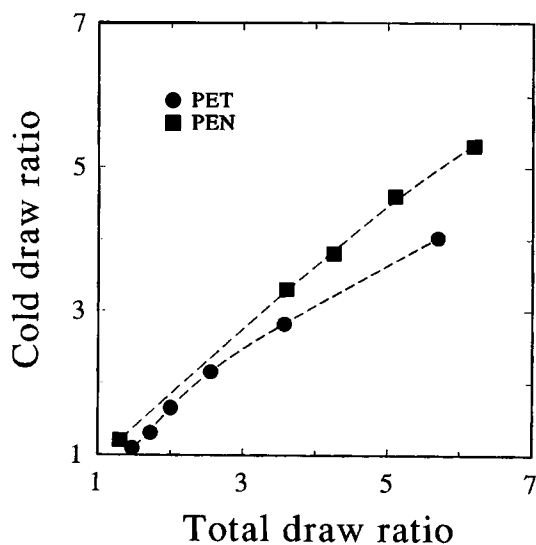
<sup>c</sup> Cold drawing was not really necessary; the preoriented partly crystalline yarn could immediately be drawn in hot steam.

### Drawing of As-Spun Yarns and Structural Aspects

Data on the drawing processes are shown in Table III. The total draw ratio is shown as a function of the spinning speed in Figure 4. The higher orientation of PEN in the as-spun yarns results in lower total draw ratios. The indicated total draw ratios resulted in drawn PEN yarns having an elongation at break of 6–8%. Drawing to an elongation at break of 10%—making the results more comparable with the PET



**Figure 4** Total draw ratio as a function of spinning speed for PEN and PET. Dashed lines are locally weighted regression fits.



**Figure 5** Cold draw ratio as a function of total draw ratio for PEN and PET. Dashed lines are locally weighted regression fits.

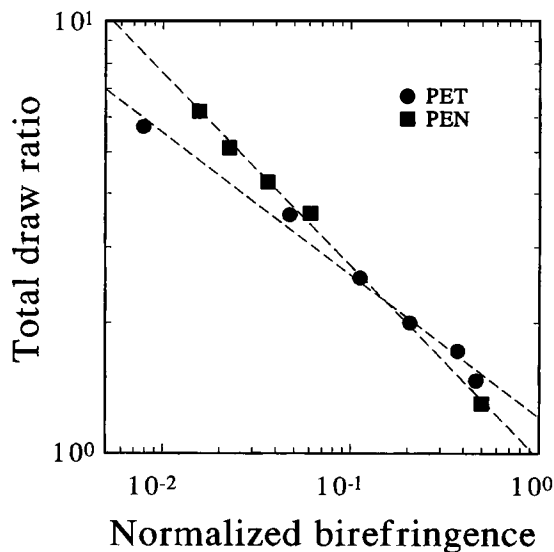
data—would have resulted in even lower draw ratios. Conversely, drawing PET to 6–8% elongation at break is almost impossible. Therefore, drawing without fluffs and breaks to low elongation at break values is much easier for PEN than for PET.

The drawing processes for PEN and PET have some remarkable differences. The first difference is that the cold draw ratio is so high for PEN. Approximately 90% of the total drawing of PEN takes place on the hot pin, whereas the total drawing of PET on this pin is approximately 70–80%. This behavior is illustrated in Figure 5. Secondly, pin drawing of PET takes place at 75°C, which is exactly the DSC glass transition temperature of this polymer. For PEN, the glass transition temperature, as measured by means of the DSC technique, is 125°C, but the temperature of the draw pin(s) must be higher, preferably 135°C. At too low temperatures, PEN yarn gets a milky appearance, the number of broken filaments is high, and the resulting tenacity is low. The nature of the milky appearance was not studied, but crazing or void formation is a possible cause. Even if the pin temperature is set at 135°C, drawing does not yet proceed without complications. The as-spun PEN yarn has a tendency to neck when contacting the hot pin, while the temperature is still too low. Smooth drawing, with a correct positioning of the neck on the draw pin, was only achieved if the yarn had been preheated to 115–120°C just before the pin. A slight predrawing of the yarn on the preheated roll or hot plate is then observed. Drawing tensions are lower for PEN than for PET. Almost indepen-

dent of the spinning speed drawing tensions of 100–140 mN/tex after the pin were measured for PEN, whereas the tension of PET varied between 150 and 200 mN/tex. Also, in a second drawing step, in hot steam the drawing tensions were lower for PEN: 100–120 mN/tex, as against 180–220 mN/tex for PET. Tension measurements were made with a Schmidt DTM-4K apparatus, having a range up to 4000 cN.

The observed higher as-spun orientation (birefringence) and lower draw ratio of PEN, when compared with those of PET, are, of course, interrelated. When the total draw ratio ( $DR_{total}$ ) is plotted as a function of birefringence in a double logarithmic plot, there seems to be a difference between PEN and PET. However, as mentioned before, PEN has a much higher intrinsic birefringence. Therefore, the birefringence was normalized, using the birefringence values for fully oriented PEN and PET yarns. The new relation, illustrated in Figure 6, shows small differences, albeit higher draw ratios are found for PEN at a low birefringence level.

On hot drawing, the physical structure of the as-spun PEN yarns changes dramatically. The orientation increases substantially and so-called  $\alpha$ -crystals<sup>22</sup> are formed. In contrast with the above-mentioned as-spun yarns, the equatorial X-ray scans of drawn semicrystalline PEN yarns perform sharp reflection peaks of  $\alpha$ -crystals (see Fig. 3). A number of structural parameters of a fully drawn PEN and a PET yarn are summarized in Table IV. From these data, it follows that the crystal size, the crystallinity,



**Figure 6** Total draw ratio as a function of the normalized birefringence for PEN and PET. Dashed lines are locally weighted regression fits.

**Table IV Physical Properties of Fully Drawn PEN and PET Yarns<sup>a</sup>**

	PEN	PET
Density (kg/m <sup>3</sup> )	1365.4	1402.3
Crystal density (kg/m <sup>3</sup> )	1405	1502
Crystalline fraction	0.38	0.37
Crystal size (Å <sup>3</sup> · 10 <sup>-5</sup> )	5.0	4.2
Crystalline orientation	0.99	0.98
Birefringence	0.3430	0.1823
Sonic modulus (GPa)	40.2	18.9
Amorphous orientation factor	0.85	0.78
Melting point (°C)	274	248/254

<sup>a</sup> For a detailed description of the calculation of the structure parameters, we refer to refs. 16 and 17.

and the crystalline orientation are about the same for drawn PEN and PET yarns. However, the amorphous orientation factor of PEN is higher, which leads to a higher modulus of the drawn PEN yarns.

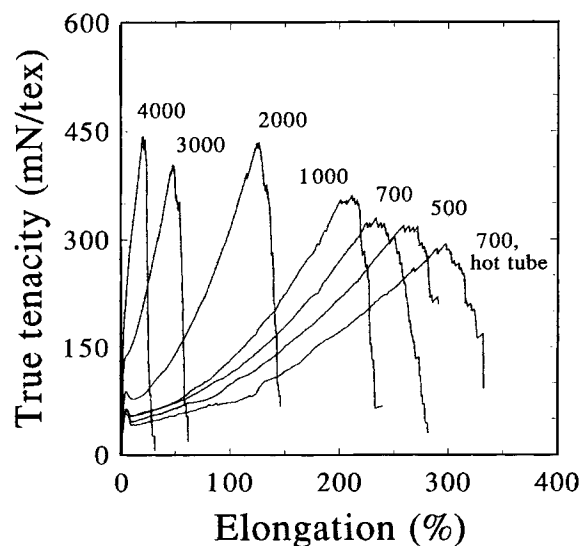
#### Mechanical Properties of As-Spun PEN Yarns

Load–elongation curves typical of as-spun PEN materials are shown in Figure 7. This figure illustrates the large effect of spinning speed on the tensile response of the as-spun PEN fibers. Increasing the spinning speed results in an increase in (true) breaking tenacity, and in a decrease of the elongation at break. Rupture of the yarn samples is not so pronounced, due to the small number of filaments in the yarn. A distinct yield point is observed for spinning speeds up to 3000 m/min. The yield stress increases with increasing spinning speed. A hot tube causes an extended load–elongation curve. The values for the shrinkage in hot air of the as-spun PEN yarns are provided in Table II as a function of the spinning speed. The shrinkage increases up to about 70% in the range of 2000 to 3000 m/min, and decreases to about 20% at 4000 m/min. Application of a hot tube lowers the shrinkage.

The molecular orientation (from birefringence data) of the as-spun PEN yarns increases with the spinning speed, as a result of which the modulus and tenacity of the as-spun PEN yarns become higher. Up to 2000 m/min the shrinkage increases also, because oriented amorphous molecules have a stronger tendency to coil at elevated temperatures. At 2000 m/min, however, the shrinkage passes through a maximum (see Table II). This maximum coincides with the strong increase in density (see Fig. 2), which is probably due to the formation of

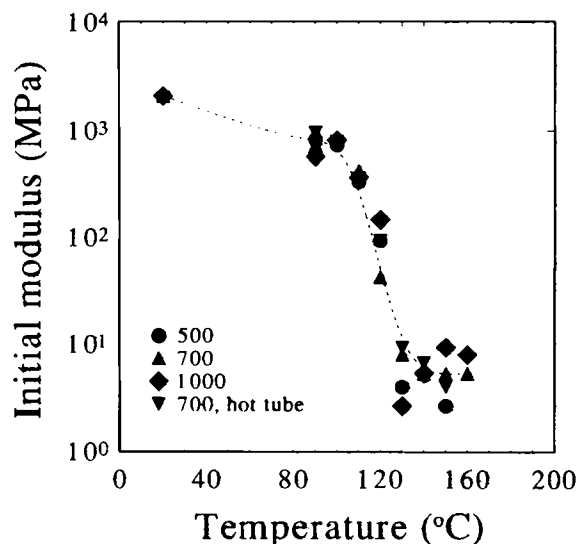
crystallites. These crystallites will act as crosslinks, which hinder the coiling of the oriented amorphous molecules. This phenomenon is also known for as-spun PET yarn.<sup>21,23</sup>

The temperature variation of the stress–strain relations of the PEN yarns spun at speeds ranging from 700 m/min up to 1000 m/min inclusive has been investigated. Results are presented elsewhere in more detail.<sup>24</sup> At the lowest temperatures, the stress–strain curve shows a clear yield point and a subsequent decrease in conventional stress. This means that necking and cold drawing take place. The yield stress diminishes up to 130°C. From this temperature and over, the stress–strain curves display rubber-like behavior. From the change in the shape of the load–elongation curve it is concluded that the glass transition temperature is in between 120 and 130°C. The temperature variation of the initial modulus of the four different PEN fibers spun at the lowest speeds is provided in Figure 8. A sharp decrease in modulus is observed between 110 and 130°C. The temperature dependence of the modulus and the decrease of about three orders of magnitude are characteristic of the glass–rubber transition. In addition, the variation in yield stress is found to decrease (linearly) in the temperature range from 90 to 120°C. From these experimental results it can be concluded that the glass transition temperature is about 125°C. This value is in very good agreement with the transition temperature found from DSC experiments. On the basis of the above indication, the appropriate temperature for drawing on hot pins is expected to be in the range of about 120 to 130°C.



**Figure 7** True stress–strain curves of as-spun PEN yarns; spinning speeds as indicated.





**Figure 8** Temperature variation in the initial modulus of amorphous as-spun PEN filament. Spinning speeds (m/min) as indicated. Dashed line connects data points for 700 m/min.

A slightly higher pin temperature (135°C), indeed, gave good drawing results. Quite remarkable is the low yield stress of PEN compared with that of PET. The yield stress of PEN is about twice as low as that of PET. Due to the low yield stress, the drawing process of PEN yarn is more critical to handle than that of PET fibers. This result agrees with the observed tensions for PEN and PET during drawing experiments. The difference between the yield behavior of PEN and PET yarn may originate from the stiffer chain of PEN. The following picture may apply. PET molecules resemble boiled spaghetti strands, whereas PEN molecules behave more like raw spaghetti. Spaghetti strands slide more easily along each other before boiling than after boiling because of the higher number of entanglements in the latter case. The same stiffness might favor orientational ordering of PEN molecules, which is, indeed, observed (see Table II). The suggested difference in number of entanglements between PET

and PEN also explains qualitatively the observed higher cold draw ratio of PEN (at the same spinning speed).

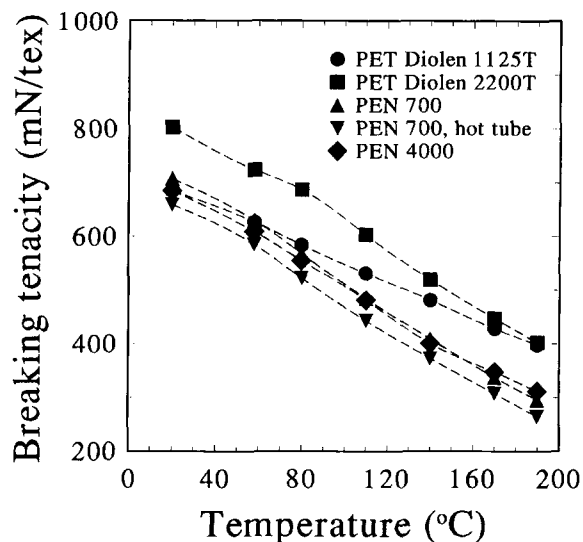
### Mechanical Properties of Drawn Yarns

PEN yarns with varying mechanical properties were obtained by changing the applied (total) draw ratio. Increasing the draw ratio leads to higher breaking tenacities up to about 800 mN/tex, to lower elongations at break down to about 4.5%, and to higher initial moduli up to about 23 N/tex. For the sake of simplicity, we prefer to compare the mechanical properties of PEN yarns spun under different conditions with an elongation at break of 6% instead of comparing series of fully drawn yarns. By interpolating the data we obtained the values of the breaking tenacity, initial modulus, and hot air shrinkage for a PEN yarn with an elongation at break of 6%. The value of 6% is approximately in the middle of the elongation at break region covered by our drawing experiments. The mechanical properties of PEN yarns spun at 700 m/min without and with a hot tube and at 4000 m/min are compared in Table V. The application of a hot tube (at 700 m/min) increases the breaking tenacity and initial modulus, whereas the hot air shrinkage remains equal for both conditions. Raising the spinning speed from 700 m/min to 4000 m/min (without hot tube) slightly decreases the breaking tenacity and initial modulus, and lowers the level of the hot air shrinkage. Consequently, breaking tenacities that are equal to or slightly less than those obtained for PET yarn can be attained for PEN yarn, but the corresponding value of the elongation at break is lower for PEN than for PET yarn. The initial modulus of drawn PEN yarns is about twice as high as that for PET yarn (e.g., about 10 N/tex for Diolen 2200T or Diolen 1125T). The thermal shrinkage of PEN yarns is only half or even less than that of commercial PET yarns spun at the same speed. It is concluded that the dimensional stability of PEN

**Table V** Mechanical Properties of PEN Yarns Spun under Different Conditions, the Elongation at Break Being 6%

Spinning Speed (m/min)	Breaking Tenacity (mN/tex)	Initial Modulus (N/tex)	Hot Air Shrinkage (%)
700	580	17.2	2.30
700*	670	19.0	2.28
4000	560	16.8	2.09

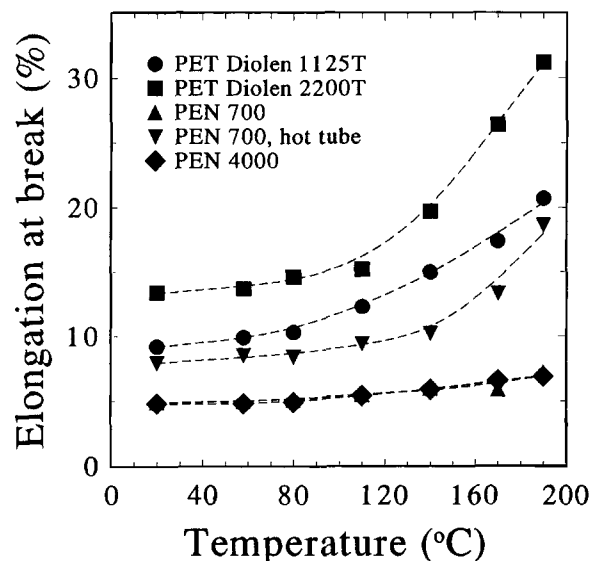
\* Hot tube applied.



**Figure 9** Temperature variation in breaking tenacity of some PEN and PET yarns. Dashed lines are locally weighted regression fits.

yarn exceeds the stability of PET yarns as a consequence of the much higher initial modulus and the much lower thermal shrinkage of PEN yarn. Variation of spinning speed seems to affect the properties, e.g., the hot air shrinkage, of drawn PEN yarns much less than those of PET yarns. Again, the observed difference between the properties of drawn PEN and PET yarns may be attributed to the stiffer chain of PEN.

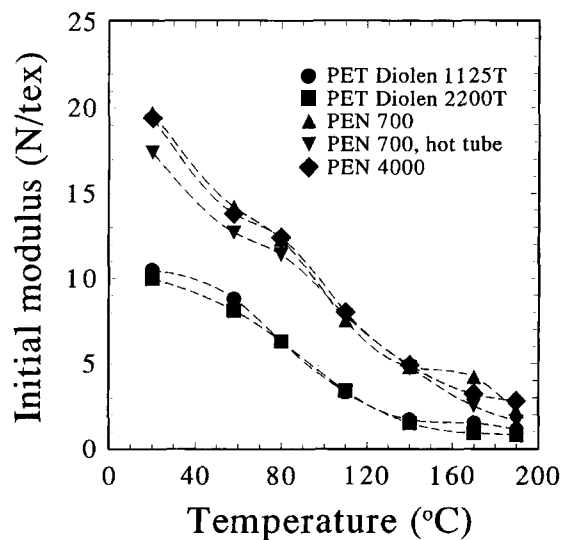
The temperature dependence of some tensile properties of both PEN and PET yarns is illustrated in Figures 9–11. Three representative drawn PEN yarns and two commercially available PET yarns (Diolen 1125T and Diolen 2200T) were selected. Figure 9 shows that the breaking tenacity of all the yarns decreases with increasing temperature. The relation between breaking tenacity and temperature is nearly linear. The relative decrease in breaking tenacity from 20°C to 190°C is slightly larger for PEN than for Diolen 2200T, *viz.* about 58% and 50%, respectively. The smallest decrease (42%) is obtained for the high-modulus low-shrinkage PET yarn Diolen 1125T. The yarns break at a higher elongation at higher temperatures (see Fig. 10). The PEN yarns spun without a hot tube exhibit a minor increase in elongation at break. The increase is much higher for the PEN yarn spun with a hot tube and for the PET yarns. The initial modulus of the PEN yarns is higher than that of the PET yarns over the entire temperature range from 20°C to 200°C (see Fig. 11). The modulus decreases with increasing temperature. At 190°C, the modulus value of the



**Figure 10** Temperature variation in elongation at break of some PEN and PET yarns. Dashed lines are locally weighted regression fits.

PEN yarns is approximately 12% of the value at room temperature, whereas a relative value of about 9% is obtained for the PET yarns. The temperature dependence of the breaking tenacity, elongation at break, and initial modulus illustrate as a whole the better thermal resistance of the PEN yarns than of the PET yarns.

The temperature variation of the (complex) modulus obtained by dynamic mechanical experiments is shown in Figure 12 for a drawn PEN yarn



**Figure 11** Temperature variation in initial modulus of some PEN and PET yarns. Dashed lines are locally weighted regression fits.

that was spun at 1000 m/min and a commercial PET yarn, Diolen 1125T. The storage modulus and the loss factor  $\tan \delta$  ( $\tan \delta = E_2/E_1$ , where  $E_2$  is the loss modulus and  $E_1$  the storage modulus) are given as a function of temperature in Figure 12. The storage modulus of the PEN yarn is (about 1.5 times) higher than for Diolen 1125T. As expected, the storage modulus decreases with increasing temperature. The  $\alpha$ -relaxation of PEN and PET are found at approximately 175°C and 140°C, respectively. The  $\beta$ -relaxations are found at about 70°C and -40°C for PEN and PET. The observed difference in temperature dependence of the dynamic modulus of the PEN and PET yarn illustrates that the stiffness of the naphthalene moiety in PEN is higher than the stiffness of the phenyl moiety in PET.

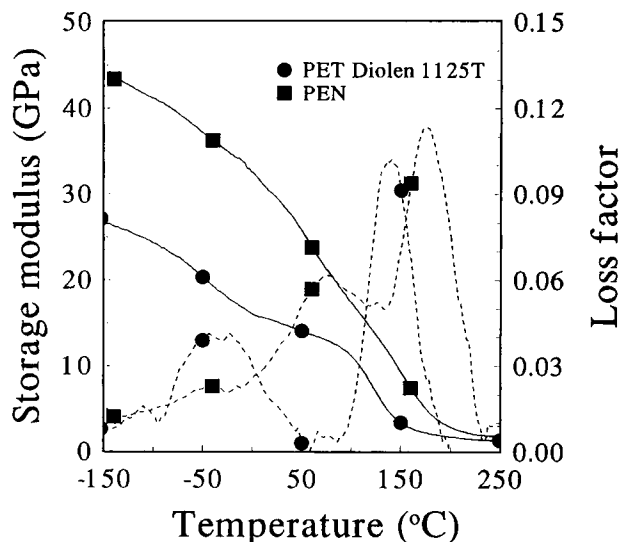
In summary, spinning and drawing of PEN is analogous to PET apart from the higher temperatures. Mechanical and thermal properties of PEN yarns are equivalent to or better than those of PET. Consequently, PEN yarns are very competitive with PET yarns with respect to performance. However, the high cost price of the PEN monomer has so far made the price/performance ratio too high for industrial fiber applications.

## CONCLUSIONS

The spinning process of PEN resembles that of PET. The orientation in the spinline is more pronounced for PEN than for PET at the same spinning speed. Measurements of stress-strain relations and initial modulus of low-speed as-spun PEN fibers indicate a glass-rubber transition temperature at about 125°C, which is about 50°C higher than that of amorphous PET. The yield stress of PEN fibers is about twice as low as that for PET. Consequently, PEN yarn can more easily be drawn in the first step of the drawing process. Also, in the subsequent hot drawing step, the drawing tension is relatively low, yet results in high modulus yarns.

Breaking tenacities of PEN yarns can be obtained at the same level as that of PET yarns, albeit at a lower elongation at break. The thermal shrinkage of PEN yarns is lower and the initial modulus is higher than that of PET yarns. Consequently, PEN yarns have a better dimensional stability than PET yarns.

Elevated temperatures up to about 200°C have a less negative effect on mechanical properties, such as breaking tenacity, elongation at break, and initial modulus, of PEN yarn than on those of PET yarn.



**Figure 12** Temperature variation in storage modulus (solid line) and in loss factor  $\tan \delta$  (dashed line) at 10 Hz of a drawn PEN yarn and PET Diolen 1125T yarn.

Therefore, the thermal resistance of PEN yarns is better.

## REFERENCES

1. S. Buchner, D. Wiswe, and H. G. Zachmann, *Polymer*, **30**, 480 (1989).
2. S. Z. D. Cheng and B. Wunderlich, *Macromolecules*, **21**, 789 (1988).
3. S. Z. D. Cheng and B. Wunderlich, *Thermochim. Acta*, **134**, 161 (1988).
4. J. G. Cook, H. P. W. Huggill, and A. R. Lowe (ICI), BP 604,073 (1948).
5. I. Hamana, Y. Fujiwara, and S. Kumakawa (Teijin Ltd.), BP 1,445,464 (1976).
6. I. Hamana, Y. Fujiwara, and S. Kumakawa (Teijin Ltd.), US 4,001,479 (1977).
7. K. Yamamoto, H. Niimi, and N. Kumura (Mitsui Petrochem. Ind., Ltd.), EP 0,383,324 (1990).
8. H. Wakumoto and T. Yatsu (Mitsui Petrochem. Ind., Ltd.), EP 0,394,751 (1990).
9. *Chem. Marketing Reporter*, July 12, 1993.
10. *Chem. Week*, 7 (March 6, 1991).
11. S. Z. D. Cheng, J. J. Janimak, A. Zhang, J. Guan, and A. L. Chu, *Polym. Bull.*, **20**, 449 (1988).
12. I. Ouchi, H. Aoki, S. Shimotsuna, T. Asai, and M. Hosoi, *Proc. 17th Jpn Congr. Mater. Res.*, 217 (1974).
13. M. Cakmak, Y. D. Wang, and M. Simhambhatla, *Polym. Eng. Sci.*, **30**, 721 (1990).
14. M. Ito, K. Honda, and T. Kanamoto, *J. Appl. Polym. Sci.*, **46**, 1013 (1992).

15. See, e.g., I. M. Ward, *Mechanical Properties of Solid Polymers*, 2nd ed., Wiley and Sons, Chichester, 1983, p. 332.
16. R. Huisman and H. M. Heuvel, *J. Appl. Polym. Sci.*, **37**, 595 (1989).
17. H. M. Heuvel and R. Huisman, *J. Appl. Polym. Sci.*, **30**, 3069 (1985).
18. C. J. M. van den Heuvel, experiments in progress.
19. R. A. Huijts and S. M. Peters, *Polymer*, **35**, 3119 (1994).
20. W. J. Jackson, *Macromolecules*, **16**, 1027 (1983).
21. H. M. Heuvel and R. Huisman, *J. Appl. Polym. Sci.*, **22**, 2229 (1978).
22. Z. Mencik, *Chem. Prum.*, **17**, 78 (1967).
23. S. D. Long and I. M. Ward, *J. Appl. Polym. Sci.*, **42**, 1921 (1991).
24. R. A. Huijts and A. J. de Vries, *Int. J. Polym. Mater.*, **22**, 231 (1993).

Received January 31, 1995

Accepted March 8, 1995