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High strength and high modulus fibers of poly(p-xylylene)

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Summary

High strength and high modulus fibers of poly(p-xylylene) (PPX) were obtained by drawing of as-polymerized films (molecular weight 5×10^5) at 420 ^{0}C in the conformationally disordered β_2 phase. Fibers of PPX have been obtained having a tensile strength at break of 3.0 GPa, a Young's modulus of 102 GPa and a strain at break of 3 %. The theoretical strength of PPX was calculated to be 23 GPa.

Introduction

The generation of ultra-high strength and ultra-high modulus fibers of polymers has been subject to extensive research for many years. Essentially two different classes of polymers have been used to achieve these properties: flexible and rigid chain polymers.

Flexible chain polyethylene of ultra-high molecular weigth ($\sim10^6$) can be gel-spun and subsequently hot-drawn, resulting in fibers having high performance mechanical properties (1). Using ultra-high molecular weigth polyethylene in solutions of low concentrations reduces the number of topological defects in the gel-spun fiber, leading to improved tensile properties. However, a minimum number of molecular entanglements is required in order to constitute a network having good chain-extendibility.

Of the rigid chain polymers, poly(p-phenylene terephtalamide) (PPTA) has deserved most interest. It exhibits lyotropic behaviour and fibers having high performance tensile properties can be spun from a nematic solution of high concentration of low molecular weigth PPTA in sulfuric acid (2). Such fibers are likely to contain mostly defects due to chain ends, but are non-drawable due to strong hydrogen bonding between adjacent chains in the crystal lattice.

From this point of view, we decided to examine the possible mechanical properties of a semi-rigid chain polymer. PPX then deserves special attention. It was first prepared by Szwarc (3) by pyrolysis of p-xylene, and by now can be readily prepared in relatively high molecular weight by the method of Gorham (4). The crystallization upon polymerization, crystal structure and thermal behaviour have been extensively studied by Wunderlich and co-workers (5,6,9,10). Semicrystalline PPX exhibits a glass transition at 13 ^{0}C; crystalline PPX melts at 427 ^{0}C. PPX has been shown to possess three crystalline polymorphs: the lower temperature crystals of the α polymorph change at 231 ^{0}C to the β_1 polymorph, then, at 287 ^{0}C to the β_2 polymorph (5). The crystal structures of both the α and the β form have been eludicated (6,7). Both the β_1 and β_2 polymorphs are assumed to be conformationally disordered (condis) crystals. Esspecially the high temperature β_2

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polymorph can be expected to have considerable freedom of motion between the different conformations (5), and has been shown to allow creep in studies by Niegisch (8).

Considering these thermal properties, it seemed of interest to examine the mechanical properties of PPX fibers, drawn from as-polymerized films at temperatures below the melting point, in the β_2 phase region.

As a consequence of the polymerization process at low temperatures, as-polymerized films of PPX can be expected to contain only a relatively small number of crystal defects like molecular entanglement-type if any. Upon drawing in the β_2 condis phase the number of defects might be decreased more easily, due to the considerable freedom of motion of the chains, than for example in drawing of polyethylene fibers below the melting point. These advantages are counterbalanced, however, by the fact that thermal degradation of PPX already takes place just above the melting point (5) and from that it is likely that degradation may already occur under stress below the melting point, having negative effects on mechanical properties of the drawn fibers.

Experimental

PPX specimens (Parylene N, MW 5×10^5) were kindly supplied to us by Union Carbide Co..

The as-polymerized film, prepared by the Gorham method (4), was cut into ribbons of 2.0 x 30.0 mm size. The initial film was about 35 µm thick. The ribbons were clamped at either side in aluminum clips attached to wires and were lead into a tubular oven at a selected temperature through a glass tube. A nitrogen stream was let in at the entrance of the glass tube to prevent degradation due to presence of oxygen. The velocity of the ribbon entering the oven was 25 mm/min. Drawing was accomplished by means of increasing the speed of the wind-up drum, whereas the speed of the wind-off drum remained unchanged.

After drawing the ribbon was cut into fibers of 45 mm in length. Actual draw ratios and cross-sectional areas of the fibers were calculated from weight and length. The density was taken to be the theoretical density of the β form of 1158 kg/m^3 (7), since the α to β transition is irreversible unless annealing in the β_2 phase region for a long period of time had been performed (5,9).

Tensile tests were performed using an Instron 4301 tensile tester at a cross-head speed of 7.2 mm/min and a sample length of 15 mm at 20 ^{0}C.

Results and discussion

The as-polymerized PPX films consisted of folded chain crystals of the α form. It has been shown that these lamellar crystals are preferentially oriented with the (010) plane parallel to the film surface (10).

Tensile testing of the as-polymerized film revealed relatively poor mechanical properties: a tensile strength at break of 40 MPa and a Young's modulus of 3.2 GPa. In a typical stress-strain curve of this material, stress increases up to a strain of 2 %, then abruptly levels off, whereas fracture occurs at 6.5 % strain. Optical polarizing microscopy of the drawn film showed lense-shaped crazes containing birefringent material that exhibited extinction between crossed polarizers along the drawing direction (see fig. 1). Inspection of the fracture surfaces showed that breakage had occured in such crazes.

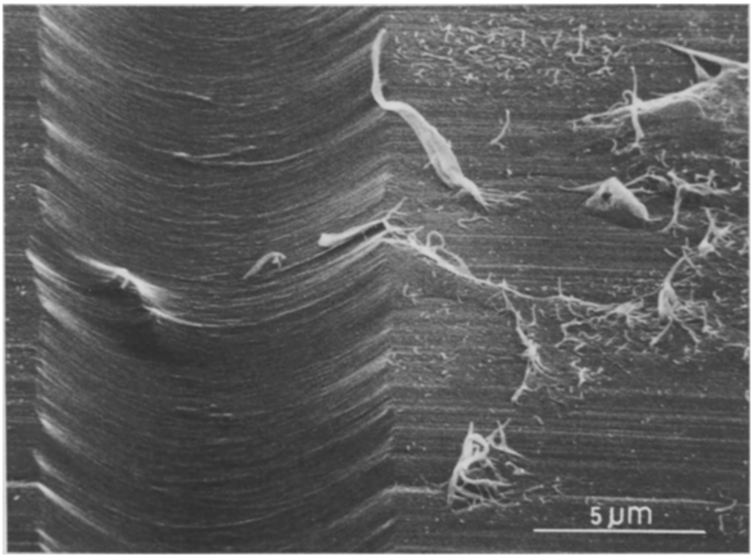

Fig. 1. SEM-micrograph of a cold-drawn as-polymerized PPX film.

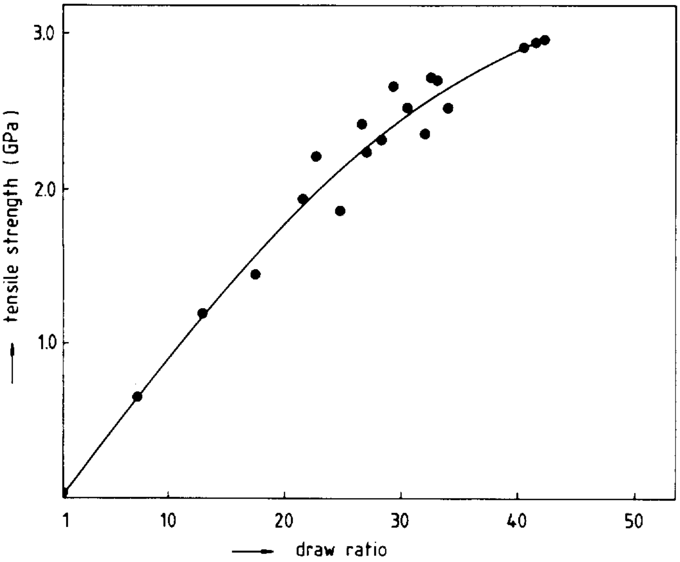

Fig. 2. Tensile strength at break versus draw ratio of fibers drawn at 420 °C.

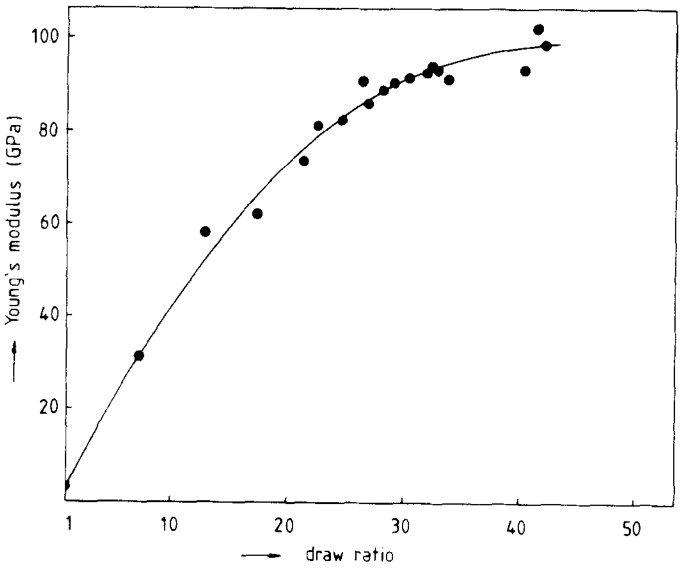

Fig. 3. Young's modulus versus draw ratio of fibers drawn at 420 °C.

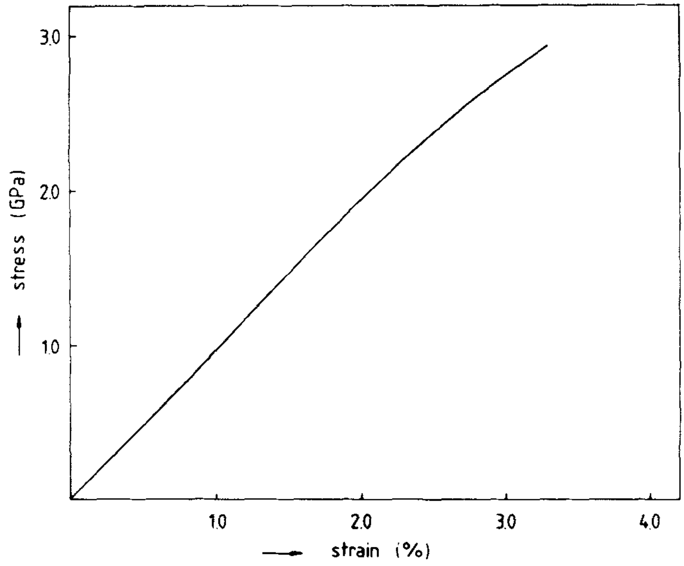

Fig. 4. Stress-strain curve of a fiber drawn at 420 °C to a draw ratio of 43.

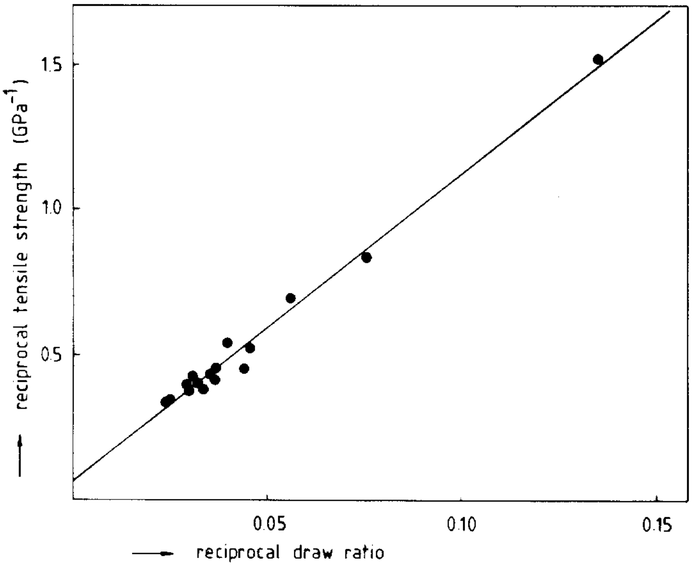

Fig. 5. Reciprocal tensile strength at break versus reciprocal draw ratio of fibers drawn at 420 °C.

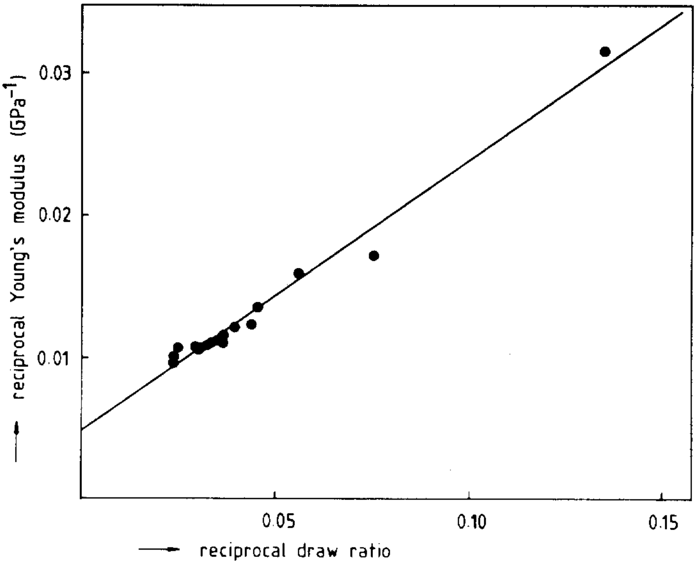

Fig. 6. Reciprocal Young's modulus versus reciprocal draw ratio of fibers drawn at 420 °C.

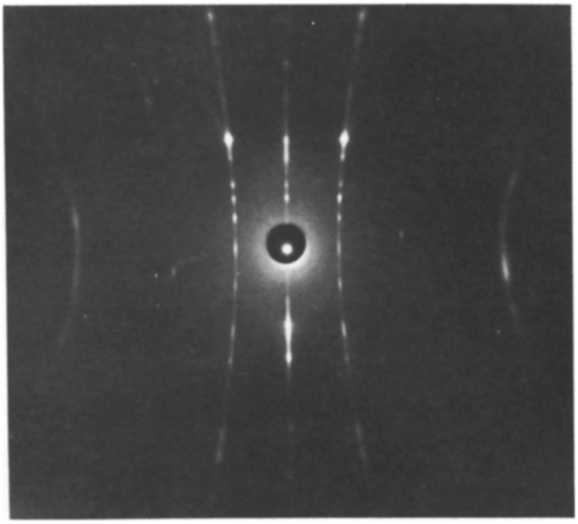

Fig. 7. WAXS-pattern of a fiber drawn at 390 °C to a draw ratio of 36.

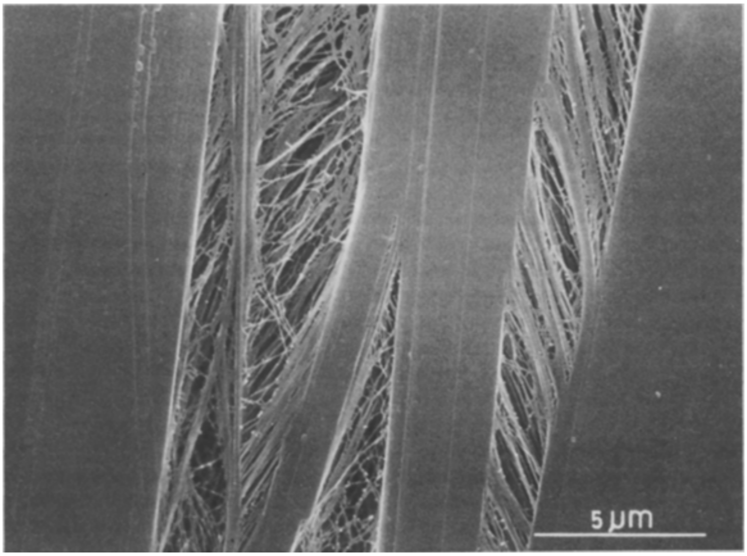

Fig. 8. SEM-micrograph of a tensile tested fiber drawn at 390 °C to a draw ratio of 43.

Considering the material being above its glass transition point, it can be concluded that orientation of the material occurs along the drawing direction upon cold-drawing. Furthermore the smoothness of the crazes suggests that presence of molecular entanglements in the as-polymerized films is not likely, as can be expected from the method of polymerization.

The mechanical properties were investigated on fibers drawn at 420 ^{0}C, just below the melting point. We found the normal increase of tensile strength at break and Young's modulus for increasing draw ratios, as shown in fig. 2 and fig. 3. The maximum draw ratio was found to be 43 and the ultimate mechanical properties were a tensile strength at break of 3.0 GPa, a Young's modulus of 102 GPa and a strain at break of 3 %. A typical stress-strain curve for such a fiber is shown in fig. 4.

The theoretical strength of PPX can be calculated using the approach of de Boer (11). For this, we assumed that the strength of PPX is limited by the intrinsic bond strength of the carbon-carbon bond between methylene groups connecting benzene rings. From thermal degradation studies, Schaefgen determined the latter value to be 244 kJ/mole (12). The force constant of this carbon-carbon bond was assumed to be 5.2×10^2 Nm^{-1} (13). The force necessary to break the carbon-carbon bond was then found to be 5.1×10^{-9} N. From this, and the unit cell parameters of the α and β form of PPX (6,7), a theoretical strength at break of 23 GPa for both crystal forms was calculated. For comparison, the corresponding theoretical value for polyethylene is 32.5 GPa.

In order to estimate the ultimately obtainable mechanical properties for PPX fibers drawn at 420 ^{0}C, the reciprocal tensile strength at break and the reciprocal Young's modulus were plotted versus the reciprocal draw ratio, as shown in fig. 5 and fig. 6. Extrapolating towards infinite draw ratio, *i.e.* zero reciprocal draw ratio, an ultimate tensile strength at break of 16.4 GPa and an ultimate Young's modulus of 208 GPa were found. Thus the theoretical strength at break agrees fairly well with the extrapolated value. The fact that for the drawn fibers a maximum tensile strength at break of 3.0 GPa was obtained, must at first instance be attributed to the fairly low molecular weigth of the polymer. Furthermore, drawing at 420 ^{0}C might involve stress-induced degradation of the material.

A WAXS-pattern of a drawn fiber is shown in fig. 7, clearly demonstrating that orientation has occured upon drawing. The fiber period can be identified as the c-axis. The non-symmetry of the pattern indicates double orientation, originating from the fact that in the starting material the molecules are oriented with the b-axis normal to the film plane, whereas upon drawing the c-axis gets aligned along the fiber direction. A drawn fiber exhibits a smooth surface, but generally has many narrow cracks of varying length along the fiber direction. After tensile testing to breakage of a drawn fiber, some of the cracks are widened perpendicular to the fiber direction and reveal the fibrillar nature of the drawn material (see fig. 8). Upon breaking the drawn fiber usually splits up indicating that the process of failure starts in such longitudinal cracks.

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