High-modulus fibres of nylon-6 prepared by a dry-spinning method

S. Gogolewski* and A. J. Pennings

Department of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands
(Received 2 January 1985)

Nylon-6 filaments with tensile strengths at break up to 1 GPa and initial moduli in the range of 16 to 19 GPa have been produced by dry-spinning of solutions of nylon-6 in cosolvent mixtures of formic acid and chloroform followed by hot-drawing at 200°C–240°C. Tensile strengths and elastic moduli of the nylon-6 fibres were strongly dependent on the draw ratio, on the molecular weight of the polymer, on the polymer concentration in the spinning solution and on concentration of nonsolvent in the spinning solution. At high concentrations of nonsolvent in the spinning solution, the as-spun fibres of nylon-6 were composed of ball-like structural units, formed possibly due to the liquid-liquid phase separation in the polymer/solvent/nonsolvent ternary system. Formation of ball-like structures reduced the ultimate mechanical properties of hot-drawn fibres of nylon-6.

(Keywords: nylon-6, dry spinning from solvent-nonsolvent system; high-modulus fibres; hot-drawing)

INTRODUCTION

Much effort during the last decade has been spent on producing ultra-high modulus polymers[1]. Spinning from the liquid-crystalline state[2], surface-growth fibres[3], hot-drawing of gel-spun fibres[4], hydrostatic extrusion[5], solid-state extrusion[6] or zone-annealing[7] are some of the techniques leading to high modulus and high strength polymeric materials. While from flexible high molecular weight polyethylene the fibres with tensile strength at break of 4.7 GPa[8] and modulus up to 160 GPa[9] were recently prepared, it is still difficult to produce high strength and high modulus fibres of common polyesters and polyamides.

Although it is claimed that the theoretical modulus of nylon fibres is in the range of 183–263 GPa[10,11] and a value for the theoretical strength should be in the range of 1/10 of the theoretical modulus[12], the typical commercial nylon fibres have moduli of 5 GPa and tensile strengths of about 0.5 GPa.

As nylon fibres are widely used e.g. as tyre yarns, attempts have been made to increase the modulus of the oriented aliphatic nylons. Solid-state coextrusion of nylon-6 plastified with ammonia[13] results in an enhanced tensile modulus up to 13 GPa. Drawing of fibres prepared by melt-spinning of nylon-6/lithium bromide or nylon-6/lithium chloride mixtures, led to the fibres with moduli in the range of 9–13 GPa[14,15].

Zone-annealing of commercial nylon-6 fibres increased tensile strength up to 1 GPa and modulus up to 10 GPa[16]. Also dry-spinning of nylon-6 from formic acid/chloroform cosolvent mixtures followed by hot-drawing, led to the fibres with modulus up to 12 GPa and tensile strength up to 0.7 GPa[17].

The present publication gives more details on the dry-spinning of high modulus fibres of nylon-6, with the molecular weight in the range of 1.2×10^4 to 3.5×10^6, from formic acid and formic acid/chloroform cosolvent mixtures.

EXPERIMENT

Samples

Nylon-6 with weight-average molecular weight in the range 1.2×10^4 to 4.7×10^4 was obtained by fractionation of nylon-6 from Toyo Rayon, Japan[18]. Nylon-6 with molecular weight in the range 9.4×10^4 to 3.5×10^6 was kindly supplied by Enka Research Institute, Arnhem, The Netherlands. Viscosities of the samples (1% w/v solutions) were measured in m-cresol at 25°C[19]. The weight-average molecular weight of the samples was calculated according to:

$$[\eta] = 6.7 \times 10^{-3} \times \bar{M}_w^{0.51}$$

This relationship was obtained by Markhorst and Goedhart[20]. It differs from the formulae discussed by Tuzar, Kratochvil and Bohdanecký[19] because the nylon-6 samples used in this study are likely to be branched as detected by Berk[22]. Characterization of the samples used in the experiments is given in *Table 1*.

### Dry-spinning, hot-drawing procedure

Dry-spinning and hot-drawing of nylon-6 fibres were carried out using the apparatus described previously[21]. Prior to spinning the polymer was dried for 20 h at 60°C in a vacuum oven. Spinning solutions were prepared by dissolving the polymer at room temperature in 98% formic acid and in formic acid/chloroform cosolvent mixtures (75/25, 60/40, 50/50 v/v). Concentrations of the polymer in the spinning solutions were in the range of 10

* Present address: INVENTING, SA., Chemin du Devin 94, CH-1012 Lausanne, Switzerland.

Table 1 Materials used for the experiments

$\bar{M}_w \cdot 10^4$	$[\eta]$ (dl/g)	T_m (°C)	ΔH_m (J/g)
1.2*	0.80	220	56.4
4.7*	1.62	221	59.2
4.7	1.62	222	59.0
9.4	2.30	223	57.3

$\bar{M}_w \cdot 10^6$	$[\eta]$ (dl/g)	T_m (°C)	ΔH_m (J/g)
1.6	9.7	225	58.5
2.6	12.6	226	57.7
3.5	14.6	226	58.5

* fractionated polymers
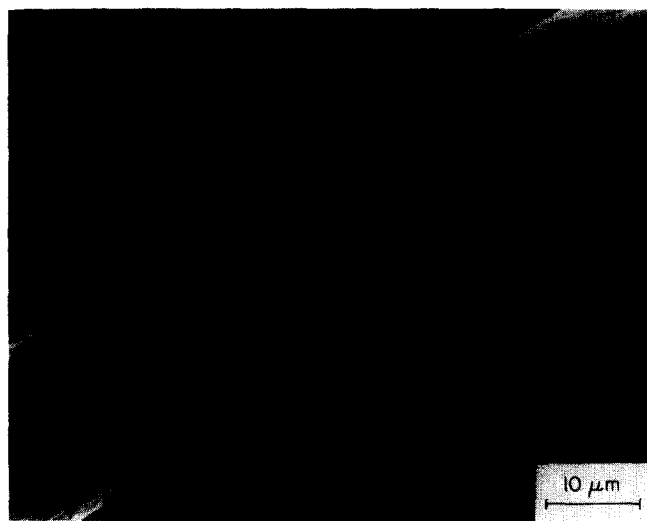
Figure 1 Scanning electron micrograph of a nylon-6 fibre with $\bar{M}_w = 2.6 \times 10^6$ spun at room temperature from formic acid 75/chloroform 25 cosolvent mixture

to 90 (w/v) % depending on the molecular weight of nylon-6 samples. Fibres were extruded through a conical die with a diameter of 0.5 and 1.0 mm and a length of 5 mm, and collected on sand-blasted glass bobbins at speeds in the range of 0.02 to 1.2 m.min^{-1}.

Fibres used for hot-drawing experiments were dried at room temperature and completely freed from solvents. The rate of solvent evaporation was in the range of 5 to 40% per hour.

Characterization of the fibres

The fibre shape and morphology were characterized using an ISI-DS 130 scanning electron microscope. Mechanical properties of the nylon-6 fibres were measured at room temperature using a Zwick tensile tester at a crosshead speed of 12 mm min^{-1}. The length of the samples was 25 mm.

RESULTS AND DISCUSSION

Fibre morphology

Figures 1 to *5* show the scanning electron micrographs of the nylon-6 fibres with a viscosity-average molecular weight $\bar{M}_v$ of 2.6×10^6 dry-spun from formic acid/ chloroform cosolvent mixture.

Figure 1 is a scanning electron micrograph of a nylon-6 as-spun fibre extruded from a formic acid 75/chloroform
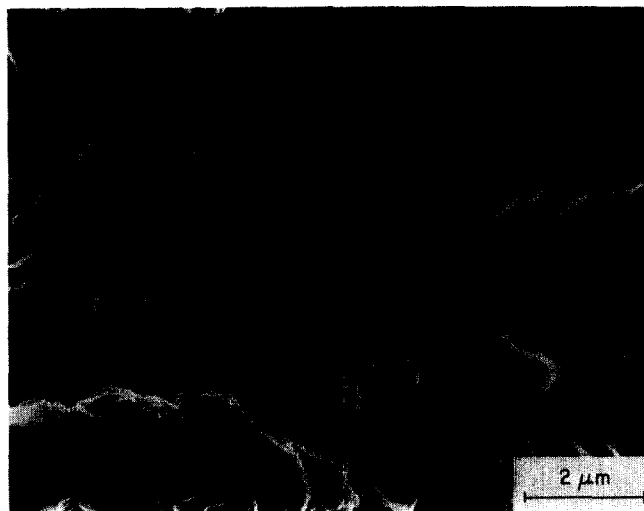
Figure 2 Scanning electron micrograph of a nylon-6 fibre with $\bar{M}_w = 2.6 \times 10^6$ spun at room temperature from formic acid 50/chloroform 50 cosolvent mixture. The fibre was collected without additional stress
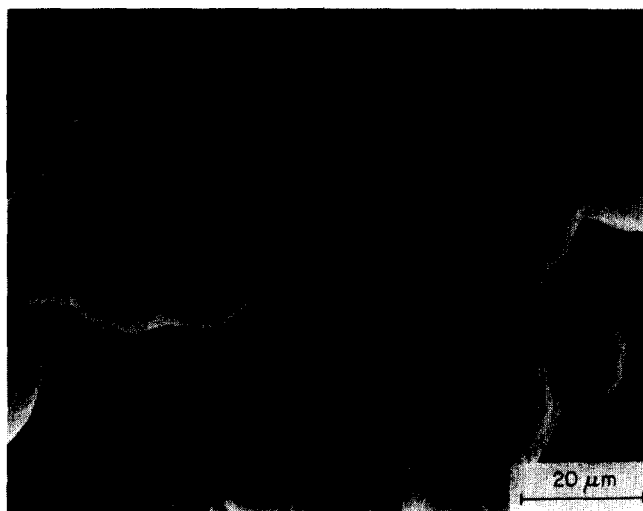
Figure 3 Scanning electron micrograph of a nylon-6 fibre with $\bar{M}_w = 2.6 \times 10^6$ spun at room temperature from a formic acid 50/chloroform 50 cosolvent mixture. The fibre was collected at 0.12 m min^{-1}
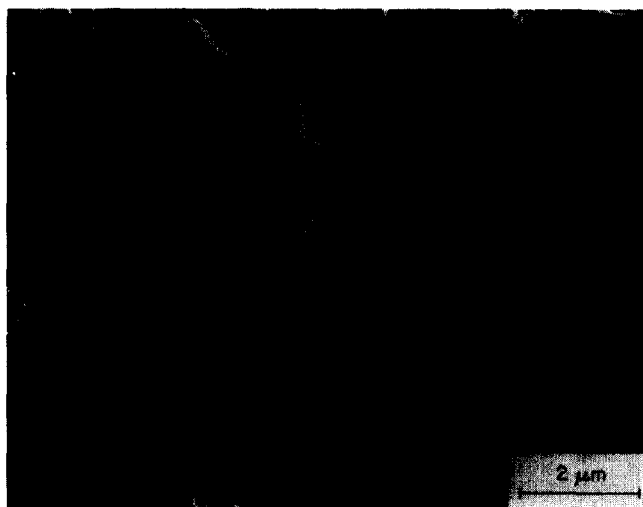
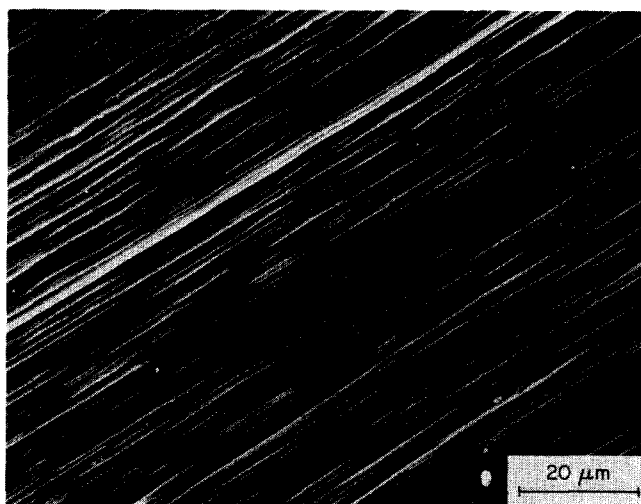**Figure 4** Higher magnification of the fibre shown in *Figure 3*. Note the grain boundaries

Figure 5 Nylon-6 fibre shown in *Figure 3* after hot-drawing at 240°C to $\lambda = 5$. Note an extensive fibrillation

25 mixture. The fibre exhibits a compact structure and a relatively smooth surface.

Figure 2 shows a scanning electron micrograph of a nylon-6 as-spun fibre extruded from a formic acid 50/ chloroform 50 cosolvent mixture. The fibre was collected on the bobbin without applying any additional stress $(0.02 \text{ m min}^{-1})$. The dry fibre maintained its initial length when it was removed from the bobbin. The fibre has a porous, lamellar-like structure.

Figure 3 is an electron micrograph of nylon-6 as-spun fibre produced from formic acid 50/chloroform 50 cosolvent mixture. The fibre was collected at a speed of 0.12 m min^{-1}, which resulted in additional stress applied to the fibre. Completely dry fibres when removed from the bobbin showed a shrinkage of about 5 to 10% of its initial length in the swollen state. Applying a stress to the swollen fibre resulted in formation of a ball-like porous structure. The balls are the fibrillar spherulites as are demonstrated in *Figure 4* which is a higher magnification of the fibre shown in *Figure 3*. The formation of this ball-like structure is possibly due to the stress-induced liquid–liquid phase separation which takes place in nylon-6/solvent/nonsolvent ternary system at a high concentration of nonsolvent.

This ball-like structure reduces coherence of the fibre elements and gives rise to an extensive fibrillation of the filament upon hot-drawing, accompanied by a substantial decrease of tensile strength and modulus. Fibrillation of the fibre is illustrated in *Figure 5* which shows the surface of this fibre after hot-drawing at 244°C to $\lambda = 5$.

Mechanical properties

Figure 6 shows typical stress–strain dependences for nylon-6 fibres with $\overline{M}_w = 2.6 \times 10^6$ spun from formic acid 75/chloroform 25 cosolvent mixture and drawn at 234°C to different ratios. The shape of this dependence for higher draw ratios is characteristic for highly oriented high molecular weight fibres of polyethylene[4,8].

Fibres A, B and C with the highest moduli were slowly dried at ambient temperature and had a crystallinity prior to drawing of 27%. Fibre D was dried much faster in a vacuum oven at 60°C. Its crystallinity, as judged from d.s.c. measurements, was 40%. This higher crystallinity ap-

parently allows a much lower ultimate draw ratio at 234°C of only 2, which is also reflected in much lower values for the modulus and tensile strength. These results clearly indicate that one needs a very low initial crystallinity in order to achieve a high modulus after drawing. Highly oriented nylon-6 fibres spun from solvent-nonsolvent systems usually break at elongations of 5 to 7%. Elongation at break for nylon-6 fibres spun from formic acid/chloroform cosolvent increases with molecular weight of the polymer (*Figure 7*), reaching a maximum at $\overline{M}_w = 1.6 \times 10^6$, and then decreasing gradually with increasing of $\overline{M}_w$. Similar effect of molecular weight on ultimate elongation was also reported by Margalies[23] for compression moulded HDPE.

Figure 8 shows the dependence of the tensile strength at break on the draw ratio for nylon-6 fibres with $\overline{M}_w = 2.6 \times 10^6$. The fibres were spun from formic acid/ chloroform cosolvent mixture of various compositions and hot-drawn at optimum draw temperature of 235°C. As is the case with other oriented polymer systems[1], the tensile strength of nylon-6 fibres under investigation increases with the draw ratio. The maximum draw ratio achieved in the present study was 10. The highest draw ratios obtained here for nylon-6 fibres dry-spun from solvent/ nonsolvent systems are almost two times higher than those obtained for the melt-spun fibres, however they are ten times lower than the draw ratios achieved in ultra-high modulus, high strength polyethylene fibres[9]. Thus al-
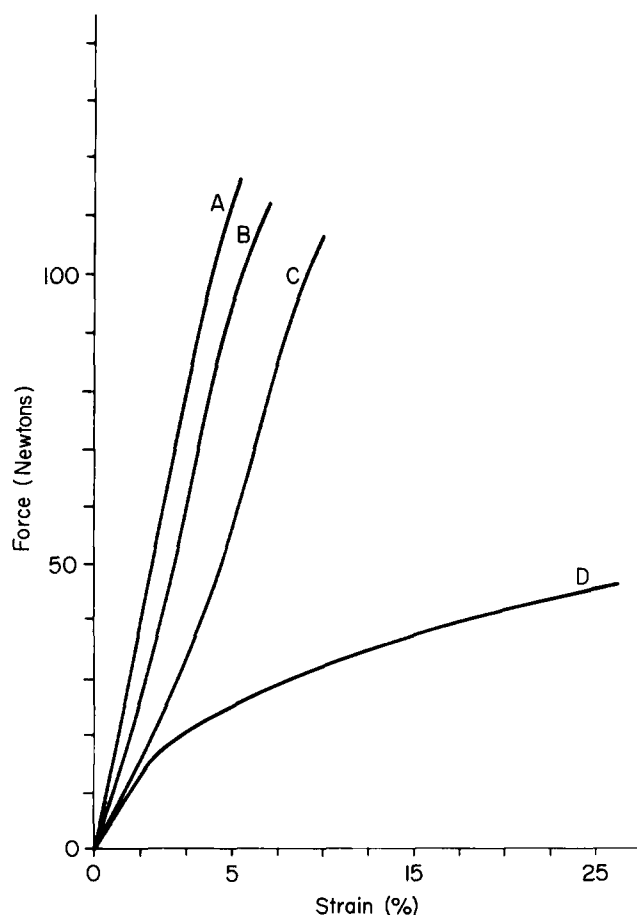

Figure 6 Typical stress–strain dependence of nylon-6 fibres with $\overline{M}_w = 2.6 \times 10^6$ spun from a formic acid 75/chloroform 25 cosolvent mixture and drawn at 234°C to different draw ratios. A, 10; B, 8; C, 6; D, 2
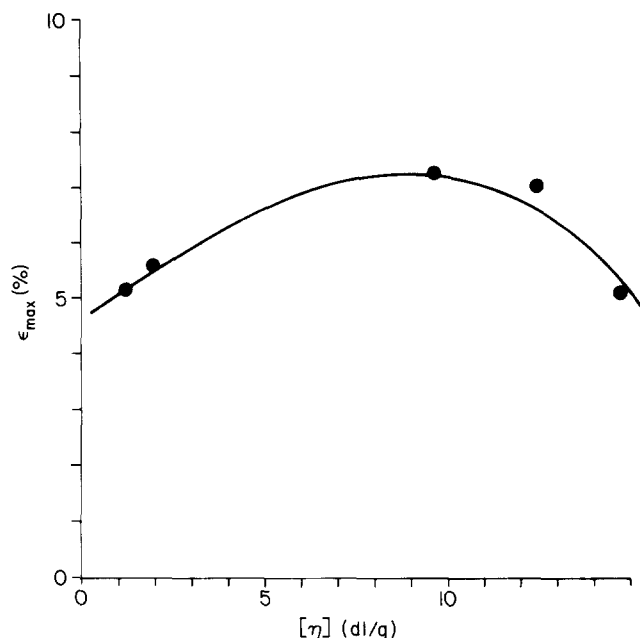
Figure 7 Dependence of ultimate elongation of nylon-6 fibres spun from a formic acid/chloroform cosolvent mixture on molecular weight (intrinsic viscosity). Fibres were hot-drawn at optimum draw temperature

though the presence of nonsolvent in the nylon spinning solution enhances formation of better entanglement network and improves the drawability of fibres, the presence of long chain branches and hydrogen bonds in the system is likely to restrict the slippage of the chains and chain defects through the crystal lattice, which will hinder achieving higher draw ratios, and better orientation.

As opposed to polyethylene, where the chain movements in the crystal require only breaking of the van der Waals bonds, in polyamide in addition to the van der Waals bonds also fracturing of hydrogen bonding networks is necessary to unfold the chains. At a length of the chain in the polyamide crystal equal to 60–80 Å, the overall strength of van der Waals forces and hydrogen bonds is equal to the strength of a covalent bond in the main chain. Thus, upon applying a stress to the fibre, the chance that the main chain will undergo scissioning is the same as the chance that the chain will be pulled out of the crystal and assume an extended conformation. The tensile strength of nylon-6 fibres produced from solvent/nonsolvent systems is also strongly dependent on the content of nonsolvent in the spinning solution. For the concentration of nonsolvent in the spinning solution up to 25 (v/v) %, the tensile strength of nylon-6 fibres increased on increasing the concentration of nonsolvent in the mixture, and then decreases gradually with increasing concentration of nonsolvent.

It should be noted here that nylon-6 fibres spun from pure formic acid always reached lower draw ratios(i.e. the tensile strength) than those spun from formic acid/nonsolvent mixtures. It suggests that in the presence of nonsolvent in the spinning solution, a better entanglement network is formed which contains fewer topological irregularities, e.g. entangled intermolecular chain portions, which could hardly be removed upon hot-drawing. Formation of such an optimum entanglement network can be enhanced by increasing a rate of fibre drying, which reduces a chance of the chains being involved in numerous

newly formed entanglements. This explanation is corroborated by the observation that under identical preparation conditions nylon-6 fibres spun from formic acid/chloroform systems got dry almost twice as fast and had lower crystallinity than those spun from pure formic acid.

However, hot-drawing of nylon-6 fibres spun from a solvent/nonsolvent system at a high nonsolvent concentration reduces again the ultimate tensile strength of the fibres. This might be mainly due to the liquid–liquid phase separation, which results in formation of a ball-like structure in the as-spun fibre. Due to the weak coherence forces between the balls, it is not possible to draw the fibre to high draw ratios and thus to produce a maximum degree of orientation. This results in a much lower ultimate tensile strength as compared with the fibres spun from a solution with the optimum solvent/nonsolvent composition. The occurence of the liquid–liquid phase separation in this case may also have been affected by the flow field. The spinning rate was in the range of 60 to 120 cm min^{-1}. Even for a spinning rate of 50 cm min^{-1} the tensile properties turned out to be rather poor (TS of 0.3 GPa). Therefore the spinning rates in the range 12 to 40 cm min^{-1} were applied in order to obtain optimum properties. It was also noticed that in the case of low flow rates, the filament leaving the orifice could be stretched much further before fracture took place. The tensile strength of nylon-6 fibres prepared by hot-drawing of the fibres dry-spun from solvent/nonsolvent systems is greatly dependent on concentration of the polymer of the spinning solution and its molecular weight (*Figure 9*).

For concentrations of the polymer in the spinning solution in the range of 1 to 10 (w/v) %, the tensile strength of fibres hot-drawn at identical conditions increases with increasing concentration. For polymer concentrations in
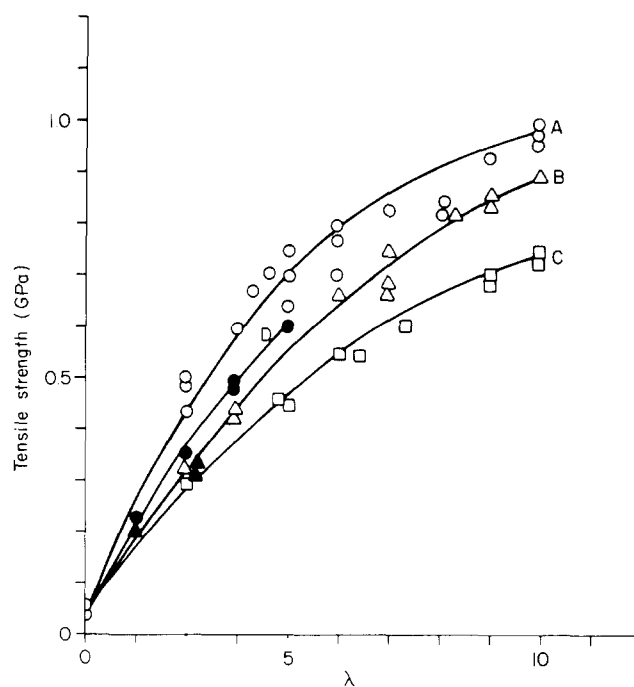

Figure 8 Dependence of tensile strength at break of nylon-6 fibres with $M_w = 2.6 \times 10^6$ on the draw ratio. Fibres were spun from formic acid/chloroform cosolvent mixtures and hot-drawn at optimum draw temperature. A, formic acid 75/chloroform 25; B, formic acid 60/chloroform 40; C, formic acid 50/chloroform 50; D, formic acid; ▲, formic acid, solution prepared from precipitated nylon-6
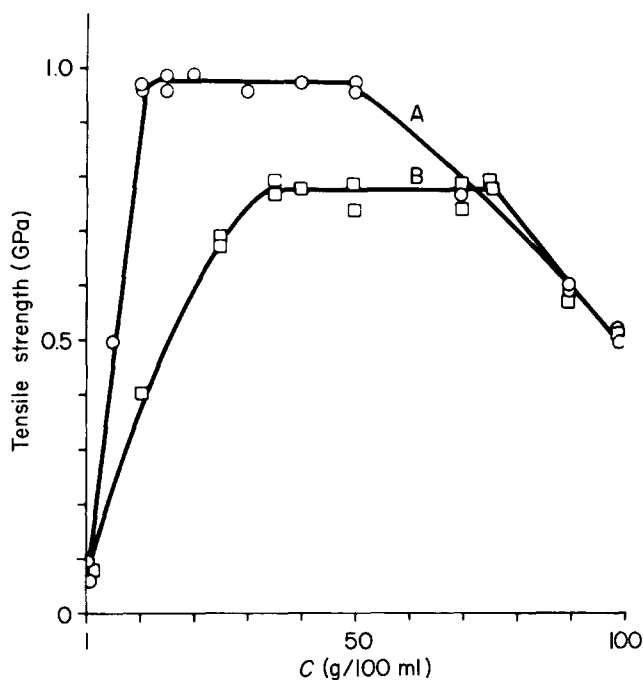
Figure 9 Dependence of tensile strength at break of nylon-6 fibres on concentration of polymer in the spinning solution, A, $M_w = 2.6 \times 10^6$, B, 9.4×10^4. Fibres were drawn at optimum draw temperature to maximum draw ratio
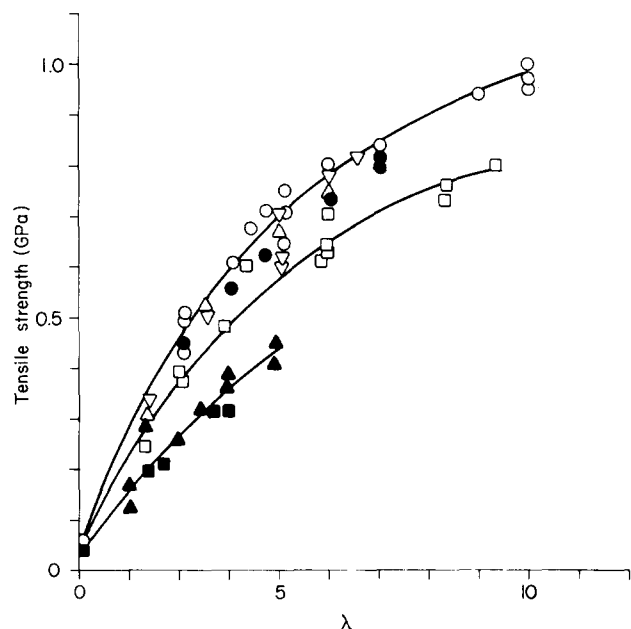

Figure 10 Dependence of tensile strength at break on the draw ratio for nylon-6 fibres with different molecular weight, spun from formic acid 75/chloroform 25 cosolvent mixtures. Fibres were hot-drawn at optimum draw temperature.
□, 3.5×10^6, ○, 2.6×10^6, ●, 1.6×10^6, ▽, 9.4×10^4, △, 4.7×10^4 (whole polymer), ▲, 4.7×10^4 (fractionated polymer), ■, 1.2×10^4 (fractionated polymer)

the range 10 to 50 (w/v) %, the tensile strength of nylon-6 fibres maintains a constant value, while above that range the tensile strength at break drops abruptly with increasing polymer concentration. A similar phenomenon was also observed for dry-spun fibres of poly(L-lactide)[21] and was related to the topology of the entanglement network and the entanglement density in the spinning solution, as well as to the presence of flaws in the fibre surface.

Figure 10 illustrates the effect of the draw ratio and molecular weight of polymer on the tensile strength at break. Fibres were spun from formic acid 75/chloroform 25 cosolvent mixture, and hot-drawn at the optimum temperature. As is the case with other polymers[1,8,9,21], higher draw ratios are achievable for nylon-6 of higher molecular weight, while removal of the low molecular weight fraction from the polymer (see data for fractionated samples), reduces the drawability and thus the tensile strength. Effect of molecular weight on tensile strength and Young's modulus of nylon-6 fibres dry-spun and hot-drawn at optimum conditions is shown in *Figure 11*. For the range of molecular weights under investigation (1.2×10^4 to 3.5×10^6), the tensile strength and modulus increase with molecular weight which is especially pronounced for the molecular weights in the range of 1.2 to 4.7×10^4.

Figure 12 shows the dependence of initial modulus vs. draw ratio for nylon-6 fibres with various molecular weights. The fibres were spun from a formic acid 75/chloroform 25 cosolvent mixture and hot-drawn at the optimum draw temperature of 234°C. In the Figure, the values of modulus obtained by Richardson and Ward for fibres spun from nylon-6/lithium chloride mixtures[15] were also included. A maximum modulus found in the present study for nylon-6 fibres dry-spun from formic acid/chloroform cosolvent mixtures was 19 GPa for a draw ratio of 10, although even at draw ratios of 7 to 8, the fibres with modulus of 16 GPa could easily be produced. The latter finding has an important technological implication.

Figure 13, 14 and *15* illustrate the effect of draw temperature on the tensile strength, elastic moduli and molecular weight (intrinsic viscosity) of nylon-6 fibres dry-spun from formic acid 75/chloroform 25 cosolvent mixture. Tensile strength and moduli increase upon increasing of draw temperature, achieving a maximum at 220°C
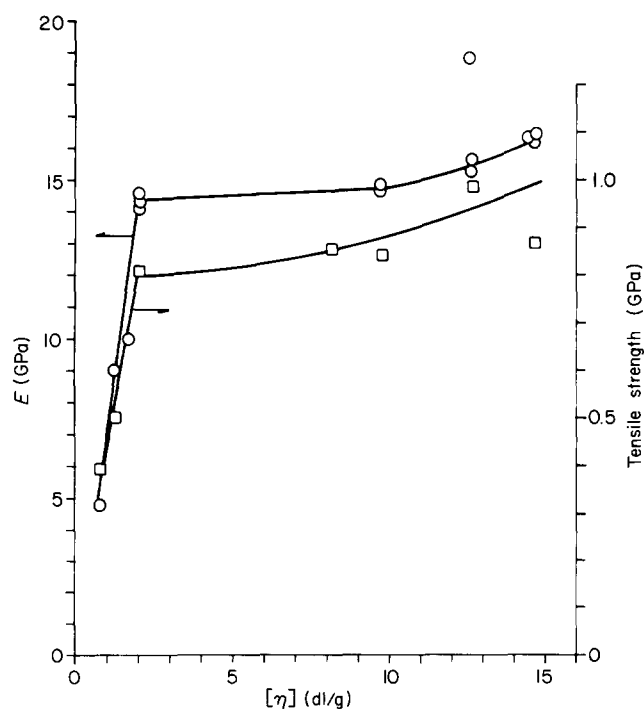

Figure 11 Initial modulus and tensile strength at λ_{max} vs. molecular weight (intrinsic viscosity). Fibres were drawn at optimum draw temperature
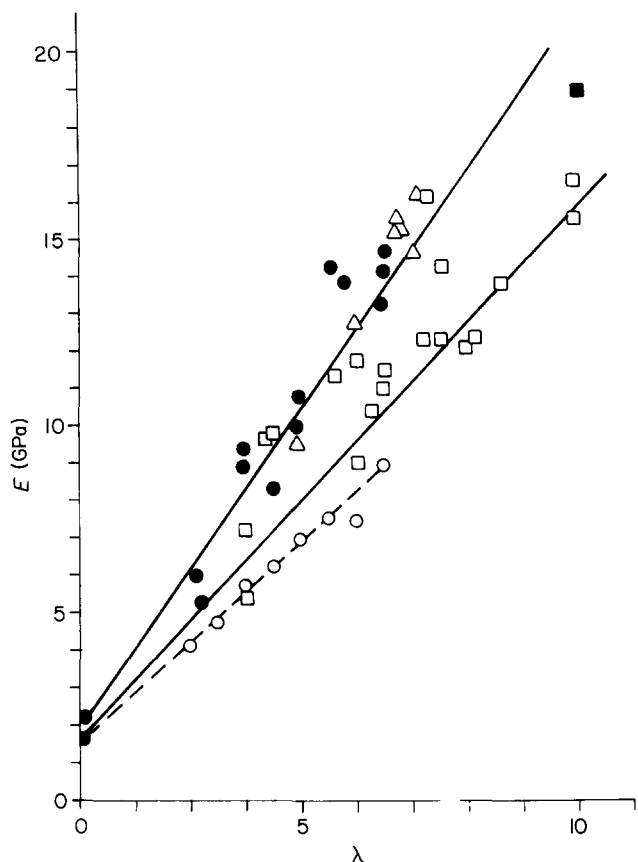
Figure 12 Initial modulus vs. draw ratio for nylon-6 fibres with various molecular weights. Fibres were spun from acid 75/chloroform 25 cosolvent mixtures and hot-drawn at 234°C.
△, 3.5 × 10⁶, ▢, 2.6 × 10⁶, ■, 2.6 × 10⁶ (formic acid 60/chloroform 40), ●, 9.4 × 10⁴, ○, N6/2%LiCl (ref. 15)

to 240°C for fibres with the high molecular weight (1.6 to 3.5 × 10⁶) and in the range of 200°C to 220°C for fibres with lower molecular weight (1.2 to 9.4 × 10⁴).

Similar dependence of tensile strength on draw temperature was also reported by Prevorsek *et al.*[24] for nylon-6 fibres drawn in a two-stage process. At draw temperatures above 250°C, the tensile strength and elastic moduli
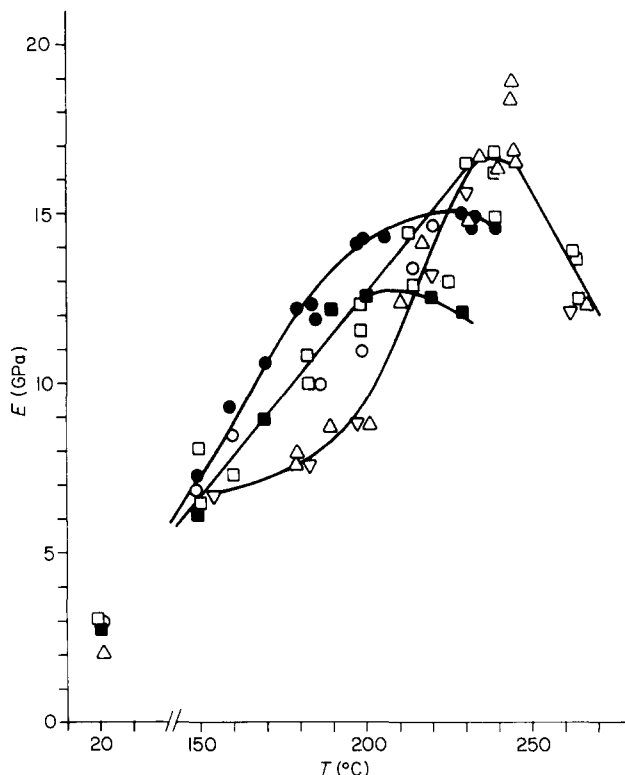

Figure 14 Initial modulus at λ_{max} on the draw temperarure for nylon-6 fibres with different molecular weights. Fibres were spun from formic acid 75/chloroform 25 cosolvent mixture. ▢, 3.5 × 10⁶, △, 2.6 × 10⁶, ▽, 1.6 × 10⁶, ●, 9.4 × 10⁴, ○, 4.7 × 10⁴, ■, 1.2 × 10⁴
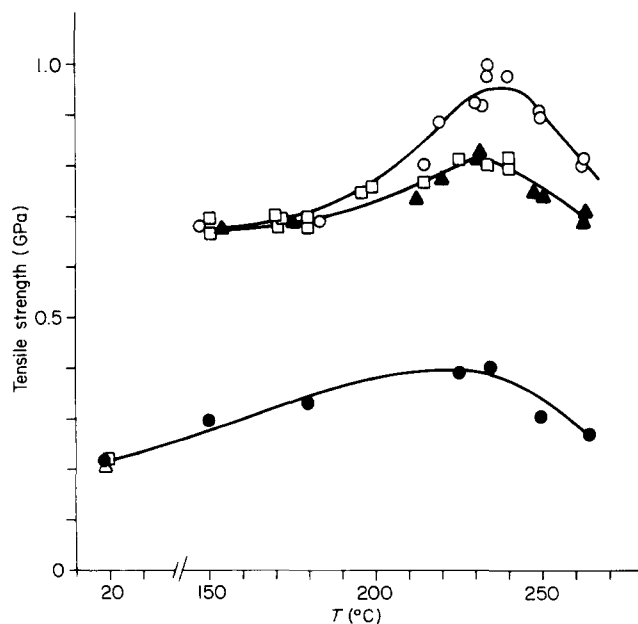

Figure 13 Dependence of the tensile strength at λ_{max} on the draw temperature for nylon-6 fibres with different molecular weight. Fibres were spun from formic acid 75/chloroform 25 cosolvent mixture.
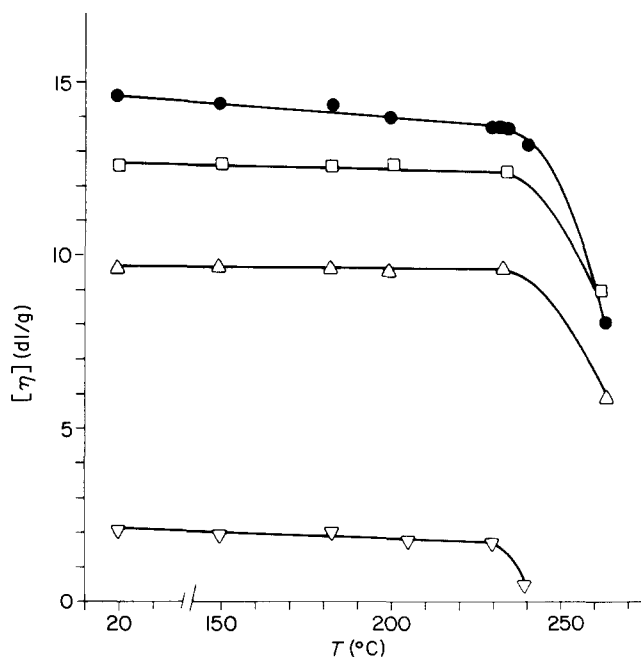▲, 3.5 × 10⁶, ○, 2.6 × 10⁶, ●, 2.6 × 10⁶ (polymer purified by precipitation), ▢, 9.4 × 10⁴

Figure 15 Dependence of molecular weight (intrinsic viscosity) on draw temperature for nylon-6 fibres of different molecular weight. ●, 3.5 × 10⁶, ▢, 2.6 × 10⁶, △, 1.6 × 10⁶, ▽, 9.4 × 10⁴

of nylon-6 fibres dry-spun from a solvent/nonsolvent system drop abruptly. This is due to extensive thermal degradation of the polymer as it can be concluded from *Figure 15*. Nylon-6 fibres with similar mechanical properties were also produced upon hot-drawing of fibres dry-spun from formic acid/camphor, formic acid/ethanol and formic acid/hexamethylbenzene cosolvent mixtures. Formic acid/acetone cosolvent system led to fibres with poorer mechanical properties.

CONCLUSIONS

(1) Dry-spinning of nylon-6 fibres from formic acid-/chloroform cosolvent mixtures is of technological interest.

(2) Nylon-6 fibres with the tensile strength at break up to 1 GPa and initial elastic modulus up to 19 GPa can be produced by hot-drawing of fibres prepared by this method.

(3) Optimum draw temperature for these fibres is in the range of 200°C to 240°C, depending on the molecular weight of nylon-6.

(4) Presence of nonsolvent in the spinning solution facilitates the formation of a better drawable entanglement network.

(5) Presence of chain branches and hydrogen bonds in the polymer are restrictions for achieving very high draw ratios in these fibres.

ACKNOWLEDGEMENTS

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