Preparation and properties of block copolyamide fibres

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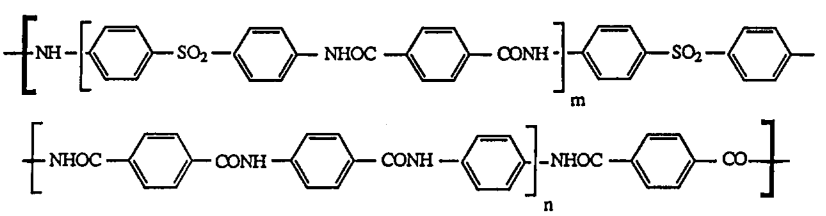
Block copolymers of aromatic polyamides have been synthesized. The polymers contain stiff, liquid crystal forming blocks and flexible blocks. A series of polymers with differing lengths of the flexible block have been prepared. The polymers have been spun into fibres from liquid crystalline solutions and the properties of as spun and heat treated (500 and 370°C) fibres have been determined. The incorporation of flexible blocks in the stiff polymer resulted in a decrease in Young's modulus and tensile strength while the elongation at break was largely unaffected. The heat treatment resulted in an increase in the Young's modulus of the fibre. The fibre containing the longest flexible block became brittle and stiff towards bending upon heat treatment. The results are discussed in terms of the influence of the block copolymer structure on the fibre morphology.

(**Keywords: aromatic polyamide; block copolymer; fibres; tensile properties**)

INTRODUCTION

During the last 20 years there has been a great interest in aromatic polyamides concerning both the synthesis of the polymers and their conversion into fibres with exceptional mechanical properties[1–11]. Investigations of the behaviour of aromatic polyamides in solution disclosed the liquid crystalline properties of the all *para* oriented systems[9–12]. These liquid crystalline solutions could be spun into high strength and high stiffness fibres according to a wet spinning technique. In this process the liquid crystals become oriented along the fibre axis. This results in a particular fibre morphology, which has been thoroughly investigated[13–15]. The orientation of liquid crystals leads to a strong anisotropy of the fibre properties[16], i.e. high tensile strength and stiffness along the fibre axis and low strength and stiffness in the cross direction of the fibre. Apart from this, the compressive strength of the fibres is low both along and across the fibre axis. These circumstances present a serious disadvantage for the use of this type of fibre in many applications where wear resistance and compressive strength are of great importance. Copolymers and block copolymers containing aromatic polyamides have been studied both from a general polymer synthesis point of view[17–21] and with a view towards applications in fibres[22] and molecular composites[23–26].

This paper reports a study of aromatic block copolyamides of the following general structure:



The incorporation of somewhat flexible sulphone containing blocks into the stiff chain aromatic polyamide and the effects of this modification on the fibre properties are the main objectives of this study. The introduction of flexible blocks into the rigid polyamide chain caused an overall decrease in both Young's modulus and tensile strength of the fibres compared to the stiff polymer. At the same time the elongation at break increased somewhat. The as spun fibres showed a well defined yield point. Heat treatment of the fibres up to 500°C resulted in a two- to three-fold increase in Young's modulus while the elongation at break decreased drastically. The tensile strength of the fibres remained almost constant. The fibres spun from a polymer containing 50% flexible blocks became very brittle upon heat treatment at 500°C. All fibres were spun from liquid crystalline solutions.

EXPERIMENTAL

Materials

N-methylpyrrolidone (NMP) was of commercially available quality and was passed through highly activated alumina (Woelm Super 1 Neutral) prior to use. Lithium chloride was oven dried. Tetrabutylammonium tetrafluoroborate was prepared via an ion pair extraction technique. 4,4'-Diaminobenzanilide was prepared from the corresponding dinitro compound (Nobel Chemicals)

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by catalytic hydrogenation in methanol over a palladium catalyst. The product was recrystallized from aqueous ethanol. 4,4′-Diaminodiphenylsulphone was of commercially available quality and was recrystallized from methanol. Terephthaloyl chloride was of commercially available quality and was recrystallized from hexane.

Polymerization

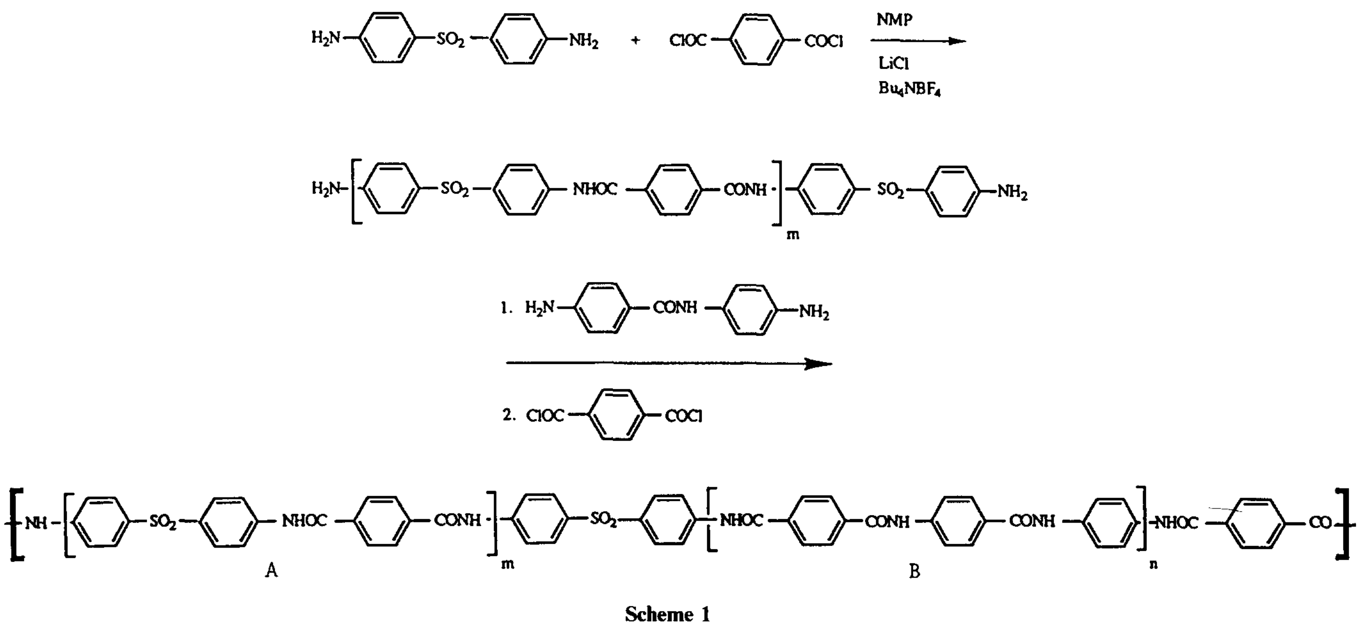
A typical polymerization experiment took place as follows: a resin flask was equipped with a powerful mechanical stirrer and a nitrogen inlet. 4,4′-Diaminodiphenylsulphone (30 mmol), lithium chloride (4.0 g) and tetrabutylammonium tetrafluoroborate (0.8 g) were placed in the flask and dissolved in dry NMP (200 ml). To this solution terephthaloyl chloride (29.4 mmol) was added under vigorous stirring to form the flexible block (A in *Scheme 1*). After 40 min 4,4′-diaminobenzanilide (30 mmol) was added and the mixture was heated to 50–60°C to effectuate dissolution. After cooling to room temperature terephthaloyl chloride (30.6 mmol) was added under vigorous stirring. All additions of solid material to the reaction mixture were followed by addition of dry NMP (25 ml) to wash all of the material into the solution. Within 5 min of the last addition the solution turned into a stiff gelatinous lump as the stiff block (B in *Scheme 1*) was formed. A few hours of kneading broke up the gelatinous lump into smaller pieces. The polymer was precipitated with water in a kitchen blender, washed thoroughly with water and oven dried. The inherent viscosity (η_{inh}) of the polymer was determined in $0.5\,g\,dl^{-1}$ solution in concentrated sulphuric acid at 25.0°C. For the polymer above described $\eta_{inh} = 3.80\,dl\,g^{-1}$.

Fibre spinning

The spinning of fibres from the polymers was performed with a small scale wet spinning unit from Bradford University Research Ltd. The polymers were dissolved in concentrated sulphuric acid with 10% fuming sulphuric acid added to reduce the water content. Spinning solutions were prepared in batches of polymer (7.5 g) in sulphuric acid (25 ml). All these solutions showed the stir opalescence typical of liquid crystalline solutions. The stiff polymers dissolved into low viscosity stir opalescent solutions while the polymers containing flexible blocks gave rather stiff stir opalescent gelatinous solutions. On spinning the solution was extruded through a single hole (50 μm diameter) spinneret into the air ~10 mm above the coagulation bath (dry-jet wet spinning). The high viscosity of the gelatinous solutions resulted in very high pressures building up during the extrusion of these solutions through the spinneret. The fibre was coagulated in water and washed with water before reaching the final take-up reel. To ensure complete removal of sulphuric acid the reels with fibre were immersed in water for 2 h after spinning and then oven dried at 60°C. After drying some fibres were heat treated at either 370 or 500°C.

Tensile testing

The tensile testing of the fibres was carried out according to the procedure of Andersson and Warren[27] using an Instron tensile tester equipped with either a 5 N or a 20 N cell (both of A grade). The clamps on the tester were of pneumatic type. The fibres were mounted with an epoxy adhesive in two L-formed paper frames held together by a paper clip. The paper clip was released when the specimen had been mounted in the tester. Three different fibre lengths (10, 50 and 100 mm) were tested and 10 individual tests were performed on each fibre length. All fibres were kept in an atmosphere of 60% relative humidity at 23°C for at least 24 h before testing. In the evaluation of the tensile tests the apparent elongations were plotted against the lengths of the specimens and hence the true elongation of the fibre could be calculated. The true elastic moduli were obtained by plotting the reciprocal of the measured modulus against the reciprocal of the fibre length and extrapolating to the reciprocal of the fibre length being equal to zero. This procedure eliminates the effects of small extensions, which do not originate from the fibres. After testing, the fibre diameters were measured using a Watson split image micrometer.



Scheme 1

Thermogravimetric analysis

The thermal stability of the fibres was measured in both nitrogen and air using a Perkin-Elmer 7 series thermal analysis system. The experiments were run at 10°C min^{-1} between 40°C and 595°C.

RESULTS AND DISCUSSION

Polymer system and synthesis

The polymer system chosen for this study was a multiblock copolymer composed of the terephthalamide from 4,4′-diaminobenzanilide for the stiff blocks and the corresponding amide from 4,4′-diaminodiphenylsulphone for the flexible blocks. The system was easily prepared due to the good stability of the diamines towards oxidation. The use of the sulphone to introduce flexibility was possible because of the 120° angle between the phenyl groups over the sulphur atom. In a flexible polymer the mobility introduced by this angle was enough to prevent the polymer from forming liquid crystals and it also resulted in good solubility of the polymer in, for instance, NMP.

The preparations of block copolymers (*Scheme 1*) were all carried out according to a one-pot, two-step procedure starting with the synthesis of the flexible block (A). As this unit was readily soluble and formed low viscosity solutions in the solvent system the incorporation of the flexible blocks in the polymer was readily achieved during the second step, the polymerization of the stiff block (B). The size of the blocks was governed by the stoichiometry of the two reactants. The excess of the amine component in the formation of the flexible segment was always kept at a constant amount in order to theoretically generate the same number of molecules independent of the chain length. The monomers for the stiff chain were always added in the amounts needed to produce stoichiometric balance in the system. In this way the chain length of the flexible block was varied while the chain length of the stiff block was kept constant.

Table 1 Polymer data

Fibre no.	η_{inh} (dl g^{-1})	Amount of flexible block (% w/w)	Block length[a] Stiff (n)	Flexible (m)[b]
I	9.30	0	–	–
II	3.26	22	49	14
III	4.16	29	49	20
IV	3.80	50	49	49

[a] Theoretical degree of polymerization based on stoichiometry

[b] m and n refer to *Scheme 1*

The characterization of stiff chain aromatic polyamides is difficult because of the low solubility of the polymers in anything but concentrated sulphuric acid. However the flexible polymer was readily dissolved in NMP. The fact that no polymer could be extracted from the samples with NMP showed that the polymers were true block copolymers. The inherent viscosities of the polymers studied together with the percentage of flexible block and the block lengths are listed in *Table 1*.

When the polymers were dissolved in concentrated sulphuric acid the stiff polymers formed a rather low viscosity stir opalescent solution, a behaviour well known for liquid crystal forming rigid rod polymers[10]. The block copolymers on the other hand formed stir opalescent high viscosity gelatinous solutions. This occurred because the flexible blocks formed tie molecules between the liquid crystalline arrays formed by the stiff blocks which resulted in physical crosslinking of the system. This also showed that the polymers are true block copolymers as a mixed solution of stiff and flexible polymers in sulphuric acid did not show this behaviour.

Fibres and fibre properties

Tensile properties of as spun fibres from four different polymers with a flexible block content ranging from 0 to 50% are shown in *Table 2*. As is evident from *Table 2* both the initial Young's modulus, the tangent modulus[28] after the yield point and the tenacity of as spun fibres decreased drastically when flexible blocks were introduced into the stiff polymer. The elongation at break of the fibres was largely unaffected by the incorporation of flexible blocks in the polymers.

However, it is evident from *Table 2* that when fibres II, III and IV are compared there is no effect by the length of flexible blocks on the strength and stiffness of the as spun fibres. Consequently for fibres II, III and IV the tensile properties of the as spun fibres seem to be dependent upon the stiff block which is held constant in length in these polymers. The lower tensile properties of fibres II, III and IV compared to fibre I are an effect of the presence of flexible blocks and possibly their influence on the order of the fibres.

Heat treatment of the fibres at 370 or 500°C results in changes in the mechanical properties of the fibres (*Table 3*). When the fibres were heat treated a drastic increase in Young's modulus was observed together with a decrease in elongation at break. This is a well known behaviour for this type of fibre upon heat treatment[10]. However, fibre IV containing 50% flexible blocks turned extremely brittle when heat treated at 500°C.

The thermogravimetric data in *Table 4* reveal a weight

Table 2 Tensile properties of as spun fibres

Fibre no.	Amount of flexible block (% w/w)	E_1[a] (GPa)	E_2[b] (GPa)	Yield point σ (GPa)	ε (%)	σ_B[c] (GPa)	ε_B[d] (%)
I	0	52	40	0.43	0.6	1.87	4.2
II	22	24	6	0.26	0.9	0.61	5.6
III	29	28	13	0.29	0.9	0.86	4.1
IV	50	24	11	0.34	1.8	0.69	5.5

[a] Young's modulus

[b] Tangent modulus after yield point

[c] Tensile strength

[d] Elongation at break

Table 3 Tensile properties of heat treated fibres

Fibre no. /temp. (°C)	Amount of flexible block (% w/w)	E_1 (GPa)	E_2 (GPa)	Yield point σ (GPa)	Yield point ε (%)	σ_B (GPa)	ε_B (%)
I/370	0	65	–	–	–	1.82	2.5
I/500	0	105	–	–	–	1.88	0.7
II/500	22	65	–	–	–	0.64	1.9
III/370	29	40	32	0.30	0.5	0.93	2.1
IV/500	50	54	–	–	–	0.75	0.5

Table 4 Thermogravimetric data of the fibres

Fibre	Mass loss (%) <150°C	Mass loss (%) <550°C
I	1.5	7
II	3.1	17
IV	3.6	30
I/500[a]	0.6	5
IV/500[a]	1.6	15

[a] Temperature for heat treatment

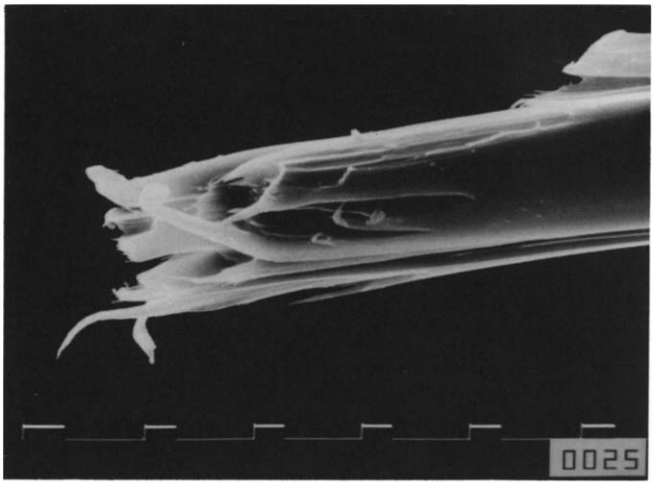


Figure 1 Fracture surface of as spun fibre I

loss at temperatures up to 150°C which is probably due to the loss of water. As water is known to be a plasticizer for aramides and the thermal treatment decreased the water content of the fibres a stiffening resulted. However, this is not enough to explain why fibre IV, heat treated at 500°C, behaves like a stiff molecular composite.

The influence of the flexible blocks on the solution behaviour of the block copolymers was clearly demonstrated by the formation of a physically crosslinked gel where the flexible blocks acted as tie molecules between liquid crystalline domains. When this liquid crystalline gel is spun into fibres it is reasonable to assume that this type of crosslinking will also be present in the fibre. The behaviour of fibre IV after heat treatment is in agreement with this type of crosslinking of the fibre.

However, fibres II and III containing shorter flexible blocks did not show this embrittlement and bending stiffness. This can only mean that there are no links between the crystallites in these fibres. Hence the flexible blocks are too short and it is energetically most favourable for all the stiff blocks of a polymer molecule to arrange within the same crystallite.

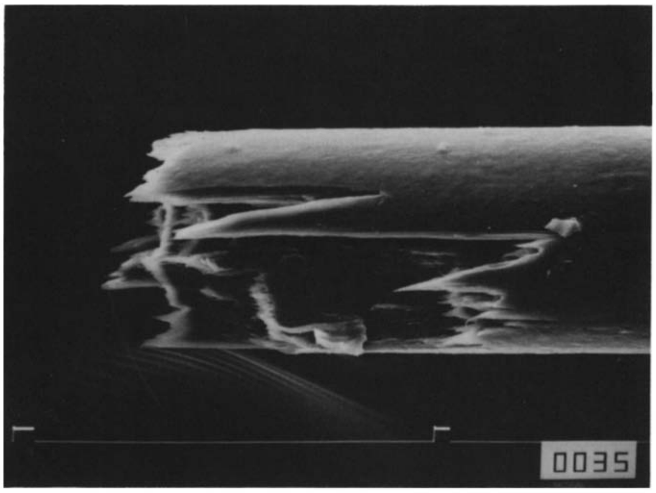


Figure 2 Fracture surface of as spun fibre III

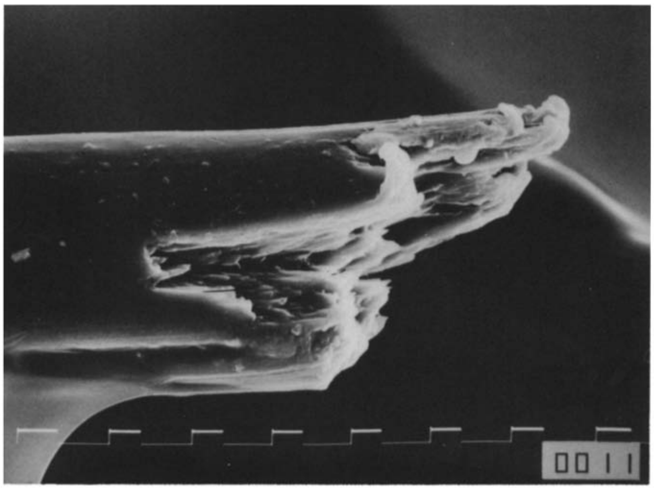


Figure 3 Fracture surface of as spun fibre IV

The fracture surfaces from as spun fibres shown in *Figures 1–3* clearly show a decreasing tendency of the fibres to form fibrils at rupture as flexible blocks of increasing length are introduced in the polymer.

CONCLUSIONS

Aromatic block copolyamides containing stiff and flexible blocks have been synthesized. Upon dissolution in concentrated sulphuric acid the polymers form liquid crystalline gels. The fibres spun from these gels showed a decrease in Young's modulus and tensile strength compared to fibres from the stiff polymer. The elongation at break of the fibres was largely unaffected. The Young's modulus increased and the elongation at break decreased when the fibres were heat treated. The fibre containing the longest flexible segment became brittle and stiff towards bending upon heat treatment. The tendency of the stiff fibres to form fibrils at rupture decreased when flexible blocks were introduced in the polymer. The effects are explained in terms of the influence of the flexible block on the fibre morphology.

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