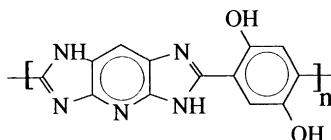


Design, synthesis and properties of a novel rigid rod polymer, PIPD or 'M5': high modulus and tenacity fibres with substantial compressive strength

Doetze J. Sikkema*

Akzo Nobel Central Research, P.O. Box 9300, 6800 SB Arnhem, The Netherlands
 (Received 2 September 1997; accepted 5 November 1997)

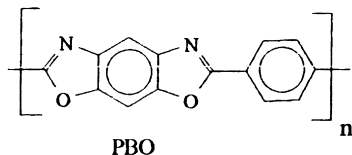
A rigid rod polymer with strong hydrogen bonds between the polymer chains was found in polypyridobisimidazole based on 2,3,5,6-tetraaminopyridine and 2,5-dihydroxyterephthalic acid (D. J. Sikkema and V. Lishinsky, WO 94/25506). The strong interchain forces translate into the highest compressive strength found in polymer fibres by far, and the polarity of the polymer seems to contribute to easy adhesion in advanced composite manufacture. The modulus and tenacity are as expected for a rigid rod polymer in the general class of the earlier PBZT and PBO fibres. © 1998 Elsevier Science Ltd. All rights reserved.



(Keywords: polypyridobisimidazole; rigid rod polymers; polymer fibres)

INTRODUCTION

Two methods have proved effective in preparing high-modulus, high-tenacity polymer fibres: (a) perfecting the drawing technique of precursor fibres in order to attain draw ratios way above 10, as in the well-known polyethylene Dyneema and Spectra yarns^{1–3}; and (b) manipulating rigid-rod-like molecules into fibres that are already very highly oriented in the as-spun state, as in PpPTA fibres (for reviews, see Refs. 4–6). Work has been directed at much stiffer rigid-rod-like materials in an effort that originated from the US Air Force, culminating in the PBO fibre that is now becoming commercially available from Toyobo after much development at Wright–Patterson AFB, at SRI International and at Dow Chemical (for reviews, see Refs. 4, 5, 7 and 8).



Although PBO shows very impressive tensile properties, its performance under compression has been disappointing, and much work has been done in various ways to correct the problem but without making much headway, however. Various schemes have been tried to increase lateral strength

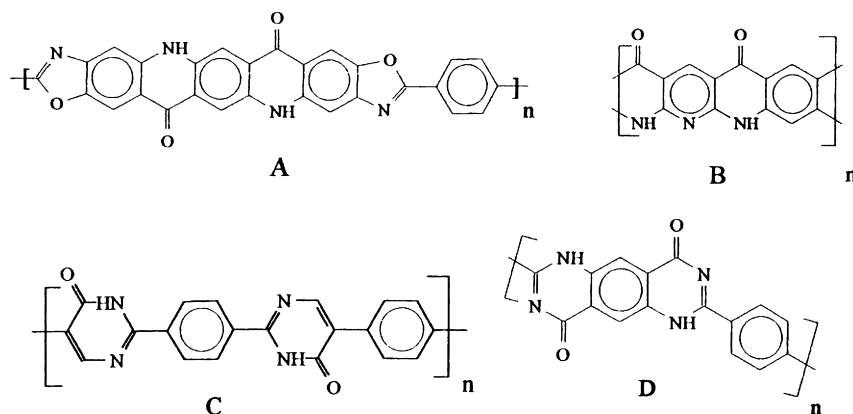
in PBO after fibre formation^{9–14} (also, for a review, see Ref. 15, often by cross-linking. One attempt at introducing hydrogen bonds in such a polymer did not afford the improved compression performance hoped for. Its lack of success in attaining improved compression properties was attributed to the hydrogen bonds being formed intramolecularly rather than intermolecularly¹⁶.

It has been the ambition of this author to create polymers that are as rigid-rod-like as PBO, with strong intermolecular hydrogen bonds.

Initial work was concerned with polymer systems that were rather different from PBO with a view to developing a route which does not employ the extremely oxygen-sensitive aromatic tetrafunctional nucleophiles that are characteristic of the PBO-like approach. Parts of this early work have been reported^{17–20}.

For various reasons, no attractive polymers or fibres have proved to be accessible by these routes, and we turned our attention to the well-proven (albeit experimentally challenging^{1,7,8}) polymerization of one-ring aromatic tetrafunctional nucleophiles. An example of high merit appeared to be 2,3,5,6-tetraaminopyridine: 2,6-pyridinediamine, a commercial product, is fairly easily accessible by Chichibabin amination (we found a more economical route to 2,6-diaminopyridine²¹), and, importantly, nitration was expected to be highly selective for production of the 3,5-dinitro isomer. Literature reports exist with regard to this nitration, albeit with low yield after purification^{22,23}, as well as to the polymerization of the tetraamine, starting with the HCl salt (along USAF-SRI lines^{1,7,8} for PBO), with isophthalic acid to prepare a thermally stable polymer (Ref. 24; see also Refs. 17–19).

* Tel.: 0031 26 3663459; fax: 0031 26 3665175; e-mail: Doetze.Sikkema@AHM.AkzoNobel.nl



EXPERIMENTAL

Nitration of 2,6-diaminopyridine.

A 10 l beaker was charged with 6 l of ethanol, and after heating to 60°C, 2000 g (18.34 mol) of 2,6-diaminopyridine (DAP) were added in portions with rapid stirring. After the solution became clear (2 h), 900 g of concentrated sulfuric acid (9.18 mol) were added over 2 h. The final pH should be checked to be between 3 and 5, and can be adjusted by the further addition of DAP or H₂SO₄. The mixture was cooled to room temperature and the DAP sulfate (2563 g, 88%) was filtered off and dried for 24 h at 50°C at 2 mbar. Using the mother liquor for the next preparation of DAP sulfate increased the yield to essentially quantitative. If desired water, can be used as the reaction solvent for preparing the sulfate.

A 10 l double-walled reactor was charged with 1200 ml of 20% oleum. After cooling to 0°C, 375 g (2.37 mol) of DAP sulfate were added slowly, with vigorous stirring, keeping the temperature below 30°C, over 2 h. A 299 g (4.75 mol) amount of 100% HNO₃ was added over 2 h with rapid stirring, keeping the temperature below 20°C. The reaction mixture was quenched with 6 kg of ice (energetic stirring to avoid hot spots; final temperature, 2°C), and the yellow product was filtered off and washed three times with water, then finally with dilute ammonia to produce 434 g of 2,6-diamino-3,5-dinitropyridine (DADNP) (92%). The DADNP produced in this way contains trace amounts, or up to several percent, of the aminohydroxy hydrolysis product, depending on the success of the quenching operation.

Product characteristics were as follows. IR (KBr, transmission) (cm⁻¹): 3580, 3460, 3290(w), 1670(s), 1560, 1500, 1440, 1420, 1375, 1330, 1275, 1085, 995, 880, 815, 770. ¹H NMR (DMSO) (ppm): 8.27 (s, 2H: NH₂), 8.43 (s, 2H: NH₂), 9.00 (s, 1 H: δ-C-H), from TMS. The hydrolysis product can be seen (if present) at 9.10 ppm (δ-C-H). Traces of H₂SO₄ appear as a triplet at 7.08 ppm. ¹³C NMR (DMSO) (ppm): 120.5, 135.8, 155, from TMS.

2,3,5,6-Tetraaminopyridine.

Phosphate. In a 1 l autoclave, 100 g of DADNP, 628 ml of H₂O, 116 g of 85% phosphoric acid and 5 g of 10% Pd-on-C were slurried; air was displaced with nitrogen and 20 bar of hydrogen were supplied; the temperature was raised to 50°C and stirring was continued with the supply of hydrogen at 20 bar until the hydrogen consumption ceased (30 h). Without the introduction of air, 150 g of 38% aqueous HCl were added, and the mixture was extruded through a filter from the autoclave with 5 bar of H₂ within 5 min into a flask flushed with nitrogen. Through

a septum, 110 ml of deaerated aqueous 25% NH₃ were added to the vigorously stirred solution; upon cooling a rich slurry of yellow crystals was formed which was filtered off in a glove box under nitrogen, washed twice with water (resulting in important losses) and twice with alcohol. After flushing the crystals for 1 h with a nitrogen stream, the virtually dry crystals could be transferred from the glove box to a drying oven without discolouration; drying for 20 h at 50°C and 1 mbar yielded 54.44 g, 45.7% of ochre-yellow TAP.H₃PO₄. This product yielded only a modest molecular weight (MW) polymer.

Hydrochloride. A hydrogenation was conducted employing 1575 ml of water, 925 ml of 85% phosphoric acid, 429 g of DADNP and 9.4 g of Pd/C (10%). After catalyst filtration, 1 l of 36% aqueous HCl was added, followed by 2 l of THF and 1 l more of concentrated HCl. After about 1 min, a precipitate of very light tan plates began to form. Filtering under nitrogen and drying for 18 h at 1 mbar and 50°C yielded 487 g (85%) of polymer grade TAP.3HCl.1H₂O. Substituting concentrated HCl for the THF during the crystallization step gave an equivalent result.

The product characteristics were as follows. ¹H NMR (D₂O): 7.65 (s, 1H), from TMS. ¹³C NMR (D₂O): 103.0, 134.9 and 147.8 ppm, from TMS. IR (DRIFT, Kubelka-Munk) (cm⁻¹): very strong band at 3500–2500 peaking at 3349, 3141, 2820 and 2600; weak bands at 2225, 2004; strong band peaking at 1682, 1606 and 1548; more peaks at 1490, 1385, 1343, 1296, 1129, 1088, 990, 856, 800, and 578.

Dimethyl 2,5-dihydroxyterephthalate.

In a 20 l reactor with stirrer, thermometer, reflux head and dropping funnel, dimethyl succinoylsuccinate (1980 g, 8.676 mol) was dispersed in 9.9 l of acetic acid, the dispersion was heated with stirring to 111°C, and 9.9 g each of iodine and potassium iodide were added. Without external heating, 886 ml of 30% H₂O₂ were added at a reaction temperature of 105–114°C in the course of 190 min. (Caution: if the reaction temperature drops below 105°C, external heating should be provided up to 108–110°C, otherwise H₂O₂ build-up in the reactor may result). Ten minutes after the last hydrogen peroxide addition, 4 l of warm and 3 l of cold water were stirred through the reaction mixture. After cooling to room temperature, the slurry was filtered and washed twice with water. For the next step, drying of the filter cake is unnecessary. Drying the product (24 h; 50°C; 1 mbar) yielded 1430.5 g of DMDHT (6.324 mol, 73%), M.P. 148.6–154.6°C (10°C min⁻¹). Product characteristics were

as follows. IR (DRIFT-Kubelka–Munk): 3291, 3067 (w), 3009, 2856 (w), 1680, 1493, 1440, 1356, 1329, 1198, 1098, 957, 895, 866, 790, 698, 602, 513, 452 cm^{-1} . NMR (DMSO- d_6) (ppm): ^1H 3.89 (6H), 7.26 (2H), 9.83 (2H); ^{13}C 53.0, 118.0, 120.1, 150.9, 167.5, from TMS.

2,5-Dihydroxyterephthalic acid (DHTA)

In a 20 l reactor with stirrer, dropping funnel, thermometer, reflux head and nitrogen inlet, NaOH (792 g, 19.8 mol) was stirred into 3 l of warm water. A 1430.5 g amount of dry DMDHT (see above, 6.324 mol) was slurried in 3 l of water, and the slurry was added to the alkali. Under nitrogen, the mixture was heated to 95°C. This resulted in a colour change: the yellow DMDHT formed the red phenolate salt as it dissolved, which was instantly converted to the greenish-yellow DHTA salt. External heating was discontinued (cooling to room temperature at this stage would crystallize the DHTA Na_2 salt in high purity) and in 2 h, 1725 ml of 36% HCl were added with the reaction mixture at or near boiling. After cooling to room temperature, the DHTA was filtered off, washed with water three times and dried at 80°C and 1 mbar for 20 h to yield 798.7 g of DHTA (4.03 mol, 64%). Product characteristics were as follows. M.P.: sublimes above 270°C, fast sublimation above 330°C, melting with boiling at 342–355°C, traces of (polymeric?) material remain above 360°C (20°C min^{-1}). IR (DRIFT-KM) (cm^{-1}): wide band at 3500–2400 peaking at about 3100, 1656, 1497, 1429, 1358, 1291, 1202, 899, 849, 796, 758, 699, 499, 440. NMR (DMSO- d_6) (ppm): ^1H 7.33, ^{13}C 117.7, 119.4, 152.5, 170.7, from TMS. The O–H type protons gave rise to an indifferent non-zero baseline above 9 ppm.

2,3,5,6-Tetraaminopyridinium 2,5-dihydroxyterephthalate (TD salt)

In a 5 l reactor with a powerful, high-speed, anchor-type stirrer, 132.08 g of DHTA were dissolved with 170.76 g of NaOH in 2 l of degassed water under nitrogen by heating to 55°C. In a 1 l Erlenmeyer flask connected to the reactor with tubing, 177.72 g of TAP.3HCl.1H₂O were dissolved with stirring and slight warming in degassed water under nitrogen to a total volume of 900 ml. With rapid stirring, the TAP solution was added via the tubing to the DHTA solution, with a slight nitrogen stream aiding the transport. The clear solution was treated without further delay with a mixture of 243.04 g of 85% phosphoric acid and 350 ml of water (degassed) in about 5 min, with high-energy stirring. When about half the amount of phosphoric acid had been passed into the reactor, the precipitate was at its heaviest and special care was needed to maintain a high stirrer speed. During the addition of the remaining phosphoric acid, the slurry again became easier to stir. Finally, 10.0 g of acetic acid (diluted to 30 ml with degassed water) were stirred through the mixture. The slurry was cooled with slow stirring in an ice bath, and filtered under nitrogen; the product was washed twice with 0.5–1 l of degassed water and finally with a similar volume of degassed ethanol to facilitate drying. Prior to transfer to a drying oven, nitrogen was flushed through the filter cake for about 1 h. The pH of the combined filtrates was checked ($4 < \text{pH} < 5.5$) and the product was dried for 24 h at 50°C and 1 mbar to produce 218.14 g (97% yield) of the yellow TD salt (a slight greenish tinge would be acceptable).

The addition of a small amount of sodium dithionite to the alkaline DHTA solution seemed to protect the TD salt against discolouration upon minor intrusions of air during

the handling of the wet product; no adverse effects were noted upon the polymerization of the TD salt resulting from such a preparation in the presence of some dithionite. The quality cannot yet be checked by a method other than (trial) polymerization.

Upon scaling-up, the TD salt proved more convenient to prepare in a continuous reactor system where aqueous streams of acidic TAP and alkaline DHTA were vigorously mixed to produce a slurry of the salt in a mother liquor at pH 4.5–5.

Polymerization example (18% of polymer in 81.6% polyphosphoric acid)

Into a 200 ml reactor with a powerful, low-speed, anchor-type stirrer, were charged 62.54 g of polyphosphoric acid (PPA; 83.69% of P_2O_5), 22.88 g of TD salt, 14.76 g of P_2O_5 and 0.12 g of tin powder; part of the PPA was added first, then the solids and finally the remainder of the PPA. The reactor was closed and air was displaced by nitrogen by repeated evacuation and nitrogen blanketing. The mixture was heated to 100°C (taking into account an exotherm appearing from about 70°C to about 100°C) and the doughy mass was homogenized for 1 h. The mixture was then heated to 140°C and stirred for 1 h more, followed by further heating to 180°C. The reaction mass became opalescent at 149°C and the stirring energy dissipated decreased substantially. The viscosity of the mixture increased again during stirring at 180°C for a total of 2 h; after 1 h the viscosity increase became very slow. The bottom part of the reactor was taken down and the product was transferred from the stirrer, where most of the viscous polymer solution remained, into the cylinder of a piston-type spinning machine. The relative viscosity η_{rel} was 25.6 (0.25 g dl^{-1} in methanesulfonic acid).

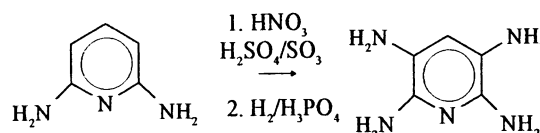
Size exclusion chromatography

Using a Zorbax PSM Trimodal-S column, g.p.c. experiments with methanesulfonic acid as the mobile phase proved uneventful. Detection was by UV (Kratos Spectroflow); calibration was performed by comparison with well-characterized Twaron aramid specimens.

RESULTS AND DISCUSSION

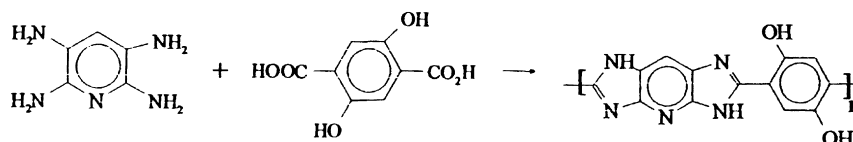
Monomer selection and syntheses

Synthesis of 2,3,5,6-tetraaminopyridine (TAP) along the lines of Refs 22 and 23, with low yield after nitration, and including reduction with tin/hydrochloric acid, afforded our early samples of TAP. Early attempts at catalytic reduction of the nitro compound were unsuccessful, mainly because of the truly horrific oxidative lability of TAP as the free base. A workable procedure was found in using dilute phosphoric acid as the medium for catalytic hydrogenation, thus avoiding ever handling the TAP free base.



Later, we succeeded in such a complete elimination of oxygen from our installations that the hydrogenation and catalyst filtration could be done with the free base in water (eliminating phosphoric acid from the recipe). In early work, we isolated TAP as the hydrochloride salt and used it in the polymerization^{4,5,7,8}. The nitration problems were

soon seen to reside in the production of 2-amino-6-hydroxy-3,5-dinitropyridine, a hydrolytic degradation product of the desired diaminodinitropyridine. We could stop this degradation pathway by modifying the nitration medium—changing from concentrated sulfuric acid^{22,23} to oleum²⁵ provided the means of exposing the hydrolysable product to strong aqueous acid only during the rapid aqueous quench after the reaction. Thus, we could isolate high-purity products at 90–95% from the nitration, and an 85% yield of polymer-grade-purity crystal from the reduction (TAP.3HCl.1H₂O).



Having a sufficient supply of TAP in hand, we tackled the polymerization. Reaction according to the method developed in Refs. 7 and 8 with terephthalic acid produced almost instantaneous precipitation of a very low MW oligomer; we also observed this when oleum was used rather than polyphosphoric acid as the polymerization medium-cum-dehydrating agent.

Polymerization with 2,5-dihydroxyterephthalic acid seemed desirable in itself (even though disappointing results were reported in Ref. 16 with this monomer) because the hydroxyl groups could contribute to the hydrogen bond network envisioned; it led to high molecular weight products, in contrast with unsubstituted terephthalic acid. Thus, not only did an enhanced-polarity polymer proved accessible, in fact the analogue with fewer active protons could not be prepared in a usable form. Concentrations of almost 20 wt.% of polymer in solution in PPA could be attained. By contrast, 1,2,4,5-tetraaminobenzene²⁶ (which likewise gives an insoluble very low MW material with terephthalic acid; see Ref. 27—note that a reasonable MW was reached in polymerizing a tosylated monomer) proved to have a solubility limit in its high MW polymer with 2,5-dihydroxyterephthalic acid of about 8.5%, in related work in our laboratory. (At 8–9% of polymer in PPA consisting, at the end of the polymerization, of 81.0% of P₂O₅ and 19.0% of water, η_{rel} values of about 100 (0.25 g dl⁻¹ in methanesulfonic acid) could be reached when starting with a tetraaminobenzene–DHTA (1:1) complex. Lower MW products of this were described earlier²⁸.)

2,5-Dihydroxyterephthalic acid (DHTA) is described in the literature as the product of the bromine/sulfuric acid-mediated aromatization²⁹ of diethyl succinoylsuccinate, a commercial product, followed by hydrolysis. The aromatization can also be effected with sulfur, analogous to the aromatization step in Refs. 17 and 20 (where succinoyl succinate is boiled with a slight excess of sulfur in NMP for 20–30 min as the temperature rises from about 150°C (H₂S evolution) to about 200°C, and dilution with water then precipitates dimethyl dihydroterephthalate, which is hydrolyzed with hot aqueous NaOH), or with sulfur with a Pd/C

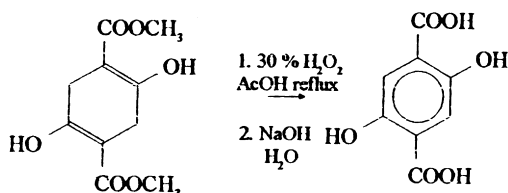
catalyst¹⁶. We found a convenient and non-noxious procedure in aromatizing the succinoylsuccinate in acetic acid at reflux with 30% aqueous hydrogen peroxide with a sodium iodide catalyst.

After hydrolysis, more than 90% of polymer-grade DHTA from succinoylsuccinate can be isolated upon acidification. (We found a more economical synthesis of DHTA: see Ref. 30.) Alternatively, the sodium salt of DHTA can be crystallized from the hydrolysis reaction mixture in high purity and somewhat lower yield (about 87%).

Polymerization

Right from the outset of our work with TAP hydrochloride and DHTA, we avoided the experimental difficulties inherent in the traditional^{4,5,7,8} method which involved adding most of the phosphorus pentoxide and the organic diacid only after driving off the hydrochloric acid by heating in ('weak') PPA. When working on a small scale at least, we could add all the ingredients at the outset of a heating cycle that involved^{4,5,7,8} many hours of heating at about 100°C while evacuating, in order to eliminate the hydrochloric acid. An important improvement was found in isolating TAP as its phosphoric acid salt, resulting not only in a much faster polymerization cycle, but also eliminating the corrosion-type difficulties implicit in the earlier route. TAP phosphate is, however, oxidatively much more fragile than the hydrochloride, necessitating the utmost care in its isolation and use. A much greater step forward was achieved by the synthesis of the TAP.DHTA (1:1) complex, or TD salt. This complex is somewhat more stable against oxidation than TAP phosphate and it precipitates in a high yield from the combination of aqueous solutions of the TAP HCl salt and DHTA, Na or K salt. It proved possible to make a high MW polymer from the TD salt prepared from acidified hydrogenation liquor and alkaline DHTA solution, without first crystallizing TAP.3HCl. A fast polymerization cycle (typically 4–5 h rather than over 24 h according to Refs. 4, 5, 7 and 8) now yields high MW polymer much more consistently than in the case when amine and acid components are weighed separately: relative viscosities (0.25 g dl⁻¹ in methanesulfonic acid) above 20 could be reached routinely, 100 being unremarkable, and values as high as 350 were seen when special care was taken. A further significant advantage of using the TD salt rather than separate components is that the delay in the process due to the slow dissolution of DHTA crystals which proved to require attention before, was now eliminated: the disintegration of TD salt in the PPA medium generates DHTA in a highly dispersed state.

We did not succeed in preparing the terephthalic acid salt of TAP, which we attribute to the weaker acidity of terephthalic acid. (Curiously, Rosenberg *et al.* describe an easy preparation of the terephthalate salt of 4,6-diaminoresorcinol³¹.) Thus, copolymers employing both DHTA and terephthalic acid (TPA) necessitated the use of TAP phosphate and TPA next to the TD salt. Such copolymers showed lower relative viscosities when more TPA was used as a comonomer and became insoluble in the polymerization medium when more than 50% of DHTA was substituted by TPA.



The polymerization of homopolymer consists of placing the TD salt, polyphosphoric acid and P₂O₅ with a trace of tin powder in the reactor, displacing air by nitrogen and heating to 140°C, and mixing for 1.5–2 h at that temperature (alternatively, first for 1 h at 100°C, then 1 h at 140°C) before taking the mixture to 180°C and stirring for another 1–2 h. When the mixture reaches 150°C it becomes liquid crystalline; after 1 h at 180°C the polymerization is essentially complete in most cases. Work on the mechanism of PBO polymerization has been reported recently^{32,33}.

The P₂O₅ content of the solvent system controls the final molecular weight, albeit that different purities of the TD salt require different PPA strengths, and obviously only the highest purity TD salt will deliver the highest MW polymers. The solubility limit of high MW homopolymer in 80.5–83% PPA (*i.e.* PPA consisting of 80.5–83% of P₂O₅, the balance being water) is 19 wt.%. At 180°C, the solution (18 wt.% of polymer) is a nematic solution with long relaxation times of orientation. Upon cooling it crystallizes at about 110°C; the crystallized solution melts at about 140°C. A further thermal transformation can be seen at about 80°C in DMA. Crystallosolvate fibres of astoundingly high and perfect crystallinity could be prepared under special conditions³⁴.

Spinning

Conventional air gap wet spinning of the as-polymerized solutions of polymers with M_w 60 000–150 000 (SEC with Twaron aramid calibration in methanesulfonic acid) at 180°C into a water or dilute phosphoric acid bath proceeded readily; spindraw ratios attainable depend on the spinning orifice diameter and the result normally delivers filaments with a diameter of 8–14 μm, which are further washed to a low phosphorus content and drawn (by a few per cent at most) at high temperature (above 400°C) to produce the final, high-modulus product.

Evolution of the fibre structure and morphology, and its properties, during the manufacturing process are discussed in separate papers^{34,35}.

Fibre properties

Even though much optimization remains to be done, we

soon achieved promising mechanical properties and structure data for our new 'M5' fibres (see *Table 1*). The crystal structure features hydrogen bonds in both the *x* and the *y* direction (*z* being the polymer main chain direction)³⁵. Moduli over 300 GPa, tenacities of well over 2 N tex⁻¹ (3.4 GPa), elongation at or above 1.5% and compressive strain in the Elastica test of 0.4% (corresponding to a compressive strength of 1.2 GPa) were recorded—the highest compressive strength by far shown in this test by any polymer fiber. The first composite test bars that were tested for longitudinal compressive strength confirmed the high compressive properties of the new fibre in composite form³⁶. This is in contrast with the behaviour of PBO, where a much lower compressive strength was found in composites than was suggested by the (already poor) Elastica loop test results^{9–15}.

Work is proceeding on spinning fibres with properties exceeding the values given above for early experimental samples of the new fibre.

Applications

The mechanical properties of the new fibre make it competitive with carbon fibre in most applications (*i.e.* in those areas where design compressive strains are limited similarly to aluminium). The high processing speeds inherent in organic fibres should inspire hope that the new fibre can compete economically with the carbon fibre type cited above, at an enhanced level of performance. The high electrical resistance of the new fibre should enable it to perform in areas where carbon fibre presents problems (corrosion in metal contacts) or is completely unsuitable, such as in electrical and electronic contexts. The high polarity of M5 aids in easy adhesion to a variety of matrix materials, judging by bundle pull-out tests performed with various epoxy, unsaturated polyester, and vinyl ester resins—where better adhesion was recorded than with adhesion-activated Twaron type 1001, and much better than with regular (non-activated) Twaron type 1000 aramid yarns. These gratifying results were obtained without any optimization, suggesting possibilities of even higher or (if needed) specifically tailored adhesion levels, depending on the application.

Table 1 Provisional characterization of M5 fibre spun on the bench-scale

Property	Twaron HM	C HS ^a	PBO ^b	M5 experiment ^c
Tenacity (GPa)	3.2	3.5	5.5	4
Elongation (%)	2.9	1.5	2.5	1.2
<i>E</i> Modulus (GPa)	115	230	280	330
Compr. str. (GPa) ^d	0.58	2.1	0.4	1.6
Compr. strain (%) ^d	0.5	0.9	0.15	0.5
Density	1.45	1.8	1.56	1.7
Water regain (%)	3.5	0	0.6	2
LOI (% O ₂)	29	— ^e	68	> 50
Onset of thermal degradn., air	450	800	550	530
Electr. conduction	—	++	—	—
Impact resistance	++	--	++	++
Damage tolerance	+	--	— ^e	++
Weaving props.	+	—	+	+
Knot strength	+	--	0	0

^aThe mechanical properties of carbon are evaluated in resin-impregnated strands in order to protect the material against premature brittle failure in the tensile testing machine. The organic fibres are tested as such; filament averages at a 10 cm gauge length are presented

^bToyobo data

^cMeasured in UD composite test bars, three-point bending test, onset of deflection for the organic fibre-reinforced composites; catastrophic failure for the carbon composites. M5 composites proved to be able to carry much higher loads than the load at the onset of deflection, and to absorb much energy at high strains in a mode analogous to the flow behaviour in steel being damaged

^eNo data

ACKNOWLEDGEMENTS

Among the many people who contributed to this study, special thanks are due to Vadim Lishinsky for his tenacious zeal in thinking about and making pyridine derivatives; to Antoine Duindam for his indefatigable efforts in improving our synthesis and polymerization procedures, and to Menno Lammers, Henk ter Maat, and Bert-Jan Lommerts for their pioneering work in spinning the new polymer. The invaluable help of Noor van Andel to make this project survive in the corporate environment is also gratefully acknowledged.

REFERENCES

1. Kalb, B. and Pennings, A. J., *Polymer Bulletin*, 1979, **1**, 871.
2. Smith, P., Lemstra, P. J., Kalb, B. and Pennings, A. J., *Polymer Bulletin*, 1979, **1**, 733.
3. Smith, P. and Lemstra, P. J., *Journal of Materials Science*, 1980, **15**, 505.
4. Northolt, M. G. and Sikkema, D. J., in *Liquid Crystal Polymers, from Structures to Applications*, ed. A. A. Collyer, Elsevier Applied Science, 1992.
5. Northolt, M. G. and Sikkema, D. J., *Advances in Polymer Science*, 1990, **98**, 115.
6. Vollbracht, L., in *Comprehensive Polymer Science*, Vol. 5, ed. G. Allen, Pergamon Press, Oxford, 1989, Chapter 22.
7. Wolfe, J. F., in *Encyclopedia of Polymer Science and Engineering*, Vol. 11, 2nd edn., Wiley-Interscience, New York, 1988, p. 601.
8. Adams, W. W., Eby, R. K., McLemore, D. E. (Eds.), The materials science of rigid-rod polymers, in *Materials Research Society Symposium Proceedings*, Vol. 134, 1989.
9. Sweeny, W., *Journal of Polymer Science, Part A*, 1992, **30**, 1111.
10. Rakas, M. A. and Farris, R. J., *Journal of Applied Polymer Science*, 1990, **40**, 823.
11. Sahafeyan, M. and Kumar, S., *Journal of Applied Polymer Science*, 1995, **56**, 517.
12. Dotrong, M., Dotrong, M. H. and Evers, R. C., *ACS Polymer Preprints*, 1993, **34**(2), 408.
13. Dang, T. D. and Arnold, F. E., *ACS Polymer Preprints*, 1995, **36**(1), 455.
14. McGarry, F. J. and Moalli, J. E., *Polymer*, 1991, **32**, 1816.
15. Kozey, V. V., Jiang, H., Mehta, V. R. and Kumar, S., *Journal of Materials Research*, 1995, **10**, 1044.
16. Tan, L.-S., Arnold, F. E., Dang, T. D., Chuah, H. H. and Wei, K. H., *Polymer*, 1994, **35**, 3091.
17. Sikkema, D. J., *Synthesis*, 1993, 1211.
18. Duindam, A., Lishinsky, V. L. and Sikkema, D. J., *Synthetic Communications*, 1993, **23**, 2605.
19. Sikkema, D. J. and Reichwein, J., *Macromol. Chem. Phys.*, 1994, **195**, 273.
20. Sikkema, D. J. and van Guldener, D. B., *Polymer*, 1993, **34**, 4373.
21. NL 1000360, 1995.
22. Gerber, A. H., *Journal of Polymer Science (Chem.)*, 1973, **11**, 1703.
23. Williams, L. and Cohen, S. A., *Journal of Heterocyclic Chemistry*, 1971, **8**, 841.
24. Gerber, A. H., US Patent A-4533692, 1973.
25. NL 1001238, 1995.
26. Nietzki, R. and Schedler, A., *Berichte der Deutschen Chemischen Gesellschaft*, 1897, **30**, 1666.
27. Kovar, R. F. and Arnold, F. E., *Journal of Polymer Science (Chem.)*, 1976, **14**, 2807.
28. Dang, T. D., Tan, L. S. and Arnold, F. E., *ACS PMSE*, 1990, **62**, 86.
29. Dang, T. D., Chuah, H. H., Tan, L. S. and Arnold, F. E., US Patent 5041552, 1991.
30. NL 1001628, 1995.
31. WO 93/08156, 1995.
32. So, Y.-H., Heeschen, J. P. and Murlick, C. L., *Macromolecules*, 1995, **28**, 7289.
33. So, Y.-H. and Heeschen, J. P., *Journal of Organic Chemistry*, 1997, **62**, 3552.
34. Lammers, M., Klop, E. and Northolt, M. and Sikkema, D. J., *Polymer*, 1998, **39**(24), 5999–6005.
35. Klop, E. and Lammers, M., *Polymer*, 1998, **39**(24), 5987–5998.
36. van der Jagt, O., *Polymer*, in press.