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The synthesis and characterisation of reactive poly(*p*-phenylene terephthalamide)s: A route towards compression stable aramid fibres

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ABSTRACT

Herein we report on the synthesis of reactive poly(*p*-phenylene terephthalamide) (PPTA) oligomers and the preparation and characterisation of aramid fibres thereof. Methacrylate and maleimide reactive end-groups were found to be sufficiently stable in H_2SO_4 at 85 °C and they were used to prepare reactive PPTA oligomers. Lyotropic spin-dopes could be prepared with up to 20 wt% of reactive oligomer (M_n = 3900 g mol^{-1}) and this modification did not interfere with the fibre spinning process and had no effect on the fibre tensile properties. The as-spun fibres did indeed show a modest (+0.1 GPa) improvement in compression strength. A high temperature treatment at 380 °C resulted in fibres which all show a significant increase in compressive strength over their as-spun precursors, *i.e.* from 0.7 to 0.9 GPa. When fibres were treated at 430 °C the compression values of the oligomer-modified fibres dropped somewhat, whereas unmodified PPTA displayed a compressive strength of 1.1 GPa. Other favourable fibre properties such as modulus and tenacity were not compromised.

1. Introduction

High performance polymeric fibres such as poly(*p*-phenylene terephthalamide) (PPTA), poly(pyridobisimidazole), or PIPD (a fibre which is currently marketed under de name 'M5') and ultra high molecular weight polyethylene fibres (Dyneema) show specific linear tensile properties based on which they outperform their inorganic counterparts like carbon and glass fibres [1–4]. A major concern is, however, their strength under compressive loading which in general is found to be lower then 1 GPa and this significantly limits their use in structural applications [5]. At present, there is general consensus that the low compressive strength of polymeric fibres finds its origin in the mediocre lateral interactions between the polymer chains, *i.e.* the poor inter-molecular interactions result in a low inter-molecular shear-strength. This idea is supported by the increasing compressive strengths when comparing high-modulus fibres of comparable tensile properties such as UHMWPE, *para*-aramid, and PIPD fibres. In these fibres, the lateral interactions between the molecular chains are the results of van der Waals forces, hydrogen bonds forming one-dimensional (*para*-aramid) and hydrogen bonds forming two-dimensional networks (PIPD). Since the compressive strength increases from 0.02 to well above 1.0 GPa, this trend strongly suggests that stronger lateral interactions indeed increase the fibre compressive strength. It should be noted that strong lateral interactions are not only limited to hydrogen bonds, but can also involve other favourable electrostatic interactions such as dipole–dipole, π–π and molecular polarizability.

Several attempts to enhance lateral interactions via crosslinking adjacent polymer chains have been explored in the past. During the mid-90s a series of articles were published on the synthesis of 1,2-dihydrocyclobutabenzene-3,6-dicarboxylic acid monomer and its successful incorporation into PPTA fibres [6–9]. The formation of crosslinks raised the strain to kink band formation and decreased the kink band density at a given strain. Although strong evidence for the control over the compressive behaviour was presented, no numerical data on the compressive strengths were reported. At the same time another monomer, disulfonediamine, was explored by Suter and co-workers [10,11] and incorporated into fibres using this monomer as a substituent for *p*-phenylene diamine. The fibres, however, displayed poor mechanical properties, which is likely to be the result of the distortion of the crystal structure due to the bulkiness of the DSDA monomer. Other chemical modifications include the incorporation of halogenated monomers into PPTA and PBZT fibres by Sweeny leading to significant deterioration of tensile properties [12]. Incorporation of methyl-pendant monomers into PBI and PBZT fibres by Jenkins et al. resulted in higher tensile but lower compressive strengths upon heat treatment [13], and

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diacetylene functionalised PPTA fibres with improved tensile properties were prepared by Beckham and Rubner [14]. Instead of introducing monomers capable of forming covalent bonds, Xue and Hara [15,16], and less successfully by Glomm and co-workers [17], made use of ionic moieties to enhance the cohesive forces between adjacent polymer chains. Xue and Hara's results showed that the number of kink bands decreased as a result of the presence of lateral ionic bonds.

Other attempts to enhance lateral interactions via crosslinking rely on the addition of a crosslinking agent or infiltration of crosslinkable polymers rather than on changing the polymer backbone chemistry. The most successful attempt at present is the development of a new polymer, PIPD, which is capable of forming a 2 dimensional hydrogen bonded network. As a result of the high lateral interactions between polymer chains, compressive strengths as high as 1.7 GPa were reported [18]. This polymer is rather expensive and the compressive properties appear to be sensitive to water, which reduces compressive performance over time [19–21].

We report here on a novel approach towards the synthesis of compression stable aramids by incorporating reactive end-groups on the poly(*p*-phenylene terephthalamide) (PPTA) chain ends. This new concept is based on PPTA-compatible reactive oligomers, which are added to the standard PPTA spin-dope prior to the fibre spinning process and which are activated in a thermal post-processing step. This approach was inspired by our previous work on reactive all-aromatic thermotropic oligomers. The processing and toughness of all-aromatic liquid crystal polymers could be improved significantly when crosslinkable end-groups were introduced at the polymer chain ends [22,23]. In case of PPTA, the oligomers with reactive end-groups were designed to match the molecular packing preferences of PPTA-based fibres and not to interfere with the lyotropic spinning process. In particular, we describe here a systematic approach for careful selection of suitable end-groups and a route to incorporate them into PPTA fibres. The spinning process carried out in sulphuric acid (>98.5%) at 85 °C requires any end-group to be incorporated into the PPTA fibre to be chemically stable in 85 °C sulphuric acid for at least the duration of the spinning process. *i.e.* no chemical degradation or premature crosslinking reactions are allowed. In addition, the conditions for activating the reactive end-groups should not result in degradation of the polymer backbone chemistry or disrupt the final fibre structure and morphology. In order to gain more insight in the chemical stability, amide model compounds were prepared and investigated by NMR. An overview of the end-groups that were selected to prepare these model compounds is shown in Fig. 1. Maleimides and phenylethynyl end-groups are known for their use in high performance polymers [24]. Adding substitutes such as a methyl group, or phenyl ring, possibly shield the reactive double bond in the acid environment by steric hindrance. In addition, we also tested a series of acrylates, which were anticipated to be stable in acidic environments since their synthesis often involves acidic reaction conditions [25,26], thus suggesting a good chemical stability. Furthermore, it was believed that the fluorine atoms might have a shielding effect protecting the reactive double bound. Aniline was used to prepare oligomers with a non-reactive end-group.

Based on results of the aforementioned analyses, chemically stable end-groups were selected and used to end-cap aramid oligomers, which were incorporated in aramid fibres. These fibres were extensively tested to determine the effect of our approach – *i.e.* incorporating reactive oligomers into fibres and subjecting them to a thermal post-treatment – on the linear tensile properties and in particular on the critical compressive stresses. Since literature results showed that a high concentration of crosslinkable functionalities (>5 mol%) resulted in a modest increase in compressive strength but a drop in other favourable fibre properties such as tenacity and elongation at break, we decided to keep the concentration of the reactive oligomers low.

2. Experimental

2.1. Materials

All materials were obtained from Sigma–Aldrich and used as-received unless stated otherwise. Acetic anhydride 97% was obtained from J.T. Baker, *p*-phenylene diamine pellets from DuPont, terephthaloylchloride and the methylmaleimido benzamide end-

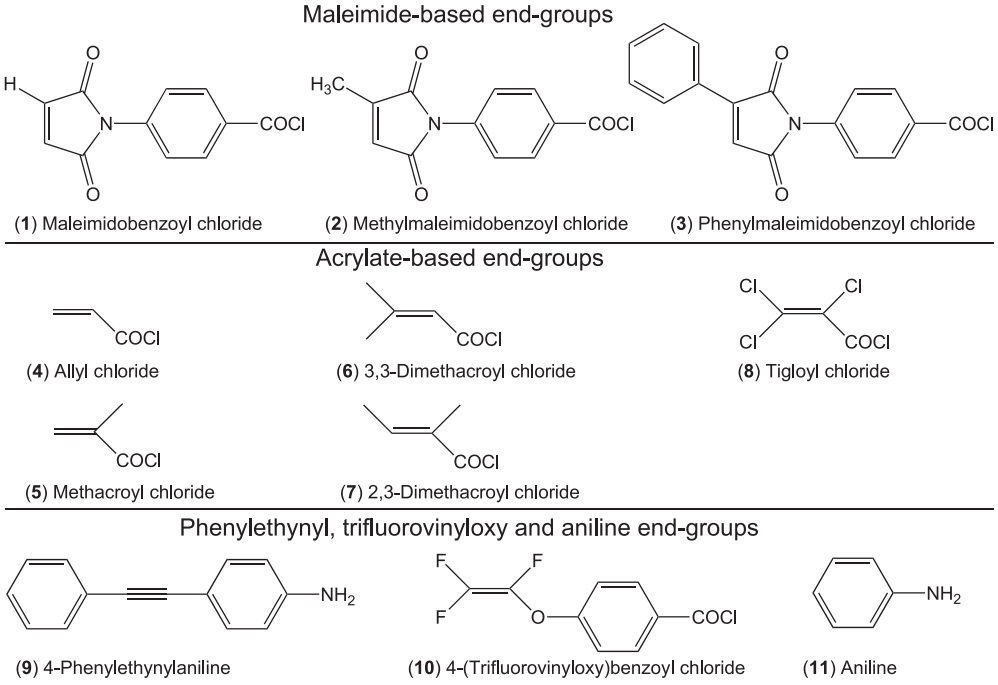
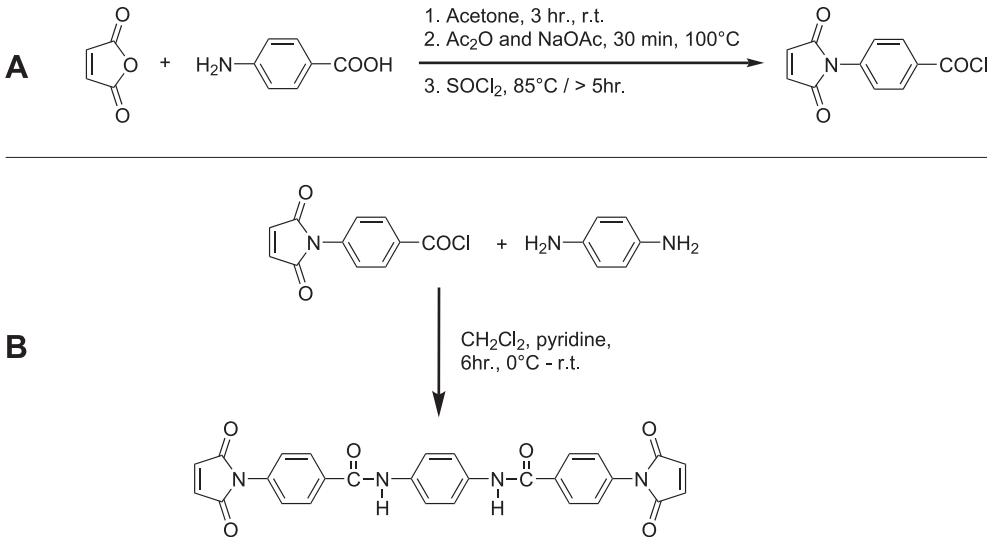


Fig. 1. Selection of reactive end-groups used for the preparation of amide model compounds.



Scheme 1. Synthetic route (A) towards maleimidobenzoyl chloride (**1**) and (B) the coupling of (**1**) with p-phenylene diamine to prepare the amide model compound (**I**).

groups from Teijin Aramid B.V. Tigloyl chloride (98+%) was purchased from TCI Europe and 4-(trifluorovinyloxy)benzoyl chloride from Fluorochem Ltd.

2.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity INOVA 300 spectrometer operated at 300 and 75 MHz respectively. Chloroform-*d* ($CDCl_3$) and dimethyl sulfoxide-d_6 (DMSO-d_6) were used as solvents and sulphuric acid-d_2 (98 wt% in D_2O, with 99.5 atom% *D*) was used as the solvent for determining the chemical stability of the model compounds under acid conditions at 85 °C. For such measurements, reference spectra were recorded at room temperature in DMSO-d_6 and D_2SO_4. Next, the sample was heated to 85 °C within the spectrometer and 3 subsequent spectra were recorded at time intervals of 10 min.

In order to acquire information on the oligomer molecular weight distribution, size exclusion chromatography (SEC) experiments were performed. The oligomers were dissolved in 100% sulphuric acid (0.1 mg mL^{-1}) and eluted over a Zorbax GPC column (250 × 6.2 mm). For detection a UV detector (340 nm) was used. The molecular weight values were calculated using Cirrus version 1.1 GPC software (Polymer Laboratories). As references, a high molecular weight PPTA (yarn type 1010) and a PPTA-based trimer were used.

Thermal properties of end-groups and model compounds were investigated using a PerkinElmer Pyris Diamond TG/DTA and a PerkinElmer Sapphire DSC. Unless stated otherwise, samples of typically 5 mg were investigated while heating at 10 °C min^{-1} and using nitrogen as a purge gas. Curing experiments were done using a Linkham THMS hot-stage pre-heated to the desired temperatures and purged with nitrogen.

The linear fibre properties were determined on an Instron 5543 tensile tester. For each fibre 10 filaments with a gauge length of 100 mm were tested at a speed of 10 mm min^{-1}. Experiments were performed under standard laboratory conditions of 21 °C and 65% relative humidity. The compressive properties of single filaments were determined by the elastica single filament compression test [27,28].

X-ray diffraction was used to determine the crystal unit cell parameters and the apparent lateral crystal size. The XRD measurements were carried out on a Bruker D8 diffractometer in $\theta/2\theta$ geometry, equipped with parallel beam optics. The optics consists of a primary 60 mm Göbel focussing mirror, a parabolic Ni/C multilayer device, providing Cu-Kα radiation, and 0.12° Soller slits. The diffractometer is equipped with scintillation detector and auto-changer.

2.3. Synthesis of reactive end-groups

2.3.1. Maleimidobenzoyl chloride (1)

The synthesis of the maleimide reactive end-group was performed using standard synthetic procedures as summarised in Scheme 1. The maleimidobenzoyl chloride was prepared from maleic anhydride and *p*-aminobenzoic acid according to a literature procedure [29].

The title compound was purified via recrystallisation (CH_2Cl_2: hexane, 50:50) or sublimation. ^{1}H NMR ($CDCl_3$) δ(ppm): 6.9 (s, 2H), 7.6 (d, J = 8.7 Hz, 2H), 8.2 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ (ppm): 125.1, 131.7, 132.2, 134.6, 137.7, 167.5, 168.6; T_m = 157 °C. The melting point was found to be in agreement with literature [30].

2.3.2. Phenylmaleimidobenzoyl chloride (3)

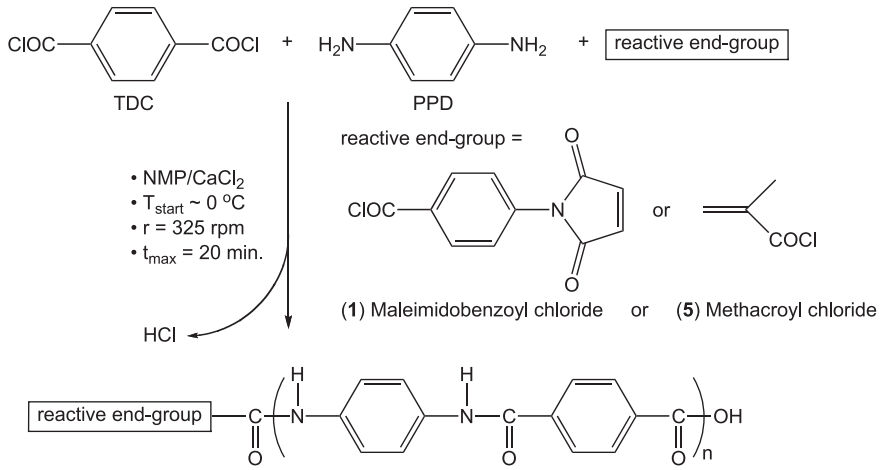
The phenyl-substituted maleimide was synthesised from phenylmaleic anhydride and *p*-aminobenzoic acid employing the previously described [25]. ^{1}H NMR (DMSO-d_6) δ(ppm): 7.5–7.6 (m, 6H), 8.1 (m, 4H). ^{13}C NMR (DMSO-d_6) δ(ppm): 126.2, 127.1, 129.4, 129.6, 130.4, 130.6, 131.8, 136.3, 143.6, 167.4, 169.5, 169.8; T_m = 261 °C. The acid functionality was converted into an acid chloride by refluxing the product in $SOCl_2$ and removing the excess by distillation. The acid chloride was used immediately in the next step.

2.3.3. 4-Phenylethynylaniline (9)

4-Phenylethynylaniline was prepared via a palladium-catalysed coupling of ethynylbenzene and 4-iodoaniline [31,32]. The product was recrystallised from *n*-heptane/ethylacetate (9:1) yielding brown flakes. TLC(4/1 hexane/ethyl acetate) t_r = 0.10 (one spot); ^{1}H NMR ($CDCl_3$) δ(ppm): 3.8 (b, $-NH_2$) 6.6 (d, J = 8.6, 2H), 7.23–7.35 (m, 5H), 7.47–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ(ppm): 87.35, 90.15, 112.61, 114.75, 123.92, 127.65, 128.27, 131.35, 132.95, 146.66. MS (*m*/*z*): 193 (M+).

2.4. Synthesis of model compounds

In order to further investigate the end-groups with respect to their stability in strong acidic environments, well-defined amide-



Scheme 2. Synthetic route towards poly(p-phenylene terephthalamide) oligomers with reactive maleimide (**1**) or methacryloyl (**5**) end-groups.

based model compounds were synthesised via a condensation coupling of the amine, or acid (chloride) functionalised end-groups, with either terephthaloylchloride (TDC) or *p*-phenylene diamine (PPD). As a representative example, the synthesis of a maleimide (**I**) end-capped model compound is described below. All other model compounds were prepared using a similar procedure.

*2.4.1. Maleimide (MIBC) amide (**I**) or N,N′-1,4-phenylenebis[4-(2,5-dihydro-2,5-dioxo-1H-pyrrol-1-yl)-benzamide [33]*

Maleimidobenzoyl chloride 1.55 g (6.6 mmol) was charged into a 100 mL round bottom flask and immediately dissolved in 40 mL anhydrous CH_2Cl_2. After cooling to 0 °C, 0.328 g (3.0 mmol) *p*-phenylenediamine (PPD) dissolved in 30 mL CH_2Cl_2 was slowly added (step B in Scheme 1) to the maleimide benzoyl chloride solution, resulting in an instant change of the reaction mixture to an opaque yellow/brown colour. Anhydrous pyridine (2 mL, 24.8 mmol) was added as an acid scavenger, and the mixture was allowed to warm up to room temperature overnight. Finally the solvent was evaporated and the product was precipitated in demineralised water and collected by filtration. The final product was refluxed in excess tetrahydrofuran (THF) in order to remove any remaining starting material. The beige coloured solids were then collected by filtration and dried under vacuum (50 °C). T_{exo} = 289/315 °C (onset to/peak of reaction exotherm); ^{1}H NMR (D_2SO_4) δ(ppm): 6.27 (4H, s), 6.71 (4H, d), 6.99 (4H, d), 7.44 (4H, s); ^{13}C NMR (D_2SO_4) δ(ppm): 126.3, 129.1, 131.1, 132.5, 133.5, 133.7, 135.9, 171.8, 174.7

*2.4.2. Methylmaleimide amide (**II**) or N,N′-1,4-phenylenebis[4-(2,5-dihydro-3-methyl-2,5-dioxo-1H-pyrrol-1-yl)-benzamide*

T_{exo} = 376/417 °C; ^{1}H NMR (D_2SO_4) δ(ppm): 2.08 (6H, s,), 6.70 (4H, s,), 7.41 (4H, d,), 7.69 (4H, d,), 8.13 (4H, s,)

*2.4.3. Phenylmaleimide amide (**III**) or N,N′-1,4-phenylenebis[4-(2,5-dihydro-3-phenyl-2,5-dioxo-1H-pyrrol-1-yl)-benzamide*

T_m = 363 °C, T_{exo} = 376/379 °C. ^{1}H NMR (D_2SO_4) δ(ppm): 7.4–8.3 (m, 24H)

*2.4.4. Acrylate amide (**IV**) or N,N′-p-phenylenebisacrylamide*

T_m = 276 °C (242 °C [34]), T_{exo} = 282/289 °C. ^{1}H NMR (DMSO-d_6) δ(ppm): 5.8 (m, 2H), 6.3 (m, 2H), 6.5 (m, 2H), 7.6 (s, 4H); ^{13}C NMR (DMSO-d_6) δ(ppm): 119.6, 126.4, 131.5, 134.4, 162.8

*2.4.5. Methylmethacrylate (MMA) amide (**V**) or N,N′-p-phenylenebis methacrylamide*

T_m = 256 °C (248 °C [34]) ^{1}H NMR (DMSO-d_6) δ(ppm): 2.0 (s, 6H,), 5.5 (s, 2H, vinyl group), 5.8 (s, 2H), 7.6 (s, 4H), 9.8 (s, 2H); ^{13}C NMR (DMSO-d_6) δ(ppm): 18.4, 119.6, 120.2, 134.3, 140.0, 166.4.

*2.4.6. 3,3-Dimethacrylate amide (**VI**) or N,N′-p-phenylenebis-3,3-dimethacrylamide*

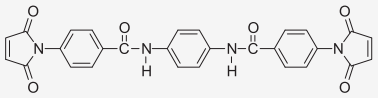
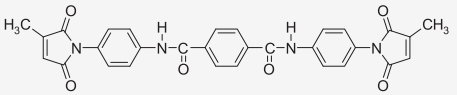
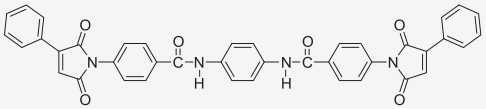
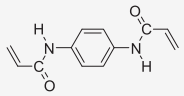
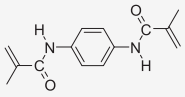
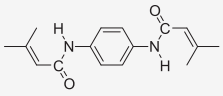
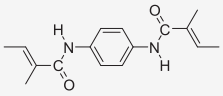
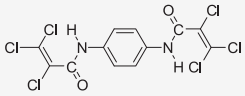
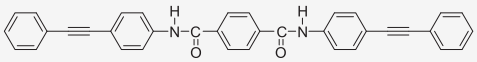
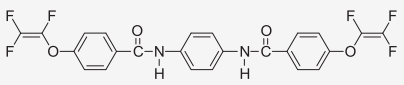
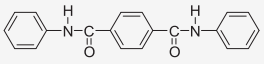
T_m = 264 °C; ^{1}H NMR (DMSO-d_6) δ(ppm): 1.9 (s, 6H), 2.1 (s, 6H), 5.8 (s, 2H), 7.5 (s, 4H), 9.8 (s, –NH); ^{13}C NMR (DMSO-d_6) δ(ppm): 19.3, 26.9, 119.1, 119.2, 134.7, 150.7, 164.2.

Table 1
Starting materials used for the synthesis of poly(p-phenylene terephthalamide) oligomers end-capped with reactive groups.

Oligomer	Selected end-group		PPD	TDC
PPTA-ANIL-5K	Aniline	0.94 g (0.010 mol)	21.60 g (0.20 mol)	40.56 g (0.20 mol)
PPTA-MMA-5K	Methacryloyl chloride	1.05 g (0.010 mol)	21.60 g (0.20 mol)	40.56 g (0.20 mol)
PPTA-MIBC-5K	Maleimidobenzoyl chloride	2.07 g(0.0087 mol)	19.46 g (0.18 mol)	36.54 g (0.18 mol)
PPTA-ANIL-2.5K	Aniline	1.97 g (0.021 mol)	21.17 g (0.20 mol)	39.73 g (0.20 mol)
PPTA-ANIL-10K	Aniline	0.46 g (0.005 mol)	21.17 g (0.20 mol)	39.74 g (0.20 mol)
PPTA-MMA-0.5K-I[a]	Methacryloyl chloride	4.80 g (0.045 mol)	13.00 g (0.12 mol)	12.20 g (0.06 mol)
PPTA-MMA-1K-I[a]	Methacryloyl chloride	2.27 g (0.022 mol)	10.46 (0.10 mol)	14.74 (0.07 mol)
PPTA-MMA-2.5K-I[a]	Methacryloyl chloride	0.79 g (0.008 mol)	9.31 g (0.09 mol)	15.89 g (0.08 mol)
PPTA-MMA-2.5K-II[b]	Methacryloyl chloride	2.35 g (0.022 mol)	12.07 g (0.11 mol)	20.40 g (0.10 mol)
PPTA-MIBC-1.2K-I[a]	Maleimidobenzoyl chloride	11.41 g (0.048 mol)	10.47 g (0.10 mol)	14.74 g (0.07 mol)
PPTA-MIBC-2.5K-II[b]	Maleimidobenzoyl chloride	3.12 g (0.013 mol)	7.14 g (0.07 mol)	12.07 g (0.06 mol)

[a] Calculations based on the exact molecular weight of an oligomer backbone.
[b] Calculations based on Carothers general equation modified for end-capping both polymer chain ends.

Table 2
Chemical and thermal properties of the reactive model compounds.

	Molecular structure	Stable in H_2SO_4[a]	T_m (°C)[b]	T_{exo} (°C)[c]
I		Y	–	289/315
II		N	–	376/417
III		N	363	376/379
IV		N	276	282/289
V		Y	256	–
VI		N	264	–
VII		Y	230	–
VIII		Y	–	–
IX		N	391	394/404
X		N	–	274/301
XI		N	345	–

– Not observed.
[a] Chemically stable in 85 °C sulphuric acid (>98.5%) for 30 min.
[b] Onset to melt.
[c] Onset/Peak value for exotherm.

*2.4.7. Tigloyl amide (**VII**) or N,N′-p-phenylenebis-2,3-dimethacrylamide*

T_m = 230 °C; ^{1}H NMR (DMSO-d_6) δ(ppm): 1.8 (m, 12H), 6.4 (m, 2H), 7.6 (s, 4H), 9.5 (s, –NH); ^{13}C NMR (DMSO-d_6) δ(ppm): 13.2, 14.5, 120.9, 130.7, 133.3, 135.5, 168.2.

*2.4.8. Trichloroacrylate amide (**VIII**) or N,N′-p-phenylenebis-2,3,3-trichloroacryl-amide*

^{1}H NMR (DMSO-d_6) δ(ppm): 7.62 (s, 4H), 11.00 (s, NH); ^{13}C NMR (DMSO) δ(ppm): 120.22, 121.86, 124.35, 134.26, 158.21.

*2.4.9. Phenylethynyl amide (**IX**) or N,N′-diphenylethynyl-1,4-benzenedi-carboxamide*

$T_m = 392$ °C, $T_{exo} = 394$ °C. ^{1}H NMR (D_2SO_4) δ(ppm): 7.3–8.4 (m, 22H)

*2.4.10. 4-(Trifluorovinyloxy) amide (**X**) or N,N′-1,4-phenylenebis[4-[(trifluoroethenyl) oxy]-(9 cl) benzamide*

^{13}H NMR (DMSO-d_6) δ(ppm): 7.5 (d, 4H), 7.7 (s, 4H), 8.1 (d, 4H), 10.3 (s, –NH). ^{13}C NMR (DMSO-d_6) δ(ppm): 106.7, 116.2, 121.4, 130.0, 132.6, 135.6, 157.0, 164.8. ^{19}F NMR (DMSO-d_6) δ(ppm): –117.2 (1F, dd, cis CF=CF_2), –125.3 (1F, dd, trans CF=CF_2), –134.4 (1F, dd, CF=CF_2).

*2.4.11. Aniline (ANIL) amide (**XI**) or N,N′-diphenyl-1,4-benzenedicarboxamide*

$T_m = 345$ °C. ^{1}H NMR (DMSO-d_6) δ(ppm): 7.13 (t, 2H), 7.38 (t, 4H), 7.81 (d, 4H), 8.11(s, 4H), 10.39 (s, 2H). ^{13}C NMR (DMSO-d_6) δ(ppm): 121.2, 124.6, 128.4, 129.4, 138.2, 139.7, 165.5.

2.5. Synthesis of oligomers

All oligomer variations were prepared according to the synthetic procedure as shown in Scheme 2. As a representative example, we describe the preparation of a 5000 g mol^{-1} maleimidobenzoyl chloride end-capped oligomer. In preparation of the synthesis, all glassware were pre-dried in an air-circulation oven at 120 °C for at least 60 min. NMP was dried over and distilled from P_2O_5 and stored under a continuous nitrogen flow. $CaCl_2$ was dried in a vacuum oven at 200 °C for at least 12 h prior to the experiments. The final solvent mixture generally contained less then 200 ppm H_2O.

PPTA-MIBC-5K. A 2 L reactor vessel equipped with a mechanical stirrer, nitrogen inlet and vacuum connection was charged with ~270 mL NMP/$CaCl_2$ (8.5 wt%) and 19.46 g (0.18 mol) *p*-phenylene diamine (PPD). After closing the reactor, a vacuum was applied on the reaction mixture followed by a nitrogen purge. This procedure was repeated at least 3 times in order to remove all traces of moisture and air. This mixture was stirred (150 rpm) for 30 min while heating at 60 °C and sonicating for 10 min in order to dissolve all PPD monomer. This mixture was cooled to ~0 °C and 36.54 g (0.18 mol) terephthaloylchloride (TDC) and 2.07 g (0.0087 mol) maleimidobenzoyl chloride (MIBC) were added. The stirring rate was increased to 320 rpm and the reaction mixture was stirred for at least 20 min while monitoring torque and temperature. Directly following the addition of the TDC/MIBC components the temperature increased to around 37 °C and the reaction mixture formed a yellow thick slurry, which transformed into a claylike substance towards the end of the reaction.

The final product was coagulated in demineralised water and washed 4 times before being collected by filtration. The yellow fibrous product was then dried for 24 h in an 80 °C vacuum (~25 mbar) oven and another 24 h in a 50 °C vacuum oven (<1 mbar). After drying, 37 g (83%) oligomer was collected for further processing and characterisation. The quantities of starting materials used for the syntheses are summarised in Table 1. The yields were generally found to be above 80%.

2.6. Fibre spinning

In preparation of the dry-jet wet spinning process for the manufacturing of the fibres, spin-dopes containing 20 wt% 5000 g mol^{-1} oligomer and 80 wt% high molecular weight (M_n = 10,000 g mol^{-1}) PPTA polymer were prepared. Both oligomer and polymer were ground, filtered and at a temperature of –20 °C mixed with sulphuric acid (99.8%) flakes and stirred overnight, which resulted in a spin-dope with a maximum PPTA content of 19.8%. In a twin-screw extruder the spin-dope was heated to 85 °C and pushed though a spinneret, stretched within the air-gap and finally coagulated in water with a temperature of around ~5 °C. After drying, fibres were annealed at temperatures at either 380 or 430 °C in order to induce crosslinking via the reactive end-groups. All fibres were spun at a line speed of 200 m min^{-1}. The fibres were labelled according to the end-group used. For example, ANIL20-200 refers to a fibre based on 20 wt% aniline terminated oligomer spun at a line speed of 200 m min^{-1}, whereas ANIL20-200HT refers to the same fibre but heat-treated at 380 °C.

3. Results and discussion

3.1. Synthesis and characterisation of end-groups, model compounds and oligomers

The model compounds were synthesised following a straightforward condensation coupling of the acid chloride or amine functionalised end-group with either *p*-phenylenediamine or terephthaloylchloride. The end-groups that were used are readily available or easy to synthesise via standard literature procedures. Final products were purified by recrystallisation or by washing them with hot THF to remove any remaining starting materials or side products. NMR using either D_2SO_4 or DMSO-d_6 as a solvent confirmed the structure of all model compounds.

Thermal analysis revealed that maleimide (**I**) and methyl (**II**) maleimide end-capped model compounds, did not show a well-defined melt-transition and that the phenyl maleimide melted at 363 °C. The starting temperature for the endothermic reaction of the maleimide functionality (289 °C) in the unsubstituted maleimide (**I**), is influenced by the presence of a substituent such as a methyl (**II**) or phenyl (**III**) group and increases towards 376 °C for the latter ones – a shift of approximately 90 °C. An overview of all model compounds and their thermal properties is provided in Table 2.

In contrast, melting temperatures for acrylates were rather low and in a range of 230–276 °C. Immediately upon melting, the unsubstituted acrylate (**IV**) shows an exothermal peak in the DSC curve whereas no exothermal reactions could be detected for the substituted acrylates (**V**–**VIII**). Both the phenylethynyl (**IX**) and the trifluorovinyloxy (**X**) compound show distinct curing reactions in the liquid and solid phase respectively. The aniline (**XI**) end-capped model compound, synthesised as inert reference only melted upon heating.

3.2. Chemical stability of end-groups in strong acid environment

Good chemical stability of the end-groups in 85 °C sulphuric acid is important to survive the fibre spinning process and to be effective in the subsequent heat treatment process. This means that the end-groups should not undergo any premature reactions that prevent proper crosslinking in the latter heat treatment step or even interfere with the fibre spinning process, resulting in deterioration of tensile properties. The spin-dope has to remain stable for at least 30 min at 85 °C before the fibres are spun, coagulated in water and washed. The most important technique that we employed for investigating the chemical stability was the evolution of ^{1}H NMR spectra, recorded every 10 min with D_2SO_4 as the solvent at 85 °C. Where possible or required, additional NMR methods were employed, *i.e.* ^{13}C NMR and ^{19}F NMR.

The ^{1}H NMR reference spectrum of the methacrylate (**V**) end-capped model compound, as shown in Fig. 2(a), was obtained at 24 °C immediately after dissolving this compound in D_2SO_4. Upon inspection of the proton spectra all-aromatic and -allylic peaks can be accounted for, *i.e.* a single peak for the methyl protons, two

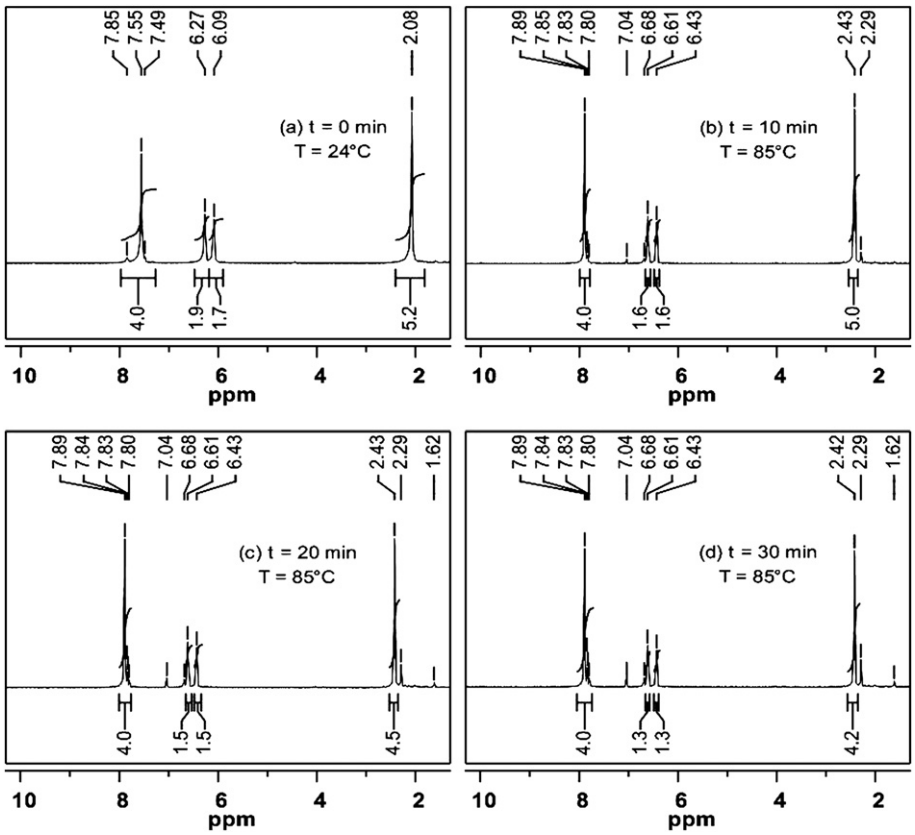


Fig. 2. ^{1}H NMR spectra of the methacrylate (**V**) end-capped model compound in D_2SO_4 recorded at $t = 0$ (a), $t = 10$ (b), $t = 20$ (c) and $t = 30$ (d) minutes, at temperatures of 24 °C (a) and 85 °C (b, c and d) respectively.

single peaks that can be assigned to the vinyl protons and a single peak for the aromatic protons. Compared to the DMSO-d_6 spectrum (Experimental section) a small downfield chemical shift for the peaks can be detected, which can be explained by the change of solvent, *i.e.* DMSO-d_6 to D_2SO_4. It is well-known that the chemical shifts are solvent dependent and in this case, the downfield shift is the result of an increased de-shielding of the protons due to an increase in solvent polarity [35]. The results, however, clearly indicate that upon dissolving of the model compound, no or at least no fast reactions take place between the sulphuric acid and the reactive methacrylate terminated model compound.

Immediately after recording a reference spectrum at 24 °C/$t = 0$, the temperature of the sample was increased to 85 °C. After increasing the temperature, new spectra were recorded after 10, 20 and 30 min, respectively. The spectra for the methacrylate (**V**) end-capped model compound as a function of time at 85 °C are shown in Fig. 2 (b–d).

To acquire information on the effects of temperature and time on sulphuric acid exposures, spectra (a) to (d) (Fig. 2) are compared. The 7.6 ppm peak, corresponding to the central phenyl ring, was selected as a reference peak, since this aromatic moiety is relatively stable under these acidic conditions at elevated temperatures. The first noticeable change is the peak shift from 7.6 to 7.8 ppm of the reference peak after heating the sample from room temperature to 85 °C. A similar shift is also present for all other peaks and is due to the increase in temperature. A second, and more important observation is the slow change of the appearance of small peaks at 7.04 and 2.29 ppm. This is indicative of the fact that acid catalyzed chemistry might be taking place at the reactive double bond at elevated temperatures. It is possible that the double bond undergoes an addition reaction with the sulphuric acid. It is known that a double bond (SP_2–SP_2) structure can react with HSO_3^- via an electrophilic addition type reaction [36]. The reaction is slow, however, and only takes place at elevated temperatures and based on the integration the change in concentration is well below 5% and therefore the methacrylate (**V**) end-cap seems to be a suitable candidate as a potential crosslink group in aramid fibres.

A second example is the maleimide (**I**) end-capped model compound, which is shown in Fig. 3. The proton NMR experiments at 85 °C in D_2SO_4 show that the model compound is affected at two different sites. In the first place, there are noticeable changes of the two doublets corresponding to the phenyl ring adjacent to the maleimide end-group (Fig. 3b). It is possible that this phenyl ring is susceptible towards sulfonation. This reaction, however, will not affect the ability of the maleimide group to form crosslinks or to undergo chain extension and is therefore not considered a problem. The second reaction, as indicated by the appearance of small peaks around the 7.0 ppm maleimide proton peak, indicates a reaction at the aforementioned maleimide reactive side (the maleimide double bond).

Extended testing of the chemical stability of the maleimide bond showed that the model compound remains stable in sulphuric acid even after a 24-h exposure time at room temperature, see Fig. 3c. This result combined with the fact that the reaction at the maleimide double bond is relatively slow even at 85 °C indicates that the maleimide group is another suitable candidate for crosslinking aramid fibres.

Following the approach as described above, all reactive model compounds were investigated on their chemical stability and the results are summarised in Table 2. Based on their ease of synthesis and commercial availability, maleimidobenzoyl chloride (**1**) and methacryloyl (**5**) chloride, were incorporated in PPTA and spun into fibres. In addition aniline (**11**) was used as a non-reactive end-group.

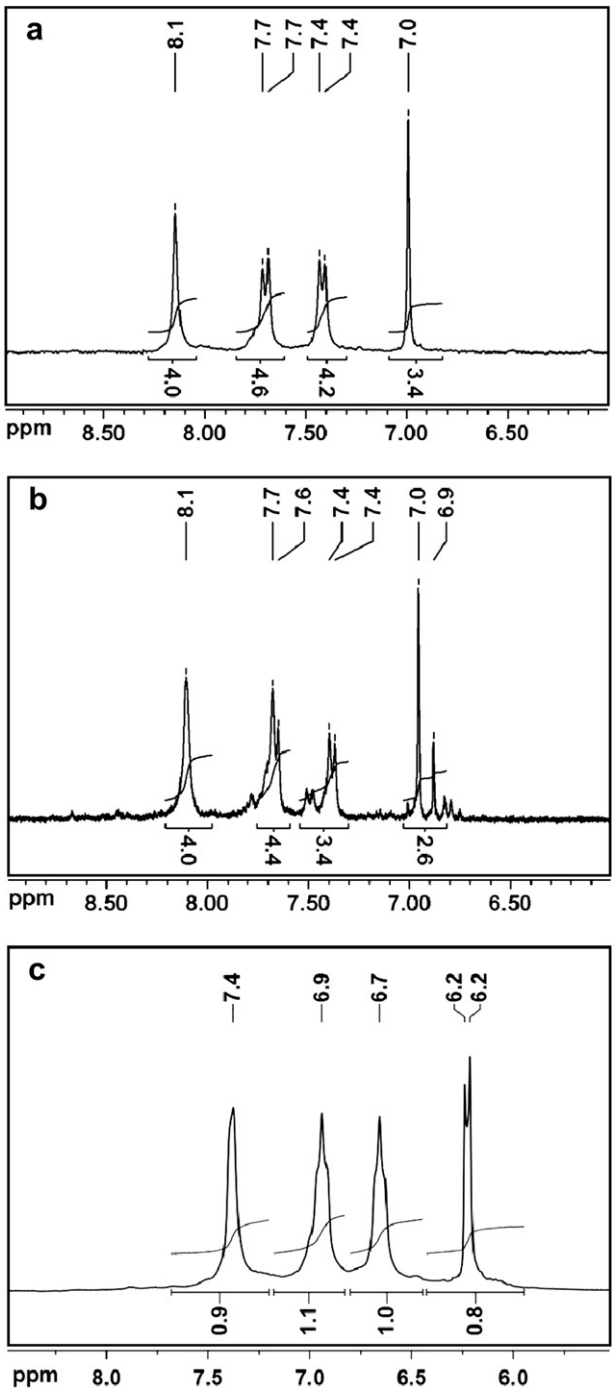


Fig. 3. ^{1}H NMR spectra of the maleimide (**I**) end-capped model compound recorded in D_2SO_4 at (a) room temperature, (b) after 15 min at 85 °C and (c) after 24 h at room temperature in D_2SO_4.

3.3. Curing behaviour of model compounds

In order to investigate the solid-state thermal curing of the reactive end-groups, as will be the case once the reactive groups are incorporated in PPTA fibres, qualitative solubility experiments were conducted before and after heat treatment. For the three compounds, *i.e.* maleimidobenzoyl chloride (**1**) and methacrylate (**5**) end-capped model compounds and the aniline (**11**) end-capped reference, dimethyl sulfoxide (DMSO) was found to be a suitable solvent to prepare solutions of 0.5 wt% of the selected model compounds. Before the heat treatment, fresh samples of approximately 10 mg were prepared in aluminium cups. Samples were heated for 30 s at three different temperatures, *i.e.* of 300, 350 and 400 °C using an Argon (Ar) purged hot-stage. When removed from the hot-stage all samples were quenched to room temperature and transferred to a sample vial where ~2 mg DMSO was added. The samples were stirred at room temperature for at least 24 h prior to recording their solubility, as summarised in Table 3.

Table 3
Solubility of sulphuric acid stable model compounds (**I** and **V**) and an aniline (**XI**) end-capped reference compound, as measured in DMSO-d_6 after a 30 s heat treatment (under Ar) at various temperatures.

Type of end-cap	300 °C	350 °C	400 °C
Aniline (**XI**)	+	+	+
Maleimidobenzoyl chloride (**I**)	−	−	−
Methyl methacryloyl chloride (**V**)	+	+	+

(− not soluble, + soluble).

The results in Table 3 show that the "inert" aniline-based reference model compound (**XI**) remains soluble over the whole range of heat treatment temperatures. The aniline end-group, therefore, is a suitable end-cap to be used in synthesis as a non-reactive reference compound. In addition it becomes clear that the aramid-like structure does not undergo any thermally induced polymerisation or crosslinking by itself. Unlike the aniline end-capped compound (**XI**), model compound (**I**) is the only compound to become insoluble after the heat treatment. This indicates that at relatively high concentrations the maleimide end-group effectively forms an insoluble network after heat treatment in the solid-state. These results are supported by the literature, from which it is known that maleimide–maleimide crosslinks are formed at temperatures in excess of 250 °C [24,37]. The third model compound (**V**) is found to remain soluble after the heat treatments. A possible explanation for this result is decomposition of the sample during the heat treatments, which was confirmed by TG/DTA experiments, where we observed rapid decomposition after melting at 256 °C. As will be discussed in more detail later, methacrylate (**V**) end-capped oligomers display improved thermal stabilities over their low molecular weight analogs, and appear more suitable for our solid-state crosslinking experiments.

3.4. Oligomer synthesis and characterisation

3.4.1. Molecular weight analysis

Large-scale synthesis (~40 g scale) of the oligomers could be performed without noticeable problems and with yields above 80%. The number average molecular weight (M_n) for all (non)-reactive oligomers used for fibre spinning experiments are summarised in Table 4. For all oligomers the measured number average molecular weight (M_n) seems to be lower than the targeted M_n and is probably due to the presence of moisture during the reaction or premature phase separation. Water will hydrolyse the acid chloride-based monomers, which reduces their reactivity and finally results in a lower molecular weight of the oligomers.

3.4.2. Thermal analysis

Since our fibres will be exposed to a thermal post-treatment step, in order to activate the reactive end-groups, it is important to investigate whether our oligomers display the required thermal stability. Thermogravimetric experiments (TGA), performed at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere, show that severe degradation of the oligomers starts at temperatures well above 500 °C which is comparable to their high molecular weight PPTA counterpart [38]. The small amount of weight lost

Table 4
Typical values found for the number average molecular weights as measured by SEC (H_2SO_4 was used as the eluent).

Oligomer	M_n (g mol^{-1})	M_w (g mol^{-1})	D
PPTA-ANIL-2.5K	1400	2700	2.0
PPTA-ANIL-5K	2100	5133	2.4
PPTA-ANIL-10K	2900	7500	2.6
PPTA-MMA-5K	3900	9833	2.5
PPTA-MIBC-5K	3900	10 867	2.6
Twaron 1010 ref.	10 300	31 400	3.0

For all oligomers the measured number average molecular weight (M_n) seems to be lower than the targeted M_n and is probably due to the presence of moisture during the reaction or premature phase separation. Water will hydrolyse the acid chloride-based monomers, which reduces their reactivity and finally results in a lower molecular weight of the oligomers.

(approximately 1%) upon heating at 100 °C is related to the loss of water. This was confirmed by DSC, where the endothermic peaks around 100 °C disappeared upon a second heating. Due to the low concentration of reactive end-groups, we could not detect exothermic events associated with the chain extension or crosslink chemistry.

3.4.3. Nuclear magnetic resonance spectroscopy

The presence of the end-groups in the oligomers was investigated by ^{1}H NMR analysis. Because of their limited solubility, 3900 g mol^{-1} oligomers were not suitable to prepare proper samples. Instead, low molecular weight equivalents were used as a proof of principal. The spectra, recorded in D_2SO_4 at room temperature, are shown in Fig. 4. For PPTA-MMA-0.5K three peaks could be observed and assigned to the methacrylate end-group. Those are the peaks at 6.3 and 6.1 ppm, which can be assigned to the vinylic protons, and the peak at 2.1 ppm, which belongs to the protons of the methyl group. Evidence for the presence of the maleimide moiety in the spectrum of the PPTA-MIBC-1.2K oligomer is found at 7.0 ppm, and can be assigned to the maleimide double bond.

3.4.4. Curing behaviour

The ability of the oligomer to form crosslinks was investigated following a similar approach as was used for investigating the model compounds. An NMP/$CaCl_2$ (5 wt%) mixture was preferred over sulphuric acid to prevent possible degradation of the crosslinks that were formed during the heat treatment. Oligomers with M_n = 3900 g mol^{-1} were found to have a too low solubility (much lower than 0.5 wt%), therefore oligomers with an M_n of 2000–2500 g mol^{-1} were used for these experiments instead. The results are summarised in Table 5. Before any heat treatment, all oligomers were readily soluble and formed fully transparent solutions. Upon heat treatment, a decreased solubility was observed for all oligomer modifications, where both PPTA-ANIL-2.5K and PPTA-MMA-2.5K-II became fully insoluble and the maleimide end-capped PPTA-MIBC-2.5K-II became partially insoluble. These results are in contrast with the solubility experiments of the model compounds, as discussed in Section 3.3. Especially aniline, which was concluded to be an "inert" end-cap, appears to be reactive when used in an oligomer. A major difference is the higher thermal stability (T_{dec} > 500 °C) of the oligomer when compared to the model compound (T_{dec} = 333 °C). The high post-treatment temperatures are likely to be sufficient to cause chain extension/crosslinking via un-reacted acid- and amine-functionalities, leading to an insoluble product.

Table 5
Solubility of oligomers in NMP/$CaCl_2$ (5 wt%) before and after a 60 s/350 or 380 °C heat treatment under nitrogen atmosphere. (+soluble, ± partially soluble and − insoluble).

Oligomer	No treatment	350 °C	380 °C
PPTA-ANIL-2.5K	+	−	−
PPTA-MMA-2.5K-II	+	−	−
PPTA-MIBC-2.5K-II	+	±	±

Heat treatment of the methacrylate end-capped PPTA-MMA-2.5K-II also resulted in an insoluble product, likely to be the result of crosslinking. The thermal stability is significantly higher for the oligomer and therefore the vinyl end-group can be thermally activated before degradation starts. PPTA-MIBC-2.5K-II becomes partially insoluble after the various heat treatments. Thermal degradation at high temperatures competing with chain extension/crosslinking could be the reason that part of the materials dissolves even after heat treatment [39]. In general, however, it is shown here that oligomers with an M_n of ~2000 g mol^{-1} are able to undergo polymerization, *i.e.* via chain extension or crosslinking.

3.5. Fibre spinning and characterisation

Incorporation of (reactive) oligomers was shown to be fully compatible with the 'classic' PPTA fibre spinning process [40]. Spindopes could be prepared following the traditional procedure and the fibre spinning process itself was also carried out without noticeable problems. Typical stress–strain curves for the as-spun and heat-treated experimental fibres are shown in Fig. 5. Fig. 5a indicates that the incorporation of 20 wt% reactive PPTA oligomers is of minor influence on the stress–strain behaviour. Careful observation reveals an initial linear behaviour up to the point of yielding where the slope of the curves changes. Upon further straining of the fibre, an increase in slope is observed. This tensile

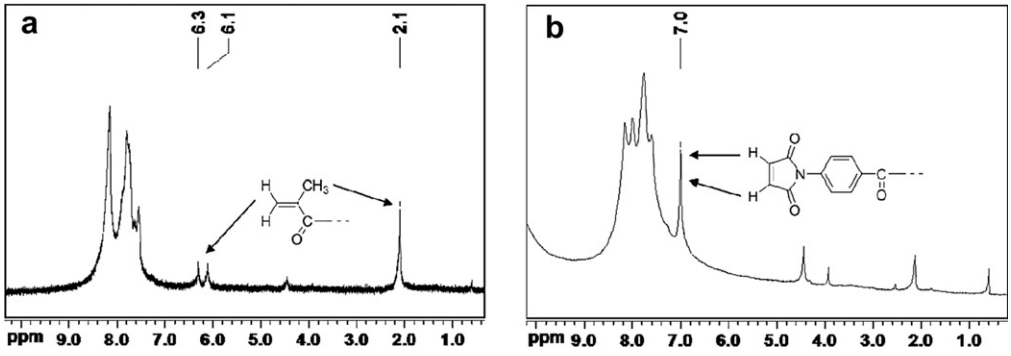


Fig. 4. ^{1}H NMR spectra in D_2SO_4 of (a) PPTA-MMA-0.5K at room temperature and (b) PPTA-MIBC-1.2K at 85 °C. The spectra confirm the presence of the methacrylate and maleimide end-groups in the oligomers.

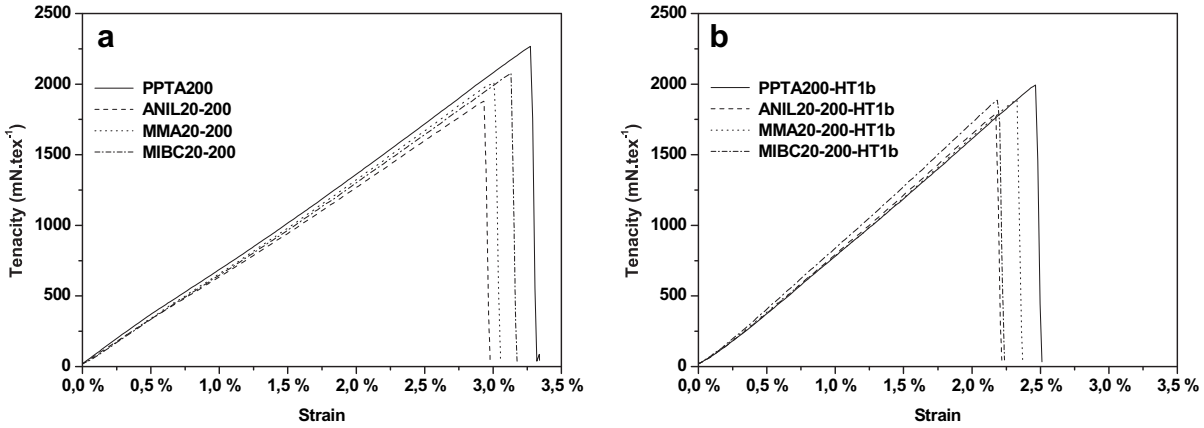


Fig. 5. Stress–strain curves as measured for as-spun (a) and heat-treated at 380 °C (HT) (b) filaments based on standard PPTA polymer (PPTA-200) or on a mixture of 80 wt% standard PPTA polymer and 20 wt% of a 5000 g mol^{-1} (reactive) end-capped oligomer spun at a line speed of 200 m min^{-1}.

behaviour was explained by Northolt and co-workers and attributed to the onset of a sequential and plastic orientation mechanism of the chains brought about by the resolved shear stress [3,41,42]. In other words yielding occurs when the stress increases and the corresponding shear stresses within a domain reaches a critical shear level. One could argue that the addition of low molecular weight oligomers could have been of influence on this critical shear level resulting in a more distinct yielding behaviour. This is, however, not the case for our fibres as shown by the curves in Fig. 5a. In line with the underlying theory, yielding becomes even less pronounced (see Fig. 5b) as the initial orientation of the domains in the fibre is higher due to the heat treatment at 380 °C.

Mechanical data of as-spun fibres, as summarised in Table 6, shows that the incorporation of oligomers did not affect the characteristics of the stress–strain curves but resulted in a modest decrease (max 9%) of the tenacity while leaving the moduli largely unaffected. The fibre based on the 20 wt% aniline end-capped oligomer performs the worst and shows a drop in tenacity of 17%. This is likely to be the result of the average molecular weight being lower than the anticipated 5000 g mol^{-1} resulting in less effective stress-transfer.

The heat treatment had an overall effect on all fibres, *i.e.* decreasing the tenacity with an average of 8% compared to the as-spun precursors. The strength retention of the PPTA reference fibre annealed at 430 °C shows that high temperature post-treatments are possible without a penalty in fibre strength. As expected, all moduli increase upon heat treatment. No correlations were found between fibre strength or fibre stiffness on one hand, and oligomer chemistry, or oligomer concentration on the other hand. Data, as obtained via the 'elastica' single filament compression test indicated that the as-spun fibres did indeed show a modest (+0.1 GPa) improvement in compression strength. When exposed to a high temperature (380 °C) heat treatment, both the reference PPTA fibres and the oligomer-modified fibres showed a significant increase in compression strength, *i.e.* from 0.7 to 0.9 GPa. Increasing the post-treatment temperature to 430 °C, however, reduces the compressive properties again, with the sole exception of the PPTA reference fibre, where we measured a compression strength of 1.11 GPa. This value comes close to the 1.29 GPa reported for the M5 fibre [43], which is considered the polymeric fibre with the best compressive strength to date. We believe at this point that the concentration of end-groups is too low to have positive contribution on the compressive strength. This was confirmed by 'elastica' single filament compression test, as well as by Raman experiments [44]. WAXS experiments (Table 6) showed that the incorporation of oligomers has no measurable effect on the fibre crystal structure. The values for the apparent crystallite size, *i.e.* Λ 110 and Λ 200, are similar for the fibres based on 20 wt% 3900 g mol^{-1} oligomers when compared to the PPTA reference fibres. We are currently exploring whether higher concentrations of reactive oligomers, *i.e.* 40 and 50%, results in an improvement in compression strength.

Table 6
Physical and mechanical properties of fibres based on high molecular weight PPTA and 3900 g mol^{-1} end-capped PPTA oligomers. Fibres subjected to a thermal post-treatment at 380 °C are encoded HT. All fibres were spun at a line speed of 200 m min^{-1}.

Fibre	LD (dtex)	Tenacity (mN tex^{-1})	Modulus (GPa)	Elongation at break (%)	Compressive strength (GPa)[b]	Λ 110 (nm)[c]	Λ 200 (nm)[d]
PPTA200	1.75	2195	91.2	3.22	0.65 ± 0.04	55	52
ANIL20-200	1.78	1879	87.0	2.95	0.74 ± 0.11	55	50
MMA20-200	1.73	2019	93.5	3.01	0.71 ± 0.07	55	51
MIBC20-200	1.74	2080	93.7	3.12	0.77 ± 0.07	54	50
PPTA200-HT	1.69	2019	115.4	2.47	0.90 ± 0.06	90	67
ANIL20-200-HT	1.65	1787	114.7	2.19	0.98 ± 0.11	87	65
MMA20-200-HT	1.65	1860	113.9	2.30	0.90 ± 0.06	91	67
MIBC20-200-HT	1.64	1911	121.1	2.24	0.98 ± 0.08	89	66
PPTA-250-HT2[a]	1.27	2079	137	2.1	1.11 ± 0.17	96	72

[a] PPTA reference fibre spun at 250 m min^{-1} and heat-treated at 430 °C.
[b] Average of 5 experiments.
[c] Λ 110: apparent lateral crystal size in the direction perpendicular to the plane through the diagonal of the basal plane and the *c*-axis.
[d] Λ 200: apparent lateral crystal size in the *a*-direction.

4. Conclusions

We have synthesised and characterised a series of amide model compounds end-capped with various types of reactive end-groups. It was shown by NMR spectroscopy using D_2SO_4 as a solvent that maleimide benzoyl chloride, methacryloyl chloride, tigloyl chloride and trichloro acryloyl chloride could be coupled to PPD and that the resulting end-groups are chemically stable in 85 °C sulphuric acid (>98.5%). Maleimide benzoyl chloride and methacryloyl chloride were successfully used for end-capping aramid oligomers with molecular weights up to 3900 g mol^{-1}. The addition of up to 20 wt% oligomers did not interfere with the spinning process and fibre tensile strengths were maintained between 1879 and 2080 mN tex^{-1} for as-spun fibres based on 20 wt% oligomers, which is somewhat lower then the 2195 mN tex^{-1} found for the PPTA reference fibre. Upon heat treatment, a decrease in tensile strength was measured with values of 1787–1911 mN tex^{-1} for oligomer-based fibres. Fibre moduli remained unaffected by the incorporation of oligomers but we found that the compressive strengths improved significantly upon heat treatment. The reference fibres based on high molecular weight PPTA polymer, however, showed similar improvements suggesting that the incorporation of up 20 wt% reactive oligomers does not result in an additional measurable increase in compressive strength. We found that the PPTA-based fibres without reactive oligomers and post treated at 430 °C exhibit compressive strengths of 1.11 GPa. We believe that this significant improvement will expand the application range of aramid fibres and closes the performance gap with other, more expensive, high-modulus fibres such as M5 and PBI.

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