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Synthesis and characterization of a water-soluble rigid-rod polymer

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Abstract

Water-soluble polyaramides have been prepared from 2,5-diaminobenzene-sulphonic-acid activated by TMSCl and terephthalic-acid-chloride. Using this method, we achieved molecular weights of our polymers up to 18,000 g mol^{-1}. Two model compounds were synthesized in order to establish the effect of trimethylsilyl-chloride, which was used as the activating agent for this reaction. The resulting sulphonated poly-aramides were characterized by: inherent viscosity measurements, size exclusion chromatography (SEC), DMA, TGA, flame absorbance atomic spectroscopy (FAAS), NMR spectroscopy and optical polarisation microscopy. In all cases, the polymers were easily soluble in hot water up to concentrations of 20 wt%. Upon cooling lyotropic alignment of molecular aggregates is observed at low polymer concentrations, typically 2–5 wt%. Polymers with low molecular weights do not show this behaviour. Films made from these sulphonated aramide polymers showed good thermal stability, and have interesting mechanical properties. Our results indicate the presence of a structure consisting of molecular aggregates.

Keywords: Sulfo-PPTA; Silylated diamines; Molecular aggregates

1. Introduction

Poly(p-phenylene-terephthal-amide) (PpPTA, commercial name: Kevlar or Twaron) is a polymer of great technical interest [1–4]. High modulus fibres can be spun from lyotropic PpPTA solutions. In sulphuric acid (98%) [5], polymer chains are aligned forming a nematic solution. Films and fibres resulting from the processing of these solutions, i.e. by the removal of the solvent by coagulation in water, have impressive mechanical properties. This is probably due to the strong hydrogen bonding between the amide groups of adjacent molecules. The main drawbacks in the processing of these polymers are their lack of meltability and poor solubility (Fig. 1) [6].

Introducing steric hindrance along the main chain by using side groups chain may improve solubility and meltability [7–9]. Kricheldorf et al. [10–13] have described the use of monomers substituted with bulky flexible side-groups to enhance solubility, but the resulting polymers were poorly soluble in most organic solvents, and few of them showed lyotropic behaviour.

Vandenberg et al. have described a polymerisation, where a sulphonated monomer was incorporated into the main chain of poly(p-phenylene-terephthal-amide), see Fig. 2. The main goal of this study was to obtain a polymer that was easily soluble in water or volatile organic solvents [14]. This methodology enhanced the solubility of the polymer samples [15]. Direct sulphonation [16] of PpPTA as an alternative route for obtaining such a polymer was not successful for two main reasons: 1—the degree of substitution was very low (sulphur content 0.5 wt%), and 2—chain degradation occurred during the process [17]. In addition, the sulphonic group was randomly incorporated into the main chain. For all polymers prepared by the Vandenberg method [18,19], no lyotropic behaviour in solution has been reported. Most likely this is because the molecular weight of these polymers was too low to achieve alignment. We believe that this tendency to form low molecular weight polymers is due to the poor reactivity of the sulphonated diamine. To our knowledge, methods for increasing the reactivity of the sulphonated diamine have never been reported.

In the present work, we report the synthesis of a high molecular weight, water-soluble polyaramide. Using the sulphonic group on the main chain improves the water solubility, and enhances the possibility to observe lyotropic behaviour of the polymer [20]. Obtaining high molecular

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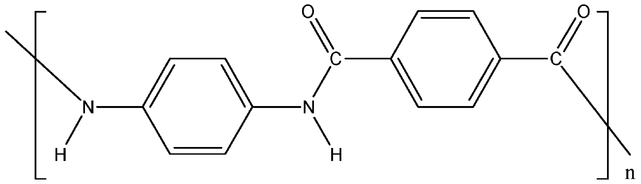

Fig. 1. PPTA, poly(*p*-phenyleneterephthalamide).

weight polymers is achieved by activation of the sulphonated diamine with trimethylsilyl-chloride, TMSCl (**3**). The activation of the diamines by this method is studied using two model reactions. In our synthesis, the activation and polymerisation are a 'one-pot' reaction. Finally, the characterization of the polymers using NMR and FAAS spectroscopy, inherent viscosity, SEC, TGA and DMA is discussed.

2. Experimental

2.1. Materials

Chlorotrimethylsilane (**3**) (99.99% Aldrich Sure Seal®), and *N*,*N*′-dimethylacetamide (99.99% Aldrich Sure Seal®) were used as received. Lithium chloride (technical grade) was dried under vacuum in an oven at 250 °C overnight. Other solvents are technical grade. 2,5-Diaminobenzenesulfonic acid (**1**) (98%, Fluka) was purified by recrystallisation three times from demineralized water. The first time the solution is boiled in the presence of active carbon and filtered through Celite. White needles are obtained. After the third recrystallisation, the white needles are washed with dry hexane, dried overnight under vacuum at 80 °C, and then stored under nitrogen. 1,4-Benzenedicarbonyl dichloride (**2**) (99%, Aldrich) is purified by sublimation and then stored under nitrogen. Benzoyl Chloride (**4**) (99%, Aldrich) was used as received.

2.2. Measurements

Both ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz UR-400S Varian NMR spectrometer in DMSO-d_6. Size exclusion chromatography (SEC) was performed by dissolving the sample in concentrated sulphuric acid (1 mg ml^{-1}) and separating this using a modified Zorbax column (250 × 6.2 mm), using concentrated sulphuric acid as the mobile phase (0.1 ml min^{-1}). A UV detector operating at 340 nm was used for detection. From the chromatograms, the Mw values were calculated using Cirrus version 1.1 GPC software (Polymer Labs). As references in the SEC analysis, a Twaron (PpPTA) yarn, type 1010 and an aramid trimer were used. The lithium (Li) content in our polymers has been determined by FAAS on a Perkin–Elmer Plasma 40 Flame Atomic Absorbance Spectrometer. The sulphur content in our samples has been determined by XRF on a LECO CS-225. The polymer samples were dissolved in hot water and ultrasonic mixing at 60 °C for 2 h prior to analysis. TGA measurements were performed in nitrogen, with a Perkin–Elmer TGA 7a with a heating rate of 10 °C per minute from 25 to 400 °C. DMA measurements were performed using a Perkin–Elmer DMA 7a with a heating rate of 5 °C per minute from 25 to 225 °C.

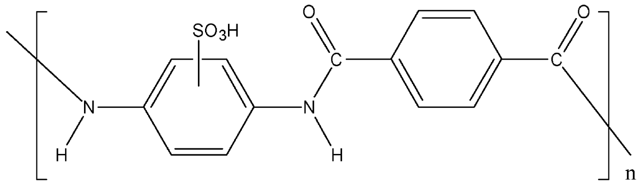

Fig. 2. Sulfo-PPTA, poly(*p*-sulfo-phenyleneterephtalamide).

2.2.1. 2,5-Bis-benzoylamino-benzenesulfonic acid (5) with TMSCl (3)

A 250 ml 3 necked flask was dried using a flame prior to use and was mounted with a cooler, a dropping funnel and a thermoprobe. 6.38 g (0.06 mol) of **3** was added drop wise to the reaction mixture containing 5 g (26.5 mmol) of **1** in 75 ml of DMAc. The flask was cooled at 0 °C with an ice bath vigorously stirred with magnetic stirrer during 1 h, and then 7.42 g (53 mmol) of **4** were added drop wise during 15 min. The flask was left to vigorously stirred at 0 °C in the ice bath for 1 h and then at room temperature for a further hour. Subsequently, the standard temperature sequence is applied: 40 °C for 1 h and 75 °C for 90 min using a thermostated oil bath. The mixture is poured into 400 ml of water. The solvent is removed with a rotary evaporator leaving a purple powder, which was washed with ether (2 × 200 ml). The yield was 6.40 g (61%). ^{1}H NMR (DMSO-d_6) δ 11.4 ppm (1H, s), 10.4 ppm (1H, s), 8.5 ppm (1H, d, $J = 9$ Hz), 8.2 ppm (1H, d, $J = 2$ Hz), 8 ppm (5H, dd), 7.92 ppm (1H, dd, $J = 9$, 2 Hz), and 7.6 ppm (6H, dd).

2.2.2. 2,5-Bis-benzoylamino-benzenesulfonic acid (5) without TMSCl (3)

The same set-up as described above was used. 5 g (26.5 mmol) of **1** was added and dissolved by heating at 75 °C during 1 h in 75 ml of DMAc. The reaction was done under an inert argon atmosphere. The solution was cooled down with an ice bath to 0 °C, and then 7.42 g (53 mmol) of **4** are added drop wise during 15 min. The flask was vigorously stirred at 0 °C for 1 h and then at room temperature for a further hour. Then the standard temperature sequence is applied: 40 °C for 1 h and 75 °C for 90 min. The mixture is poured in 400 ml of water. The solvent is removed with a rotary evaporator leaving a purple powder, which was washed with ether. The yield was 5, 10 g (48%). ^{1}H NMR (DMS0-d_6) δ 11.4 ppm (1H, s), 10.4 ppm (1H, s), 9 ppm (4H, COOH, unreacted 4 hydrolysed into carboxylic acid during the extraction procedure), 8.5 ppm (1H, d, $J = 9$ Hz), 8.2 ppm (1H, d, $J = 2$ Hz), 8 ppm (18H, dd, aromatic protons from terminal benzyl ring and from unreacted **4**), 7.92 ppm (1H, dd, $J = 9$, 2 Hz), and 7.6 ppm (12H, dd, aromatic protons from terminal benzyl ring and unreacted **4**).

2.3. General procedure for the one-pot silylation and polymerisation

2.3.1. Silylation

The polymerisation and all transfer operations were carried out in flame-dried glassware and under argon, due to the high moisture sensitivity of the silylated-diamines. Just after assembly, the equipment was heated and flushed with argon to remove any adsorbed moisture. During the reaction, argon was flushed slowly into the reactor. The reactor mounted with: a cooler with argon outlet, a thermometer, a mechanical stirrer and a argon inlet was charged with 10 g of **1** (53 mmol), 200 ml of DMAc and 4.7 g of LiCl. (0.111 mol), the solution was heated at 85 °C until complete dissolution of LiCl after which the solution turned yellow. The solution was cooled with dry ice, the temperature drops to −25 °C. The dropping funnel was filled with 30 ml of **3**, and added drop wise during 30 min causing an increase of the temperature from −25 to 0 °C. After the complete addition the reaction mixture was cooled down again to −25 °C.

2.3.2. Polymerisation

The dropping funnel was filled with 10.8 g of **2** (53 mmol) and dissolved in 60 ml of DMAc. The solution was added drop wise for 15 min, during this time the temperature increases from −25 to 0 °C. After addition of this solution, the ice bath was removed, until room temperature is reached. At the end, the mixture is heated step by step with a heating mantle: 40 °C for 1 h and 75 °C for 90 min. The yellow, viscous solution was precipitated into 1200 ml of methanol and filtered through a P2 glass frit. The fluffy precipitate was dissolved in hot DMF (205 °C), followed by precipitation in 2 l of ether. The yellow powder is subsequently washed with 500 ml of methanol, 500 ml of acetone and 500 ml ether. The goldish powder was dried under vacuum at 60 °C overnight, the yield being 19 g (91%). ^{1}H NMR (DMSO-d_6) δ 11.5 ppm (1H, s, NHCO), 10.5 ppm (1H, s, NHCO), 9.9 ppm (2H, t), 8.6 ppm (tt, 2H), 8.1 ppm (t, 3H), ^{13}C NMR (DMSO-d_6)): 164 ppm, 162 ppm C=O, δ 145.2, 142.8, 138.3, 135.8, 129.7, 129.2, 128.2, 127.8, 127.6, 127.4, 127.1, 126.8.

3. Results and discussion

3.1. Model reactions

Model compound **5** shown in Figs. 4 and 6, was synthesized to confirm the effect of **3** (**TMSCl**) on the reactivity of **1**. In the procedure described by Vandenberg [14], only one monomer is activated (see Fig. 3): i.e. the terephthalic acid chloride (**2**).

The presence of the SO_3H group has a detrimental effect on polymerisation compared to 1,4-phenyl-diamine. The nucleophilicity of the two amino groups of **1** notably the one at the 2 position is very low due to the presence of the electron-withdrawing sulphonic group [18] causing a decrease in the reactivity of the diamine [19]. The relation between the low reactivity of the sulfo-diamine and the low molecular weight of the final polymer is confirmed by previous results [20–22]. No polymers were obtained with a molecular weight higher than 10,000 g mol^{-1} (Figs. 4–7).

It has been reported before that TMSCl is suitable to increase the reactivity of diamines [23,24] but to our knowledge this is the first time its use has been reported for a sulphonated-phenyl-diamine. The activation of **1** by **3** using the Imai method [25,27], can be monitored by ^{1}H NMR, by comparing two spectra: Figs. 5 and 7.

By reacting **4** with silylated **1**, the ^{1}H NMR spectra obtained are in accordance with the expected structure of **5**. The peak attribution is shown below. A significant difference is found when comparing this to the ^{1}H NMR spectra of the compound obtained without the use of TMSCl, **3**.

The purple powder obtained after the purification procedure (same procedure in both cases) is a mixture of benzoic acid, formed by the hydrolysis of unreacted **4** and the model compound **5**. The integration values in the aromatic region and especially for the two peaks at 8 and 7.6 ppm are high; this indicates the presence of benzoic acid. The large peak at 8 ppm is due to a carboxylic proton from benzoic acid. The reaction between **1** and **4** is not complete due low reactivity of **1**. The results clearly show a low conversion, so low molecular weight polymers are, therefore, expected for a polymerisation reaction without TMSCl activation. Different reaction times do not influence this result.

3.2. Polymer synthesis

In order to compare the efficiency of TMSCl as an activator, the same conditions as described for the model reactions were used, see Fig. 8. The ^{1}H and ^{13}C NMR spectra do not indicate any formation of side-products. In order to compare our results to the inactivated route of Vandenberg [15], we also synthesized reference polymers using their procedure. From the large increase in molecular weight observed with TMSCl activation compared to these reference polymers (see below), we conclude that the silylated diamine is formed before the polymerisation process. The polymerisation procedure was done at 40 °C and finished at 75 °C, this temperature sequence gives the best result in terms of molecular weight increase [26,27]. Finishing, the polymerisation procedure with a lower temperature gives a lower molecular weight. Increasing the time of reaction does not increase the final molecular

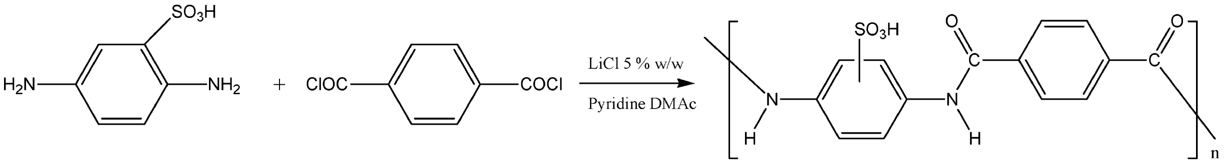

Fig. 3. Polymerisation method by Vandenberg [14].

weight and consequently, it was not possible to obtain a molecular weight higher than 20,000 g mol^{-1}, which may be due to the precipitation of the polymer that occurs during the synthesis. This aspect is confirmed by the fact that polymerisation without the use of the LiCl only gave low molecular weight polymers. It has been already shown that the addition of salt during the polymerisation enhances the solubility [2], due to the salt disrupting hydrogen bonding between the polymer chains. FAAS has been used to estimate the lithium content of our polymer. Generally, the lithium concentration in the final polymer is in a range of 0.20–0.5 wt%. This means that about 10–25% of the sulphonic groups are lithiated since 2 wt% Li corresponds to complete substitution.

4. Characterization

4.1. Molecular mass determination

4.1.1. Viscosimetry

Viscosimetry in sulphuric acid is used in order to determine the M_w. An approximate M_w value is calculated using the relationship between intrinsic viscosity and molecular weight for PpPTA [30]. The M_w values obtained via the TMSCl activated method are compared to the values obtained by the non-activated method as shown in Table 1. These results clearly show a threefold increase in molecular weight obtained by TMSCl activation.

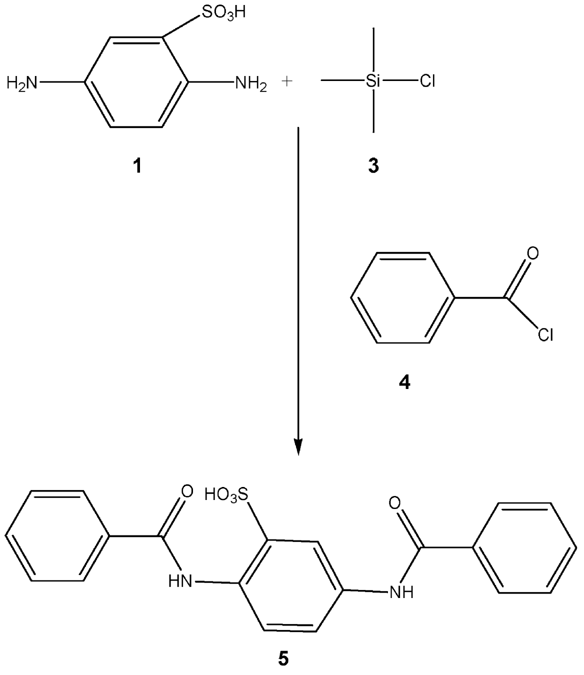

Fig. 4. Reaction route for the model compound with **3** (TMSCl).

4.1.2. SEC analysis

The results obtained by SEC are displayed in Table 2 below. Flexible polymers show globular coils in solution with the diameter of such coils being directly correlated with the M_w of the polymer. However, using the SEC method to exclude rigid rod molecules is limited by the fact that the polymer conformations will have a different shape [28]. Another aspect to take into account is that the calibration of the column is not based on sulfo-PPTA standard but PS standard in THF, which means two different components are changed: the standard and the solvent [29].

Nevertheless, the results obtained by SEC confirm the increase of the molecular weight of the polymer using TMSCl activation. The values for the molecular weight averages are low compared to the values obtained by viscosimetry, which presumably is due to the used calibration of the SEC column. The polydispersity index is close to 2, as expected for a step-growth (poly-condensation) reaction. This is illustrated by the SEC curve plotted below (Fig. 9).

4.2. Solution behaviour

The polymer solutions were prepared by dissolving the polymer powder in water. The solution was boiled for 15 min in a sealed tube and then ultra-sonic mixed for 2 h at 60 °C. Gel formation occurs when the samples cool down. Isotropic gels are observed for low polymer concentrations of typically below 2 wt% polymer in water. At concentrations between 2 and 25 wt%, spontaneous alignment is observed by optical polarisation microscopy, as shown in Fig. 10. The picture shows a typical birefringent optical texture formed by molecular aggregates of sulfo-PPTA chains [31].

We note that previous reports have described the possible

Table 1
Viscosities and molecular weight of the polymers samples obtained with and without TMSCl activation

	Unactivated route	Activated route
η_{inh} (dl g^{-1})	0.7	1.4
M_w [19] (g mol^{-1})	5000	18000
Yield	70%	95%

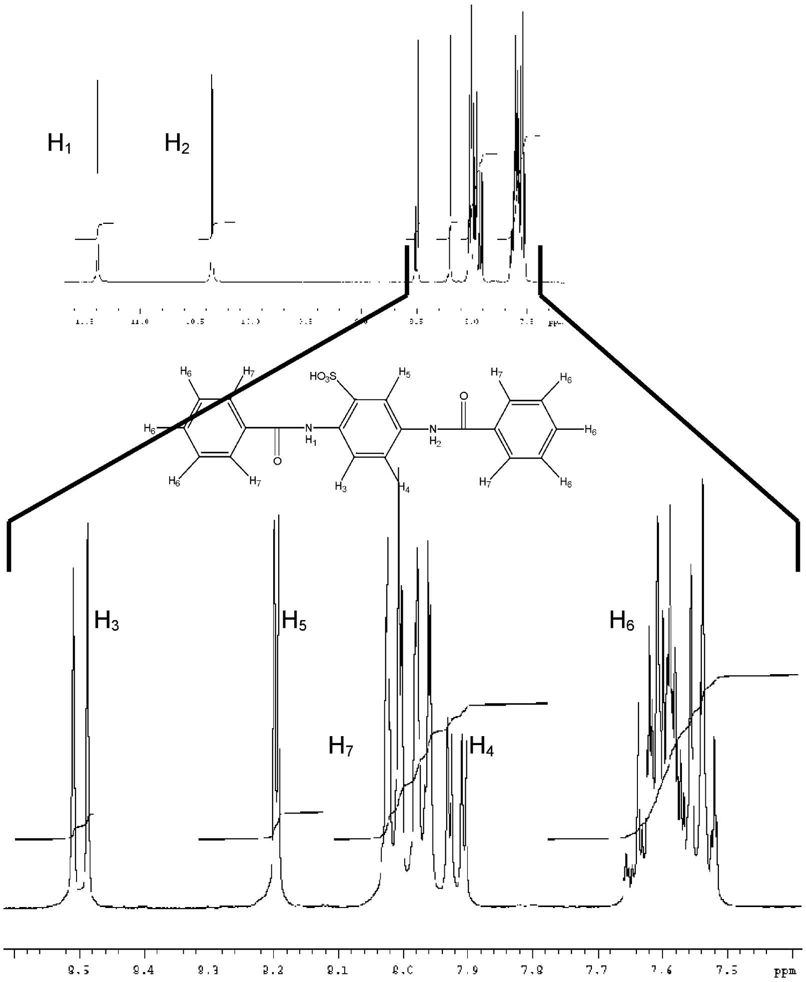

Fig. 5. NMR spectra of model compound with **3** (TMSCl).

formation of aggregates of the sulfo-PPTA polymer chains [19]. In our experiments, the evidence for the formation of molecular aggregates is from the observed turbidity (light haze) of the solutions upon gel formation after cooling down, while the solutions are fully transparent at elevated temperatures. The turbidity itself does not appear to be related to the formation of a lyotropic liquid crystalline structure as this haze is also observed in the isotropic gels. In addition, in aged gels we have observed the presence of fine fibrillar structures using optical microscopy, which suggests that the underlying structures in the fresh gels are also fibrillar in nature. SEM of dried films of sulfo-PPTA has confirmed this hypothesis (Fig. 11). In this picture, a section of fibrillar structure can be observed in the fracture surface. This picture also reveals the weakness of these aggregates as is confirmed by the mechanical analysis.

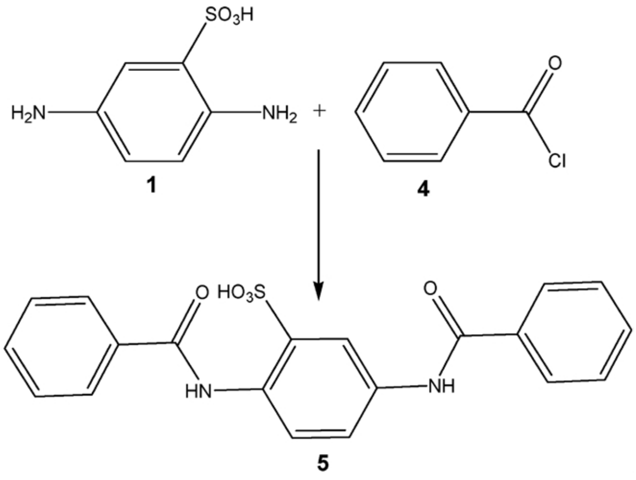

Fig. 6. Reaction route for the model compound without **3** (TMSCl).

Additional evidence for this structure was found using small-angle neutron scattering, which was reported in a recent paper [32].

Table 2
M_n and M_w values as obtained by SEC

Sample	M_n	M_w	PDI
Unactivated route	1200	1600	1.3
Activated route	4200	7800	1.8

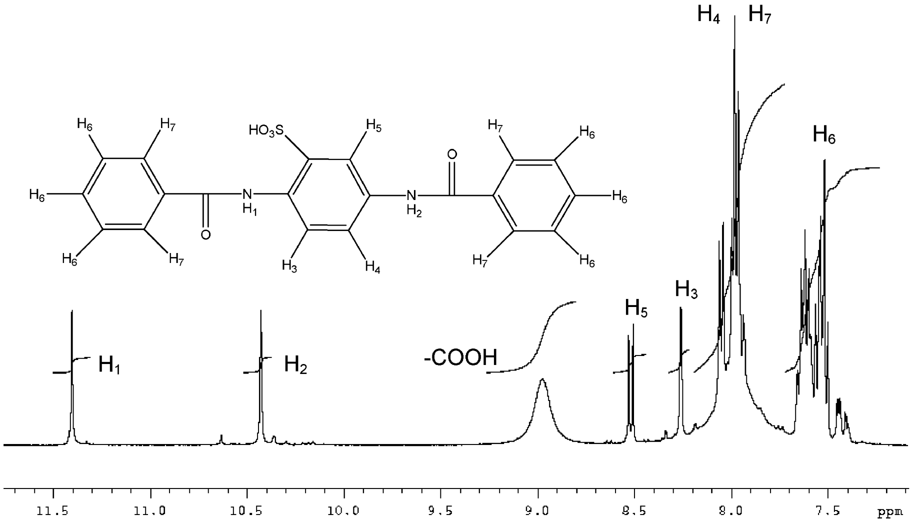

Fig. 7. NMR spectra of model compound without **3** (TMSCl).

4.3. Thermal analysis

TGA measurements have been done in nitrogen in order to evaluate the thermal stability of our polymer; standard PPTA with a comparable M_w has been used as a comparison.

The curve shows two reductions in mass: at 280 °C (25%) due to the departure of the sulphonic group, and finally at 580 °C (25%) due to degradation of the amide bonds. In the PPTA curve is observed around 280 °C. Since the sulphonic group represent 25 wt% in the repeating unit, therefore, all sulphonic groups have degraded and this is confirmed by FTIR [33], no peaks [34] were found around 1050–1000 cm^{-1}. Further investigations have been done using XRF in order to determine the content of sulphur in the sample before and after exposure at 350 °C, we found for the starting polymer: 8.0% in mass of sulfur (calculated 10.04%), and after exposure 0.1% in mass of sulphur (calculated 0%). Therefore we can conclude that the first weight loss is due to the departure of the sulfonic groups.

From this result we believe that it may be possible to

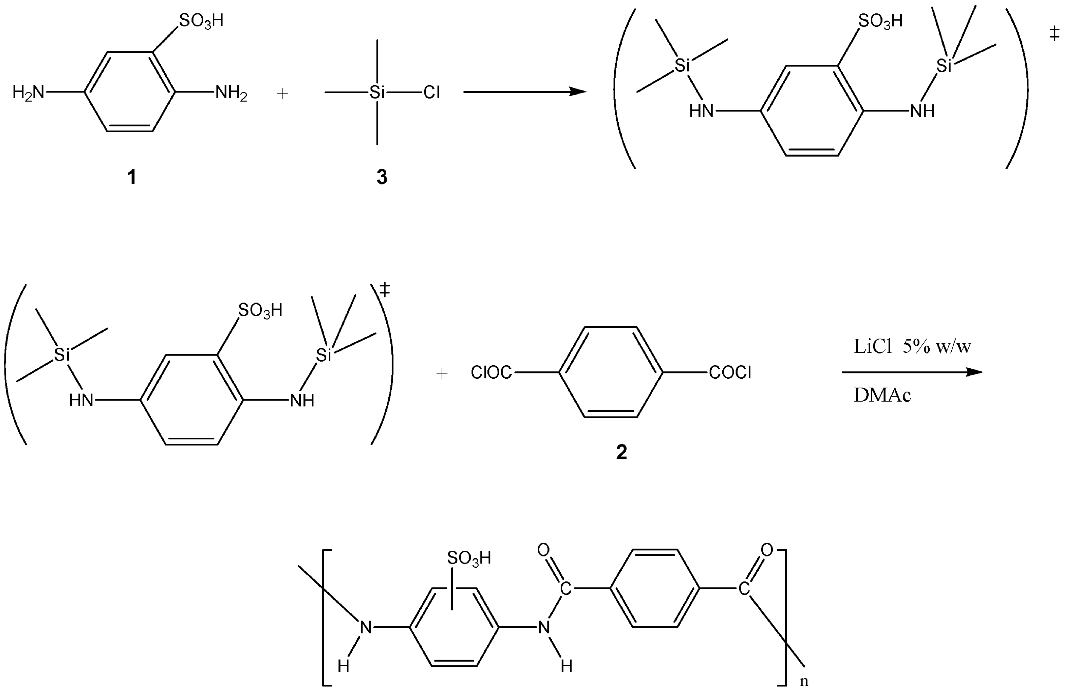

Fig. 8. TMSCl activated route for water-soluble sulfo-PPTA.

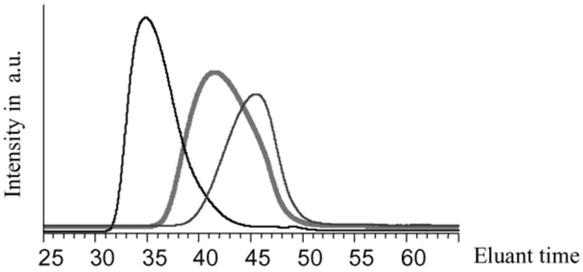

Fig. 9. SEC curve with PPTA 1010 (plain) as a reference, (blue line) sulfo-PPTA synthesised with silylated diamine, (red line) sulfo-PPTA obtained with the standard diamine.

process our materials by spin coating followed by curing it at 400 °C in order to obtain a PPTA-like structure.

4.4. Dynamic mechanical analysis

DMA measurements were performed in order to evaluate the mechanical properties of freestanding films, which were obtained by evaporation of the casting solvent. The obtained films are very brittle. Interestingly, the polymer shows a storage modulus of 3 GPa and a loss modulus of 2.5 GPa. In comparison for unoriented PPTA films of a similar M_w a storage modulus of 6 GPa and a loss modulus of 60 MPa is reported in the literature [15]. The DMA results on our polymer, therefore, show the same order of magnitude for E′, but the value of the loss modulus E″ is exceptionally high, both in relative and in absolute terms, especially when considering that we are very far below the glass transition or melting point of the material. This intriguing result may be due the structures of the films where the structural units are not single polymer chains but instead consist of fibrillar aggregates that are loosely bound together.

In standard PPTA films, made from sulphuric acid solution, the polymer chains are aligned and strongly bonded together, see Fig. 12.

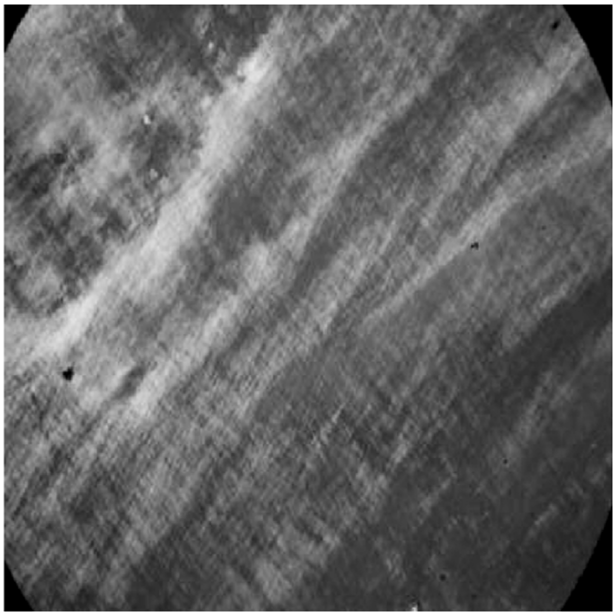

Fig. 10. Optical polarisation microscopy image from sulfo-PPTA, at 2% wt.

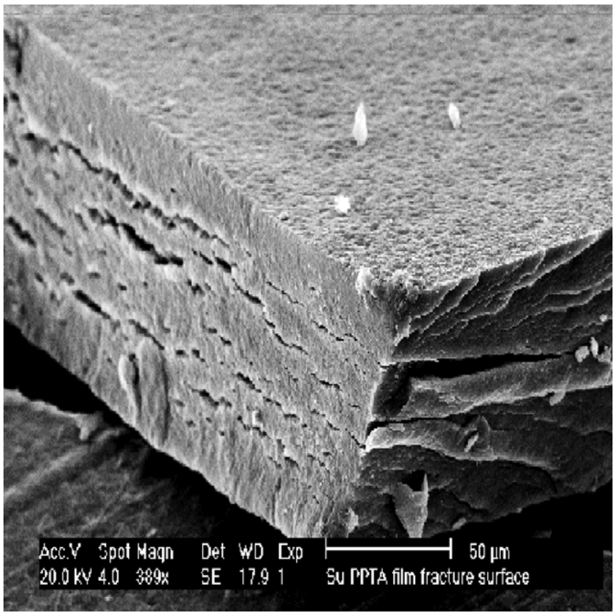

Fig. 11. SEM picture of dried film of sulfo-PPTA.

Conversely, in sulfo-PPTA films the high value of the loss modulus indicates a structure consisting of loosely bound molecular aggregates see Fig.13. We may assume that these objects are formed by the aggregation of several polymer chains during gel formation in solution and that they are then become partially aligned during further solvent evaporation. However, it appears from the DMA results that the aggregates are not strongly bonded like in the case of PPTA and can move rather easily. We can further assume that in sulfo-PPTA, the hydrogen bonding between the polymer chains has been disrupted to some extent by the presence of the sulphonic group, i.e. the sulphonic groups may cause unfavourable stacking due to steric hindrance. This would also lead to an additional explanation of the very high value of the loss modulus in our material.

5. Summary and conclusions

Sulfo-PPTA as obtained by using sulphonated phenyldiamine shows good water solubility. The use of activation

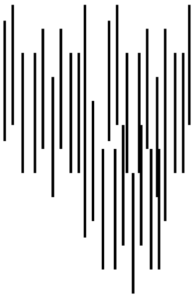

Fig. 12. Schematic morphology of a PPTA film.

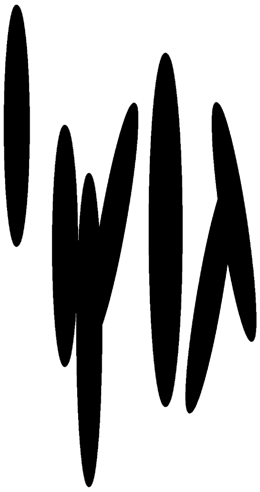

Fig. 13. Schematic morphology of a sulfo-PPTA film.

via TMSCl triples the molecular weight of the polymer when compared to previous results. Without chlorotrimethylsilane (**3**), 2,5-diaminobenzenesulfonic acid (**1**) is less reactive, and the resulting reaction between benzoyl chloride (**4**) and 2,5-diaminobenzenesulfonic acid (**1**) is not complete. To our knowledge, this is the first report of a reaction between an aromatic diamine (sulfonated phenyldiamine) and chlorotrimethylsilane. The value of the molecular weight obtained by viscosimetry is higher that the values obtained by SEC although the trends are the same.

The sulfo-PPTA polymer is soluble in water at room temperature at polymer concentrations between 0 and 20 wt%. Gel formation appears for the sample all polymers concentrations. Alignment of sulfo-PPTA in H_2O solution is observed at concentrations between 2 and 25 wt%. The alignment mechanism is not completely clear but preliminary results suggest that molecular aggregates are formed and it is these that can be aligned.

The form, the shape and the composition of the aggregates have to be explored further. The aggregate formation may be due to the limited solubility of our partially sulfonated polymer and their ability to form hydrogen bounds. The steric hindrance caused by the presence of the sulphonic groups along the main chain may act to decrease the strength of the molecular H-bonding interactions. In conjunction with this the formation of films consisting of assemblies of molecular aggregates seems to provide an explanation of the anomalously high loss modulus found form DMA measurements in thin films of sulfo-PPTA.

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