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Preparation of Aromatic Polyamide Polyanions: A Novel Processing Strategy for Aromatic Polyamides

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ABSTRACT: The reaction of aromatic polyamides such as poly(*p*-phenylene terephthalamide) (PPTA) with a variety of strong bases to yield dimethyl sulfoxide (DMSO) soluble polyanions has been explored. At least 60% of the amide groups must be deprotonated to give soluble polyanions of PPTA. Little loss of molecular weight was observed under 40 °C. Solution viscosity was highly dependent on the cation, with potassium giving lower viscosity solutions than sodium. The viscosity of the PPTA solutions increased with the degree of deprotonation, suggesting an increase in chain stiffness. Addition of proton donors, such as methanol, to the reaction of base with the aromatic polyamide in DMSO significantly enhanced the rate of polymer dissolution and gave higher solubilities and lower solution viscosities. Deprotonation of dibenzoyl-*p*-phenylenediamine was studied as a model compound for PPTA, confirming the results from the polymer. A single-crystal X-ray diffraction study of the model compound as its dianion revealed a short C–N bond and a long C–O bond in the amide groups indicative of increased conjugation through the backbone chain. Properties of films and fibers from processing the isotropic anion solutions are also described.

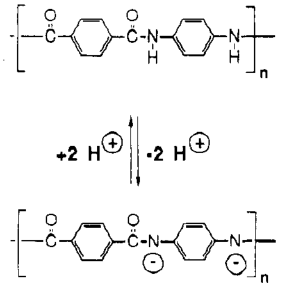
Introduction

Rodlike macromolecules such as poly(*p*-phenylene terephthalamide) (PPTA) are important in fibers and films because of their high strength and stiffness as well as their heat and solvent resistance.[2] Normally the rodlike aromatic polyamide PPTA is soluble only in strongly acidic media.[2] However, a completely new approach to dissolving PPTA, first described by Takayanagi, is the discovery that the amide groups of PPTA can be deprotonated by the strong base sodium methyl sulfinyl carbanion to yield a polyanion, Na$^+$PPTA$^-$, as shown in Scheme I. This polyanion is soluble in the simple organic solvent dimethyl sulfoxide (DMSO).[3,4] We were intrigued by the possibility that the PPTA polyanion solutions could represent a new approach to the processing of PPTA, which is otherwise very difficult. We have therefore explored the chemistry of the PPTA polyanion with an emphasis on novel methods of processing.

Takayanagi and co-workers have described the reaction of PPTA with NaH in DMSO to form red gelatinous solutions of Na$^+$PPTA$^-$ at low concentrations (ca. 1 wt %).[3a,c] These solutions have been used for the preparation of N-alkylated aromatic polyamide derivatives as well as graft copolymers of PPTA by means of grafting reactions at the deprotonated amide bond.[3a,c,e,f,4d] Additionally molecular composites have been prepared by coprecipitating PPTA with other polymers from the DMSO solution.[3d,g,h] Recent publications by Takayanagi and others have emphasized the use of the aramid polyanion chemistry to effect reactions at the surfaces of PPTA fibers.[3b,i-k,4a,b] Nevertheless, basic information on the solution properties of the aromatic polyamide polyanions was otherwise unavailable.

We have discovered that the solution properties of the poly(arylamide) polyanions are markedly influenced by the counterion, a liquid crystalline regime being observed for some of the salts, and that complete deprotonation of the amide bonds of the PPTA is not necessary to render the polymer soluble in DMSO. We have found that proton donors, such as alcohols or water, reduce the PPTA polyanion solution viscosities in DMSO and allow much higher solution concentrations of the PPTA polyanion to be achieved. Possible mechanisms of this effect are discussed. We have demonstrated that the aromatic polyamide polyanion solutions can be used for the preparation of high-quality isotropic films, fibers, and coatings of PPTA. These investigations are the subject of this report.

Scheme I



Results and Discussion

Preparation of PPTA Polyanion Solutions. PPTA is dissolved by reaction of sodium methyl sulfinyl carbanion (prepared by reaction of NaH with DMSO) to give red viscous solutions of Na$^+$PPTA$^-$ as an approximately 1 wt % solution in DMSO, as described by Takayanagi.[3a] Higher concentrations of high molecular weight polymer ($\eta_{inh} \geq 4$ dL/g), reacted under Takayanagi's conditions,[3a] give thick gels that are essentially nonprocessible. Furthermore, efficient formation of sodium methyl sulfinyl carbanion requires anhydrous conditions since water is a stronger acid than DMSO by several orders of magnitude.

We have discovered that high molecular weight PPTA can be dissolved in DMSO as the PPTA polyanion by a variety of strong bases such as alkoxides and amides. Additionally, solutions of the PPTA polyanion can be straightforwardly prepared as their Li$^+$, Na$^+$ and K$^+$ salts with solubilities and solution viscosities that depend mark-

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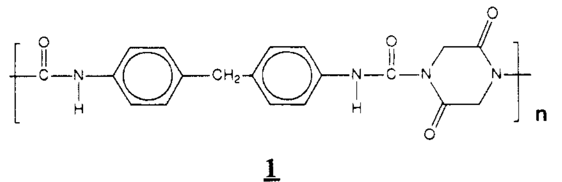
edly on the choice of cation. The sodium salt of the PPTA polyanion forms highly viscous solutions in DMSO, while the potassium salt forms free-flowing solutions at comparable concentrations. The lithium salt likewise forms relatively free-flowing solutions at concentrations of approximately 1 wt %, although the lithium salt forms only slowly at room temperature. For example, reaction of lithium methyl sulfinyl carbanion in DMSO (prepared by reaction of butyllithium with DMSO) requires approximately 1 week at room temperature to fully dissolve PPTA to a concentration of 1 wt %, while the analogous reaction with potassium methyl sulfinyl carbanion goes to completion within 24 h to give 1.5 wt % solutions in DMSO at room temperature. In general the potassium salt gave the highest solubilities.

We have found that high concentrations of the aramid polyanion can be easily prepared by judicious choice of base and counterion and with use of a proton donor as an additive to the solution, permitting preparation of higher concentration solutions than without the proton donors. In this way, PPTA (η_{inh} = 5.5 dL/g) was reacted with potassium *tert*-butoxide in DMSO in the presence of 4 equiv of methanol per amide bond to give a solution that was 10 wt % PPTA polyanion salt in DMSO. Under similar conditions, poly(*m*-phenylene isophthalamide) was dissolved to yield 20 wt % solutions. The order of addition of base, proton donor, and polymer to the DMSO is unimportant.

DMSO and analogous alkyl sulfoxides such as tetramethylene sulfoxide are the only solvents we have found for the PPTA polyanion. Other dipolar, aprotic solvents such as *N*-methylpyrolidinone, tetrahydrofuran, and dialkyl sulfones are compatible with the PPTA polyanion, but these are not by themselves solvents for the PPTA polyanion in the absence of DMSO. The unique capacity of DMSO in this regard possibly can be attributed to the ability of this solvent to solvate both anionic and cationic species.[5]

The scope of polymers dissolved by this technique includes hydrogen-bonded polymers such as aromatic polyamides (but not aliphatic nylons), polybenzimidazoles, and polyureas. It includes PPTA, poly-1,4-benzamide, and meta isomers of this polymer such as commercially available poly(*m*-phenylene isophthalamide) as well as various copolymers of these materials. Aromatic–aliphatic polyamides are also dissolved by this approach providing that aromatic groups are bonded directly to the amide nitrogen to render the amide hydrogen relatively acidic. We have dissolved polyurea (1) shown below by this technique. The polybenzimidazoles dissolved in this way include poly-2,5(6)-benzimidazole (2) and poly(2,6-(*p*-phenylene)dimidazobenzene)[6] (3).



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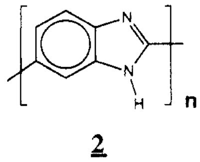

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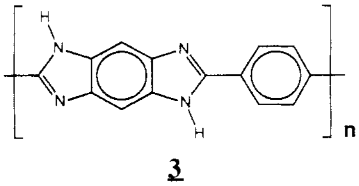

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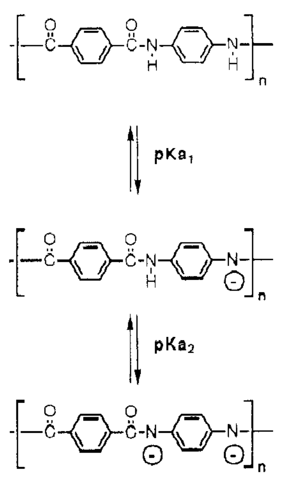
Scheme II



The PPTA polyanion undergoes only slow molecular weight loss under anhydrous conditions at moderate temperatures. For example, a 1-week old sample of K^+PPTA^- polyanion was precipitated with water and dried. This sample had an inherent viscosity in concentrated sulfuric acid of 4.57 dL/g compared to 5.41 dL/g for the control sample of PPTA.

Acidity of Aromatic Polyanions. The pK_a's of aromatic polyamides are unknown in the literature. However, we can approximate that PPTA has two pK_a's: one for deprotonation of the first hydrogen ion from the PPTA repeat unit and a second pK_a for the deprotonation of the second hydrogen ion, as shown in Scheme II.[7] The pK_a of benzanilide is 18.8 in anhydrous DMSO,[8] and therefore the pK_{a1} of PPTA should be approximately 19. It is known from the literature that weak organic acids related by a *p*-phenylene linkage should have first and second pK_a's differing by about 10 pK_a units.[9] Therefore, we propose that pK_{a2} of PPTA is about 29 in DMSO. In principle, then, any base whose conjugate acid has a pK_a in DMSO greater than 29 should fully deprotonate PPTA, and any base whose conjugate acid has a pK_a greater than 19 should effect 50% deprotonation of PPTA. Hence, we have found that potassium *tert*-butoxide (*tert*-butyl alcohol, pK_a = 32), sodium methoxide (methanol, pK_a = 29), potassium hydroxide (water, pK_a = 32), and sodium amide (ammonia, pK_a = 41),[10] among others, are all useful to prepare the anionic form of aramids such as PPTA, poly(*m*-phenylene isophthalamide), and poly-1,4-benzamide in DMSO.

Poly(*m*-phenylene isophthalamide) is a stronger acid in DMSO than is PPTA as evidenced by the following observation. Cosolutions of poly(*m*-phenylene isophthalamide) and PPTA were prepared. The typical procedure was to prepare a 16 wt % solution of the partially deprotonated poly(*m*-phenylene isophthalamide) polyanion as its potassium salt in DMSO. Aliquots of this solution were then mixed with varying amounts of 1.3 wt % fully deprotonated PPTA as its potassium salt. When the ratio of poly(*m*-phenylene isophthalamide) polyanion to PPTA polyanion was 50:1, the PPTA precipitated out of solution as the unionized polymer, identified by solubility characteristics and by infrared spectroscopy of the precipitate. Presumably the protons from the partially deprotonated poly(*m*-phenylene isophthalamide) were transferred to the more basic PPTA polyanion, protonating the PPTA polyanion sufficiently to cause it to precipitate. When the ratio of poly(*m*-phenylene isophthalamide) polyanion to PPTA polyanion was less than

50:1, the two solutions were miscible with one another, allowing them to be cast together into films or cospun into fibers. Resonance structures for the two polyanions suggest why PPTA is less acidic than its meta isomer. Resonance structures for PPTA polyanion allow for much less charge separation than the analogous resonance structures for the meta isomer, providing for greater resonance stabilization of the conjugate base.

Sodium amide generated the PPTA polyanion in DMSO only very slowly. Carrying out this reaction in the presence of 2 equiv of additives with pK_a's lower than that of DMSO but higher than that of aramid significantly accelerated the reaction. Aniline (pK_a = 30.6), primary alkyl amines (p$K_a \cong 35$), or acetamide (pK_a = 25.5) significantly enhanced the formation of the PPTA polyanion from sodium amide.[10] However, with phenol (pK_a = 18)[10] or acetic acid (pK_a = 12.3)[10] present, PPTA did not react with base to form a solution. Because the pK_a of DMSO is 35, this result implies that methyl sulfinyl carbanion formation is not a prerequisite for the deprotonation reaction.[10] Similarly, lithium dimethylamide, despite being a stronger base than sodium amide, gave aramid solutions only when an additive such as formamide or benzamide was present in DMSO.

Solubility of the polymer anions was enhanced significantly be addition of fair amounts of proton donors, such as alcohols, water, and selected amides. This again demonstrates that formation of the methyl sulfinyl carbanion is not prerequisite for anion formation since the alcohols and water are significantly stronger acids than DMSO. For optimum solubility of various polyamides we use 1 equiv of base for every polymer amide group and 3–4 equivalents of alcohol. Five or greater weight percent of PPTA in DMSO is readily obtained in this way. Methanol, benzyl alcohol, ethylene glycol, and 2-propanol are all effective for this purpose. Octanol is effective as well, although solubility limits of the polymer are strained because of the high weight percent of additive used (approximately 15% of total solvent).

Although the proton donors aid in the dissolution, they also compromise the molecular weight stability of the aromatic polyamide polyanions. Thus, while the hydrolytic stability of the polymer solutions containing the alcohol proton donors is good at room temperature, little change in polymer inherent viscosity has been observed with the PPTA polyanion solutions containing methanol when stored at room temperature for several months. Above 40 °C, however, the drop in solution viscosity became appreciable and was highly dependent on the added proton donor, as a result of molecular weight loss. With 2-propanol as the donor, little drop in viscosity took place over 25 h even at 70 °C. With ethylene glycol, at the same molar concentrations, the solution viscosity dropped at 50 °C to one-fifth of its original value. In relative terms loss in solution viscosity up to 80 °C was 8/5/3/1 for ethylene glycol/methanol/benzyl alcohol/2-propanol. This effect is depicted in Figure 1. Qualitatively, the loss in solution viscosity as a result of molecular weight loss induced by proton donors is much greater for poly(*m*-phenylene isophthalamide) than it is for PPTA.

Model Studies. To gain insight into the solution structure of the PPTA polyanion and into the extent of deprotonation of the polyanion, the simple three-ring oligomer dibenzoyl-*p*-phenylenediamine has been studied as a model for PPTA. This oligomer is only sparingly soluble in DMSO. However, when reacted with a DMSO solution of the potassium salt of methyl sulfinyl carbanion, the resulting dianion is highly soluble in DMSO. Addition of equal volumes of THF and pentane to the DMSO solution causes precipitation of the dianion, which can be further recrystallized from DMSO/THF/pentane mixtures to yield an analytically pure, white, microcrystalline solid. It is noteworthy that this dianion, despite being white as an analytically pure solid, forms yellow solutions in DMSO. NMR, IR, and elemental analyses are all consistent with the formulation of this product as the simple potassium salt of the PPTA oligomer.

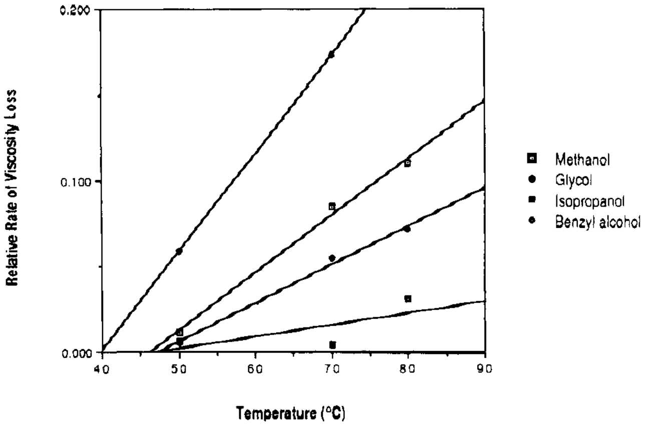


Figure 1. Plot of relative rate of viscosity loss of a 5.6 wt % solution of K^+PPTA^- in DMSO induced by various proton donors as a function of temperature (see text).

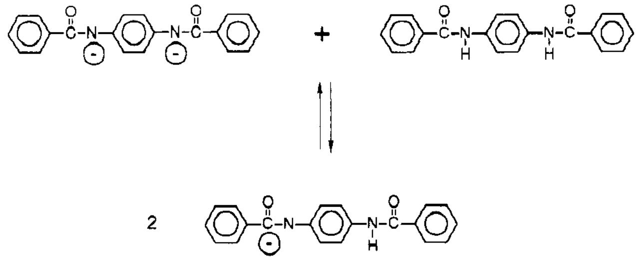


Figure 2. Equilibrium between a slurry of the unionized PPTA model compound and a solution of the monoionized and diionized PPTA model compounds. The equilibrium lies very far to the side of the monoionized model compound as determined by ^{1}H NMR spectroscopy.

The potassium ions can readily be complexed with 18-crown-6 by addition of the crown ether to DMSO solutions of the PPTA oligomer dianion. The K(18-crown-6)$^+$ salt is much more soluble than the simple K^+ salt, soluble even in THF. Also, the K(18-crown-6)$^+$ salt is yellow as an analytically pure compound, and the yellow color is observed for the solution as well.

Reaction of a DMSO solution of the dianion with 1 equiv of the parent dibenzoyl-*p*-phenylenediamine as a slurry in DMSO results in complete dissolution of the oligomer to form the new monoprotonated PPTA oligomer as shown in Figure 2. This monoanion has been isolated as an analytically pure, white, microcrystalline solid and characterized by NMR and IR spectroscopy. Like the parent dianion, this compound is white as a pure solid but yellow in solution. The significance of this experiment is that it demonstrates that protons can be exchanged between the PPTA oligomer and the deprotonated PPTA oligomer and that partially deprotonated arylamides can be formed. The equilibrium shown in Figure 2 lies very far to the side of the monoprotonated oligomer as evidenced by NMR spectroscopy and by the fact that no undissolved parent oligomer remains in the reaction vessel. These results suggest that the PPTA polymer could itself be partially protonated to give a soluble species, the extent of deprotonation depending on the stoichiom-

Table I
Viscometry Data for K^+PPTA^- Polyanion Solutions in DMSO by the Bubble Rise Time Method[a]

concn, wt %	extent of deprotonatn,[b] %	viscosity,[c] stokes
	As K^+ Salt	
1.33	100	44.1 (0.7)
1.33	90	22.9 (0.4)
1.33	75	15.6 (0.3)
	As $[K(18\text{-crown-}6)]^+$ Salt	
1.33	100	18.2 (0.4)
1.33	90	11.9 (0.1)
1.33	75	11.3 (0.3)

[a] $T = 25$ °C, ASTM D 1545-76. [b] Extent of deprotonation defined as the fraction of amide bonds that are deprotonated as determined by the stoichiometry of the acid–base reactions (see text). [c] Determined with Cargille viscosity tubes meeting ASTM D 1545-76 specifications. Viscosities represent the average of three to four determinations, with the standard deviation given in parentheses.

etry between the reaction of PPTA and base, and that protons could be rapidly exchanged between PPTA and the PPTA polyanion. Extending these results for the model compound to the PPTA polymer itself are described below.

Partially Deprotonated PPTA Polyanion Solutions. Three preparations of partially deprotonated PPTA were devised: 1, addition of excess PPTA to preformed solutions of fully deprotonated PPTA; 2, addition of strong acid to preformed solutions of fully deprotonated PPTA; and 3, use of a deficiency of base in the reaction with PPTA. All these preparations yield red homogeneous solutions with no evidence for unreacted PPTA by visual inspection or by examination of representative solution samples under a polarizing microscope.

Most significant was the observation that the viscosity of the partially reprotonated PPTA polyanion solutions was lower than that of the fully deprotonated polyanion solutions at comparable concentrations. The lowest viscosity achieved was when less than 70% but more than 60% of the amide bonds had been deprotonated. These samples were prepared by reaction of PPTA with 1 equiv of potassium methyl sulfinyl carbanion per amide bond and subsequent addition of acetic acid to give the desired level of partial deprotonation. To support these qualitative observations, a series of viscosity measurements were carried out by means of bubble rise time. These are given in Table I for 1.33 wt % solutions of the K^+PPTA^- polyanion in DMSO.

In this way the solubility of the PPTA polyanion in DMSO is enhanced. For example, solutions that are 9.5 wt % K^+PPTA^- as 75% deprotonated PPTA can be prepared by using only conventional mechanical laboratory stirrers. These concentrations are consistent with what can be achieved with methanol as an additive, as described above.

Possible Mechanism of Protic Additives on PPTA Polyanion Solutions. We have found that addition of small amounts of alcohols, especially methanol, to the DMSO/base solution enhances the rate of formation of the PPTA polyanion solutions, and they give solutions with lower viscosity than the corresponding solutions without the protic additives. This effect of protic additives forms the basis for the observed enhanced solubility of the PPTA polyanion in the presence of protic additives. The effect of methanol is optimal when there are 3–4 equiv of methanol per amide bond.

We believe that small amounts of protic additives serve to partially reprotonate the PPTA polyanion, and reprotonation therefore is the basis for the viscosity lowering observed with the protic additives. A second equally important effect of the alcohols is a kinetic one: the protic additives enhance the rate of formation of the polyanion. It is known from the literature that alcohols enhance the rate of proton exchange reactions between carbon, nitrogen, and oxygen acids in DMSO solutions (see Scheme III).[11] The basis of this effect is the stability of the known alcoholate species in DMSO (Scheme III).[11] A similar effect applied to PPTA, itself a nitrogen acid, would account for the observed rate enhancement.

Table II
Capillary Viscometry Data for K^+PPTA^- Polyanion Solutions in DMSO[a]

concn, wt %	extent of deprotonatn,[b] %	inherent viscosity,[c] dL/g
	As K^+ Salt	
0.133	100	11.07 (0.03)
0.0665	100	13.35 (0.08)
0.0133	100	26.37 (1.02)
0.00665	100	29.90 (0.32)
0.133	85	9.44 (0.13)
0.0665	85	11.66 (0.09)
0.0133	85	20.87 (1.37)
0.00665	85	21.02 (0.36)
0.133	75	8.89 (0.08)
0.0665	75	10.65 (0.23)
0.0133	75	16.78 (0.16)
0.00665	75	22.32 (1.26)
	As $[K(18\text{-crown-}6)]^+$ Salt	
0.0133	100	24.65 (1.10)
0.0133	75	23.76 (0.25)

[a] $T = 25$ °C. Viscosities determined by using a size 150 Cannon Fenske viscometer maintained at 26.6–27.0 °C by using an oil bath. [b] Extent of deprotonation defined as the fraction of amide bonds that are deprotonated as determined by the stoichiometry of the acid–base reactions (see text). [c] Inherent viscosities represent the average of three or four determinations. The standard deviation is given in parentheses.

Scheme III

$$ROH\cdots OR^- \rightleftharpoons RO^-\cdots HOR$$

$$R'CONRH\cdots OR^- \rightleftharpoons R'CONR^-\cdots HOR$$

The proton donors may aid in solvation of the aramid polyanion after the aramid polyanion is formed by means of hydrogen bonding to the PPTA polyanion as the solution species.[12,13] Infrared and NMR spectroscopy did not reveal any evidence for such hydrogen-bridged species.

Polyelectrolyte Behavior of PPTA Polyanion Solutions. We have measured the viscosity of the potassium salt of the PPTA polyanion over the concentration range 0.0066–1.3 wt % in DMSO as a function of the extent of deprotonation of the amide bonds at constant potassium ion concentration. The bubble rise time method was used for the 1.3 wt % solutions, while capillary viscometry was used for the lower concentration solutions (Tables I and II). As is evident from the viscosity data, the inherent viscosity increases with decreasing concentration regardless of the degree of deprotonation of the amide bonds. This observation is consistent with polyelectrolyte effects analogous to what is normally observed for random coil polymers and suggests that the chain becomes stiffer and more expanded as the polymer chains are diluted.

We have found that the inherent viscosity of the PPTA polyanion decreases inversely with reprotonation, even at very low concentrations. We interpret these observations as follows: Decreasing the degree of deprotonation

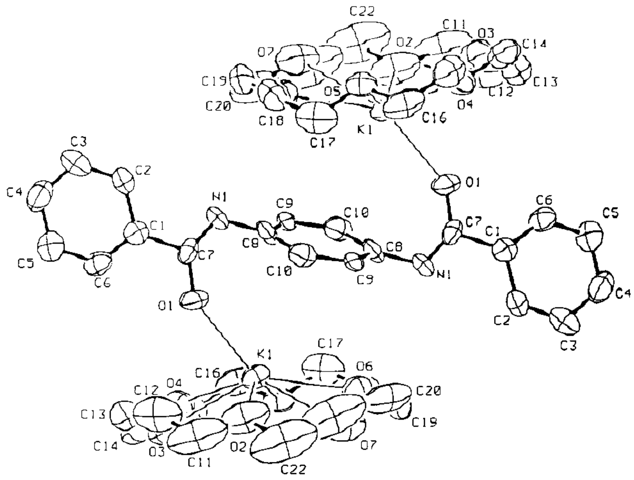


Figure 3. ORTEP drawing from the single-crystal X-ray diffraction study of the PPTA model compound bis(*p*-*tert*-butylbenzoyl)-*p*-phenylenediamine dianion as its salt with [K(18-crown-6)]$^+$ Hydrogen atoms are omitted for clarity.

reduces the charge density along the length of the polymer chain, and therefore the electrostatic driving force for chain expansion of the polyelectrolyte is reduced.

The data in Table II shows that the use of the [K(18-crown-6)]$^+$ salt, instead of the simple potassium salt of the PPTA polyanion, decreases the inherent viscosity of the solutions at concentrations greater than 0.1 wt % but has no effect at lower concentrations. This suggests that ion pairing increases the stiffness of the polymer chain, but dilution below 0.1 wt % disfavors ion pairing to the PPTA polyelectrolyte.

These results all suggest that deprotonation of the amide bonds of PPTA gives a polyelectrolyte that is actually a stiffer, more expanded chain than the parent PPTA polymer. This observation is somewhat surprising given the fact that PPTA is already an extended semi-rigid-rod polymer.[14] For that reason we have sought independent corroboration of this conclusion. Light scattering studies of the PPTA polyanion solutions proved impossible because these polyanions absorb strongly in the UV–vis region of the spectrum with absorption maxima that are concentration dependent. However, we have successfully completed a single-crystal X-ray diffraction study of the model compound bis(*p*-*tert*-butylbenzoyl)-*p*-phenylenediamine dianion as its salt with [K(18-crown-6)]$^+$. An ORTEP drawing from this crystal structure of the model compound is given in Figure 3, and the details of the crystal structure are given in the supplementary material. The carbon–oxygen bonds are long, and the C–N bond of the amide linkage is short relative to uncharged aryl–amide bonds (1.287 and 1.258 Å for the anionic model compound vs 1.226 and 1.359 Å for the unionized model compound).[15] These metric parameters are therefore consistent with a structural model in which the negative charge is localized primarily on the carbonyl oxygen with extensive double-bond character on the C–N amide bond.[16]

Liquid Crystalline PPTA Polyanion Solutions. Because the PPTA polyanion is a rodlike polymer much like the parent PPTA polymer, we anticipated that the PPTA polyanion could form a lyotropic liquid crystalline phase. Although the PPTA polyanion solutions were generally prepared at approximately 1–3 wt % in DMSO, higher concentration solutions could be prepared with high torque mixers or by evaporation of the solvent by means of vacuum distillation. In this way, we have prepared PPTA polyanion solutions up to approximately 12 wt %. Polarizing optical microscopy demonstrated that these high concentration solutions are liquid crystalline. Solutions at different polymer concentrations were prepared as the sodium salt and as the potassium salt, and the results of the microscopy studies are summarized in Table III.

Table III
Birefringent Properties of PPTA Polyanion Solutions

concn, wt %	optical properties
	Sodium Salt
1.5	isotropic, shear birefringent
2.1	biphasic, birefringent regions
2.7	biphasic, more birefringent regions
4.4	mostly birefringent
5.3	birefringent
6.3	birefringent
	Potassium Salt
1.7	isotropic
6.3	isotropic, shear birefringent
8.6	isotropic, shear birefringent
11	mostly birefringent
13	birefringent

A Na$^+$PPTA$^-$ polyanion solution in DMSO is isotropic at 1.5 wt % but shows some shear birefringence. The solution is biphasic in the range of 2–5 wt %, with birefringent regions and optically isotropic regions being observed simultaneously. Samples of the sodium salt of fully deprotonated PPTA polyanion are entirely birefringent above 5 wt %. These observations are temperature invariant from +30 to +80 °C. No textural changes or changes in light intensity were observed over a period of several hours at +30 °C.

Solutions of the potassium salt of the PPTA polyanion also form anisotropic phases but at much higher polymer concentrations than for the sodium salt. For example, a 1.7 wt % solution of the K$^+$PPTA$^-$ polyanion salt is completely isotropic with no shear birefringence. At higher concentrations (6.3–8.6 wt %) the solutions are isotropic but exhibit shear birefringence. Above 12 wt % the potassium salt of the fully deprotonated PPTA polyanion becomes fully birefringent. No liquid crystalline behavior was observed for solutions of poly(*m*-phenylene isophthalamide) polyanion.

Differential scanning calorimetry investigations of these PPTA polyanion solutions showed that the melting point was elevated in the presence of the sodium salt of the PPTA polyanion solutions. For example, the peak maximum for the melting of DMSO occurred at 16.4 °C by DSC. At 4.4 wt % Na$^+$PPTA$^-$ in DMSO, the peak maximum was 17.3 °C, while the peak maxima were 22.4 and 23.1 °C for 5.3 and 6.3 wt % solutions, respectively. Similar melting point elevations were observed for the potassium salts.

Films and Fibers from PPTA Polyanion Solutions. Isotropic solutions of the PPTA polyanion in DMSO and in DMSO/methanol mixtures have been used for the preparation of strong PPTA films and fibers. Typically solutions were used with a polymer concentration ranging from 1 to 5 wt %. Polyanion solutions were cast on a solid support. Then the solution was immersed in water to reprotonate the PPTA and extract DMSO. This procedure left the PPTA in the form of a gel film. The gel film was extracted liberally with water and dried under restraint to give a fully densified PPTA film which was then finally dried at 180 °C. The films were clear and tough and isotropic. Typical properties for a 2 × 10^{-4} in. thick film were as follows: tensile modulus, 800 kpsi; tensile strength, 24 kpsi; elongation at break, 5%; Elmendorf tear strength, 7 g/mm. Density was 1.354 g/mL. These films had a moisture regain of 5.3% at 21 °C and

65% relative humidity, significantly higher than, for example, Kapton polyimide films, which had a moisture regain of 1.0% under identical conditions.[19] PPTA films have previously been reported from anisotropic and isotropic sulfuric acid solutions.[20] PPTA films have also been very recently prepared by an electrodeposition process from the PPTA polyanion solutions.[21]

Films of poly(*m*-phenylene isophthalamide) have been prepared by similar procedures using 2 wt % solutions of the potassium salt of the corresponding polyanion and no proton donor. Typical properties for a 1.5×10^{-3} in. thick film were as follows: tensile modulus, 530 kpsi; tensile strength, 13 kpsi; elongation at break, 4%. Therefore, while these films are strong and stiff, they only have small elongation at break.

Fibers were readily prepared by wet spinning 3–5 wt % isotropic solutions of PPTA of η_{inh} = 5.7 dL/g in DMSO/methanol/potassium *tert*-butoxide into methanol containing a small amount of acetic acid. After drying at constant length and annealing at 500 °C, the fiber had tensile properties: tenacity, 5.6 g/denier; elongation, 2%; modulus, 340 g/denier. These unoptimized spinning conditions have so far yielded unexceptional tensile properties, being typical of PPTA spun from isotropic solutions in concentrated sulfuric acid.[22] In our hands, the liquid crystalline PPTA polyanion solutions have had viscosities too high to be spun. Monolithic objects of PPTA have also been prepared from the PPTA polyanion solutions. Poly(*m*-phenylene isophthalamide) of inherent viscosity 1.6 dL/g was spun from an 18 wt % solution in DMSO/methanol/potassium *tert*-butoxide into a bath of 10% acetic acid in water, using a 0.5 in. air gap. After being soaked in acetic acid and then washed in acetone, the fibers were drawn 350% over a hot surface at 120 °C followed by annealing at 295 °C. Tensile properties were as follows: tenacity, 4.4 g/denier; elongation, 14%; modulus, 103 g/denier, typical of commercial poly(*m*-phenylene isophthalamide)[23] (Nomex Aramid[24]), which is dry spun from isotropic solution.[23]

Summary. We have explored the rich acid–base chemistry of aromatic polyamides. On the basis of acid–base properties, we have described an altogether new approach to processing these materials making use of their weak acidity to convert the aromatic polymers to the conjugate base, a DMSO-soluble species, which is readily reconverted back to the parent polymer by water or other acidic media.

We have examined the solution properties of the aromatic polyanions in DMSO and found that the solution viscosity is a function of the counterion, the state of ion pairing, as well as the fraction of amide bonds that are deprotonated. Consequently the concentrations of aromatic polyanions that can be achieved are influenced by counterion and degree of deprotonation as well as by proton donor additives that function uniquely to provide control over the degree of deprotonation and the rate at which the polymers are deprotonated. Model studies and qualitative investigations of the polyelectrolyte effects of these solutions suggest that the PPTA polyanion is a stiffer chain than is PPTA itself.

PPTA films with good properties have been prepared by this aramid polyanion chemistry, although the properties of fibers prepared in this way have thus far been lower than those obtained from spinning anisotropic solutions of PPTA in concentrated sulfuric acid.

Experimental Section

General Procedures. Except where otherwise noted, all experiments were performed under an inert atmosphere using a dry nitrogen filled drybox, on a standard Schlenk line with argon source, or by blanketing the reaction under dry nitrogen. THF, hexane, and pentane were distilled from sodium benzophenone ketyl. DMSO was Aldrich Gold Label brand and was used when the water content was 85 ppm or less by Karl-Fischer titration. Potassium *tert*-butoxide, potassium hydride, sodium hydride, and lithium diethylamide were purchased from Aldrich. Tetramethylene sulfoxide, methanol, ethylene glycol, 2-propanol, and benzyl alcohol were purchased from Aldrich as reagent grade and were used as received. PPTA was commercially available as Kevlar Aramid[24] pulp or as Kevlar-49 Aramid[24] fibers obtained from the Du Pont Co. ($\eta_{inh} \geq 5.3$ dL/g). Inherent viscosities were determined by using 0.10 wt % PPTA solutions in concentrated sulfuric acid. Poly(*m*-phenylene isophthalamide) was obtained as commercially available Nomex Aramid[24] staple fiber (from the Du Pont Co.). Polymer samples were dried in an oven at 130 °C for a minimum of 12 h before use. Sodium salts of the PPTA polyanion were prepared by the literature procedure.[3a] Representative preparations of other PPTA polyanion solutions are given below.

Preparation of a 1.3 wt % PPTA Polyanion Solution as the Potassium Salt. An argon- or nitrogen-flushed 1-L three-neck flask equipped with a nitrogen inlet, mechanical stirrer, and septum cap on the third neck was charged with 8.75 g (76.4 mmol) of KH as a 35% suspension in mineral oil. The KH was added to the flask against a heavy flow of inert gas. DMSO (600 mL) was then added by means of syringe through the septum cap. Approximately 50 mL of dry hexane was then added to the flask to extract the mineral oil that was suspended in the DMSO. The hydrocarbon layer was then removed by means of a syringe and discarded. After several minutes the KH dissolved. Aliquots (5.00 mL) were withdrawn and quenched with 20.00-mL aliquots of 0.100 M HCl solution. Phenolphthalein indicator was added, and the solution was titrated with 0.100 M NaOH solution to give the total base concentration in the DMSO. PPTA, 9.10 g as pulp, was then added to give 1 equiv of amide bonds/equiv of base. Stirring the resulting slurry for 36–48 h gave a red homogeneous solution of the polyanion, with no detectable unreacted fibers. The concentration of the resulting solution was 1.3 wt %.

Use of Methanol for the Preparation of a PPTA Polyanion Solution as the Potassium Salt. An argon- or nitrogen-flushed 1-L three-neck flask equipped with nitrogen inlet, mechanical stirrer, and septum cap on the third neck was charged with 17.1 g (0.15 mol) $K^{+-}O$-*t*-Bu. DMSO (600 mL) was then added by means of a syringe through the septum cap. PPTA, 18.2 g as pulp, was then added, followed by 19.6 g (24.7 mL, 0.61 mol) of methanol. Stirring the resulting slurry for 4 h gave a red homogeneous solution of the polyanion, with no detectable unreacted fibers. The concentration of the resulting solution was 2.8 wt %. The viscosity of this solution was approximately that of the 1.3 wt % solution prepared without proton donors.

Preparation of a Solution of Poly(*m*-phenylene isophthalamide) Polyanion as the Potassium Salt. An argon- or nitrogen-flushed 100-mL three-neck flask equipped with nitrogen inlet, mechanical stirrer, and septum cap on the third neck was charged with 5.7 g (0.050 mol) of $K^{+-}O$-*t*-Bu. DMSO (35 mL) was added, followed by 6.0 g of poly(*m*-phenylene isophthalamide) and 6.5 g (8.2 mL, 0.20 mol) of methanol. The reaction was stirred for 2 h at room temperature to give a clear, pale yellow 11.7 wt % solution of the poly(*m*-phenylene isophthalamide) polyanion as its potassium salt with no evidence for undissolved polymer.

Preparation of High Concentration PPTA Polyanion Solutions. Solutions (1.3 wt %) of PPTA polyanion either as the potassium salt or as the sodium salt were concentrated to give higher concentration, liquid crystalline solutions by vacuum distillation of DMSO. The higher concentration solutions were examined for liquid crystallinity by means of polarizing optical microscopy.

In a variation of this procedure, a blender was filled with liquid nitrogen. The low concentration polyanion solutions were added to the liquid nitrogen filled blender to give the polyanion solution in the form of a finely divided frozen solution. The finely divided frozen solution was then concentrated by means of freeze-drying to give the higher concentration, liquid crystalline solutions. The optical properties of these materials were determined with an optical microscope equipped with cross polarizers (see Results and Discussion).

Preparation of Polybenzimidazole Polyanion Solutions. A reaction vessel was charged with 1.0 g (8.6 mmol of polymer repeat units) of poly-2,5(6)-benzimidazole (η_{inh} = 0.8 dL/g), 100 g of DMSO, 5 g (44.6 mmol) of potassium *tert*-butoxide, and 1 g (31.3 mmol) of methanol. The reaction was stirred for 24 h at 20 °C to give a dark brown solution of the PBI polyanion solution from which films could be cast. A similar procedure was used to dissolve poly[2,6-(*p*-phenylene)diimidazobenzene].

Preparation of PPTA Films. In a typical procedure, a 2.6 wt % solution of the PPTA polyanion as the potassium salt was used with or without proton donor additives. The solution was cast on a glass plate by means of a "doctor's blade", to give a thickness of 0.025 in. The glass plate was immersed in water to reprotonate the PPTA polyanion and extract DMSO leaving a gelatinous film that was repeatedly extracted with water. The gel film was mounted on metal frames, air-dried to bring about densification of the gel, and finally oven-dried at 130 °C. The resulting film was 6.6×10^{-4} in. thick, with a density of 1.354 g/cm^3 and tensile properties as reported in the Results and Discussion. Poly(*m*-phenylene isopohthalamide) films were prepared similarly.

Determination of the Rate of Viscosity Loss of PPTA Polyanion as the Potassium Salt Induced by Proton Donors. Four samples of high concentration K^+PPTA^- solutions in DMSO were prepared from 6.5 g of PPTA (η_{inh} = 5.7 dL/g), 6.5 g of potassium *tert*-butoxide, and 117 g of DMSO using procedures described above. Proton donors were added to the solutions to give a ratio of 3.5 equiv of hydroxyl groups for every amide bond. Thus, one solution contained 6.5 g of methanol, another 6.5 g of ethylene glycol, a third solution contained 13.0 g of 2-propanol, and a final solution contained 22.1 g of benzyl alcohol. The solutions were mixed at 25 °C for 3 days, using a constant temperature bath. The samples were then heated to the appropriate reaction temperature by means of a constant temperature bath. Samples were withdrawn periodically, which were allowed to equilibrate at 25 °C. Viscosity measurements were then made with a Brookfield viscometer. The rate of viscosity loss in arbitrary units was determined from the slope of the log of viscosity versus time plot (see supplementary material). These rates are then plotted against temperature for the various proton donors as shown in Figure 1.

Viscosity Measurements. Dilute solution viscosity measurements were determined with size 150 Cannon Fenske capillary viscometers or by means of the bubble rise time method using Cargille viscosity tubes. Solutions were equilibrated in baths at 26.6–27.0 °C.

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Supplementary Material Available: Synthesis, characterization, and X-ray crystal structure of the model compounds bis(*p*-*tert*-butylbenzoyl)-*p*-phenylenediamine dianion salt and dibenzoyl-*p*-phenylenediamine dianion salt and viscosity data for 5.5 wt % K^+PPTA^- polyanion solutions in DMSO with various proton donors as a function of temperature (10 pages). Ordering information is given on any current masthead page.

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Registry No. (PPTA)·K (copolymer), 122545-45-3; (PPTA)·K (SRU), 122507-01-1; (PPTA)·Na (copolymer), 105176-75-8; (PPTA)·Na (SRU), 105096-56-8; dibenzoyl-*p*-phenylenediamine, 13755-08-3; dibenzoyl-*p*-phenylenediamine dianion, 124244-56-0; (isophthalic acid)(*m*-phenylenediamine)·K (copolymer), 124244-62-8; (isophthalic acid)(*m*-phenylenediamine)·K (SRU), 124244-59-3; (2,5-benzimidazole) (SRU), 124244-60-6.

The Molecular Structure of Low-Density Polyethylene. 1. Long-Chain Branching and Solution Properties

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ABSTRACT: Light scattering, viscosity, gel permeation chromatography (GPC), and ^{13}C NMR measurements were carried out on fractions of linear high-density polyethylene (HDPE) and branched low-density polyethylene (LDPE). GPC spectra show that the molar mass distribution of branched LDPE can be well fitted by the three-parameter distribution of Hosemann and Schramek. Its nonuniformity coefficient is 10 times larger than one corresponding to the linear polymer of the same molar mass. ^{13}C NMR measurements indicate that the branched LDPE's contain both short (favorably *n*-butyl) and long branches. A comparison of the number-average of long branches per 1000 CH$_2$, estimated by ^{13}C NMR spectroscopy, with the one calculated by light scattering indicates that the branch points are predominantly tetrafunctional if one assumes random branching. However, an adequate interpretation of the experimental data can also be given by the heterogeneous comb model, developed by Solensky and Casassa. Thus, there exists some doubt concerning the true structure of the branched polymers. Additionally, it seems that LDPE's, prepared by different companies, possess slightly different structures of branching. The following paper, dealing with the particle scattering factor, will hopefully give a deeper understanding of this problem.

Introduction

The behavior of branched chain polymers in solution is of major interest with respect to both technological problems and basic theoretical questions. Branching, which may be characterized as long chain or short chain, can arise through chain-transfer reactions during free-radical polymerization at high pressure or by copolymerization with α-olefins. Short-chain branches influence the morphology and solid-state properties of semicrystalline polymers, whereas long-chain branching has a remarkable effect on solution viscosity and melt rheology. Therefore it is important to get as much information as possible concerning the nature and number of these branches.

This paper, presented here, is part of a series of two papers. Here, we report experimental data of three linear high-density and three branched low-density polyethylene samples by means of light scattering, ^{13}C NMR, GPC, and viscosity measurements to provide data on number- and mass-average molar masses, intrinsic viscosities, mean square radii of gyration, and osmotic second virial coefficients. These data are presented along with treatments allowing the estimation of unperturbed dimensions and long-chain branching indices according to several theories, whereby the "long branch content", estimated by GPC and light scattering, is compared with the equivalent content, obtained by ^{13}C NMR spectroscopy. Two types of branched structures are considered in some detail: (1) randomly branched macromolecules with tri- and tetrafunctional branch points; (2) heterogeneous comb molecules. These classes of structures are of special interest because Kuhn and Krömer[1] showed that randomly branched LDPE is only obtained if the polymerization is carried out in an ideally stirred reactor with the same temperature, pressure, and conversion prevailing all over the reactor. These are conditions that are not fulfilled in almost all large-scale LDPE polymerization processes so that practically all available commercial LDPE types are not randomly branched. A gain in realism can be made by introducing the heterogeneous comb model, derived by Solensky and Casassa.[2]

On the other hand, one cannot expect that a LDPE molecule represents a simple comb molecule because it is an enormous, if not insoluble, task to synthesize molecules with such an architecture, monodisperse with respect to structure. Thus, the real structure of a branched molecule should lie somewhere between that of a comb and that of a random branched tree, where the content of the predominant kind of branching depends on the condition of preparation. Consequently, different companies should produce LDPE's of slightly different structures of branching. To prove these statements, we researched the physicochemical properties of three different LDPE's purchased from two different companies.

It is well-known, however, that much more information on the structure of a polymer can be extracted from the curve of the particle scattering factor than a mere determination of the relationships between the parameters, mentioned above, can yield. The following paper will provide the relevant information.

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