N-Alkylation and Hofmann Elimination from Thermal Decomposition of R_4N^+ Salts of Aromatic Polyamide Polyanions: Synthesis and Stereochemistry of N-Alkylated Aromatic Polyamides

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ABSTRACT: The reaction of aromatic polyamides such as poly(*p*-phenyleneterephthalamide) (PPTA) with $(n\text{-Bu})_4N^+{}^-OH$ or $Et_4N^+{}^-OH$ gives dimethyl sulfoxide (DMSO) soluble polyanions as the $(n\text{-Bu})_4N^+$ or Et_4N^+ salts derived from deprotonation of the amide hydrogen. The $n(R_4N^+)PPTA^{n-}$ salts thermally decompose by Hofmann elimination to yield neutral PPTA, olefin, and NR_3. Dissolving PPTA by deprotonation and thermally decomposing the R_4N^+ salt can be used to process the polymer. Films cast from DMSO solutions of $nR_4N^+PPTA^{n-}$ convert from polyanion to a PPTA film when heated to about 200 °C, removing solvent and volatile byproducts, and leaving a crisp PPTA film. Model studies show that N-alkylation competes with the Hofmann elimination of $nR_4N^+PPTA^{n-}$. Whereas $n(n\text{-Bu})_4N^+PPTA^{n-}$ undergoes extensive N-butylation, $nEt_4N^+PPTA^{n-}$ shows only trace amounts (<1%) of ethylated product. N-Alkylation changes the stereochemistry of the amide bond from trans to cis, causing the N-alkylated PPTA derivatives to behave as a random coil rather than a rigid rod in solution. N-Alkylation comprises the mechanical properties of PPTA films.

Introduction

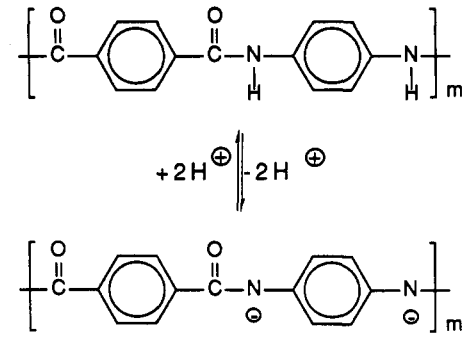
Distinctive properties of rigid-rod aromatic polyamides include high-temperature stability, high strength and stiffness, and low thermal expansion, making them attractive in many applications.[1] However, the high glass transition temperatures, high melting points, and poor solubility of these polymers make processing difficult.[1] We recently described a processing strategy for aromatic polyamides[2] taking advantage of the acidity of the amide hydrogens of these polymers to form polyanions that are soluble in dimethyl sulfoxide (DMSO, Scheme I).[3] The aromatic polyanion salt solutions can be cast as films or spun into fibers.[2] Quenching with water reprotonates the amide bonds and extracts the alkali-metal cations and DMSO. The aqueous quench could limit use of this chemistry in some applications. Furthermore, alkali-metal salts left as impurities from inadequate quenching are particularly undesirable in electronic applications. In this context, aromatic polyanion salt solutions that do not require metal salts or an aqueous quench should be especially useful.

The Hofmann degradation of quaternary ammonium salts ($R_4N^+{}^-X$) giving olefin, trialkylamine, and a protonated counterion, HX (eq 1), is a well-established reaction

$$(C_2H_5)_4N^+{}^-X \xrightarrow{\text{heat}} C_2H_4 + (C_2H_5)_3N + HX \qquad (1)$$

pathway.[4] We therefore anticipated that PPTA polyanions with quaternary ammonium cations would thermally regenerate PPTA (PPTA = poly(*p*-phenyleneterephthalamide)). To this end, we now report the preparation of tetraethylammonium and tetrabutylammonium PPTA polyanions, $n(n\text{-Bu})_4N^+PPTA^{n-}$ and $nEt_4N^+PPTA^{n-}$, respectively, where *n* is the charge on the polymer chain. As expected, the quaternary ammonium ion (R_4N^+) is thermally "fugitive".[5] When heated to ~200 °C, polyanion films cast from $nEt_4N^+PPTA^{n-}$ solutions convert to dense PPTA films as the Hofmann elimination takes place and as the solvent evaporates. We also find the N-alkylation competes with the Hofmann elimination in thermal decomposition of $nR_4N^+PPTA^{n-}$. Whereas $n(n\text{-Bu})_4N^+PPTA^{n-}$ undergoes extensive N-butylation, $nEt_4N^+PPTA^{n-}$ shows only trace amounts (<1%) of ethylated product.

Scheme I



Results and Discussion

Poly(*p*-phenyleneterephthalamide) (PPTA) and poly(*m*-phenyleneisophthalamide) (MPIA) are both dissolved by DMSO solutions of $(n\text{-Bu})_4N^+{}^-OH$ or $Et_4N^+{}^-OH$ to give $(n\text{-Bu})_4N^+$ and Et_4N^+ salts of the corresponding aromatic polyamide polyanions. The formation of DMSO-soluble aromatic polyamide polyanions by deprotonation with tetraalkylammonium hydroxide is identical with the reaction of aromatic polyamides with alkali-metal salts of strong bases giving soluble polyanions as previously reported (Scheme I).[2,3] The pK_a of water in DMSO is 32,[6] and therefore hydroxide deprotonates aromatic polyamides, which typically have pK_a's in DMSO ≤29.[2] The R_4N^+ salts of the PPTA polyanion form deep red solutions in DMSO, while the corresponding MPIA salts are yellow in DMSO solution. Both the $(n\text{-Bu})_4N^+$ and Et_4N^+ salts of the PPTA polyanion form free-flowing, isotropic solutions in DMSO at low concentration (<4 wt%) but are optically birefringent at higher concentrations (~14 wt%). Similar behavior is observed for PPTA polyanions as alkali-metal salts (nA^+PPTA^{n-}, where $A^+ = Li^+$, Na^+, or K^+).[2] We

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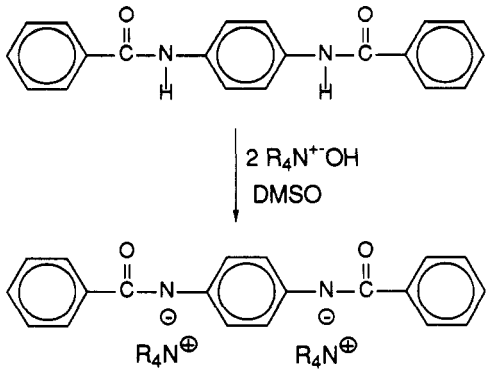
Scheme II



have not been able to quantify the extent of deprotonation of the R_4N^+ salts of the aromatic polyamide polyanions. However, infrared spectra of DMSO solutions of these salts show a stretch at 3320 cm^{-1}, presumably for the N–H bond. We have previously shown that greater than approximately 60% of the N–H protons must be deprotonated to make PPTA soluble in DMSO.[2] Therefore, at least 60% of the N–H bonds are deprotonated by the R_4N^+–OH reagents.

The chemistry of the R_4N^+ salts of the aromatic polyamide polyanions was studied by using dibenzoyl-*p*-phenylenediamine as a model for PPTA. Deprotonation of the amide hydrogens of the model compound with 2 equiv of $(n\text{-}Bu)_4N^+$–OH or Et_4N^+–OH in DMSO gives the tetraalkylammonium salts $2[R_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ (Scheme II), which are isolated as yellow microcrystalline solids. NMR and IR spectroscopies show no evidence for N–H protons, suggesting that both amide protons are removed by the reaction of $(n\text{-}Bu)_4N^+$–OH with the model compound. Elemental analysis (see Experimental Section) is consistent with the formulation $2[Bu_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$. However, spectroscopic analysis of the Et_4N^+ salt shows water is present in the isolated salt: N–H bonds detected by IR spectroscopy (3320 cm^{-1}) show that the compound is not completely deprotonated under these conditions, and the ^1H NMR (DMSO-d_6) shows a resonance for free water molecules in solution at +3.60 ppm. The integration shows that the ratio of free water in solution to Et_4N^+ cations is approximately 1:1. Integration of the ^1H NMR resonances for the ethyl hydrogens compared to the aromatic hydrogens shows that the degree of deprotonation is approximately 93%.

Thermal gravimetric analysis (TGA) of $2[Et_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ shows a 17% weight loss at approximately 104 °C, presumably due to loss of water. An additional 34% weight loss occurs at approximately 155 °C consistent with loss of triethylamine and ethylene. The remaining 49% weight loss occurs at 352 °C when $C_6H_5C(O)NHC_6H_4NHC(O)C_6H_5$ vaporizes. Solid-state pyrolysis of $2[Et_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ at 200 °C gives a white powder with an infrared spectrum and mass spectrum consistent with quantitative formation of $C_6H_5C(O)NHC_6H_4NHC(O)C_6H_5$. However, mass spectrometry (MS) also showed weak parent ions for the two N-ethylated species $C_6H_5C(O)N(Et)C_6H_4N(Et)C(O)C_6H_5$ and $C_6H_5C(O)NHC_6H_4N(Et)C(O)C_6H_5$. The intensity of these two parent ions was less than 1% of the intensity of $C_6H_5C(O)NHC_6H_4NHC(O)C_6H_5$. Triethylamine and ethylene were identified as the volatile byproducts by mass spectrometry (MS).

TGA of the $(n\text{-}Bu)_4N^+$ analogue shows a 55% mass loss at 179 °C for loss of butene and tributylamine, as confirmed by the MS of the volatiles. The product of solid-state pyrolysis of $2[(n\text{-}Bu)_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ is extensively butylated as shown by MS and NMR and IR spectroscopies: Although the ^1H NMR spectrum in DMSO-d_6 of the pyrolysis product showed $C_6H_5C(O)N(Bu)C_6H_4N(Bu)C(O)C_6H_5$ was the major product of the pyrolysis, IR and MS analyses of the solid product showed that $C_6H_5C(O)NHC_6H_4NHC(O)C_6H_5$ and $C_6H_5C(O)NHC_6H_4N(Bu)C(O)C_6H_5$ are also formed. Thermal decomposition at 220 °C of $2(Me_4N^+)[C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$, lacking β hydrogens, gave exclusively *N,N*-dimethyldibenzoyl-*p*-phenylenediamine in addition to 2 equiv of trimethylamine.

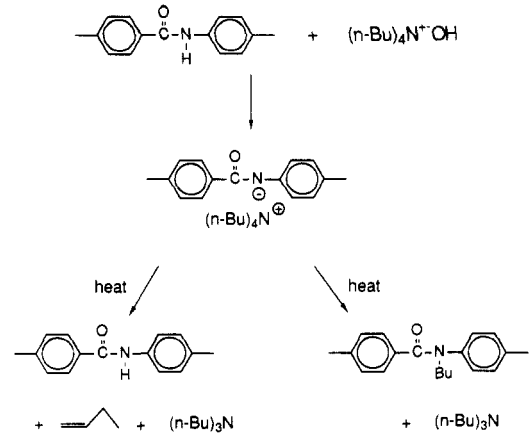


Figure 1. Summary of the synthesis and thermal degradation of tetraalkylammonium salts of aromatic amide anions. The major pathway for decomposition of the $(n\text{-}Bu)_4N^+$ salt is elimination of protons, tributylamine, and butene. A competitive pathway is N-butylation of the aromatic amide. The Et_4N^+ salt shows no tendency to alkylate.

We have also monitored the thermal degradation of $2[(n\text{-}Bu)_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ in DMSO-d_6 solution (concentration = 0.26 M) by ^1H NMR spectrometry in a torch-sealed NMR tube at 180 °C. Under these conditions, $2[(n\text{-}Bu)_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ is 95% decomposed after 10 h. Integration of the spectrum shows that 10% of the deprotonated amide bonds are butylated in the decomposition process. Bu_3N and 1-butene are formed in the ratio 1.2:1, while the ratio of dibenzoyl-*p*-phenylenediamine to Bu_3N was 1:2.1. No intermediates and no other butene isomers were detected by NMR or GC-MS analyses in this reaction. Therefore, the distribution of products depends on the concentration during the decomposition: alkylation is extensive in a solid-state pyrolysis, while Hofmann elimination dominates in dilute solution.

The thermal degradation of $n(R_4N^+)PPTA^{n-}$ parallels the thermal degradation of the salts of the model compounds. The Et_4N^+ and $(n\text{-}Bu)_4N^+$ polyanion salts, cast as films on a glass support, thermally decompose at 200 °C to yield dense PPTA films, as confirmed by IR. Visually this decomposition is seen as a color change from deep red to orange and finally pale yellow for neutral PPTA as olefin, trialkylamine, and DMSO vaporize. The films from the Et_4N^+ salt qualitatively are strong and stiff, with IR spectra showing no evidence of N-alkylation. In contrast, the films derived from Hofmann elimination of the $(n\text{-}Bu)_4N^+$ salt are weak and brittle. Their IR spectra show extensive N-alkylation, which contributes to the weakness of the films, as discussed below. This reaction sequence is summarized in Figure 1.

Conceivably the mechanism of $n(R_4N^+)PPTA^{n-}$ decomposition is exclusively through N-alkylation followed by thermal decomposition of the resulting N-alkylated derivative. However, TGA analysis of authentic poly(*N,N*-dibutylphenyleneterephthalamide) shows that this poly-

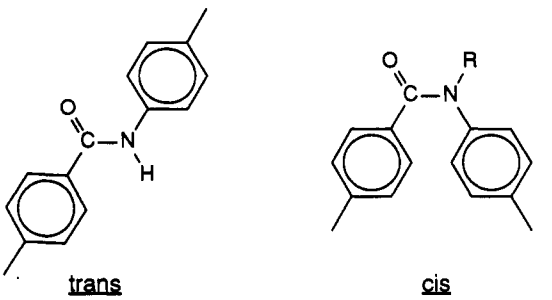
mer is stable at the temperature for $n(R_4N^+)PPTA^{n-}$ decomposition and that butene loss commences at 430 °C. These observations are consistent with the two distinct pathways for $n(R_4N^+)PPTA^{n-}$ decomposition shown in Figure 1.

Thermal decomposition is accompanied by some chain scission of PPTA. PPTA isolated from pyrolysis at 220 °C for 30 min of $n(Et_4N^+)PPTA^{n-}$ had η_{inh} = 0.63 dL/g compared to 5.47 dL/g for the starting polymer. We previously reported[2] that proton donors enhance the rate of chain scission reactions of aromatic polyamide polyanions. On this basis, it is possible that the water generated as a byproduct of the deprotonation of PPTA by $R_4N^+{}^-OH$, as well as residual methanol from the $R_4N^+{}^-OH$ causes much of the observed chain scission. Consistent with this proposal, nK^+PPTA^{n-}, prepared under strictly aprotic conditions, when pyrolyzed under identical conditions and then quenched with water, gave PPTA with much less chain scission (η_{inh} = 2.60 dL/g). Some chain scission, however, is not a problem for certain applications of this chemistry, such as bonding PPTA fibers together using PPTA polyanion solutions to give sheet structures of these fibers with enhanced mechanical properties.[7]

The fact that $n(n\text{-}Bu)_4N^+PPTA^{n-}$ thermally decomposes to give PPTA that is partially N-butylated as a film with poorer mechanical properties than films derived from the Et_4N^+ salt prompted a study of *N*-butylated PPTA films. We have prepared a series of partially alkylated PPTA polymers by partial alkylation of the nK^+PPTA^{n-} salt.[8,9] This method should leave the degree of polymerization relatively unaffected.[8,9] We find that alkylation of PPTA also degrades the tensile properties of films prepared from those polymers. When 2% of the amide bonds in PPTA were alkylated and the polymer cast as a film, the film had the following properties: tensile modulus, 530 kpsi; tensile strength, 11 kpsi; elongation at break 3%. For comparison, the tensile properties of PPTA films are as follows: tensile modulus, 800 kpsi; tensile strength, 24 kpsi; elongation at break, 5%.[2] When more than 8% of the amide nitrogens are alkylated, the films are already too weak for mechanical testing. The tensile properties of N-octadecylated PPTA (degree of N-alkylation ~92%)[9] have also been reported and are likewise highly diminshed relative to unsubstituted PPTA.[9]

We believe the poor mechanical properties of N-alkylated PPTA films are due to two structural features of the alkylated derivative. First, N-alkylation hinders interchain interactions and interferes with hydrogen bonding that is crucial to crystallization of PPTA.[10] Furthermore, *N*-alkyl groups cannot pack into the unit cell for crystalline PPTA,[10] which disrupts PPTA crystallization.[11] Second, N-alkylation changes the stereochemistry of the amide bond.[12] The aromatic rings in aromatic polyamides normally have a trans stereochemical relationship about the amide bond, with the carbonyl group, the nitrogen, the amide hydrogen, and the two aromatic carbon atoms coplanar. However, a recent single-crystal X-ray diffraction study by Kim and Calabrese[12] of the PPTA model compound *N,N*-diallyldibenzoyl-*p*-phenylenediamine shows a cis stereochemistry of the aromatic rings about the amide bond (Scheme III). Also, the substituents on the amide bond are no longer coplanar in this model compound.[12] N-Butylation should have similar effects on amide bonds, and, therefore, alkylation changes the PPTA structure from a rigid rod or semirigid rod to that of a coiled structure. Similar cis–trans structural isomerism has been observed for aliphatic polyamides[13] and was proposed for poly(*N*-methyl-*p*-benzamide).[14] Chain scission further contributes to the diminished tensile properties of the $n(n\text{-}Bu)_4N^+PPTA^{n-}$-derived films.

Scheme III



trans cis

Table I
Effect of N-Alkylation on Solution Properties of PPTA

% alkylation[a]	η_{inh},[b] dL/g	% alkylation[a]	η_{inh},[b] dL/g
0	5.31	5	2.73
1	4.63	20	1.24
2	4.06	83	0.73[c]

[a] The alkyl group was *n*-butyl. [b] Inherent viscosity (η_{inh}) determined on 0.5 wt % solutions in concentrated H_2SO_4 at 30 °C. [c] This sample was soluble in DMSO-d_6, allowing NMR determination of the percent alkylation. All other samples were insoluble. See Experimental Section.

Table II
Effect of N-Alkylation on Solution Properties of PPTA Polyanion

% alkylation[a]	solution viscosity,[b] s	% alkylation[a]	solution viscosity,[b] s
0	32.9	5	3.2
1	26.6	20	0.8
2	17.4	100	<0.1

[a] The alkyl group was *n*-butyl. [b] Determined for K^+ salt, $[K^+]$ = 0.11 M, PPTA polyanion concentration = 1.3 wt %, using the bubble rise time method (ASTM D 1545-76) at 21 °C. The viscosity represents the average of three or four determinations.

Viscosity studies of partially alkylated PPTA suggest that the cis stereochemistry of the N-alkylated PPTA persists in solution. Viscosity studies of N-alkylated PPTA in sulfuric acid solution and of N-alkylated PPTA polyanion in DMSO solution are summarized in Tables I and II. The data in Table I show that the inherent viscosity of the alkylated PPTA solutions in sulfuric acid decreases drastically as the fraction of amide bonds that are alkylated increases. Because the series of alkylated polymers all have nearly the same degree of polymerization,[8,9] the change in the inherent viscosity reflects a change in polymer stiffness. The alkylation changes the stereochemistry of the amide bond from all-trans for PPTA to trans with cis at the alkylated amide bonds in the partially alkylated polyamides and ultimately to all-cis for the fully alkylated PPTA. The extremely low viscosity of the fully alkylated PPTA polymer solutions suggests a random coil structure in solution. Similar effects on solution viscosity are found for the partially alkylated PPTA polyanion solutions (Table II).

We note that N-alkylated PPTA and graft copolymers of PPTA prepared by grafting at the deprotonated amide bond have been used for the preparation of molecular composites[15] and for surface modification of PPTA films.[16] Because of the cis stereochemistry at the substituted amide bond, it is doubtful that the PPTA functions as a rigid or semirigid rod in these systems. Rigid-rod poly(benzimidazoles) can similarly be N-alkylated by reaction with strong base in DMSO[2,17] followed by reaction with RX.[17] By contrast, the stereochemistry of poly(benzimidazole) is fixed and therefore unaffected by N-alkylation, although the solid-state structure could be disrupted. Conceivably polyelectrolytes such as poly(*p*-phenyleneterephthal-

amidopropanesulfonate) may be rigid in solution due to polyelectrolyte effects.[18]

Experimental Section

General Procedures. Except where otherwise noted, all experiments were performed in an inert atmosphere by using either a nitrogen-filled drybox or a standard Schlenk line with argon source or by blanketing reactions under dry nitrogen. THF and diethyl ether were distilled from sodium benzophenone ketyl. DMSO (Aldrich Gold Label) contained 85 ppm or less water (determined by Karl-Fischer titration). Tetrabutylammonium hydroxide, 1.0 M solution in methanol, tetramethylammonium hydroxide, 25 wt% solution in methanol, and tetraethylammonium hydroxide, 40 wt% solution in water, were purchased from Aldrich. Tetraethylammonium hydroxide, 25 wt% solution in methanol, was purchased from Sigma. Anhydrous methanol was used as received (Aldrich). PPTA, commercially available as Kevlar Aramid[19] pulp or as Kevlar-29 Aramid[19] fibers, was obtained from the Du Pont Co. ($\eta_{inh} \geq 5.3$ dL/g). Inherent viscosities were determined by using 0.50 wt% PPTA solutions in concentrated sulfuric acid at 30 °C. The poly(*m*-phenyleneisophthalamide) used was commercially available Nomex Aramid[19] staple fiber (Du Pont Co.). Polymer samples were dried in an oven at 130 °C for a minimum of 12 h before use. Tensile properties of film samples were measured on an Instron testing device. ^{1}H NMR spectra were recorded at 300 MHz on a GE QE-300 system with chemical shifts relative to $Si(CH_3)_4$. MS was carried out by electron impact using a ZAB-2F double-focusing VG instrument. Pyroprobe measurements were done at 220 °C with a Varian GC 3700 using a DB1 column and a VG MM16 mass spectrometer.

Preparation of 2[(*n*-Bu)$_4$N$^+$][C$_6$H$_5$C(O)NC$_6$H$_4$NC(O)C$_6$H$_5$]$^{2-}$. A nitrogen-flushed reaction flask equipped with a stir bar was charged with approximately 10 mL of anhydrous DMSO and 6.40 mL of a 1.0 M solution of $(n\text{-Bu})_4N^+OH^-$ solution in methanol (6.40 mmol). The methanol and a small amount of DMSO were removed by means of vacuum distillation. $C_6H_5C(O)NHC_6H_4NHC(O)C_6H_5$ (1.0 g, 3.16 mmol), was then added to the reaction vessel against a heavy stream of inert gas. The resulting mixture was stirred for 3 h at room temperature. The $2[(n\text{-Bu})_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ salt was precipitated in pure form by addition of approximately 100 mL of dry diethyl ether. The salt was isolated by filtration and dried in a vacuum for 15 h at room temperature. ^{1}H NMR (DMSO-d_6, 25 °C) δ +8.05 (dd, 4 H, J = 7.5, 2.0 Hz), +7.15 (s, 4 H), +7.07 (m, 6 H), +3.04 (m, 16 H), +1.48 (m, 16 H), +1.12 (m, 16 H), +0.86 (t, 24 H, J = 15.9 Hz). Elemental anal. (Pascher) found: 77.39, C; 10.80, H, 6.97, N. Calc for $C_{52}H_{86}N_4O_2$: 78.20, C; 10.78, H; 7.02, N. TGA showed loss of 55% of the mass at 179 °C, for loss of butene and tributylamine, which was confirmed by mass spectra of the volatiles evolved. Solid-state pyrolysis of $2[(n\text{-Bu})_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ at 220 °C gave an off-white solid. ^{1}H NMR of the soluble components of the pyrolysis product was the same as the product of the reaction of $2K^+C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ with BuI (2 equiv), in addition to small amounts (<10%) of unconverted $2[(n\text{-Bu})_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$. Nearly all the sample was soluble, suggesting most of the pyrolysis product was alkylated, since nonalkylated arylamides are insoluble in DMSO. The IR spectrum of a KBr pellet of the pyrolysis product was a superposition of spectra of $C_6H_5C(O)NHC_6H_4NHC(O)C_6H_5$, $C_6H_5C(O)N(Bu)C_6H_4N(Bu)C(O)C_6H_5$, and uncoverted $2[(n\text{-Bu})_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$, the butylated product being dominant. MS showed three parent ions at 316 amu for $C_{20}H_{16}N_2O_2$, 372 amu for $C_{24}H_{24}N_2O_2$, and 428 amu for $C_{28}H_{32}N_2O_2$.

Preparation of 2[Et$_4$N$^+$][C$_6$H$_5$C(O)NC(O)C$_6$H$_5$]$^{2-}$. A 125-mL erlenmeyer flask was charged with 1.00 g of $C_6H_5C(O)NHC_6H_4NHC(O)C_6H_5$ and 10 mL of DMSO. Separately, 1.00 g of $Et_4N^+OH^-$ (isolated by evaporation of methanol from the as-received 25 wt% $Et_4N^+OH^-$ solution in methanol) was dissolved in 10 mL of DMSO. The solution frothed considerably as the salts dissolved. The $Et_4N^+OH^-$ solution was combined with the slurry of $C_6H_5C(O)NHC_6H_4NHC(O)C_6H_5$ yielding, after 1 h of stirring, a yellow homogeneous solution. Addition of 100 mL of dry diethyl ether created an oil. The supernatant was decanted from the oil. The oil was treated with approximately 4 mL of dry THF to give yellow crystals, which were isolated by filtration and dried in a vacuum for 15 h at room temperature. ^{1}H NMR (DMSO-d_6, 25 °C) δ +8.05 (dd, 2 H, J = 7.5, 2.0 Hz), +7.25 (s, 2 H), +7.18 (m, 3 H), +3.60 (br s, width at half-height ≈20 Hz, H_2O, aproximately 13% of the intensity of the NCH_2 resonances), +3.07 (quart., J = 7.40 Hz, 15.2 H, NCH_2), +1.08 (tt, $J_{H\text{-}H}$ = 7.40 Hz, $J_{N\text{-}H}$ = 2.07 Hz, 21.8 H, NCH_2CH_3). The IR (KBr pellet) spectrum showed bands for N–H and/or O–H stretches at 3502 (s), 3415 (s), 3320 (s), 3295 (s), 3200 (m), 3155 (m) cm^{-1} and an amide CO stretch at 1648 (vs) cm^{-1}. Solid-state pyrolysis of this compound at 200 °C gave a strong parent ion at 316 amu for $C_{20}H_{16}N_2O_2$ in addition to very weak parent ions at 372 amu and 428 amu for the two ethylated species, which were less than 1% of the intensity of the parent ion at 316 amu. Mass spectrometry of the volatile pyrolysis products showed that triethylamine formed.

Preparation of 2[Me$_4$N$^+$][C$_6$H$_5$C(O)NC$_6$H$_4$NC(O)C$_6$H$_5$]$^{2-}$. $Me_4N^+OH^-$ (2.40 g, 6.59 mmol) as a 25 wt% solution in methanol was dissolved in 10 mL of DMSO. The methanol was vacuum distilled from this solution. Dibenzoyl-*p*-phenylenediamine (1.00 g, 3.16 mmol) was added as a solid. The resulting slurry was stirred for 18 h at room temperature to give a clear yellow solution. Addition of 100 mL of Et_2O precipitated 0.84 g of $2[Me_4N^+][C_6H_5C(O)NC_6H_4NC(O)C_6H_5]^{2-}$ as a yellow microcrystalline solid (1.45 g theoretical). ^{1}H NMR (DMSO-d_6, +25 °C) δ +8.05 (dd, 2 H, J = 7.5, 2.0 Hz), +7.20 (s, 2 H), +7.14 (m, 3 H), +3.03 (s, 12 H). TGA showed loss of 26% of the mass of the sample at 195 °C, consistent with loss of 2 equiv of trimethylamine. MS showed a parent ion at 344 amu for $C_{22}H_{20}N_2O_2$, with no other parent ions observed. The IR spectrum (KBr pellet) showed 3060 (w), 3040 (w), 2940 (w), 1630 (vs), 1600 (w), 1575 (w), 1515 (m), 1449 (w), 1427 (w), 1365 (m), 1302 (w), 1108 (m), 1022 (w) cm^{-1}. ^{1}H NMR (DMSO-d_6, +25 °C) δ +7.28 (m, 2 H), +7.15 (m, 3 H), +7.00 (s, 2 H), +3.27 (s, 3.5 H, NCH_3).

Preparation of *n*Et$_4$N$^+$PPTA^{n-}. A round-bottom flask was charged with 12.5 g of a 25 wt% solution of $Et_4N^+OH^-$ in methanol (21.5 mmol). Methanol was removed from this solution by vacuum distillation until the solution volume was approximately 9 mL. This base solution was then transferred to a three-neck flask containing 55 mL of DMSO and 2.5 g of PPTA pulp (10.5 mmol of repeat units). The PPTA dissolved in this medium to give a solution that was 3.6 wt% polymer. A film of this polyanion solution was cast on a glass plate with a 25-mil doctors knife under a dry nitrogen atmosphere. The film was heated to 220 °C (also under nitrogen) to give a dense PPTA film.

Preparation of *n*(*n*-Bu)$_4$N$^+$PPTA^{n-}. $(n\text{-Bu})_4N^+OH^-$ (25.2 mL, 1 M) in methanol (25.2 mmol) was dissolved in 65 mL of DMSO. The methanol was removed from the solution by vacuum distillation. The remaining 55–60 mL of clear colorless solution was transferred by cannulation to a three-neck flask containing 3.0 g of PPTA pulp (12.6 mmol of repeat units). After 16 h of stirring at room temperature, the PPTA pulp had dissolved to form a clear, deep red solution with no evidence of undissolved PPTA as determined by examination of samples by optical microscopy. A film of this polyanion solution was cast on a glass plate with a 25-mil doctors knife and placed in a nitrogen-purged oven at 205 °C. The DMSO evaporated, leaving a reddish orange film. After ~30 min at 205 °C, the reddish orange color changed to the tan color characteristic of PPTA films. The final film, after 24 h at 205 °C in vacuum, was pale tan and very brittle similar to N-butylated PPTA films. The IR spectrum of this film showed stretches at 3028 (w), 2962 (s), 2939 (m), 2878 (w) cm^{-1}, indicating the presence of alkyl groups. MS showed that butene, tributylamine, and DMSO are produced during pyrolysis at 175 and 220 °C.

Birefringent Solutions of *n*(*n*-Bu)$_4$N$^+$PPTA^{n-}. A nitrogen-flushed three-neck flask equipped with mechanical stirrer was charged with 120 mL of anhydrous DMSO and 50.4 mL of tetrabutylammonium hydroxide as a 1 M solution in methanol (50.4 mmol). The methanol was removed by vacuum distillation and PPTA pulp (6.0 g, 25.2 mmol of repeat units) was added, which dissolved in 16 h to give an optically anisotropic, ~4 wt% solution.

Isolation of $n(n\text{-Bu})_4N^+PPTA^{n-}$. The birefringent solution (21 g, 4 wt%, prepared as described above) was added slowly to approximately 500 mL of THF with rapid stirring. A red solid precipitated that weighed 2.57 g after drying. The solid was predominately $n(n\text{-Bu})_4N^+PPTA^{n-}$, the remainder being solvent. The solid (1.0 g) was redissolved in 2.9 g of DMSO to give a highly viscous, somewhat pasty, mixture that flowed as a solution. The pasty solution was optically birefringent as determined by optical microscopy with cross polarizers.

Alkylation of PPTA. This procedure is a modification of the literature procedure.[3] A solution of 210 g of a 1.3 wt% K^+PPTA^- solution[2] was treated with a solution of 0.060 g (0.47 mmol) of *n*-propyl bromide in 10 mL of DMSO added dropwise with stirring over 1 h. The solution was stirred for an additional 24 h and then quenched by pouring it into a large excess (2 L or more) of water in a blender. The polymer was isolated by filtration, washed liberally with water followed by acetone, and finally dried in a vacuum oven for 36 h at 110 °C. This procedure yields polymer with 2% of the amide bonds alkylated. Similar procedures were used for other levels of alkylation and also for preparation of *N*-butyl derivatives of PPTA. The extent of alkylation was determined by the stoichiometry of the reaction between the deprotonated amide bonds and the alkylating agent. When the stoichiometry was one butyl iodide for every amide bond, the resulting polymer was soluble in DMSO-d_6 and hexafluoroisopropyl alcohol. ^1H NMR (DMSO-d_6, +25 °C) spectroscopy showed weak, broad resonances at δ +10.38 and 10.20 for N*H* in intensity ratio 1:3 and accounting for approximately 1.7% of the total spectral integration, aromatic resonances at +8.00, +7.70, +7.60, +7.35, +7.25, +7.00, +6.92 ppm, and aliphatic resonances at +3.82, +1.30, +1.17, +0.85 ppm. The integration of aliphatic to aromatic resonances was 1.875, for approximately 83% N-butylation. GPC (hexafluoroisopropyl alcohol) M_n = 19 200, M_w = 77 100, relative to poly(ethyleneterephthalate) standards. η_{inh} (H_2SO_4, 0.5 wt%, +30 °C) = 0.73 dL/g. Polyanion solutions could then be prepared from this partially alkylated PPTA.

Preparation of $n\text{Et}_4N^+MPIA^{n-}$. A 250-mL three-neck flask was charged with 3.33 g (22.7 mmol) of $Et_4N^+{}^-OH$, 2.00 g (8.45 mmol) of repeat units poly(*m*-phenyleneisophthalamide), and 80 mL of DMSO. The reaction was stirred with a mechanical stirrer for approximately 7 days at room temperature. Examination of an aliquot of the solution under a microscope revealed a small amount of undissolved particles. Therefore, a 10-mL aliquot of the solution was filtered through a plug of glass wool to give a clear, homogeneous, yellow solution with no evidence of undissolved particles. Approximately 0.5 mL of this filtered solution was spread on a glass microscope slide and heated to 210 °C for 5 min. IR spectra of the resulting hazy colorless film revealed that it was poly(*m*-phenyleneisophthalamide), identical with starting material, with no evidence of alkylation, residual tetraalkylammonium cation, or trialkylamine.

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