Poly((*p*-phenyleneterephthalamido)propanesulfonate): A New Polyelectrolyte for Application to Conducting Molecular Composites

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ABSTRACT: A new water-soluble polyelectrolyte has been synthesized by the alkylsulfonation of the aramid poly(*p*-phenyleneterephthalamide) (PPTA) to form poly((*p*-phenyleneterephthalamido)propanesulfonate) (PPTA-PS). This polyelectrolyte is soluble in water to greater than 18% by weight when the aramid is alkylsulfonated to 66%. Characterization and structural analysis of the polyelectrolyte were facilitated by a ^{13}C NMR study of the model compound benzanilide and its alkyl and alkyanesulfonate derivatives, as well as of an alkyl derivative of PPTA. The preparation of a molecular level composite of polypyrrole and PPTA-PS has been pursued by electrochemical polymerization of pyrrole using PPTA-PS as both the electrolyte and the polymeric dopant ion. The composite materials exhibit conductivites of 1 Ω^{-1} cm^{-1} and improved thermal stabilities when compared to poly(pyrrolyl tosylate).

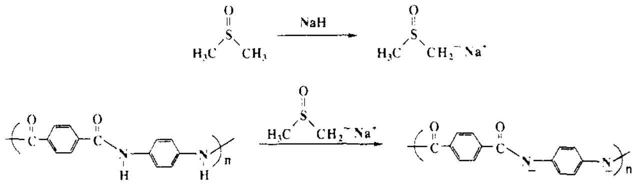
Introduction

The ability to electrochemically prepare electrically conductive composites of polyheterocycles with various carrier polymers has led to materials with enhanced mechanical and electrochemical properties. Ideally, the composites retain the desirable properties of each component polymer, exhibiting the electronic conducting ability of the polyheterocycle and the good thermal and mechanical properties of the carrier polymer. Since conducting polyheterocycles have generally poor flexibility and thermal stability, carrier polymers with exceptional qualities are needed.

The first materials of this class were prepared by in situ electropolymerizations in thermoplastic matrices[1-9] or ionomeric membranes such as Nafion, which results in an ionically conductive medium.[10-13] A very useful method for the preparation of these conductive molecular composites is heterocycle electropolymerization in the presence of solubilized polyelectrolyte.[14-21] This method allows not only variation of the structure of the respective polymer components but control of the material properties of a particular composite by variation of certain aspects of the electropolymerization technique itself. For example, Wegner et al.[17] have used the polarity of the medium to control the solution properties of the polyelectrolyte, which then directly affects the conductivity of the formed composite. A recent study by Takayanagi et al.[22] involved electropolymerization of pyrrole, with tosylate as dopant, into a matrix formed by electrodeposition of the anion of poly(*p*-phenyleneterephthalamide) onto the electrode surface.

In this paper, we report on a facile derivatization of the aramid poly(*p*-phenyleneterephthalamide) (PPTA) to form a highly water-soluble polyelectrolyte. This represents the first report of a water-soluble polyelectrolyte derivative of PPTA. Previous derivatizations resulted in grafting of polymeric side chains onto the aramid backbone.[23,24] Other rigid chain, water-soluble aramids have been prepared by polymerization of sulfonated aromatic diamines with terephthaloyl chloride.[25-27] The characterization of our polyelectrolyte was aided by the synthesis and NMR analysis of another derivatized PPTA, poly(*N*-ethyl-*p*-phenyleneterephthalamide), as well as the derivatization of benzanilide and structural assignments of two model compounds, *N*-ethylbenzanilide and benzanilidopropanesulfonate.

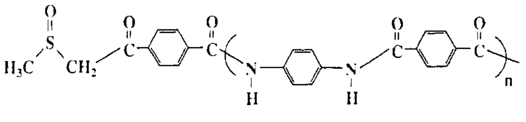
Scheme I



We have used the polyelectrolyte as both electrolyte and polymeric dopant ion in the electrochemical synthesis of conducting molecular composites with pyrrole. In addition to high conductivity, these composites exhibit enhanced thermal stability when compared with typical polypyrroles.

Results and Discussion

Polyelectrolyte Synthesis. 1. Poly(*p*-phenyleneterephthalamide) (PPTA) Anion. The PPTA anion is formed as previously reported[28] by the reaction shown in Scheme I. Kevlar pulp is treated with "dimsyl" anion that is generated when NaH abstracts a proton from DMSO. With care, the possible side reactions of this process can be avoided as detailed below. Use of 1 equiv of NaH per nitrogen atom on the polymer chain prevents formation of excess dimsyl anion, which might attack the polymer carbonyl sites and result in chain cleavage and formation of a chain terminus with structure **1**. In addition, cooling the dimsyl solution to slightly above room temperature before the PPTA is added prevents reaction at the carbonyl oxygen of the resonance-delocalized anion when treated with alkylating agent. In the presence of strong base, N-alkylation is greatly preferred to O-alkylation for primary and secondary amides (except when the counterion is silver),[29] but at higher reaction temperatures the extent of O-alkylation increases. Limited alkylation reaction times were found to help control the extent of O-alkylation (**2**). Provided the anion solution is isolated from air, moisture, and light, it is stable for an indefinite period of time. An experiment was performed in which PPTA anion solution was left in the dark for 8 weeks and subsequently reacted with iodo-



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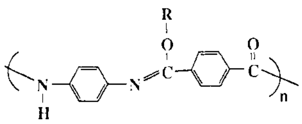

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ethane. The product showed no increase in the amount of O-alkylation product (see NMR discussion below).

When treated with an alkylating agent, the PPTA anion solution shows an almost immediate decrease in viscosity and lightening of color from the anion's characteristic deep red. Once the solution is precipitated in THF, several days of stirring are required in order to allow for collection of the product. The precipitate turns into a gel when the solvent mixture is removed unless sufficient stirring time after precipitation is given. This is presumably due to the time required for the THF to displace the strongly solvating DMSO molecules that are interacting with the polymer chains.

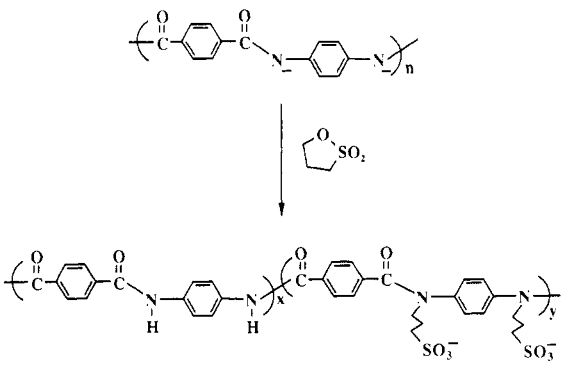
2. Poly((*p*-phenyleneterephthalamido)propanesulfonate) (PPTA-PS). The addition of the propanesulfonate side chain to PPTA to form PPTA-PS polyelectrolyte is accomplished by reaction of 1,3-propane sultone with the PPTA anion as shown in Scheme II. It is expected that alkylsulfonation occurs with a random placement of ionic groups along the PPTA backbone. The structure of the product in Scheme II is only meant to represent the extent of alkylsulfonation and not polymer microstructure. After several hours, the solution has lightened to a yellow/orange color, which indicates that the reaction is complete. The polymer is obtained as a yellow/orange powder that is extremely hygroscopic. Thermal analysis of the air-dryed powder shows an approximate 15% retention of DMSO in the apparently dry material. Vacuum oven treatment at 100 °C and 2 Torr for several hours followed by flushing with nitrogen is required to effectively remove bound solvent.

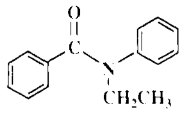
Calculation of the sulfur to nitrogen ratio of the polyelectrolyte determined by elemental analysis indicates the extent of alkylsulfonation of the polymer backbone. This value varies from batch to batch, and a range of 50–66% alkylsulfonation of the backbone has been realized. The 66% alkylsulfonated powder can be dissolved in water in concentrations of 18 wt %. Exact values of elemental percentages were not obtained, most likely due to entrapment of solvent and general difficulties encountered in the combustion analysis of polymers.

NMR Spectroscopy. Due to the structural complexity of PPTA-PS, an NMR study was done to analyze the polyelectrolyte, model compounds, and an alkyl-derivatized PPTA. ^{13}C solution analysis was chosen over ^{1}H methods because of the poor resolution and large line widths in the proton spectra.

1. Benzanilide Model Study. Benzanilide was used as a model compound to verify the proposed reactions of the polymer, as well as to assist in its structural assignment. Ethylbenzanilide (**3**) and benzanilidopropanesulfonate (**4**) were prepared using procedures similar to the one followed for the preparation of the PPTA-PS (see Experimental Section below).

Scheme II





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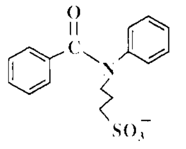

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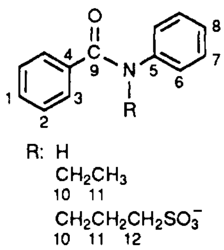
The ^{13}C chemical shifts for benzanilide and its two derivatives are shown in Table I. The aromatic peak assignments for benzanilide were made by calculating the incremental shifts from benzene of the aromatic carbons of monosubstituted benzene rings. The assignments of the aromatic resonances in the substituted benzanilides are tentative, due to uncertainties in the calculated chemical shifts. The farthest upfield aromatic carbons in benzanilide (C6 and C8) are shifted significantly downfield by alkyl substitution at the nitrogen. This shift is due to the inductive effect of the substituent, which increases the electron density on the nitrogen. This increases the C5–N bond order, leading to some conjugation across the amide linkage and decreasing the electron density of the ring. There is a similar downfield shift in the carbonyl carbon with alkyl substitution at the nitrogen atom. Observation of this shift allows assignment of the carbonyl peaks in derivatized PPTA as discussed below.

Inspection of the chemical shifts for the ethyl group in ethylbenzanilide and for the propanesulfonate group in benzanilidopropanesulfonate allows assignment of the alkyl resonances in the spectra. The farthest upfield peak is assigned to the middle carbon in the benzanilidopropanesulfonate side chain, which is the least deshielded. For comparative purposes, the ^{13}C spectrum for pyrrol-1-ylpropanesulfonate[30] shows resonances at 27.6, 47.7, and 48.4 ppm. Because of the similarity in environments of the first and third carbons in the side chains of benzanilidopropanesulfonate and pyrrol-1-ylpropanesulfonate, it can be assumed that the resonances at 49.2 and 49.6 ppm in benzanilidopropanesulfonate's spectrum are caused by C12 and C10. This is a reasonable area of the spectrum for C10 since the carbon next to the nitrogen in ethylbenzanilide has a chemical shift of 45.3 ppm, less than 5 ppm away.

Proton NMR also confirms the composition. Ethylbenzanilide shows a triplet/quartet couple centered at 2.65 ppm, and benzanilidopropanesulfonate shows peaks at 3.75 (triplet), 2.70 (quintet), and 1.82 (triplet) ppm.

2. Poly(*p*-phenyleneterephthalamide) (PPTA). Figure 1 shows the solid-state CP/MAS ^{13}C NMR spectrum of the starting material, Kevlar aramid pulp type 979 (Du Pont). The spectrum is externally referenced to glycine, whose carbonyl resonance is taken to be at 176 ppm relative to TMS. As expected, there is a single carbonyl resonance for the amide carbon at 162 ppm. Detailed assignment of the ring carbons has not been

Table I
^{13}C NMR Chemical Shift Data (ppm) for Benzanilide and Its Derivatives



R	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
H	131.5	127.6	128.3	134.9	139.1	120.3	128.5	123.6	165.5			
C_2H_5	129.4	128.0	129.0[a]	136.5	143.8	127.6	129.1[a]	126.4	169.2	45.3	13.1	
$C_3H_6SO_3^-$	129.3	128.0	127.7	136.5	142.8	128.1	129.3	126.7	169.5	49.6[a]	23.3	49.2[a]

[a] These assignments may be interchanged.

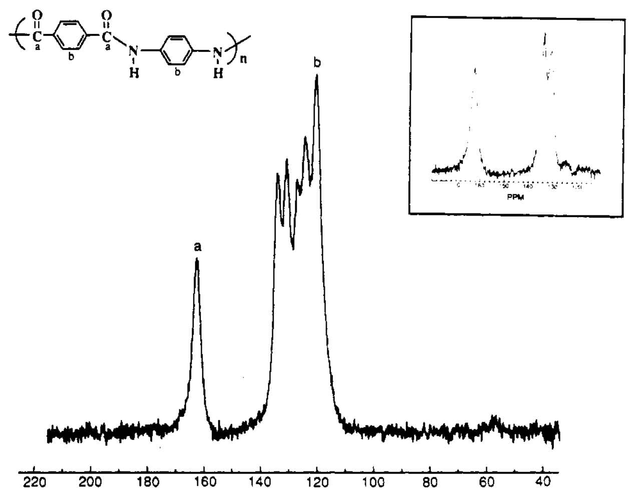
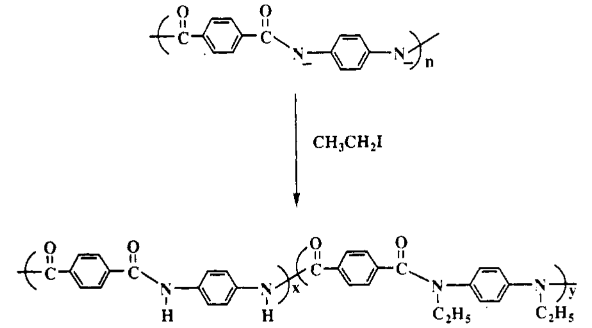


Figure 1. Solid-state CP/MAS ^{13}C NMR spectrum of PPTA externally referenced to glycine. Inset shows nonquaternary suppression (NQS) spectrum of the same material.

Scheme III



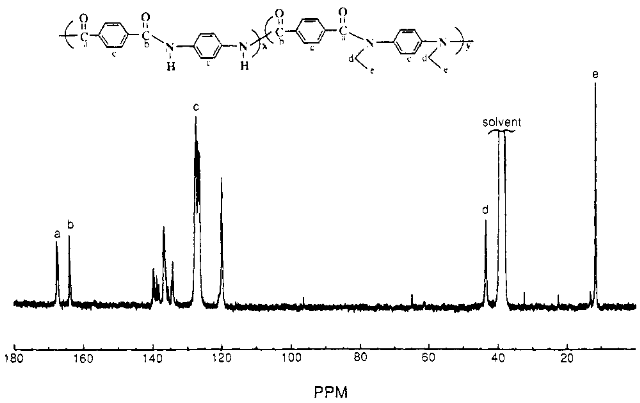


Figure 2. ^{13}C NMR spectrum of Et–PPTA carried out at ~10% in DMSO-d_6 by using an inverse gated decoupling pulse program and a 30-s delay.

attempted since the number and positions of resonances may be quite complicated due to geometrical isomerism and solid-state packing effects. However, the quaternary resonances were easily identified by a nonquaternary suppression (NQS) experiment, shown as an inset in Figure 1, where only the carbonyl and nonprotonated carbons are apparent.

3. **Poly(*N*-ethyl-*p*-phenyleneterephthalamide) (Et–PPTA).** The PPTA anion was reacted with 1-iodoethane in order to introduce an ethyl side-chain onto the polymer backbone as shown in Scheme III. The yellow powder obtained was soluble in DMSO. The ^{13}C NMR spectrum for the ethyl derivative of PPTA is shown in Figure 2. The use of inverse gated decoupling and a sufficiently long delay time resulted in a complete suppression of the NOE and allowed integration of protonated to nonprotonated carbon atoms. The validity of the integration was checked by examination of the ratio of carbonyl to aryl carbon atoms and was found to be 1:6, as expected for PPTA. Comparison of the areas of the carbonyl peaks (a and b in Figure 2) suggests that approximately 50% of the nitrogen atoms on the polymer backbone are alkylated. This conclusion is based on the assumption that the appearance of two carbonyl carbons results from the presence of an adjacent substituted nitrogen atom, with the substituted carbonyl being farthest downfield. The assignment is substantiated by the shift in the carbonyl peak in substituted benzanilide. The spectrum clearly shows the resonances for the two alkyl carbons at 44.4 and 12.5 ppm, which correspond very closely to the ethyl group resonances in ethylbenzanilide (see Table I).

4. **Poly(*p*-phenyleneterephthalamide) (PPTA–PS).** The NMR spectrum of PPTA–PS is shown in Figure 3. It also shows the presence of two different carbonyl peaks due to proximity to substituted or unsubstituted nitrogens. By comparison of the areas of these peaks, it is seen that slightly less than 50% of the nitrogen atoms in the PPTA are substituted with a propanesulfonate group. When the derivatization reaction was done with excess dimsyl anion, a third carbonyl peak at 162 ppm was seen. We expect this was the result of products of a chain cleavage reaction resulting from attack of the dimsyl anion at the carbonyls of the aramid as illustrated in structure 1. To address this, dimsyl anion was reacted with benzoyl chloride to yield a model compound having a similar functional group sequence to 1. The ^{13}C NMR spectrum of the product exhibited a carbonyl resonance at 164 ppm, consistent with the β-keto sulfoxide. By comparison to benzanilidopropanesulfonate, the side-

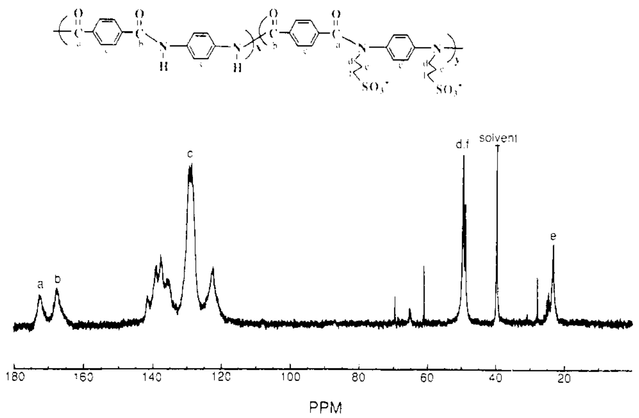


Figure 3. ^{13}C NMR spectrum of PPTA-PS on a ~10% solution in D_2O obtained by using inverse gated decoupling and a 30-s delay.

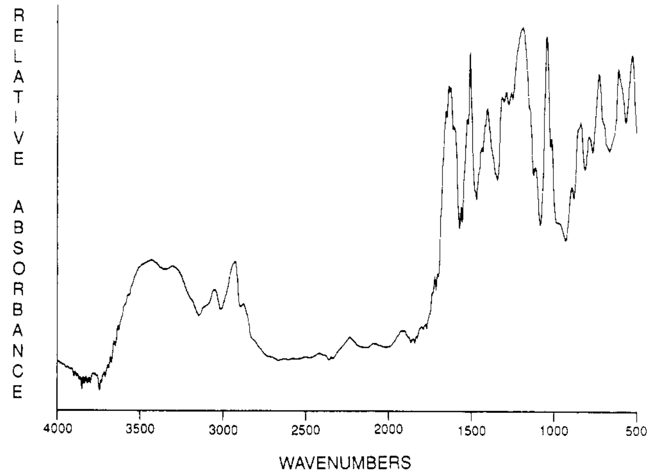


Figure 4. Diffuse reflectance infrared spectrum of PPTA-PS in a KBr dispersion.

chain carbon assignments have been made for chemical shifts of 49.4, 48.7, and 23.2 ppm. PPTA-PS made at higher temperatures and longer reaction times showed small resonances at 69.5, 60.9, and 27.7 ppm. A possible explanation for these peaks may be the occurrence of a small amount of O-alkylated product (structure 2). This product is not a substantial contaminant, however, since the carbonyl to aryl integration has the proper ratio, indicating that the extent of O-alkylation is not significant. Although the intensities of the O- and N-alkylated side-chain peaks vary with reaction conditions, the location of peaks in the spectrum is completely reproducible in various syntheses of PPTA-PS.

Further Characterization of PPTA-PS. The IR spectrum of PPTA-PS is shown in Figure 4. The spectrum corresponds well with that of the PPTA except for the addition of the sp^3 C-H stretches at 2969 cm^{-1} and two major peaks at 1207 and 1049 cm^{-1}. These peaks result from the symmetrical and asymmetrical stretching vibrations of the sulfur to oxygen double bond of the sulfonate moiety. Similar peaks are seen at 1220 and 1064 cm^{-1} in a spectrum of benzenesulfonic acid and at 1207 and 1050 cm^{-1} for butanesulfonic acid.

Thermogravimetric analysis of the polyelectrolyte carried out in N_2 is compared to that of PPTA in Figure 5. PPTA is very thermally stable and shows no degradation until nearly 600 °C. After derivatization, the PPTA-PS shows retention of thermal integrity until approximately 420 °C, at which temperature a 30% weight loss occurs. This loss is followed by a steady degradation to 40 wt % at 800 °C. The initial decrease in mass at 420 °C is most likely due to side-chain degradation.

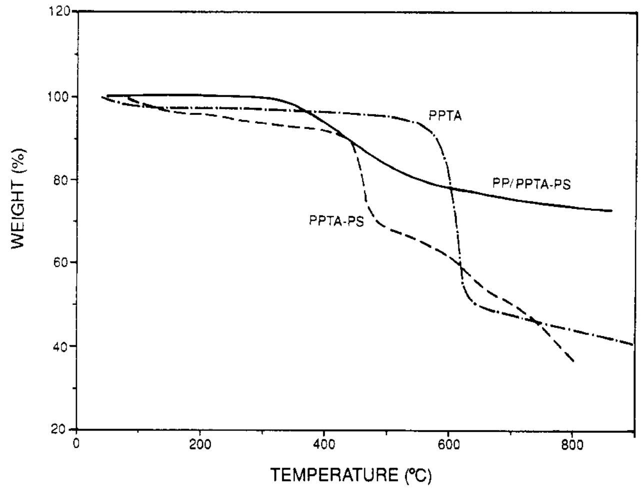


Figure 5. Thermograms of PPTA, PPTA-PS, and PP/PPTA-PS carried out under a nitrogen atmosphere at a heating rate of 20 °C/min.

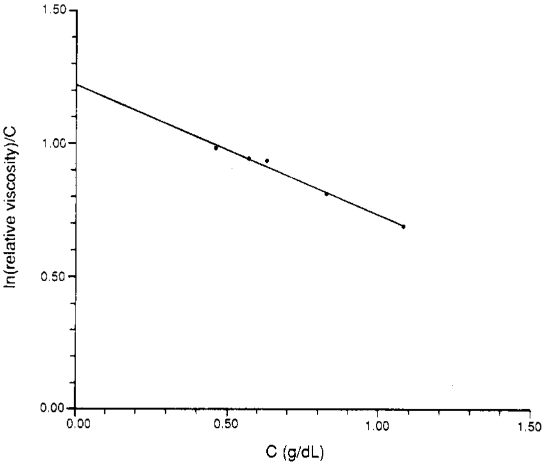


Figure 6. Instrinsic viscosity determination of aqueous solutions of PPTA-PS.

An inherent viscosity of 0.96 dL/g for an aqueous 0.5% solution of PPTA-PS was obtained. Comparable values have been reported for sulfonated aramids in sulfuric acid solution at the same weight percentage.[25-27] The intrinsic viscosity determined with aqueous solutions of less than 1 wt % PPTA-PS is 1.2 dL/g (see Figure 6). At these concentrations (≥0.4 g/dL), the polyelectrolyte effect was not observed. No viscosity maximum occurred in aqueous solutions between 1.5 and 18 wt % PPTA-PS, indicating that at these concentrations no lyotropic liquid crystalline behavior is occurring.

Size exclusion chromatography of the polyelectrolyte, in aqueous solution, indicated that the polymer had a hydrodynamic volume too large to be accommodated by the column. The column was calibrated with poly(ethylene oxide) standards; the maximum standard used had a molecular weight of 30 000.

Conducting Molecular Composites. The molecular level composite films resulting from electrochemical polymerization of pyrrole in an aqueous solution of PPTA-PS are shiny black, free standing, and exhibit four probe conductivities of ~1 Ω^{-1} cm^{-1}. The conductivity varies minimally with the variation of the system parameters (Table II) and is comparable to other polypyrrole molecular composites.[9,10] The materials are very strong and are somewhat brittle due to the utilization of the aramid polyelectrolyte.

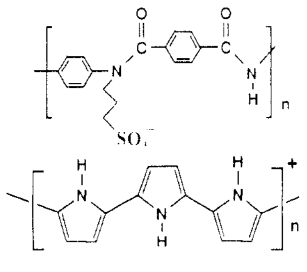
Aqueous solutions of 1% by weight PPTA-PS were used in the electrochemical polymerization of pyrrole. This

Table II
Variation of Conductivity of PP/PPTA-PS Molecular Composite with System Parameters

electrode material	current density, mA/cm^2	voltage	conductivity, Ω^{-1} cm^{-1}
glassy carbon	1.0	3.5 ± 0.2	0.8
glassy carbon	2.0	4.2 ± 0.2	0.7
stainless steel	1.5	3.1 ± 0.1	0.5
stainless steel	1.0	2.9 ± 0.1	0.3

weight precentage corresponds to 0.026 M based on a repeat unit weight of 432 g for 66% alkylsulfonated PPTA. Purging the solution with nitrogen was used to disperse the poorly soluble pyrrole into the solution as well as to deoxygenate the system. Both glassy carbon and stainless steel electrodes were used with equal success. As Table II shows, the voltage maintained in the system varies only slightly during the electropolymerization process, depending on electrode composition and current density employed. With a vertical orientation of the electrodes, the surface of the film is ridged, presumably due to gravity. When the electrochemical cell is sealed and oriented horizontally, a very smooth film surface is realized.

The electropolymerization/deposition of conductive polypyrrole films is generally accepted to proceed via an electrochemically activated step growth coupling mechanism. The first step of this reaction is the oxidation of the pyrrole monomer to form a radical cation, which then couples with another radical cation or reacts with a neutral monomer molecule to form a dimer. This doubly charged dimer can then lose two protons to rearomatize to form a stable dimer species. The dimer is somewhat more easily oxidized than the monomer and may participate in additional oxidation/radical coupling reactions to form oligomers and eventually polymer. The polymer is insoluble in the solvent, water, and precipitates as a film on the electrode surface. Because the polymer is still in contact with the electrode surface, it is further oxidized and must incorporate anions from the electrolyte to maintain charge neutrality. For our case of a polymeric electrolyte, the anions are covalently bound to a polymer chain, so the two polymer backbones are intimately mixed. Thus the term molecular level composite is pertinent. Structure 5 is a schematic representation of the composite.



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One of the desired benfits of using a sulfonate-derivatized Kevlar as the charge-compensating ion in oxidatively doped polypyrrole films was the possibility of improving the thermal stability of the conductive polymer. Figure 5 includes the thermogram of the molecular composite along with PPTA and PPTA-PS. As discussed above, the PPTA shows 100% weight retention to above 600 °C, and the polyelectrolyte is stable to ~400 °C before onset of side-chain cleavage. The thermal analysis of the PP/PPTA-PS composite shows enhanced properties over typical polypyrroles, in that virtually complete mass retention to 330 °C in both N_2 and air is seen, at which point side-chain cleavage is presumed to begin occurring. As can be seen in Figure 7, when compared to poly(pyrrolyl tosylate), the onset of degradation is higher for PP/PPTA-PS. In addition, the PP/PPTA-PS shows 80% mass retention at 900 °C in N_2, which is greater by 15% than the amount of residual char at this temperature for a poly(pyrrolyl tosylate) film.

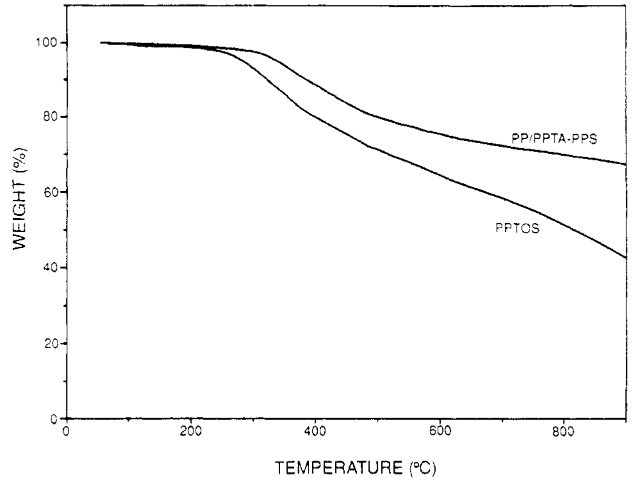

Figure 7. Thermal analyses of PP/PPTA-PS and poly(pyrrolyl tosylate) carried out under a nitrogen atmosphere at a heating rate of 20 °C/min.

Experimental Section

Poly(*p*-phenyleneterephthalamide) (PPTA) Anion. In a typical preparation, the PPTA anion[28] was prepared by charging 400 mL of anhydrous dimethyl sulfoxide (Aldrich) and 1.20 g (0.04 mol) of an 80% sodium hydride dispersion in mineral oil (Aldrich) into a dry three-necked round-bottomed flask flushed with nitrogen and equipped with an overhead mechanical stirrer and thermometer. After the mixture was reacted at 75 °C for 1 h and cooled to 40 °C, 4.76 g (0.04 mol) of vacuum-dried PPTA (Kevlar aramid pulp type 979, Du Pont) was added. The mixture was stirred vigorously for 48 h. The resulting anion solution was dark red, extremely viscous, moisture sensitive, and contained no solid PPTA residue.

Poly((*p*-phenyleneterephthalamido)propanesulfonate) (PPTA-PS). The propanesulfonate side chain was introduced by adding 4.89 g (0.04 mol) of 1,3-propane sultone (Aldrich) as a solid to the PPTA anion solution with stirring at 40 °C for 24 h. The PPTA-PS solution was clear, yellow, and much less viscous than the PPTA anion solution. The PPTA-PS was precipitated, as a yellow-orange powder, into a large excess of distilled tetrahydrofuran (Aldrich). After decantation of the DMSO/THF mixture, replacement with fresh THF, and several days of stirring, the product was collected by vacuum filtration under nitrogen and dried in a vacuum oven. Yields of ~60% have been attained: IR (KBr) 3306, 3051, 2969, 1639, 1512, 1408, 1319, 1273, 1207*, 1118, 1049*, 1018, 895, 864 cm^{-1} (* indicates sulfonate stretching frequencies).

Poly(*N*-ethyl-*p*-phenyleneterephthalamide) (Et-PPTA). One equivalent per reactive site on the PPTA anion of 1-iodoethane (Aldrich) was syringed into the anion solution for the introduction of an ethyl group to the polymer backbone. The mixture was stirred at 40 °C for 24 h. A color change from red to orange was observed, along with a reduction in solution viscosity. The product was isolated as a yellow powder by precipitation into distilled tetrahydrofuran (Aldrich), followed by centrifugation, washing with ether, and drying under dynamic vacuum.

Benzanilidopropanesulfonate. In a typical derivatization reaction, a flame-dried, nitrogen-flushed 250-mL three-necked round-bottomed flask fitted with a thermometer and mechanical stirrer was charged with 100 mL of anhydrous DMSO

(Aldrich) and 0.60 g (0.020 mol) of NaH in an 80% dispersion in mineral oil (Aldrich). This mixture was heated to 75 °C for a period of ~1 h until the solid NaH all dissolved and the solution took on a greenish tinge. After the mixture cooled to 40 °C, 4.00 g (0.020 mol) of benzanilide (Aldrich) was added as a solid to the solution. The solid dissolved immediately, and stirring was continued for 1.5 h. To the resulting yellow/green solution, 2.44 g (0.020 mol) of solid 1,3-propane sultone (Aldrich) was added. The sultone dissolved and an immediate lightening of the color of the solution occurred. After stirring overnight (~24 h), the solution was light yellow in color. The DMSO was removed by careful distilling to dryness under vacuum. The solid was then redissolved in a minimum of water, filtered, and dried to obtain a completely water soluble product. The yellow solid is hygroscopic with a melting point of 154–156 °C: yield 3.32 g, 52%. The infrared spectrum of the product corresponds to that of benzanilide with the addition of sp^3 stretching bands at 2940 and 2874 cm^{-1} and sulfonate vibration bands at 1212 and 1055 cm^{-1}. NMR was performed in D_2O solutions at ~10% by weight.

Ethylbenzanilide. The ethyl side chain was introduced onto benzanilide by syringing 3.12 g (0.020 mol) of iodoethane into the benzanilide anion solution prepared as described above. After 1 day of stirring, the yellow solution was dripped into cold, stirred THF to precipitate the NaI from the solution, followed by gravity filtration. The filtrate, containing the product, was distilled to remove the THF/DMSO mixture leaving a yellow oil. Column chromatography on alumina with a 30% THF/70% hexane elutant mixture was used to isolate the product. DMSO-d_6 was the NMR solvent.

Polypyrrole/Poly((*p*-phenyleneterephthalamido)propanesulfonate) (PP/PPTA–PS). Electrochemical syntheses were utilized for the production of the PP/PPTA–PS molecular composite. Two 100-cm^2 plate electrodes were oriented horizontally at a distance of 2 cm in a rectangular cell. Both glassy carbon (Atomergics) and stainless steel electrodes were used. Polishing with diamond paste and soaking in nitric acid prior to electropolymerization was required for the glassy carbon. The pyrrole was purified by passing over alumina, and aqueous solutions of 0.2 M pyrrole and 1% by weight PPTA–PS were deoxygenated with nitrogen. A nitrogen blanket was kept over the solution during electropolymerization. Constant current densities of 1–2 mA/cm^2 were employed, and polymerizations were carried out for 4–6 h. The resulting films, with thicknesses of 70–130 μm, were easily removed from the electrode surface with a flat spatula after loosening the edges with a razor blade and were pressed dry.

Characterization. Infrared spectroscopy using the diffuse reflectance technique and KBr dispersions were carried out on a Digilab FTS-40 spectrophotometer. Thermal analyses were performed on a Du Pont 9900 TA system equipped with TGA, DSC, and DMA. GPC was done on a Waters 440 system liquid chromatograph with an Ultrahydrogel 250 column. The exclusion limit of the column is 80 000, and the pore size is 250 Å. C, H, N, and S elemental analyses were done by Texas Analytical Laborotories, Inc., of Tallahassee, FL. An Ostwald viscometer suspended in a constant-temperature bath thermostated at 30 °C was used for viscosity determinations.

NMR spectroscopy was carried out on a Bruker 300-MSL spectrometer on 10% by weight solutions in DMSO-d_6 and D_2O. In all cases, the spectra were referenced to a resonance caused by residual DMSO that was assigned a chemical shift of 39.5 ppm. Spectra of the Kevlar derivatives Et–PPTA and PPTA–PS were obtained by using inverse gated decoupling and a delay time of 30 s. Solid-state NMR was carried out on the same instrument using a Doty Scientific solids probe. The PPTA fibers were packed into a standard 5-mm Doty Scienific rotor and spun at 9000 Hz, with a sweep width of 25 kHz, acquisition time of 0.035 s, and a relaxation delay of 4 s. The reference peak of glycine was assigned a value of 176.0 ppm.

Four probe conductivities were determined on samples that had been dried at ~5 torr at ambient temperature for 24 h and showed no residual solvent by TGA. A Keithly 197 autoranging microvolt digital multimeter was used for the resistance determinations. Conductivities were also calculated after using a Keithley 224 programmable current source in combination with a Keithley 181 nanovoltmeter to determine the resistance of the samples. Samples for thermal analyses were dryed under vacuum as described above for the conductivity samples.

Conclusions

In this work, we have reported, for the first time, a method of derivatizing the thermally stable aramid, poly(*p*-phenyleneterephthalamide), to produce and characterize a highly water soluble polyelectrolyte, poly((*p*-phenyleneterephthalamido)propanesulfonate). An NMR study involving the model compound benzanilide and its derivatives, as well as an alkylated derivative of PPTA, has been useful in characterization. This polyelectrolyte is soluble to at least 18 wt % in water with approximately 66% alkylsulfonation of the reactive nitrogen sites. We have utilized this polymer as the polyelectrolyte in the electrochemical synthesis of an electrically conductive polypyrrole molecular composite where the PPTA–PS is incorporated as the dopant ion. Conductivities of about 1 Ω^{-1} cm^{-1} were obtained on glassy carbon and stainless steel electrodes with current densities between 1 and 2 mA/cm^2. In addition to high electronic conductivities, these molecular composites exhibit similar mechanical properties and enhanced thermal stability when compared to poly(pyrrolyl tosylate).

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Water-Soluble Copolymers. 35. Photophysical and Rheological Studies of the Copolymer of Methacrylic Acid with 2-(1-Naphthylacetyl)ethyl Acrylate

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ABSTRACT: Fluorescence and dilute solution viscosity behavior of a 20:80 mol % copolymer of 2-(1-naphthylacetyl)ethyl acrylate (NAEA) and methacrylic acid (MAA), respectively, have been studied. The fluorescence spectra of this copolymer showed an almost 4-fold increase in excimer emission relative to monomer emission (I_E/I_M) upon increasing from pH 5 to 9. Similarly, as the pH of the medium increases, reduced viscosity increases, indicating a transition from a compact coil to a more expanded coil at pH 7.5. This behavior is unlike that previously reported presumably due to the extent of naphthyl group substitution, the hydrophobic character of both the naphthyl groups and the pendant methyl groups of MAA, and effective decoupling of the chromophore from the polymer backbone by a spacer group. The effects of urea, a water-structure breaker, and of polymer concentration indicate that, at high pH, NAEA–MAA forms an intramolecular "hypercoil". High quenching efficiencies of both monomer and excimer fluorescence by copper(II) ions result from ionic binding of the quencher ions with the copolymer.

Introduction

Recently, polyelectrolytes containing pendant aromatic chromophores such as naphthalene or phenanthrene have attracted a great deal of attention, particularly as models for artificial photosynthetic systems.[1–4] These polymers have been reported to exist in dilute aqueous solution as "hypercoils", which are characterized by hydrophobic aromatic groups clustered toward the center of the coil and hydrophilic ionic groups located in the aqueous boundary.[5–7] The microenvironment produced by the polyelectrolytes to which the hydrophobic chromophores are covalently attached often dramatically affects both the photophysical and photochemical properties of the chromophore. Most investigations to date have primarily been conducted on solutions of polymers in the electrolyte form. To date few comprehensive studies directed toward understanding the effect of pH on the conformation, and consequently the photophysical and rheological properties, of these "pseudomicellar" polymers have been conducted.

In this paper, we report the results of both fluorescence emission and viscosity studies of a polymer of methacrylic acid containing 20 mol % of 2-(1-naphthylacetyl)ethyl acrylate. Data suggest that the observed behavior relates, at least in part, to hydrophobic naphthyl group associations along the polymer chain.

Experimental Section

Materials. The synthesis of 2-(1-naphthylacetyl)ethyl acrylate (NAEA) has been outlined elsewhere.[8] Poly[2-(1-naphthylacetyl)ethyl acrylate-*co*-methacrylic acid) (NAEA–MAA) was prepared by 2,2′-azobis(isobutyronitrile) (AIBN) (1.0 mol %) initiated radical polymerization of NAEA (20 mol %) and MAA (80 mol %) in degassed *N,N*-dimethylformamide (DMF) solution at 65. After 6 h, the sample was precipitated into diethyl ether, redissolved into DMF, and reprecipitated into diethyl ether. A dialysis/HPLC technique indicated <0.1 mol % residual NAEA in the copolymer. The composition of the polymer was determined from both elemental analysis (MHW Laboratories, Phoenix, AZ) and the UV absorption spectrum of NAEA–MAA in DMF (ϵ = 6745 M^{-1} cm^{-1} at 280 nm). The polymer consists of 20.5 mol % NAEA and 79.5 mol % MAA.

Urea (Aldrich, 99+%) was recrystallized three times from methanol. Copper nitrate (Aldrich 99.99%) was used as received.

The polymer solutions were prepared in deionized water. Due to the inherent hydrolytic instability of NAEA,[9] solutions were discarded after 48 h and fresh solutions prepared for subsequent studies.

Methods. Polymer Characterization. UV absorbance measurements (Perkin-Elmer Lambda 6B) and elemental analysis (MHW Laboratories, Phoenix, AZ) were used to determine the composition of the copolymer. The copolymer contained 20.5 mol % NAEA and 79.5 mol % MAA. The number average molecular weight, M_n, of the copolymer was estimated to be 140 000, based on osmotic pressure measurements (Knauer Osmometer with 600W membrane, Arro Laboratories, Inc.) in *N,N*-dimethylacetamide.

Fluorescence Spectroscopy. The concentration of polymer in solution was ca. 0.01 g/dL (unless otherwise noted) such that the concentration of naphthyl moieties in solution was always $<10^{-4}$. Sample solutions were degassed with N_2 for 15 min prior to emission measurements. Steady-state fluorescence spectra were measured on a Perkin-Elmer 650-10B spectrophotometer;

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