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**Electronic and Ionic Transport in Processable Conducting Polymers**

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

Melinda B. Gieselman and John R. Reynolds

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Poly(*p*-phenyleneterephthalamide 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 alkyl sulfonation of the aramid poly(*p*-phenyleneterephthalamide) (PPTA) to form poly(*p*-phenyleneterephthalamide propanesulfonate) (PPTA-PS). This polyelectrolyte is soluble in water to greater than 18% by weight when the polyaramid is alkyl sulfonated to 66%. Characterization and structural analysis of the polyelectrolyte was facilitated by a  $^{13}\text{C}$  NMR study of the model compound benzanilide and its alkyl and alkyl sulfonate 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 conductivities of  $1\ \Omega^{-1}\text{cm}^{-1}$  and improved thermal stabilities when compared to poly(pyrrole 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<sup>1-9</sup> or ionomeric membranes such as Nafion, which results in an ionically conductive medium.<sup>10-13</sup> A very useful method for the preparation of these conductive molecular composites is heterocycle electropolymerization in the presence of solubilized polyelectrolyte.<sup>14-21</sup> 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<sup>17</sup>, 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.<sup>22</sup> 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.<sup>23,24</sup> Other rigid chain, water soluble polyaramids have been prepared by polymerization of sulfonated aromatic diamines with terephthaloyl chloride.<sup>25-27</sup> The characterization of our polyelectrolyte was aided by the synthesis and NMR analysis of another derivitized PPTA, poly(*N*-ethyl-*p*-phenyleneterephthalamide), as well as the derivatization of benzanilide and structural assignments of two model compounds, *N*-ethyl benzanilide and benzanilide propanesulfonate.

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<sup>28</sup> by the reaction shown in Scheme I.

Insert Scheme I

Kevlar pulp is treated with "dimethyl" 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 one equivalent of NaH per nitrogen atom on the polymer chain prevents formation of excess dimethyl 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 dimethyl 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 counter ion is silver)<sup>29</sup>, 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).

#### Insert Structures 1 and 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 eight weeks, and subsequently reacted with iodoethane. 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 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*-phenyleneterephthalamide propanesulfonate) (PPTA-PS).

The addition of the propane sulfonate 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.

#### Insert Scheme II

It is expected that alkyl sulfonation 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 alkyl sulfonation 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 yellow/orange powder that is extremely hygroscopic. Thermal analysis of the air-dried 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 alkyl sulfonation of the polymer backbone. This value varies from batch to batch, and a range of 50% - 66% alkyl sulfonation of the backbone has been realized. The (5% alkyl sulfonated powder can be dissolved in water in concentrations of 18 weight percent. 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.  $^{13}\text{C}$  solution analysis was chosen over  $^1\text{H}$  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. Ethyl benzanilide (3) and benzanilide propanesulfonate (4) were prepared using similar procedures to the one followed for the preparation of the PPTA-PS. (See experimental section below.)

#### Insert Structures 3 and 4

The  $^{13}\text{C}$  chemical shifts for the benzanilide and its two derivatives are shown in Table I. The aromatic peak assignments for the 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 ethyl benzanilide and for the propane sulfonate group in benzanilide propanesulfonate allows assignment of the alkyl resonances in the spectra. The farthest upfield peak is assigned to the middle carbon in the benzanilide propanesulfonate side-chain which is the least deshielded. For comparative purposes, the  $^{13}\text{C}$  spectrum for pyrrole-N-propanesulfonate<sup>30</sup> 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

benzanilide propanesulfonate and pyrrole-N-propanesulfonate, it can be assumed that the resonances at 49.2 and 49.6 ppm in benzanilide propane sulfonate'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 ethyl benzanilide has a chemical shift of 45.3 ppm, less than 5 ppm away.

Proton NMR also confirms the composition. Ethyl benzanilide shows a triplet/quartet couple centered at 2.65 ppm, and benzanilide propanesulfonate 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  $^{13}\text{C}$  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 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 non-quaternary suppression (NQS) experiment, shown as an inset in Figure 1, where only the carbonyl and non-protonated 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  $^{13}\text{C}$  NMR

#### Insert Scheme III

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 which 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 ethyl benzanilide (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 propane sulfonate group. When the derivatization reaction was done with excess dimethyl 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 dimethyl anion at the carbonyls of the aramid as illustrated in structure 1. To address this, dimethyl anion was reacted with benzoyl chloride to yield a model compound having a similar functional group sequence to 1. The  $^{13}\text{C}$  NMR spectrum of the product exhibited a carbonyl resonance at 164 ppm, consistent with the  $\beta$ -keto sulfoxide. By comparison to benzanilide propanesulfonate, the side-chain carbon assignments have been made for chemical shifts of 49.4, 41.7, 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  $\text{sp}^3$  C-H stretches at  $2969\text{ cm}^{-1}$ , and two major peaks at  $1207\text{ cm}^{-1}$  and  $1049\text{ cm}^{-1}$ . 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  $1220\text{ cm}^{-1}$  and  $1064\text{ cm}^{-1}$  in a spectrum of benzene sulfonic acid, and at  $1207\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$  for butane sulfonic acid.

Thermogravimetric analysis of the polyelectrolyte carried out in  $\text{N}_2$  is compared to that of PPTA in Figure 5. PPTA is very thermally stable and shows no degradation until nearly  $600^\circ\text{C}$ . After derivatization, the PPTA-PS shows retention of thermal integrity until approximately  $420^\circ\text{C}$ , at which temperature a 30% weight loss occurs. This loss is followed by a steady degradation to 40 weight percent at  $800^\circ\text{C}$ . The initial decrease in mass at  $420^\circ\text{C}$  is most likely due to side chain degradation.

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.<sup>24,26</sup> The intrinsic viscosity determined with aqueous solutions of less than 1 weight percent PPTA-PS is 1.2 dL/g (see Figure 6). At these concentrations ( $\geq 0.4\text{ g/dl}$ ) the polyelectrolyte effect was not observed. No viscosity maximum occurred in aqueous solutions between 1.5 and 18 weight percent 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  $\sim 1 \Omega^{-1}\text{cm}^{-1}$ . The conductivity varies minimally with the variation of the system parameters (Table II), and is comparable to other polypyrrole molecular composites<sup>9,10</sup>. The materials are very strong and are somewhat brittle due to the utilization of the rigid-rod polyaramid polyelectrolyte.

Aqueous solutions of 1% by weight PPTA-PS were used in the electrochemical polymerization of pyrrole. This weight percentage corresponds to 0.026 M based on repeat unit weight of 432 g for 66% alkyl sulfonated PPTA. Purging the solution with nitrogen was used to disperse the poorly soluble pyrrole into the solution as well as deoxygenate the system. Both glassy carbon and stainless steel electrodes were used with equal success. As Table III 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, so 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.

Insert Structure 5

One of the desired benefits 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<sub>2</sub> 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(pyrrole tosylate), the onset of degradation is higher for the PP/PPTA-PS. In addition, the PP/PPTA-PS shows 80% mass retention at 900 °C in N<sub>2</sub>, which is greater by 15% than the amount of residual char at this temperature for a poly(pyrrole tosylate) film.

## Experimental

**Poly(*p*-phenyleneterephthalamide) (PPTA) anion.** In a typical preparation, the PPTA anion<sup>17</sup> was prepared by charging 400 mL of anhydrous dimethyl sulfoxide (Aldrich) and 1.20 g (0.04 moles) of an 80% sodium hydride dispersion in mineral oil (Aldrich) to a dry three-necked round bottomed flask flushed with nitrogen and equipped with an overhead mechanical stirrer and thermometer. After reacting at 75 °C for 1 hour, and cooling to 40 °C, 4.76 g (0.04 moles) of vacuum dried PPTA (Kevlar aramid pulp type 979, DuPont) was added. The mixture was stirred vigorously for 48 hours. The resulting anion solution was dark red, extremely viscous, moisture sensitive, and contained no solid PPTA residue.

**Poly(*p*-phenyleneterephthalamide propanesulfonate), (PPTA-PS).** The propane sulfonate side chain was introduced by adding 4.89 g (0.04 moles) of 1,3-propane sultone (Aldrich) as a solid to the PPTA anion solution with stirring at 40 °C for 24 hours. 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<sup>-1</sup>. (\* 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 hours. 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.

**Benzanilide propanesulfonate.** In a typical derivatization reaction, a flame dried, nitrogen flushed 250 mL 3-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 moles) of NaI in an 80% dispersion in mineral oil (Aldrich). This mixture was heated to 75 °C for a period of ~1 hour until the solid NaI all dissolved and the solution took on a greenish tinge. After cooling to ~40 °C, 4.00 g (0.020 moles) of benzanilide (Aldrich) was added as a solid to the solution. The solid dissolved immediately, and stirring was continued for 1.5 hours. To the resulting yellow/green solution, 2.44 g (0.020 moles) 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 hours), the solution was light yellow in color. The DMSO was removed by carefully 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.

**Ethyl Benzanilide.** The ethyl side-chain was introduced onto benzanilide by syringing 3.12 g (0.020 moles) of iodoethane into the benzanilide anion solution prepared as described above. After a 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 and a 30% THF/70% hexane elutant mixture was used to isolate the product. DMSO- $d_6$  was the NMR solvent.

**Polypyrrole/poly(p-phenyleneterephthalamide 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 to 6 hours. The resulting

films, with thicknesses of 70 to 130 microns, 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 was carried out on a Digilab FTS 40 spectrophotometer. Thermal analyses were performed on a DuPont 990 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 angstroms. C, H, N, and S elemental analyses were done by Texas Analytical Laboratories, 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 using inverse gated decoupling and a delay time of 30 seconds. 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 Scientific rotor, spun at 9000 Hz, with a sweep width of 25 KHz, acquisition time of 0.035 s, and a 4 s relaxation delay. 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  $\sim 5$  torr at ambient temperature for 24 hours 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 dried 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*-phenyleneterephthalamide 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 weight percent in water with approximately 66% alkyl sulfonation 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  $1 \Omega^{-1}\text{cm}^{-1}$  were obtained on glassy carbon and stainless steel electrodes with current densities between 1 and 2 mA/cm<sup>2</sup>. In addition to high electronic conductivities, these molecular composites exhibit similar mechanical properties and enhanced thermal stability when compared to poly(pyrrole tosylate).

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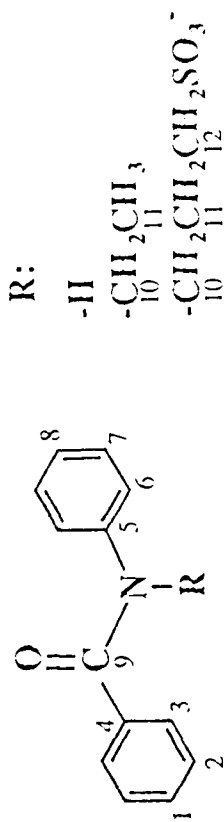
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Table I  
<sup>13</sup>C NMR Chemical Shift Data for Benzanilide and Its Derivatives



| 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 <sub>2</sub> H <sub>5</sub>                              | 129.4 | 128.0 | 129.0* | 136.5 | 143.8 | 127.6 | 129.1* | 126.4 | 169.2 | 45.3  | 13.1  | ----- |
| -C <sub>3</sub> H <sub>6</sub> SO <sub>3</sub> <sup>-</sup> | 129.3 | 128.0 | 127.7  | 136.5 | 142.8 | 128.1 | 129.3  | 126.7 | 169.5 | 49.6* | 23.3  | 49.2* |

\* These assignments may be interchanged.

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

| Electrode Material | Current Density<br>(mA/cm <sup>2</sup> ) | Voltage       | Conductivity<br>( $\Omega^{-1}\text{cm}^{-1}$ ) |
|--------------------|------------------------------------------|---------------|-------------------------------------------------|
| glassy carbon      | 1.0                                      | $3.5 \pm 0.2$ | 0.8                                             |
| glassy carbon      | 2.0                                      | $4.2 \pm 0.2$ | 0.7                                             |
| stainless steel    | 1.5                                      | $3.1 \pm 0.1$ | 0.5                                             |
| stainless steel    | 1.0                                      | $2.9 \pm 0.1$ | 0.3                                             |

**FIGURE CAPTIONS:**

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

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

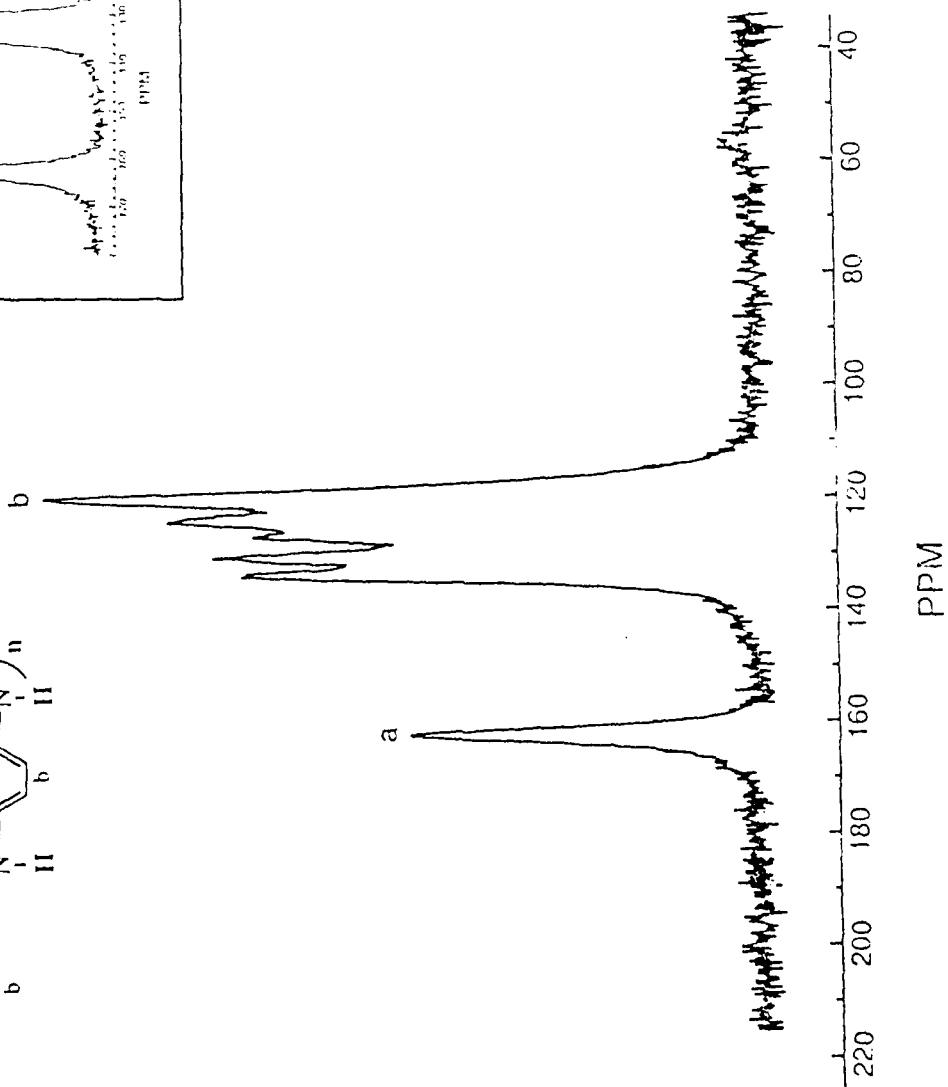
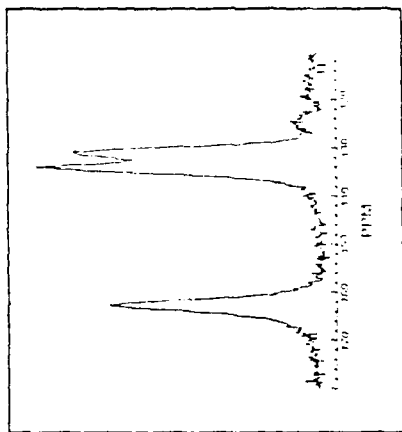
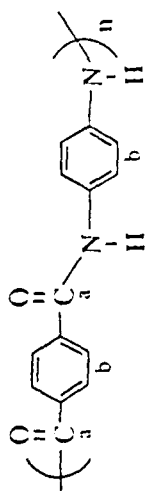
Figure 3.  $^{13}\text{C}$  NMR spectrum of PPTA-PS on a ~10% solution in  $\text{D}_2\text{O}$  using inverse gated decoupling and a 30 s delay.

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

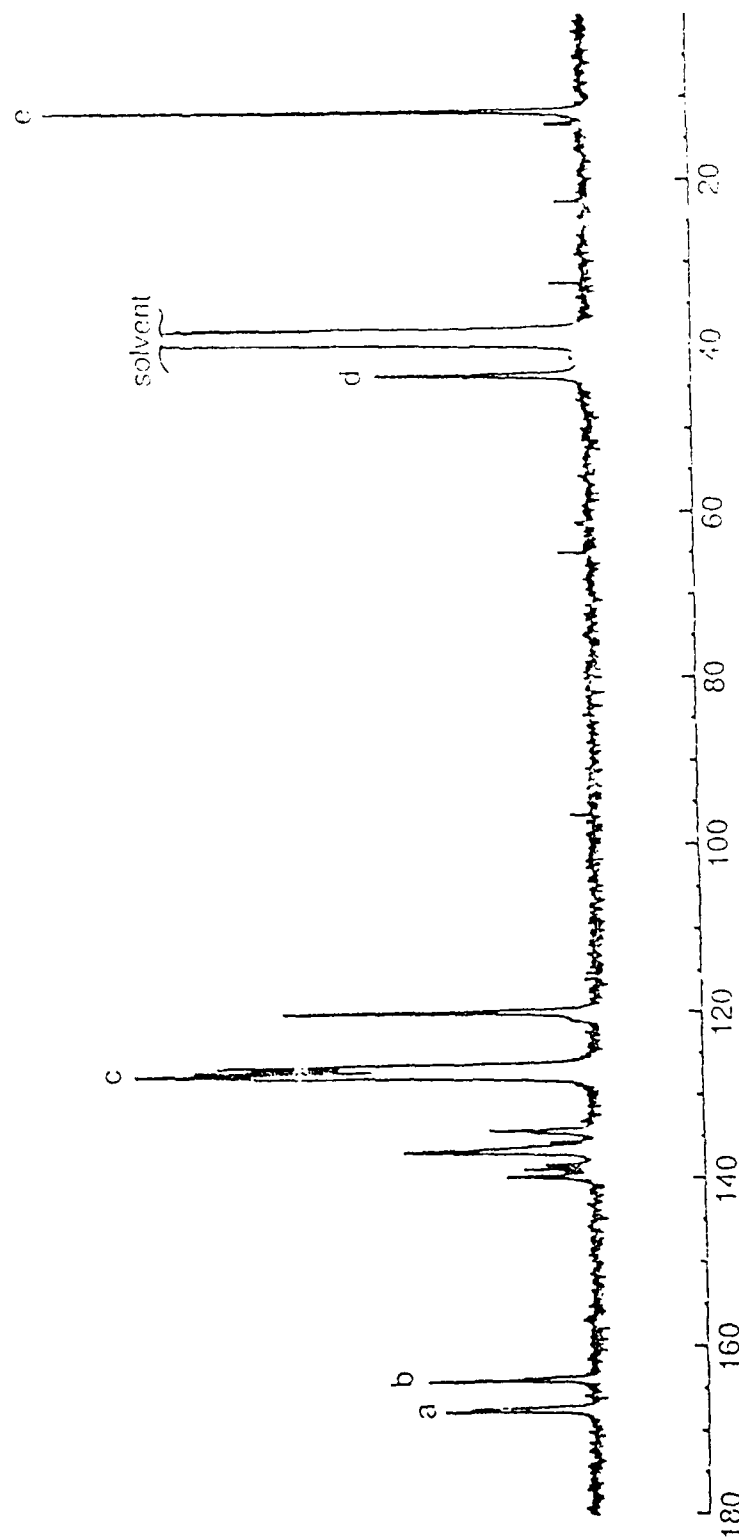
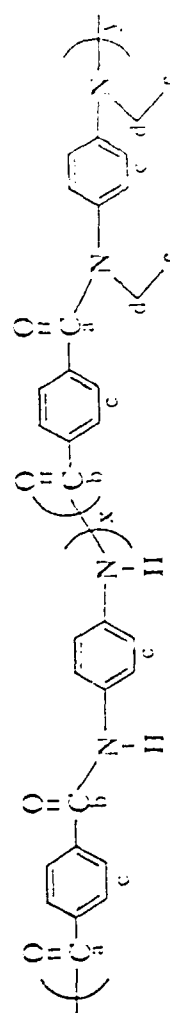
Figure 5. Thermograms of PPTA, PPTA-PS, and PP/PPTA-PS carried out under a nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$ .

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

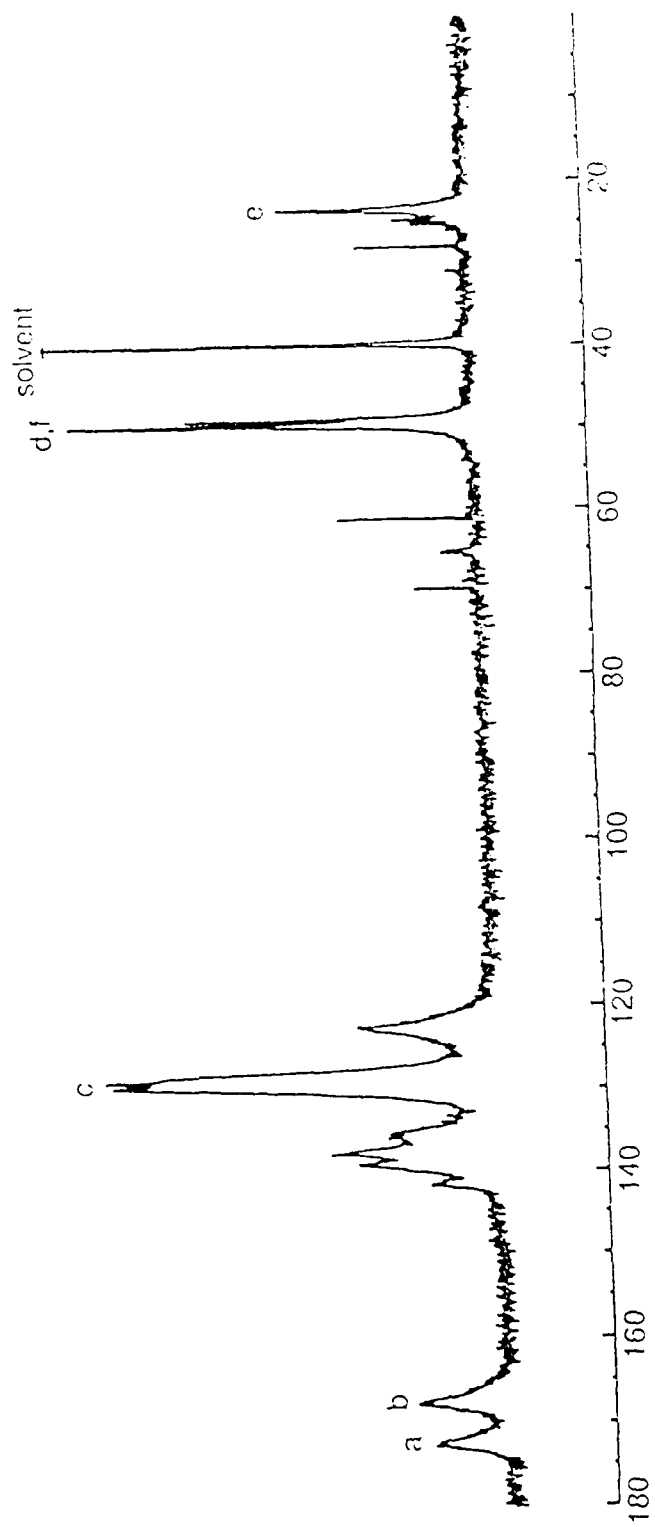
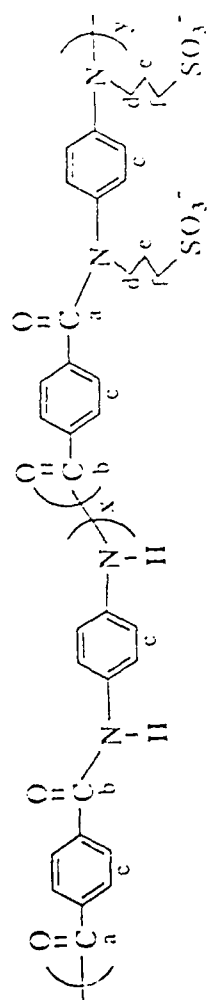
Figure 7. Thermal analyses of PP/PPTA-PS and poly(pyrrole tosylate) carried out under a nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$ .

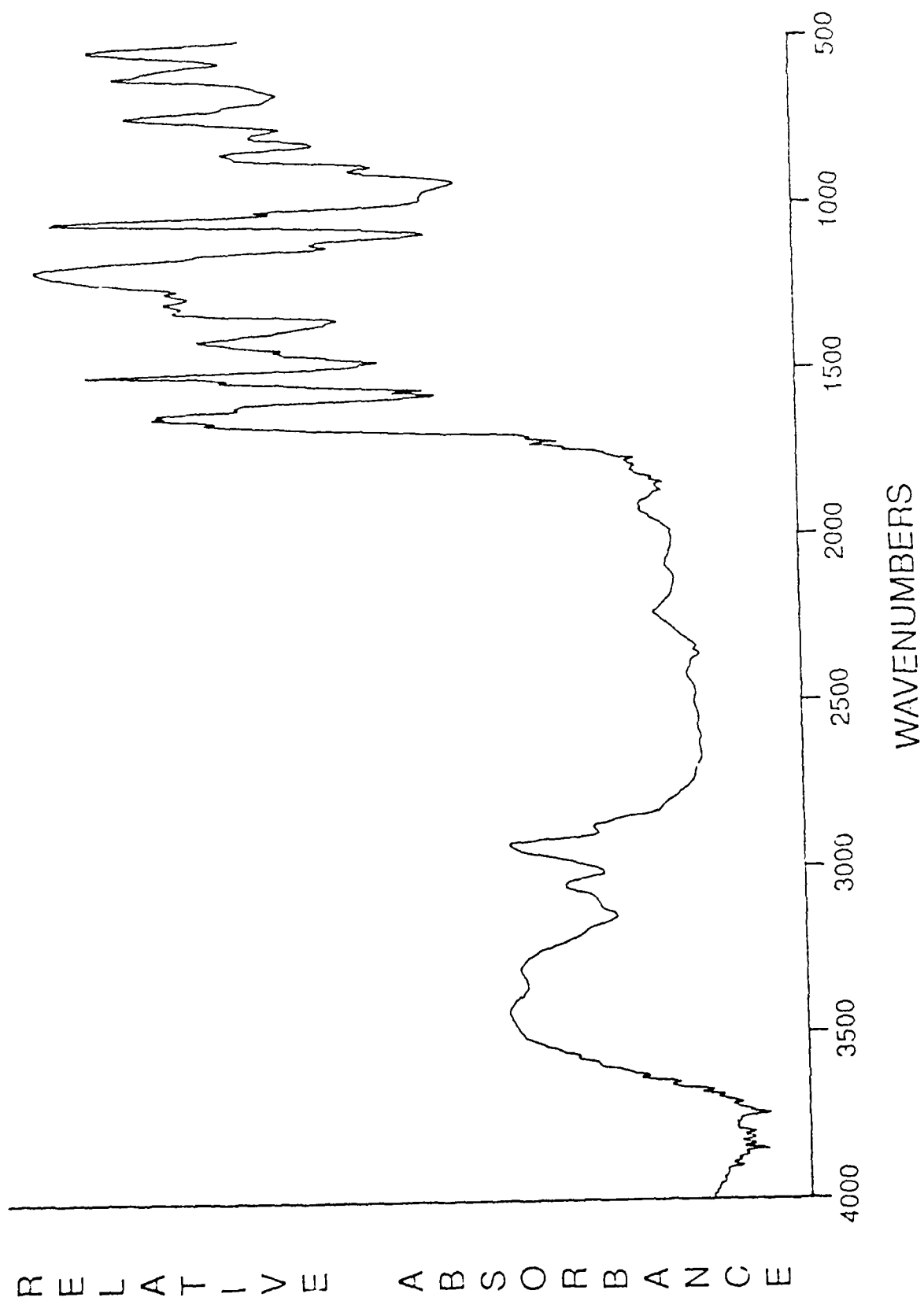


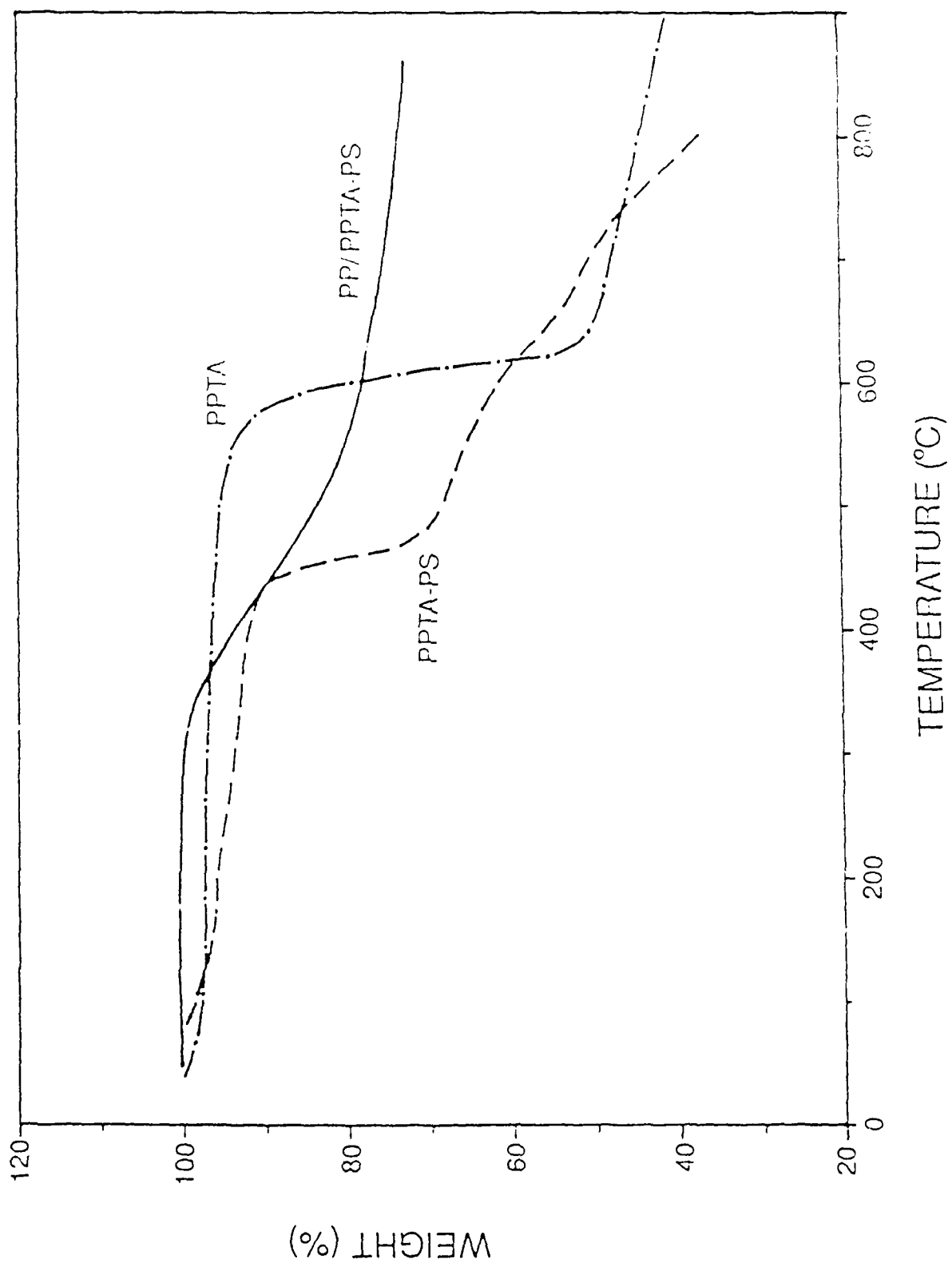
F2



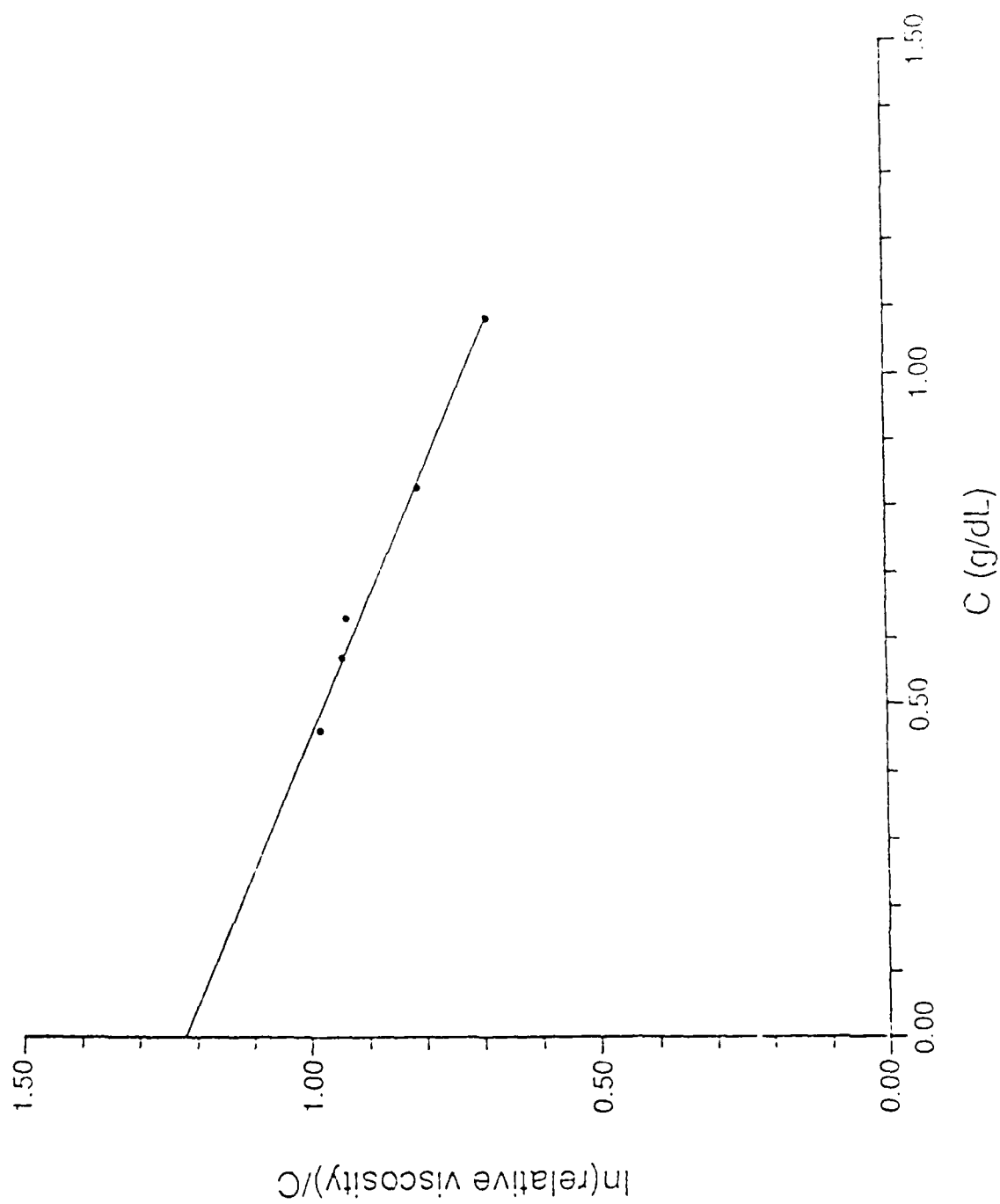
PPM

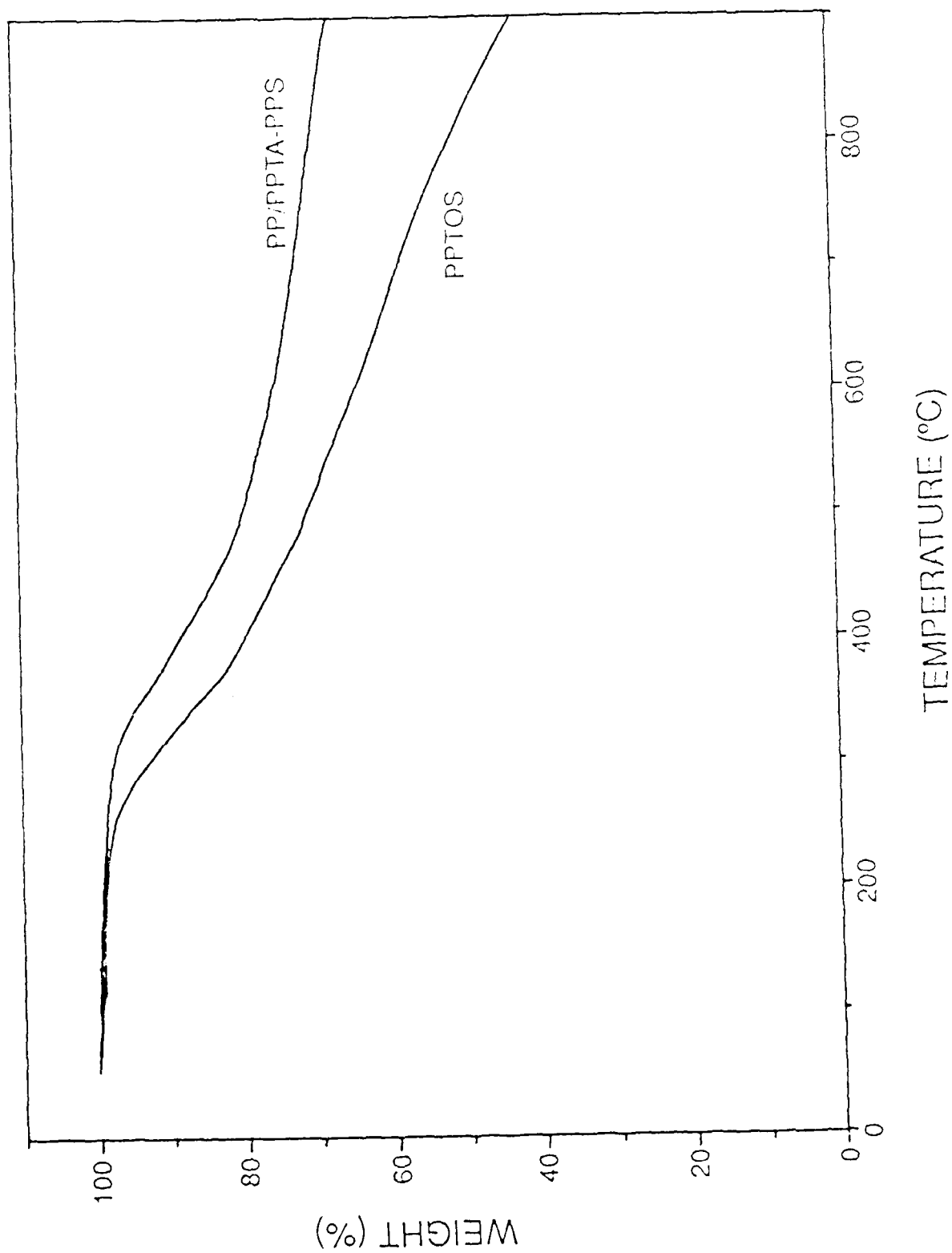


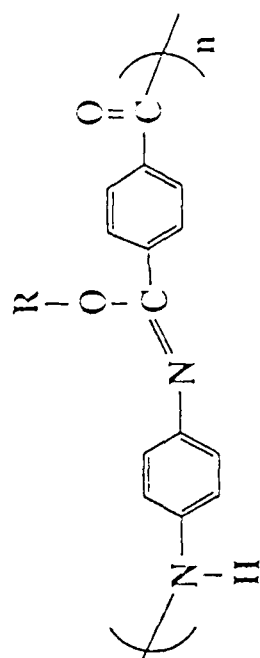
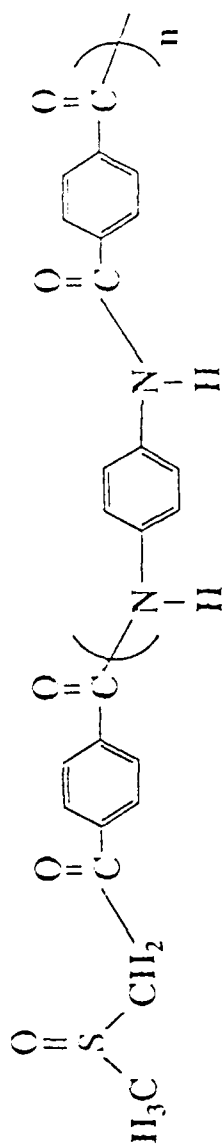




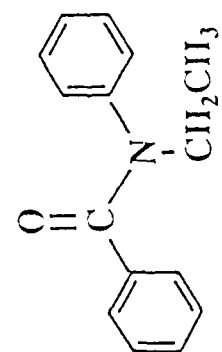
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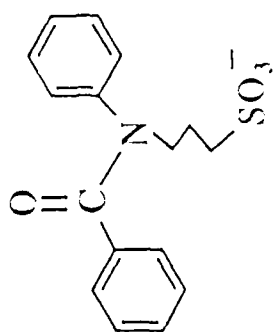




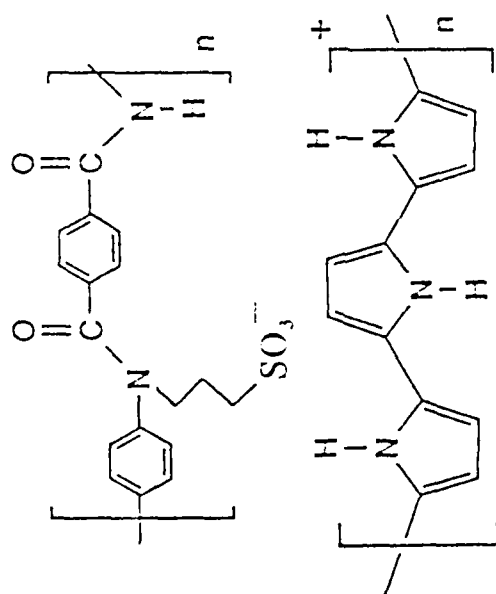
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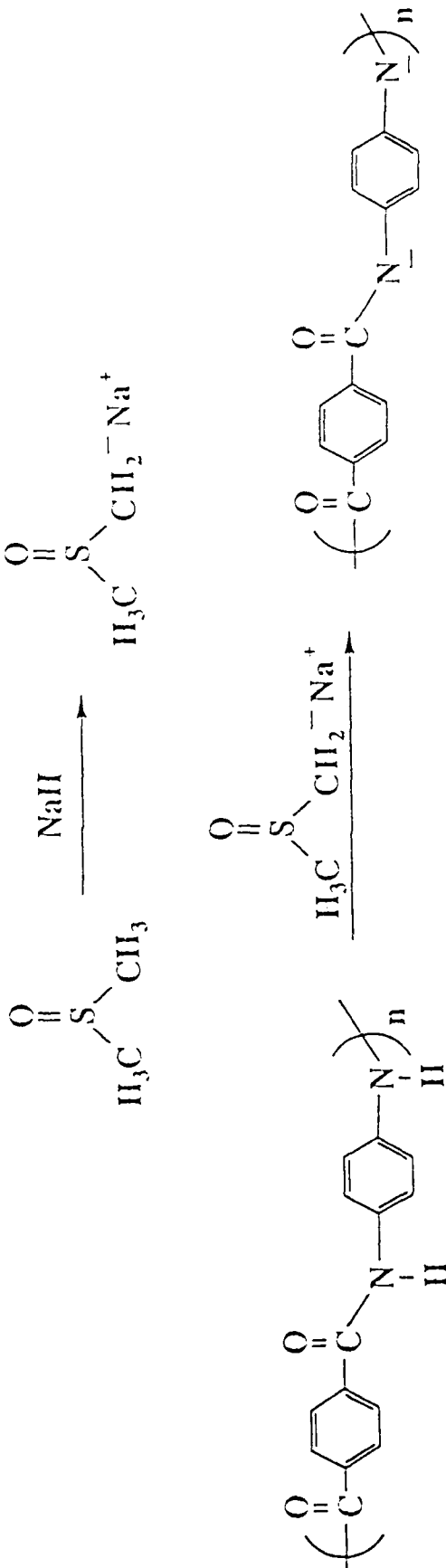
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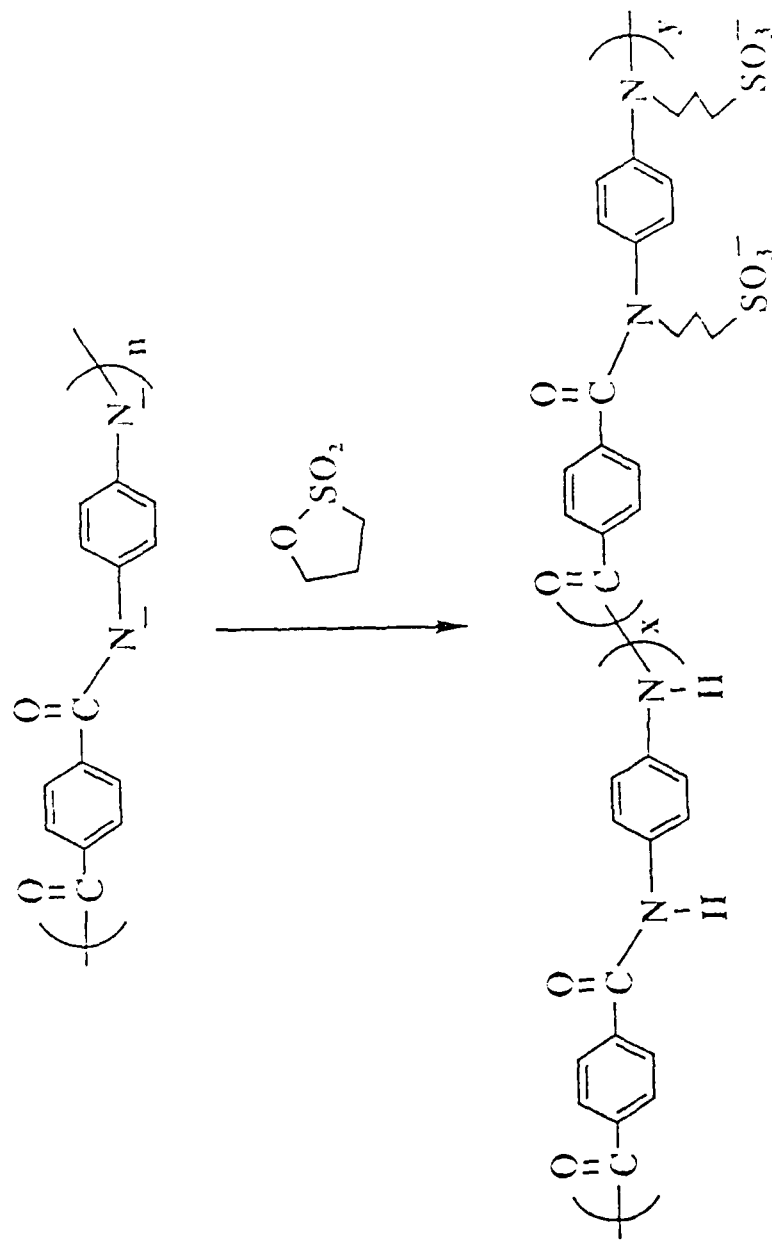
4



## Scheme I



Scheme II



Scheme III

