Use of Tanninsulfonic Acid in the Synthesis of Water-Dispersible Polyaniline

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ABSTRACT: Polyaniline was synthesized in the presence of tanninsulfonic acid to yield a product tanninsulfonic acid-doped polyaniline (TANI-PANI) that is water-dispersible. Several samples ranging from 0 to 70% tanninsulfonate (TS) were prepared. These samples were then evaluated for differences in dispersibility, particle size, and conductivity. As the percent of TS in the samples was increased, the water-dispersibility of the TANI-PANI also increased. The particle size of the samples as well as the conductivity of the samples decreased with increasing percentages of TS in the samples. After extensive washings, however, the conductivity remained fairly constant ($\sim$0.5 S/cm) regardless of the amount of TS in the samples. Additionally, elemental analysis, TGA, and IR data were used to demonstrate that the TS may be grafted to polyaniline during the synthesis of TANI-PANI. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2113–2119, 2007

Key words: FTIR; conducting polymers; NMR; graft copolymers; particle size distribution

INTRODUCTION

Polyaniline is an intrinsically conductive polymer (ICP) that has the potential for use in a number of applications such as light emitting diodes,[1] rechargeable batteries,[2] electromagnetic interference shielding,[3] and smart windows.[4] One particularly promising application is in the area of corrosion prevention. It has been found that ICPs, such as polyaniline, can inhibit corrosion when applied to a metal surface.[5,6]

Conventional polyaniline, however, is limited by its processability.[7] Emeraldine base, the nonprotonated, nonconducting form of polyaniline, for example, has only limited solubility in organic solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, and N,N-dimethylformamide. Polyaniline doped with most acids is insoluble in common organic solvents.

Several methods have been developed to help improve the processibility of polyaniline. One involves the use of acids that generate soluble counter-ions when the base form of the polymer is doped. A variety of sulfonic acids have been used as dopants because of the solubility of the sulfonate counter-ion.[8] In addition to monosulfonic acids, polysulfonic acids have also been used as dopants.[9] Tanninsulfonic acid is a poly-sulfonic acid that can be used in the synthesis of polyaniline to form a water-dispersible product, tanninsulfonic acid-doped polyaniline (TANI-PANI). It is highly dispersible in polar aprotic solvents such as dimethyl sulfoxide and tetrahydrofuran in its conducting state. This is because of the high solubility of the tanninsulfonate (TS) incorporated as a dopant.[10,11]

Tannins are polyphenols found in the vascular tissue of plants.[12] Plant tannins bind proteins to form both insoluble and soluble tannin–protein complexes. The insoluble tannin–protein complex is the driving force behind the tanning process in which animal hides are turned into leather.[13] The phenolic groups on tannin are easily oxidized to form semiquinones and quinones. This oxidized form of tannin is electrophilic and forms covalent bonds with nucleophiles, such as the amino group of proteins.[14] Sulfonation, or sulfomethylation of these tannins, an example of which is shown in Figure 1, results in a highly water soluble product. These derivatized tannins are readily available from industries that deal with oil recovery.

Several graft copolymers of aniline and/or tannin-like polymers have previously been prepared. Jo and coworkers have shown that aniline can be grafted onto poly(styrenesulfonic acid-co-aminostyrene), resulting in a polymer with improved solubility.[15] Yang et al. also demonstrated improved solubility when grafting chitosan and polyaniline.[16] Several researchers have also reported the successful grafting of lignin, which has a structure similar to tannin, to various copolymers.[17–22] Additionally, Joseph and coworkers have demonstrated that polymers formed via free radical
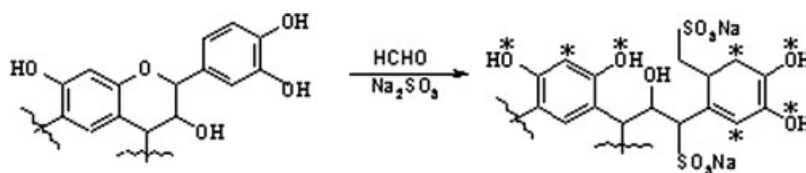
Figure 1 A typical sulfonated/sulfomethylated tannin monomer unit. The asterisks denote possible aniline binding sites.

mechanisms can be covalently grafted to tannins, resulting in a homogenous dispersion of the polymer in water.[23] Possible sites of grafting polyaniline to the TS are indicated by an asterisk in Figure 1.

This article presents evidence in the form of elemental analysis, TGA, and IR data that suggests that tanninsulfonic acid not only acts as a dopant but also grafts to the polyaniline during the synthesis of TANI-PANI.

EXPERIMENTAL

Materials

Sodium persulfate (98%), aniline (99%), iron(II) sulfate heptahydrate (ACS reagent), sulfuric acid (95–98%), hydrochloric acid (37%), sodium hydroxide pellets, and potassium bromide (FTIR grade) were purchased from Sigma–Aldrich (St. Louis, MO). The D3 tanninsulfonate was provided by CP Chem (Orfom Grade D3 Tanninsulfonate) (Houston, TX). All reagents were used without further purification, except aniline, which was distilled once prior to use.

Synthesis of emeraldine base polyaniline

A 4.00-mL sample of distilled aniline was added to 134 mL of deionized (DI) water, which was adjusted to a pH of 4.00 using concentrated hydrochloric acid. After the addition of aniline, the solution was brought back to pH 4.00 using hydrochloric acid. The solution was then oxidatively polymerized at 0°C using sodium persulfate as the oxidant in a 1 : 1.1M ratio of aniline to sodium persulfate. After 4 h, sodium hydroxide was added to bring the pH to 11. The solution was then taken through a series of washings as described in The Removal of Excess Tanninsulfonic Acid section to keep the preparation as close to the TANI-PANI preparation as possible. After the washings were complete, the sample was collected through vacuum filtration and dried in a vacuum oven.

Synthesis of tanninsulfonic acid doped polyaniline

TANI-PANI was prepared by dissolving sodium tanninsulfonate (between 0.4542 g for 10% and 9.5389 g for 70%) in 134 mL of DI water. The sodium salt was then protonated by titration with a strong acid, such as hydrochloric acid or sulfuric acid, to bring the pH of

the solution to 4.00. To this aqueous solution of tanninsulfonic acid was added 4.00 mL of distilled aniline. The solution was then oxidatively polymerized at 0°C by adding 11.48 g of sodium persulfate as the oxidant (1 : 1.1M ratio between aniline and the persulfate). After 4 h, the product was collected by vacuum filtration and washed with DI water.

Although the majority of polyaniline syntheses are performed in environments with a starting pH of less than 1, TANI-PANI is synthesized at an initial pH of 4 to reduce the competition between the sulfuric acid (or hydrochloric acid) and the tanninsulfonic acid as the dopant. Preparing the solutions at a pH 4 would ensure that the majority of the acid initially available for doping is the tanninsulfonic acid. A consequence of the decomposition of persulfate is that additional acid is introduced into the system, resulting in a pH less than 1.

Samples with various ratios of tanninsulfonate (TS) to aniline were prepared. The percentage of TS in the starting reaction mixture for these samples ranged from 10 to 70% by weight based on total dry weight of aniline and TS.

Removal of excess tanninsulfonic acid

After the TANI-PANI reaction had progressed for 4 h, the pH of the reaction mixture was brought to 11.00 using sodium hydroxide. The dedoped TANI-PANI was then washed successively with 400 mL of (3%) sodium hydroxide solution, 200 mL of DI water, 200 mL of 1.2M hydrochloric acid or sulfuric acid, 200 mL water, and 200 mL sodium hydroxide. The filtered solid was then redispersed in 400 mL sodium hydroxide solution using a high speed homogenizer (18,000 rpm) for 5 min. The washing was then repeated an additional 6 times, followed by redispersion. After the seventh washing, the product was washed with 2000 mL of DI water. The precipitate was collected and vacuum dried. The dried product was pulverized and sent to a laboratory for elemental analysis.

Synthesis of ex-situ doped tanninsulfonic acid doped polyaniline

Freshly prepared tanninsulfonic acid was added to a wet cake of emeraldine base and was stirred overnight. The amount of TS was equivalent to that added to the

20% TANI-PANI (meaning 20% TS to 80% aniline before synthesis). Tanninsulfonic acid was prepared by passing a solution of TS through a column containing Dowex cation exchange resin.

FTIR analysis

FTIR analysis was performed on KBr pellets using a Nicolet Magna 550 FTIR.

Conductivity studies

Conductivities of pressed pellets were measured using an Alessi 4-point probe in conjunction with a Keithly voltmeter and programmable current source.

Thermogravimetric analysis

TGA was performed on the samples using a Mettler-Toledo TG50 controlled by a PC. Approximately 30 mg of sample in a crucible was placed in the oven. The samples were heated from 40 to 1000°C at 10°C/min in air.

Elemental analysis

C, H, N, and S elemental analyses were performed by Galbraith Laboratories (Knoxville, Tennessee).

Particle size analysis

Particle size analysis measurements were performed using Leeds and Northrup Microtrac FRA 9200 Series Instrument and Programs. Several 100-mL samples of a 0.02% solution were prepared for each of the TANI-PANI samples synthesized. The solutions were each blended at 18,000 rpm for 60 s. Particle size analyses were performed in triplicate on each sample and the average of these 3 runs was recorded.

Nuclear magnetic resonance

Proton NMR spectra were obtained using a Bruker 200 MHz superconducting multinuclear nuclear magnetic resonance (NMR) spectrometer. Solutions were prepared by dissolving 0.100 g of sample in 1.00 mL of deuterated dimethylsulfoxide (DMSO-d_6) containing a 1% (v/v) TMS. After thorough mixing, the solution was filtered through glass wool and collected in an NMR tube.

RESULTS AND DISCUSSION

Characterization of doped TANI-PANI samples

Each synthesized sample was evaluated for differences in dispersibility, particle size, and conductivity. Dispersibility was visually observed to improve with increasing amounts of TS. This was demonstrated qualitatively by dissolving approximately equal amounts of wet TANI-PANI (percent solids in wet sample had previously been determined) containing various percentages of TS. There was a noticeable difference between samples containing 50 and 60% TS in the TANI-PANI preparation. Although the samples containing 10–50% dispersed readily in the water, they completely precipitated after a few days. The 60% TANI-PANI sample, however, showed no signs of precipitation even after months of remaining undisturbed. To further understand this phenomenon, samples containing 50, 52, 54, 56, 58, and 60% TS were synthesized. Dispersions were prepared as described earlier and left undisturbed for 1 week. The samples containing 50 and 52% TS completely precipitated, while the samples containing 54% and greater TS exhibited significant green color in the supernate as shown in Figure 2. Complete precipitation of these samples was never observed.

For a quantitative comparison, particle size analysis was performed on each of the samples. The results of these analyses are shown in Figure 3. As expected, when the amount of TS is increased from 20 to 60% in
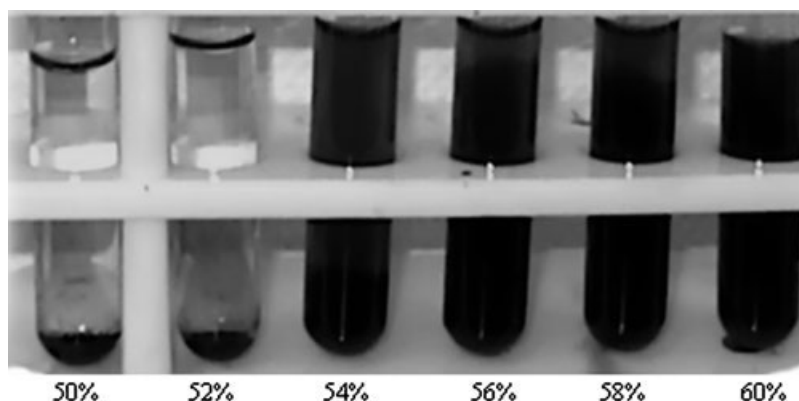
Figure 2 Dispersibility of TANI-PANI samples after being allowed to stand for over a week in test tubes.
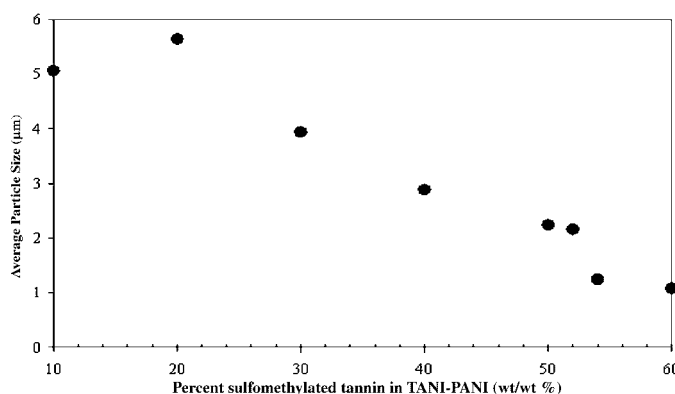
Figure 3 Various percentages of TANI-PANI are shown versus the average particle size of a 0.02% solution.

the samples, the particle size decreases. A significant drop in particle size occurred between the samples containing 52 and 54% TS. These results indicate a significant change in the physical nature of the TANI-PANI moiety.

The distribution profile, which gives the best picture of what is occurring in the solution, also changes considerably with increased TS, as shown in Figure 4. The profile of the sample containing 10% TS (bottom panel of Fig. 4) shows a trimodal distribution that begs explanation. The profiles for the samples containing 20 and 30% TS indicate a bimodal distribution. It is suspected that these 2 peaks correspond to 2 distinct polymeric species: homopolymer doped by sulfuric acid and TS grafted/doped PANi. The second peak, which has a larger particle size, is attributed to the H_2SO_4 doped PANi, since it is less dispersible. The first peak is due to the more dispersible TANI-PANI. This is further confirmed by the magnitude of the 2 peaks. For the sample containing 20% TS, the second peak is larger. For the sample containing 30% TS, however, the first peak is the larger, indicating that with increasing TS TANI-PANI becomes the dominant species. This conclusion is supported by the monomodal distribution of the remaining samples containing greater amounts of TS. It can be inferred from the monomodal distribution, as well as the decreasing particle size, that these samples contain only TANI-PANI.

Conductivities were also determined for each of the samples as shown in Figure 6. With the exception of an initial increase in conductivities over the PANi sample, conductivities decreased with increasing amounts of TS.

Determination of grafting

Although experimental observations indicate that the incorporation of TS results in a more dispersible PANi, further experiments were performed to determine whether the TS was permanently incorporated into the polymeric species. Elemental analysis was

performed for each sample to identify the amount of TS that was grafted to the polyaniline. The samples were prepared in the same way as the other samples,
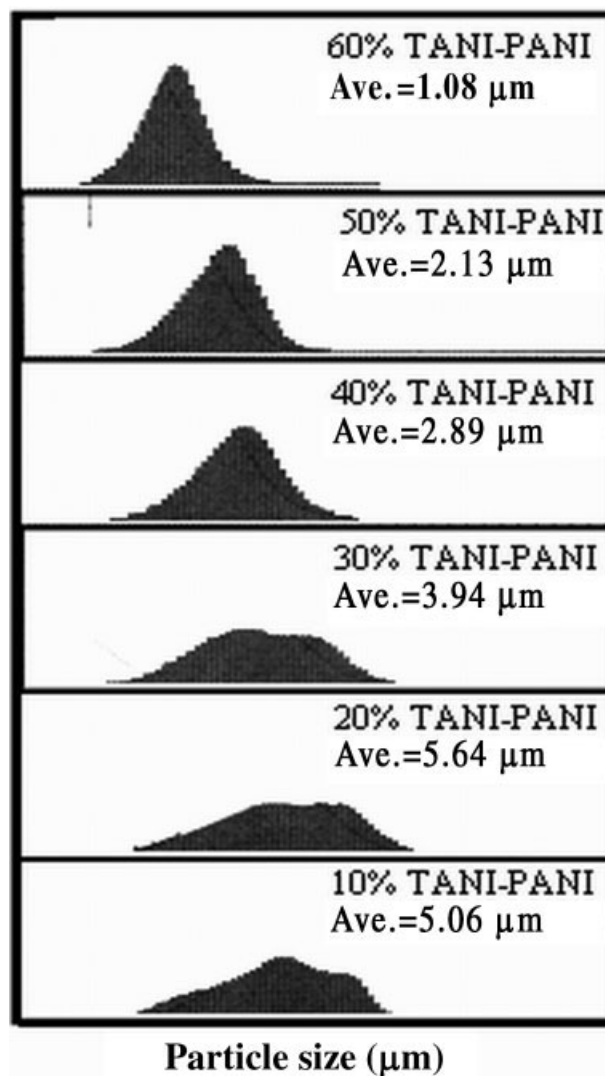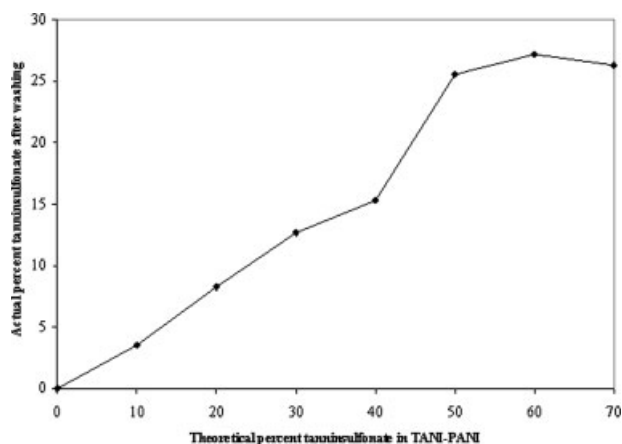

Figure 4 Profiles of the particle size analysis of the various percentages of D3 TANI-PANI.

TABLE I
Elemental Analysis Results of the TANI-PANI

Sample	% Sulfur	% Carbon	% Hydrogen	% Nitrogen
PANi	0.23	74.95	4.94	14.48
TANI-PANI (%)				
10	0.31	41.35	7.62	7.92
20	0.93	69.99	4.63	13.23
30	0.84	46.78	6.62	8.46
40	1.33	64.01	4.13	11.41
50	1.91	62.00	4.31	10.38
60	2.00	63.32	4.40	10.27
Comparison	0.23	73.42	4.93	14.09

but then washed thoroughly as described in the experimental section using acid, base, and water to ensure that all impurities and dopants were removed. These dried dedoped samples were then sent off for elemental analysis and the results are shown in Table I. The only sources of sulfur are the oxidant and the TS while the only source of nitrogen is the polyaniline. To account for the amount of sulfur present from the oxidant, elemental analysis was performed on a PANi sample prepared containing no TS. A plot of the sulfur to nitrogen ratio (S/N) shows an excellent correlation which increases with increasing amounts of TS up to 50%, as shown in Figure 5. The 50% through 70% ratio, however, remains fairly constant, showing that a maximum amount of TS has been incorporated. The S/N ratio was used to account for varying amounts of water present in the samples as indicated by TGA.

It is possible that some TS remaining in the samples after washing is a result of physical interactions and not grafting. To determine the magnitude of this interaction, a control sample in which the TS acted only as a dopant was prepared (Comparison in Table I). This sample was synthesized by adding freshly prepared tanninsulfonic acid to dedoped HCl-PANi. This solution was allowed to stir overnight to ensure maximum doping. The amount of tanninsulfonic acid added was equivalent to the amount of TS present in the synthesis of 20% TANI-PANI. Elemental analysis confirms that only a very small amount of TS remains in the sample after the washings are complete. The S/N of the comparison is slightly higher (0.01632) than that of pure PANi (0.01588) but considerably lower than that of the 10% TANI-PANI sample (0.03914). This indicates that only a small amount stays bonded throughout all the washings when it is acting as a dopant. The amount of TS remaining in the TANI-PANI samples after 7 washes, therefore, must be due to something more than the TS acting as a dopant.

Elemental analysis also indicates that there is a maximum amount of TS that can be grafted onto PANi. This maximum is reached when greater than 50% TS is used in the reaction mixture. The presence of this maximum precludes occlusion from being the cause of the persistent presence of TS in the washed samples. Particle size analysis data that was previously shown in Figure 4 supports the results from elemental analysis. The particle size distribution profile of the samples above 40% all show a monomodal distribution, indicating a single grafted polymer species.

The conductivities of the HCl redoped samples are shown in Figure 6. Samples that were only washed once with DI water demonstrated a fairly predictable trend of decreasing conductivities (Fig. 6, dashed line) with increasing amounts of TS. When the samples were washed 7 times *vide supra*, however, this trend is disrupted and the conductivities remain fairly constant (Fig. 6, solid line) with increasing amounts of TS. The decrease in conductivities for the samples washed only with water is likely due to excess TS present in the
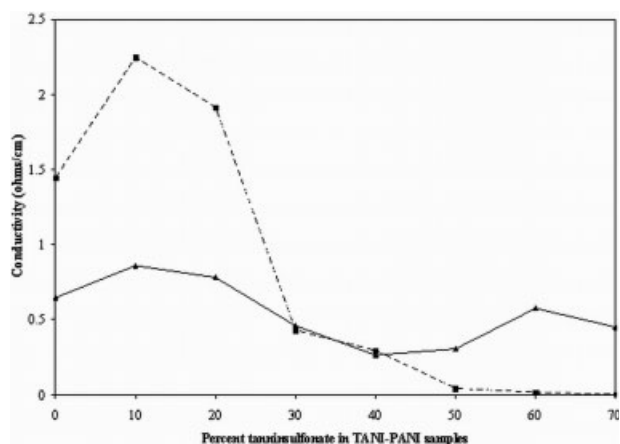

Figure 5 The percent tanninsulfonate remaining in the washed samples as calculated from the elemental analysis results versus the percent tanninsulfonate added in the synthesis.

Figure 6 Conductivities of various percent tanninsulfonates after being washed once with water (dashed line) and washed seven times (solid line) as explained in the experimental section.
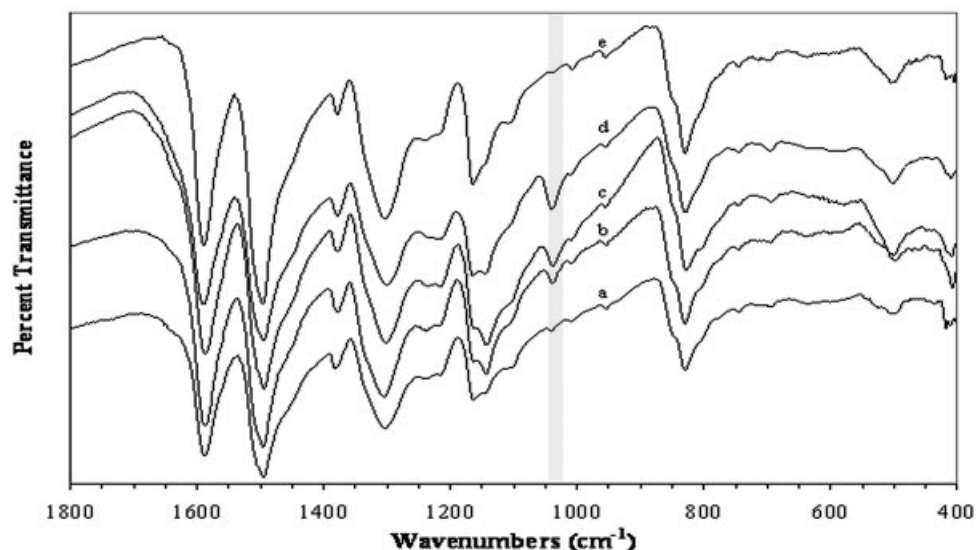
Figure 7   Normalized and offset IR spectra of (from bottom to top) (a) PANI, (b) 20% TANI-PANI, (c) 40% TANI-PANI, (d) 60% TANI-PANI, and (e) TS PANI (control). The 1030 cm^{-1} peak is highlighted showing increasing amounts of tannin.

sample. Tanninsulfonate is an insulator and should, therefore, decrease the conductivity. After repeated washings, however, all the excess TS should have been removed. This, in turn, should allow the conductivities to remain fairly constant with increasing amounts of TS. The overall low conductivities of the washed samples are most likely a result of inefficient redoping.

Additional evidence of grafting is shown in the infrared spectrum of the dedoped samples (Fig. 7). The peak at 1030 cm^{-1} is attributed to a sulfur–oxygen stretch that is present in TS. A very small peak is seen at 1030 cm^{-1} for the PANI sample presumably due to the oxidant [Fig. 7(a)]. The remaining samples show a definite increase in absorbance at 1030 cm^{-1} for the 20, 40, and 60% TANI-PANI samples [Fig. 7(b–d)]. The spectrum for the comparison sample in which TS was only a dopant is also shown [Fig. 7(e)]. The very small amount remaining is evidenced by the small peak at 1030 cm^{-1}. The peak is smaller than that of the PANi sample synthesized with no TS. This, in additional to the elemental analysis results, indicates that the tanninsulfonic acid is not acting only as a dopant, but actually is grafted to the PANi.

Proton NMR data was also obtained for various samples. Unfortunately, however, the D3 tanninsulfonate is virtually transparent, even though it has a large number of hydrogens. Small peaks are observed at 1.8 and 6.5 ppm. Both these peaks are masked by the PANi which also reveals peaks in both of these locations.

CONCLUSIONS

The incorporation of TS during the synthesis of PANi results in a water-dispersible conducting polyaniline.

Dispersibility of this polymer was found to increase as the amount of TS in the reaction mixture was increased from 0 to 54%. After 54% no appreciable improvement was observed.

Conductivities, on the other hand, are observed to decrease for the unwashed polymer with increasing amounts of TS as a result of its inherent insulating properties. When the polymers were washed repeatedly with acid and base to remove any untreated TS, however, the samples demonstrated consistent conductivities after redoping.

Finally, through FTIR and elemental analysis of the thoroughly washed samples, it was shown that the TS is acting as a dopant. Also, there is a significant permanent incorporation of the TS presumably through a grafting mechanism. Results indicate that a maximum of ∼ 50% TS can be incorporated.

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