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Articles

Highly Conductive and Thermally Stable Self-doping Propylthiosulfonated Polyanilines

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ABSTRACT: A new type of highly conductive self-doping polyaniline, MPS−Pan, containing a sulfonic acid moiety covalently bonded to the polymer backbone through an electron-donating propylthio linkage has been successfully prepared via a novel concurrent reduction and substitution route. At a similar self-doping level, the resultant MPS−Pans displayed much higher conductivity than the corresponding sulfonated polyaniline (S−Pan). Furthermore, for fully doped samples, contrary to the trend of decreasing conductivity with the sulfonation degree in S−Pan, the conductivity of MPS−Pan was found to increase with its substitution degree. These results agreed with the expectation that electron-deficient charge carriers (e.g. semiquinone radical cations) on acid-doped polyaniline chains will be better stabilized by the electron-donating alkylthio substituent. Surprisingly, TG and XPS studies showed that MPS−Pan was thermally much more stable than S−Pan, with S−Pan starting to lose its sulfonic acid dopant at 185 °C, while MPS−Pan remained intact up to ∼260 °C.

Owing to their unique electrooptical properties and market potential, polyanilines have been one of the recent focuses in the field of conducting polymer research.[1] The insulating emeraldine base form of polyaniline can be conveniently doped with a simple protonic acid (e.g. HCl) to form a highly conductive emeraldine salt (1−5 S/cm).[2] However, the susceptibility of the labile acid dopant to evaporation and rain flushing loss is detrimental to long term thermal and environmental stabilities. Therefore, a self-doping polyaniline[3−6] that contains a stable/immobile, covalently bonded acid moiety on the backbone is highly desired.

Self-doping polyanilines can be prepared either from the polymerization of an acid-containing aniline monomer[3] or by a postreaction to attach an acid moiety directly to the phenyl rings (via ring-sulfonation)[5,6] or indirectly through an alkyl or aryl linker to the nitrogen sites[4] via nucleophilic substitution. Despite their improved thermal stability and water resistance,[5] these self-doping polyanilines have rather poor conductivity (10^{-2} to 10^{-9} S/cm)[3,4] with the exception of ring sulfonated polyaniline (S−Pan).[5,6] Regarding S−Pan, wide discrepancies in conductivity have been reported, with values ranging from 0.1 S/cm to less than 10^{-2} S/cm for a 50 mol % self-doping level sample[5] and from 1 to 0.08 S/cm for an unusually high (75 mol %) self-doping level sample.[6] Such discrepancies may be caused by the rather complicated nature of the sulfonation reaction, which involved a highly reactive (hence nonselective) reagent, nonspecific reaction sites, and the following contemporaneous events: the slow dissolution of the polymer sample in the concentrated sulfuric acid medium; a very fast concurrent sulfonation reaction with the SO_3 (via rather complicated reaction patterns including homogeneous, heterogeneous, and multiple sulfonation); and a hydrolysis decomposition[7] of the polymer backbone by the strong acid. Thus, the sulfonation results should be highly sensitive to the reaction conditions and the history of the reaction process, which could lead to a wide variety of structures between individual polymer chains, regarding the degree of backbone and phenyl-ring sulfonation as well as the distributions of sulfonic acid groups for a given average sulfonation degree. As a result, it will be extremely difficult to reproduce samples of the same quality among different research groups or operators, which, in turn, will affect the conductivity being reported. Therefore, it is highly desirable to devise a new and better-controlled method for the consistent preparation of self-doping polyanilines.

Recently, we have discovered an interesting concurrent reduction and substitution (CRS) method[8] that can be used to derivatize the polyaniline backbone with various alkylthio substituent groups without adversely affecting its conductivity.[9] For example, such a derivatized polyaniline containing 38 mol % of the bulky butylthio group was found to have a reasonable conductivity of 3−4 S/cm, similar to that for its parent unsubstituted polyanilines (2−3 S/cm).[9] Interestingly, the substitution reaction was also found to occur only at the diiminoquinoid rings, a structure believed to be regularly distributed among the nonreactive diaminobenzenoid rings. The introduction of a substituent will reduce and convert a diiminoquinoid ring into an unreactive derivatized diaminobenzenoid ring. Since the

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initial amount of diiminoquinoid ring can be conveniently controlled by the oxidation state of the polyaniline sample, thus, the degree of substitution can also be readily controlled. We believe this novel CRS method is an almost ideal synthetic tool for the preparation of a new type of self-doping polyaniline having a very ordered structure, a critical key for enabling a conducting polymer to have a high conductivity.

We report herein the preparation and characterization of a new self-doping polyaniline, MPS−Pan (mercaptopropanesulfonic acid substituted polyaniline), via the CRS method by derivatizing polyaniline emeraldine base with MPS. Interestingly, the resultant MPS−Pans are found to be much more conductive than the corresponding sulfonated polyanilines (at the same self-doping levels), and they also possess higher thermal stability.

Experimental Section

Free-standing polyaniline emeraldine base films (∼10 μm thick) used for this work were cast from a solution of 0.48 wt % polyaniline emeraldine base in NMP, following a literature method[10] with slight modifications. Polyaniline emeraldine thin films on Pt or ITO (indium−tin oxide) glass electrodes were grown in a three-electrode electrochemical cell, using Pt or ITO glass plates as working electrodes, a platinum plate as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. All the electrochemical polymerization reactions were controlled with a potentiostat (EG&G 273) under a constant current density of 13.3×10^{-6} A/cm^2 for 25 min, in a 0.5 M H_2SO_4 aqueous solution that contained 0.1 M aniline. The polyaniline thin film thus obtained on the working electrode was further dedoped by 5% aqueous Na_2CO_3 to convert it into emeraldine base form. The thickness of the film (of about 100 nm) was determined by SIMS (secondary ion mass spectroscopy) depth-profiling and an α-step.

A typical self-doping polyaniline, mercaptopropylsulfonic acid-substituted polyaniline (MPS−Pan), was prepared by reacting a polyaniline emeraldine base film with 0.1 M 3-mercapto-1-propanesulfonic acid sodium salt (MPS−Na) in MeOH under a N_2 atmosphere at room temperature for appropriate time, for example, 14 h, to allow for the completion of the CRS reaction. A catalytic amount of protonic acid, for example, 0.01 M acetic acid, was sometimes added to accelerate the reaction. The resultant self-doped polyaniline film was thoroughly rinsed and soaked with methanol (to remove any MPS−Na residue), followed by soaking in 5% aqueous Na_2CO_3 (to remove the acetic acid catalyst and/or any nonbonded 3-mercapto-1-propanesulfonic acid residue), deionized H_2O (to remove Na_2CO_3), and dried acetone (to remove H_2O), before being blown dried with nitrogen gas to remove the acetone.

The attenuated total reflectance infrared (ATRIR) spectra of the resultant polyaniline films on the Pt electrode were obtained with a Perkin-Elmer 2000 FTIR spectrometer equipped with a Graseby Specac single reflection diamond ATR accessory under a nitrogen atmosphere. The active area of the diamond contact probe was 0.6 mm × 0.6 mm. By assigning the refractive index of the polyaniline films as 1.5, the corresponding theoretical surface penetration depths of the incident IR beam, from 400 to 4000 cm^{-1}, were calculated and found to be from 2.3 to 0.23 μm. A constant clamping pressure, applied by using a torque wrench set at 60 cNm/m, was employed to mount all polyaniline film specimens, to ensure good and consistent surface contact between the polyaniline film and the diamond probe head. XPS (X-ray photoelectron spectroscopy) spectra of the resultant polyaniline films were collected with a Physical Electronics ESCA PHI 1600 spectrometer, using Mg Kα as X-ray source. The excitation area was 800 μm × 800 μm; the step-sizes for the survey and the chemical state spectra were 1.6 and 0.025 eV, respectively. SIMS analysis of the resultant polyaniline films was performed on a Cameca IMS-4f instrument, using Cs as the primary ion source. A raster area of 250 μm × 250 μm and an analysis area of 60 μm × 60 μm were employed. UV−vis−NIR spectra of the polyaniline films on ITO glass electrodes were obtained, using a Hitachi U3501 spectrophotometer. Conductivity measurements were made on $HClO_4$-doped or self-doped samples using a standard four-in-line probe method[11] with a constant current source (Keithley 220) and a multimeter (Keithley 196). The fully doped samples were prepared by soaking the above substituted and unsubstituted polyaniline films twice with an aqueous solution of 1 M $HClO_4$ for 1 h; the self-doped samples were prepared by soaking the fully doped polyaniline films twice with deionized water for 1 h to remove the $HClO_4$ external dopant. Thermogravimetric analysis (TG) was performed with a Seiko Instruments model SSC5200 analyzer. Samples for TG studies were heated from 30 to 1000 °C with a heating rate of 10 °C/min using nitrogen or air, at a flow rate of 100 mL/min.

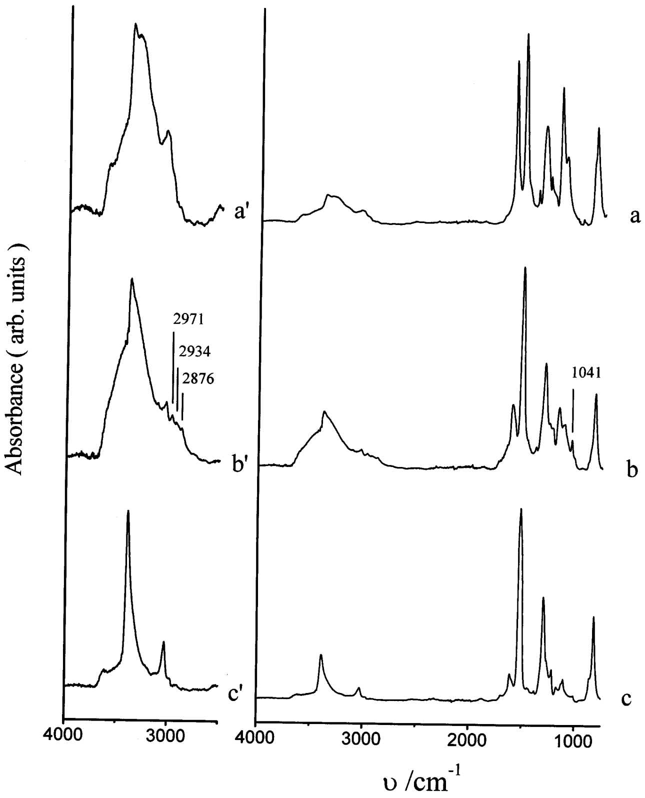


Figure 1. ATRIR spectra for the polyaniline coated electrodes: (a) before and (b) after soaking treatment with a 0.1 M methanolic solution of MPS−Na for 14 h; (c) as in its fully reduced leucoemeraldine state. Traces a′−c′ show the corresponding enlarged 2500−4000 cm^{-1} region (with arbitrary magnifications).

Results and Discussion

Preparation and Characterizations of MPS−Pan.

The new self-doping MPS−Pan was prepared by soaking a polyaniline emeraldine base film in a 0.1 M methanolic solution of mercaptopropanesulfonic acid sodium salt (MPS−Na) for 14 h, after which the polyaniline film turned from blue to neutral gray, as the polyaniline backbone converted from blue emeraldine base form to colorless leucoemeraldine base form. Further studies with ATRIR and XPS indicated that the polyaniline backbone has been not only reduced but also substituted with a propylthiosulfonate group. The ATRIR spectrum (Figure 1b) of the resulting polyaniline film clearly showed reduction in the intensities of the diiminoquinoid ring associated peaks at 1600 cm^{-1} (C=C stretching[11]), 1169 cm^{-1} (diiminoquinoid ring

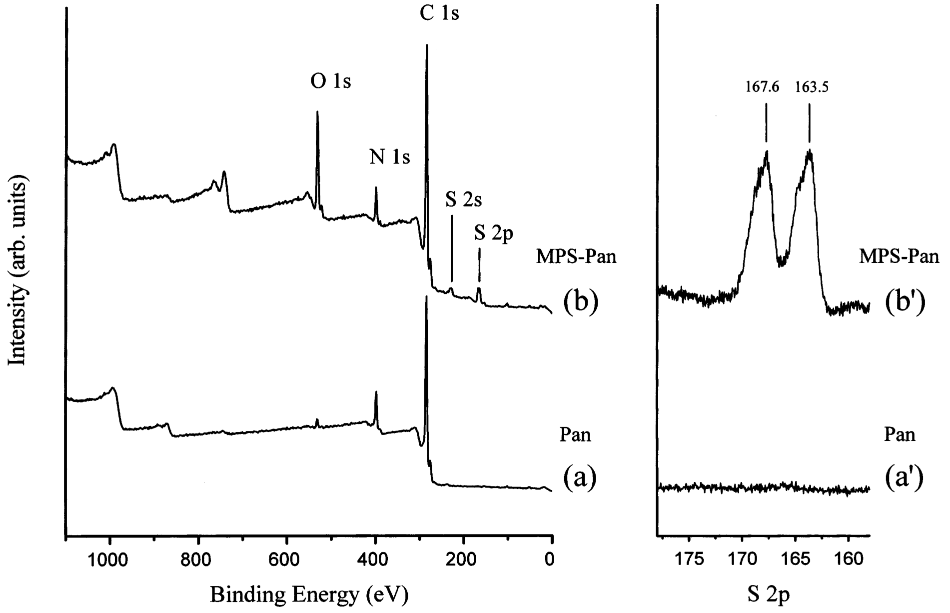


Figure 2. XPS spectra for (a) the original undoped polyaniline film and (b) the polyaniline film after soaking treatment with a 0.1 M methanolic solution of MPS−Na for 14 h. The chemical state spectra of S 2p for the corresponding polyaniline films are displayed in a′ and b′.

vibration[12]), and 820 cm^{-1} (C−H out-of-plane vibration of the 1,4-ring[12]). A similar intensity reduction of these three peaks has also been observed when polyaniline emeraldine base (Figure 1a) was reduced by hydrazine to leucoemeraldine base (Figure 1c). The same ATRIR spectrum of the MPS−Na treated film also showed the presence of a new peak at 1041 cm^{-1}, attributable to the symmetric SO_3 stretching of the newly introduced MPS substituent.[13] The position of this new peak was consistent with the original thiol MPS−Na (1062 cm^{-1}) and sulfonated polyaniline (1080 cm^{-1})[5a] Also shown in the same IR spectrum were three barely detectable small new peaks at about 2971, 2934, and 2876 cm^{-1}, which can be attributed to the asymmetric (2971, 2934 cm^{-1}) and symmetric (2876 cm^{-1}) $-CH_2-$ stretching of the MPS substituent.[13] Similar weak C−H stretching peaks for MPS−Na were observed at 2974, 2939, and 2860 cm^{-1}, with intensities less than one-tenth of that for its SO_3 asymmetric stretching peak at 1194 cm^{-1}.

The presence of the new sulfonic-acid-containing alkylthio substituent in the resultant polyaniline film was also confirmed by X-ray photoelectron spectroscopy (XPS). In addition to the original C 1s (with a binding energy of 284.6 eV) and N 1s (399.2 eV) lines, the XPS survey spectrum of the MPS−Na treated film (Figure 2b) showed a newly appearing O 1s line at 531.5 eV and a S 2p line at around 160−170 eV. The more detailed S 2p chemical state spectrum for the same film (Figure 2b′) indicated that there were two new S $2p_{3/2}$ lines appearing at 163.5 and 167.6 eV, attributable to the sulfide linkage and the sulfonic acid end group, respectively. [8,9,14]

Results from a secondary ion mass spectroscopy (SIMS) depth-profiling study (Figure 3) indicated a homogeneous distribution of the alkylthio substituents throughout the thickness of all films, including a 10 μm free-standing film. Thus, the substitution degrees, as measured by XPS, were also valid for the bulk film.

These reduced and derivatized polyanilines can be reoxidized by air or via a precisely controlled electrochemical means. Figure 4 displays the UV−vis−NIR spectra for a MPS−Pan thin film on an ITO glass electrode, after being electrochemically forced at different oxidation states (e.g. 0.5, 0.3, 0.1, or −0.1 V vs SCE) in 0.5 M aqueous H_2SO_4 and then undoped with 5% aqueous Na_2CO_3. The spectra all showed a typical $\pi-\pi^*$ transition band of the benzenoid rings[15a] at ∼328−336 nm and an exciton band of the quinoid rings (an excitation transition between a benzenoid ring and a quinoid ring)[15b] at ∼636−652 nm. As the polyaniline backbone became more reduced, the intensity of the exciton band decreased in accordance with the reduced number of quinoid rings; and the peak wavelengths of both $\pi-\pi^*$ transition and exciton bands were simultaneously red-shifted in accordance with the expectation that a more reduced polyaniline backbone would have a higher electron density. When the MPS−Pan was at the oxidation state of 0.3 V, the exciton bands were located at 334 and 648 nm, respectively, which were both red-shifted from the corresponding bands of its parent unsubstituted polyaniline (330 and 640 nm) at

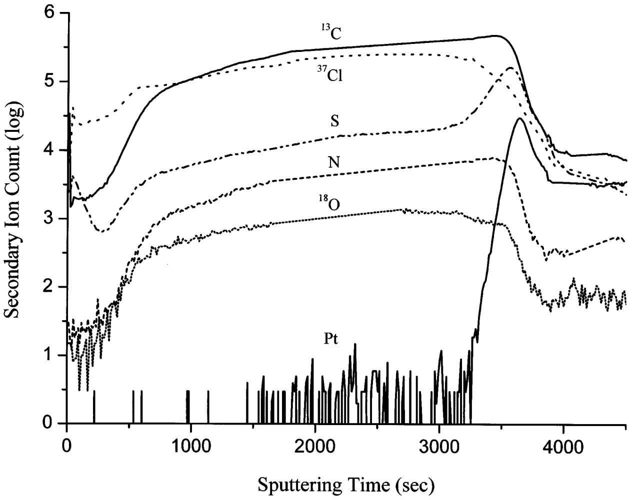


Figure 3. Secondary ion mass spectrum of a polyaniline film (ca. 10 μm thick and 1 cm × 1 cm in size) after soaking treatment with a 0.1 M methanolic solution of MPS−Na for 14 h. The film specimen was fixed on a Pt plate by applying a conductive carbon paste to the four corners of the film.

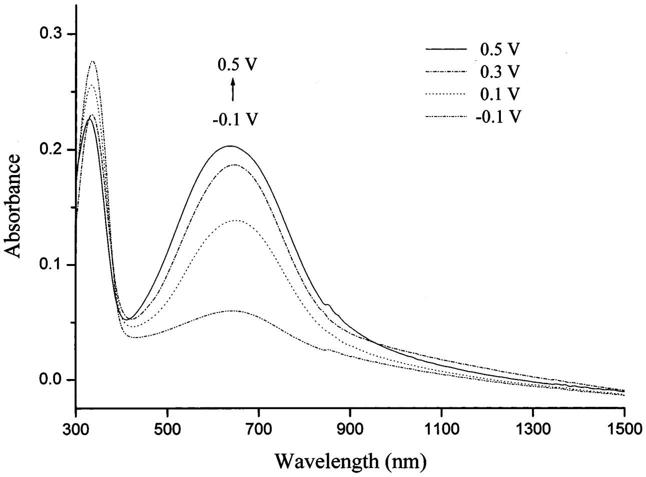


Figure 4. UV–vis–NIR spectra of undoped MPS–Pan (MPS–Pan-14) films on ITO glass at different oxidation potentials (vs SCE).

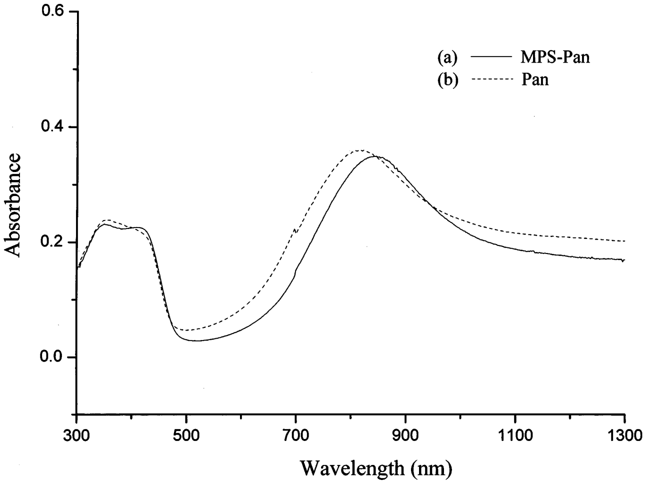


Figure 5. UV–vis–NIR spectra of H_2SO_4-doped films (on ITO glass) of (a) MPS–Pan (MPS–Pan-14) and (b) its parent unsubstituted polyaniline.

the same oxidation state. A similar red-shifting effect has also been previously observed for the methoxy-substituted[16] and butylthio-substituted[9] polyaniline. The results suggested that addition of these electron-donating propylthiosulfonate groups indeed increased the electron density of the polyaniline backbone. When the above 0.3 V MPS–Pan was redoped in a 0.5 M aqueous H_2SO_4 (Figure 5), two new polaron band transitions[17] appeared at ~423 and 845 nm at the expense of the exciton band, while the $\pi-\pi^*$ transition band red-shifted to 352 nm. Under the same conditions, the parent unsubstituted polyaniline showed the corresponding two polaron bands (421, 830 nm) and $\pi-\pi^*$ transition at 352 nm. The fact that both the MPS–Pan and the parent polyaniline showed a similar typical localized polaron band suggests that the original compact coiled chain conformational structure of the parent unsubstituted polyaniline film was essentially retained during the solid-state CRS reaction in the absence of any effective secondary dopant.[18]

The cyclic voltammogram, scanned between −0.1 and 0.6 V (vs SCE) at 30 mV/s in 0.5 M H_2SO_4 aqueous solution, for the resultant MPS–Pan (Figure 6) showed a quasi-reversible redox process similar to that of unsubstituted polyaniline. Unlike the sulfonated polyaniline (S–Pan), which, owing to the electron-withdrawing effect of the attached sulfonic acid group, has an oxidation potential $E°$ (0.163 V) significantly higher (by ~0.064 V) than that of its parent unsubstituted polyaniline (0.099 V), the oxidation potential $E°$ of the resultant MPS–Pan (0.098 V) was however found to be very close to that of the parent polyaniline (0.099 V). These results confirmed that the electron-withdrawing influence of the sulfonic acid group could be avoided by placing a propylthio spacing group between the polymer backbone and the sulfonic acid group.

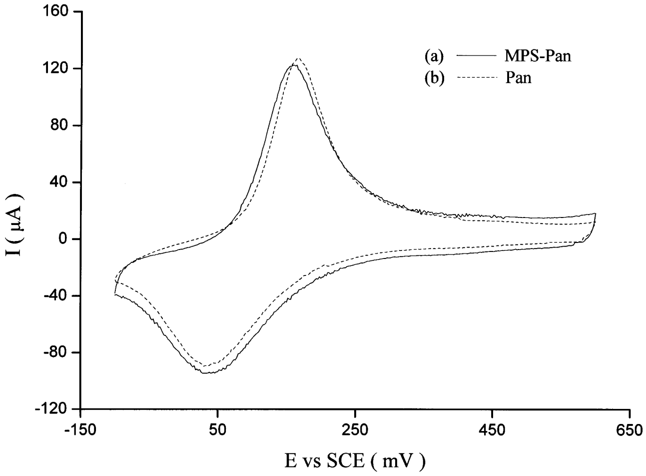


Figure 6. Cyclic voltammograms of (a) MPS–Pan (MPS–Pan-14) and (b) its parent unsubstituted polyaniline.

Further study indicated that the substitution degree of the resultant MPS–Pan, although increased with reaction time initially, eventually leveled off at about 26 mol % after 14 h of reaction time in the presence of a catalytic amount of proton. This saturated substitution degree is consistent with the fact that a polyaniline emeraldine base contains about 25 mol % of the diiminoquinoid ring, thus supporting the hypothesis that the CRS reaction only happened at the diiminoquinoid sites.

Conductivity Results

For the conductivity study, free-standing MPS–Pan films (~10 μm thick) were first reoxidized at 0.3 V in 0.5 M aqueous H_2SO_4, followed by rinsing with a copious amount of deionized water and then soaking twice in fresh deionized water for 1 h to remove any residual H_2SO_4. After drying, the self-doping conductivity (i.e., free of any external dopant) of the resultant films was measured and summarized in column 4 of Table 1 (entries 2–4). The results clearly show that as the substitution degree increased from 15 to 26 mol %, the self-doping conductivity of MPS–Pan increased from 0.017 to 0.77 S/cm, attributable to the increase of the doping level. Similar behavior has been previously observed for the S–Pans[5c] (the results also summarized in entries 5–8, Table 1). Interestingly, these new types of self-doping MPS–Pans were found to be much more conductive than the corresponding S–Pans having a similar substitution degree (i.e., self-doping degree). For example, at the same self-doping level of 26 mol %, the conductivity of MPS–Pan (0.77 S/cm; entry 4, Table 1) was found to be ~5 orders of magnitude higher than that of S–Pan (10^{-5} S/cm; entry 6, Table 1). This result implies that the self-doping groups of MPS–Pan may be distributed in a way much more conducive to the conductivity than that of S–Pan. Such different distribution behaviors may be associated with the different

Table 1. Conductivity Results for Self-doping Polyanilines

entry	polyaniline[a]	self-doping degree[b] (mol %)	self-doped conductivity[c] (S/cm)	fully doped conductivity[e] (S/cm)	source
1	Pan	0	$<10^{-8}$ [d]	2.0 ± 0.5[f]	this work
2	MPS−Pan-6A	15	0.017	3.8	this work
3	MPS−Pan-14	20	0.42	12.1	this work
4	MPS−Pan-14A	26	0.77	19.5	this work
5	S−Pan	11	10^{-8}	1.2	ref 5c
6	S−Pan	26	10^{-5}	0.63	ref 5c
7	S−Pan	50	0.01−0.023	0.01−0.023	ref 5c, 5d
8	S−Pan	50	0.1	0.1	ref 5b

[a] Pan, polyaniline; MPS−Pan, polyaniline after treatment with MPS−Na for 6 or 14 h, with or without the addition of 0.01 M acetic acid (A); S−Pan, sulfonated polyaniline. [b] The mole percent of repeat units that contain a self-doping sulfonic acid moiety. For entries 2−4, the values were based on the atomic ratio (S/2N) measured by XPS. For entries 5−8, the values were adopted from the corresponding specified references. [c] Conductivity of the self-doped polyanilines without the presence of any external dopants. [d] Undoped polyaniline. [e] Conductivity of the fully doped polyanilines with the presence of a self-doping sulfonic acid moiety plus external dopants. The external dopant was $HClO_4$ for entries 1−4 and HCl for entries 5−8. The total doping degrees, that is, the self-doping plus external doping, for entries 1−4 were estimated to be about 50 ± 2%, as measured by the atomic ratio (Cl + 0.5S)/N using XPS. [f] The averaged conductivity value for the untreated polyaniline film (doped with a 1 M aqueous solution of $HClO_4$) was obtained using four different control sample specimens. This value is comparable with the results reported for a polyaniline film that was fully doped with HCl (ref 2).

chemical nature of their respective substitution reactions. In the case of MPS−Pan, the substitution reaction can only occur at the diiminoquinoid rings, with each being uniformly separated by three diaminobenzenoid rings and accounting for ∼25 mol % of the repeating unit of the emeraldine form. Therefore, as the CRS reaction reached the completion state (i.e., as in the case of the 26 mol % substituted MPS−Pan), the MPS groups should also be uniformly attached and distributed on every polyaniline chain, with each chain reaching the same substitution level (i.e., ∼25 mol %). On the contrary, the sulfonation of polyaniline involves the electrophilic substitution of the SO_3 electrophile to the electron-rich diaminobenzenoid rings, which accounted for ∼75 mol % of the repeating unit of an emeraldine polyaniline chain. Therefore, when the averaged sulfonation degree of a bulk sample is far below the theoretical saturation level (e.g., 75 mol % in the case of monosulfonation for each benzenoid ring), as in the case of the 26 mol % sulfonated polyaniline, the distribution of those sulfonic acid groups among different polymer chains can differ and vary widely according to the employed reaction conditions. In other words, the individual polyaniline chain within the reaction mixture can have a wide range of sulfonation level, ranging from 0 to 75 mol % or even above. In extreme cases of such inhomogeneous distribution, the highly sulfonated (thus better conductive) polyaniline chains might be completely isolated from each other by those lightly or barely sulfonated (thus poor conductive or even insulating) polyaniline chains. Under such unfavorable conditions, the resultant S−Pan matrix may display an unusually low self-doping conductivity but can still gain a fairly good conductivity after being fully doped with compensating external dopants. For example, the 26 mol % S−Pan showed a very poor self-doping conductivity (10^{-5} S/cm; entry 6, column 4) but still displayed a fairly good conductivity after being fully doped (0.63 S/cm; entry 6, column 5). The above phenomenon may account for the wide discrepancy of the previously reported conductivity values between different research groups for the 50 mol % (entries 7 and 8, Table 1) and 75 mol % sulfonated polyanilines.[5,6] The uneven attachment of the sulfonic acid groups should also lead to a lower dopant utilization efficiency, which seems to explain why S−Pan requires a much higher self-doping level (i.e. 75 mol %) to achieve an optimal conductivity, whereas the externally doped (substituted or unsubstituted) polyanilines often reach their maximal conductivity at a common optimal doping level of ∼45−50 mol %. For example, the 75 mol % sulfonated polyaniline showed an unexpected higher conductivity (0.08−1 S/cm), compared to that of the 50 mol % sulfonated polyaniline (0.01−0.1 S/cm).[5,6]

Since all the obtained MPS−Pans in the present study had a self-doping degree much less than the optimal doping degree (i.e., 50 mol %), they were further doped with 1 M $HClO_4$ aqueous solution for 2 h to provide the compensating external dopant (i.e. $HClO_4$) for reaching a total doping level of ∼50 mol %. The results, summarized in Table 1 (column 5), clearly showed that the conductivity of the fully doped MPS−Pan increased with the amount of its MPS substituent, with MPS−Pan having 15, 20, and 26 mol % MPS substituent showing conductivity values of 3.8, 12.1, and 19.5 S/cm, respectively, which are all higher than the 2.0 S/cm for the parent polyaniline film (entry 1, Table 1). On the contrary, the fully doped S−Pans actually showed a distinct reverse trend, with the conductivities for the 11, 26, and 50 mol % sulfonated polyanilines being 1.2, 0.63, and 0.1−0.01 S/cm, respectively (entries 5−8, Table 1).[5c] These results may be attributed to the different electronic effects between the MPS and the sulfonic acid substituents. As the number of the electron-donating MPS groups increases, the electron density of the MPS−Pan backbones will also increase and, in turn, enhance the stabilization of electron-deficient charge carriers such as semiquinone radical cations and/or cationic bipolarons generated from the doping of polyaniline with protonic acid.[19] Such a stabilization effect can then lead to the induction of a higher effective concentration of charge carriers at the same given doping level and thus results in higher conductivity. On the contrary, for S−Pan, as the number of the electron-withdrawing sulfonic acid group increases, the electron density of the S−Pan backbone is reduced, leading to a lower conductivity. Such an expectation is supported by our preliminary EPR studies on a butylthio-substituted polyaniline (also prepared by the same CRS method), which was found to have a higher number of delocalized Pauli spins and a higher density of state at the Fermi level than its parent unsubstituted polyaniline under the same doping and EPR measurement conditions.

Similar to the case of a typical self-doping polyaniline,[5b] the conductivity of MPS−Pan was also found to be pH independent for pH < ∼7, while its parent unsubstituted polyaniline was essentially undoped and became insulating at pH values greater than 4.

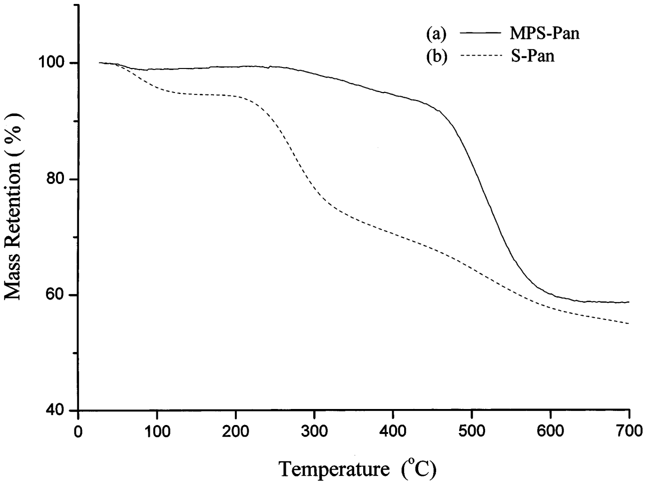


Figure 7. Thermogravimetric analysis traces of (a) MPS−Pan (MPS−Pan-14) and (b) its parent unsubstituted polyaniline.

Since the above CRS reaction was performed in a solid matrix of polyaniline film without using any effective secondary dopant and primary/functional dopant, the conformations of the polyaniline chains are not expected to be significantly altered. This assumption is again supported by the electronic absorption results (Figure 5) that both MPS−Pan and its parent unsubstituted polyaniline showed similar UV−vis−NIR spectral features for a localized polaron band. In light of such conformational similarity, the high conductivity associated with these MPS−Pans may most likely result from the electron-donating influence of the alkylthio-substituent instead of the conformational change effect of the polymer backbone.[18]

Thermal Stability

Since the dopant moiety is covalently bonded to the polymer backbone, the thermal stability of a self-doping polyaniline is expected to be better than that of the unsubstituted polyaniline doped with an external dopant. S−Pans has been previously reported to be thermally much more stable than its parent unsubstituted polyaniline doped with HCl.[5e] The thermal stabilities of this new type of self-doping MPS−Pans were also examined by thermogravimetric analysis (TG). The TG result for a 20 mol % substituted MPS−Pan is displayed in Figure 7a. In addition to the small water-losing event at below ~120 °C, the TG curve showed a minor weight loss event between 260 and 400 °C followed by a major weight loss event at 524 °C. The minor weight loss event has an initialization temperature at ~260 °C and an onset temperature of ~270 °C. The major weight loss event has an onset temperature at ~470 °C with the initialization temperature being obscured by the proceeding minor event. For comparison, a 55.8 mol % S−Pan, prepared according to the previously reported method,[5b] was also examined under the same TG conditions, and the result is shown in Figure 7b. The result indicated that, in addition to the initial water loss event at below ~120 °C, the weight loss of the S−Pan showed a continuous multistage feature, with an initialization temperature at ~185 °C, an onset at ~230 °C, and a first major decomposition at ~273 °C. Similar initialization and major decomposition temperatures at 190 and 275 °C, respectively, for a 50 mol % S−Pan have been previously reported by Chen.[5d]

Table 2. S/N Atomic Ratios of MPS−Pan and S−Pan after Being Heated at Different Temperatures

temp[a] (°C)	MPS−Pan (S/N)[b]	S−Pan (S/N)[b]
30	0.395	0.558
100	0.393	0.540
210	0.388	0.382
240	0.391	0.224
270	0.298	0.182
340	0.153	0.089
420	0.136	0.038

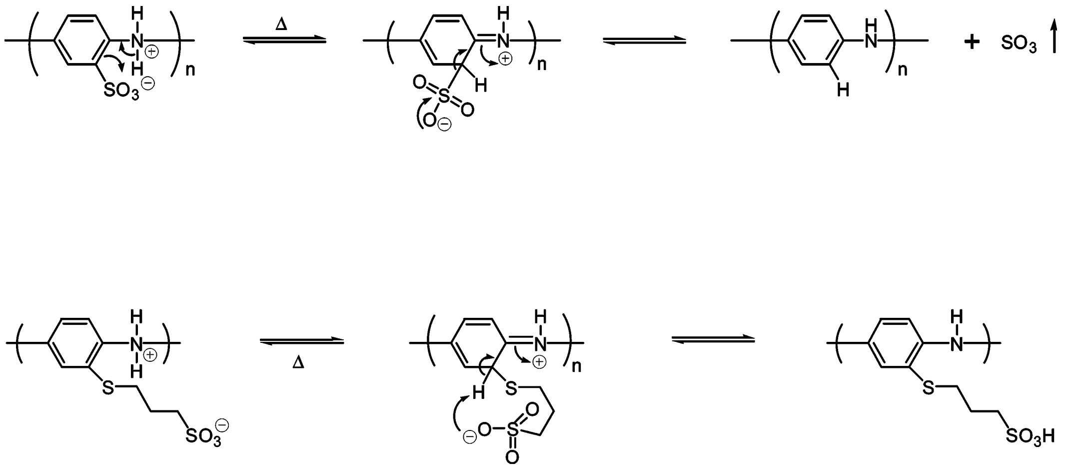
[a] The samples were heated at the given temperature for 1 h under 1 atm of N_2. [b] The S/N atomic ratio as measured by XPS.

Attempts were made, using XPS studies, to elucidate the cause of the observed TG weight loss and gain insights on the thermal degradation chemistry of different samples. A series of the above samples of MPS−Pan and S−Pan were heated at a predetermined temperature (e.g., 30, 100, 210, 240, 270, 340, and 420 °C) under N_2 atmosphere for 1 h, and their S/N atomic ratios were examined by XPS. The results on MPS−Pan samples showed that, within experimental error, the S/N ratios were almost unchanged at 0.392 ± 0.02, after they were heat treated at below 240 °C, whereas the S/N ratio of S−Pan treated at a similar temperature decreased significantly from 0.558 (heated at 30 °C), through 0.382 (at 210 °C), to 0.224 (at 240 °C). These results indicated that the structure of MPS−Pan was intact up to at least 240 °C, whereas a significant amount of the sulfonic acid group on S−Pan was cleaved at 210 °C. Results from Table 2 showed that a further increase of the treatment temperature led to a steady decrease of the S/N atomic ratio, suggesting a continuous loss of sulfur-containing moieties from the polyanilines. Further detailed XPS chemical state studies indicated that the reduction in S/N ratio of the MPS−Pan initiated at 260 °C was mainly caused by the loss of the terminal SO_3^- group, while the sulfide linkage remained intact until ~300 °C. Therefore, from the TG and heat treatment studies, one can suggest that the thermal degradation of S−Pan involved the loss of a sulfonic acid group (initiated at 185 °C) probably followed by backbone decomposition, whereas MPS−Pan degradation also involved the loss of a sulfonic acid group, but initiated at a much higher temperature of 260 °C.

Additional TG studies were made to investigate the oxidative stability of different samples, using air as purge gas. Preliminary results showed, under oxidative conditions, that the initialization temperatures for the first minor degradation weight loss event of both S−Pan (195 °C) and MPS−Pan (270 °C) were about 10 °C higher, with the preinitialization thermal stability being unchanged in both cases, indicating a similar initial degradation trend as in nitrogen. These oxidative TG results, in conjunction with the above-mentioned XPS studies, suggested that the oxidative or non-oxidative thermal stabilities of both S−Pan and MPS−Pan are probably associated with the loss of the substituted sulfonate moiety.

In general, the results indicated that a self-doping MPS−Pan has thermal stability not only higher than that of HCl-doped polyaniline but also much higher than that of the self-doping S−Pan. Although further detailed studies on the degradation of MPS−Pan are underway to understand the cause for the much higher thermal stability of MPS−Pan, a plausible mechanism as illustrated in Scheme 1 is proposed. For the decomposi-

Scheme 1



tion of S−Pan, a thermally activated, reversible 1,3-hydrogen shift may first occur between the protonated imine site and the sulfonated ortho-carbon site, following by a subsequent irreversible desulfonation due to the evaporation of the SO_3 byproduct at elevated temperatures. For MPS−Pan, although a similar 1,3-hydrogen shift may still happen between the protonated imine site and the MPS-substituted ortho-carbon site, the ortho-proton is readily removed by the terminal $-SO_3^-$ group (through a relatively easier accessible eight-member-ring arrangement) to convert the unstable nonaromatic intermediate to the stable aromatic benzenoid ring, thus neutralizing the decomposition.

Conclusion

A new type of highly conductive self-doping polyaniline, MPS−Pan, containing a sulfonic acid moiety covalently bonded to the polymer backbone through a propylthio moiety has been successfully prepared via the novel concurrent reduction and substitution method performed within the solid matrix of polyaniline emeraldine base. Compared with their parent unsubstituted polyaniline; the undoped MPS−Pan showed more red-shifted UV−vis absorption bands and a slightly lower oxidation potential, suggesting that the electron density of MPS−Pan is increased by the presence of these electron-donating propylthiosulfonate groups.

The resultant MPS−Pans are found to have a much higher self-doping conductivity than the S−Pans at the same self-doping level, attributable to the more homogeneous distribution of the self-doping MPS groups among the polymer chains and within each individual polymer chain. After providing compensated external dopant to achieve a total doping level of ~50 mol %, these MPS−Pans revealed a full-doping conductivity even higher than that of the parent unsubstituted polyaniline; and the conductivity was found to clearly increase with the degree of substitution. On the contrary, the S−Pans showed a lower full-doping conductivity than that of their parent unsubstituted polyaniline, with the conductivity further decreased as the degree of the sulfonation increased. These results suggested that the increased electron density on the polymer backbones of MPS−Pan could help stabilize the electron-deficient charge carriers (e.g., semiquinone radical cations, or cationic bipolarons), thus increasing their effective concentration and leading to a higher conductivity.

Most interestingly, both TG and XPS studies confirm that MPS−Pan is thermally much more stable than S−Pan, with MPS−Pan retaining its sulfonic acid groups until ~260 °C, whereas S−Pan started to lose its sulfonic acid groups at a much lower temperature of about 185 °C. Just like a typical self-doping polyaniline, MPS−Pan is also soluble in 0.1 N NaOH aqueous solutions, and it has a conductivity that is rather pH-insensitive at values between 0 and 7, whereas its parent unsubstituted polyaniline became essentially undoped and insulating at pH values higher than ~4.

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