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Redox Behavior of Poly(2-methoxyaniline-5-sulfonic acid) and Its Remarkable Thermochromism, Solvatochromism, and Ionochromism

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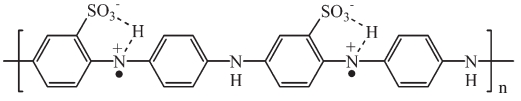
ABSTRACT: A detailed investigation has been carried out of the redox behavior of poly(2-methoxyaniline-5-sulfonic acid) (PMAS) in aqueous solution. Oxidation of PMAS emeraldine salt with aqueous 0.10 M ammonium persulfate proceeded in an analogous fashion to that observed with unsubstituted polyaniline, generating a pale purple species with λ_{max} at 330 and 540 nm, consistent with the fully oxidized pernigraniline base form of PMAS. Subsequent protonation with dilute acid yielded the blue PMAS pernigraniline salt (λ_{max} 670 nm). In contrast to the behavior of previously studied polyanilines, the hydrazine reduction of PMAS emeraldine salt produced an equilibrium mixture of two leucoemeraldine base forms with λ_{max} at 335 and 408 nm, respectively. These PMAS leucoemeraldine base species, believed to be conformers with differing degrees of planarity along their polymer chains, exhibit remarkable thermochromism, solvatochromism, and ionochromism that is unprecedented in polyaniline chemistry.

Introduction

Polyaniline is one of the most widely studied organic conducting polymers because of its good environmental stability, its ready switching between three oxidation states, and the good electrical conductivity (typically 1−10 S cm^{-1}) of its emeraldine salt form. However, a disadvantage for processing has been its insolubility in water. The introduction of sulfonic acid groups into polyaniline (either directly onto the aniline rings[1−7] or in side chains[8,9]) has proved a useful approach to enhancing water solubility. In their seminal studies, Epstein et al.[1−3] reported that 50% or 75% of the aniline rings of polyaniline can be substituted with sulfonic acid groups via reaction of fuming sulfuric acid with emeraldine base (EB) or leucoemeraldine base (LB), respectively. The so-called SPAN products are in the conducting emeraldine salt form, in which sulfonic acid substituents form six-membered self-doping structures with radical cation nitrogen sites along the polymer chains, as illustrated in **1** for 50% sulfonated SPAN.

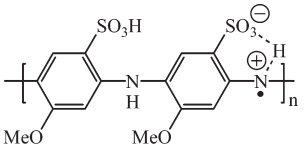


1 (SPAN)

SPANs possess useful electrical conductivity (from 0.02 to 1.0 S cm^{-1} at room temperature) and exhibit similar electronic spectra and redox properties to unsubstituted polyaniline emeraldine salts.[1−7] However, they are markedly more resistant to alkaline dedoping to the insulating emeraldine base form. Whereas unsubstituted polyanilines become insulators at pH ≥ 4,[8] the conductivities of 50% and 75% sulfonated SPANs are pH-independent up to pHs of 7.5 and ≤14, respectively.[2,3] This imparts a major advantage in cases where the polymer may be exposed to highly alkaline environments. Unfortunately, the 50−75% sulfonated SPANs possess very limited water solubility, while a more soluble 80% sulfonated SPAN recently obtained by reacting EB with chlorosulfonic is believed to be complicated by the presence of interchain −SO_2− or −SO_2NH− linkages.[5,6]

Considerable recent interest[9−21] has consequently focused on the first fully sulfonated polyaniline, poly(2-methoxyaniline-5-sulfonic acid), PMAS. This has been synthesized in its emeraldine salt PMAS(ES) form using either chemical[9,10] or electrochemical[11,12] polymerization of 2-methoxyaniline-5-sulfonic acid monomer (MAS). In the dimer repeat unit of PMAS(ES) one sulfonic acid is involved in self-doping to a radical cation nitrogen site while the other is "free". The steric effect of the sulfonate and methoxy ring substituents in PMAS would be expected to increase the torsional angle between adjacent aniline rings, leading to lower electrical conductivity. However, PMAS(ES) still exhibits moderate electrical conductivity (0.01−0.04 S cm^{-1}).[9−12] Its exceptionally high water solubility (up to 10% w/v) is of major benefit in its processing for potential applications. In addition, we have also found that it is even more resistant to alkaline dedoping than SPANs, remaining in the conducting emeraldine salt form in up to 2.0 M NaOH.[13]

PMAS(ES)



The present paper reports a detailed investigation of the redox properties of aqueous PMAS(ES), using complementary cyclic voltammetry, UV−vis−near-infrared spectroscopy, and light scattering studies. Oxidation is found to parallel that previously observed for unsubstituted polyaniline emeraldine salts, giving an analogous fully oxidized pernigraniline base PMAS(PB) form. However, reduction of PMAS(ES) with aqueous hydrazine reveals marked differences to the behavior of parent polyaniline. The product is an equilibrium mixture of two species, believed to be conformers of the fully reduced leucoemeraldine base PMAS(LB)

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form. These leucoemeraldine base species undergo unprecedented thermochromism, solvatochromism, and ionochromism.

Experimental Section

Materials. High-molecular-weight PMAS(ES), synthesized and purified using the improved cross-flow dialysis procedure developed by Masdarolomoor et al.,[10] was available in our laboratories. The presence of "free" SO_3H groups was confirmed by the acidic pH of aqueous PMAS(ES) solutions (e.g., pH ca. 5 for a 4×10^{-5} M solution). Ammonium persulfate, hydrazine monohydrate, and *N*-methylpyrrolidinone (NMP) were purchased in the purest grades available from Aldrich, while methanol was obtained from Ajax. Aqueous solutions of reagents were prepared using Milli-Q quality water and filtered through a 0.45 μm filter prior to use.

Chemical Oxidation and Reduction of Aqueous PMAS(ES). Unless otherwise stated, all redox reactions were performed at room temperature (20−25 °C).

An aqueous PMAS(ES) concentration of ca. 4×10^{-5} M (based on a dimer repeat unit) was employed in all cases, except in two hydrazine reductions where [PMAS] of 8×10^{-6} and 1.6×10^{-3} M were used to determine the influence of polymer concentration. The polymer concentrations were estimated from the absorbance at 473 nm (λ_{max}) by reference to Beer's law plots constructed with known concentrations of aqueous PMAS(ES).

Oxidation of aqueous PMAS(ES) emeraldine salt to its pernigraniline base form, PMAS(PB), was carried out using 0.10 M ammonium persulfate as oxidizing agent. The reduction of PMAS(ES) emeraldine salt to its leucoemeraldine base PMAS(LB) form was performed with hydrazine hydrate as reducing agent, using a range of aqueous hydrazine concentrations ($[N_2H_4] = 0.01-0.40$ M) and temperatures. In a few cases, the PMAS(ES) was dissolved in phosphate buffer (0.20 M NaH_2PO_4/Na_2HPO_4, pH 7) prior to reduction.

The progress of each of the oxidations and reductions was followed by monitoring the UV−vis spectral changes between 250 and 1100 nm.

Thermochromism, Solvatochromism, and Ionochromism of Reduced PMAS(LB). The PMAS(LB) employed in these studies was typically prepared *in situ* via the rapid (< 1 min) reduction of PMAS(ES) in aqueous 0.10 M hydrazine at room temperature (20−25 °C).

Thermochromism of the PMAS(LB) product was examined by monitoring the UV−vis spectral changes when its aqueous solution was maintained at various temperatures using a thermostated cell block in the spectrophotometer. In related studies, the thermochromism of PMAS(LB) was quantified by carrying out the reduction of aqueous PMAS(ES) with 0.40 M hydrazine at temperatures between 0 and 50 °C and then maintaining the PMAS(LB) product at the same temperatures until equilibrium was reached (as indicated by no further changes in the UV−vis spectra).

Solvatochromism of the aqueous PMAS(LB) was examined by adding various amounts of methanol, NMP, or acetone and monitoring the subsequent UV−vis spectral changes. *Ionochromism* of aqueous PMAS(LB) was similarly investigated by adding a variety of alkali metal and alkaline earth metal salts (0.40 M LiCl, NaCl, KCl, $MgCl_2$ and $CaCl_2$, or 0.20 M Na_2SO_4) and the ammonium salts NH_4Cl and Bu_4NCl.

Aerial Reoxidation of Reduced PMAS(LB). Aerial reoxidation of the above PMAS(LB) samples back to PMAS(ES) emeraldine salt was achieved by lowering the pH of the reduced solutions to 1−2.

Spectroscopic Studies. UV−vis spectra of polymer solutions were recorded with a Schimadzu UV-1601 spectrophotometer using matched 1 cm quartz cells, except for the hydrazine reduction using the high PMAS(ES) concentration of 1.6×10^{-3} M where a 0.1 cm cell was employed. For the thermochromism studies on aqueous PMAS(LB) carried out at specific temperatures, a thermostated cell block was employed. The UV−vis−near-infrared spectrum of a PMAS(ES) film on glass was measured between 300 and 2600 nm with a Cary 500 spectrophotometer.

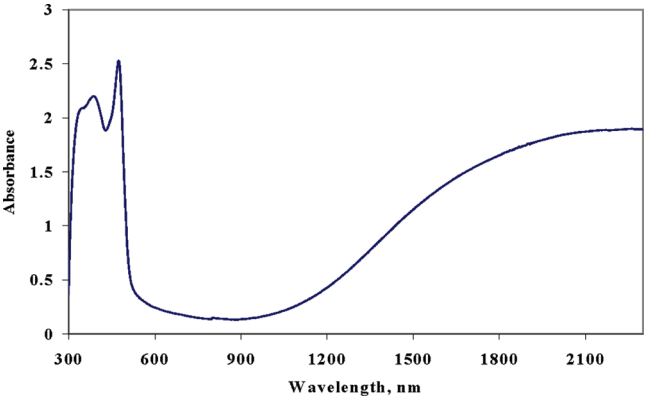


Figure 1. UV−vis−near-IR spectrum of a PMAS(ES) film spin-cast from aqueous solution.

Particle Size Measurements. Particle size measurements for solutions of PMAS(ES) emeraldine salt and its reduced PMAS(LB) leucoemeraldine base were carried out via dynamic light scattering using a Malvern Nano-ZS Zetasizer and 8° angled backscattered light. All solutions were passed through a 0.45 μm filter prior to recordings. The PMAS(LB) solutions were generally produced via the reduction of aqueous 6×10^{-5} M PMAS(ES) with 0.10 M hydrazine at 25 °C, although PMAS(ES) concentrations of 3.0×10^{-5} and 1.2×10^{-4} M were also employed in a few cases.

Measurements were typically performed at room temperature 25 °C. However, particle sizes of the aqueous PMAS(LB) solutions were also measured after thermostatting at a range of other temperatures (4, 10, 40, and 60 °C). The influence of added methanol on the particle size of aqueous 6×10^{-5} M PMAS(LB) was determined by reducing 1.2×10^{-4} M PMAS(ES) with aqueous 0.10 M hydrazine and then divided into samples that were separately diluted with equal volumes of water or 20−60% (v/v) methanol, giving solutions containing 6×10^{-5} M PMAS(LB) and 10−30% methanol.

Results and Discussion

UV−Vis−NIR Spectrum and Conformation of PMAS(ES) Emeraldine Salt. Self-doped SPANs such as **1** in which 50% of the aniline rings are sulfonated give green aqueous solutions that exhibit a localized polaron band at ca. 830−850 nm, together with a further polaron band at 420−435 nm and a $\pi-\pi^*$ band at ca. 313−320 nm.[2,4] These spectroscopic features are characteristic of emeraldine salts in the "*compact coil*" conformation.[22] The presence of the methoxy and sulfonate groups on the aniline rings of PMAS(ES) has a major impact on the UV−vis spectrum and conformation adopted by the polymer. In contrast to the SPANs, aqueous PMAS(ES) is yellow-green in color and shows no localized polaron band around 800 nm−the absorption being near zero from 600 to 900 nm (Figure 1). Instead, a characteristic strong band is observed at 473 nm together with overlapping bands at 320−380 nm, which we have assigned to a low wavelength polaron band and $\pi-\pi^*$ transitions, respectively (each red-shifted compared to corresponding electronic transitions for SPANs).[13] A strong, broad near-infrared band is also clearly observed for a film of PMAS(ES) spin-cast onto glass (Figure 1). This latter band, centered at ca. 2200 nm, may be attributed to a delocalized polaron band. These spectroscopic features for PMAS(ES) are characteristic

of emeraldine salts in which the polymer chains have adopted an "*extended coil*" conformation.[22]

The contrasting conformations adopted by the polymer chains in aqueous PMAS(ES) and 50% sulfonated SPAN **1** may be rationalized in terms of their different degrees of sulfonation. For both polymers, a sulfonic acid group on every second aniline ring is involved in self-doping of an adjacent radical cation nitrogen site. In the case of the fully sulfonated PMAS(ES), an anionic sulfonate group is also present on each alternate aniline ring along the polymer chain. Assuming incomplete masking by the counterions (H^+ or NH_4^+), electrostatic repulsion between these negatively charged "free" sulfonate substituents would be expected to promote extension of the PMAS(ES) chains into an "*extended coil*" conformation. In contrast, with 75% sulfonated SPAN there is only one "free" sulfonate group in the tetramer repeat unit, while with 50% sulfonated SPAN **1** there are no "free" sulfonate substituents. The markedly fewer negative sulfonate groups along the SPAN polymer chains would therefore favor the adoption of a "*compact coil*" conformation.

Preference for a more fully expanded "*extended coil*" conformation for aqueous PMAS(ES) is also consistent with the expected strong interactions between its sulfonate groups and water solvent. These polymer−solvent interactions would be enhanced by the more open "extended" polymer chain arrangement and diminished in the more folded "*compact coil*" conformation. Furthermore, polymer−polymer interactions (favoring a "*compact coil*" conformation) might be expected to be considerably weaker in PMAS(ES) compared to unsubstituted PAn (or partly substituted SPANs) due to electrostatic repulsion between the PMAS(ES) chains caused by the negative sulfonate substituents.

Redox Switching of PMAS between Different Oxidation States. Recent cyclic voltammetry studies of aqueous PMAS(ES) have shown[10] that, like unsubstituted polyanilines, it can be redox switched between three oxidation states. When sweeping the potential anodically, two oxidation peaks were observed at ca. 0.4 and 0.8 V (vs Ag/AgCl) that may be assigned to the successive oxidations of PMAS from the fully reduced leucoemeraldine state to the emeraldine salt and then to the fully oxidized pernigraniline form. Corresponding reduction peaks were observed in the reverse cathodic sweep at ca. 0.7 and 0.3 V, from which $E_{1/2}$ values of ca. 0.35 and 0.75 V are derived for the successive redox transitions.

In the present work, further insights into the redox switching behavior of PMAS have been obtained from studies of its chemical oxidation and reduction.

i. Oxidation with Ammonium Persulfate. The room temperature treatment of an aqueous 4×10^{-5} M PMAS(ES) solution with 0.10 M ammonium persulfate oxidant caused a color change from yellow-green to pale purple (mauve) over 30 min. The accompanying changes in the UV−vis spectrum of the polymer are shown in Figure 2. The polaron band of the initial PMAS(ES) emeraldine salt at 473 nm decreased with time, as did the absorption in the near-infrared region, while two new peaks grew at 330 and 540 nm. Three isosbestic points were observed at 380, 500, and 685 nm from 1 min until completion of the reaction in 30 min, indicating a clean process between two species. The product bands at 330 and 540 nm are characteristic[23−25] of the pernigraniline base form of polyaniline, confirming oxidation of PMAS(ES) emeraldine salt to its fully oxidized pernigraniline base PMAS(PB) form, as shown in Scheme 1.

Further supporting a pernigraniline base structure for the above PMAS(PB) was its facile conversion to the protonated pernigraniline salt PMAS(PS) form by lowering the pH to

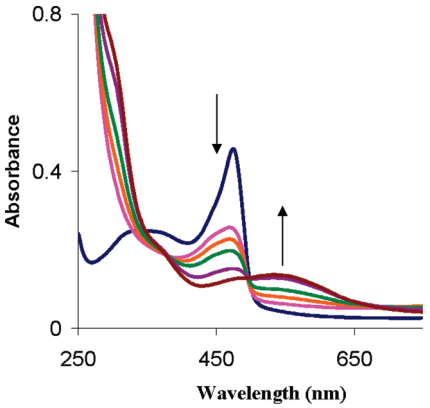
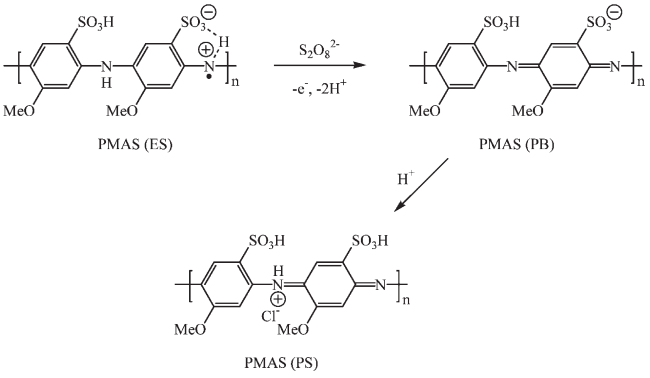


Figure 2. UV−vis spectral changes during oxidation of aqueous 4×10^{-5} M PMAS(ES) with 0.10 M $(NH_4)_2S_2O_8$ (pH 4.5−5). Spectra recorded at 1, 3, 5, 15, and 30 min.

Scheme 1



1.7 with added dilute hydrodrochloric acid (Scheme 1). Within a few minutes the color changed from mauve to blue, and the 540 nm band of PMAS(PB) was replaced by a peak at ca. 670 nm, close to the λ_{max} reported[25,26] for the pernigraniline salt form of unsubstituted polyaniline. The protonated PMAS(PS) polymer was unstable in acid solution, as evidenced by a gradual decrease in intensity of its 670 nm absorption band with time, a feature also characteristic of unsubstituted polyaniline.[25,27] Treatment of the aqueous PMAS(PS) with NaOH caused rapid deprotonation and reversion to the mauve PMAS(PB) with its characteristic band at 540 nm, confirming facile pH switching of the pernigraniline form of PMAS.

ii. Reduction with Aqueous Hydrazine. By analogy with the behavior of unsubstituted polyanilines,[23,24,28,29] the hydrazine reduction of PMAS(ES) emeraldine salt was expected to lead to the leucoemeraldine base form, PMAS(LB). However, whereas polyaniline leucoemeraldine bases reported to date exhibit a single characteristic absorption band at ca. 310−330 nm (assigned as a $\pi-\pi^*$ transition[24]), the room temperature reduction of aqueous PMAS(ES) with 0.10−0.40 M hydrazine unexpectedly led to the rapid (< 1 min) replacement of the initial emeraldine salt absorption bands with an intense, sharp peak at 408 nm together with a shoulder at ca. 360 nm for the PMAS(LB) product (e.g., Figure 3). This surprising behavior, unprecedented in the redox chemistry of unsubstituted polyanilines, has also recently been noted briefly by Hirao and co-workers in the reduction of PMAS(ES) with the vanadium(IV) species $VOSO_4$.[20]

The UV−vis spectrum of the initial PMAS(LB) product (formed rapidly in 0.10 or 0.40 M hydrazine) changed slowly at room temperature over the next few hours to give an

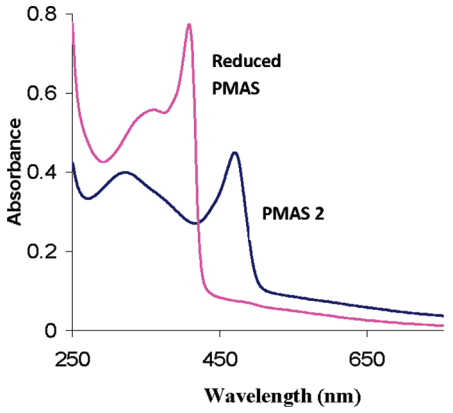


Figure 3. UV−vis spectral change upon the rapid (< 1 min) reduction of aqueous 4.0×10^{-5} M PMAS(ES) with 0.40 M hydrazine (pH 9.5) at room temperature.

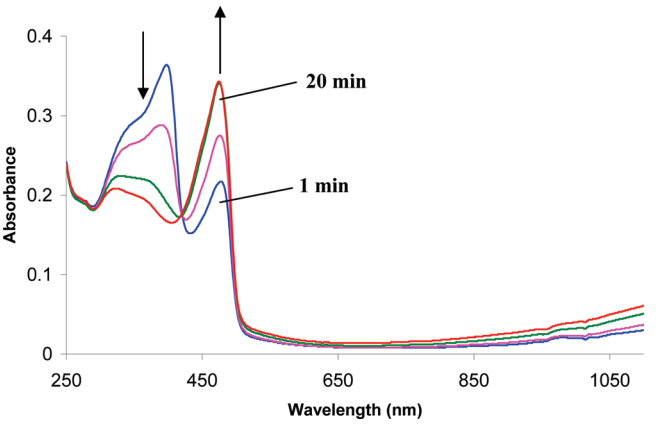
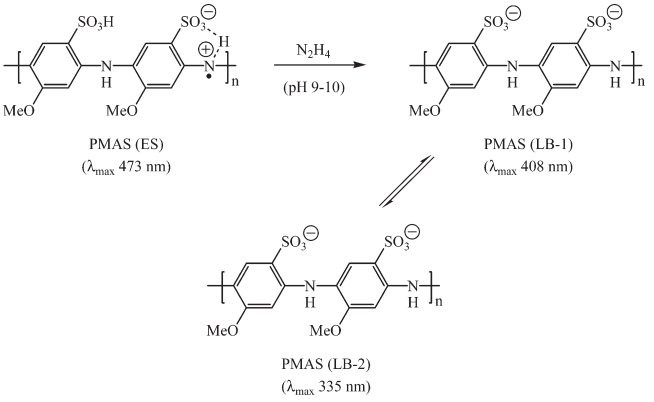


Figure 4. UV−vis spectral changes during the room temperature reduction of aqueous 4×10^{-5} M PMAS(ES) with 0.01 M hydrazine in pH 7 phosphate buffer.

Scheme 2



equilibrium mixture in which the λ_{max} 408 nm species PMAS-(LB-1) still dominated, but in which a distinct peak had now appeared at 344 nm consistent with the expected PMAS leucoemeraldine base product, PMAS(LB-2). Subsequent studies, described in detail below, showed that heating the initial PMAS(LB) product mixture PMAS(LB-1)/PMAS-(LB-2), or the addition of organic solvents such as methanol or acetone, resulted in the partial or complete loss of the intense 408 nm band of species PMAS(LB-1) and its replacement with a strong peak at ca. 335 nm due to its conversion to PMAS(LB-2). These observations are summarized in Scheme 2.

Varying the hydrazine concentration between 0.01 and 0.10 M in room temperature (25 °C) reductions of PMAS-(ES) at a constant pH of 7 (0.20 M phosphate buffer) confirmed that the rate of polymer reduction was strongly dependent on the concentration of hydrazine employed, as expected for a bimolecular process. The reduction with 0.10 M hydrazine was complete within 1 min, and the product solution again exhibited a strong, sharp peak at 408 nm {species PMAS(LB-1)} together with a shoulder at ca. 360 nm associated with PMAS(LB-2). The same product absorption spectrum was obtained for an analogous reduction of PMAS(ES) using 0.01 M hydrazine (Figure 4). However, the latter reduction was much slower than that in 0.10 M hydrazine, taking 60 min to proceed to completion. Three isosbestic points were observed at 305, 423, and 496 nm throughout the slow reduction, confirming a clean redox process.

In contrast, the PMAS(ES) concentration had little influence on the reduction process, as shown by a series of reactions employing 0.10 M hydrazine (pH 9.5) at room temperature while varying the polymer concentration over the range 8×10^{-6}−1.2×10^{-3} M. In each case, the reduction was complete within a minute, and a similar ratio of the reduced product species PMAS(LB-1) (λ_{max} 408 nm) and PMAS(LB-2) (λ_{max} ca. 340 nm) was observed.

On the basis of its facile thermochromic and solvatochromic conversion to PMAS(LB-2) (vide infra), we believe that the unprecedented PMAS(LB-1) (λ_{max} 408 nm) species formed preferentially during room temperature hydrazine reduction of PMAS(ES) is a leucoemeraldine base form of PMAS possessing a different conformational arrangement of its polymer chains to that adopted by PMAS(LB-2). Its π−π^* band is red-shifted by ca. 70 nm from that of PMAS-(LB-2) (λ_{max} = 335 nm). This suggests a considerably greater conjugation length for the chains of PMAS(LB-1), possibly arising from a more planar arrangement (with less twisting of adjacent aniline rings) and increased π overlap along the polymer chains. The λ_{max} of 408 nm exhibited by PMAS(LB-1) equates with a π−π^* band gap of only 3.04 eV, considerably lower than that found for other polyaniline leucoemeraldine bases (ca. 3.75−4.0 eV). The enhanced planarity for PMAS-(LB-1) may be associated with weak H-bonding between amine H centers and methoxy oxygens on adjacent aromatic rings along the polymer chain.

Reoxidation of PMAS Leucoemeraldine Base. The PMAS-(LB) species formed in each of the above hydrazine reductions may be reoxidized to PMAS(ES) emeraldine salt by lowering the pH of the solutions to 1−2 by addition of concentrated HCl. The protonated hydrazine so formed is no longer a reducing agent, and by analogy with studies[28−30] on unsubstituted polyaniline, it was anticipated that dissolved oxygen in the aqueous solutions would lead to reoxidation of the PMAS(LB) back to the PMAS(ES) emeraldine salt form. This was confirmed by the disappearance over ca. 20 min of the PMAS(LB-1) and PMAS(LB-2) peaks (at 408 and 335 nm) and the reappearance of a strong peak at 473 nm together with near-infrared absorbance above 1000 nm characteristic of PMAS(ES) emeraldine salt (e.g., Figure 5). The reoxidations proceeded cleanly, as indicated by the presence of a sharp isosbestic point at 420 nm.

Thermochromism of PMAS(LB). The species PMAS(LB-1) (λ_{max} 408 nm), formed as the major initial product in the rapid room temperature reduction of PMAS(ES) emeraldine salt by aqueous 0.10 M (or 0.40 M) hydrazine, exhibited remarkable thermochromism when subsequently heated at 40 °C. Within 1 min, its 408 nm peak showed a marked decrease

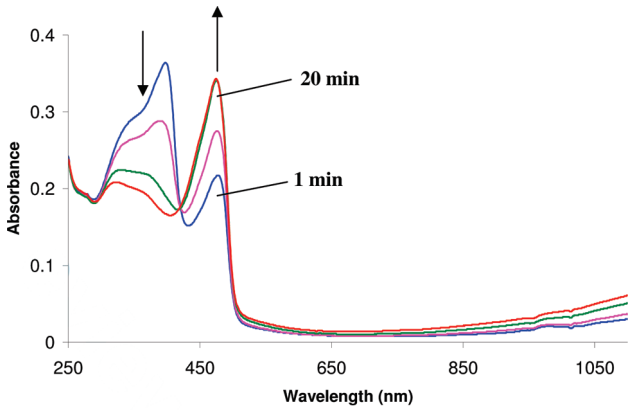


Figure 5. UV−vis spectra during aerial reoxidation of reduced PMAS-(LB) (formed in 0.10 M hydrazine/pH 7 phosphate buffer) after reacidification with HCl to pH 1.5.

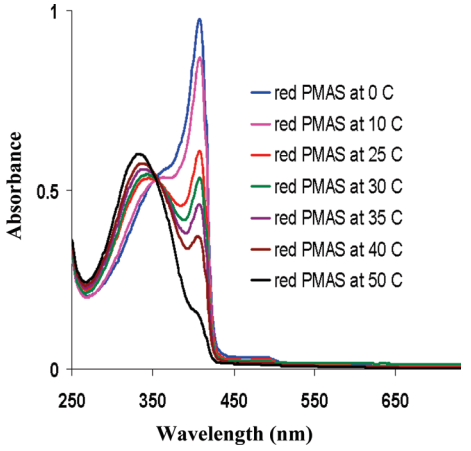


Figure 6. UV−vis spectrum immediately after reduction of aqueous 4×10^{-5} M PMAS(ES) with 0.40 M N_2H_4 (pH 10) at room temperature and following subsequent heating at 40 °C for 1, 5, 10, 20, and 30 min.

in intensity, accompanied by a blue shift of the original shoulder at ca. 360 nm (Figure 6). Over the next 30 min at 40 °C, the 408 nm peak continued to decrease significantly. Equilibrium was achieved within an hour, by which stage the dominant peak appeared at ca. 340 nm, characteristic of PMAS(LB-2) leucoemeraldine base. The sharp isosbestic point observed at 350 nm during these spectral changes indicated a clean interconversion between only two species. However, the transformation of PMAS(LB-1) to PMAS-(LB-2) did not proceed to completion at 40 °C, and the spectral changes were slowly reversed by cooling to 0 °C, confirming a temperature-dependent equilibrium as shown in eq 1.

$$\underset{(\lambda_{max}\ 408\ nm)}{\text{PMAS(LB-1)}} \overset{K_{eq}}{\rightleftharpoons} \underset{(\lambda_{max}\ 335\ nm)}{\text{PMAS(LB-2)}} \qquad (1)$$

When a similar aqueous PMAS(LB-1)/PMAS(LB-2) mixture was held at 50 °C, the thermal conversion of PMAS(LB-1) to PMAS(LB-2) was considerably more rapid and proceeded almost to completion. In contrast, heating at 30 °C resulted in slower interconversion and a greater preference for PMAS(LB-1). The thermochromism of PMAS(LB) is clearly revealed in Figure 7, which compares the UV−vis spectra of aqueous PMAS(LB) solutions generated by reducing PMAS(ES) with 0.10 M hydrazine at various temperatures between 0 and 50 °C and maintaining these temperatures

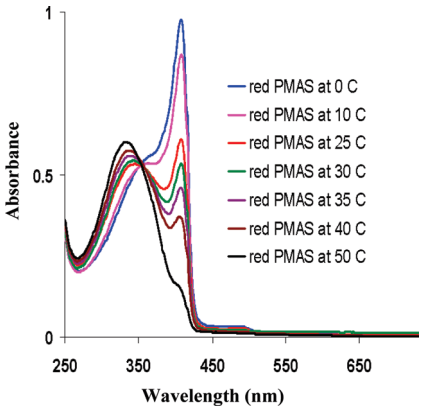


Figure 7. UV−vis spectra of aqueous PMAS(LB) solutions held at various temperatures between 4 and 50 °C until equilibrium is achieved. The PMAS(LB) solutions were generated by the room temperature reduction of 4×10^{-5} M PMAS(ES) with 0.40 M N_2H_4.

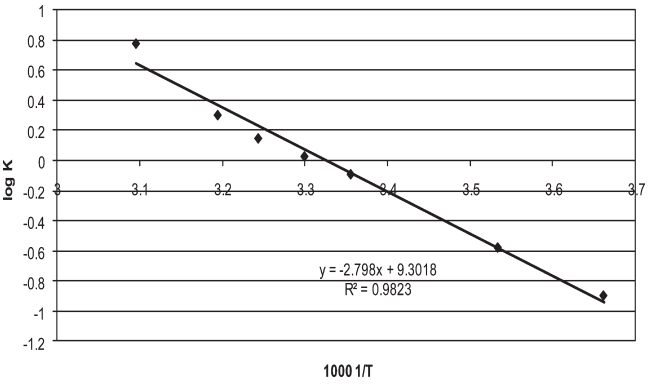


Figure 8. Plot of log K_{eq} vs $1/T$ for the equilibrium interconversion of PMAS(LB-1) species to PMAS(LB-2).

Table 1. Temperature Dependence of the Equilibrium Constant (K_{eq}) for the Thermal Interconversion of PMAS(LB-1) to PMAS(LB-2)

temp (°C)	0	10	25	30	35	40	50
K_{eq}	0.126	0.263	0.807	1.06	1.40	2.00	5.95

Table 2. Influence of Temperature on the Particle Size of Aqueous 6×10^{-5} M PMAS(LB)

temp (°C)	4	10	25	40	60
particle size (nm)[a]	166 (±3)	154 (±2)	172 (±4)	178 (±4)	173 (±12)

[a] Values in parentheses are the standard deviations of four separate measurements.

until equilibrium was reached. The presence of a sharp isosbestic point at 353 nm for the UV−vis spectra in Figure 7 is again consistent with a clean equilibrium process of type (1).

The concentrations of the PMAS species PMAS(LB-1) and PMAS(LB-2) present at each equilibrium temperature were determined from Figure 7 and the corresponding equilibrium constants (K_{eq}) calculated using eq 2. The temperature dependence of K_{eq} is summarized in Table 1, while a plot of ln K_{eq} vs $1/T$ is shown in Figure 8. From the slope ($-\Delta H°/R$) of this linear plot a standard enthalpy $\Delta H°$ value of +12.8 kcal/mol was calculated. From this value and the K_{eq} value of 0.807 at 25 °C (Table 2), a standard entropy $\Delta S°$ value of +43 eu was determined.

$$K_{eq} = [\text{PMAS(LB-1)}]/[\text{PMAS(LB-2)}] \qquad (2)$$

Assuming there are no overriding solvent effects, the positive $\Delta S°$ value for the conversion of PMAS(LB-1) to

PMAS(LB-2) indicates a less ordered conformation for the leucoemeraldine base chains in the latter species. This is consistent with thermal cleavage of weak H-bonds between adjacent amine and methoxy oxygen centers in PMAS(LB-1), leading to PMAS(LB-2) with decreased planarity and more twisting along the polymer chains, together with a blue shift (from 408 to 340 nm) in the observed $\pi-\pi^*$ band gap. Both PMAS(LB) conformers are expected to adopt an overall "extended coil" conformation in water due to their highly ionic nature.

The marked thermochromism exhibited here by PMAS(LB) is unprecedented for a reduced polyaniline species. In the only previous study of such thermal behavior, MacDiarmid and co-workers[24] observed only a small blue shift of ca. 10 nm in the position of the 330 nm $\pi-\pi^*$ band for the leucoemeraldine base of unsubstituted polyaniline when an NMP solution was heated to 85 °C. No evidence was seen for a 408 nm species at lower temperatures. Reversible thermochromic behavior is, however, well-known for neutral poly(alkylthiophene)s. For the latter polymers, heating causes a large blue shift of the highest wavelength $\pi-\pi^*$ band of the polymers, which has been attributed to a rearrangement of the polythiophene chains from a highly ordered, almost planar conformation to a less ordered, nonplanar conformation.[31−33]

Varying the PMAS concentration over a 150-fold range from 8×10^{-6} to 1.2×10^{-3} M in the reductions with 0.10 M hydrazine was found to have very little effect on the [PMAS(LB-1)]/[PMAS(LB-2)] product ratios. This strongly suggests that the observed thermochromism of PMAS leucoemeraldine base is a single-chain phenomenon rather than being associated with interchain aggregation. This conclusion is supported by particle size measurements of PMAS(LB) solutions at various temperatures. As seen in Table 2, increasing the temperature of a solution of PMAS(LB) from 4 to 60 °C had only a small effect on the polymer particle size (increasing from ca. 166 to 175 nm). This indicates that the observed thermochromism is not due to changes in the degree of aggregation of the PMAS chains with temperature.

Solvatochromism of PMAS(LB). The UV−vis spectrum of the PMAS(LB) leucoemeraldine base was also found to be very sensitive to changes in solvent. Parts a, b, and c of Figure 9 show the effects of adding the solvents methanol, NMP, and acetone, respectively, to an aqueous solution of PMAS(LB) at room temperature. In each case, the solvatochromism observed involved similar spectroscopic changes to those seen above with increasing temperature, consistent with a similar conversion between the PMAS(LB) leucoemeraldine base conformers PMAS(LB-1) and PMAS(LB-2). The λ_{max} 408 nm peak found in aqueous solution was shifted progressively to 335 nm as increasing amounts of organic solvent were added. Almost complete conversion to PMAS(LB-2) (λ_{max} 335 nm) was achieved by addition of 30% (v/v) methanol (Figure 9a), with a clean isosbestic point observed at 365 nm for solutions containing between 5% and 30% methanol. Only 10% (v/v) of added NMP was required to achieve the same interconversion (Figure 9b), while with added acetone complete conversion to PMAS(LB-2) (λ_{max} 335 nm) occurred with 20% organic component (Figure 9c).

The observed solvatochromism PMAS(LB-1) to PMAS(LB-2) is not due to an organic solvent-initiated redox process, since methanol, NMP, and acetone do not reduce PMAS or other polyanilines. The influence of added methanol on the particle size of reduced PMAS(LB) (prepared by reducing 6×10^{-5} M aqueous PMAS(ES) with 0.10 M hydrazine at 25 °C) is summarized in Table 3. Increasing the amount of methanol in the solvent mixture from 0 to 30% (v/v) caused the polymer particle size to increase from 175 to 526 nm, indicating increased polymer aggregation. This is consistent with the "poorer" nature of methanol compared to water as a solvent for the highly ionic sulfonated PMAS(LB) polymer. However, the increase in aggregation of PMAS(LB) upon adding organic solvents is not considered to contribute significantly to the observed UV−vis spectral changes, since aggregation was found to play no role in the extremely similar spectroscopic changes observed above in the related thermochromism studies.

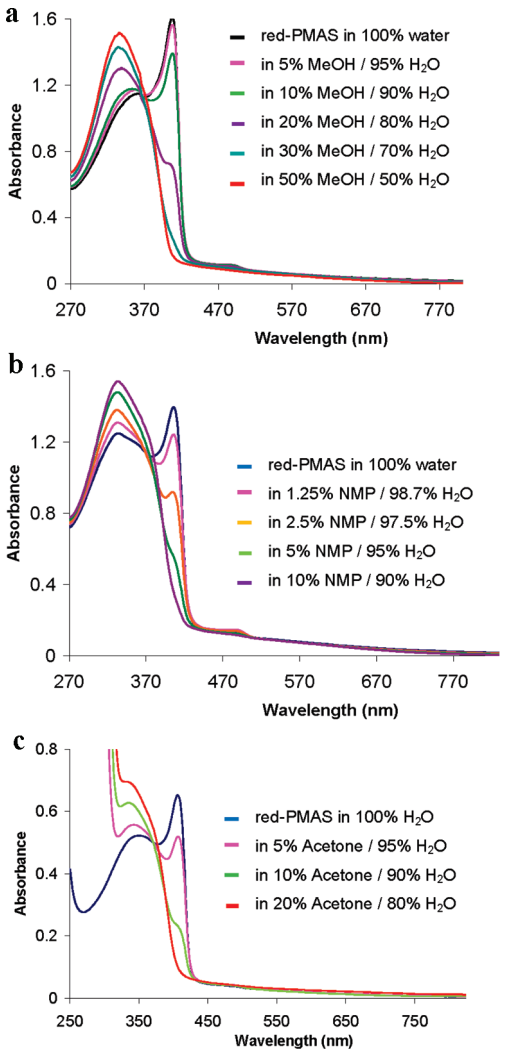


Figure 9. (a) UV−vis spectrum upon reduction of aqueous 4×10^{-5} M PMAS(ES) with 0.10 M hydrazine (pH 9.5) at room temperature, and immediately after subsequent addition of 5−50% (v/v) methanol. (b) UV−vis spectra upon reduction of aqueous PMAS(ES) with 0.10 M hydrazine at room temperature and immediately after subsequent addition of 1.25−10% (v/v) NMP. (c) UV−vis spectra upon reduction of aqueous PMAS(ES) with 0.10 M hydrazine at room temperature and immediately after subsequent addition of 5−20% (v/v) acetone.

Table 3. Particle Sizes of PMAS(LB) in Various Methanol/Water Mixtures at 25 °C

% MeOH (v/v)	0	10	20	30
particle size (nm)	175	240	410	526

Ionochromism of PMAS(LB). We have previously reported[13] that the presence of added alkali and alkaline earth metal ions can cause marked changes in polymer chain conformation for aqueous PMAS (ES) emeraldine salt. Remarkable ionochromism is also observed in the present study for PMAS(LB) leucoemeraldine base. The addition of

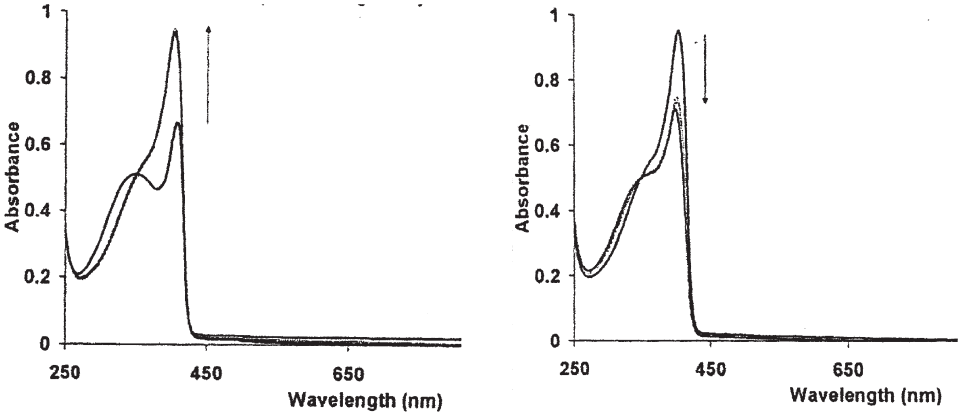


Figure 10. UV−vis spectral changes (a) upon adding 0.20 M Na_2SO_4 to an aqueous mixture of PMAS(LB-1) and PMAS(LB-2) (formed via the room temperature reduction of PMAS(ES) with 0.10 M hydrazine) and (b) when the PMAS(LB) formed in (a) in the presence of 0.20 M Na_2SO_4 was heated at 50 °C for 5, 15, and 45 min.

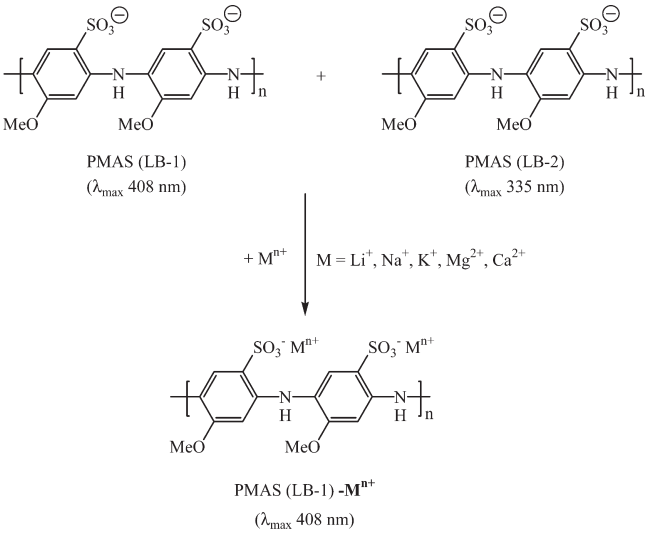
0.20−0.40 M Na_2SO_4 to a mixture of PMAS(LB-1) and PMAS(LB-2) (produced by the room temperature reduction of PMAS(ES) with 0.10 M hydrazine at pH 9.5) caused the rapid (seconds) and virtually complete conversion of conformer PMAS(LB-2) (λ_{max} 335 nm) to PMAS(LB-1) (λ_{max} 408 nm) (Figure 10a). Similar rapid and near-quantitative conversion of conformer PMAS(LB-2) to PMAS(LB-1) was caused by the addition of 0.40 M LiCl, NaCl, KCl, $CaCl_2$, or $MgCl_2$ to a preformed PMAS(LB) mixture.

The added alkali metal ions also had a marked effect on the subsequent thermochromism of PMAS(LB). For example, heating to 50 °C the solution of predominantly PMAS-(LB-1) (λ_{max} 408 nm) formed in Figure 10a in the presence of Na_2SO_4 led to only a small shift of equilibrium (1) toward species PMAS(LB-2) (λ_{max} 335 nm) (Figure 10b). This behavior was in marked contrast to that observed above for aqueous PMAS(LB) mixtures in the absence of added metal salts, where heating at 50 °C caused virtually complete conversion of PMAS(LB-1) to PMAS(LB-2) (see Figure 7). It is clear that the presence of added metal salts such as Na_2SO_4 preferentially stabilizes the λ_{max} 408 nm conformer PMAS(LB-1).

We believe that these marked ionochromic effects arise from electrostatic binding of the alkali and alkaline earth metal ions to sulfonate groups on the PMAS(LB) polymer chains. Similar binding of these metal ions to sulfonate groups of related, nonconducting polyelectrolytes such as poly(styrenesulfonate) and poly(vinylsulfonate) is well established.[34,35] In reduced PMAS(LB), all of the sulfonate groups on the polymer chains are "free", since the polymer no longer possesses self-doping sites (see Scheme 2). Strong binding of the PMAS(LB) sulfonate groups to the metal ions is expected to stabilize the more planar, ordered PMAS(LB-1) (λ_{max} 408 nm) conformer (Scheme 3), in a similar fashion to the stabilization of the planar conformation of some poly(3-alkoxy-4-methylthiophene)s reported by Leclerc and co-workers.[36] Metal ion coordination to the sulfonate ring substituents should also partly screen the electrostatic repulsions between the SO_3^- negative charges along the chains, resulting in less tendency to adopt an "extended coil" conformation.

We subsequently observed a similar rapid conversion of PMAS(LB-2) to PMAS(LB-1) upon addition of 0.40 M NH_4Cl to an aqueous PMAS(LB) mixture at room temperature. Electrostatic binding of the NH_4^+ cation to "free" sulfonate groups on the PMAS(LB) chains would again appear to be the most likely cause of this ionochromic behavior. The possibility that the preference for conformer

Scheme 3



PMAS(LB-1) in the presence of added metal ions and the NH_4^+ cation arises from nonspecific masking of the sulfonate negative charges by the increased ionic strength was eliminated by the failure of 0.40 M Bu_4NCl to cause similar ionochromism. Binding of this large ammonium ion to the polymer SO_3^- groups is expected to be hindered by its steric bulk.

The above ionochromic behavior suggests an explanation for the unprecedented formation of the PMAS(LB-1) (λ_{max} 408 nm) conformer in the hydrazine reduction of aqueous PMAS(ES), a behavior not seen in the analogous reduction of unsubstituted polyaniline. Conformer PMAS(LB-1) may be a hydrazinium salt, $[NH_3NH_3^{2+}]$PMAS(LB-1), formed via interaction of excess hydrazine with free sulfonic acid (SO_3H) groups along the PMAS chains. Support for this comes from the strong ionochromism observed above upon adding the related NH_4^+ cation. In principle, hydrazine (with its two amine termini) should have the ability to bind simultaneously (either intramolecularly or intermolecularly) to two sulfonic acid substituents on the PMAS(LB) chains. Partial masking of the negative charges of the sulfonate groups by the hydrazinium cations may, in a similar fashion to alkali and alkaline earth metal ions, favor a less "extended coil" conformation PMAS(LB-1), λ_{max} 408 nm, for the leucoemeraldine base polymer.

The observed thermochromism of PMAS(LB) may be similarly rationalized in terms of conversion between conformers

with differing degrees of order along their polymer chains. Heating would be expected to diminish the electrostatic binding of hydrazinium cations to PMAS sulfonate groups, thereby facilitating conversion of the initially favored more planar, ordered conformer PMAS(LB-1) (λ_{max} 408 nm) to the alternative more twisted conformation PMAS(LB-2) (λ_{max} 335 nm). This conclusion is supported by the positive $\Delta S°$ value of +43 eu calculated at 25 °C from the temperature dependence of the equilibrium constant K_{eq} for the conversion of PMAS(LB-1) to PMAS(LB-2) (Table 1 and Figure 8). The relatively small conversion of PMAS(LB-1) to PMAS-(LB-2) observed upon heating PMAS(LB) when in the presence of Na^+ ions may be explained by the stronger binding of this alkali metal ion to PMAS sulfonate groups than that achieved by hydrazinium cations, resulting in the more planar PMAS(LB-1) conformer remaining favored even at elevated temperatures.

Conclusion

The chemical oxidation of the fully sulfonated poly(2-methoxyaniline-5-sulfonic acid) PMAS(ES) emeraldine salt with aqueous ammonium persulfate proceeds in a similar fashion to that previously observed with unsubstituted polyaniline, producing the fully oxidized pernigraniline base PMAS(PB) form with a characteristic absorption band at 540 nm. This oxidized species can be protonated in dilute acid to give the corresponding pernigraniline salt PMAS(PS) form of PMAS which has a characteristic absorption band at 670 nm.

PMAS(ES) exhibits unprecedented behavior upon reduction with aqueous hydrazine. Unlike previously examined polyanilines, the PMAS(LB) leucoemeraldine base product exists as an equilibrium mixture of two species, PMAS(LB-1) and PMAS-(LB-2) with λ_{max} at 408 and 335 nm, respectively. This aqueous equilibrium mixture shows remarkable thermochromism and solvatochromism, in which increasing temperature or the addition of organic solvents such as methanol, acetone, and NMP converts the initially favored PMAS(LB-1) (λ_{max} 408 nm) conformer to the PMAS(LB-2) (λ_{max} 335 nm) conformer. On the basis of these spectroscopic studies and related ionochromism exhibited by PMAS(LB) in the presence of alkali and alkaline earth metal ions and NH_4^+ cations, the two PMAS leucoemeraldine base species are assigned as conformers with differening degrees of planarity and order along their polymer chains.

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