ESR, Raman, and Conductivity Studies on Fractionated Poly(2-methoxyaniline-5-sulfonic acid)

Lynn Dennany, Peter C. Innis,* Fatemeh Masdarolomoor, and Gordon G. Wallace

ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, AIIM Facility, Innovation Campus, University of Wollongong, NSW 2522, Australia

Synthesis methods used to produce poly(2-methoxyaniline-5-sulfonic acid) (PMAS), a water-soluble, self-doped conducting polymer, have been shown to form two distinctly different polymer fractions with molecular weights of approximately 2 kDa and 8−10 kDa. The low molecular weight (LMWT) PMAS fraction is redox inactive and nonconducting, while the high molecular weight (HMWT) PMAS is electro-active with electrical conductivities of 0.94 ± 0.05 S cm^{-1}. Previous investigations have illustrated the different photochemical and electrochemical properties of these fractions but have not correlated these properties with the structural and electronic interactions that drive them. Incomplete purification of the PMAS mixture, typically via bag dialysis, has been shown to result in a mixture of approximately 50:50 HMWT:LMWT PMAS with electrical conductivity significantly lower at approximately $0.10-0.26$ S cm^{-1}. The difference between the electrical conductivities of these fractions has been investigated by the controlled addition of the nonconducting LMWT PMAS fraction into the HMWT PMAS composite film with the subsequent electronic properties investigated by solid-state ESR and Raman spectroscopies. These studies illustrate strong electronic intereactions of the insulating LMWT PMAS with the emeraldine salt HMWT PMAS to substantially alter the population of the electronic charge carriers in the conducting polymer. ESR studies on these mixtures, when compared to HMWT PMAS, exhibited a lower level of electron spin in the presence of LMWT PMAS indicative of the formation of low spin bipolarons without a change in the oxidation state of the conducting HMWT fraction.

Introduction

Poly(2-methoxyaniline-5-sulfonic acid) (PMAS) is a fully sulfonated polyaniline that is highly soluble in water in the conducting state providing a unique solution processing route.[1,2] Photoluminescence- and photoredox-induced reactions have been reported for PMAS in its emeraldine salt state.[1−7] These studies were carried out on PMAS fractions prepared via chemical oxidation of a 2-methoxyaniline-5-sulfonic acid (MAS) monomer, as shown in Scheme 1. It is known that PMAS synthesized via either chemical or electrochemical oxidation routes contains two distinct fractions that can be crudely separated by membrane dialysis.[8−10] More recently, these fractions have been isolated in high purity with the high molecular weight (HMWT) PMAS fraction having a M_w of ca. 8−10 kDa, while the low molecular weight (LMWT) PMAS fraction is an oligomer with M_w of ca. 2 kDa.[11] The oligomeric LMWT PMAS fraction is believed to be a phenazine-like structure similar to products reported for the polymerization of aniline at high pH's.[12]

Previous investigations into the photoluminescence of fractionated PMAS have shown that LMWT PMAS is a photoluminescent species.[2−4] Pure HMWT PMAS, in contrast, is a quencher, consistent with it being in the emeraldine salt form.[2] Examination of the mixtures of both fractions revealed that HMWT PMAS statically quenched the photoluminescence of the LMWT PMAS. It was shown that two quenching mechanisms were dominant in mixtures of these fractions driven via an inner filter quenching (or radiative energy) effect and a nonradiative energy transfer process. This latter quenching

SCHEME 1: Reaction of HMWT PMAS Synthesis
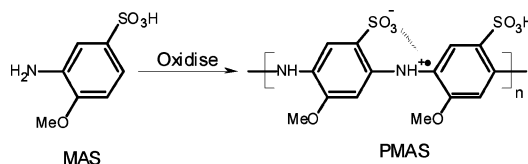
mechanism was successfully modelled by the nonlinear Perrin static quenching model that predicts a strong association of the two PMAS fractions in solution due to them being diffusionally restricted macromolecules.[2]

The strong association of these fractions may also impact significantly the electronic properties of PMAS. The magnitude of conductivity in a conducting polymer will be dependent upon the extent of charge carrier (polaron) delocalization, the charge carrier mobility, as well as the existence of structural disorder resulting from tail-to-tail propagation. The delocalization of charge along the PMAS structure is typically ascribed to the formation of high spin radical cations or polarons.[13,14] The nature and evolution of high-spin radical cations (polaron) through to the formation of the zero spin diacation (bipolaron), which form at higher doping levels in a conducting polymer, can be examined effectively using both Raman and electron spin resonance (ESR) spectroscopy.[15−21] Importantly, ESR can not only demonstrate the presence of unspin paired electrons, indicative of polarons, but also directly measure the relative concentration of polarons within the polymer by measuring spin concentration.[22,23]

In this work, we have studied the influence of these two distinctly different, but interrelated, PMAS fractions upon each

* To whom correspondence should be addressed. Phone: +61 2 4221 3127. Fax: +61 2 4298 1499. E-mail address: innis@uow.edu.au.

TABLE 1: Mixed Solutions of HMWT PMAS and LWMT PMAS Utilized within this Study

% w/w HMWT PMAS	volume LWMT PMAS (μL)[a]	volume HMWT PMAS (μL)[b]	volume H₂0 (μL)	total volume (μL)
100.0	0	400	0	400
50.0	200	200	0	400
46.7	200	175	25	400
42.9	200	150	50	400
38.5	200	125	75	400
33.3	200	100	100	400
27.3	200	75	125	400
20.0	200	50	150	400
11.1	200	25	175	400
0.00	200	0	200	400

[a] Stock aqueous solution of LWMT PMAS was 2.5 mg/mL.
[b] Stock aqueous solution of HMWT PMAS was 2.5 mg/mL.

other. These studies were made to gain further insight into how the LMWT PMAS influences the resultant electronic and chemical properties of the HMWT PMAS to describe the behavior observed in the nonfractionated (as synthesized) PMAS that has been used with little or no postsynthesis purification or fractionation.

Experimental Section

Materials and Reagents. 2-Methoxyaniline-5-sulfonic acid (MAS) was provided by Mitsubishi Rayon, Japan, and purified by acid base crystallization prior to use. Polystyrenesulfonic acid sodium salt (PSS) gel permeation calibration standard with a molecular weight of 2 kDa (PDI 1.0) was purchased from Sigma Aldrich and used without modification. PMAS emeraldine salt was prepared via the chemical synthesis method, reported previously.[9,11] The as-synthesized material was fractionated via a previously described cross-flow dialysis system.[11] The fractionated PMAS samples are identified hereafter as high molecular weight HMWT PMAS (M_w 8−10 kDa, PDI 1.4) and low molecular weight LMWT PMAS (M_w 2 kDa, PDI 1.1). All other reagents used were of analytical grade, and solutions were prepared in Milli-Q water (18 MΩcm).

Sample Preparation. PMAS and fractionated mixtures of HMWT and LMWT PMAS were dissolved in water at loading levels shown in Table 1. Aliquots of 20 μL of these solutions were micropipetd onto the tip of a microcapillary tube, dried, and inserted into a 2.0 mm inner diameter ESR tube (Bruker). The ESR tube was then inserted into the ESR spectrometer resonator and left at a fixed position for all subsequent measurements. The microcapillary tubes rather than the ESR tube were removed from the resonator to produce reproducible resonator cavity tuning. All experiments were run in triplicate, and their average response was reported. Immediately after each ESR study, Raman spectra of the deposit at the tip of the microcapillary tube were acquired to minimize sample aging.

Apparatus. ESR spectra were recorded on a Bruker EMX ESR spectrometer under identical conditions: microwave frequency of 9.861 GHz, attenuator of 30.0 dB, sweep width of 30 G, modulation frequency of 100 kHz, modulation amplitude of 0.25 G, time constant of 40.96 ms, conversion time of 163.84 ms, and sweep time of 671 s were employed unless otherwise stated.

Raman spectra were recorded on a Jobin Yvon Horiba HR800 Raman microscope. A He−Ne (632.8 nm) laser was utilized with a 300-line grating providing a resolution of ±1.25 cm⁻¹.

Conductivity measurements were performed on dried films of 10 μm thickness (obtained by evaporative air casting on a
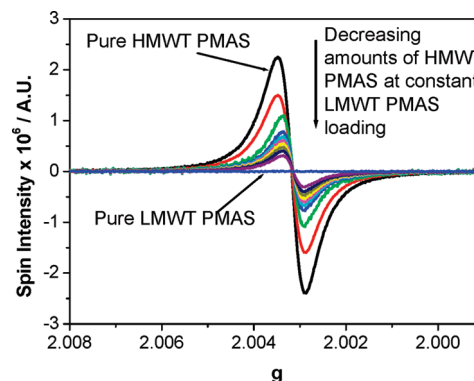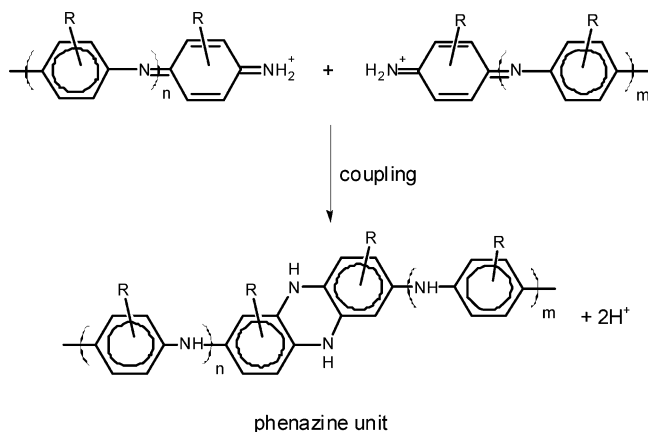

Figure 1. Typical ESR responses of solid state samples of decreasing amounts of HMWT PMAS at constant LMWT PMAS loading. The overall polymer concentration was kept constant at 2.5×10^{-4} M with the ratio of the two fractions changing. A microwave frequency of 9.861 GHz, attenuator of 30.0 dB, sweep width of 30 G, modulation frequency of 100 kHz, modulation amplitude of 0.25 G, time constant of 40.96 ms, conversion time of 163.84 ms, and sweep time of 671 s were employed.

glass slide substrate) using a JANDEL resistivity system (model RM2) with a linear four-point probe head.

Results and Discussion

ESR Properties. Extensive ESR studies have been made to identify the nature of the charge carrier formed in a conducting polymer.[24] ESR has been frequently used to investigate the nature of the quasi-particle responsible for the charge transport and their interactions with each other. Various quasi-particles[25−28] such as excitons,[26] solitons, polarons,[25] and bipolarons[27] have been described to explain the physical properties of these materials. ESR allows investigations on the nature and evolution of polarons and bipolarons in conducting polymers.[27] Polaronic quasi-particles,[22,28] where $s = \pm 1/2$, are responsible for a single resonance line located close to the g factor of 2.003, while the zero spin bipolaron ($s = 0$) presents no ESR spectrum. It has been reported that the polaron concentration can be effectively measured in conducting polymers, where the single-line ESR spectrum can be attributed to its presence. However, at higher doping or conductivity levels, polaron recombination will result in the formation of the spinless bipolaron reducing the overall observed ESR signal.[29,30] For the emeraldine salt form of HMWT PMAS, the ESR spectrum is typical of a polaronic state (Figure 1). The LMWT PMAS exhibited a very different ESR response with no spin being observed, consistent with its inert chemical and active photochemical properties reported previously.[2,5] A single-line ESR spectrum was obtained for each sample containing the HMWT PMAS, showing that the charge carriers have a spin of $s = \pm 1/2$.[31] The g factor of the HMWT PMAS solid state ESR signal was found to be in the range of 2.003−2.004 as shown in Figure 1. This result was close to the free electron g factor (2.0023) and was indicative of resonance that results from electron delocalization across the conjugated π-system.[32] The slightly higher g factor observed is typical of a heteroatom system where the spins are more localized on the nitrogen sites.[33−37] The observed ESR spectra exhibited no hyperfine structure and were characteristic of delocalized free radicals.[7] The peak-to-peak line width, ΔG, of this ESR signal was approximately 3.483 G. The relative electron spin concentration, indicative of the population of nonspin paired electrons, was determined by double integration of the observed ESR signal and found to be $\sim(4.2 \pm 0.3) \times 10^{10}$ for a 50 μg HMWT PMAS sample.

ESR, Raman, and Conductivity Studies on PMAS

J. Phys. Chem. B, Vol. 114, No. 7, 2010 **2339**

SCHEME 2: Proposed Reaction Resulting in the Formation of Phenazine-Like Defects Which May Contribute to the Formation of LMWT PMAS[1,7,38]

phenazine unit

Figure 2. Relative spin concentration of HMWT PMAS upon interaction with either LMWT PMAS (blue line) or PSS (red line).

In contrast to the above, the LMWT PMAS showed no ESR response. The apparent lack of spin does not necessarily indicate the presence or absence of spinless bipolarons in this material. Previous studies indicate that the LMWT PMAS fraction was redox inactive.[2] It has been suggested that these materials have phenazine-like defects (Scheme 2) that are incapable of supporting a delocalized polaron due to the break in conjugation resulting from these defects.[2,7,38] It is postulated that this type of reaction results in the formation of shorter polymer chains as seen for the LMWT PMAS fraction.[2,7,38] Definitive identification of this fraction by NMR and mass spectroscopic techniques has proven to be challenging due to the combined anionic and polymeric nature of these materials.

The intensity of the ESR signal was found to reduce with decreasing loadings of HMWT PMAS when mixed with the LMWT PMAS, as shown in Figure 1. The 100% HMWT PMAS signals were acquired in the absence of the LMWT PMAS to provide a comparative baseline signal. In all other instances, the amount of LWMT PMAS was kept constant. The observed ESR responses were attributed to solely the presence of the HMWT PMAS as the LMWT PMAS had no observable electron spin. A linear quantitative decrease in spin concentration would be predicted as the HMWT PMAS concentration was reduced in the presence of the ESR inactive LMWT PMAS, such that a 50% dilution should result in a similar reduction in the observed spin. However, a dramatic decrease in the relative spin intensity by 4 orders of magnitude from 4.2×10^{10} to 2.8×10^6 was observed. This result indicated that a different mechanism was dominating the electronic character of the HMWT PMAS (Figure 2). Under the experimental conditions, in this study the background relative spin concentration was observed to be of the order ca. 10^6, which was considered to be a zero spin state. The presence of this signal arises from the presence of paramagnetic impurities in the microcapillaries, ESR tubes, and other instrumental anomalies.

A comparative study of the HMWT PMAS with a fully sulfonated 2 kDa polystyrenesulfonate (PSS) oligomer, chosen as a nonconducting analogue to the LMWT PMAS, exhibited the predicted dilution behavior, as seen in Figure 3. The decrease in spin concentration was substantially smaller than the LMWT PMAS, with observed relative electron spin decreasing from 4.2×10^{10} to 1.1×10^{10} (Figure 2).

Interestingly, solution state ESR studies of these mixtures made prior to casting did not demonstrate the influence of the LMWT PMAS on the high-spin ESR signal observed for the
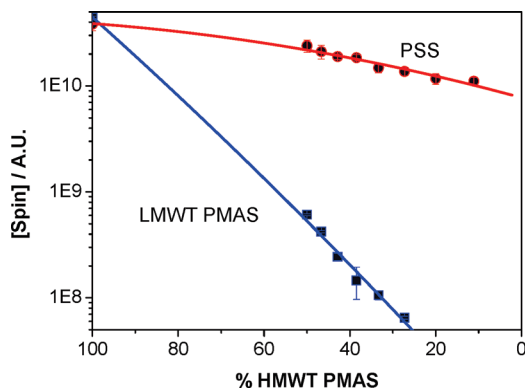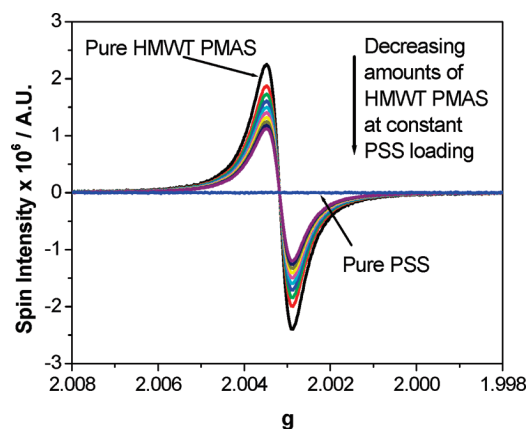

Figure 3. Typical ESR responses of solid state samples of decreasing amounts of HMWT PMAS at constant PSS loading. The overall polymer concentration was kept constant at 2.5×10^{-4} M with the ratio of the two fractions changing. A microwave frequency of 9.861 GHz, attenuator of 30.0 dB, sweep width of 30 G, modulation frequency of 100 kHz, modulation amplitude of 0.25 G, time constant of 40.96 ms, conversion time of 163.84 ms, and sweep time of 671 s were employed.

HMWT PMAS fraction. Previous fluorescence studies suggested that these PMAS fractions were interacting in solution in a paired manner with their interactions restricted by slow macromolecular diffusion processes as predicted by the Perrin model.[2] Similar behavior has also been reported for photo- and redox-active materials electrostatically bound to the HMWT PMAS where their interactions were detectable in the solid state but not in solution.[4,5] In this study, it was apparent that the electronic interactions required close association of both PMAS fractions, where the LMWT PMAS is not free to move and thereby is capable of perturbing the unspin-paired polaron charge carrier in the conducting HMWT PMAS.

The presence of the chemically inert LMWT PMAS fraction does not influence the oxidation state of the conducting HMWT fraction, as reported previously.[2] UV−vis spectroscopy studies in this earlier work indicate that these two materials behave in an additive manner.[2,5] The dramatic decrease in spin concentration can therefore be attributed to the transformation of the emeraldine salt form of the HMWT PMAS fraction from a high-spin polaronic state to a mixed polaron−bipolaron state when HMWT and LMWT PMAS are combined in the solid state. This effect was clearly illustrated in Figure 2 where spinless bipolarons were formed when these two PMAS fractions interacted in the solid state.

Conductivity. The magnetic properties and therefore the conductivity of a conducting polymer are intrinsically related

to the population and mobility of the polaron and bipolaron charge carriers. As such, the conductivity of the solid state samples containing the LMWT PMAS should result in conductivities lower than those containing only HMWT PMAS. Electrical conductivities of the purified HMWT PMAS fraction of 0.94 ± 0.05 S cm^{-1} were observed. This conductivity dropped significantly upon the addition of LMWT PMAS to 0.12 ± 0.02 S cm^{-1} for a 50:50 mixture of the two fractions. This result was also consistent with bag dialyzed materials, which are nonfractionated and have conductivities typically of the order of 0.10 to 0.26 S cm^{-1}. The conductivity of PMAS containing the LMWT fraction was substantially lower than would be expected for the addition of insulating filler. Such a result was indicative that the nonconducting LMWT PMAS fraction interacts strongly with the electronic structure of the HMWT PMAS limiting interchain charge transfer processes within the HMWT PMAS necessary for electrical conductivity. Electrical conductivities of a 50:50 mixture of HMWT PMAS with PSS of 0.38 ± 0.02 S cm^{-1} were observed. This conductivity was consistent with the predicted dilution effects of a noninteracting filler as observed for the ESR spectra acquired in the presence of the PSS, as discussed above.

ESR studies confirmed that the presence of the LMWT PMAS forced the composite toward a bipolaronic electronic structure. However, a shift to a spinless bipolaronic state does not necessarily imply a lower electrical conductivity in a conducting polymer. It is well-known that bipolaronic states generally form as the population of polarons increases at higher oxidation and doping levels and subsequently higher polymer conductivity. These bipolarons themselves may also undergo reversible conversion to the polaron and back.[38] In this case, it is the inability of the LMWT PMAS fraction to facilitate electron transfer, coupled with the evidence for strong association of this fraction to the HMWT PMAS backbone, that inhibits intracharge transfer to adjacent polymer chains. It can be concluded from this study that these interactions forced the preferential formation of zero spin bipolaron states.

Conductivity studies have been reported for polyaniline (PAni) and its behavior in the presence of oligomers.[11,38] As with the two fractions of PMAS, the materials isolated at the early stages of oxidative polymerization of the aniline monomer under aprotic or basic conditions have been reported to result in the formation of phenazine-like structures. Such structures form as a result of ortho-coupling of aniline monomers with an accompanying intramolecular cyclization.[2,38] Like the LMWT PMAS, these initial oligomeric materials were nonconducting, and their presence was noted to lower the final conductivity of the PAni emeraldine salt.

Mechanistic studies on the formation of phenazine-like defects have been reported by Viva et al. for the electrosynthesis of PMAS at pH 0.[39] They reported that the event of ortho-coupling resulted in the formation of a phenazine-like defect, which inhibited further chain propagation, thereby limiting molecular weight. The chemical and physical properties of the oligomeric LMWT PMAS formed in the present study are similar to those of the above phenazines, suggesting that the oligomeric PMAS may possess ortho-coupling structures analogous to those in Scheme 2. This would also support the findings in this study with regard to the decreased conductivity that was observed for the LMWT PMAS and for solid-state samples containing a mixture of the two oligomers.[2]

Raman Spectroscopy. Raman spectroscopy is a very powerful technique for the analysis of intrinsically conducting polymers. It has been applied to the study of structural changes
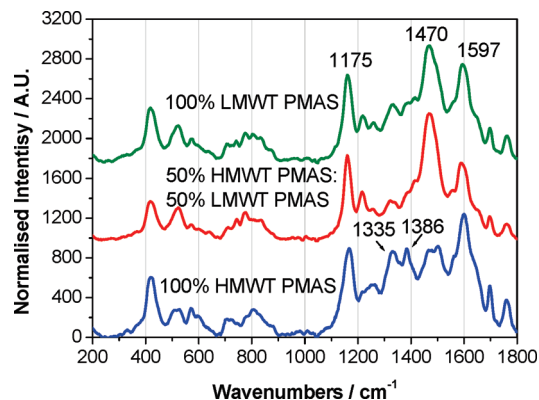

Figure 4. Raman spectra of solid state HMWT PMAS, LMWT PMAS, and 1:1 LMWT:HMWT PMAS mixture at a 632 nm Raman excitation wavelength.

related to the presence of sulfonated substituents.[18,40,41] To investigate the structural modifications that occur when the two fractions of PMAS are combined, Raman spectra of films containing 100% HMWT PMAS and 100% LWMT PMAS and an equal mixture of both were acquired, and the spectra were normalized to the C–H bending modes at 1175 cm^{-1}, as shown in Figure 4. The different modes of vibration observed have been assigned as C–H bending between 1100 and 1700 cm^{-1}, the C–N stretching modes (amines, imines, polarons) between 1210 and 1520 cm^{-1}, and the rings C=C quinoid stretching at ca. 1600 cm^{-1}.[17,41,42]

The Raman spectrum of HMWT PMAS exhibits a broad polaron doublet, with components at 1333 and 1386 cm^{-1} that have been assigned, by others, to the presence of the C–N$^{•+}$ polaron.[17,18,43] Upon addition of LMWT PMAS to the HMWT PMAS, there was a significant change in the intensity of these polaron peaks. This decrease in intensity also correlated with the decrease in the observed ESR spin as discussed above. Additionally, a decrease in relative intensity of the –C=C– quinoid band centered at ca. 1600 cm^{-1} strongly correlated with the decrease in the concentration of polarons upon mixing with the LWMT PMAS.[17]

Accompanying these changes was an increase in the peak at 1470 cm^{-1} with increasing LWMT PMAS content. The vibration has been associated with the stretching vibration of the C=N group and directly correlates with the formation of unprotonated imine (=N–) typically observed in the nonconducting emeraldine base and the fully oxidized pernigraniline forms of PAni.[17,41,44] In sulfonated PAni, Niaura et al. have also reported the presence of this band as being indicative of strong charge localization as a result of the SO$_3$$^-$ localizing or pinning of the polaron making it immobile, subsequently resulting in a lower conductivity.[41]

The effect of PSS on the Raman spectra of HMWT PMAS was also investigated. Upon addition of PSS and subsequent normalization of the Raman spectra, the spectra of HMWT PMAS and 1:1 HMWT PMAS:PSS were indistinguishable. Both show characteristic bands typical of the HMWT PMAS as described. This result was also consistent with the ESR findings where PSS, a fully sulfonated analogue to the LWMT PMAS, had no influence upon the electronic structure of the HMWT PMAS as an emeraldine salt.

Conclusions

For the first time, an explanation of why the strong interaction between the two fractions of poly(2-methoxyaniline-5-sulfonic

ESR, Raman, and Conductivity Studies on PMAS

J. Phys. Chem. B, Vol. 114, No. 7, 2010 **2341**

acid) (PMAS) severely impacts the electronic properties of mixtures of the two found in the as-synthesized polymer has been presented. It has been shown that the presence of a nonconducting, redox inactive, low molecular weight (LMWT) PMAS oligomer, formed as a byproduct during the aqueous synthesis of PMAS, will interact strongly with the emeraldine salt form of the high molecular weight (HMWT) PMAS. This interaction is reflected in a substantial decrease in the electrical conductivity by an order of magnitude greater than would be expected for insulating and inert filler at similar loadings. Accompanying the decrease in conductivity was an associated loss of electron spin associated with the presence of the polaronic charge carriers. The loss of electron spin, also confirmed by Raman spectroscopy, is a result of these polarons interacting with each other to preferentially form spinless bipolarons. Significantly, this process occurs without the polymer composite itself undergoing an oxidation state change which is usually associated with a change in electrical conductivity. This finding is indicative that the nonconducting LMWT PMAS fraction interacts strongly with the electronic structure of the HMWT PMAS, such that it not only hinders interchain charge transfer to adjacent conducting HMWT PMAS chains but also distorts the intrachain charge transfer processes within the HMWT PMAS.

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