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An ESR Study of the Electrochemical Reduction and Oxidation of Poly(*p*-nitrostyrene)

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ABSTRACT: Electron spin resonance (ESR) spectroscopy is applied to study the electrochemical oxidation and reduction of poly(*p*-nitrostyrene) solutions in situ. The electrochemical reduction in dimethylformamide solution leads to production of the anion radical of poly(*p*-nitrostyrene). The ESR spectrum of the reduced polymer is unusual in that it consists of a single homogeneously narrowed line, with no observed hyperfine couplings. On the basis of the temperature and concentration behavior of the ESR spectrum, it is concluded that the electron spin is involved in an intramolecular hopping along the pendant nitrophenyl groups in the polymer. At room temperature the rate of this process is approximately 55 MHz. The activation energy for this process is 1.5 kJ/mol in solution and 0.18 kJ/mol in the solid state. Electrochemical oxidation of poly(*p*-nitrostyrene) gives rise to a radical with resolved hyperfine coupling to ^{14}N. The oxidized radical is evidently not a simple cation radical. The electrochemical oxidation is not reversible, and the same radical can be produced by oxidation in air.

Introduction

Charge transfer between two dissimilar powders forms the basis for the development step in conventional xerography. This transfer of charge is realized when the two materials are mixed such that there is contact between their surfaces, hence the name contact electrification or triboelectrification. In spite of the tremendous importance of this process, the mechanism for the charge exchange still remains basically unknown. We have focussed our efforts in the past few years on the feasibility of applying electron spin resonance (ESR) spectroscopy as a spectroscopic probe for detection of triboelectrification.

Our initial efforts have concentrated on electron transfer to and from a variety of pigments by using an in situ electrochemical cell to transfer electrons.[1] Pigments are known to play a significant role in the transfer of charge between toner and carrier particles in xerographic developers.[2] These experiments were done to determine whether pigments do undergo reversible electron-transfer reactions and whether ESR can detect these reactions. It turns out that carbon blacks can accept electrons reversibly. With chemically oxidized carbon blacks, the accepted electrons localize on surface sites giving rise to a narrow ESR signal.[1,3] With an unoxidized black, reduction leads to a narrow conduction ESR signal.[4] ZnO particles can also undergo electrochemical reduction, and these changes can be monitored by both the generation of an ESR signal and an increase in dielectric loss.[5] Finally the organic pigment, metal-free phthalocyanine (H_2Pc), undergoes both reduction and oxidation giving rise to ESR spectra which are readily differentiated.[6] Of course the polymers in both toner and carrier also play a significant role in both the direction and amount of charge transferred. It is therefore important to determine whether polymers can also accept or donate electrons and if we can detect these redox reactions with ESR. This present work then details our initial efforts at extending this study to polymers.

The utilization of electroactive polymers to chemically modify electrodes has been known for some time now.[7] Polymers such as poly(nitrostyrene),[8] poly(vinylferrocene),[9] poly(vinylanthraquinone),[10] and polyimide[11] have all been

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studied electrochemically. For example, a Pt electrode coated with poly(nitrostyrene) and immersed in an electrolyte will, upon the application of a potential, reversibly donate electrons to the nitrophenyl moieties of the coated polymer.[8] Albery and Jones[10,12] have taken this one step further and demonstrated that ESR can successfully detect this charge transfer for several polymers including poly(*p*-nitrostyrene) when they are coated on a platinum electrode.

Because of this prior work, we have selected poly(*p*-nitrostyrene) as the polymer for our initial experiments. We, however, look at the polymer in solution rather than as a film. As we shall demonstrate in this report, poly(*p*-nitrostyrene) not only accepts charge in solution but also can donate electrons through oxidation. Additionally, from analysis of the ESR spectra, new insights emerge into intramolecular electron transfer along the nitrophenyl groups of a polymer chain.

Experimental Section

The electrochemistry was carried out in either dimethylformamide (DMF) or dichloromethane ($MeCl_2$) from Aldrich. The electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP) from Eastman. The poly(*p*-nitrostyrene), or PNS, and the *p*-nitrostyrene (NS) monomer were both from Polysciences. All chemicals were used as received, except for monomer-free PNS, which was obtained by the following procedure. PNS was dissolved in a minimum volume of DMF and then precipitated with $MeCl_2$. Flocculation of the precipitate was accomplished by addition of small amounts of TBAP. The precipitate was filtered and washed with $MeCl_2$. This procedure was repeated five times to remove the last traces of residual monomer. Oxygen was removed from all solutions by bubbling for at least 1 h with N_2 gas before use.

ESR spectra were obtained on a commercial Varian E109E spectrometer equipped with an E-238 TM-110 cavity and an E-257 variable-temperature accessory. All ESR spectra are plotted with field increasing from left to right. The Mn^{2+} signal from a SrO sample was used as a reference for measurement of *g* values, absolute radical concentrations, and an internal standard for the temperature dependence of signal intensities. For absolute radical concentrations the SrO signal was referenced against a standard solution of 4-oxo-TEMPO. All electrochemical oxidation and reductions were done in situ. The ESR cell for variable-temperature studies was a small standard quartz flat cell that fit into the quartz Dewar of the ESR variable-temperature accessory. For electrochemical studies a Pt electrode was inserted through a rubber stopper at the top of the cell into the ESR sensitive region to serve as the working electrode. A second Pt electrode inserted from the bottom of the cell served as the counter electrode. A silver wire served as a pseudo-reference electrode. The reduction of *p*-benzoquinone was used as a standard in this cell to relate these potentials to those versus SCE in 0.1 M TBAP in DMF. For studies at room temperature a larger electrochemical flat cell from Wilmad was used.

Simulation of ESR spectra was accomplished by using a Nicolet 1180 Data Processor with NTCESR software.

Results and Discussion

Electrochemical Reduction of PNS (1). Electrochemical reduction of polynitrostyrene (PNS) at −1.0 V versus SCE in 0.1 M TBAP in DMF solution gives rise to an ESR spectrum consisting of a broad signal ($\Delta H_{pp} = 6$ G) and a signal showing hyperfine structure. Both signals have identical *g* values of 2.0045, as would be expected for nitrogen centered aromatic radicals (a *g* value of 2.0044 is observed for nitro-substituted benzenes[14]). Electrochemical reduction of 0.1 M TBAP in DMF does not give rise to an ESR signal, ruling out nitrogen-centered radicals on DMF. Removing the applied potential with the circuit closed results in a slow decrease in the ESR signal intensity, which can be accelerated by changing the potential to more anodic values. This electrochemical reaction appears to be qualitatively reversible.

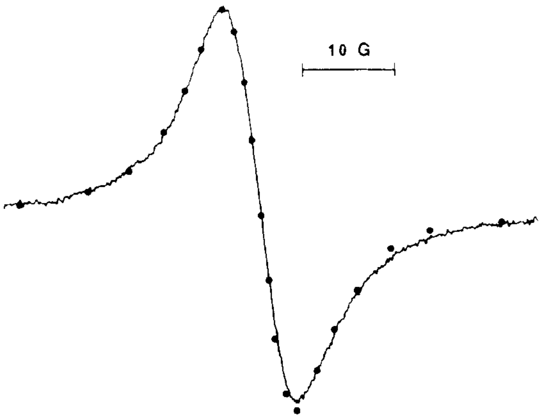
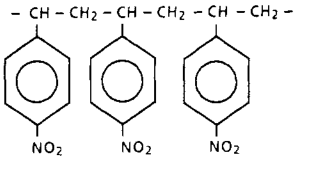


Figure 1. ESR spectrum of electrochemically reduced poly(*p*-nitrostyrene) in DMF solution after removal of residual monomer. The points show the fit to a Lorentzian line shape. The data were obtained at a temperature of 233 K with 1-G modulation, 10-mW microwave power, and [PNS] = 10^{-3} M and [TBAP] = 0.1 M.

One possibility for the radical giving rise to the ESR component with hyperfine structure is the anion radical of residual *p*-nitrostyrene (NS) monomer (2) in the PNS sample. To separate the residual monomer from the polymer, we added dichloromethane ($MeCl_2$) to a DMF solution of PNS, precipitating the polymer. Residual NS monomer is soluble in $MeCl_2$ and thus should remain in solution. Electrochemical reduction of the supernatant solution ($E_{1/2} = -0.86$ V vs SCE) gave rise to the same hyperfine spectrum seen in the untreated polymer, with no indication of a broad component. Unfortunately, it is difficult to definitively assign the observed spectrum to the radical anion of the NS monomer. The ESR spectrum from the $MeCl_2$ extract of the polymer is similar to that obtained from a commercial sample of NS monomer and to that previously presented in the literature.[15] However, the observed intensities are different, and there are additional resonances in the $MeCl_2$ extract. In addition, the changes in the spectra on changing solvents suggests that there may be more than one radical present. Further work to identify these impurities in the polymer were not considered necessary for the present work. All further discussion will deal with polymer that has been purified by $MeCl_2$ extraction.

Electrochemical reduction of a DMF solution of the $MeCl_2$-insoluble polymer ($E_{1/2} = -1.0$ V vs SCE) from the PNS sample gives rise to the ESR spectrum shown in Figure 1. This spectrum is identical with the broad component observed from the untreated commercial PNS sample. In the $MeCl_2$-extracted polymer there is no indication of the component with hyperfine structure. The broad unresolved spectrum shown in Figure 1 is very similar to the one shown previously for electrochemically reduced *solid films* of PNS.[10] In that work the authors suggested that this ESR signal arose from the radical anion of the PNS polymer (1), although no work was shown to confirm the identity of this ESR signal. The ESR signal in the present work clearly does arise from PNS in *solution*, not electrochemically deposited on the electrode surface. The PNS radical is quite stable, and the ESR spectrum could be observed in the DMF solution after the cathode had been removed.

A number of workers have studied the cyclic voltammetry of the reduced *solid* PNS films on Pt electrodes in acetonitrile.[8,10,12,22] In the solid they have found reduction potentials of $E_{1/2} = -1.5$ to -1.7 V vs Ag|Ag$^+$. Using a value[23] of −0.30 V for the potential of SCE vs Ag|Ag$^+$ (ignoring differences in junction potentials in the two dif-



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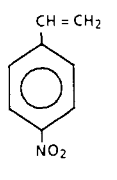

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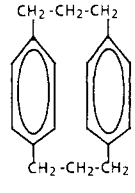

3

ferent solvents) gives $E_{1/2} = -1.30$ V vs Ag|Ag$^+$ for the PNS solution in DMF in the present work, slightly less negative than that observed in the solid. The present work also indicates that residual nitrostyrene monomer (and possibly other $MeCl_2$ extractable species) may make a contribution in the electrochemical reduction of this polymer.

The ESR signal for the radical from PNS reduction has a *g* value of 2.0045, suggesting that it is a nitrosubstituted aromatic anion radical, as expected for the PNS polymer 1. It would also be expected to show hyperfine couplings to the aromatic and aliphatic protons and to the nitrogen of the nitro group. Since the hyperfine coupling to nitrogen should be approximately 10 G (it is 9.75 G in NS$^-$ in DMF), while a single narrow line with $\Delta H_{pp} = 6.0$ G is observed at room temperature, the ESR line is clearly homogeneously narrowed by an exchange interaction. As illustrated in Figure 1 for a temperature of 233 K, this signal is Lorentzian over a temperature range of 100–300 K, again in agreement with a homogeneously narrowed signal (a Gaussian line shape is expected from a heterogeneous envelope of unresolved couplings). The width of the ESR signal appears to be essentially independent of either PNS concentration, [PNS], or the concentration of the reduced PNS radical, [PNS$^-$], when they are changed by a factor of 100. There is an increase in the line width from 6 to 10 G as the temperature is lowered from 300 to 100 K.

There are a number of possible exchange mechanisms which could give rise to narrowing in the "fast"-exchange region, where $\upsilon_{ex} > \gamma_e \Delta a_N$. Here υ_{ex} is the rate of the exchange, Δa_N is the separation of lines with the largest hyperfine coupling (that to ^{14}N) in gauss, and γ_e is 2.8-MHz G^{-1}. The rate of exchange is thus greater than 30 MHz. One possible mechanism is the exchange interaction between two adjacent electron spins[16] (Heisenberg exchange), as has been observed in solutions of DPPH[17] and as was tentatively suggested[10] for the previously observed ESR signal in solid PNS. For a polymer this type of exchange interaction may occur via an *intermolecular* mechanism or via an *intramolecular* mechanism between electron spins that are located on the same polymer chain. In any event, both the intermolecular and intramolecular cases would be expected to show $\Delta H_{pp} \propto 1/[PNS^-]$,[16] which is not observed. ΔH_{pp} was observed to be independent of [PNS$^-$] over a wide range. In addition, the maximum concentration of radical sites that was produced was 10% of the total number of nitrophenyl moieties after extensive reduction and was typically only 1%. For an *intramolecular* exchange, if the reduced sites are distributed at random, then the probability that two adjacent moieties are both reduced is less than 2%. This makes it seem very unlikely that the narrowing in the bulk of the sample is by intramolecular electron–electron exchange. In terms of an *intermolecular* exchange, the [PNS] was typically 10^{-2}–10^{-4} M. With even 10% of these sites reduced, the [PNS$^-$] would be extremely low to result in any significant electron–electron exchange.[16]

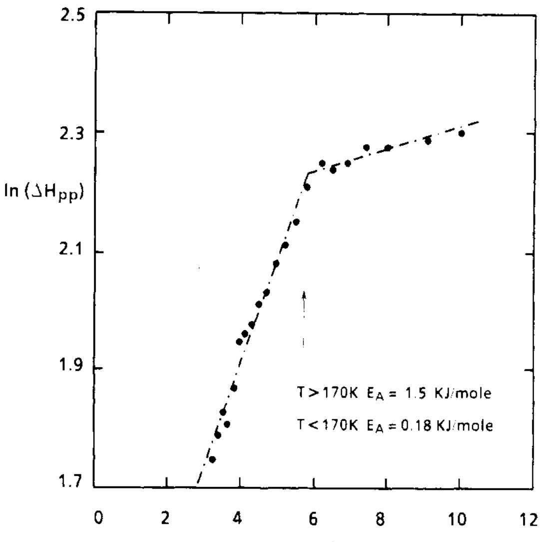

Figure 2. Temperature dependence of the ESR line width, ΔH_{pp}, of the poly(*p*-nitrostyrene) radical anion, in DMF solution. The activation energy of the intramolecular exchange is shown based on eq 1. The arrow shows the observed freezing point of the solution. The data were obtained with 1-G modulation, 10-mW microwave power, and [PNS] = 10^{-3} M and [TBAP] = 0.1 M in DMF.

The other possible mechanism is a chemical exchange interaction between PNS and PNS$^-$ which would occur in a bimolecular collision of the radical anion and the neutral molecule. Following Ward and Wiessman,[19] for a bimolecular exchange we can write $1/\tau = k[PNS]$, where τ is the mean lifetime of PNS$^-$ and k is the rate constant for the collision. Applying this to the equation of Piette and Anderson,[20] for the case of fast exchange

$$(1/T_2)_{\mathrm{eff}} - 1/T_2 = \nabla\tau \qquad (1)$$

gives an exchange narrowed line width that is inversely proportional to [PNS], while the observed line width is essentially independent of [PNS]. In eq 1 $(1/T_2)_{\mathrm{eff}} = {}^1/_2\sqrt{3}\Delta H_{pp}$, $1/T_2 = {}^1/_2\sqrt{3}(\Delta H_{pp})_0$, ΔH_{pp} is the observed exchange narrowed line width, $(\Delta H_{pp})_0$ is ΔH_{pp} in the absence of exchange, ∇ is the second moment of the spectrum, and τ is the correlation time for the exchange.

Again, however, in the polymer *intramolecular* collisions along the polymer chain are highly probable. In the case of *intramolecular* collisions, the exchange will appear to be unimolecular (i.e. independent of [PNS]) and thus $1/\tau = k$. Inserting this in eq 1 gives

$$\ln \{(1/T_2)_{\mathrm{eff}} - 1/T_2\} = \ln \{\nabla/A\} + E_A/RT \qquad (2)$$

Here A and E_A are the Arrhenius parameters for the exchange. Thus a plot of ΔH_{pp} (assuming $\Delta H_{pp} \gg (\Delta H_{pp})_0$) versus $1/T$ should be linear, with a slope of E_A/R, and will be independent of both [PNS] and [PNS$^-$]. As noted above, the observed ΔH_{pp} is essentially independent of [PNS] and [PNS$^-$], in agreement with this model.

The assumption in Figure 2 (the plot of eq 2) is that ΔH_{pp} is large compared to $(\Delta H_{pp})_0$, the natural line width in the absence of exchange. This assumption can be shown to be reasonable in a number of ways. Simulations of the solution spectra of the oxidized PNS radical (where exchange is much slower, as is discussed later) suggests that $(\Delta H_{pp})_0$ must be less than 2 G in the oxidized radical at room temperature, compared to the observed line width of $\Delta H_{pp} = 6$ G in reduced PNS. However, some of the 2-G line width in the oxidized radical could be due to exchange effects in that radical, and $(\Delta H_{pp})_0$ could be much less. Indeed, the fact that the plot in Figure 2 is linear at the highest temperatures suggests that $(\Delta H_{pp})_0$ is considerably smaller than 2 G. A value of $(\Delta H_{pp})_0$ greater than 0.5 G gives rise to an obvious curvature at the highest temperatures away from the vertical axis of the plot. If $(\Delta H_{pp})_0 = 0.5$ G, then the value of the rate constant k decreases by 15%, and the value of the activation energy E_a increases by 10%. Finally, $(\Delta H_{pp})_0$ would be expected to be strongly viscosity dependent (assuming it is dominated by dipolar, anisotropic g factor or anisotropic hyperfine interactions) and thus should be dependent on the PNS concentration. Since the observed line width appears to be independent of polymer concentration, $(\Delta H_{pp})_0$ does not appear to be significant.

From eq 1 with $1/\tau = k$, the value of the rate constant k can be determined if the value of ∇ is known. From the spectrum of the reduced PNS radical where the exchange has been slowed considerably (as discussed later and shown in Figure 4) the value of ∇ can be estimated and is found to be approximately 102 G^2. Thus at room temperature that rate of the intramolecular electron exchange in the reduced PNS is 55 MHz.

The plot of eq 2 is shown in Figure 2. The plot shows two linear regions of different slopes. Above about 170 K the slope yields an activation energy of 1.5 kJ/mol, while below 170 K the activation energy is only 0.18 kJ/mol. The transition shown in Figure 2 at 170 K corresponds to the freezing point of the DMF solution. Thus, according to this mechanism the activation energy for the transfer of the electron spin along the nitrophenyl side groups of the polymer is 8 times *lower* in the solid state than in solution. This strongly suggests that the TBAP electrolyte is not involved in this electron transfer, as the mobility of this salt is very low in the solid state (the electrochemical current drops by a factor >100 on freezing), which would result in a greatly increased activation energy in the solid. Note also that the observed ΔH_{pp} is independent of [TBAP] from 0.1 to 2 M.

The lower activation energy in the solid can be explained by a simple model, where the electron transfer occurs between adjacent aromatic rings that are approximately parallel. Evidence has been previously presented for intramolecular electron transfer between two aromatic rings in the anion radicals of [2,2]paracyclophane and [3,3]-paracyclophane (**3**), where two aromatic rings are locked into a parallel conformation by aliphatic bridges.[21] In this locked structure, the electron exchange between the two rings is apparently extremely rapid, although it is not clear if this is an electron hopping between the two rings or if there is sufficient overlap of molecular orbitals to result in electron delocalization over the entire molecule. The homology in the structures of [3,3]paracyclophane (**3**) and PNS (**2**) is clear. In solution, rapid motion of the polymer chains would tend to minimize such parallel associations in PNS. In the solid, however, the polymer would tend to form a helix with staggered, approximately parallel aromatic rings to minimize intramolecular packing energy. The constraints of the solid-state lattice would also tend to minimize motions that could interrupt this favorable alignment. The net result would be a lower activation energy in the solid state compared to solution.

Although the unpaired electron spin appears to be hopping along the aromatic rings down the polymer chain at a rate 55 MHz, the electron spin occupies localized molecular orbitals, not a conduction band as observed in conducting polymers. This is illustrated in Figure 3, which shows the temperature dependence of the ESR intensity of the PNS^- radical. The intensity very clearly shows Curie Law behavior as expected for a localized radical. In a conduction band the intensity would be essentially independent of temperature.

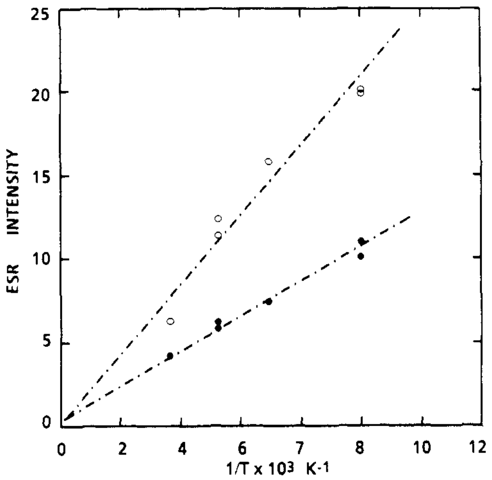

Figure 3. Temperature dependence of the ESR signal intensity of the poly(p-nitrostyrene) radical anion. The line shapes remain Lorentzian at all temperatures, and thus the intensities were corrected for line-width changes by multiplying by $(\Delta H_{pp})^2$. The signal intensity of Mn^{2+} is also shown for an internal SrO reference. The data were obtained with 1-G modulation, 2-mW microwave power, and [PNS] = 10^{-3} M and [TBAP] = 0.1 M in DMF: ○, PNS^-; ●, Mn^{2+} from internal SrO.

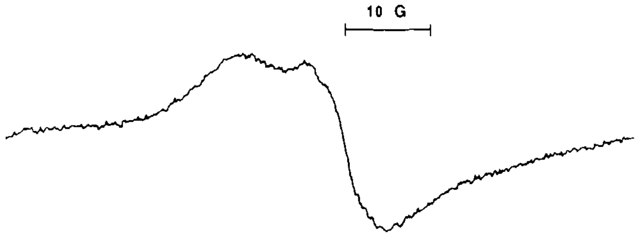

Figure 4. Room-temperature spectrum of poly(p-nitrostyrene) radical anion in DMF solution with 5% v/v H_2O. The data were obtained with 1-G modulation, 10-mW microwave power, and [PNS] = 10^{-3} M and [TBAP] = 0.1 M.

Previous studies have shown that nitrobenzene anion radicals are strongly solvated by adding water to the acetonitrile[25] or DMF[26] solvent in which the reduction is done. This results in an increase in the ^{14}N hyperfine coupling for the nitro group and a large decrease in the exchange rate between nitrobenzene and its radical anion. Reduction of PNS in DMF with 5% v/v H_2O at room temperature results in the ESR spectrum shown in Figure 4. Note that the PNS remains in solution in this solvent mixture. The broadened asymmetric ESR spectrum shows very clearly the hyperfine coupling to ^{14}N, with a g value identical with that in pure DMF. Comparing Figure 4 with Figure 1 shows that the added H_2O has disrupted the electron hopping that gave rise to the exchange-narrowed ESR resonance, so that the rate of exchange must now be less than 30 MHz. This experiment gives strong evidence that the resonance observed for PNS^- in DMF (Figure 1) is indeed a homogeneously exchange narrowed resonance rather than a heterogeneously broadened line arising from unresolved hyperfine couplings. The broadness of the ESR spectrum in Figure 4 is in part due to the fact that the rate of electron hopping is now intermediate to the fast- and slow-exchange regions. In addition, the observed asymmetry and some of the line broadening is due to the low mobility of the polymer chain in solution. The effect of

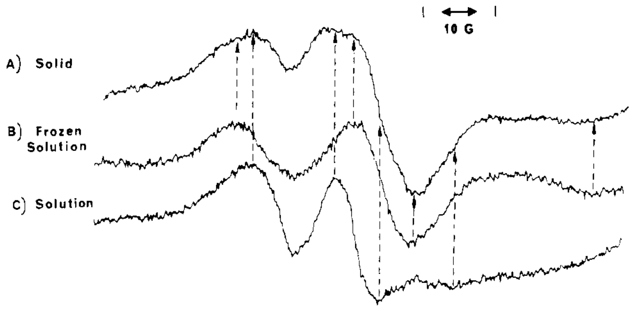

Figure 5. ESR spectra of oxidized poly(*p*-nitrostyrene) after removal of residual monomer: (A) solid powder after 1 day at room temperature exposed to air; (B) frozen solution (170 K) of poly(*p*-nitrostyrene) after electrochemical oxidation in DMF, with [PNS] = 10^{-3} M and [TBAP] = 0.1 M; (C) solution of poly(*p*-nitrostyrene) after electrochemical oxidation in DMF, with [PNS] = 10^{-3} M and [TBAP] = 0.1 M. All data were obtained with 1-G modulation and 10-mW microwave power.

mobility on line shapes has been extensively studied in nitroxide radicals.[24]

Electrochemical Oxidation of Poly(*p*-nitrostyrene). Attempts to oxidize DMF solutions of commercial poly(*p*-nitrostyrene) were not successful, presumably due to the presence of an antioxidant in the commercial material. The antioxidant, however, is apparently extracted from the polymer with $MeCl_2$ along with the monomer. The extracted solid polymer, in fact, oxidizes readily in air (in the dark or light) over a period of days to give the ESR spectrum shown in Figure 5A. The air oxidation is apparently thermally induced, as irradiation with a UV-visible source did not noticeably affect the rate of radical formation. The broadened, asymmetric ESR spectrum in Figure 5A shows very clearly the hyperfine coupling to ^{14}N, and the *g* value appears to be the same as in the PNS^- radical and the monomer anion radical. The spectrum of the oxidized PNS is in fact very similar to that observed for PNS^- in DMF with 5% v/v H_2O, with the line broadening and asymmetry being due to the low mobility of the oxidized radical in the solid state.

If DMF solutions of the extracted polymer are degassed with N_2, then essentially the same ESR signal can be produced electrochemically in solution ($E_{1/2} = +0.27$ V vs SCE in 0.1 M TBAP in DMF), as shown in Figure 5C. The spectrum is narrower and more symmetric in solution than in the solid. However, the radical is still reorienting slowly even in solution, which supports the assumption that it is associated with the polymer. On freezing this DMF solution, the ESR spectrum broadens further as shown in Figure 5B. Comparison of the ESR spectrum in the neat solid (a polycrystalline powder) with that in solution and in the frozen solution suggests that the spectrum of the neat solid has two components. The neat solid appears to be composed of a broad, nearly "immobile" radical (corresponding to the frozen solution radical) and a narrower, more mobile radical (corresponding to the solution radical). Indeed, freezing the neat solid results in an "immobile" spectrum very similar to that of the frozen solution in Figure 5B. It is suggested that the mobile radical in the neat solid is associated with lower molecular weight material which is produced as a result of the oxidation. This is supported by the observation that the ratio of the "mobile" signal to the "static" signal increases over a period of weeks, as the total radical concentration increases. Thus it appears oxidation results in both radical formation and chain scission.

Although the cation radical has the *g* value and the ^{14}N hyperfine coupling expected of a N-centered radical, the identity of the radical on oxidation is not clear. In the case of the reduced PNS^- radical, the reversibility of the reaction suggested that the species was a simple anion radical of 1. In the case of the oxidized radical, it can be produced both thermally and by an applying a potential. In addition, turning off the applied potential with a closed circuit or reversing the potential to cathodic values does *not* result in disappearance of the ESR signal due to the oxidized radical, even up to the appearance of the reduced species. The oxidation also appears to lead to the production of low molecular weight radical species. These effects argue against a simple cation radical for the oxidized species. In addition, the hopping of the electron spin that was observed in the reduced anion radical is not apparent in the oxidized species. Simulations of the spectrum of the oxidized radical in solution suggest a line width of 2 G, which could be partially due to some electron hopping. Using the slow-exchange equation of Piette and Anderson[20] gives a rate constant for the exchange at room temperature that must be less than 7 MHz, at least an order of magnitude less than for the reduced PNS. It is not apparent why there would be such a difference in behavior for a cation radical compared to an anion radical. Thus it appears the oxidized species is not a simple cation radical.

Registry No. PNS, 24936-54-7.

References and Notes

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