Proton ENDOR Studies of Soliton Wave Functions and Dynamics in Polyacetylenes[†]

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Electron nuclear double resonance (ENDOR) studies were carried out over a range of temperatures for five different preparations of polyacetylenes (PAs): Shirakawa (trans-PA), Shirakawa (cis-PA), Durham PA, Naarmann PA, and "enolic PA". EPR and magnetic susceptibility (SQUID) measurements were also performed and correlated with ENDOR measurements. Whereas the same quasi-delocalized paramagnetic defect ("soliton") appears to give rise to the ENDOR spectra for all preparations, the extent and dynamics of the soliton defect vary significantly with different preparations illustrating the importance of the lattice (cross-links, residual catalyst, elimination products, adjacent polyene chains, etc.) surrounding and terminating a soliton in defining apparent delocalization of the observed soliton. The analysis of the temperature dependence of ENDOR spectra is complicated by the relatively high concentration of paramagnetic solitons, which may facilitate exchange narrowing of ENDOR spectra. The ambiguity of whether spectral narrowing with increasing temperature arises from exchange interactions (spin diffusion) or from modulation of hyperfine interactions by soliton diffusion (real translational diffusion) cannot be resolved by the analysis of ENDOR spectra. The ENDOR spectra of enolic polyacetylene is unique in reflecting hyperfine interactions of only one sign compared to other forms of polyacetylene, which exhibit features associated with both positive and negative hyperfine interactions. The spectra of the enolic form suggest a restriction of the soliton to one side of the polyacetylene chain (centered on carbons containing protons but not on a carbons containing oxygen), i.e., removal of the degeneracy of the normally degenerate two solitons that can exist on either sides of a polyacetylene chain.

Introduction

Charge displacement (atomic or molecular hyperpolarizability) is critical to the realization of large nonlinear optical effects such as electric field-dependent changes in the index of refraction. Charge transport is critical to electronics. Organic polymers exhibiting π-electron conjugation over nanometer dimensions have received considerable attention in recent years because of their potential for large molecular hyperpolarizability and high conductivity. There is little disagreement that polyacetylene can be considered to be the prototypical conjugated π-electron polymer; and its discovery and characterization by Shirakawa and co-workers[1,2] sparked a growing research effort in electroactive polymers that has led to battery, light emitting, nonlinear optical, and photovoltaic device applications.[3−11] Central to the quantitative understanding of molecular hyperpolarizability and conductivity is an unambiguous experimental basis from which one can distinguish between static and dynamic quasi-delocalization. In an effort to define the soliton wave function (static quasi-delocalization) and soliton dynamics (dynamical delocalization), a number of researchers have conducted electron paramagnetic resonance (EPR), electron spin−echo (ESE), electron nuclear double resonance (ENDOR), and ESE-ENDOR experiments.[12−48] Most of these studies have been carried out on polyacetylenes prepared by the method of Shirakawa and co-workers.[1,2] Within the framework of assumptions about the shape and extent of the soliton wave function and the nature (e.g., 1-dimensional) of soliton diffusion, various simulations of spectroscopic results have been executed and reported.[12−48]

It is generally recognized that simulations of the "powder" EPR spectra of disordered organic radicals are not usually unique as the spectral intensity variations will depend in a complex way on all of the electron−nuclear hyperfine interactions, the number of nuclei associated with each of the hyperfine interactions, the spatial relationship of all hyperfine and Zeeman tensors, and the details of dynamics that modulate hyperfine interactions. Indeed, Kahol and Mehring[13] concluded that the analysis of the EPR spectra of polyacetylenes does not provide a unique description of the soliton.

Since the resonance frequencies of ENDOR transitions vary as $\nu_\pm = \nu_n \pm A/2$, where ν_n is the nuclear Larmor frequency and A is the hyperfine interaction associated with a particular type of nucleus (e.g., protons), ENDOR spectral shapes have the potential for reflecting the distribution of hyperfine interactions even for disordered materials. That is, the contribution made by one hyperfine interaction can be independent of other hyperfine interactions and is potentially independent of the electron Zeeman interaction. In reality, the analysis of ENDOR "powder patterns" is not straightforward because the detailed shapes depend strongly on electron, nuclear, and cross relaxation times; upon spectral (spin) diffusion; upon both the anisotropy of hyperfine and g-tensors; and upon the anisotropies in dynamics mechanisms. As shown by Dalton and Kwiram, spectral diffusion can actually simplify the analysis of the

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ENDOR spectra of disordered materials by eliminating the "orientation selection" feature of ENDOR spectra (that is, the dependence of spectra upon the region of the EPR spectra irradiated by the microwave field).[49] Moreover, this phenomenon accounts for the "matrix" signal that arises at the nuclear Larmor frequency.[50] Nevertheless, there are many phenomena that make the analysis of ENDOR spectra of disordered materials difficult. The first is the typically modest signal-to-noise associated with ENDOR and ESE-ENDOR spectra. Spectra can also be distorted by instrumental artifacts such as radio frequency pick-up or by radio frequency power variations with ENDOR frequency. For ^{13}C or ^{2}H enriched samples, higher harmonics of strong matrix ENDOR signals can also complicate analyses of spectra.[21,22] Transitions associated with different hyperfine interactions can also be influenced by different relaxation times (as relaxation times can depend on hyperfine interactions); thus, ENDOR intensities do not necessarily relate in a simple way to number of nuclei. This also applies to the dependence of spectral intensities on magnetic anisotropy (the relationship between the hyperfine tensor and the applied static magnetic field); note that the hyperfine interaction in organic radicals is typically aniso-tropic (and highly anisotropic for alpha proton type interactions). Moreover, ENDOR spectra will be influenced by soliton dynamics including the dimensionality of various dynamics. This includes diffusional dynamics that modulate hyperfine inter-actions and exchange phenomena that also can modulate hyperfine interactions (i.e., real and spin diffusion). In summary, the analysis of ENDOR and ESE-ENDOR spectra must be approached with great care, and simulation of spectra is a necessary but not sufficient condition that a particular model for the soliton wave function and dynamics is correct. Indeed, in this paper, we present data that provide support for the concept that the paramagnetism of polyacetylenes is associated with a soliton-like defect. Moreover, the work presented here emphasizes the importance of matrix interactions (interchain, "impurity", sp^3 defects) in defining the observed features of solitons existing on polyacetylene chains. Interchain interactions (e.g., via spin exchange) likely influence magnetic resonance spectra in a manner analogous to the way that they influence electrical conductivity.

Most EPR and ENDOR studies have been carried out on polyacetylenes prepared by the Shirakawa method.[12-48] De-pending on the exact details of preparation, two limiting forms of polyacetylene can be prepared by the method of Shirakawa: the thermodynamically favored trans isomeric form and the kinetically favored cis isomeric form. Of course, *cis*-PA is converted in time and by heating into *trans*-PA. Also, the soliton defects can exist only in *trans*-PA segments and, as might be expected, are present at much higher concentrations in prepara-tions rich in the trans isomer. Quantitative estimates of soliton concentrations have been made by EPR measurements; however, these should not be considered to be highly reliable because of the difficulty in measuring spin concentrations precisely in the resonant cavity structures used in EPR experiments (i.e., in precisely measuring microwave field intensities across the sample). Nevertheless, there is little doubt that soliton concen-trations are significantly (e.g., an order of magnitude or more) higher in *trans*-PA rich samples. Electron spin lattice relaxation times are also at least an order of magnitude shorter in trans isomer rich samples, and this may reflect the greater soliton concentrations and soliton-soliton interactions contributing both to spin diffusion and enhanced electron-spin lattice relaxation.

Two limiting forms of proton ENDOR spectra are obtained for trans-rich and cis-rich polyacetylene samples. For trans-rich samples, a single nearly Lorentzian resonance line centered at the nuclear Larmor frequency is observed at temperatures above 77 K. As the temperature is decreased from ambient tempera-tures, this resonance is observed to broaden from somewhat greater than 100 kHz peak-to-peak line width to widths of several hundred kHz. At 2K (the lowest temperature practically accessible for ENDOR measurements), the ENDOR spectra of cis and trans polyacetylene samples are similar but the spectrum of the trans rich PA is noticeably narrower: the spectra appear to be limited to the region 12−17 MHz with the two most prominent features separated by only approximately 1 MHz.

For cis-rich samples, the spectral extent of the ENDOR spectrum is greatly increased (with spectral widths exceeding 10 MHz in some samples) and some features appear to be resolved. Of course, the exact spectral shape observed for cis-rich PA samples varies with cis isomer concentration and hence with preparation and handling. Indeed, preparation of ^{13}C enriched samples resulted in spectra with apparent increased broadening and resolution of spectral features. Thomann and co-workers[14,15,31] demonstrated nearly quantitative simulation of such spectra assuming that the powder pattern arises from two unique hyperfine tensors as would be expected for a soliton localized on a trans-segment existing between two cis segments. Such localization would have the effect of "squaring" or "flattening" the tanh (hyperbolic function)-like distribution of hyperfine interactions associated with theoretical predictions of a "self-localized" soliton defect.[51,52] Other researchers have offered other explanations of the observed features including harmonics of the ^{13}C matrix signals or sum and difference of ^{13}C and ^{1}H matrix signals.[21,22] What is generally agreed upon is that turning points associated with positive and negative hyperfine interactions are observed in the spectra of cis-rich samples. Thomann and co-workers[37] demonstrated that such variation in hyperfine interactions (spin density) is to be expected as the result of electron Coulomb interactions. Thus, both electron Coulomb and electron phonon interactions play important roles in defining the soliton wave function.[53,54] The most definitive statement that can likely be made about the ENDOR and ESE-ENDOR spectra of cis-rich polyacetylene samples is that the greatest observed spectral width (between low and high frequency turning points of 9 and 19.5 MHz) is 10.5 MHz. This establishes the value of the largest principal element of the largest hyperfine interaction. Taking the ratio of this value to that of the other most prominent turning point suggests a ratio of negative to positive soliton spin densities of approximately 0.5. TRIPLE experiments have been used to determine that these spectral features are associated with hyperfine interactions of opposite sign. A word of caution should be added that only the turning points at the very extremes of the spectra are determined unambiguously and even these determinations are limited by signal-to-noise considerations. Because of the potential for modulation of hyperfine interactions by both Heisenberg exchange and soliton diffusion, it is impossible to carry out a truly meaningful quantitative analysis of the temperature dependence of the ENDOR spectra of trans-rich samples.

Other reasons for not attempting quantitative analysis of ENDOR spectra are more subtle but probably worth noting. The assumption made by all in carrying out analysis of ENDOR and ESE-ENDOR spectra is that defects with different orienta-tions with respect to the dc magnetic and microwave fields sense the microwave field equally; that is, "orientation selection" (typically observed for inorganic samples with large g-anisotropy

but seldom for randomly oriented organic radicals) does not influence the ENDOR of polyacetylene samples and that relaxation rates do not vary with ENDOR frequency (magnitude of hyperfine interactions) or with orientation of the polyacetylene polymer chains in the sample. This is a tempting and even potentially reasonable approximation to make; however, there is no experimental proof that such an approximation is warranted. Also, there is no way of knowing whether the soliton is a self-localized defect or one that is artificially confined by pinning defects (lattice effects such as interchain interactions, residual catalyst, elimination products, cross-links or sp^3 defects, etc.). Comparison of the predictions of theory[53,54] with experimental spectra requires the assumption that the observed spectrum corresponds to a self-localized defect and that both lattice effects and dynamical effects are turned-off. This does not say that theory is incorrect; indeed, enough features of soliton theory are observed in experimental results to suggest that theory is probably largely correct. The point is to avoid over-interpreting experimental results.

In summary, ENDOR and ESE-ENDOR studies of Shirakawa polyacetylene samples appear to provide support for the general quantum mechanical descriptions of the soliton, particularly with respect to the role of electron Coulomb interactions as well as electron−phonon interactions in defining the soliton wave function (as evident by spin densities that vary in sign as one progresses from the center of the soliton defect between two phases of bond alternation). What is less clear is whether results can be related to detailed theoretical predictions of the "self-localized" soliton shape and spatial extent. This is particularly the case in that ENDOR spectral widths are observed to vary widely with sample preparation; although the general features remain throughout. Indeed, Thomann and Baker[47,48] have provided compelling experimental data and analysis that exchange mechanisms dominate soliton translational diffusion in defining spectral narrowing in *trans*-PA.

To support a broader perspective, we report ENDOR, EPR, and SQUID magnetic susceptibility measurements on a large number of polyacetylene samples prepared by different synthetic methods. The data reported here largely derives from the Ph.D. dissertation of Dr. C. L. Young, which also reports studies of polaron defects in a number of polymers of the symmetry type -(A=B)$_n$-.[55] Although the data reported here do not answer the outstanding question as to the precise form of the "self-localized" soliton wave function, new insights can be gained from this previously unpublished data. In particular, the role of lattice in defining observed spectra is clearly apparent and further general support for a soliton type species is provided. The results reported here appear to be consistent with the conclusions of Thomann and Baker.[47,48]

Experimental Section

EPR and ENDOR measurements were carried out employing commercial (a Bruker ER200D EPR with ENDOR accessory or a Varian E-line EPR with E1700 ENDOR accessory) spectrometers. Microwave frequency (for g-value measurements) was measured using an EIP model 545A microwave frequency counter. Details of measurement, including over various temperature ranges, have been discussed elsewhere.[24−39,55] ENDOR spectra were taken employing both amplitude and frequency modulation of the applied radio frequency field. For the sake of simplicity, only spectra recorded employing frequency modulation are discussed in this communication. Such spectra appear as the "derivative" of the absorption ENDOR spectra; thus, "turning points" associated with principal elements of

hyperfine tensors are more easily recognized. Spectra were recorded at several positions in the EPR spectra; no evidence of orientation selection in the ENDOR was observed. Spectra were investigated extensively as a function of experimental conditions and every effort was made to avoid spectral artifacts. The spectra reported here are representative and do not represent spectra selected for best signal-to-noise.

Magnetic susceptibilities were measured using an S. H. E. magnetic VTS susceptometer (model 905). Gram susceptibilities were recorded at temperatures ranging from 6 to 300 K. The applied field was 10 kiloGauss.

Preparation and Handling of Shirakawa PA. Shirakawa polyacetylenes were prepared using the relatively high concentrations of Ziegler−Natta (ZN) catalyst, originally used by Shirakawa, incorporated into a solution consisting of a 1:4 ratio of tetrabutoxytitanium (TBOTi) in toluene and triethylaluminum (TEA). This solution is stirred at room temperature for a few minutes and then cooled to dry ice temperatures (−78 °C) and degassed at reduced pressure for a minimum of 30 min. Polymerization occurs interfacially with the flow of acetylene gas over the surface of the catalytic film (coating the sides of the reaction flask). Film thickness is controlled by the duration of the acetylene flow. The resultant polymer was purified by extensive washing with toluene and a methanol/hydrochloric acid mixture. The resultant material was an insoluble, black, lustrous film. The proportion of cis to trans isomer was controlled by control of temperature with high conversion to the trans form taking place at 140 °C.

The synthesized films were sealed under vacuum in clear fused quartz (CFQ) EPR tubes, with exposure to oxygen being kept at below 5 ppm.

Preparation and Handling of Durham PA. In an attempt to remove the metallic contamination due to the ZN catalyst, Edwards and Feast[56] (Durham, England) developed a synthetic route to PA that involves a soluble precursor polymer. This soluble precursor can be precipitated out of solution, separating it from catalyst. The two stage synthesis involves a ring opening metathesis polymerization of 7,8-bis(trifluoromethyl)-tricyclo-[4,2,2,0]deca-3,7,9 triene in chlorobenzene with a freshly prepared catalyst solution of tetramethyl tin and tungsten hexachloride. The polymerization is carried out at 15 °C and is stirred for approximately 20 min until the mixture becomes viscous. Precipitation from solution with cold methanol produces a white powder. When this precursor polymer powder is dissolved in acetone, films can be extruded from solution. Transformation from a white to silvery film is visually observable by noting color changes upon heating (which produces elimination of the hexafluoroxylene product and promotes cis−trans isomerization). The white film becomes yellow then orange then red then darker red to brown then purple and finally silver, with a metallic luster similar to aluminum foil. The films resulting from this method are nonfibrous and of a fully dense, compact morphology.

Syntheses of Durham PA samples were carried out under an inert atmosphere in a Vacuum Atmospheres glovebox. Samples were kept under an argon atmosphere and then sealed in EPR tubes under a vacuum of less than 10^{-4} Torr.

Static magnetic susceptibilities were measured on samples placed in standard aluminum sample buckets. The sample lids were sealed in place with standard epoxy for anaerobic static susceptibility measurements.

Preparation and Handling of Naarmann PA: A polyacetylene that displays doping-induced conductivity on the order of that of copper has been developed by Theophilou and Naar-

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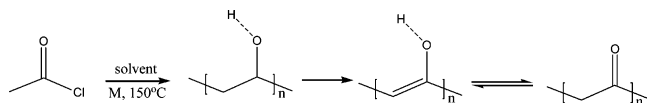**SCHEME 1: Preparation of Enolic Polyacetylene**

TABLE 1: Reaction Conditions for Polymerization of Acetyl Chloride to Produce Enolic Polyacetylene

protocol	Lewis acid catalyst	reaction time (h)	reaction temp. (°C)
1	AlCl₃ (10%)	18	150
2	AlCl₃/TiCl₄	18	150
3	TiCl₄ (10%)	9	150
4	TiCl₄	9	150
5	TEA (equimolar)	18	150

mann[57] of BASF. The procedure is similar to that of Shirakawa et al. but has added features in that the polymerization is catalyzed by an aged ZN solution and takes place in a silicon oil medium. In Naarmann PA, there is a higher degree of regularity and crystallinity in well-defined parallel planes. Naarmaan PA also appears to be more stable under atmospheric conditions. It has been speculated that Naarmaan PA has many fewer sp^3 defects.

Naarmann PA was investigated as a function of uniaxial stretching. Three degrees of stretching were investigated: $L = 1$, $L = 4$, and $L = 6$ where $L = l/l_0$ where l is the final length after stretching and l_0 is the original length before stretching. These films were kept in an inert environment then cut into strips that could be oriented in a quartz EPR tube. The EPR tubes could, in turn, be rotated in the applied magnetic field. These samples were also sealed under a vacuum of less than 10^{-4} Torr.

Preparation and Handling of Enolic PA. Acetyl halides can be incorporated into coordination polymerizations to produce a variety of oxygen-substituted polyacetylenes. The dehydrohalogenation polymerization of an acetyl chloride, which has been reacted with AlCl₃ and other Lewis acid halides at temperatures around 150 °C, produces a polyketene (or polyoxyacetylene) that is in equilibrium with the enolic tautomer.[58] The typical synthetic scheme is shown in Scheme 1, where M is a catalytic mixture of titanium and aluminum halides.[58] Different solvent environments and reaction temperatures are influential in defining the electronic and structural properties of the resultant typically intractable polymers.[58] Chien et al.[59] synthesized a similar material, an acetylene and CO copolymer. The structure that resulted exhibited two types of carbonyl stretches associated with either −CH=CH−C(=O)−CH=CH− or −CH₂−C(=O)− structures. These materials, upon doping, behaved similarly to Shirakawa polyacetylene.

Samples of enolic PA were handled in the manner of other samples described above. Samples prepared by five different protocols (see Table 1) were investigated using *n*-heptane as a solvent.

For reasons that are not clear, we were unable to synthesize samples of Enolic PA enriched with ^{13}C.

Results and Discussion

In Figure 1, the temperature dependence of EPR peak-to-peak line widths (H_{pp}, in Gauss) is shown for unstretched samples of trans-rich Shirakawa, Durham, and Naarmann polyacetylenes. The results of EPR measurements on stretched samples of Naarmann PA are shown in Table 2. The line width measured for the magnetic field oriented along the stretch direction is denoted by $H_{pp,\parallel}$ and that perpendicular to the stretch
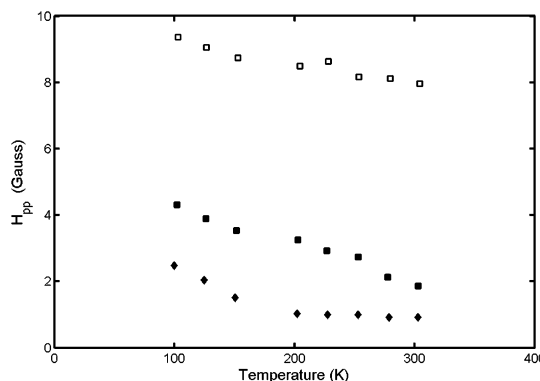

Figure 1. Temperature dependences of the peak-to-peak EPR line widths of trans-rich Durham (open squares), Naarmann (closed squares), and Shirakawa (diamonds) polyacetylenes are shown.
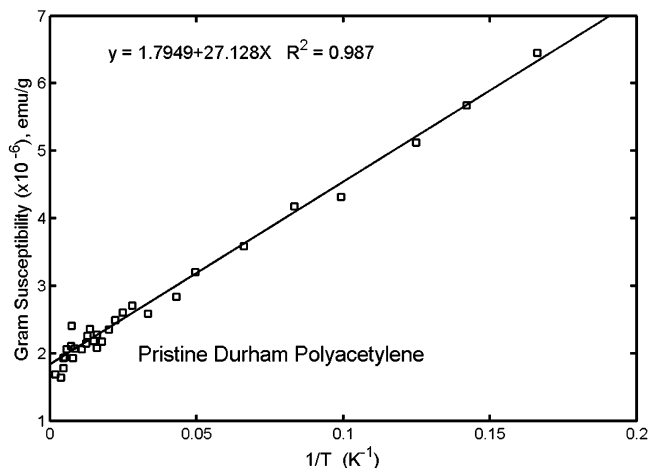

Figure 2. Gram magnetic susceptibility of Durham polyacetylene exhibiting Curie behavior.

TABLE 2: EPR Linewidth Measurements on Stretched Samples of Naarmann PA

L	T (K)	$H_{pp,\parallel}$	$H_{pp,\perp}$	L	T (K)	$H_{pp,\parallel}$	$H_{pp,\perp}$
1	308	2.24 G	2.05 G	6	298	1.99 G	1.86 G
	210	2.91 G	2.85 G		125	3.55 G	3.65 G
	109	4.40 G	4.11 G				

TABLE 3: EPR g Value and Linewidth Measurements for Various Preparations of Enolic PA

preparation	g value	H_{pp}	relative intensity
1	2.0030	6.25 G	1.51
2	2.0032	5.50 G	2.82
3	2.0031	4.25 G	2.02
4	2.0031	8.50 G	2.54
5	2.0031	7.25 G	1.00

direction is denoted by $H_{pp,\perp}$. In Table 3, we summarize the EPR measurements for various preparations of enolic polyactylene described in Table 1. The relative intensities are for equal weights of sample. The g values for enolic PA samples are consistently somewhat larger than g values observed for Shirakawa PA ($g = 2.0026$), Durham PA ($g = 2.0025$), and Naarmann PA ($g = 2.0025$). The line widths observed for enolic PA samples are closer to that for Durham PA ($H_{pp} = 7.6$ G) than for Shirakawa *cis*-PA ($H_{pp} = 4.0$ G). Magnetic susceptibility data for Durham PA and enolic PA samples are shown in Figures 2 and 3, respectively. The static susceptibility for Durham PA is higher than that for Shirakawa trans-PA sug-
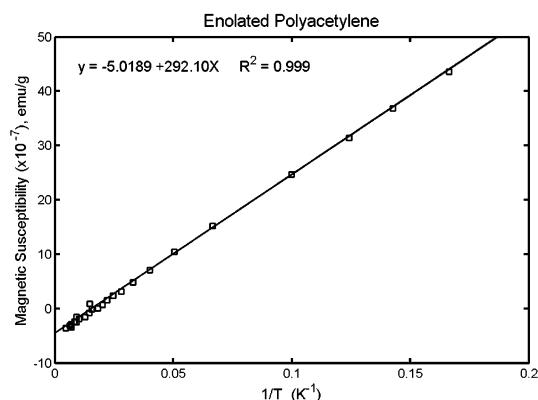
Figure 3. Gram magnetic susceptibility of enolic polyacetylene as a function of temperature.
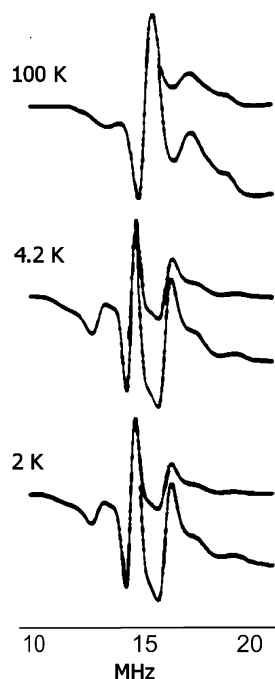

Figure 4. Temperature dependence of the proton ENDOR spectra of Durham polyacetylene.

gesting about 1 spin per 1000 carbon atoms compared to about 1 spin per 3000 carbons for Shirakawa trans-PA samples and about 1 spin per 30 000 carbon atoms for Shirakawa cis-PA samples. Susceptibility measurements showed that the bulk character of the enolic PA samples to be diamagnetic. The paramagnetism responsible for the strong EPR and ENDOR signals is not dominant throughout the sample.

In Figures 4 and 5, typical ENDOR spectra are shown for Durham and enolic PA samples. The ENDOR spectrum of the Durham PA samples remains relatively unchanged between 4.2 and 2 K and broaden only modestly between 100 K and liquid-helium temperatures. Like the spectra of Shirakawa cis-PA rich samples, ENDOR spectra of Durham samples are characterized by a relatively narrow matrix ENDOR line and by features that probably can be associated with negative and positive hyperfine interactions. If the four (two high frequency and two low frequency) observed "turning points" of the spectra are associated with the largest elements of the positive and negative hyperfine interactions, then it is reasonable to assume that the ratio of negative to positive spin densities is approximately 0.5 as previously determined. Such a ratio is consistent with theoretical calculations.[53,54]

TABLE 4: Naarmann PA ENDOR Linewidth Data as a Function of Film Elongation and Temperature

L	T (K)	ν_{pp}
1	298	166.0 kHz
	120	195.3 kHz
4	298	234.4 kHz
	120	332.0 kHz
6	298	175.8 kHz
	125	224.6 kHz

The ENDOR spectra observed for samples of enolic PA are particularly interesting because spectral contributions associated with negative spin densities do not appear to be present; only spectral contributions that can be associated with positive spin densities appear to be present. Although the strength of ENDOR signals varied somewhat with preparation protocol, the ENDOR spectral shape remained relatively constant and changed little as temperature was lowered to helium temperatures. The separation (e.g., approximately 10 MHz at 133 K) between extreme high and low-frequency spectral turning points (the largest hyperfine tensor element measured) was very similar to that measured for Shirakawa and Durham PA samples (e.g., 9−10.5 MHz). The ENDOR spectral shapes observed for enolic PA samples are the most consistent with the theoretically predicted tanh variation of hyperfine interactions for the self-localized soliton defect in *trans*-PA segments.[51] The fact that only half of the ENDOR transitions observed for other polyacetylene samples appear in the ENDOR of enolic polyacetylene requires that only solitons centered on carbons bonded to protons exist. Those that are centered on carbons bonded to oxygen cannot exist for they would give rise to positive hyperfine interactions, which are not observed. Clearly, replacement of half of the protons of a polyacetylene chain by oxygens lifts the degeneracy of solitons localized on "opposite sides" of the chain but we can offer no more insightful explanation for the observed absence of one of the two types of solitons.

The ENDOR spectra of Naarmann PA samples above 100 K are characterized by a single Lorentzian shaped resonance centered at the proton Larmor frequency. ENDOR line width data for unstretched and stretched samples are summarized in Table 4. The line widths measured to Naarmann PA samples are very similar to those measured for Shirakawa trans-rich PA samples. Because we cannot separate the effects of stretching on order and upon dynamics, we cannot provide a detailed analysis of the experimentally observed spectra. The spectra are consistent in a general way with our expectations for the behavior of a trans-segment localized soliton.

In overview, the dependence of apparent soliton quasi-localization upon PA preparation is most dramatic for the Naarmann samples. The results do not correlate in a simple way with spin concentration although it should be noted that spins are not necessarily homogeneously distributed in samples. With Durham polyacetylene, some of the elimination product bis-fluoroxylene may be trapped in the films acting to pin soliton defects or affect interchain interactions. Stretching Naarmann PA films produces a significant change in ENDOR spectra. This is not necessarily just a change in the degree of order of polyacetylene chains with respect to the direction of film elongation. Stretching may also significantly alter interchain interactions.

Considering the various preparations, it is clear that a variety of perturbations associated with catalyst particles, sp^3 defects, trapped elimination products, oxygen-counterion interactions, etc. may influence the shape and dynamic properties of soliton wave functions. Moreover, various effects can influence both
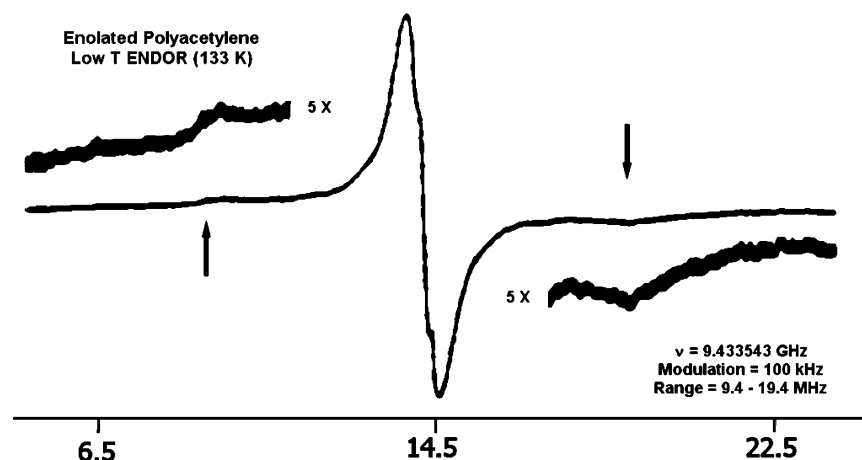
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Figure 5. Proton ENDOR of enolic PA at 133 K. The spectrum consists of a sharp matrix line at the proton Larmor frequency and what appears to be spectral features attributable to a distribution of negative hyperfine interactions. The turning points (more clearly seen in the X 5 amplified spectrum) correspond to the largest hyperfine interaction (i.e., the hyperfine interaction associated with the central carbon of the soliton bond phase alternation defect).

interchain (hence, Heisenberg exchange interactions and the dimensionality of soliton diffusion) as well as on-chain diffusion of solitons. ENDOR spectra do not permit a quantitative analysis of self-localized soliton wave function dynamics but do provide important information about the extent of delocalization. For example, Mehring et al.[13] found that the ENDOR spectra of Shirakawa tPA, when cooled to very low temperatures, could be simulated by a delocalized spin density wave. The original wave function of Su et al.[51] did not provide a quantitative agreement with the ENDOR. However, an alternative form of the spin density wave, using a sech function, and a width of 12 units, did fit the ENDOR spectra extremely well. This function gives a density profile that is extensive: 75% of the total spin density is contained in the first 40 monomeric units. If one assumes a uniform distribution over 40 monmeric units, then the standard distribution width, which is the parameter comparable to that used in the sech function, would be 12, which is the same as the value used in the sech function. Therefore, one can see why a square distribution over 40−50 units also gives a reasonable accounting of the density profile. The sech function is a gradual falloff function, somewhat like the original function suggestion of Su et al.,[51] but of much greater extent. The sech function gives a better understanding of the extent of delocalization of the soliton in tPA. This does not explain what causes the delocalization. However, given the qualitative similarity to the results of Su et al., one might infer that the simple model of Su et al.[51] provides a qualitatively correct theoretical explanation for soliton confinement.

Conclusions

The *g* values and ENDOR spectra observed for various polyacetylene preparations are consistent with a soliton-like defect. The observation that branches of the ENDOR spectra can be associated with spin densities of the opposite sign (both negative and positive spin densities) is consistent with theoretical predictions that both electron Coulomb and electron-phonon interactions are important in defining the details of the soliton wave function.[37,53,54] Our results obtained for an enolic form of polyacetylene are consistent with this picture suggesting that positive spin densities occur at carbon atoms bonded to hydrogens while negative spin densities occur at carbon atoms bonded to oxygens. The interaction of oxygens in the enolic form with metal counterions (from the catalyst) and with

hydrogen may promote an enhanced order. The spectra observed for enolic PA are the closest to that theoretically predicted for the self-localized soliton as observed for any form of PA; this is particularly the case in that the spectra appear to be simplified by the absence of contributions from hyperfine interactions associated with negative spin densities. The variation of ENDOR intensities with frequency (hyperfine interactions) appear to map the function assumed by Mehring et al.[13] as a self-localized soliton.

Although the data presented are consistent with the general concept of soliton-like defects localized on trans-PA segments, no definitive insight is provided into the details of soliton dynamics or to the precise nature of the self-localized soliton wave function. Alternative interpretations exist for most of the ENDOR spectral features except for the extreme turning points. The best resolution is obtained for enolic PA where the matrix ENDOR contribution is relative small and contributions from positive hyperfine interactions are absent. These spectra appear to correlate with the positive spin density branch of ENDOR spectra observed for cis-rich Shirakawa and Durham polyacetylenes. However, even for these spectra, care must be exercised in that little is known about interchain interactions or the influence of metal cations on the detailed shape (localization) of the soliton wave function.

The most striking observation is the strong dependence of ENDOR spectra upon the details of the lattice surrounding and terminating individual trans-polyacetylene chain segments. Sample heterogeneity may play a significant role in defining experimental results. Indeed, electrical conductivity measurements have emphasized the importance of interchain interactions in charge transport and such interactions likely play a significant role in defining magnetic resonance and relaxation data. Given the apparent importance of interchain interactions and defects, the data reported here would appear to be consistent with the interpretations of Thomann and Baker.[47,48]

The results presented here do indicate significant delocalization of the soliton even for the most tightly confined soliton wave functions. Such delocalization is important for realizing significant optical nonlinearity and charge transport (including facilitating charge transport by interchain hopping). The complexities observed for the intractable samples of this study certainly played a role in motivating the search for soluble and processible forms of electroactive polymers.

Young et al.

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