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Electron nuclear double resonance spectra of *cis*-rich and *trans*-rich polyacetylenes between 1.9 and 4.2 K

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The electron nuclear double resonance (ENDOR) spectra of "*cis*-rich" and "*trans*-rich" polyacetylenes have been recorded at temperatures in the range 4.2–1.9 K. The striking feature of these spectra is the similarity in both forms to the high-temperature ENDOR spectra of *cis*-rich polyacetylene reported previously. This observation demonstrates the existence of a common defect, a delocalized π electron or soliton, in both materials. In the temperature range from 4.2 to 1.9 K, the hyperfine tensors are observed to be temperature independent for *cis*-rich polyacetylene. The hyperfine interactions for *trans*-rich polyacetylene are observed to be temperature dependent and can be characterized by a 1-K activation energy. At higher temperatures (6–300 K), the *trans*-polyacetylene material is characterized by a 400-K activation energy for modulation of the hyperfine interactions. The consequences of these results for current soliton theories are discussed.

Examining the electron nuclear double resonance (ENDOR) spectra of "*cis*-rich" polyacetylene at temperatures between 77 and 300 K, Thomann *et al.*[1] have reported ^{13}C and ^{1}H tensors (see Table I) that are compatible with two unique spin densities, $\rho_{\text{odd C}} = +0.06$ (25 carbons) and $\rho_{\text{even C}} = -0.02$ (24 carbons) that alternate along a 49-carbon polyene segment. The sign variation was established by electron nuclear-nuclear triple resonance (TRIPLE)[2] and arises from electron-Coulomb interactions; indeed, this result has stimulated considerable theoretical interest[2–8] and appears compatible with an on-site electron-Coulomb potential of approximately 3 eV (see Table I).[2]

Heeger and Schrieffer[9] have interpreted the results of Thomann *et al.*[1] by assuming that the soliton wave function calculated by Su, Schrieffer, and Heeger (SSH)[10] is rapidly averaged over a 49-carbon polyene segment. Such rapid averaging yields a time-independent (on the ENDOR time scale) wave function characterized by two unique spin densities in exact agreement with the experimental results. The question immediately arises as to the source of the (49 ± 10)-carbon polyene-segment confinement regions. Recently, the suggestion[11] has been made that such confinement results from *cis*-polyacetylene segments which describe at least 5% of the polymer on even "pure" *trans*-polyacetylene synthesized by the Shirakawa method.[12] Interchain crosslinks and chain kinks also have been suggested as sources of soliton confinement, and Maki[13] has suggested that solitons will tend to localize at the ends of chains. An alternate interpretation is to assume that the experimentally determined wave function[1] defines the intrinsic form of the self-localized solution.[8,14,15] This latter model differs from the SSH model in the form of the spin-density variation and by the absence of fast soliton diffusion.

A further point reflecting upon the significance of the results of Thomann *et al.*[1] is that doubt has been raised as to whether the results reported for the *cis*-rich material have

TABLE I. ^{1}H and ^{13}C hyperfine tensors for *cis*-rich polyacetylene (element values in MHz).[a]

^{1}H tensor		^{13}C tensor
	Site 1	
$A_{xx} = -1.4$		$A_{xx} = +3.1$
$A_{yy} = -6.8$		$A_{yy} = +3.1$
$A_{zz} = -3.2$		$A_{zz} = +7.0$
	Site 2	
$A_{xx} = +0.5$		$A_{xx} = -1.3$
$A_{yy} = +2.1$		$A_{yy} = -1.3$
$A_{zz} = +1.1$		$A_{zz} = -2.1$

[a] Assignment of signs of hyperfine tensor elements is based upon TRIPLE resonance experiments and upon the consideration of Coulomb interactions following the theory of Karplus and Fraenkel [M. Karplus and G. K. Fraenkel, J. Chem. Phys. 35, 1312 (1961)]. The consideration of Coulomb interactions leads to a somewhat different assignment of ^{13}C elements as discussed elsewhere [H. Kim, A. Morrobel-Sosa, H. Thomann, L. R. Dalton, J. F. Cline, and B. M. Hoffman (unpublished)].

any relevance for *trans*-polyacetylene—the model for theoretical calculations.

We report here a study of both "*cis*-rich" and "*trans*-rich" polyacetylene that addresses the above concern. The temperature dependence of the ENDOR spectra recorded in this study also provide new insight into the influence of activated processes upon hyperfine interactions.

The polyacetylenes employed in the present work were synthesized by the Shirakawa method[12] as discussed previously.[1] ENDOR spectra were recorded employing 100-kHz Zeeman modulation, using an ENDOR spectrometer discussed elsewhere.[16] For measurements, the microwave resonator, containing radio-frequency coils, is immersed in liquid helium. The temperature is varied by pumping on the liquid helium and is measured from the vapor pressure of helium.

Because of the long relaxation times that characterize the spins in *cis*-rich polyacetylene, the ENDOR spectra for this material in the temperature range 4.2–1.9 K depend upon modulation conditions, i.e., exhibit passage effects. Because of the existence of passage effects in these spectra, the accuracy of the measurement of hyperfine tensors is reduced. Although analysis of such effects permits an independent confirmation of relaxation times measured by pulse techniques[17–19] and provides insight into nuclear spin diffusion rates, such discussion is beyond the scope of the present work. Relaxation rates in the *trans*-rich polyacetylene material are sufficiently fast that passage effects are not observed.

Typical ENDOR spectra of *cis*-rich and of *trans*-rich polyacetylenes are shown in Fig. 1. These spectra show both distant ENDOR signals at the proton Larmor frequency and local ENDOR signals shifted away from the Larmor frequency by $A_i/2$, where A_i are components of the electron-proton hyperfine interaction tensors. The striking feature of these spectra is their similarity to each other and to the high-temperature spectra of *cis*-rich polyacetylene reported previously.[1] There can be little doubt as to the fact that the same type of delocalized π-electron defect gives rise to the ENDOR response for both materials. The only difference appears to be a slight reduction in π-electron delocalization over the *trans*-polyene backbone as reflected in differing ENDOR peak positions, longer relaxation times in the *cis*-rich material as reflected in ENDOR signal intensities and passage phenomena, and in the temperature dependence of the ENDOR peak positions, i.e., in hyperfine interactions.

The ENDOR spectra of *cis*-rich polyacetylene are temperature independent in the region 4.2–1.9 K, but those of the *trans*-rich polyacetylene are not. The temperature dependence of the hyperfine interactions measured by ENDOR can be analyzed in terms of a motional process producing a dynamic modulation of the hyperfine interactions characterized by a correlation time τ which varies with temperature as $1/\tau = Ae^{-\Delta E/T}$. The motional correlation time is, in turn, obtained from the measured hyperfine interactions by assuming the interactions are modulated by a simple two site jump process.[20] The results are presented in Fig. 2, which also schematically represents the high-temperature data.

Strictly speaking, ENDOR cannot distinguish between a dynamic process which modulates hyperfine interactions and a temperature-dependent spin density associated with changing Boltzmann distributions among low-lying states. We note that the 1-K activation energy observed here is compatible with the temperature dependence of the electron-spin lattice relaxation (ESLR) rates if these rates are assumed to be determined by a local-mode process.[18,21] The correlation between ENDOR and ESLR data also appears to hold for *cis*-rich polyacetylene, where no temperature dependence is observed and the local mode ESLR is not observed.

As a consequence of these results, the dynamics of the soliton model for *trans*-polyacetylene should, perhaps, be considered in the light of two activated processes. The 400-K process observed earlier (see Fig. 2) likely can be associated with substantial movement, perhaps depinning, of the soliton, whereas the cause of the 1-K process remains less clear. The latter may simply be associated with spin-phonon interaction or may be associated with fast one-dimensional diffusion.

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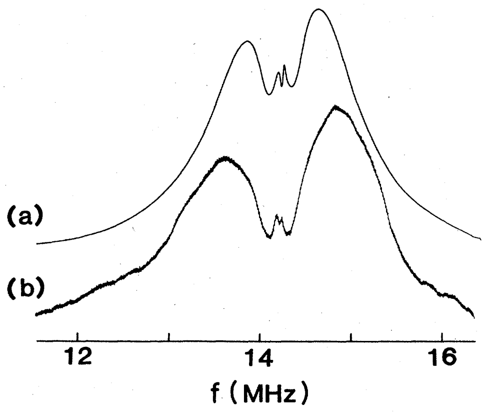

FIG. 1. ENDOR spectra of (a) *cis*-polyacetylene and (b) *trans*-polyacetylene. The spectra are recorded using a 100-kHz field modulation of 0.5 G. *ENDOR conditions:* Microwave frequency, 9.53 GHz; $H_0 = 3380$ G; $T = 2.0$ K; microwave power, 2 μW; rf power, 20 W; rf scan rate, 1.0 MHz/sec.

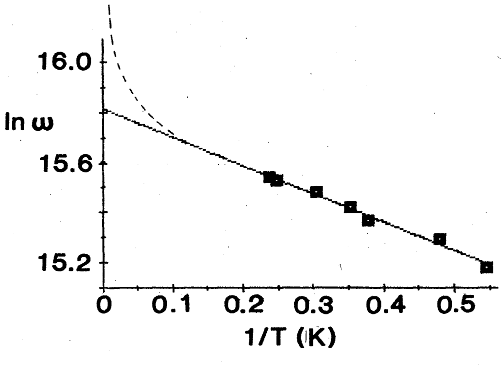

FIG. 2. Logarithmic plot of the motional correlation time $\omega (= 1/\tau)$ vs reciprocal temperature for *trans*-polyacetylene. A limiting hyperfine interaction of 3.1 MHz was assumed. The slope yields an activation energy of 1.1 K. The high-temperature data (Ref. 20) are represented schematically by the dashed line.

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