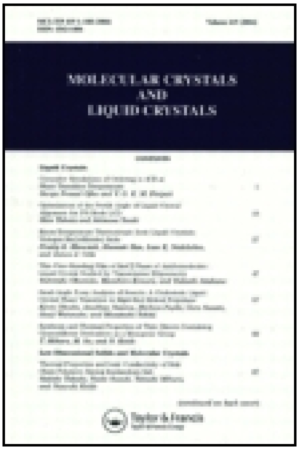

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Magnetic resonance properties of polyacetylene

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Version of record first published: 14 Oct 2011.

To cite this article: H. Thomann, L. R. Dalton, Y. Tomkiewicz, N. S. Shiren & T. C. Clarke (1982): Magnetic resonance properties of polyacetylene, Molecular Crystals and Liquid Crystals, 83:1, 33-48

To link to this article: http://dx.doi.org/10.1080/00268948208072153

Mol. Cryst. Liq. Cryst., 1982, Vol. 83, pp. 33–48
0026-8941/82/8301–0033$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

MAGNETIC RESONANCE PROPERTIES OF POLYACETYLENE

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Received for publication January 5, 1982

Electron-nuclear double resonance (ENDOR) spectra have been recorded for samples of pristine *cis*- and *trans*-polyacetylene at temperatures ranging from 15°K to 290°K. The ENDOR spectra of *cis*-polyacetylene consist of resolved contributions arising from distant and local ENDOR mechanisms. The temperature dependence of the peak positions of the local ENDOR spectra is analyzed in terms of a simple two-site electron jump model resulting in modulation of a 1.8 MHz isotropic hyperfine coupling. This analysis leads to an activation energy of 34°K. The ENDOR spectra of *trans*-polyacetylene at temperature above 70°K consist of a single line centered at the free proton Larmor frequency and exhibiting a temperature-dependent linewidth. These spectra are assumed to be composed of distant and local ENDOR contributions with motional narrowing of the local ENDOR structure accounting for the temperature dependence of the ENDOR linewidths. This assumption is supported by observation of two-component ENDOR spectra below 40°K. Analysis of the linewidth variations of the high temperature spectra suggests that the linewidths are determined by modulation of an approximately 1.4 MHz hyper-fine interaction by a dynamic process characterized by a 400-K activation energy. These numbers are in excellent agreement with values obtained from analysis of electron spin echo (ESE) spin-spin relaxation data establishing that the same process determines both ENDOR and ESE data. No evidence is obtained from ENDOR spectra for the existence of large hyperfine interactions. Thus, the EPR, ESE, and ENDOR results for *trans*-polyacetylene are dominated by an intermediate motion process (τ = 10^{-6} to 10^{-9} sec) modulating approximately 2 MHz hyperfine couplings and characterized by a relatively high activation energy (400°K) and not by a fast, highly directional motion modulating large hyperfine interactions as suggested by recent soliton theory analysis of EPR spectra.

INTRODUCTION

The conducting organic polymer polyacetylene has been extensively studied by electron paramagnetic resonance (EPR) spectroscopy[1-15] in an effort to define the magnetic susceptibility by analysis of integrated signal intensities and to elucidate the electron dynamics by an analysis of EPR linewidths. The magnitude and temperature dependence of EPR linewidths were initially analyzed in terms of a highly one-dimensional soliton motion.[3,8]

Recently, electron spin echo (ESE),[16] microwave-induced nuclear polarization,[13,17] and nuclear spin-lattice relaxation[13,17] measurements have shown that the major contribution to EPR linewidths cannot be assigned to a fast, highly dimensional soliton motion but rather appears to be characterized by a motion with a correlation time of approximately 10^{-8} to 10^{-9} sec at ambient temperatures. Moreover, the ESE results indicate that at temperatures below 200°K the EPR spectrum of *trans*-polyacetylene is inhomogeneously broadened. This observation, together with predictions of the magnitude of the modulated hyperfine interactions derived from quantitative analysis of the ESE spin-spin relaxation data, led us to perform electron- nuclear double resonance (ENDOR) measurements on protonated *cis*- and *trans*-polyacetylene. Local ENDOR frequencies are given by the expression

$$\nu_{ENDOR} = \nu_p \pm \frac{1}{2}\left[A_c + D\Sigma \int \frac{\sigma_i}{|r_p - r_i|^3}(3\cos^2\theta_i - 1)d\tau\right] \qquad (1)$$

where $\nu_p = g_N \beta_N H_0$ is the free proton frequency associated with the nuclear Zeeman effect. A_c is the Fermi contact hyperfine interaction or coupling constant; σ_i is the unpaired electron spin density on the ith atom in the molecule; D is a constant reflecting the magnetic moments of the interacting spins, $\boldsymbol{r}_i$ and $\boldsymbol{r}_p$ are vector distances from the origin of the ith atom and the nucleus (e.g., proton) respectively, θ_i is the angle between H_0 and $(\boldsymbol{r}_p - \boldsymbol{r}_i)$ and $d\tau$ is the volume element in the electron distribution. From Eq. (1) it is clear that the spectral position of an ENDOR resonance line is linearly related to the hyperfine interaction experienced by that class of protons. Such is not the case for conventional EPR where the position of any resonance line is dependent upon all hyperfine interactions and the number of nuclei experiencing each particular hyperfine interaction. This feature of ENDOR spectroscopy results in a great simplification in the analysis of ENDOR spectra as compared to the analysis of EPR spectra.[18-26]

Local ENDOR spectra intensities depend upon induced transition probabilities which predict a quadratic dependence upon ν_{ENDOR} and upon various relaxation rates.[19,25,26] If relaxation rates are isotropic, the analysis of even complex distributions of hyperfine interactions is possible. On the other hand, if relaxation rates, such as proton spin-lattice relaxation rates, are anisotropic, then quantitative analysis of ENDOR spectra is difficult if not impossible, although qualitative insight can still be obtained into the magnitude of hyperfine interactions.

A second possible contribution to the ENDOR spectrum may arise from a distant ENDOR mechanism.[25,27] A schematic representation of this mechanism is shown in Fig. 1. The polarization reflected in the local ENDOR effect may, in favorable cases, be transmitted to distant nuclei by simultaneous nuclear spin flips (a process called nuclear spin diffusion.[28]) The transition frequencies and hence lineshape of the distant ENDOR spectrum is determined by nuclear Zeeman and nuclear dipole-dipole interactions. Distant ENDOR spectra are centered at the free nuclear Larmor frequency and exhibit spectral widths that are substantially less than the widths of the local ENDOR spectra, reflecting the smaller magnitude of nuclear dipolar interactions as compared to hyperfine interactions. Distant ENDOR transition intensities depend strongly upon relaxation rate includ-

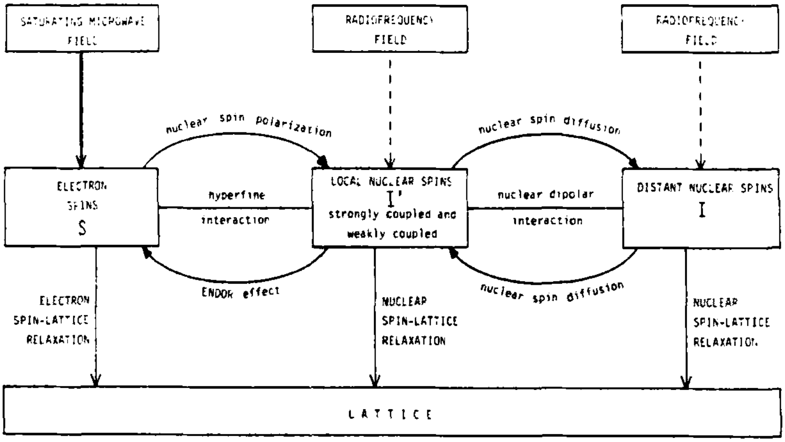

FIGURE 1 A schematic representation of the interactions and energy transfer processes relevant to the ENDOR experiment is shown. Nuclear spins are divided into two classes according to whether they experience finite (local nuclear spins) or no (distant nuclear spins) hyperfine interaction with paramagnetic electrons.

ing nuclear spin-diffusion rates; in the simplest case, spectra are determined by the ratio of the nuclear spin-diffusion rate to the nuclear spin-lattice-relaxation rate.

EXPERIMENTAL

ENDOR measurements were performed employing two different ENDOR spectrometers. The first system consisted of a Varian E-1700 ENDOR accessory interfaced with a Varian E-12 EPR spectrometer equipped with an E-272B field/frequency lock accessory. A variety of modulation schemes are available with this instrument as has been described elsewhere.[29,30] The second system consisted of an IBM Instruments ER-250 Computer-Controlled ENDOR/TRIPLE accessory interfaced to an Aspect 2000 computer controlled ER 220 EPR system (12 inch electromagnet). This EPR spectrometer was also equipped with a field/frequency lock accessory. Modulation schemes available with the IBM ENDOR include frequency or amplitude modulation of the radiofrequency field.

Variable temperature operation between liquid nitrogen and ambient temperatures was accomplished employing either a Varian E-257 accessory or an IBM Instruments 4111 accessory. Variable temperature operation between liquid helium and ambient temperatures was accomplished employing either a Varian ESR-9A accessory or an IBM Instruments ER 4112 HV accessory (or an Oxford ESR-9 variable temperature unit). Temperatures at the sample were measured as described previously.[31]

Spectra were recorded employing all of the possible modulation schemes and the essential spectral shapes were found to be independent of modulation scheme employed. Spectra were also investigated as a function of microwave and radiofrequency field intensities. The spectral shapes of the spectra reported here were found to be independent of field intensities, i.e., free from radiofrequency coherence effects[32] and modulation broadening.[26]

RESULTS

Extensive investigation of ENDOR spectra as a function of modulation and detection scheme, type of microwave cavity, and type of radiofrequency coil structure demonstrated that the spectra shown in Figs. 2-5 are free from instrumental artifacts and are representative of *cis*- and *trans*-polyacetylene, respectively.

With both *cis*- and *trans*-polyacetylene samples, an exhaustive search was made for large hyperfine interactions. The baseline at high frequencies was established as a zero ENDOR effect baseline by standard procedures.[25,26,33] As shown in Fig. 2, no features[19] that could be associated with large hyperfine interactions were observed.

Analyses of ENDOR spectra were carried out assuming that a simple two-site jump process modulates isotropic hyperfine interactions. The expression used for analysis of the effect of electron dynamics upon the separation of the peaks of the ENDOR spectra of *cis*-polyacetyene is

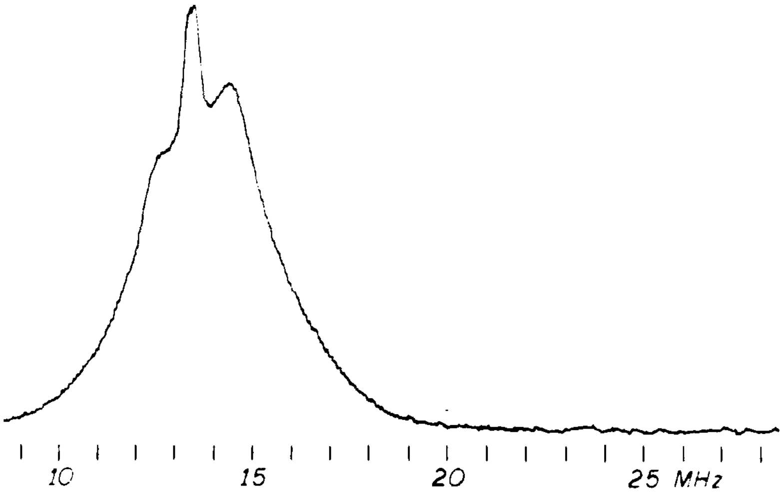

FIGURE 2 A typical single scan ENDOR spectrum of *cis*-polyacetylene, recorded employing amplitude modulation of the radiofrequency field, is shown. This spectrum, obtained at a sample temperature of 15°K, demonstrates the absence of large hyperfine couplings. The spectral regions 1-9 MHz and 30 to 100MHz were also exhaustively investigated with the result that no evidence of large hyperfine interactions was found.

$$\frac{1}{\tau(T)} = \frac{\pi}{\sqrt{2}}(\Delta\nu^2_{T=0} - \Delta\nu^2_T)^{1/2} \qquad (2)$$

where $\tau(T)$ is the correlation time for the electron motion, $\Delta\nu_{T=0}$ is the low-temperature limiting value of the splitting of the ENDOR spectra and $\Delta\nu_T$ is the value of the splitting measured at temperature T. In the analysis presented here $\Delta\nu_{T=0}$ was taken as 1.8 MHz. As can be seen in Fig. 6, this value of 1.8MHz optimizes the linearity of the plot of $-\ln \tau(T)$ versus 1/T. Eq. (2) assumes the dynamics are in the slow exchange region.

The variation of the ENDOR linewidth for *trans*-polyacetylene with temperature was conducted assuming two independent contributions to the linewidth. The resolution of these two contributions at low temperature is evident in Fig. 5. The first contribution is a temperature- independent contribution from a distant ENDOR signal. This contribution determines the residual linewidth and arises from proton dipole-dipole

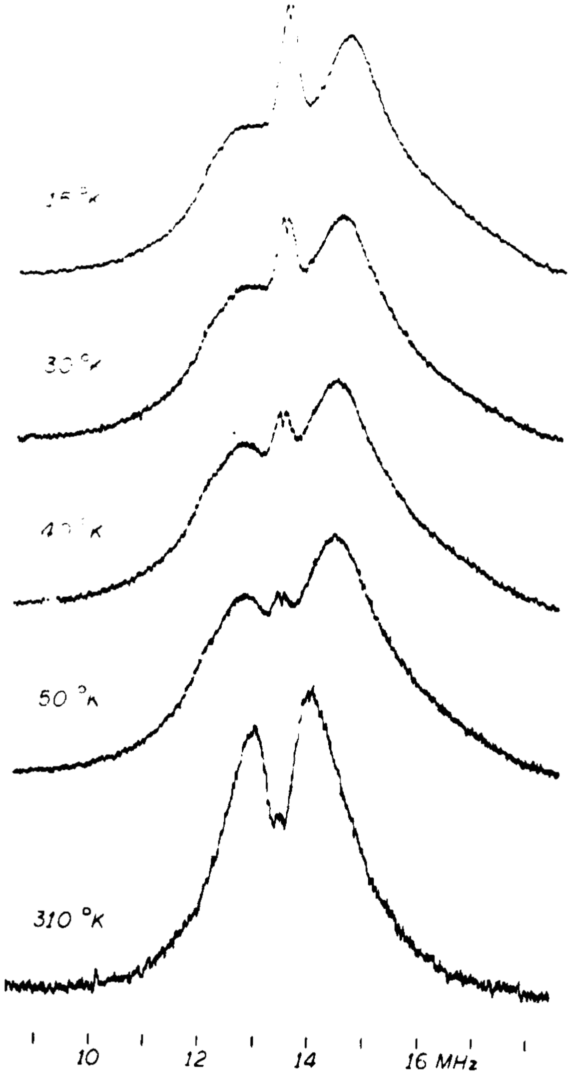

FIGURE 3 Typical ENDOR spectra for *cis*-polyacetylene, recorded employing amplitude modulation of the radiofrequency field, are shown as a function of temperature. The spectra shown are single scan spectra. Computer averaging was used to improve signal-to-noise for detailed lineshape analysis. These spectra are composed of local and distant ENDOR contributions.

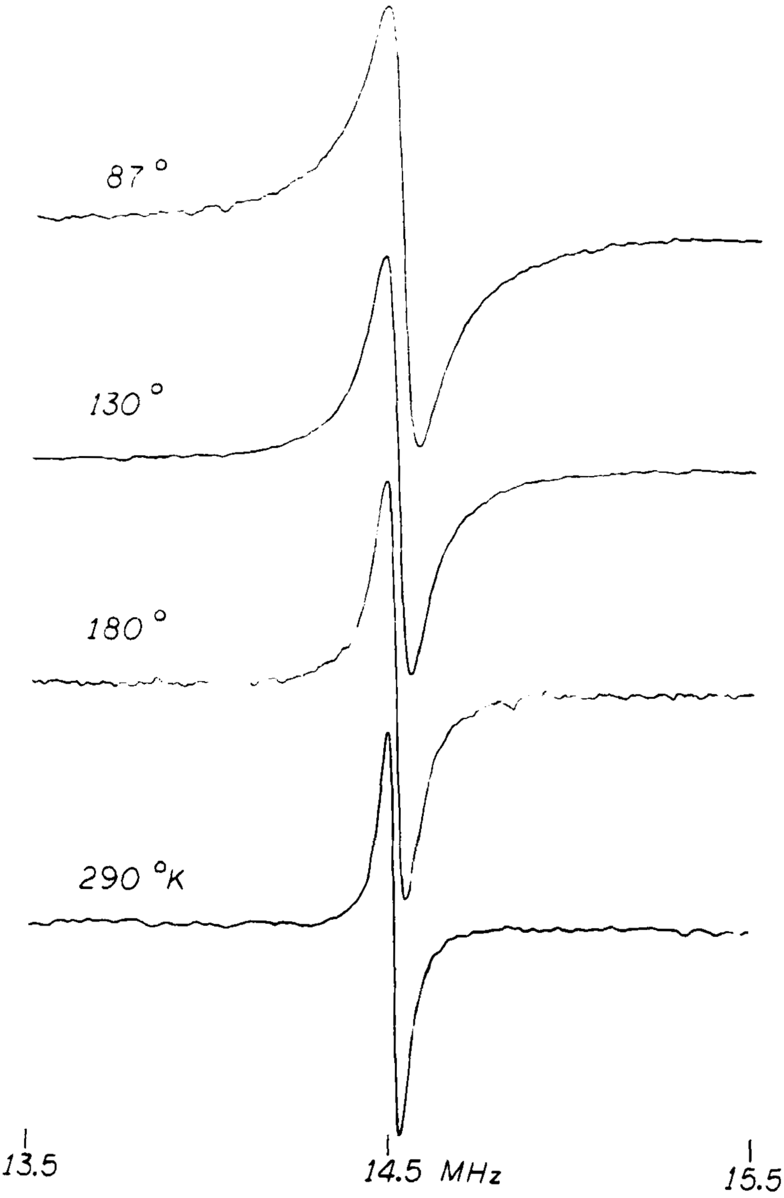

FIGURE 4 Typical ENDOR for *trans*-polyacetylene, recorded employing 10 khz frequency modulation of radiofrequency field, are shown as a function of temperature.

interactions. The magnitude of the proton dipolar interactions are calculated from structural data for *trans*-polyacetylene[34,35] assuming a point-dipole approximation.[27] The second contribution to the ENDOR linewidth arises from the motional narrow-

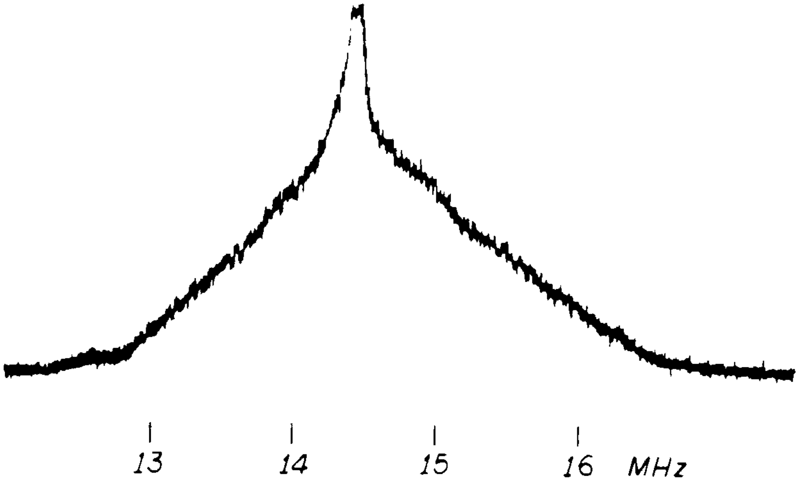

FIGURE 5 An ENDOR spectrum of *trans*-polyacetylene recorded at 24°K employing amplitude modulation of the radiofrequency field is shown. The high sensitivity IBM spectrometer was not available for measurements on *trans*-polyacetylene between 15 and 80°K so measurements were carried out on the Varian system. With this system, quantitative linewidth measurments were not possible but the systematic broadening of the spectra to a two component spectrum such as shown in this figure was observed qualitatively. The characteristic spectrum does not appear to change between 30 to 15°K; the appropriate local ENDOR linewidth in this temperature region is 1.4 MHz.

ing of the local ENDOR couplings by electron dynamics. The following equation assumes that the electron dynamics are in the fast motion region

$$\frac{1}{\tau(T)} = \frac{\pi}{\sqrt{3}}(\Delta\nu^2_{T=0})[\delta\nu_T - \delta\nu_{RESIDUAL}]^{-1} \qquad (3)$$

where $\delta\nu_{RESIDUAL}$ is the temperature-independent residual linewidth determined by the distant ENDOR signal and $\delta\nu_T$ is the ENDOR linewidth measured at temperature T. A value of $\delta\nu_{RESIDUAL}$ of 40 kHz was calculated and used in the analysis discussed here.

The correlation times obtained from the simple two-jump model are plotted versus 1/T in Figs. 6 and 7. Activation energies of 34°K and 400°K are obtained for *cis*- and *trans*-polyacetylene, respectively.

DISCUSSION

The ENDOR spectrum of *cis*-polyacetylene obviously consists of two components. The narrow component detected at the free proton Larmor frequency is very likely a distant ENDOR. The linewidth of this component does not appear to change with temperature; however, accurate measurement of the linewidth is hindered by overlap of a broader local ENDOR spectrum. Moreover, the assignment of the distant ENDOR component must be approached with care as this signal may arise from "*trans*-polyacetylene domains" in the nominally *cis*-polyacetylene sample.

The temperature dependence of the local ENDOR peak separations (i.e., hyperfine interactions in the simplest model) is shown in Fig. 8. Clearly, this graph suggests a limiting value of 1.8 MHz or a simple isotropic hyperfine coupling of 1.8 MHz. Employing this limiting value in the simple two-site jump model yields correlation times which in turn yield a highly linear activation energy plot. Other values of $\Delta\nu_{T=0}$ lead to substantially less linear plots. While the justification for the simplicity of this model may be disputed, the excellent linearity of the activation plot is suggestive and it is clear that no large hyperfine interactions contribute to the ENDOR spectrum within the limits of instrumental sensitivity.

It is clear from simple visual observation that the ENDOR spectra of *cis*-polyacetylene are composed of two components. As a working hypothesis, it is assumed that the high-temperature ENDOR spectra of *trans*-polyacetylene are also composed of the same two components. This hypothesis is supported by observation of two-component ENDOR spectra at low temperatures. The distant ENDOR spectrum is computed from structural information and the assumption of proton point dipolar interactons determining the spectral width. The hyperfine interactions which are modulated by the electron dynamics and give rise to the local ENDOR linewidths were adjusted to optimize the linearity of the plot of ln τ versus $1/T$ yielding a "best fit" hyperfine interaction

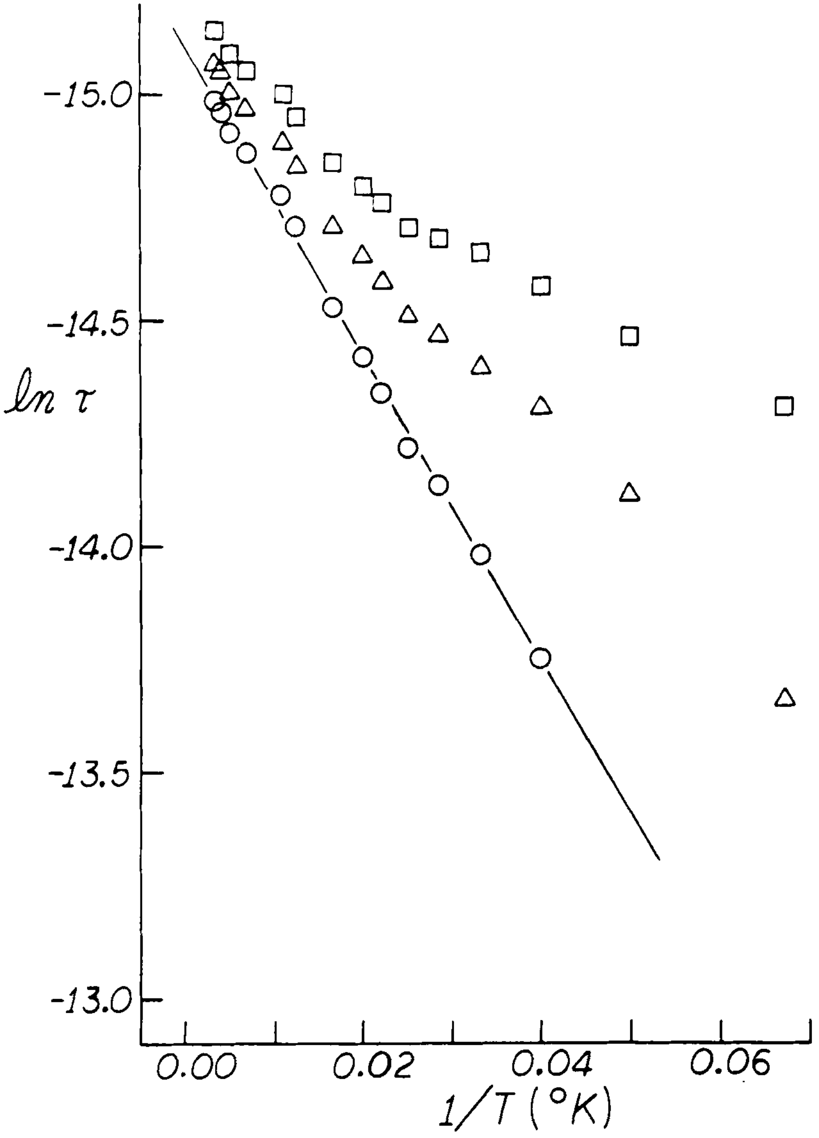

FIGURE 6 The plot of calculated logarithm of the motional correlation time versus reciprocal temperature for *cis*-polyacetylene is shown for three model calculations. In the first calculation (squares) a limiting hyperfine interaction of 2.0 MHz was assumed to be modulated by electron diffusion (two site hopping). In the second model (triangles) a 1.9 MHz hyperfine

interaction was assumed while in the third model (circles) a 1.8 MHz interaction was assumed. The improved linearity for the value of 1.8 MHz suggests that this model may be correct. The slope yields an activation energy of 34°K.

of 1.4 MHz. The value of the activation energy and of the hyperfine interaction obtained from analysis of the *trans*-polyacetylene ENDOR linewidths are in good agreement with values obtained from analysis of the magnitude and temperature dependence of spin-spin relaxation times measured by electron spin-echo spectroscopy. Clearly, the same process determines both ENDOR linewidths and spin-spin relaxation times and the linearity of all plots suggests but does not prove the appropriateness of a single-jump model analysis. Both ENDOR and ESE data are determined by the modulation of small hyperfine interactions on the order of 2 MHz for protonated samples. ESE data are also affected by the modulation of electron-electron dipolar interactions as is demonstrated from the isotopic dependence of measured spin-spin relaxation times.

While the presently available magnetic resonance data do not conclusively prove the absence of a fast motion modulating large hyperfine interactions as suggested by the soliton model, such a process does not contribute to the observed ENDOR or ESE data. Both ENDOR and ESE data for *trans*-polyacetylene are determined by a process that is characterized by a rather high activation (400°K), and which modulates a rather small hyperfine interaction, 2 MHz. If the simple analysis of ENDOR spectra is correct, there exists only a narrow distribution of hyperfine interactions.

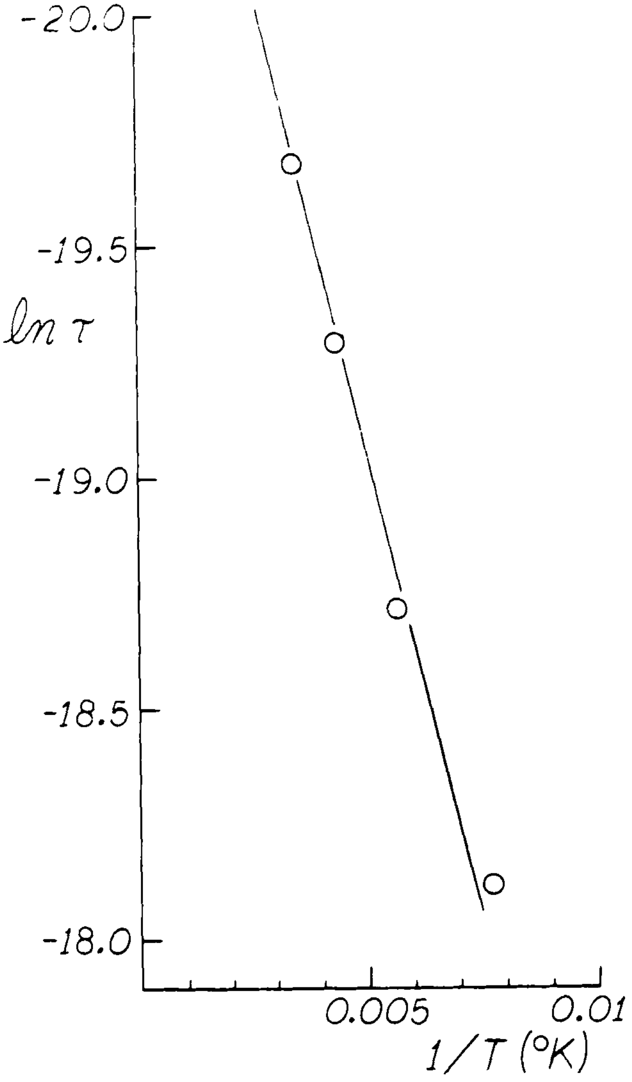

FIGURE 7 The plot of calculated logarithm of the motional correlation time versus reciprocal temperature for *trans*-polyacetylene is shown. A residual linewidth of 40 kHz was used in the analysis and a hyperfine interaction of 1.4 MHz was assumed to be modulated by the motion. The slope yields an activation energy of 400°K.

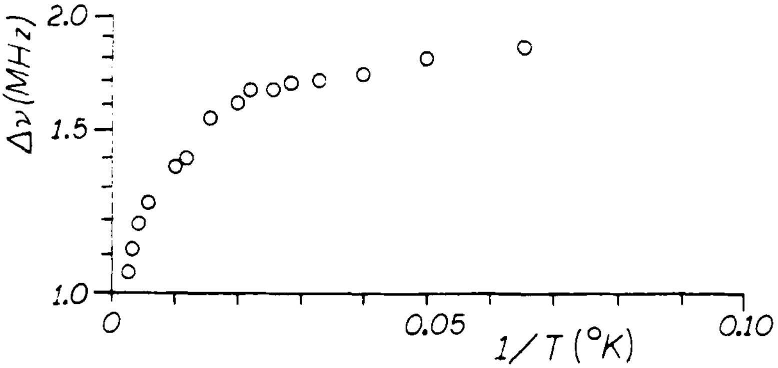

FIGURE 8 The ENDOR peak separation (or equivalently the hyperfine interaction for purely isotropic couplings) for *cis*-polyacetylene is shown as a function of temperature. The low temperature limiting value is 1.8 MHz.

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