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Electron nuclear double resonance studies on polyacetylene

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ENDOR measurements have been carried out on *trans*-polyacetylene and on 0.5 mol % ReF_6 doped 70% *cis*-polyacetylene at 4 K. The pure *trans*-polyacetylene yields only a single line, but the ReF_6 doped material yields two hyperfine couplings to hydrogens of 0.2 and 1.7 MHz. Calculations suggest the average chain length of the soliton is 93 carbon atoms. The absence of fluorine hyperfine coupling suggests that ReF_n molecular units are in the C, H molecular plane of the *trans*-polyacetylene.

INTRODUCTION

There have been a large number of papers analyzing the contribution to the linewidth of the electron spin resonance spectrum of doped and pristine polyacetylene polymer. In all of these papers, no hyperfine coupling has been observed to ^{13}C or ^1H of the polyacetylene, nor to dopant nuclei. The temperature dependence and magnitude of the linewidths have been analyzed in terms of a highly one-dimensional soliton model^{1,2} and electron spin-echo,³ and microwave induced nuclear polarization and nuclear spin relaxation experiments^{4,5} have shown that below 200 K the linewidth is inhomogeneously broadened. One means of directly measuring unresolved hyperfine interactions is to make electron nuclear double resonance (ENDOR) measurements. A feature of ENDOR spectroscopy is that the magnitudes of the hyperfine interaction to different sets of equivalent nuclei may be determined together with an assignment of which nucleus that coupling is associated with.

In this paper, we report our ENDOR measurements on pristine *trans*-polyacetylene and on 0.5 mol % ReF_6 doped 70% *cis*-polyacetylene (i.e. 30% *trans*-70% *cis*) at tempera-

tures down to 4 K. ESR and electrical conductivity measurements on ReF_6 doped material will be reported separately.

EXPERIMENTAL

Cis-rich polyacetylene was prepared by the method of Ito *et al.*⁶ and converted to the *trans* isomer by heating to 100 °C. The doped sample was made by exposing the *cis*-rich polyacetylene to the vapor of ReF_6 in a high vacuum apparatus. ESR spectra were recorded on a Bruker ER200D spectrometer with a computer controlled ENDOR (ER250) accessory interfaced to an Aspect 2000 computer. Measurements at 4 K were carried out using an Oxford Instruments ESR9A cryostat.

RESULTS

The ENDOR spectrum of undoped pure *trans*-polyacetylene consisted of a single narrow line centered on the free proton nuclear frequency at all temperatures from 4–293 K (Fig. 1). The linewidth varied from ~0.25 to 0.12 MHz as the temperature varied from 4 to 293 K (Fig. 2).

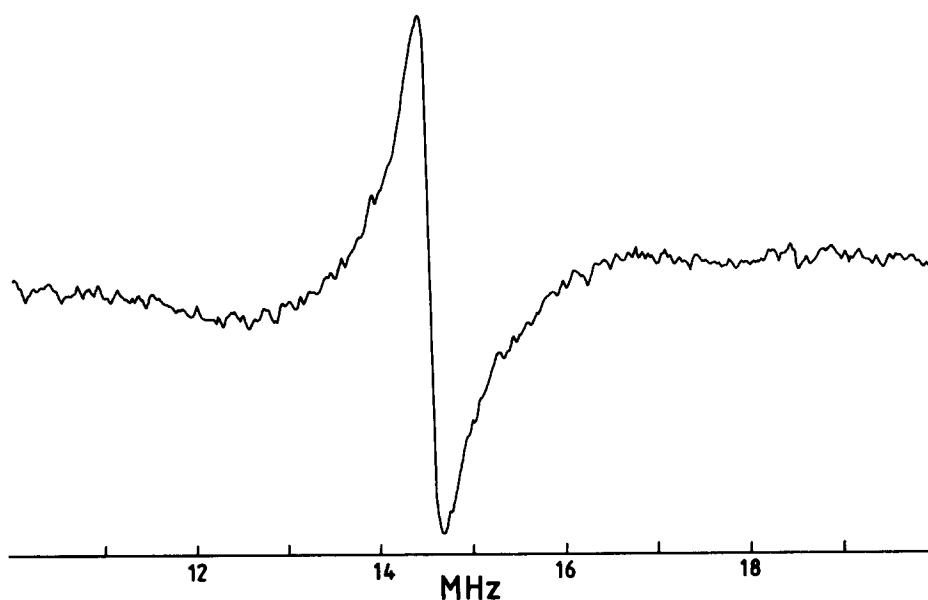


FIG. 1. ENDOR spectrum of pristine *trans*-polyacetylene at 4 K.

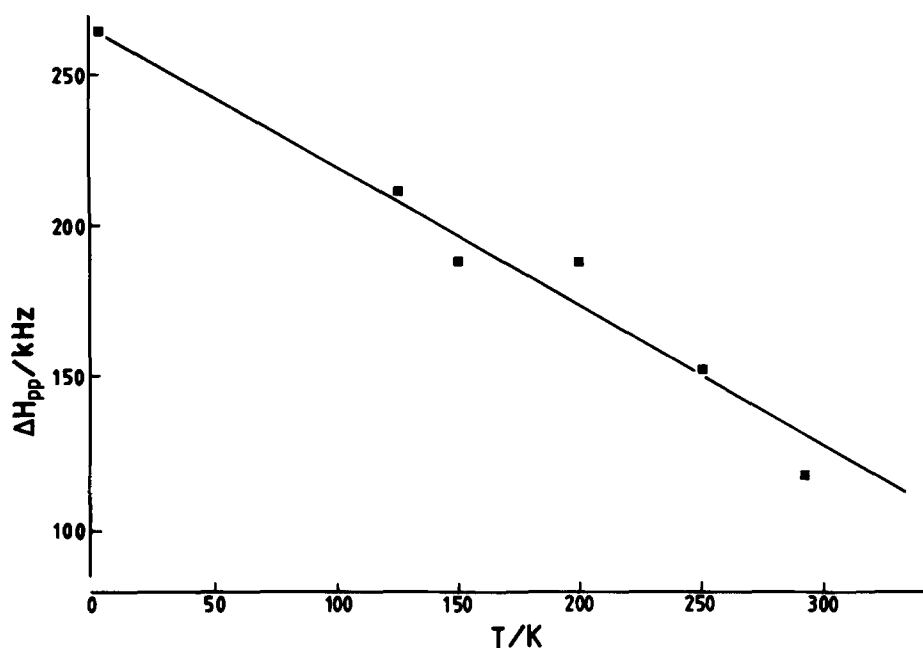


FIG. 2. Temperature variation of the peak to peak linewidth of the ENDOR spectrum of pristine *trans*-polyacetylene.

The ENDOR spectrum of 0.5 mol % ReF_6 doped 70% *cis*-polyacetylene shows two well-resolved features. A narrow line is superimposed on a broad pair of lines, both have Lorentzian line shape and are centered on the proton nuclear frequency (Fig. 3). The narrow line becomes much more intense relative to the other as the temperature is lowered (Fig. 4) from 200 K, and at 4.2 K it splits into a poorly resolved pair of lines. The splitting of the broad pair of lines increases linearly as the temperature is lowered (Fig. 5). No resolved ENDOR spectra could be obtained > 200 K. Computer simulation gives hyperfine couplings of 1.7 and 0.2 MHz at 4.2 K. ENDOR spectra down to 77 K of 3 mol % ReF_6 doped sample were almost identical to those on a 0.5% doped sample.

DISCUSSION

Trans-polyacetylene

The variation in linewidth of the single ENDOR line as a function of temperature is very similar to that found by Thomann *et al.*⁸ The cause of the linewidth variation is attributed to motional narrowing of the local ENDOR coupling by electron dynamics.⁷ In *trans*-polyacetylene, there are long chains of *trans* isomer separated or broken by small lengths of *cis* isomer. The spin density on each carbon atom in the solitons is very low and the proton hyperfine coupling will be so small that it is unlikely to be measurable even by ENDOR spectroscopy.

0.5 mol % ReF_6 doped 70% *cis*-polyacetylene

At 4.2 K, the hyperfine coupling to two different protons is seen, with magnitudes 0.2 and 1.7 MHz. Couplings of this magnitude in a polyene system may be accounted for by comparison with those predicted by e.g., Beveridge and Dobosh in their Hartree-Fock SCF spin-unrestricted and spin-annihilated INDO calculations.⁸ Theory predicts that there

will be alternating spin densities at C atoms resulting in alternate negative proton hyperfine couplings and much smaller positive proton hyperfine coupling. The soliton

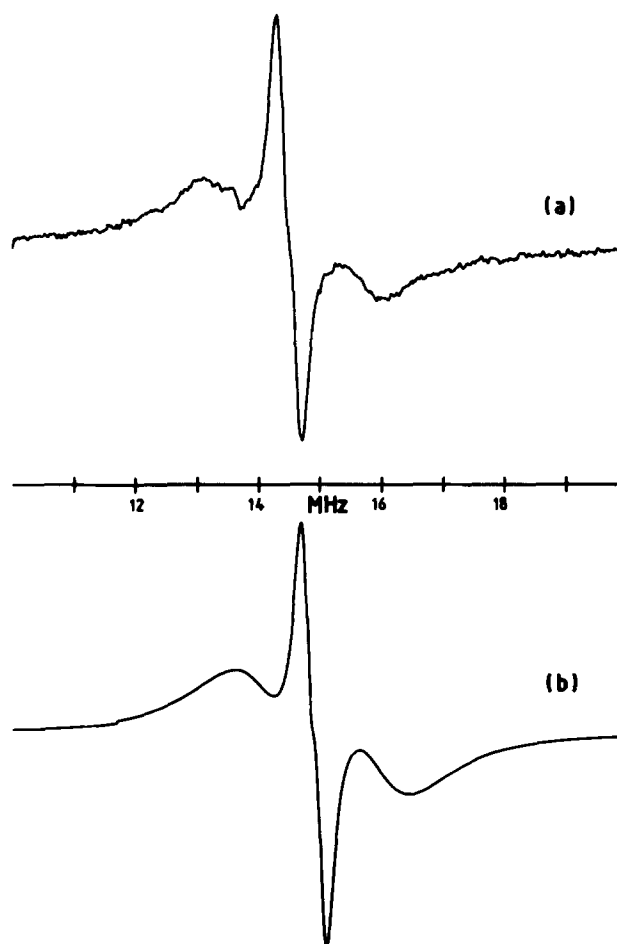


FIG. 3.(a) ENDOR spectrum of 0.5 mol % ReF_6 doped 70% *cis*-polyacetylene at 4 K; (b) computer simulated spectrum.

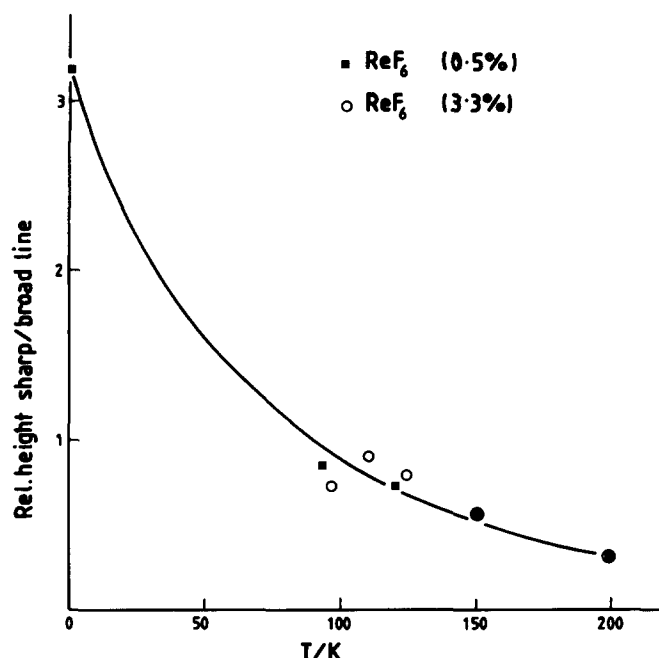


FIG. 4. Relative height of the sharp and broad ENDOR lines of 0.5 and 3 mol % ReF_6 doped 70% *cis*-polyacetylene as a function of temperature.

model is based on this. Using the McConnell Q value of -70 MHz for the short polyenes,⁹ the chain length can be calculated from the sum of the observed proton hyperfine couplings, taking the signs as -1.7 and $+0.2$ MHz. From this a soliton of length averaging 93 carbon atoms is predicted at 4.2 K. At 200 K, the splitting is smaller (1.2 MHz) and suggests a longer chain length for the soliton.

The broadness of the pair of ENDOR lines with larger coupling can be explained on the soliton wave model which predicts a decreasing electron density on alternate carbon atoms nearer the boundary of the soliton. There will thus be

a wide range of couplings resulting in the overlap of many lines. In addition, each soliton will have a different length. The resultant line shape is the sum of these different couplings and the measured splitting is an average hyperfine coupling.

It is difficult to find a convincing reason for the temperature dependence of the ENDOR peak heights (Fig. 4), although it could be due to different relaxation mechanisms for the two signals.

The absence of both hyperfine coupling to ^{19}F and any shift in the g value shows that the rhenium fluoride molecular unit (ReF_n) must be diamagnetic and remote from the soliton. If the ReF_n were above or below the π -molecular orbital of the soliton, then some delocalization of the unpaired electron onto the fluorines would be expected. A more likely position is adjacent to the soliton in the nodal plane of the π -molecular orbital, i.e., the plane containing the C and H atoms. Its position could be stabilized by hydrogen bonding but the distance of the F atoms from the C π orbital is too great for it to be subject to electron polarization which gives apparent unpaired electron spin density on the hydrogens.

Comparison with other work

Thomann has presented ENDOR results on pure *cis*-polyacetylene in two papers.^{7,10} It is difficult to reconcile the results in the two papers although they were submitted within 9 months of each other. In the first paper,⁷ the spectrum at 15 K is very similar to that of ours for 0.5 mol % ReF_6 in 70% *cis*-polyacetylene with a proton hyperfine splitting of 1.8 MHz and a central unresolved sharp line. The similarity is encouraging since short lengths of ESR detectable *trans* isomer must be present in the parent *cis* isomer which would be diamagnetic if pure. The chain length is similar in both systems. More puzzling is the second paper by Thomann¹⁰ in

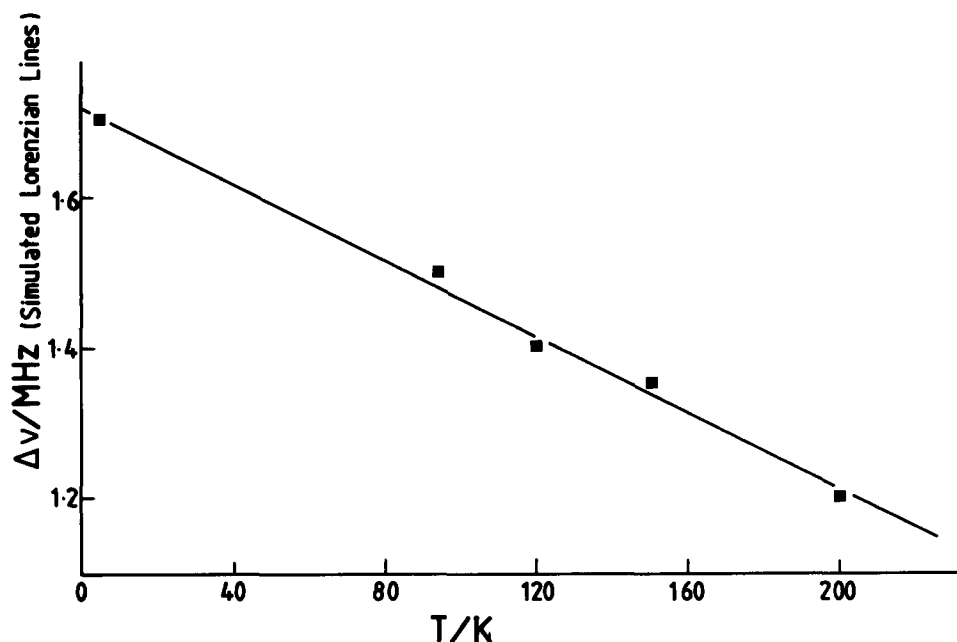


FIG. 5. Variation of the splitting of the broad pair of ENDOR lines (Fig. 3) as a function of temperature.

which ENDOR measurements at 136 K yield a well resolved pair of lines, with some shoulders, separated by about 1 MHz, and another set with splittings ranging from 1.8–7 MHz. No central line is observed. ^{13}C couplings are also measured. From these results, they calculate a chain length of ~ 30 carbon atoms.

Several papers report results of calculations based on an analysis of the ESR linewidth of undoped polyacetylenes. From the change in linewidth of deuterated *cis*-rich polyacetylene relative to undeuterated material, Weinberger estimated the chain length of the soliton to be 10–14 carbons,² while a theoretical analysis of the linewidth of *trans*-polyacetylene by Nechtschein *et al.* suggested a chain length of 10–17 carbons.¹¹ Our estimate is a much longer chain length of 93 carbons in the case of the ReF_6 doped 70% *cis*-polyacetylene. This suggests that dopant molecules are capable of stabilizing longer solitons.

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