Brief Reports

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Time-domain analysis of EPR measurements of polyacetylene and soliton diffusion

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A novel analysis of EPR measurements on polyacetylene is demonstrated by the analysis of the conventional line shape in time domain. Quantitative results of the hyperfine-coupling constant, the on-chain diffusion rate, and the off-chain hopping rate were extracted by nonlinear curve fitting to the time-domain signals, and they are consistent with the soliton model of polyacetylene.

I. INTRODUCTION

The dynamics of paramagnetic defects in undoped *trans*-polyacetylene has been studied extensively by magnetic resonance spectroscopies.[1-7] Experiments indicate that the impurities are neutral in charge and are highly mobile along the chain. These observations have been suggested as evidence for the existence of topological neutral solitons (the kinks in bond-alternation domain wall).[8,9]

In the conventional line-shape studies in frequency domain,[3,4,10] only qualitative analysis on the dimensionality of the diffusive process was usually made. However, quantitative results of the hyperfine coupling constant, the on-chain diffusion rate, and the off-chain hopping rate were obtained by other means such as the electron-spin echo (ESE)[6] and nuclear-spin-relaxation measurements.[3] Because of the spectrometer deadtime, most ESE measurements were performed only on deuterated samples which have a long-phase memory time. Although the hyperfine constant can be measured on *cis*-polyacetylene,[4] the value for *trans*-type samples could be made only at very low temperatures so that the solitons are almost localized. In this Brief Report, we present a novel analysis of EPR measurements on both *trans*- and *cis*-polyacetylene. By nonlinear curve fitting to the time-domain signals, we were able to extract these parameters. Although the same information is present in both time-domain and frequency-domain signals, time-domain analysis is more direct and efficient.

II. THEORY AND EXPERIMENTS

The time-domain signals were a Fourier transformation of absorption spectra which were first obtained by integrating the conventional derivative spectra. Standard EPR measurements were made on stretched films of undoped *trans*- and *cis*-polyacetylene $(CH)_x$, with about 80% C-H chains preferentially oriented parallel to magnetic field. The field-domain derivative spectra were recorded for a 100-G sweep field range, with the use of 0.4-G field modulation and 0.2-mW microwave power.

If one assumes a one-dimensional diffusive motion of the soliton, a Gaussian distribution of spin delocalization [$(\sqrt{2\pi}N)^{-1}\exp(-n^2/2N^2)$ at the nth monomer unit] with half-width Nl, and a Lorentzian hopping process between chains,[7,10] it can be shown that the correlation function $g(\tau)$ is given by

$$g(\tau)=(\Delta\omega)^2 e^{-\gamma\tau}\frac{1}{\sqrt{1+\alpha\tau}} \tag{1}$$

and

$$(\Delta\omega)^2=\frac{I(I+1)}{3}\frac{a_H^2}{\sqrt{\pi}2N}\ , \tag{2}$$

$$\alpha=D/N^2l^2\ , \tag{3}$$

where D is the on-chain diffusion constant and γ is the off-chain hopping rate. The effective diffusion rate α is scaled by a factor $1/N^2$, and the effective second moment of the hyperfine field $\Delta\omega^2$ is also scaled by $1/\sqrt{\pi}2N$. By use of the correlation function stated in Eq. (1) and Kubo's formula for the time-domain signal[11,12] $S(t)$, it can be shown that

$$-\frac{\ln S(t)}{\Delta\omega^2}=\sqrt{\pi/\alpha\gamma^3}e^{\gamma/\alpha}\left[\frac{\gamma}{\alpha}(1+\alpha t)-1/2\right]\left\{\mathrm{erf}\left[\left[\frac{\gamma(1+\alpha t)}{\alpha}\right]^{1/2}\right]-\mathrm{erf}(\sqrt{\gamma/\alpha})\right\}+\frac{1}{\alpha\gamma}(e^{-\gamma t}\sqrt{1+\alpha t}-1)\ , \tag{4}$$

where erf(x) is the error function.

Although the above expression is rather complicated, some of its limits are simple and particularly interesting: (1) For $\alpha, \gamma << 1/t$, $S(t) \propto \exp(-\frac{1}{2}\Delta\omega^2 t^2)$ is characterized by a Gaussian form. (2) For $\alpha >> \gamma >> 1/t$,

$$S(t) \propto \exp[-(\Delta\omega)^2\sqrt{\pi/\alpha\gamma}\,t]$$

has a simple exponential decay form. (3) For $\gamma >> \alpha, 1/t$,

$$S(t) \propto \exp(-\Delta\omega^2 t/\gamma)$$

is again characterized by an exponential decay form. (4) For $\alpha >> 1/t >> \gamma$,

$$S(t) \propto \exp[-(\Delta\omega)^2(4/3\sqrt{\alpha})t^{3/2}]$$

has a $t^{3/2}$ dependence in the exponent which is a characteristic associated with one-dimensional diffusive processes.

The exponential behavior in the long-time limit has been observed experimentally for a wide range of temperatures from 8 K to room temperature. As an example illustrated in Fig. 1(a), the time-domain signal at 75 K shows an exponential decay tail for $t \geq 20$ nsec. The data in the tail portion were least-squares fitted by $C\exp(-At^B)$ with three variable parameters A, B, and C. The fitting converges to the best fit with $B = 1.00 \pm 0.05$, which corresponds to an exponential decay. The exponential decay tail indicates the existence of the off-chain hopping processes.[10] From the time when the data begins to show exponential decay behavior, the off-chain hopping rate is estimated to be roughly about 5×10^7 s^{-1}. The value agrees to previous nuclear-relaxation measurements on T_1 and $T_{1\rho}$.[5]

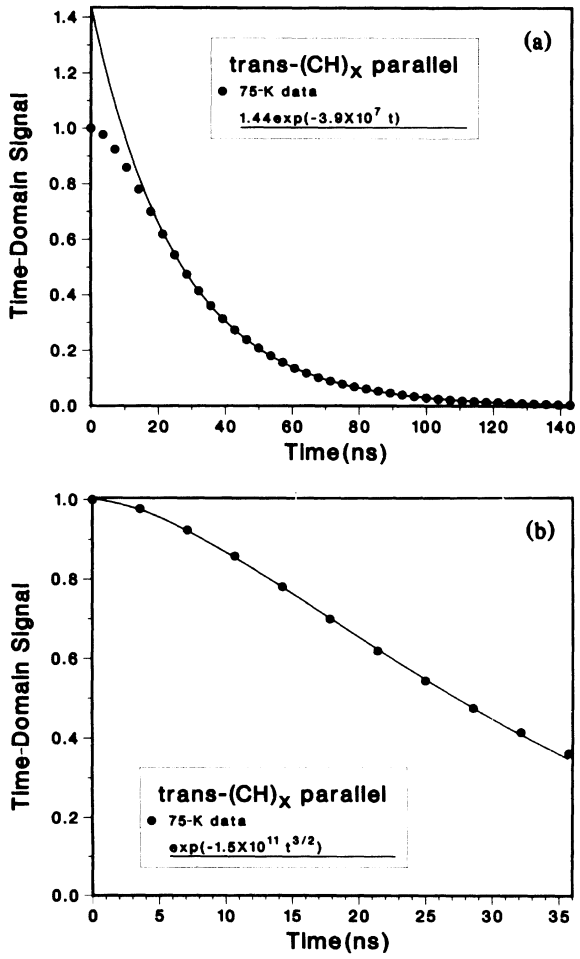

FIG. 1. (a) Time-domain signal at 75 K and its best fit for the tail portion. The data show an exponential decay tail for $t > 20$ ns which indicates an off-chain hopping rate of about 5×10^7 s^{-1}. (b) Short-time behavior of the time-domain signal at 75 K and its best fit. The characteristic $t^{3/2}$ dependence in the exponent is due to the one-dimensional diffusion process.

The short-time behavior ($t \leq 35$ nsec) of the same data as shown in Fig. 1(b) is evidently nonexponential. The data were found to be best fitted by $1.44\exp(-1.5\times10^{11}t^{1.5})$. The characteristic $t^{3/2}$ dependence is strong evidence of a one-dimensional diffusive process.

Generally, the time-domain signal at higher temperatures is almost exponential. Although the exponential rate $(\pi/\alpha\gamma)^{1/2}(\Delta\omega)^2$ can be determined accurately, the curve fitting of data at high temperature using the complete expression in Eq. (4) does not converge to a unique fit. However, the low-temperature data which are significantly nonexponential can be fitted uniquely. It is found that $\Delta\omega$ does not change significantly (less than 10%), and γ varies by a small factor. Recent NMR results have also indicated a small temperature dependence of γ.[13] By holding both $\Delta\omega$ and γ fixed at 9.4×10^7 and 6.2×10^7 s^{-1}, respectively, the diffusion rate α at the three temperatures 8, 35, and 48 K are found to be 1.8×10^8, 5.9×10^8, and 9.4×10^8 s^{-1}, respectively, as shown in Fig. 2.

The effective hyperfine field for *cis*-$(CH)_x$ is obtained by fitting the time-domain signal of the sample at 8 K by $\exp[-\frac{1}{2}(\Delta\omega)^2t^2]$. It is found that $\Delta\omega = 9.8\times10^7$ s^{-1}, which is very close to the value for *trans*-$(CH)_x$ samples. One possible interpretation is that solitons have a similar spin distribution for both types of structure although the solitons in *cis*-$(CH)_x$ are not very mobile.

If one takes $a_H/2\pi = 31$ G,[14] the hyperfine constant for an unpaired spin localized to a single C-H unit, the half-width of soliton in the Gaussian model is estimated to be 2.3. In the Su-Schrieffer-Heeger (SSH) model the hyper-

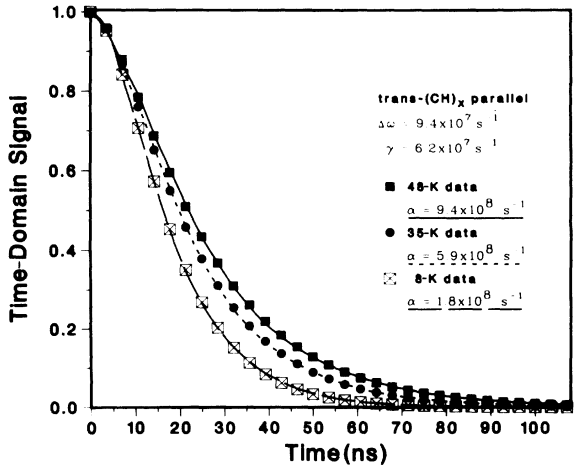

FIG. 2. Time-domain signals at three low temperatures and their best fits. γ is the off-chain hopping rate and α is the on-chain diffusion rate. The observed hyperfine field $\Delta\omega$ is smaller than that of localized spin and serves as evidence for spin delocalization.

fine constant at the nth monomer unit is given by

$$(1/N)a_H \operatorname{sech}^2(n/N)\cos^2(n\pi/2) ,$$

with N about 7. If one omits the odd-number sites which have zero-spin density, the envelope of the spin-density distribution by the SSH model is very close to a Gaussian form $\exp(-n^2/2N^2)$, with N about 5. Interpretation of the effective hyperfine field in Eq. (2) is model dependent. It can be shown that, by assuming the spin distribution function in the SSH model, $(\Delta\omega)^2 = 2I(I+1)a_H^2/9N$. The resulting delocalization factor $N \simeq 5.5$, which is close to the prediction of the SSH model. With use of the same values of $\Delta\omega$ and γ at low temperature, the effective diffusion rate for the *trans*-$(CH)_x$ sample at room temperature is estimated to be about 1.5×10^{10} s^{-1}. This implies an anisotropy ratio of diffusion rate at room temperature about 240. If the scaling factor N^2 ($N=2.3$ for the Gaussian model) is taken into account, the actual anisotropy ratio of the diffusion constant is then about 1300.

III. CONCLUSION

In conclusion, the effects of one-dimensional diffusion of solitons on EPR measurements of undoped *trans*-$(CH)_x$ were analyzed in the time domain. It is found that the time-domain signal generally exhibits an exponential tail which could be the consequence of interchain hopping. The one-dimensional diffusive process is consistent with the observed $\exp(-at^{3/2})$ dependence in short-time behavior. The effective hyperfine fields $\Delta\omega$ for both types of *trans*- and *cis*-$(CH)_x$ were found to be very close. It may indicate a similar spin distribution for both types of structures. If one assumes a Gaussian distribution of spin density for the soliton, it is found that the spin is delocalized over five sites. However, if one used the spin-density function of the SSH model, spin delocalization over 11 sites is found. The value is closer to the prediction by the model. Measurements of the temperature dependence of the diffusion constant now in progress should serve as a test for predictions of the Wada-Schrieffer[15] or Maki[16] theories.

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