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## Temperature Dependence of Soliton Diffusion

in Trans-Polyacetylene

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## Abstract

The temperature dependence of 1-D diffusion rate of solitons in trans-polyacetylene is determined by time-domain analysis of ESR measurements. The diffusion rate appears to obey a simple power law. Monte Carlo simulation of 1-D diffusion process in impure chains indicates that overall diffusion can be much slower than that without traps.

## I. INTRODUCTION

Pristine polyacetylene,  $(\text{CH})_x$ , has recently been studied extensively by magnetic resonance spectroscopies.<sup>1-9</sup> The diffusion rate of unpaired spins inferred from ESR measurements is smaller than that by nuclear relaxation measurements. Reconciliatory arguments assuming the existence of two spin species were proposed by Nechtschein et al.<sup>7</sup> In their analysis of the diffusion constant, a homogeneous lorentzian lineshape is assumed for the whole range of 4 K to room temperature. However, it is known that below 100 K the ESR lineshape deviates from lorentzian and contains inhomogeneous components. As a consequence, their analysis on the temperature dependence of the diffusion constant cannot be complete. In a previous paper,<sup>9</sup> we have pointed out that quantitative results of the on-chain diffusion rate can be extracted by time-domain analysis of ESR measurements even if the lineshape is not lorentzian. In this paper, we present results on the temperature dependence of one dimensional (1-D) diffusion rate process in trans- $(\text{CH})_x$  by time-domain analysis. A simple model of diffusion in impure chains is provided to explain why the apparent observed diffusion rate of spins decreases if traps are present.

## II. THEORY AND EXPERIMENTS

In the bond-alternation domain-wall (soliton) model,<sup>10-12</sup> the unpaired spins are delocalized over about fourteen C-H units, and are highly mobile along the chain. If one assumes a 1-D diffusive motion of the soliton, and a lorentzian hopping process between chains, it has been shown that the spin correlation function is given by<sup>9</sup>

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

where  $\gamma$  is the off-chain hopping rate,  $\alpha$  is the 1-D diffusion rate, and  $\Delta\omega^2$  is the effective second moment of the hyperfine and dipolar field. The 1-D diffusion rate is scaled by a factor  $1/N^2$  as a consequence of spin delocalization over  $2N$  C-H units.<sup>10,11</sup> The time-domain signal can be derived by Kubo's formula<sup>13</sup> as

$$S(t) = \exp \left( \int_0^t (t-\tau) g(\tau) d\tau \right). \quad (2)$$

The analytical expression of the above integration is given in our previous paper.<sup>9</sup>

Standard X-band ESR measurements were performed on stretched films of both air-exposed and unexposed  $\text{trans}-(\text{CH})_x$ , with about 80% of the C-H chains preferentially oriented along magnetic field. The exposed sample was degassed and sealed in helium atmosphere after the exposure. The field-domain derivative ESR spectra were recorded for 40 and 100 G sweep field ranges, employing from 0.01 to 0.05 G field modulation with microwave power of 0.01 to 0.1 mW. The time-domain signal can be obtained by a Fourier transformation of the absorption spectrum obtained by integrating the first derivative spectrum. The values of  $\Delta\omega^2$  and  $\gamma$  were first obtained by fitting data at liquid helium temperature where the 1-D diffusion rate is negligibly small as compared to  $\gamma$ . To improve the accuracy of fitting time-domain data at various temperatures, both  $\Delta\omega^2$  and  $\gamma$  were fixed, and only one parameter, the 1-D diffusion rate, was varied. The assumption of constant  $\gamma$  is justified by both NMR results<sup>14</sup> and the small temperature dependence of the ESR linewidth of  $\text{cis}-(\text{CH})_x$ . The off-chain hopping of spins may involve Heisenberg exchange.

By curve fitting, we find that  $\Delta\omega = 8.7 \times 10^7 \text{ rad s}^{-1}$ ,  $\gamma = 1.1 \times 10^8 \text{ s}^{-1}$  for the unexposed sample, and  $\Delta\omega = 9.1 \times 10^7 \text{ rad s}^{-1}$ ,  $\gamma = 1.1 \times 10^8 \text{ s}^{-1}$  for the sample exposed at room temperature to air for ten minutes. Assuming a spin distribution function as in the Su-Schrieffer-Heeger model,<sup>11</sup> it was shown that<sup>9</sup>  $\Delta\omega^2 = 2I(I+1) a_H^2/9N$ , where  $a_H/2\pi$  ( $\sim 31\text{G}$ ) is the hyperfine constant for an unpaired spin localized to a single C-H unit.<sup>15</sup> The delocalization factor  $N$  for both samples is found to be about 6 and is close to the theoretical prediction. The slight difference in  $\Delta\omega$  between two samples may be due to the difference in the dipolar interaction.

The 1-D diffusion rates of both samples at various temperatures are shown in Fig. 1(a) and 1(b). The data appear to be linear in the log-log plot. The slope for the unexposed sample in Fig 1(a) is 2.6, and the slope of the air-exposed sample in Fig 1(b) is about 2.3. The temperature dependence of diffusion rate is different from Nechtschein's analysis<sup>7</sup> and is much simpler. The observed temperature dependence is different from the prediction by the Wada-Schrieffer model<sup>16</sup> of a quadratic dependence. Our data also differ from Maki's prediction of a power law  $\alpha \propto T^{(2-d)/2}$  where  $d$  is the spatial dimension of the acoustic phonon involved.<sup>17</sup> Such disagreement is not unexpected because the latter two models do not consider the effects of trapping centers, the observed temperature dependence of diffusion rate can be very different from ideal cases.

The measured 1-D diffusion rate at room temperature is about  $10^{10} \text{ s}^{-1}$ . If the scaling factor  $N^2$  ( $N \sim 7$  for Su-Schrieffer-Heeger model) is taken into account, the actual diffusion rate is about  $5 \times 10^{11} \text{ s}^{-1}$ . This value is two orders of magnitude smaller than that from NMR relaxation measurements.<sup>3</sup> The apparent discrepancy may be due to a difference in the time-scale to which ESR linewidth measurements and NMR relaxation measurements are sensitive. In the

ESR linewidth broadening process, slow motions at a rate comparable to hyperfine field are important. However, in the NMR spin-lattice relaxation process, fast motion close to electron Larmor frequency dominates. As a result, the ESR linewidth senses the long time behavior of the diffusive process and NMR spin-lattice relaxation senses a much shorter time behavior. To support this argument, a Monte Carlo simulation of a 1-D random walk process in the presence of trapping centers was performed.

In the long time limit where  $\alpha_L t \gg 1$  ( $\alpha_L$  is the escape rate from trapping sites), the effective diffusion rate is significantly reduced in the presence of a small amount of traps if the escape rate is much smaller than the diffusion rate of non-trapping sites,  $\alpha_D$ . The effective diffusion rate in the long time limit from Monte Carlo simulation is shown in Fig. 2 and appears to follow a simple relation as<sup>18</sup>

$$\alpha_{\text{eff}}/\alpha_D = \frac{\alpha_L/\alpha_D}{p + (1-p)\alpha_L/\alpha_D} \quad (3)$$

where  $p$  is concentration of trapping centers. In the short time limit,  $\alpha_L t \ll 1 \ll \alpha_D t$ , however, the effective diffusion rate deviates from the above relation and is close to  $\alpha_D$ . In this limit, one may deal with two distinct spin species and may assume that only the spins at non-trapping sites contribute to nuclear spin relaxation<sup>7</sup>. However, in the long time scale of ESR linewidth broadening (which is about three orders of magnitude longer than time scale involved in NMR relaxation process) one may not distinguish these two spin species, but rather observes a slower overall effective diffusion rate. These simulated results support the view that the effective diffusion rate being measured depends on the time scale to which a particular spectroscopic tool is most sensitive. As a consequence, it is not unexpected that

the effective diffusion rate inferred from ESR linewidth measurements is smaller than that by NMR nuclear spin relaxation measurements.

### III. CONCLUSIONS

In conclusion, the temperature dependence of the 1-D diffusion rate of solitons is determined by time-domain analysis of ESR measurements. Even though the lineshape is no longer lorentzian at low temperature, the diffusion rate can be determined by curve fitting to time-domain data. The dependence of the diffusion rate on temperature follows a simple power law. The presence of oxygen increases the ESR linewidth and decreases slightly the power of the temperature dependence of diffusion rate. Monte Carlo simulations of the 1-D diffusion process in presence of traps indicates that the effective diffusion rate is reduced if observed in a longer time scale. These results may explain why the diffusion rate observed by ESR linewidth measurements is slower than that by NMR spin-lattice relaxation measurements.

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## FIGURE CAPTIONS

FIG. 1. Temperature dependence of 1-D diffusion rate  $\alpha$  in units of 1/nanosecond. Both sets of data obey a simple power law as  $\alpha \propto T^n$ , where  $n = 2.6$  for the unexposed sample (Fig. 1.(a)) and  $n = 2.3$  for the sample exposed to air for ten minutes (Fig. 1.(b)).

FIG. 2. Results of Monte Carlo simulation of 1-D diffusion process with traps. The calculated diffusion rates for various trap concentration follow closely the relation shown in eq. (3) as represented by the solid and dashed lines.





