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EPR of Naarmann-Theophilou polyacetylene: Critical role of interchain interactions

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Electron-paramagnetic-resonance (EPR) experiments have been carried out on pristine Naarmann-Theophilou polyacetylene N-$(CH)_x$. It is found that there is a significantly increased interchain spin exchange in *trans*-(N-$(CH)_x$) compared with that of *trans*-Shirakawa $(CH)_x$. We propose that the intrachain soliton diffusion range in *trans*-(N-$(CH)_x$) is greatly enhanced. Studies of spin-lattice relaxation and oriented polymers support this conclusion. We discuss possible origins for the higher conductivity of I_2-doped N-$(CH)_x$ in light of the enhancement of the soliton diffusion range.

Polyacetylene has been extensively studied since the report by Shirakawa *et al.* in 1977 that polyacetylene [denoted here as S-$(CH)_x$] goes through an insulator-metal transition upon doping with I_2 and other dopants.[1] For the heavily doped "metallic" $(CH)_x$, the conductivity (σ) reaches 10^2–10^3 S/cm at room temperature. In 1987 a different route to synthesize $(CH)_x$ was reported by Naarmann and Theophilou[2] [denoted as N-$(CH)_x$]. This N-$(CH)_x$, when doped with I_2, has σ (295 K) approaching 10^5 S/cm,[3–5] a value close to that of copper. Since then N-$(CH)_x$ has become a focus of extensive studies aimed at revealing its difference from S-$(CH)_x$.[4–9] The earlier ^{13}C NMR studies indicated[2] a reduction of sp^3 defect concentration in N-$(CH)_x$. This was suggested as the origin of the high σ.[2,3] However, further experiments showed that this difference is questionable.[8] Optical absorption, photoinduced absorption, and magnetic susceptibility experiments[4] revealed almost identical electronic structures for the two polymers. Thermoelectric power, magnetoresistance,[7,10] and spin concentration[4] of I_2-doped N-$(CH)_x$ and S-$(CH)_x$ are also similar. Some difference in crystalline coherence ξ have been reported though the crystalline percentage is similar.[8,9] The intrachain $\xi_\parallel$ of N-$(CH)_x$ is found to ~160–180 Å, slightly greater than that of S-$(CH)_x$ (~100–130 Å). However, the transverse $\xi_\perp$ of N-$(CH)_x$ is shorter (~50 ± 3 Å) compared with $\xi_\perp \sim 75 \pm 15$ Å in S-$(CH)_x$. The difference between N-$(CH)_x$ and S-$(CH)_x$ thus still remains a puzzle.

In this Rapid Communication, we report experimental results which reveal a significant difference between *undoped* N-$(CH)_x$ and S-$(CH)_x$. We have performed electron-paramagnetic-resonance (EPR) experiments on pristine N-$(CH)_x$ and compare the results with those of S-$(CH)_x$. We find EPR line shapes of these two polymers are significantly different. There is more than an order of magnitude increase in the interchain spin-exchange interaction in the N-$(CH)_x$ as compared to that in S-$(CH)_x$. In addition, the spin-lattice relaxation time of N-$(CH)_x$ is reduced to a larger extent in going from *cis* to *trans* samples by thermal isomerization. We propose that these differences reflect an increase in intrachain soliton diffusion range in *trans*-(N-$(CH)_x$) which increases the interchain spin exchange and the spin-orbit coupling. The conclusion is further supported by the comparison of unoriented *trans*-$(CH)_x$, oriented *trans*-$(CH)_x$, and *cis*-$(CH)_x$. This increased soliton diffusion range suggests that the origin of the increased σ of I_2-doped N-$(CH)_x$ may lie in a subtle difference in interchain as well as intrachain order.

The experimental results are summarized as follows. The EPR peak-to-peak linewidth ΔH_{pp} of unoriented *trans*- and *cis*-(N-$(CH)_x$) are plotted versus temperatures (T) in Fig. 1. The $\Delta H_{pp}(T)$ of *trans*-(N-$(CH)_x$) is al-

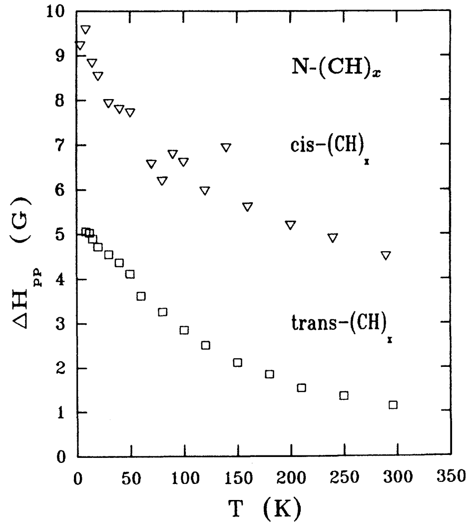

FIG. 1. Temperature dependence of EPR peak-to-peak linewidth ΔH_{pp} of N-$(CH)_x$ in the *cis* form (▽) and *trans* form (□).

most identical to that of *trans*-(S-(CH)$_x$) while *cis*-(N-(CH)$_x$) has smaller $\Delta H_{\rm pp}$.[11] Analyses of EPR line shapes of *trans*-(N-(CH)$_x$) and *trans*-(S-(CH)$_x$) (Ref. 11) at 295 K are shown in Fig. 2, where the single integral $I(H)$ of EPR derivative signal normalized to its maximum $[I(H_0)]$ is plotted versus the square of the difference in magnetic field H from H_0 normalized by half-width at half power of the spectrum $\Delta H_{1/2}$. The linewidths and line shapes are reproducible for different batches. The noise is negligibly small in the range of 10–15 times the linewidth. Also shown in Fig. 2 are the theoretical line shapes expected for quasi-one-dimensional (1D) spin diffusion with different interchain couplings J'. The *trans*-(N-(CH)$_x$) has a line shape very close to a Lorentzian or 3D shape while the *trans*-(S-(CH)$_x$) line shape[11] is in between Lorentzian and that of ideal 1D spin diffusion. Figure 3 shows the line shapes of *cis*, 500% oriented *trans*, as well as unoriented *trans*-(N-(CH)$_x$). We can see that the room-temperature line shape of the *cis* sample is very close to the ideal 1D shape and that of unoriented *trans* is close to the ideal 3D shape; the line shape of oriented *trans* is in between. It is noted that the experimental line shapes for all the samples differ substantially from Gaussian shape (i.e., immobile, noninteracting spins). Figure 4 shows saturation characteristics of EPR (single integral) signals. Spin-lattice relaxation time T_1 is calculated[12] according to $T_1 = 4.56 \times 10^{-7} \Delta H_{1/2}/gH_1^2$, where $\Delta H_{1/2}$ is defined above, g is the Landé g factor, and H_1 is the applied microwave frequency magnetic field for maximum signal amplitude. The H_1 is related to microwave power P as $H_1^2 = 0.628P$ where coefficient 0.628 is found by measuring the resonance frequency shift induced by a metallic sphere.[12] We find $T_1 \sim 3.5 \times 10^{-4}$ (sec) for *cis*-(N-(CH)$_x$) and $T_1 \sim 2.3 \times 10^{-5}$ (sec) for *trans*-(N-(CH)$_x$). For comparison, we note that S-(CH)$_x$ has[13] $T_1 \sim 5.4 \times 10^{-5}$ (sec) (*cis*) and $\sim 2.7 \times 10^{-5}$ (sec) (*trans*). Though in the *cis*-(N-(CH)$_x$) T_1 is much larger than that of *cis*-(S-(CH)$_x$), T_1 of *trans*-(N-(CH)$_x$) is dramatically reduced to become comparable with that of *trans*-(S-(CH)$_x$). Thus the isomerization process reduces T_1 of N-(CH)$_x$ more significantly.

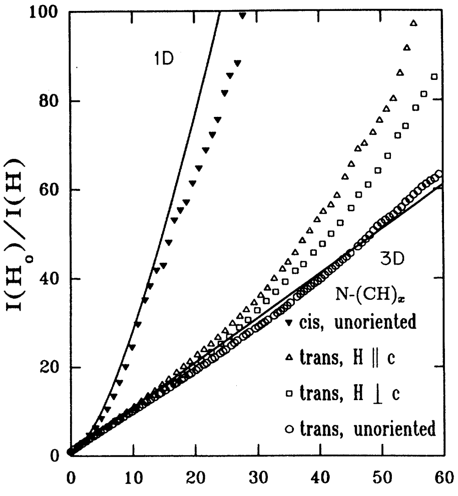

FIG. 3. Comparison of room-temperature EPR line shapes of N-(CH)$_x$ with theoretical line shapes of 1D and 3D spin diffusion (solid lines). The line shape of unoriented *cis* (▲), 500% stretched *trans* (△, $H \parallel c$; □, $H \perp c$), and unoriented *trans* (○) samples are presented.

The similar EPR linewidths of N-(CH)$_x$ and S-(CH)$_x$ indicate similar spin or neutral soliton diffusion rate for *trans* samples since a EPR linewidth of *trans*-(CH)$_x$ is narrowed by spin diffusion.[11,14] The earlier studies suggest[14] that there exist both mobile solitons (moving with approximately the speed of sound) and localized solitons.

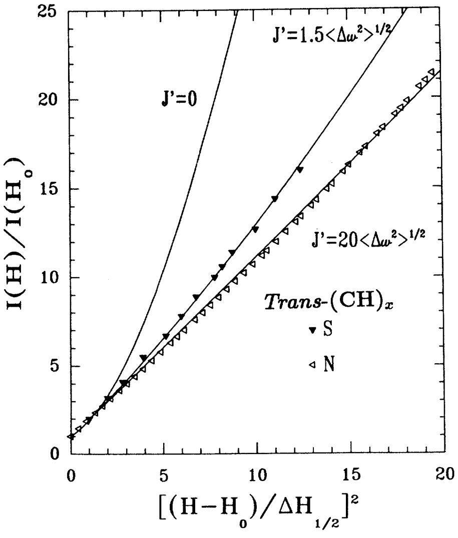

FIG. 2. Comparison of room-temperature EPR line shapes of *trans*-(N-(CH)$_x$) (△) and *trans*-(S-(CH)$_x$) (▲) with the theoretical line shapes of quasi-one-dimensional spin diffusion with different interchain exchange J'; see text.

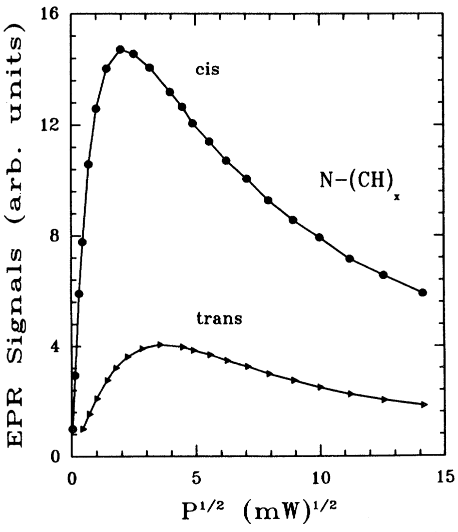

FIG. 4. EPR saturation characteristics of N-(CH)$_x$ in its *trans* form (▲) and *cis* form (●).

Since we observe a single homogeneously broadened EPR line in all cases, the exchange rate between mobile and fixed spins must be greater than the resonance frequency. Hence the observed soliton diffusion rate includes effects of both mobile and fixed spins. Note that the *cis*-(N-(CH)$_x$) shows smaller ΔH_{pp} than *cis*-(S-(CH)$_x$).[11] This is probably due to higher *trans* concentration in the sample [$\sim$15% in N-(CH)$_x$ (Ref. 2) vs $\sim$5% in S-(CH)$_x$ (Ref. 1)].

The EPR line-shape analyses indicate an increased intrachain soliton diffusion range in *trans*-(N-(CH)$_x$). For a 3D spin motion, the transverse magnetization varies as $\Phi(t) \sim \exp(-\eta t)$, resulting in a Lorentzian shape. For a strictly 1D spin motion, $\Phi(t) \sim \exp[-(\beta t)^{3/2}]$, resulting in the 1D shape in Figs. 2 and 3. For a quasi-1D spin motion, we have[15]

$$\begin{aligned}
\Phi(t) &= \exp[-\phi(t)]\,, \\
\phi(t) &\approx \frac{\langle \Delta\omega^2 \rangle}{(J'/\hbar)^2} F(t/t_0)\,, \\
F(t/t_0) &= \int_0^{t/t_0} [(t/t_0) - x]\, x^{-1/2} \\
&\quad \times \exp(-4x^{3/2}) I_0^2(2x^{3/2})\, dx\,,
\end{aligned} \tag{1}$$

where $\langle \Delta\omega^2 \rangle$ is the second moment of an unnarrowed line, J' is spin interchain coupling, I_0 is the modified zero-order Bessel function, and t_0^{-1} is the interchain transfer rate for spin polarization[15]

$$t_0^{-1} \approx (J'/J)^{1/3} J'/\hbar\,, \tag{2}$$

where J is spin intrachain coupling. The line shape represented by Eq. (1) is in between the 1D and Lorentzian line shape. Fitting the line shape of *trans*-(N-(CH)$_x$) and *trans*-(S-(CH)$_x$) to Eq. (1) (see Fig. 2) we obtain $J'/\hbar \sim 1.5\langle \Delta\omega^2 \rangle^{1/2}$ for S-(CH)$_x$ and $J'/\hbar \sim 20\langle \Delta\omega^2 \rangle^{1/2}$ for N-(CH)$_x$. The difference in interchain coupling J' is likely due to the difference in *interchain spin exchange;* the interchain charge-transfer rate must be the same since σ is the same for both polymers.[3,16] Since the spin concentration is similar, the origin for the increased J' in N-(CH)$_x$ must be caused by increased soliton diffusion range so that two solitons on neighboring chains can approach closer to one another and hence exponentially increase their spin exchange interaction.

The comparison of T_1 of N-(CH)$_x$ and S-(CH)$_x$ is consistent with the EPR line-shape analyses. Spin-orbit coupling is suggested to be a major spin-lattice relaxation mechanism in (CH)$_x$,[13] which is increased in the vicinity of an impurity.[13] If a spin can move in a larger range there will be a higher chance for the spin to approach near impurities thereby reducing T_1. In the *cis*-rich (CH)$_x$ spins are confined to short *trans* segments inside the *cis* structure while in the *trans*-(CH)$_x$ spins can move a larger distance, hence T_1 is decreased. The more significant decrease of T_1 in *trans*-(N-(CH)$_x$) suggests a *greater soliton diffusion range* compared to that of *trans*-(S-(CH)$_x$).

EPR line-shape analyses of oriented N-(CH)$_x$ further support this conclusion. A soliton is the "kink" between regions of differing phases of bond alternation (A phase and B phase).[1] These two phases are degenerate for an isolated chain.[1] However if we consider interchain coupling, this degeneracy is lifted since there is a small energy difference ($\sim$10 K/C) for in-phase and out-of-phase coupling between two neighboring chains.[17] Thus solitons are confined so that the energetically favored interchain phase correlation is maximized. Since interchain disorder tends to destroy the phase correlation between the neighboring chains, it suppresses the soliton confinement. However, as the polymer chains are oriented, the interchain order is improved which would result in the increase of soliton confinement and hence the decrease of interchain exchange J'. This is what is observed if we compare EPR line shapes of oriented and unoriented samples (Fig. 3). Furthermore, since the soliton is confined to the short *trans* segments in the *cis*-rich samples, the line shape is even closer to the 1D line shape (Fig. 3). Therefore the dimensionality of EPR line shape is directly related to the intrachain soliton diffusion range.

The increased soliton diffusion range in *trans*-(N-(CH)$_x$) suggests a possible origin for its high σ when doped with I$_2$. It is well known that a charge is localized in a strictly 1D system with any weak disorder due to the interference of a forward wave with a backscattering wave.[18] However, the charge is significantly delocalized if it is in a 3D (though highly anisotropic) system. The increased soliton diffusion range in *trans*-(N-(CH)$_x$) suggests weaker interchain order in the undoped polymer (in agreement with the shorter $\xi_\perp$). This may allow easier reorganization of polymer chains upon exposure to I$_2$ to the ideal crystal structure for the I$_2$-doped phase, resulting in increased 3D order and 3D charge delocalization in I$_2$-doped N-(CH)$_x$ as compared to S-(CH)$_x$. Thus higher σ may result.

In conclusion, we observed increased soliton interchain exchange and isomerization effects on T_1 in N-(CH)$_x$. These effects are attributed in to the increased soliton diffusion range in N-(CH)$_x$. The results might be useful for the understanding origin of the high σ in some polymers.[7,19]

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[1] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc. Chem. Commun. 578 (1977). For a summary of related works see *Handbook of Conducting Polymers,* edited by T. A. Skotheim (Dekker, New York, 1986), Vols. I and II; *Proceedings of the International Conference on Science and Technology of Synthetic Metals (ICSM'88), Sante Fe, NM,* edited by M. Aldissi

[Synth. Met. **27**, (1989)]; *Proceedings of the International Conference on Science and Technology of Synthetic Metals (ICSM'90), Tübingen, Germany,* edited by M. Hanack, S. Roth, and H. Schier [Synth. Met. **41**, (1991)].

[2] H. Naarmann and N. Theophilou, Synth. Met. **22**, 1 (1987).

[3] A. J. Heeger, S. A. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[4] N. Theophilou, D. B. Swanson, A. G. MacDiarmid, A. Chakraborty, H. H. S. Javadi, R. P. McCall, S. P. Treat, F. Zuo, and A. J. Epstein, Synth. Met. **28**, D35 (1989).

[5] N. Basescu, Z. X. Liu, D. Moses, A. J. Heeger, H. Naarmann, and N. Theophilou, Nature (London) **327**, 403 (1987); T. Schimmel, W. Reiss, J. Gimeiner, G. Denninger, M. Schwoerer, H. Naarmann, and N. Theophilou, Solid State Commun. **65**, 1311 (1988).

[6] S. A. Kivelson and A. J. Heeger, Synth. Met. **22**, 371 (1988).

[7] H. H. S. Javadi, A. Chakraborty, C. Li, N. Theophilou, D. B. Swanson, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. B **43**, 2183 (1991).

[8] N. Theophilou, D. B. Swanson, A. G. MacDiarmid, J. G. Mantovani, B. K. Annis, and A. J. Epstein, in *Electronic Properties of Conjugated Polymers III,* edited by H. Kuzmany, M. Mehring, and S. Roth (Springer-Verlag, Berlin, 1989), p. 14.

[9] D. Djurado, J. Ma, N. Theophilou, and J. E. Fischer, Synth. Met. **30**, 395 (1989).

[10] G. Thummes, F. Korner, and J. Kotzler, Solid State Commun. **67**, 215 (1988).

[11] B. R. Weinberger, E. Ehrenfreund, A. Pron, A. J. Heeger, and A. G. MacDiarmid, J. Chem. Phys. **72**, 4749 (1980).

[12] C. P. Poole, *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques* (Wiley, New York, 1967), p. 711.

[13] J. C. W. Chien, Gary E. Wnek, Frank E. Karasz, J. M. Warakomski, A. J. Heeger, and A. G. MacDiarmid, Macromolecules **15**, 614 (1982).

[14] K. Holczer, J. P. Boucher, F. Devreux, and M. Nechtschein, Phys. Rev. B **23**, 1051 (1981); M. Nechtschein, F. Devreux, F. Genoud, M. Guglielmi, and K. Holczer, *ibid.* **27**, 61 (1983).

[15] M. J, Hennessy, C. D. McElwee, and P.M. Richards, Phys. Rev. B **7**, 930 (1973).

[16] G. Du (unpublished); interchain intersoliton hopping was considered as the origin of J' (see Ref. [11]).

[17] D. Baeriswyl and K. Maki, Phys. Rev. B **28**, 2068 (1983).

[18] Y. A. Firsov, in *Localization and Metal Insulator Transition,* edited by H. Fritzsche and D. Adler (Plenum, New York, 1985), p. 471; W. Apel and T. M. Rice, J. Phys. C **16**, L1151 (1983).

[19] Z. H. Wang, C. Li, E. M. Scherr, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. Lett. **66**, 1745 (1991); Z. H. Wang, A. Ray, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. B **43**, 4373 (1991).