Study of anisotropic spin dynamics in pristine trans-
polyacetylene by means of 2 mm EPR spectroscopy

V. I. Krinichnyi, A. E. Pelekh, L. I. Tkachenko and G. I. Kozub
Department of Kinetics and Catalysis, Institute of Chemical Physics,
USSR Academy of Science, Chernogolovka 142 432 (USSR)

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Abstract

Spin–lattice and spin–spin relaxation times of paramagnetic centres in initial and partly
oriented trans-polyacetylene have been measured by a saturation method at 2 mm
waveband EPR in the 90–300 K temperature range. Temperature dependences of the
intrachain diffusion and interchain hopping rates of the paramagnetic centres in the latter
samples are evaluated. Spin dynamics in the oriented sample has been shown to depend
on its orientation in a magnetic field and is in good agreement with Kivelson’s theory
of charge transport in trans-polyacetylene via intersoliton electron hopping. Temperature
evaluation of the neutral soliton width has been investigated.

Introduction

trans-Polyacetylene (trans-(CH)$_x$) is the simplest linear conjugated system
with a doubly degenerate ground state on bond alternation leading to the
formation of the charge-neutral topological kink, a soliton, with $\sim 6m_e$ effective
mass and spin $\frac{1}{2}$ [1]. According to the alternative Maki [2] and Wada and
Schrieffer [3] approaches, the soliton in trans-(CH)$_x$ is transferred along the
separate chain with a quasi one-dimensional (1-D) diffusion rate of $\nu_{1D} \sim 10^{14}$
s$^{-1}$ at room temperature and with $T^{-0.5}$ and $T^{2.0}$ temperature dependences,
respectively. However, in real polymer systems soliton hopping between
chains with frequency $\nu_{3D}$ occurs besides 1-D motion. In order to clarify
electron spin dynamics in trans-(CH)$_x$ the dynamic proton nuclear polarization
and the $\nu_e^{-0.5}$ resonant frequency dependence of $^1$H NMR $T_1$ [4], the above-
mentioned frequency dependence of the narrowing via the spin diffusion
linewidth at low operation fields (5–450 MHz) [5] and X-band EPR [6],
5–450 MHz EPR $T_1$ [7] and the $T_M$ at X-band EPR [8] were studied with
a variety of conclusions.

The 1-D diffusion rate in chaotically oriented [4, 6, 7, 9–11] and partly
oriented [12] trans-(CH)$_x$ samples by both EPR and $^1$H NMR methods was
determined to be equal to $\nu_{1D} \sim 10^{11} - 10^{14}$ s$^{-1}$ at room temperature and to
have a $T^\alpha (\alpha = 4.5 - 1.5)$ temperature dependence. Besides 1-D motion, the
soliton can hop between polymer chains with frequency $\nu_{3D}$. Thus, from the
analysis of the trans-(CH)$_x$ EPR line shape and frequency dependence of
$^1$H NMR and EPR $T_1$, the spin diffusion anisotropy $\nu_{1D}/\nu_{3D}$ was evaluated to be in the range $\approx 10^8$–$10^8$ [7, 9, 13] in this polymer.

Thus, the data concerning spin dynamics in pristine trans-(CH)$_x$ determined by complementary magnetic resonance methods are not compatible to date. In order to explain the above-mentioned discrepancy in experimental results, as well as between theoretical predictions and experimental data, the existence of both diffusive and $O_2$-trapped paramagnetic centres (PCs) and the possibility of the hopping of the former PCs were suggested [4].

In previous papers [14, 15] we have shown that the asymmetric 2 mm waveband EPR spectrum of the PCs in cis-(CH)$_x$ is attributed to the solitons localized in short polymer chains, thereby the EPR spectrum of trans-(CH)$_x$ is the superposition of the asymmetric and symmetric ones belonging to immobile and mobile solitons, respectively. Thus, cis–trans isomerization leads to the appearance of mobile solitons; however the portion of such PCs is only up to 5%. Electron spin–lattice ($T_1$) and spin–spin ($T_2$) relaxation times of both types of PCs were determined independently by a saturation method at 2 mm waveband EPR in a wide temperature interval. Recently, we have determined the $\nu_{1D} < 10^{12}$ s$^{-1}$ and $\nu_{1D}/\nu_{3D} < 10^3$ values at room temperature for neutral soliton dynamics in trans-(CH)$_x$ [16]. It has been shown that the $T^{-2.4}$ temperature dependence of the former value differs from those predicted theoretically [2, 3] as well as from those deduced from $^1$H NMR $T_1$, EPR $T_1$ and EPR linewidth analysis [4, 8, 9]. In addition, it has been shown that our experimental results concerning spin dynamics in trans-(CH)$_x$ may be explained even better within the intersoliton isoenergetic electron hopping formalism proposed by Kivelson [17].

In this report we discuss the anisotropy of soliton dynamics and its temperature dependence in partly oriented trans-(CH)$_x$ in the temperature range 90–300 K. In terms of the 1-D diffusion of neutral solitons we show clearly that field-dependent spin dynamics in partly oriented trans-(CH)$_x$ may be explained within the above-mentioned Kivelson formalism. Finally, we show the temperature evaluation of the neutral soliton width.

**Experimental**

cis-(CH)$_x$ film of 200 µm thickness was synthesized by the usual Shirakawa method in the presence of a Ziegler–Natta catalyst [18]. One portion of the sample was thermally transferred to the trans-isomer in the evacuated quartz tube which was placed in an oil bath at 450 K for several minutes. Another part of the film was isomerized after mechanical stretching up to approximately 50%.

All EPR experiments were performed on an EPR5-01 spectrometer [19] with a cavity, operated in the H$_{011}$ mode. Operation was made in the 2 mm waveband ($\nu_e=140$ GHz), with 100 kHz field modulation for phase-lock detection. The capillaries together with the samples occupying the axis of the cavity were attached to one of the cavity plungers and rotated together with it. EPR spectra were recorded for dispersion ($\chi'$) and absorption ($\chi''$)
signals. For this purpose, as well as to account for detector nonlinearities, the single crystal (DBTTF)$_2$PtBr$_4$ lateral standard was used. The total spin concentration in the initial and stretch-oriented trans-(CH)$_x$ samples was determined to be 200 ppm. $T_1$ and $T_2$ values of these samples were measured using the saturation method at 90–300 K.

Results and discussion

Signals from PCs, namely, sp$^3$ and immobile solitons, exhibit at room temperature weakly axial-symmetric spectra with $g_L = 2.002\ 83$, $g_B = 2.002\ 36$ and peak-to-peak linewidths $\Delta H_{pp}^{in} = 12.3$ G for the initial and $\Delta H_{pp}^{str} = 14.5$ G for the stretch-oriented cis-(CH)$_x$ samples. For the latter, the $\Delta H_{pp}^{str}$ value as well as other magnetic parameters remain invariant under sample rotation. For chaotic cis-(CH)$_x$ relaxation times were $T_1 = 3.2T^{-2.0}$ s and $T_2 = 9.1 \times 10^{-3}T^{0.9}$ s. The values for stretched cis-(CH)$_x$ were $T_1 = 4.3 \times 10^{-2}T^{-1.2}$ s and $T_2 = 3.8 \times 10^{-8}T^{0.6}$ s, which weakly change under sample rotation. Here $T$ is the absolute temperature.

The cis–trans isomerization leads to increase in frequency exchange between the spins via soliton motion and to decrease in variance of the local hyperfine fluctuating frequency of the spin packets $\langle \Delta \Omega \rangle$ [14]. This causes narrowing of the linewidth of chaotic trans-(CH)$_x$ up to approximately 7.3 G at 300 K. This value for stretch-oriented trans-(CH)$_x$ varies monotonically under rotation from 6.0 to 6.8 G at room temperature. The EPR spectrum for both trans-(CH)$_x$ samples is the overlapping of the line of the localized solitons with the above-indicated width and a narrower one with $\Delta H_{pp}^s = 3.0$ G and averaged via spin motion $\langle g \rangle = 2.002\ 69$ attributed to mobile solitons [14].

Figure 1 shows the results for temperature evaluation of the $T_1$ (a) and $T_2$ (b) values for the initial (curve 3) and stretch-oriented trans-(CH)$_x$ samples. Here $\psi$ is the angle between the external magnetic field and the stretching direction. $T_1(T)$ and $T_2(T)$ dependences of chaotic trans-(CH)$_x$ have no sensitivity to angle $\psi$. Indeed as one can clearly see from this Figure these values in the case of oriented trans-(CH)$_x$ are functions changing with $\psi$. This fact may be explained by the motion hindering of part of the solitons.

In order to explain our experimental results, we consider the intrachain 1-D diffusive motion of the delocalized PCs with rate $\nu_{1D}$ within the restrictions of the 1-D model and its cutoff by 3-D Lorentzian hopping between chains with frequency $\nu_{3D}$. In this case the probability for the fluctuations of the both types of spins may be written as [20]

$$P = P_{1D}P_{3D}$$

$$= (1 + 4 \pi \nu_{1D} |t|)^{-0.5} \exp \left[ -\frac{(r-r_0)^2}{4 \nu_{1D}^2 t} \right] \exp(-2 \pi \nu_{3D} t)$$

where $\nu_{1D} = \nu_{1D} N^{-2}$ is the diffusion rate of a soliton of half-width $Nc$, $c$ is the lattice constant and $(r-r_0)$ is the change in spin position at time $t$. 

Fig. 1. Temperature dependences of spin–lattice $T_1$ (a) and spin–spin $T_2$ (b) relaxation times for initial trans-(CH)$_n$ (curve 3) and trans-(CH)$_n$ oriented by the stretching direction relative to the external magnetic field with angle $\psi=90^\circ$ (curve 1), $60^\circ$ (curve 2), $30^\circ$ (curve 4) and $0^\circ$ (curve 5).
This equation becomes independent of variable \( r \) if the approximation \( \nu'_{1D} > \nu_e > \nu'_{3D} \) is assumed. For the Fourier fluctuation power spectrum of the 1-D spin motion, \( \varphi(\nu) \), one obtains [21]

\[
\begin{align*}
\varphi(\nu) &= (4\pi \nu'_{1D} \nu_e)^{-0.5} \quad \text{if} \ \nu_e \to \infty \quad (2a) \\
\varphi(\nu) &= (4\pi \nu'_{3D} \nu_e)^{-0.5} \quad \text{if} \ \nu_e \to 0 \quad (2b)
\end{align*}
\]

In trans-(CH)\(_x\) electron relaxation times, \( T_1 \) and \( T_2 \), are determined mainly by dipole interaction between the mobile and localized spins through 1-D diffusive motion of the former ones and, to a certain extent, by hyperfine interaction between the electron and nuclei spins. For the spin–spin dipole modulation these values are expressed [20]

\[
\begin{align*}
T_{1}^{-1} &= \frac{3}{2} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma_e^2 \hbar^2 S (S + 1) \left[ J_1(\nu) + J_2(2\nu) \right] \quad (3a) \\
T_{2}^{-1} &= \frac{3}{8} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma_e^2 \hbar^2 S (S + 1) \left[ J_0(0) + 10J_1(\nu) + J_2(2\nu) \right] \quad (3b)
\end{align*}
\]

where \( \gamma_e \) and \( S \) are the hydromagnetic ratio and the spin of the electron, respectively, \( J_i(\nu) = n \varphi(\nu) P_i \) is the spectral density of the soliton motion, \( n = n_1 + n_2/\sqrt{2} \) is the total concentration of the trapped \( (n_1) \) and mobile \( (n_2) \) solitons per \( C \) atom, \( P_i = \sum p_i \cos \theta_i \gamma_2 \) is the random interaction function modulated by 1-D motion of the soliton and \( \theta \) is the angle between vectors \( r_1 \) and \( r_2 \).

In the case of the partly oriented trans-(CH)\(_x\), the equations above consist of two parts and can be written as

\[
\begin{align*}
T_{1}^{-1} &= A \langle \omega^2 \rangle \left[ \varphi(\nu)P_1 + \varphi(2\nu)P_2 \right] + (1 - A) \langle \Delta \omega^2 \rangle \left[ \varphi(\nu)P'_1 + \varphi(2\nu)P'_2 \right] \quad (4a) \\
T_{2}^{-1} &= \frac{A}{4} \langle \omega^2 \rangle \left[ \varphi(0)P_0 + 10\varphi(\nu)P_1 + \varphi(2\nu)P_2 \right] \\
&\quad + \frac{1 - A}{4} \langle \Delta \omega^2 \rangle \left[ \varphi(0)P'_0 + 10\varphi(\nu)P'_1 + \varphi(2\nu)P'_2 \right] \quad (4b)
\end{align*}
\]

where \( A \) is the degree of orientation (here \( P_1 \) and \( P'_1 \) designate the oriented and chaotic chains of trans-(CH)\(_x\), respectively) and \( \langle \omega^2 \rangle = \frac{3}{4} \frac{\mu_0}{4\pi} \gamma_e^2 \hbar^2 S (S + 1)n \).

Using \( P_0 = 4.3 \times 10^{58} \sin^4 \psi, \quad P_1 = 4.8 \times 10^{57}(1 - \cos^4 \psi), \quad P_2 = 4.8 \times 10^{57}(1 + 6\cos^2 \psi + \cos^4 \psi), \quad P'_0 = 1.6 \times 10^{58}, \quad P'_1 = 2.7 \times 10^{57}, \quad P'_2 = 1.1 \times 10^{58} \) \( \text{m}^{-6} \) [7, 12], we can simplify eqns. (4a) and (4b) for stretch-oriented trans-(CH)\(_x\):

\[
T_1^{-1} = \frac{5.0 \times 10^9 n}{(\nu'_{1D} \nu_e)^{1/2}} \left[ 6.8 - A(1.1 - 14.0 \cos^2 \psi + \cos^4 \psi) \right] \quad (5a)
\]
\[ T_2^{-1} = \frac{1.4 \times 10^{30} n}{(\nu_{1D}^{'})^{1/2}} \left[ \frac{1 - A + A \sin \psi}{(\nu_{3D}^{'})^{1/2}} + \frac{2.1 + A(1.1 + 1.3 \cos^2 \psi - 2.9 \cos^4 \psi)}{(\nu_{c})^{1/2}} \right] \]  

(5b)

Figure 2 displays the temperature dependences of rates \( \nu_{1D}^{' \, a} \) and \( \nu_{3D}^{' \, b} \) for chaotic \((A = 0)\) and stretch-oriented \((A = 0.07)\) \(\text{trans-}(\text{CH})_x\) samples calculated according to eqns. (5a) and (5b) and using the data presented in Fig. 1. Indeed, the Figure shows that both 1-D diffusive and 3-D hopping rates of the soliton have a sensitivity to the orientation of the latter sample in a external magnetic field due to 1-D soliton motion. It can be seen from the Figure that the phase of the \( \nu_{1D}^{' \, a} \) for the oriented sample is opposite to that of \( \nu_{3D}^{' \, b} \). Since the orientation of the c-axis in chaotic \( \text{trans-}(\text{CH})_x \) remains arbitrary, these values are averaged over angle \( \psi \). Moreover, the averaged \( \nu_{1D}^{' \, a} \) value is well described by equation \( \langle \nu_{1D}^{' \, a} \rangle = \nu_{1D}^{' \, a} \sin^2 \psi + \nu_{1D}^{' \, a} \cos^2 \psi \), where \( \nu_{1D}^{' \, a} \) and \( \nu_{1D}^{' \, b} \) are the extremes of the \( \nu_{1D}^{' \, a}(\psi) \) function. Note that a similar functional form describes an effective spin diffusion in low dimensional systems [22]. Thus, the \( \nu_{1D}^{' \, a} < \nu_{1D}^{' \, b} \) inequality displays spin delocalization over a soliton. Taking into account that the soliton is limited in its hopping by the interchain lattice constant and that the value of the average square of its diffusive hopping step along the c-axis is \( \langle N^2 c^2 \rangle \), we can determine the soliton width as

\[ N^2 = \nu_{1D}^{' \, a}/\nu_{1D}^{' \, b} \]  

(6)

Figure 3 shows the temperature evolution of the soliton width calculated from the data of Fig. 2(a) using eqn. (6). \( 2N_{300K} = 14.8 \) is in good agreement with that theoretically predicted by Su et al. [1] and that derived from magnetic resonance experiments [4, 23]. Extrapolation to the region \( T < 90 \) K allows us to determine the temperature region (~60 K) where the soliton width starts to increase.

Note that at such temperatures the break in the experimental \( \nu_{1D}(T) \) function as well as the difference in the experimental results from theory [4, 8] occur.

Finally we can determine the spin dynamics anisotropy \( \nu_{1D}^{' \, a} N^2/\nu_{3D}^{' \, b} \) in \( \text{trans-}(\text{CH})_x \) samples under study. This value was determined to be nearly temperature independent and equal to 30 for chaotic and to 45 for stretch-oriented \( \text{trans-}(\text{CH})_x \) samples.

The data of Fig. 2 indicate that the maximum value of \( \nu_{1D} \) does not exceed \( 7 \times 10^{12} \text{ s}^{-1} \) at room temperature. This value is two orders of magnitude lower than that theoretically predicted and derived from magnetic resonance measurements. As in an earlier study [16] our present experimental results concerning spin dynamics in \( \text{trans-}(\text{CH})_x \) can be more acceptably explained in terms of the phonon-assisted intersoliton electron hopping model proposed by Kivelson [17]. According to this model, the probability of such an electron transition depends on the temperature as \( W(T) \sim T^{-(\beta+1)} \) (or \( \sim T^\beta \)) with RF field presence (or absence). At sufficiently high RF fields the total conductivity
Fig. 2. Temperature dependences of intrachain diffusive $\nu_1$ (a) and interchain hopping $\nu_2$ (b) rates for initial (curve 3) and stretch-oriented trans-(CH)$_x$ with orientation degree of 0.07 and oriented by the polymer $c$-axis relative to the external magnetic field by $\psi=90^\circ$ (curve 1), $60^\circ$ (curve 2), $30^\circ$ (curve 4) and $0^\circ$ (curve 5). A.c. conductivities (dashed lines) calculated using eqn. (7) (see the text) with $K'=9.3 \times 10^{-17}$ S cm$^{-1}$ s K, $\beta=8.0$ for the initial sample (curve 3) and $K'=6.3 \times 10^{-16}$ S cm$^{-1}$ s K, $\beta=11.6$ for the stretched sample (curve 5) vs. temperature are also presented.
of trans-(CH)$_x$ is determined by the a.c. term, namely [24]

$$\sigma_{AC}(T) = K' \nu_c T^{-\frac{1}{2}} \left[ \ln(\nu_c BT^{-\beta-1}) \right]^4$$

(7)

where $K'$ and $B$ are constants and $\beta \approx 10$. Note that a similar functional form was used by Kivelson and Epstein to explain the $\sigma(\nu, T)$ dependence for trans-(CH)$_x$ [24].

Temperature dependences of a.c. ($\nu_c = 1.4 \times 10^{11}$ s$^{-1}$) conductivity calculated by means of eqn. (7) for initial ($K' = 9.3 \times 10^{-17}$ S cm$^{-1}$ s K, $\beta = 8.0$) and 0°-oriented ($K' = 6.3 \times 10^{-16}$ S cm$^{-1}$ s K, $\beta = 11.6$) trans-(CH)$_x$ samples are presented in Fig. 2(a). In fact, the Figure shows the $\nu'_{1D}(T)$ and $\sigma_{AC}(T)$ dependences for both the initial and oriented trans-(CH)$_x$ samples to be comparable. Moreover, from the room temperature $\sigma_{AC} \approx 4 \times 10^{-2}$ S cm$^{-1}$ (see Fig. 2(a)) and $\sigma_{DC} \approx 7 \times 10^{-5}$ S cm$^{-1}$ [24], the ratio $\sigma_{AC}/\sigma_{DC} \approx 10^4$ is obtained. This value is also in good agreement with Kivelson theory. Thus, the spin dynamics in the samples under study may be undoubtedly better explained in terms of isoenergetic intersoliton electron hopping.

Hence, the charge transport process in pristine trans-(CH)$_x$ may be described in the following manner. In cis-(CH)$_x$ the solitons trapped in short chains are the dominated spins. The possibility of electron intersoliton hopping is very small, hence $\sigma_{DC} \approx 10^{-13}$ S cm$^{-1}$. The length of the $\pi$-conjugated chains increases in (CH)$_x$ during its cis–trans isomerization, and a mobility of about 5% solitons appears. Thus the spin mobility causes the drastic increase in probability of the tunnelling electron hopping between solitons in trans-(CH)$_x$ and thus in its conductivity up to $\sigma_{DC} \approx 10^{-5}$ S cm$^{-1}$. It should be stressed that because the solitons play an auxiliary role, the described charge transport mechanism may be correct, however, for pristine and lightly
doped trans-(CH)$_x$ only. At higher doping levels the electron intersoliton hopping is unlikely to be the dominant charge transport mechanism and the conductivity is determined mainly by other parallel processes.

Conclusions

Millimetric EPR spectroscopy undoubtedly gives the possibility of determining the nature of PCs, their relaxation parameters and hence dynamics of the neutral soliton in trans-(CH)$_x$. Despite the discrepancy between our experimental results and soliton theory and the fact that the solitons are not the dominant type of defects, we have nevertheless also shown the reality of the soliton mobility as the cause of drastic change in the dynamics of charge carriers in trans-(CH)$_x$.

We have discussed the soliton dynamics and its dimensionality in a typical trans-(CH)$_x$ sample. However, the concentration, relaxation and other (i.e., π-conjugated average length) parameters of trans-(CH)$_x$ films of different thickness, and history etc., differ from sample to sample [15]. Thus, these parameters should be determined independently in each case.

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References