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

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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 ν_{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 ^1H 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 ^1H 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^α ($\alpha = 4.5 - -1.5$) temperature dependence. Besides 1-D motion, the soliton can hop between polymer chains with frequency ν_{3D}. Thus, from the analysis of the *trans*-$(CH)_x$ EPR line shape and frequency dependence of

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^{1}H NMR and EPR T_1, the spin diffusion anisotropy ν_{1D}/ν_{3D} was evaluated to be in the range $\sim 10^5$–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 $\nu_{1D} \leqslant 10^{12}$ s^{-1} and $\nu_{1D}/\nu_{3D} \leqslant 10^3$ 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 (χ') and absorption (χ'')

signals. For this purpose, as well as to account for detector nonlinearities, the single crystal $(DBTTF)_3PtBr_6$ 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 $g_\perp = 2.002\,83, g_\parallel = 2.002\,36$ 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 ΔH_{pp}^{str} value as well as other magnetic parameters remain invariable under sample rotation. For chaotic *cis*-$(CH)_x$ relaxation times were $T_1 = 3.2T^{-2.0}$ s and $T_2 = 9.1 \times 10^{-9} T^{0.9}$ 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 $\langle \Delta\Omega_i \rangle$ [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].

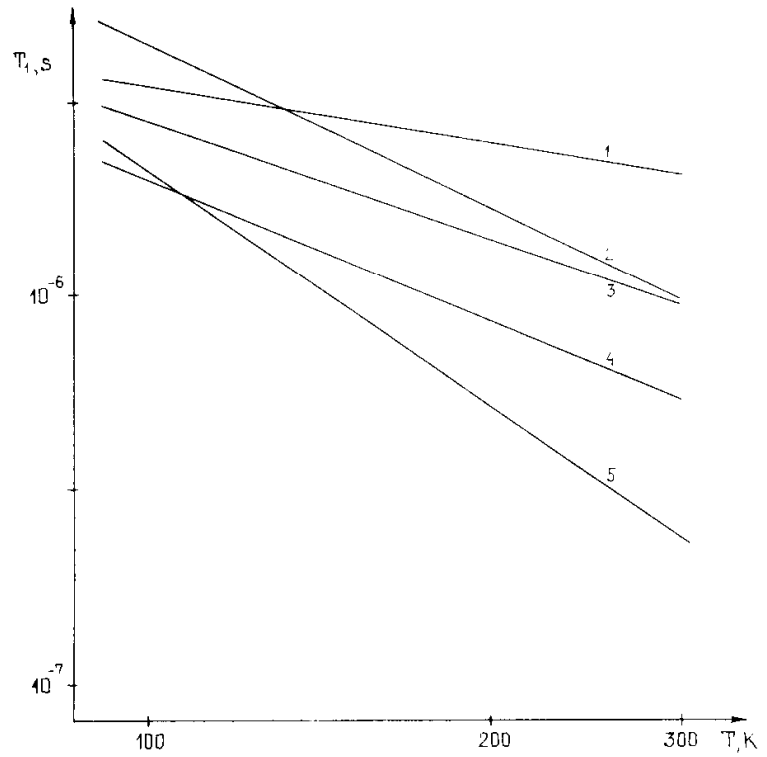
Figure 1 shows the results for temperature evaluation of the T_1 (a) and T_2 (b) values for the initial (curve 3) and stretch-oriented *trans*-$(CH)_x$ samples. Here ψ is the angle between the external magnetic field and the stretching direction. $T_1(T)$ and $T_2(T)$ dependences of chaotic *trans*-$(CH)_x$ have no sensitivity to angle ψ. Indeed as one can clearly see from this Figure these values in the case of oriented *trans*-$(CH)_x$ are functions changing with ψ. 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 ν_{1D} within the restrictions of the 1-D model and its cutoff by 3-D Lorentzian hopping between chains with frequency ν_{3D}. In this case the probability for the fluctuations of the both types of spins may be written as [20]

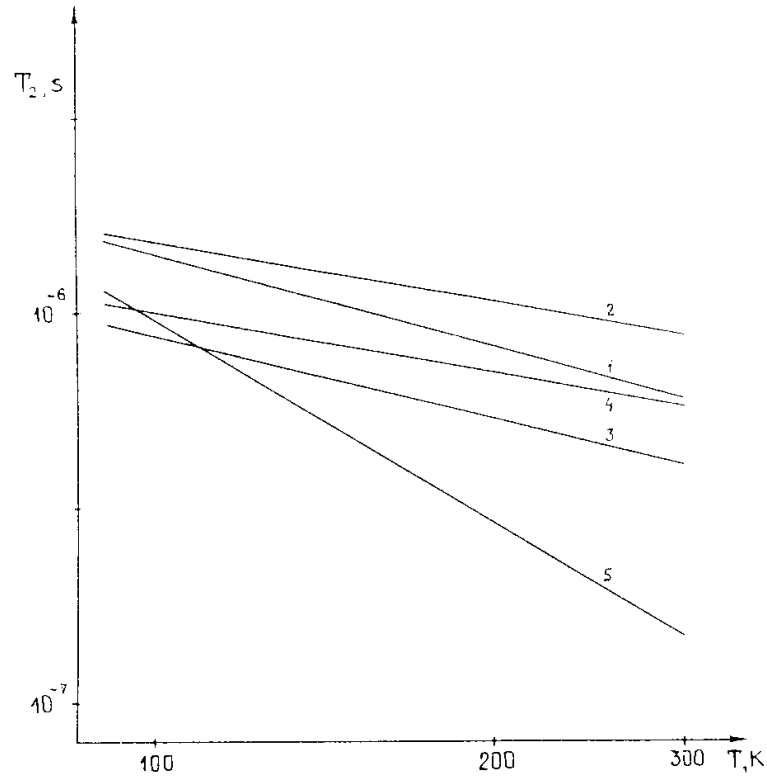
$$P = P_{1D} P_{3D}$$

$$= (1 + 4\pi\nu'_{1D}|t|)^{-0.5} \exp\left[- \frac{(r - r_0)^2}{4\nu'_{1D} t} \right] \exp(-2\pi\nu_{3D} t) \qquad (1)$$

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.



(a)



(b)

Fig. 1. Temperature dependences of spin–lattice T_1 (a) and spin–spin T_2 (b) relaxation times for initial *trans*-$(CH)_x$ (curve 3) and *trans*-$(CH)_x$ oriented by the stretching direction relative to the external magnetic field with angle $\psi = 90°$ (curve 1), 60° (curve 2), 30° (curve 4) and 0° (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]

$$\varphi(\nu) = (4\pi\nu'_{1D}\nu_e)^{-0.5} \qquad \text{if } \nu_e \to \infty \tag{2a}$$

$$\varphi(\nu) = (4\pi\nu'_{3D}\nu_e)^{-0.5} \qquad \text{if } \nu_e \to 0 \tag{2b}$$

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]

$$T_1^{-1} = \frac{3}{2}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_e^4 \hbar^2 S(S+1)[J_1(\nu) + J_2(2\nu)] \tag{3a}$$

$$T_2^{-1} = \frac{3}{8}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_e^4 \hbar^2 S(S+1)[J_0(0) + 10J_1(\nu) + J_2(2\nu)] \tag{3b}$$

where γ_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, $P_i = \Sigma p_i \cos \vartheta_{1,2}/r_1^3 r_2^3$ is the random interaction function modulated by 1-D motion of the soliton and ϑ is the angle between vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.

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

$$T_1^{-1} = A\langle\omega^2\rangle[\varphi(\nu)P_1 + \varphi(2\nu)P_2] + (1-A)\langle\Delta\omega^2\rangle[\varphi(\nu)P'_1 + \varphi(2\nu)P'_2] \tag{4a}$$

$$T_2^{-1} = \frac{A}{4}\langle\omega^2\rangle[\varphi(0)P_0 + 10\varphi(\nu)P_1 + \varphi(2\nu)P_2] + \frac{1-A}{4}\langle\Delta\omega^2\rangle[\varphi(0)P'_0 + 10\varphi(\nu)P'_1 + \varphi(2\nu)P'_2] \tag{4b}$$

where A is the degree of orientation (here P_i and P'_i designate the oriented and chaotic chains of *trans*-$(CH)_x$, respectively) and $\langle\omega^2\rangle = \frac{3}{2}[\mu_0/4\pi]^2\gamma^4\hbar^2 S(S+1)n$.

Using $P_0 = 4.3\times10^{58}\ \sin^4\psi$, $P_1 = 4.8\times10^{57}(1-\cos^4\psi)$, $P_2 = 4.8\times10^{57}(1+6\cos^2\psi+\cos^4\psi)$, $P'_0 = 1.6\times10^{58}$, $P'_1 = 2.7\times10^{57}$, $P'_2 = 1.1\times10^{58}$ (m^{-6}) [7, 12], we can simplify eqns. (4a) and (4b) for stretch-oriented *trans*-$(CH)_x$:

$$T_1^{-1} = \frac{5.0\times10^9 n}{(\nu'_{1D}\nu_e)^{1/2}}[6.8 - A(1.1 - 14.0\cos^2\psi + \cos^4\psi)] \tag{5a}$$

$$T_2^{-1} = \frac{1.4\times10^{20}n}{(\nu'_{1D})^{1/2}}\left[\frac{1-A+A\sin\psi}{(\nu'_{3D})^{1/2}} + \frac{2.1+A(1.1+1.3\cos^2\psi-2.9\cos^4\psi)}{(\nu_e)^{1/2}}\right] \tag{5b}$$

Figure 2 displays the temperature dependences of rates ν'_{1D} (a) and ν'_{3D} (b) for chaotic ($A=0$) and stretch-oriented ($A=0.07$) *trans*-$(CH)_x$ 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 ν'_{1D} for the oriented sample is opposite to that of ν'_{3D}. Since the orientation of the c-axis in chaotic *trans*-$(CH)_x$ remains arbitrary, these values are averaged over angle ψ. Moreover, the averaged ν'_{1D} value is well described by equation $\langle\nu'_{1D}\rangle = \nu^{\parallel}_{1D}\sin^2\psi + \nu^{\perp}_{1D}\cos^2\psi$, where $\nu^{\parallel}_{1D}$ and $\nu^{\perp}_{1D}$ are the extremes of the $\nu'_{1D}(\psi)$ function. Note that a similar functional form describes an effective spin diffusion in low dimensional systems [22]. Thus, the $\nu^{\parallel}_{1D} \ll \nu^{\perp}_{1D}$ 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 $\langle N^2c^2\rangle$, we can determine the soliton width as

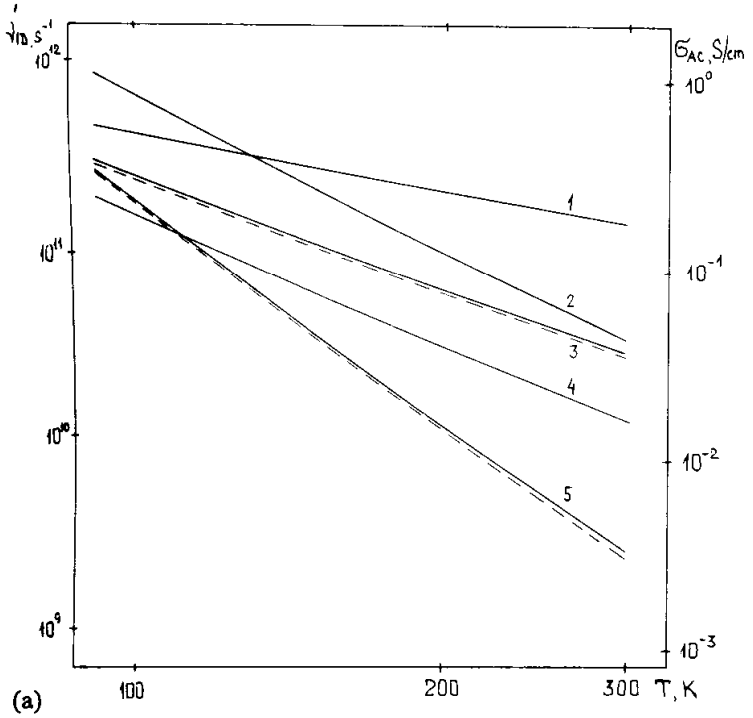
$$N^2 = \nu^{\perp}_{1D}/\nu^{\parallel}_{1D} \tag{6}$$

Figure 3 shows the temperature evolution of the soliton width calculated from the data of Fig. 2(a) using eqn. (6). $2N_{300\,K} = 14.8$ 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 $\nu'_{1D}N^2/\nu'_{3D}$ in *trans*-$(CH)_x$ samples under study. This value was determined to be nearly temperature independent and equal to 30 for chaotic and to 45 for stretch-oriented *trans*-$(CH)_x$ samples.

The data of Fig. 2 indicate that the maximum value of ν_{1D} does not exceed $7\times10^{12}\,s^{-1}$ 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 *trans*-$(CH)_x$ can be more acceptably explained in terms of the phonon-assisted intersoliton electron hopping 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



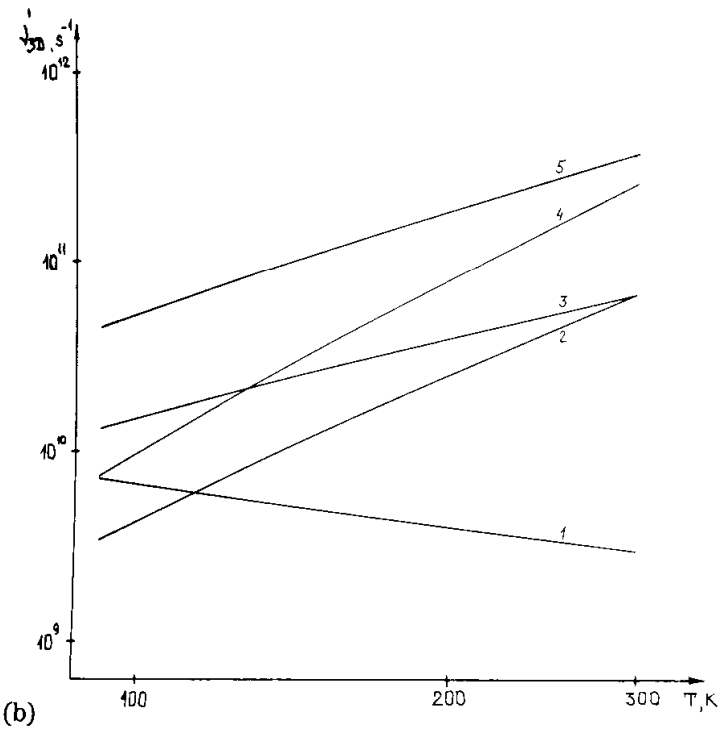


Fig. 2. Temperature dependences of intrachain diffusive ν'_{1D} (a) and interchain hopping ν'_{3D} (b) rates for initial (curve 3) and stretch-oriented *trans*-$(CH)_x$ with orientation degree of 0.07 and oriented by the polymer *c*-axis relative to the external magnetic field by $\psi = 90°$ (curve 1), 60° (curve 2), 30° (curve 4) and 0° (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.

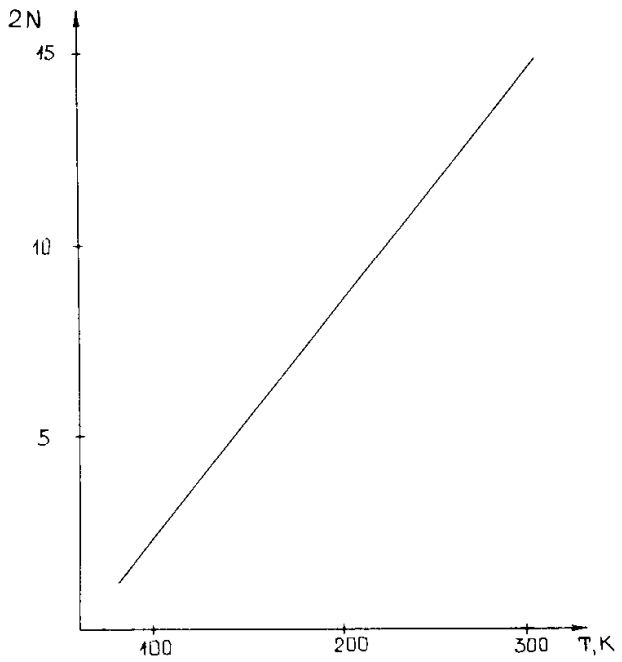


Fig. 3. Temperature dependence of the effective width $2N$ or the neutral soliton in *trans*-$(CH)_x$.

of *trans*-$(CH)_x$ is determined by the a.c. term, namely [24]

$$\sigma_{AC}(T) = K' \nu_e T^{-1} [\ln(\nu_e B T^{-\beta-1})]^4 \tag{7}$$

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. ($\nu_e = 1.4 \times 10^{11}$ 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 $\sigma_{DC} \approx 7 \times 10^{-6}$ S cm^{-1} [24], the ratio $\sigma_{AC}/\sigma_{DC} \sim 10^4$ 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 π-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 $\sigma_{DC} \sim 10^{-5}$ 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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