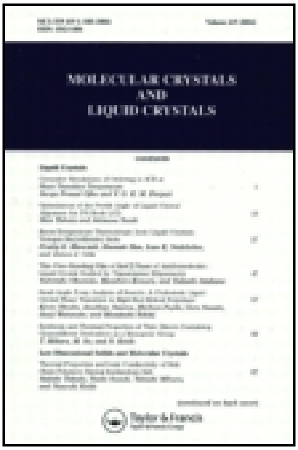

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Electron Spin Echo Study on Polyacetylene

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ELECTRON SPIN ECHO STUDY ON POLYACETYLENE

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Abstract Electron Spin Echo (ESE) measurements on stretch-oriented films of polyacetylene are reported. The electron dipole-dipole interaction is estimated. Effect of oxygen on the phase memory decay has been studied.

ESE is one of various techniques in magnetic resonance which have been applied to study the motion of spin in polyacetylene.[1-2] We present the results of ESE (X-band) measurements on stretch-oriented films. In the $\parallel$ direction, the molecular chains are oriented (chain allignment parameter $\langle\cos^2\alpha\rangle \sim 0.8$) through the allignment of the fibrils along the stretched direction. In the $\perp$ direction, the summed spectra of the random orientations perpendicular to the chains (or spectrum averaged in plane perpendicular to the chains) should result.

DIPOLE-DIPOLE INTERACTION AT LOW TEMPERATURE

In both trans-$(CH)_x$ and trans-$(CD)_x$, instantaneous spin diffusion phenomenon was observed below $\sim$200K. The dipole-dipole interaction $(\Delta H_{1/2})_{dip}$ was determined by measuring the time constant b of the echo envelope decay as a function of the tilting angle θ of the

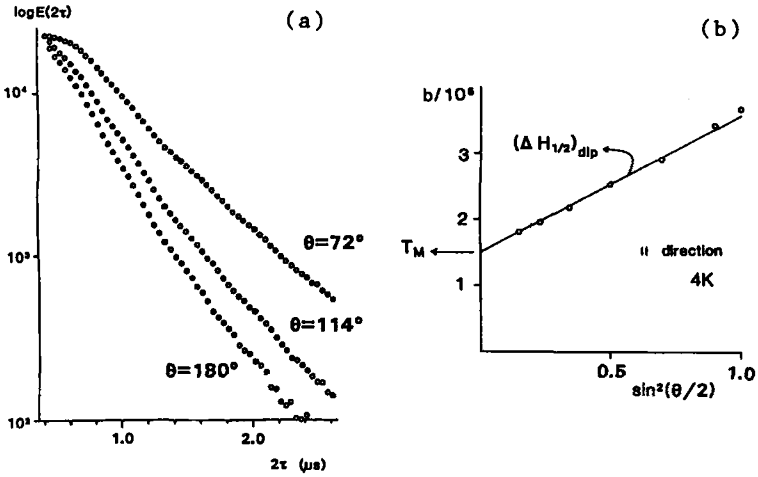

FIGURE 1 Instantaneous spin diffusion in trans-$(CD)_x$
(a) Echo envelope decay for various values of θ
(b) Linear relationship between b and $\sin^2(\theta/2)$

second pulse.[3] In trans-$(CD)_x$, $(\Delta H_{1/2})_{dip}$ is obtained as 1.2G at 4K, which decreases as temperature increases (0G at ~200K). The anisotropy of $(\Delta H_{1/2})_{dip}$ for ∥ and ⊥ directions of applied field to the chains is small, under ~200ns minimum pulse separation used. Based upon the observed $(\Delta H_{1/2})_{dip}$ and a point-dipole approximation, the average distance between the spins is estimated to be 34Å. The estimated spin concentration of one per ~2500 carbon atoms gives us the average distance of 36Å. Therefore, in trans sample at low temperature, there are two possibilities, the spins are distributed uniformly, or those spins with the smaller interspin distance might not be detected under the limited pulse strength and the limited minimum pulse separation used. In cis-$(CD)_x$, $(\Delta H_{1/2})_{dip}$ (at 115K, 0.49G and 0.54G for ∥ and ⊥ , respectively) decreases slightly as temperature increases.

DIPOLAR ANISOTROPY AT HIGH TEMPERATURE

At the higher temperature above 300K of motionally narrowed range ($\Delta H_{1/2}=(\gamma T_M)^{-1}$), the anisotropy of T_M is different between trans-$(CH)_x$ and trans-$(CD)_x$; $(T_M)_{\parallel} < (T_M)_{\perp}$ for trans-$(CH)_x$ and $(T_M)_{\parallel} > (T_M)_{\perp}$ for trans-$(CD)_x$. The hyperfine anisotropy[4] dominates in trans-$(CH)_x$ wheras dipolar anisotropy dominates in trans-$(CD)_x$. Since the hyperfine contribution to second moment $(\Delta H^2)_{hfX}$ is proportional to $g_{nX}^2 I_X(I_X+1)$ (X=H,D), the dipolar contribution can be separated by using a simple model of motional narrowing:

$$(\gamma T_M)^{-1} = (\Delta H^2)_{hf}\cdot\tau_c + (\Delta H^2)_{dip}\cdot\tau_c$$

where $(\Delta H^2)_{dip}$ and τ_c are common for both trans-$(CH)_x$ and trans-$(CD)_x$. We take $(\Delta H^2)_{hf}$ from the observed cis-$(CH)_x$ spectrum of Gaussian lineshape at 48K.

TABLE I Effective dipolar field and τ_c

		300K	324K	344K	363K	383K
$\Delta H_{1/2}$ (G)						
trans-$(CH)_x$	$\parallel$	0.612	0.521	0.451	0.404	0.349
	$\perp$	0.472	0.401	0.349	0.313	0.276
trans-$(CD)_x$	$\parallel$	0.170	0.153	0.141	0.127	0.120
	$\perp$	0.220	0.197	0.177	0.160	0.141
$\sqrt{(\Delta H^2)_{dip}}$ (G)	$\parallel$	3.6	3.8	4.0	4.0	4.3
	$\perp$	4.5	4.7	4.9	5.0	5.0
τ_c (ns)		0.57	0.49	0.41	0.37	0.32

As the chain length has a distribution around 500 carbons,[5] the unpaired electron in trans sample is expected to be about one per 5 chains. The dipolar anisotropy is explained qualitatively as follows. If the spins are moving along nearby chains and are able to come close together, the dipole-dipole interaction is expected to be largest in the direction perpendicular to the chains. On the other hand, when the spins are far apart on nearby chains, the dipole-dipole interaction has the maximum value in the direction parallel to the chains. Discussions of the motion of spins based on the dipole-dipole interaction will be described elsewhere.

EFFECT OF OXYGEN

Around room temperature, the 2-pulse phase memory decay of trans-$(CH)_x$ is biexponential. The echo-detected ESR with various values of τ confirms that there are two species of spins, to be denoted here as mobile spins (short T_M, large concentration C_m) and fixed spins (long T_M, small concentration C_f). The inhomogeneous linewidth of the fixed spins is similar to that of cis spectrum. The linewidth of cw-ESR spectrum of Lorentzian lineshape corresponds to T_M of the mobile spins. The weak signal of the fixed spins underneath the strong signal of the mobile spins has not been separated by cw-ESR ($C_f/C_m \sim 0.003$ at 300K). The linewidth of the mobile spins, which is sensitive to oxygen contamination, has been ascribed to a rapid exchange between diffusive state and trapped state.[6] In case that we know the linewidth of the trapped state and the ratio between time spent in the trapped state and that in the diffusive state f_t/f_d, the intrinsic linewidth of the diffusive state free from the oxygen trapping centers can be estimated. After exposing to air (60min) followed by degassing, the ratio C_f/C_m increases and T_M of the mobile spins decreases. C_f/C_m decreases as temperature increases, while the ratio of C_f/C_m between the air-exposed and unexposed films is nearly independent of temperature ($\sim$2.1) in the high temperature range. By assuming that the ratio of f_t/f_d between the air-exposed and unexposed films should be equal to the ratio of C_f/C_m between the two, (i.e. at each temperature, the shallow trap concentration should increase when the deep trap concentration increases by air-exposure), and by using the linewidth of cis-

$(CH)_x$ for that of the trapped state, $\Delta H_{1/2}$ of the diffusive state is estimated to be, at 344K and 383K, respectively, 0.24G, 0.20G for $\parallel$ and 0.20G, 0.15G for $\perp$ direction of applied field.

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