

Localized electronic states in individual polyacetylene molecules

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Localized electronic states in individual polyene molecules in solution have been studied by ESR. A hysteresis has been found in the paramagnetic susceptibility. This hysteresis stems from the preservation of some of the stable localized spin states during *p*-type doping. The difference in the shapes of the ESR signals in the presence and absence of a polarizing voltage is analyzed.

The reason for the steady interest in one-dimensional conducting systems such as polyacetylene, $(\sim\text{CH}\sim)_n$, where $n \gg 1$, is the search for soliton-like states and quasi-particles with unusual spin and charge relations in this material. Much of the corresponding theoretical work has been carried out in the molecular-field approximation for an isolated polyene chain,¹⁻⁴ $(\sim\text{CH}\sim)_n$. The crystal field has been taken into account in a continuum model by Brazovskii.^{5,6} Most of the experimental work has been on amorphous or partially crystallized polyacetylene, whose macroscopic properties depend on the spatial packing of the chains. Our purpose in the present study was to learn about localized electronic states in individual polyene molecules $(\sim\text{CH}\sim)_n$ with $n \gg 100$. The only previous research on the optical properties of polyenes has been on individual molecules in solutions.⁷

A technique for producing crystalline polyacetylene at the interface between an inorganic phase and a polyvinylchloride solution has been described elsewhere.⁸ The process by which the crystals are formed here is a typical first-order phase transition in the concentration of the polyene molecules. There is accordingly a unique possibility for studying the properties of individual polyene molecules if the crystallization conditions do not hold, i.e., at concentrations below the critical value. This situation is arranged by using polyvinylchloride in very low concentrations to synthesize the polyacetylene solutions. Here we will discuss only the experiments in which the solvent in the synthesis was nitrobenzene; the critical concentrations in this case were $\sim 1.5\%$.

The working cell was a cylindrical capillary with Pt electrodes, used for doping the polyacetylene molecules at the interface by an electrochemical method. The electric field in the cell was directed along the axis of the capillary. The lower part of the cell was filled with an aqueous solution of KCl ($\sim 50\%$), while the upper part was filled with a solution of nitrobenzene and the individual polyene molecules. We studied the effect of the field on the "through" electrical conductivity of these solutions and on the number of paramagnetic centers, while varying the potential difference. The concentration of ESR centers was estimated from the magnitude of the ESR signals on an RE 1306 spectrometer with a wavelength $\lambda \sim 3$ cm by the standard procedure.⁹ In parallel, we measured the current-voltage characteristics of the solutions. The presence

of K^+ and Cl^- ions in the solution made it possible to carry out an n -type or p -type doping by simply changing the polarity of the applied voltage.

Let us examine the properties of individual polyene molecules when they are doped at the interface between an organic phase and an inorganic phase. We are primarily interested in the appearance of localized spin states and their relationship with the number of current carriers. In the original solution, their number is zero in the absence of a polarizing voltage. As the voltage is increased, with the positive potential being applied to the aqueous solution of KCl , an electrochemical reaction occurs at the interface, accompanied by the reduction of K^+ and the oxidation of the polyacetylene. This reaction leads to the generation of spin states. Figure 1 shows the number of spin states, N_s , as a function of the potential difference across the electrodes. We see that the spin states arise above a certain equilibrium potential $\varphi_{eq} \sim (-1.0) - (-1.2)$ V. Later, N_s reaches saturation at a potential difference $\sim 8-10$ V. A comparison of this curve with the current-voltage characteristic of the solution reveals that the regimes of the current flow through the cell are completely identical to the regimes of the buildup of spin states in the individual polyene molecules: There is a coincidence of the equilibrium potential and the diffusion-kinetics regime at a $8-10$ V (or the limiting-current regime). When the cell is overpolarized, the number of spin states remains nonzero even in the absence of a potential difference, while it is zero if the polarity is reversed. The apparent reason for this hysteresis in the paramagnetic susceptibility is that some of the stable localized spin states persist in the volume of the solution. Hence, we can draw another important conclusion: The spin states in individual polyene molecules are generated only by a p -type dopant, which in the case at hand is K^+ . The electrochemical reaction at the interface between the solutions in this case is $([\sim CH\sim]) + K^+ \rightarrow (\sim CH\sim)_n^- + K$. Actually, this reaction could lead to the formation of either a coupled spin-charge pair, i.e., a positive polaron, or a

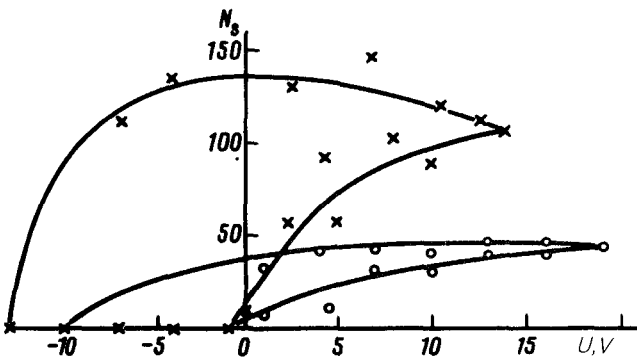


FIG. 1. The number of paramagnetic centers, N_s , and the paramagnetic susceptibility of the samples corresponding to N_s (i.e., $\chi \approx 2S/\pi\omega_0$, where S is the integral intensity of the resonant absorption, and ω_0 is the resonant frequency) versus the potential difference across the electrodes, $\varphi_A - \varphi_B$. These curves were recorded after a fourfold cycling.

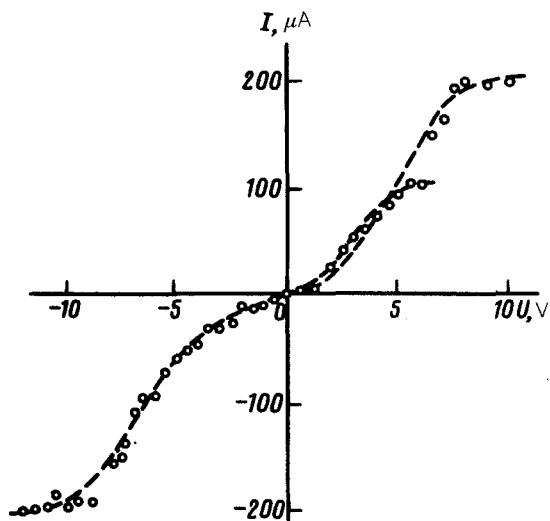


FIG. 2. Current-voltage characteristic of a solution of $(\sim\text{CH}\sim)_n^+$ molecules. The first plateau at $u > 0$ apparently corresponds to a limiting current of $(\sim\text{CH}\sim)_x^+$ ions, while the second corresponds to the conductivity due to K^+ and Cl^- ions.

soliton with a spin $S = 1/2$ and zero charge and also a positive soliton with $q = -e$ and $S = 0$ in the polyacetylene molecules. Just what happens can be found from the width of the ESR line: The observed lines have a width $\sim 1.6\text{--}2$ Oe (Fig. 3). Since the hyperfine structure is 23 Oe, because of the interaction with the proton for the spin of an immobile electron, we find an estimate of the extent of the delocalization of the spins: over $\sim 100\text{--}150$ nodes. Such values correspond to solitons with a spin $S = 1/2$ and a zero charge, since a positive polaron is a strictly localized state, which is localized by the confinement of π bonds.¹⁰

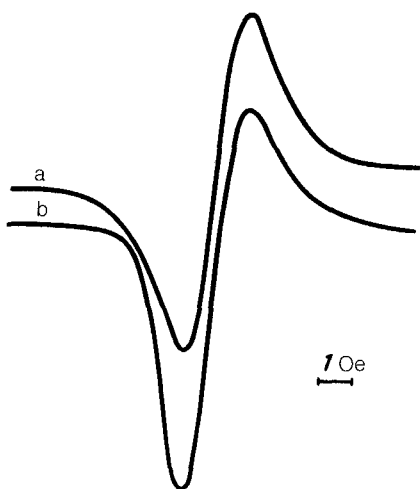


FIG. 3. Shape and width of the lines. a— $u = 15$ V; b— $u = 0$ V.

Note the difference between the ESR signals in the presence and absence of a polarizing voltage (Fig. 3). This difference stems from the appearance of an asymmetry of the signal, which can easily be attributed to a degeneracy of the fine structure of the lines for a strictly fixed orientation of the spins on the chain during the motion of the soliton. This conclusion is based on the following considerations. Conducting chains with a trans-isomer length of 100–150 atoms can be oriented well in an electric field, since the dielectric susceptibilities along the chain (ϵ_{\parallel}) and across it (ϵ_{\perp}) are different, with $\epsilon_{\parallel} \gg \epsilon_{\perp}$, $\epsilon_{\parallel} \gg 1$. Since the stabilizing moment varies as $\epsilon_{\parallel} E^2$, an induced nematic liquid-crystal phase with a degree of order $S \sim \epsilon_{\parallel} E^2$ appears.¹¹ The shape of the ESR signal is then determined exclusively by the value of the g -factor perpendicular to the axis of the chain, g_{\perp} . At $g_{\parallel} \sim 0$, and in the absence of an orienting electric field, there is an averaging of the absorption at fields $H \gg H_0$. The result is an asymmetric differential signal of the type in Fig. 3.

We turn now to the doping with n -type chlorine ions. In this case, spin-zero charged soliton states with $g = e$ and $S = 0$ apparently form. The degree of delocalization of such states is not found in these experiments, however.

We will conclude by pointing out a distinction between the properties of isolated chains and those of the condensed phase. In the condensed phase, aside from the monoclinic modification of polyacetylene,¹² the solitons are immobile. Another surprising result which we described above is that the linear geometry of the individual

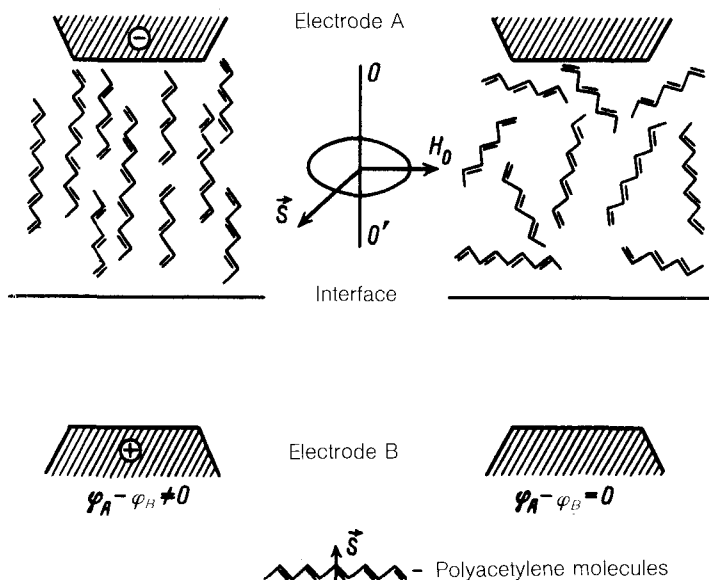


FIG. 4. Orientation of the polyene molecules, $(\sim\text{CH}\sim)_n$, in an electric field. Shown at the right is the situation in the absence of an electric field. The inset shows the orientation of the spin S with respect to the axis of the molecule. OO' —Axis of polyacetylene molecule; H_0 —magnetic field.

key: 1) Polyacetylene molecules

polyenes persists in solutions over a length $\sim 250\text{--}300 \text{ \AA}$, as follows from the width of the ESR line. Folds and bends of chains would signify a physical limitation on the region in which a soliton with $q = 0$ and $S = 1/2$ moves. We thus see the mechanism for the formation of crystals by polyene molecules above the critical concentration; this mechanism can be understood on the basis of Flory's two-dimensional lattice model for long rods.¹³

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