Solitons in Polyacetylene Produced and Probed by Positive Muons

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(Received 19 June 1984)

Positive muons were injected into both *trans*- and *cis*-$(CH)_x$ as well as $(CD)_x$. A marked difference was found in the field dependence of the muon spin-relaxation functions between *cis*- and *trans*-polyacetylene. A quantitative explanation was obtained by considering the unpaired electron produced by a muon: It is localized at the nearby carbons in *cis*-polyacetylene forming a radical state; on the other hand, in *trans*-polyacetylene, it becomes highly mobile and takes a one-dimensional solitonlike motion as clearly indicated by the inverse-root field dependence found for the relaxation rates.

PACS numbers: 76.90.+d, 61.40.Km, 76.80.+y

Since the development of thin-film formation by use of special catalyzing materials,[1] *trans*-polyacetylene has attracted both theoretical and experimental interests, because of the proposed existence of solitons which can be ascribed to one-dimensional diffusion of unpaired electrons associated with a different phase of bond alternation.[2] There have been many experimental studies by magnetic resonances[3,4] and other methods, but understanding of the basic properties of the soliton in *trans*-polyacetylene still seems unclear.

In the present study, we probed this celebrated system by the μ^+ spin-rotation method.[5] Positive muons are produced 100% longitudinally polarized and decay with the mean lifetime of 2.2 μs by emitting positrons asymmetrically with respect to the spin direction. In the muon spin-rotation experiment, the time evolution of the angular asymmetry of decay positrons reflects the relaxation of the muon spin due to local magnetic interaction. The role of μ^+ is quite significant in the studies of polyacetylene: μ^+, when stopped in a hydrocarbon with double bond, generally produces an unpaired electron and forms a muonium radical[5]; depolarization of the μ^+ in a *trans* isomer may reflect the dynamics of soliton in a *trans* chain. Here we found that the positive muon produces an unpaired electron which is highly mobile like a soliton in *trans*-polyacetylene, and that the observed relaxation rate is quantitatively explained by this picture. A preliminary stage of the muon spin-rotation studies with limited data on $(CH)_x$ has been reported elsewhere.[6]

The experiment was carried out at UT-MSL BOOM (Booster Meson Facility of the Meson Science Laboratory, University of Tokyo),[7] located at the Booster Synchrotron Utilization Facility of KEK. At the $\mu 1$ port of the BOOM facility, pulsed (50-ns width and 50-ms separation) and polarized (80%) backward (60 MeV/c momentum) muons were stopped in a polyacetylene target composed of a stack of thin films (in total, 4 cm×4 cm×1 g/cm^2). We used four types of samples, namely, *cis*-$(CH)_x$, *cis*-$(CD)_x$, *trans*-$(CH)_x$, and *trans*-$(CD)_x$, all of which were prepared by the Shirakawa method.[1] They were sealed into thin polyethylene bags in an argon atmosphere. We used a standard muon spin-rotation setup at BOOM, and detected decay positrons by the digital method of pulsed muon spin rotation using sixteen channel scintillation counter telescopes in both forward and backward directions to the beam.[7]

First, muon spin rotation was measured for both *cis*- and *trans*-polyacetylene under a 100-G transverse field at room temperature. A clear difference was found between *cis*- and *trans*-isomers: The μ^+ polarization at $t=0$ is largely lost in *cis*-polyacetylene, while it is kept in *trans*-polyacetylene, suggesting that the positive muon forms a paramagnetic (radical) state in the *cis*-isomer, while it is in a diamagnetic state in the *trans*-isomer. In order to study this difference more clearly, the longitudinal relaxation of μ^+ was measured under various applied longitudinal fields. The result is shown in Fig. 1(a) for *cis*-$(CH)_x$ and in Fig. 1(b) for *trans*-$(CH)_x$, where the decay e^+ asymmetry is displayed as a function of time, representing a longitudinal relaxation function $G_z(t)$. The pulsed muon beam is quite powerful for these muon spin-rotation measurements of long time range because of the substantially reduced background.

As clearly seen in Fig. 1(a), the μ^+ asymmetry in

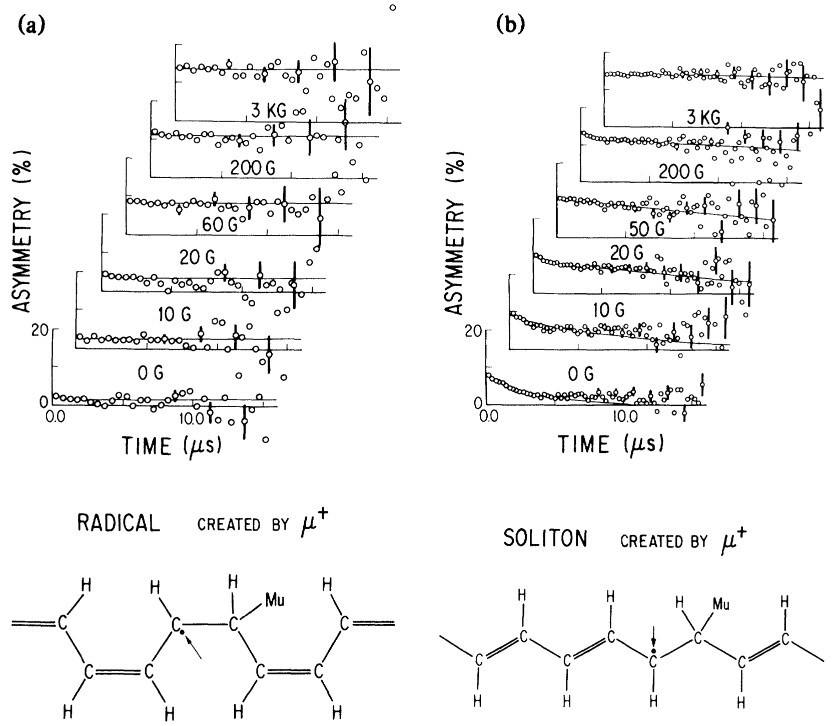

FIG. 1. Time spectra of decay positron asymmetry (longitudinal spin-relaxation functions) for μ^+ in (a) *cis*-$(\mathrm{CH})_x$ and (b) *trans*-$(\mathrm{CH})_x$ at room temperature for various applied longitudinal fields. The curves are best-fitted exponential relaxation functions. The proposed pictures for the muonium (represented by $\mathrm{Mu} = \mu^+ e^-$) states in these two isomers are also shown.

the *cis* isomer is recovered to the maximum asymmetry by increasing the applied field, where no damping is seen in the time spectra. The result is consistent with a typical decoupling pattern for a muoniumlike paramagnetic state. From the analysis of the decoupling curve of the asymmetry versus field, we found that the hyperfine coupling constant between the muon and the unpaired electron is around 200 MHz. Details of the analysis will be published elsewhere. The obtained result suggests the following picture: The μ^+ picks up an electron forming muonium during the slowing-down processes and attaches itself to one of the π bonds of *cis*-polyacetylene. In this process, an electron pair is formed with one of the π electrons, leaving the other unpaired π electron to form a muonium radical, as shown in the lower part of Fig. 1(a).

As shown in Fig. 1(b), the *trans* isomer, the μ^+ asymmetry at $t = 0$ is close to full asymmetry in zero field and changes only slowly with the change of the applied field from 10 G to 3 kG; at the same time the relaxation rate depends strongly on the field. In view of the nearly identical physical properties between *cis*- and *trans*-polyacetylene, e.g., ionization energy, bond length, etc., the marked contrast as shown in Figs. 1(a) and 1(b) is really surprising. We are naturally tempted to consider that this difference is related to the mobility of the produced unpaired electron: In the *cis* isomer, the unpaired spin is localized at the carbons next to the muon, while in the *trans* isomer the degenerate structure between two phases of bond alternation makes it possible for the unpaired electron to diffuse far away.

The observed relaxation functions $G_z(t)$ for *trans*-polyacetylene were fitted by assuming an exponential-type relaxation function e^{-t/T_1}. The relaxation rates (T_1^{-1}) for both *trans*-$(\mathrm{CH})_x$ and -$(\mathrm{CD})_x$ are plotted as a function of the applied field in Fig. 2. We found that the relaxation rate can be represented by an $H^{-1/2}$ dependence for a wide range of the external field H, from 10 to 3000 G at 293 K. Its rate was $3.2(2)\times10^5 H^{-1/2}\ \mathrm{s}^{-1}$ for $(\mathrm{CH})_x$ and $2.3(2)\times10^5 H^{-1/2}\ \mathrm{s}^{-1}$ for $(\mathrm{CD})_x$ where H is given in gauss. On the other hand, at 4.2 K, we found an upward deviation from the $H^{-1/2}$ dependence below 50 G. In this case, above 50 G the data were represented by $1.9(4)\times10^5 H^{-1/2}\ \mathrm{s}^{-1}$ for $(\mathrm{CH})_x$ and $1.7(3)\times10^5 H^{-1/2}\ \mathrm{s}^{-1}$ for $(\mathrm{CD})_x$.

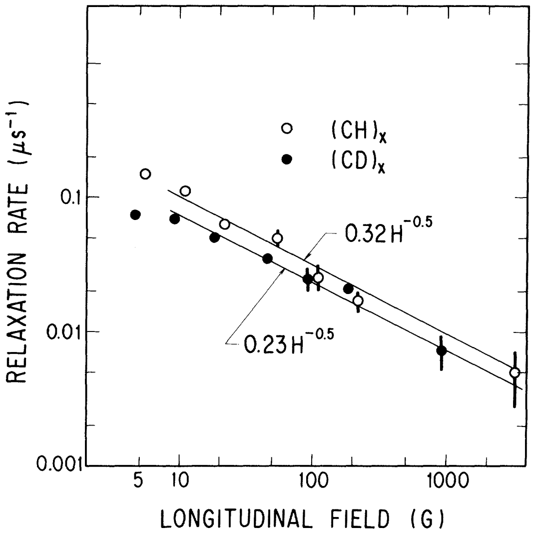

FIG. 2. The observed relaxation rates vs external field for μ^+ in *trans*-$(CH)_x$ and *trans*-$(CD)_x$ at 293 K.

To explain these field dependences, three relaxation mechanisms have been considered: nuclear dipolar field, cross relaxation due to spin diffusion to fixed paramagnetic defects, and one-dimensional diffusion of the unpaired electron which we may call here a soliton. First, the effect of the nuclear dipolar fields on the longitudinal relaxation of the μ^+ was calculated by a Monte Carlo simulation. It was found that this dipolar effect can be almost completely decoupled by the longitudinal field above 10 G. Furthermore, the small difference seen between $(CH)_x$ and $(CD)_x$ precludes this mechanism. Secondly, the contribution of spin diffusion, which could produce $H^{-1/2}$ dependence,[4] can be neglected in muon spin rotation since the muon is a perfectly dilute impurity.

Therefore, the only possible mechanism that can explain the $H^{-1/2}$ dependence is the one-dimensional diffusion of unpaired electron. In this case, the spin-lattice relaxation for μ^+ can be expressed as[8]

$$T_1(\mu)^{-1} = \tfrac{1}{4} n_s \left[\tfrac{3}{5} d^2 f(\gamma_\mu H) + (a^2 + \tfrac{7}{5} d^2) f(\gamma_e H)\right], \quad (1)$$

where a and d are the isotropic and the dipolar hyperfine coupling constants between electron and muon, respectively, γ_e and γ_μ are the electron and the muon gyromagnetic ratios, respectively, n_s is the density of unpaired electron per carbon atom, and $f(\omega)$ is the spectral density function containing $H^{-1/2}$ dependence for one dimensionally diffusing unpaired electrons. Let us compare $T_1(\mu)^{-1}$ to that of ^1H obtained by NMR, which is around $2.4 \times 10^3 H^{-1/2}$ s^{-1} at room temperature.[3] The observed $T_1(\mu)^{-1}$ for the μ^+ in both $(CH)_x$ and $(CD)_x$ is two orders of magnitude larger than $T_1(p)^{-1}$ at the same external field. Let us assume that one of the protons is replaced by the muon and that a difference in the relative position of the μ^+ from that for the proton with respect to the unpaired electron can be neglected. Then, the ratio of $T_1(\mu)^{-1}$ and $T_1(p)^{-1}$ should be scaled by the square of the gyromagnetic ratio, $\gamma_\mu^2/\gamma_p^2 \cong 10$. After this correction there still remains a difference of around a factor of 10 in the ratio of T_1^{-1}.

Here, we introduce the picture of unpaired-electron formation by the muon, which yields another enhancement due to the increased local density of the soliton at the μ^+: The μ^+ produces one soliton on the same chain; in ^1H NMR, the proton spins are relaxed by the solitons located at particular chains (1 per n_c chains) which are produced during the thermal isomerization. This reduction factor $1/n_c$ for ^1H NMR is estimated to be around 1/6, which is expected when we consider $T_1(p)^{-1}$ in terms of the chain length and the paramagnetic spin concentration.[9] Thus, this difference in number of solitons per probe between that produced by the muon and that studied by ^1H NMR, together with the difference in γ_μ and γ_p, can almost explain the observation that $T_1(\mu)^{-1}$ is nearly $100 \times T_1(p)^{-1}$.

In conclusion, we have found a new interesting phenomena of solitons revealed by muon spin rotation, namely, a soliton produced by the muon itself. The absolute relaxation rate and its $H^{-1/2}$ dependence can be solely attributed to this soliton. It is interesting to consider a possible scattering effect of the produced soliton at the "muon boundary": The soliton should be reflected at the muon site, where the muon fixes the bond-alternation phase. The deviation from the $H^{-1/2}$ dependence at 4.2 K may reflect a possible slowing down of soliton motion or confinement of the soliton. Further experiment and analysis along this line are now in progress.

We thank Dr. J. Imazato, Dr. T. Suzuki, and Mr. Y. Morozumi for their collaborations at various stages of the present work. Helpful information from Professor H. Nagasawa and Professor K. Kume and discussions with Professor J. H. Brewer and Professor D. G. Fleming are also acknowledged. The present work was partly supported by the Grant in Aid of the Japanese Ministry of Education, Culture, and Science.

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