Diffusion Properties of the Muon-Produced Soliton in *trans*-Polyacetylene

K. Ishida, K. Nagamine, T. Matsuzaki, Y. Kuno, and T. Yamazaki
Meson Science Laboratory, University of Tokyo, Bunkyo-ku, Tokyo, Japan

E. Torikai
Doctoral Course in Human Culture, Ochanomizu University, Bunkyo-ku, Tokyo, Japan

H. Shirakawa
Institute of Materials Science, University of Tsukuba, Sakura-mura, Ibaraki, Japan

and

J. H. Brewer
Department of Physics and TRIUMF, University of British Columbia, Vancouver, British Columbia, Canada

(Received 11 June 1985)

We have measured the longitudinal spin-relaxation functions of positive muons injected into *trans*-$(\mathrm{CH})_x$ at various temperatures and external fields. They showed non-single-exponential functions and were fitted by a model which takes into account both the on-chain diffusion and the disappearance of the muon-produced soliton. It was found that the on-chain diffusion rate $D_{\parallel}$ is almost constant from 29 to 290 K, while the disappearance rate D_3 slightly increases with temperature.

PACS numbers: 66.30.Lw, 72.80.Le, 76.90.+d

Recently, the behavior of the unpaired electrons in *trans*-polyacetylene has been extensively studied, both experimentally and theoretically, since it is proposed to be related to the properties of solitons.[1] There seem, however, to remain many unclear aspects to be studied concerning, in particular, on-chain and interchain diffusion properties of the soliton. In the present experiment, we studied this problem by the muon-spin-relaxation method, which is expected to probe the soliton in polyacetylene from a different viewpoint compared to conventional ESR or NMR.

In a previous paper,[2] we reported the following observations concerning positive muons in *trans*-polyacetylene: The positive muon, when it is added to a double bond in *trans*-polyacetylene, produces an unpaired electron; the unpaired electron exhibits soliton-like one-dimensional diffusion, as demonstrated by the $H^{-1/2}$ dependence of the longitudinal relaxation rate of the muon spin on the longitudinal magnetic field H. The soliton produced and probed by the muon has different properties from the usual soliton probed by NMR, ESR, etc.: (1) There is no mechanism similar to nuclear spin diffusion which affects the rate of muon spin relaxation because the muon is an "infinitely" dilute probe; (2) the soliton is created at the time of the muon arrival so that the time evolution of the soliton dynamics can be observed time-sequentially with reference to this "birth" time; and (3) the soliton is confined to one side of the chain from the boundary determined by the muon location, because the conjugation is terminated here. In this paper, we describe a further experiment in which particular attention was paid to deducing the disappearance of the soliton from the chain.

The on-chain spin diffusion rate $D_{\parallel}$ of the unpaired electron and its temperature dependence are interesting, because they reflect the interaction between the soliton and phonons. Theoretically, Wada and Schrieffer[3] have proposed that $D_{\parallel}$ should obey a T^2 temperature dependence, while Maki[4] predicted a $T^{-1/2}$ temperature dependence for $D_{\parallel}$. Experimentally, from the inverse-root–type frequency dependence of the proton spin-lattice relaxation rate (T_1^{-1}), it has been concluded that the spin diffusion is highly one-dimensional with $D_{\parallel} = 4\times 10^{13}\ \mathrm{s}^{-1}$ and that the interchain diffusion rate D is less than $10^8\ \mathrm{s}^{-1}$ at room temperature.[5] However, it was also pointed out that the nuclear spin diffusion to a fixed paramagnetic spin also reproduces the same frequency dependence[6] so that the above-mentioned interpretation is still unsettled. Recently, the frequency dependence of T_1^{-1} of the unpaired electron was directly observed by ESR,[7] where $D_{\parallel}$ and D were found to be 4×10^{13} and $2\times 10^7\ \mathrm{s}^{-1}$, respectively, at room temperature. This result was almost consistent with that of NMR. However, the temperature dependence of the diffusion rates is not yet clear: The T_1^{-1} of proton NMR obeys a $T^{1/4}$ dependence,[5] while that of ESR was proportional to the temperature.[8]

The experiment was carried out at the M20 muon channel at TRIUMF, the Tri-University Meson Facility in Vancouver, Canada. There, surface muon beams were stopped in a *trans*-polyacetylene target composed of a stack of thin films (in total, 2 cm × 2 cm × 80 mg/cm^2). The sample was prepared by the Shirakawa-Ikeda method[9] and sealed into a thin polyethylene bag of 88 μm thickness with an argon atmosphere. The temperature dependence of the longitudinal relaxation above 29 K was measured with a standard muon-spin-relaxation apparatus on the M20 channel, where we applied a longitudinal field of up to 4 kG. Samples were cooled by a helium exchange gas contained in a cryostat vessel, where the vessel itself was cooled by thermal contact with a cold finger cooled by liquid-helium flow. The temperature stability was around ±0.5 K.

The measured longitudinal relaxation functions $G_z(t)$ are shown in Fig. 1 for temperatures of both 29 and 281 K, showing the field dependence for 0, 10, 20, and 50 G. A significant temperature dependence can be seen by comparing these two data; the long-lived asymmetry (after 5 μs) is consistently reduced for the data at 29 K compared to those at 281 K. The relaxation rates decrease as the external field is increased at all the temperatures.

In a previous paper,[2] the relaxation functions were fitted by a single exponential relaxation function, where the main relaxation mechanism was considered to be due to the interaction between the muon spin and the one-dimensionally moving unpaired electron (soliton) produced by the μ^+. However, in the present 281-K data, the relaxation seems to cease after about 5 μs, indicating the need of a more complicated relaxation function. Since the nuclear dipolar fields must contribute to the muon spin relaxation $[G_z^n(t)]$, we calculated $G_z^n(t)$ by a Monte Carlo method considering mutual interactions between μ^+ and surrounding protons,[10] and took the ratio $G_z^e(t) = G_z(t)/G_z^n(t)$. Then we fitted the data of $G_z^e(t)$ with an exponential relaxation function by changing the analysis time region in a 2-μs step. All the data above 200 K were combined, since there seemed to be almost no temperature dependence above 200 K. The result shown in Fig. 2 exhibited a decrease of the relaxation rate itself with time. This result indicates a model in which the source of the relaxation, namely the soliton, disappears from the chain with time after it is created by the muon arrival.

Before going further, we have to consider several other possible mechanisms which may cause a change in the muon-spin-relaxation function from a single exponential type. Here, let us consider the following three possibilities: (1) As was shown in the time-domain analysis of ESR,[11] for the time before the effect of interchain diffusion becomes significant, the relaxation function could become $\exp(-\alpha t^{3/2})$. In our case, however, this time range is estimated to be only before about 20 ns, which is too short for the change in the relaxation function to be observed. (2) The muon-spin-relaxation rate will be reduced when the

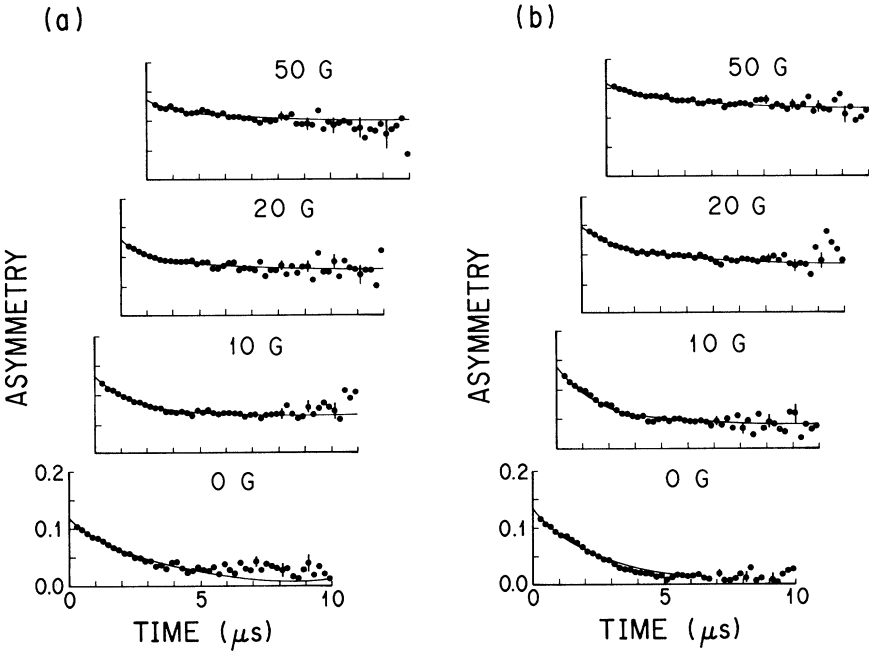

FIG. 1. Longitudinal spin relaxation functions for the μ^+ in *trans*-$(CH)_x$ (a) at 281 K and (b) at 29 K for longitudinal fields of 0, 10, 20, and 50 G. The curves are best-fitted functions by Eq. (3) after correction for the contribution of nuclear dipolar field to the relaxation function.

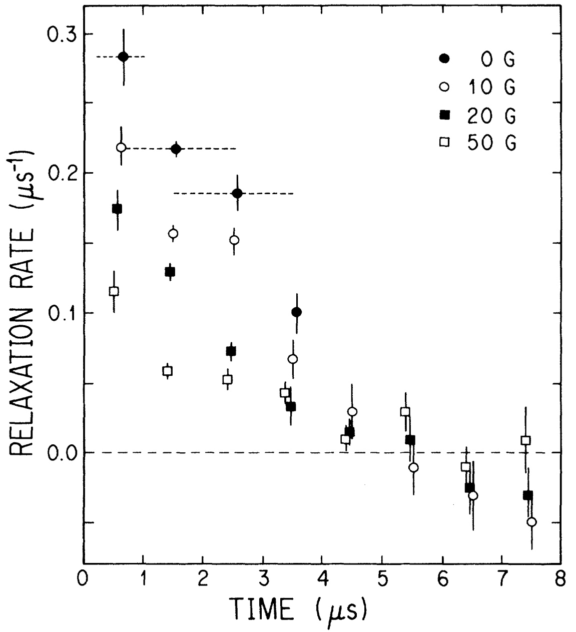

FIG. 2. Time dependence of the relaxation rate of μ^+ in *trans*-$(CH)_x$. The time window for the analysis is 1 μs for the earliest-time data, while it is 2 μs for the others, as shown in the figure. All the data above 200 K were summed up and used in this analysis. The effect of nuclear dipolar field has been already subtracted before the analysis. The 0-G data after 4 μs are not shown because of the unsatisfactory fit due to a small asymmetry.

electron spin associated with the soliton is left polarized. The electron spin-lattice relaxation rate measured by ESR, which is 10^7 s^{-1} at room temperature,[7] is much faster than the typical muon-spin-relaxation times so that this effect is considered to be small. (3) The location of the muon is considered to be randomly distributed on the chain. The relaxation rate is expected to be proportional to the probability of existence of the soliton around the muon; the rate is proportional to the inverse of the distance between the muon location and the end of the chain. This effect was calculated, but the result was found to be not much different from a single exponential relaxation.[10]

Since the above-mentioned three effects cannot explain the observed relaxation function, we will now consider the effect of the disappearance of the soliton from the chain. As shown in a previous paper,[2] the relaxation rate of the muon spin is proportional to the density of the soliton which remains on the chain. Thus, when the soliton disappears, the relaxation rate may change with time. Now, we introduce the disappearance rate D_3 of the soliton. Then, the time-dependent relaxation rate $R(t)$ may be written as

$$R(t) = R_0 \exp(-D_3 t), \tag{1}$$

where R_0 is the T_1^{-1} at $t=0$. From the rate equation for the relaxation function of the muon spin $G_z^e(t)$,

$$dG_z^e(t)/dt = -R(t)G_z^e(t), \tag{2}$$

we obtain

$$G_z^e(t) = \exp\{-(R_0/D_3)[1-\exp(-D_3 t)]\}. \tag{3}$$

We fitted D_3 and R_0 simultaneously for the data above 200 K. It was found that D_3 is almost field independent, while R_0 obeys an $H^{-1/2}$ dependence. This indicates that the muon spin relaxation comes mainly from the one-dimensionally diffusing unpaired electron and that the disappearance is due to a dynamical effect independent of the magnetic field. Next, the temperature dependences of R_0 and D_3 were obtained by a fit to the data at all fields, where D_3 was fixed at each temperature. The fitted results are shown in Figs. 3(a) and 3(b) for R_0 and D_3, respectively. Here, the relaxation rate R_0 was around 3 times larger than that which we obtained using a single exponential function.[2] However, this difference does not change our basic interpretation in the previous paper.[2]

The temperature dependence of R_0 reflects mainly

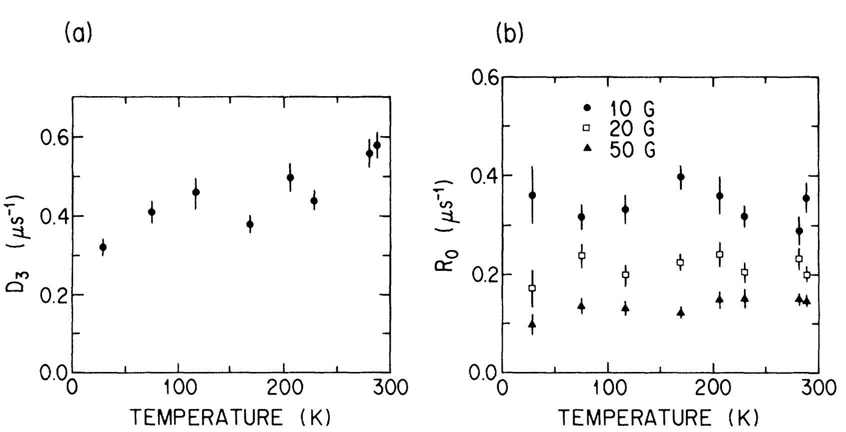

FIG. 3. Temperature dependence of (a) soliton disappearance rate D_3 and (b) the muon spin relaxation rate R_0.

the temperature dependence of $D_{\parallel}$. As shown in Fig. 3(b), it is almost temperature independent. Above 150 K, this is consistent with the ESR and the NMR results. But below 150 K, our result does not agree with these results. This is because the muon-spin-rotation method observes different aspects of the soliton dynamics from the other methods, e.g., the effect of the soliton trapping may be smaller in the muon-spin-rotation studies.

The soliton disappearance rate D_3 can be related to the interchain diffusion rate D of the soliton. The value of D obtained from the cutoff frequency in the ESR is $2\times10^7\ \mathrm{s}^{-1}$ at room temperature.[7] Since the mutual spin flip between solitons as well as the interchain hopping of the soliton itself contributes to the relaxation in the ESR experiment, it is not surprising that D is larger than the D_3 obtained in the present experiment. D_3 slightly increases with temperature, which indicates that hopping between the chains has a small activation energy.

In conclusion, we have measured the temperature dependence of the muon-spin-relaxation function in *trans*-polyacetylene. The observed relaxation function was well reproduced by considering both the muon spin relaxation due to the soliton and the disappearance of the soliton from the chain to which the muon is attached. The relaxation rate was almost temperature independent. The disappearance rate D_3 increased only slightly with temperature.

We thank Dr. R. Keitel, Dr. S. R. Kreitzman, Dr. D. R. Noakes, and Dr. M. Senba for their help during the Tokyo group's stay at TRIUMF. The Tokyo group is also grateful to E. W. Vogt and staff members of TRIUMF for their hospitality. Helpful information from Professor K. Kume is also acknowledged. The present work was supported partly by a Grant in Aid of the Japanese Ministry of Education, Culture, and Science, and partly by the Natural Sciences and Engineering Research Council of Canada.

---

[1] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979).

[2] K. Nagamine, K. Ishida, T. Matsuzaki, K. Nishiyama, Y. Kuno, T. Yamazaki, and H. Shirakawa, Phys. Rev. Lett. **53**, 1763 (1984).

[3] Y. Wada and J. R. Schrieffer, Phys. Rev. B **18**, 3897 (1978).

[4] K. Maki, Phys. Rev. B **26**, 2181, 2187, 4539 (1982).

[5] M. Nechtschein, F. Devreux, F. Genoud, M. Guglielmi, and K. Holczer, Phys. Rev. B **27**, 3938 (1983).

[6] N. S. Shiren, Y. Tomkiewicz, H. Thomann, L. Dalton, and T. C. Clarke, J. Phys. (Paris), Colloq. **44**, C3-223 (1983).

[7] K. Mizoguchi, K. Kume, and H. Shirakawa, Solid State Commun. **50**, 213 (1984); K. Kume, K. Mizoguchi, and H. Shirakawa, Mol. Cryst. Liq. Cryst. **117**, 469 (1985).

[8] L. R. Dalton, H. Thomann, A. Morrobel-Sosa, C. Chiu, M. E. Galvin, G. E. Wnek, Y. Tomkiewicz, N. S. Shiren, B. H. Robinson, and A. L. Kwiram, J. Appl. Phys. **54**, 5583 (1983).

[9] H. Shirakawa and S. Ikeda, Polym. J. **2**, 231 (1971).

[10] K. Ishida, thesis, University of Tokyo, 1985 (unpublished).

[11] J. Tang, C. P. Lin, M. K. Bowman, J. R. Norris, J. Isoya, and H. Shirakawa, Phys. Rev. Lett. **50**, 533 (1983).