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^{1}H and ^{19}F NMR Relaxations of Electroconducting Polypyrrole and Polythiophene Trifluoromethanesulfonates

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Synopsis. The NMR relaxation time T_1 of ^{1}H and that of ^{19}F were determined for polypyrrole and polythiophene doped with trifluoromethanesulfonate (triflate) or perchlorate ions. The ^{1}H T_1 is governed by the paramagnetism of the polymer chains. The ^{19}F T_1 of the triflate ions is explained by the combined effect of the F-F dipolar interaction and the electron-nucleus coupling. The activation energy for CF_3 reorientation about the C_3 axis was 7.5 kJ mol^{-1} for polypyrrole triflate and 15 kJ mol^{-1} for the corresponding polythiophene.

The electrical conductivities of doped polypyrroles and polythiophenes are strongly dependent on the nature of dopant anions as well as dopant concentration.[1,2] The molecular geometry and the molecular motion of anions may be affecting factors. In the present work, we have studied the molecular motion of trifluoromethanesulfonate (abbreviated as triflate) ions in polypyrrole and polythiophene with the aid of ^{19}F NMR.

Experimental

The materials used in this study were $[(C_4H_3N)(ClO_4)_{0.31}\cdot 0.4H_2O]_n$ (with a conductivity of 25 S cm^{-1} at 300 K), $[(C_4H_3N)(CF_3SO_3)_{0.3}\cdot 0.36H_2O]_n$ (1 S cm^{-1}), $[(C_4H_2S)(ClO_4)_{0.17}\cdot 0.25H_2O]_n$ (3 S cm^{-1}), and $[(C_4H_2S)(CF_3SO_3)_{0.2}\cdot 0.15H_2O]_n$ (0.15 S cm^{-1}), which were prepared by the methods reported in our previous papers.[3—6]

The relaxation time T_1 was determined by a 180°—τ—90° pulse sequence method with the aid of home-made pulsed NMR spectrometers.[7,8] The ^{19}F T_1 was determined at the Larmor frequency of 42 MHz. The ^{1}H T_1 was measured at 20 and 45 MHz. The sample was sealed with helium gas after pumped down for 3—4 h. The sample temperature was controlled between 80 and 300 K by flowing cold nitrogen gas.

Results and Discussion

Polypyrroles. The ^{1}H NMR of the polypyrrole triflate exhibited a single exponential free induction decay (FID) curve. When the sample was exposed to air, a non-exponential FID curve consisting of two components was observed at room temperature. One of the components had a T_2* of ca. 30 μs, which was identical with that of the oxygen-free sample. The other had a T_2* of ca. 1 ms. It weakened with decreasing temperature, and disappeared below ca. 250 K. The two components had an identical T_1 value, which agreed with that of the oxygen-free sample. This oxygen-absorption effect was reversible. As shown in Figs. 1 and 2, the ^{1}H T_1 was substantially temperature-independent except at temperatures above ca. 200 K. Since the relaxation time was constant with respect to the resonance frequency (Figs. 1 and 2), the temperature-independent relaxation process is dominated by the spin dynamics in the paramagnetic polymer chains, the unpaired electrons of which are originated from polarons and/or chain defects.[6] The weak temperature dependence at high temperatures may be attributed to an additional effect arising from a molecular motion of polymer chains and/or water of

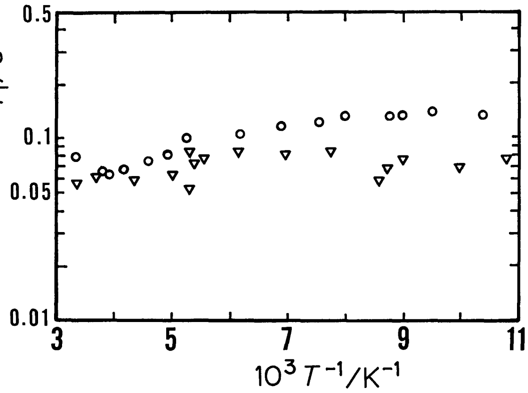

Fig. 1. ^{1}H relaxation time T_1 observed for polypyrroles at 20 MHz: perchlorate $[(C_4H_3N)(ClO_4)_{0.31}\cdot 0.4H_2O]_n$ (○) and triflate $[(C_4H_3N)(CF_3SO_3)_{0.3}\cdot 0.36H_2O]_n$ (▽).

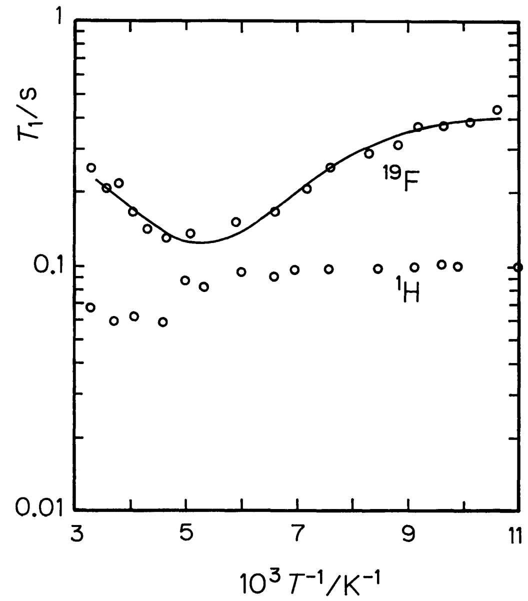

Fig. 2. ^{19}F relaxation time T_1 (top) and ^{1}H T_1 (bottom) observed for polypyrrole triflate: the Larmor frequency was 45 MHz for ^{1}H and 42 MHz for ^{19}F. The curve was calculated by Eq. 3 in the text.

hydration.

For the ^{19}F NMR of the triflate ions in the polymer, an exponential FID curve was observed throughout the temperature range investigated, and it was not influenced by the adsorption of oxygen. As shown in Fig. 2, the temperature dependence of the ^{19}F T_1 exhibited a well-defined T_1 minimum. This temperature dependence was different from that of ^{1}H T_1. A cross relaxation, therefore, is not operative between ^{19}F and ^{1}H nuclei. The absence of the cross relaxation is supported by the fact that the ^{1}H T_1 of the triflate shows an identical temperature dependence with that of the perchlorate as shown in Fig. 1.

The ^{19}F relaxation due to a reorientation of a CF_3 group is usually explained by the BPP theory:[9)]

$$T_1^{-1}(\mathrm{BPP}) = (2/3)\gamma^2\Delta M[\tau/(1+\omega^2\tau^2) + 4\tau/(1+4\omega^2\tau^2)], \tag{1}$$

where ΔM is a second-moment decrease due to motional narrowing and ω is the angular resonance frequency. The correlation time τ of the CF_3 reorientation about its C_3 axis is assumed to be given by the Arrhenius equation with the activation energy δ:

$$\tau = \tau_0 \exp(\delta/kT). \tag{2}$$

The observed ^{19}F T_1 vs. T^{-1} curve shows a well-defined minimum (Fig. 2). In contrast to the BPP curve, however, the slopes of the high- and low-temperature sides are not identical with each other. The paramagnetism of the polymer chains may contribute to the ^{19}F T_1 in addition to the BPP process. The ^{19}FT_1 is, therefore, given by:

$$T_1^{-1}(^{19}\mathrm{F}) = T_1^{-1}(\mathrm{el}) + T_1^{-1}(\mathrm{BPP}), \tag{3}$$

where, T_1^{-1}(el) is the inverse of a relaxation time due to the paramagnetic process.[10)] Since this process is expected to govern the ^{19}F T_1 via the same electron spin dynamics as for the ^{1}H T_1, T_1^{-1}(el) in Eq. 3 can be assumed to be proportional to ^{1}H T_1:

$$T_1^{-1}(\mathrm{el}) = cT_1^{-1}(^1\mathrm{H}), \tag{4}$$

here $T_1^{-1}(^1\mathrm{H})$ is the inveres of the ^{1}HT_1, which is 96 ms at 45 MHz. Figure 2 shows that Eq. 3 well explains the observed ^{19}F T_1. The best fit was obtained when c=0.23, ΔM=2.5 G^2, δ=7.5 kJ mol^{-1} and $1/T_{\min}$ (reciprocal temperature of the T_1 minimum)=5.3× 10^{-3} K^{-1}. The second moment of an isolated CF_3 group in a rigid lattice was calculated to be 6.5 G^2 on the basis of geometrical parameters determined for dimethylgold triflate hydrate.[11)] When the CF_3 group rapidly reorientates about its C_3 axis, the ΔM amounts to ca. 5 G^2 due to the molecular motion.[12)] When a molecular motion cannot be defined by a single correlation time, a ΔM value is smaller than 5 G^2.[13)] The small ΔM, 2.5 G^2, obtained in this study suggests that the correlation time of the CF_3 reorientation is different from one group to another in the polymer material. The activation energy δ=7.5 kJ mol^{-1} determined for the CF_3 reorientation is much smaller than 25 kJ mol^{-1} reported for Ag(CF_3CO_2),[14)] and is comparable to 5.5 kJ mol^{-1} of copper(I) trifluoroacetate[12)] in which the CF_3 groups undergo almost free reorientation about the C_3 axis.

Polythiophenes. The ^{1}H FID curves observed for the triflate and the perchlorate showed essentially the same nature as for the corresponding polypyrrole salts. The absorption of oxygen showed the same effect on the FID as observed for the polypyrroles. The ^{1}H T_1 gradually decreased with decreasing temperature as shown in Figs. 3 and 4. Undoped polythiophene was stable enough to provide reliable NMR data. A single ^{1}H FID curve was observed without an oxygen-adsorption effect. The ^{1}H T_1 increased with decreasing

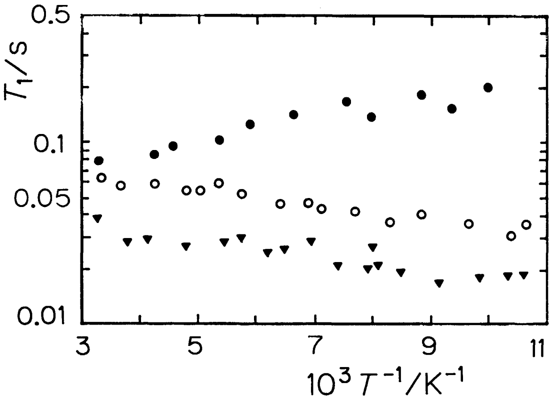

Fig. 3. ^{1}H relaxation time T_1 observed for polythiophenes at 20 MHz: perchlorate $[(C_4H_2S)(ClO_4)_{0.17} \cdot 0.25H_2O]_n$ (○), triflate $[(C_4H_2S)(CF_3SO_3)_{0.2} \cdot 0.15H_2O]_n$ (▼), and undoped polythiophene (●).

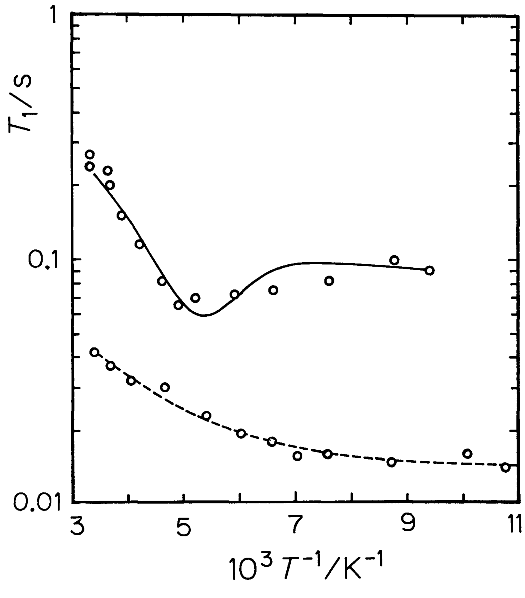

Fig. 4. ^{19}F relaxation time T_1 (top) and ^{1}H T_1 (bottom) observed for polythiophene triflate: the Larmor frequency was 45 MHz for ^{1}H and 42 MHz for ^{19}F. The solid curve was calculated by Eq. 3 and the broken curve by Eq. 5 in the text.

temperature (Fig. 3), in contrast to the doped polythiophene. The ^{1}H T_1 of the doped polymer, therefore, should be interpreted by a correlation with the polaron spin. As shown in Fig. 4, the ^{1}H T_1 of the triflate shows a clear temperature dependence, which can be explained by the sum of a temperature-independent term and a thermally activated term:

$$T_1(^1\mathrm{H}) = A + B\exp(-E/kT). \qquad (5)$$

The broken curve in Fig. 4 was obtained with A=0.014 ms, B=0.23 ms and E/k=620 K. A probable origin of the second term is an interchain spin diffusion that is thermally activated.

The ^{19}F FID curve of the triflate was exponential throughout the temperature range investigated. The temperature dependence of the T_1 showed a shallow minimum at ca. 200 K (Fig. 4). The ^{19}F relaxation in the polythiophene triflate is expected to be governed by the same process as for the corresponding polypyrrole. When Eq. 5 is substituted in Eqs. 3 and 4, Eq. 3 well explains the observed ^{19}F T_1 as shown in Fig. 4: the solid curve was obtained with the parameters c=0.16, ΔM=4.3 G^2, δ=15 kJ mol^{-1} and $1/T_{\mathrm{min}}$=5.3$\times$ 10^{-3} K^{-1}.

In conclusion, the ^{19}F T_1 in the triflates is governed by the combined effect of the fluorine–fluorine dipolar coupling and of the electron–fluorine interaction. The activation energy δ and the second moment decrease ΔM obtained for the CF$_3$ reorientation in the polypyrrole triflate is significantly smaller than the corresponding values in the polythiophene triflate. This reflects the difference between the environment around a CF$_3$ group in polypyrrole and that in polythiophene. The ^{1}H T_1 of the polypyrrole perchlorate is longer than that of the corresponding triflate. There is the identical relation in the polythiophenes. This suggests that the more conductive salt has the shorter correlation time of the spin diffusion.

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References

1) M. Salmon, A. F. Diaz, A. J. Logan, M. Krounbi, and J. Bargon, *Mol. Cryst. Liq. Cryst.*, **83**, 265 (1982).

2) Proc. Int. Conf. Science Technol. Synth. Met., Santa Fe, NM, U. S. A., 1988, *Synth. Met.*, **28**, (1989).

3) M. B. Inoue, E. F. Velazquez, and M. Inoue, *Synth. Met.*, **24**, 223 (1988).

4) M. M. Castillo-Ortega, M. B. Inoue, and M. Inoue, *Synth. Met.*, **28**, C65 (1989).

5) M. Inoue, A. R. Mendivil-Sol, H. Grijalva, and M. B. Inoue, *Inorg. Chim. Acta*, **161**, 179 (1989).

6) M. Inoue, M. B. Inoue, M. M. Castillo-Ortega, M. Mizuno, T. Asaji, and D. Nakamura, *Synth. Met.*, **33**, 355 (1989).

7) L. S. Prabhumirashi, R. Ikeda, and D. Nakamura, *Ber. Bunsen-Ges. Phys. Chem.*, **85**, 1142 (1981).

8) S. Gima, Y. Furukawa, R. Ikeda, and D. Nakamura, *J. Mol. Struct.*, **111**, 1983 (1983).

9) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

10) K. Mizoguchi, M. Nechtschein, J. P. Travers, and C. Menardo, *Synth. Met.*, **29**, E417 (1989).

11) S. Komiya, J. C. Huffman, and J. K. Kochi, *Inorg. Chem.*, **16**, 2138 (1977).

12) A. Kubo, R. Ikeda, J. A. Sampedro, M. Inoue, and D. Nakamura, *Bull. Chem. Soc. Jpn.*, **58**, 2947 (1985).

13) Y. Ito, T. Asaji, R. Ikeda, and D. Nakamura, *Ber. Bunsen-Ges. Phys. Chem.*, **92**, 885 (1988).

14) M. Punkkinen, L. P. Ingman, D. G. Taylor, and P. S. Allen, *J. Phys. C*, **8**, 2159 (1985).