^{1}H NMR study of spin dynamics in the I$_2$-doped PBMPV conducting polymers

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We have studied the room-temperature spin dynamics in a series of I$_2$-doped poly[2-buthoxy-5-methoxy phenylenevinylene] (PBMPV) conducting polymers by means of ^{1}H NMR in the Larmor frequency range 20 to 45 MHz. The nuclear magnetization recovery of the I$_2$-doped (PBMPV) conducting polymers showed a stretched-exponential form, and the spin-lattice relaxation rate was inversely proportional to the square root of the ^{1}H Larmor frequency. Our results are consistent with the one-dimensional spin diffusion of the mobile spin-carrying polarons along the main chain, and gave the intrachain diffusion constant as a function of the electrical conductivity.

I. INTRODUCTION

The conducting polymers have recently been the subject of much experimental studies. When doped with electron donors or acceptors, they can give remarkable electrical conductivities.[1] The electrical conductivity is known to be governed by the one-dimensional diffusion of the charge-carrying solitons or polarons. Electron paramagnetic resonance and nuclear magnetic resonance (NMR) are powerful tools for spin dynamics,[2–11] and have been employed to study polyacetylene,[5] polypyrrole,[6] polythiophene,[7] and polyaniline.[8,9] In this work, we have investigated the ^{1}H NMR line shapes and the nuclear spin-lattice relaxations at various Larmor frequencies in a series of I$_2$-doped poly[2-buthoxy-5-methoxy phenylenevinylene] (PBMPV) samples.

The main charge-transfer mechanism in conducting polymers is known to be the intrachain diffusion and the interchain hopping of polarons and/or bipolarons.[12,13] In one-dimensional structured systems, the nuclear spin-lattice relaxation rate is expressed in terms of the intrachain diffusion constant $D_\parallel$ and the interchain diffusion constant $D_\perp$ as[2–11]

$$\frac{1}{T_1} = \left(\frac{c}{4}\right)\left\{\left[\left(\frac{3}{5}\right)d^2 f(\omega_n) + \left[a^2 + \left(\frac{7}{5}\right)d^2\right]f(\omega_e)\right\},\quad (1)$$

$$f(\omega) = \frac{1}{\sqrt{4D_\parallel D_\perp}}\left(\frac{1+\sqrt{1+(\omega/2D_\perp)^2}}{1+(\omega/2D_\perp)^2}\right)^{1/2},\quad (2)$$

where ω_n and ω_e are the nuclear and electronic Larmor frequencies, respectively. c is the spin concentration, a the scalar coupling constant, and d the dipolar hyperfine coupling constant. Thus, the spin-lattice relaxation rate is inversely proportional to the square root of the NMR Larmor frequency in the one-dimensional spin-diffusion case, i.e., in the limit of small interchain diffusion constant $D_\perp$.

II. EXPERIMENT

The structure of PBMPV, a derivative of PPV (polyphenylenevinylene), is shown in Fig. 1. The PBMPV conducting polymer samples were prepared by spin coating and iodine doping, and the iodine concentration was determined as previously described.[14] The thin-film samples were a few micrometers thick, and visual inspection showed some inhomogenity. The four-in-line-probe method was employed for the conductivity measurements.

The samples were sealed in helium atmosphere for ^{1}H NMR measurements in the Larmor frequency range 20–45 MHz at room temperature. The spin-lattice relaxation was measured by the inversion recovery method, and the line shapes were obtained from the solid echoes. All the fits for the experimental data were made using the least-squares method.

III. RESULTS AND DISCUSSION

The electrical conductivity for various degrees of doping is shown in Fig. 2. The conductivity increases rapidly, before becoming saturated at heavier doping. The maximum conductivity is about 10^1 S/cm.

The ^{1}H NMR line shape for the undoped PBMPV and that for a heavily doped one are shown in Fig. 3. They consist of a relatively broad and a narrow component. The narrow component can be attributed to the main chain ^{1}H sites experiencing modulated magnetic fields by the mobile charge carrier spins, while the broad component can be attributed to the side chain ^{1}H sites, which are less affected by the mobile spins.
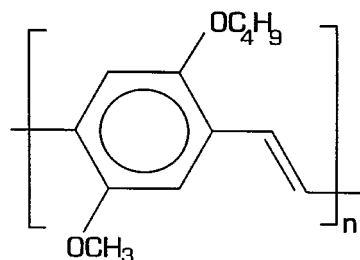
The typical magnetization recovery in I$_2$-doped PBMPV
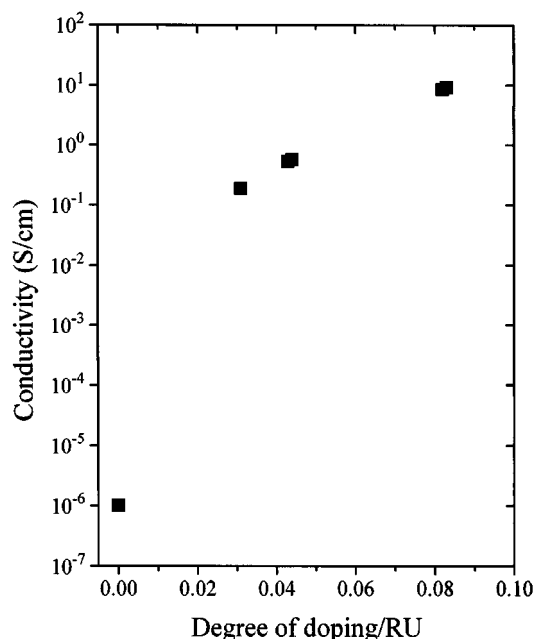

FIG. 1. The PBMPV structure.

FIG. 2. Electrical conductivity as a function of the degree of doping.

FIG. 4. Nuclear spin-lattice magnetization recovery in an I$_2$-doped PBMPV sample with a conductivity of $\sim$ 10 S/cm.

is shown in Fig. 4. It is not well described by a single- or a double-exponential function, but can only be well described by a stretched-exponential form, $M(t) = M_0[1 - \exp(t/T_1)^n]$, with $n = 0.8 \pm 0.03$. A stretched-exponential form is characteristic of a system with a distribution of the correlation time,[15] which is believed to arise from the inhomogenious charge-carrier environments created by the I$_2$ doping in our case. This seems to reflect relative inhomogeneity in this series of PBMPV samples.

Figure 5 shows the Larmor frequency dependence of the spin-lattice relaxation rate $(1/T_1)$ for samples with various conductivities. It is seen that the spin-lattice relaxation rate has a linear $\omega^{-1/2}$ dependence over the frequency range in-
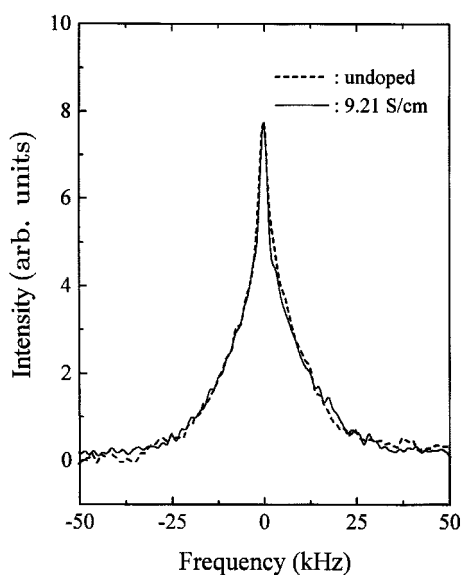
vestigated for all the samples, indicating that the main spin-lattice relaxation mechanism is the one-dimensional spin diffusion. Assuming that the degree of doping is proportional to the spin concentration c and that the interchain diffusion constant $D_\perp$ is negligible as is indicated in Fig. 5, the slopes in Fig. 5 and Eqs. (1) and (2) can give a relation between the intrachain diffusion constant $D_\parallel$ and the dc conductivity, which is shown in Fig. 6. It shows that $D_\parallel$ increases with the conductivity, roughly obeying a power law.[16]

Figure 7(a) shows the spin-lattice relaxation rate T_1^{-1} vs the dc conductivity σ at various NMR frequencies. A single

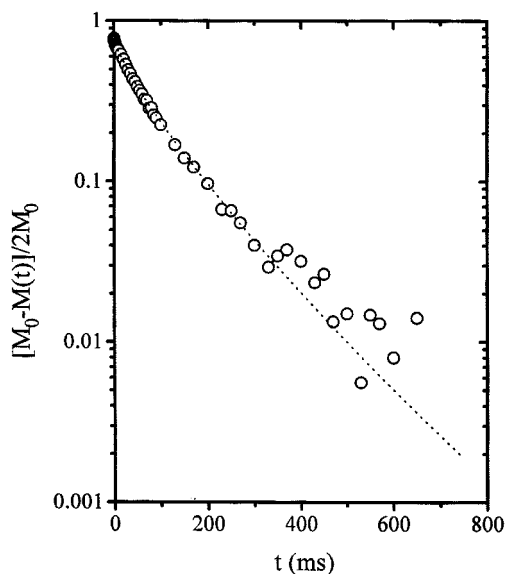FIG. 3. ^{1}H NMR line shape for the undoped PBMPV sample and that for an I$_2$-doped sample with a conductivity of $\sim$ 10 S/cm.
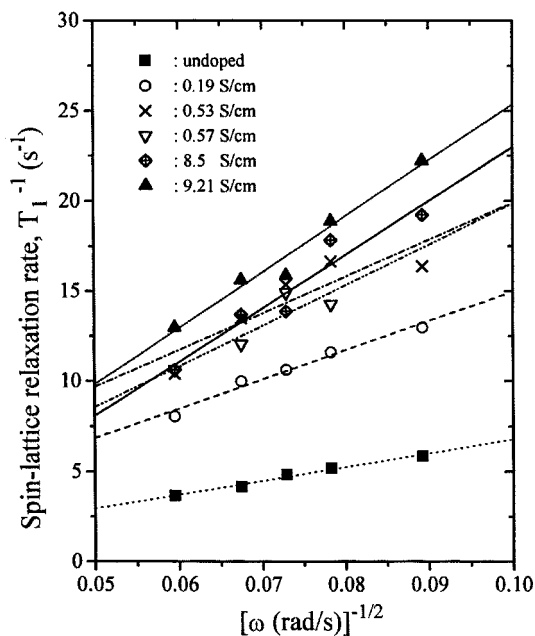

FIG. 5. Larmor frequency dependence of the spin-lattice relaxation rate $1/T_1$ for samples with various electrical dc conductivities. The data scatter in the range 0.5 S/cm is simply due to the smaller sample quantity resulting in a poorer signal-to-noise ratio.
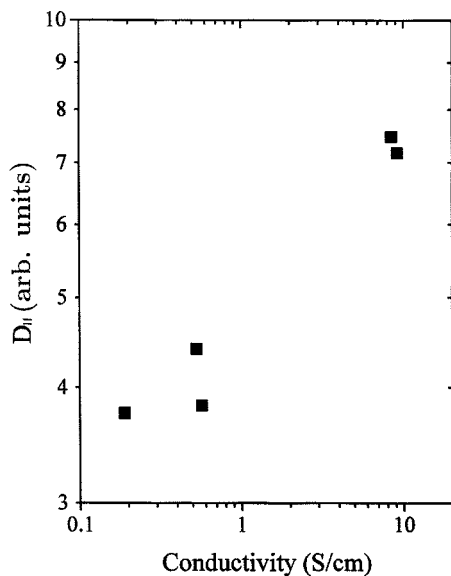
FIG. 6. Intrachain diffusion constant $D_\parallel$ vs the electrical conductivity.

power-law relation was sought, and the relation $T_1^{-1} = A\sigma^n + b$ gave a resonable fit at all the frequencies with $n = 0.08 \pm 0.007$ and $b = 0.3 \pm 0.07$. However, the A values were dependent on the NMR frequency, which is shown in Fig. 7(b). This is believed to reflect the frequency dependence of the electrical conductivity in our NMR frequency range.

In summary, we have measured the ^{1}H NMR spin-lattice relaxation times over a Larmor frequency range from 20–45 MHz in I_2-doped samples of PBMPV conducting polymers. For all the samples with various conductivities, the ^{1}H spin-lattice relaxation rate was inversely proportional to the square root of the ^{1}H Larmor frequency, and no dimensional crossovers were observed in our frequency range. It can be concluded that the conduction mechanism in I_2-doped PBMPV is dominated by the one-dimensional spin diffusion along the main chain. In addition, the intrachain diffusion constant could be obtained as a function of the spin concentration (or degree of doping) and the electrical conductivity.
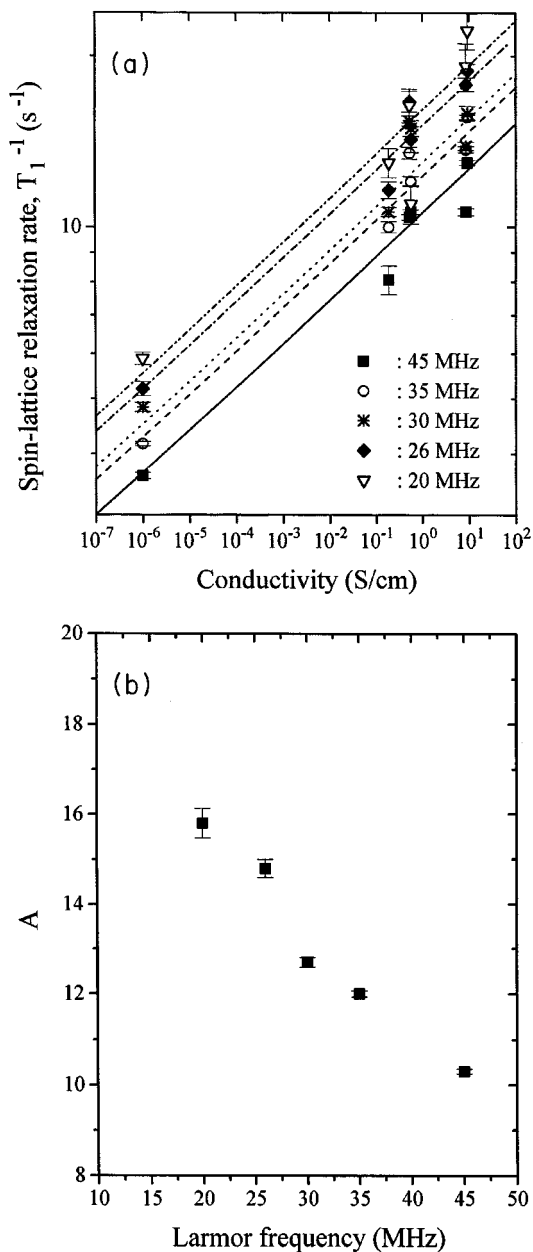
ACKNOWLEDGMENTS

FIG. 7. (a) Spin-lattice relaxation rate vs the dc conductivity. (b) The coefficient A vs the NMR frequency.

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