Anisotropic Polaron Motion in Polyaniline Studied by Muon Spin Relaxation

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Muon spin relaxation has been used to probe the highly anisotropic motion of polaronic charge carriers in the emeraldine base form of polyaniline. The measured diffusion rate along the polymer chain for negative polarons shows a metalliclike temperature dependence, which is saturated at low temperatures but becomes limited by phenylene ring librational scattering above 150 K. The interchain transport at room temperature is more than 4 orders of magnitude slower than the intrachain process and becomes further suppressed on cooling. [S0031-9007(97)04231-2]

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Conducting polymers such as polyaniline (PANI) have been attracting considerable attention recently due to the high conductivities achievable by doping and their potential as highly tailorable semiconducting materials for use in electronics and optoelectronics [1]. Although an understanding of the mechanisms of polaron motion in such materials is of great importance both for fundamental and technological reasons, the correct description of the transport mechanisms and their relation to the underlying polymer structure and the modifications produced by doping are still only poorly understood. One reason for this is that macroscopic electronic transport measurements such as conductivity studies are dominated by the slowest component of the transport process, which is strongly dependent on the degree of order in the sample morphology [2]. On the other hand, microscopic spin dynamics probes such as ESR, NMR, and muon spin relaxation (μSR) are much better placed to focus on the intrinsic transport processes governing the mobility of an electronic excitation traveling along a polymer chain. In a highly anisotropic polymer system the dominant character of this motion is expected to be a one-dimensional diffusion process. The first clear demonstration of such a characteristic 1D diffusion was made using ESR in undoped *trans*-polyacetylene where neutral kink solitons are the mobile spin species [3].

For polymers like PANI having a more complex structure than polyacetylene, spin dynamical studies using NMR and ESR have been used to observe the motion of polarons [4]. μSR is an alternative spin dynamical probe technique which measures the time dependence of the spin polarization of a positive muon implanted into the sample [5]. ESR and NMR work best for the *doped* case, since the motional linewidth contributions are proportional to the carrier density. In contrast, the positive muon is a uniquely sensitive microscopic probe of polaron excitations in the *undoped* state of a conducting polymer, as the muon implantation process itself generates an excitation which is initially close to the muon site. The dynamical properties of this muon-generated excitation can then be studied via the time evolution of the muon spin polarization, which is deduced from the asymmetric emission of positrons following muon decay. This was first demonstrated for solitons in polacetylene [6] and subsequent studies were reported for a range of conducting polymers where polarons are the mobile species [7]. We report here muon measurements of polaron dynamics in undoped PANI, where we have been able to measure the temperature dependence of both the on-chain diffusion rate $D_{\parallel}$ and the interchain diffusion rate $D_{\perp}$. We find a metallic type of temperature dependence for $D_{\parallel}$ over the whole measured temperature range 6–300 K, whereas an activated behavior is seen for $D_{\perp}$.

High molecular weight samples (MW $\sim$ 150 000) of the emeraldine base form of PANI (PANI:EB) were prepared as powder using procedures described elsewhere [8]. This powder was pressed into pellets for the muon measurements. Muon spin relaxation was measured using 27 MeV$/c$ positive surface muons at the RIKEN-RAL muon facility, where the relaxation function could be measured over the time range from $\sim$50 ns to $\sim$25 μs.

As in other unsaturated organic systems [9], the muon picks up an electron to form muonium as it slows down in the polymer. This muonium then reacts with the polymer, resulting in the muon analog of a hydrogenation reaction. The electronic structure of emeraldine in its pristine, hydrogenated, and protonated forms was calculated by Duke *et al.* [10]. Hydrogenation corresponds to adding a single electron to the lowest unoccupied molecular orbital (LUMO) of emeraldine. Following rapid electronic and structural relaxation of the surrounding molecule, a negative polaron is formed, which is centered on the quinoid ($=C_6H_4=$) ring of the molecule. In the emeraldine polymer the polaron can easily move away from its initial site and diffuse through the system. As the polaron diffuses, spin flip can occur due to spin-lattice relaxation and interaction with magnetic impurities. This relaxation of the polaron spin will be transferred to the muon via a hyperfine coupling mechanism, but only while the mobile polaron is within interaction range of the muon site. By studying the longitudinal magnetic field dependence of the muon relaxation, important information about the polaron motion can be obtained.

In the earlier muon studies of conducting polymers [6,7], NMR theory was adapted to the muon case and the muon spin relaxation was fitted to an exponential decay function. However, it has always been clear that a simple exponential does not describe the relaxation well over a wide time range. Risch and Kehr (RK) recently derived a function that more properly describes the spin relaxation of a muon interacting with a spin defect which is rapidly diffusing along a one-dimensional chain [11]. The corresponding longitudinal muon spin relaxation function has the form: $G(t) = \exp(\Gamma t)\,\mathrm{erfc}(\sqrt{\Gamma t}\,)$ for $\lambda t_{\max} \gg 1$, with erfc signifying the complementary error function, λ the electron spin flip rate, $t_{\max}$ the experimental time scale, and Γ a relaxation parameter. This relaxation function goes as $t^{-1/2}$ at long times rather than decaying exponentially. We have found that the measured relaxation is well described by this RK function over a wide range of experimental conditions. After correcting for the diamagnetic component of asymmetry, which is measured in a small transverse field, the data are fitted with only two parameters, the initial amplitude of the asymmetry and the relaxation parameter Γ. Some muon spin relaxation measurements for PANI:EB are shown in Fig. 1(a) together with fits to the RK function. Figure 1(b) shows the improved fit using the RK function compared to an exponential fitting function.

In finite magnetic field the RK relaxation parameter Γ is given by $\Gamma = \lambda/(1 + \sqrt{2\omega_e\lambda}\,D_\parallel/\omega_0^2)^2$ where ω_e is the electronic Larmor frequency, ω_0 is the muon-electron hyperfine coupling, and $D_\parallel$ is the intrachain diffusion rate. In the fast diffusion limit, which applies for all the measurements here, $D_\parallel \gg \omega_0^2/\sqrt{2\omega_e\lambda}$ and Γ has an inverse magnetic field dependence $\Gamma = \omega_0^4/2\omega_e D_\parallel^2$, which is independent of the spin flip rate and allows straightforward determination of $D_\parallel$. As the field is reduced there will be a cutoff in the $1/B$ field dependence of Γ due to a crossover to a 3D diffusion regime, which occurs when ω_e becomes smaller than the interchain diffusion rate $D_\perp$. In the 3D diffusion regime the relaxation rate is expected to be independent of field. Although RK did not consider interchain diffusion and the 3D diffusion regime, we can estimate the interchain diffusion rate from the low-field departure of the measured relaxation from 1B dependence by assuming the form $\Gamma = \Gamma_0/[1 + (B/B_c)]$ for the field dependence of the relaxation. A straightforward estimate of $D_\perp$ is then given by $\gamma_e B_c$. When the applied field is below ~10 G, the nuclear dipole fields seen by the diamagnetic muon fraction are no longer fully decoupled and provide an additional contribution to the muon relaxation which can be difficult to separate accurately from the paramagnetic relaxation. In addition, polaron reflection by chain ends or conjugation defects introduced by impurities or cross-linking can also lead to an increased muon relaxation rate at low fields. All these effects limit the accurate estimation of slower interchain diffusion rates.

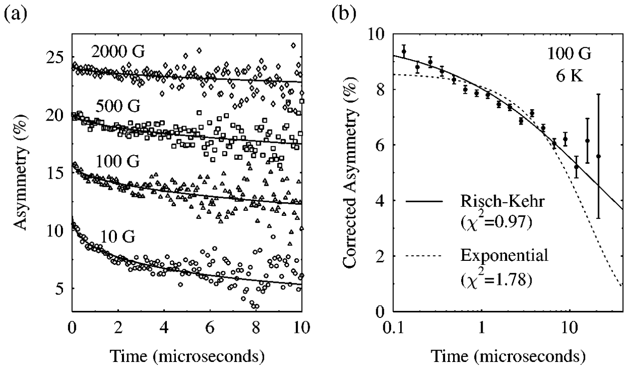

FIG. 1. (a) Positron emission asymmetry showing muon spin relaxation in PANI:EB at 6 K for several values of longitudinal magnetic field. The lines show fits to the RK relaxation function. (b) The data for 100 G shown on a logarithmic time scale after subtraction of the nonrelaxing diamagnetic asymmetry $a_D = 6.7\%$. It can be seen that the exponential function provides a very poor fit, whereas the RK function provides an excellent fit over 2 orders of magnitude in time.

The field dependence of the fitted RK relaxation parameter Γ is shown in Fig. 2 for high and low temperatures. It can be seen that at 6 K the one-dimensional $1/B$ regime holds down to below 10 G, whereas at 300 K the $1/B$ regime only holds down to 300 G or so. This indicates that $D_\perp$ increases by around 2 orders of

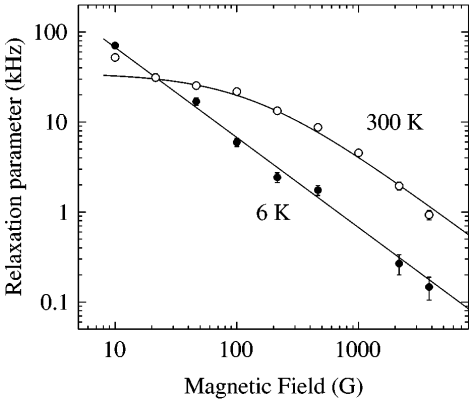

FIG. 2. Relaxation parameter Γ versus field for PANI:EB at 6 and 300 K. The high-field behavior shows the 1/B dependence which is characteristic of 1D diffusion in the Risch-Kehr relaxation model. At 300 K the interchain diffusion is sufficiently fast to observe a 3D diffusion regime below a crossover field of around 100 G. For an explanation of the fitted lines see the text.

magnitude between 6 and 300 K, where it reaches a value of $\sim 2 \times 10^9$ rad/s.

Since, at 500 G and above, the one-dimensional $1/B$ field dependence is obeyed over the full temperature range studied, a field of 1 kG was chosen for a more detailed study of the temperature dependence of the relaxation. This is shown in Fig. 3, where it can be seen that there is a rapid increase in the relaxation above ~150 K. We associate this with polaron scattering by phenylene ring librational modes which are known to couple strongly to the electronic excitations [12]. Inelastic neutron scattering indicates that these modes have energy bands centered around 7 meV for benzenoid ($\text{—}C_6H_4\text{—}$) and 10 meV for quinoid ($\text{═}C_6H_4\text{═}$) ring librations [13]. Mechanical studies have also shown that these modes become strongly excited in the 180–220 K region [14].

In order to derive the diffusion rate from the relaxation we take a value for the hyperfine coupling $\omega_0 = 2\pi \times 150$ MHz, as estimated from the longitudinal decoupling field of the initial muon asymmetry. The diffusion rate $D_\parallel$ calculated from Γ is shown in the inset to Fig. 3. It shows a weak metallic type temperature coefficient at low temperatures, becoming stronger above 150 K. Well above 150 K it becomes inversely proportional to temperature, which is suggestive of phonon limited metallic transport. The data can be fitted well by a simple model for the transport in which $D_\parallel \propto 1/(\Sigma_0 + \Sigma_r)$, where Σ_0 is a temperature independent scattering term and Σ_r is a phonon scattering term proportional to the number of ring libration modes excited, i.e., $\Sigma_r \propto 1/[\exp(E_r/kT) - 1]$. The energy of the librational mode E_r is estimated from our data to be 11.7 ± 0.6 meV, which is entirely consistent with the broad 10 meV quinoid libration band seen in neutron scattering [13]. Perpendicular diffusion rates were estimated from the cutoff fields; below ~100 K the estimated values should be taken as upper limits for the reasons mentioned earlier. The parallel and perpendicular diffusion rates are shown together in Fig. 4 along with previous ESR data in the protonated metallic state for comparison [15]. In contrast to $D_\parallel$, it can be seen that the interchain diffusion $D_\perp$ shows an activated semiconducting behavior, and it increases sharply in the region above 150 K where $D_\parallel$ is decreasing with temperature. This strongly suggests that the librational motion is *assisting* the interchain transport, whereas it *hinders* the metalliclike intrachain motion. The overall values for $D_\parallel$ at 300 K and for the temperature dependence of $D_\perp$ are quite similar here to the ESR values measured for the protonated metallic state, but the fully metallic temperature dependence of $D_\parallel$ seen here is in marked contrast to the semiconducting behavior seen below 150 K in the doped case.

Acoustic-phonon-limited polaron transport was considered in polyacetylene by Jeyadev and Conwell [16]. Their calculated diffusion coefficient showed a broad peak at a temperature below 100 K with the parameters appropriate for *trans*-polyacetylene. A $1/T$ dependence was predicted at high temperature. Optical phonons were included in addition to the acoustic phonons in an earlier analysis of

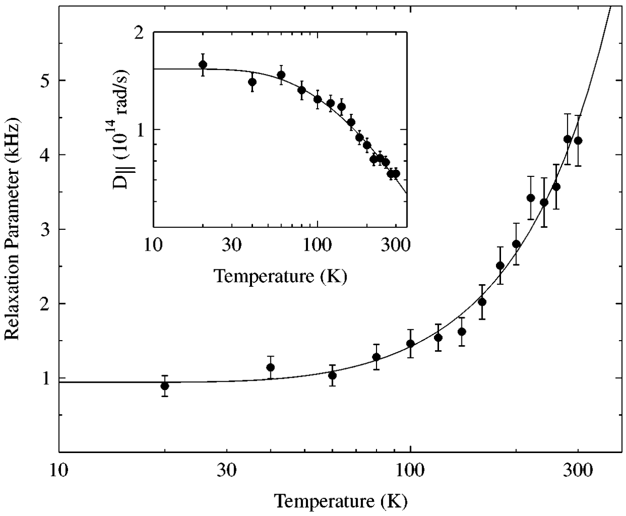

FIG. 3. Temperature dependence of the relaxation parameter Γ for PANI:EB at 1 kG. The inset shows the polaron intrachain diffusion rate $D_\parallel$ derived from the 1 kG relaxation using the value $\omega_0 = 2\pi \times 150$ MHz. The solid lines show the fitted temperature dependence for polaron scattering from ring librational modes.

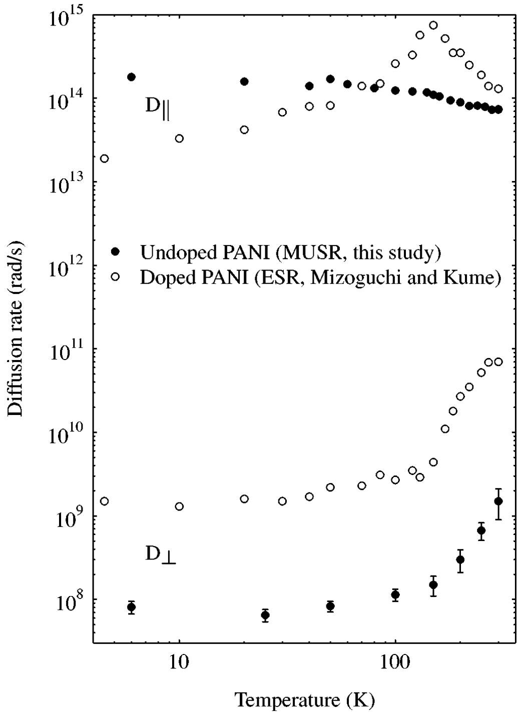

FIG. 4. Temperature dependence of the parallel and perpendicular diffusion rates for negative polarons in PANI:EB compared with previous ESR measurements of positive polaron diffusion in the doped state [15].

soliton diffusion by Maki [17], and these give a scattering contribution proportional to the phonon number. This is consistent with our measured high temperature behavior. One of the most significant differences between polyaniline and polyacetylene is the lack of charge conjugation symmetry (CCS) in the former, and Sum *et al.* [18] extended the work of Jeyadev and Conwell to include CCS-breaking effects. These produce dramatic differences between the mobilities of positive and negative polarons. Whereas the negative polaron is relatively mobile, movement of a positive polaron requires large ring rotations which make it much more massive and immobile. Since protonation produces positive polarons, whereas muonium addition produces a negative polaron, the different behavior of the measured on-chain diffusion rates in doped and undoped PANI can be understood as resulting from the negative polaron being intrinsically more mobile at low temperatures.

A solitary wave acoustic polaron [19], like the polyacetylene kink soliton [20], is theoretically expected to have a maximum velocity c comparable to the sound velocity in the polymer v_s. This has been confirmed by recent dynamical simulations [21]. Since the on-chain diffusion constant $\mathcal{D}_\parallel$ may be expressed as $\mathcal{D}_\parallel = D_\parallel a^2 = c^2 \tau = cl$, where a is jump distance for the polaron, τ the scattering time, and l the mean free path, it can be seen that at low temperatures $D_\parallel$ will be a constant determined by the mean free path resulting from defects. At low enough temperatures the thermalized polaron velocity is no longer expected to be saturated, and the diffusion rate should fall. From the data measured here, this fall in diffusion rate would have to be below 6 K. Taking $v_s \sim 2.5 \times 10^3$ m/s, this sets an upper limit on the negative polaron's "rest" mass at $\sim 30 m_e$. If the polaron jump distance is taken as the quinoid ring separation $a \sim 20$ Å, the low temperature mean free path can be estimated to be $l \sim 160a$. Since the average chain length is $L \sim 400a$, this implies 2–3 scattering defects per chain.

In conclusion, we have used the positive muon to probe the anisotropic diffusion of negative polarons in polyaniline. We have found clear evidence that the on-chain diffusion is controlled by scattering from ring librational modes at temperatures above ~ 150 K, whereas it becomes limited by defect scattering at low temperatures. The polaron velocity appears to be fully saturated down to 6 K in agreement with theoretical expectations for a 1D solitary wave acoustic polaron. Finally, the enhanced mobility of negative polarons compared to positive polarons has been demonstrated in this system.

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