

Muon-spin relaxation study of anisotropic charge carrier motion in polyphenylene vinylene-based polymers

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 9987

(<http://iopscience.iop.org/0953-8984/14/42/311>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 18/05/2010 at 15:13

Please note that [terms and conditions apply](#).

Muon-spin relaxation study of anisotropic charge carrier motion in polyphenylene vinylene-based polymers

S J Blundell^{1,4}, F L Pratt², I M Marshall¹, C A Steer¹, W Hayes¹,
A Husmann¹, C Fischmeister³, R E Martin³ and A B Holmes³

¹ Clarendon Laboratory, Oxford University Department of Physics, Parks Road,
Oxford OX1 3PU, UK

² ISIS Muon Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK

³ The Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of
Cambridge, Pembroke Street, Cambridge CB2 3RA, UK

E-mail: s.blundell@physics.ox.ac.uk

Received 15 August 2002

Published 11 October 2002

Online at stacks.iop.org/JPhysCM/14/9987

Abstract

Muon-spin relaxation (μ SR) experiments on the conducting polymers poly(2, 3-dibutoxy-1, 4-phenylene vinylene) and poly(2, 5-bis(dimethyloctylsilyl)-1, 4-phenylene vinylene) probe the dynamics of the highly mobile polarons created by the muon-implantation process in which muonium reacts with the polymer forming a radical state. The fluctuating spin density induced by the electronic spin defect rapidly diffusing up and down the chain leads to a characteristic relaxation, the temperature and field dependences of which permit the extraction of intrachain and interchain diffusion rates. The intrachain diffusion rate decreases with temperature and can be fitted to a model of phonon-limited transport. The interchain diffusion rate increases with temperature and can be fitted to an activated temperature dependence.

1. Introduction

The production of various electronic and optical devices based upon conducting polymers has arisen because of the ability to dope conjugated organic polymers over the full range from insulator, through semiconducting behaviour to metallic regimes [1, 2]. The recent advances in polymer light-emitting diodes have come about because of new electroluminescent materials prepared using one particular family of polymers based on polyphenylene vinylene (PPV) [3–5]. Organic electroluminescent materials are especially suited to large-area displays as they can be readily deposited from solution by spin-coating, and PPV shows the tensile strength

⁴ Author to whom any correspondence should be addressed.

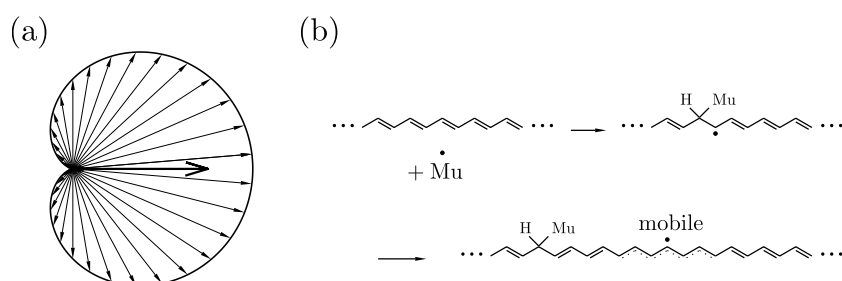
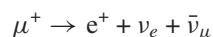


Figure 1. (a) The angular distribution of emitted positrons with respect to the initial muon-spin direction. The figure shows the expected distribution for the most energetically emitted positrons. (b) Muonium interaction with *trans*-polyacetylene to produce a diamagnetic radical and a mobile neutral soliton.

expected for a chain-extended polymer so that durable displays can be produced. PPV can also be used in the fabrication of molecular wires [6]. It is therefore important to understand in greater detail the anisotropic motion of carriers in PPV-based materials. Muon-spin relaxation (μ SR) is a powerful technique for probing polaron motion in undoped conducting polymers because it is possible to study the *dynamics of a single electronic defect*, one introduced by the muon itself. In this paper we present recent experimental results which we have obtained on samples of substituted PPV using implanted muons.

The μ SR technique is an important tool in condensed matter physics (for reviews see [7–9]). The decay of the positive muon (μ^+) follows the following reaction:



where ν_e and $\bar{\nu}_\mu$ are neutrinos. Each muon (average lifetime 2.2 μ s) decays into a positron (e^+) which is emitted preferentially along the instantaneous direction of the muon spin (see figure 1(a)). By analysing the time dependence of the asymmetry of the positron decay, one can infer the time evolution of the muon-spin polarization.

Depending on its chemical environment, the implanted muon can pick up an electron during its (very rapid) thermalization process and form a neutral atomic state called muonium (abbreviated Mu = μ^+e^-) which is an analogue of atomic hydrogen. In muonium the electronic spin and the muon spin are coupled by a hyperfine interaction. The reaction between muonium and *trans*-polyacetylene [10–12] produces a diamagnetic, neutral muon defect and a highly mobile unpaired spin (see figure 1(b)). Because the unpaired spin is mobile, the hyperfine coupling between it and the muon defect is intermittent [13]. In other polymers, such as polyaniline, the muon-induced defect is a negatively charged polaron [14, 15] and we have found that muons are uniquely sensitive to the motion of this defect in undoped materials [16]. In non-conducting polymers such as polybutadiene, the muon-generated radical states remain localized near the site of the muon [17].

The same kind of effect observed in polyaniline [16] is expected in PPV, as illustrated in figure 2. This excitation diffuses up and down the chain but cannot cross the point at which the muon is bonded to the chain which therefore acts as a barrier. Every time the excitation briefly revisits the muon, the muon–electron hyperfine coupling is turned on and then off, so that successive visits progressively relax the muon polarization. Measurement of the magnetic field dependence of this relaxation yields the spectral density function associated with the excitation random walk and can be used to infer the dimensionality of the diffusion [10, 18]. This occurs because the relaxation rate is connected with the noise power (or spectral density), $J(\omega_\mu)$, in the fluctuating magnetic field at the muon Larmor frequency, $\omega_\mu = \gamma_\mu B$, associated

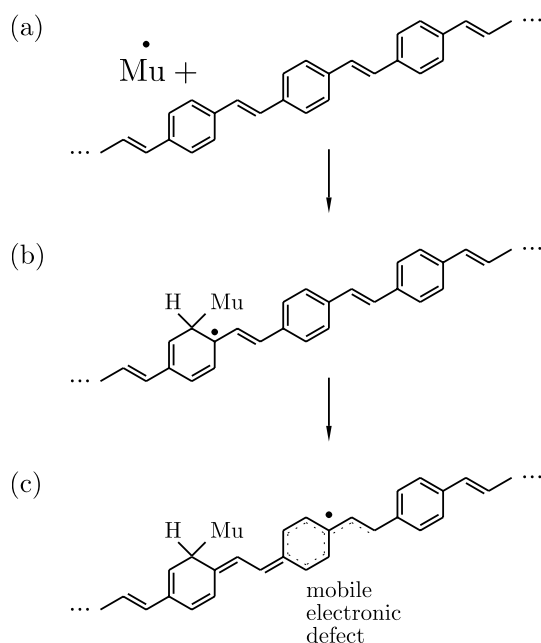


Figure 2. Schematic diagram showing muon implantation in PPV. (a) Muonium adds to PPV to produce (b) a muonated radical. This injected electronic excitation can diffuse along the chain as a polaron and is thus (c) a mobile electronic defect.

with that particular magnetic field B , where γ_μ is the muon gyromagnetic ratio. Sweeping the magnetic field allows one to extract the frequency distribution of the fluctuations.

Polaronic motion in doped conducting polymers can be measured using NMR and ESR [19]; for these techniques the motional linewidth contributions are proportional to the carrier density and so measurements on PPV-based polymers are restricted to doped materials (see e.g. [20]). Muons are uniquely sensitive to polaron transport in undoped materials [16] (in which there is no significant carrier density to provide an NMR or ESR signal). In contrast to transport experiments, which provide results which are inevitably dominated by the slowest component of the transport process, muon measurements can provide information on the intrinsic transport processes governing the mobility of an electronic excitation along a chain. In PPV-based polymers, as in polyaniline, the defect is likely to be a polaron.

2. Experimental details

Our experiments were performed on the EMU beamline at the ISIS facility. Initial experiments were performed on the π M3 beamline at the PSI facility. In all our experiments positrons are detected by scintillation counters which are positioned in front of and behind the sample with respect to the initial muon momentum direction. The μ SR function $G(t)$ (also known as the asymmetry) is defined by $G(t) = [N_B(t) - \alpha N_F(t)]/[N_B(t) + \alpha N_F(t)]$, where $N_B(t)$ and $N_F(t)$ represent the number of positron counts in the backward and forward detectors respectively as a function of time; α is an experimental calibration constant which is usually close to unity.

Long side chains can be added to PPV in order to produce PPV derivatives that are soluble and are thus solution processible. The long side chains keep the polymer backbones apart and this can have a beneficial effect on the polymer's fluorescence and

electroluminescence quantum yields [5]. Samples of two PPV-based polymers [21, 22], poly(2, 3-dibutoxy-1, 4-phenylene vinylene) (abbreviated henceforth to DB-PPV [23]) and poly(2, 5-bis(dimethyloctylsilyl)-1, 4-phenylene vinylene) (abbreviated henceforth to BDMOS-PPV [24]), were each wrapped in a 25 μm silver foil and mounted on a silver backing plate in the cryostat. Silver is used because it gives a non-relaxing muon signal, and hence only contributes a temperature-independent constant to $G(t)$. A preliminary analysis of the data for DB-PPV was reported earlier [25].

3. Risch–Kehr model

The measured muon relaxation data were fitted using the theory of Risch and Kehr [26] for a muon interacting through hyperfine coupling ω_0 to the spin density on the chain site to which it is bonded (this is illustrated in figure 3). In this model, when the hyperfine coupling is switched on, the muon electron system evolves according to a Hamiltonian given by

$$\mathcal{H} = \frac{\hbar}{4}\omega_0\boldsymbol{\sigma} \cdot \boldsymbol{\tau} - \frac{\hbar}{2}\omega_\mu\sigma_z + \frac{\hbar}{2}\omega_e\tau_z \quad (1)$$

where $\boldsymbol{\sigma}$ and $\boldsymbol{\tau}$ are the Pauli spin matrices for the muon and electron respectively, $\omega_e = \gamma_e B$ is the electron Larmor frequency and γ_e is the electron gyromagnetic ratio. When the hyperfine coupling is switched off, the electron and muon spins are decoupled and separately evolve according to the Zeeman terms in the Hamiltonian. In addition, the electron spin is subject to random spin-flips at a rate λ . The fluctuating spin density induced by an electronic spin defect rapidly diffusing up and down the one-dimensional chain leads to a relaxation function of the form $G(t) = \exp(\Gamma t)\text{erfc}(\sqrt{\Gamma t})$ for $\lambda t_{\text{max}} \gg 1$, with erfc signifying the complementary error function, t_{max} the experimental timescale and Γ a relaxation parameter. For $D_{\parallel} > \omega_0 > \lambda$, Γ has an inverse magnetic field dependence given by

$$\Gamma = \frac{\omega_0^4}{2\omega_e D_{\parallel}^2}. \quad (2)$$

The delocalization of the electronic defect in the neighbourhood of the attached muonium is not known, but a neutral spin- $\frac{1}{2}$ defect is believed to be delocalized over six lattice constants in finite-*trans* polyacetylene on the basis of calculations [27]. In the Risch–Kehr model, the Brownian motion of an extended defect is replaced by an effective hopping process of a localized defect [26].

4. Results

μSR data for DB-PPV are shown in figure 4 for two temperatures and are well fitted by the following relaxation function:

$$G(t) = a_0 + a_1(B) \exp(\Gamma(B)t) \text{erfc}(\sqrt{\Gamma(B)t}), \quad (3)$$

where a_0 is a constant, $a_1(B)$ is a field-dependent relaxing amplitude and $\Gamma(B)$ is a field-dependent Risch–Kehr relaxation parameter. The raw data shown in figure 4 demonstrate that the relaxation has a rich field and temperature dependence. The figure also shows the increase in initial asymmetry as a function of field which is due to the repolarization of the muonium states [28].

The field dependence of $\Gamma(B)$ at two temperatures is shown in figure 5. The relationship $\Gamma(B) \propto 1/B$, indicative of intrachain diffusion, holds at high field at both low and high temperature. However at low field there is a crossover to a three-dimensional diffusion regime

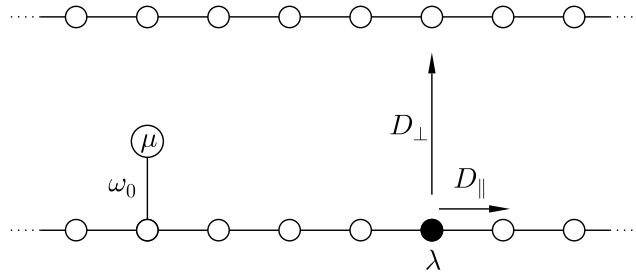


Figure 3. Schematic diagram of the polaron diffusion model used in the text which is based on that of Risch and Kehr but including interchain diffusion (after [17]). The muon interacts through hyperfine coupling ω_0 to the spin density on the chain site to which it is bonded. The electronic spin defect (black filled circle) rapidly diffuses up and down the chain with intrachain and interchain diffusion rate D_{\parallel} and D_{\perp} respectively. λ is the electron spin flip rate, assumed faster than the reciprocal of the experimental timescale.

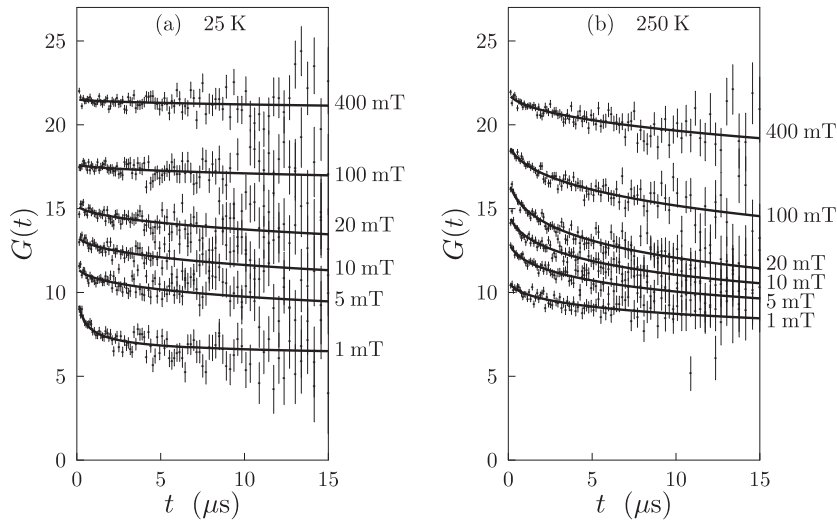


Figure 4. μ SR data in DB-PPV at (a) 25 K and (b) 250 K for a range of longitudinal magnetic field values. The solid curves are fits to equation (3).

which occurs when the electron Larmor frequency becomes smaller than D_{\perp} [16]. This is clearly observable in the high temperature data, demonstrating that D_{\perp} increases with increasing temperature. When the applied field is below ~ 1 mT, 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 is difficult to separate from the paramagnetic relaxation with any degree of accuracy.

In order to calculate the intrachain diffusion rate we take a value for the hyperfine coupling $\omega_0 = 2\pi \times 450$ MHz, as estimated from the longitudinal decoupling field of the initial muon asymmetry [28]. The high field $\Gamma(B)$ is fitted for each temperature to the expression $\Gamma(B) = \omega_0^4 / 2\gamma_e B D_{\parallel}^2$ and D_{\parallel} extracted. The resulting estimate of the intrachain diffusion rate D_{\parallel} is shown in figure 6. It shows a temperature dependence which is suggestive of phonon-limited metallic-style transport, as found in μ SR studies of polyaniline [16]. These data are fitted well by a simple model for the transport in which $D_{\parallel} \propto (\Sigma_0 + \Sigma_r)^{-1}$ where Σ_0 is a

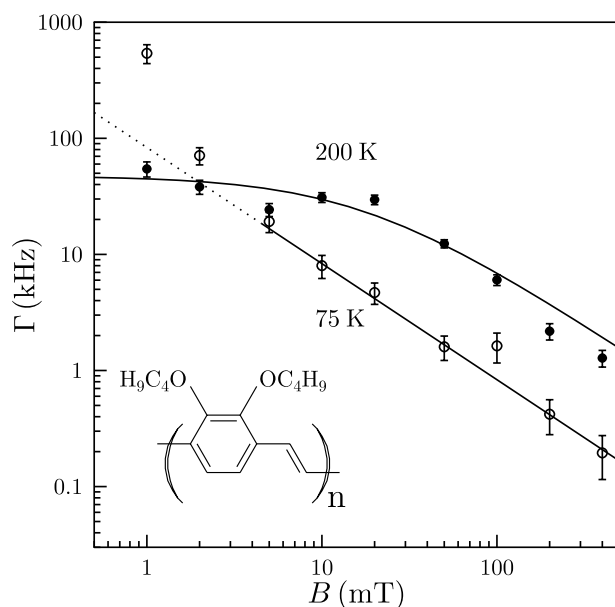


Figure 5. Field dependence of the RK relaxation rate in DB-PPV for two temperatures. The inset shows the chemical structure of DB-PPV.

temperature-independent scattering term and Σ_r is a phonon scattering term proportional to the number of modes excited, so that it is proportional to $(\exp(E_r/k_B T) - 1)^{-1}$. A scattering contribution proportional to phonon number is expected in theories of phonon-limited polaron transport [29, 30]. The energy of the phonon mode is thus estimated to be 22(1) meV. This is in agreement with a mode associated with whole chain librations or mixed chain torsions and ring librations which has been observed in inelastic neutron scattering of pure PPV [31]. A similar mode was found in an earlier experiment on polyaniline [16].

The field B_c , at which crossover to a three-dimensional diffusion regime is observed, can be used to estimate the interchain diffusion rate $D_{\perp} \approx \gamma_e B_c$ and this is shown in the inset to figure 6. This is estimated by fitting $\Gamma(B)$ to a phenomenological functional form proportional to $(1 + B/B_c)^{-1}$ [16]. A crossover is only observed for $T \geq 175$ K; below this temperature D_{\perp} must be undetectably small, i.e. much less than 10^9 rad s $^{-1}$. As found in polyaniline [16, 17, 33], the interchain transport is assisted by thermal motion, rather than hindered by it.

Results for BDMOS-PPV are shown in figure 7. The values of the intrachain diffusion can be extracted from the high field dependence of $\Gamma(B)$ in an analogous manner and are found to be slightly lower than in DB-PPV at low temperature, although comparable in magnitude at room temperature. The energy of the phonon mode, 11(8) meV, is also lower, though still within the main band of spectral weight (10–30 meV) in the vibrational density of states observed in inelastic neutron scattering of pure PPV [31]. The addition of side-chains will however greatly affect the electronic [32] and vibrational [31] interchain coupling, which is likely to have a marked effect on the vibrational density of states. The crossover to the three-dimensional diffusion regime can also be used to estimate the interchain diffusion (shown in the inset to figure 6) which as in DB-PPV also appears to increase with temperature. Both show an activated temperature dependence as shown in figure 8 with activation energies equal to 130(10) and 21(3) meV for DB-PPV and BDMOS-PPV respectively.

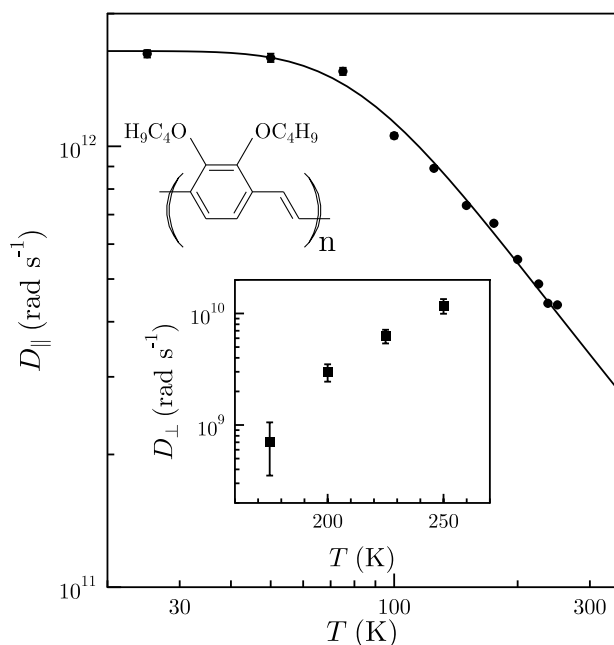


Figure 6. The temperature dependence of the intrachain polaron diffusion rates in DB-PPV derived from the μ SR. The main figure shows D_{\parallel} , and the solid curve is a fit to a simple model of the transport, with a phonon activation energy of 22 meV. The inset shows an estimate of the interchain diffusion rate D_{\perp} .

The value of D_{\parallel} in both polymers can be used to obtain the diffusion constant $\mathcal{D} = D_{\parallel}a^2$, where $a \approx 7 \text{ \AA}$ is the length of the monomer unit, and hence estimate the mobility μ via the Einstein–Smoluchowski relation $\mu = \mathcal{D}/(k_{\text{B}}T/e)$. This gives a value of $\approx 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K in both samples (rising to about $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 30 K for DB-PPV). This is comparable to results obtained using pulse radiolysis time-resolved microwave conductivity measurements on a soluble dialkoxy derivative of PPV; these gave a value for the intrachain electron mobility of $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature [34]. The obtained mobilities using μ SR and pulse radiolysis are several orders of magnitude larger than those obtained using time-of-flight measurements [35–37], current–voltage measurements [38, 39] and admittance spectroscopy [40], techniques which are much more influenced by domain and grain boundaries and the presence of deep trapping sites [41]. A large intrinsic mobility of up to $0.1\text{--}10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K has also been found within nanometre-sized regions using voltage-modulated millimetre-wave spectroscopy [42], demonstrating that the mobility of PPV can locally be very high. The size of these high mobility regions is found to increase with increasing electric field, increasing the overall mobility, although the millimetre-wave experiments were not performed in electric fields below $40 \text{ V } \mu\text{m}^{-1}$ (at which point the mobility is $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Our measurements probe the intrinsic mobility locally and are performed in zero electric field, so that our value of $\approx 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ appears to be consistent with these results.

5. Conclusion

In conclusion, we have used implanted positive muons to probe the anisotropic diffusion of negative polarons in DB-PPV and BDMOS-PPV. The intrachain diffusion is controlled by scattering from librational and torsional modes; this scattering hinders intrachain transport but promotes interchain transport.

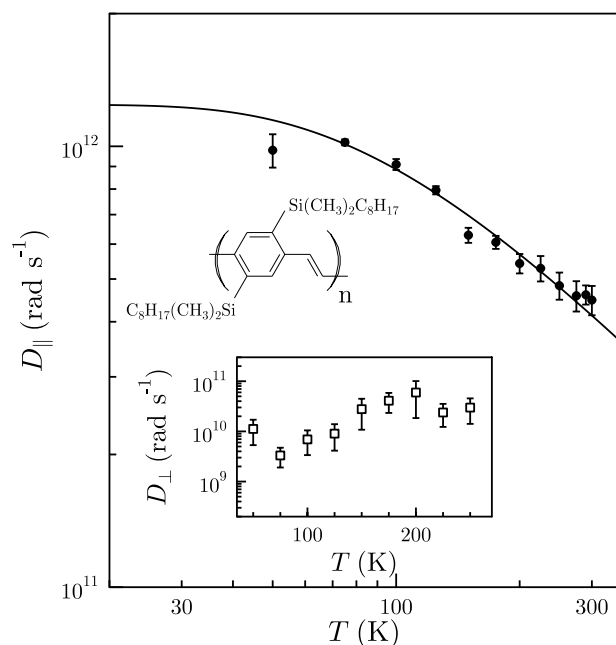


Figure 7. The temperature dependence of the intrachain polaron diffusion rates in BDMOS-PPV derived from the μ SR. The main figure shows D_{\parallel} , and the solid curve is a fit to a simple model of the transport, with a phonon activation energy of 11 meV. The inset shows an estimate of the interchain diffusion rate D_{\perp} .

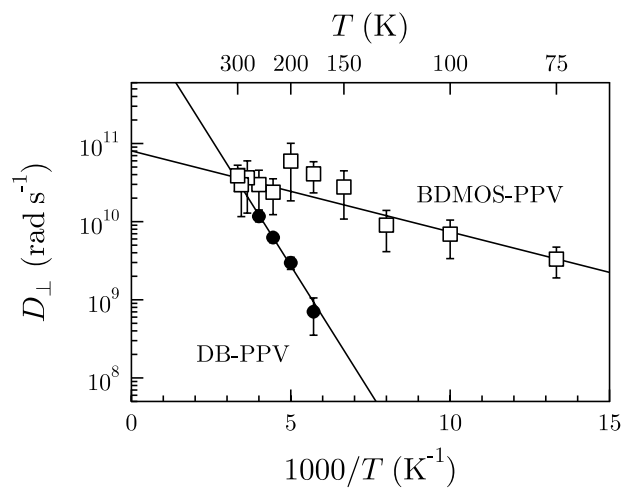


Figure 8. The temperature dependence of the interchain polaron diffusion rates in DB-PPV and BDMOS-PPV. The fitted activation energies are 130(10) and 21(3) meV.

Acknowledgments

We thank the EPSRC (UK) for financial support and the staff of the ISIS and PSI muon facilities for experimental assistance. SJB is grateful to the Nuffield Foundation. We thank L D A Siebbeles and S F J Cox for stimulating discussions.

References

- [1] Heeger A J 2001 *Rev. Mod. Phys.* **73** 681
- [2] MacDiarmid A G 2001 *Rev. Mod. Phys.* **73** 701
- [3] Burroughes J H, Bradley D D C, Brown A R, Marks R N, Mackey K, Friend R H, Burn P L and Holmes A B 1990 *Nature* **347** 539
- [4] Friend R H *et al* 1999 *Nature* **397** 121
- [5] Kraft A, Grimsdale A C and Holmes A B 1998 *Angew. Chem. Int. Edn.* **37** 402
- [6] Davis W B, Svec W A, Ratner M A and Wasielewski M R 1998 *Nature* **396** 60
- [7] Cox S F J 1987 *J. Phys. C: Solid State Phys.* **20** 3187
- [8] Dalmas de Réotier P and Yaouanc A 1997 *J. Phys.: Condens. Matter* **9** 9113
- [9] Blundell S J 1999 *Contemp. Phys.* **40** 175
- [10] Nagamine K, Ishida K, Matsuzaki T, Nishiyama K, Kuno Y and Yamazaki T 1984 *Phys. Rev. Lett.* **53** 1763
- [11] Pratt F L, Hayes W, Mitchell G R, Rossi B, Kiani M S, Malhotra B D, Pandey S S, Milton A and Monkman A P 1993 *Synth. Met.* **55** 677
- [12] Hayes W 1995 *Phil. Trans. R. Soc. A* **350** 249
- [13] Jestädt Th, Sivia D S and Cox S F J 1997 *Hyperfine Interact.* **106** 45
- [14] Pratt F L, Valladares R M, Pattenden P A, Blundell S J, Hayes W, Fisher A J, Monkman A P, Malhotra B D and Nagamine K 1995 *Synth. Met.* **69** 231
- [15] Pratt F L, Ishida K, Nagamine K, Pattenden P A, Jestädt T, Chow K H, Blundell S J, Hayes W and Monkman A P 1997 *Synth. Met.* **84** 943
- [16] Pratt F L, Blundell S J, Hayes W, Ishida K, Nagamine K and Monkman A P 1997 *Phys. Rev. Lett.* **79** 2855
- [17] Pratt F L *et al* 2000 *Physica B* **289** 612
- [18] Pratt F L, Blundell S J, Pattenden P A, Hayes W, Chow K H, Monkman A P, Ishiguro T, Ishida K and Nagamine K 1997 *Hyperfine Interact.* **106** 33
- [19] Mizoguchi K 1995 *Japan. J. Appl. Phys.* **34** 1
- [20] Mizoguchi K 2001 *Synth. Met.* **199** 35
- [21] Martin R E, Geneste F, Riehn R, Chuah B S, Cacialli F, Friend R H and Holmes A B 2000 *Chem. Commun.* 291
- [22] Martin R E, Geneste F, Riehn R, Chuah B S, Cacialli F, Holmes A B and Friend R H 2001 *Synth. Met.* **119** 43
- [23] Chuah B S, Cacialli F, dos Santos D A, Feeder N, Davies J E, Moratti S C, Holmes A B, Friend R H and Brédas J L 1999 *Synth. Met.* **102** 935
- [24] Chu H Y, Hwang D-H, Do L-M, Chang J-H, Shim H-K, Holmes A B and Zyung T 1999 *Synth. Met.* **101** 216
- [25] Blundell S J, Pratt F L, Marshall I M, Husmann A, Hayes W, Martin R and Holmes A B 2001 *Synth. Met.* **119** 205
- [26] Risch R and Kehr K W 1992 *Phys. Rev. B* **46** 5246
- [27] Boudreaux D S, Chance R R, Brédas J L and Silbey R 1983 *Phys. Rev. B* **28** 6927
- [28] Pratt F L 1997 *Phil. Mag. Lett.* **75** 371
- [29] Jeyadev S and Conwell E M 1987 *Phys. Rev. B* **35** 6523
- [30] Maki K 1982 *Phys. Rev. B* **26** 2181
- [31] Papanek P, Fischer J E, Sauvajol J L, Dianoux A J, Mao G, Winokur M J and Karasz F E 1994 *Phys. Rev. B* **50** 15 668
- [32] Gomes da Costa P, Dandrea R G and Conwell E M 1993 *Phys. Rev. B* **47** 1800
- [33] Pratt F L, Blundell S J, Lovett B W, Nagamine K, Ishida K, Hayes W, Jestädt T and Monkman A P 1999 *Synth. Met.* **101** 323
- [34] Hoofman R J O M, de Haas M P, Siebbeles L D A and Warman J M 1998 *Nature* **392** 54
- [35] Meyer H, Haarer D, Naarman H and Hörhold H H 1995 *Phys. Rev. B* **52** 2587
- [36] Lebedev E, Dittrich Th, Petrova-Kpoch V, Karg S and Brütting W 1997 *Appl. Phys. Lett.* **71** 2686
- [37] Hertel D, Bäessler H, Scherf U and Hörhold H H 1999 *J. Chem. Phys.* **110** 9214
- [38] Lee C H, Yu G, Moses D and Heeger A J 1994 *Phys. Rev. B* **49** 2396
- [39] Bozano L, Carter S A, Scott J C, Malliaras G G and Brock P J 1999 *Appl. Phys. Lett.* **74** 1132
- [40] Martens H C F, Huiberts J N and Blom P W M 2000 *Appl. Phys. Lett.* **77** 1852
- [41] Antoniadis H, Abkowitz M A and Hsieh B R 1994 *Appl. Phys. Lett.* **65** 2030
- [42] Martens H C F, Hilt O, Brom H B, Blom P W M and Huiberts J N 2001 *Phys. Rev. Lett.* **87** 086601