Muon spin relaxation study of spin dynamics in poly(triarylamine)

Jing He [a,b], Jinglei Du [a,b], Theo Kreouzis [c], Francis L. Pratt [d], James S. Lord [d], Mark T.F. Telling [d], Alan J. Drew [a,c], Nicola A. Morley [e,*], Maureen Willis [a,b,**]

[a] College of Physical Science and Technology, Sichuan University, Chengdu, Sichuan 610064, PR China
[b] Sino-British Materials Research Institute, Sichuan University, Chengdu, Sichuan 610064, PR China
[c] School of Physics and Astronomy, Queen Mary, University of London, Mile End, London E14NS, UK
[d] ISIS Muon Facility, Rutherford Appleton Laboratory, Didcot OX11 0QX, UK
[e] Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, UK

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ABSTRACT

Organic semiconductors (OSCs) have been of great interest over the last couple of decades on account of their mechanical flexibility, ease of processing and high tunability as well as being readily available. Polymers, in particular, possess the two desirable properties, print processing and electronic tunability. These properties are both necessary for the application of these materials in devices such as organic solar cells and spin valves being engineered for hard disks and logic devices. Much focus in recent years has been given to researching electron and hole dynamics, transport mechanisms and spin relaxation in order to utilise these OSCs in novel organic devices. Here the μSR technique is applied to perform an in depth study of the electron dynamics and spin relaxation in the commonly used poly(triarylamine) polymer (PTAA). Strong evidence shows that the electron wave function can be considered localised to the aromatic rings giving rise to a strong hyperfine coupling interaction with the attached muon. Additionally, an electron spin relaxation (eSR), similar to that previously reported in the small organic molecule series (in the order of $0.25\,\mu s^{-1}$), is shown to exist with a value of $0.31\,\mu s^{-1}$ at room temperature.

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1. Introduction

Organic semiconductors (OSCs) have been of great interest over the last couple of decades owing to their mechanical flexibility, ease of processing, high tunability and availability. Indeed, they are now used in a wide range of applications including Organic LED television and mobile phone screens, RFIDs and Solar cells [1–16]. One area of OSCs of increasing interest is polymers as they possess many of the desirable properties, most importantly print processing and tunability of the electronic properties. These are both necessary for application in devices such as organic solar cells and spin valves being engineered for hard disks and logic devices [17–20]. Despite their availability on the commercial market, a number of fundamental properties are still not fully understood. In order to integrate them in to organic spintronics, a detailed understanding of their spin properties is crucial. To fully realise their potential the charge carrier transport requires further understanding and optimisation. Consequently, much focus has been given in recent years to researching electron and hole dynamics, transport mechanisms and spin relaxation in OSCs in order to utilise them in novel organic devices [21]. Two devices of particular interest for their impact on commercial energy production and computing technology are organic solar cells and spinvalves. In the case of organic solar cells high efficiencies are necessary to become economically viable, whilst spin valves require good spin transport to integrate the spin property of the charge carriers. These processes all depend on the charge transport and mobility of the organic materials, therefore bringing about detailed studies of these properties in the polymers used in such devices.

One of the many challenges is finding a suitable technique to measure these fundamental properties with some of the current methods for determining mobility and spin relaxation time being magnetoresistance and time of flight measurements [15,22,23]. However, such techniques include additional effects from the contacts, interfaces and bottlenecks in the devices being measured. Muon spin relaxation (μSR) has recently been shown as a crucial technique in the study of electron spin relaxation (eSR) in OSCs [24–27]; offering a unique way to study the electron dynamics in organic systems without the effects described above. The

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* Corresponding author.
** Corresponding author at: College of Physical Science and Technology, Sichuan University, Chengdu, Sichuan 610064, PR China. Tel.: +86 15528065560.
E-mail addresses: n.a.morley@sheffield.ac.uk (N.A. Morley), m.willis@scu.edu.cn (M. Willis).

μSR research in small organic molecules [24,25] and polymers [26,27] has already shown the ability to probe both inter and intra-molecular interactions of eSR as well as electron dynamics in both bulk materials and devices. Indeed it was recently revealed that an additional intra-molecular eSR exists in the small organic molecule systems [24]. This relaxation is mediated by the spin orbit interaction, which previously was thought not to play a significant role, as the hyperfine interaction was understood to be stronger in these systems. However, both interactions are relatively weak. An obvious question is whether polymers exhibit the same types of electron dynamics and relaxation processes as small molecules or if different mechanisms are at play.

Here the μSR technique is applied to carry out an in depth study of the electron dynamics and spin relaxation in the commonly used poly(triarylamine) polymer (PTAA). It is shown that the electron wave function can be considered localised to the aromatic rings providing a strong hyperfine coupling interaction with the muon. In addition an eSR is shown to exist with a value of 0.31 μs^{-1} at room temperature and is comparable to the value previously reported in the small organic molecule series of 0.25 μs^{-1}.

2. Experimental methods

In a typical μSR experiment, 100% spin polarised positively charged muons are implanted into a sample. Once inside the sample, the muon's kinetic energy is firstly reduced to a few keV via inelastic scattering processes. Then a proportion of the muons capture an electron from a molecule forming a hydrogen like species, called muonium. Muonium can then bind to a molecule to form a muoniated radical. A key point to understand is that during the thermalisation process the muon spin polarisation is preserved. The muons then decay into a positron, muon-antineutrino and an electron-neutrino. As a result of the particle decay cross section there is an asymmetry of the positron emission, for which the direction depends on the orientation of the muon spin at the instant of the decay. The spatial distribution of the positron emission is governed by the equation

$$dW(\epsilon, \theta) = \frac{e^{t/\tau_\mu}}{\tau_\mu}[1 + a(\epsilon)\cos\theta]n(\epsilon)d\epsilon d\cos\theta \, dt$$

where $a(\epsilon) = (2\epsilon - 1)/(3 - 2\epsilon)$, $n(\epsilon) = 2\epsilon^2(3 - 2\epsilon)$ and the reduced positron energy ϵ is defined as $\epsilon = E/E_{max}$, where E_{max} is the maximum positron energy $E_{max} = 52.83$ MeV. It is thus possible to place a series of detectors around the sample environment that are capable of detecting the positron emission direction. Hence, it is possible to track the evolution of the muon's spin as a function of time. In the case of the ALC measurements reported here the measurement is carried out under a longitudinal applied magnetic field (parallel to the muons spin) with detectors at the front and back of the sample environment. The asymmetry between the detectors then contains all the necessary spin relaxation information and is given by

$$A(t) = A_0 P(t)$$

A weighted average of this time dependant signal is then taken to obtain a single asymmetry point for each field. In the case of organic semiconductors, a majority of the muons are in a stable bound state with an electron, i.e. the muonium. The muon and electron spins are coupled by the hyperfine (HF) interaction, which can be either isotropic or anisotropic. As mentioned above in an organic sample, the muonium can form a bond with the molecules in the last step of the thermalisation process, joining a molecule at a site with high electron concentration, such as the aromatic rings present in the PTAA. The degree of localisation of the electron's wave function, determines the value of the HF constant to the muon, and can vary by a significant amount between different muon adduct

sites, even those next to each other on the same molecule. Hence, the HF coupling constant strongly varies between sites, however, it can be readily calculated using Density Functional Theory (DFT) [28]. The more localised the wave function the higher the HF constant. As well as the isotropic HF coupling constant, there can also be an anisotropic HF interaction between the muon and electron. The energy eigenvalues of the resultant muonium system are given by the following equations and have both a triplet and singlet component [29].

$$E_1 = \frac{\hbar}{4}[A + 2B(\gamma_e - \gamma_\mu)],$$

$$E_2 = \frac{\hbar}{4}\left[A - 2B\sqrt{A^2 + B^2(\gamma_e + \gamma_\mu)}\right],$$

$$E_3 = \frac{\hbar}{4}[A - 2B(\gamma_e - \gamma_\mu)],$$

$$E_4 = \frac{\hbar}{4}\left[A + 2B\sqrt{A^2 + B^2(\gamma_e + \gamma_\mu)}\right].$$

It can easily be shown using a spin density matrix formulism that the energy levels undergo a level crossing at a field determined by the isotropic hyperfine interaction. Furthermore this becomes an avoided level crossing (i.e. an ALC) in the presence of cross relaxation effects arising from additional spins. At a given field corresponding to the ALC a depolarisation of the muon spin occurs, and gives rise to the observed ALC resonances, even in the absence of electron spin relaxation (eSR) [30,31]. Since the spins of the electron and of the muon in muonium are coupled, if an eSR mechanism is effective in the material it causes a further relaxation of the muon spin through spin flip and/or dephasing processes. It is shown in much literature that this is detected in the ALC as an increase in amplitude without significant change to the shape or width of the resonance [25,32] (more detailed information about the technique is reported in Ref. [32] and the Supplemental Material of Ref. [24]). A quantitative estimation of the eSR at room temperature can be obtained by modelling of the ALCs via the "Quantum" software and the method well documented in the literature [25,32,33].

The HiFi spectrometer at ISIS (Rutherford Appleton Laboratory, Oxford UK) was used to perform all the μSR measurements and the sample was mounted in a 20 mm × 20 mm silver (99.9% pure) 25 μm foil packet in the solid form.

3. Results and discussion

In order to establish the possible muon adduct sites, the ALCs for a monomer unit of PTAA were firstly calculated using DFT. The calculation is performed by first carrying out a semiemperical unrestricted Hartree-Fock PM3 optimisation of the monomer unit. This allows for a much better relaxation of the crystal structure addressing some of the solid state effects that pose a challenge in such calculations. This crystal geometry is then used in a DFT calculation to obtain the HF coupling constants for each adduct position and spin distribution across the molecule. The exchange and correlation functional B3LYP is used in conjunction with a standard 6-31G Gaussian basis set with no additional functions. The results in previous literature have shown this to be accurate to within 1–5%. The results of the calculations are shown in Fig. 1. The first point to observe is that the monomer unit of PTAA has ten possible adduct sites to which the muon in the form of muonium can join. In addition, at each site the two positional conformations (above and below the plane of the aromatic ring) are non-equivalent, hence doubling the adduct site possibilities to 20 in total. Each of these has a corresponding ALC shown in Fig. 1. Another feature to note is that the calculated ALCs are very close for some of the sites. The consequence of this is that these ALCs may be unresolvable within the limitations of the technique and instead present as an individual