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He, J., Du, J., Kreouzis, T. et al. (2015) Muon spin relaxation study of spin dynamics in poly(triarylamine). Synthetic Metals, 208. pp. 21-25. ISSN: 0379-6779

https://doi.org/10.1016/j.synthmet.2015.05.010

Muon Spin Relaxation Study of Spin Dynamics in Poly(triarylamine)

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Abstract

Organic semiconductors (OSCs) have been of great interest over the last couple of decades owing to their mechanic flexibility, ease of processing, high tuneability and availability. One area of OSCs that is of growing interest is polymers as they possess many of the desirable properties, in particular print processing and tunability of electronic properties, necessary for application in devices such as organic solar cells and the spin valves being engineered for hard disks and logic devices. Much focus has been given in recent years to the areas of research including the electron and hole dynamics, transport mechanisms and spin relaxation in OSCs in order to utilise them in novel organic devices. In this paper 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 wavefunction can be considered localised to the aromatic rings providing a strong hyperfine coupling interaction with the muon. In addition the presence of an electron spin relaxation (eSR) is demonstratated that resembles that previously reported in the small organic molecule series.

Keywords: Organic semiconductors, Polymers, Spin relaxation, Spintronics, MuSR

1. Introduction

Organic semiconductors (OSCs) have been of great interest over the last couple of decades owing to their mechanic flexibility, ease of processing, high tuneability 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 that is of growing interest is polymers as they possess many of the desirable properties, in particular print processing and tunability of electronic properties, necessary for application in devices such as organic solar cells and the spin valves being engineered for hard disks and logic devices [17–20]. Despite their availability on the commercial market there still remain some fundamental properties of these materials that need to be understood. In order to integrate them in to orgainc spintronics a detailed understanding of their spin properties is needed. Furthermore to fully realise their potential the charge carrier transport needs to be understood further and optimised. Consequently, much focus has been given in recent years to the areas of research including the electron and hole dynamics, transport mechanisms and spin relaxation in OSCs in order to utilise them in novel organic devices. 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 required to become economically viable, while 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 so consequently the properties of the polymers used in such devices are being studied in great detail.

One of the challenges is finding a suitable technique to measure these fundamental properties with some of the current methods including magnetoresistance and time of flight measurements. However such techniques include additional effects from the contacts, interfaces and bottlenecks in the devices being measured. Muon

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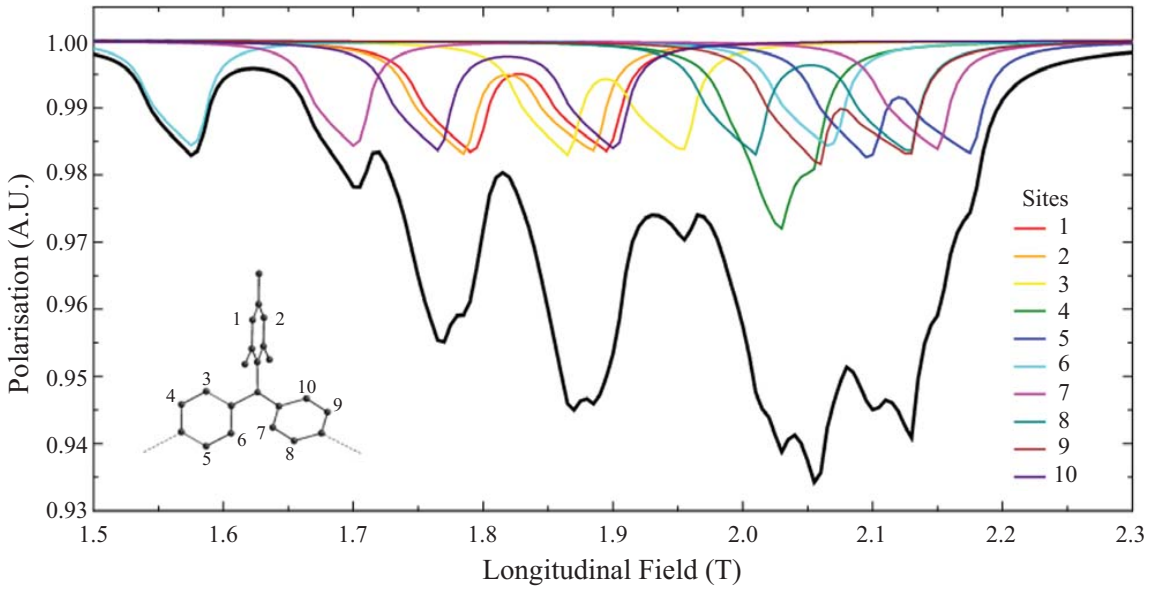

Figure 1: DFT calculated ALC resonances for PTAA monomer unit and inset: PTAA structure and site allocation.

Spin Relaxation (μSR) has recently been shown as a crucial technique in the study of electron spin relaxation in OSCs [21–24], offering a unique way to study the electron dynamics in organic systems without the effects described above. The μSR research in small organic molecules [21, 22] and polymers [23, 24] has already shown the ability to probe both inter and intra-molecular interactions of the electron spin relaxation and dynamics in both bulk materials and devices. Indeed it was recently revealed that an additional intra-molecular electron spin relaxation exists in the small organic molecule systems [21]. This relaxation is mediated by the spin orbit interaction, which was previously thought not to play a significant role as the hyperfine interaction was understood to be stronger in these systems, although 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.

In this paper 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 wavefunction can be considered localised to the aromatic rings providing a strong hyperfine coupling interaction with the muon. In addition the presence of an electron spin relaxation (eSR) is demonstratated that is similar to that previously reported in the small organic molecule series.

2. Experimental Methods

In a typical μSR experiment 100% spin-polarized muons are implanted into the OSC. During the thermalisation process, 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. In an Avoided Level Crossing (ALC) experiment a magnetic field is applied parallel to the initial muons spin direction. At a particular value of the magnetic field, due to cross relaxation effects, a depolarisation of the muon spin occurs, and gives rise to the observed ALC resonances, even in the absence of eSR [25, 26]. Since the spins of the electron and of the muon in Muonium are coupled, if an electron spin relaxation mechanism is effective in the material it causes a further relaxation of the muon spin. This is detected as an increase in amplitude of the ALC resonance [22, 27] (more detailed information about the technique is reported in Ref. [27] and the Supplemental Material of Ref. [21]). A quantitative estimation of the eSR at room temperature can be obtained by modelling of the ALCs as described in the literature [22, 27, 28]. At lower fields (in the region called the repolarisation region) the time resolved polarisation spectra can be fitted with a relaxation function to extract the muon spin relaxation rates. Studied as a function of field these relaxation rates can be modelled to extract the diffusion rates and hence mobilities, via the Einstein relation, both along and between the polymer chains in

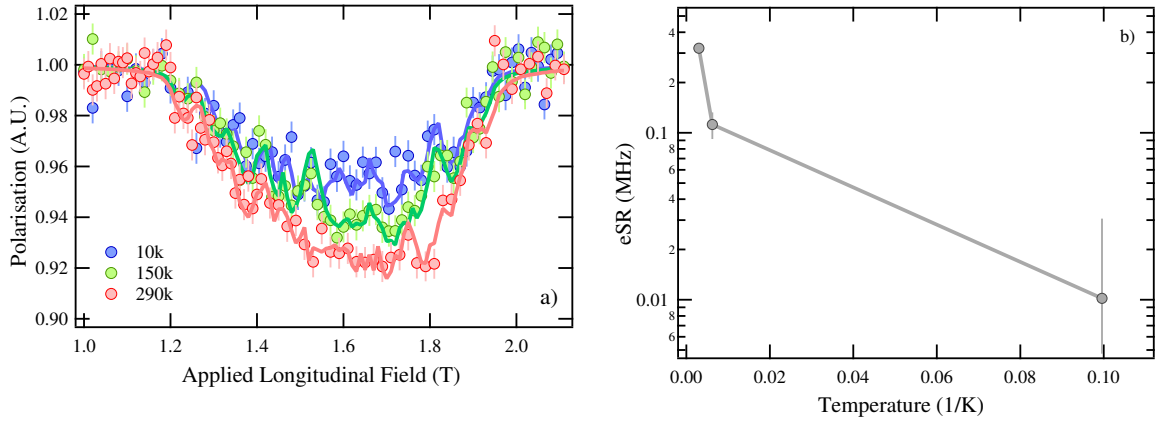

Figure 2: a)ALC resonances for PTAA n=10 at 10 K, 150 K and 290 K (modelling solid lines) and b) eSR as function of temperature on Arrhenius scale.

the sample. The μSR measurements were all carried out on the HiFi instrument at ISIS in a Longitudinal Field setup. The samples are packed in to 25 m silver foil packets, 25X25 mm in dimension, and mounted on to a solid Aluminium sample holder with 1 additional layer of silver foil to act as a degrader. At high fields (5000-20000G), the avoided level crossing (ALC) resonance was measured for the as-purchased PTAA. All data was taken at temperatures between 10K and 300K.

3. Results and Discussion

It was mentioned earlier that a large amount of research on the electron spin relaxation (eSR) in the small molecule AlQ3 with MuSR has been carried out [21, 22, 27]. Although PTAA is a polymer, its monomer unit, as shown in the inset of Figure 1 is quite similar to that of ALQ3 and it therefore may be expected to exhibit similar eSR properties. Owing to its similarity in structure, PTAA can provide a useful first step system between small molecules and polymers. For this reason the same MuSR measurements were performed on the PTAA system to provide a suitable comparison.

In order to establish the possible muon adduct sites, the ALCs for a monomer unit of PTAA were calculated using Density Functional Theory (DFT), the results of which are shown in Figure 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 position 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 Figure 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 resolution of the technique and instead present as an individual broader ALC. Such a consequence would affect the dipolar coupling values in the modeling. Another result of the many sites is the entire width of the ALC is very broad as shown in Figure 1.

Figure 2a shows the measured ALC data at three temperatures (10 K,150 K and 290 K) for the PTAA sample. The first point to note is the position of the ALC, which is relatively high at 1.75 T. This field position corresponds to isotropic hyperfine coupling constants in the region of those observed by Roduner et al. in their study of Benzene. In this case the strong localisation of the wavefunction to the aromatic ring and hence the muon radical site produces such high couplings and consequently high field values [29]. This is in agreement with the calculated values from the DFT and would suggest that indeed in the PTAA the wavefunction is confined to the aromatic rings on the monomer units where the muon adduct positions are and does not delocalise strongly along the polymer chains. It is worth noting at this point that the DFT calculations are shifted by around 3000G to a higher field. This could be attributed to several factors including the fact that the calculations are performed on a single monomer and do not take in to account the effects of a chain. Also there may be a difference in the thermal factor and quantum factor both of which are included in the calculation and both of which can induce a lateral shift in the ALC field value. The second point of interest is the broad nature of the ALCs. This can be attributed to two factors. Firstly, the effects

Table 1: PTAA n=10 ALC model parameters where A, D and E are in MHz and eSR is in μs^{-1} for 10 K, 150 K and 290 K

	ALC1	**ALC2**	**ALC3**	**ALC4**	**ALC5**	**ALC6**	**ALC7**	**ALC8**	**ALC9**	**ALC10**	**ALC11**
	10K									**Ave. eSR**	0.01
A	332±5	359±5	378±5	394±5	407±5	421±5	441±5	465±5	483±5	505±5	522±5
D	6.0±2	7.0±2	9.0±2	4.0±2	6.0±2	7.0±2	10.0±2	9.0±2	8.0±2	8.0±2	6.0±2
E	6.0±2	7.0±2	9.0±2	4.0±2	6.0±2	7.0±2	10.0±2	9.0±2	8.0±2	8.0±2	6.0±2
eSR	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	150K									**Ave. eSR**	0.11±0.02
A	334±5	355±5	375±5	393±5	405±5	427±5	443±5	465±5	483±5	505±5	522±5
D	6.0±2	7.0±2	9.0±2	4.0±2	7.0±2	8.0±2	10.0±2	9.5±2	8.0±2	8.0±2	6.0±2
E	6.0±2	7.0±2	9.0±2	4.0±2	-5.0±2	8.0±2	10.0±2	9.5±2	8.0±2	8.0±2	6.0±2
eSR	0.05	0.05	0.05	0.10	0.08	0.05	0.08	0.10	0.25	0.10	0.30
	290K									**Ave. eSR**	0.31±0.02
A	335±5	356±5	375±5	393±5	407±5	422±5	442±5	464±5	486±5	504±5	525±5
D	6.0±2	7.0±2	9.0±2	5.0±2	8.0±2	9.0±2	11.0±2	10.0±2	8.0±2	8.0±2	6.0±2
E	6.0±2	7.0±2	9.0±2	5.0±2	5.0±2	9.0±2	11.0±2	10.0±2	8.0±2	8.0±2	6.0±2
eSR	0.50	0.20	0.18	0.15	0.10	0.13	0.25	0.20	0.90	0.15	0.70

of polymer chain folding provide slight variations in the hyperfine coupling frequencies that are not resolvable and hence result in what appears as broadening of the individual ALCs. Secondly, as mentioned above, some of the ALCs are extremely close in position and consequently it is not possible to resolve them within the limitations of the measurement. In this case the ALCs are convoluted and appear as a broader single ALC resonance. In order to ascertain with more certainty the ALC positions future measurements in the transverse field regime can be performed to extract some of the hyperfine couplings. Lastly it is clear that the ALC amplitude is increasing with the increasing temperature. As in the case of the small molecules the width and shape does not appear to change significantly. This would imply that a similar process as the reported eSR is occurring as expected. In order to gain a more qualitative analysis of the eSR the data was modelled for all three temperatures. It is worth noting that whilst it is not possible to model the positions accurately it is possible to model the data sufficiently to extract an initial eSR value to compare with that of the small molecules. In order to achieve reasonable dipolar hyperfine constants a total of 11 ALCs were required to model the data. Reasonable constraints from the DFT results were applied to the modelling to ensure a more accurate eSR was extracted. The amplitude at 10K of the individual ALCs allow for the determination of the scaling factors to be determined. These initial amplitudes are strongly influenced by the muonium formation probabilities, which varies in different samples.

The parameters of each ALC are shown in Table 1 and the results of the modelling are shown as solid lines in Figure 2a. The eSR at 10K is assumed to be 0.01 within the errors of the modelling as the phonons in the system are essentially frozen out and hence there is no resultant effect on the spin orbit interaction. It is immediately clear that the amplitude of each ALC and thus the eSR is indeed increasing with increasing temperature. This is consistent with the eSR reported in the small molecules in which all the ALCs increased wihout any change to the shape or width. This would suggest the same process is occurring in the PTAA polymer. It is also to clear to observe from the modelling parameters that the dipolar couplings do not vary significantly as expected in the case of an eSR effect. In order to compare the result to those reported by Nuccio et al. the element with the highest Z number is taken, which is N in the case of the monomer unit (Z=7). Indeed the eSR in the PTAA is consistent with the results of Nuccio et al suggesting the PTAA polymer has "small molecule like" spin relaxation properties. The eSR as a function of temperature is plotted on an Arrhenius scale in Figure 2b. As there is only three temperatures in the case of the PTAA it is not possible to make a direct comparison of the temperature dependance of the eSR with the small molecules, although initially in the PTAA the dependance would appear non-linear. Further measurements at additional temperatures are required to determine if the eSR in the PTAA does follow an Arrhenius behaviour with two regimes, similar to that reported for the small organic molecules.

4. Conclusions

In this paper it is shown that the monomer unit of PTAA has 20 possible muon adduct sites resulting in a broad ALC resonance. The DFT calculations show that the electron wavefunction is confined to the aromatic rings on the isolated monomer units and does not strongly delocalise along the polymer chain. This is confirmed by the high isotropic hyperfine coupling frequencies obtained for the ALC resonances at the adduct positions. Furthermore, the presence of an additional eSR is determined like that reported in the small molecule series. The eSR value at 290 K is comparible to those previously reported in the study of the spin orbit interaction in small organic molecules. The PTAA monomer unit reflects the AlQ_3 system and can provide a useful stepping stone between polymer and small organic molecule systems in future study.

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