Field and Temperature Dependent Charge Transport Characteristics in Regio-regular Poly(3-octylthiophene-2,5-diyl) Studied by Muon Spin Relaxation

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Abstract. Spin dynamic of regio-regular Poly(3-octylthiophene-2,5-diyl) has been investigated with longitudinal field (LF) muon-spin-relaxation ($\mu$SR) techniques. The LF dependent muon-spin depolarization rate indicates the occurrence of dimensional crossover from one-dimensional intra-chain spin diffusion to three-dimensional inter-chain spin diffusion at 50 K.

1. Introduction

Polythiophene (PT) and its derivative are among the conducting polymers which have been of great research interest due to their chemical and thermal stability [1] as well as their broad applications and possibilities of new applications [2]. They are also easily grafted with side changes for property modifications [3]. In particular, the PT derivative of poly(3-alkylthiophene) (P3AT) has been attracted intensive study because of the effective modification of its properties by variations of the alkyl side-chain length [4]. For instance, conductivity was reported to decrease with increasing alkyl side chain length while stronger luminescence was observed in the case longer chain length [5]. The dependence of hole mobility on the alkyl chain length has also been reported, with the poly(3-hexylthiophene) showing the highest hole mobility among the series of P3AT [6].

We have studied the microscopic and intrinsic charge transport processes in both regio-regular and regio-random poly(3-hexylthiophene-2,5-diyl) (P3HT) by measuring their of longitudinal field (LF) muon-spin-relaxation ($\mu$SR) behaviors [7, 8]. The muonium, being made up of a positive muon and an electron, is readily formed as slows down to a near stop in the sample and picks up an electron from a carbon double bond in the polymer, thereby attaching itself to the carbon atom by sharing the electron. This leaves an unpaired electron at the neighbor carbon atom. Following a rapid electronic and structural relaxation of the surrounding polymer,
a negative polaron, a quasiparticle composed of an unpaired electron plus its accompanying polarization field, is formed. The mobile polaron will move away from its initial site and diffuse up and down the polymer chain, giving rise to intra-chain charge transport, which may or may not be accompanied by inter-chain hopping in the conducting polymer [9, 10, 11]. The experimental results for poly(3-hexylthiophene-2,5-diyl) show that the temperature-dependent charge carrier mobility depends on their regio-regularity and exhibits abrupt change associated with the "transition" from intra-chain diffusion to inter-chain diffusion at 25 K and 50 K for the regio-regular and regio-random samples, respectively [7, 8].

Here, we report the study of intrinsic charge transport processes in the regio-regular poly(3-octylthiophene-2,5-diyl) (P3OT) along and perpendicular to the chain by LF-μSR method. The analysis of the field and temperature dependent effects on the intra-chain hopping mechanism and inter-chain coupling effect in the polymers is performed on the basis of commonly accepted theoretical model. In this connection, the possible chain length effect on the diffusive spin motion in the regio-regular P3AT is also discussed.

2. Experimental

The regio-regular Poly(3-octylthiophene-2,5-diyl) (Sigma-Aldrich) samples were pressed and wrapped in a 25 μm silver foil and mounted on a silver plate in the cryostat for muon measurements. The μSR measurements were performed at temperature varied from 10 K to 300 K in longitudinal magnetic field ranging from 0 to 350 mT using a pulsed positive surface muon beam [12, 13] at the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the UK.

The μSR function known as asymmetry parameter $A(t)$ at a time $t$ is defined as $A(t) = [F(t) - \alpha B(t)]/[F(t) + \alpha B(t)]$, where $F(t)$ and $B(t)$ are total muon events counted by the forward and backward counters, respectively, and $\alpha$ is the calibration factor reflecting the relative counting efficiencies between the forward and backward counters.

3. Results

Asymmetry parameters at various longitudinal magnetic fields are shown in figure 1 for two temperatures of 10 K (a) and 300 K (b). The initial asymmetries in both cases increase monotonously with increasing field as a results of repolarization of the muonium states [14]. In each case, the dynamical variation of the asymmetry parameters display visible field dependencies, while comparison between Fig 1(a) and (b) also shows perceptible temperature effect. In order to obtain the detailed information of polaron diffusion on the polymer chains, all the time spectra were analyzed using the following two-component function:

$$A(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)$$

where $A_1$ and $A_2$ are the initial asymmetries and $\lambda_1$ and $\lambda_2$ are the corresponding depolarization rates associated with the fast and slow components, respectively. The solid line in Figure 1 is the best fit obtained using the diffusion model mentioned above. According to Butler et al. [15], the LF dependence of the dynamical depolarization rate reflects the dimensionality of the spin diffusion. That is, the depolarization rate is proportional to $aH^{-0.5}$ for the one-dimensional intra-chain diffusion and while it is characterized by a $c - bH^{0.5}$ curve for the three-dimensional inter-chain diffusion where $H$ is the applied longitudinal field and $a, b, c$ are constant.

Figure 2 shows the longitudinal-field (LF) dependence of the muon-spin depolarization rate ($\lambda_1$) in regio-regular P3OT at temperatures of 300 K, 75 K, 50 K and 10 K. At the low temperatures below 50 K, the relaxation rate displays $aH^{-0.5}$ field-dependence characteristic of one-dimensional intra-chain diffusion, implying that below 50 K, the charge transport is dominated by mobility along (intra) the polymer chain. Upon increasing the temperature,
Figure 1. The Asymmetry data of regio-regular poly(3-octylthiophene-2,5-diyl) at (a) 10 K and (b) 300 K for various longitudinal magnetic field values. The solid lines are best fits to equation (1).

Figure 2. The longitudinal-field dependence of relaxation rate $\lambda_1$ of regio-regular poly(3-octylthiophene-2,5-diyl) at 300 K, 75 K, 50 K and 10 K. The solid line are the best fit using three-dimensional model (a, b) and one-dimensional model (c, d), respectively.
the charge carrier mobility deviates drastically from one-dimensional intra-chain diffusion and crossover completely to three-dimensional inter-chain diffusion as demonstrated by the well fitted $c = -6H^{0.5}$ field-dependent variation of the relaxation rate. A similar tendency of LF dependent variation of $\lambda_2$ was also observed although the values of $\lambda_2$ are two orders of magnitude smaller than that of $\lambda_1$. The present results have thus revealed the dimensional crossover of charge transport in regio-regular P3OT at 50 K.

Comparing with $\mu$SR data of regio-regular P3HT that shows dimensional crossover at 25 K [7], it is apparent that inter-chain polaron diffusion process in the present case (P3OT), requires the assistance of higher temperature. While an accurate and more thorough explanation of this difference is not available from this experiment, it may nonetheless be related to the difference side chain length in the alkyl. Clearly, longer side chain leads to larger distance between the chains which implies in turn the need of large thermal energy to support the inter-chain hopping process.

4. Conclusion
We have studied the spin dynamics in regio-regular poly(3-octylthiophene-2,5-diyl) by means of LF-$\mu$SR techniques. Our experimental results have revealed a characteristic spin diffusion in one-dimension intra-chain transport at low temperatures below 50 K and in three-dimension inter-chain diffusion at temperatures above 50 K. The present result has thus demonstrated the crossover from one-dimensional intra-chain diffusion to three-dimensional diffusion featuring strong temperature-induced inter-chain hopping effect. In addition comparison of our present result with a previous result also indicated the dependence of side chain length on the dimensional crossover of the charge transport.

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