Abstract. We have carried out longitudinal field (LF) muon-spin-relaxation (μSR) measurements in polythiophene based polymers of Poly(3-hexylthiophene-2,5-diyl) with regio-regular structure to elucidate the intra- and inter-chain hopping mechanisms. The LF dependent muon-spin depolarization rate indicates the occurrence of dimensional crossover from 1 dimensional intra-chain spin diffusion to 3 dimensional inter-chain spin diffusion at 25 K.

1. Introduction
The studies of conducting polymers have been attracting much attention due to many new possibilities for wide ranging and growing applications in many fields such as those for the development of devices combining unique optical, electrical, and mechanical properties [1, 2]. One of the materials being intensively studied is the polythiophene (PT) based polymers. Polythiophene is produced by polymerization of thiophenes, a sulfur heterocycle. Compared with other systems of conducting polymers, the polythiophene forms an important class for reason of its certain practical advantages. For instance, it is easily synthesized and doped with various dopant, it is chemically, thermally and environmentally stable in air and humid environment both in doped and undoped states [3]. It is also easily grafted with side changes for property modifications [4]. As such, it has potential applications for field-effect transistors [1], solar cells, batteries and light-emitting diodes [2].

One of the most notable properties of these materials is their electrical conductivity resulted from the delocalization of π-electrons in the conjugated chain backbone induced via doping. This property is related with the charge carrier transport and its mobility along (intra) and perpendicular (inter) to the polymer chain [5, 6, 7].

So far, the macroscopic electronic transport measurements of PT based polymers have been reported to exhibit strong dependence of the conductivity on their structures. For instance, the conductivity of the polymer depends on its regio-regularity (regio-random or regio-regular). A regio-random copolymer of 3-methylthiophene for example, possesses a conductivity of 50 S/cm, while a more regio-regular copolymer configurations has a higher conductivity of 140 S/cm [8].
Meanwhile, the photo luminescent property of PT is strongly affected by the chain length of its alkyl substituents. Hidayat et al., reported the photoluminescence characteristics of poly(3-alkylthiophene) (PAT) which were influenced by the preparation methods of the thin films and molecular composition of their side chains [4]. However, most of the previous studies on those structural effects were conducted by means of transport measurements and photo luminescent spectroscopic measurements, which did not reveal directly the intrinsic and local effects.

We have studied the microscopic intrinsic charge transport processes in the regio-regular polythiophene based polymers of Poly(3-hexylthiophene-2,5-diyl) along and perpendicular to the chain by means of longitudinal field (LF) muon-spin-relaxation (μSR) method. It is aimed to elucidate the intra-chain hopping mechanism and inter-chain coupling effect, which can be related to the electrical and optical properties of the polymers.

2. **Experimental**

The samples of regio-regular Poly(3-hexylthiophene-2,5-diyl) (RR-P3HT)(Sigma-Aldrich) were pressed and wrapped in a 25 μm silver foil and mounted on a silver plate in the cryostat for muon measurements. The LF-μSR measurements were performed in magnetic field ranging from 0 to 395 mT and at temperature varied from 10 K to 300 K at the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the UK using a pulsed positive surface muon beam.

In this measurement, the muonium, made up of a positive muon and an electron, is readily formed as the muon slows down in the sample and the muonium reacts with the polymer. Following rapid electronic and structural relaxation of the surrounding polymer, a negative polaron, a quasiparticle composed of an electron plus its accompanying polarization field, is formed. The polaron will move away from its initial site and diffuse up and down the polymer chain, giving rise to intra-chain charge transport or hops between chains giving rise to inter-chain charge transport as well in the conducting polymer [9, 10, 11].

3. **Results**

The asymmetry parameter \( A(t) \) at a time \( t \) is defined as \( A(t) = \frac{[F(t) - \alpha B(t)]}{[F(t) + \alpha B(t)]} \), 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. In order to obtain the detailed information of polaron diffusion on the polymers chain, 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 corresponding the depolarization rates associated with the fast and slow components, respectively. According to Butler et al., the LF dependence of the dynamical depolarization rate reflects the dimensionality of the diffusion of the spin-excited state. That is, the depolarization rate is proportional to \( H^{-0.5} \) for 1 dimensional intra-chain diffusion and \( C-H^{0.5} \) for 3 dimensional inter-chain diffusion [12].

Figure 1 shows the longitudinal-field (LF) dependent variation of the raw asymmetry at temperatures of 300 K and 10 K. The solid line is the best fit obtained using the diffusion model mentioned above. Both asymmetries have a field and temperature dependence. The initial asymmetries increase monotonously with increasing field as a results of repolarization of the muonium states [13].

Figure 2 shows the longitudinal-field (LF) dependence of the muon-spin depolarization rate (\( \lambda_1 \)) in RR-P3HT at temperatures of 300 K and 10 K. At the low temperature of 10 K, the relaxation rate displays \( H^{-0.5} \) field dependence characteristic of 1 dimensional intra-chain diffusion, implying that at low temperatures the charge transport is dominated by mobility.
Figure 1. The Asymmetry data of regio-regular Poly(3-hexylthiophene-2,5-diyl) (RR-P3HT) 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-hexylthiophene-2,5-diyl) (RR-P3HT) at 10 K and 300 K.

along (intra) the polymer chain. Upon increasing the temperature to 300 K, the charge carrier mobility deviates drastically from 1 dimensional intra-chain diffusion and changes completely to 3 dimensional inter-chain diffusion as characterized by its field-dependent variation which is relaxation rate well fitted by $C - H_{LF}^{0.5}$ curve at low field regions up to 20 mT. The initial sign of change was actually observed around the low temperature of 25 K. A similar behavior was also observed in the LF dependent variation of $\lambda_2$. However the values of $\lambda_2$ are two order magnitude smaller than that of $\lambda_1$, implying that the contribution of the second component to the muon
spin relaxation is much smaller than the first component. The present results have thus revealed
the dimensional cross over of charge transport in RR-P3HT at 25 K. The dimensional cross over,
that is related to the voltage-induce metal-insulator transition, was also reported by Dhoot et
al., in RR-P3HT field-effect transistors (FETs) [14]. Different from a previous report [15] which
indicated the metallic behavior induced by increasing dopant concentration, the present results
show a thermal-motion induced change of metallic behavior. The present data also clarified
the origin of increasing step in voltage-shorted-compaction (VSC) resistance ratio below 30 K
[15]. Comparing with other conducting polymers such as PANI and PPV [16], the observation
of dimensional cross over in the lower temperature regime indicates that RR-P3HT has higher
charge mobility, particularly stronger inter-chain hopping mobility.

4. Conclusion
We have studied the microscopic intrinsic charge transport processes in the polythiopene
based polymers of Poly(3-hexylthiophene-2,5-diyl) with regio-regular structure along and
perpendicular to the chain by means of longitudinal field (LF) μSR method. Our experimental
results have elucidated the intra-chain transport mechanism and inter-chain hopping effect,
which can be related to the electrical and optical properties of the polymers. We found that the
temperature-dependent charge carrier mobility exhibits a perceptible change from intra-chain
diffusion to inter-chain diffusion at 25 K. The present result has thus revealed the crossover
from 1 dimensional intra-chain diffusion to 3 dimensional diffusion featuring strong temperature-
induced inter-chain hopping effect.

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