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Intra- and Inter-chain polaron diffusion in regio-random polythiophene studied by muon spin relaxation

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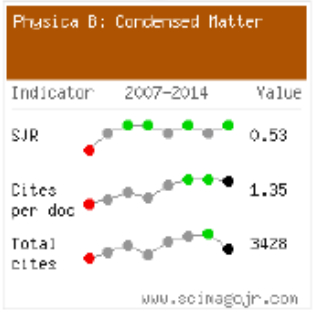

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Intra- and inter-chain polaron diffusion in regio-random polythiophene studied by muon spin relaxation

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ABSTRACT

Longitudinal field (LF) muon-spin-relaxation measurements have been performed for polythiophene based polymers of regio-random poly(3-hexylthiophene-2,5-diyl) to elucidate the intra- and inter-chain hopping mechanisms. The LF dependent muon-spin depolarization rate indicates the occurrence of pronounced shift in the relative dominance of charge transport mechanism from intra-chain diffusion to inter-chain diffusion at 50 K which is higher than the 25 K observed previously for the regio-regular case.

1. Introduction

The studies of conducting polymers in general have constituted a subject of great research interest due to the wide ranging possibilities for their novel applications in various fields. One of the materials being intensively studied is the polythiophene (PT) based polymers [1–3] which form an important class for its certain practical advantages. They can be easily synthesized with various dopants, and they are chemically as well as thermally stable in air [4]. These polymers can also be readily grafted with different side chains for their property modifications. Specifically, the photo luminescent property and field-effect charge mobilities in PT grafted with alkyl side chain have been reported to be strongly affected by the chain length of its alkyl substituents [3,5].

One of the most notable properties of these materials is, nevertheless, the observed enhancement of their electrical conductivity induced by the presence of appropriate dopants. The transport measurements of PT have also revealed strong dependence of the conductivity on their molecular structures, such as its regio-regularity (regio-regular or regio-random). A regio-random 3-methylthiophene for example, possesses a conductivity of 50 S/cm, while a more regio-regular configurations has a higher conductivity of 140 S/cm [6]. However, most of the previous studies on those structural effects were conducted by means of macroscopic transport measurements, which did not provide direct information on structure dependent local charge mobility in the polymer.

Prior to this work, we have studied the microscopic charge transport processes in regio-regular poly(3-hexylthiophene-2,5-diyl) by means of longitudinal field (LF) muon-spin-relaxation (μSR) method. The result shows that the temperature-dependent charge carrier mobility exhibits abrupt change associated with the "transition" from intra-chain diffusion (along to the polymer chain) to inter-chain diffusion (perpendicular to the polymer chain) at 25 K [7]. Here, we report the study of temperature-dependent spin diffusion dynamics of the charge carrying polarons in the regio-random poly(3-hexylthiophene-2,5-diyl) along and perpendicular to the chain by LF−μSR method for the purpose of determining the relative contributions of the intra-chain hopping mechanism and inter-chain coupling effect to the charge transport processed in the polymers.

2. Experimental

The regio-random poly(3-hexylthiophene-2,5-diyl) (Sigma-Aldrich) samples were prepared by pressing and wrapping the samples 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 to 300 K in longitudinal magnetic field ranging from 0 to 395 mT at the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the UK using a pulsed positive surface muon beam [8,9]. The μSR function known as the 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,

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