

Slow polymer dynamics in poly(3-hexylthiophene) probed by muon spin relaxation

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The local molecular dynamics of regioregulated poly(3-hexylthiophene) P3HT has been revealed by muon spin relaxation (μ SR) [1]. The response of the μ SR spectra to a longitudinal magnetic field (B_{LF} , parallel to the initial muon spin direction) indicates that the implanted muons form both muonated radicals localized on the thiophene ring and diamagnetic states with comparable yields. Moreover, the unpaired electron in the radical undergoes hyperfine interactions with muon bound to thiophene and with neighboring protons (see Fig.1), whose fluctuations can serve as a

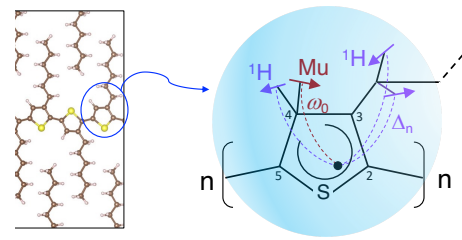


Fig.1 Local electronic structure of muonated radical observed in regioregular P3HT, where ω_0 and Δ_n refer to the hyperfine and nuclear hyperfine parameters.

measure for the molecular dynamics. The B_{LF} dependence of the longitudinal muon spin relaxation rate ($1/T_{1\mu}$) measured in detail at several temperatures is found to be well reproduced by the spectral density function $J(\omega)$ derived from the local susceptibility that incorporates the Havriliak-Negami function used in the analysis of dielectric relaxation, $\chi(\omega) \sim 1/[1-i(\omega/\nu)^\delta]^\gamma$ (where ν is the mean fluctuation rate, and $0 < \gamma, \delta \leq 1$) [2]. The magnitude of ν and its temperature dependence deduced from the analysis of $1/T_{1\mu}$ are found to be consistent with the motion of hexyl chains and thiophene rings suggested by ^{13}C -NMR. The present result marks a methodological milestone in the application of μ SR to the dynamics of complex systems with coexisting fluctuations over a wide range of time scales, such as polymers.

References

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