Saturation Transfer EPR Spectroscopy of Hexylated Polymers with Acene Cores

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Introduction

Our interests lay in the comparative study of ABA systems comprised of benzene (B), naphthalene (N), and anthracene (A) cores disubstituted with easily oxidized heterocyclic aromatics. Previous studies of systems containing naphthalene and anthracene have shown the potential for the formation of localized aromatic sextets orthogonal to the charge transport pathway and the subsequent restriction of π-electron delocalization.[1] Building on these findings, we undertook a high frequency saturation transfer EPR (ST-EPR) analysis of oxidized bithiophene-acene-bithiophene chemical polymers (**Figure 1**) where the effects of the core on charge transport were seen by monitoring changes in spin diffusion rates.

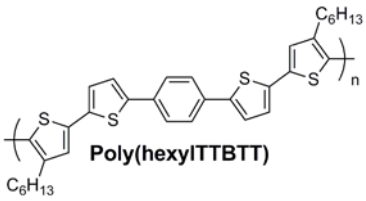

Figure 1. The hexylated polymer with a benzene core, naphthalene and anthracene systems were also synthesized.

Experimental

ST-EPR measurements were obtained using the 12.5 T heterodyne EPR spectrometer at 240 GHz between 4 K and 20 K, as the right combination of relaxation times and saturation effects exists at this field such that the in-phase and quadrature terms from the dispersion signal can be used to calculate relaxation times from the u_1-u_3 components (**Figure 2**) using the slow passage equations:[2]

$$T_1 = \frac{\pi u_3}{2\omega_m u_1} \qquad T_2 = \frac{\pi u_3}{2\omega_m (u_1 + 11u_2)}$$

where ω_m is the frequency of the modulation field. The polaron intra- (1D) and interchain (3D) spin diffusion rates can be calculated from the relaxation times using the equations:[2]

$$T_2^3 = T_{2_0}^4 v_{1D} \qquad T_2 = T_{2_0}^2 v_{3D}$$

where T_{2_0} is the relaxation time without spin mobility, $v_{1,3D}$ is the spin diffusion rate.

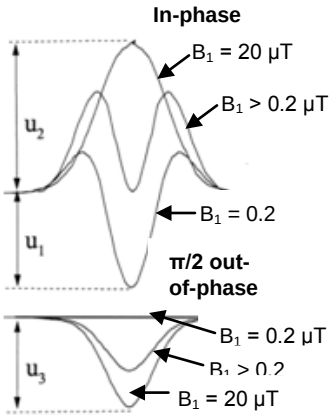

Figure 2. u_1–u_3 components of the 1st derivative dispersion spectra.[2]

Results and Discussion

The polymer relaxation times at 4 K or 5 K are similar (T_1 ~ 2.5 μs and T_2 ~ 0.14 μs), suggesting similar polymer dynamics. The 1D and 3D diffusion rates are also similar; an increase in 1D diffusion is seen as the acene core is changed from benzene to naphthalene to anthracene (**Table 1**), where a faster rate suggests less restriction of spin delocalization.

Table 1. The calculated inter- and intrachain spin diffusion rates for the poly(hexylTTXTT) systems.

	Poly(hexylTTBTT)	Poly(hexylTTNTT)	Poly(hexylTTATT)
1D Diffusion Rate (s^{-1})	1.96×10^{12}	1.25×10^{13}	2.13×10^{14}
3D Diffusion Rate (s^{-1})	4.68×10^{9}	8.68×10^{9}	2.23×10^{10}

Conclusions

At 4 K to 20 K, the 1D spin diffusion rate is higher for poly(hexylTTATT) than for the other polymers. As anthracene was found to restrict charge transport in earlier studies, the most likely explanation for this finding is that spin diffusion is limited to the hexylthiophene subunits versus diffusion through the acene cores in the other polymers. The 3D diffusion rates are more similar, likely because polymer stacking is defined by the hexyl chains.

Acknowledgements

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References

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[2] Krinichnyi, V.I., Synth. Met., **108**, 173-222 (2000).