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Chain Dynamics, Relaxation Times, and Conductivities of Bithiophene−Acene Copolymers Measured Using High Frequency Saturation Transfer EPR

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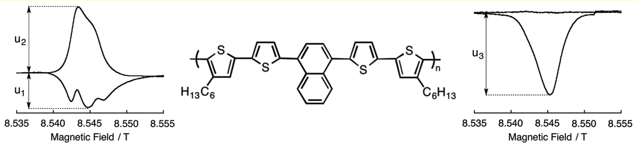
Supporting Information



ABSTRACT: We present a study to probe the formation of localized aromatic sextets and their effects on the charge transport properties in polymers with acene cores. Bithiophene−acene copolymers containing benzene, naphthalene, or anthracene as acene cores were synthesized using Yamamoto polymerization. Drop-casted polymer films were chemically doped and analyzed using high frequency saturation transfer EPR (HF ST-EPR), a method which has proven useful in the study of conducting polymers. The spin−spin and spin−lattice relaxation times were determined for these polymers at low temperatures (4 to 20 K) and used to obtain inter- and intrachain spin diffusion rates and conductivities. Similar interchain spin diffusion rates were seen across all polymer systems; however, anthracene containing polymer poly(hexylTTATT) was found to have the largest intrachain spin diffusion rate. The poly(hexylTTATT) intrachain spin diffusion rate may be artificially high if the anthracene ring restricts the diffusion of spin to the hexylated quaterthiophene segment in poly(hexylTTATT) whereas the spins diffuse through the acene cores in the benzene and naphthalene derivatives. Alternatively, as both the spin diffusion rates and conductivities vary unpredictably with temperature, it is possible that the π-electron localization previously seen in the anthracene core could be relieved at lower temperatures.

INTRODUCTION

Organic π-conjugated conducting polymers are the subject of a considerable amount of research due to their use in a variety of applications including organic light emitting diodes (OLEDs), molecular wires, solar cells, and organic field effect transistors (OFETs). Many of the interesting properties of these materials arise from the creation, migration and/or annihilation of charge carriers generated via photonic or electrical inputs, so it is essential to understand the nature of these charged species. Upon oxidation of prototypical polyaromatic conjugated polymers (such as those containing benzene or thiophene repeat units), radical cations (polarons) are formed that become progressively more delocalized as the polymer undergoes local structural reorganizations from aromatic to quinoidal states. The quinoidal structure is maintained during further oxidation to the spinless dication or bipolaron form. The properties of the spin-bearing radical ions of organic conducting polymers and their monomer precursors have been investigated using EPR in conjunction with a number of electrochemical techniques such as cyclic voltammetry, conductivity measurements, and spectroelectrochemistry. This combination of techniques is used to follow the creation and electronics of charged species such as polarons, polaron pairs, and bipolarons. Many p-type hole transporting materials consist of heteroaromatics, including poly(alkylthiophenes) and poly(3,4-ethylenedioxythiophene, EDOT). These heterocycles are used because of their ease of oxidation, the stability of their oxidized spin-bearing forms, and the high polarizability of the sulfur atoms which facilitates intramolecular and intermolecular electronic delocalization.[1] Joint electrochemical EPR studies have been used to characterize the oxidation of thiophene or EDOT containing polymers including a 3-methyl- and 3-hexylthiophene copolymer[2] as well as dodecyl EDOT homopolymer.[3]

EPR studies of organic conducting polymers are often performed at X-band frequencies (~10 GHz), typically in conjunction with another instrumental technique such as UV/vis or cyclic voltammetry. Although these measurements are typically used to study the creation of polarons and bipolarons, low to mid frequency EPR instruments have also been used to study spin dynamics in conducting polymers. X-band frequencies were used to determine polaron dynamics in alkylthiophene oligomers of defined lengths.[4] Mizoguchi and co-workers showed that the spin dynamics of organic polymers could be obtained from a multifrequency analysis of spectral line widths on the order of a few MHz to 24 GHz.[5] In addition, pulsed EPR techniques have been frequently used to determine spin−spin and spin−lattice relaxation times of organic

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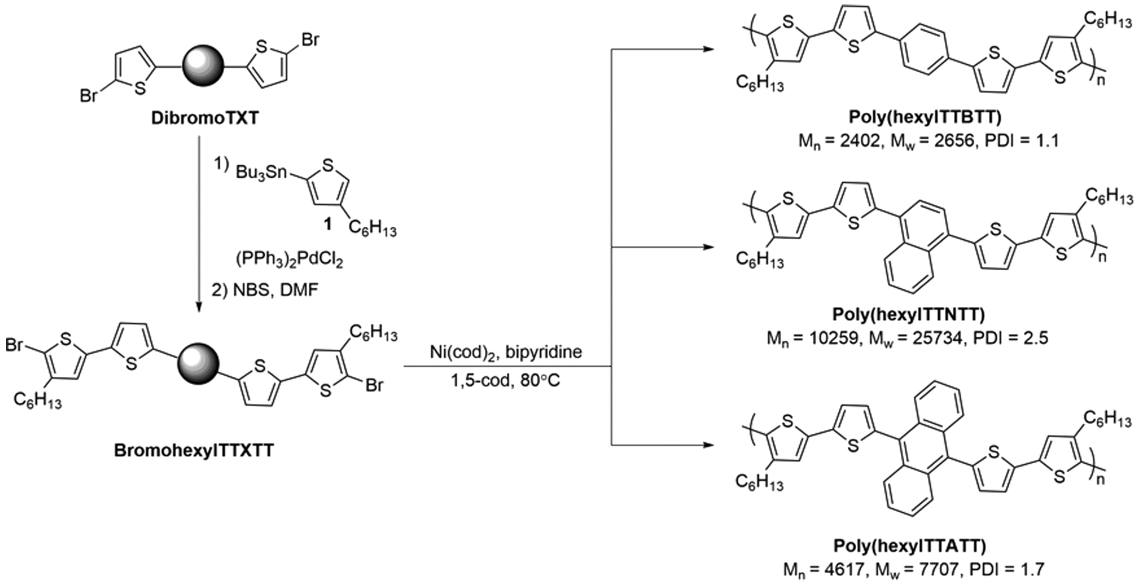
Scheme 1. Synthesis and Structures of HexylTTXTT Polymers, Where X = 1,4-Phenylene (B), 1,4-Naphthylene (N), or 9,10-Anthrylene (A)



polymeric systems.[6,7] However, the development of high frequency EPR (HF-EPR) instruments using microwave frequencies ≥95 GHz has allowed for further quantitation of molecular motion in solution, solid state and oriented media,[8−11] and of various properties of oxidized organic conducting polymers including the rotational dynamics of polymer chains,[12] the orientational dependence of polymer films,[13] and polaron spin diffusion rates.[14] Continuous wave HF-EPR has several advantages over lower frequency experiments including increases in the *g*-factor resolution and spin sensitivity.

The dynamics of polymer chains, with correlation times of 10^{-7}−10^{-3} s, can only be studied using high frequency saturation transfer EPR (HF ST-EPR).[15] These measurements cannot be performed at X-band because of poor spectral resolution and the interference of relaxation processes on signal shape. HF ST-EPR has several advantages over standard X-band including increased sensitivity of the HF ST-EPR method, decreased probability of radical cross relaxation meaning that paramagnetic species do not interact at this frequency, and the right combination of relaxation times and saturation effects exists at these fields.[15] Therefore, at higher fields a more complete picture of the structure, relaxation, and molecular dynamics of conducting polymers can be obtained. An increase in sensitivity to the anisotropy of molecular rotation is also seen when Q-band (35 GHz) EPR is used, but at this frequency the anisotropy of the resonant field of the radical centers is comparable with the anisotropy of superfine interaction, leading to difficulties in spectral interpretation and modeling.[16]

Although a wealth of information can be obtained with HF ST-EPR, the method is not commonly used. In the biochemical field, Fajer and co-workers used HF ST-EPR to study the rotational molecular motion of several spin labeled proteins, demonstrating the method's utility in the study of chemical biology problems.[17] HF ST-EPR has been used in the study of conductive polymers, specifically to probe the effects of temperature on polymer conductivity mechanisms including conduction along polymer chains, hopping between chains, and tunneling between conducting regions separated by less conductive portions. Krinichnyi and co-workers have demonstrated the use of the HF ST-EPR method to probe inter- and intrachain electronic processes in oxidized conducting polymers including polythiophenes with solublizing alkyl chains, polyaniline, and polytetrathiafulvalene.[15] The high resolution and the appropriate time scale of HF ST-EPR, especially at frequencies ~140 GHz, enabled the analysis of the anisotropic character of superslow molecular motions generally on the order of 10^{-7} s and allowed quantification of the mobility of charge carriers in low-dimensional organic semiconductors.[15] The separation of intrinsic charge dynamics along polymer chains from interchain, interglobular, and related processes using other experimental methods is quite difficult.[18] In addition, magnetic resonance studies of charge dynamics also allow for a separate analysis of both intra- and interchain spin dynamics.[18]

In the context of the development of photochromic organic electronic materials, we studied polymers and molecular models with orthogonal degrees of ring fusion pendant to the main-chain conjugation pathway, specifically through comparative studies of benzene, naphthalene, and anthracene cores disubstituted with easily oxidized heterocyclic aromatics.[19] Our interests were to interrogate the natures of the charged states resulting from chemical or electrochemical oxidation, while similar motifs have attracted interest elsewhere in the area of molecular electronics.[20−22] We demonstrated that systems containing naphthalene and anthracene have the potential for the formation of localized aromatic sextets orthogonal to the charge delocalization pathway and thus the subsequent restriction of π-electron circulation.[23] Although these conclusions were supported by cyclic voltammetry and UV/vis studies of the polymers and their respective monomers, the results were largely influenced by the analysis of the EPR hyperfine splitting constants of the oxidized monomers which were synthesized with methyl groups in the α-thienyl positions to block polymerization yet allowing for the generation of persistent and observable intermediates.[19] Building on these findings, we report here a HF ST-EPR and pulsed EPR study of chemically synthesized bithiophene-acene copolymers in order to elucidate the charge transport properties in the solid state.

EXPERIMENTAL SECTION

Synthesis. All syntheses were performed on a Schlenk line using standard air-free techniques. Ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone before use. All other reaction solvents were degassed before use. All reaction solvents were passed through activated alumina and degassed before use; polymerization solvents were degassed over 4 Å molecular sieves, 1,5-cyclooctadiene was distilled prior to use. Palladium catalysts were purchased from Strem Chemicals, all other reagents and chemicals were purchased from Aldrich and used as received. Monomers for polymerization were prepared from their respective TXT precursors[23] by NBS bromination yielding dibrominated dithienyl arenes (Scheme 1) to which alkylated thiophene units were added via Stille couplings with stannylated 3-hexylthiophene (**1**). The resulting hexylTTXTT monomers were brominated again using NBS and then polymerized using Yamamoto methodology mediated by Ni(cod)$_2$.[24] Polymers were purified by Soxhlet extraction using methanol and hexane, chloroform was used to redissolve the desired polymers. The identities and purities of all compounds were verified by ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) obtained on a Bruker Avance spectrometer. High resolution electron impact/chemical ionization (EI/CI) mass spectrometry was obtained on a VG Instruments VG70S magnetic sector mass spectrometer. Synthesis details and molecular characterization data can be found in the Supporting Information.

Gel Permeation Chromatography (GPC). Polymer molecular weights were determined using GPC on a Waters 1515 Isocratic HPLC equipped with two 5 mm Waters Styragel HR4 and HR3 columns (300 nm ×7.8 mm) connected in series with increasing pore size, and a Waters 2489 UV/vis detector. The polymers were dissolved in HPLC grade THF (0.5−1 mg/mL) and filtered through a 0.2 mm PVDF filter. The GPC was run with submicrometer filtered HPLC grade THF (Fisher) at 1 mL/min. The polymer molecular weights and polydispersities were determined from a calibration curve based on linear polystyrene standards.

Polymer Film Preparation. Polymer drop casting and doping was performed in a glovebox, samples were transferred to a Schlenk line in an airfree manner. Chloroform used for polymer drop casting was run through a plug of basic alumina, degassed over 4 Å molecular sieves, distilled, and freeze pump thawed prior to use. Acetonitrile used for polymer doping was degassed over K_2CO_3 followed by 3 Å molecular sieves, distilled, and freeze−pump−thawed prior to use. Films for high frequency EPR were prepared on polyethylene terephthalate (PET) supports and sonicated in hexane for 10 min followed by ethanol for 10 min and dried. With the exception of poly(hexylTTBTT), 10 mg/mL solutions of the polymers were made up in chloroform. The poly(hexylTTBTT) solution was 4 mg/mL due to low solubility. A small amount of solution (0.2 mL) was drop casted onto a 1 in. by 6 cm strip of PET support and the film was annealed at 50 °C for 20 min. Films were cut into approximately 3 mm by 4 cm long strips and doped by immersion for several seconds (when a color change was seen) in an approximately 40 mg/mL solution of $NOPF_6$ in acetontrile. The strips were placed in 4 mm OD EPR tubes and attached to a Wilmad-LabGlass EPR tip-off manifold to allow airfree transport to a Schlenk line where they were evacuated and flame-sealed using a natural gas/oxygen torch.

High Frequency EPR Spectroscopy. The EPR samples were studied in a home-built EPR spectrometer at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, FL.[25,26] The instrument was fitted with quadrature detection, allowing a simultaneous measurement of absorption and dispersion. In general the spectral signals obtained were a mixture of absorption and dispersion, with a 90° phase difference. The out-of-phase signals with respect to field modulation for both of these were also recorded, and allows for saturated signals to be obtained. A microwave phase shift of about 200° and a small correction to the modulation phase of the order of few degrees was performed to obtain an in-phase absorption signal. The in-phase dispersion signal (a sum of the derivative of the dispersion and the nonderivative absorption) was processed by subtracting a proportion of the out-of-phase signal to obtain the in-phase derivative of the dispersion signal. A sample of 1,3-bis(diphenylene)-2-phenylallyl radical (BDPA) in polystyrene containing a known amount of spins per gram was used for spin counting. The samples were run at 239 GHz between 290 and 4 K.

Surface Profilometry. Film thicknesses were measured using a DekTak3 surface profile measuring system. Prior to measurements, the films were scratched with a razor blade to provide a step edge, taking care not to scratch the PET support.

Electrochemistry. Electrochemical films were grown or dropcasted on a 2 mm^2 platinum button working electrode with a quasi-internal Ag/Ag$^+$ reference electrode (silver wire immersed in 0.01 M $AgNO_3$ and 0.1 M TBAP in acetonitrile, separated from the cell with a porous Vycor frit) and a platinum wire counter electrode using a scan rate of 100 mV/s. The half-wave potential of the Fc/Fc$^+$ couple (recorded at 289 mV and 144 mV vs Ag/Ag$^+$ in CH_2Cl_2 and MeCN, respectively) was used as an external standard. The potentials were cycled using an Autolab PGSTAT 302 bipotentiostat. A saturated solution of poly(hexylTTNTT) (30 mg) was prepared in 5 mL of anhydrous 0.1 M n-Bu_4NPF_6 (TBAP)/dichloromethane electrolyte. The polymer precipitated onto a working electrode during solution cyclic voltammetry (CV) measurements. Nothing was observed to precipitate from a 0.5 mM poly(hexylTTATT) electrolyte solution (in anhydrous 0.1 M TBAP/MeCN) during CV, so this solution was dropcasted onto the electrode and the resulting thin film was allowed to soak for 1 h before recording the polymer film CV. Both polymer films were studied in 0.1 M TBAP/MeCN electrolyte.

UV/Vis. UV/vis measurements were taken with a Varian Cary 50 Bio UV/vis spectrophotometer in $CHCl_3$. Because of low solubility, poly(hexylTTBTT) was first dissolved in o-DCB and then added to $CHCl_3$.

RESULTS AND DISCUSSION

We sought to better understand the solid state electronic properties of these bithiophene-acene-bithiophene systems by modifying the known TXT architectures into polymerizable monomers (Scheme 1). This was achieved through a three-step sequence of TXT bromination, Stille cross-coupling, and final bromination of the α-positions of the bithiophene units. These monomers were then polymerized via Yamamoto homocoupling. Solubilizing hexyl groups were added to improve the processability of the resulting polymers whose molecular weights were determined by GPC. Poly(hexylTTNTT) was found to be the longest polymer chains at 16−41 subunits, followed by poly(hexylTTATT) at 7−11 subunits. Poly-

(hexylTTBTT) had the shortest polymer chains at 4−5 subunits, likely due to very low solubility.

UV/Vis and Cyclic Voltammetry. Solution UV/vis measurements of the neutral polymers were taken to determine the effective conjugation lengths (ECLs) of the systems in the absence of solid-state packing effects. The poly(hexylTTBTT) absorption λ_{max} at 443 nm is red-shifted compared to the naphthyl (λ_{max} = 397 nm) and anthracenyl (404 nm) counterparts (Figure 1). The UV/vis spectrum of poly(hexylTTATT) is polymodal with a broad absorption at 342 nm, and vibronic features at 361, 383, and 404 nm, similar to those observed for anthracene (340, 360, and 380 nm). The higher energy features seen in the polymers with naphthalene and anthracene cores versus poly(hexylTTBTT) suggest that the additional π-electrons in these extended acene cores remain localized in the neutral polymers. These results corroborate our previous findings in neutral TTXTT monomers[23] and their methyl blocked counterparts[19] while also verifying that the addition of bulky hexyl chains did not significantly perturb the electronics of these systems.

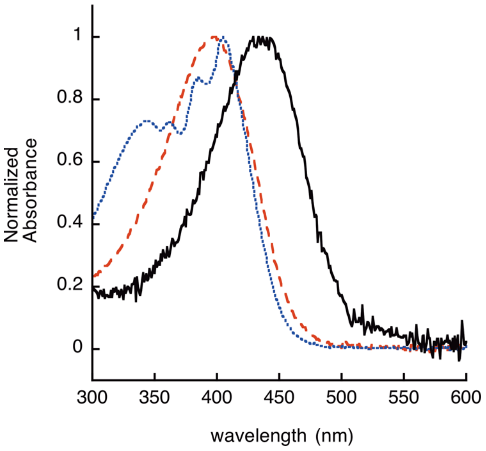


Figure 1. Normalized UV/vis spectra of the neutral polymers recorded in $CHCl_3$ [poly(hexylTTBTT), solid black; poly(hexylTTNTT), dashed red; poly(hexylTTATT), dotted blue]. Because of low solubility, poly(hexylTTBTT) was dissolved in minimal *o*-dichlorobenzene and added to $CHCl_3$.

Cyclic voltammetry (CV) of the polymer films provides information about solid state redox properties. Differences in how the films were deposited on the electrode for study by CV may have an effect on the data, because poly(hexylTTNTT) electrodeposited on the platinum working electrode during the CV experiment in a polymer solution whereas poly(hexylTTATT) needed to be drop casted onto the platinum electrode. A CV of poly(hexylTTBTT) could not be obtained due to low solubility. The results show that poly(hexylTTNTT) is easier to oxidize than its anthracenyl counterpart with half wave potentials ($E_{1/2}$) of 0.66 and 0.79 V, respectively (Figure 2). This data further suggests that the additional π-electrons in the anthracene core do not contribute to the ECL of the neutral polymer.

Pulsed and HF ST-EPR. The hexylTTXTT polymers were dropcasted onto solid supports, oxidized, and placed into EPR tubes. Oxidized films were then studied by HF ST-EPR to obtain a more complete picture of charge delocalization in these systems. With the appropriate phase tuning, HF ST-EPR can be used to determine the spin relaxation times of a polymer. The relaxation times are affected by lattice oscillations, global tumbling, polymer torsional motions, and fast electron spin diffusion.[13] The relationship between relaxation times and spin diffusion can be used, in conjunction with equations described below, to determine polymer inter- and intrachain spin diffusion rates as well as conductivities. A description of the mathematics used to describe the physical processes at play can be found in the Supporting Information.[14]

The u_1, u_2, and u_3 components measured from the magnitudes of the π/2-out-of-phase and in-phase components of the poly(hexylTTXTT) first derivative dispersion signals (Figure 3) were used to calculate the spin−spin and spin−lattice relaxation times for all poly(hexylTTXTT) samples (Table 1). Since the signal strength falls off rapidly with increasing temperature, we averaged the measured the T_1 and T_2 values over a narrow temperature range (depending on the polymer used).

Relaxation times were determined for all poly(hexylTTXTT) samples at 4 or 5 K and the T_1 and T_2 values are found to be very similar, suggesting similar polaron dynamics. The poly(hexylTTNTT) and poly(hexylTTATT) relaxation times at a slightly higher temperature (10 K) also show some variation which may indicate differences in electronic processes

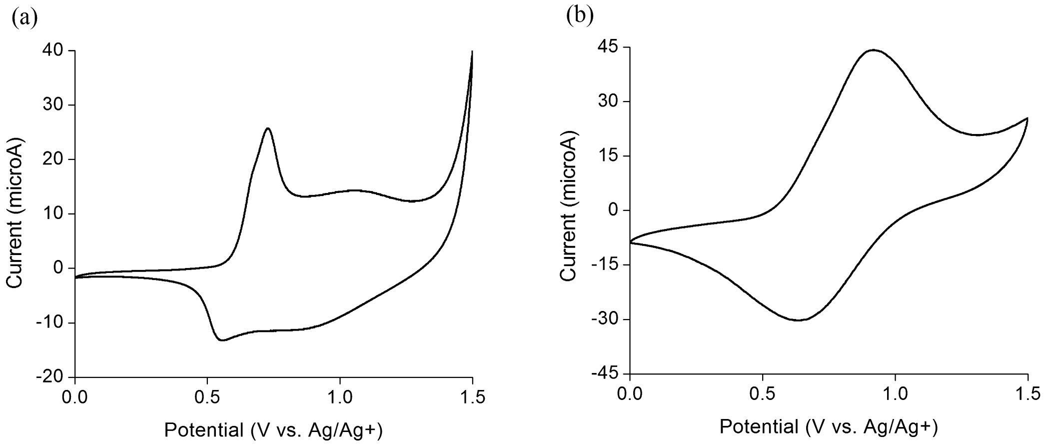


Figure 2. CV profiles of (a) poly(hexylTTNTT) that electropolymerized during oxidation of a saturated polymer electrolyte solution and (b) poly(hexylTTATT) dropcasted from a 2 mg/mL solution onto the working electrode, recorded on a 2 mm^2 Pt button working electrode in 0.1 M TBAP/MeCN using a 100 mV/s scan rate; the Fc/Fc^+ half-wave potential (averaged from the two profiles) fell at 144 mV in 0.1 M TBAP/MeCN.

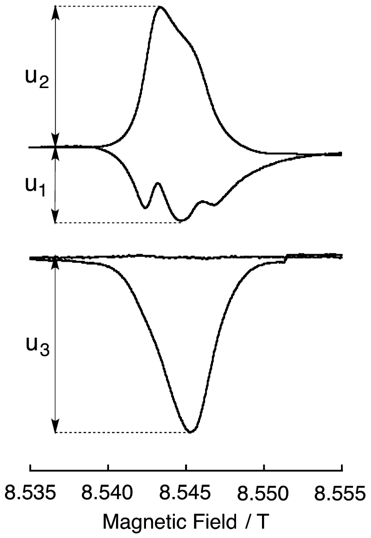


Figure 3. In phase (above) and $\pi/2$-out-of-phase (below) dispersion spectra of polyTTNTT polarons obtained at 20K. The u_1 measurements were taken at 0 db attenuation, u_2 measurements at 28 db attenuation, and u_3 measurements at 0 and 28 db attenuation.

Table 1. Spin–Lattice and Spin–Spin Relaxation Times Calculated for Each Polymer at Various Temperatures Using the Equations for Slow Passage Conditions

sample	T_1 (s)	T_2 (s)
poly(hexylTTBTT); average of values measured at 5 and 7 K	2.16×10^{-6}	8.94×10^{-8}
poly(hexylTTNTT); average of values measured at 4, 10, and 20 K	2.90×10^{-6}	1.66×10^{-7}
poly(hexylTTATT); measured at 5 K	3.74×10^{-6}	1.54×10^{-7}

at this temperature. Comparison of these relaxation times with previously reported values for other organic polymers is difficult because these values do not change in a predictable fashion with temperature. The hexylTTXTT polymer signals saturated only around 20 K and below whereas measurements for related polymers were taken between 90 and 293 K. Unfortunately, low spin concentrations of $<10^{16}$ spins/m^3 (Table 3) likely restricted the measurements to such low temperatures as doped organic conducting polymers generally contain 10^{22}–10^{27} spins/m^3.[14] At 90 K, doped poly(3-octylthiophene) has a T_2 of about 5×10^{-7} s, similar to our values at much lower temperatures.[16] However, the T_1 is considerably slower at about 1×10^{-4} s.[16] Again, as relaxation times change unpredictably with temperature, the implication of this finding with respect to differences in the charge transport processes between doped poly(3-octylthiophene) and the poly(hexylTTXTT) systems cannot be determined with certainty. The differences in T_1 can be due to a variety of differences between the two systems including spin diffusion processes, temperature, spin concentration, film thickness, and dopant.[14,27]

The relaxation times, and further results such as spin diffusion rates and conductivities which are calculated using these values, depend on the doping level of the polymers.[14] Therefore, a sample containing a known amount of 1,3-bis(diphenylene)-2-phenylallyl radical in polystyrene was used as a standard to determine the doping level of the poly(hexylTTXTT) films (Table 3). As the instrument did not contain a double resonator for simultaneous study of the standard and polymer sample and the data had to be taken at room temperature where the polymer EPR intensities were quite low, there is likely an error associated with these measurements. Despite difficulties with spin counting, the counts are quantitatively supported by an analysis of the peak to peak height and width of the HF-EPR absorption spectra where poly(hexylTTNTT) is the highest doped sample, followed by poly(hexylTTBTT), and last poly(hexylTTATT).

Using the relaxation times calculated for the poly(hexylTTXTT) systems, the inter- and intrachain spin diffusion rates can be determined using the following equations:

$$T_2^{\;3} = T_{2_0}^{\;4}\nu_{1D} \tag{1}$$

$$T_2 = T_{2_0}^{\;2}\nu_{3D} \tag{2}$$

Here T_2 is the spin–spin relaxation time, T_{2_0} is the spin–spin relaxation time without spin mobility, and ν_{1D} and ν_{3D} are the intra- and interchain spin diffusion rates, respectively.[14] T_{2_0} is calculated to be 4.37×10^{-9} s for all samples from the peak to peak line width at the point where this measurement does not change significantly with temperature,[28] and the T_2 values for each polymer sample used in these equations are averaged. The intrachain (1D) and interchain (3D) diffusion rates are relatively similar for all of the polymers; a slight increase in diffusion is seen as the acene core is changed from benzene to naphthalene to anthracene (Table 2). The poly(hexylTTXTT) spin diffusion rates are on the order of other organic conducting polymers, with room temperature measurements of $\nu_{1D} = 3.2 \times 10^{12}$ s^{-1} for polythiophene and $\nu_{3D} = 2.1 \times 10^{10}$ s^{-1} for poly(3-octylthiophene), although the literature data were determined at higher temperatures.[14,29]

Table 2. Calculated Low Temperature Inter- and Intrachain Spin Diffusion Rates for the Poly(hexylTTXTT) Systems Determined Using eqs 1 or 2 and T_2 Values from Table 1

polymer	1D diffusion rate (s^{-1})	3D diffusion rate (s^{-1})
poly(hexylTTBTT)	1.96×10^{12}	4.68×10^{9}
poly(hexylTTNTT)	1.25×10^{13}	8.68×10^{9}
poly(hexylTTATT)	2.13×10^{14}	2.23×10^{10}

As there are too few spins in the poly(hexylTTATT) sample to obtain a count, it is surprising that this polymer appears to have the highest intrachain (1D) spin diffusion rate of all the poly(hexylTTXTT) systems. The rate is about 15 times that of poly(hexylTTNTT) but more than 100 times that of poly(hexylTTBTT). It was expected that the low number of spins in the hexylTTATT polymer sample combined with the π-electron localization previously seen in the anthracene core upon oxidation would lead to a lower spin diffusion rate in this system compared to its naphthalene and benzene counterparts. The variation in interchain spin diffusion rates is much smaller, only about a 5-fold difference exists between the highest and lowest rate.

Although the diffusion rates are not directly related to the diffusion lengths, a faster rate suggests less restriction of spin delocalization. Additionally, the rings over which the spin diffuses cannot be determined. It is possible that the anthracene ring restricts the diffusion of spin to the hexylated quaterthiophene segment in poly(hexylTTATT) whereas the spins diffuse through the acene cores in poly(hexylTTNTT) and poly(hexylTTBTT). This could give an artificially high intrachain spin diffusion rate in the anthracene containing polymer. The interchain diffusion rates are largely dependent on charge hopping thus a smaller variation in rates is to be expected since the polymer stacking is influenced by the hexyl chains.

The inter- (1D) and intrachain (3D) conductivity of the polymers with temperature were determined using the following equations:[16]

$$\sigma_{1D} = \frac{N_s e^2 \nu_{1D} c_{1D}{}^2}{k_B T} \tag{3}$$

$$\sigma_{3D} = \frac{N_s e^2 \nu_{3D} c_{3D}{}^2}{k_B T} \tag{4}$$

where N_s is the number of spins, e is the elementary charge, k_B is the Boltzmann constant, T is temperature, c_{1D} and c_{3D} are the intra- or interchain lattice constant, respectively (Table 3). The calculated conductivities are likely rough estimates as we used the X-ray scattering lattice constants of c_{1D} = 0.785 nm and c_{3D} = 0.480 nm reported for oriented poly(3-octylthiophene)[30] and due to the previously mentioned difficulties with spin counting. Taking into consideration these complications, there is likely an error associated with the determination of conductivities for the poly(hexylTTXTT) systems. In addition, no estimate could be obtained for poly(hexylTTATT) as there was no signal at room temperature.

Table 3. Number of Spins and the Corresponding Low Temperature Inter- and Intrachain Conductivities for the Intrinsic, Undoped Poly(hexylTTXTT) Systems

polymer	number of spins	1D conductivity (S/m)	3D conductivity (S/m)
poly(hexylTTBTT)	3.29×10^{14}	4.28×10^{-7}	1.11×10^{-10}
poly(hexylTTNTT)	1.08×10^{16}	1.41×10^{-5}	3.65×10^{-9}
poly(hexylTTATT)	N/A	N/A	N/A

The calculated conductivities are easier to analyze as they vary with the polymer spin concentrations and diffusion rates. As expected, a larger number of spins and higher diffusion rates lead to a higher intra- and interchain conductivities in poly(hexylTTNTT) compared to poly(hexylTTBTT). As for the spin diffusion rates, the conductivities are only valid at low temperatures (4–20 K) and changes in these measurements with increasing temperature cannot be predicted.

Although the polymer film thickness was not accounted for in the conductivity calculation, for film thicknesses on the order of micrometers, conductivity generally decreases as thickness increases.[30−32] Surface profilometer measurements of our dropcast polymer films provide an average thickness of 1.2 μm for poly(hexylTTNTT), increasing to 4.5 μm for poly(hexylTTATT) and 9.0 μm for poly(hexylTTBTT). With identical charge carrier densities in these films, we would anticipate the conductivity to increase from poly(hexylTTBTT), to poly(hexylTTATT), with poly(hexylTTNTT) having the largest conductivity if there are no significant differences in the packing of these systems.

■ CONCLUSIONS

This study elucidated the charge transport behavior of oxidized bithiophene-acene copolymer films in the solid state. Data obtained at room temperature mirrored results found previously in our laboratory, where the presence of naphthalene or anthracene cores appears to restrict π-electron delocalization compared to their benzene counterpart. HF ST-EPR provided a more quantitative study of the polymers' charge transport properties, however due to low concentration of spins these measurements could only be obtained at low temperatures. The spin–lattice and spin–spin relaxation times obtained from the ST-EPR method are similar for all of the polymers, suggesting similar polymer dynamics. Further analysis of the data shows that, at low temperatures, the intrachain spin diffusion rate is significantly higher for poly(hexylTTATT) than for the other hexylTTXTT polymers whereas the interchain spin diffusion rates are more similar. The interesting intrachain spin diffusion results suggest either a relief in the π-electron localization previously seen in the anthracene containing systems or, more likely, that spin diffusion is limited to the oligothiophene subunits in the anthracene based system and not in the benzene or naphthalene counterparts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b11212.

> Description of the mathematics used to calculate relaxation times, dispersion spectra and film thickness measurements, ^{1}H and ^{13}C NMR data, gel permeation chromatography traces, and the reaction procedures used for monomer and polymer synthesis (PDF)

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⊥Taken in part from the thesis of A.M.F. (Ph.D., Johns Hopkins 2012)

Notes

The authors declare no competing financial interest.

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