Spin Dynamics and Conductivity in Polyaniline

In a recent Letter,[1] Mizoguchi et al. presented the frequency dependences at room temperature of proton NMR T_1 and ESR linewidth of the emeraldine form of polyaniline as a function of protonation level. They determined that the on-chain electron-spin-diffusion rate $D_{\parallel}$ is independent of protonation level $y \equiv [Cl]/[CN]$, while the transverse diffusion $D_{\perp}$ exhibits a sudden drop at a percolation threshold, $0.21 < y_c < 0.27$. These data were shown to confirm the "granular polymeric metal" picture earlier proposed,[2,3] but it was concluded on the basis of the spin-dynamics data that a given conducting island consists of just a single conducting chain and it was suggested that the conductivity was governed by interchain hopping.

In this Comment we point out an alternate perspective on these data based upon results of x-ray diffraction, electron-spin resonance, and related studies, as well as theoretical results for the one-dimensional metallic state. We conclude that doped emeraldine salt (ES) forms three-dimensional metallic islands with a percolation threshold of metallic islands in the vicinity of $0.2 < y_c < 0.3$ and barriers remaining between the islands for $y > y_c$. Localization effects within the islands are important when the island size is small and their crystalline structure is distorted, corresponding to $y < y_c$.

X-ray structural studies coordinated with temperature-dependent static and electron paramagnetic resonance (EPR) determination of magnetic susceptibility (χ) demonstrate that a metallic Pauli susceptibility is observed only when three-dimensional crystalline regions (islands) are formed.[3] The average size of the ES-I islands increases with y, reaching values of about 50 Å in parallel and perpendicular directions for $y \sim 0.5$. With increasing y the d spacings in the crystalline part of ES-I change until y_c, then remain constant for larger y. Only the size of the individual crystalline domains still increase above y_c.[4] Protonation in the amorphous regions leads to an essentially spinless material indicating that a Fermi glass does not form.[3] EPR of protonated $y = 0.5$ ES has a nearly ideal Lorentzian line shape for $T > 10$ K indicative of isotropic diffusion of the electron spins in contrast with the more one-dimensional diffusion line shape for the polytoluidine.[5] In contrast, substitution of a CH_3 for one of the H on the C_6 rings (polytoluidine) leads to a polymer with similar crystallinity, yet one-dimensional localization[5] due to increased separation between polymer chains.[5] This result, combined with temperature-dependent microwave conductivity experiments[6] suggests that the increase in $D_{\perp}$ as y increases beyond $y \sim 0.2$ parallels the change in interchain spacing in crystalline ES-I or the formation[3] of doped ordered islands in ES-II so that localization no longer dominates. It is unlikely y_c is a percolation between random long chains, since the percolation threshold for long chains is expected to occur at a very low concentration. Instead,

y_c likely represents the crossover between localization and delocalization. The agreement of the calculated conductivity[1] with an experimental value only at room temperature is suggestive that the agreement itself is fortuitous, especially in light of the fiftyfold increase in the conductivity of ES upon orientation while maintaining the same temperature dependence.[7]

It is difficult to quantitatively compare the results of Mizoguchi et al.[1] for the "metallic" state with those of earlier work. The data for $y = 0.62$ imply a composition with a 25% greater protonation than that previously accepted as necessary for emeraldine salt[8] suggesting either chlorination at the C_6 rings (Cl replacing H) or protonation of amine (-NH) sites with formation of $(-NH_2)^+$, leading in either case to increasing localization.

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