Three Dimensionality of "Metallic" States in Conducting Polymers: Polyaniline

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Anisotropic-conductivity (σ), thermopower, and dielectric-constant studies show that oriented polyaniline salt is representative of a class of quasi-one-dimensional disordered conductors where coupled parallel chains form "metallic" bundles in which electron wave functions are extended three dimensionally. This is in contrast to isolated conducting chains in conventional 1D conductors. The bundles correspond to crystalline regions of the polymer. The results are important for understanding the stabilization of metallic states and achievement of high σ in conducting polymers.

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The study of the dimensionality of quasi-one-dimensional (quasi-1D) conducting polymers is important for understanding the absence of Peierls instability[1] and 1D localization[2,3] in their heavily doped "metallic" form. In contrast, these two phenomena play important roles in charge-transfer salts of tetracyanoquinodimethane (TCNQ).[3-6] Despite their absences in metallic polymers it is generally believed[1,7] that the polymer chains are 1D conductors with only weak interchain coupling; most of the theoretical studies ignore the interchain interactions.[7,8] However the 1D models cannot explain the stabilization of the polymer metallic state against the Peierls instability,[7] nor the high σ (close to that of copper) of doped Naarmann polyacetylene $(CH)_x$,[1,9,10] where electron states are not localized.[9] Kivelson and co-workers thus suggested[9] that interchain interaction in the $(CH)_x$ may suppress the Peierls instability and avoid 1D localization. Javadi *et al.*[11] further pointed out that 3D metallic states may be formed in the highly conducting $(CH)_x$. Theoretically, the electron states of a quasi-1D disordered system (DS) become three dimensional (3D) if the interchain coupling is comparable with the scattering rate due to the disorder.[2] In the case of a quasi-1D DS consisting of N coupled parallel chains, the electron wave functions become extended uniformly over the N chains,[2] similar to thin metallic wires where Thouless localization plays an important role.[12] Until now experimental studies of conducting polymers have been inadequate to determine the dimensionality of their conducting states with results even for the highly conducting $(CH)_x$ being ambiguous.[10,11,13] Detailed studies of the anisotropy of the conducting polymers are essential in order to determine the dimensionality of their conducting states and hence the origin of their high σ as well as the stabilization of their metallic states.

We present the transport studies of the anisotropy of one class of metallic conducting polymers, the emeraldine salt of oriented polyaniline (PAN-ES). The experiments find that thermopower $S(T)$ is proportional to temperature T $[S(T) \propto T]$ at high T (> 100–200 K) and is independent of stretching ratios, which suggest 3D metallic behavior. The low-T value of transverse dielectric constant $\epsilon_\perp$ ($= 26$) is also independent of stretching ratios; it corresponds to transverse localization length $L_1 \approx 20$ Å, much larger than the interchain separation of the polymer chains [3.5 Å (Ref. 14)]. Our results hence point out the 3D character of the metallic states in PAN-ES. We propose that PAN-ES represents a class of quasi-1D disordered conductor which consists of bundles of coupled parallel chains in which electron wave functions are three dimensionally delocalized, different from conventional 1D conductors.[3-6] The size of the bundle is related to crystalline coherence length ξ of the polymer.[14] Hence the formation of the bundles is attributed to significant interchain coherence[9] as well as interchain coupling.[2] Our results contradict the "single conducting chain" models of PAN-ES.[8,15]

Films of the emeraldine base form of polyaniline (PAN-EB) (Fig. 1) were cast from N-methyl-2-pyrrolidinone[16] (NMP) and stretched up to fourfold (1:4) at temperatures $T > 110\,°C$.[16] The bulk density is about 1.04 g/cm^3 for the unoriented PAN-EB films and 0.9 g/cm^3 for the 1:4 stretched films, compared with 1.34 g/cm^3 obtained by flotation techniques. Thus the compactness of the films is 0.7 ± 0.1, depending on the stretching ratios. Samples were doped to [Cl]/[N] $= 50\%$ to form PAN-ES (Fig. 1) by equilibrating with 1-mole HCl solution. Samples of lower doping levels were also studied.[17] The experimental techniques have been reported earlier.[18]

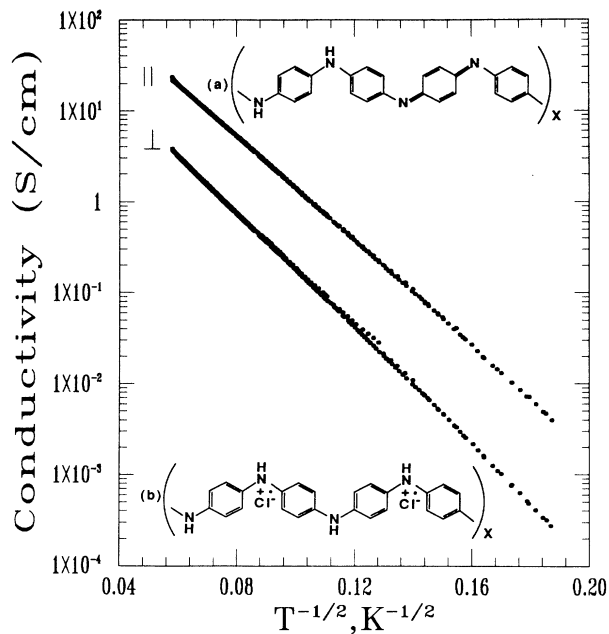Figure 1 shows the dc $\sigma(T)$ for 1:4 stretched samples.

FIG. 1. Temperature dependence of dc conductivity of 50% doped 1:4 stretched PAN-ES (HCl) films in the directions parallel and perpendicular to the stretching direction. Inset: Schematic structures of (a) PAN-EB and (b) PAN-ES.

FIG. 2. Comparison of temperature dependence of thermoelectric power of PAN-ES at stretching ratios 1:4 ($\square$), 1:3 (∇), and 1:1 ($\circ$).

The relation $\sigma(T) \propto \exp[-(T_0/T)^{1/2}]$ is the best fit to the data for samples at all doping levels. The $S(T)$ for different stretching ratios ($l_0:l = 1:4, 1:3, 1:1$) is shown in Fig. 2. All the data show aspects of a U-shaped T dependence, similar to that of poly(o-toluidine) salt[18] (POT-ES) and SPAN,[19] two derivatives of PAN-ES. Note that $S_{\parallel}(T)$, the parallel component of $S(T)$, is always more positive than $S_{\perp}(T)$, the perpendicular component. Except for a negative constant, both $S_{\parallel}$ and $S_{\perp}$ are linear with T at high T ($T > 100$–200 K) and their slopes are *independent* of stretch ratios. This is true for all doping levels.[17] However, at low T, $S_{\parallel}$ and $S_{\perp}$ have different T dependences and are *dependent* on the degree of orientation. The values of ϵ at the low-T limit for different stretching ratios are shown in the inset of Fig. 3. The error bars account for uncertainties in geometric factors and compactness of the samples. The values of $\epsilon_{\parallel}$ strongly depend on stretching ratios. For 1:4 stretched samples, anomalously large $\epsilon_{\parallel}$ (~ 3000 at 295 K and ~ 100 at $T \to 0$) were obtained (Fig. 3). However, the low-T value of $\epsilon_{\perp}$ is essentially *independent* of stretching ratios within the experimental uncertainties.

Before going on to discussion, we briefly review some relevant theoretical models. Let us consider a quasi-1D DS consisting of N coupled parallel chains. Interchain transfer integral $t_{\perp}$ and intrachain mean free time τ are assumed. If interchain coupling is weak so that $t_{\perp} < 0.3\hbar/\tau$, the electron wave functions are localized essentially to a single chain.[2] In this case quasi-1D vari-
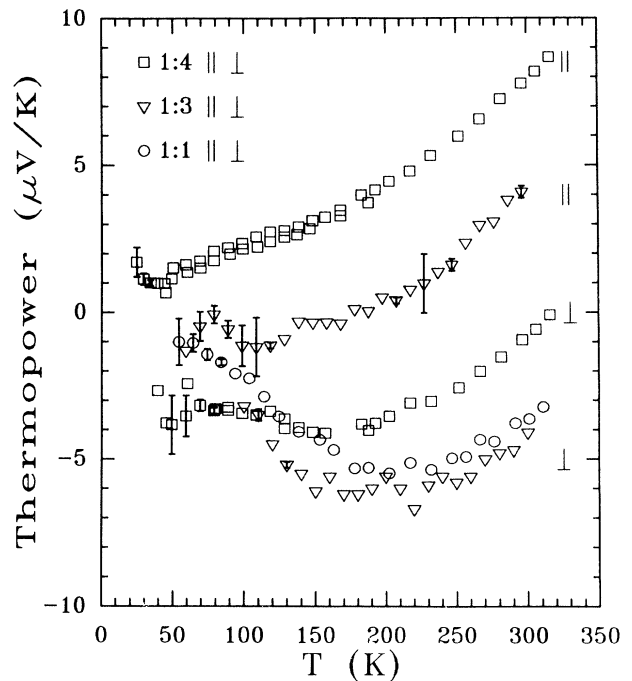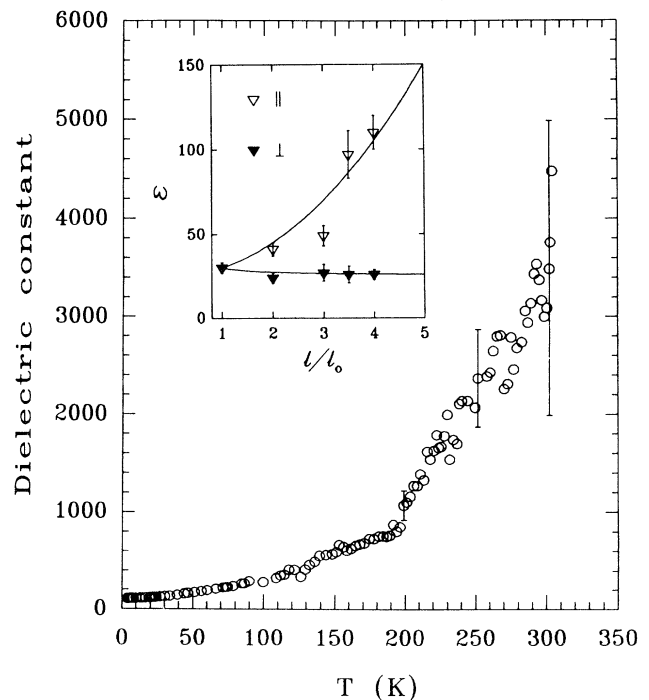

FIG. 3. Temperature dependence of the dielectric constant for a 1:4 stretched sample in the electric field F parallel to the stretching direction. Inset: The comparison of $\epsilon(T \to 0)$ at different stretching ratios. The solid lines represent $\epsilon_{\parallel} = \epsilon_{3D} + \gamma(l/l_0)^2$ and $\epsilon_{\perp} = \epsilon_{3D} + \gamma(l_0/l)$, where γ is a constant.

able range hopping (quasi-1D VRH) is expected to dominate the conduction at low T.[3,20] For interchain quasi-1D VRH, $\sigma \propto \exp[-(T_0/T)^{1/2}]$, where $k_B T_0 = 16/L_3 \times N(E_F)z$ (Refs. 18 and 20) [L_3 is the intrachain electron localization length, $N(E_F)$ the density of states, and z the number of nearest-neighboring chains]. $S(T)$ is a constant.[18] For intrachain quasi-1D VRH, $\ln\sigma \sim -T^{-1}$ (Ref. 20) and $S(T) \sim 1/T$.[18] Combining the contributions of both interchain and intrachain VRH, $S(T) = S_0 + B/T$. On the other hand, if $t_\perp > 0.3\hbar/\tau$, the electron wave functions extend uniformly over the N chains.[2] L_3 is then enhanced N times ($L_3 \sim Nl$, where l is for the isolated chains) and $L_1 \sim Nb$. In this case $S(T)$ is expected to be metallic ($\propto T$).

$S(T)$ reflects contributions from both the crystalline (metallic) and amorphous (localized) components in the polymer. The relation $S(T) = S_0 + B/T$ is followed by both POT-ES ($T < 300$ K)[18] and SPAN ($T < 250$ K).[19] We find that S_0 is always *negative* and B/T is always *positive*.[18] The similarity of $S(T)$ between PAN-ES and POT-ES or SPAN leads us to apply the expression $S(T) = S_0 + B/T$ to PAN-ES at low T (< 100 K) where $S(T)$ is dominated by the amorphous regions. This is supported by the following consideration. Since $S_0 < 0$ and $B/T > 0$ are contributions from interchain and intrachain quasi-1D VRH, respectively, it is expected that $S_\parallel$ is *more positive* than $S_\perp$, confirmed by the experiment (Fig. 2). Also, $S_\perp$ should not contain a $1/T$ term which is due to intrachain VRH. Thus the $1/T$ contribution to $S_\perp$ at low T should decrease as orientation increases. This is in accordance with a comparison of $S_\perp(T)$ for 1:3 and 1:4 stretched polymers (Fig. 2). For the high-T regime, since the linear T dependence is *independent* of orientation, we propose that it results from nearly free charge carriers transporting in 3D metallic (crystalline) regions of the polymer.

The ϵ data support the existence of these 3D metallic regions. It is noted that a giant ϵ was also observed in many TCNQ salts[5] (along the highly conducting axis). The major difference of PAN-ES and TCNQ salts is that PAN-ES has much larger $\epsilon_\perp$ (≈ 26) at low T [for (tetrathiafulvalene) TTF-TCNQ, $\epsilon_\perp = 6$]. Since $\epsilon_\perp$ is independent of stretching ratio, it is unlikely due to the contribution of $\epsilon_\parallel$ from misaligned chains. Also, the mosaic spread of 1:4 stretched polymer chains is $\pm 7°$ for crystalline regions,[14] too small to account for the observed $\epsilon_\perp$. We suggest that $\epsilon_\perp$ is mainly due to transverse polarization of electrons. Three origins were proposed for the large $\epsilon_\parallel$ in TCNQ salts: pinned charge-density-wave (CDW) states,[21] small band gaps,[5] and (quasi-1D) conductors with finite localization lengths.[3,22] The T dependence of σ, the susceptibility,[23,24] and the optical-absorption spectra[25] do not support the existence of band gaps or CDW states in PAN-ES. Assuming that the large $\epsilon_\parallel$ is the signature of a conductor with finite localization lengths, the relatively large $\epsilon_\perp$ in PAN-ES support that the electron wave functions extend beyond a

single chain since $\epsilon \propto L^2$,[3,22,26] where L is the measurement of the range of electron wave function. To estimate L, we consider the electrons limited in a rectangular box of side length $L_1 = L_2 < L_3$: $\epsilon = \epsilon_0 + (2^{9/2}/\pi^3) \times e^2 N(E_F) L_i^2$ ($i = 1,2,3$),[26] where ϵ_0 is from core polarization [4 for $\epsilon_\perp$ and 10 for $\epsilon_\parallel$ (Ref. 17)], e the electron charge, and $N(E_F) \sim 1.6$ states/eV 2-ring.[24] Hence $L_3 = 40$ Å for 1:4 stretched PAN-ES using $\epsilon_\parallel - \epsilon_0 \approx 100$ and $L_1 = L_2 = 20$ Å for $\epsilon_\perp - \epsilon_0 \sim 21$. The value 20 Å is much larger than the interchain separation of polymer chains [3.5 Å (Ref. 14)]. It confirms that the conduction electrons are delocalized transversely beyond a single conducting chain. On the contrary, $\epsilon_\perp$ at low T is 6 for TTF-TCNQ (Ref. 5) and 7 for POT-ES.[18] For these materials the contribution of conduction electrons is small (ϵ is mainly from the core polarization), apparently due to the limitation of electrons to the single conducting chains. We thus consider PAN-ES as a quasi-1D conductor consisting of bundles of N coupled parallel chains, rather than many isolated chains proposed by other authors.[8,15] This result is consistent with the $S(T)$ at higher T (> 100 K) where 3D metallic behavior was observed (Fig. 2). The metallic bundles are associated with the crystalline regions of the polymer since the values of L_i are similar to ξ_i (20–50 Å).[14] It is noted that L_i are underestimated values since the measured ϵ is an average of ϵ from the crystalline and the amorphous regions (where ϵ is expected to be much reduced).

Now we consider the σ data. Based on the studies of $S(T)$ and $\epsilon(T)$, the signatures of both quasi-1D VRH in amorphous regions and the existence of "cigar-shaped" metallic regions are observed. The behavior $\sigma(T) \propto \exp[-(T_0/T)^{1/2}]$ may be due to either the quasi-1D VRH[18,20] or hopping between the metallic bundles.[27] The electric-field dependence of σ at low T (Ref. 17) favors the quasi-1D VRH model. The similarity of σ of PAN-ES and its derivatives (POT-ES and SPAN)[18,19] also favors the quasi-1D VRH model. Based on the quasi-1D VRH model and $T_0 = 4500$ K, we obtain $L_3 \sim 60$ Å. This value is consistent with the estimates from ϵ (40 Å). These data support that the moderate value of dc σ in PAN-ES is due to the limitation of charge transport through the amorphous regions.

We conclude that the metallic states of PAN-ES are essentially 3D states and that PAN-ES represents a class of quasi-1D disordered conductors. The major difference with conventional quasi-1D conductors is that PAN-ES is composed of bundles of coupled parallel chains instead of isolated chains. The electrons are three dimensionally delocalized within the bundles. PAN-ES can be compared to thin metallic wires where Thouless localization plays an important role. The formation of the "metallic wires" in PAN-ES is attributed to strong interchain coupling and interchain crystalline order. Our results point out the important roles played by interchain coupling in stabilizing the metallic states against the "Peierls instability" and avoiding 1D electron localization in conduct-

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