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by

A.J. Epstein and A.G. MacDiarmid

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University of Pennsylvania
Department of Chemistry
Philadelphia, PA 19104-6323

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STRUCTURE, ORDER, AND THE METALLIC STATE IN POLYANILINE AND ITS DERIVATIVES

A.J. EPSTEIN

Department of Physics and Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210-1106 USA

A.G. MACDIARMID

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323
USA

ABSTRACT

The origin of high conductivity in various conducting polymers remains of considerable interest. The polyaniline family of polymers provides a means of sensitively testing the effects of crystal structure, coherence, order and chain separation on the conductivity. Extensive comparative study of emeraldine hydrochloride, oriented emeraldine hydrochloride, poly(orthotoluidine) hydrochloride, and sulfonated polyaniline demonstrate the importance of interchain diffusion of charge in achieving high conductivities. These results are in accord with magnetotransport studies of polyacetylene which similarly demonstrate the importance of three-dimensional charge diffusion.

INTRODUCTION

The report of polyacetylene of conductivity approaching 10^5 S/cm [1] lead to extensive studies to establish the electronic state and to determine the origin for the thousand-fold increase in conductivity over usual Shirakawa polyacetylene [2-5]. Recent magnetotransport studies together with magnetic susceptibility and thermopower results lead to the conclusion that the microscopic electronic phenomena in the highly doped new polyacetylene as compared with the earlier studied Shirakawa polyacetylene has not been changed, rather there is an increase in the relaxation time along the chain or interchain charge transfer that helps to avoid entrapment of charge within a single

chain. This leads to the three-dimensional delocalization of electrons responsible for the high conductivity [6].

The extension of the concept of three-dimensional delocalization of charge to other polymers has been hampered by the absence of extremely highly conducting samples. However, the advent of the polyaniline and its ease of derivatization and processing enables a critical assessment of the role of three-dimensional delocalization in obtaining highly conducting polymer systems. The results of coordinated synthetic, structural, transport and magnetic studies point to the key role of coherent interchain charge transport in the avoidance of electron localization. Hence, the development of three-dimensional order in these polymers is critical to the obtaining of high conductivity.

EXPERIMENTAL TECHNIQUES

The synthesis of polyanilines has recently been reviewed [7]. Figure 1 summarizes the chemical structure of the insulating forms of polyaniline, including leucoemeraldine base (LEB), emeraldine base (EB) and pernigraniline base (PNB), the conducting emeraldine hydrochloride salt form, as well as schematic structures for the monomethyl substituted polyaniline, poly(orthotoluidine) (POT), in the emeraldine base oxidation state and the self-doped sulfonic acid substituted polyaniline, SPAN.

Recent advances in the processing of the polyanilines enable the study of the orientation and crystallinity of dependence of the charge transport mechanisms. In particular, the emeraldine base can now be processed to form oriented films [8, 9]. Both emeraldine base [9, 10] and emeraldine salt [11] can be processed to obtain highly oriented fibers. The techniques used for structural studies [12, 13] and charge transport measurements [14, 15] have been previously described.

RESULTS AND DISCUSSION

Figure 2 represents the conductivity measured along the fiber direction for polyaniline fibers that were drawn (in water) from emeraldine base solution in N-methylpyrrolidinone and subsequently stretched to preselected lengths at 140°. These fibers, from the same batch, were then equilibrated with 1 M HCl to produce a dopant concentration of $x \equiv [Cl]/[N] = 0.5$. Data, measured in air, show a dramatic increase of conductivity of the polyaniline with orientation. Further studies of x-ray diffraction of the fibers show an increase in crystallinity and orientation with draw ratio [10].

The study of the parallel and perpendicular conductivity of four-fold stretch oriented polyaniline, Fig. 3, shows an anisotropy of the conductivity of approximately a factor of 10 and a small difference of temperature dependence in the parallel and perpendicular directions. The anisotropy in the dielectric constant and thermoelectric power are even more dramatic [14]. The conductivity, thermopower and dielectric constant of unoriented samples of emeraldine hydrochloride more closely resemble the behavior in the

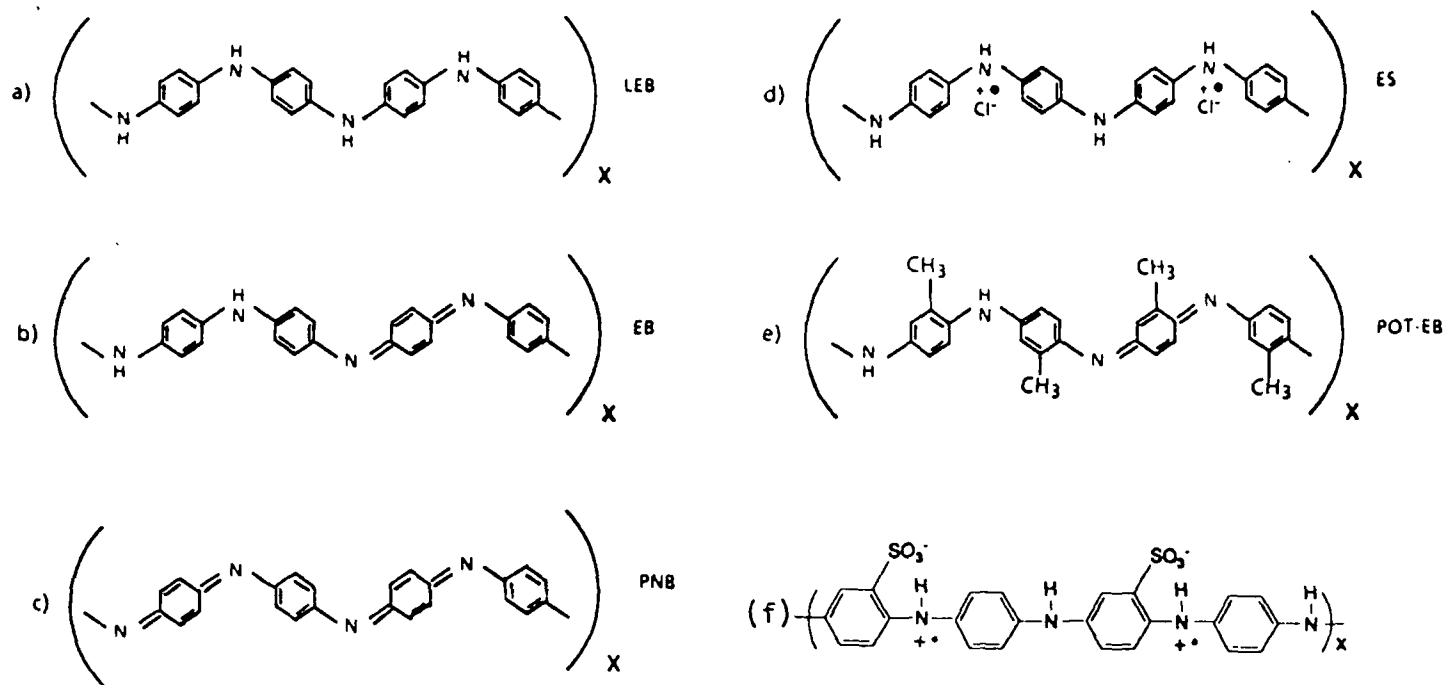


Fig. 1 (a) leucoemeraldine base; (b) emeraldine base; (c) pernigraniline base; (d) emeraldine hydrochloride salt polymer; (e) poly(orthotoluidine) (emeraldine base form); (f) sulfonated polyaniline (self-doped salt form).

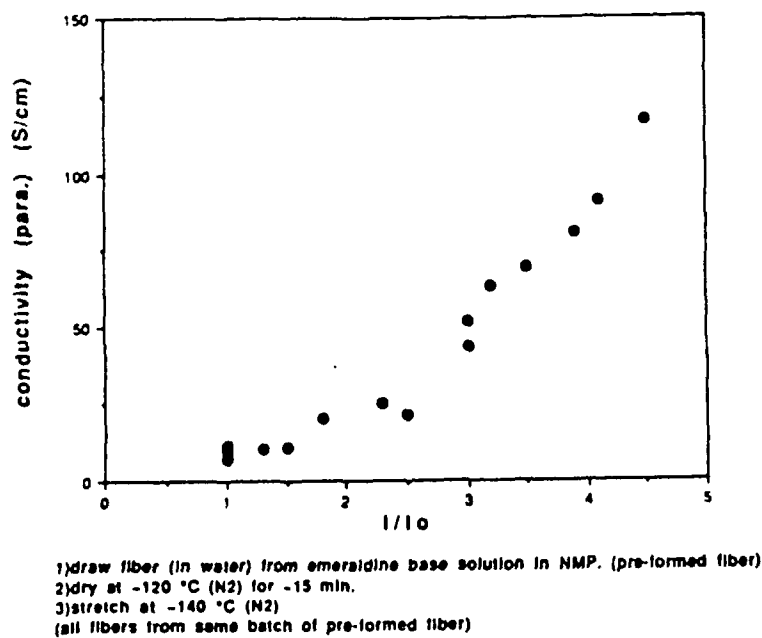


Fig. 2 Conductivity (parallel) vs. draw ratio (l/l₀) of polyaniline (emeraldine base) fibers (doped with 1M HCl)

perpendicular direction of the oriented samples. Extensive studies of unoriented poly(orthotoluidine) hydrochloride show a behavior similar to the perpendicular transport phenomena of oriented emeraldine hydrochloride [15]. Unoriented sulfonated polyaniline is similar to poly(orthotoluidine) hydrochloride in its transport.

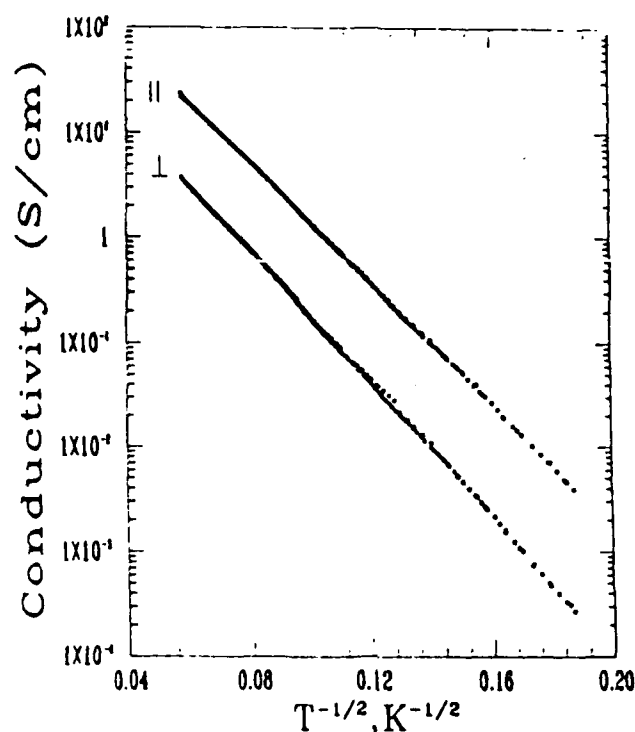


Fig. 3 Temperature dependence of dc conductivity of 50% doped 1:4 stretched PAN-ES (HCl) films in the directions parallel and perpendicular to the stretching directions.

Extensive x-ray diffraction studies show that for emeraldine there is an increase in crystallite size and decrease in interchain separation with protonation level. This corresponds with the increasing three-dimensional delocalization of charge with protonation [16, 17].

The temperature and orientation dependences of thermoelectric power and dielectric constant of oriented emeraldine hydrochloride suggest a "cigar" shaped metallic region in which electron states are extended and also signs of quasi-one-dimensional variable range hopping. The quasi-1-D variable range hopping [$\sigma(T) \propto \exp[-(T_0/T)^{1/4}]$] likely results from hopping within the amorphous regions. Utilizing the quasi-1-D variable range hopping model we estimate a localization length in the parallel direction of $\sim 30 \text{ \AA}$ similar to the localization length determined by low temperature microwave dielectric constant studies and to the coherence length for the crystalline regions measured by x-ray diffraction. Perpendicular dielectric constant studies lead to a low temperature localization length in the perpendicular direction of $\sim 10 \text{ \AA}$, considerably larger than the interchain separation in the crystalline regions. Thus, in partially crystalline

emeraldine hydrochloride, the conduction electrons appear delocalized over bundles of chain within the ordered regions. Thouless-like localization may occur at low temperatures within the finite rigid ordered domains. The lower conductivity of unoriented poly(orthotoluidine) hydrochloride and sulfonated polyaniline correspond with much shorter localization lengths ($\sim 5\text{-}9\text{\AA}$) so that quasi-one-dimensional variable range hopping appears to dominate the charge transport in these derivatized systems. Improvement of local order, both along the chain and in the interchain direction, may lead to crossover to the 3-D delocalized regime.

CONCLUSION

The highly conducting polyacetylene and oriented polyanilines represent a new class of behavior for conducting polymers and quasi-one-dimensional systems. Analysis of x-ray structure together with transport and derivatization data leads to the suggestion that there is significant three-dimensional delocalization of charge within the bundles of chains in crystalline regions. Hopping and localization effects in disordered regions continue to dominate the dc conductivity. Improved orientation and crystallinity should lead to a dramatic increase in conductivity.

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