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| <p>Electron localization in HCl salt form of polyaniline (PAN-ES) and its methyl ring-substituted derivative, poly(o-toluidine)(POT-ES), has been investigated by optical, transport and magnetic studies. Compared with PAN-ES, POT-ES has increased electron localization though the band structure, crystallinity and intrachain coherence length are similar for the two polymers. The localization is proposed to be induced by a CH<sub>3</sub> group on each C<sub>6</sub> ring which decreases the interchain diffusion rate through reduction of interchain coherence and increased interchain separation.</p> |       |                                      |                                                                                      |                                                                  |                    |
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ELECTRON LOCALIZATION IN POLYANILINE AND ITS DERIVATIVES

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## ABSTRACT

Electron localization in HCl salt form of polyaniline (PAN-ES) and its methyl ring-substituted derivative, poly(o-toluidine)(POT-ES), has been investigated by optical, transport and magnetic studies. Compared with PAN-ES, POT-ES has increased electron localization though the band structure, crystallinity and intrachain coherence length are similar for the two polymers. The localization is proposed to be induced by a  $\text{CH}_3$  group on each  $\text{C}_6$  ring which decreases the interchain diffusion rate through reduction of interchain coherence and increased interchain separation.

## INTRODUCTION

The achievement of high conductivity  $\sigma$  for polymers has both theoretical and practical importance. Often high  $\sigma$  has been attributed to increase of conjugation length[1]. Though the decrease of conjugation length does decrease the conductivity[2], other factors may be more important in control of very high conductivity of polymers. It is well-known that in a strictly one-dimensional disordered system (1d-DS) all electron states are localized with any weak disorder[3]. However polymer systems are quasi 1d-DS (q1d-DS) where interchain diffusion is not negligible. The interchain diffusion rate  $w$  plays an important role in electron localization of a q1d-DS[4,5]. It can be shown[4,5] that with increase of  $w$  the electron localization length  $\alpha^{-1}$  and  $\sigma$  of a q1d-DS increase. The value of  $w$  depends on interchain transfer integral  $t_{\perp}$ , interchain coherence length  $\xi_{\perp}$  and intrachain coherence length  $\xi_{\parallel}$ [4,5] or conjugation length. Thus the increase of the conjugation length or  $\xi_{\parallel}$  does increase  $\alpha^{-1}$  and  $\sigma$  of polymers. However the other two factors may also play important roles in electron localization. We explore their importance in this paper.

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PAN and POT were synthesized in the base and salt form as described earlier[5](Fig.1a). Pressed pellets were used for most of the transport measurements, with the exception of microwave studies where films cast from N-Methyl-2-Pyrrolidinone were used. A four-probe technique was utilized for  $\sigma_{dc}$  measurements. The 'cavity perturbation' technique was adopted for the microwave measurement. EPR X-band measurements utilized a Bruker EPS 300 spectrometer. The static  $\chi$  was measured by Faraday technique[5].

The EPR peak-to-peak linewidth (Fig. 1b) of POT-ES monotonically decreases from 2.7 G to 0.7 G as T increases from 4 K to 300 K, however that of PAN-ES has very little T-dependence ( $\sim 0.3$  G). The optical absorption spectra of PAN-ES and POT-ES in aqueous 80% acetic acid (inset of Fig. 1b) are qualitatively the same. For both polymers  $\sigma \propto \exp[-(T_0/T)^{1/2}]$ , but  $T_0 = 5000$  K for PAN-ES and 30000 K for POT-ES (Fig. 2a). The room temperature  $\sigma$  of PAN-ES is about  $10^0 \sim 10^1$  S/cm, and that of POT-ES is  $10^{-3} \sim 10^{-2}$  S/cm, depending on moisture, ageing, doping, etc. The dielectric constants  $\epsilon$  at frequency 6.5 GHz increases with T, from 20 to 100 for PAN-ES and 7 to 10 for POT-ES as T from 50 K to 300 K. The thermoelectric powers  $S(T)$  of the two polymers have similar U-shape T-dependence (inset of Fig. 2b). The minimum of  $S(T)$  for PAN-ES is between 150 K and 200 K and for POT-ES it is approximately 300 K. At low T ( $< 300$  K),  $S(T)$  of POT-ES can be expressed as  $A + B/T$ [5], while  $S(T)$  of PAN-ES can be approximately decomposed into  $A + B/T + CT$ [7].

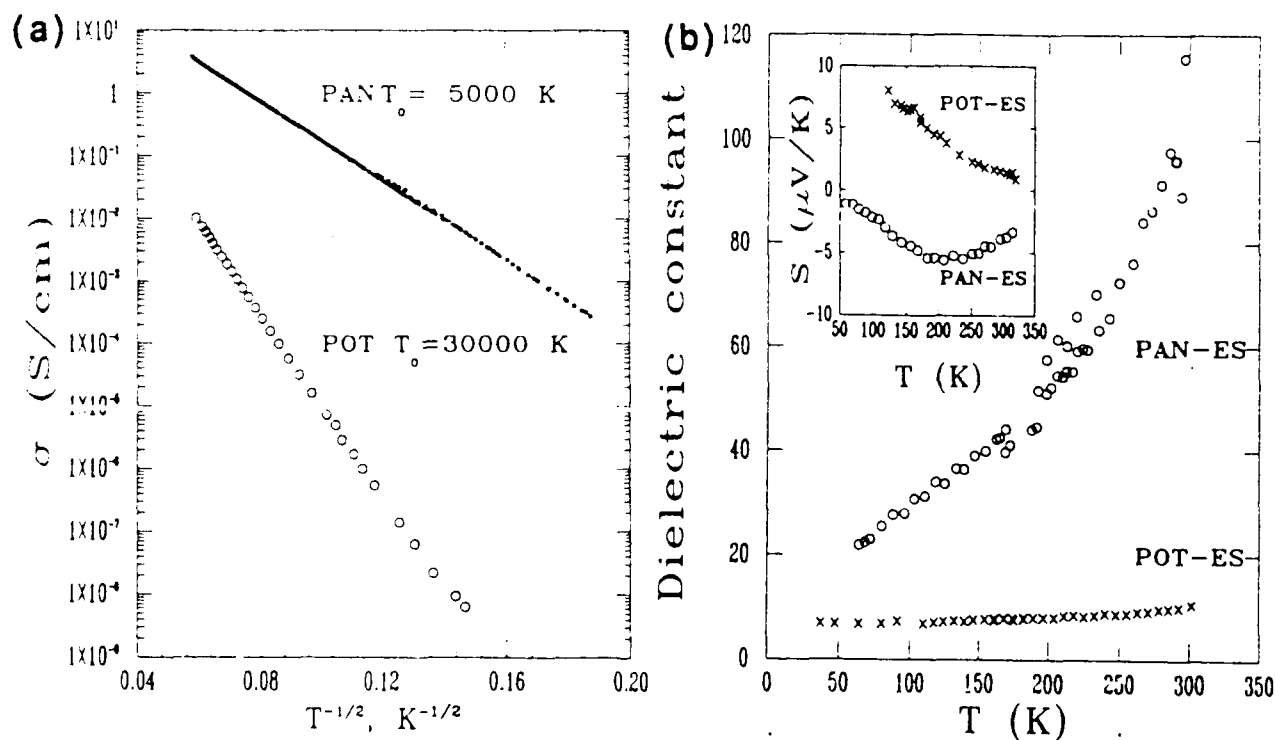


Fig.2 (a) DC conductivity of PAN-ES ( $\bullet$ ) and POT-ES ( $\circ$ ). (b) Dielectric constant of unoriented PAN-ES ( $\circ$ ) (Javadi et al, *Phys. Rev. B*, 39 (1989) 3579.) and POT-ES ( $\times$ ). Inset is thermoelectric power of PAN-ES ( $\circ$ ) and POT-ES ( $\times$ ).

We compare here two polymers, the HCl salt form of polyaniline (PAN-ES) and its methyl ring-substituted derivative, poly(o-toluidine) (POT-ES) (Fig.1a)[5]. They have similar electronic structures, crystallinity and more importantly  $\xi_{\parallel}$ , but different  $\xi_{\perp}$  and interchain space or  $t_{\perp}$ [5,6]. Analyses of T-dependent DC conductivity  $\sigma_{dc}(T)$ , electric field dependent  $\sigma(E)$ , thermopower  $S(T)$ , microwave conductivity and dielectric constant  $\epsilon$  at 6.5 GHz, susceptibility  $\chi$ , and electron paramagnetic resonance (EPR) linewidth and lineshape together show that there is greater electron localization in POT-ES as compared with that in PAN-ES[5]. Our study together with the results of X-ray studies[6] suggests that the increased electron localization in POT is associated with the increased one-dimensionality induced by decreased interchain diffusion rate due to (i) the increased interchain separation and (ii) greater interchain disorder within the crystalline regions. Both are due to existence of  $\text{CH}_3$  on  $\text{C}_6$  rings. The  $\text{CH}_3$  has larger size than H and its location at the "a" or "b" position of  $\text{C}_6$  ring (Fig.1a) is dependent on ring flipping. Hence it induces an increase of interchain spacing and disorder. The transport data suggest that conduction is due to quasi-1d variable range hopping [5]. Based on this model quantitative analyses show  $\alpha^{-1}$  for POT-ES is several Å, while for PAN-ES is a few tens Å.

## EXPERIMENTAL TECHNIQUES AND RESULTS

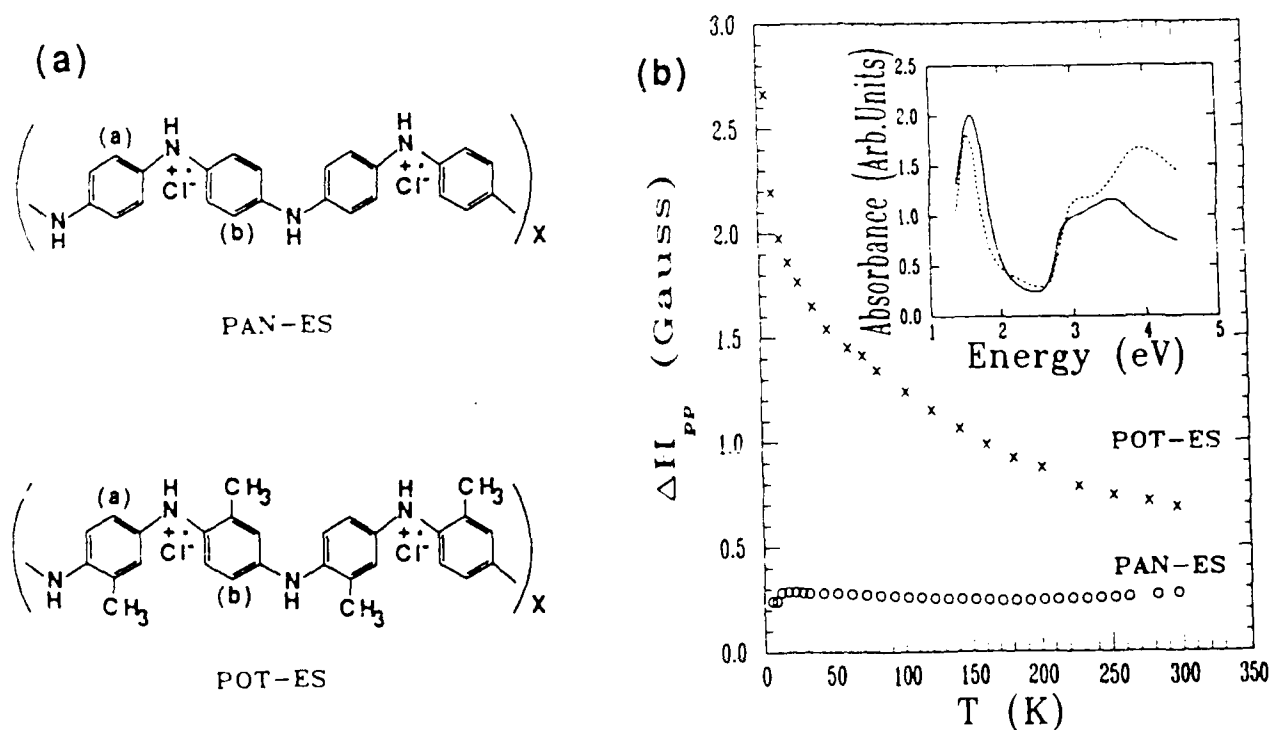


Fig.1 (a) Schematic structure of PAN-ES and POT-ES. (b) EPR peak-to-peak linewidth of PAN-ES (o) (from P. Vaca et al, to be published) and POT-ES (x). Inset is the optical spectra of PAN-ES (solid line) and POT-ES (dashed line) in aqueous 80% acetic acid.

## DISCUSSION

The EPR linewidth, DC conductivity, microwave dielectric constant and thermoelectric power altogether reflect increased electron localization in POT-ES compared with PAN-ES. The narrowed EPR linewidth indicates a strong spin motional or exchange narrowing[5]. The greater EPR linewidth as well as lower conductivity and dielectric constant in POT-ES is a signature of increased spin localization in POT-ES[5]. The T-dependence of  $\sigma(T) \propto \exp[-(T_0/T)^{1/2}]$  and  $S(T) \propto A + B/T$  (at low temperatures) indicating a q1d-VRH of charges between nearest neighboring chains[5]. Within the model,  $T_0 = 16\alpha/N(E_F)k_B z$ [5] where  $N(E_F)$  is density of states at Fermi energy,  $k_B$  is the Boltzmann constant and  $z$  is the number of nearest neighboring chains. Utilizing  $N(E_F) = 3.5$  (PAN-ES) and 1.7 (POT-ES) states/eV-2rings[5], we obtain  $\alpha^{-1} \sim 30 \text{ \AA}$  for PAN-ES and 9  $\text{\AA}$  for POT-ES.

Two polymers have very similar electronic structures and crystallinity, but very different electron localization and transport properties. Based on the EPR lineshape analyses[5] and x-ray studies[6], the increased electron localization is attributed to the decreased interchain diffusion rate, associated with the decrease of  $\xi_{\perp}$  and increased interchain separation (decrease of  $t_{\perp}$ ), not with the change in conjugation length. The studies of oriented PAN-ES[7] suggest that PAN-ES represents a new class of q1d disordered conductors where electrons are delocalized to a bundle of chains with the dimension determined by  $\xi_{\perp}$ [7] while POT-ES remains as a non-metal. Our results demonstrate that maximizing interchain coherence and transfer integral is essential to improve the conductivity of polymers.

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## REFERENCES

- 1 Handbook of Conducting Polymers, Vol.2, ed. by T.A. Skotheim (Dekker, NY, 1986).
- 2 F. Zuo, A.J. Epstein, X.Q. Yang, D.B. Tanner, G. Arbuckle, and A.G. MacDiarmid, Synth. Met., **17**, (1987) 433.
- 3 A.A. Gogolin, Phys. Rept., **1**, (1982) 1 ; **5** (1988) 269.
- 4 Y.A. Firsov, in H. Fritzsche and D. Adler (eds.), Localization and Metal Insulator Transition, Plenum Press, 1985, p.477; S. Kivelson and A.J. Heeger, Synth. Met., **22**, (1988) 371.
- 5 Z.H. Wang, H.H.S. Javadi, A. Ray, A.G. MacDiarmid, and A.J. Epstein, Phys. Rev. B, **42**, 1990 5411; Z.H. Wang, A. Ray, A.G. MacDiarmid, and A.J. Epstein, *ibid*, in press.
- 6 M.E. Józefowicz, R. Laversanne, H.H.S. Javadi, J.P. Pouget, X. Tang, and A.G. MacDiarmid, Phys. Rev. B, **39**, (1989) 12958; Synth. Met., in this volume.
- 7 Z.H. Wang, C. Li, E. Scherr, A.G. MacDiarmid, J. Yue, and A.J. Epstein, to be published.