



Time: Four per response, including the time for reviewing instructions, searching existing data sources, collection of information, and comments regarding this burden estimate or any other aspect of this Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

2

1. AGENCY USE ONLY (Leave blank) 2. REPORT DATE June 5, 1992 3. REPORT TYPE AND DATES COVERED Technical - 5/31/91 - 6/30/92

4. TITLE AND SUBTITLE "ELECTRONIC PHENOMENA IN POLYANILINES" 5. FUNDING NUMBERS G-N00014-90-J-1559

6. AUTHOR(S) A.J. Epstein and A.G. MacDiarmid

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Pennsylvania Department of Chemistry Philadelphia, PA 19104-6323 8. PERFORMING ORGANIZATION REPORT NUMBER 1992-9

DTIC
SELECTED
SEP 01 1992
S B D

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Sponsoring Agency: DARPA 3701 N. Fairfax Drive Arlington, VA 22203-1714 Monitoring Agency: ONR 800 N. Quincy Street Arlington, VA 22217-5000 10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT Distribution Unlimited 12b. DISTRIBUTION CODE

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

13. ABSTRACT (Maximum 200 words) Polyanilines have been known for over one hundred years. Recent studies of this chemically flexible polymer have demonstrated unusual chemical, electrical, and optical phenomena, both in insulating forms and conducting forms. Polyaniline has three stable insulating forms, leucoemeraldine base (LEB), emeraldine base (EB), and pernigraniline base (PNB). These three forms exhibit differing phenomena ranging from intramonomer luminescing excitons and ring rotation polarons in LEB, to nonluminescing charge transfer excitons and also ring rotational polarons in EB, to a degenerate ground state with bond order parameter solitons and ring order parameter polarons in PNB. The LEB form can be p-doped (oxidatively doped), the EB form can be protonic acid doped and the PNB form can be n-doped (reductively doped) to form conducting systems. Charge conduction studies of oriented films and fibers demonstrate that three-dimensional order between chains is critical for high conductivities. The ability to derivatize polyaniline at ring and nitrogen positions allows one to test concepts for the control of conductivity as well as improved processing.

92 8 28 097

278975

92-23995



1488

14. SUBJECT TERMS leucoemeraldine base (LEB), emeraldine base (EB), pernigraniline base (PNB), films, fibers, charge transfer excitons, ring rotation polarons, bond order parameter solitons, three dimensional order, conductivity. 15. NUMBER OF PAGES 12 16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified 18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified 19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified 20. LIMITATION OF ABSTRACT UL

OFFICE OF NAVAL RESEARCH

GRANT NO.: N00014-90-J-1559

R & T CODE NO.: A400004DF3

TECHNICAL REPORT NO.: 1992-9

"ELECTRONIC PHENOMENA IN POLYANILINES"

by

A.J. Epstein and A.G. MacDiarmid


Accepted for Publication in
Frontiers of Polymer Research (1991)

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

June 5, 1992

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Electronic Phenomena in Polyanilines

Arthur J. Epstein

Department of Physics and Department of Chemistry
The Ohio State University
Columbus, OH 43210-1106 U.S.A.

Alan G. MacDiarmid

Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104-6323 U.S.A.

DTIC QUALITY INSPECTED 3

ABSTRACT

Polyanilines have been known for over one hundred years. Recent studies of this chemically flexible polymer have demonstrated unusual chemical, electrical, and optical phenomena, both in insulating forms and conducting forms. Polyaniline has three stable insulating forms, leucoemeraldine base (LEB), emeraldine base (EB), and pernigraniline base (PNB). These three forms exhibit differing phenomena ranging from intramonomer luminescing excitons and ring rotation polarons in LEB, to nonluminescing charge transfer excitons and also ring rotations polarons in EB, to a degenerate ground state with bond order parameter solitons and ring order parameter polarons in PNB. The LEB form can be *p*-doped (oxidatively doped), the EB form can be protonic acid doped and the PNB form can be *n*-doped (reductively doped) to form conducting systems. Charge conduction studies of oriented films and fibers demonstrate that three-dimensional order between chains is critical for high conductivities. The ability to derivatize polyaniline at ring and nitrogen positions allows one to test concepts for the control of conductivity as well as improved processing.

FREQUENCY RESPONSE

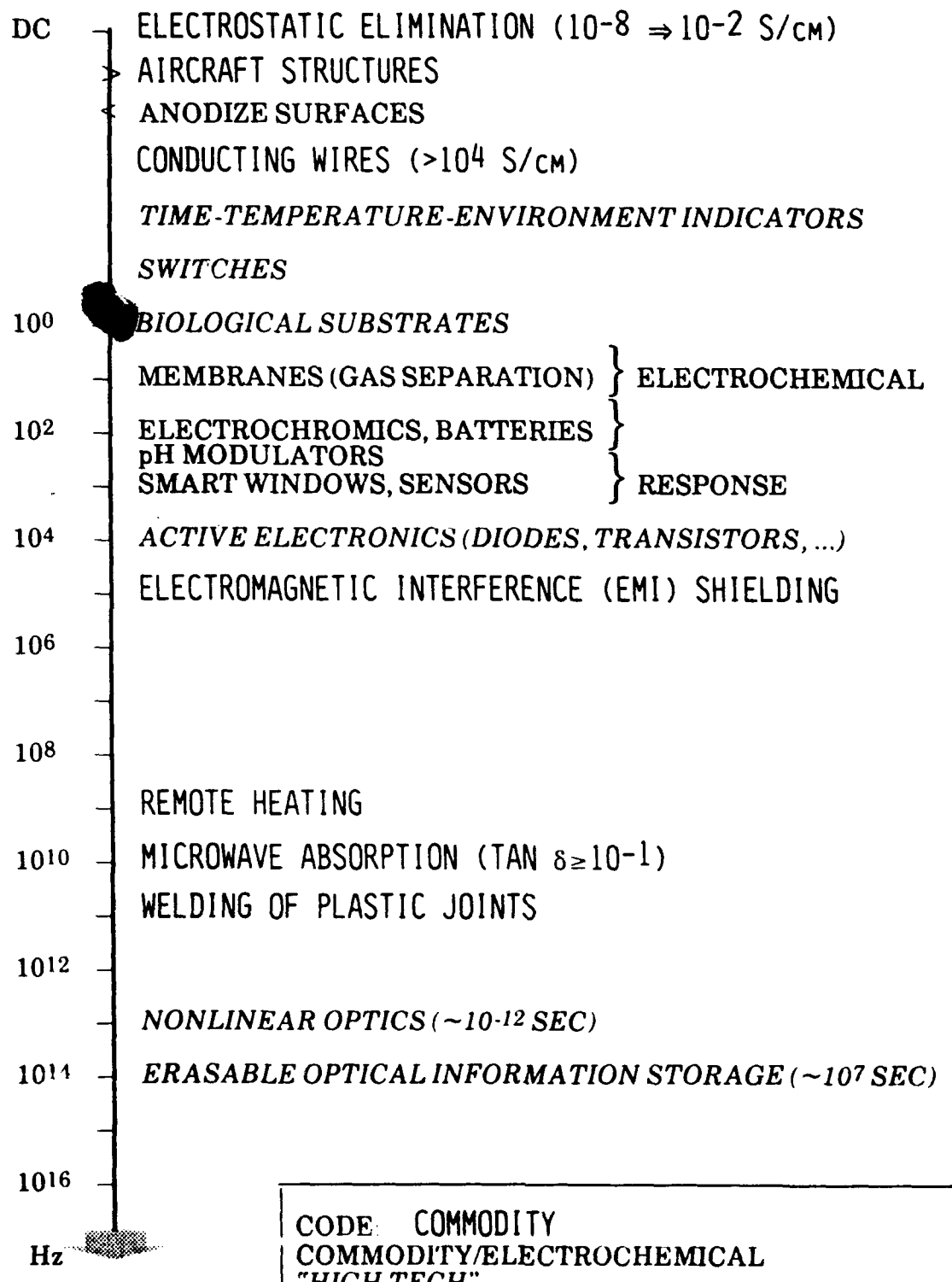


Fig. 1 Potential applications of electronic polymers.

INTRODUCTION

The polyanilines are among the oldest known synthetic organic polymers, having been first reported in 1862 [1]. Since the mid-1980's there has been a mushrooming interest in this family of polymers [2-8]. Synthesis of polyanilines and their derivatives have been extensively described [7]. The facile chemistry of this system and its ability to be processed into oriented films [9,10] and fibers [11-13] have opened the opportunity to design in properties for function. This has led to interest in the potential use of polyanilines and related conducting polymers in a variety of commodity, commodity/electrochemical, and high tech type applications [14, 15]. Figure 1 summarizes the range of technologies proposed. It is noted that a wide range of resistivities from insulating through highly conducting are of potential utility.

We review here the essential differences in the physics of the three different polyaniline insulating forms as well as present a summary of the critical aspects controlling conductivity in the emeraldine salt system. The effects of derivatization are briefly indicated. The parent polyaniline can be prepared in a range of oxidation states ranging from the fully reduced form, leucoemeraldine base (LEB), $\text{-(NH-C}_6\text{H}_4\text{-NH-C}_6\text{H}_4\text{)}_x\text{-}$ (Fig. 2a.), to the fifty percent oxidized emeraldine base (EB), $\text{-(NH-C}_6\text{H}_4\text{-NH-C}_6\text{H}_4\text{-N=C}_6\text{H}_4\text{=N-C}_6\text{H}_4\text{)}_x\text{-}$ (Fig. 2b), to the fully oxidized pernigraniline base (PNB), $\text{-(N=C}_6\text{H}_4\text{=N-C}_6\text{H}_4\text{)}_x\text{-}$ (Fig. 2c) [7,16]. The three base forms are insulators. Protonation of EB or oxidation of LEB leads to formation of the conducting emeraldine salt (ES) shown in Fig. 2d as the hydrochloride salt.

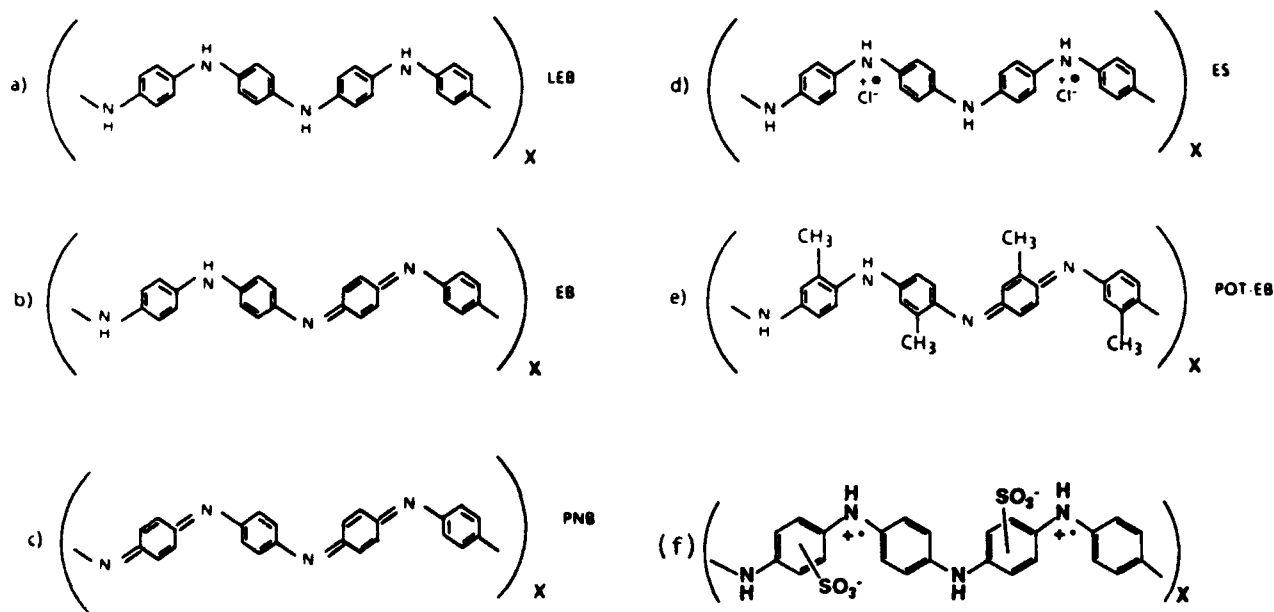


Fig.2. (a) leucoemeraldine base; (b) emeraldine base; (c) pernigraniline base; (d) emeraldine hydrochloride salt polymer; (e) poly(orthotoluidine) (emeraldine base form); (f) sulfonated polyaniline (self-doped form).

DERIVATIZATION

The polyanilines are easily derivatized at the ring [17-19] and nitrogen [20] positions. For example, replacement of one H of each ring with a CH_3 group to form poly(*o*-toluidine), Fig. 2e, enables testing of the roles of interchain separation and crystalline order in determining electronic properties [17,21,22], while replacement of a H on one-half the rings with a sulfonic acid group, $-\text{SO}_3\text{H}$, Fig. 2f, leads to a self-doped polymer the conductivity of which is independent of pH for $\text{pH} \lesssim 7.5$ [18,19] (Fig. 3) and exhibits greater thermal and environmental stability [23]. The change in doping level with temperature for emeraldine hydrochloride and ring-sulfonated polyaniline is estimated by assuming that the entire weight loss measured by thermogravimetry is due to loss of HCl and SO_3H , respectively, Fig. 4. In actuality, loss of polymer fragments may occur as well.

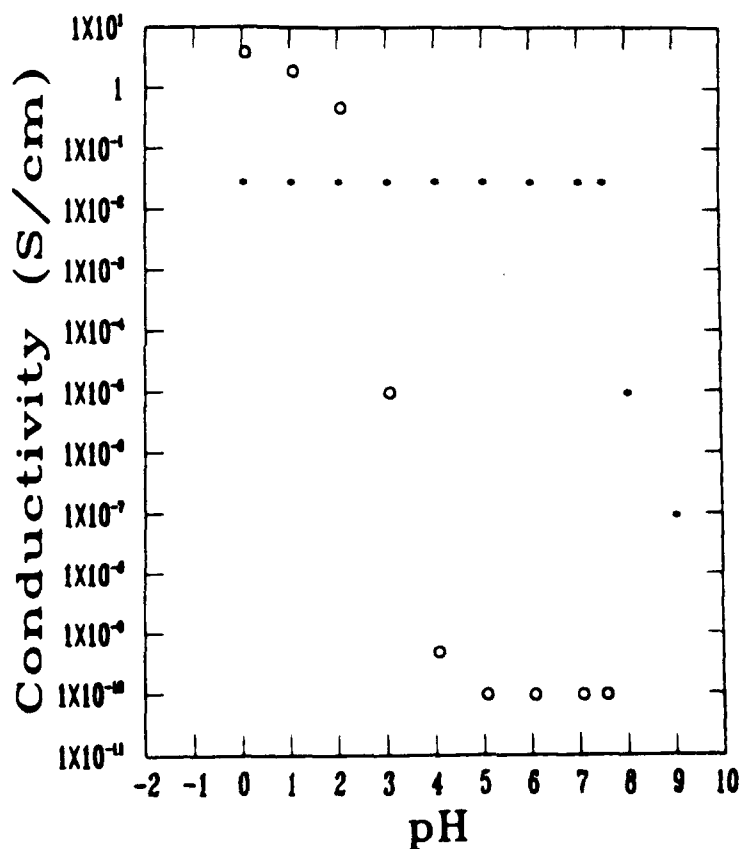


Fig. 3. pH dependence of conductivity of ring-sulfonated polyanilines (*) and the emeraldine hydrochloride form of polyaniline (o) (from Ref. 19).

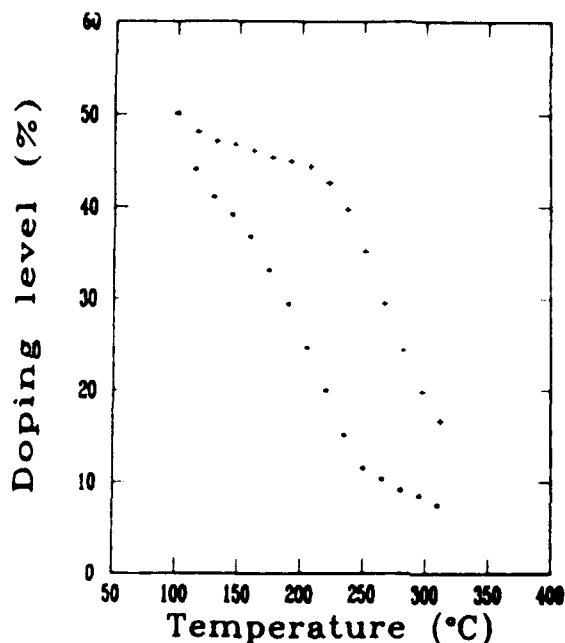


Fig. 4. Doping levels determined by thermogravimetry of emeraldine hydrochloride (*) and sulfonated polyaniline (+) as a function of temperature assuming that the entire weight loss for each polymer is due only to loss of HCl and SO₃H respectively (from Ref. 23).

SPECTROSCOPY AND PHOTOEXCITATION SPECTROSCOPY

The optical absorption spectrum of LEB [24] is shown in Fig. 5 together with the results of a Hückel calculation for the electronic band structure of LEB carried out assuming that the repeat unit is a single (C₆H₄NH) unit [25,26]. This simple calculation reproduces most of the band structure features obtained in more extensive calculations [27,28,29]. The seven energy bands are derived from the six p_z energy levels of benzene together with the p_z energy level of nitrogen. The lower four energy bands are completely filled while the upper three are empty. It is noted that the valence band is relatively broad (its breadth depending upon the ring torsion angle) while the conduction band is dispersionless. Hence, charge conjugation symmetry is absent in leucoemeraldine base. The exact width and separation of each of the bands are sensitive to the torsion angle the C₆ rings make with respect to the plane defined by the nitrogen atoms [25,29].

Excitation of leucoemeraldine solutions in *N*-methylpyrrolidone (NMP) with bandgap light produces an intense luminescence peak at 3.5 eV [30], Fig. 6. The magnitude of the luminescence intensity decreases linearly with increasing concentration of imine groups within the polymer chain. The luminescence is nearly zero when the emeraldine base oxidation state is achieved. The decay

time for the luminescence has been measured and found to be ~ 4 ns at room temperature [30]. The presence of a similar luminescence in three-ring oligomers [30] and also in the aniline ($C_6H_5NH_2$) monomer [31] supports that the luminescence derives from radiative decay of an intramonomer polaronic exciton [32].

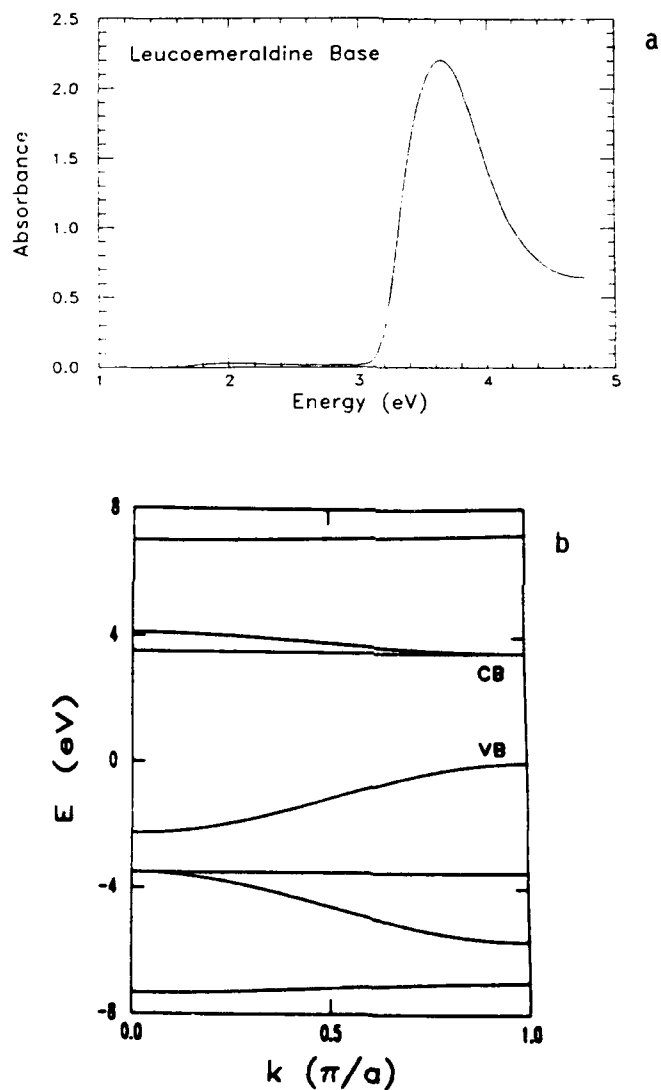


Fig. 5.(a) Absorption spectrum of leucoemeraldine base in NMP (from Ref. 33); (b) Hückel electronic band structure of leucoemeraldine (from Ref. 25).

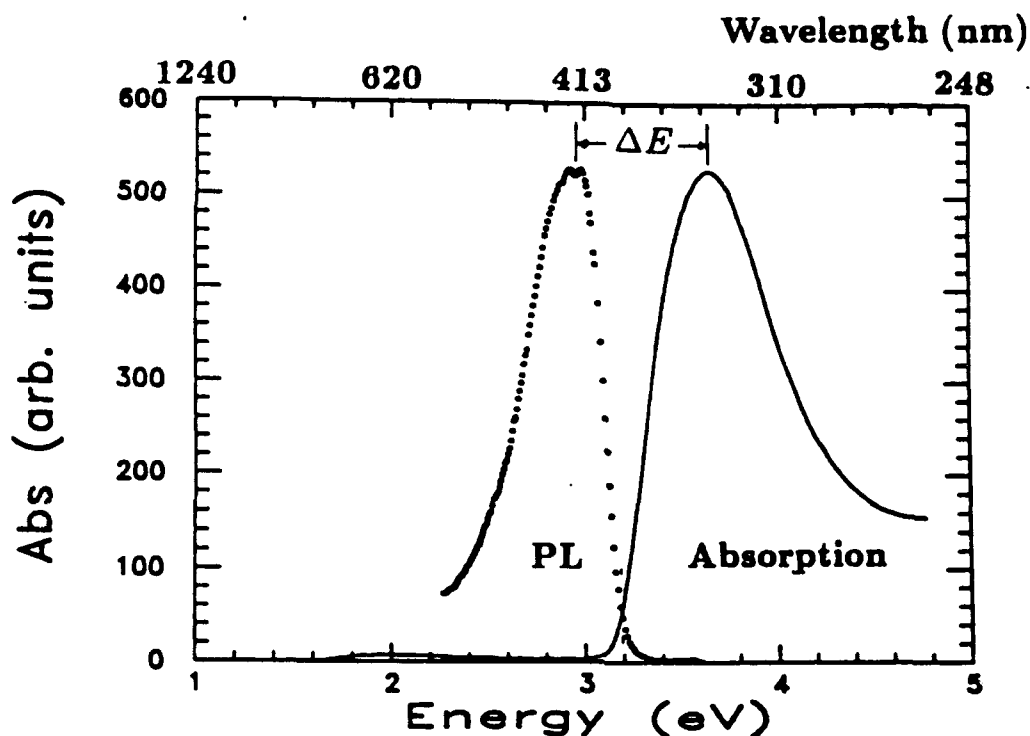


Fig. 6. Absorption and photoluminescence spectra for leucoemeraldine base in NMP, the exciting wavelength for the PL spectrum is ~ 345 nm (from Ref. 30).

Photoexcitation of LEB films and powders with superbandgap light leads to new intragap absorptions centered at 0.7 eV and 2.9 eV [24,33]. This photoinduced absorption has been described in terms of formation of a ring rotation polaron [24-26, 33]. Because of the large charge conjugation asymmetry in the system there is only one energy level introduced into the gap by the distortion of the ring torsion angles. This polaron differs substantially from earlier studied polarons in polythiophene and polypyrrole and their derivatives in that it has a very large effective mass ($\sim 50m_e$) due to the effects of a large moment of inertia involved in rotating the polyaniline rings about the N-N axis. Also observed in the photoexcitation spectrum is a bleaching at ~ 2.0 eV associated with the presence of some residual imine groups in the otherwise pure LEB. At long times a photoinduced absorption at ~ 1.4 eV is stable. This absorption is associated with a ring rotation polaron trapped adjacent to a quinoid ring. This trapped ring rotation polaron is readily observed in the photoexcitation spectra of emeraldine base [24,33]. Comparison of the magnitude of the photoinduced *ir* active vibrations and electronic absorption confirms the large mass of the photoexcited defects.

The optical absorbance of pernigraniline base though similar to that of EB is different in origin. In particular, the 2.3 eV absorption in PNB has been assigned to the excitation across a Peierls energy gap. This Peierls gap has been proposed to arise from two independent contributions, variation in bond length order parameter and variation in ring torsion angle order parameter, [25,34,35]. The effects of these two order parameters recently have been shown to vary additively [29]. Steady state photoinduced absorption experiments show the presence of a photoinduced charge defect of effective $\sim 5 m_e$ and a photoinduced charge defect of effective mass $\sim 300 m_e$. Because of the enormous difference in their effective mass and their lifetimes, the low energy peak is associated with a solitonic defect in the bond length order parameter while the middle energy peak is associated with a polaronic defect in the ring torsion angle order parameter [36]. Light induced electron spin resonance studies support these assignments [37]. This is the first known material where two order parameters contribute independently to the bandgap and sustain separate excitations.

CHARGE TRANSPORT

The increase in conductivity of emeraldine salt fiber as a function of elongation ratios (l/l_0) demonstrates the importance of orientation and crystallinity (which increases with stretch ratio [13-15]). The conductivity, $\sigma(T) \sim \exp[-(T_0/T)^{1/2}]$ suggests the relevance of two models: quasi-one-dimensional variable range hopping (VRH) [21, 22,38] and hopping of charge carriers between granular metallic regions [39]. The dc conductivity of the hydrochloric salt of poly(orthotoluidine) (POT-ES) has the same temperature dependence but with a six-fold larger T_0 indicative of greater localization of the charge carriers. The thermoelectric power for POT-ES shows only a term for variable range hopping without any temperature range where a metallic-like thermopower dominates [21,22]. Self-doped sulfonated polyaniline (SPAN) [19] provides a similar case study.

The temperature dependence of the microwave frequency (6.5GHz) dielectric constant for unoriented emeraldine hydrochloride (PAN-ES) [40], POT-ES [21,22] and self-doped sulfonated polyaniline [41], Fig. 7, graphically illustrates the importance of interchain interaction in delocalization. Analysis of these data and the data for stretch oriented emeraldine hydrochloric film [30] suggests that the localization length for positive charges in SPAN-ES is $\sim 6\text{\AA}$ while that for POT-ES is $\sim 8\text{\AA}$. Both of these systems have conductivity dominated by quasi-one-dimensional variable range hopping. In contrast, PAN-ES has a parallel localization length in the order of 50\AA and a perpendicular localization length $\sim 20\text{\AA}$ even at low temperatures [38]. These dimensions which coincide with the estimated size of the crystalline regions strongly support that the three-dimensional delocalization of charge carriers occurs within the crystalline regions of PAN-ES.

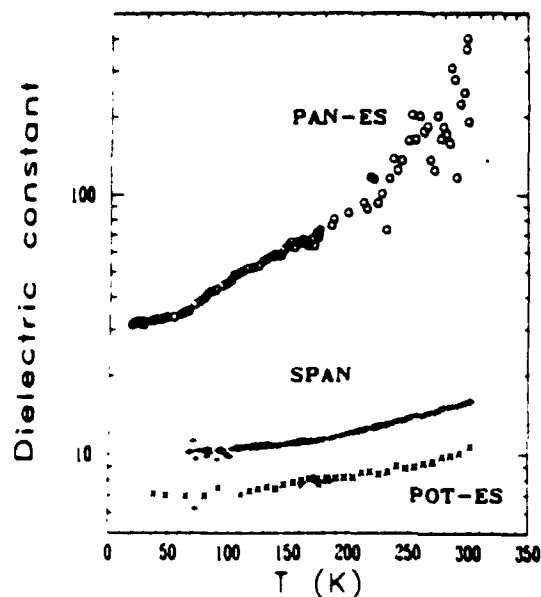


Fig. 7. Microwave frequency dielectric constant vs. temperature for unoriented PAN-ES (from Ref.38) unoriented POT-ES (from Ref. 22) and sulfonated polyaniline (from Ref. 41).

SUMMARY

The varied chemistry and ability of the polyanilines to be processed together with their environmental stability makes the systems suitable for scientific and technological studies. Several important concepts have emerged including the essential roles of ring rotations in electronic phenomena, and three-dimensional order for high conductivity. These materials remain a laboratory for study of chemical, physical, and technological opportunities in conducting polymers.

The authors acknowledge the important contribution of their students, postdoctoral fellows and collaborators. This work is supported in part by the Defense Advanced Research Projects Agency through a grant monitored by the U.S. Office of Naval Research.

REFERENCES

1. H. Letheby, J. Chem. Soc. 15:161 (1862).

2. B.D. Humphrey, J-C. Chiang, W-S. Huang, A.F. Richter, N.L.D. Somarisi, A.G. MacDiarmid, X.Q. Yang, A.J. Epstein and R.W. Bigelow, Bull. Phys. Soc. 30:605 (1985).
3. J.P. Travers, J. Chroboczek, F. Devreux, F. Genoud, M. Nechtschein, A. Syed, E.M. Genies and G. Tsintavis, Mol. Cryst. Liq. Cryst. 121:195 (1985).
4. A.G. MacDiarmid, J-C. Chiang, M. Halpern, W-S Huang, S-L. Mu, N.L.D. Somasiri, W. Wu and S.I. Yaniger, Mol. Cryst. Liq. Cryst. 121:173 (1985).
5. E.W. Paul, A.J. Ricco and M.S. Wrighton, J. Phys. Chem. 89:1441 (1985).
6. P.M. McManus, S.C. Yang and R.J. Cushman, J. Chem Soc. Chem. Commun. 1556 (1985).
7. A.G. MacDiarmid and A.J. Epstein, Faraday Discuss. Chem. Soc. 88:317 (1989).
8. For recent progress, see Proc. Int. Conf. on Science and Technology of Synthetic Metals, Kyoto, Japan, June 1986 (Synth. Met. 17-19 (1987)); Sante Fe, NM, June 1988 (Synth. Met. 27-29 (1989)); Tübingen, Germany, September 1990 (Synth. Met. 41-43 (1991)).
9. K.R. Cromack, M.E. Jozefowicz, J.M. Ginder, R.P. McCall, A.J. Epstein, E. Scherr and A.G. MacDiarmid, Bull. Am. Phys. Soc. 34:583 (1989) .
10. K.R. Cromack, M.E. Jozefowicz, J.M. Ginder, R.P. McCall, G. Du, J.M. Leng, K. Kim, C. Li, Z. Wang, A.J. Epstein, M.A. Druy, P.J. Glatkowski, E.M. Scherr and A.G. MacDiarmid, Macromolecules xx, xxx (1991).
11. X. Tang, E. Scherr, A.G. MacDiarmid and A.J. Epstein, Bull. Am. Phys. Soc. 34:583 (1989).
12. A. Andreatta, Y. Cao, J.C. Chiang, A.J. Heeger and P. Smith, Synth. Met. 26, 383 (1988); A. Andreatta, S. Tokito, P. Smith and A.J. Heeger, Mat. Res. Soc. Symp. Proc. 173:269 (1990).
13. E.M. Scherr, A.G. MacDiarmid, S.K. Manohar, J.G. Masters, Y. Sun, X. Tang, M.A. Druy, P.J. Glatkowski, K.R. Cromack, M.E. Jozefowicz, J.M. Ginder, R.P. McCall and A.J. Epstein, Synth. Met. (1991).
14. A.G. MacDiarmid and A.J. Epstein, "Science and Application of Conducting Polymers," W.R. Salaneck, D.T. Clark and E.J. Samuelsen, eds., Adam Hilger, New York, p.117 (1991).

15. A.J. Epstein and A.G. MacDiarmid, "Science and Application of Conducting Polymers," W.R. Salaneck, D.T. Clark and E.J. Samuelsen, eds., Adam Hilger, New York, p.141 (1991).
16. Y. Sun, A.G. MacDiarmid and A.J. Epstein, J. Chem. Soc. Commun. 7:529 (1990).
17. Y. Wei, W.W. Focke, G.E. Wnek, A. Ray and A.G. MacDiarmid, J. Phys. Chem. **93**, 495 (1989); A. Ray, A.G. MacDiarmid, J.M. Ginder and A.J. Epstein, Mat. Res. Soc. Symp. Proc. 173:353 (1990).
18. J. Yue and A.J. Epstein, J. Am. Chem. Soc. 112:2800 (1990).
19. J. Yue, Z.H. Wang, K.R. Cromack, A.J. Epstein and A.G. MacDiarmid, J. Am. Chem. Soc. 113:2665 (1991).
20. S.K. Manohar, A.G. MacDiarmid, K.R. Cromack, J.M. Ginder and A.J. Epstein, Synth. Met. **29**, E349 (1989).
21. Z.H. Wang, H.H.S. Javadi, A. Ray, A.G. MacDiarmid and A.J. Epstein, Phys. Rev. B 42:5411 (1990).
22. Z.H. Wang, A. Ray, A.G. MacDiarmid and A.J. Epstein, Phys. Rev. B 43:4373 (1991).
23. J. Yue, A.J. Epstein, Z. Zhong, P. Gallagher and A.G. MacDiarmid, Synth. Met. **xx**, xxx (1991).
24. R.P. McCall, J.M. Ginder, M.G. Roe, G.E. Asturias, E.M. Scherr, A.G. MacDiarmid and A.J. Epstein, Phys. Rev. B 39:10,174 (1989).
25. J.M. Ginder and A.J. Epstein, Phys. Rev. B 41:10,674 (1990).
26. J.M. Ginder, A.J. Epstein and A.G. MacDiarmid, Solid State Commun. 72:987 (1989).
27. D.S. Boudreaux, R.R. Chance, J.F. Wolf, L.W. Shacklette, J.L. Bredas, B. Themans, J.M. Andre and R. Silbey, J. Chem. Phys. 85:4584 (1986).
28. S. Stafstrom and J.L. Brédas, Synth. Met. 14:297 (1986).
29. J.L. Brédas, C. Quattrocchi, J. Libert, A.G. MacDiarmid, J.M. Ginder and A.J. Epstein, Phys. Rev. B 44:xxx (1991).
30. J.G. Masters, A.G. MacDiarmid, K. Kim, J.M. Ginder and A.J. Epstein, Bull. Am. Phys. Soc. 36:377 (1991).
31. I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, 2nd ed., Academic Press (1971).
32. N.F. Colaneri, D.D.C. Bradley, R.H. Friend, P.L. Burn, A.B. Holmes and C.W. Spangler, Phys. Rev. B 42:11,670 (1990).

33. R.P. McCall, J.M. Ginder, J.M. Leng, H.J. Ye, S.K. Manohar, J.G. Masters, G.E. Asturias, A.G. MacDiarmid and A.J. Epstein, Phys. Rev. B 41:5202 (1990).
34. J.M. Ginder and A.J. Epstein, Phys. Rev. Lett. 64:1184 (1990).
35. M.C. dos Santos and J.L. Brédas, Phys. Rev. Lett. 64:1185 (1990).
36. J.M. Leng, J.M. Ginder, R.P. McCall, H.J. Ye, Y. Sun, S.K. Manohar, A.G. MacDiarmid and A.J. Epstein, to be published.
37. K.R. Cromack, A.J. Epstein, J.G. Masters, Y. Sun and A.G. MacDiarmid, Synth. Met. xx, xxx (1991).
38. Z.H. Wang, C. Li, E.M. Scherr, A.G. MacDiarmid and A.J. Epstein, Phys. Rev. Lett., 55:1745 (1991).
39. F. Zuo, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein, Phys. Rev. B 36:3475 (1987).
40. H.H.S. Javadi, K.R. Cromack, A.G. MacDiarmid and A.J. Epstein, Phys. Rev. B 39:3579 (1989).
41. Z.H. Wang, K.R. Cromack, J. Yue and A.J. Epstein, to be published.