

Study of Vibrational Spectra of Polyaniline Doped with Sulfuric Acid and Phosphoric Acid

MANJU ARORA,¹ VANDNA LUTHRA,²
RAMADHAR SINGH,¹ AND S. K. GUPTA*,¹

¹National Physical Laboratory, Dr. K. S. Krishnan Road,
New Delhi 110012, India, E-mail: skgupta@csnpl.ren.nic.in;
and ²Physics Department, Gargi College, Sirifort Road,
Delhi University, New Delhi 1110049, India

Abstract

Vibrational spectra of insulator emeraldine base (EB) form of polyaniline and electrical conductive sulfuric acid- and phosphoric acid-doped emeraldine salts (ES) were studied in the region of 4000–400 cm⁻¹ at ambient temperature by Fourier transform infrared spectroscopy. Infrared transmittance spectra of EB and ES were investigated to understand the bonding behavior of different organic and inorganic groups present in the polymeric chains and their structural variations on protonation by sulfate or phosphate ion inclusion in the polymer salt network. These studies revealed the para-coupling of deformed disubstituted benzenoid (B) and quinoid (Q) rings with ends capped predominantly by (B4Q1) units. The deformation of B and Q rings was confirmed by the appearance of many weak bands, very weak bands, and satellite structures in strong transmittance peaks of polymeric chain-constituting groups. Protonation takes place at the nitrogen sites of Q rings and forms semiquinone radical ions in ES. The vibrational bands pertaining to B rings, Q rings, B4Q1 units, semiquinone segment, sulfate ions, and phosphate ions were observed and assigned from these measurements. The shift in peak position of some bands with gain or loss in intensity and appearance of some new bands were observed in sulfuric acid- and phosphoric acid-doped ES spectra. These variations are attributed to the formation of new structural groups in ES on protonation and a change in crystalline field by sulfate and phosphate ion doping for crosslinking the polymeric chains.

Index Entries: Vibrational spectra; polyaniline; sulfuric acid; phosphoric acid.

*Author to whom all correspondence and reprint requests should be addressed.

Introduction

Polyaniline (PANI) is a conjugated conducting polymer that finds use in a large number of practical applications (1–10) in the fields of electroluminescent devices, optoelectronics, microelectronics, sensors, electromagnetic shieldings, anticorrosion coatings, storage devices, and so on. The extensive utilization of this polymer in various devices for controlling electrical, optical, and chemical properties is attributed to its transitions from insulator state to metallic state or vice versa, ease of processibility, and stability. Chemically, PANI is the polymerized form of poly(*p*-phenylene-amineimines) containing *p*-phenyleneamine as reduced units and *p*-phenyleneimine as oxidized units in polymeric chains. These units exist in different ratios in three principal insulator forms of PANI: as leuco-emeraldine fully reduced form (poly *p*-phenyleneamine), semioxidized emeraldine form containing 50% oxidized (poly *p*-phenyleneimine) and 50% reduced units (poly *p*-phenyleneamine), and pernigraniline completely oxidized form (poly *p*-phenyleneimine). The number of electrons present on the polymer chains of three insulating states of PANI remain the same, and they can be made conductive by varying the number of protons on the polymer chain through protonation-deprotonation reaction with acids or bases and redox reaction. The electronic structure of emeraldine base (EB) is modified by protonation through acids to produce a semiquinone radical structure that transfers its positive charge to the polymeric chain for generating mobile charge carriers to improve the conductivity of polymer.

In the present studies, EB was protonated with sulfuric acid and phosphoric acid to add protons at $-N=$ (imine nitrogen) sites of quinoid (Q) ring in polymer chains and their crosslinking by sulfate ions and phosphate ions to form conductive emeraldine salts. Sulfuric acid- and phosphoric acid-doped polymer salts exhibit strong electron lattice coupling by presenting strong and sharp vibrational bands in their infrared (IR) transmittance spectra, which can be associated with the changes in chemical bonding behavior and increase in crystallinity.

The purpose of the present investigation was to analyze vibrational spectra of the EB form of PANI and its sulfuric acid- and phosphoric acid-doped salts to reveal bonding arrangements of benzenoid (B) and Q rings and their structural deformations on the protonation and nature of doping of sulfate ions and phosphate ions in a polymeric salt network by high-resolution Fourier transform infrared (FTIR) spectroscopic technique.

Materials and Methods

The EB form of PANI was prepared by the chemical oxidative polymerization method (11) using 0.5 M aniline in 1 M aqueous HCl at -5°C (268 K) and 0.5 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (ammonium persulfate) as oxidant. The powdered EB form was protonated with H_2SO_4 and H_3PO_4 acids at pH 0.0 to obtain the respective emeraldine salts (ES).

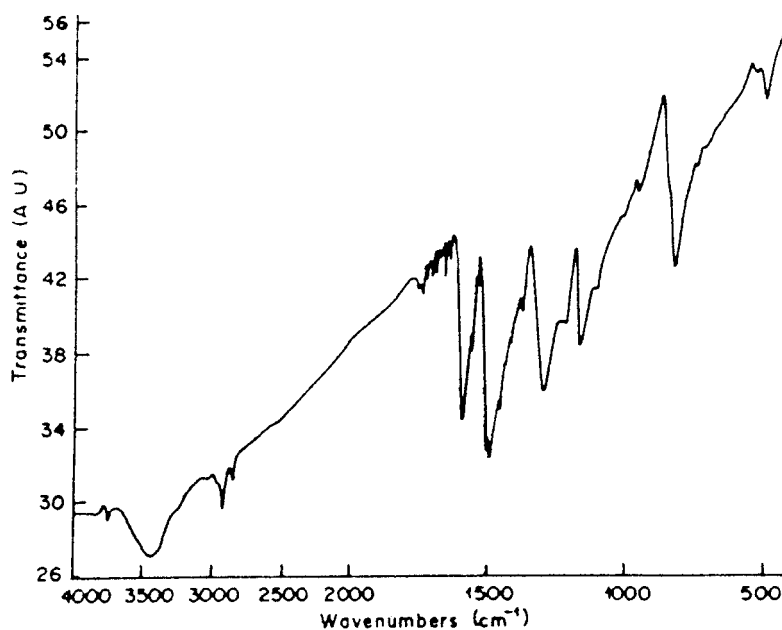


Fig. 1. IR transmission spectrum of EB in the region of 4000–400 cm^{-1} . a.u., arbitrary units.

High-resolution and high-performance Nicolet FTIR spectrophotometer model MAGNA 750 was used to record the transmission spectra of EB and its sulfuric acid- and phosphoric acid-doped salts in the region of 4000–400 cm^{-1} . The instrument was purged with pure nitrogen gas, and a DTGS pyroelectric IR detector was used to detect the IR signal. Each spectrum consisted of an average of 200 scans and measured at 4 cm^{-1} resolution. Samples in the form of KBr pellets were used in these measurements.

Results and Discussion

IR transmittance spectra of EB and ES of sulfuric acid and phosphoric acid recorded in the region of 4000–400 cm^{-1} at ambient temperature are presented in Figs. 1, 2, and 3, respectively. The peak position of various bands obtained in these spectra along with their tentative assignments are given in Table 1. The different vibrational bands obtained in the IR transmittance spectra of these polymers were assigned by comparing their values with theoretical results (12–15) considering the basic repeating oligomer unit in polymeric chains. These studies were used to reveal the structural details of insulating EB form and electrical conductive doped ES in terms of the chemical transformation of Q rings into semiquinone radical ions and the role of sulfate and phosphate ion doping in polymeric salt structure. IR transmittance spectra of these polymers showed strong electron-lattice coupling by the appearance of strong and fine vibrational bands.

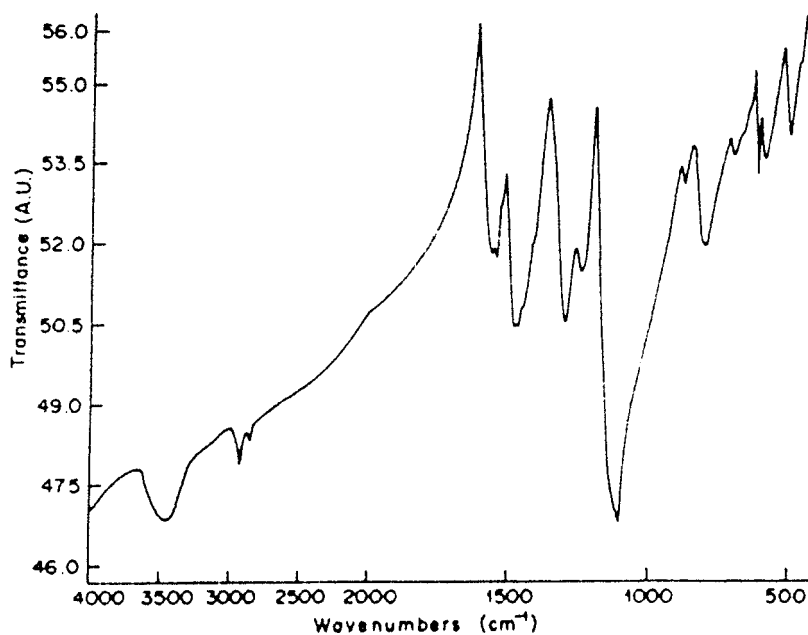


Fig. 2. IR transmission spectrum of sulfuric acid-doped ES in the region of 4000–400 cm⁻¹. a.u., arbitrary units.

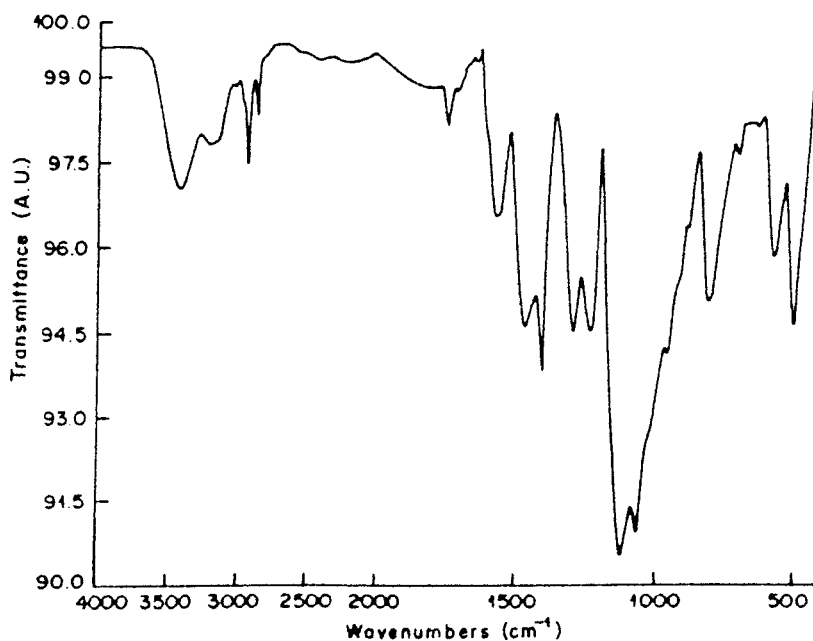


Fig. 3. IR transmission spectra of phosphoric acid-doped ES in the region of 4000–400 cm⁻¹. a.u., arbitrary units.

Table 1
Peak Positions (cm⁻¹) of Different Bands Along
with Tentative Assignments as Observed in IR Transmission Spectra of EB,
Sulfuric Acid-Doped ES:SO₄ and Phosphoric Acid-Doped ES:PO₄

Peak position (cm ⁻¹) ^a			Assignment
EB	ES:SO ₄	ES:PO ₄	
3410.2 (b, s)	3456.6 (b, s)	3405.3 (s) 3195.3 (s)	N-H stretch. mode of sec. amine
2927.1 (m)	2944.4 (m)	2927.1 (s)	C-H asym. stretch. mode of polymerized B ring and/or alkyl group
2851.3 (w)	2857.8 (w)	2857.1 (m)	C-H sym. stretch. mode of polymerized B ring and/or alkyl group
1586.0 (vs) 1550.0 (vw) 1533.3 (vvw) 1505.6 (vw)	1570.5 (m) _I 1548.1 (m) _{II}	1566.6 (m) 1545.1 (m)	C=C stretch. mode of Q ring with C-H bend. mode
1493.8 (vs)	1480.7 (vs) _I	1461.8 (vs) _I	C=N asym. stretch. mode and C-H bend. mode of B ring
1466.7 (vvw)	1466.7 (vs) _{II}	1400.0 (vs) _{II}	C-H bend. + C-C stretch. modes of B ring
1427.8 (vvw)			
1380.36	—	—	C-C stretch. mode of Q ring
1296.0 (vs)	1298.2 (vs) _I	1293.0 (vs) _I	C-H bend. B ring and C-N asym. stretch. mode of Q ring
1214.6 (sh)	1239.3 (vs) _{II}	1229.1 (vs) _{II}	
1162.2 (s)	—	—	C=N asym. stretch mode and C-H bend. mode of Q ring
—	—	1118.5 (vs) _I 1063.3 (vs) _{II}	Asym. stretch. of v ₃ PO ₄ ³⁻ ion
—	1107.4 (vs)	—	Asym. stretch. of v ₃ SO ₄ ²⁻ ion
1101.1 (vvw)	—	—	C-H bend. Q ring and ring deformation of B ring
1016.0 (vw)	—	—	Ring deformation of B ring
955.6 (w)	951.1 (w)	949.8 (w)	C-H bend and ring deformation of Q ring
827.1 (s)	809.8 (s)	804.4 (s)	Para-coupling of disubstituted B ring
755.6 (vw)	722.2 (w)	705.4 (w)	C-N=C bend. imine group
—	—	577.6 (m)	Asym. bend. of v ₄ PO ₄ ³⁻ mode
—	618.9 (m) _I 588.1 (m) _{II}	—	Asym. bend. of v ₄ SO ₄ ²⁻ mode
592.3 (vw)	—	—	Planar ring deformation of Q ring
504.7 (m)	506.7 (s)	504.7 (s)	N-H torsional oscillation
446.2 (vw)	—	—	C-C out-of-plane bend. of B ring
—	—	410.0 (w)	O-P-O bend. of bridging P

^avs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak; sh, shoulder; b, broad. Abbreviations stand for the intensity of band given along with peak positions. Stretch, stretching; asym, antisymmetric; sym, symmetric; bend, bending; Q and B represents the quinoid and benzenoid rings of polymeric chains.

Region of 3500–2000 cm⁻¹

N-H stretching vibration of secondary amine (>NH) was obtained as a broad strong band in the region of 3500–3000 cm⁻¹ with peak maxima at 3410.2 cm⁻¹ in EB, which shifted to 3456.6 cm⁻¹ in ES:SO₄, and this mode degenerated into two components at 3405.3 and 3195.3 cm⁻¹ in ES:PO₄ salt. The broadness and gain in intensity of this band in both protonated ES showed the existence and strengthening of hydrogen bonding on protonation (16,17). The removal of degeneracy in ES:PO₄ salt indicated the lowering of site symmetry and structural deformation of the Q ring in polymer chains by protonation reaction. The strong and broad bands with maxima at 3405.3 and 3319.3 cm⁻¹ in ES:PO₄ salt were assigned to antisymmetric stretching and symmetric stretching modes of the NH group, respectively.

Stretching vibrations of the C-H group in B ring occurred in the region of 3100–3000 cm⁻¹ (16), which shift to low wave numbers on polymerization owing to a change in ring electron density and changes in resonance of polymeric chains, as suggested by Hatchett et al. (18). These vibrational modes shifted to the region of 3000–2800 cm⁻¹, where alkyl group C-H stretching vibrations also appear (16). In these polymers, the alkyl group impurities may enter from acetone, diethyl ether, and methanol solvents during preparation. IR transmittance bands observed at 2927.1 and 2851.3 cm⁻¹ in the prepared EB sample spectrum may be owing to antisymmetric stretching and symmetric stretching of the C-H group in the polymerized B ring and/or to alkyl group impurities present in the polymeric network. In protonated ES of sulfuric acid and phosphoric acid, these bands gained intensity with a small shift in peak positions, showing the strengthening of C-H bonds in B rings on protonation.

Region of 2000–1000 cm⁻¹

IR transmittance spectra of EB, ES:SO₄, and ES:PO₄ for the region of 2000–1000 cm⁻¹ contain fundamental and combination vibrational bands of B and Q rings and ν_3 antisymmetrical stretching modes of sulfate ion and phosphate ion. C=C stretching vibration of the Q ring coupled to the C-H bending mode appeared as a strong band at 1586.0 cm⁻¹ in EB with very weak band components at 1550.0 and 1533.0 cm⁻¹. This band was observed as a medium-intensity band degenerated into two components in protonated salts and shifts to low wave numbers. The peak positions of this band's components for ES:SO₄ and ES:PO₄ salts are given in Table 1. The presence of weak components in this vibrational peak were attributed to the coupling of the quadrant stretching motion of the C=C bond with the C-H in-plane bending mode, which confirmed the disubstitution of B rings and predominance of B4Q1 segments in the polymeric chains of EB and its protonated sulfuric acid- and phosphoric acid-doped salts. The decrease in intensity of this mode in protonated salts was associated with the structural deformation of polymeric chains by the doping of sulfate and phosphate ions and formation of neutral amine to charged amine salt. The

charged salt formation shows the increase in quinoid character in polymeric chains by the greater contribution from the --C=C-- and --C=N vibrational modes. The strong peak at about 1580 cm^{-1} is characteristic of charged amine salt in protonated ES. The combination modes of $[\text{C=N stretch of Q} + \text{C-H bend of B rings}]$ and $[\text{C-C stretch of B} + \text{C-H bend of B rings}]$ were obtained as very strong bands in the region of $1510\text{--}1400\text{ cm}^{-1}$, with peak maxima at 1493.8 cm^{-1} with very weak and very very weak components on both sides of the main peak in EB. This band degenerated into two band components in both protonated salts with a decrease in intensity and shifted to lower frequencies. The assignments and positions of these combination modes are given in Table 1. The minor shifts in peak component frequency and intensity proved the ring deformation of the Q rings bonded adjacent to the tetra-amine unit of polymer chain. The C-C stretching mode of the Q ring appeared as a weak band at 1380.4 cm^{-1} only in the EB spectrum. The combination vibration of C-H bending of the B ring and C-N antisymmetric stretching of the deformed Q ring was observed as a broad band with two components at 1296.0 and 1212.6 cm^{-1} in EB showing the presence of 2C-N bands of different nature in EB, as suggested by Stafstrom et al. (19). This mode is characteristic of reduced amine units in polymer chains. These components shift to higher frequency with an increase in intensity in protonated ES spectra, and their positions are presented in Table 1.

A coupled vibration of the C=N group with the C-H bending mode of the Q ring in the polymer chain appeared as a strong band in EB at only 1162.2 cm^{-1} . The coupling vibration of the C-H bending mode of the Q ring with ring deformation of B and ring deformational mode of B ring were observed as very very weak bands at 1101.1 and 1016 cm^{-1} , respectively, only in the EB spectrum. In addition to the skeletal vibrations of various polymer chain-constituting groups, the ν_3 antisymmetric stretching fundamental mode of sulfate and phosphate ions appeared as a very strong band at 1107.4 , 1118.6 , and 1063.3 cm^{-1} , respectively. The existence of this fundamental vibration confirmed the doping of sulfate and phosphate ions in polymer chains and their involvement in crosslinking of polymer chains.

Region of $1000\text{--}400\text{ cm}^{-1}$

The region of $1000\text{--}400\text{ cm}^{-1}$ constitutes the vibrations of ring deformation of Q ring, para-substitution of B ring, imine group (of oxidized units of polymeric chains), and planar ring deformation of Q and B rings with fundamental and bridging modes of sulfate and phosphate ions. The C-H bending mode, along with ring deformation of the Q ring, appeared as a very weak band at 955.6 cm^{-1} in the EB spectrum. This band gained intensity in protonated ES of sulfuric acid and phosphoric acid with small shifts in peak position. The para-coupling of disubstituted B ring was confirmed by the presence of a strong 827 cm^{-1} band. This band shift to lower frequency on protonation showed the change in crystalline field by structural deformation in the polymeric network through proton addition and crosslinking of polymeric chains via sulfate and phosphate ions. The existence of the

C-N=C (imine) group was characterized by the observation of a very weak bending mode at 755.6 cm^{-1} in EB that shifted to low wave numbers on protonation with an increase in intensity; their values are listed in Table 1. Very weak planar ring deformation of Q ring and weak C-C out-of-plane B ring deformation modes were obtained in EB IR spectra at 592.3 and 446.2 cm^{-1} , respectively. N-H torsional oscillation appeared as a medium-intensity band at 504.7 cm^{-1} in EB and gained intensity in protonated ES with a minor shift in peak position.

IR bending (ν_4) fundamental vibration of sulfate and phosphate ion and a bridging vibration of the O-P-O mode were also observed in the region of $1000\text{--}400\text{ cm}^{-1}$. The ν_4 bending mode of sulfate appeared as a doublet band with maxima at 619.0 and 588.1 cm^{-1} and phosphate ion at 577.6 cm^{-1} as medium-intensity vibrations. In addition to this fundamental mode, weak O-P-O bending vibration of bridging phosphorus of phosphate ion appeared at 410 cm^{-1} in ES:PO₄ salt.

Conclusion

IR vibrational spectra of EB and ES of sulfuric acid and phosphoric acid revealed the dominance of B4Q1 units and para-substitution of B rings in polymer chains. Protonation took place at the nitrogen sites of the imine group of oxidized units of EB. This was confirmed by the disappearance of 1162.2 cm^{-1} vibration in protonated salts and an increase in quinoid character in doped ES. B and Q rings have a deformed ring structure in polymeric chains, which may induce anharmonicity and activity of IR combination modes and the coupled vibrations. Sulfate and phosphate ions have tetrahedral symmetry and are involved in crosslinking of polymeric chains through hydrogen bonding. This may cause the change in intensity and vibrational frequency of skeletal polymeric chain-constituting groups by the variations in crystalline field and the lowering of site symmetry through reorientational ordering of B and Q rings.

References

1. Hu, S. S., Luo, J., and Cui, D. (1999), *Anal. Sci.* **15**, 585–588.
2. Cantu, M. L. and Romero, P. G. (1999), *J. Electrochem. Soc.* **146**, 2029–2033.
3. Gazoti, W. A., DePaoli, M. A., CasalboneMiceli, G., Geri, A., and Gazotti, W. A. (1999), *J. Appl. Electrochem.* **29**, 753–757.
4. DePaoli, M. A., CasalboneMiceli, G., Giroto, E. M., and Gazotti, W. A. (1999), *Electrochimica Acta* **44**, 2983–2991.
5. Bairachnyi, B. I., Vasilchenko, A. V., Lyashok, L. V., Orekhova, T. V., and Baikova, T. F. (1999), *Russian J. Appl. Chem.* **72**, 225–228.
6. Heeger, A. J. (1995), *Trends Polymer Sci.* **33**, 39–47.
7. Wilson, E. G. (1985), *Mol. Cryst. Liq. Cryst.* **121**, 271–275.
8. Genies, E. M., Syed A. A., and Tsintavis, C. (1985), *Mol. Cryst. Liq. Cryst.* **121**, 247–254.
9. Ellis, J. R. (1986), in *Handbook on Conducting Polymers*, vol. 1, Skotheim, T. K., ed., Marcel Dekker, NY, 501–506.
10. Bredas, J.-L., Salaneck, W. R., and Wegner G., eds. (1994), *Organic Materials for Electronics*, Elsevier Science, North Holland.

11. Singh, R., Arora, V., Tandon, R. P., Chandra, S., and Mansingh, A. (1997), *Polymer* **38**, 4897–4902.
12. Boyer, M. I., Quillard, S., Rebourt, E., Louran, G., Buisson, J. P., Monkman, A., and Lefrant A. (1998), *J. Phys. Chem. B* **102**, 7382–7392.
13. Shacklette, L. W., Wolf, J. F., Gould, S., and Baughman, R. H. (1988), *J. Chem. Phys.* **88**, 3395–3961.
14. McCall, R. P., Ginder, J. G., Leng, J. M., Ye, H. J., Manohar, S. K., Masters, J. G., Asturias, G. E., and MacDiarmid, A. G. (1990), *Phys Rev. B* **41**, 5202–5213.
15. Dasilva, J. E. P., Temperini, M. L. A., and Torrieri, S. C. (1999), *Electrochemica Acta* **44**, 1887–1891.
16. Silverstein, R. M., Bassler, G. C., and Morrill, T. C. (1976), *Spectrometric Identification of Organic Compound*, 3rd ed., John Wiley & Sons, NY.
17. Herzberg, G. (1947), *Molecular Spectra and Molecular Structure, Part II Infrared & Raman Spectra of Polyatomic Molecules*, D. Van Nostrand, NY.
18. Hatchett, D. W., Josowicz, M., and Janata, J. (1999), *J. Phys. Chem. B* **103**, 10,992–10,998.
19. Stafstrom, S., Bredas, J. L., Epstein, A. J., Woo, H. S., Tanner, D. B., Huang, W. S., and MacDiarmid, A. G. (1987), *Phys. Rev. Lett.* **59**, 1464–1467.