

Photoacoustic Spectroscopy of Polyaniline Films

To cite this article: Taro Toyoda and Hiroki Nakamura Hiroki Nakamura 1995 *Jpn. J. Appl. Phys.* **34** 2907

View the [article online](#) for updates and enhancements.

You may also like

- [Photoacoustic tomography in absorbing acoustic media using time reversal](#)
Bradley E Treeby, Edward Z Zhang and B T Cox
- [Advanced photoacoustic and thermoacoustic sensing and imaging beyond pulsed absorption contrast](#)
Fei Gao, Xiaohua Feng and Yuanjin Zheng
- [Photoacoustic imaging for guidance of interventions in cardiovascular medicine](#)
Sophinese Iskander-Rizk, Antonius F W van der Steen and Gijs van Soest

Photoacoustic Spectroscopy of Polyaniline Films

Taro TOYODA and Hiroki NAKAMURA*

*Department of Applied Physics and Chemistry, The University of Electro-Communications,
1-5-1 Chofugaoka, Chofu, Tokyo 182, Japan*

(Received November 28, 1994; accepted for publication February 18, 1995)

Photoacoustic spectra as well as optical absorption spectra were measured to study the heat generation by non-radiative processes in electrodeposited polyaniline films in the wavelength range of 310 to 800 nm. The shapes of both spectra depend on the pH for polymerization of electrodeposited polyaniline films. The shapes of infrared spectra also show the pH dependence. Photoacoustic spectra show that the changes of signal intensity are different from those of optical absorption spectra, suggesting the character of lattice relaxation of a low-dimensional system.

KEYWORDS: photoacoustic spectroscopy, photothermal effect, conducting polymer, polyaniline, total rate of optical energy absorption, infrared spectroscopy

1. Introduction

Polyaniline is a very attractive conducting polymer because it exhibits good stability in air or water and the redox mechanisms involve the exchange of protons and electrons.¹⁾ Polyaniline has attracted much attention because of fundamental interest and possible applications such as batteries, electrochromic displays, and others.^{2–5)} In contrast to other conducting polymers, polyaniline shows two separate oxidation and reduction processes during its electrochemical cycling.^{6,7)} The fully reduced form of polyaniline is electrically insulating and consists of benzenoid rings. In the first oxidation process, the electronic band structure and the chemical structure are strongly modified, resulting in a highly conducting state consisting of semiquinoid rings. The second oxidation process results in an insulating state where the semiquinoid form relaxes to benzenoid and quinoid rings.⁷⁾ However, recent literature on this material is subject to controversy regarding qualitative discussion of transport and optical properties.^{6,7)}

Although several investigations have been carried out on the optical absorption of polyaniline, there are few investigations on the photothermal effect due to nonradiative processes. Photothermal spectroscopy (PTS) involves the detection of temperature changes resulting from nonradiative processes following light-energy absorption. PTS of polyaniline might provide useful information on lattice relaxation that cannot be detected by optical absorption spectroscopy measurements, because polyaniline shows one-dimensional conductivity. PTS complements optical absorption and excitation spectra measurements, and it is not affected by problems of scattered or stray light. Photoacoustic spectroscopy (PAS) developed by Rosencwaig and Gersho in solids is one of the PTS methods.⁸⁾ In microphone PAS, the sample to be studied is placed inside a closed cell containing a gas and a sensitive microphone. The sample is then illuminated with modulated monochromatic light. Photoacoustic spectra are ob-

tained as analog signals from the microphone using a phase-sensitive detector. In the present work, we show the detailed experimental results of the photoacoustic spectra in electrodeposited polyaniline films together with results from optical absorption measurements in the wavelength range of 310 to 800 nm.

2. Experimental

Polyaniline films were deposited on indium-tin-oxide (ITO) glasses by constant-potential electrolysis (+0.7 V versus Ag/AgCl electrode (RE)) in aqueous solution containing 0.5 M aniline in 1.0 M HCl (5 min.). NaOH was added in order to investigate the influence of pH on the polymerization processes of aniline. Then potentiostatic oxidation was carried out at +0.6 V versus RE (2.5 min.) in 0.1 M HCl following reduction at -0.2 V versus RE (2.5 min.). Scanning electron microscopy (SEM) showed that the films exhibited a granular morphology and the thickness was approximately 0.5 μm for all the samples.

The body of the PAS cell was an aluminum cylinder with a small channel in its periphery in which the microphone was inserted. The window of the cell was of silica glass. The sample was affixed to silica glass which was placed inside the cell. The inside volume of the cell was approximately 1.0 cm^3 . The cell was suspended by four rubber wires in order to avoid outside vibrations. The light source was a 500 W xenon arc lamp. The light beam was focused on the sample through a monochromator with an impinging area of 0.16 cm^2 . A cut-off filter was used above the 600 nm wavelength region to eliminate higher-order diffraction. Modulation frequency for PAS measurements was 33 Hz using a mechanical chopper, and the measurements were carried out at room temperature in the wavelength range of 310 to 800 nm. The photoacoustic (PA) signal intensities were monitored by passing the microphone signal first through a preamplifier and then into a two-phase lock-in amplifier. The data were usually averaged in the lock-in amplifier to improve S/N ratio. The spectra were normalized by the PA signals of carbon black sheet. The optical transmission spectra (visible and infrared regions) were measured by conventional methods.

*Present address: Nippon Oil Co., Ltd., Minato-ku, Tokyo 105, Japan.

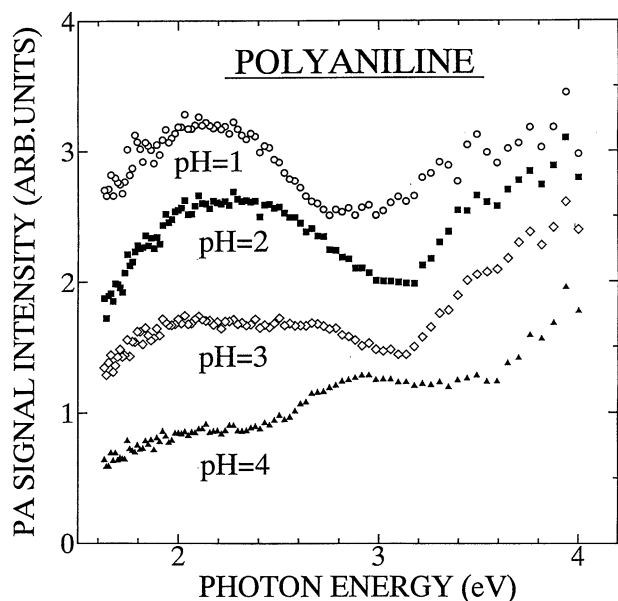


Fig. 1. Photoacoustic signal intensity of electrodeposited polyaniline films for different pH values as a function of photon energy.

3. Results and Discussion

Figure 1 shows the PA signal intensity of electrodeposited polyaniline films polymerized at various pH values at 33 Hz modulation frequency as a function of photon energy. Two bands are present in the PA spectra except for the case of pH=4. One is between 1.8 and 2.6 eV with maximum absorption around 2.1 eV and the other is around 3.8 eV. There are three bands in the case of pH=4 with maximum peaks are 2.1, 3.0, and 3.8 eV, respectively. Figure 2 shows the modulation frequency (f) dependence of the PA signal intensity at $\lambda=620$ nm (2.0 eV photon energy) for polyaniline film polymerized at pH=1. The PA signal exhibits a $f^{-1.0}$ modulation-frequency dependence within the experimental accuracy ($\sim 5\%$) predicted for optically transparent and thermally thin sample by the thermal diffusion model for the generation of PA signal.⁸⁾

Figure 3 shows the total rate of optical energy absorption, $1-T-R$ (T : transmission, R : reflectance), of electrodeposited polyaniline films for different pH values as a function of photon energy. Two bands are present in the $1-T-R$ spectra except for the case of pH=4. Maximum absorption peaks are 2.1 and 3.8 eV, which are qualitatively similar to those of PAS. There are three bands in the case of pH=4 with maximum peaks are 2.1, 3.0, and 3.8 eV, respectively. The energetic stability and electronic structure of heavily oxidized (protonated) polyaniline showed that the formation of a polaron lattice is energetically more stable than bipolaron couplings.⁹⁾ Also, the results of magnetic susceptibility and optical measurements on heavily oxidized polyaniline have suggested that a polaron lattice model is reasonably appropriate for the electric conduction, rather than the formation of bipolarons even in the heavily oxidized form of polyaniline.¹⁰⁻¹²⁾ According to the scheme of band levels for conducting polymer reported

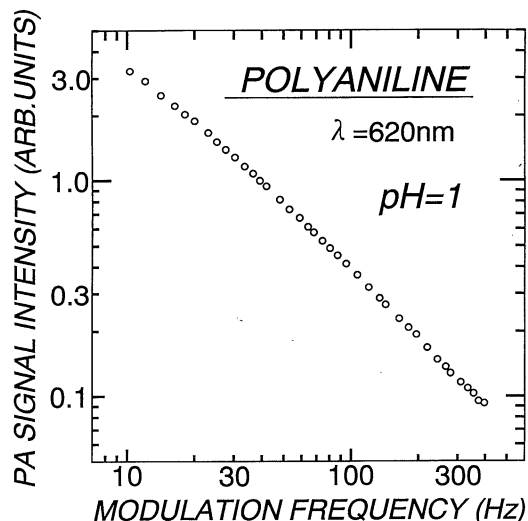


Fig. 2. Modulation-frequency dependence of the photoacoustic signal intensity at $\lambda=620$ nm for polyaniline film polymerized at pH=1.

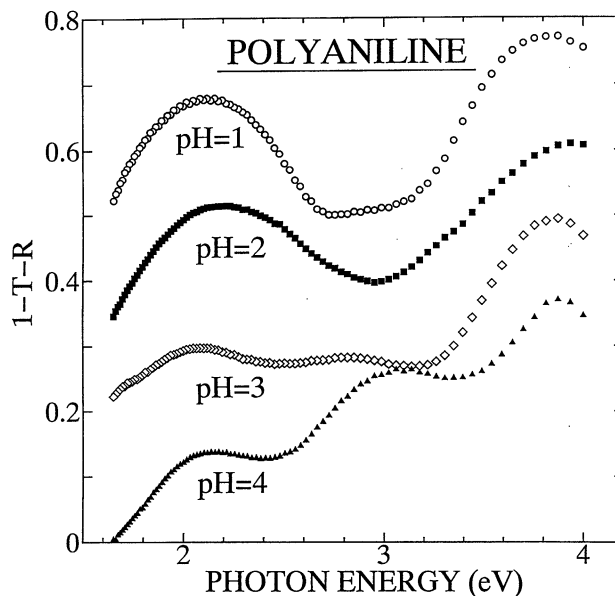


Fig. 3. Total rate of optical energy absorption, $1-T-R$ (T : transmission, R : reflectance), of electrodeposited polyaniline films for different pH values as a function of photon energy.

by Genies and Lapkowski¹⁾ and the above discussions, the first band at 2.1 eV could be assigned to the transition between bonding cation level and antibonding cation level, and the second, to the band gap of polyaniline. The maximum absorption peak at 3.0 eV in pH=4 could be assigned to the transition between bonding cation level and conduction band.

Figure 4 shows pH dependence of the PA signal intensity (\bullet) and $1-T-R$ (\circ) of electrodeposited polyaniline films at (a) $\lambda=325$ nm and (b) 620 nm (3.82 and 2.00 eV photon energy, respectively). The PA signal intensity and $1-T-R$ decrease as pH increases in both bands and they show linear dependence on pH. However, the slope of PA signal intensity at $\lambda=620$

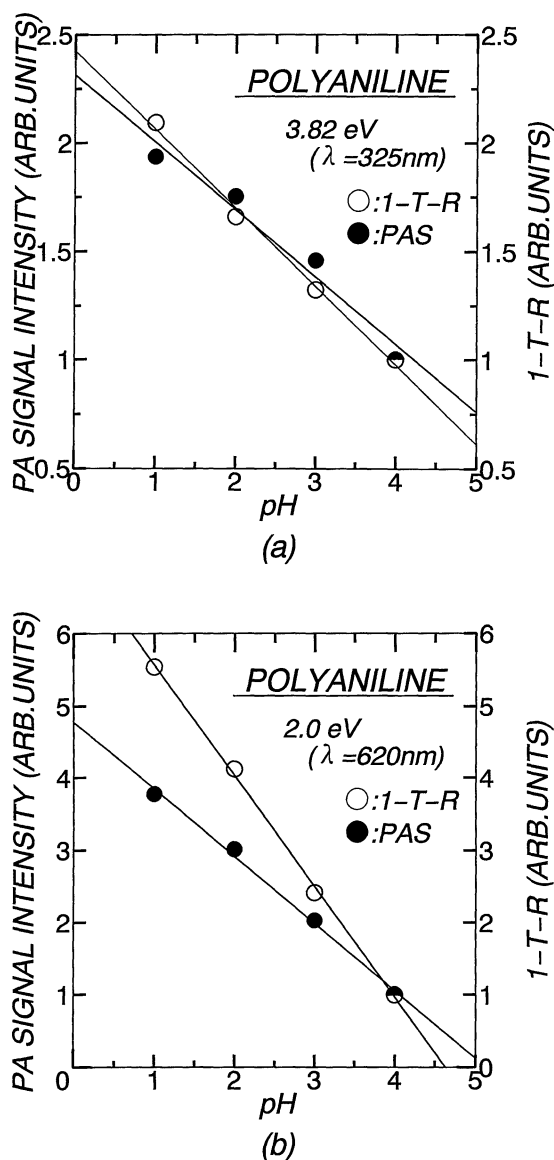


Fig. 4. pH dependence of the photoacoustic signal intensity (●) and 1-T-R (○) of electrodeposited polyaniline films. (a) $\lambda = 325 \text{ nm}$ (3.82 eV), (b) $\lambda = 620 \text{ nm}$ (2.00 eV).

nm is smaller than that of 1-T-R, indicating the difference between optical energy absorption and thermal conversion efficiency in electrodeposited polyaniline film under different polymerization conditions. The slopes of PA signal intensity and 1-T-R at $\lambda = 620 \text{ nm}$ are steeper than those at $\lambda = 325 \text{ nm}$, suggesting that the formation of bonding or antibonding cation level and nonradiative processes are greatly influenced by pH for polymerization.

In order to investigate increases and changes of both PAS and 1-T-R, PA signals were divided by 1-T-R ($\text{PAS}/(1\text{-T-R})$). Figure 5 shows the ratio, $\text{PAS}/(1\text{-T-R})$, of electrodeposited polyaniline films for different pH values as a function of photon energy. The result indicates that the increases and changes of the PAS are different from those of 1-T-R, the total rate of optical energy absorption, and they depend on the pH for polymerization. A maximum peak at 2.7 eV can be seen for the cases of pH = 1 and 2, and 2.5 eV for pH = 3 and 4.

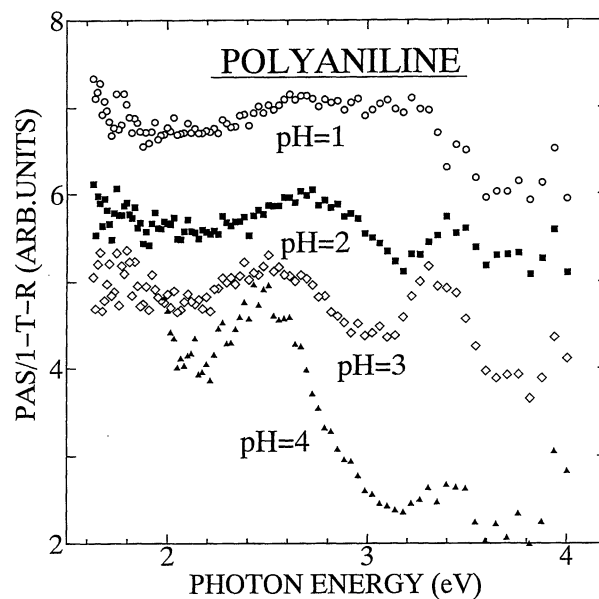


Fig. 5. Ratio of the photoacoustic signal intensity (PAS) and total rate of optical energy absorption (1-T-R) of electrodeposited polyaniline films for different pH values as a function of photon energy.

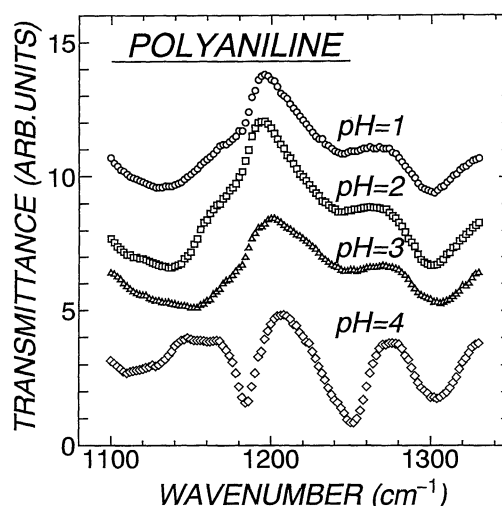


Fig. 6. Infrared transmittance of electrodeposited polyaniline films for different pH values as a function of wave number.

The band shape for the case of pH = 4 is different from the rest and it shows rapid changes near the maximum peak. Figure 5 suggests that there is a photon-energy dependence of the nonradiative and radiative quantum yields and the quantum yields are related to the polymerization processes in aniline. In order to consider the molecular structure changes due to polymerization of aniline at different pH values, infrared (IR) transmission spectra of polyaniline films were measured. Figure 6 shows the IR transmittance of electrodeposited polyaniline films for different pH values as a function of wave number. The spectra for the cases of pH = 1, 2, and 3 resemble each other, indicating the same molecular structures. and they correspond to those reported by Sariciftci *et al.*⁷⁾ However, the spectrum for the case of pH = 4 is different from the rest, indicating mole-

cular structure changes caused by the decrease of H^+ ions in polymerization processes.

- 1) E. M. Genies and M. Lapkowski: J. Electroanal. Chem. **220** (1987) 67.
- 2) A. G. Macdiarmid, J. Chiang, A. Richter and A. J. Epstein: Synth. Met. **18** (1987) 285.
- 3) E. M. Genies, M. Lapkowski, C. Santier and E. Vieil: Synth. Met. **18** (1987) 631.
- 4) L. W. Shacklette, M. Maxfield, S. Gould, J. F. Wolf, T. R. Yow and R. H. Baughman; Synth. Met. **18** (1987) 611.
- 5) G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger: Nature **357** (1992) 477.
- 6) A. F. Diaz and A. J. Logan: J. Electroanal. Chem. **111** (1980) 111.
- 7) N. S. Sariciftci, M. Bartonek, H. Kuzmany, H. Newgebauer and A. Neckel: Synth. Met. **29** (1989) E193.
- 8) A. Rosencwaig and A. Gersho: J. Appl. Phys. **47** (1976) 64.
- 9) K. Tanaka, S. Wang and T. Yamabe: Synth. Met. **36** (1990) 129.
- 10) S. Stafstroem, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang and A. G. MacDiarmid: Phys. Rev. Lett. **59** (1987) 1464.
- 11) A. J. Epstein and A. G. MacDiarmid: Mol. Cryst. Liq. Cryst. **160** (1988) 165.
- 12) A. J. Epstein, J. M. Ginder, F. Zuo, R. W. Bigelow, H.-S. Woo, D. B. Tanner, A. F. Richter, W.-S. Huang and A. G. MacDiarmid: Synth. Met. **18** (1987) 303.