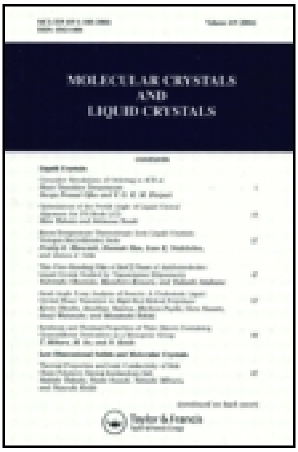

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photothermal Spectroscopy of Polyaniline Films

J. E. De Albuquerque [a] , W. L. B. Melo [b] & R. M. Faria [c]

[a] Departamento de Física, Universidade Federal de Viçosa, Viçosa, MG, 36571-000, Brazil E-mail:

[b] CNPDIA, EMBRAPA Instrumentação Agropecuária, C.P. 741, São Carlos, SP, 13560-970, Brazil

[c] Instituto de Física de São Carlos, USP, C.P. 369, São Carlos, SP, 13560-970, Brazil

To cite this article: J. E. De Albuquerque, W. L. B. Melo & R. M. Faria (2002): Photothermal Spectroscopy of Polyaniline Films, Molecular Crystals and Liquid Crystals, 374:1, 379-384

To link to this article: http://dx.doi.org/10.1080/10587250210453

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 379-384
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00

Photothermal Spectroscopy of Polyaniline Films

J. E. DE ALBUQUERQUE[1], W. L. B. MELO[2] and R. M. FARIA[3]

[1]*Departamento de Física, Universidade Federal de Viçosa, Viçosa, 36571-000, MG, Brazil, jeduardo@mail.ufv.br,*
[2]*CNPDIA/EMBRAPA Instrumentação Agropecuária, C.P. 741, São Carlos, 13560-970, SP, Brazil and*
[3]*Instituto de Física de São Carlos/USP, C.P. 369, São Carlos, 13560-970, SP, Brazil*

In this work, we obtained photoacoustic spectra (PAS) of undoped and doped poly(o-methoxyaniline) (POMA). The fittings for the PAS spectra are obtained from equation for the photoacoustic signal. For these curves, the thermal parameters obtained from the Photopyroelectric Spectroscopy (PPES) were used.[1] Two Gaussian curves, which fit well the UV-Vis absorption spectrum of undoped POMA, plus a third Gaussian centered at 820 nm, which fit well the UV-Vis absorption spectrum of doped POMA, were used for these fittings. The PAS signal was used to obtain the optical characteristics of the POMA films, like the optical absorption coefficient β and the optical gap between the valence and the molecular exciton band of the undoped POMA. The values of β in the maximum of the absorption bands agree very well with the intensities of the Gaussian curves used for the PPES fittings. The optical gap obtained here agrees with the value of the literature obtained from the UV-Vis optical absorption.

Keywords Polyaniline; Photothermal Spectroscopies; Optical Parameters

INTRODUCTION

Photothermal spectroscopies — Photopyroelectric and Photoacoustic — have been extensively and successfully applied to solid state materials for obtaining their thermal and optical parameters.[1–3] Recently, we obtained thermal parameters of polyaniline (PANI) films using the PPES, such as thermal diffusivity α, thermal conductivity k and specific heat c.[1] In these techniques a pulsed light beam is absorbed in a solid sample and the converted heat (non-radiative conversion) diffuses into the bulk structure; the sample expansion, or the temperature gradient, is then detected by an adequate sensor system. The detected signal depends on the optical and thermal properties of the sample: the optical absorption coefficient $\beta(\lambda)$ (λ being the light wavelength), the non-radiative conversion efficiency $\eta(\lambda)$, the thermal conductivity, and the thermal diffusivity coefficient. It also depends on experimental controlled parameters as the chopping frequency f and the incident light beam.

Polyaniline and its derivatives are considered promising conducting polymers for several applications[4,5] because they present good doping characteristics, high environmental stability, and easily solubility and processability.[6,7] In spite of the large number of experimental and theoretical studies devoted to their physical properties, thermal characteristics of polyaniline have so far been relatively disregarded.

SAMPLES OF POLYANILINES

The monomeric unit of polyaniline is composed by four aromatic rings, consisting of a sequence of oxidized $[-(C_6H_4)-N=(C_6H_4)=N-]$ and reduced $[-(C_6H_4)-(NH)-(C_6H_4)-(NH)-]$ units. Three distinct forms have been identified among them, leucoemeraldine, emeraldine and pernigraniline, and can be converted one into another.[8] The emeraldine form containing equal number of oxidized and reduced segments has been the most frequently studied. Upon protonation, emeraldine changes its conductivity from that characteristic of poorly conducting semiconductor, $\sigma \sim 10^{-10}$ S/cm, to metal, $\sigma \sim 10^{2}$ S/cm.

Emeraldine base — EB-POMA — was chemically synthesized and doped according to a method described elsewhere.[9] The photoacoustic spectra were obtained for POMA transparent films assembled in quartz plates by spin coating technique. The thickness of the films was about 0,18 μm. Strong doped samples were obtained immersing the sample in a HCl solution of 1 M, for 30 seconds.

PHOTOPYROELECTRIC AND PHOTOACOUSTIC SPECTROSCOPY

The photothermal spectrometer used in our experiments is schematically shown in Figure 1. It comprises an optical part (light source, monochromator, and chopper), the custom-made pyroelectric or photoacoustic chamber, and the measuring system. When the monochromator is used, a optical cable can be connected to the photothermal chamber, substituting the mirror. The measuring system is composed by a lock-in amplifier, locked in the chopper frequency, connected to a microcomputer that stores the data and controls the experiment. The mechanical slotted wheel chopper modulates the incident light. The absorption of this modulated pulsed light gives rise to a periodic heating of the sample owing to nonradiative relaxation of excited states. The nonradiative conversion efficiency $\eta(\lambda)$ is very near to the unity, because luminescence effects in PANI have very low efficiency, approximately 10^{-4}.

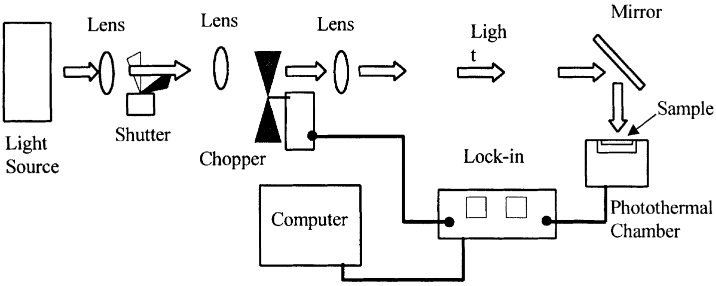

FIGURE 1 Photothermal experimental setup.

In the case of the PAS spectroscopy, the heat propagation across the whole chamber is governed by heat diffusion equations of each medium coupled via the boundary conditions at the interfaces ($T_a = T_b$ and $k_a dT_a/dx = k_b dT_b/dx$,), as established by Rosencwaig theory,[10] whose normalized photoacoustic signal produced by the microphone, that is, pressure variation of the gas, is:

$$\Delta \mathrm{Pn} = \frac{\eta_s r_s b_{bs}}{r_s^2 - 1}\left[(r_s - 1)(b_{bs} + 1)e^{\sigma_s L_s} - (r_s + 1)(b_{bs} - 1)e^{-\sigma_s L_s} + 2(b_{bs} - r_s)e^{-\beta_s L_s}\right] \tag{1}$$

$$\div\left[(b_{gs} + 1)(b_{bs} + 1)e^{\sigma_s L_s} - (b_{gs} - 1)(b_{bs} - 1)e^{-\sigma_s L_s}\right]$$

where $r_s = \beta_s/\sigma_s$, $\sigma_s = (1 + \mathrm{i})a_s$ with $a_s = (\pi f/\alpha_s)$, $b_{nm} = k_n a_n / k_m a_m$ ($n = g$, s, b, that is, g=gas, s=sample, b=backing), and L_s is the sample thickness. This equation, which is obtained in function of the optical, thermal and geometrical parameters of the system, can be simplified for some special cases of physical interest and it is used for the fittings that will be given next below.

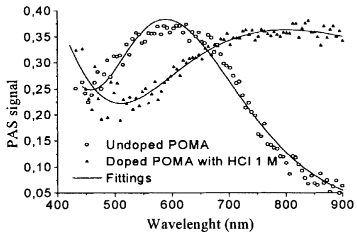

FIGURE 2 PAS of POMA with the fittings.

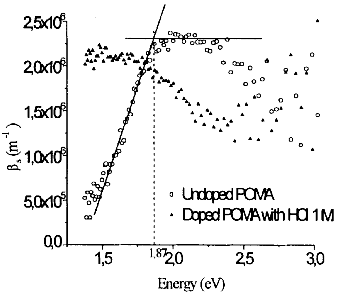

FIGURE 3 Optical absorption and optical gap of POMA.

RESULTS AND DISCUSSIONS

The PAS spectra were obtained for the POMA transparent films, and the light modulation was 10 Hz. Figure 2 shows the PAS spectra of undoped and doped samples where dots represent experimental results and full lines the fittings. The continuous lines that fit the PAS spectra of this figure are obtained from equation (1) for the photoacoustic signal. For these curves, the thermal parameters obtained from the PPES were used.[1] Two Gaussian curves, which fit well the UV-Vis absorption spectrum of undoped POMA, plus a third Gaussian centered at 820 nm, which fit well the UV-Vis absorption spectrum of doped POMA, were used for these fittings. Like the PPES,[1] the intensity of this third Gaussian is two orders of magnitude smaller than the others being, therefore, not observed in the PAS spectrum of the undoped sample. Analogously, the 600 nm band in the doped sample presents intensity one order of magnitude than the others two. This explains the fact that even in strongly doped samples undoped regions may exist. Thus, for the doped samples there exists doped and undoped regions and vice-versa, corroborating the PPES results.

The PAS signal was used to obtain the optical characteristics of the POMA films, like the optical absorption coefficient β and the optical gap between the valence and the molecular exciton band of the undoped POMA. The Rosencwaig equation given by the equation (1) is very complicated and not much efficient for the attainment of the optical absorption coefficient β. For some special cases we can simplify the equation, making it more simple. For the case the sample is optically transparent ($\beta_s^{-1} > L_s$) and thermally thin ($\mu_s >> L_s$ e $\mu_s > \beta_s^{-1}$), we obtain:

$$\Delta\text{Pn} = \frac{\eta_s \beta_s L_s b_{bs} (r_s - b_{bs})}{r_s (b_{gs} + b_{bs})} \tag{2}$$

This equation is a complex function because presents the term r_s. Determining the module of the equation (2), and using the values of b_{bs} for the undoped and doped sample and the thermal parameters obtained by the PPES, we obtain the spectra shown in Figure 3. The values of β_s in the maximum of the absorption bands agree very well with the intensities of the Gaussian curves used for the PPES fittings. Also, this figure shows the optical gap of the undoped sample, obtained from the shoulder of the curve, that is, by the intersection of the two lines fitted in the linear regions.[2] The optical gap obtained here agrees with the value of the literature obtained from the UV-Vis optical absorption[8] and with the value obtained from the PPES.[1]

CONCLUSIONS

This work shows the application of the particular photothermal technique, photoacoustic spectroscopy, in optical studies of POMA films. In the special case of PANI films of different doping degrees, we show the data obtained from the PPES for the thermal properties as k_s, α_s and c_s in the reference [1]. Here, we saw that, besides the PPES and PAS similarities, they possess their own different characteristics due to distinct detection systems. In particular, the PPES technique presents a major utility to obtain thermal parameters. The PAS technique comes to confirm these thermal data, so it was of great utility to obtain the optical absorption coefficient and optical gap through a very simple method.

ACKNOWLEDGMENTS

FAPESP, CAPES and FAPEMIG.

REFERENCES

1. Albuquerque, J. E. de; Melo, W. L. B.; Faria, R. M. J Polym Sci Polym Phys **38**, 1294 (2000).
2. Melo, W. L. B.; Pawlicka, A.; Sanches, R.; Mascarenhas, S.; Faria, R. M. J Appl Phys **74**, 1 (1993).
3. Melo, W. L. B.; Faria, R. M. Appl Phys Lett **67**, 3892 (1995).
4. Genies, E. M.; Lapkowski, M.; Tsintavis, C. New J Chem **12**, 181 (1988).
5. Angelopoulos, M. Synth Met **41-43**, 1109 (1991).
6. Cao, Y.; Treacy, G. M.; Smith, P.; Heeger, A. J. Appl Phys Lett **80**, 2711 (1992).
7. Leclerc, M.; Guay, J.; Dao, L. H. Macromolecules **22**, 649 (1989).
8. Albuquerque, J. E. de; Mattoso, L. H. C.; Balogh, D. T.; Faria, R. M.; Masters, J. G.; MacDiarmid, A. G. Synth Met **113**, 19 (2000).
9. Mattoso, L. H. C.; Faria, R. M.; Bulhões L. O. S.; MacDiarmid, A. G. J Polym Sci Polym Chem **32**, 2147 (1994).
10. Rosencwaig, A. Photoacoustics and photoacoustic spectroscopy; John Wiley & Sons, New York (1980).