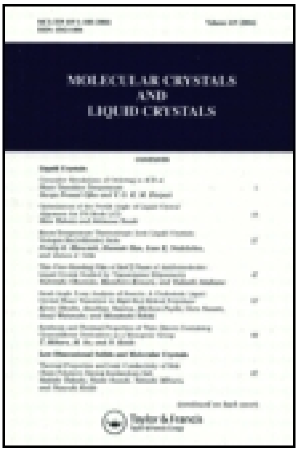

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Walter Mendes De Azevêdo [a] , Eduardo Henrique Lago Falcão [a] & Dmitrii Vassilievitch Petrov [a]
[a] Departamento de Química Fundamental, Universidade Federal de Pernambuco, Recife, PE, 50670-901, Brazil

Version of record first published: 29 Oct 2010

To cite this article: Walter Mendes De Azevêdo, Eduardo Henrique Lago Falcão & Dmitrii Vassilievitch Petrov (2002): First Hyperpolarizability and Multiphoton Induced Fluorescence in Different Forms of Polyaniline, Molecular Crystals and Liquid Crystals, 374:1, 481-486

To link to this article: http://dx.doi.org/10.1080/713738303

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 481-486

1058-725X/02 $12.00 + .00

First Hyperpolarizability and Multiphoton Induced Fluorescence in Different Forms of Polyaniline

WALTER MENDES DE AZEVÊDO, EDUARDO HENRIQUE
LAGO FALCÃO and DMITRII VASSILIEVITCH PETROV

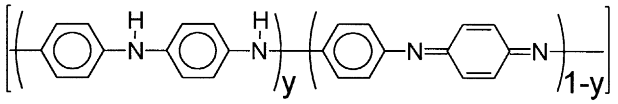
*Departamento de Química Fundamental, Universidade Federal
de Pernambuco, Recife-PE, 50670-901, Brazil*

The first hyperpolarizability β per monomeric residue of polyaniline in three oxidation states and in the doped emeraldine salt form was determined by hyper-Rayleigh scattering. Multiphoton induced fluorescence was observed and, together with light absorption at the fundamental (ω) and double (2ω) frequencies was taken into account in the calculation of β.

Keywords: polyaniline; first hyperpolarizability; hyper-Rayleigh

INTRODUCTION

Since the discovery of electrical conductivity in polyacetylene, more than 20 years ago, conducting polymers have been intensively studied due to fundamental knowledge concerns and to the possibility of applications in advanced technologies. Polyaniline (PANI), one of such polymers, can be represented by the formula



where y may in principle vary between 0 and 1 [1]. For y=1, the polymer is in the completely reduced state, leucoemeraldine (LE). The other extreme, y=0, is the totally oxidized form, pernigraniline (PE). The half-oxidized form (y=0.5), emeraldine base (EB), when protonated on the imine nitrogens, drastically changes its physical and chemical properties, being known as emeraldine salt (ES). Its good environmental stability, low cost and easy synthesis, as well as the possibility of both protonic and oxidative control of conductivity and other properties, make PANI attractive for several applications.

In the field of nonlinear optics, much work has been done on third order properties of PANI [2, 3], but substantially less attention has been devoted to second order properties [4].

In this respect, hyper-Rayleigh scattering (HRS) [5, 6] has proven to be a very versatile and reliable technique to study the first hyperpolarizability β of molecules in solution. The scattering phenomenon is originated from orientation fluctuations of molecules in solution, which momentarily break its centrosymmetry, and scatter light with frequency doubling [6].

Linear light absorption, both at the fundamental and second harmonic frequencies, and multiphoton absorption induced fluorescence (MPIF) are two problems met by HRS, which result in ambiguous evaluation of β values. To overcome these problems, correction terms must be added to the fundamental equation normally used. Thus, the HRS equation becomes

$$I_{2\omega} = BI_{\omega}^{2}\left\{N_{sol}\left\langle\beta_{sol}^{2}\right\rangle + N_{smp}\left\langle\beta_{smp}^{2}\right\rangle + N_{smp}\Phi\right\}\left\{\frac{1-\exp(-2\alpha_{\omega}L_{1})}{2\alpha_{\omega}}\exp(-\alpha_{2\omega}L_{2})\right\}$$

where $I_{2\omega}$ is the intensity of the second harmonic scattered light, B is a geometrical factor, I_{ω} is the intensity of the incident, fundamental light and N and $\langle\beta^2\rangle$ are the concentration and the orientation averaged first hyperpolarizability squared, respectively. The indexes sol and smp refer to solvent and sample, respectively, and Φ is the MPIF quantum yield. The last terms account for linear absorption, where $\alpha(\omega)$ and $\alpha(2\omega)$ are the absorption coefficients at the fundamental and double frequencies, L_1 is the fundamental beam path length and L_2 is the scattered light propagation length.

In this work we determined the first hyperpolarizability of PANI in solution, in the acid and base forms of emeraldine and in the pernigraniline and leucoemeraldine states. We observed the presence of MPIF for all the samples, although in different intensities. MPIF and the effects of linear light absorption were taken into account in the calculations of β.

EXPERIMENTAL

Polyaniline was chemically synthesized with ammonium persulfate in aqueous hydrochloric acid at 0-5°C, in a procedure adapted from literature [1], and converted to the emeraldine base form by treatment with NH_4OH 1M. EB was dissolved in DMSO or in formic acid, typically in concentrations of 1.5 mg/mL, from which we determined the number of monomeric residues (MR) per volume unit in the solutions. We considered the set carbon ring plus one nitrogen atom as a MR, irrespective of its oxidation state. PE and LE solutions were obtained by treating EB/DMSO solutions with $(NH_4)_2S_2O_8$ or hydrazine hydrate. The solutions (ES in formic acid, EB, PE and LE in DMSO) were characterized by UV-Vis-NIR spectroscopy.

The second harmonic and MPIF signals [7] were created inside a glass cell containing the samples using the 10 ns, up to 30 mJ pulses at 1064 nm by a Q-switched Nd-YAG laser. The scattered light was collected by a photomultiplier tube after passing through a monochromator, and the signal was processed by a gated acquisition data system. The external reference method was used [8], with *para*-nitroaniline (*p*NA) as the reference.

RESULTS AND DISCUSSION

Figure 1 shows the emission spectra of all the studied forms of PANI. We can see that MPIF has a very pronounced contribution for PE, EB and ES. Leucoemeraldine, on the other hand, almost only displays the HRS signal.

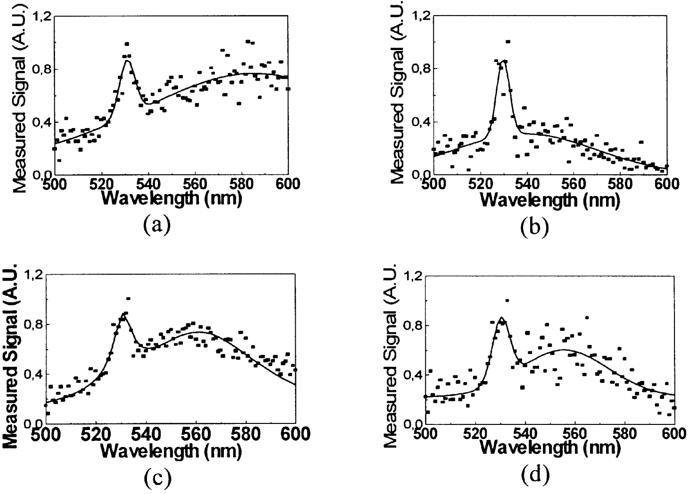


FIGURE 1. Normalized emission spectra (1064 nm excitation) of PE/DMSO (a); LE/DMSO (b); EB/DMSO (c); ES/formic acid (d).

The contribution for the total signal at 532 nm due to MPIF was evaluated from the emission spectra, and the absorption coefficients at 532 and 1064 nm were obtained from the linear absorption spectra. The calculated β per MR for all the studied forms of PANI is shown in Table 1. For comparison, β for *p*NA in methanol (the reference used) is also shown. From these results we can see that PE presents the highest β value. It is more than ten times the value found for LE and it is higher even than for ES. As expected, β increases upon doping (EB to ES).

TABLE 1. Experimental results

Studied form	Solvent	β (10^{-28} esu)	$\lambda_{Max(MPIF)}$ (nm)
Pernigraniline	DMSO	3.2	580
Emeraldine Base	DMSO	0.8	560
Leucoemeraldine	DMSO	0.2	540
Emeraldine Salt	Formic Acid	2.0	555
Para-Nitro Aniline	Methanol	0.15	—

Analyzing only the neutral forms, we can see that β progressively increases with the oxidation degree. This trend was attributed to a progressive increase in the bond conjugation of the polymer chain when it is oxidized. In fact, PE is a degenerate ground state polymer, just like polyacetylene, and it has been suggested that this feature could lead to potentially high optical nonlinearities [9]. From this reason, the intermediate value found for EB could also be accounted for.

Comparing ES with EB, we can see that β increases almost twice upon protonation. Since there is a large increase in the conjugation upon doping [10] and also a polaronic lattice is formed [11], such an increase of β would be expected. An even more impressive comparison is made between ES and LE: now, the effect of electron withdrawing causes a ten-fold increase in the hyperpolarizability. The polaronic lattice formation, however, does not seem to be enough to overcome the large value of β found in PE.

Symmetry considerations can also be important, since it is known that PANI is not a perfectly linear, coplanar chain [12]. Hence, when the centrosymmetry that could be present in such a perfect chain is removed, it allows the appearance of the second order nonlinearity [13]. Due to the quinoid structure, the possibility of *E/Z* configurations is another symmetry breaking feature, along with chain folding, ring torsions and so on. All these features must have their own importance according to the considered form of PANI, but were not quantitatively considered here. A theoretical work is in progress to better clarify contributions from symmetry.

Finally, the observed MPIF for the neutral forms also showed a systematic behavior, similar to the value of the hyperpolarizability. The fluorescence was more intense in the more oxidized form of PANI, and almost absent in LE. Furthermore, a red shift was also observed with oxidation degree. We concluded that MPIF must be associated to the oxidized units.

CONCLUSION

The first hyperpolarizabilities for PANI (in DMSO) in three oxidation states, and for doped emeraldine (in formic acid), were determined by hyper-Rayleigh scattering. We found that β per monomeric residue progressively increases from LE to PE by more than one order of magnitude, and from EB to ES by nearly twice. Multiphoton induced fluorescence was observed for all samples. MPIF and linear absorption of light, both at fundamental and at second harmonic frequencies, are well accounted by the data treatment used. This procedure allows one to use HRS to determine β even in systems with such biasing effects.

ACKNOWLEDGEMENTS

Work partially supported by FINEP, CNPq, CAPES and FACEPE .

REFERENCES

[1] W. S. Huang, B. D. Humphrey, A. G. MacDiarmid, J. Chem. Soc., Faraday Trans. I **82** (1986), 2385

[2] C. Halvorson, Y. Cao, D. Moses, A. J. Heeger, Synth. Met. **55-57** (1993), 3941

[3] G. S. Maciel, C. B. de Araújo, R. R. B. Correia, W. M. de Azevêdo, Optics Commun. **157** (1998), 187

[4] O. Aktsipetrov, A. Ermushev, A. Petukhov, L Daikhin, M. Levi, V. Vereta, Synth. Met. **54** (1993), 327

[5] R. W. Terhune, P. D. Maker, C. M. Savage, Phys. Rev. Lett. **14** (1965), 681

[6] E. Hendrickx, K. Clays, A. Persoons, Acc. Chem. Res. **31** (1998), 675

[7] N. W. Song, T. I. Kang, S. C. Jeoung, S. J. Jeon, B. R. Cho, D. Kim, Chem. Phys. Lett **261** (1996), 307

[8] M. A. Pauley, H. W. Guan, C. H. Wang, A. K.Y. Jen, J. Chem. Phys. **104** (1996), 7821

[9] M. C. dos Santos, J. L. Brédas, Phys. Rev. Lett. **62** (1989), 2499

[10] S. Stafström, Synth. Met. **18** (1987), 387

[11] S. Stafström, J. L. Brédas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang, A. G. MacDiarmid, Phys. Rev. Lett. **59** (1987), 1464

[12] R.H. Baughman, J.F. Wolf, H. Eckhardt, L.W. Shacklette, Sinth. Met. **25** (1988), 121

[13] P. N. Prasad, D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, John Wiley & Sons (New York, 1991), Ch. 2