J. Braz. Chem. Soc., Vol. 19, No. 7, 1306-1310, 2008.
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0103 - 5053 $6.00+0.00

Article

Time Resolved Emission Spectroscopy of Poly(2,5-dicyano-*p*-phenylene-vinylene) Films

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Filmes finos de poli(2,5-diciano-*p*-fenileno vinileno), DCNPPV, foram produzidos por síntese eletroquímica com variação do potencial aplicado de – 0,15 até – 1,0 V, e depositados sobre camada fina de ouro sobre vidro. A cinética de estado excitado destes materiais foi investigada por medidas de decaimentos de fluorescência. Os filmes apresentam decaimentos com três componentes, uma rápida da ordem de 200-400 picossegundos, e outra duas componentes de aproximadamente um e cinco nanossegundos, na temperatura de 293 K. O decaimento de fluorescência ocorre pela desativação em sítios de baixa energia na cadeia polimérica conjugada e por supressão do estado excitado por monômeros bromados terminais da cadeia e íons brometo aprisionados durante o crescimento eletroquímico do filme. A mudança do ânion do eletrólito suporte de brometo para perclorato reduziu de modo significativo essa contribuição de supressão do estado excitado como resultado da troca iônica por uma espécie não supressora.

Films of poly (2,5-dicyano-*p*-phenylene vinylene), DCNPPV, were obtained by electrochemical synthesis over gold thin layer (20 nm) transparent electrode deposited on a glass plate. The DCNPPV films of 4 μm thickness were produced by electropolymerization process of α,α,α´,α´-tetrabromo-2-5-dicyano-*p*-xilene at different applied potentials (–0.15, –0.25, –0.40, –0.60, –0.80, and –1.0 V) using 0.1 mol L^{-1} of tetraethylammonium bromide in acetonitrile as the supporting electrolyte. The emission decays have three exponential components: a fast component in the picosecond range (200-400 ps), and two other of about one and five nanoseconds at 293 K. The fluorescence quenching process seems to occur by exciton trapping in a low-energy site and quenching by residual bromine monomer attached at the end of the polymer chain. However, the electrochemical synthesis generates entrapped bromide or ion pairs during the growth step of the film which also contributes to the deactivation. The change of the electrolyte from bromide to perchlorate reduces significantly this additional quenching effect by allowing ion exchange of formed bromide with the nonquenching perchloride anion.

Keywords: conjugated polymer, PPV, excited-state dynamics, fluorescence decay

Introduction

Conducting organic polymers are special materials that have been explored for light-emitting diodes, in organic field transistors, photovoltaic cells, and in chemical sensors.[1-4] Besides these applications, several fundamental topics related with charge and exciton transport in conducting organic polymers have been investigated, and the results are very important in the molecular design of new materials in order of optimizing their applications.[5] The preparation of conducting or conjugated polymers with high defined properties is a important issue,[6] and routes based on electrochemical synthesis of PVP-type polymers have been introduced in the last years.[7–10] However, the electropolymerization process usually results in polymer films with properties that depend on the controlled parameters like applied potential, film growth rate, and solvent medium.[10]

The study of the electronic excited state dynamics of conducting polymer using excitation and emission spectroscopy has provided important information about exciton diffusion, migration, trapping and quenching in aggregates like excimers or its deactivation in low energy charge-transfer states.[11–15] These processes are closely related to the luminescence yields and stability of several optoelectronic devices based on conjugated polymers.

In this work, films of poly (2,5-dicyano-p-phenylene vinylene), DCNPPV, obtained by electrochemical synthesis under different cathodic potentials and solvent compositions,

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are studied by time-resolved emission spectroscopy. The goal is to investigate how the preparation conditions can lead to materials with different time resolved emission properties.

Experimental

Materials and methods

Films of poly (2,5-dicyano-p-phenylene vinylene), DCNPPV, were obtained by electrochemical synthesis over gold thin layer (20 nm) transparent electrode deposited on a glass plate (for polymer molecular structure see Figure 1). The DCNPPV films of about 4 μm thickness were produced by electropolymerization process of α,α,α´,α´-tetrabromo-2-5-dicyano-*p*-xilene at potentials of −0.15, −0.25, −0.40, −0.60, −0.80, and −1.0 V, and using 0.1 mol L^{-1} of tetraethylammonium bromide in acetonitrile as supported electrolyte. A second series of thin films were produced by the same procedure but the electrolyte had perchlorate instead of bromide anion. Additional details of the electrochemical synthesis of DCNPPV and film characterization have been reported elsewhere.[10]

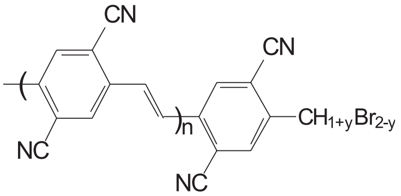

Figure 1. Molecular structure of DCNPPV (y = 0–2).

The polymeric film obtained over a gold thin layer on glass plate is an extremely insoluble material, but a soluble polymer fraction was produced during long-term electrolysis experiment using stirred mercury pool as electrode. In this case, the formation of the non-conductive film is avoided, and it is possible to produce a certain amount of a polymer powder, which yields a small fraction of soluble material in acetonitrile. This fraction was analyzed by size exclusion chromatography (SEC) using Schimadzu (RID-6A detector), with ASAHIPAK column and polystyrene as molecular weight standard. The result is that the major part of the soluble fraction of DCNPPV is formed by short oligomers (*ca.* 4 monomeric units), but the first shoulder of the SEC profile corresponding to 10% indicates a soluble polymer fraction with a weight of 1377 g mol^{-1}, which would correspond to about 9 monomeric units per chain (data not shown). Thus, it can be inferred that the non-soluble part of DCNPPV deposited as a film should contain chains with more than ten monomers.

Luminescence decays of the films were measured by time correlated single-photon counting technique using a CD-900 Edinburgh spectrometer equipped with Glan-Thompson polarizers (set at magic angle configuration) and a cooled PMT Hamamatsu R955. The light pulse at 402 nm was provided by frequency doubling the 200 fs laser pulse of Mira 900 Ti-Sapphire laser pumped by a Verdi 5 W Coherent. The laser pulsed frequency was reduced by using a Conoptics pulse picker system.[16] Before spectral measurements, the films over the glass plate were rinsed with acetonitrile and dried at low pressure. The film samples were then kept in a low-pressure optical compartment to avoid the oxygen quenching and oxidation effects, and were disposed in front-face configuration at room temperature (20 ºC). The soluble fraction in acetonitrile was also investigated by time resolved emission measurements, and it will provide a comparison with the photophysical properties of the films. The decays measured were analyzed by reconvolution of the instrument response function with exponential decay models (up to three components) of the Edinburgh Instruments software.

Results and Discussion

The DCNPPV sample forms a yellow film with a broad electronic absorption band with maximum at 420 nm, and emission spectra centered at 575 nm.[10] The electronic transitions are red shifted when compared with PPV samples, and this effect is ascribed to a stabilization of the conduction band edges due to the charge-transfer character and further delocalization of the electron density in excited state promoted by the presence of CN groups in the unsaturated polymer backbone. They are highly emissive films, and the luminescence decay behavior is a function of the electrochemical deposition parameters. Decay profiles of films obtained at different reduction potentials (– 150, – 400, and – 600 mV) are illustrated in Figure 2.

The excited-state relaxation is strongly multiexponential, and in general the decay becomes faster as the film is grown

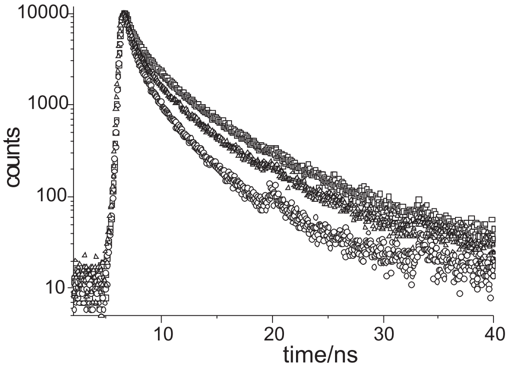

Figure 2. Decays of DCNPPV films obtained at different reduction potentials of –150 mV (top , □), – 400 mV (middle, Δ) , and – 600 mV (lower trace, O). λ_{exc} = 402 nm and λ_{em} = 555 nm.

at higher reduction potential. The relaxation of the excited state of PPV-type conducting polymer is wavelength dependent.[11] In our samples, this character is also observed by the change of the three decay time components with the emission wavelength as given in Figure 3. The decay becomes slower as the emission scans to the red part of the spectrum. This effect can be ascribed to the dynamics of exciton in the polymer chain, its trapping in excimer-like dimer forming at the intramolecular contact regions of chromophores, and the distribution of defects with different quenching rates.[11,12] The effect of the width of the molecular weight distribution in the excited-state dynamics could account partially to the behavior observed, but the separation of this contribution is not trivial. The fast component with decay in the range of 200-400 ps is within the decay times observed for PPV-type polymers reported in the literature.[11]

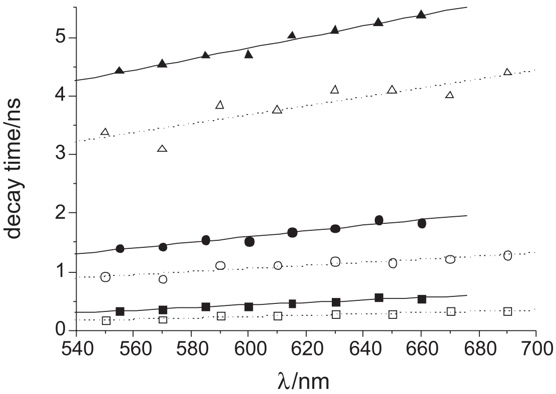

Figure 3. Decay components from three-exponential fitting of DCNPPV films obtained at reduction potentials of –150 mV (solid symbols) and – 600 mV (open symbols) with λ_{exc} = 402 nm.

This inhomogeneous character of the relaxation of DCNPPV films can also be seen from the time-resolved emission spectra (TRES). A typical TRES data is given in Figure 4.

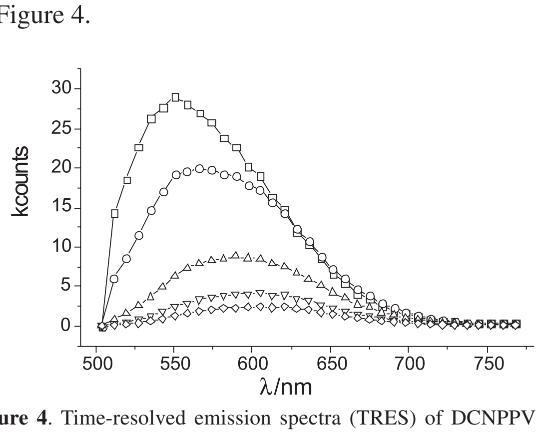

Figure 4. Time-resolved emission spectra (TRES) of DCNPPV film obtained at – 800 mV at 0 (□), 0.5 (O), 1.0 (Δ) 1.7 (∇), and 2.5 (◊) ns after the maximum of the laser pulse in the instrument response function. λ_{exc} = 402 nm.

In a few ns, the emission maximum that starts at 555 nm shifts about 60 nm to the red region, which corresponds to an energy change of 176 cm^{-1}, which is comparable to what was observed in MH-PPV at room temperature.[11] However, in pure PPV film, red shift in TRES analysis was only clearly observed at low temperature measurements of 77 K.[12] But, strong red shifted emission is common in cyano-substituted PPV, like CN-PPV, and also they have longer decay times when compared with PPV. [17] These two effects observed both in film and in poor solvent solution of CN-PPV are related to interchain excited states due to intermolecular interactions or strong folding of the chain in solution of a poor solvent.

Similar trends of the excited state relaxation of DCNPPV films with emission wavelength (λ_{em}) and cathodic potential are recorded from the analysis of the average decay time ⟨τ⟩. This parameter is given by,

$$\langle\tau\rangle = \frac{\sum b_i \tau_i^2}{\sum b_i \tau_i} \qquad (1)$$

where b_i and τ_i are the amplitude and decay time of each component (i = 1, 2, 3 for three exponential fitting), respectively. Values found for ⟨τ⟩ increase with λ_{em} and decrease with applied potential (a rate of 140 ± 20 ps/nm from the slopes of the linear fits). A typical set of results is given in Figure 5.

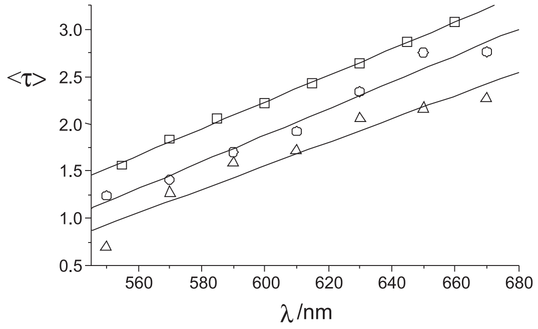

Figure 5. Average decay time ⟨τ⟩ of DCNPPV films obtained under reduction potentials of –150 mV (□), – 400 mV (O), and – 600 mV (Δ). λ_{exc} = 402 nm.

The non-exponential behavior and the increase of the lifetime with the emission wavelength was also observed in films of didodecylstilbenevinylene, a PPV-type polymer with application to light emitting devices, and the values reported showed an increase from 2.3 ns (510 nm) to 5.9 ns (650 nm).[18] In general, it is assumed that the increase of the applied potential in electropolymerization produces polymer with low molecular weight and higher disorder in the chain packing.[10] Thus the fast decay observed in films obtained at high reduction potentials could be explained by the formation of a polymer with lower molecular weight (M_w) and a film with more disordered chain packing. The density of quenching sites by interchain excimer formation or by the residual bromine monomer at the chain end is expected to increase as the M_w decreases. The quenching by heavy atom effect has been observed in studies using bromine-substituted distyrylbenzenes as model compounds.[19] In addition to these two competing quenching processes, the electrochemical synthesis can lead to a trapping of the supporting electrolyte species during the growth of the film. In our first film preparation, standard 0.1 mol L^{-1} of tetraethylammonium bromide in acetonitrile was used as supporting electrolyte. In this case, an additional luminescence quenching path could occur by the trapping of bromide or ion pairs (well recognized as fluorescence quencher of aromatics) in the film, forming point defects, which would contribute significantly to the deactivation of excited-state. Note that bromide ion is also a byproduct formed during the electropolymerization process. In order to investigate such effect of bromide, the supporting electrolyte was changed to perchlorate ions as the anion species. In fact, the decay of the films formed with perchlorate ion in the supporting electrolyte is slower than the decay of the previous sample, and therefore, larger values of $\langle\tau\rangle$ are observed upon change of the electrolyte of the electrochemical synthesis of DCNPPV. A comparative result of the average decay time $\langle\tau\rangle$ of films at a fixed emission wavelength, and obtained under similar reduction potential for the two types of supporting electrolyte, is given in Figure 6.

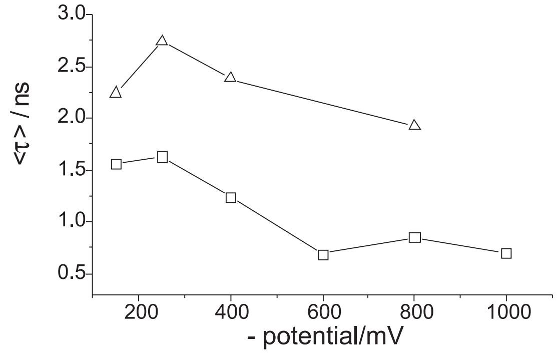

Figure 6. Average decay time $\langle\tau\rangle$ of DCNPPV films as a function of reduction potential and obtained using different supporting electrolyte: 0.1 mol L^{-1} of tetraethylammonium bromide in acetonitrile (☐), and 0.1 mol L^{-1} of tetraethylammonium perchoride in acetonitrile (Δ). λ_{em} = 555 nm.

There is an appreciable increase of $\langle\tau\rangle$ with the change of supporting electrolyte. This result is ascribed to the removal of the bromide ion quencher *via* ion exchange by perchlorate non-quencher species at the polymer-solution interface during electrochemical synthesis. In the samples measured, no evidences of delayed fluorescence were observed. A long lived decay could result from geminate pair recombination of charge carriers or from triplet-triplet annihilation.[20,21] However, cyano-substituted PPV, does not create triplet state in a considerable yield,[21] and as the quenching by bromine end group should form a lone triplet, both factors explain the lack of a second-order process like triplet-triplet annihilation and delayed fluorescence in our materials.

Finally, the soluble DCNPPV fraction in acetonitrile was analyzed and its spectral properties were compared with those of the films. The absorption and emission spectra of the short DCNPPV oligomer is shown in Figure 7, and as expected only a decreasing optical density above 380 nm is observed, which contrast with the absorption band of DCNPPV films with maximum at 420 nm (see data in reference 10).

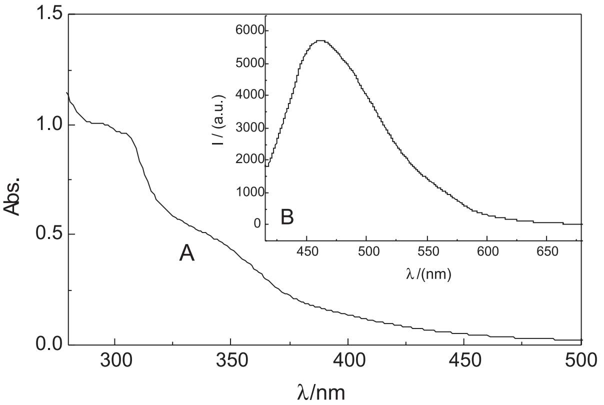

Figure 7. Absorption (A) and emission (B, λ_{exc} = 400 nm) spectra of the soluble fraction of DCNPPV oligomers in acetonitrile at room temperature.

On the other hand, the emission of the soluble fraction is well defined and it has a maximum at about 460 nm, well below the emission maximum of DCNPPV in the films that occurs at about 575 nm. Excitation spectrum (data not shown) is very similar in shape to the absorption spectrum, which indicates that emission is a result of contribution of all fractions of the oligomer distribution with different polymer chain length. Its fluorescence decay is nonexponential, but contrasting with the decay in the films, the three components observed are wavelength independent, and the whole decay surface formed by 17 decay traces spanning from 400-600 nm was globally analyzed with linked decay components (global chi-square of 1.049). The decay components found are 0.7 ± 0.1, 1.8 ± 0.2, and 5.3 ± 0.6 ns. The average lifetime at the emission of 450 nm is 2.3 ns. This value approaches to the average lifetime of the DCNPPV films obtained by using tetraethylammonium perchlorate in acetonitrile as supporting electrolyte (see Figure 6), and the reason is that the oligomers soluble fraction is also free of adsorbed bromide ions. The TRES data of the soluble fraction of DCNPPV in acetonitrile is shown in Figure 8, and from it is clear the absence of red shift effect with time, contrasting to what was observed in the film samples as illustrated in Figure 4.

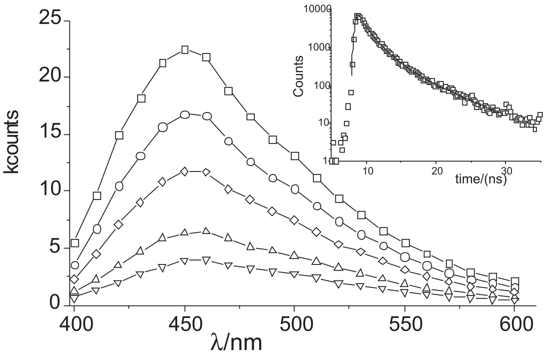

Figure 8. Time-resolved emission spectra (TRES) of soluble fraction of DCNPPV in acetonitrile at the 0 (☐), 0.5 (O), 1.0 (◊) 2.0 (Δ), and 3.0 (∇) ns after the maximum of the laser pulse in the instrument response function. Inset is a typical multiexponential decay observed in the transients (λ_{exc} = 385 nm and λ_{em} = 460 nm).

Both samples of DCNPPV, the films and the soluble fraction of oligomers, are polydisperse and the size distribution accounts for the multiexponential character of the fluorescence decay of these systems. The conjugation length or delocalization of the exciton is affected by the size of the DCNPPV chain, and therefore distinct fraction of DCNPPV may provide different decay times of the excited state. However, the absence of dynamical red shift of the emission band in acetonitrile would indicate that the oligomers of the DCNPPV are not able to form red sites or low-energy chromophores when in a dilute solution, but the polymer does form when it is in solid film. These red sites are ascribed to conjugated chain contacts, which cause a local lowering of the exciton energy due to π stacking. Such a process is favored in films, but less probable with oligomers in solution.

In conclusion, a better protocol of electrochemical synthesis of highly emissive DCNPPV film pointed out in this study is the use of low reduction potential (– 250 mV *vs*. Ag/AgBr is appropriate), and a supporting electrolyte without bromide ion. Further improvements of film emission properties would be achieved with elimination of the residual bromine end monomer by hydrolysis of this group, but such chemical treatment is expected to change the film morphology, and it was not investigated in the present work.

Acknowledgments

The authors thank FAPESP and CNPq for the financial support.

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Received: December 20, 2007
Web Release Date: August 8, 2008

FAPESP helped in meeting the publication costs of this article.