EUROPEAN Polymer Journal

European Polymer Journal 42 (2006) 228-233

Short communication

Solvent and concentration effects on fluorescence emission in MEH-PPV solution

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Received 29 April 2005; received in revised form 13 June 2005; accepted 25 June 2005 Available online 10 August 2005

Abstract

We systematically studied the excitation and the fluorescence steady-state spectroscopy of poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylene vinylene] (MEH-PPV) in two solvents and several concentrations. Fluorescence spectra were recorded for solutions in several concentrations $(10^{-5} \text{ mg/ml} \text{ to } 10^{-3} \text{ mg/ml})$, showing that tetrahydrofuran (THF) and toluene solvate the polymer chain differently. Dilute solution (10^{-5} mg/ml) in THF exhibit broader fluorescence spectra due to greater conformation disorder. The degree of the aggregation depends on both the solvent and the polymer concentration. Aggregation is promoted in toluene solution and hindered in THF solvent. © 2005 Elsevier Ltd. All rights reserved.

Keywords: MEH-PPV; Solvent effect; Flourescence; Aggregation

1. Introduction

Conjugated polymers are novel materials that combine the optoelectronic properties of semiconductors with the mechanical properties and processing advantages of plastics [1]. The ease of polymer processing compared with conventional inorganic semiconductors offers the potential for enormous cost-saving in applications that require visible band-gap semiconductors. Thus, conjugated polymers offer the possibility for use in devices such as plastic LEDs [2], photovoltaics [3], transistors [4], and in completely new applications such as flexible displays.

One important aspect of the emission properties of conjugated polymer is the assignment of its emissive centers. Apart from the intrinsic chemical composition and macromolecular architecture, the emission wavelength depend on two main parameters: the torsion angle of the conjugated backbone, which determines the conjugation length [5]; and the occurrence of interchain interactions, leading to the formation of excimers, aggregates, and/or polaron pairs [6].

Poly[2-methoxy-5-(2'-ethylhexoxy)-p-phenylene vinylene] (MEH-PPV) is one of the first PPV derivatives with alkoxy groups on phenyl rings. Several studies with MEH-PPV are reported showing the photoluminescence

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^{0014-3057/\$ -} see front matter © 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.eurpolymj.2005.06.025

in solutions and in films prepared by distinct techniques (spin coating and casting from solutions) in an attempt to understand the morphology of the films and to optimize the performance of the electroluminescent device [7–9]. The role of the solvent depends on its solvation power as a whole, as well as on its selectivity: it has been shown that some solvents, like THF and chloroform, have a preferential salvation of the lateral groups, while others, like chlorobenzene, xylene and toluene, mainly solvate the polymer backbone, resulting in different macromolecular conformations [10-12]. This way, the distribution of the effective conjugation length and, consequently, the emission profile are changed. Moreover, the conformations in solution are partially maintained in the polymer films prepared from distinct solvents (memory effect) [13,14].

Here we report the systematic study of the concentration on the photophysical properties of MEH-PPV in an attempt to describe the evolution of the aggregation process. We have systematically studied the photophysical properties of MEH-PPV solutions of different concentrations to follow the sequential aggregation. The degree of the aggregation depends on both the solvent and the polymer concentration. Aggregation is promoted in solvents in toluene solution and hindered in THF solvent.

2. Experimental

Poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylene vinylene] (MEH-PPV) sample was obtained from South China University of Technology. The average molecular weight and poly dispersity index (PDI) for the employed material are 700 kg/mol and 3.25 respectively. Spectroscopic-grade toluene and tetrahydrofuran (THF) purchased from J&K Chemical Limited, and were purified following standard methods before use.

Photoluminescence studies of solutions of the poly[2-methoxy-5-(2'-ethylhexoxy)-*p*-phenylene vinylene] (MEH-PPV) in toluene and tetrahydrofuran were prepared by dissolving the appropriate amount of polymer into the measured solvent and stirring for several hours. The concentration ranges from 10^{-5} mg/ml to 10^{-3} mg/ml. Solutions were stored in sealed vials in an inert atmosphere in the dark when not in use.

UV–Visible absorption spectra were recorded on Shimadzu UV-3101PC spectrometer using tungsten and deuterium lamps as light sources. Photoluminescence (PL) spectra and photoluminescence excitation (PLE) were measured by spectrofluorometer (Spex Fluorolog-3) using a xenon lamp for the excitation source. All the experiments were performed at room temperature.

3. Results and discussion

UV–Vis electronic absorption spectra of MEH-PPV solutions show an intense absorption band at 495 nm (2.51 eV) whose peak position is practically independent of the solvent. Absorbances of solutions with several concentrations show a deviation from Lambert–Beer's law for concentrations greater than 10^{-3} mg/ml. On the other hand, for dilute samples, the excitation band peaked at 470 nm, which differs from the maximum of the absorption spectra.

Steady-state fluorescence spectroscopy using three excitation wavelengths: at the blue-edge ($\lambda_{exc} = 410$ nm), at the peak ($\lambda_{exc} = 490$ nm) and at the red-edge ($\lambda_{exc} = 520$ nm) of the excitation band, was performed at several concentrations (from 10^{-5} mg/ml to



Fig. 1. Normalized fluorescence ($\lambda_{exc} = 410 \text{ nm} -$, $\lambda_{exc} = 490 \text{ nm} -$ -, $\lambda_{exc} = 520 \text{ nm} -\Delta$ -) and excitation ($\lambda_{em} = 566 \text{ nm}$) spectra of MEH-PPV in THF (a) and toluene (b) respectively. Concentration: 10^{-5} mg/ml .

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 10^{-3} mg/ml), in solutions of toluene and THF of MEH-PPV.

Fig. 1 shows the excitation and fluorescence emission spectra of MEH-PPV, at the lowest concentration, 10^{-5} mg/ml, in both solvents. As noted, the emission is virtually independent of the excitation wavelengths characteristic of the emission from an isolated excited state singlet intrachain exciton [6]. Fluorescence peaks lie at 552 and 555 nm for MEH-PPV solutions in THF and toluene, respectively, independent of the excitation wavelengths. Fluorescence emission spectra are slightly blue shifted in THF relative to toluene.

The spectral intensity is approximated by the superposition of transitions between the vibrational frequencies of the ground and the excited electronic states. In the emission process the probability of the 0th vibronic excited state to the *n*th vibronic ground state is given by

$$I_{0\to n} = \frac{\mathrm{e}^{-S}S^n}{n!} \tag{1}$$

where S is the Huang–Rhys factor [15].

It was noted that the Huang–Rhys factor (S) correlates with conformational disorder [16]. The more conformational disorder is, the larger the Huang–Rhys factor (S) will be. Table 1 shows concentration effect on the relative intensity and Huang–Rhys factors in tol-

Table 1 Concentration effects on the relative intensity and Huang–Rhys factors

Concentration (mg/ml)	THF		Toluene	
	I_{0-0}/I_{0-1}	S factor	I_{0-0}/I_{0-1}	S factor
10^{-5}	2.63	0.38	3.12	0.32
10^{-4}	2.38	0.42	2.43	0.41
10^{-3}	1.27	0.79	1.38	0.72

uene and THF respectively. The relative intensities of the 0–0 and 0–1 vibronic bands are taken from the experimental curves. It can be deconvoluted in three vibronic bands (Fig. 2) using the software origin version 6.0 with the spectrum in wavenumber scale and fitting the peak profile with Gaussian functions. The Huang–Rhys factor (S) was calculated using the above equation.

As we can see, greater conformational disorder exists in THF than toluene. The difference is attributed to the different group of the preferential solvation. Toluene has a preferential interaction with the backbone of the polymer chain, and thus the MEH-PPV chains adopt a rigid, open and straight conformation in solution, which is best to maximize favorable solute-solvent interaction. THF, on the other hand, preferentially solvates the polymer's side groups. MEH-PPV chains form a much tighter coil as the polymer curls up to minimize unfavorable interaction with the solvent in solution. Since the lateral groups can display several possible special orientations, several types of partially folded conformations can take place and, as a consequence, conformational disorder increases, which results in broader spectra emission. Diftoluene solvents undergo preferential ferently, interaction with the conjugated polymer backbone (vinylene-phenylene groups), which adopt more planar conformations [17,18,14]. One unequivocal experimental demonstration of the preferential solvation of the lateral groups by non-aromatic solvents was the orientation of these groups perpendicular to the macromolecular backbone making the film surface more polar whereas the coplanar orientation were observed when the film was spun using aromatic solvents [9]. Consequently, greater constraints are imposed on the backbone that limit the possible number of conformations. More limited distributions of conformers always lead to narrower fluorescence bands because the number of emissive Franck–Condon (FC) states is reduced [19].



Fig. 2. Normalized fluorescence spectra of MEH-PPV experimental curve (solid curves). The dashed curves show Guassian fits to the three visible peaks of the fluorescence spectra. Concentration: 10^{-5} mg/ml in (a) THF and (b) toluene, $\lambda_{exc} = 490$ nm.

Fluorescence spectra of MEH-PPV in more concentrated solutions, 10^{-4} mg/ml (Fig. 3), are slightly red shifted (2–3 nm) compared with the spectra of a 10^{-5} mg/ml solution (Fig. 1). This red shift is independent of the excitation wavelengths, as often observed for concentrated solutions [19]. The excitation spectra at the emission peak (557–560 nm) are also similar to those obtained at 10^{-5} mg/ml (data not shown).

However, some evidence of preliminary aggregation of the polymer is revealed by the small change of the relative intensity of vibronic bands 0–0 and 0–1, I_{0-0}/I_{0-1} (shown in Table 1), compared with that for the 10^{-5} mg/ml solutions. Moreover, the degree of aggregation we observed depends on both the choice of solvent and the polymer concentration. Aggregation is promoted in solvents such as *toluene* in which the chains have a relatively open coil and hindered in solvents such as THF where the chains tend to coil tightly. The aggregates of MEH-PPV emit at 598 nm in coincidence with the vibronic 0-1 band of the intra-chain isolated chromophore, which explains the relative increase of the intensity at 598 nm [20–22].

As noted in Fig. 4, the fluorescence emissions for solutions of 10^{-3} mg/ml are also red shifted compared with the spectra of samples with lower concentration. For MEH-PPV in THF the fluorescence emission is practically independent of the excitation wavelengths ($\lambda_{\rm exc} = 410$ nm, $\lambda_{\rm exc} = 490$ nm and $\lambda_{\rm exc} = 520$ nm), for toluene solutions the lower intensity band at 598 nm has a higher intensity if the excitation takes place at the red-edge of the excitation band, ca. $\lambda_{\rm exc} = 520$ nm. In addition, there is a remarkable decrease of the I_{0-0}/I_{0-1} ratio, compared with the 10^{-5} mg/ml solutions.

As previously commented, the red-shift of the fluorescence spectra resulted from: (i) the conformational changes of the polymer chain that modify the effective size of the conjugation; (ii) the formation of aggregates that increases the relative intensity of the red-edge 0-1



Fig. 3. Normalized fluorescence spectra of MEH-PPV in (a) THF and (b) toluene, with several concentrations: 10^{-5} mg/ml to 10^{-3} mg/ml. $\lambda_{exc} = 490$ nm.



Fig. 4. Normalized fluorescence emissions for solutions of 10^{-3} mg/ml with different excitation in (a) THF and (b) toluene respectively.

vibronic band (598 nm) and, (iii) interaction with the solvent, producing solvatochromic effects. The enhancement of the intensity at 598 nm can be attributed to, at least, two major reasons: aggregation of the polymer chains in more concentrated solutions and changes of the conformational disorder. Nevertheless, there are several reasons for our belief that aggregation predominates over the conformational disorder: (i) there is a relative increase of the band at 598 nm where the emission of aggregates predominates; (ii) this relative intensity is more pronounced for higher concentration; (iii) there is a remarkable decrease of the entire intensity signal, which is compatible with the decrease of the quantum yield of aggregates compared to the isolated luminophores. On the other hand, increase of the conformational disorder should produce different types of changes of the spectral profile, such as: (i) broadening of the emission band occurs when the conformational disorder increases; (ii) more flexible conformations produce shorter conjugation lengths leading to the blueshift of the emission spectrum. Thus, considering that none of these two behaviors were observed and considering that the solubility decreases with the increase of the molecular weight, we conclude that the major reason for the relative increase of the intensity at 598 nm is the aggregation of the polymer in concentrated solutions.

Differences of the solvation abilities of TFH and toluene play an important role in controlling the shape of the emission band. For toluene solution the excitation on the blue-edge of the excitation band ($\lambda_{exc} = 410 \text{ nm}$) leads to the emission of higher energy specie, the isolated form, while excitation at the red-edge ($\lambda_{exc} = 520 \text{ nm}$) preferentially excites the lower energy aggregates that emit at the red-edge of the emission band. Although in toluene we observe site-selective excitation, in THF solutions the emission is independent of the excitation wavelengths even though the higher relative intensity of the band at 598 nm evidenced the presence of aggregates.

Because of the difference in solvation ability, we assume that toluene undergoes a preferential solvation of the back-bone inducing a more planar structure. With the backbone open and exposed, it is straightforward for the π -electrons on one chain to overlap with those on a neighboring chain. Increasing the concentration offers a greater number of segments available for interaction; as a result, the extent of aggregation is increased. Under this condition, site-selective emission can be observed. On the other hand, preferential solvation of lateral groups by THF leads to a more flexible backbone, several conformations are possible. Emission bands become broader and site-selective emission is not observed. Although a precise explanation for these observations requires additional data, for example time resolved spectra, we suggest that in less ordered systems additional energy transfer or migration processes occur and the relative quantum efficiencies of the emission of isolated and aggregate forms are maintained constant. On contrary, successive energy transfer or migration was inhibited when higher energy specie is preferentially excited either because the radiative process is more efficient or because the lower energy specie (aggregate) is inaccessible. In any case this point requires further studies.

4. Conclusions

We have shown that two solvents for MEH-PPV (toluene and THF) undergo different interactions with the polymer, bringing about different conformations in solution that are reflect in the photoluminescence properties. The solvation abilities play important roles with respect to the photoluminescence properties of MEH-PPV in solutions. Some evidence of preliminary aggregation of the polymer is revealed with increasing the concentration. The degree of the aggregation depends on both the solvent and the polymer concentration. We observe site-selective excitation in more concentration toluene solution (10^{-3} mg/ml) .

Since the conformation in solution is partly retained in the films, the solvent effects described can have an important role in the electroluminescence properties of this material, which is its most important application.

Acknowledgements

The authors thank State key project of basic research (No. 2003CB314707), Beijing NOVA Program (No. 2004B10), NSFC (No. 10434030), and RFDP (No. 20020004004) for the financial support.

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