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Chemical Physics Letters

Counter ion effects on the energy transfer processes in PPV

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ARTICLE INFO

ABSTRACT

We report an enhanced luminescence of cast films of poly(p-phenylenevinylene) (PPV), where the energy transfer among adjacent polymer chains was controlled by varying the concentration of counterions in the synthesis. Using as precursor poly(xylylidenetetrahydrothiophenium) with dodecylbenzenesulfonate as counter ions (PTHT-DBS) in 1:3 M basis led not only to the strongest but also the most polarized emission. Both the intensity and degree of polarization could be controlled, provided that the conversion temperature was considerably lower than the T_g of PPV. These results may be exploited in optimizing organic electronic devices, for which annealing is needed.

1. Introduction

Enhancing the electroluminescence efficiency of organic light-emitting diodes (OLEDs) requires new synthesis strategies for conjugated organic molecules or polymers, in addition to optimized processing techniques for large-area displays [1–5]. A major difficulty in device fabrication is associated with thermal annealing normally used to modify morphology and remove residual solvents from the active layer [6]. For polymeric devices (PLEDs), this annealing step is often performed close to the glass transition temperature (T_g) [7,8], which might bring about deleterious effects because charge injection may be decreased [9]. Therefore, in order to optimize device performance one may need to understand the effects from thermal annealing or even avoid annealing at high temperatures altogether. This calls for further strategies to control emission properties, and one possibility is the control of energy transfer processes within the device. Indeed, polarized emission can be increased considerably if energy transfer is reduced [10], which can be performed by varying the counter ions in the synthesis as demonstrated for poly[3-octylthiophene] synthesized by chronocoulometry [10]. For poly(p-phenylenevinylene)-LiCl films, other possible control variables are counter ion concentration and the temperature of thermal annealing [11].

In this Letter, we investigate the effects of the conversion temperature and counter ion concentration on the emission efficiency of poly(p-phenylenevinylene) (PPV) cast films, for which dodecyl-sulfonic acid (DBS) was used as counter ion associated with the precursor, in various degrees of substitution of the original chloride

ions of PTHT. DBS is advantageous for two main reasons [12]: it allows conversion into PPV at a much lower temperature than T_g, with less structural defects, and permits fine control of emission properties. Indeed, upon replacing the chloride counter ions of the precursor by DBS ions, it is possible to thermally convert into PPV at lower temperatures (100 °C), thus decreasing substantially the number of structural defects [12]. Moreover, the DBS counter-ion has a long aliphatic chain that is useful as spacer between adjacent polymer chains, increasing the free volume and consequently reducing the polymer/polymer interaction. That in turn will allow the control of the amount of energy transfer among the photoexcited carriers during the synthesis process. These advantages were exploited with emission being probed with ellipsometry, from which energy transfer processes could be inferred. We found that an ideal concentration of DBS exists for enhanced emission, which also affords a larger degree of polarization.

2. Materials and methods

Poly(p-phenylenevinylene) (PPV) was synthesized following the procedures established in reference [13], starting with the soluble precursor poly(xylylidenetetrahydrothiophenium) chloride (PTHT – Aldrich®). Cast films were produced by dropping aqueous solutions of PTHT (0.011 M) and of the counter-ion dodecylbenzenesulfonate (DBS – Aldrich®), in various molar ratios (PTHT:DBS) (mol:mol), namely 1:0.1, 0.2, 1.0, 2.0, 3.0, 4.0, 5.0, 10, 15, and 20. The PPV-DBS films were obtained by thermal conversion of PTHT-DBS cast films in vacuum (10^{-3} atm) at 100 °C and 200 °C during 2 h.

Polarized absorption and absorption measurements were made with a UV–VIS 800XI Femto spectrophotometer. Photoluminescence

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spectra were obtained by pumping the samples with an air cooled argon ion laser (Stellar-Pro ML/150 of Modu Laser) at 458 nm. All measurements were carried out at room temperature ($\sim$22 °C) under vacuum (10^{-6} atm). Emission ellipsometry experiments were performed with the setup described by Alliprandini et al. [14], whose details are given in the Supplementary Information (SI).

3. Results and Discussion

Figure 1 shows the absorption and emission spectra for cast films of PTHT-DBS before and after conversion at two distinct temperatures, namely T_c = 100 °C and 200 °C , leading to PPV-DBS films. The spectrum for the PTHT DBS film in Figure 1a displays the well-known absorbance peaks at ca. 225 nm, due to the π–π^* electronic transitions of benzene, and at 320 and 360 nm owing to the π–π^* electronic transitions of tetrahydrothiophene aromatic rings and of stilbene and stilbene aggregates, respectively [11,15]. At high DBS concentrations, absorption in the low wavelength region increases considerably since DBS also absorbs in the spectral region of aromatic π–π^* transitions (benzene ring) and probably because DBS hampers chain aggregation in PTHT. This is consistent with the reduction in aggregation induced by the ion Li, which also depended on the Li concentration [11]. The absorption spectra for the converted PPV-DBS films in Figure 1b and c exhibit the non-localized PPV π–π^* transitions above 350 nm, with the band at 400 nm depending on the amount of DBS [11,15]. The films are isotropic according to their polarized absorption spectra

shown in the Supplementary Information (SI), as expected for cast films. Regarding the emission in Figure 1d–f, the addition of DBS led to a broadening of the photoluminescence (PL) spectrum of PTHT, with a small red shift in the maximum, probably owing to stilbene aggregation.

Significant differences were observed among the PL spectra of converted PPV-DBS films, depending on the conversion temperature. The film containing no DBS and converted at 200 °C displayed a considerably broader spectrum, which was relatively well resolved in the large wavelength region with vibrational progression peaks at 548 nm. Upon incorporation of DBS, the electron-vibrational coupling decreased and so did the intensity of this peak, in comparison with the DBS-free PPV film thermally converted in the conventional procedure (for zero DBS in Figure 1f). Since the PL line shape was the same for the PPV-DBS film converted at 100 °C and the non-converted PTHT + DBS film, two effects need to be considered. The first brings about a red shift due to thermal conversion [11,16,17], while the second is responsible for a blue shift owing to interchain de-aggregation [18–20]. When the conversion temperature was increased to 200 °C , the emission peak was red-shifted by 10 nm to 532 nm because at this temperature the PTHT lateral groups are completely eliminated by complexation with the Cl counter ions. This yields an increase in the effective conjugation length with a larger extent of polymer entanglement and aggregation. Additionally, an increase in the vibrational peak intensity was observed which could be assigned to structural defects arising mainly from oxidative process such as carbonyl group formation, as is well documented in literature with FTIR
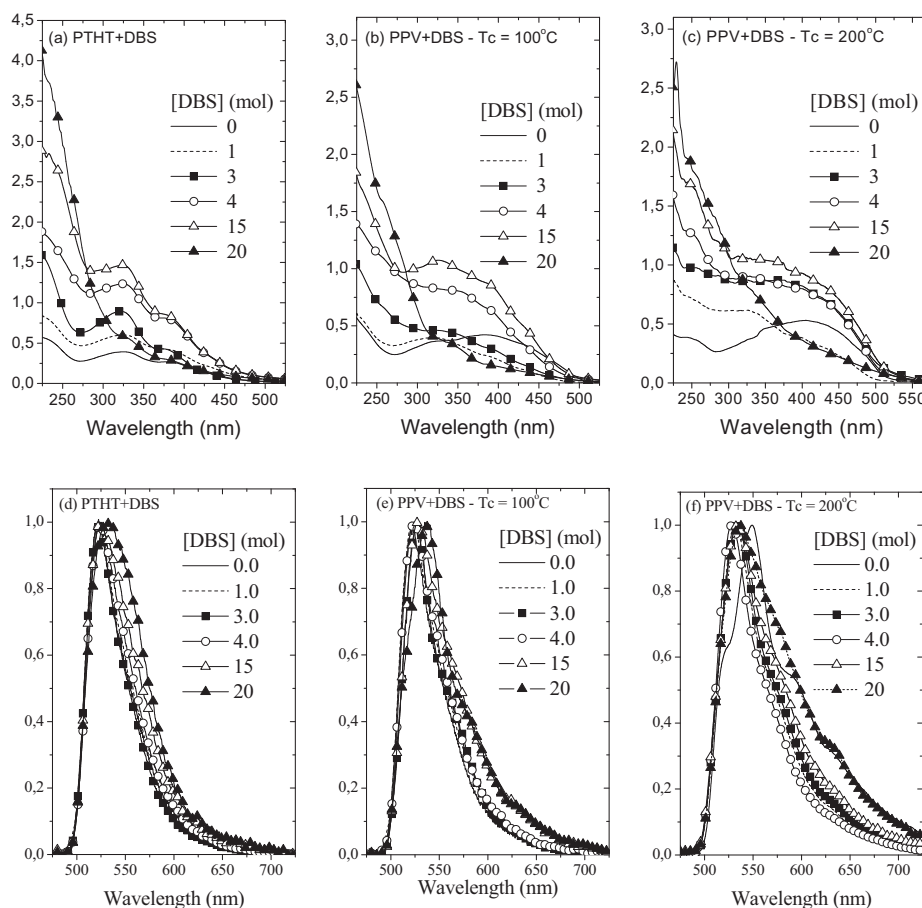

Figure 1. Absorption spectra for cast films of (a) PTHT + DBS, (b) PPV + DBS converted at T_c = 100 °C, and (c) PPV + DBS converted at T_c = 200 °C. Normalized PL spectra for cast films of (d) PTHT + DBS, (e) PPV + DBS at T_c = 100 °C, and (f) PPV + DBS at T_c = 200 °C. The PTHT:DBS concentrations were 1:0, 1:1, 1:3, 1:4, 1:15 and 1:20 mol. All measurements were performed at room temperature of 25 °C.

and other methods [11,12,16,17,21,22]. The excess added DBS in relation to the original chloride ions was needed to ensure complete substitution. The high molecular weight and entanglement of the precursor hindered the access to all substitution sites. Nevertheless, it is quite possible that some DBS excess remained in solution.

The spectral mass center, λ_{SMC}, for the emission of PTHT + DBS and PPV-DBS cast films was calculated using:

$$\lambda_{SMC} = \frac{\int_{\lambda_i}^{\lambda_f} I(\lambda) \lambda d\lambda}{\int_{\lambda_i}^{\lambda_f} I(\lambda) d\lambda} \tag{1}$$

and the values are given in Table SI1 in the Supplementary Information [SI], where $I(\lambda)$ is the emission intensity in the spectral range from λ_i to λ_f.

The energy transfer of photoexcited carriers may be assessed by determining the polarization of the emitted light [10,23,24]. Here we performed emission ellipsometry experiments with which the polarization could be obtained from the Stokes parameters. The emission intensity is [13,14,25,26]:

$$I = \frac{1}{2}[A + B\sin(2\theta) + C\cos(4\theta) + D\cos(4\theta)] \tag{2}$$

where I is the emission intensity at a specific wavelength, θ is the angle between the achromatic linear polaroid (vertical direction) and the rapid axis of rotation quarter wave plate, $A = S_0 - \frac{S_1}{2}$, $B = S_3, C = -\frac{S_1}{2}, D = -\frac{S_2}{2}$ and S_0, S_1, S_2 and S_3 are the Stokes' parameters. The polarization degree P of the emitted light is calculated as [13,14,25,26]:

$$P = \frac{\sqrt{S_1^2 + S_2^2 + S_2^2}}{S_0} \tag{3}$$

Figure 2 displays typical curves of emission ellipsometry for PTHT + DBS and converted PPV + DBS films at $T_c = 100\,^\circ C$ and $200\,^\circ C$ (Figure 2c) films, for 3.0 mol of DBS. The solid lines were obtained by fitting the data ($I(\lambda)$) with Eq. (2). The Stokes parameters and P are listed in Table SI2 in the Supplementary Information [SI] for all samples. Polarized emission was obtained by exciting the sample with a linearly polarized light even for isotropic cast films because the polymer chains with the highest probability to emit are those with the transition electric dipole moment in the same direction of the polarization of the exciting light. No polarization was observed for excitation with circularly polarized light.

The normalized emission efficiency was calculated as the ratio between the number of emitted and absorbed photons as:

$$\eta \sim \frac{I_{PL}}{P_{abs}(\lambda_{exc})} \tag{4}$$

The dependence on the DBS concentration for the features characterizing emission, viz. spectral mass center (λ_{SMC}), degree of polarization (P) and relative emission efficiency (η_{rel}), is depicted in Figure 3 for all cast films. Significantly, the maximum in emission efficiency and in the degree of polarization coincides with the minimum in the spectral mass center at 1:3.0 mol ratio of PTHT-DBS, regardless of the conversion temperature, and even whether there was not any conversion into PPV. It means that at this concentration DBS acts as a spacer with optimized performance. DBS actually reduces the chain–chain interaction in the polymer, thus decreasing the energy transfer from photoexcited carriers; as a consequence, the emission efficiency increases and so does the degree of polarization. Note that for a solid sample the emission of polarized light with a linearly polarized excitation cannot be attributed to the emission being faster than the molecular diffusion [24] since there is no free volume for molecular diffusion. The reason why λ_{SMC} is minimum at 3 mol of DBS is also due to de-aggregation of polymer chains induced by DBS. The effects on λ_{SMC}, P and η_{rel} do not increase further upon increasing DBS concentration because at higher concentrations the formation of micelles may occur which will cause PPV to aggregate. Also worth noting is that the effects are much less significant for the PPV-DBS film converted at $200\,^\circ C$ in Figure 3c, since the action of DBS as spacer is diminished when the film is thermally treated at a temperature close to the glass transition temperature ($T_g \sim 200\,^\circ C$) [27,28].

One could argue that the information on energy transfer could be obtained with the anisotropy parameter from fluorescence measurements. However, the anisotropy parameter does not vary when the polarization direction of the excitation is changed, which is the reason why we had to resort to emission ellipsometry. This is clearly seen by inspecting the anisotropy parameter for emission defined as [23]

$$r = \frac{I_{\parallel,\parallel} - GI_{\parallel,\perp}}{I_{\parallel,\parallel} + 2GI_{\parallel,\perp}} \tag{5}$$

where $I_{\parallel,\parallel}$ is the emission intensity excited by a parallel polarized light (first index) in the parallel direction (second index), $I_{\parallel,\perp}$ is the emission intensity for parallel excitation measured in the
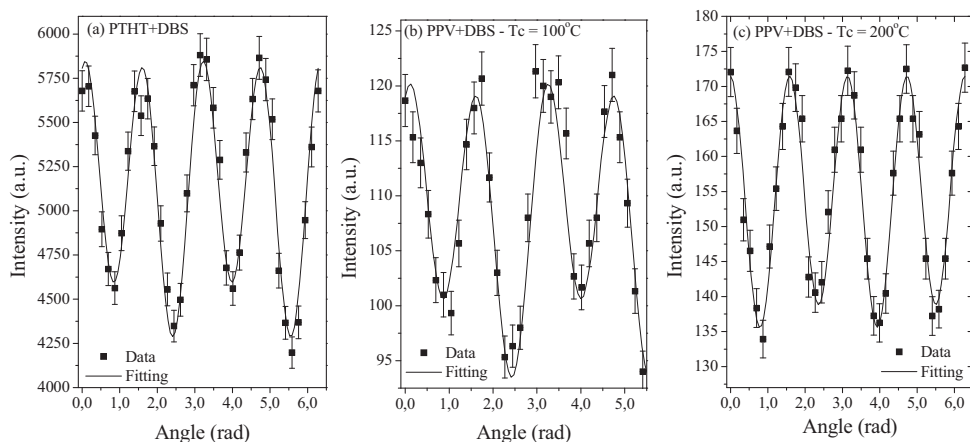

Figure 2. Emission ellipsometry measurements (solid squares) for cast films of (a) PTHT-DBS, (b) PPV-DBS converted at $T_c = 100\,^\circ C$, and (c) PPV-DBS at $T_c = 200\,^\circ C$. The PTHT:DBS concentration was 1:3.0 mol ratio. The samples were excited with linear polarization (vertical direction) at 457 nm and the solid lines represent the fitting using Eq. (2).
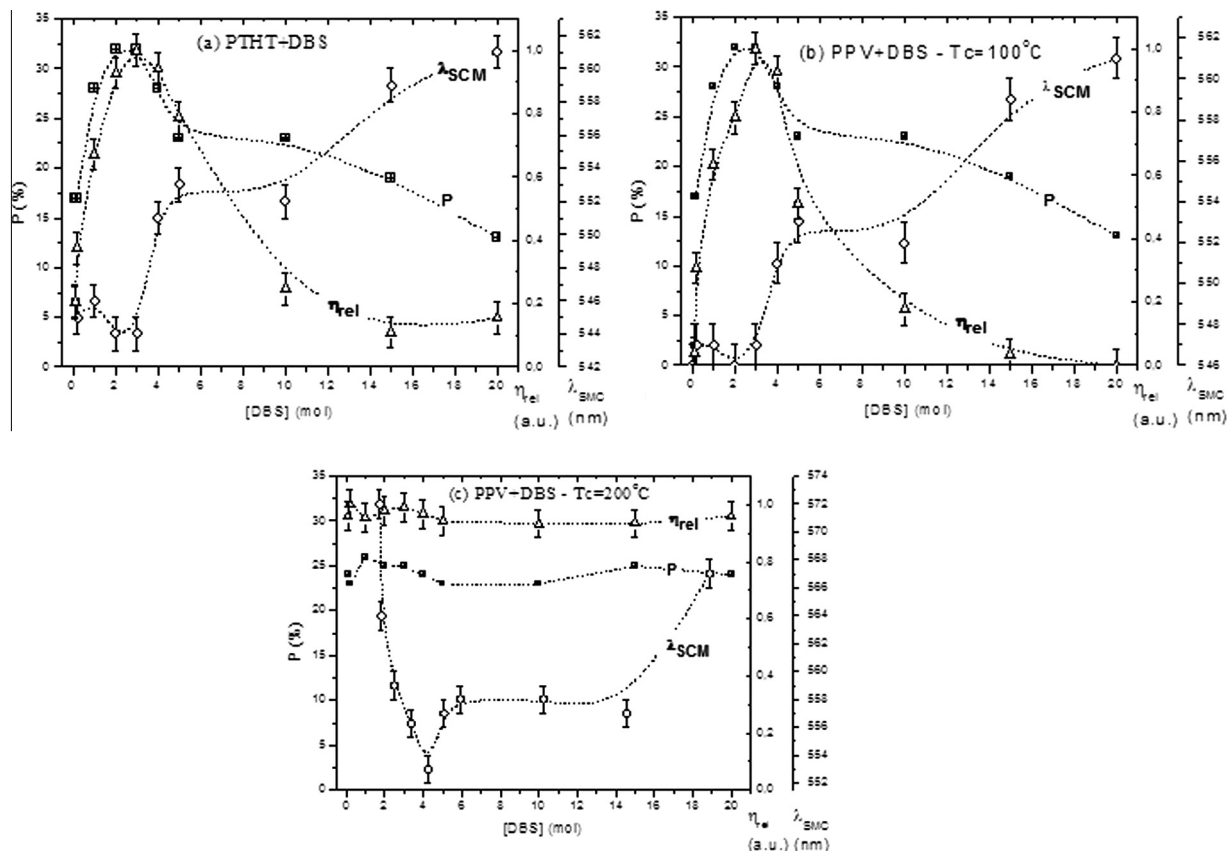
Figure 3. Spectral mass center – λ_{SMC} (Eq. (1)), polarization degree – P (Eq. (3)), and relative emission efficiency – η_{rel} (Eq. (4)) for PTHT + DBS (a), PPV + DBS T_c = 100 °C (b), and (c) PPV + DBS T_c = 200 °C cast films in function of the DBS concentration.

perpendicular direction, and G is a geometric factor introduced to compensate the difference in transmission in the spectrometer diffraction grating for vertically and horizontally polarized light given by [23]:

$$G = \frac{I_{\perp,\parallel}}{I_{\perp,\perp}} \tag{6}$$

Where $I_{\perp,\parallel}$ is the emission intensity for perpendicular excitation measured at the parallel direction, and $I_{\perp,\perp}$ is the emission intensity for perpendicular excitation in the perpendicular direction. Note that if index $\parallel \rightarrow \perp$, that is with a 90° rotation of the sample, the anisotropy factor in Eq. (5) may be invariant. It means that the anisotropy parameter does not depend on the positioning of the sample in the experimental setup if the correct factor G is used. This result also demonstrates that it is not possible to photoselect the chromophores with changes in the excitation if only the fluorescence anisotropy parameter is used for an isotropic medium.

Finally, the explanation presented here is consistent with the experimental results but it cannot be taken as a proof that energy transfer is the sole factor to determine the change in emission polarization, particularly because morphology, which also affects energy transfer, was not considered.

4. Conclusions

We have shown that using DBS as counter ion in the synthesis and conversion of PPV films can lead to an optimized emission, with larger degree of polarization, which is observed when the relative concentration is 1:3 PTHT/DBS mol ratio. This was proven with

emission ellipsometry with which the polarization state of the emitted light could be described in the scope of the Stokes theory for the electromagnetic field. As expected, the emission was partially linearly polarized for PTHT-DBS and PPV-DBS cast films excited with linearly polarized excitation, but showed no polarization when excitation was performed with circularly polarized excitation. This level of control was ascribed to the possible tuning of the energy transfer processes in the films. Interestingly, such control was only possible for the films converted at the lower temperature, well below the T_g of PPV; only in this case was the interchain interaction reduced and controllable. It should be remarked that in addition to the interest for basic physics, the control of energy transfer processes is also crucial for organic electronic applications. For example, with such control one may enhance the performance of organic photovoltaic cells, such as those based on heterojunctions where the use of thermal treatment and dopants is commonplace, or obtain optical gain in emission.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2014.05.018.

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