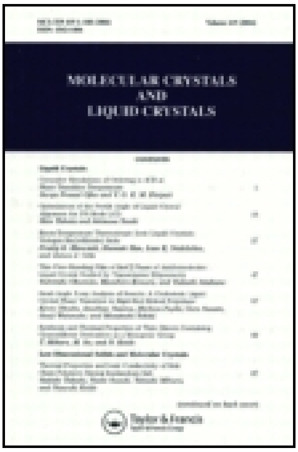

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Optical Properties of Poly(p -phenylene vinylene) Derivatives with Ion-Coordinating Side Groups

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Optical Properties of Poly(*p*-phenylene vinylene) Derivatives with Ion-Coordinating Side Groups

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The optical properties of poly(*p*-phenylene vinylene) (PPV) derivatives with ion-coordinating side groups (ICSG) films and respective blends with poly(ethylene oxide) (PEO) complexed with lithium triflate are studied by means UV-visible absorption and photoluminescence (PL) spectroscopy. These PPV-derivatives were synthesized with the objective to improve the physical properties of PPV-derivative: PEO: lithium salt blends to be used in light emitting electrochemical cells (LECs). We have synthesised two homopolymers: the poly(2-methoxy, 5-(triethoxymethoxy)-1,4-phenylene vinylene) (MTEM-PPV) and the poly(2-methoxy,5-(2'ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV); and a statistical copolymer: the poly(2-methoxy, 5-(2'ethylhexyloxy)-co-2-methoxy, 5-(triethoxy-methoxy) -1,4-phenylene vinylene) (MEH-co-MTEM)-PPV. The analysis of PL spectra of PPV derivatives blended with salt or PEO-salt showed that PPVs with higher amount of ICSG present higher quenching effect on the PL efficiency in the presence of lithium salt complexes.

Keywords: Optical properties; poly(1,4-phenylene vinylene) and derivatives; polymeric blends; light-emitting devices.

INTRODUCTION

Polymer light-emitting diodes (PLEDs) have attracted much attention, since their discovery by Burroughs *et. al.* in 1990 [1]. Five years later, a new type of polymeric light-emitting device, the light-emitting electrochemical cell (LEC) was proposed by Pei *et. al.* [2], presenting improved physical features in comparison to conventional PLEDs. The structure used in LEC devices is similar to the configuration used in LEDs, except by the active layer that is composed by a blend of an electroluminescent polymer and a polymeric solid electrolyte.

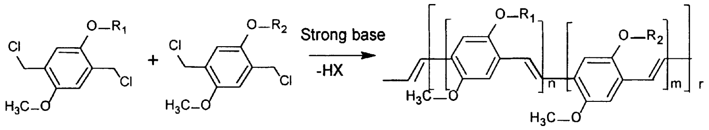
The disadvantage of LECs, although, is the great phase separation in the blended films, due to the distinct polar nature of the non-polar luminescent polymer and the polar polymer electrolyte which may originate undesired device properties as high response time, mechanical instability and short lifetime. In order to avoid this problem, alternatives to improve the blend miscibility have been proposed as the use of surfactant-like additives [3] and the synthesis of conjugated polymers containing ion-coordinating side groups (ICSG), such as ethylene oxide olygomers groups, introduced in the polymer backbone [4].

Conjugated polymers with ICSG are particularly promissory materials to be used in LECs since ICSG promotes a higher interaction of the luminescent polymer with PEO as well as they can take part in the ionic transport of the device. Morphological studies in a similar system [5] have shown that a good refinement of blend microstructure can be reached by using PPV derivatives containing ICSG.

In this work we analyse the optical properties of poly(*p*-phenylene vinylene) derivatives with ICSG, and their blends with PEO:CF_3SO_3Li by UV-vis absorption and photoluminescence spectroscopy, in comparison to conventional PPV derivatives and blends.

EXPERIMENTAL

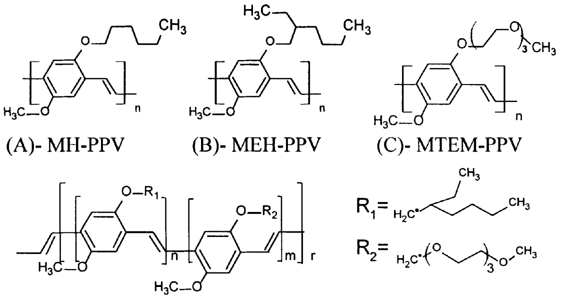
The synthesis of PPV derivatives were based on Gilch and Wudl methods [6, 7], following a dehydrohalogenation condensation polymerization in which the monomers, bis (halomethyl) benzene with substituting groups, react in the presence of a strong base. To obtain the statistical copopolymer, poly(2-methoxy,5-(2'ethylhexyloxy)-co-2-methoxy,5-(triethoxymethoxy)-1,4-phenylene vinylene) (MEH-co-MTEM-PPV), the monomers of MEH-PPV and MTEM-PPV were, respectively, used at the proportion n:m of 3:7, as shown in the synthetic route summarized in Figure 1. The poly(ethylene oxyde) (PEO) (MW = 5.000.000 g.mol^{-1}, and the lithium triflate salt, CF_3SO_3Li were purchased from Aldrich.



m= 0, MEH-PPV; m:n=3:7, MEH-co-MTEM-PPV; n=0, MTEM-PPV

FIGURE 1 Scheme of the polymerisation step of a general PPV derivative.

Figure 2 shows the synthesized PPV derivatives that were used to produce films and blends with PEO-salt. The degree of polymerisation was obtained from the molecular weight (determined by gel permeation chromatography GPC): $DP_{(A)}$= 130, $DP_{(B)}$= 135, $DP_{(C)}$= 51, $DP_{(D)}$= 66 (See Figure 2).



(A)- MH-PPV (B)- MEH-PPV (C)- MTEM-PPV

(D)- MEH-co-MTEM-PPV

FIGURE 2 Synthesized PPV derivatives.

The studied films were prepared by spin coating chloroform solutions of the pure PPV derivatives and of the blends onto quartz substrates. The solutions were prepared by dissolving separately PPV derivatives and PEO in anhydrate chloroform and CF_3SO_3Li in anhydrate acetonitrile. Blended solutions were obtained, therefore, by mixing the original pure solutions in adequate proportions to produce solutions in the desired mass compositions.

UV-visible absorption spectra were performed by a Hitachi U-2001 model spectrophotometer whereas photoluminescence measurements were carried out using a PL system composed by a monochromator coupled to a cooled photomultiplier for spectra acquisition and an argon laser ($\lambda_{exc} = 458$ nm) as the excitation source.

RESULTS AND DISCUSSION

Absorption spectra of pure polymers films and respective blends in the 1:1:0.18 proportion (w/w) are depicted in Figure 3. Considering that the four polymers have similar functional structures, no great differences in the shape of the absorption curves were indeed expected.

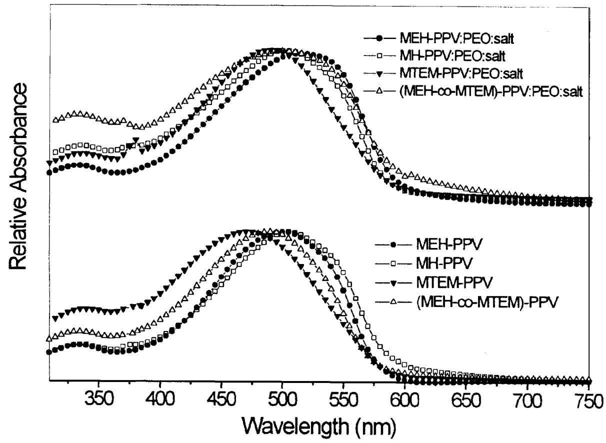


FIGURE 3: Relative absorption spectra of the four synthesized polymers and respective PEO:lithium salt blends.

However, in the case of pure polymers with ICSG, the absorption spectra exhibit a small blue shift in comparison to the derivatives without these groups, being more evident for the MTEM-PPV. This blue shift can be associated to a reduction of the effective conjugation length of the PPV derivatives containing ICSG, as a result of the steric interactions of this side chains over the backbone, leading to higher band gap energy. In the blends spectra, it is observed that the band gap of all polymers suffers a slight red shift by blending, except to the MTEM-PPV blend spectrum, which remains almost invariable. This red shift might be related to an increase of the effective conjugation length of the luminescent polymer due to the interactions with the PEO chains. Since the MTEM-PPV has a better affinity to the PEO than the other PPV derivatives, the introduction of the PEO probably does not change significantly the conformational properties of the polymer and, therefore, its effective conjugation length.

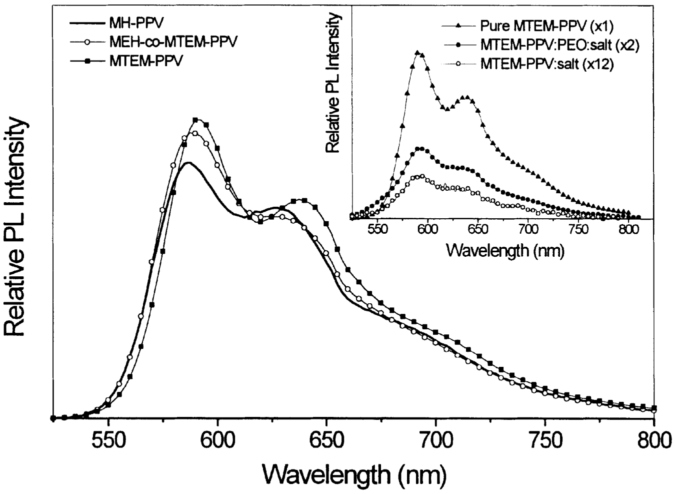


FIGURE 4: Relative photoluminescence (λ_{exc} = 458 nm) spectra of the pure polymers. Inset: decrease of the PL efficiency of MTEM-PPV systems by blending.

Figure 4 shows the relative PL spectra of the synthesized polymers excited at 458 nm. Considering that the spectra were normalized by the absorption coefficient at the excitation wavelength, these spectra allow evaluating the relative PL efficiency of the films. It was observed that all the pure polymers presented comparable values of PL efficiency which were differently affected when blended with PEO:salt. The PL efficiency of the homopolymer MTEM-PPV was particularly affected by blending with PEO:lithium salt (inset of Figure 4), presenting a decrease by a factor of about 6 in comparison to the pure polymer efficiency. Such decrease was even more abrupt by the simple addition of lithium salt (1:10 w:w) to the pure polymer. This result indicates that even though the use of ICSG PPV derivatives in LECs generally improves the electrical properties of devices, one must be aware to the possibility of decreasing the luminescent efficiency at high lithium salt concentrations.

CONCLUSIONS

Introduction of ion coordinating side groups into the backbone of luminescent conjugated polymers has shown to be very useful in the synthesis of polymers to be used in light-emitting electrochemical cells. However, the strong quenching effect in the PL efficiency in the presence of lithium salt in such materials is an indicative that non-radiative processes might be taking place in the blend structure. The understanding of these processes may provide important information in order to improve the performance of LECs based on such materials.

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