

Control of polymer–electrode interactions: the effect of leaving group on the optical properties and device characteristics of EHPPV

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Poly[2-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (EHPPV) was prepared *via* chloro, *S*-methyl xanthate and *O*-ethyl xanthate precursor polymers. The choice of leaving group used was found to control the optical and device properties of the EHPPV with the variations arising from the differing chemical interactions of the leaving groups with indium tin oxide (ITO). The leaving group–ITO interactions were found to dominate the properties of EHPPV when formed from the commonly used chloro precursor polymer and this problem could be solved by use of xanthate leaving groups which were found not to react with the contact.

Controlling polymer–electrode chemical interactions is an important issue for polymer based light-emitting diodes (LEDs). It is particularly important for precursor polymer routes as the by-products from the elimination process could react with the electrode materials. The precursor polymer route was the original method used for the preparation of LEDs based on conjugated polymers.¹ The precursor route involves the synthesis of a polymer that is soluble and processable. The precursor polymer is then processed, for example, by spin-coating into a thin film and then converted, usually thermally, to the conjugated polymer.^{2,3} In many cases the conjugated polymer is insoluble. Insoluble conjugated polymers have some attractive features for use in LEDs. For example, many of the more efficient LEDs contain more than one layer. If the light-emitting polymer layer is rendered insoluble then another layer such as electron transport material can be easily deposited by solution processing without the polymer layer being removed. In addition, the fact that the conjugated polymer is insoluble means that patterning of an LED becomes simpler as the deposited material will be more stable to solvents that might be used in the patterning process. Also the conversion reaction has a second advantage in that it ensures that the processing solvent is driven off. In spite of these potential advantages much of the recent research of conjugated polymers for LEDs has concentrated on soluble conjugated polymers. This is in part due to the fact that soluble polymers are relatively easily synthesised and processed, and can often have high photoluminescence quantum yields (PLQYs). Soluble conjugated polymers also have disadvantages including removal of the processing solvent and that the more efficient multilayer devices can be harder to prepare. However, recently there have been reports of conjugated polymers prepared *via* precursor routes that have high PLQYs.^{4,5} This coupled with their potentially superior physical properties suggests that more effort should go into the study of insoluble conjugated polymers.

For precursor polymer routes to conjugated polymers to reach their full potential, the chemical interactions between the leaving groups and electrode materials need to be understood and controlled. This is particularly important during LED fabrication where the precursor polymer is generally deposited on an electrode material before the thermal conversion. There are a number of precursor routes to poly(1,4-phenylenevinylene) (PPV) and its derivatives including sulfonium,^{3,6} sulfide,⁷ halo,^{4,8} and xanthate.⁹ Of these precursor routes the details of the leaving group–electrode interactions have only been reported for the sulfonium leaving group.^{10,11} With the sulfonium precursor to PPV it has been clearly shown that the hydrogen chloride given off during the conversion process can react with the ITO and the products, possibly indium chloride, can quench the PL.^{10,11} Attempts to modify the leaving group electrode interactions have wholly concentrated on the layer on which the polymer is deposited. For example, the introduction of a conducting polymer layer between a “sulfonium” precursor to PPV and an ITO electrode can moderate the leaving group–electrode interactions.⁵ It has also been shown that the properties of PPV prepared *via* the sulfonium precursor can be affected by the reactivity of the metal electrode.¹²

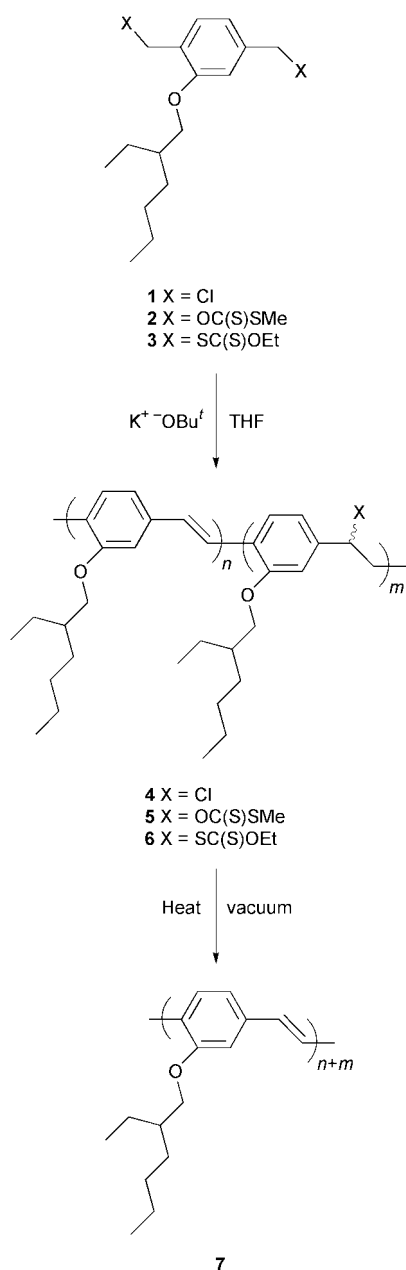
However, what has not been studied is whether the leaving group–electrode interactions can be controlled by choice of leaving group or whether such interactions are general for all polymers. The latter point is beyond the scope of this paper. The potential for the choice of leaving group giving control over the chemical interaction with the electrode was illustrated in a report that compared the sulfonium precursor to PPV with a new *O*-ethyl xanthate† precursor route. It was found that LEDs containing PPV prepared *via* the *O*-ethyl xanthate precursor route were more efficient than those in which the PPV was produced *via* the more traditional sulfonium precursor route.⁹ The improvement in LED efficiency was attributed to the amorphous nature of the “PPV” produced *via* the *O*-ethyl xanthate precursor route, the amorphous nature of the “PPV” being due to it containing some saturated links as well as *cis* and *trans* linkages. However, there are two important alternative explanations for the improved device efficiencies. First, the PPV prepared *via* the *O*-ethyl xanthate precursor might be inherently more luminescent than PPV prepared *via* the sulfonium route. Second, the by-products from the elimination reaction from the *O*-ethyl xanthate precursor might be less damaging to the electrode material, in this case indium tin oxide.

†*O*-Ethyl xanthate = *O*-ethyl dithiocarbonate.

This communication shows how the choice of leaving group may be used to control the leaving group–electrode interactions. We describe a systematic study that differentiates between the inherent photophysical properties of EHPPV prepared *via* three different precursor polymers and the effect the interactions of the leaving group–electrode have on those properties. We show that the correct choice of leaving group can avoid detrimental reactions with the underlying electrode during the thermal conversion to leave the photophysical properties of the polymer unchanged. In this study EHPPV was prepared from chloro **4**, *S*-methyl xanthate **5**, and *O*-ethyl xanthate **6** precursor polymers and the electrode material was chosen to be the commonly used ITO.

Results and discussion

The synthesis of poly[2-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (EHPPV) **7** from the three different precursor routes is shown in Scheme 1 and is described in detail elsewhere.⁴ The precursor polymers **4–6** were prepared by base catalysed polymerisation of their respective monomers **1–3**. It is important to note that precursor polymers produced *via* this



Scheme 1 Structures of the polymers used in this study.

route can have some degree of conjugation caused by competition between the polymerisation and base catalysed elimination of the leaving groups on the formed polymer. In addition, although not shown, there can also be a small number of phenylene units connected *via* ethylene and therefore 1,2-disubstituted (with leaving groups) ethylene units which arise from head-to-head and tail-to-tail couplings during the polymerisation. The precursor polymers **4–6** can all be thermally converted to form EHPPV **7**. Although the EHPPV is drawn fully conjugated the presence of the chemical defects in the precursor polymer must also give rise to a small percentage of ethylene units and possibly acetylene units in the final polymers.^{13,14} Infrared analysis of EHPPV prepared *via* the three different precursor routes showed that in all cases the conversion had gone to completion. In addition, the infrared spectra showed that the chemical structure of the EHPPV was essentially independent of the precursor route used suggesting that differences in the photophysical properties were likely to arise from differences in the polymer's morphology. Finally, the PL spectra of EHPPV prepared *via* the three different routes on quartz are all very similar suggesting that the longest effective conjugation length for EHPPV is also independent of precursor route.

In this study the PLQYs of thin films of EHPPV **7** on quartz prepared from the chloro **4**, *S*-methyl xanthate **5**, and *O*-ethyl xanthate **6** precursor polymers converted at 240 °C for 15 h at 0.02 mbar were measured to be 50%, 23%, and 17% respectively. The properties of the EHPPV prepared *via* the *S*-methyl xanthate **5** precursor polymer were found to be sensitive to the batch of the material studied but the PLQY was always higher than that of EHPPV prepared from **6** and lower than EHPPV made from **4**. We believe that the differences observed are due to the fact that **5** has a relatively low molecular weight when compared with **4** and **6** and morphological effects in film formation play an important role. On the basis of PLQY measurements alone, it would appear that the chloro precursor is most promising for LEDs. However, the possibility of interactions between the by-products of the elimination and ITO must also be considered. This was investigated by spin-coating each of the three precursor polymers onto ITO and converting them to EHPPV under the same conditions. The UV–visible and PL spectra (Fig. 1–3) and PLQYs were recorded. The first thing to note is that the UV–visible spectra of EHPPV prepared from the two different xanthate precursors, **5** and **6**, are similar whether they are prepared on glass or ITO (Fig. 2 and 3). In the case of EHPPV prepared *via* the *S*-methyl xanthate **5** precursor polymer there is a small blue shift in the onset of absorption but the absorption maximum is the same (Fig. 3). This suggests that there are no strong interactions or chemical reactions of the xanthate by-products with the ITO. This argument is strengthened by the fact that the PL spectra of EHPPV prepared *via* **5** are

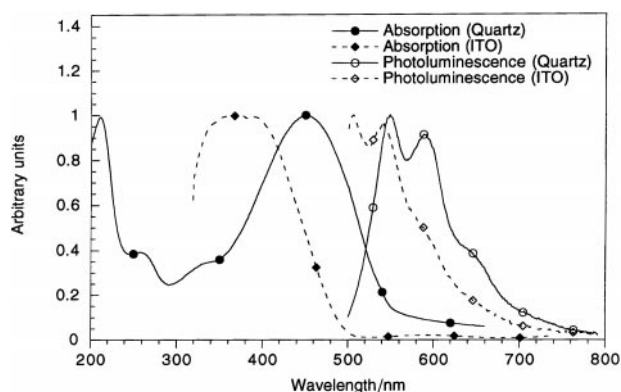


Fig. 1 UV–visible and PL spectra of EHPPV prepared *via* the chloro precursor polymer **4** on quartz and ITO.

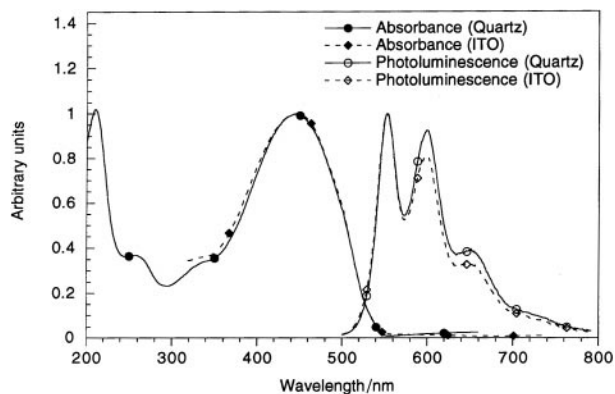


Fig. 2 UV-visible and PL spectra of EHPPV prepared *via* the *O*-Et xanthate precursor polymer **6** on quartz and ITO.

identical whether prepared on quartz or ITO (Fig. 3). A similar result is also seen for EHPPV prepared from **6** (Fig. 2). In contrast, there was a strong blue shift in the UV-visible and PL spectra of EHPPV produced *via* the chloro precursor polymer **4** on the ITO compared to when it was prepared on quartz (Fig. 1). The fact that there is an interaction between the eliminated hydrogen chloride and the ITO is not surprising given that the hydrogen chloride given off during the conversion of the sulfonium precursor to PPV reacts with the ITO.^{10,11} However, in the case of PPV prepared *via* the sulfonium precursor there was no blue shift observed in the PL spectra. The blue shift in the PL and UV-visible spectra of EHPPV prepared *via* the chloro precursor **4** could be due to a number of reasons including incomplete conversion, increased conformational disorder caused by the elimination by-products, or oxidative doping of the sample. Also, it may be possible that some polymer scission process occurs during the conversion, shortening the conjugation length, and giving rise to the blue shift. At this stage we cannot determine which are important contributors although we feel that incomplete conversion is unlikely under the reaction conditions given the smooth conversion on quartz. In addition, we believe that oxidative doping is not the cause of the blue shift as we would expect to see absorptions at long wavelength due to the oxidised species and these were not present.

The PLQYs of the EHPPVs prepared on ITO were measured with the excitation through the substrate or from the top of the polymer film. The PLQY of EHPPV prepared *via* the chloro precursor polymer **4** was found to fall from 50% on quartz to only 8% on ITO whilst the yields for EHPPV prepared *via* the two different xanthates, **5** and **6**, remained essentially constant. For the *S*-methyl xanthate precursor polymer **5** the PL quantum yields on quartz and ITO were 23% and 24% respectively whilst for the *O*-ethyl xanthate precursor polymer

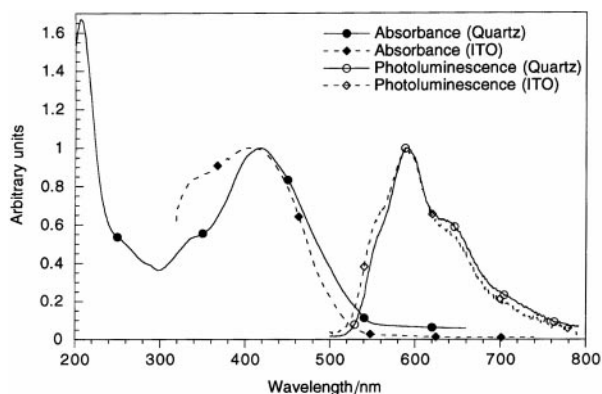


Fig. 3 UV-visible and PL spectra of EHPPV prepared *via* the *S*-Me xanthate precursor polymer **5** polymer on quartz and ITO.

6 the results were 17% for quartz and 16% for ITO. There was no difference in the spectra or PL quantum yields whether the measurement was taken through the glass or at the air-polymer interface. The PLQY results confirm the suggestion from the UV-visible and PL spectra that there were minimal chemical interactions with the by-products from the xanthate eliminations with the ITO. The drop in PL quantum yield for the chloro precursor on ITO is consistent with the results observed for the sulfonium precursor to PPV.¹⁰

One measure of how effective a conjugated polymer will be in a device is how luminescent the material is. However, two other important device factors that must be considered are charge injection into the polymer layer and transport through it. All three of these factors can be affected by the morphology of the polymer. With EHPPV produced *via* the chloro **4**, *S*-methyl xanthate **5**, and *O*-ethyl xanthate **6** precursor polymers we have a unique opportunity to explore these factors. If the PLQY measurements were only carried out on quartz the chloro precursor polymer might have been thought to be the ideal device candidate. However, by converting the precursor polymers on ITO the order of device efficiency based only on PLQY would change with EHPPV from the *S*-methyl xanthate giving the most efficient devices and the chloro the least. To test this we made single layer devices (ITO/EHPPV/Al) using each of the three precursor polymers and measured their efficiencies and EL spectra. We found that the device efficiency followed the same trend as the PLQY on ITO with EHPPV prepared from the *S*-methyl xanthate **5** being the most efficient and the EHPPV prepared *via* the chloro leaving group **4** being least efficient. The external EL efficiencies were measured over several devices on a single substrate and the average efficiencies were found to be $5 \times 10^{-3}\%$, $1 \times 10^{-2}\%$, and $4 \times 10^{-2}\%$ for EHPPV prepared *via* the chloro, *O*-ethyl xanthate, and *S*-methyl xanthate respectively. The external EL efficiencies measured for EHPPV *via* the xanthate precursor polymers are of the same order of magnitude as that reported for PPV prepared *via* the *O*-ethyl xanthate precursor route.⁹

Interestingly, we found that in contrast to the PL spectra the EL spectra of the three devices were the same (Fig. 4). Given the blue shift in the PL spectrum of EHPPV prepared *via* **4** on ITO when compared with EHPPV prepared *via* the xanthate precursor polymers this was something of a surprise. We do not understand at this stage why EL spectra of all the EHPPVs are the same but it may be due to the position of the light-emitting region in the LED. In the PL experiment most of the film is excited, whereas in EL light can be emitted from a narrow recombination zone. EHPPV **7** is expected to be predominantly a hole transport material (similar to MEHPPV). In the device set up used (ITO/EHPPV/Al) it would be anticipated that the recombination zone would be close to the relatively high work-function cathode. Therefore, the EL spectra of EHPPV prepared *via* the chloro precursor **4** suggests that the by-products arising from the hydrogen chloride and ITO, and

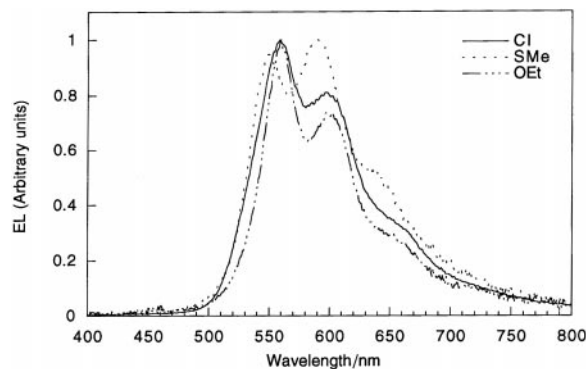


Fig. 4 Electroluminescence spectra of EHPPV prepared *via* chloro **4**, *S*-Me xanthate **5**, and *O*-Et xanthate **6** precursor polymers.

which cause the blue-shift in the PL spectrum, are not present in the recombination zone. This could potentially arise from the fact that the by-products have not migrated to the interface or indeed that there is another set of chemical reactions between the by-products and the deposited cathode. This will have to be investigated further.

Conclusion

This study shows that a family of precursor polymers with different leaving groups provides a powerful way of studying how polymer–substrate interactions affect the photophysical and device properties. In particular we find that the by-products from the chloro leaving group interact strongly with ITO, whereas the by-products from the two xanthate leaving group polymers do not. This means that although the EHPPV produced from the chloro precursor polymer **4** is the most luminescent on quartz it is least luminescent on ITO and gives the least efficient LED. For most polymers studied PLQY is used as a guide as to their potential performance. The results show that for precursor polymers to reach their full potential the polymer–electrode interactions must be considered and controlled.

Experimental

For the electroluminescence studies films of the precursor polymers were spin-coated from tetrahydrofuran onto ITO coated glass substrates to give films with thicknesses around 90 nm. The ITO was cleaned by ultrasonification, first in acetone and then hot propan-2-ol. The precursor polymer films were converted under vacuum ($\sim 10^{-5}$) at 240 °C for 15 h. The devices were completed by evaporation of Al at pressures of typically 10^{-6} mbar. The current–voltage and light–output–current measurements were performed simultaneously using a Keithley source-measure unit and a calibrated photodiode. The external quantum efficiency was deduced from the light–output–current data following a reported method.¹⁵ The electroluminescence spectra were recorded using a CCD spectrograph. Thin films for optical studies were prepared by spin-coating the precursor polymers from tetrahydrofuran onto quartz or ITO coated glass substrates. The precursor polymer films were converted under vacuum (0.02 mbar) at 240 °C for 15 h. The thin films for the optical measurements had relative absorbances in the region of 1–2. Absorption spectra were measured using a Perkin Elmer Lambda 19 spectrophotometer. Photoluminescence spectra were measured using a CCD spectrograph. The excitation was provided by the 488 nm line of a CW Ar-ion laser (Spectra Physics). Photoluminescence quantum yields (PLQYs) were measured using an

integrating sphere (Labsphere) in accordance with the method outlined by Greenham *et al.*¹⁶

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