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LUMINESCENCE PROPERTIES OF PPV DERIVATIVES CARRYING ANTHRACENE PENDENT GROUPS

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Abstract : Photo- (PL) and electroluminescence (EL) properties of three different PPV derivatives carrying the 9,10-diphenylanthracene units are compared. One (polymer **1**) of the polymers contains the 9,10-diphenylanthracene structure as an integral part of the main chain, but the other two have it as the pendent group attached to the main chain through either oxyethyleneoxy (polymer **2**) or oxyhexamethyleneoxy (polymer **3**) spacer. Polymers **1** and **2** exhibit very similar PL and EL spectra that are more or less of superimposed feature of the spectra from the backbones and the anthracene pendents. In contrast, polymer **3** shows an EL spectrum that is completely different from its PL spectrum. Whereas the PL spectrum of polymer **3** appears to be a combination of the spectra from the main chain and the pendents, as for polymer **1** and **2**, the EL spectrum of polymer **3**, however, looks as if the lights were emitted only from the backbone. This difference is explained in terms of excited state electronic interactions between the main chain and the pendents.

INTRODUCTION

The Cambridge group's reports in 1990 and later years (Refs. 1-3) on the electroluminescence (EL) properties of PPV and its derivatives, sparked strong interests on the luminescence characteristics of and light-emitting diodes (LED) based on the polyconjugated organic

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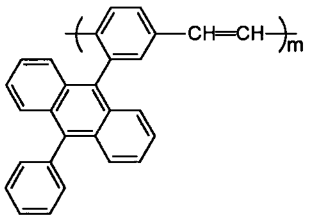
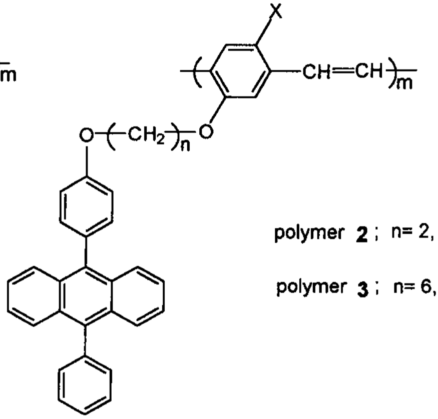
polymers (Refs. 4-8). Although EL devices composed of conjugated polymers appear to be entering the stage of commercial development, there are still many unresolved problems in chemistry as well as in device engineering.

While we (Refs. 9-14) were studying the relationship between the structure of PPV derivatives and their electrical conductivities and also nonlinear optical properties, we became interested in the photo- (PL) and electroluminescence (EL) properties of PPV derivatives having the anthracene moieties as an integral part of the main chain or as pendents. The structures of the polymers are shown below :



polymer **1**



polymer **2** ; n= 2, X= OC_4H_9

polymer **3** ; n= 6, X= H

As one can see from the above structural formulas, in polymer **1** the 9,10-diphenylanthracene structure is the integral part of the main chain, but in polymer **2** and **3** it is bound to the chain as the pendent. In the latters, the 9,10-diphenylanthracene group is attached to the backbone through a saturated spacer; oxyethyleneoxy spacer in polymer **2** and the longer oxyhexamethyleneoxy spacer in polymer **3**. Although polymer **2** carries the second substituent, the n-butoxy group, bonded to the phenylene ring of the main chain, it should not influence much of our comparison of their luminescence behavior. It is very well established (Ref. 15) that 9,10-diphenylanthracene exhibits very high quantum efficiency in PL. But PL properties of the PPV derivatives carrying the 9,10-diphenylanthracene units have not yet been fully studied and reported. We (Ref. 16) have previously reported preliminary findings on the PL and EL characteristics of polymer **1** and polymer **3**.

This article describes the similarities and also differences observed in the PL and EL behavior of the three polymers. Although a preliminary report on the PL and EL properties of polymer **1** and **3** was published recently by us (Ref. 16), the comparison of the PL and EL behavior of polymer **2** with those of polymer **1** and **3** gives a better perspective on the influence of the length of the spacers and also on the importance of intramolecular excited state electronic energy transfer in the luminescence characteristics of the polymers. Therefore, it is inevitable that many of our earlier data are utilized in this presentation for the sake of a clearer discussion.

RESULTS AND DISCUSSION

Fig. 1 compares the UV-vis spectra of the present polymers. They exhibit strong absorptions over the wavelength range of about 325-400 nm overlapped with much weaker, broad absorptions over the region of about 400-500 nm. The absorptions in the shorter wavelength region are originated from the anthracene group and the ones in the longer wavelength region from the main chain. The absorption maxima of the anthracene groups in the polymers appear slightly red-shifted when compared with those of the 9,10-diphenylanthracene molecule that shows absorption maxima at 337, 355, 374, and 394 nm.

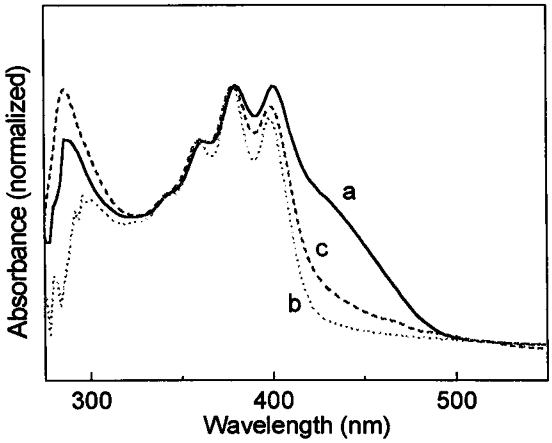


Fig. 1. UV-vis spectra of the thin films of a) polymer **1**, b) polymer **2** and c) polymer **3**

These shifts must be due either to slight electronic interaction between the main chain and the pendent (polymer **1**) or to the presence of the alkoxy substituent(s) on the phenyl group attached to the anthracene center (polymer **2** and **3**). Direct electronic interaction in the ground state between the main chain and the pendent in polymer **1**, however, appears to be minimal in light of the very small shift in the absorption positions. Similar observations were made by us (Ref. 17) earlier for PPV derivatives carrying the styryl substituents.

Photoluminescence (PL) characters of the present polymers are not too much different from each other; all of them show an emission from about 400 to 550 nm originated from the anthracene residue and additional ligth-emission in the longer wavelength region that is emitted from the main chain (Fig. 2). In other words, basically their PL spectra appear to be simple overlaps of the PL spectra of the backbone and the pendents. It is conceivable that lights of different wavelengths are emitted simultaneously from the main chain and the anthracene pendents, because the PL spectra were obtained for the excitation wavelength of 365 nm which is absorbed by the both parts of the polymer molecules. It is also very possible , in particular, for polymer **1** that there is an excited state electronic interactions or exciton migrations between the π -systems in the main chain and the pendents because the pendents are directly bound to the backbone. In fact, a detailed study on the time-resolved PL spectra of the present polymers indicates that exciton migration from the pendents to the backbone is most facile in polymer **1**, but it is practically inhibited in polymer **3**. The behavior of polymer **2** lies inbetween.

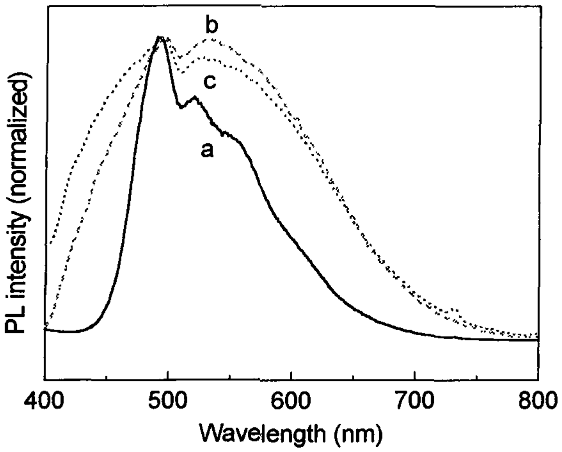


Fig. 2. Photoluminescence spectra of the thin films of a) polymer **1** , b) polymer **2** and c) polymer **3** (excitation wavelength : 365 nm)

Evidently, exciton migration between the pendents and the backbone strongly depends on the length of the spacer connecting the two parts of the molecules. A detailed report (Ref. 18) on this point will be published by us soon elsewhere. It is also very possible for all of the three polymers that a part of emitted light by the anthracene pendents is reabsorbed by the backbone resulting in the additional luminescence from the main chain. The PL spectrum of polymer **2** covers the broadest wavelength region among the three, starting from the blue to the red region. This polymer carries two alkoxy substituents attached on to the phenylene ring in the main chain, whereas others have either only one alkoxy group or the anthracene moiety attached to the backbone ring. Clearly, the presence of the two electron-donating groups on the phenylene ring in polymer **2** gives rise to the emission in the longer wavelength region covering broader wavelength regime.

In contrast to the PL properties, polymer **3** exhibits a very different electroluminescence (EL) behavior from the other two polymers. While the EL spectra of polymer **1** and **2** are about the same as their PL spectra, in the case of polymer **3** the EL spectrum is much different from its PL spectrum (Fig. 3). In fact, polymer **3** emits light only from the main chain, but not any from the diphenylanthracene pendents. This peculiar phenomenon can be explained by the assumption that the excited state electronic energy transfer or exciton migration between the backbone and the pendent group occurs in polymer **1** and **2**, but not in polymer **3**. Since the main chain should have a lower ionization potential and a higher electron affinity (Ref. 19) than the anthracene moiety (Ref. 20), it is conceivable that initial hole-injection as well as electron-injection will occur preferentially to the backbone part of the molecule resulting in the initial formation of excitons only along the main chain. But in polymer **1** and **2** these initially injected charges and excitons formed therefrom must interact with the pendent 9,10-diphenylanthracene moieties giving rise to the light emission not only from the backbone but also from the pendents. Therefore, this type of interactions generates light emission in the blue region from the pendents as well as in the green-red region from the backbones for both polymer **1** and **2**.

It is rather surprising that polymer **2** allows for such excited state electronic energy transfer to occur between the two parts of the molecule, i.e., the main chain and the backbone, through the σ - bonded oxyethyleneoxy spacer connecting the two structural elements. In other words, the energy transfer or exciton migration must occur through the spacer via the through-bond interaction mechanism (Ref. 21). Evidently, due to the longer length of the spacer, such

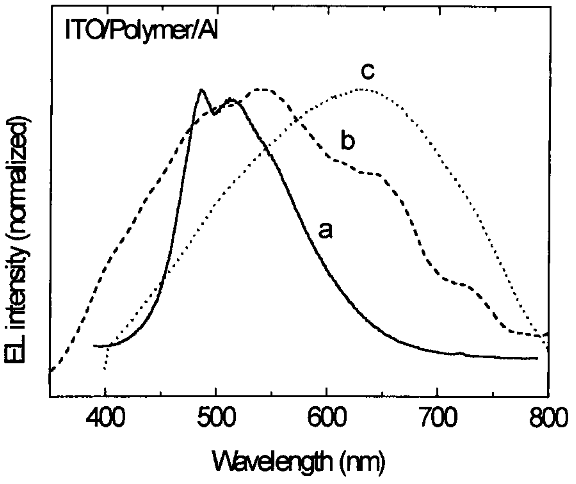
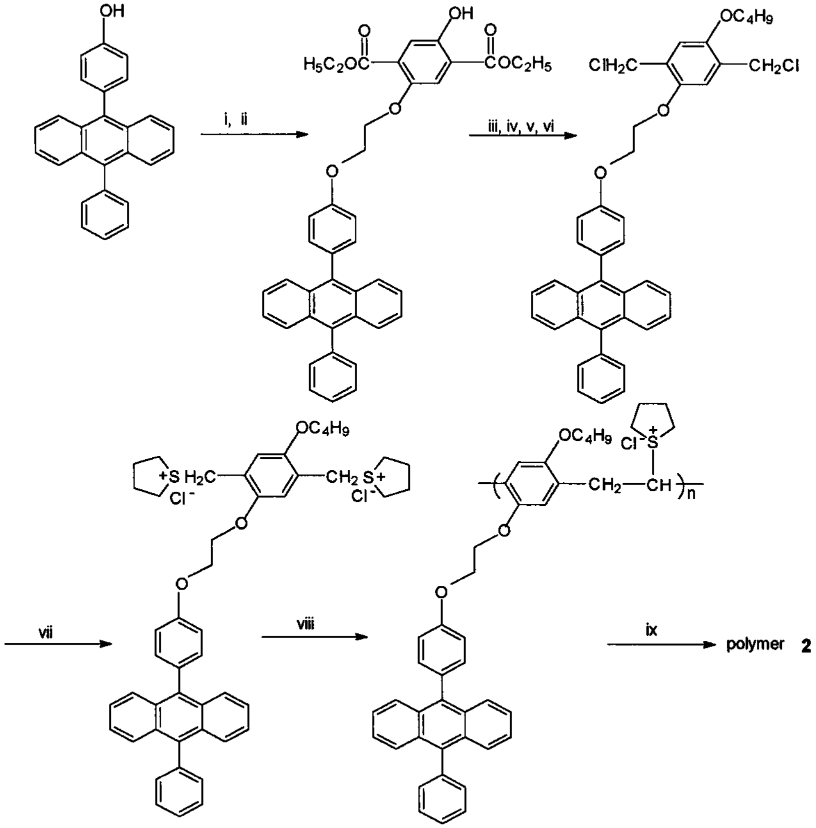


Fig. 3. Electroluminescence spectra of the thin films of a) polymer **1** (Eapp.= 13V), b) polymer **2** (Eapp.= 22V) and c) polymer **3** (Eapp.= 18V)

interactions are not possible in polymer **3**. Otherwise, these polymers are expected to show a similar EL behavior, if so-called the through-space mechanism (Ref. 21) for the excited state energy transfer is applicable. Earlier, Dexter (Ref. 22) showed that energy transfer through the electron exchange mechanism decreases rapidly with the distance between the two sites involved. The penetration probability (Ref. 23) for a quantum leakage through tunneling mechanism also predicts a similar dependence on the distance. It is conjectured that similar transfer mechanisms are applicable to the present cases. We, however, do not yet know the critical length of the spacer that would prohibit completely such energy transfer between the main chain and the pendents. It is emphasized that consideration of the possible intramolecular electronic interactions described in this article should pave an important road to the design and synthesis of new light-emitting organic polymers by which the emitted light colors may be tunnable with higher efficiencies.

EXPERIMENTAL

Synthesis of polymer **1** and **3** were briefly explained in one of our earlier reports (Ref. 16), and only the synthetic procedure of polymer **2** is given in Scheme I.



Scheme I. Synthetic route to polymer **2** ; Reagents and conditions;

i. $Br(CH_2)_2Br$, K_2CO_3, acetone, reflux, 48 h, 84 %; ii. $(CH_3CH_2OOC)_2C_6H_2(OH)_2$, K_2CO_3, acetone, reflux, 48 h, 74 %; iii. $Br(CH_2)_3CH_3$, K_2CO_3, acetone, reflux, 3 days, 82 %; iv. KOH, ethanol, reflux, 10 h, 84 %; v. $LiAlH_4$, THF, reflux, 4 h, 68 %; vi. $SOCl_2$, DMF, reflux, 4 h, 88%; vii. tetrahydrothiophene, methanol, 50℃, 40 h, 74 %; viii. TMAH, DMF/H_2O (15/1 by vol.), 15℃, 5 days; ix. 250℃, 6 h in vacuo (ca. 0.1 torr).

All of the PL spectra of the thin films (ca. 0.3 μm thick) were obtained at the excitation wavelength of 365 nm. The EL spectra were obtained for the devices in which the light-emitting polymer layer of about 0.1 μm thick was sandwiched between the aluminum cathode and the ITO glass anode. Polymer **1** and **3** are soluble in toluene and their number-average MWs measured by GPC against polystyrene standard were 10,500 and 11,000, respectively. Polymer **2** is less soluble and its inherent viscosity value measured at 30 ℃ for 0.2 g/dL solution in 1,1,2,2-tetrachloroethane was 0.72.

ACKNOWLEDGEMENT

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