EFFECT OF CONJUGATION LENGTH ON PHOTOPHYSICAL PROPERTIES OF A CONJUGATED-NON-CONJUGATED MULTIBLOCK COPOLYMER

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Abstract

The synthesis, structural characterization and photophysical properties of copolymers built by conjugated PPV type units of variable length and an aliphatic spacer are described. The aliphatic spacer provided good film forming capability and solubility. The effective conjugation extension was determined and its influence on the bandgap was evaluated, complementing theoretical and experimental data, since the PV units were oligomeric in size but with the mobility of longer chains. Aggregation phenomena were investigated; ground state dimers or higher associated forms were detected. The electrical and photovoltaic properties were studied in devices built with the neat polymers or containing a heterojunction with fullerene (C₆₀), the photovoltaic responses were in agreement with the photoluminescence results. The most efficient photovoltaic device was based on the polymer containing the longest conjugated block, which also the most luminescent material.

Keywords: PPV type copolymer, aliphatic spacer, conjugation length.

Introduction

The increasing interest in electroluminescent polymers is due to promising technological applications such as large area displays, apart from the scientific interest in this new class of materials. The great majority of electroluminescent polymers are built up by a fully conjugated backbone, leading to the formation of chromophores with different energy gaps because the effective length of conjugation is statistically distributed. However, in the mixture, the chromophores with lower energy gaps will be the emitting species because of energy transfer. To solve this problem several approaches have been developed. The confinement of the conjugation into a well-defined length of the chain is one of the most successful strategies developed so far, and can be achieved by tailoring the polymer structure several ways, like inserting kink (ortho and meta) linkages or imposing steric distortions [1]. A very effective means of confining the conjugation in a well defined region of the chain is the insertion of aliphatic spacers along the chain, forming conjugated-non conjugated multiblock copolymers (CNCMBC’s) [2]. Those conjugated–non-conjugated copolymers are soluble, homogeneous in terms of conjugation length, and can be designed to emit in any portion of the visible spectrum [3]. In such structures energy transfer from high band gap to lower band gap sequences in which excitons may be partially confined will
provide higher luminescence efficiency when compared to similar structures of uniform conjugation [4]. This method was used to prepare a well defined (CNCMBC’s), having p-phenylene vinylene blocks (so called 2 1/2 PPV units) intercalated by an aliphatic spacer which was the first blue soluble emitter (465 nm).

This work aims to explore the possibilities of a conjugated-non-conjugated multiblock copolymer, in which the chromophores are PPV type emitting segments, interspersed among inert methylene groups, to access the effect of the conjugation length on the emission properties of the active block. The same architecture has been addressed before with twofold objectives: separation of the emitting units facilitating solubility and enhancing film formation capability [5,6,7].

The optoelectronic properties of three copolymers with variable conjugation length were studied using absorption and fluorescence spectroscopy and the transport/photovoltaic properties were investigated using sandwich devices based on the different polymers, neat and in heterojunction with C₆₀. The molecule C₆₀ presents high electroaffinity value allowing ultra-fast charge transfer from the polymers to the molecule [8]. We have used it to improve the exciton dissociation in a bi-layer geometry measuring appreciable photocurrent [9,10]. It was reported that all excitons available near the interface polymer/C₆₀ contributes to the photocurrent [10,11]. As the number of excited states available near the interface depends on the polymer properties and the device geometry (layer thickness) [12,13] we have used the same geometry, applying equal thickness for the different polymers and molecule layers. Therefore, it was possible to correlate the photoluminescence spectra of the polymers with the action spectra of the devices.

Experimental

Chemical Procedures

Monomer synthesis

1,2-bis(4-formyl-2,6-dimethoxyphenoxy)octane – dial

The procedure was similar to the one previously described in literature [4] which consisted in the reaction of 3,5-dimethoxy-4-hydroxybenzaldehyde (seringaldehyde) with 1,8-dibromooctane in dimethylformamide (DMF) in the presence of anhydrous potassium carbonate. The product was filtered and, recrystallized in ethanol. The melting point of the collected white solid was 89.6°C.

Polymer Syntheses

The procedure was similar to the one previously described in literature [4,18] and could be briefly described as follows: the monomer 1,2-bis(4-formyl-2,6-dimethoxyphenoxy)octane was prepared through the Williamson reaction (alkylation of alkoxides with alkyl halides). Thus dial, 0.0312g (0.23 mmol) reacted with terephthal dicarboxaldehyde, and p-xylene
bis(triphenylphosphonium bromide) in the presence of potassium t-butoxyde in anhydrous ethanol). The polymer was separated by filtration and purified by successive precipitations from chloroform into ethanol/water mixture.

According to their composition the copolymers were labeled poly 10-90, poly 20-80 and poly 50-50, the first figure represents the terephthaldehyde and the second the dialdehyde containing the spacer, named dial. For example, the polymer 10-90 had 10 terephthaldehyde units and 90 dial units, in a molar basis. The structure with 2.5 PV units (obtained without terephthaldehyde) was used for comparison purposes and was labelled as LaPPS 08 [18].

**Optical band gap measurements**

The optical band gap (Eg) was calculated using the relationship \( E_g = \frac{1242}{\lambda_0} \) [14,15].

\( \lambda_0 \) stands for the highest wavelength where absorption is detected for solutions of concentration \( 10^{-5} \) mol/L.

**Molar masses measurements**

The molar masses were measured by gel permeation chromatography (GPC). As is common with complex structures, the molar masses measured by GPC using monodisperse polystyrene samples for calibration cannot be taken as absolute values, but as simple reference figures. The interaction of the sample with the stationary phase and solvent can vary with the chemical nature and hydrodynamic volume of the sample.

**Thermal Characterization**

The glass transition temperatures (measured by DSC) of the copolymers, and the onset of weight loss (measured by TGA) are presented in Table 2. In DSC the instrumental average deviation of the measured values are, according to the instrument supplier of 0.2% at maximum. However, one can also consider a delay due to the heat capacity of the sample, which mass was around 7 mg, adding in a extra 0.25% error, allowing for a total error of 0.45% in each measurement. Each experiment was run in duplicate with fair good agreement. In relation to the thermogravimetric analysis, the temperature delay is somewhat larger, since the TGA pan is made of ceramic material, as compared to the DSC one which is made of aluminum. The increase in temperature delay is due the difference in heat conductivity between these materials and in the thermogravimetric analysis is estimated in \( 1^\circ C/°C/min \). Taking into account that the measurements were performed at a rate of \( 5^\circ C/min \) and a variation of \( 1^\circ C \) per each scanned \( 0.5^\circ C \), a total average deviation of about \( 3^\circ C \) can be considered a fair range of variation for each measurement.
Devices

Two kinds of devices differing by the active layer, were prepared. The first were neat polymer layer devices, and the other used a layer C_{60} (TechnoCarbo, 99%) inserted between the polymer and the cathode (photovoltaic devices). Both devices were built in a similar way, in a sandwich geometry (active area = 4 mm^2) starting with the hole collector electrode, a transparent layer of PEDOT(PSS) (poly(3,4-ethylene dioxythiophene), (Baytron–Bayer AG) doped with polystyrenesulfonate, deposited by spin coating (thickness 60 nm) onto patterned fluorine doped tin oxide (FTO Flexitec Ltd)/glass substrate. The polymers were deposited by spin coating from a chloroform solution onto the PEDOT(PSS)/FTO electrode, with the final thickness of, 50 nm. In the photovoltaic bi-layer devices the C_{60} layer was deposited by spin coating resulting in a final thickness of 30 nm. The second electrode (Al) was vacuum evaporated through a shadow mask defining the active area, in both kinds of devices. The current–voltage (JxV) measurements were performed in the dark using a Keithley picoammeter with power supply, model 6487 with a home made SICADI software, in dark and under illumination in the case of photodiodes. The spectral response of the photovoltaic devices was measured using a Keithley picoammeter and a known intense monochromatic light from a 150 W Xenon lamp/MS157 Oriel monochromator system.

Results and Discussion

A widely used route to CNCMBC’s involves the Wittig type coupling of dialdehydes with bis(phosphoranylidene)s [16,17]. This route (as with other condensation routes) does not lead to high molecular weight polymers because these become insoluble after a certain degree of polymerization is reached. Two dialdehydes were used, one containing a phenylene ring (terephthaldehyde) and the other containing an aliphatic segment (-(CH₂)₈-). The conjugation length was set by the ratio between those two dialdehydes. The molar ratio between the sum of the dialdehydes and p-xylenebis(triphenyl fosfonium bromide) was the unity. In order to minimize the content of cis linkages, that are defect forming in the conjugated chain, the vinylene groups were isomerized, thus increasing the trans/cis ratio in the copolymers. The copolymers poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene] were prepared through the Wittig polycondensation which chemical steps and resulting copolymers structure are shown in Figure 1.
NMR analysis

Each flexible group incorporated into the copolymer backbone contributes with 12 protons with a NMR shift of 1-2 ppm that is, six inner methylenes (those not attached to the phenolic oxygens) Each non flexible (PPV block) contributes with zero methylene protons and 12 protons attached to sp² carbon atoms with a chemical shift in the range of 6-8ppm. With these numbers the theoretical forecast of the composition was easily done.

The assignment of the NMR peaks made it possible to confirm the obtainment of the desired structure, and the quantitative amount of each segment was determined from the ratio of the aromatic/aliphatic areas. The integration of the absorptions at 7.03 ppm (trans) and 6.51 ppm (cis) gave the cis/trans ratio of the vinylenic bonds. Representative FTIR and NMR spectra of the copolymers are depicted in Figures 2 and 3.
The composition of the copolymers is shown in Table 1, along with the molar masses. The discrepancies found between the theoretical and experimental results was attributed to the higher reactivity of the spacer dialdehyde (dial) towards the phosphine in relation to that of the terephthaldehyde, and also to premature precipitation of the polymers containing longer PPV sequences. The more the reaction is allowed to proceed, the greater the proximity to the theoretical composition. For this reason, the polymer with the shortest PPV block (LaPPS 08, Figure 1), used as a model compound, had the largest molar mass and was more soluble.

Table 1- Composition and molar masses of the copolymers.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$M_n$ (Kg/mol)</th>
<th>$M_w$ (Kg/mol)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPPS 08</td>
<td>29</td>
<td>41</td>
<td>1.400</td>
</tr>
<tr>
<td>Poly 10-90</td>
<td>3.212</td>
<td>10.370</td>
<td>3.200</td>
</tr>
<tr>
<td>Poly 20-80</td>
<td>1.383</td>
<td>9.158</td>
<td>3.000</td>
</tr>
<tr>
<td>Poly 50-50</td>
<td>2.638</td>
<td>10.730</td>
<td>4.100</td>
</tr>
</tbody>
</table>

D= molar mass dispersity

The molar masses values are in accordance with those reported for Wittig polymers. The low values were attributed to the precipitation that occurs when a certain PV chain size is attained.

Table 2 - $T_g$ and onset of weight loss of the copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
<th>Onset of weight loss (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPPS 08</td>
<td>31.8</td>
<td>188</td>
</tr>
<tr>
<td>Poly 10-90</td>
<td>45.5</td>
<td>209</td>
</tr>
<tr>
<td>Poly 20-80</td>
<td>47.6</td>
<td>244</td>
</tr>
<tr>
<td>Poly 50-50</td>
<td>58.6</td>
<td>310</td>
</tr>
</tbody>
</table>

The shift to higher temperatures with increases in the conjugated segment length was expected, due to higher interchain interaction and less molecular flexibility. TGA traces of the copolymers showed that they are thermally stable materials, with an onset of weight loss in the range 200-300°C.

Optical Properties

Figures 4 show the absorption characteristics of the three copolymers in solution (chloroform C=10^{-5} mol/L) and in film form. It was observed that the increase of the conjugation...
length of the phenylenevinylene units brought about increases in the absorption intensity and at the same time redshifted the emission. The UV-vis spectra of the copolymers in solid state (film) were similar to the spectra of the same copolymers in chloroform solution, but with broader bands. The loss of vibronic structure in solid state is generally attributed to freezing of different conformations with solvent evaporation, resulting in a more disordered situation.

Figures 5 present the fluorescence spectra of the copolymers in solution (chloroform C=10^{-5} mol/L) and in film form, acquired with the excitation wavelength corresponding the absorption maximum of each copolymer. As noted previously in absorption spectra, increases in conjugated phenylenevinylene segments brought about increases in the intensity and a redshifting of the spectra.
The effect of the PV segment length on the optical band gap of the polymers is displayed in Figure 6 and Table 3.

![Figure 6- Dependence of the optical gap on the length of the PV segments.](image)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \lambda_0 ) (nm)</th>
<th>( E_g ) (eV)</th>
<th>PVunits</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPPS 08</td>
<td>425</td>
<td>2.920</td>
<td>2.5</td>
</tr>
<tr>
<td>Poly 10-90</td>
<td>459</td>
<td>2.706</td>
<td>3.0</td>
</tr>
<tr>
<td>Poly 20-80</td>
<td>467</td>
<td>2.660</td>
<td>3.5</td>
</tr>
<tr>
<td>Poly 50-50</td>
<td>471</td>
<td>2.630</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**Electrical Properties**

The forward JxV characteristics, in dark, of diodes based on poly 10-90, poly 20-80, poly 50-50 and LaPPS 08, are presented in Figure. 7. One can notice that the current density has an exponential dependence on voltage increasing from poly 10-90, poly 20-80, poly 50-50 to LaPPS 08. Apart from the energy levels of the polymers and electrodes (barrier height), charge injection on polymer diodes depends on the dipoles, interfacial layers, between the polymer/electrodes and/or doping impurities. Two classical situations can be found: the current in the diodes can be either contact limited current or bulk limited current [19]. The bulk limited or space charge limited (SCL) current is established when the one of the electrodes supplies more current than the semiconductor can transport and the exit contact can not inject sufficient opposite charges carriers to compensate for the internal space charge. Often it is the case of conjugated polymer diodes because of their low mobility. In the insert the J(V) dependence is plotted on log-linear scale in order to compare the power law behavior among the different materials. It suggests that the increasing in PPV units, thus the conjugation length, improves the transport properties of the polymers. The conductivity of...
LaPPS 08 was higher than the other copolymers and that was probably due to its higher molecular weight, with less chain ends.

![Diagram](image-url)

Figure 7 – Current vs. voltage characteristics of the diodes based on, poly 10-90, poly 20-80, poly 50-50 and LaPPS 08 using FTO/PEDOT as anode and Aluminum as cathode. The inset presents the contribution of the bulk transport properties in Log-linear scale after 1V, to the electrical behavior of the diodes.

The spectral response of FTO/PEDOT:PSS/ polymer/C₆₀/Al devices of the four polymers is presented in Figure 8. The spectral response is expressed by the external quantum efficiency (IPCE) which is the ratio of the photocurrent to incoming photons flux: IPCE=1240 Jph/ λI₀, where Jph is the photocurrent density (A/cm²), I₀ is the light intensity (W/m²), and λ is the wavelength (nm).

![Diagram](image-url)

Figure 8 – External quantum efficiency (IPCE) of the diodes based on poly 10-90, poly 20-80, poly 50-50 and LaPPS 08 polymers using FTO/PEDOT as anode and Aluminum as cathode, at zero bias.
The spectra of the photodiodes follow the absorption coefficient dependence on wavelength of the polymers and C\(_{60}\), reflecting the contribution of the polymer and the C\(_{60}\) molecule to the photocurrent. The comparison of the action spectra of the four photodiodes shows that the efficiency of poly 50-50/C\(_{60}\) devices is several times higher than those of the other three polymers. LaPPS08 presented a somewhat higher IPCE than poly 10-90 and poly 20-80 mostly due to the fact that its conductivity is better than the other copolymers; it may have compensated the IPCE by the improved transport characteristics.

The electrical characteristics follow the trend observed in the photoluminescence behavior, in which the poly 50-50 presented the highest photoluminescence, i.e., more excited states (excitons) are available to undergo dissociation in the interface polymer/C\(_{60}\), transferring charges to the acceptor molecule, thus delivering free electrons to the Al electrode improving the photocurrent. The current-voltage characteristics of FTO/PEDOT:PSS/ poly 50-50/C\(_{60}\)/Al in dark and under illumination are shown in Figure 9. The open circuit voltage for this device is around 0.5V which is the difference between the energy levels of the polymer and the C\(_{60}\) molecule [20]. The electrical behavior of the other diodes is similar but the photocurrent magnitude is smaller, following the efficiency (IPCE) dependence.

![Figure 9 – Current-Voltage characteristics of FTO/PEDOT:PSS/ poly 50-50/C\(_{60}\)/Al device in dark and under illumination of 8.25 W/m\(^2\) and wavelength of 350nm. The inset presents log-linear plot of the modulus of the current versus voltage.](image)

Conclusions

The comparison of the emission properties of the three copolymers showed that increases in the effective conjugation length brings about increases in emission intensity and spectra red
shifting. Apart from that, aggregation might be operating as well, giving rise to emission from excimers and/or ground state preformed dimers that also contribute to batochromic effects. The lowering of the bandgap with increasing PV segment length leveled off at 4-5 PV units, indicating that this is probably the effective conjugation length. The present work complements theoretical and experimental work done with oligomers and long chain precursor routes to PPV in the sense that the PV units are oligomeric in size but with the mobility of long polymer chains. Photovoltaic devices based on these copolymers presented spectral response following the photoluminescent dependence on conjugation length, the efficiency of devices depends on the effective conjugation length of the copolymers.

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References