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Highly Regioregular Poly-3-alkylthiophenes: Influence of the Structure on Photoluminescence

Alberto Bolognesi*, **Chiara Botta,** and **William Porzio**

Istituto di Chimica delle Macromolecole, I-20133 Milano, Italy

Summary. A class of regioregular poly-3-alkylthiophenes was synthesized *via* a new and simple synthetic procedure. These polymers exhibit a regioregularity as high as 95–100% and show different thermal behaviour depending on the length of the side chain. The high conjugation length reached is responsible for a red-orange emission with photoluminescence (PL) quantum efficiencies of about 45% in solution. The study of the PL of spin coated films at different temperatures allows to correlate the PL spectra with the structure of the polymers as detected by XRD.

Keywords. Poly-3-alkylthiophenes; Polymerization; Photoluminescence; Phase transitions.

Introduction

The study of well-defined conjugated polymeric structures is a very important field for a better understanding of the relations between structure and electrooptical properties of these materials. Among the great amount of structures currently being investigated, poly-3-alkylthiophenes (*PAT*s) have attracted attention because of their potential use in light emitting diodes (LEDs) [1], field effect transistors [2], or photovoltaic cells [3].

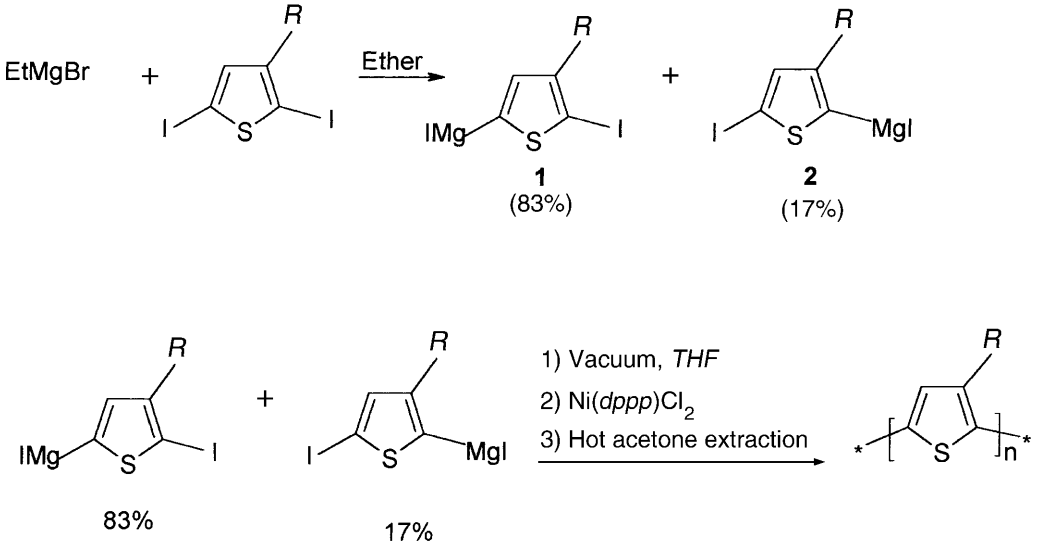
*PAT*s are characterized by a conjugated stiff backbone surrounded by flexible chains. The thermal behaviour of these two parts is quite unlike, affecting, in a different way, the relation between thermal properties and structure. Moreover, the structural evolution of these polymers is strictly related to the electrooptical properties such as photoluminescence (PL) and electroluminescence (EL). In this paper we try to give an interpretation of the observed PL and EL data obtained for two *PAT*s which differ in the lengths of the side chain.

Results and Discussion

Employing Ni-catalyzed polymerization [4], we were able to obtain highly regioregular *PAT*s. The synthetic procedure followed is outlined in Scheme 1 for a series of *PAT*s containing an oxygen atom in the side chain.

GC of the reaction mixture before introduction of the catalyst showed that the amount of compound **2** in the monomer mixture after reaction with EtMgBr is 17%,

* Corresponding author



Scheme 1

whereas the amount of compound **1** is 83%. According to the polymerization mechanism [5], the presence of both **2** and **1** induces regioregularity defects in the polymer backbone: a regioregularity of the polymer of about 80% can be expected on the basis of the ratio between **2** and **1**. On the contrary, the polymer fraction resulting from residue to hot acetone extraction [4] shows regioregularities higher than 80%, whereas the low molecular polymer fraction extracted by hot acetone exhibits a high concentration of defects. These observations suggest that the coupling between the positions 2 and 2′ of the two monomeric units **2** and **1**, leading to an irregular enchainment, is a process which is kinetically unfavourable as compared to the coupling between positions 2 and 5′ of two equivalent monomeric units, responsible for regular connection. In fact, the highest defect concentration is found in the low molecular weight and more soluble fraction which, in our opinion, did not reach a high polymerization degree because of the reduced growing rate in the coupling reaction between **1** and **2**.

The difference in regioregularity of the two fractions is also evidenced by the different UV/Vis absorption spectra of the polymer solutions as shown in Fig. 1. The fraction extracted from hot acetone shows a maximum at 435 nm, whereas the residue to hot acetone extraction has its maximum red-shifted by about 15 nm, indicating a higher conjugation length.

The degree of regioregularity has been found to be in the range of 96%–100% for the three polymers; it was determined by ^{1}H NMR spectroscopy in $CDCl_3$ solution [4].

Depending on the length of the side chains, different thermal behaviours corresponding to different arrangements in the solid state are found for these polymers. We have investigated in more details the behaviour of *P5*OMe and *P6*OMe. For polymer *P6*OMe, the XRD patterns at room temperature and at 120°C (Fig. 2) are different, indicating, in agreement with DSC (Fig. 3), that a phase

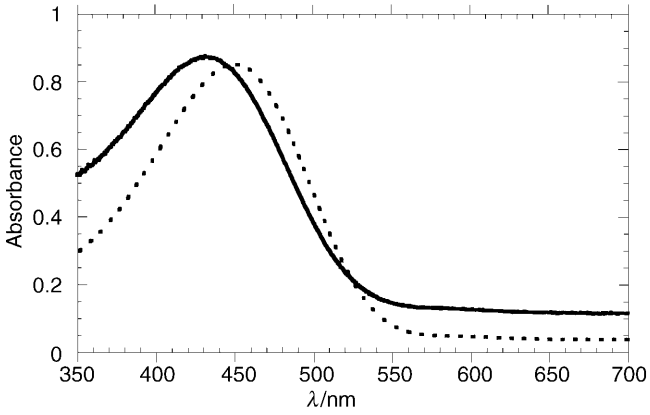


Fig. 1. UV/Vis absorption spectra of *P6*OMe in $CHCl_3$; dotted line: residue to hot acetone extraction, full line: extracted from hot acetone

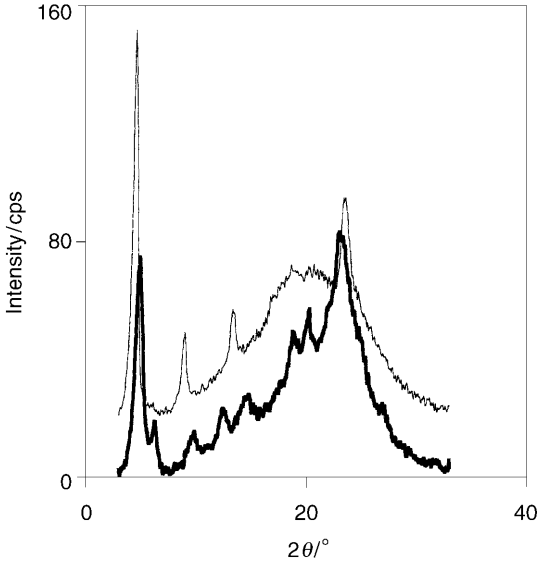


Fig. 2. XRD patterns of *P6*OMe; thick line: room temperature, thin line: 120°C

transition occurs below 120°C. In fact, a *P6*OMe DSC scan shows an endothermal peak at 110°C attributed to a phase transition and an endothermal peak due to melting at 180°C. On the other hand, polymer *P5*OMe, whose XRD pattern is shown in Fig. 4, does not show any DSC peak up to 207°C where melting of the polymer occurs as detected by optical microscopy in polarized light. Moreover, the XRD pattern of this polymer does not change up to the melting point.

By comparing the XRD patterns of *P6*OMe and *P5*OMe it is obvious that the structure of *P6*OMe above the first transition is equivalent to the structure of *P5*OMe at room temperature. The only difference between the XRD pattern of *P5*OMe and of *P6*OMe is in the peak position at low angle, related to the a spacing of 17.85 Å and 18.05 Å for *P5*OMe and *P6*OMe, respectively. These values are

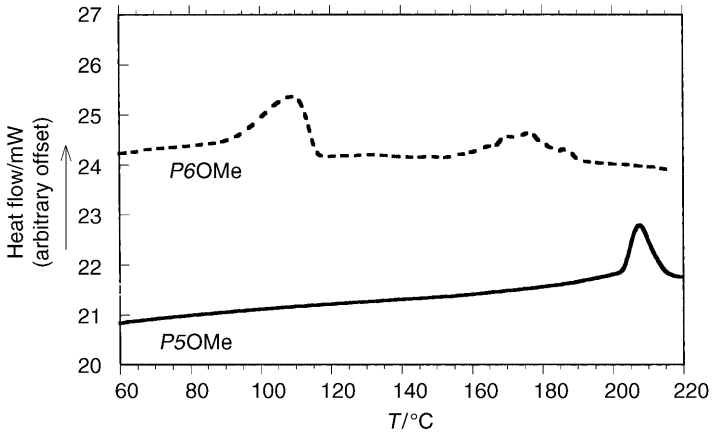


Fig. 3. DSC scan of *P6*OMe (dotted line) and *P5*OMe (full line); 20°C/min, N_2 atmosphere

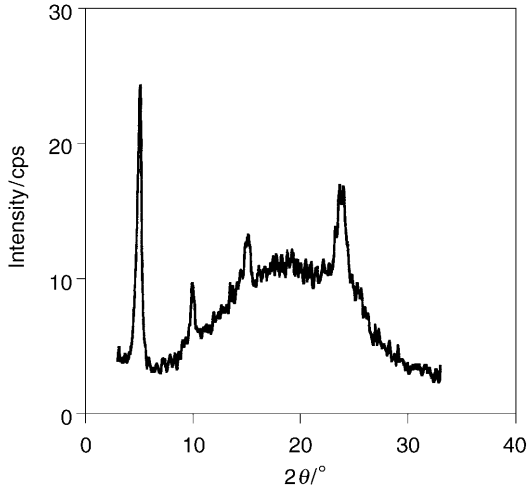


Fig. 4. XRD pattern of *P5*OMe at room temperature

related to different interchain distances due to the difference in the side chain length for the two polymers.

We have investigated the PL change of both *P5*OMe and *P6*OMe spin coated films by increasing the temperature of the samples, thus obtaining a variation in intensity and position of the PL peaks. The spectroscopic evolution is shown in Fig. 5.

For *P5*OMe, two PL peaks at 720 and 640 nm increase in intensity. The peak at 640 nm, whose position is close to that of the PL from solution, has been attributed to the emission from a disordered, amorphous structure, whereas the peak at 720 nm has been assigned to emission from a more ordered phase. For *P6*OMe, a change in shape and position is observed at a temperature corresponding to the first endothermal peak observed in the DCS scan. Above this temperature, the *P6*OMe PL spectroscopic shape closely resembles that of *P5*OMe with two main peaks at 720 and 640 nm.

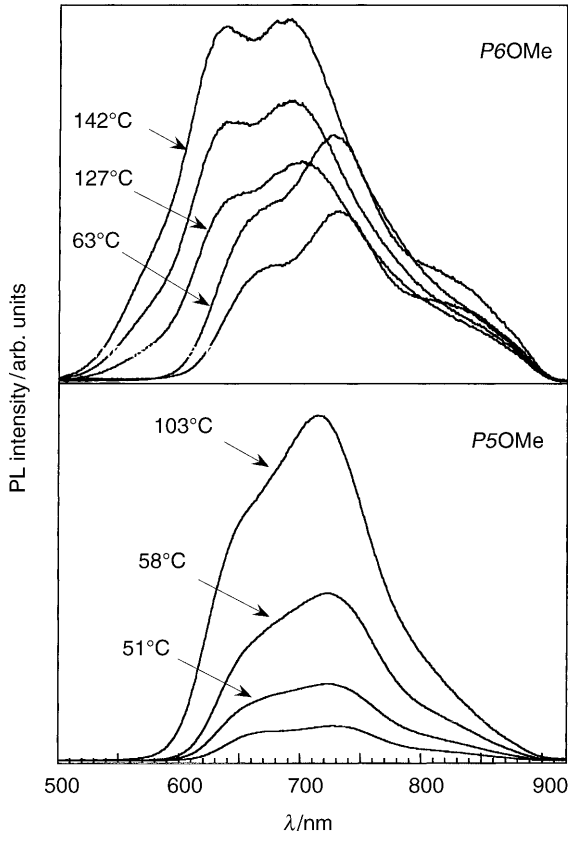


Fig. 5. PL evolution of *P6*OMe and *P5*OMe with temperature

It is worthwhile to point out that, as reported above, above 110°C the XRD pattern of *P6*OMe powders is equivalent to that of *P5*OMe powders, indicating that the two structures are isomorphous: the same spectroscopic feature of PL for both *P5*OMe and *P6*OMe seems to arise from the same structural arrangement in the solid state.

However, a direct correlation between the structure of the polymers as powder and as spin coated film is very difficult. In fact, whereas powders give diffraction peaks, spin coated films result in featureless spectra, even though the PL spectroscopic shape of spin coated films and of powders are almost identical. This fact can be explained by assuming that (*i*) PL is more sensitive to the intrachain structural situation than to the chain packing, and (*ii*) XRD and PL measurements are of different sensitivity with respect to detecting the degree of order.

Assuming that the emission from *P6*OMe arises from a well-ordered phase exhibiting high conjugation length, in the spin coated film this phase may also be present in an amount almost undetectable by XRD. Its photoluminescence emission, however, is well detectable by PL measurements as a result of an energy transfer from an amorphous region with a high concentration of low conjugation length segments to a better ordered phase containing segments of higher conjugation length [6]. We therefore believe that the change of the PL peak for *P6*OMe observed above 110°C reflects both the change in conformation of the chain which looses a

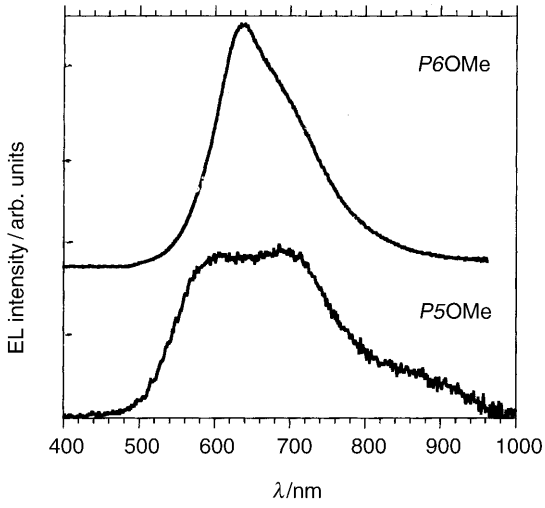


Fig. 6. Comparison between the EL of *P5*OMe and *P6*OMe

certain degree of order and the change of structure in the ordered domains as evidenced by XRD on powders.

The correlation between the PL behaviour of spin coated films and of powders at different temperatures has been put forward for poly-3-octylthiophene whose thermal/structural behaviour has been studied [7]. The knowledge of the PL behaviour at different temperatures can be helpful in understanding the different electroluminescence (EL) behaviour of both polymers. We have found that PL quantum yields in solution for *P5*OMe and *P6*OMe are different (48 and 38%, respectively). On this basis, a higher electroluminescence efficiency should be found for a LED with *P5*OMe as active electroluminescent layer. Unexpectedly, the external quantum yields are lower for *P5*OMe LEDs (*ca.* 10^{-4}–10^{-5}%) than for *P6*OMe ones (*ca.* 10^{-3}%). This can be explained by comparing the two EL spectra at the same driving voltage (Fig. 6). Whereas *P5*OMe LEDs still show the two components as already observed in PL in the EL spectrum, thus highlighting the presence of two phases, EL from *P6*OMe exhibits only the component at higher energy, indicating that emission arises from the less ordered, almost amorphous phase. In this phase the mobility of the side chains is high, increasing their bulkiness and contributing to an increased distance among the conjugated backbone. These factors improve the radiative decay [8].

The difference found for the EL of the two polymers can also be understood by comparing both DSC runs: the thermal stability of *P5*OMe is higher than that of *P6*OMe. *P5*OMe starts to loose its ordered arrangement at 200°C, at least 50°C above the corresponding value for *P6*OMe. During the working time of a LED, prolonged heating at temperatures even below the melting of *P6*OMe results in the melting of the ordered domains responsible for the electroluminescence at lower energy. The thermal stability of two almost identical polymers, differing only in one carbon atom in the side chains, is responsible for two EL efficiency values [4].

The structural features for both polymers as detected by XRD indicate, as mentioned previously [4], that the preferred arrangement is of the smectic type. Upon heating *P6*OMe and *P5*OMe on a hot stage of a cross-polarized microscope, birefringence is lost at 170° and 207°C for *P6*OMe and *P5*OMe, respectively. This strongly supports the possibility to obtain oriented structures of these materials because of their liquid crystalline nature. In fact it has been reported recently that conjugated polymers exhibiting liquid crystalline behaviour may be aligned by a proper annealing on highly oriented polyimide (PI) films. The process has been described by *W. Knoll et al*. in Ref. [9]. Attempts to apply these methods to *P6*OMe and to *P5*OMe failed, resulting in no alignment of the conjugated polymer chains with respect to the PI oriented films as detected by UV/Vis absorption in polarized light.

The direct rubbing of *P5*OMe and *P6*OMe films by a rotating cylinder covered with velvet was successful in obtaining orientation of the polymers as reported by *Yoshino et al*. [10]. This method, which is currently under investigation, has allowed to reach a dichroic ratio of nearly 5 in the UV/Vis absorption spectra, whereas the same samples used as active layers in a LED exhibit a polarization ratio of about 8. Work in this direction will be reported elsewhere [11].

Experimental

The synthetic procedure for the preparation of *P5*OMe and *P6*OMe has been described in Ref. [4] together with the characterization of the polymers.

UV/Vis spectra were recorded with a Cary 2400 spectrophotometer. DSC were run on a Perkin Elmer Pyris 1 instrument under a nitrogen atmosphere. XRD patterns were obtained with a computer controlled Siemens D-500 instrument with *Bragg-Brentano* geometry using CuK_α radiation. PL and EL were measured with a SPEX 270 M polychromator equipped with a liquid N_2 cooled CCD detector. For PL measurements, the 457.8 nm line of an Ar+ laser was used as excitation line.

Light emitting diodes were prepared from spin coated films on ITO covered glass. The second electrode was prepared by evaporating aluminum under 10^{-5} mm Hg. The apparatus for external efficiency measurements has been described elsewhere [12].

Acknowledgements

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References

[1] Dyreklev P, Berggren M, Inganäs O, Andersson MR, Wennerström O, Hjertberg T (1995) Adv Mater **43**: 7
[2] Sirringhaus H, Brown PJ, Friend RH, Nielsen MM, Bechgaard K, Langeveld-Voss BMW, Spiering AJH, Janssen RAJ, Meijerr EW, Herwig P, Leeuw DM (1999) Nature **401**: 685
[3] Roman LS, Mammo W, Pettersson AAL, Andersson MR, Inganäs O (1998) Adv Mater **10**: 774
[4] Bolognesi A, Porzio W, Bajo G, Zannoni G, Fanning L (1999) Acta Polymerica **50**: 151
[5] Yamamoto T, Hayashi Y, Yamamoto A (1978) Bull Chem Soc Jpn **51**: 2091
[6] Lemmer U, Ochse A, Deussen M, Mahrt RF, Gobel EO, Bassler H, Haring Bolivar P, Wegmann G, Kurz H (1996) Synth Met **78**: 289
[7] Bolognesi A, Botta C, Porzio W, Provasoli A (Macromol Chem Phys, submitted)

[8] Cornil J, dos Santos DA, Crispin X, Silbey R, Bredas JL (1998) J Am Chem Soc **120**: 1289
[9] Grell M, Knoll W, Lupo D, Meisel A, Miteva T, Neher D, Nothofer HG, Scherf U, Yasuda A (1999) Adv Mater **11**: 671
[10] Hamaguchi M, Yoshino K (1997) Polymer for Adv Tech **8**: 399
[11] Bolognesi A, Botta C, Martinelli M, Porzio W, Organic Electronics (accepted for publication)
[12] Bolognesi A, Bajo G, Paloheimo J, Östergård T, Stubb H (1996) Adv Mater **9**: 121

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