

## Chiral Polyalkylthiophenes for Organic Light Emitting Diodes

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### ABSTRACT

Chiral polyalkylthiophenes are noncentrosymmetric organic materials which can be used both in second harmonic-generation devices and in polarized light emitting diodes. In this work we present the synthesis and the characterization of a polyalkylthiophene with a chiral center very close to the conjugated backbone: poly(3-[(S)-2-methylbutyl]thiophene) (PMBT). Circular dichroism (CD) measurements have been carried out to ascertain the chirality of these materials. The CD spectra show intense signals both in mixed solvents and in the solid state. The strong Cotton effect can be associated to a highly ordered aggregated phase whose nature is still under investigation. We also present the photo and electroluminescence characterization of single layer light emitting diode (LED) with the following configuration: ITO (Tin Indium Oxide)/PMBT/Al.

### INTRODUCTION

Polyalkylthiophenes have been widely studied for their electrical and electronic properties in view of their potential applications [1]. The study of polythiophenes with chiral substituents has been motivated by the aim to obtain promising materials for sensors due to their possible conformational changes induced by the interaction with chemicals and/or the temperature [2]. Indeed, Meijer *et al* have demonstrated that polyalkylthiophenes with chiral substituents exhibit, in mixed solvents large circular dichroism signals which monitor conformational changes due to small aggregates or microcrystallites with inter-chain interactions [3]. Different examples of thermochromism both in solution and in the solid state have been described in the literature [4]. Circular Dichroism (CD) spectroscopy represents one of the best tools among the chiroptical techniques to estimate the structural characteristics of these materials [5]. It has been demonstrated that the CD signals are very sensitive to the enchainment of thiophene units and that regioregularity is an important factor in the development of chiral structures [6]. Moreover optical activity is due to a chiral supramolecular organization both in solution and in the solid state [7].

This work is focused on the chiroptical and absorption/emission characterization, in solution and in the solid state, of a polyalkylthiophene with a short chiral alkyl group close to the thiophene backbone: poly[3-[(S)-2-methylbutyl]thiophene] also named PMBT. We have studied the modification of the CD, UV-Visible spectra in solution of good solvent (chloroform) and in mixtures of good and bad solvent (chloroform/methanol). The same investigation was performed

in the solid state on PMBT thin films with different degree of order. We present also photoluminescence (PL) and electroluminescence (EL) characterization of a single layer light emitting diode with PMBT as active layer.

## EXPERIMENTAL DETAILS

Regioregular poly[3-(S)-2-methylbutyl]thiophene] (PMBT) was prepared with Ni(dppp)Cl<sub>2</sub> catalyst using the McCullough method [8]. The regioregularity of the polymer as determined by <sup>1</sup>H-NMR spectroscopy was >98%. The average molecular weight (M<sub>w</sub>) determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) against polystyrene standards was 25 kg/mol with dispersity D=1.7. Thermogravimetric analysis (TGA) measurements for PMBT showed a 2.5% weight loss at about 400°C. The differential scanning calorimetry (DSC) curves exhibit an endothermic melting peak between 220 and 245°C upon heating and an exothermic peak between 200 and 160°C upon cooling.

The samples for solvatochromism studies were prepared by dissolving the polymer (C = 4.1x10<sup>-3</sup> M) in chloroform (CHCl<sub>3</sub>) with an increasing amount of methanol (CH<sub>3</sub>OH). Cast films of PMBT were also prepared from mixed solution (CHCl<sub>3</sub>/CH<sub>3</sub>OH). The PMBT films for both optical characterization and LED preparation were obtained by a spin coating technique at 2000 turns/minute using a 20 mg/ml polymer solution in CHCl<sub>3</sub>. The PMBT characterizations were performed on freshly prepared films and on the same sample after a thermal annealing consisting in a heating to 240 °C followed by slow cooling to room temperature.

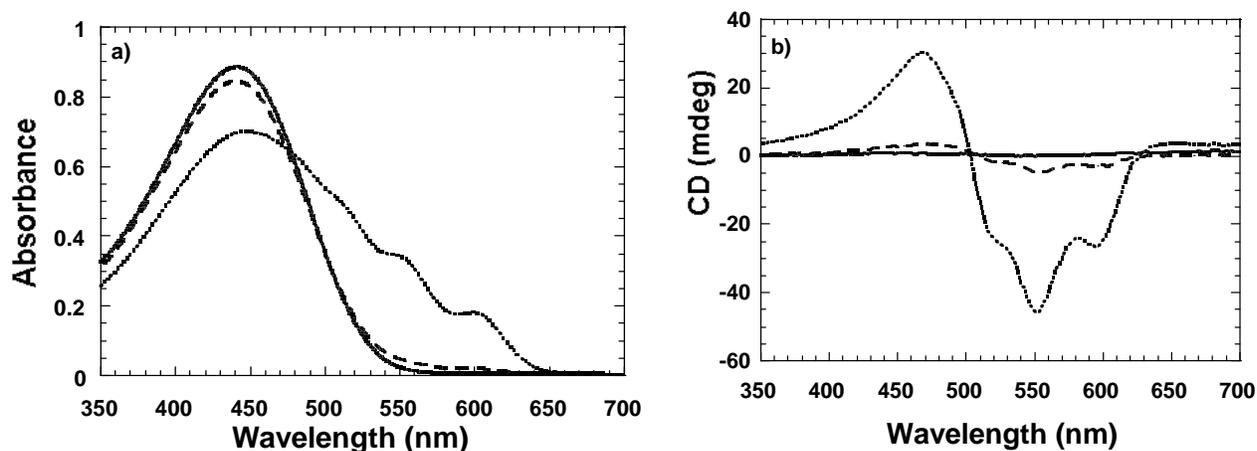
CD spectra were recorded on a Jasco J-500 spectropolarimeter flushed with dry nitrogen. For each measurement, the following conditions were used: 100 nm/min scanning rate, 2 nm band width, 1 s time constant and 8 scans. A cylindrical quartz cell with optical path length of 1 cm was used for solutions. The electronic absorption spectra were recorded with a Perkin-Elmer spectrophotometer Lambda 9. Photoluminescence was measured at room temperature by means of a flat field monochromator and a CCD detector on films kept in nitrogen flux to prevent oxygen quenching. The light source used for photoluminescence measurements was Ar<sup>+</sup>-laser with power incident of 1 mW. The laser beam was focalized with cylindrical lens with 200 mm focal length. The single layer light emitting device was prepared by spin casting onto an ITO covered glass a chloroform solution (10 mg/ml) of PMBT. The cathode was formed by evaporating aluminium in vacuum (4x10<sup>-5</sup> mm Hg).

## DISCUSSION

The optical activity of chiral polythiophenes is strongly dependent upon the supramolecular organization of the conjugated chains both in solution and in the solid state. We have studied the modification of optical and chiroptical properties of poly[3-(S)-2-methylbutyl]thiophene with the increasing of the inter and intrachain organization induced in solution by the addition of a non-solvent and in the solid state by a thermal annealing.

Electronic absorption and CD characterisations of PMBT have been performed at room temperature in chloroform solution and in chloroform/methanol mixed solvent. In the good solvent a single absorption maximum was observed at 438 nm. Upon increasing the percentage of poor solvent ( $\text{CH}_3\text{OH}$ ) a red shift of the absorption maxima and a vibronic structure appears in the spectra (figure 1a). This fine structure is related to the coupling of the C=C stretching mode of the conjugated backbone to the  $\pi-\pi^*$  transition [9,10]. The red shift of the absorption band is associated with an increase of the mean conjugation length. However inter-chain coupling, which varies with the tridimensional chain order, may also affect the absorption features.

The CD spectra in chloroform reveal conformationally disordered polymer chains without optical activity as shown on figure 1b. Upon addition of  $\text{CH}_3\text{OH}$ , a positive Cotton effect appears at 468 nm and a negative one at 520, 550 and 594 nm in correspondence with the extra bands of the absorption spectra. The three negative CD features differ by  $1273\text{ cm}^{-1}$  and  $1459\text{ cm}^{-1}$  which are characteristic of intramolecular vibration according to our Vibrational Circular Dichroism (VCD) results [11].

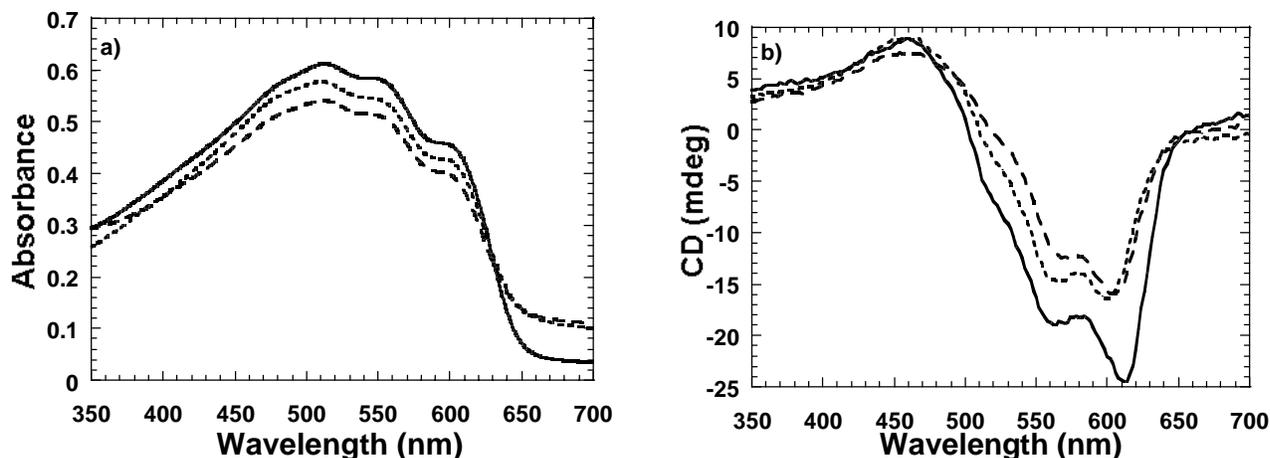


**Figure 1.** a) UV/Vis absorption spectra and b) CD spectra of PMBT in various  $\text{CHCl}_3/\text{CH}_3\text{OH}$  mixtures (—100%  $\text{CHCl}_3$ , - - - 93%  $\text{CHCl}_3$ ; .....86%  $\text{CHCl}_3$ ).

The polymer in mixed solvents shows an aggregation of the chains. We have prepared cast films from these solutions with the aim to increase the degree of chain organization. Figure 2a shows the absorption spectra of these films; all the samples present a vibronic structure with three major bands at 472, 509 and 552 nm. On the basis of numerous publications dealing with the study of poly(3-alkylthiophenes) in the solid state, it is generally agreed that the structure consists mainly of stacks of nearly co-planar extended chains that explain the red shift observed going from the solution to the solid state. The cast films have also quite high CD signals as shown in figure 2b. All films exhibit a small positive Cotton effect located at ca 450 nm and a larger negative one at 500, 550 and 600 nm.

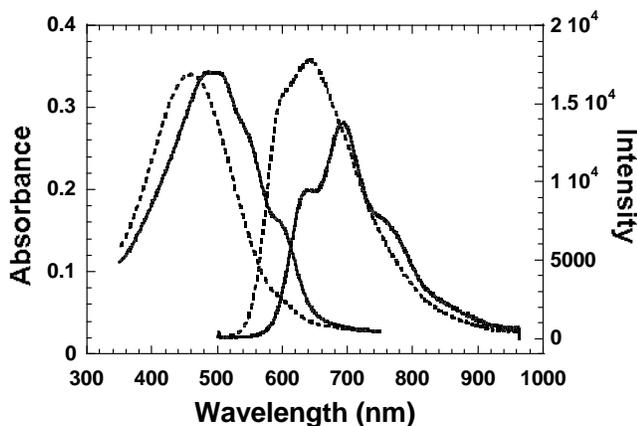
In order to investigate the aggregation process induced in the solid state by the temperature, we have studied the optical properties of spin coated films of PMBT before and

after annealing. This thermal process consists in heating the film to the melting point and cooling slowly to room temperature.



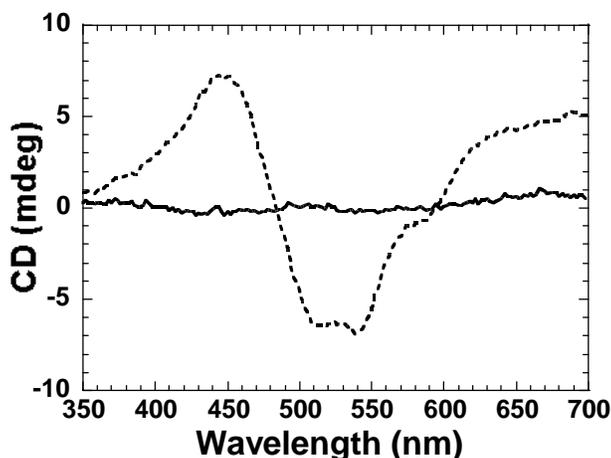
**Figure 2.** a) UV/Vis absorption spectra and b) CD spectra of PMBT films (thickness about 100 nm) obtained by evaporation from solution in mixed solvent (—93%  $\text{CHCl}_3$ ; - - - 86%  $\text{CHCl}_3$ ).

In figure 3 we display the UV-VIS absorption and the photoluminescence spectra of a spin coated film before and after thermal treatment. Before annealing PMBT exhibits an absorption spectrum with  $\lambda_{\text{max}} = 460 \text{ nm}$ , with a weak shoulder at 600 nm which is usually ascribed, for polyalkylthiophene, to the presence of an ordered phase; the emission spectrum is broad and peaked at 642 nm, with a shoulder at 600 nm. After thermal treatment there is a red shift of the absorption spectrum and the shoulder at 600 nm increases in oscillator strength, and a vibronic structure appears in the spectrum; the emission is also red shifted and exhibits a quite evidently vibronically structured shape with three peaks at 635 nm, 694 nm and 761. These changes clearly demonstrate that upon thermal treatment there is the formation of an ordered phase.



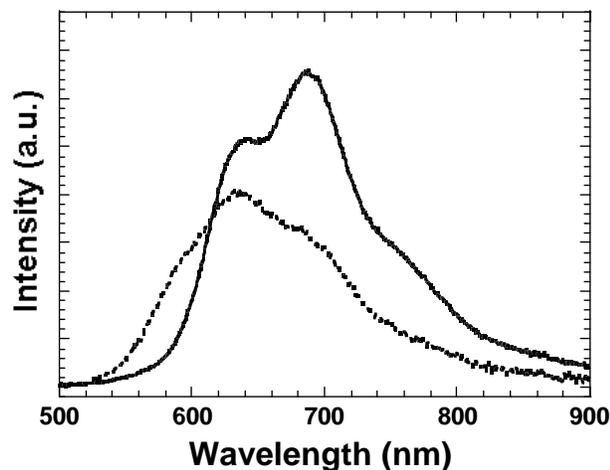
**Figure 3.** Absorption and emission spectra of PMBT films (thickness about 70 nm) before (dashed line) and after annealing (solid line);  $\lambda_{\text{ex}} = 488 \text{ nm}$ .

Spin coated PMBT samples do not show optical activity at room temperature as monitored by the CD spectrum in figure 4. After annealing a clear bisignated Cotton effect appears with a positive signal at 450 nm and three negative ones at 500, 550 and 600 nm. We note that the intensity ratio of the positive to negative Cotton effect and the intensity distribution among the three negative peaks of the couplet change from solutions to the solid state. This feature probably indicates that the PMBT segregated phases in the mixed solvent solution and in the solid state are different.



**Figure 4.** CD spectra of spin coated PMBT film (thickness about 70 nm) before (solid line) and after annealing (dashed line).

In figure 5 the EL spectra of a single layer device (ITO/PMBT/Al) are reported at two different device working times. The dashed line spectrum has been obtained within 40 sec of the device working time while the full line spectrum after 1 minute. As can be clearly observed the latter spectrum is red shifted with respect to the former one and the appearance of vibronic structures indicates a better ordered arrangement for the polymer. The EL spectral evolution of figure 5 is in agreement with the PL change upon thermal annealing, as shown in figure 3. We suggest that during the working time of the device the polymer film is heated by Joule effect, the increase of temperature being responsible for the change in the structural arrangement.



**Figure 5.** EL spectra of ITO/PMBT/Al LED (PMBT film thickness about 70 nm) at two different device working times

## CONCLUSIONS

The CD spectra of PMBT show intense signals both in mixed solvents and in the solid state. In chiral polythiophenes the strong Cotton effect can be associated to a highly ordered aggregated phase, even though the nature of this phase is not yet known. The data demonstrate that the three-dimensional organization responsible of the chiroptical properties is different in solution in cast and spin coated films. We have also shown that the change of the chain aggregation induced in the solid state by temperature is also affecting the electroluminescence properties in a single layer devices. X ray studies are underway to discern the nature of the different three-dimensional organizations of PMBT presented in this work.

## ACKNOWLEDGMENTS

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