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Polarized photoluminescence and electroluminescence in oriented films of regioregular poly(3-alkylthiophenes)

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Abstract

We report polarized photoluminescence (PL) and electroluminescence (EL) from regioregular poly(3-alkylthiophene) thin films oriented by means of the rubbing technique. With a proper thermal annealing of the rubbed films we have increased the anisotropy reaching values up to 8 both in PL and EL. We have evidenced that the orientation in the rubbing direction is higher for the longest conjugation segments than for the less conjugated ones. Moreover polarized PL study demonstrates that emission takes place after migration of the excitation from shorter, less oriented, to longer, more oriented conjugation segments. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The almost one dimensionality of conjugated polymeric systems offers the possibility to prepare well-oriented thin films [1–3] useful for many electronic applications, such as polarized electroluminescence (EL) suitable for backlights in liquid crystal displays [4], as recently reported in literature [5–7]. Several methods have been described for aligning conjugated macromolecules in one direction; they have been recently summarized in a work by Grell and Bradley [5].

Different dichroic ratios, photoluminescence (PL) and EL anisotropies were found depending

on the polymer structure and on the orientation method. For disubstituted polyfluorene [6] a polarization ratio of about 15 was obtained in EL by liquid crystalline (LC) self-organization of the polymer on pre-oriented substrates. In the case of unsubstituted poly(*para*-phenylenevinylene) a value of 12, obtained through the rubbing induced alignment, seems to be the upper limit [7].

Poly(3-alkylthiophenes) (PATs) have also been oriented, but lower anisotropies both in EL and in PL have been found. Inganäs and coworkers [8] reported in 1995 that polarized EL with a polarization ratio of 2.4 can be reached from a light emitting diode (LED) having as active layer a thin film of oriented poly(3-octylthiophenes) obtained by a mechanical stretching procedure.

In previous works we have reported that conveniently functionalized PATs may be obtained as thin multilayered structure by means of the

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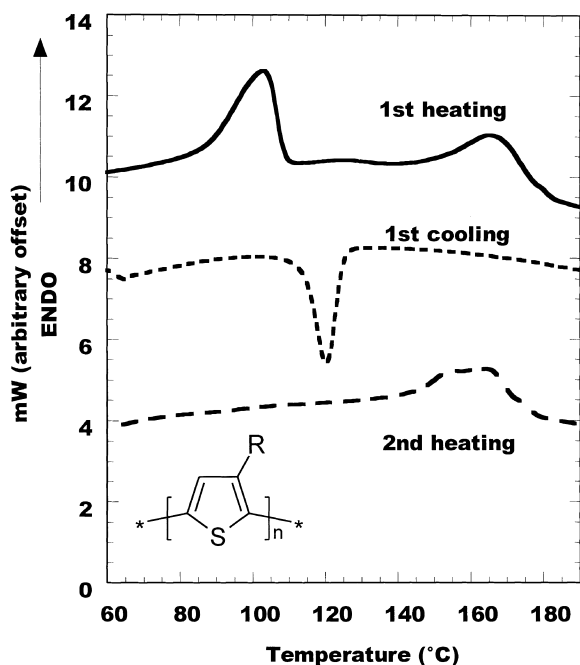


Fig. 1. DSC scan of P6OMe polymer – in the inset the structure of the polymer, $R = -(CH_2)_6OCH_3$.

Langmuir Blodgett (LB) technique [9,10]. It was reported, in agreement with results from other authors [11] on different polymeric materials, that during the transfer process, a good orientation of the chains in the dipping direction occurs. However, the EL anisotropy in a PAT single layer device, with the active layer prepared by the LB technique [12], was lower than 2.

More recently Hamaguchi and Yoshino [13] have studied the effect of rubbing on thin films of PATs with different length of the side chains. The higher orientation was reached with a side chain as long as 12 carbon atoms. With the procedure described an anisotropy of 2.6 was found both for absorption and EL.

With the aim of improving these values in the PAT family, we have recently undertaken a study on a new synthesized regioregular poly[3-(6-methoxyhexyl)thiophene] (P6OMe, see the inset of Fig. 1) showing an LC phase [14].

In this work we present some recent data on the polarized EL and PL obtained in our laboratories on oriented P6OMe. The polymer orientation was

obtained by means of the rubbing method combined with LC self-organization.

The differential scanning calorimetry (DSC) trace of P6OMe powders is reported in Fig. 1. The first scan consists of two broad endotherms whose maxima are at 110°C and 170°C. The higher temperature transition has been attributed, on the basis of XRD analysis and optical microscopy observation in polarized light, to the clearing point of the polymer [14]. The endotherm at 110°C has been suggested to be due to a phase transition from a three-dimensional ordered phase to an LC phase, as deduced from XRD at two different temperatures [14]. On fast cooling from the melt ($-20^\circ\text{C}/\text{min}$) only an exothermic peak appears at 120°C, having the same intensity of the peak at 170°C observed in the heating scan. The following heating from room temperature evidences only the transition at 170°C indicating that the initial three-dimensional phase is not recovered. This occurs even after slow cooling from the melt. No evidence of a T_g was found even by heating the sample from -30°C .

XRD of films either cast or spin coated, obtained by quenching from the melt gave no diffraction peak indicating the presence of a glassy material. As a matter of fact the optical microscopy observation in polarized light onto the same sample indicated an LC pattern. Hence the LC phase can be obtained in a glassy situation, this behaviour being already described by Bradley et al. in [15].

The UV–VIS absorption spectrum of the spin coated film from chloroform solution is reported in Fig. 2. It shows three shoulders at 605, 555, 522 nm, usually attributed to vibronic structures.

The film prepared by spin coating has been easily oriented by rubbing onto a rotating cylinder covered with velvet. This process is responsible for macromolecules orientation mainly at the film surface. In fact thin films exhibit higher dichroic ratios than thick films.

However, as will be shown below, we have found that the degree of orientation of the rubbed film is increased after a proper annealing of the sample. The best results were obtained by heating the oriented samples at 105°C (in the region where the first endotherm takes place) in vacuum, followed by either slow or fast cooling.

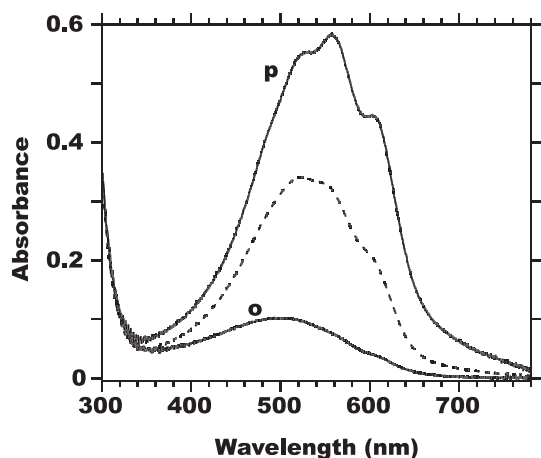


Fig. 2. Optical absorption of a spin coated P6OMe film (---) and polarized optical absorption of the rubbed-annealed film, with light polarized parallel (*p*) and orthogonal (*o*) to the rubbing direction.

The high degree of orientation reached in the samples seems thus to be the results of two different processes:

1. Orientation of the film surface through the rubbing. This is a phenomenon interesting mainly the film surface as described by many authors on different polymeric materials (PPV films were also oriented in this way [7]).
2. The surface orientation is extended through a proper thermal treatment to the remaining volume of the polymer. This annealing process, at a temperature where the LC phase is stable, has the effect of increasing the size of the aligned domain, as happens in a process occurring near the thermodynamic equilibrium. Moreover after this thermal treatment we do not observe a marked dependence of the anisotropy on the film thickness.

XRD on the rubbed and annealed spin coated samples does not yet show any peak, indicating that crystallization of the polymer does not occur in these conditions. The film orientation is detected by the UV–VIS spectrum in polarized light, as reported in Fig. 2 where the spectra *p* and *o* are obtained from rubbed-annealed samples with light polarized parallel and orthogonal to the rubbing

direction, respectively. The UV–VIS spectrum of the film which was only rubbed, not reported here, is similar to the spectra of the rubbed-annealed sample, the main difference being an increase of the dichroic ratio (obtained as the ratio of the area of the spectra measured with light polarized parallel *p* and orthogonal *o* to the rubbing direction) from 3.3 (rubbed film) to 5.2 (rubbed-annealed film). This increased degree of orientation for the annealed samples, suggests that a proper thermal treatment, in the region of the first endotherm transition, induces a reorganization in the oriented films able to increase the domain size of the oriented aggregates.

As clearly seen the spectra *p* and *o* in Fig. 2 have a different shape and different maxima at 558 nm (*p*) and 498 nm (*o*). This behaviour has been already put forwards [13,7] and it was attributed to a different degree of orientation for long and short conjugation segments in polymers having a distribution of conjugation lengths. Long segments are well oriented in the rubbing direction, while the shortest remain mainly unoriented. As a consequence, the anisotropy of the absorption strongly depends on the wavelength (increases at longer wavelengths) and can therefore be expressed in different ways. The ratio between *p* and *o* absorbances at the *p* absorption maximum is about 8, while a value of 6.7 is obtained as the absorbance ratio at the maxima of the two absorption spectra. We note that the spectrum of the oriented sample shows very well resolved vibronic structures and its maximum position is red shifted of about 30 nm with respect to the spectrum of the unoriented sample. This observation seems to indicate that rubbing increases the average conjugation length of the film, suggesting that it can reduce the conformational defects of the backbones. A similar situation was already found in multilayer structures of PATs obtained with LB technique [9].

The polarized PL spectra, obtained with unpolarized incident light, shows an anisotropy $R_{PL} = 8$ (obtained as the ratio of the area of the emissions polarized parallel and orthogonal to the orientation direction) for the rubbed-annealed sample and 4.3 for the only rubbed sample. The PL spectra obtained with polarized incident light are reported in Fig. 3, where the first index indicates the direction of the incident polarization, the second index

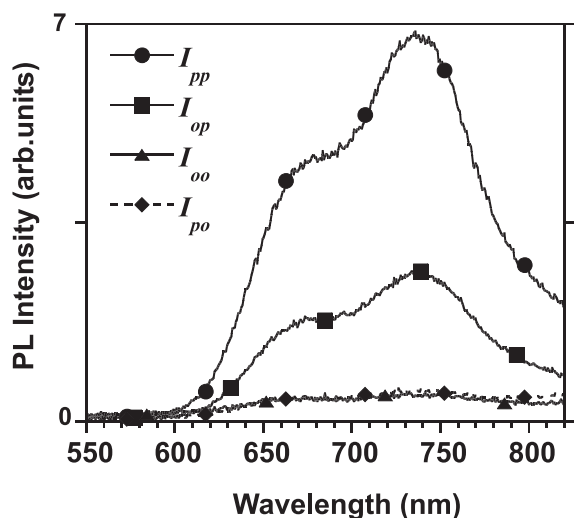


Fig. 3. Polarized PL spectra of the rubbed-annealed film of P6OMe. The first index is the incident polarization, the second index is the emitted polarization, as defined in Fig. 2.

the direction of the polarization of the analysed emission, parallel (p) or orthogonal (o) to the rubbing direction and I is the intensity as deduced from the area of the spectrum. After corrections for the different photon absorptions at the exciting wavelength, it is obtained $I_{pp} \approx I_{op}$. This means that the intensity of the emission polarized along the alignment direction is independent of the polarization of the exciting light, indicating that an energy transfer process [16,17] takes place from shorter to longer conjugation segments, leading to the emission from more oriented chains. The suggested mechanism is in agreement with the observation that the lowest intensities I_{oo} and I_{po} are obtained when the emission is analysed orthogonal to the rubbing direction, being $I_{op} \approx 7I_{oo} \approx 14I_{po}$. In this case the emission polarized orthogonal to the chain direction is less favoured for the crossed exciting polarization (parallel to the chains). This is again indicative of the fact that energy migration does not generally occur from oriented to unoriented chains but vice versa. When the longer, better oriented chains are excited, the excitation is more easily localized within oriented domains giving good polarization memory ($I_{pp} \gg I_{po}$).

The higher anisotropy observed in PL, with respect to absorption, is thus a consequence of

exciton migration from short to long conjugation segments, which takes place before radiative recombination. All these data indicate that the emission originates from well aligned and almost defect free PAT chains, whose absorption is related to the well resolved structures in the spectrum observed with light polarized along the rubbing direction.

The polarized EL spectra are reported in Fig. 4, showing an anisotropy $R_{EL} = 8$ for the annealed samples, equivalent to the PL anisotropy. The spectral position of the EL is blue shifted of about 25 nm with respect to the PL. This different spectral position has already been reported for PATs, and is probably due to heating and/or degradation effects at the polymer/Al interface [18].

The data we have reported indicate that oriented films of PATs can be obtained by rubbing and successively annealing spin coated films reaching high degree of orientation. PL originates from the more oriented chains after energy transfer processes from shorter to longer conjugation segments. The regioregularity of the polymer together with the presence of an LC phase are key factors for the obtained improvement of the chain

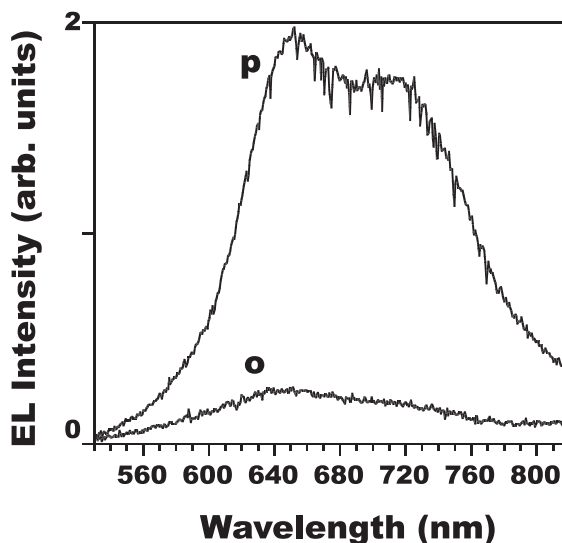


Fig. 4. Polarized EL of a rubbed-annealed film of P6OMe parallel (p) and orthogonal (o) to the rubbing direction. Applied voltage 3.5 V, $I = 4$ mA.

orientation of PATs. Even though the anisotropies both in PL and in EL are lower with respect to other conjugated emitting polymers, to our knowledge the values reached are the highest for a red emitting polymer.

2. Experimental

P6OMe was synthesized according to [14]. M_w as detected from GPC and referred to a calibration curve on polystyrene standards was 24.000 with an M_w/M_n ratio of 1.6. All the data reported in the text are referred to the polymer obtained as residue to hot acetone extraction. The regioregularity of the polymer, as determined by $^1\text{H-NMR}$ investigation, was 98%.

DSC scans were performed at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen atmosphere with a Perkin Elmer Pyris 1 instrument.

XRD patterns were obtained from a Siemens D-500 diffractometer with soller slits and narrow windows (both aperture and receiving) using $\text{CuK}\alpha$ monochromated radiation.

In order to obtain oriented samples the spin coated films were repeatedly rubbed by a velvet cloth on a rotating cylinder. After this treatment the samples were heated at 105°C in vacuum (10^{-3} mmHg) for 1 h. The temperature was then slowly decreased ($-1^\circ\text{C}/\text{min}$) down to room temperature. Typical film thickness was about 50 nm.

Polarized absorption spectra were measured with a Cary 2400 spectrometer using a couple of sheet polarizers on both the sample and the reference beam, whose baseline was previously recorded for both the polarizations. Polarized PL and EL were obtained with a SPEX 270M polychromator equipped with a liquid N_2 cooled CCD detector. The emission was analysed with a sheet polarizer and a polarization scrambler was used to avoid polarization dependences of the gratings and detection system. The sample was kept under inert atmosphere during the PL measurements, performed in the backscattering geometry by exciting with the 457.8 nm line of an Ar^+ ion laser, whose polarization was changed with a polarizing prism. The spectra are corrected for the spectral response

of the instrument, measured using a calibrated lamp.

The devices were obtained by spin coating the chloroform polymer solution (13 mg/ml) onto Indium Tin Oxide (ITO) ($50 \Omega/\text{cm}^2$) coated glass. The film on ITO was then rubbed and annealed as described above. The second electrode was formed by aluminium evaporated (10^{-5} mmHg) on the top of the rubbed-annealed film. The onset voltages of the LEDs are in the range of 3–4.5 V and the external efficiencies are about $10^{-4}\%$.

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