Solid-State Optical and Structural Modifications Induced by Temperature in a Chiral Poly-3-alkylthiophene

Marinella Catellani,* Silvia Luzzati, Fabio Bertini, and Alberto Bolognesi

Istituto per lo Studio delle Macromolecole-CNR, via Bassini 15, 20133 Milano, Italy

France Lebon, Giovanna Longhi, and Sergio Abbate

Dipartimento di Scienze Biomediche e Biotecnologie, Università di Brescia, via Valsabbina 19, 25123 Brescia and INFM—Istituto Nazionale di Fisica della Materia, UdR Brescia, via Valotti 9, 25133 Brescia, Italy

Antonino Famulari and Stefano Valdo Meille

Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta" del Politecnico di Milano, Via Mancinelli 7, 20133 Milano, Italy

Polyalkylthiophenes bearing enantiomerically pure side chains are noncentrosymmetric materials that can be used in polarized photo- and electroluminescence areas and enantio-selective sensing. In this work we present the characterization of a polyalkylthiophene with a chiral center very close to the conjugated backbone: poly-3-(*S*)-2-methylbutylthiophene (PMBT). Differential scanning calorimetry and X-ray diffraction measurements have been performed to characterize the thermal transitions and the structural organization of this polymer. Thin films of PMBT exhibit interesting thermochromism phenomena that affect absorption, emission, and circular dichroism properties. The influences of both the film processing and the thermal treatment on the conjugated polymeric chains have been studied by UV–visible, FTIR, and Raman spectroscopies. Thermochromism has been monitored by in situ electronic absorption, circular dichroism, and photoluminescence experiments. Electroluminescence properties and the electrical characterization of a single-layer light-emitting diode are also presented. The optical and structural changes induced by the temperature are discussed in terms of the peculiar three-dimensional order found for this polymer with respect to other poly-3-alkylthiophenes.

Introduction

The interest in conjugated organic polymers stems from their optical, electrical, and photoelectrical properties that make them applicable in electronic and photonic devices as photo- and electroactive materials.[1] The synthetic effort toward π-conjugated systems having well-defined architectures and specific properties is stimulated by the possibility to modulate both electrical and optical characteristics via control of the molecular structure.[2] Along with the development of polymeric materials and their applications in electronic devices, fundamental research is required to gain a better understanding of the relationship between chemical structure and electronic properties.

Among conjugated macromolecules, thiophene-based polymers make up a wide class of stable and processable materials whose electronic properties can be easily tailored by functionalization of the monomers.[3] In particular, chiral polythiophenes have recently received much attention due to their potential use as nonlinear optical, circularly polarized luminescent and enantio-sensor materials.[4] These polymers contain typically one or two enantiomerically pure side chains attached to the thiophene rings and their chiroptical properties can be evidenced, both in solution and in the solid state, when the conjugated backbones aggregate into chiral supramolecular structures. The optical activity of chiral polythiophenes is strongly influenced by the regioregularity and by the nature of chiral substituents, and the intensity of circular dichroism (CD) signals depends on the conformational changes induced by temperature or by interactions with chemicals. Meijer and co-workers have performed a complete study on these optically active materials by using techniques such as optical rotation, CD, circular polarized luminescence, and small-angle X-ray diffraction.[5–8] However, the nature

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(1) Skotheim, T. A.; Elsembaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*; Marcel Dekker Inc.: New York, 1998.
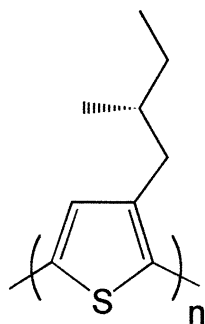(2) Roncali, J. *Chem. Rew.* **1997**, *97*, 173.
(3) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93.
(4) Pu, L. *Acta Polym.* **1997**, *48*, 116.
(5) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Christiaans, M. P. T.; Meskers, S. C. J.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 4908.
(6) Langeveld-Voss, B. M. W.; Waterval, R. J. M.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1999**, *32*, 227.

Scheme 1

of the chiral aggregated states and their detailed backbone conformation are not fully clarified. The processing conditions that favor optical activity in the solid state organization of these polymers are still poorly defined and require further studies.

In this paper we study the optical and the structural modification induced by temperature in a chiral polythiophene with a short alkyl substituent having an asymmetric carbon close to the conjugated backbone: poly-3-(S)-2-methylbutylthiophene (PMBT) (see Scheme 1). Regioregular PMBT was previously prepared by Langeveld-Voss et al.[9] in the context of a broad screening study of a number of optically active polyalkylthiophenes. In the present investigation we have synthesized PMBT using a modification of the McCullough method,[10] obtaining a regioregular polymer with an average molecular weight higher than the one found in previously prepared polymers. Similar to other chiral polythiophenes, PMBT shows, in solution of good and poor solvents, an intense circular dichroism signal that can be associated with the formation of a highly ordered aggregated phase.[11,12] Thin films of the polymer exhibit an interesting thermochromism that affects absorption, emission, and CD properties.

With the aim of correlating the optical changes induced by temperature-varying supramolecular organization, we have studied both thermal and structural properties of PMBT by differential scanning calorimetry and X-ray diffraction. We have subsequently investigated the thermochromism of thin films prepared by casting from solution or by spin-coating deposition. The influence of the processing conditions and the chain modification induced by temperature has been evaluated by UV−visible FTIR and Raman spectroscopies. Changes in the optical properties of spin-coated films during the heating process from room temperature to polymer melting have been monitored by in situ electronic absorption, CD, and photoluminescence experiments. Moreover, we have prepared a single-layer light-

emitting diode (LED) having PMBT as an active layer. This device shows a modification of the electroluminescence spectrum during the working time: we have explained this variation in terms of structural changes due to devices heating.

Experimental Section

Synthesis. 3-(S)-2-Methylbutylthiophene monomer was synthesized from (S)-(+)-1-bromo-2-methylbutane (Aldrich) and 3-bromothiophene following the literature.[13] Regioregular poly-3-(S)-2-methylbutylthiophene (PMBT) was prepared with Ni(dppp)Cl$_2$ catalyst using the McCullough method.[10] ^{1}H NMR (CDCl$_3$, 270 MHz, ppm): 6.88 (s, H ar), 2.72 (m, 1H), 2.55 (m, 1H), 1.71 (m, 1H), 1.43 (m, 1H), 1.18 (m, 1H), 0.87 (m, 6H). The regioregularity of the polymer as determined by ^{1}H NMR spectroscopy was >98%. The average molecular weight determined by size exclusion chromatography was Mw = 25 kg/mol with dispersity D = 1.7. The thermogravimetric analysis of PMBT performed under a nitrogen atmosphere showed a 1% weight loss at 350 °C.

Thin film samples were obtained starting from 10 mg/cm^3 chloroform solutions by casting or by spin coating. Films about 80-nm thick for the in situ UV−visible, photoluminescence, and CD experiments and for the single-layer light-emitting diode were prepared by spin coating (1 drop at 3000 runs/min) on a glass substrate or ITO glass substrates.

Measurements. ^{1}H NMR spectra were recorded in deuterated chloroform solution with a Bruker 270-MHz instrument. The molecular weight (Mw) of the polymers was obtained with a Waters modular SEC system equipped with a 490E UV−visible detector, using a Waters Ultrastyragel column. The experimental conditions were as follows: tetrahydrofuran as the mobile phase at 35 °C, 1 mL/min flow rate, and a sample concentration of 0.5 mg/mL. The calibration curve, polynomial third-order fit, was constructed using polystyrene standards with the molecular weight ranging from 162 to 3.28 × 10^6 g/mol.

The thermogravimetric analysis was carried out with a Perkin-Elmer TGA 7 thermobalance.

Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Pyris 1 instrument equipped with a liquid nitrogen subambient device. The sample, typically 5−7 mg, was placed in a sealed aluminum pan and the measurements were carried out using heating and cooling rates of 20 °C/min.

PMBT samples were crystallized from the melt by slow cooling (5 °C/min) or quenched from the melt into a liquid nitrogen bath. Minute fragments of <1 mg of polymer sample were mounted on a glass fiber and X-ray diffraction patterns were recorded using graphite monochromated Cu Kα radiation (λ = 1.54179 Å), on a Siemens P4 diffractometer equipped with a HiStar 2D detector.

FTIR absorption spectra were recorded with a Bruker IFS66 FT-IR spectrometer on films prepared by casting or spin coating on KBr pellets.

Raman spectra were obtained with a Bruker FRA106 Raman attachment, exciting at 1064 nm with a Nd:YAG laser.

The absorption, emission, and CD characterizations of PMBT were performed on spin-coated films on a glass substrate during thermal heating from room temperature to the melting point. The in situ experiments have been carried out on films, under a nitrogen atmosphere, in a Mettler FP5 oven that allows heating rate control from room temperature to 260 °C.

Electronic absorption spectra were performed with a Perkin-Elmer Lambda 9 spectrophotometer.

Photoluminescence (PL) spectra were recorded using the 488-nm Argon laser light excitation by means of a Spex 270M flat field monochromator coupled to a N$_2$-cooled CCD detector.

(7) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W. *J. Mol. Struct.* **2000**, *521*, 285.

(8) Brustolin, F.; Goldoni, F.; Meijer, E. W.; Sommerdijk, A. J. M. *Macromolecules* **2002**, *35*, 1054.

(9) Langeveld-Voss, B. M. W.; Christiaans, M. P. T.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1998**, *31*, 6702.

(10) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250.

(11) Lebon, F.; Longhi, G.; Abbate, S.; Catellani, M.; Wang, F.; Polavarapu, P. L. *Enanantiomers* **2002**, *7*, 207.

(12) Lebon, F.; Longhi, G.; Abbate, S.; Catellani, M.; Luzzati, S.; Bolognesi, A. *MRS Symposium: Organic Optoelectronic Materials, Processing and Devices*; Bao, Z., Bulovic, V., Ermer, S. P., Jen, A. K-Y., Malliaras, G. G., McGehee, M. D., Eds.; Material Research Society: Pittsburgh, 2002; Vol. 708, p. BB10.28.

(13) Tamao, K.; Komada, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347.
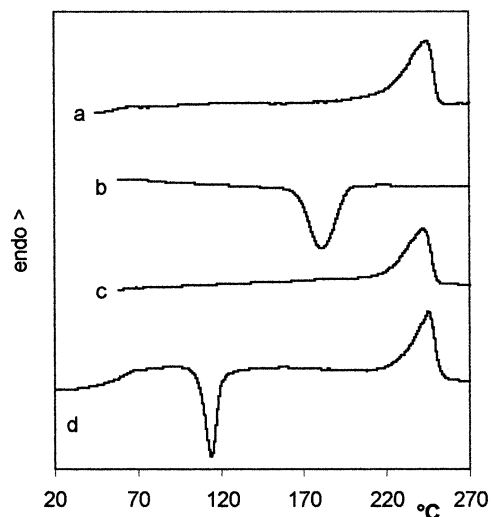
Figure 1. DSC thermograms of PMBT with a heating and cooling rate of 20 °C/min: (a) heating of the pristine polymer; (b) cooling; (c) heating; (d) molten and liquid nitrogen quenched sample.

The same spectrometer was used to measure the electroluminescence spectra.

CD spectra were recorded on a Jasco J-500 spectropolarimeter flushed with dry nitrogen. For each measurement, the following conditions were used: 200 nm/min scanning rate, 2-nm bandwidth, 1-s time constant, and 3 scans.

A single-layer LED was prepared by spin coating PMBT from chloroform solution (10 mg/mL) onto ITO-covered glass at 3000 rpm. The cathode was formed by evaporation of aluminum in a vacuum (4×10^{-5} mmHg).

Result and Discussion

Differential Scanning Calorimetry. The thermal behavior of native poly-3-(*S*)-2-methylbutylthiophene (PMBT) was analyzed in the bulk using differential scanning calorimetry (DSC). The PMBT thermal analysis is reported in Figure 1, where successive scans are displayed. First heating runs on the native sample (Figure 1a) show an endothermic transition at 244 °C with a heat flow of 25 J/g due to the crystal melting. The relatively small heat of fusion is consistent with data reported in the literature[14] and is typical of regioregular polyalkylthiophenes. In the cooling scan (Figure 1b), an exothermic peak centered at 181 °C ($\Delta H = 22$ J/g), is present. Finally, the second heating curve (Figure 1c) is similar to the first one, showing an endothermic peak at around 242 °C ($\Delta H = 21$ J/g). The heating run of the PMBT sample melted and quenched in liquid nitrogen is shown in Figure 1d where three transitions could be observed. The glass transition event at ≈59 °C is consistent with a highly amorphous sample. It is followed by the occurrence of a cold crystallization exotherm, centered at 114 °C, due to the crystallization of the amorphous phase during heating from the glassy state. Finally, the melting of the crystalline PMBT occurs at 245 °C with a heat flow of 20 J/g.

X-ray Diffraction. X-ray diffraction patterns of PMBT samples are reported in Figure 2. Profile I is the diffraction pattern from a highly crystalline sample, obtained by slow cooling from the melt PMBT in a DSC
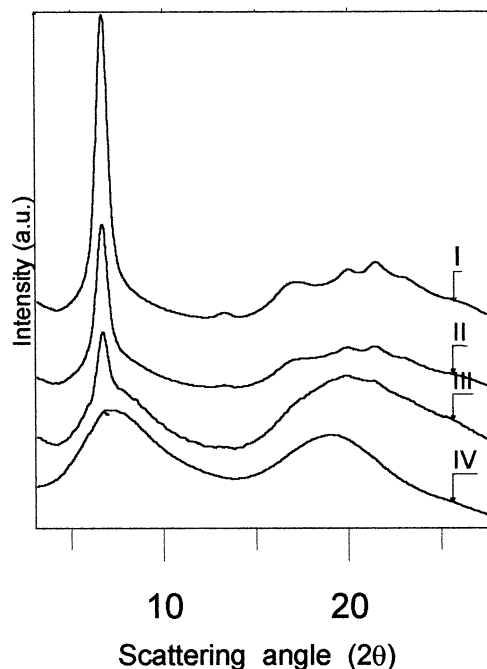
Figure 2. X-ray diffraction patterns of (I) highly crystalline PMBT, melt-crystallized and annealed (IV) fully amorphous PMBT, melted and quenched in liquid nitrogen. Profiles (II) and (III) show co-presence of the two phases in different proportions.
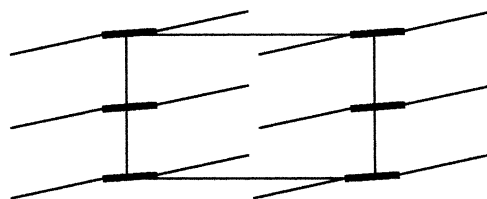
Figure 3. Schematic view of a plausible packing of PMBT and PBT in their respective unit cells.

and annealing it at 80 °C. The position of the lower angle maximum at 6.7° (2θ), corresponding to a *d* value of 13.3 Å, and of its higher order reflections at 13.3° (2θ), $d = 6.66$ Å, and 19.9° (2θ), $d = 4.44$ Å, are remarkably similar to those found in melt-crystallized regioregular poly(3-*n*-butylthiophene) (PBT) of similar molecular weight (6.8° (2θ), $d = 13.0$ Å; 13.6° (2θ), $d = 6.50$ Å; 20.3° (2θ), $d = 4.37$ Å).[15] This close analogy between crystalline PMBT and PBT suggests that also PMBT must adopt the layered structure typical of form I poly-3-alkylthiophenes,[16] with a marginally expanded layer periodicity.

Also, the few additional peaks (see Table 1) in the diffraction pattern correspond quite well to those found in PBT. For PMBT a first approximation orthorhombic lattice with $a = 13.3$, $b = 7.70$, and *c* (chain axis) = 7.76 Å, with $Z = 4$, that is, two chains in the unit cell and a calculated density of 1.27 mg m^{-3}, can be tentatively proposed (see Figure 3), showing a very modest expansion with respect to the PBT lattice ($a = 13.0$, $b = 7.63$, and *c* (chain axis) = 7.76 Å). Although these may well be subcells of the true lattices, the clear message is that

(14) Yang, C.; Orfino, F. P.; Holdcroft, S. *Macromolecules* **1996**, *29*, 6510.

(15) Meille, S. V.; Romita, V.; Catellani, M.; Luzzati, S.; Belobrzeckaja, L., in preparation.

(16) Meille, S. V.; Romita, V.: Caronna, T.; Lovinger, A. J.; Catellani, M.; Belobrzeckaja L. *Macromolecules* **1997**, *30*, 7898.

**Table 1. Observed and Calculated *d* Spacings and with Tentative Indexing for PMBT and PBT**

PMBT			PBT[a]	
d_{obs} (Å)	d_{calc} (Å)	*hkl*	d_{calc} (Å)	d_{obs} (Å)
13.3	13.3	100	13.0	13.0
6.65	6.65	200	6.50	6.50
5.04	5.06, 5.05, 5.03	111, 201, 210	5.02, 4.98, 4.95	5.0
4.44	4.43	300	4.33	4.37
4.17	4.22	211	4.17	4.16
3.85	3.85, 3.85, 3.84	020, 301, 310	3.83, 3.78, 3.77	3.82

[a] PBT is a regioregular poly-3-butylthiophene sample with a molecular mass of approximately 10 000.[16] Adopted lattice parameters were respectively $a = 13.3$, $b = 7.70$, and c (chain axis) $= 7.76$ Å for PMBT and $a = 13.0$, $b = 7.64$, and c (chain axis) $= 7.76$ Å for PBT.

the additional methyl does not perturb the basic features of the crystalline form I poly-3-butylthiophene packing. Specifically, also the intralayer interchain packing distance, corresponding to half the *b* lattice periodicity, in PMBT remains very close to the 3.83-Å value found in PBT and in other poly-3-alkylthiophenes.[15,16]

The resulting high-density crystalline organization achieved in PMBT is likely to correspond to a particularly efficient packing. This result appears to be consistent with the fact that, at least so far, we were able to crystallize PMBT in only one crystalline modification. Furthermore (see also the DSC results), we have found no evidence that PMBT may present a 2D mesophase similar to those given by other poly-3-alkylthiophenes.[16] Indeed, PMBT appears to crystallize fairly rapidly at temperatures above 70 °C both from the melt and from the glass.

Additional insights into the solid state organization of PMBT result from examination of patterns (Profile IV in Figure 2) from fully glassy samples obtained by quenching samples from the melt in liquid nitrogen. They show two well-defined maxima at 6.8° and ≈19° (2θ) corresponding to equivalent Bragg spacings of 13.0 and 4.7 Å. The first value would correspond to average interchain distances of 14.4 Å,[17] assuming a cylindrical chain shape which is doubtful in our case: in fact, a pronounced molecular anisotropy is likely for PMBT also in a projection orthogonal to the chain axis. The position of the lower angle peak is extremely close to the value found in glassy PBT, that is, 6.9° (2θ), corresponding to an equivalent Bragg spacing value of 12.8 Å. This finding indicates that a frequently occurring interchain distance somewhat larger than 13 Å, implying some degree of layered organization, must be preserved also in the amorphous phase of both polymers. On the other hand, the second amorphous peak of PBT is centered at 23.4° (2θ), that is, 3.81 Å. The difference from the value pertaining to PMBT suggests diversities in the chain organization of the two polymers in the amorphous phase. In the case of PMBT, the position of the second amorphous peak, is more similar to values found for other high polymers (e.g., polystyrene), where it is thought to arise mainly from quasi-random C···C nonbonded interactions: in this sense amorphous PMBT seems to be closer to a truly amorphous arrangement than amorphous PBT, where the 3.8-Å value may point
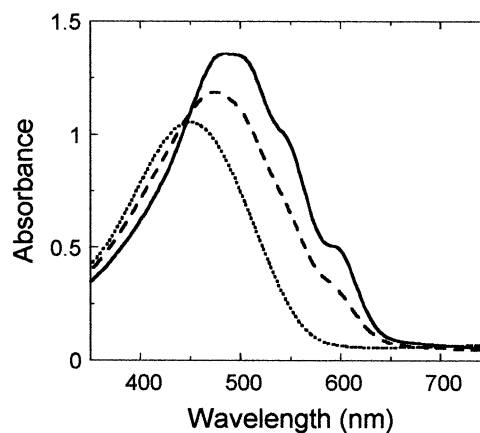
Figure 4. Electronic absorption spectra of a PMBT thin film prepared by spin coating (dotted line), a spin-coated film heated to 80 °C and cooled to room temperature (dashed line), and a film prepared by casting (solid line).

to interchain stacking interactions persisting to some degree also in the amorphous phase.

It seems important to remark that, in the case of PMBT, only two phases were observed by us, namely, the amorphous and a crystalline phase. These two phases can coexist in various proportions at room temperature, depending upon the efficiency of the quenching or crystallization procedures (see profiles II and III in Figure 2). Annealing procedures at 50 °C have minimal effects on the sample crystallinity and amorphous samples remain so, whereas at 70 °C or above (i.e., above the glass transition, see DSC results) relatively rapid and complete crystallization occurs.

Electronic Absorption. PMBT shows a strong thermochromism that can be evidenced both in solution and in the solid state.[11,12] We have studied the optical modification induced by temperature on PMBT thin films prepared with different deposition techniques. The film-growth process from solution influences both the chain supramolecular order and the backbone conjugation length of the sample.[18] Spin coating consists of a fast evaporation of the solvent that produces not well-ordered superstructures, while casting implies a slower evaporation that permits a better organization of the growing film.

The electronic absorption spectra of PMBT films are affected both by the deposition technique and by the thermal history of the sample. It can be seen in Figure 4 that the UV–visible spectrum of the spin-coated film has an absorption maximum (λ_{max}) at 450 nm. Upon heating of the sample to 80 °C followed by cooling to room temperature, the band is red-shifted and a structure appears in the spectrum. By drop casting PMBT from chloroform solutions, the spectrum is structured and has a λ_{max} at 490 nm. Similar features are obtained starting with a spin-coated film, heating it to the melting temperature and cooling slowly to room temperature.

The appearance of a structured spectrum in drop-cast films and in spin-coated films upon thermal treatment is indicative of an increased three-dimensional order with respect to the spin-coating deposition. The red shift

(17) Alexander, L. E. *X-ray Diffraction Methods in Polymer Science*; John Wiley: New York, 1969; pp 379–381.

(18) Catellani, M.; Luzzati, S.; Meille, S. V.; Romita, V.; Caronna, T. *Makromol. Chem., Rapid Commun.* **1997**, *18*, 939.
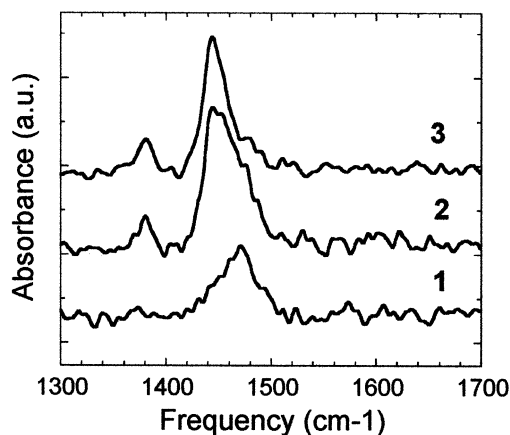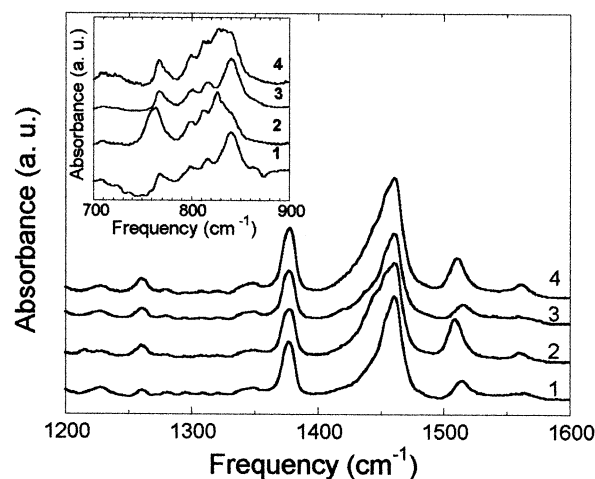
Figure 5. Raman spectra of PMBT thin films on KBr pellets: (1) spin-coated film; (2) spin-coated film heated to 80 °C and cooled at room temperature; (3) heated to 260 °C and slowly cooled.

Figure 6. FTIR spectra of PMBT thin films on KBr pellets: (1) spin-coated films, (2) cast film; (3) cast film heated to 260 °C and quenched in liquid nitrogen; (4) cast film heated to 260 °C and slowly cooled to room temperature.

of the absorption maxima may suggest longer conjugation lengths but it has to be noticed that the absorption spectra energy position can be affected by other factors like changes of the interchain coupling as a result of increased three-dimensional order. Interchain coupling has minor effects on the Raman scattering and IR absorption spectra, which are mainly probing the intrachain π-electron delocalization properties of PMBT chains.

Raman Scattering. The Raman spectra of the PMBT films obtained by different deposition processes and thermal treatments are displayed in Figure 5. The figure shows the frequency region of the most intense Raman mode, mainly due to C=C stretching vibrations which are strongly coupled to the $\pi-\pi^*$ transition. It can be seen that the C=C stretching band position depends on the film deposition technique: it has one component at 1470 cm^{-1} for the spin-coated film. When the temperature is increased up to 80 °C, two components appear in the spectrum: a main component at 1443 cm^{-1} and a still detectable shoulder at 1470 cm^{-1}. After melting and cooling to room temperature, the 1470-cm^{-1} shoulder becomes hardly detectable.

In conjugated polymers the frequency of the C=C stretching band varies with the extent of π-electron delocalization. It is known from the literature that in poly-3-alkylthiophenes the C=C stretching Raman frequency is probing the changes of conjugation due to variation of backbone planarity at a short-range scale (less than three monomers).[19,20] The usual value obtained in a film, with a 1064-nm excitation, is near 1445 cm^{-1}, independent of the degree of conjugation. In solution this mode shifts to 1477 cm^{-1} because of a more twisted backbone conformation.

Thus, the Raman spectra displayed in Figure 5 indicate that the PMBT chains in the spin-coated film have a more twisted backbone conformation with respect to other poly-3-alkylthiophenes in the solid state; upon thermal treatment there is an increase of the backbone planarity, leading to longer conjugations.

Infrared Absorption. The polyalkylthiophene infrared spectrum provides additional information on the degree of conjugation and backbone planarity by looking at two different spectroscopic signatures. The first is a ring stretching mode at 1510 cm^{-1} whose oscillator strength and frequency depends on the degree of conjugation and backbone planarity. For shorter conjugation lengths this mode decreases in intensity and shifts toward higher frequencies (from 1510 to 1515 cm^{-1}). The second spectroscopic probe of the backbone planarity is the out-of-plane deformation mode of aromatic C—H's in the β-position.[21] For slightly twisted backbone conformations this IR band has a frequency around 820 cm^{-1} while for more twisted conformations this mode shifts toward 835 cm^{-1}. In polyalkylthiophenes usually these different conformations coexist in the solid state while in solution or near the melting temperature the twisted conformation prevails.

Figure 6 shows the ring stretching mode region and, in the inset, the C—H out-of-plane frequency region for different thermal treatments and depositions. The ring stretching mode frequency is respectively at 1514 and 1515 cm^{-1} in the spin-coated film (spectrum 1) and in the molten film quenched into liquid nitrogen (spectrum 3). Its intensity is weak relative to that of the 1375-cm^{-1} umbrella deformation of the CH$_3$ alkyl chain, which can be taken as an internal standard since its frequency and intensity is generally not so sensitive to inter- or intramolecular coupling.[21] In cast films (spectrum 2) and in cast films first crystallized from the melt by slow cooling, (spectrum 4) the ring stretching mode increases in oscillator strengths while its frequency is shifted toward 1507 and 1510 cm^{-1}, respectively. This is an indication of longer conjugations lengths in drop cast films with respect to spin-coated films. The C—H out-of-plane deformation mode exhibits one component at 835 cm^{-1} both for the spin-coated film (spectrum 1) and for the molten film quenched in liquid nitrogen (spectrum 3), suggesting that the twisted conformation prevails. In the cast film (spectrum 2) and in the cast films recrystallized from the melt by slow cooling

(19) Botta, C.; Luzzati, S.; Bolognesi, A.; Catellani, M.; Destri, S.; Tubino, R. *MRS Symposium Advanced Organic Solid State Materials*; Chiang, L. Y., Chaikin, P. M., Cowan, D. O., Eds.; Material Research Society: Pittsburgh, 1990; Vol. 173, p 397.
(20) Botta, C.; Luzzati, S.; Catellani, M.; Destri, S.; Tubino, R.; Borghesi, A. *Phys. Rev.* **1992**, *B46*, 13008.

(21) Zerbi, G.; Chierichetti, B.; Ingänas, O. *J. Chem. Phys.* **1991**, *94*, 4646.
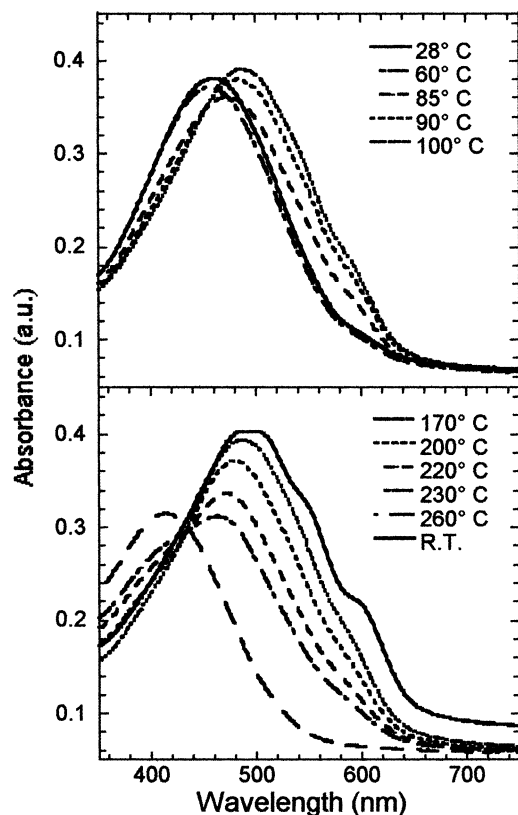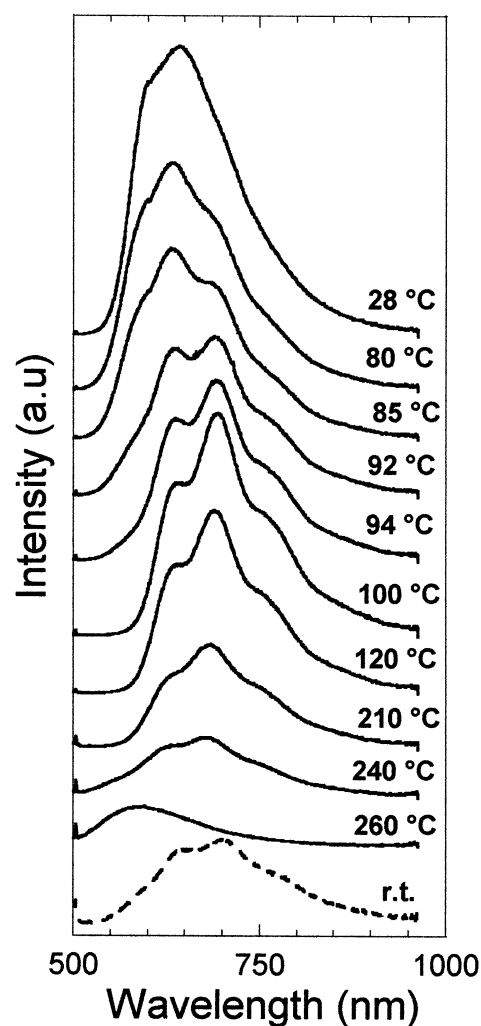
Figure 7. Electronic absorption spectra of spin-coated PMBT film during in situ heating from 28 to 260 °C and cooling to room temperature.

(spectrum 4) another component at 820 cm^{-1} appears in the spectra which can be ascribed to the presence of more planar backbone conformations.

In Situ Absorption and Emission Thermochromism. We have studied the thermochromism of PBMT spin-coated films with in situ absorption and emission experiments to correlate the optical changes during thermal treatment with structural modifications. In Figure 7 are shown the electronic absorption spectra of a PMBT film recorded during heating from room temperature to the melting of the chains. Increasing temperature up to 100 °C produces a red shift of the absorption band with the formation of a structured spectrum due to an increase of conjugation lengths and/ or of three-dimensional chains order. Raman and IR spectra prove that native spin-coated films have a more distorted backbone conformation and lower conjugation length with respect to annealed samples. These thermochromic effects are quite probably correlated with the cold crystallization detected in a DSC thermogram (Figure 1) of liquid nitrogen quenched samples. While the thermochromism from room temperature to 100 °C is due to both a disorder−order transition in the chain arrangement and an increase of the conjugation, heating the polymer above the melting temperature produces a blue shift of the absorption band typical of a shortening of the conjugation length.[14] After the sample is slow cooled to room temperature, the absorption spectra shows a structured band.

The photoluminescence (PL) spectra of a spin-coated PMBT film obtained in situ during a thermal cycle from room temperature to melting are reported in Figure 8. At 28 °C the film exhibits a main band at 642 nm and


Figure 8. Photoluminescence spectra of spin-coated PMBT film during in situ heating from 28 to 260 °C and cooling to room temperature.

a shoulder at 600 nm. Increasing temperature up to 80 °C, the main band shifts to 633 nm while a shoulder around 690 nm and a weak shoulder at 760 nm appear in the spectra. There is a substantial change of the spectral features upon further heating: (i) the 600-nm shoulder disappears; (ii) the 690-nm peak increases in intensity, becoming dominant above 100 °C; (iii) there is a noticeable reduction of the spectral broadening. From 100 to 240 °C no mayor change of band shape or position is observed in the spectra with the exception of an increase of the broadening. At 260 °C, that is, above the melting temperature, the PL spectrum displays a broad peak at 585 nm. After slow cooling to room temperature, the film exhibits a structured PL with three bands respectively at 640, 710, and 760 nm. The same PL spectrum is detected for a drop-cast film.

The band shape and frequency changes in the PL spectra can be ascribed to the structural modifications induced by temperature and can be rationalized as follows. At room temperature the PL spectrum of the spin-coated film is blue-shifted with respect to the thermally treated sample or to the drop-cast film. This is in agreement with the previously reported IR absorption and Raman characterizations, suggesting a more twisted backbone conformation in the spin-coated film.
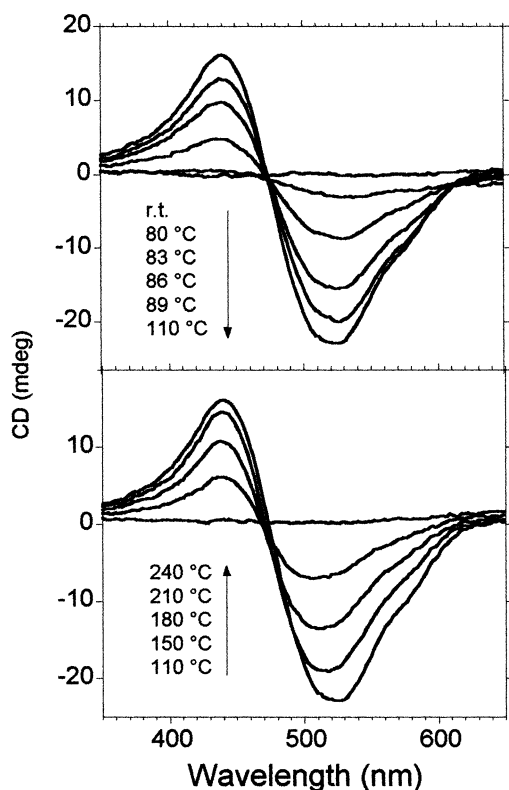
Figure 9. Circular dichroism spectra of a spin-coated PMBT film during in situ heating from 80 to 240 °C.

With increasing temperature, there is a reduction of PL inhomogeneous broadening caused by development of the three-dimensional order consistent with the crystallization detected by DSC measurements and by X-ray diffraction. The red shift of the PL can be due to an increase of backbone planarity in the crystalline phase as well as to a reduction of the stacking distance between the chains.[22] Indeed, IR and Raman measurements probe a more planar conformation of the conjugated chain and the stacking distance is also decreasing in the crystalline phase.

Upon melting the shape and position of the PL peak is very similar to the shape and position of the PL of PMBT in a good solvent solution.

Figure 8 also shows a decreasing of PL intensity upon thermal treatment. Even though the emission efficiency is also related to the structural modifications, we will not attempt to discuss these features, as we cannot completely rule out some oxygen PL quenching with our in situ experimental setup.

Circular Dichroism. In Figure 9 the CD spectra of a spin-coated PMBT film during in situ heating are reported. As observed in a previous paper,[11] the CD spectra are typical of a *laevo* supramolecular arrangement of the polymeric backbones: two nearby polythiophene strands interact via exciton coupling, giving rise to the observed positive−negative features. In the top part of Figure 9 one may notice an increasing of the CD signals with heating from room temperature to 110 °C. In the bottom part of Figure 10 the decrease of the CD signals with temperature increasing from 110 to 240 °C is shown. The CD data suggest that maximum
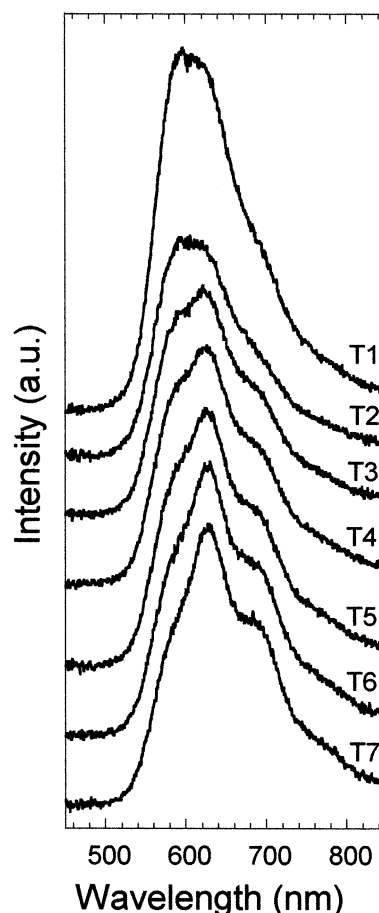
Figure 10. Evolution of electroluminescence spectra of a single-layer LED during working time; the spectra were recorded every 30 s from T1 to T7.

chiral order is attained at 110 °C, where the film becomes crystalline as evidenced by DSC measurements (see Figure 1), and it is lost at the end of the experiment after the melting has occurred. The attainment of a chiral structure is smoothly reached and an isosbestic point is observed in the top part of Figure 9. This feature suggests that during the heating two phases are present: one optically inactive and disordered that is converting in another one, which is chiral and ordered.

If we assume that chiral order is very close to a crystalline order, a combined use of X-ray data, CD, and UV-absorption data may be attempted to evaluate some parameters of the chiral geometry. As already done in the literature,[11] the use of the rotational strength R and of the dipole strength D could provide information on the distance of two nearby polythiophene strands and of their mutual orientation. Dividing the expression of R, given in refs 23 and 11, by $D = 2\mu^2$, we have

$$4R/D = \pi\nu d_{12} \sin \tau \qquad (1)$$

where d_{12} is the distance of the two interacting polythiophene backbones, τ is the angle by which the two chains are tilted with respect to each other, and ν is the wavenumber of the main absorption (corresponding, for example, to the center of the positive and negative bands of the exciton couplet). In the equation no

(22) Cornil, J.; Dos santos, D. A.; Crispin, X.; Silbey, R.; Bredas, J. L. *J. Am. Chem. Soc.* **1990**, *120*, 1289.

(23) Rodger, A.; Norden, B. *Circular Dichroism and Linear Dichroism*; Oxford University Press: Oxford, 1997; p 74.
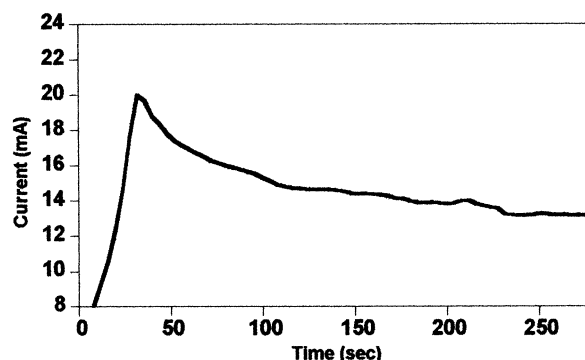
knowledge is needed for μ^2 and consequently for the film thickness. It is possible to calculate the $4R/D$ value needed in eq 1 from the optical measurements by simply integrating the CD bands (ΔA) and the UV absorption bands (A) in absorbance units. It turns out that[24]

$$4R/D = \int \Delta A \, d\lambda / \int A \, d\lambda = \Delta I / I \qquad (2)$$

From the experimental data we have $\Delta I = 0.028$ for the positive CD band and $\Delta I = 0.057$ for the negative CD band, and $I = 63.9$. Using the ΔI value of the positive CD band, we obtain from eq 2 $4R/D \cong 4.4 \times 10^{-4}$. Taking $d_{12} = 3.85$ Å as the intralayer stacking distance of polythiophene chains obtained from the X-ray data, and $\nu = 21097$ cm^{-1}, we obtain from eq 1 $\tau \approx 10°$. This result, which has a qualitative value, is quite reasonable for solid-state samples, even though the determination of τ by this method gives values too high for polymer solutions and is under discussion.[5,25] We observe that the value for $4R/D$ that we have measured here is lower than what we have previously observed for PMBT in mixed methanol/chloroform solution and much lower than what we have found for PMBT in decanol solution.[11] We can conclude that the product d_{12} sin τ is lower in the solid state than in solution, where the neighboring polythiophene backbones are more tilted and /or they are further away, probably due to the interactions between the polymeric chain and the solvent that are present also in aggregated phase.

Electroluminescence. We have prepared LEDs having PMBT films as the single layer with the configuration ITO/polymer/Al[12] and we have followed the evolution of the electroluminescence (EL) during the working time of the devices. The spectral changes observed in the device are reported in Figure 10 and are strictly related to the PL evolution during thermal treatment. In fact, as the working time of the device increases, the heating due to the Joule effect causes the same structural modification observed during the thermal treatment of PMBT thin film. The first EL spectrum T1 (see Figure 10) is equivalent to the PL spectrum obtained on the spin-coated film at 28 °C (Figure 9), indicating the same structural situation. Upon increasing of the working time (spectra T6 and T7 in Figure 10), the spectral shape changes: the intensity of the electroluminescence decreases and the emission band became similar to the PL spectrum as obtained from the spin-coated film heated at 100 °C.

This structural change has been detected also by plotting the current against working time, by keeping the voltage constant. In Figure 11 the evolution of

(24) Lightner, D. A.; Gurst, J. E. *Organic Conformational Analysis and Stereochemistry Circular Dichroism Spectroscopy*; Wiley-VCH: New York, 2000.

(25) Langeveld-Voss, B. M. W.; Beljonne, D.; Shuai, Z.; Janssen, R. A. J.; Meskers, S. C. J.; Meijer, E. W.; Bredas, J. L. *Adv. Mater.* **1998**, *10*, 1343.

Figure 11. Current intensity against working time at constant voltage (10 V) for a single-layer LED.

devices current as a function of working time is reported. It can be clearly seen that current increases up to 40 s. The material undergoes a thermal transition and the newly formed structural arrangement has an electrical behavior different from that of the starting material. Over 45−50 s working time the current decreases and reaches a plateau value, indicating a stable organization of the materials.

Conclusions

We have studied the optical and the structural modification induced by the temperature in chiral poly-3-(*S*)-2-methylbutylthiophene combining absorption, emission, and vibrational spectroscopy with thermal and structural characterizations. The optical transition from a disordered to an ordered three-dimensional assembling was clearly detected because this polymer, unlike other polyalkylthiophenes, shows only two structural phases in the solid state, namely, the amorphous and a crystalline modification. Indeed, X-ray diffraction patterns of PMBT show no evidence of a 2D mesophase similar to those given by other polyalkylthiophenes, nor a second crystal form. Raman scattering and IR spectra indicate that in spin-coated PMBT films the chains have a more twisted backbone conformation with respect to both cast films and other poly-3-alkylthiophenes. With heating to 100 °C spin-coated PMBT films produce in the UV−visible and PL spectra thermochromic changes that can be correlated with X-ray diffraction and DSC evidence of crystallization of the sample. The CD data suggest that maximum chiral order is attained at 110 °C and that during thermal treatment two phases are present: one optically inactive and disordered, which progressively converts in a chiral and ordered phase. The thermochromism was also evidenced in the EL spectrum of a light-emitting diode and explained as crystallization of PMBT films induced by the heating of the working diode. All the available evidence points, in the case of PMBT, to a particularly strong coupling between intramolecular and supramolecular order.