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Study of [Thienylene-dialkoxy phenylene] Conjugated Materials

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Summary: In this work we report on the electrochromic and optical studies of thin films of thienylene-dialkoxyphenylene. The films for the optical measurements were prepared by spin casting on glass and silicon substrates. Photoluminescence and absorption spectra were recorded in the temperature range from 300 K. The differences between the spectra of the polymer and the oligomer can be attributed to a higher mean conjugation length in the polymer than in the oligomer. We present also a first principles theoretical calculation which shows that the conjugated oligomer has an HOMO-LUMO energy around 2.0 eV, which is consistent with the experimental data.

Keywords: optical properties; thienylene-phenylene

Introduction

Increasing attention is being paid to light emitting materials due to their promising electro-optical applications. The first report of a polymer based light-emitting diode, more than a decade ago,[1] has led to growing interest in conjugated organic polymers for electro-optical devices.[2–7] In addition to easy processability, organic polymers offer unique possibilities for tuning the electronic and opto-electronic properties. The tailoring of the materials properties can be easily achieved by varying the structure of the unsaturated chain unit.[8] Poly (*p*-phenylene vinylene) proved to be of interest as electro-luminescent material for light emitting diodes and showed high photoluminescence quantum efficiency.[9] Recent reports emphasized structure/property relationships in light-emitting phenylene-vinylene copolymers.[10–12] Polythiophenes[13–15] also constitute interesting materials owing to their good stability and the easy tunability of their electronic and optical properties. Co-polymers containing phenylene and thienylene units also proved to be of interest in combining the properties associated to the two different conjugated rings. We recently reported the synthesis of well defined and oriented alternating phenylene-thienylene copolymers exhibiting interesting electro chemical and optical properties.[16,17] Also, related phenylene alkyl-thienylene copolymers have been explored in an effort to develop highly efficient thiophene-based light emitting polymers.[18] Here we report an investigation of a thienylene-phenylene copolymer and oligomer with di(ethyleneoxide) side chains (Figure 1). The presence of di(ethyleneoxide) polar side chains gives to the material a good solubility and excellent adhesion properties. These properties allowed the formation of homogeneous thin films by spin coating. We characterize the properties of this new conjugated system by means of optical measurements. We also performed first-principles calculations

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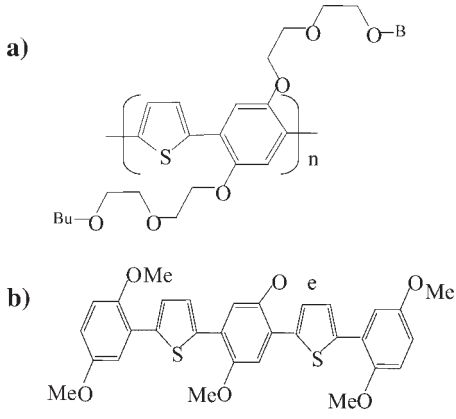

Figure 1.
Thienylene-dialkoxyphenylene organic materials with side chains, (a) copolymer ($n = 25$; Bu = C_8H_{17}), (b) oligomer (Me = CH_3).

based on the density functional theory to determine its structural and electronic properties.

Results and Discussion

Electrochemical Properties

The copolymer or oligomer was deposited on an ITO electrode by spin-casting from a solution of the materials in THF (20 mg · mL^{-1}) and studied by electrochromism using a 0.10 M solution of tetrabutyl ammonium hexafluoro electro chromism associated to the redox behaviour of the materials was observed. The absorption spectra were recorded for films deposited from solution in THF on an ITO glass support with the value of the electric potential varying between 0 and 1.0 V (Figure 2). In its neutral form (before oxidation) the spectrum of the materials showed a single band associated to an interband transition ($\lambda = 456$ nm). Upon oxidation, the absorption shifts to higher wavelength. The new band ($\lambda = 680$ nm) is associated to the appearance of bipolaronic states in the gap.

Optical Properties

The absorption spectra were recorded for films deposited from solution in THF on a glass support. The absorption spectra of the conjugated copolymer showed bands at $\lambda = 462$ nm in THF solution and $\lambda = 494$ nm ($E = 2.51$ eV) in solid state. To the oligomer, in THF solution, these bands are centered at $\lambda = 423$ nm and $\lambda = 460$ nm ($E = 2.69$ eV) in solid state. This bathchromic shift can be attributed to a higher mean conjugation length in the solid organic materials.

The emission spectrum of the copolymer and oligomer was also recorded in solid state at room temperature. An intense band at $\lambda = 600$ nm ($E = 2.06$ eV) was observed to copolymer. The shape and the energy of the photoluminescence band are close to that of polythiophene. For the oligomer, the emission band was observed at

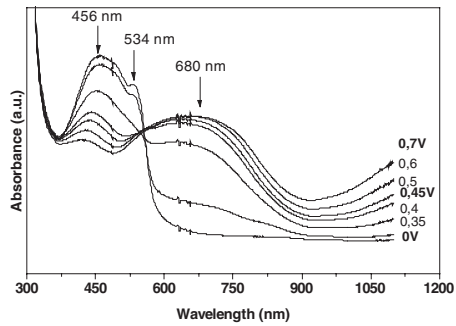

Figure 2.
Electrochromism of thienylene-dialkoxiphenylene copolymer deposited on ITO electrode.

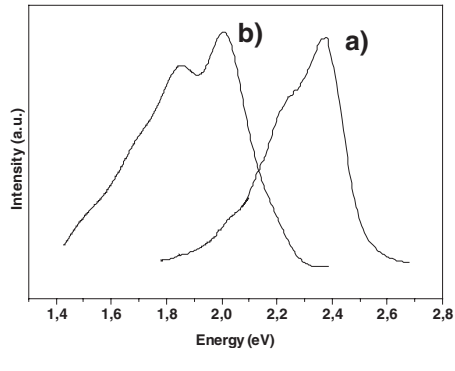

Figure 3.
Emission spectra of the (a) oligomer and (b) copolymer spin-coated on glass.

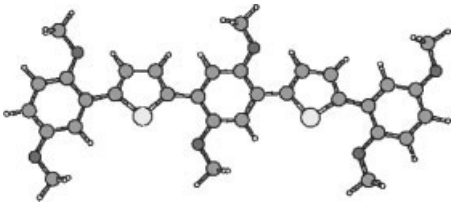

Figure 4.
The relaxed structure of the oligomer.

$\lambda = 520$ nm ($E = 2.38$ eV). This difference between copolymer and oligomer can be attributed to a higher mean conjugation length in the polymer than in the oligomer (Figure 3). First-principles calculations based on the density functional theory (DFT) show that a relaxed structure of the oligomer (Figure 4) has a HOMO-LUMO gap of 2.0 eV, which is consistent with the experimental results if we take into account that DFT is known to underestimate gap energies.[19]

Conclusion

Owing to the presence of the di(ethylene oxide) side chains, the thienylene-dialkoxyphenylene copolymer and oligomer (Figure 1) exhibited excellent glass adhesion properties and formed very homogeneous films by spin-coating. These new materials are promising candidate for the fabrication of opto- electronic devices.

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[1] H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, *347*, 539.
[2] S. Miyata, H. S. Nalwa, "*Organic Electroluminescent Material and Devices*", Gordon and Breach, Amsterdam 1997.
[3] T. Skotheim, J. Reynolds, R. Elsenbaumer, "*Handbook of Conducting Polymers*", Marcel Dekker, New York 1998.
[4] H. S. Nalwa, "*Handbook of Conducting Polymers*", Wiley, New York **1997**, Vol. 4.
[5] M. T. Bernius, M. Inbasekaram, J. O. Brien, W. Wu, *Adv. Mater.* **2000**, *12–23*, 1737.
[6] Special issues on molecular materials for electronic and optoelectronic devices, *J. Mater. Chem.* **1999**, *9*, 1853.
[7] Special issues on molecular materials for electronic and optoelectronic devices, *Acc. Chem. Res.* **1999**, *32*, 191.
[8] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 402.
[9] R. H. Friend, N. C. Greenham, in: *"Handbook of Conducting Polymers"*, T. A. Skotheim, J. R. Reynolds, R. L. Elsenbaumer, Eds., Marcel Dekker, New York 1998.
[10] M. Zheng, A. M. Sarker, E. E. Gürel, P. M. Lahti, F. E. Karasz, *Macromolecules* **2000**, *33*, 7426.
[11] Z. K. Chen, W. Wuang, L. H. Wang, E. T. Kang, B. J. Chen, C. S. Lee, S. T. Lee, *Macromolecules* **2000**, *33*, 9015.
[12] T. Ahn, S. Y. Song, H. K. Shim, *Macromolecules* **2000**, *33*, 6764.
[13] J. Roncali, *Chem. Rev.* **1992**, *92*, 711.
[14] J. Roncali, *Chem. Rev.* **1997**, *97*, 173.
[15] R. D. Mc Cullough, P. C. Ewbank, in: *"Handbook of Conducting Polymers"*, T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds, Eds., Marcel Dekker, New York **1998**, Chap. 9.
[16] J.-P. Lère-Porte, J. J. E. Moreau, C. Torreilles, *Synth. Metals* **1999**, *101*, 104.
[17] J.-P. Lère-Porte, J. J. E. Moreau, F. Serein- Spirau, C. Torreilles, A. Righi, J.-L. Sauvajol, M. Brunet, *J. Mater. Chem.* **2000**, *10*, 927.
[18] J. Pei, W. L. Yu, W. Huang, A. J. Heeger, *Macromolecules* **2000**, *33*, 2462.
[19] M. S. C. Mazzoni (private communication).

