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New thermotropic oligomers designed for FET applications

S. DESTRI[a], W. PORZIO[a], L. MARIN[a,b,c*], M. D. DAMACEANU[c], M. BRUMA[c]
[a]*Istituto di Chimica delle Macromolecole del CNR, via E. Bassini 15, 20133 Milan, Italy*
[b]*Dipartimento di Scienza dei materiali, Università Milano Bicocca, via Cozzi 53, Milan, Italy*
[c]*Institute of Macromolecular Chemistry, Aleea Gr. Ghica voda 41A, Iasi, Romania,*

We synthesised, purified and structurally confirmed three thiophene based oligomers with appreciable field effect transistor properties. The compounds present thermotropic behaviour. In order to understand the influence of liquid crystalline properties on the FET performances, differential scaning calorimetry, polarized light microscopy and thermogravimetrical analyses were performed.

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1. Introduction

Organic thin films have been widely investigated as active layers in electronic and optoelectronic devices, such as field – effect transistors (FETs), light – emitting diodes (LEDs), photovoltaic cells, organic light – emitting (field – effect) transistors (OLETs) [1]. Organic thin films transistors (OTFT) are studied like a viable alternative to traditional TFTs based on inorganic materials. Up to now, the performance in FET devices shown by small molecules is higher than that experienced with polymers although a large number of molecules need expensive methods for thin film preparation. The higher mobility in small molecules has been attributed to their ability to pack into well – organised polycrystalline films [2]. For organic semiconductors, the intrinsic carrier mobility depends critically on the extent of $\pi - \pi^*$ conjugation in the material, reflected in the HOMO – LUMO gap, and on the degree of molecular ordering; the performance of field effect based on single crystalline inorganic semiconductors such as Si and Ge, is a result of a charge carrier mobility about three orders of magnitude higher [3]. Moreover the connectivity among crystal domains is another important feature which strongly influences the device performances.

The liquid crystal state is a distinct phase of matter which combine two antagonistic features: fluidity and order: orientational order for nematic mesophases and orientational and positional order for smectic mesophases [4]. The main condition for a thermotropic behaviour is the presence of a mesogenic core which means in fact the presence of a extended conjugation.

Keeping in mind all these facts, we decided to analyse the thermotropic behaviour of three oligomers displaying appreciable FET performances [5].

Here we report the study of thermotropic behavior of three oligomers based on dithienothiophene and fluorene moieties (scheme 1) which structure is specifically selected to control both liquid-crystal and electrical properties.

2. Experimental

2.1 Chemical

The synthesis of the molecules have been performed as described in ref. 5, while the high degree of purity was achieved as detailed in a forthcoming paper.

2.2 Instrumentation

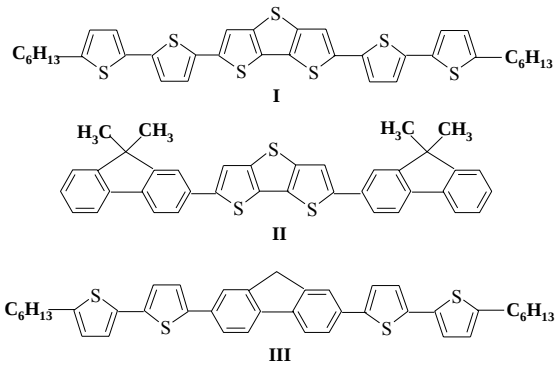
Differential scanning calorimetry (DSC) was performed with a Pirys 2 Perkin Elmer instrument, at heating rates of 10°C/min or 20°C/min, under a nitrogen atmosphere. The transition temperatures were read at the top of the endothermal and exothermal peaks. Mesophases of the oligomers were studied by observation of the texture with an Olympus BH-2 polarized light microscope under cross polarizers with a THMS600\HSF9I hot stage. The temperature at which isotropic phases occurred was taken as the isotropization temperature (T_i). Thermogravimetric analysis (TGA) was carried out by using a Perkin Elmer apparatus, at a heating rate of 10°C/min, in air.

AFM images were collected in intermitting-contact mode with a Nanoscope IIIa (Digital Instruments) using silicon cantilevers. Optical micrographs under blue light were obtained with a Nikon Eclipse TE2000-U microscope equipped with a fluorescence illuminator with a 450 – 490 nm (pyronine) band – pass excitation filter.

FETs were fabricated on heavily doped and oxidized silicon wafers in a top contact device configuration, by the thermal evaporating. The electrical properties of the FETs were measured with a HP 4155A parameter analyzer, with the sample in a dry and inert atmosphere.

3. Results and disscusion

Thiophene based oligomers designed for FET applications have been synthesised accordingly with ref. 5 paying more attention to the purification step.



Scheme 1.

The thermal behaviour of these oligomers was observed correlating the differential scanning calorimetry (DSC), polarized light microscopy (PLM) and thermogravimetrical analisis (TGA) data.

For **oligomer I**, the DSC traces (Fig. 1) have indicated the presence of LC state. At the corresponding temperatures 70 ^{o}C and 100 ^{o}C detected in DSC, birefringence in thin layers and in thick layers under shear (Figure 2a) was observed in PLM. The sample becomes fluid at 247 ^{o}C (melting point) and the isotropization (315 ^{o}C) is strongly affected by decomposition, visible in PLM. The decomposition is confirmed by the TGA analysis (figure 3); it starts about 100°C and 10 % weight loss has been seen at 350 ^{o}C.

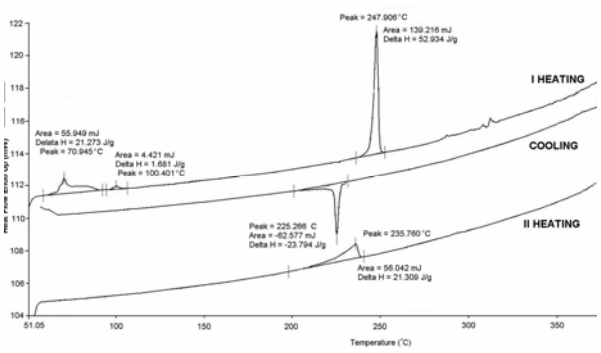
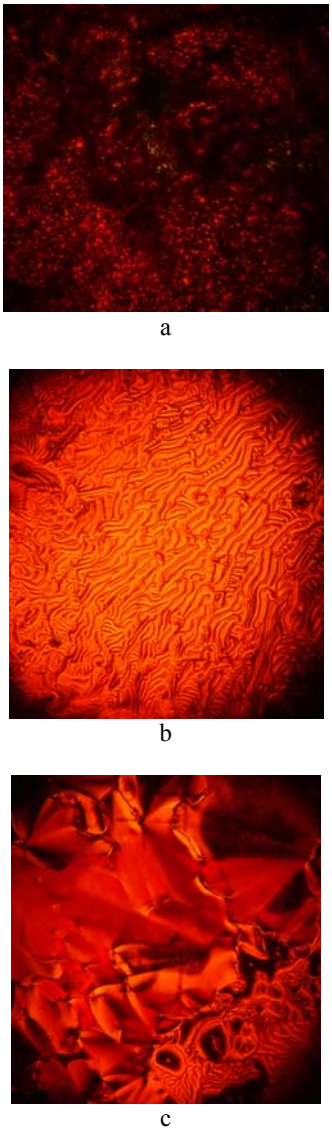


Fig. 1. DSC thermograms of oligomer I, 10 ^{o}C/min.

In order to avoid such a decomposition we have heated and cooled the sample using a speed of 90 ^{o}C/min and have obtained clear nematic and smectic textures which prove the potential ordering of this oligomer on heated substrates.

Oligomer II has an complex behaviour, unaffected by the thermal decomposition, as has been proved by DSC (Fig. 4), PLM and TGA measurements.

Its crystalline samples melt at lower temperatures when deposited in thin layers and show a mosaic texture typical of a smectic B mesophase [6] (Fig. 5a) which is visible in all the field at a temperature 20 ^{o}C higher.



a

b

c

Fig. 2. Optical polarized microphotographs, crossed polarizers; a) Oligomer I, 1H, 198 ^{o}C, 400x, 10 ^{o}C/min, fine grain texture; b) Oligomer I, 1C, 290 ^{o}C, 200x 90 ^{o}C/min , nematic phase; c) Oligomer I, 1C, 289^{o}C, 200x, fan-shaped texture.

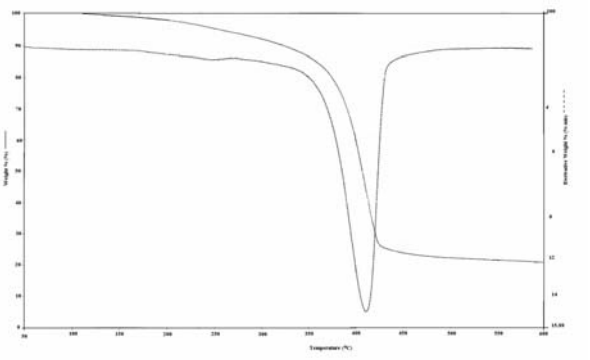


Fig. 3. TGA curves for oligomer I.

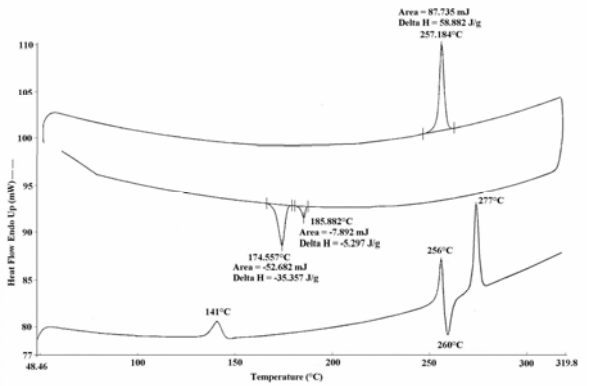


Fig. 4. DSC traces for oligomer II.

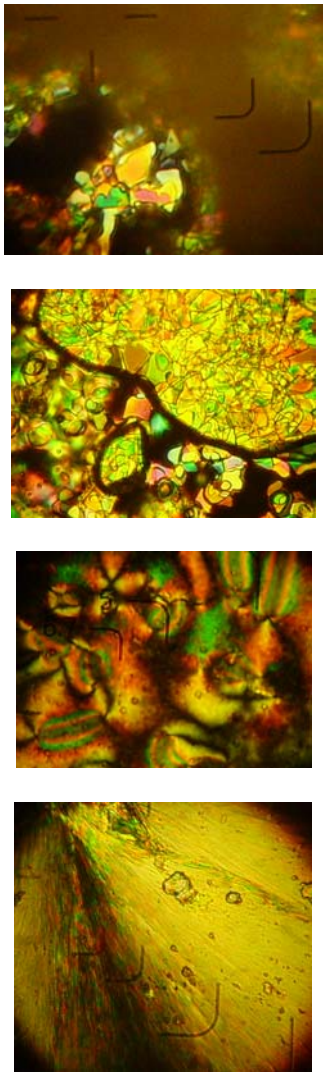


Fig. 5. Optical polarized microphotographs, crossed polarizers; a) Oligomer II, 1H, 234 ^{O}C, 400×; b) Oligomer II, 1H, 263 ^{O}C, 400×; c) Oligomer II, 1C, 224 ^{O}C, 400×, Schlieren texture; d) Oligomer II, 1C, 176 ^{O}C, 400×, crystalline state.

Interesting and unusual is the crystallization during the melting, when crystals with very good connectivity are obtained (Fig. 5b).

In the cooling scan from the isotropic state a Schlieren texture (nematic phase) appeared (Figure 5c) and have transformed in a crystalline state with huge crystals (Fig. 5d).

Oligomer III in a similar way to oligomer I presents three transitions up to 150 ^{o}C which correspond in PLM to a fine grain texture obtained under shear force. The melting temperature is higher, it occurs at 326 ^{o}C and the isotropization temperature could not be observed due to thermal decomposition.

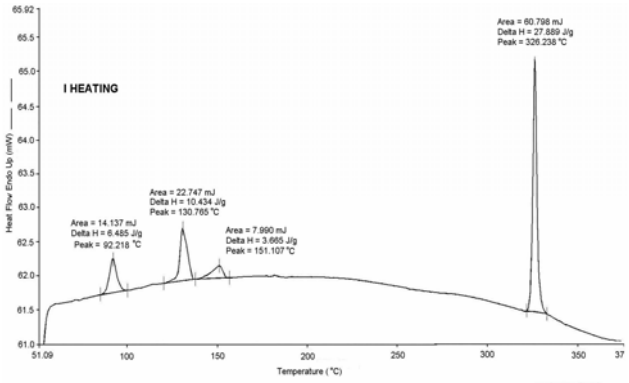


Fig. 6. DSC traces for oligomer II.

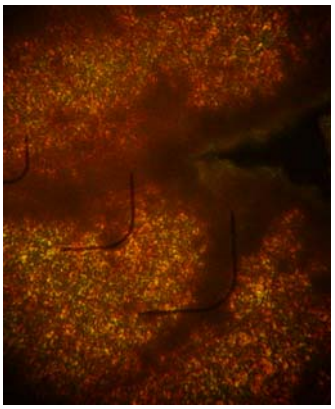


*Fig. 7. **Oligomer III**, 1H, 304 ^{O}C, 400x, fine grain texture.*

In order to check the possibility to obtain ordered layers from molten state, quenched films in the liquid crystal and crystal state have been obtained. The analysis of these films under polarized light and fluorescent light (blue light) revealed that in nematic phases continuous films (Fig. 8, a, b) can be obtained. The films obtained in smectic and crystal phases present breaks under polarized light (Fig. 8 c), but in blue light (Fig. 8 d) these breaks seem to un-affect the active layer at the organic – dielectric interface, responsible for charge transport [1].

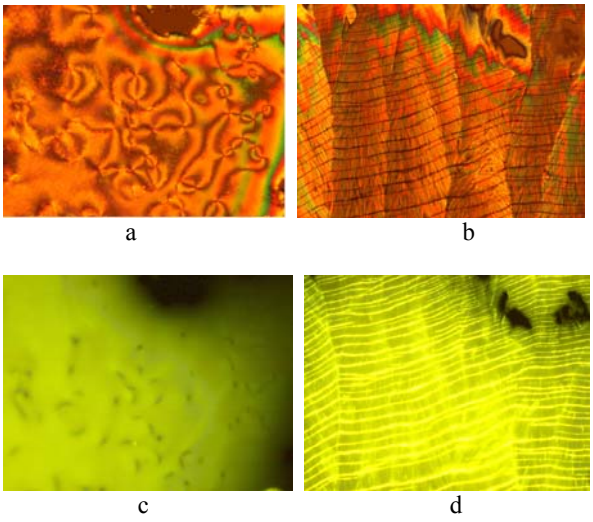


Fig. 8. Quenched films under polarized light (a, c) and blue light (b, d); a) quenched Schlieren texture; c) quenched crystalline state; b) quenched Schlieren texture; d) quenched crystalline state.

Table 1 provides data related to their optical, electrochemical, and electrical characterizations useful for evaluating their potential application in OFET and OLET devices. The electrical data have been measured using FET devices prepared by vacuum deposition. Comparing these data with those obtained for other thiophene oligomers [8-10] we observe that the mobility values and current modulation ratios are still unsatisfactory. In the light of these new thermal measurements and taking account that, during vacuum deposition, at the evaporation temperature decomposition can partially occur , we believe that solution cast films deposited on the heated substrates can provide better FET performances.

This hypothesis can be sustained by atomic force microscopy (AFM) measurements. In AFM, films of the oligomers I, II III, grown on the silica and OTS treated silica, heated at 70 ^{o}C, 60 ^{o}C, 30 ^{o}C respectively (Fig. 9) present good surface covering and a better connection when the substrate temperature is higher [7].

Table 1. Optical, electrochemical and electrical data.

Sample code	λ_{abs} (nm)	λ_{em}(nm)	$E_{g,el}$ (eV)	E_{HOMO} (eV)	μ (cm^2V/s)	I_{on}/I_{off}
OI	438	500 540	2.77	-5.23	$5*10^{-2}$	10^7
OII	403	440 475	2.85	-5.13	10^{-5}	10^3
OIII	401	440 475	3.13	-5.23	$5*10^{-3}$	10^4

λ: wavelength of the maximum absorption and emission peak in $CHCl_3$ solution; Eg, gap measured from electrochemical data; μ: mobility measured in FET devices based on vacuum deposited films.

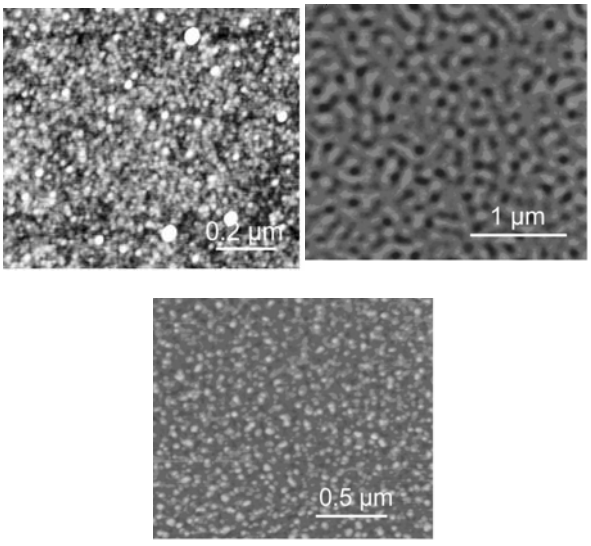


Fig. 9. AFM images of the surface of thin films of oligomer I, II, III, grown on the silica, heated substrates; a) Oligomer I, 70^{o}C; b) Oligomer II, 60^{o}C; c) Oligomer III, 30^{o}C.

4. Conclusions

The analysis of the thermal properties of the oligomers I, II, III revealed us their thermotropic behaviour.

Oligomer I has a week thermal stability and probably, for good FET results, solution cast films on the heated substrates are recommended instead of the thermal evaporation.

Oligomer II presents a crystallization on heating scan with connected crystals and huge crystals with good connectivity are obtained on cooling scan, although in different phases.

In the first heating scan of DSC of oligomers I and III, solid – solid transitions corresponding to an improved organization in supramolecular architectures have been observed.

Generally, under PLM we observed thermotropic transitions at temperatures lower for thin layers and higher for thick layers.

The quenched films from the liquid crystal and crystal states have good continuity.

The study of thermotropic behavior could provide precious information concerning the suitable methods for FET devices fabrication.

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*Corresponding author: lmarin@icmpp.ro