



# Controlling the alignment of ultra-thin films of linear and branched oligothiophenes for electronic applications

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## Report:

Functional materials for molecular electronics (e.g., organic field effect transistors - OFET) and optics (e.g., organic light emitting diodes - OLED) fabricated on the basis of pure organic oligomeric or polymeric building blocks show a large scientific and technological potential<sup>1-3</sup>.

Oligo- and polythiophenes as highly conjugated systems are promising candidates for organic electrical (semi)conductors. In the doped state they exhibit conductivities comparable to that of metals<sup>4</sup>.

For applications with respect to their electronic properties such materials have to form highly ordered structures in thin films by self-organisation processes. Strong intermolecular interactions between the heteroaromatic units of the oligothiophene molecules lead to poor solubility and processability. Hence, the formation of the thin films based on unsubstituted oligomers is limited. of non-modified is limited<sup>5</sup>. Therefore, the solution-based molecular self-assembling processes of monodisperse oligomers leading to ordered structures are particularly required. The synthetic strategy based on the combination of ring closure and metal-catalyzed coupling reactions allows to synthesize new class of  $\alpha,\omega$ -substituted septithiophenes. The use of soluble diketo-precursor preserves the good solubility of the intermediate products in the course of the multistep synthesis until the very last reaction and gives rise to good yields and high purity of the final oligomers<sup>6,7</sup>. The samples used in this study were synthesized by U. Ziener, Ulm University (Germany).

In the frame of the present project, we explored the crystalline and liquid crystalline structure of  $\alpha,\omega$ -substituted septithiophenes as a function of temperature (see Figure 1). The molecular alignment of these compounds was studied for thin films deposited on different substrates (silica, glass, PTFE-rubbed surfaces). To optimize the alignment of the oligothiophenes the role of the substrate nature and chain architecture of the substituents was investigated. The films were prepared by spin-coating of dilute solutions at room temperature. Time- and temperature-resolved WAXS and SAXS measurements were performed in grazing

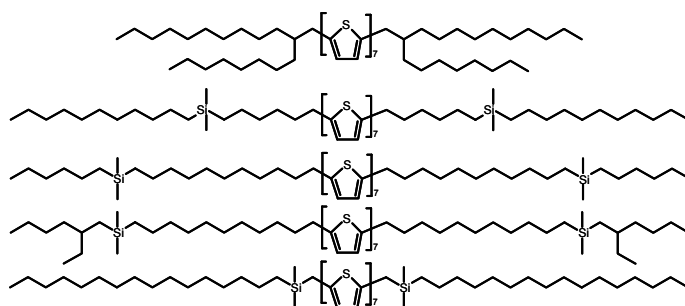


Figure 1. Chemical structure of novel  $\alpha,\omega$ -substituted septithiophenes.

incidence configuration using home-made sample holders. The experiments were carried out at the wavelength of 1.24 Å. Dynamic measurements employed heating rates of 5°/min or 10°/min using a Linkam heating stage.

At 25°C, the X-ray patterns of extruded fibers exhibit crystalline phases in which the longest spacing (c-parameter) is oriented in the direction perpendicular to the fiber axis. The X-ray results obtained on these systems are exemplified for 2-octyldodecyl-disubstituted septithiophene (referred in the following as compound 1) in Figure 2 (top). In the region of SAXS the compound displays two orders of the 001 peak corresponding to the c-distance of 33.9 Å. It is noteworthy that in this case the hk0 peaks pertinent for molecular packing in the plane of the smectic layers on the meridian. During heating the c-parameter of the smectic phase evolves significantly (Fig. 2, top). In the temperature range 25-163°C the 001 peak shifts to wide angles, which indicates a decrease of the layer thickness. At 165°C the X-ray patterns show a step-wise increase of the c-parameter indicated with an arrow. The transition temperature is close to that measured by DSC.

Within the temperature window between this transition and the isotropization point, the sample exhibits a smectic-like mesophase. It is noteworthy that the films are crystalline at room temperature. The isotropization point is reached at the temperature corresponding to the high-temperature peak in DSC, which is in agreement with the optical observations. The layer thickness of the studied LC phases is by far smaller than the molecular length in the stretched conformation (ca. 70 Å). Analysis of Patterson functions and density calculations show that the alkyl chains are inclined in respect to the smectic plane by approx. 45°.

In the case of thin films, the X-ray patterns recorded at 25°C exhibit a strong diffraction peak positioned on the meridian, which implies that the c-parameter is normal to the substrate plane (Figure 2, bottom). The spacing is in agreement with that of the crystalline 001 peak observed in bulk material. Also, upon heating, the thin films display the same behaviour than the for bulk material.

Thin layers of compound 1 were deposited on various substrates to evaluate the effect of the surface on the alignment of the molecules. The film deposited on silicon and glass substrate appears to show the meridional 001 peak with a wide angular dispersion (Fig.2, bottom left). In contrast, the film spin-coated on rubbed PTFE surface exhibits a well-oriented meridional 001 peak showing that PTFE improves molecular organization in the direction normal to the substrate (Fig.2, bottom right).

In conclusion, the studied septithiophenes are crystalline at room temperature, and at higher temperatures transform in a liquid-crystalline smectic C phases. Thus, in the unit cell, the molecules adopt a tilted conformation. The presence of substituents strongly influences the thermal behaviour of the compounds. The c-parameter is oriented normally to the surface of the films. Varying the substrate nature allows to tune quality of molecular alignment, which can have implications for the fabrication of electronic devices.

## References

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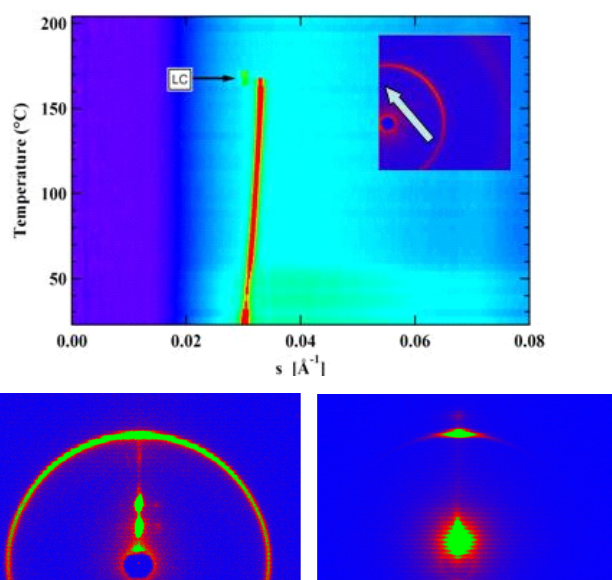


Figure 2. Top: Integrated SAXS intensity of compound 1 as a function of temperature during a heating ramp at 10°C/min. The inset shows the initial fiber pattern measured at room temperature. Bottom: SAXS pattern of compound 1 deposited on glass (left) or PTFE-rubbed substrate (right).