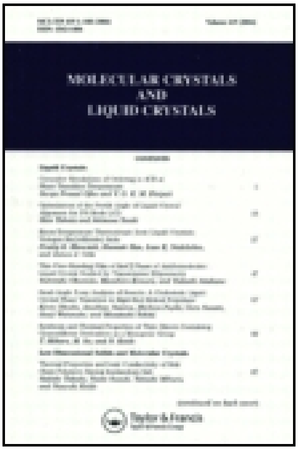

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Magnetic Field Alignment of Liquid Crystalline Pentathiophene

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MAGNETIC FIELD ALIGNMENT OF LIQUID CRYSTALLINE PENTATHIOPHENE

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Liquid crystalline α,α'-disubstituted pentathiophene was aligned using high magnetic fields ($> 5\,T$) resulting in macroscopically oriented samples. The pentathiophene crystallites were found to be aligned perpendicular to the magnetic field direction, as is evidenced by microscopy images. The samples are stable at room temperature and will be used for further investigations such as the determination of the (anisotropic) mobility and the polarization of the light emission.

The study of the physical properties of conjugated organic materials has attracted a growing amount of interest in the last decade, strongly motivated by their enormous potential for applications in electronics and photonics. Oligothiophenes have already been recognized as a promising class of materials to realize organic electrooptical devices such as solar cells [1], light emitting diodes [2], and field effect transistors [3]. The performance of such devices strongly depends on the material quality and can be improved considerably by introducing a high degree of orientational order, for example in a liquid crystalline (LC) state. Therefore, considerable efforts have been made to synthesize polymer materials with conjugated main chains and LC side chains [4,5]. Magnetic fields have already been

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proven to be a powerful tool to orient low molecular weight liquid crystals [6], but can also be used to align more complicated materials like polymer liquid crystals [7,8]. In this work we demonstrate the alignment of LC pentathiophene in high magnetic fields. Magnetic field alignment has several advantages over other alignment techniques such as mechanical stretching [9], LC self-organization [10], organic molecular beam deposition [11], and the use of alignment layers [12]. Application of a field leads to a bulk, contact free, nondestructive force, which is homogeneous throughout the sample and thus can be used for producing highly oriented bulk samples as well as thin films.

The principle of magnetic field alignment originates from the fact that most organic molecules are diamagnetic, that is when a molecule is placed in a uniform magnetic field a magnetic moment $\vec{m}$ is induced. This magnetic moment interacts with the magnetic field and the molecule will acquire an extra energy:

$$E = -\vec{m} \cdot \vec{B} = -\frac{\chi B^2}{\mu_0 N_A}$$

where χ is the diamagnetic susceptibility of the molecule and N_A is Avagadro's number. The diamagnetic susceptibility is closely related to the molecular structure and therefore it is generally anisotropic. The difference in susceptibility $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ between two orthogonal molecular axes causes a difference in energy depending on the orientation of the molecule with respect to the field. As a consequence the molecule experiences a force to orient itself with the molecular axis with the smallest susceptibility along the field direction. For single molecules the reduction in magnetic energy, at the fields that are currently available, is small compared to the thermal energy ($\Delta\chi \cdot B^2 \ll kT$), i.e. Brownian motion of the molecules is too large to achieve alignment. However, for collective molecular behavior, like in LC mesophases, the difference in magnetic energy added up for all molecules within a correlation volume (N) can become large enough ($N\Delta\chi \cdot B^2 \gg kT$) to induce magnetic alignment. This mechanism is our motivation for the alignment of pentathiophene in its LC mesophase.

The molecular structure of α, α'-disubstituted pentathiophene is shown in the inset of Figure 1. The synthetic details are described elsewhere [5]. It was shown previously that this compound exhibits a high temperature smectic liquid crystal phase [10]. Thin LC cells were prepared by spincoating a dilute solution of polymer microspheres ($\varnothing = 18\,\mu\text{m}$) in ethanol on a glass plate, where the microspheres acted as spacers. Subsequently a second glass plate was glued on the spincoated side in such a way, that the obtained cell had two open ends. The cells were filled by capillary forces with the pentathiophene compound in the isotropic phase

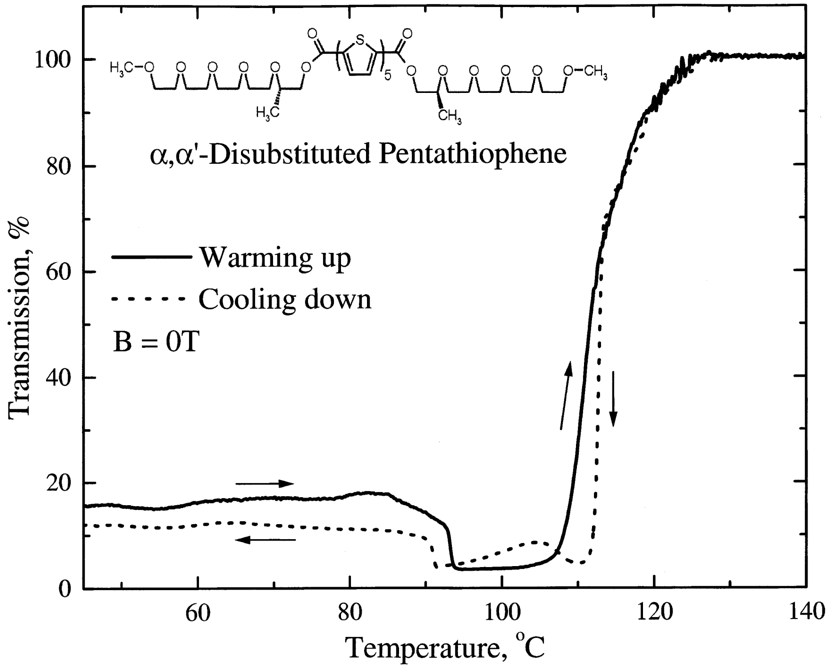

FIGURE 1 Phase diagram of LC pentathiophene obtained by transmission measurements upon heating (solid curve) and cooling (dotted curve). Inset: structural formula of the compound.

(130°C), after which both open sides were sealed. The magnetic field alignment experiments were performed in a 20 Tesla resistive magnet in the temperature range 20 ÷ 140°C. The compound was first heated up to the isotropic phase. Then the magnetic field was applied and subsequently the sample was cooled down through the LC phase to the crystal phase. Different cooling rates were applied but the best results were obtained with a ramping speed of 5°C/min. The alignment process was monitored by measuring the linear retardance (birefringence) using a polarization modulated He-Ne laser beam (wavelength 632.8 nm and a precision of 10^{-4} radian phase difference). Simultaneously the transmission of the laser beam through the sample was measured.

A typical transmission curve, measured at zero magnetic field is shown in Figure 1, and reveals the phase diagram of the substance. Upon warming up, the crystal phase, characterized by a finite transmission, remains up to ~95°C where the trasmission abruptly drops at the crystal-smectic LC phase transition. The small transmission in the smectic phase is attributed to the strong scattering by the unoriented liquid crystalline domains. This

LC phase remains up to ~114°C where the smectic LC–isotropic phase transition occurs, marked by a sharp increase of the transmitted laser intensity. Cooling down reveals a similar behavior, but with a small hysteresis, showing the isotropic–smectic LC phase transition starting at approximately the same temperature as in the heating trace.

Typical magnetic field induced retardance curves are shown in Figure 2. The curves were measured during cooling down from the isotropic state to the crystal phase at different field strengths: 0, 5, 10 and 15 T. In the isotropic phase ($T > 116°C$) a very small phase difference was measured, as expected for an uncorrelated isotropic phase, since single molecules cannot be aligned. At the isotropic–smectic LC phase transition the retardance signal steeply rises indicating the alighment of the LC material. With decreasing temperature the degree of alignment increases monotonously, until the smectic LC–crystal phase transition takes place, marked by the flattening of the retardance curves. The maximum retardation value increases with magnetic field, which is due to the higher degree of alignment at larger fields as follows from the formula above. Subsequent cooling down shows no further changes in the alignment. It is important to note

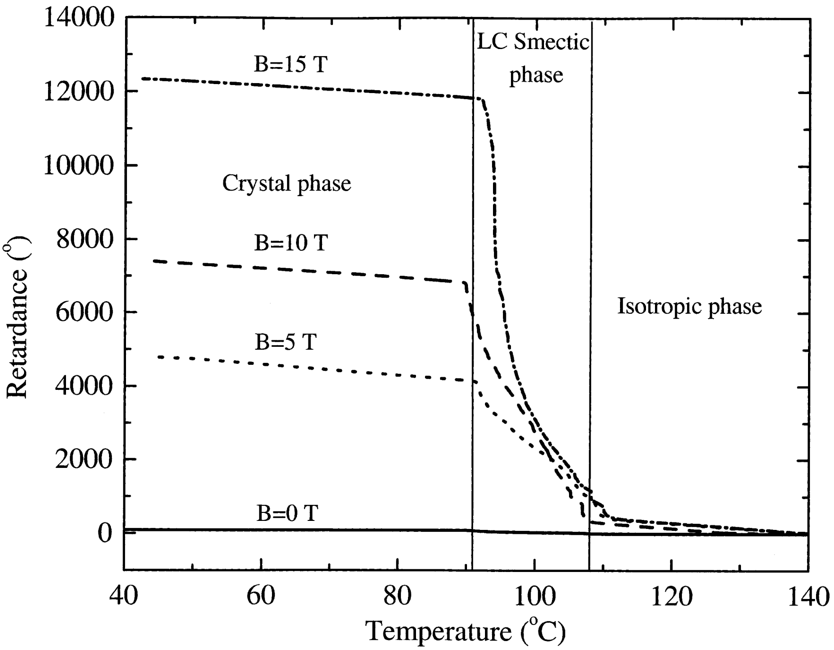

FIGURE 2 Retardance curves obtained for different magnetic fields. The alignment process occurs in the LC phase (116°C ÷ 90°C).

that in the solid phase the alignment is preserved, even after the field was switched off, which enables further investigation of the aligned material.

Figure 3 presents microphotographs of an unoriented sample (a) and of a sample aligned in 5 T (b), taken at room temperature, and corresponding to the traces depicted in Figure 2. The microphotographs taken at the same conditions for the samples oriented in 10 T and 15 T show similar features as the one taken at 5 T. Figure 3(b) clearly indicates that alignment of pentathiophene is perpendicular to the magnetic field direction. Furthermore the size of the oriented crystallites is considerably larger than that of the unaligned reference sample.

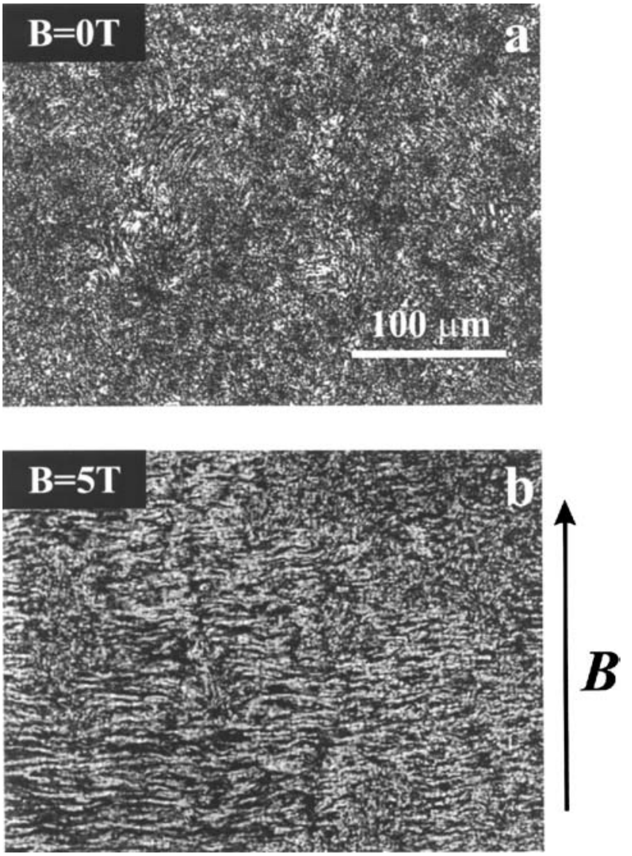

FIGURE 3 Polarized microphotographs of unoriented (a) and oriented samples at different mgnetic field values (b). All pictures are taken at room temperature i.e. in the crystal phase of the studied substance.

In conclusion, we have demonstrated an alternative method for producing macroscopically oriented samples of LC pentathiophene using high magnetic fields. The alignment was preserved in the crystal phase. The crystallites of the pentathiophene were observed to orient perpendicular to the magnetic field direction. The aligned samples are stable at room temperature and will be used for more elaborate experiments in the future.

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