Liquid Crystalline Behavior of α-Substituted Oligothiophenes

Takashi Yamada, Reiko Azumi,*[†] Hiroaki Tachibana,[††] Hideki Sakai, Masahiko Abe, Peter Bäuerle,[†††] and Mutsuyoshi Matsumoto[†]
Faculty of Science and Technology, Science University of Tokyo, 2641 Yamazaki, Noda 278-8510
[†]*Nanotechnology Research Institute, National Institute of Advanced Science and Technology,*
AIST Tsukuba Central 5-2, Tsukuba 305-8565
[††]*Correlated Electron Research Center, National Institute of Advanced Science and Technology, Tsukuba 305-8562*
[†††]*Department of Organic Chemistry II, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany*

(Received June 22, 2001; CL-010594)

Thermal behaviors of α-disubstituted oligothiophenes were investigated. 5,5''-Dicyanoterthiophene having thiophene rings as the rigid core exhibited a nematic liquid crystalline phase at 205 °C on cooling. It should be emphasized that this molecule lacks in a flexible substituent such as a long alkyl chain.

Organic semiconductors fabricated with π-conjugated polymers and oligomers have attracted much attention in the past few years.[1] In particular, polythiophenes and oligothiophenes can have high carrier mobility and emission efficiency and are extensively studied for the application to organic thin film transistors and organic light-emitting diodes. There has been a growing interest in conjugated polymers and oligomers, partly because some of them exhibit liquid crystalline phases.[2,3]

The molecular orientation of the π-conjugated polymers and oligomers is an important factor that affects the charge-carrier mobility. From this viewpoint, the liquid crystalline materials are useful, because they can be obtained as homogeneous thin films with expected high carrier mobility. Though the liquid crystalline behaviors of polythiophenes have been extensively investigated, few studies have been reported on the liquid crystalline behaviors of oligothiophenes.[4–9] As for the electric properties of the mesophase, Matharu et al. reported that bi- and terthiophene based chiral esters exhibit ferro-, ferri- and antiferroelectric behaviors.[10] Funahashi et al.[11] reported that dialkylterthiophene derivatives exhibit fast electron transport in their smectic phases. The excellent transport characteristics should be attributed to the crystal-like molecular ordering in smectic phases. For relatively small oligothiophenes, the attachment of alkyl chains to the oligothiophene core has been a prerequisite for the appearance of the liquid crystalline phases.[12] However, the presence of alkyl chains in the molecules is not preferable since they dilute the concentration of the oligothiophene core, the functional unit, in the material.

In this paper, we report on the thermal behavior of several α-substituted oligothiophenes, which have molecular shapes similar to those of typical thermotropic liquid crystals such as substituted biphenyls and terphenyls, using polarizing microscopy and differential scanning calorimetry (DSC). We have selected small and simple substituents to avoid the dilution of the oligothiophene core as much as possible. We have focused on terthiophene because the melting points of larger oligothiophenes will be very high and hence the temperatures for the appearance of liquid crystalline phases, if any, will be too high for the practical applications. The influence of the substituent at the α-position on the thermal behavior is discussed.

Several α–disubstituted oligothiophenes (Figure 1) were synthesized according to the literatures[13,14] and were identified by IR spectroscopy, mass spectroscopy, UV–vis spectroscopy and measurements of melting point. The thermal properties of the α-substituted oligothiophenes have been characterized by DSC and microscopic observations. Microscopic observations of mesophase textures were performed with a BH-2 (Olympus) with an FP80 hot stage and central processor (Mettler). The DSC measurements were performed with a DSC6200 (Seiko Instruments Inc.) at a heating and cooling rate of 10 °C·min^{-1}.

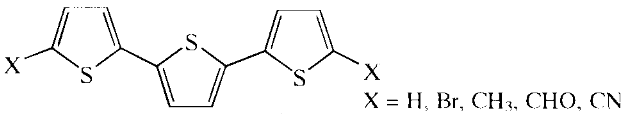
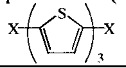


Figure 1.

Table 1. Influence of the substituent at the α-position on the thermal behavior

Substituent at the α-position (-X) 	Liquid crystalline phase
-H	none
-Br	none
-CH$_3$	none
-CHO	none
-CN	nematic phase (at 205 °C)

The influence of the terminal substituents on the phase transition was investigated. We selected small substituents such as bromo, methyl, aldehyde and cyano groups. The results are shown in Table 1. 5,5''-Dicyanoterthiophene is the only one that exhibits a liquid crystalline phase among the compounds studied. Polarizing micrograph of 5,5''-dicyanoterthiophene is shown in Figure 2. The disclination lines that are characteristic of a nematic phase are evident at ca. 205 °C on cooling. This texture was instantaneously observed. Schlieren texture was also observed under different sample conditions.

Figure 3 shows the DSC thermogram of 5,5''-dicyanoterthiophene. On cooling, an exothermic peak due to the transition between an isotropic phase and a liquid crystal phase is evident near 205 °C, which is below the melting point of the crystal. The ΔH value of the phase transition is ca. 1 kJ·mol^{-1}. The relatively small value suggests the existence of a mesophase with high symmetry.

These results suggest that the liquid crystalline phase is a nematic phase. This nematic state is monotropic and occurs

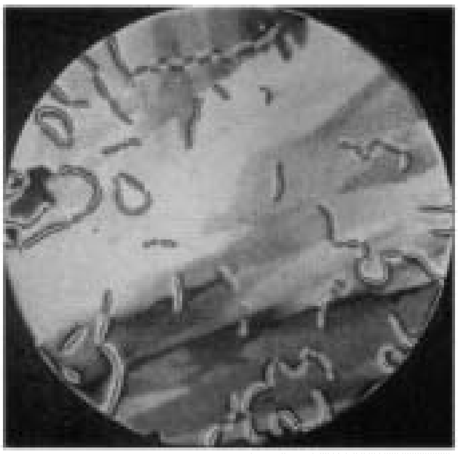


Figure 2. Polarizing micrograph of 5,5''-dicyanoterthiophene. (at 205–206 °C, on cooling) 1mm × 1mm.

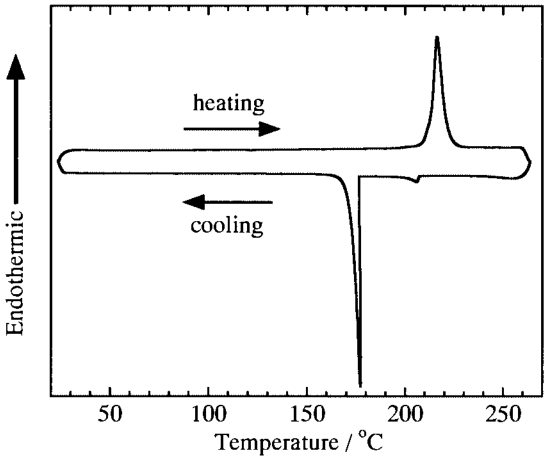


Figure 3. DSC thermogram of 5,5''-dicyanoterthiophene. (heating and cooling rate of 10 °C·min^{-1}).

only in the supercooled isotropic liquid below the melting point of the crystal. It should be noted that 5,5''-dicyanoterthiophene, which has no flexible substituent such as a long alkyl chain, exhibits a liquid crystalline phase.

The most stable conformation of terthiophene is calculated to be *anti–gauche* form, i.e., slightly twisted all-*anti* form.[15] For simplicity's sake, we assume that terthiophene takes planar all-*anti* form because the stability of this form is similar to that of *anti–gauche* form. The molecule is hence classified as C_{2v}, with dipole moment parallel to the short axis of the molecule. The substituents are inclined with respect to the long axis of the molecule and the direction of the sum of the dipole moment of the symmetrically substituted groups is the same with or opposite to that of the terthiophene core (Figure 4). The dipole moments of terthiophene, dibromoterthiophene, dimethylterthiophene, terthiophenedicarbaldehyde and dicyanoterthiophene are estimated to be 0.66, 0.83, 0.58, 1.92 and 1.90 D, respectively.[16] The increase in the dipole moment increases the dipole–dipole interaction between molecules, which will favor the appearance of a liquid crystalline phase. The different behaviors of dicyanoterthiophene and terthiophenedicarbaldehyde with similar magnitude of dipole moment may be due to the larger molecular length of the former than that of the latter. These results have revealed that the appearance of the mesophase depends strongly on the substituent at the α-position.

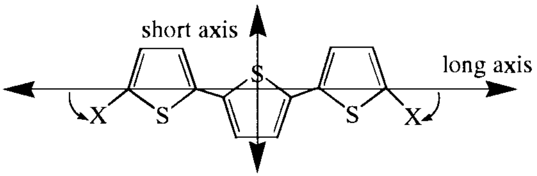


Figure 4. All-*anti* form of α-disubstituted terthiophene. The direction of the sum of the dipole moment of the two substituents is parallel to the short axis of the molecule because the directions of the substituents have the same finite angles with the long axis.

In summary, we have found that 5,5''-dicyanoterthiophene exhibits a liquid crystalline behavior at 205 °C on cooling. It was concluded that the liquid crystalline phase is a nematic phase based on the microscopic observation of mesophase and the results of thermal analysis. The appearance of the liquid crystalline properties depended strongly on the substituent at the α-position, indicating that the liquid crystalline behavior of oligothiophenes can be controlled by the appropriate selection of the substituents.

We would like to thank Dr. Günther Götz of University of Ulm for his helpful suggestions on syntheses. We also acknowledge Dr. Haruhisa Akiyama and Dr. Nobuyuki Tamaoki of AIST for providing their polarizing microscope and differential scanning calorimeter, and helpful suggestions.

References and Notes

1 P. Bäuerle, in "Electronic Materials: The Oligomer Approach," ed. by K. Müllen, and G. Wegner, Wiley-VCH, Weinheim (1998), p 105.
2 K. Akagi, H. Goto, Y. Kadokura, H. Shirakawa, S.-Y. Oh, and K. Araya, *Synth. Met.*, **69**, 13 (1995).
3 H. Tokuhisa, M. Era, and T. Tsutsui, *Adv. Mater.*, **10**, 404 (1998).
4 D. Byron, A. Matharu, R. Wilson, and G. Wright, *Mol. Cryst. Liq. Cryst.*, **265**, 61 (1995).
5 H. E. Katz, J. G. Laquindanum, and A. J. Lovinger, *Chem. Mater.*, **10**, 6335 (1998).
6 F. Garnier, R. Hajlaoui, A. El Kassmi, G. Horowitz, L. Laigre, W. Porzio, M. Armanini, and F. Provasoli, *Chem. Mater.*, **10**, 3334 (1998).
7 R. Azumi, G. Götz, and P. Bäuerle, *Synth. Met.*, **101**, 544 (1999).
8 P. Liu, H. Nakano, and Y. Shirota, *Liq. Cryst.*, **28**, 581 (2001).
9 S. Inoue, S. Nishiguchi, S. Murakami, Y. Aso, T. Otsubo, V. Vill, A. Mori, and S. Ujiie, *J. Chem. Res.* (S), 596 (1999).
10 A. Matharu, R. Wilson, and C. Grover, *Mol. Cryst. Liq. Cryst.*, **332**, 303 (1999).
11 M. Funahashi and J. Hanna, *Appl. Phys. Lett.*, **76**, 2574 (2000).
12 The appearance of a liquid crystalline phase of sexithiophene was reported by C. Taliani et al., and S. Destri et al., (C. Taliani, R. Zamboni, G. Ruani, S. Rossini, and R. Lazzaroni, *J. Mol. Electron.*, **6**, 225 (1990); S. Destri, M. Masherpa, and W. Porzio, *Adv. Mater.*, **5**, 43 (1993)) at temperatures higher than 300 °C without any indication of the clearing point up to 350 °C.
13 P. Bäuerle, F. Würthner, G. Götz, and F. Effenberger, *Synthesis*, **1993**, 1099.
14 T. M. Barclay, A. W. Cordes, C. D. MacKinnon, R. T. Oakley, and R. W. Reed, *Chem. Mater.*, **9**, 981 (1997).
15 S. Millefiori, A. Alparone, and A. Millefiori, *J. Heterocycl. Chem.*, **37**, 847 (2000).
16 The dipole moments were calculated by MOPAC. All-*anti* and planar conformation was assumed for the terthiophene core, and the most stable conformation of the side groups was employed.