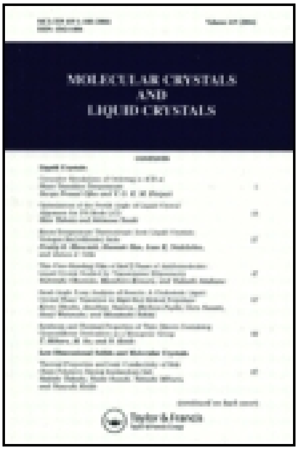

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LIQUID CRYSTALLINE BEHAVIORS OF SUBSTITUTED OLIGOTHIOPHENE BINARY MIXTURES

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Thermal behaviors were investigated of the binary mixtures of α,ω-disubstituted oligothiophenes. Smectic A phase, which is absent in the pure state of each component, was observed in the mixture of dicyano- and dimethylterthiophenes. On the other hand, the mixture of dicyanoterthiophene and terthiophene dicarboxaldhyde did not exhibit a new mesophase. Platelet texture was observed in the mixture of terthiophene dicarboxaldhyde and dimethylterthiophene although the two components did not mix well.

INTRODUCTION

π-Conjugated oligomers have been intensively studied not only as structural models of conducting polymers but also as promising materials for electronic and optoelectronic devices [1]. Oligothiophenes, in particular, are well studied as candidates for the application because of their excellent charge transport and electroluminescent properties, stability under ambient conditions and ease of chemical modification [2].

Recently, much attention has been focused on π-conjugated oligomers and polymers which exhibit liquid crystalline phases [3–6]. The orientation of the molecules in liquid crystalline phases can easily be controlled using external stimuli, which will modify the physical properties of the material.

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As α, ω-disubstituted oligothiophenes have molecular shapes similar to those of typical thermotropic liquid crystals such as substituted biphenyls and terphenyls, we can expect the appearance of their mesophase. Several oligothiophenes, often with long alkyl chains as substituents, have actually been reported to exhibit mesophases [7–10]. We have found, on the other hand, that α,ω-dicyanoterthiophene (CN3T) exhibited monotropic nematic phase [9]. It should be emphasized that this compound does not have long alkyl chains that are in many cases required to stabilize a mesophase.

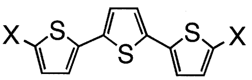
Mixing of two or more compounds is often performed to enlarge the temperature range of liquid cystalline phases. Mixing may also give rise to a new mesophase that neither of the pure components has. Here we report on the thermal behaviors of the mixture of a few terthiophene derivatives using polarizing microscopy, X-ray diffraction and differntial scanning calorimetry (DSC).

EXPERIMENTAL

Materials [11–14]

2,2′:5′,2″-Terthiophene-5,5″-dicarbonitrile (CN3T) was synthesized with a slight modification of the literature method [14]. 5,5″-dibromo-2,2″-terthiophene (2.05 g, 5.05 mol) was suspended in quinoline (50 ml) with copper(I) cyanide (1.27 g, 1.41 mmol). The reaction mixture was then refluxed for several hours. After cooling to room temperature, the mixture was poured onto 500 g of ice mixed with 50 ml of conc. HCl. The greenish-brown precipitate was filtered, washed copiously with water and ethanol, and dried *in vacuo*. The material was extracted using Soxhlet with hexane and then chloroform as solvents. After the evaporation of the solvent, the crude powder was sublimed (230–250°C, 1 mmHg) to yield yellow crystals which were collected and recrystallized from hexane/toluene. Yellow needle crystals (yield: 29%). m.p. 210–212°C. UV-vis($CHCl_3$): λ_{max} 381 nm, IR(KBr): 3094(νC–H), 2220(νC≡N), 1494, 1438(νC=C), 862, 810, 788(C–H o.o.p.d), 524(C–C o.o.p.b.)cm^{-1}, MS: m/z 298(M^+, 100%), 300(M+2, 14%).

5,5″-Dimethyl-2,2′:5′,2″-tethiophene (Me3T) was synthesized by Kumada-coupling [11]. Under an atmosphere of nitrogen 2-bromo-5-methylthiophene (5 g, 28.2 mmol) in 150 ml of ether was added dropwise to a slurry of a small excess of magnesius in ice-cooled ether, and the reaction mixture was refluxed for 4 h. The solution was transferred to the dropping funnel of a second apparatus and was added dropwise to an ether solution (150 ml) of 2,5-dibromobithiophene (2.73 g, 11.3 mmol) and [1,3-bis(diphenylphosphino)propane] nickel(II) (Ni(dppp)Cl_2, 0.06 g, 0.11 mmol). The mixture was refluxed for several hours and poured onto 500 ml of ice,



X = CN **(CN3T)**
X = CH_3 **(Me3T)**
X = CHO **(CHO3T)**

SCHEME

to which NH_4Cl was added until saturation. The organic phase was extracted with ether, dried with Na_2SO_4 and the solvent was evaporated. The brown powder was sublimed (120–140°C, 1 mmHg) to yied pale yellow crystals which were collected and recrystallized from ethanol. Platelet crystal (yield: 47%). m.p. 97–98°C, UV-vis($CHCl_3$): λ_{max} 365 nm, IR(KBr): 3065(νC-H), 2910, 2853(νCH_3), 1482, 1443(νC=C), 801, 794(C-H o.o.p.d.), 471(C-C o.o.p.b.) cm^{-1}, MS: m/z 376(M$^+$, 100%), 378(M+2, 17%).

2,2′:5′,2″-Terthiophene-5,5″-dicarboxaldehyde (CHO3T) was purchased from Tokyo Kasei.

Measurements

Mesophases of the binary mixtures were characterized by microscopic observations, X-ray diffraction measurements, and DSC measurements. Microscopic observations of mesophase textures were carried out with a Nikon S-Ke polarizing microscope equipped with a Mettler FP82 hot stage and and FP80 central processor. X-ray diffraction was collected with a Rigaku R-AxisIV (Cu$K\alpha$) equipped with a Mettler TOLEDO FP82HT hot stage and an FP90 central processor. The DSC measurements were performed with a Perkin Elmer DSC7 at a heating and cooling rate of 10°C min^{-1} under nitrogen.

RESULTS AND DISCUSSION

CN3T exhibits a monotropic nematic phase while Me3T and CHO3T do not exhibit a mesophase [9]. When CN3T and Me3T were mixed, a new mesophase was observed. Figure 1a shows a polarizing micrograph of the 1:1 mixture of CN3T and Me3T. On cooling, bâtonnet texture appeared from the isotropic liquid, and the whole compound turned into a focal-conic fan texture. A polygonal texture was also observed under different sample conditions. These textures are characteristic of a smectic A phase. The mesophase texture appeared only on cooling. When the molar ratio CN3T/Me3T was larger than unity, an excess portion of CN3T precipitated as crystals. In the mixture where Me3T was dominant, a platelet-like texture was observed (Fig. 1b).

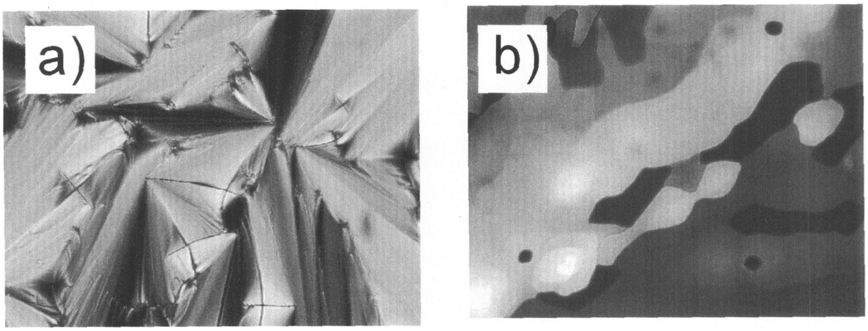


FIGURE 1 Polarizing micrograph of a binary mixture of CN3T and Me3T. a) Fan-shape texture of the 1:1 mixture (at 147°C on cooling). b) Platelet-like texture of the 1:4 mixture (at 95°C on cooling). Area: 400 µm × 300 µm.

Figure 2 shows an X-ray diffraction pattern of the 1:1 mixture of CN3T and Me3T. The appearance of a sharp peak at $2\theta = 5.73°$ (d = 15.4 Å) accompanied with a broad peak at ca. 20° is characteristic of a smectic A or C phase. Other small peaks are probably due to the crystalline phase of CN3T coexisting in the mixture. The layer distance (15.4 Å) roughly corresponds to the lengths of the longer molecular axes of CN3T and Me3T.

The above results suggest that the mesophase in the 1:1 mixture is a monotropic smectic A phase. CN3T and Me3T may form a kind of complex.

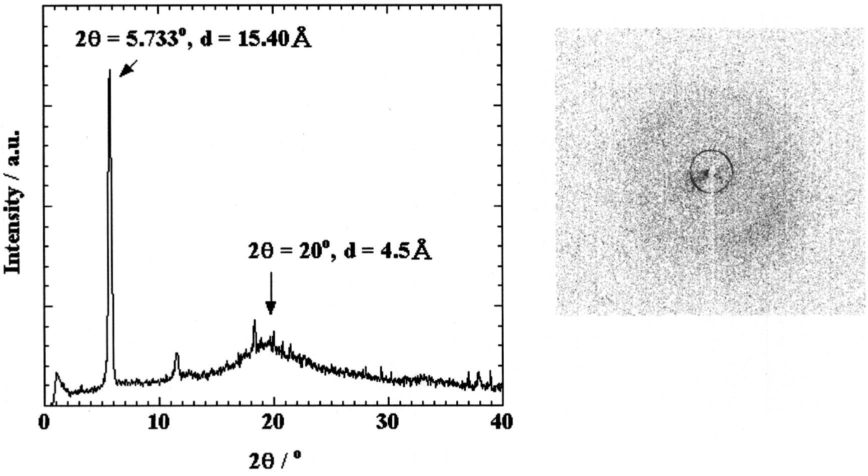


FIGURE 2 X-ray diffraction pattern of the 1:1 mixture of CN3T and Me3T at 165°C on cooling.

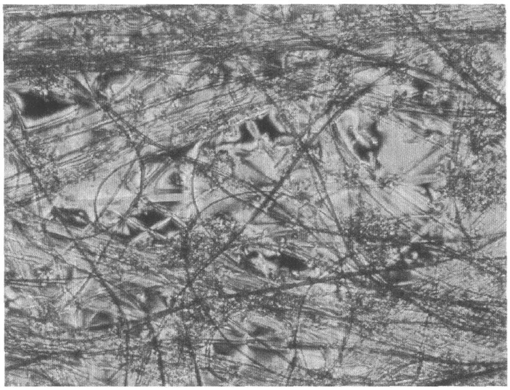


FIGURE 3 Polarizing micrograph of the 1:1 mixture of CN3T and CHO3T (at 179°C on cooling). Schlieren texture is evident between the crystals of CHO3T. Area: 400 μm × 300 μm.

The 1:1 mixture of these two compounds affords a unique foliaceous crystalline from a chloroform/ethanol mixed solution, i.e., these compounds do not precipitate separately. The obtained crystalline sample meltes at 167°C, which is far above the melting point of Me3T (97–98°C).

The mixture of CN3T and CHO3T did not exhibit a new mesophase. Figure 3 shows a polarizing micrograph of the 1:1 mixture. Schlieren texture is evident between the crystals of CHO3T, which corresponds to the pure CN3T portion. The above results suggest that these two compounds do not mix well. On the other hand, a platelet texture was observed in the

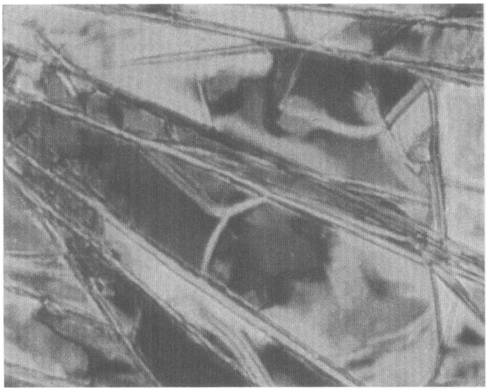


FIGURE 4 Polarizing micrograph of the 1:3 mixture of CHO3T and Me3T (at 110°C on cooling). Area: 400 μm × 300 μm.

binary mixture of CHO3T and Me3T, although needle-like crystals of CHO3T were observed even in the presence of an excess amount of Me3T (CHO3T/Me3T = 1/3, Figure 4). The observed platelet-like texture is similar to that observed in the 1:4 mixture of CN3T and Me3T (Fig. 1b), suggesting that this texture originates from Me3T and appears in the presence of a small amount of a second component.

In conclusion, a new liquid crystal phase has appeared by mixing two substituted terthiophene derivatives. The results will open up the possibilities of obtaining various kinds of liquid crystalline materials consisting of oligothiophene moieties.

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