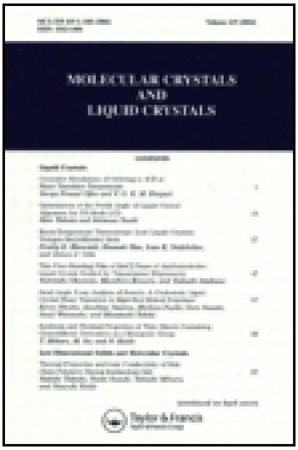

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Novel Liquid-Crystalline Phenylene-Thienylene Co-Oligomers for Photoinduced Reorientation of Liquid Crystals

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Novel Liquid-Crystalline Phenylene-Thienylene Co-Oligomers for Photoinduced Reorientation of Liquid Crystals

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Several kinds of symmetric and asymmetric phenylene-thienylene co-oligomers substituted with alkyl, alkoxy, ester or cyano groups in the ends were newly synthesized. Liquid-crystalline (LC) properties of these compounds were evaluated by differential scanning calorimetry and polarizing optical microscopy. It was found that all the compounds showed an LC phase. The photoinduced reorientation behavior of the dye-doped nematic LCs was investigated upon exposure to an Ar^+ laser beam at 488 nm. The change in refractive index was estimated to be larger than 0.1. It was revealed that the dyes synthesized act as an efficient trigger for the photoinduced reorientation.

Keywords: alignment change; liquid crystal; oligomer; thiophene

INTRODUCTION

Conjugated oligomers such as oligothiophenes have attracted much attention since the last decade. An important advantage of the conjugated oligomers is that the strict control of their chemical structures is possible by chemical methods (step by step procedures) in contrast to the existing polymerization procedures normally used to prepare

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conjugated polymers. For this reason, oligothiophenes are used as model compounds to rationalize or predict the structures and properties of electrically conductive polythiophenes [1]. Furthermore, in recent years, they are studied for nonlinear optical, photonic and electronic materials because of their higher solubility and lower viscosity than those of the polymers, which are advantageous in fabrication of devices [2].

Recently, we have synthesized a five thiophene-ring oligomer-type thiophene derivative, 5,5″-bis(5-butyl-2-thienylethynyl)-2,2′:5′,2″-terthiophene (**TR5**), and found that **TR5** can reorient liquid crystals (LCs) effectively upon exposure to an Ar^+ laser beam when doped in nematic LCs [3,4]. This reorientational behavior of LCs is interpreted in terms of selective photoexcitation of the dye molecules, followed by a consequent large change in guest-host interaction [5–9]. It is interesting to look at the oligothiophene-induced reorientation of LCs from viewpoints of not only controlling alignment of LCs by light, but also novel application of oligothiophenes. However, the effects of the molecular structure on the photoinduced reorientation and the reorientational mechanism have not been clear in detail.

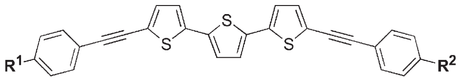
It is assumed that the high efficiency of **TR5** for photoinduced reorientation is mainly due to the change in molecular polarizability between the ground and the excited states, which is related to the intramolecular delocalization of π-electrons along the molecular long axis [10]. Therefore, other π-conjugated oligomers could induce reorientation of LCs, providing useful information for designing new dye structures. In this paper, we synthesized several kinds of phenylene-thienylene co-oligomers and demonstrated photoinduced reorientation of LCs doped with the co-oligomers as a photoactive dopant. In addition, we investigated the effect of the phenyl groups in the dye structure on reorientation of LCs.

EXPERIMENTAL

Materials

Figure 1 shows the chemical structure of phenylene-thienylene co-oligomers used in this study as the dye molecules and their abbreviations. **TP1**, **TP2**, **TP3** and **TP5** have alkyl, alkoxy, ester and cyano moieties in both ends, respectively. **TP4** possesses an asymmetric structure, a butyl group in one end and a cyano group in the other end. They were synthesized according to the literature with some modifications [3].

LC behavior and phase transition behavior were evaluated on a polarizing optical microscope (POM, Olympus, BX50) equipped with



TP1: $\mathbf{R}^1 = \mathbf{R}^2 = C_4H_9$
TP2: $\mathbf{R}^1 = \mathbf{R}^2 = OC_4H_9$
TP3: $\mathbf{R}^1 = \mathbf{R}^2 = COOC_4H_9$
TP4: $\mathbf{R}^1 = C_4H_9$, $\mathbf{R}^2 = CN$
TP5: $\mathbf{R}^1 = \mathbf{R}^2 = CN$

FIGURE 1 Chemical structure of phenylene-thienylene co-oligomers used in this study and their abbreviations.

a hot stage (Mettler, FP-90 and FP-82HT). Thermotropic properties of co-oligomers were determined with a differential scanning calorimeter (DSC, Seiko I&E SSC-5200 and DSC220C) at a heating and cooling rates of 2–10°C/min, and by thermogravimetry and differential thermal analysis (TG/DTA, Seiko I&C SSC-5200 and TG/DTA6200) at a heating rate of 5°C/min under a nitrogen atmosphere. At least three scans were performed in each sample to verify reproducibility on the DSC measurement. The UV-Vis absorption spectra were measured with a UV-Vis spectrometer (JASCO, V-550).

Preparation of Dye-Doped LC Cells and Experimental Condition

4-Pentyl-4′-cyanobiphenyl (**5CB**) was obtained from Merck Ltd., being used as a non-photosensitive host LC without further purification. Guest dye molecule and **5CB** were dissolved separately in toluene, and the solutions were mixed together at the dye concentrations from 0.05 to 0.20 mol%. After the solvent was removed completely under vacuum, the LC mixture was sandwiched between two lecithin-coated glass substrates with a 100-μm thick silica particle as a spacer. This cell with a homeotropic alignment of LCs was used as a sample for optical measurement. Clearing temperature (T_{NI}) of dye-doped cells was determined by POM at a heating rate of 0.5°C/min.

Photoinduced reorientation of dye-doped LCs was evaluated by self-diffraction measurement at room temperature. The optical setup was illustrated elsewhere [11]. A linearly polarized Gaussian beam at 488 nm with a diameter of 1.5 mm from an Ar^+ laser (NEC, GLG3280) was focused normally onto the sample cell by a lens with a focal length of 20 cm. The polarization of the laser beam was maintained as horizontal with a half-wave plate. The transmitted beam pattern created after the sample cell was observed on a screen behind the sample.

RESULTS AND DISCUSSION

Thermal Properties of Dye Molecules

The TG/DTA thermogram for **TP1** is shown in Figure 2. The weight remained unchanged until 300°C, then gradually decreased, and lost by 3 wt% from its initial weight at 403°C. Thermal properties of the dye molecules are summarized in Table 1. All the dyes showed the thermal decomposition temperature at higher than 350°C. However, it is noteworthy that a large broad exothermic peak was observed in DTA around 300°C without the weight loss. In addition, the sample was found to become from yellow to dark red after the annealing at 300°C. These results indicate that some structural change has occurred rather than thermal decomposition. This broad exothermic peak was found in all dye molecules in spite of different end substitutents. We assume, therefore, that it is attributed to the aromatic rings of dye molecule.

We previously reported that **TR5** shows a nematic phase between 191°C and 90°C and a smectic B phase between 90°C and 54°C on cooling [3]. It can be expected that LC phases appear since the new dye molecules have a structure similar to **TR5**. We examined phase structures of the dye molecules by DTA, DSC and POM. On the DTA measurement of the dye molecules, the endothermic peak due to the transition from the mesophase to an isotropic phase was not observed below 300°C.

The vast majority of literature on LCs pertaining to 1,4-disubstituted phenyl compounds clearly shows that phenylene-based materials possess higher melting and clearing temperatures than

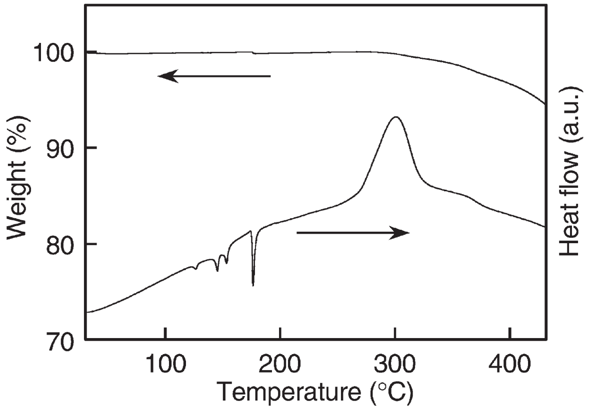


FIGURE 2 TG/DTA thermogram of **TP1**. Heating rate: 5°C/min.

TABLE 1 Thermal Properties of the Dye Molecules used in this Study[a]

Dye	Thermal decomposition temperature (°C)[b]	Phase transition temperature (°C)
TP1	403	K 151 S 175 N > 250 (heating) K 134 S 174 N > 250 (cooling)
TP2	379	K 165 S 187 N > 250 (heating) K 154 S 181 N > 250 (cooling)
TP3	366	K 162 N > 250 (heating) K 149 N > 250 (cooling)
TP4	423	K 117 S 191 N > 250 (heating) K 102 S 189 N > 250 (cooling)
TP5	>430	K 217 N > 250 (heating) K 173 N > 250 (cooling)

[a] K, crystal; S, smectic; N, nematic.
[b] Temperature at which a sample loses weight by 3 wt% from its initial weight.

the corresponding thienyl analogs [12,13]. **TP1** exhibited higher melting and clearing temperatures than the thienyl analog **TR5** as expected. Figure 3 shows the textures of **TP1** observed by POM at different temperatures. A shlieren texture was observed at 190°C with high fluidity under stresses, thus we assigned the mesophase above 174°C as a nematic phase. Between 174 and 134°C a mosaic-like texture was observed, and we assigned the phase as a smectic B phase. **TP2** showed a nematic phase above 181°C and a smectic phase between 181 and 154°C. In **TP3**, a shlieren texture was observed above 149°C, while it changed to the dark view under stresses. In addition, the conoscopic image showed a cross-shaped texture. This means that **TP3** tends to align homeotropically without any alignment layer on

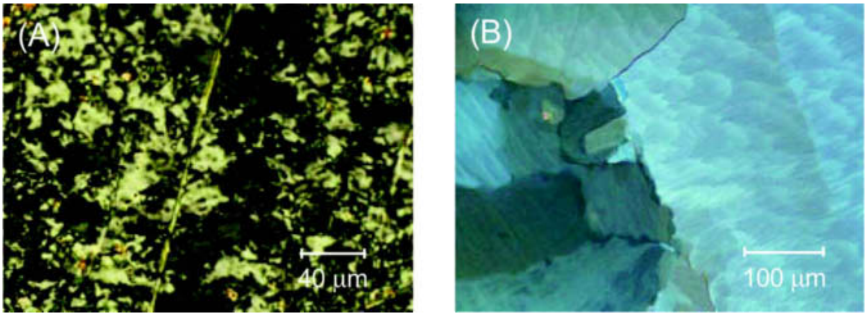


FIGURE 3 Polarizing optical micrographs of the texture of **TP1** at (A) 190°C and (B) 150°C obtained on heating and cooling, respectively.

glass substrates. A similar texture was observed in **TP4** above 189°C. On cooling, the dark view concurrently changed to a bright texture attributed to a smectic phase. It is interesting to note that **TP4** shows an LC phase, even though it has a butyl group in the terminal phenylene, which is a short flexible tail compared to 5 aromatic rings as a long mesogenic core. Taliani *et al*. reported that a rigid-rod aromatic oligomer, α-sexithiophene, without a flexible tail showed an LC phase [14]. It seems reasonable that our co-oligomer **TP5** shows an LC phase. A shlieren texture was observed at 230°C and high fluidity was appeared under stresses. From these results, it can be said that **TP5** is a unique compound that shows a nematic phase in spite of a long mesogenic core without any flexible tail. Although we identified the mesophase as a smectic phase from the texture under the POM, X-ray measurement is needed for the detailed confirmation.

Characterization of the Dye-Doped LCs

Figure 4 shows the clearing temperature of **5CB** doped with the dyes at various concentrations. The pure **5CB** in the LC cell showed nematic to isotropic phase transition at 34.7°C. With an increase of the dye concentration, the value of T_{NI} increased gradually. This indicates that the LC phase of the mixtures is stabilized by dye molecules to some extent. Particularly, when 0.20 mol% of **TP4** was doped into **5CB**, the clearing temperature increased by 2.4°C compared to the undoped **5CB**. We assume that it is due to the dipole–dipole

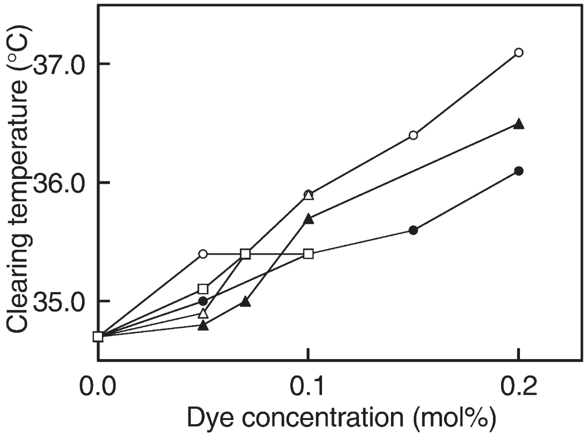


FIGURE 4 Clearing temperatures of dye-doped **5CB** as a function of the dye concentration. (▲) **TP1;** (△) **TP2;** (●) **TP3;** (○) **TP4;** (□) **TP5**.

interaction between a cyano moiety in **5CB** and a cyano moiety in **TP4**. However, **TP5** also has a cyano moiety at the end, while T_{NI} was not significantly affected by the dye concentration, unlike **TP4**. It is considered that this result may be attributed to the decrease of dipole moment of **TP5** due to its symmetric molecular structure. **TP1**, **TP3** and **TP4** could be doped into **5CB** at 0.20 mol% or more, whereas, in **TP2** and **TP5**, the phase separation was observed by POM at the concentration of 0.15 mol%. To investigate the effect of the dye molecules on the molecular order of **5CB**, we estimated order parameter, S, from the polarized absorption spectra [15]. The measurement was performed with 20-μm-thick homogeneous cells at the dye concentration of 0.10 mol%. The values of S around 0.6 were obtained in all samples, indicating that the end substituents do not affect the orientational order.

Photoinduced Reorientation of Dye-Doped LCs

Diffraction rings formed on the screen were observed due to the self-phase modulation effect upon photoirradiation of the sample cell doped with dye molecules at 0.10 mol%. Figure 5 shows a typical

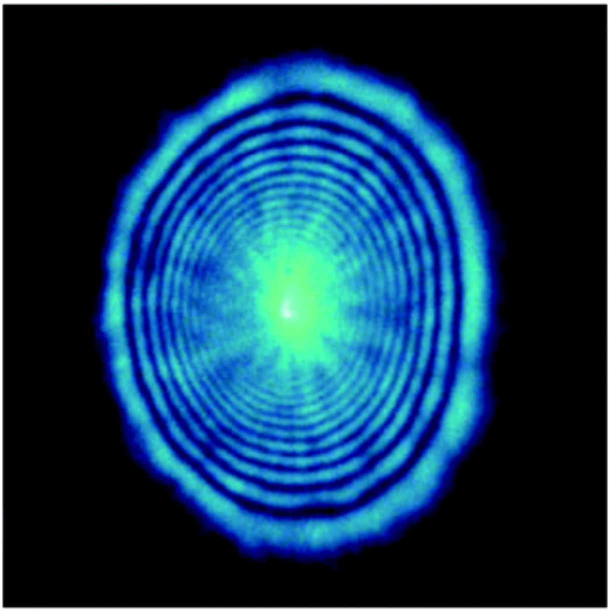


FIGURE 5 A typical diffraction pattern of **TP1**-doped **5CB** formed on a screen at 47 W/cm^2.

self-diffraction pattern observed in **TP1**-doped **5CB**. The number of diffraction rings (N) increased with the light intensity. N can be estimated from the following equation [16]:

$$N = \frac{\Delta\psi_0}{2\pi} = \frac{1}{\lambda}\int_{-d/2}^{d/2} \Delta n(z)\, dz \tag{1}$$

where $\Delta\psi_0$ is the phase shift observed by the laser beam in the beam center traversing the LC cell with thickness d, $\Delta n(z)$ is the local refractive-index change induced by the laser beam, and λ is the wavelength of the laser beam. Therefore, average Δn induced in the beam center can be estimated by Eq. (1) if $\Delta n(z)$ is assumed to be uniform along the propagation direction. It was reported that the diffraction rings also could be formed with the photothermal effect of dye molecules absorbing light in dye-doped LCs [17]. To confirm the origin of the diffraction rings, either director reorientation of LCs or photothermal refractive-index change, transmitted light through the sample cell was measured by a pump-probe method. Linearly polarized light at 633 nm from a He-Ne laser was used as a probe beam, and it was incident to the sample cell at the same position as the spot of the 488-nm laser beam. Bright diffraction rings were observed when the polarization of the probe beam and the 488-nm laser beam were parallel to each other, while no diffraction rings were formed when they were perpendicular to each other. This result is significantly different from those observed in the photothermal effect, where diffraction rings should have no polarization dependence due to heat that conducts isotropically. Therefore, it is assumed that the director reorientation of LCs causes the formation of diffraction rings. The details of mutual influences between the director reorientation and the thermal effect will be discussed elsewhere.

Change in Δn induced in the dye-doped cell as a function of light intensity is shown in Figure 6. The value of Δn was calculated with Eq. (1) by measuring the number of diffraction rings observed on the screen. Above the threshold intensity, the ring appeared and the number of the ring increased with the light intensity, indicating the increase in Δn. Further irradiation with a high-intensity laser beam brought about the distortion of the rings on the screen due to a thermal effect of dye molecules absorbing light at high intensity. The maximum values of Δn were found to be about 0.12 in all dye-doped samples, which is almost the same as those of the **TR5**-doped or undoped **5CB** [4,16]. These results suggest that end substituents and aromatic rings are irrelevant to the maximum values of Δn. On the other hand, the threshold intensity significantly depended on

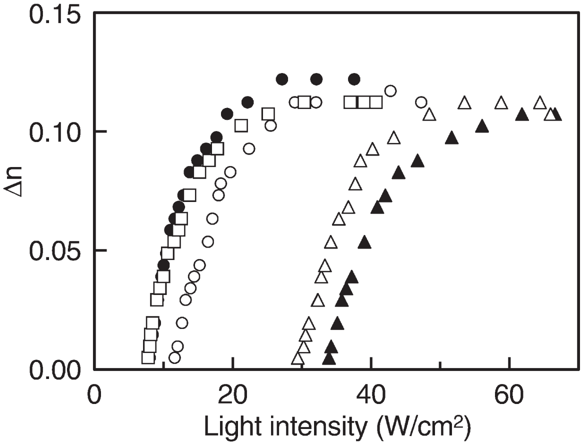


FIGURE 6 The value of Δn induced by the laser beam as a function of light intensity. (▲) **TP1;** (△) **TP2;** (●) **TP3;** (○) **TP4;** (□) **TP5**.

the dye structure: 34 W/cm^2 for **TP1**, 29 W/cm^2 for **TP2**, 8.0 W/cm^2 for **TP3**, 12 W/cm^2 for **TP4**, and 7.8 W/cm^2 for **TP5**, respectively. The introduction of cyano or ester moieties to **TP1** effectively reduces the threshold intensity by about 4 times.

CONCLUSION

The end-substituted phenylene-thienylene co-oligomers were newly synthesized. All the compounds exhibited an LC phase in a wide temperature range. By doping with only a small amount of dye molecules, the LC phases were stabilized. When the dye-doped LCs were exposed to the laser beam, the transmitted light formed diffraction patterns on a screen due to the self-modulation effect. The change in refractive index was estimated to be larger than 0.1. It was revealed that **TP3** and **TP5** act as an efficient trigger for the photoinduced reorientation of nematic LCs.

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