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Synthesis, Phase-transition Behaviors, and Birefringence Properties of Fluorinated Diphenyl–Diacetylene Derivatives

Yuki Arakawa, Sungmin Kang,* Junji Watanabe, and Gen-ichi Konishi*
Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552

(E-mail: konishi.g.aa@m.titech.ac.jp; skang@polymer.titech.ac.jp)

We designed fluorinated diphenyl–diacetylene-based liquid crystal (LC) molecules that exhibit enantiotropic nematic phases near room temperature. These LC molecules also show high birefringence ($\Delta n \approx 0.35$) similar to their non-fluorinated analogs. The introduction of fluorine atoms into LC molecules can decrease the phase-transition temperature without decreasing birefringence.

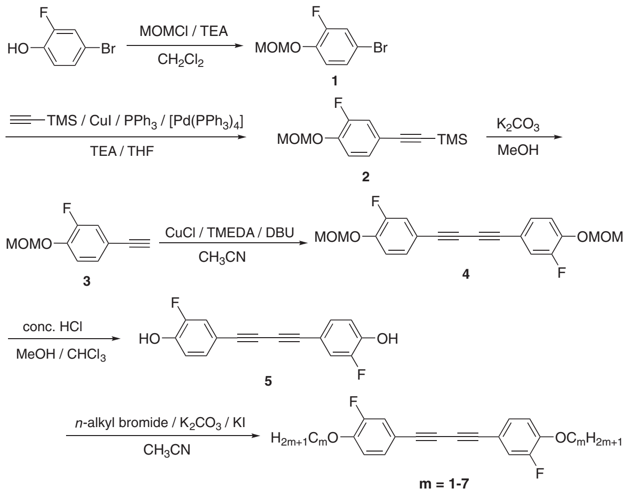
High birefringence (Δn) materials have considerable significance in liquid crystal display (LCD) technologies,[1] cholesteric (Ch) films with broad light reflection bands,[2] Ch laser films,[3] and holographic memory devices.[4] However, the high phase-transition temperatures of these materials pose a challenge, as high birefringence materials are generally constructed with highly anisotropic molecular structures.[5] Recently, we have reported that diphenyl–oligoyne systems that include alkoxy diphenyl–diacetylene derivatives (DPDA–OC*m*) exhibit high birefringence properties, but these anisotropic compounds also have high transition temperatures.[6]

As a strategy to decrease phase-transition temperatures of LC compounds, introduction of fluorine atoms into the mesogenic moiety of LC materials is often utilized.[5f,7] In addition, fluorinated LC molecules are of great interest for the basic chemistry of LCs.[8]

In this study, we synthesized 3,3′-difluoro-4,4′-dialkoxydiphenyldiacetylene (F)-DPDA–OC*m* derivatives (alkoxy number $m = 1$–7), in addition to the previously reported DPDA–OC*m* derivatives (alkoxy number $m = 1$–7), and investigated their phase-transition behaviors and birefringence properties.

A series of fluorinated diphenyl–diacetylenes with alkoxy tails, (F)-DPDA–OC*m*, were synthesized according to Scheme 1. The synthesis and characterization of the obtained compounds are described in detail in the Supporting Information.

The thermal behavior of (F)-DPDA–OC*m* was investigated using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The phase-transition temperatures and enthalpy changes measured during the cooling scans are listed in Table 1; for comparison, the data for the unsubstituted DPDA–OC*m* systems are also shown in Table 1, and the DSC thermogram of (F)-DPDA–OC6 is shown in Figure S1. The transition temperatures $T_{\mathrm{I-N}}$ (isotropic to nematic) and T_c (nematic to crystalline) of the series of (F)-DPDA–OC*m* derivatives are plotted against the number of carbon atoms *m* in Figure S2.



Scheme 1. Synthesis of (F)-DPDA–OC*m*.

Table 1. Phase transition temperatures (°C) and enthalpies (ΔH, kJ mol^{-1}) of DPDA–OC*m* and (F)-DPDA–OC*m* (cooling differential scanning calorimetry analysis at 10 °C min^{-1})

Compound	Cr	Temp. (ΔH)	N	Temp. (ΔH)	Iso	T_m[a]	N width[b]
(F)-DPDA–OC1	•	150.0 (27.9)		—	•	162.8	—
(F)-DPDA–OC2	•	134.8 (23.3)		—	•	143.1	—
(F)-DPDA–OC3	•	68.4 (15.5)	•	87.0 (0.68)	•	90.9	19
(F)-DPDA–OC4	•	70.6 (28.1)	•	104.6 (1.35)	•	101.1	34
(F)-DPDA–OC5	•	34.8 (16.9)	•	80.2 (1.01)	•	67.5	45
(F)-DPDA–OC6	•	56.3 (22.4)	•	97.7 (1.23)	•	74.6	43
(F)-DPDA–OC7	•	40.9 (15.7)	•	76.1 (0.67)	•	58.8	35
DPDA–OC1	•	98.6 (23.8)	•	183.6 (1.65)	•	141.9	85
DPDA–OC2	•	187.3 (40.8)	•	208.8 (1.66)	•	192.0	22
DPDA–OC3	•	123.4 (17.5)	•	175.2 (1.69)	•	139.5	52
DPDA–OC4	•	149.3 (42.7)	•	173.6 (2.26)	•	157.5	24
DPDA–OC5	•	110.1 (33.3)	•	153.1 (1.90)	•	119.1	43
DPDA–OC6	•	115.3 (41.8)	•	147.5 (2.01)	•	123.5	32
DPDA–OC7	•	92.7 (23.7)	•	134.6 (1.71)	•	104.6	42

[a]Measured on heating scan. [b]Evaluated from $T_{\mathrm{I-N}} - T_c$.

Almost all the compounds studied in this work exhibited a mesophase during the thermal phase transition. (F)-DPDA–OC*m* homologs with $m = 4$–7 exhibited enantiotropic nematic (N) phases, whereas (F)-DPDA–OC3 showed a monotropic N phase during the cooling scan. A POM image of (F)-DPDA–OC6 is shown in the Supporting Information (Figure S3), which exhibits a typical N phase. In contrast, (F)-DPDA–OC1 and (F)-DPDA–OC2 did not show mesophases because of the enhanced crystallinity obtained when short alkoxy chains were used. Notably, these compounds exhibited only nematic phases, despite being substituted at the position adjacent to the terminal position (the outer-edge position). Previously reported rod-like LC compounds (e.g., *p*-terphenyl derivatives) are known to exclusively form smectic C (SmC) phases when a fluorine atom is introduced at this position because fluoro substituents in the outer-edge positions fill any empty space with their polar C–F units.[9] On the basis of our previous studies, we assumed that for (F)-DPDA–OC*m*, the dumbbell-shaped mesogen would prevent microphase separation.[6a] According to previous studies, (F)-DPDA–OC*m* derivatives with $m \geq 8$ exhibit SmC behavior.[10]

As expected, the transition temperatures of the (F)-DPDA–OC*m* derivatives oscillated according to an odd–even effect with respect to the number of alkoxy tail carbons; that is, even-*m* derivatives have higher transition temperatures than odd-*m* derivatives. Both the transition temperatures, $T_{\text{I–N}}$ and T_c, of the series of (F)-DPDA–OC*m* derivatives were found to be significantly lower than those of the series of DPDA–OC*m* derivatives with the same alkoxy tails. For example, the T_c and $T_{\text{I–N}}$ values of DPDA–OC5 decreased from 110.1 to 34.8 °C, and from 153.1 to 80.2 °C, respectively, on fluorine substitution.

However, the magnitude of the temperature range for the N phase of each compound is unchanged, with the exception of (F)-DPDA–OC1 and (F)-DPDA–OC2, which, unlike their DPDA–OC*m* analogs, exhibit no liquid crystallinity. Compounds with shorter alkoxy tails are close to a crystal phase, while those with longer tails are close to a smectic phase. As a result, (F)-DPDA–OC5 and (F)-DPDA–OC6 would have the widest N width.

The enthalpy changes (ΔH) for (F)-DPDA–OC*m* and DPDA–OC*m* at $T_{\text{I–N}}$ and T_c are shown in Table 1. In all cases, the ΔH values for the (F)-DPDA–OC*m* derivatives are smaller than those for the DPDA–OC*m* derivatives. This reduction in ΔH values occurs because fluoro substitution at the lateral positions interferes with crystal packing and decreases intermolecular attractive interaction. Importantly, such reduced ΔH values may lead to good miscibility with other LC materials in eutectic mixtures. The total ΔH at $T_{\text{I–N}}$ and T_c follows an odd–even trend; that is, ΔH values are smaller for odd-*m* derivatives. In addition, the larger ΔH value at T_c for (F)-DPDA–OC1 than for DPDA–OC1 occurs because (F)-DPDA–OC1 does not have a mesophase, unlike DPDA–OC1; the ΔH value for the mesophase-to-crystal phase transition is typically larger than that of the isotropic-to-mesophase transition.

Next, to examine the effect of introducing fluorine atoms in the outer-edge position on refractive index, we measured the refractive index values of extraordinary (n_e) and ordinary rays (n_o) for fluoro-substituted and nonsubstituted compounds with the same tail length, namely (F)-DPDA–OC6 and DPDA–OC6, using microscopic spectroscopy with the multiple-beam interference (MBI) theory, as described in our previous study;[11] the gained transmitted light and fitting curve for (F)-DPDA–OC6 are shown in Figure S4.

The dependence of the n_e, n_o, and Δn ($n_e - n_o$) values of (F)-DPDA–OC6 on the wavelength is shown in Figure S5. These results show a positive wavelength dispersion, which is typical of rod-like molecules. In addition, the temperature dependence of the n_e, n_o, and Δn values at 550 nm at a reduced temperature $T_i - T$ is shown in Figure 1, which reveals that the n_e value increases, whereas the n_o value decreases when temperature is decreased, and the Δn value also increases with a decrease in temperature. As shown in Figure 1a, interestingly, the n_e and n_o values of (F)-DPDA–OC6 are lower than those of DPDA–OC6 over the entire N phase. This result suggests that the introduction of fluorine atoms leads to a decrease of the mean refractive index ($\langle n \rangle$) from 1.64 for DPDA–OC6 to 1.60 for (F)-DPDA–OC6 in their mesophases. This decrease may be caused by the lower molecular density of (F)-DPDA–OC6 owing to its expanded rotational volume, which is caused by the introduction of the fluorine atom. In contrast, the Δn values did not change upon the introduction of fluorine at a reduced temperature of 28 °C, and the Δn value for both compounds was 0.31 at 550 nm.

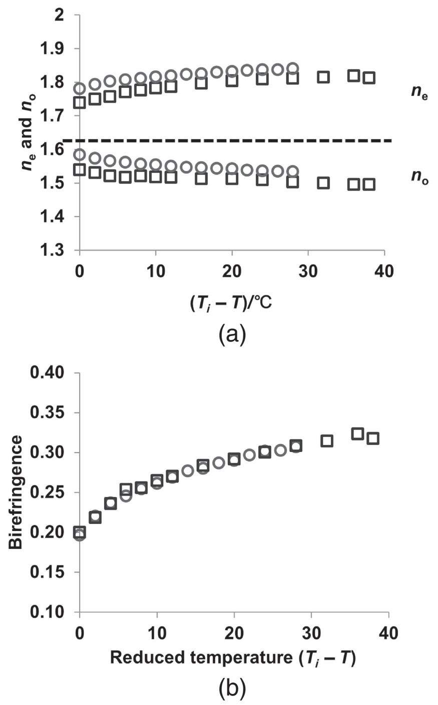


Figure 1. (a) Temperature dependence of the extraordinary (n_e) and ordinary refractive index (n_o) of (F)-DPDA–OC6 (square plot) and DPDA–OC6 (circle plot) at 550 nm. (b) Temperature dependence of birefringence (Δn) of (F)-DPDA–OC6 (square plot) and DPDA–OC6 (circle plot) at 550 nm.

Finally, the temperature dependence of Δn for (F)-DPDA–OC3–7 was measured using microscopic spectroscopy, as shown in Figure S6. The Δn values were compared at the lowest temperature measured immediately before crystallization: 72 °C for OC3, 72 °C for OC4, 39 °C for OC5, 58 °C for OC6, and 43 °C for OC7. At these temperatures, the Δn values were the highest for each compound. All the compounds exhibited very high Δn values (over 0.3), and the Δn values decreased in the following order: OC4 > OC3 > OC6 > OC5 > OC7, probably depending on each N phase range. In addition, the Δn_0 values (i.e., the associated Δn values for the perfectly aligned condition; order parameter $(S) = 1$) were estimated by fitting the curve to the following equations: $\Delta n = \Delta n_0 S$ and $S = (1 - T/T_{\text{I–N}})^{\beta}$, where T and T_i are the measurement temperature (T) and clearing temperature ($T_{\text{I–N}}$), respectively, for which the method has been described in previous reports.[6b] The exponent β depends on the molecular structure, and its value is close to 0.2. All estimated values are shown in Table 2 for (F)-DPDA–OC3–7. The Δn_0 values are very high and nearly unchanged compared with those previously reported for DPDA.[6b]

Table 2. Δn, Δn_0, and β values gained from fitting to $\Delta n = \Delta n_0(1 - T/T_i)^{\beta}$

	Δn^{a}	Δn_0	β
(F)-DPDA–OC3	0.333	0.589	0.20
(F)-DPDA–OC4	0.365	0.562	0.18
(F)-DPDA–OC5	0.356	0.540	0.22
(F)-DPDA–OC6	0.328	0.494	0.19
(F)-DPDA–OC7	0.308	0.489	0.23

[a] Evaluated at the lowest measurement temperatures.

In summary, we synthesized a series of fluorinated DPDA–OC*m* derivatives in order to obtain lower phase-transition temperatures. All these compounds exclusively exhibited enantiotropic nematic phases. Specifically, in the case of (F)-DPDA–OC5, the crystallization temperature was successfully reduced to ca. 34 °C. The birefringence and refractive index measurements revealed that the (F)-DPDA–OC*m* derivatives are good candidates for optical materials exhibiting high birefringence performance.

Supporting Information is available electronically on J-STAGE.

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