Liquid crystalline conjugated oligomers: synthesis and mesomorphic properties of laterally and terminally alkyl-substituted oligo (1,4-phenyleneethynylene)s†

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A new series of liquid crystalline conjugated oligomers, namely laterally and terminally alkyl-substituted derivatives of oligo(1,4-phenyleneethynylene)s, were synthesized, and the relationships between the molecular structures and the mesomorphic properties were investigated. The mesomorphic properties of the oligomer derivatives were examined by differential scanning calorimetry and polarizing microscopy. In the alkyl-substituted oligomers with varying core lengths, $C_8H_{17}C_6H_4CC[C_6H_2(C_2H_5)_2CC]_nC_6H_4C_8H_{17}$ where $n = 2$–5, the trimer ($n = 2$) exhibited a monotropic nematic phase, and the others showed enantiotropic nematic phases. In the alkyl-substituted tetramers, $R^1C_6H_4CC[C_6H_2(R^2)_2CC][C_6H_2(R^3)_2CC][C_6H_2(R^2)_2CC]C_6H_4R^1$ where R^1, R^2, and R^3 = alkyl chains of varying lengths and H, most of the tetramer derivatives exhibited nematic phases, whereas the others did not show any mesophases. It was found that the formation of the mesophase and the crystalline–nematic and nematic–isotropic transition temperatures are strongly affected by the structural features of the oligomer molecules: (i) the length of the oligomer core, (ii) the length, number, and position of the lateral chains, and (iii) the length of the terminal chains.

Introduction

Liquid crystals are functional self-assembling structures that combine the fluidity and orientational order of the constituent molecules.[1–5] Recently, liquid crystals formed by linear conjugated oligomers have attracted considerable attention because of their anisotropic optical and electrical properties such as photo- and electroluminescence, charge carrier mobility, *etc*.[6–18] These properties depend on both the electrons delocalized over the oligomer backbone and the liquid crystalline order of the conjugated molecules.[8,11,19,20] However, most of the recent interest has focused on the optical and electrical properties, and there have been few systematic studies of the mesomorphic properties.[21,22] The design and synthesis of conjugated oligomer derivatives for the understanding and control of the mesomorphic properties should constitute an important part of oligomer liquid crystal research.

Low molecular weight mesogens are generally composed of a rod-like core (*e.g.* biphenyl) and one or two flexible end-groups (*e.g.* alkyl and alkoxy chains).[1,23,24] When the core is a conjugated oligomer backbone, in addition to terminal chains, several lateral chains are needed to increase the solubility and to reduce the transition temperatures (Fig. 1). The mesomorphic properties of the conjugated oligomer derivatives should depend on the following structural features: (i) the shape and length of the core, (ii) the length, number, and positions of the lateral chains, and (iii) the length and number of the terminal chains. It has been reported that some derivatives of conjugated oligomers, for example, phenylene-,[25–27] fluorene-,[28–30] phenylenevinylene-,[31–34] and phenyleneethynylene-based[35,36] oligomers, exhibit liquid crystalline mesophases. In these oligomer derivatives, however, few systematic structural variations have been achieved in either the oligomer core or the lateral and terminal chains. There are too few examples to allow us to understand the relationships between the molecular structures and the mesomorphic properties of liquid crystalline conjugated oligomers.

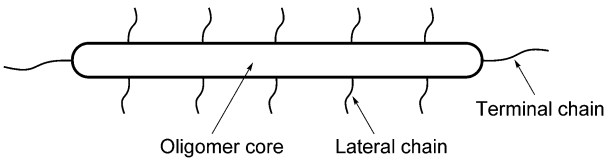

Fig. 1 Schematic representation of a conjugated oligomer with lateral and terminal chains.

We chose oligo(1,4-phenyleneethynylene) derivatives as a suitable family with which to investigate the structure–property relationships for a number of reasons. First, the tolane (diphenylacetylene) derivatives are representatives of liquid crystals that form nematic phases.[37–40] The mesophase is the simplest liquid crystal phase, in which the molecules have only orientational long-range order.[1] It has also been reported that the phenyleneethynylene-based dimers, $R(C_6H_4CC)_2C_6H_4R$ where R = alkyl[41,42] and alkoxy[43,44] chains, and the dimers with a single lateral ethyl chain, $RC_6H_4CC[C_6H_3(C_2H_5)CC]C_6H_4R$ where R = alkyl chains,[45,46] exhibit nematic phases. Therefore, it is expected that laterally and terminally alkyl-substituted derivatives of the longer oligomers will also exhibit nematic phases.

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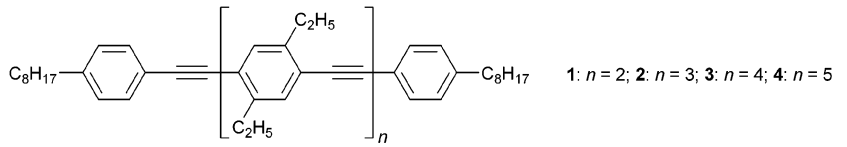
Second, the oligomer backbones are linear cores with very little conformational deviation.[47,48] One would expect it to be easier to understand the structure–property relationships of the alkyl-substituted derivatives because they have straightforward molecular structures and the simplest mesophase. Finally, convenient methods have been developed for synthesizing monodisperse linear oligomers.[49–52] The synthetic procedures involve the Sonogashira coupling reaction[53] of aryl halides with terminal alkynes and the deprotection of silylalkynes. These reactions proceed with excellent chemoselectivity under mild conditions to give the desired products with high yields. Therefore, various types of alkyl-substituted derivatives of the oligomers can be easily synthesized.

In the present study, we synthesized a series of laterally and terminally alkyl-substituted oligo(1,4-phenyleneethynylene)s, $C_8H_{17}C_6H_4CC[C_6H_2(C_2H_5)_2CC]_nC_6H_4C_8H_{17}$ where n = 2–5 (**1–4**, Fig. 2), and investigated their mesomorphic properties. Trimer **1**[54] exhibited a monotropic nematic phase, and tetramer **2**, pentamer **3**, and hexamer **4** exhibited enantiotropic nematic phases. The results show that the oligomer core length is an important factor in mesophase behavior. Next, tetramers **5a–c**, **6a,b**, and **7a–f**, which are related to tetramer **2**, were designed and synthesized. Tetramers **5a**, **6a**, and **7a–f** exhibited nematic phases, whereas tetramers **5b,c** and **6b** did not. Their mesomorphic properties were found to be strongly affected by the length, number, and position of the lateral chains. In addition, tetramers **8a–e** and **9a–e** were synthesized to investigate the effects of the lateral and terminal chains on the mesomorphic properties. We found that their transition temperatures are strongly affected by both the structure of the lateral chains and the length of the terminal chains.

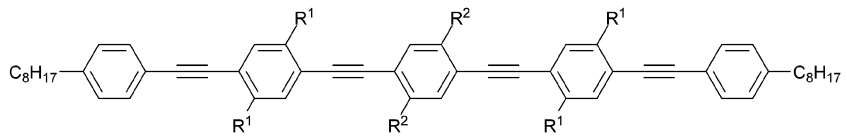
Experimental

General methods

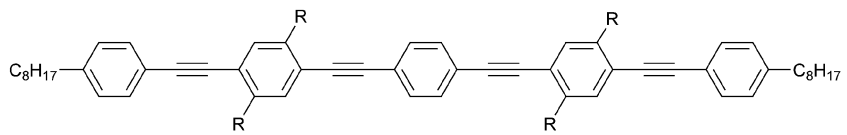
Column chromatography was performed with Merck silica gel 60 (0.063–0.200 mm). The final products were purified by high performance liquid chromatography (HPLC), which was carried out with a preparative chromatograph equipped with a JASCO PU-2086 HPLC pump, a JASCO RI-2031 refractive index detector, and two GPC columns in series (Shodex K-2002 and



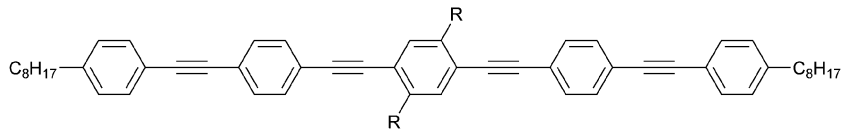
1: n = 2; **2**: n = 3; **3**: n = 4; **4**: n = 5



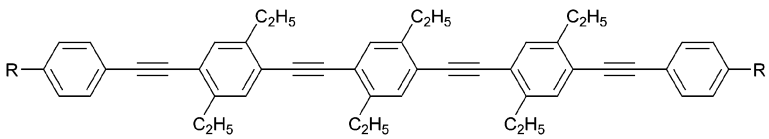
5a: $R^1 = C_2H_5$, $R^2 = C_3H_7$; **5b**: $R^1 = C_2H_5$, $R^2 = C_6H_{13}$; **5c**: $R^1 = R^2 = C_3H_7$



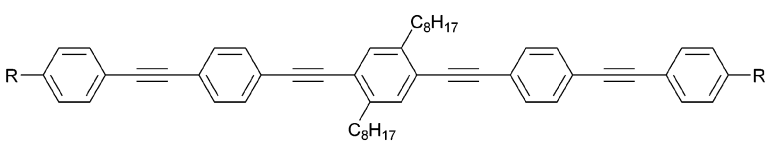
6a: R = C_2H_5; **6b**: R = C_3H_7



7a-f: R = C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_8H_{17}



8a-e: R = H, CH_3, C_2H_5, C_3H_7, C_4H_9



9a-e: R = H, CH_3, C_2H_5, C_3H_7, C_4H_9

Fig. 2 Structures of oligomers **1–4**, **5a–c**, **6a,b**, **7a–f**, **8a–e**, and **9a–e**.

2002.5). Chloroform was used as eluent at a flow rate of 3.0 or 3.5 mL min^{-1}. The chemical structures of the compounds were characterized by ^1H and ^{13}C NMR spectra, recorded in $CDCl_3$ on a Varian INOVA 400 spectrometer (400 MHz for protons, 100 MHz for carbon) using tetramethylsilane as an internal standard. The melting points were determined with a Laboratory Devices Mel-Temp II melting point apparatus and are uncorrected. Elemental analyses were carried out on a CE Instruments EA 1110. Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) was conducted using a Finnigan AQA mass spectrometer.

The mesomorphic properties of the compounds were examined by differential scanning calorimetry (DSC) and polarizing microscopy. The transition temperatures and the associated enthalpy values were determined on a Perkin-Elmer DSC 7 differential scanning calorimeter equipped with a Perkin-Elmer TAC 7/DX thermal analysis controller. The apparatus was operated at a scanning rate of 2 °C min^{-1} for both heating and cooling. Indium (156.60 °C; 28.45 J g^{-1}) was employed as a standard for calibrating temperature and enthalpy. Phase identification was performed using polarizing microscopy. The optical textures in the mesophases were observed using a Leitz Orthoplan-Pol polarizing microscope equipped with a Mettler FP82HT hot stage and a Mettler FP80 central processor.

Materials

Bis(triphenylphosphine)palladium(II) dichloride and copper(I) iodide were purchased from Tokyo Chem. Ind. (TCI) and Wako Pure Chem. Ind. (Wako), respectively. Piperidine and tetrahydrofuran were purchased from Wako and used without further purification for the Sonogashira coupling. Iodobenzene (**10a**), 4-iodotoluene (**10b**), and 1-alkyl-4-iodobenzenes where alkyl = ethyl, propyl, and butyl (**10c–e**) were purchased from Aldrich, TCI, and Wako, respectively. 1-Iodo-4-octylbenzene (**10f**) was prepared by a halogen exchange reaction[50b] with commercially available 1-bromo-4-octylbenzene from TCI. Starting with commercially available 1,4-dibromo-2,5-diethylbenzene from Junsei Chem., (2,5-diethyl-4-iodophenyl)ethynyltrimethylsilane (**11**)[55a] was prepared in the same way as that described for the dihexyl-substituted derivative.[50b]

Tetraethyl-substituted dimer **12** was prepared from iodobenzene **11** according to the procedure described for the related dimer without lateral chains.[51a] Hexaethyl-substituted trimer **13** was prepared by Sonogashira coupling of 1,4-diethyl-2,5-diethynylbenzene[55b] with iodobenzene **11** and then desilylation according to the procedure described for the hexahexyl-substituted trimer.[52a] Alkyl-substituted trimers **16a–c**, **17a,b**, and **18a–f** were also prepared by Sonogashira coupling and then desilylation using a previously described procedure.[50,52a]

Synthesis

Synthetic procedures and characterization data for intermediates **14a,b** and **15a,b** and tetramers **7c–f**, **8b–e**, and **9b–e** are described in the ESI.†

Compound 1. A mixture of **12** (180 mg, 0.533 mmol), **10f** (417 mg, 1.32 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 0.031 mmol), and CuI (22 mg, 0.12 mmol) in piperidine (10 mL) was stirred for 18 h at room temperature. Cyclohexane (50 mL) was added to the reaction mixture. The mixture was washed with an NH_4Cl aqueous solution. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel with CH_2Cl_2–hexane (1 : 4). The crude product was purified by HPLC. Yield: 312 mg (82%) of a white solid; phase transition (°C): Cr 74 I. ^1H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H), 1.23–1.36 (m, 32H), 1.57–1.66 (m, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.86 (q, J = 7.6 Hz, 4H), 2.87 (q, J = 7.6 Hz, 4H), 7.17 (d, J = 8.0 Hz, 4H), 7.39 (s, 4H), 7.45 (d, J = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 14.10, 14.73, 14.97, 22.66, 27.21, 27.26, 29.25, 29.45, 31.29, 31.87, 35.93, 87.57, 92.81, 94.37, 120.55, 122.45, 122.71, 128.51, 131.40, 131.52, 131.65. Elemental analysis: calc. for $C_{54}H_{66}$: C, 90.70; H, 9.30; found: C, 90.79; H, 9.22%. APCI-MS: m/z = 715.9 ($[M + H]^+$, calc. 715.5).

Compound 2. Synthesized by the procedure described for **1**. Quantities: **13** (259 mg, 0.524 mmol), **10f** (406 mg, 1.28 mmol), $Pd(PPh_3)_2Cl_2$ (23 mg, 0.033 mmol), CuI (22 mg, 0.12 mmol), and piperidine (10 mL). Yield: 368 mg (81%) of a pale yellow solid; phase transitions (°C): Cr 100 N 137 I. ^1H NMR ($CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 6H), 1.23–1.36 (m, 38H), 1.57–1.66 (m, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.86 (q, J = 7.6 Hz, 4H), 2.87 (q, J = 7.6 Hz, 4H), 2.88 (q, J = 7.6 Hz, 4H), 7.17 (d, J = 8.2 Hz, 4H), 7.39 (s, 4H), 7.41 (s, 2H), 7.45 (d, J = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 14.10, 14.72, 14.98, 15.00, 22.66, 27.21, 27.27, 27.30, 29.24, 29.26, 29.45, 31.29, 31.87, 35.93, 87.56, 92.77, 92.98, 94.41, 120.55, 122.41, 122.68, 122.75, 128.51, 131.40, 131.53, 131.66, 131.73, 143.23, 143.29, 143.39, 143.52. Elemental analysis: calc. for $C_{66}H_{78}$: C, 90.98; H, 9.02; found: C, 90.83; H, 8.85%. APCI-MS: m/z = 872.3 ($[M + H]^+$, calc. 871.6).

Compound 3. Synthesized by the procedure described for **1**. Quantities: **14b** (253 mg, 0.389 mmol), **10f** (378 mg, 1.20 mmol), $Pd(PPh_3)_2Cl_2$ (18 mg, 0.026 mmol), CuI (14 mg, 0.074 mmol), and piperidine–THF (1 : 1, 40 mL). Yield: 304 mg (76%) of a pale yellow solid; phase transitions (°C): Cr 122 N 201 I. ^1H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H), 1.23–1.36 (m, 44H), 1.57–1.66 (m, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.86 (q, J = 7.6 Hz, 4H), 2.87 (q, J = 7.6 Hz, 4H), 2.88 (q, J = 7.6 Hz, 8H), 7.17 (d, J = 8.2 Hz, 4H), 7.39 (s, 4H), 7.41 (s, 4H), 7.45 (d, J = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 14.10, 14.72, 14.99, 15.01, 22.67, 27.22, 27.27, 27.30, 29.24, 29.26, 29.45, 31.29, 31.87, 35.93, 87.56, 92.76, 92.94, 93.02, 94.42, 120.55, 122.40, 122.65, 122.74, 122.77, 128.51, 131.40, 131.53, 131.66, 131.75, 143.24, 143.31, 143.40, 143.53. Elemental analysis: calc. for $C_{78}H_{90}$: C, 91.17; H, 8.83; found: C, 91.10; H, 8.67%. APCI-MS: m/z = 1028.6 ($[M + H]^+$, calc. 1027.7)

Compound 4. Synthesized by the procedure described for **1**. Quantities: **15b** (259 mg, 0.524 mmol), **10f** (406 mg, 1.28 mmol), $Pd(PPh_3)_2Cl_2$ (23 mg, 0.033 mmol), CuI (22 mg, 0.12 mmol), and piperidine–THF (1 : 1, 40 mL). Yield: 387 mg (76%) of a yellow solid; phase transitions (°C): Cr 159 N 258 I. ^1H NMR ($CDCl_3$): δ = 0.89 (t, J = 6.8 Hz, 6H), 1.23–1.36 (m, 50H), 1.57–1.66 (m, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.83–2.93 (m, 20H), 7.17 (d, J = 8.2 Hz, 4H), 7.40 (s, 4H), 7.41 (s, 6H), 7.45 (d, J = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 14.10, 14.73, 14.99, 15.02, 22.67, 27.22,

27.27, 27.30, 29.26, 29.45, 31.29, 31.87, 35.93, 87.56, 92.76, 92.93, 92.97, 93.02, 94.43, 120.55, 122.40, 122.64, 122.70, 122.75, 122.77, 128.51, 131.40, 131.53, 131.66, 131.76, 143.24, 143.32, 143.41, 143.53. Elemental analysis: calc. for $C_{90}H_{102}$: C, 91.32; H, 8.68; found: C, 91.31; H, 8.49%. APCI-MS: m/z = 1184.7 ([M + H]$^+$, calc. 1184.8).

Compound 5a. Synthesized by the procedure described for **1**. Quantities: **16a** (210 mg, 0.402 mmol), **10f** (356 mg, 1.13 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.040 mmol), CuI (33 mg, 0.17 mmol), and piperidine (15 mL). Yield: 261 mg (72%) of a pale yellow solid; phase transition (°C): Cr 103 I. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H), 1.03 (t, J = 7.6 Hz, 6H), 1.23–1.36 (m, 32H), 1.57–1.66 (m, 4H), 1.70–1.81 (m, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.82 (t, J = 7.6 Hz, 4H), 2.86 (q, J = 7.6 Hz, 4H), 2.87 (q, J = 7.6 Hz, 4H), 7.17 (d, J = 8.2 Hz, 4H), 7.386 (s, 2H), 7.389 (s, 4H), 7.45 (d, J = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 14.06, 14.10, 14.69, 14.93, 22.66, 23.91, 27.20, 29.24, 29.26, 29.45, 31.29, 31.87, 35.93, 36.28, 87.57, 92.85, 93.02, 94.41, 120.55, 122.45, 122.73, 122.77, 128.51, 131.40, 131.47, 131.66, 132.56, 141.76, 143.13, 143.38, 143.52. Elemental analysis: calc. for $C_{68}H_{82}$: C, 90.81; H, 9.19; found: C, 91.12; H, 9.09%. APCI-MS: m/z = 900.3 ([M + H]$^+$, calc. 899.6).

Compound 5b. Synthesized by the procedure described for **1**. Quantities: **16b** (204 mg, 0.336 mmol), **10f** (285 mg, 0.901 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.030 mmol), CuI (20 mg, 0.11 mmol), and piperidine (20 mL). Yield: 223 mg (68%) of a pale yellow solid; phase transition (°C): Cr 91 I. ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, J = 6.8 Hz, 12H), 1.23–1.37 (m, 40H), 1.47–1.38 (m, 4H), 1.57–1.66 (m, 4H), 1.66–1.76 (m, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.83 (t, J = 7.6 Hz, 4H), 2.86 (q, J = 7.6 Hz, 4H), 2.87 (q, J = 7.6 Hz, 4H), 7.17 (d, J = 8.2 Hz, 4H), 7.38 (s, 2H), 7.39 (s, 4H), 7.45 (d, J = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 14.10, 14.70, 14.88, 22.66, 27.19, 29.24, 29.26, 29.34, 29.45, 30.81, 31.29, 31.81, 31.87, 34.31, 35.93, 87.58, 92.84, 93.04, 94.40, 120.55, 122.48, 122.71, 122.73, 128.51, 131.40, 131.44, 131.66, 132.45, 142.00, 143.12, 143.37, 143.52. Elemental analysis: calc. for $C_{74}H_{94}$: C, 90.37; H, 9.63; found: C, 90.39; H, 9.53%. APCI-MS: m/z = 984.6 ([M + H]$^+$, calc. 983.7).

Compound 5c. Synthesized by the procedure described for **1**. Quantities: **16c** (233 mg, 0.385 mmol), **10f** (348 mg, 1.10 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.030 mmol), CuI (22 mg, 0.12 mmol), and piperidine (10 mL). Yield: 281 mg (76%) of a pale yellow solid; phase transition (°C): Cr 102 I. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H), 1.01 (t, J = 7.6 Hz, 6H), 1.017 (t, J = 7.6 Hz, 6H), 1.021 (t, J = 7.6 Hz, 6H), 1.23–1.36 (m, 20H), 1.57–1.66 (m, 4H), 1.70–1.81 (m, 12H), 2.62 (t, J = 7.6 Hz, 4H), 2.77–2.85 (m, 12H), 7.17 (d, J = 8.2 Hz, 4H), 7.37 (s, 4H), 7.38 (s, 2H), 7.44 (d, J = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 14.01, 14.07, 14.10, 22.66, 23.75, 23.79, 29.24, 29.26, 29.45, 31.29, 31.87, 35.93, 36.15, 36.20, 87.79, 92.89, 93.07, 94.26, 120.59, 122.56, 122.81, 122.83, 128.52, 131.37, 132.27, 132.55, 141.61, 141.64, 141.91, 143.50. Elemental analysis: calc. for $C_{72}H_{90}$: C, 90.51; H, 9.49; found: C, 90.58; H, 9.39%. APCI-MS: m/z = 956.5 ([M + H]$^+$, calc. 955.7).

Compound 6a. Synthesized by the procedure described for **1**. Quantities: **17a** (158 mg, 0.361 mmol), **10f** (258 mg, 0.816 mmol), $Pd(PPh_3)_2Cl_2$ (13 mg, 0.019 mmol), CuI (13 mg, 0.068 mmol), and piperidine–THF (2 : 1, 15 mL). Yield: 208 mg (71%) of a pale yellow solid; phase transitions (°C): Cr 97 N 155 I. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H), 1.23–1.36 (m, 32H), 1.57–1.66 (m, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.85 (q, J = 7.6 Hz, 8H), 7.17 (d, J = 8.2 Hz, 4H), 7.39 (s, 4H), 7.45 (d, J = 8.2 Hz, 4H), 7.51 (s, 4H); ^{13}C NMR ($CDCl_3$): δ = 14.10, 14.68, 14.73, 22.67, 27.17, 29.24, 29.26, 29.45, 31.29, 31.87, 35.93, 87.52, 90.25, 93.70, 94.50, 120.52, 121.96, 122.96, 123.26, 128.51, 131.41, 131.43, 131.50, 131.55, 143.39, 143.45, 143.55. Elemental analysis: calc. for $C_{62}H_{70}$: C, 91.35; H, 8.65; found: C, 91.25; H, 8.45%. APCI-MS: m/z = 816.2 ([M + H]$^+$, calc. 815.6).

Compound 6b. Synthesized by the procedure described for **1**. Quantities: **17b** (179 mg, 0.362 mmol), **10f** (294 mg, 0.930 mmol), $Pd(PPh_3)_2Cl_2$ (18 mg, 0.026 mmol), CuI (17 mg, 0.089 mmol), and piperidine (20 mL). Yield: 221 mg (70%) of a pale yellow solid; phase transition (°C): Cr 94 I. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 6H), 1.01 (t, J = 7.2 Hz, 6H), 1.02 (t, J = 7.2 Hz, 6H), 1.23–1.36 (m, 20H), 1.57–1.66 (m, 4H), 1.69–1.80 (m, 8H), 2.62 (t, J = 7.6 Hz, 4H), 2.80 (t, J = 7.6 Hz, 8H), 7.17 (d, J = 8.2 Hz, 4H), 7.36 (s, 4H), 7.44 (d, J = 8.2 Hz, 4H), 7.50 (s, 4H); ^{13}C NMR ($CDCl_3$): δ = 14.05, 14.10, 22.66, 23.72, 23.77, 29.23, 29.26, 29.45, 31.28, 31.87, 35.93, 36.16, 87.73, 90.47, 93.57, 94.37, 120.55, 122.07, 123.07, 123.28, 128.52, 131.38, 131.40, 132.31, 132.37, 141.93, 142.00, 143.52. Elemental analysis: calc. for $C_{66}H_{78}$: C, 90.98; H, 9.02; found: C, 90.98; H, 8.89%. APCI-MS: m/z = 872.3 ([M + H]$^+$, calc. 871.6).

Compound 7a. Synthesized by the procedure described for **1**. Quantities: **18a** (156 mg, 0.408 mmol), **10f** (311 mg, 0.984 mmol), $Pd(PPh_3)_2Cl_2$ (15 mg, 0.021 mmol), CuI (17 mg, 0.089 mmol), and piperidine–THF (1 : 1, 20 mL). Yield: 231 mg (75%) of a white solid; phase transitions (°C): Cr 158 N 261 I. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 6H), 1.23–1.36 (m, 26H), 1.57–1.66 (m, 4H), 2.62 (t, J = 7.6 Hz, 4H), 2.86 (t, J = 7.6 Hz, 4H), 7.17 (d, J = 8.0 Hz, 4H), 7.39 (s, 2H), 7.45 (d, J = 8.0 Hz, 4H), 7.50 (s, 8H); ^{13}C NMR ($CDCl_3$): δ = 14.10, 14.69, 22.66, 27.15, 29.23, 29.25, 29.44, 31.23, 31.86, 35.93, 88.51, 89.99, 91.60, 93.97, 120.10, 122.44, 122.98, 123.40, 128.51, 131.39, 131.50, 131.53, 131.60, 143.50, 143.73. Elemental analysis: calc. for $C_{58}H_{62}$: C, 91.77; H, 8.23; found: C, 91.43; H, 8.00%. APCI-MS: m/z = 760.0 ([M + H]$^+$, calc. 759.5).

Compound 7b. Synthesized by the procedure described for **1**. Quantities: **18b** (157 mg, 0.383 mmol), **10f** (328 mg, 1.04 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.020 mmol), CuI (17 mg, 0.089 mmol), and piperidine–THF (1 : 1, 20 mL). Yield: 221 mg (73%) of a white solid; phase transitions (°C): Cr 140 N 209 I. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 6H), 1.01 (t, J = 7.6 Hz, 6H), 1.23–1.36 (m, 20H), 1.57–1.66 (m, 4H), 1.75 (tq, J = 7.6 Hz, 8H), 2.61 (t, J = 7.6 Hz, 4H), 2.80 (t, J = 7.6 Hz, 4H), 7.17 (d, J = 8.2 Hz, 4H), 7.37 (s, 2H), 7.45 (d, J = 8.2 Hz, 4H), 7.47–7.52 (m, 8H); ^{13}C NMR ($CDCl_3$): δ = 14.04, 14.10, 22.67, 23.74, 29.24, 29.26, 29.44, 31.24, 31.87, 35.93, 36.14, 88.51, 90.21, 91.60, 93.84, 120.10, 122.56, 123.01, 123.28, 128.51, 131.35, 131.51, 131.53, 132.43, 142.04, 143.73. Elemental analysis: calc. for $C_{60}H_{66}$: C, 91.55; H, 8.45; found: C, 91.52; H, 8.27%. APCI-MS: m/z = 788.1 ([M + H]$^+$, calc. 787.5).

Compound 8a. Synthesized by the procedure described for **1**. Quantities: **13** (158 mg, 0.320 mmol), **10a** (214 mg, 1.05 mmol), $Pd(PPh_3)_2Cl_2$ (15 mg, 0.021 mmol), CuI (15 mg, 0.079 mmol), and piperidine (15 mL). Yield: 155 mg (75%) of a pale yellow solid; phase transition (°C): Cr 177 I. ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (t, $J = 7.6$ Hz, 6H), 1.325 (t, $J = 7.6$ Hz, 6H) 1.327 (t, $J = 7.6$ Hz, 6H), 2.87 (q, $J = 7.6$ Hz, 4H), 2.877 (q, $J = 7.6$ Hz, 4H), 2.884 (q, $J = 7.6$ Hz, 4H), 7.33–7.39 (m, 6H), 7.405 (s, 4H), 7.411 (s, 2H), 7.52–7.56 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 14.74$, 14.97, 15.00, 27.21, 27.27, 27.30, 88.21, 92.86, 92.93, 94.11, 120.50, 122.64, 122.68, 123.45, 128.28, 128.38, 131.50, 131.61, 131.69, 131.75, 143.26, 143.31, 143.49. Elemental analysis: calc. for $C_{50}H_{46}$: C, 92.83; H, 7.17; found: C, 92.76; H, 6.82%. APCI-MS: $m/z = 647.6$ ($[M + H]^+$, calc. 647.4).

Compound 9a. Synthesized by the procedure described for **1**. Quantities: **18f** (170 mg, 0.309 mmol), **10a** (157 mg, 0.770 mmol), $Pd(PPh_3)_2Cl_2$ (17 mg, 0.024 mmol), CuI (19 mg, 0.10 mmol), and piperidine–THF (1 : 2, 15 mL). Yield: 157 mg (72%) of a white solid; phase transition (°C): Cr 119 I. ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (t, $J = 7.0$ Hz, 6H), 1.21–1.45 (m, 20H), 1.66–1.75 (m, 4H), 2.81 (t, $J = 7.6$ Hz, 4H), 7.33–7.38 (m, 8H), 7.48–7.56 (m, 12H); ^{13}C NMR ($CDCl_3$): $\delta = 14.11$, 22.66, 29.28, 29.50, 29.56, 30.66, 31.90, 34.13, 89.11, 90.32, 91.29, 93.76, 122.50, 123.02, 123.10, 123.25, 128.38, 128.47, 131.37, 131.56, 131.63, 132.36, 142.33. Elemental analysis: calc. for $C_{54}H_{54}$: C, 92.26; H, 7.74; found: C, 91.82; H, 7.39%. APCI-MS: $m/z = 703.8$ ($[M + H]^+$, calc. 703.4).

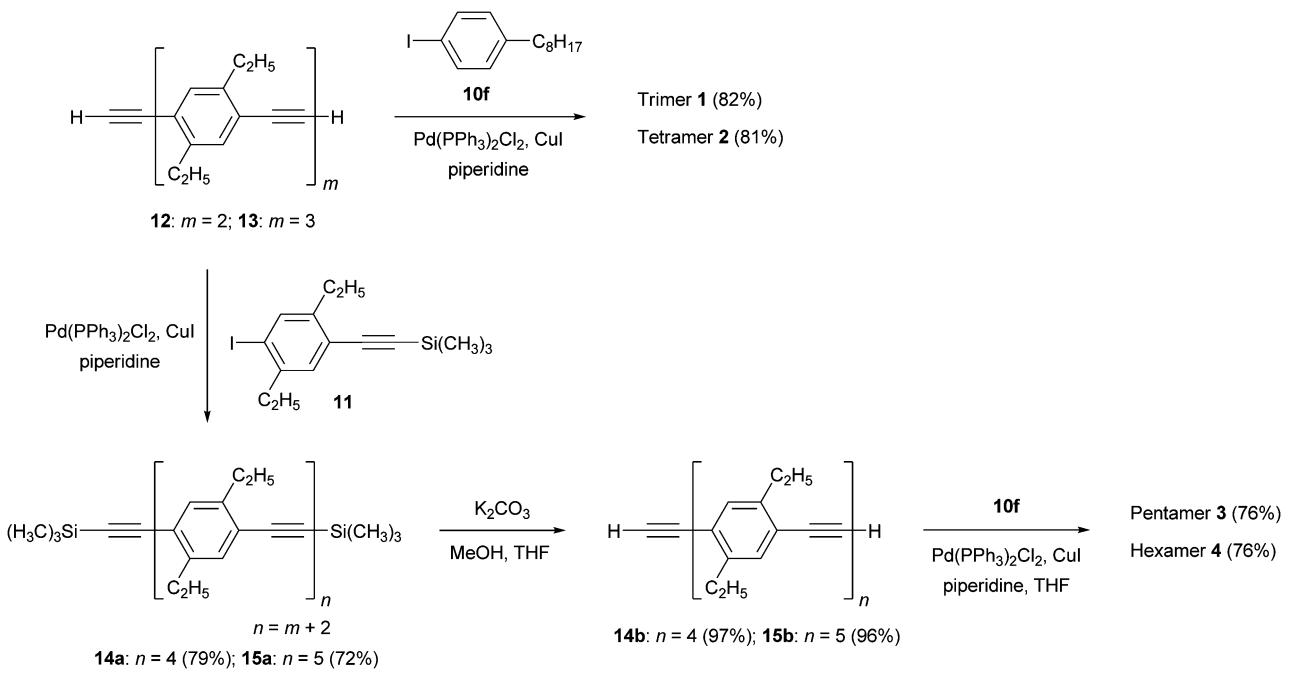
Results and discussion

Synthesis

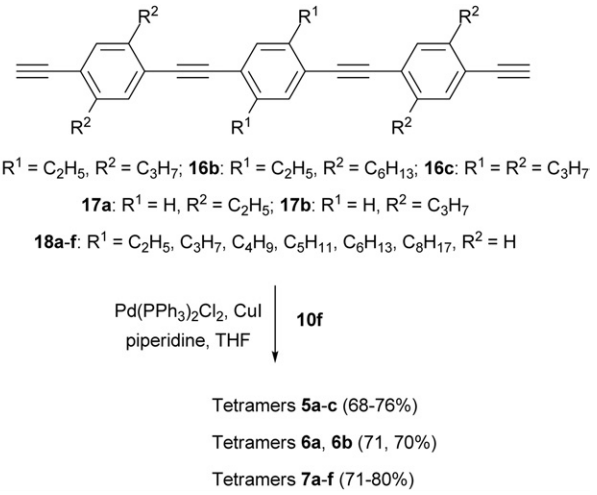
The synthesis of laterally ethyl- and terminally octyl-substituted oligomers **1–4** is shown in Scheme 1. Sonogashira coupling between phenyleneethynylene dimer **12**, with four lateral ethyl chains and two terminal acetylenes, and 1-iodo-4-octylbenzene **10f** gave trimer **1** with an 82% yield. The cross-coupling reaction of laterally hexaethyl-substituted trimer **13** with iodobenzene **10f** afforded tetramer **2** with an 81% yield. Trimer **1** is a white solid, whereas tetramer **2** is a pale yellow solid. These oligomers are soluble in common organic solvents such as hexane, dichloromethane, and THF.

Silyl-protected iodophenylacetylene **11** is a key building block for a stepwise approach to oligomers **3** and **4** by Sonogashira coupling. Thus, the cross-coupling between the building block and dimer **12** gave tetramer **14a** with a 79% yield, which was then desilylated to give tetramer **14b** with terminal acetylenes with a 97% yield. The final cross-coupling between tetramer **14b** and iodobenzene **10f** afforded the desired product **3** with a 76% yield. Hexamer **4** was synthesized in the same way starting from trimer **13**. Pentamer **3** is a pale yellow solid, and hexamer **4** is a yellow solid. These oligomers are soluble in cyclohexane, dichloromethane, THF, and hot hexane.

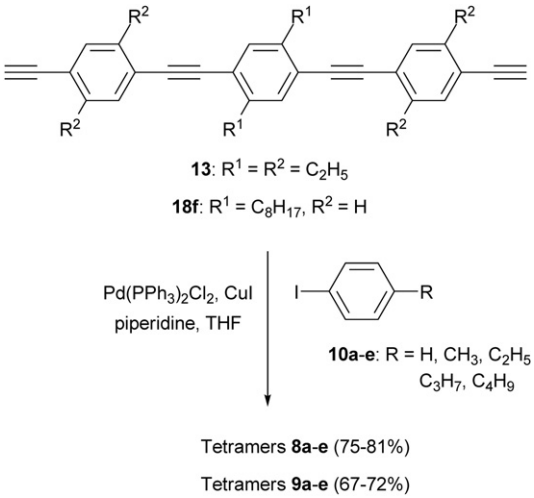
As shown in Scheme 2, tetramers **5a–c**, **6a,b**, and **7a–f**, which have lateral alkyl chains of different lengths and two terminal octyl chains, were synthesized by Sonogashira coupling. The cross-coupling between trimers **16a–c** and iodobenzene **10f** gave tetramer **5a–c** with six lateral chains with 68–76% yields. Tetramers **6a,b** with four lateral chains were prepared from trimers **17a,b** with 71 and 70% yields, respectively. Tetramers **7a–f** with two lateral chains were prepared from trimers **18a–f** with 71–80% yields. The synthesis of tetramers **8a–e**, with six ethyl lateral chains, and tetramers **9a–e**, with two octyl lateral chains, is shown in Scheme 3. Sonogashira coupling between trimer **13** and iodobenzene **10a–e** gave tetramers **8a–e** with 75–81% yields. Tetramers **9a–e** were prepared from trimer **18f** in the same way with 67–72% yields. All the alkyl-substituted tetramers are soluble in common organic solvents such as hexane, dichloromethane, and THF.



Scheme 1 Synthesis of alkyl-substituted oligo(1,4-phenyleneethynylene)s **1–4** with different core lengths.



Scheme 2 Synthesis of tetramers **5a–c**, **6a,b**, and **7a–f** with lateral alkyl chains of various lengths.



Scheme 3 Synthesis of laterally hexaethyl-substituted tetramers **8a–e** and laterally dioctyl-substituted tetramers **9a–e**.

Mesomorphic properties

The length of the oligomer core. Thermotropic data for oligomers **1–4** with different core lengths are summarized in Table 1. Trimer **1** exhibited a monotropic nematic phase. The Cr–I transition occurred at 74 °C on heating, and on cooling from the isotropic liquid a nematic Schlieren texture[56] was observed at temperatures between 72 and 35 °C (Fig. 3(a)). Slow crystallization occurred while the temperature was kept at 35 °C. Unlike trimer **1**, oligomers **2–4** exhibited enantiotropic nematic phases; the optical texture characteristics of the mesophase were observed both on heating and cooling (Fig. 3(b)–(d)). For tetramer **2** the mesophase was observed from 100 to 137 °C on heating and from 135 to 83 °C on cooling. For pentamer **3** the mesophase was observed from 122 to 201 °C on heating and from 199 to 108 °C on cooling. For hexamer **4** the mesophase occurred from 159 to 258 °C on heating and from 246 to 150 °C on cooling.

Table 1 Phase transition temperatures (°C) and transition enthalpies (in square brackets, kJ mol^{-1}) of compounds **1–4**

Compound	Phase transitions[a]
1	h: Cr 73.9 [66.6] I c: I 71.6 [−2.1] N 35.0 [−50.6] Cr
2	h: Cr 99.9 [43.2] N 136.5 [2.9] I c: I 135.1 [−2.9] N 83.1 [−41.6] Cr
3	h: Cr 122.1 [56.4] N 200.9 [4.0] I c: I 199.3 [−3.4] N 107.6 [−57.0] Cr
4	h: Cr 159.1 [52.1] N 258.4 [5.4] I c: I 246.2 [−3.6] N 150.3 [−51.5] Cr

[a] h = on heating; c = on cooling; Cr = crystalline phase; N = nematic phase; I = isotropic liquid.

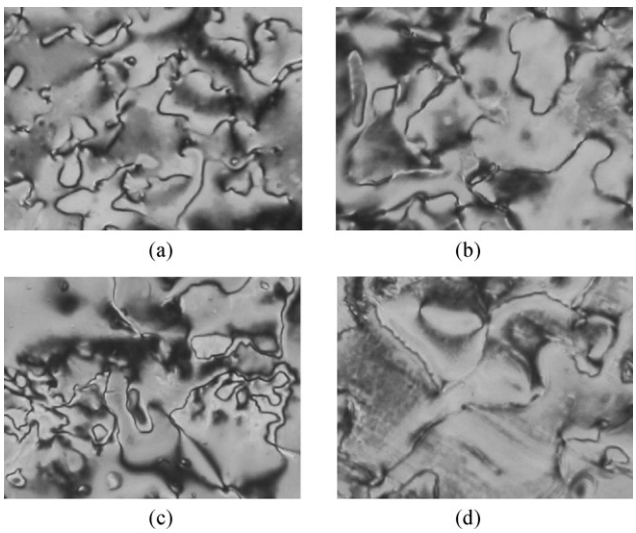


Fig. 3 Photomicrographs of the nematic phases of (a) trimer **1**, (b) tetramer **2**, (c) pentamer **3**, and (d) hexamer **4**.

In oligomers **2–4** both the Cr–N and N–I transition temperatures increased dramatically with increases in the number of diethyl-substituted phenyleneethynylene units (Cr–N: 100, 122, and 159 °C; N–I: 137, 201, and 258 °C for **2**, **3**, and **4**, respectively). In addition, a significant increase in the mesophase range was observed (37, 79, and 99 °C for **2**, **3**, and **4**, respectively).

These results show that the oligomer core length is an important factor as regards mesophase behavior. When the number of repeating units is increased, both the core length and the number of lateral chains increase. The lateral chains can disrupt the molecular packing required for mesophase generation.[1] However, the elongation of the conjugated core causes a large increase in the attractive π–π interaction between the cores, and the improved π–π interaction gives rise to increases in both the transition temperatures and the mesophase range.

Since the lateral chain of oligomers **1–4** is the shortest flexible chain, it is interesting to investigate the structure–property relationships of the oligomers with longer lateral chains. The mesomorphic properties of the tetramers with lateral alkyl chains of various lengths are discussed in the next section.

Table 2 Phase transition temperatures (°C) and transition enthalpies (in square brackets, kJ mol^{-1}) of compounds **5a–c**, **6a,b**, and **7a–f**

Compound	Phase transitions[a]
5a	h: Cr 102.5 [58.2] I c: I 100.5 [−2.7] N 87.1 [−56.5] Cr
5b	h: Cr 91.4 [48.6] I c: I 69.1 [−45.6] Cr
5c	h: Cr 101.5 [48.3] I c: I 84.4 [−46.3] Cr
6a	h: Cr 97.1 [39.4] N 154.7 [2.8] I c: I 153.4 [−2.8] N 80.6 [−43.2] Cr
6b	h: Cr 94.3 [46.9] I c: I 75.5 [−47.1] Cr
7a	h: Cr 157.8 [37.7] N 261.1 [3.8] I c: I 258.1 [−2.5] N 151.9 [−35.4] Cr
7b	h: Cr 140.2 [40.5] N 208.6 [3.5] I c: I 207.4 [−3.4] N 135.1 [−39.9] Cr
7c	h: Cr 149.7 [66.8] N 182.9 [3.5] I c: I 181.8 [−3.6] N 132.7 [−67.1] Cr
7d	h: Cr 156.4 [54.9] N 166.9 [3.2] I c: I 165.7 [−3.2] N 148.9 [−55.7] Cr
7e	h: Cr 121.5 [44.9] N 155.1 [3.1] I c: I 154.1 [−3.1] N 111.7 [−44.6] Cr
7f	h: Cr 96.3 [49.4] N 135.0 [2.4] I c: I 134.0 [−2.4] N 73.3 [−53.4] Cr

[a] h = on heating; c = on cooling; Cr = crystalline phase; N = nematic phase; I = isotropic liquid.

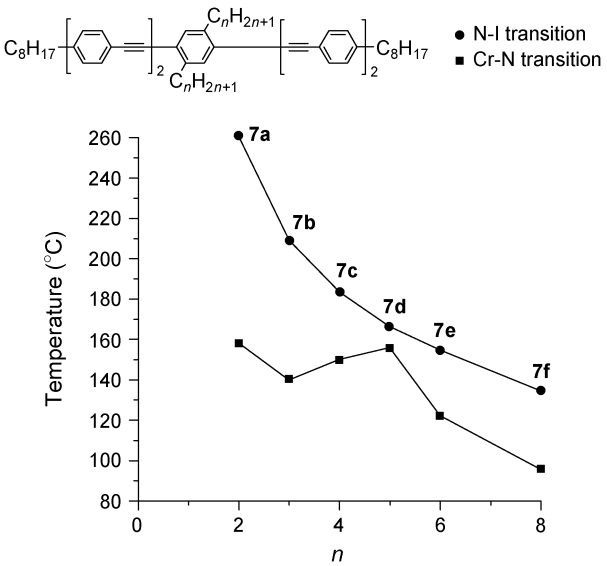


Fig. 4 Transition temperatures *vs.* number of carbon atoms (n) in the lateral chain of laterally dialkyl-substituted tetramers **7a–f**.

The length, number, and position of the lateral chains. The thermotropic data of tetramers **5a–c**, **6a,b**, and **7a–f** are listed in Table 2. Although tetramer **2** with six ethyl lateral chains exhibited the enantiotropic mesophase, tetramer **5a**, in which two propyl and four ethyl chains are attached to the central and outer phenyl rings, respectively, showed a monotropic nematic phase. The Cr–I transition occurred at 103 °C and the mesophase was observed between 101 and 87 °C on cooling. Tetramer **5b**, with two hexyl and four ethyl chains, and tetramer **5c**, with six propyl chains, both contrasted clearly with tetramers **2** and **5a** in that no mesophases were found. The Cr–I transitions occurred at 91 and 102 °C for **5b** and **5c**, respectively. Tetramer **6a** with four ethyl chains exhibited an enantiotropic nematic phase; the mesophase was observed from 97 to 155 °C on heating and from 153 to 81 °C on cooling. However, tetramer **6b** with four propyl chains showed no mesophases; the Cr–I transition occurred at 94 °C.

These observations show that, with the tetramers with four and six lateral chains, the formation of the mesophase is greatly affected by the length of the lateral chains. The replacement of the ethyl chains of tetramers **2** and **6a** with propyl chains considerably reduces the mesophase stability (N–I transition temperature) or destroys the mesophase. As a result, it appears difficult to investigate further the effects of the lateral chains on the mesomorphic properties of these systems. For a better understanding of the structure–property relationships, it will be necessary to investigate the mesomorphic properties of the longer oligomer derivatives, for example, the hexamers with several lateral alkyl chains.

Laterally dialkyl-substituted tetramers **7a–f** all exhibited enantiotropic nematic phases. As shown in Fig. 4, the N–I transition temperature decreased monotonically with increasing carbon atom number in the lateral chain (261, 209, 183, 167, 155, and 135 °C for **7a–f**, respectively). However, the change in the Cr–N transition temperature (158, 140, 150, 156, 122, and 96 °C for **7a–f**, respectively) is not as simple as that in the N–I transition temperature. Although with tetramers **7a**, **7c**, **7e**, and **7f**, which have even-numbered carbon atoms in the lateral chain, the Cr–N transition temperature decreased with increasing carbon atom number, the transition temperature of pentyl derivative **7d** was higher than that of propyl derivative **7b**. In addition to these observations, the change in the mesophase range is interesting. The mesophase range decreased with increasing lateral chain length from ethyl to pentyl (103, 68, 33, and 11 °C for **7a–d**, respectively). However, the range of hexyl derivative **7e** (34 °C) was almost the same as that of butyl derivative **7c**. Also the range of octyl derivative **7f** (39 °C) was slightly greater than that of hexyl derivative **7e**.

These results indicate that the transition temperatures of the tetramers with two lateral chains can be controlled by varying the lateral chain length. The increase in the chain length from ethyl to octyl causes a significant decrease in the mesophase stability but does not destroy the mesophase. This is quite different from the tetramers with six lateral chains; for example, tetramer **5b**, with hexyl chains attached to the central phenyl ring, exhibits no mesophases.

Comparisons between tetramers **7a**, **6a**, and **2**, with two, four, and six ethyl lateral chains, respectively, are of particular interest. Both the Cr–N and N–I transition temperatures of tetramer **7a** were considerably higher than those of tetramers **6a** and **2** (Cr–N: 100, 97, and 158 °C; N–I: 137, 155, and 261 °C for **2**, **6a**, and **7a**, respectively). The N–I transition temperature of tetramer **6a** was somewhat higher than that of tetramer **2**, whereas their Cr–N transition temperatures were very similar. In addition, the mesophase range increased significantly as the number of lateral chains decreased (37, 58, and 103 °C for **2**, **6a**, and **7a**, respectively).

These observations show that the transition temperatures and the mesophase range are strongly affected by the number and position of the lateral chains. The lateral attachment of ethyl

chains to the two phenyl rings, located separately between the central and terminal phenyl rings, causes a dramatic decrease in the transition temperatures. In addition, the use of ethyl lateral chains leads to a wide mesophase range. Therefore, such attachment should be a useful method for controlling the mesomorphic properties of alkyl-substituted derivatives of the longer oligomers.

The length of the terminal chains. Tetramer **2** has six ethyl lateral and two octyl terminal chains, whereas in tetramer **7f** four octyl chains are attached to the central and terminal phenyl rings. Although the lateral chains of tetramer **2** are quite different from those of tetramer **7f**, their transition temperatures are very similar (**2**: Cr 100 N 137 I; **7f**: Cr 96 N 135 I (°C)). To investigate the effects of the lateral and terminal chains on the mesomorphic properties, the transition temperatures of laterally hexaethyl-substituted tetramers **8a–e** were compared with those of laterally dioctyl-substituted tetramers **9a–e**. Tetramers **8b–e** and **9b–e** possess short alkyl terminal chains of various lengths (C1–C4), whereas tetramers **8a** and **9a** have no alkyl endgroups.

The thermotropic data of tetramers **8a–e** and **9a–e** are given in Table 3. Interestingly, the two tetramer derivatives are almost the same in terms of phase transitions but very different as regards transition temperatures. Tetramers **8a** and **9a** exhibited no mesophases. The Cr–I transition temperature of tetramer **8a** (177 °C) was much higher than that of tetramer **9a** (119 °C). In clear contrast to these derivatives, tetramers **8b** and **9b** with methyl endgroups exhibited nematic phases, but their phase transitions on heating were different. Tetramer **8b** showed an enantiotropic nematic phase; the mesophase was observed from 179 to 243 °C on heating and from 241 to 162 °C on cooling. Tetramer **9b**, however, exhibited a monotropic nematic phase; the Cr–I transition occurred at 156 °C and the mesophase was found at temperatures between 153 and 104 °C on cooling. The isotropization temperature of tetramer **8b** was considerably higher than that of tetramer **9b**.

Table 3 Phase transition temperatures (°C) and transition enthalpies (in square brackets, kJ mol^{-1}) of compounds **8a–e** and **9a–e**

Compound	Phase transitions[a]
8a	h: Cr 177.0 [53.4] I c: I 137.8 [−50.6] Cr
8b	h: Cr 179.2 [50.7] N 243.0 [2.7] I c: I 240.5 [−2.1] N 162.3 [−47.5] Cr
8c	h: Cr 179.6 [47.7] N 233.6 [3.1] I c: I 232.1 [−2.3] N 165.8 [−46.3] Cr
8d	h: Cr 149.3 [41.5] N 239.8 [3.9] I c: I 237.5 [−3.5] N 131.5 [−38.6] Cr
8e	h: Cr 142.4 [42.1] N 211.1 [3.4] I c: I 209.5 [−3.3] N 128.4 [−40.7] Cr
9a	h: Cr 119.1 [55.0] I c: I 103.4 [−55.7] Cr
9b	h: Cr 155.5 [68.1] I c: I 153.3 [−1.3] N 104.4 [−63.3] Cr
9c	h: Cr 123.2 [47.6] N 157.5 [1.8] I c: I 156.5 [−1.7] N 113.9 [−38.9] Cr
9d	h: Cr 109.4 [46.5] N 171.0 [2.1] I c: I 170.1 [−2.0] N 88.3 [−48.7] Cr
9e	h: Cr 100.9 [48.4] N 157.5 [2.1] I c: I 156.4 [−2.1] N 76.4 [−36.0] Cr

[a] h = on heating; c = on cooling; Cr = crystalline phase; N = nematic phase; I = isotropic liquid.

Tetramers **8c–e** and **9c–e** exhibited enantiotropic nematic phases, but the transition temperatures of tetramers **8c–e** were much higher than those of the corresponding tetramers **9c–e**. For tetramers **8c** and **9c** with ethyl terminal chains, the mesophases were observed in the 180–234 and 123–158 °C ranges, respectively. For propyl derivatives **8d** and **9d** the mesophases were observed in the 149–240 and 109–171 °C ranges, respectively. For butyl derivatives **8e** and **9e** the mesophases occurred in 142–211 and 101–158 °C ranges, respectively. In addition, the mesophase ranges of tetramers **8c–e** were consistently larger than those of the corresponding tetramers **9c–e** (54 and 34 °C for **8c** and **9c**, 91 and 62 °C for **8d** and **9d**, and 69 and 57 °C for **8e** and **9e**, respectively).

Fig. 5 shows plots of the transition temperatures *vs.* the number of carbon atoms in the terminal chain of the laterally hexaethyl- and dioctyl-substituted tetramers. The transition temperatures of the two tetramer derivatives decrease with increasing carbon atom number, but their changes in transition temperature are different. The transition temperatures of hexaethyl derivatives **8b–e** and **2** decreased more sharply than those of dioctyl derivatives **9c–e** and **7f**. With tetramers **8b–e**, both the Cr–N and N–I transition temperatures decreased in a zigzag manner with increasing terminal chain length (Cr–N: 179, 180, 149, and 142 °C; N–I: 243, 234, 240, and 21 °C for **8b–e**, respectively). With tetramers **9c–e**, the Cr–N transition temperature decreased monotonically with increasing terminal chain length (123, 109, and 101 °C for **9c–e**, respectively). The N–I transition temperatures of tetramers **9c** and **9e** were the same, and were lower than that of tetramer **9d** (158, 171, and 158 °C for **9c–e**, respectively).

These results indicate that, with the laterally hexaethyl- and dioctyl-substituted tetramers with short terminal chains, the

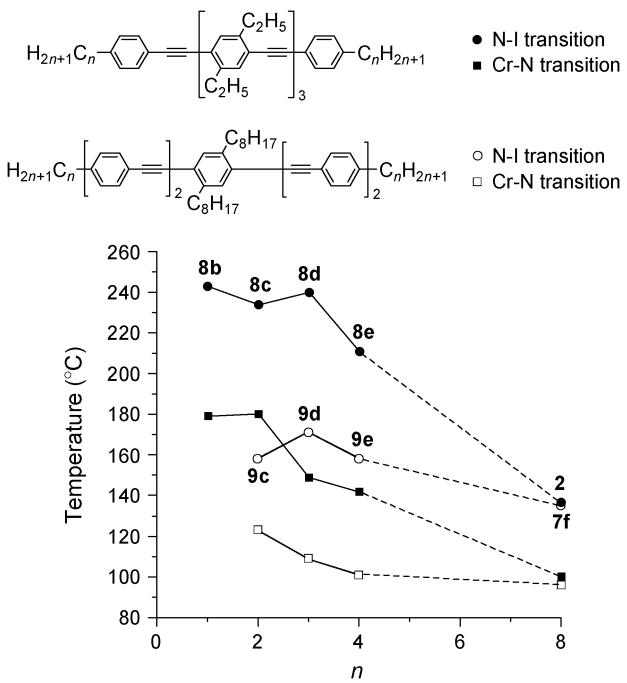


Fig. 5 Transition temperatures *vs.* number of carbon atoms (*n*) in the terminal chain of laterally hexaethyl-substituted tetramers **8b–e** and **2**, and laterally dioctyl-substituted tetramers **9c–e** and **7f**.

transition temperatures are strongly affected by both the structure of the lateral chains and the length of the terminal chains. The transition temperatures of the hexaethyl derivatives are much higher than those of the corresponding dioctyl derivatives. This difference is attributed to the bulkiness of the lateral chains. When octyl chains are attached terminally, however, the transition temperatures of the two derivatives are very similar. It appears that the molecular packing and intermolecular interaction are very similar in the two tetramers.

Conclusion

A new class of conjugated oligomers forming nematic phases, namely laterally and terminally alkyl-substituted derivatives of oligo(1,4-phenyleneethynylene)s, were synthesized and the relationships between the molecular structures and the mesomorphic properties investigated. The results showed that both the formation of the mesophase and the transition temperatures are strongly affected by the length of the oligomer core, the structure of the lateral chains, and the length of the terminal chains. However, the effects of the lateral and terminal chains on the mesomorphic properties have not yet been thoroughly explained. This will necessitate future work on the crystal structures. Nevertheless, the structure–property relationships of the newly synthesized oligomers should be useful for the molecular design of mesomorphic alkyl-substituted derivatives of the longer oligomers. We believe that systematic studies of these mesomorphic oligomers will play an important role in oligomer liquid crystal research.

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References

1 S. Singh, *Liquid Crystals: Fundamentals*, World Scientific, New Jersey, 2002.
2 D. A. Dunmur and L. D. Farrand, Functional Organic and Polymeric Materials, in *Liquid Crystals as Functional Molecular Materials*, ed. T. H. Richardson, John Wiley & Sons, Chichester, 2000, pp. 31–73.
3 C. Tschierske, *J. Mater. Chem.*, 2001, **11**, 2647.
4 T. Ikeda, *J. Mater. Chem.*, 2003, **13**, 2037.
5 T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2006, **45**, 38.
6 M. O'Neill and S. M. Kelly, *Adv. Mater.*, 2003, **15**, 1135.
7 F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491.
8 (*a*) Y. Geng, S. W. Culligan, A. Trajkovska, J. U. Wallace and S. H. Chen, *Chem. Mater.*, 2003, **15**, 542; (*b*) S. W. Culligan, Y. Geng, S. H. Chen, K. Klubek, K. M. Vaeth and C. W. Tang, *Adv. Mater.*, 2003, **15**, 1176; (*c*) Y. Geng, A. C. A. Chen, J. J. Ou, S. H. Chen, K. Klubek, K. M. Vaeth and C. W. Tang, *Chem. Mater.*, 2003, **15**, 4352; (*d*) A. C.-A. Chen, J. U. Wallace, S. K.-H. Wei, L. Zeng, S. H. Chen and T. N. Blanton, *Chem. Mater.*, 2006, **18**, 204.
9 (*a*) A. E. A. Contoret, S. R. Farrar, M. O'Neill, J. E. Nicholls, G. J. Richards, S. M. Kelly and A. W. Hall, *Chem. Mater.*, 2002, **14**, 1477; (*b*) K. L. Woon, M. O'Neill, G. J. Richards, M. P. Aldred, S. M. Kelly and A. M. Fox, *Adv. Mater.*, 2003, **15**, 1555; (*c*) M. P. Aldred, A. E. A. Contoret, S. R. Farrar, S. M. Kelly, D. Mathieson, M. O'Neill, W. C. Tsoi and P. Vlachos, *Adv. Mater.*, 2005, **17**, 1368.
10 (*a*) H. Okumoto, T. Yatabe, M. Shimomura, A. Kaito, N. Minami and Y. Tanabe, *Adv. Mater.*, 2001, **13**, 72; (*b*) H. Okumoto, T. Yatabe, A. Richter, J. Peng, M. Shimomura, A. Kaito and N. Minami, *Adv. Mater.*, 2003, **15**, 716.
11 (*a*) M. Funahashi and J. Hanna, *Appl. Phys. Lett.*, 2000, **76**, 2574; (*b*) M. Funahashi and J. Hanna, *Adv. Mater.*, 2005, **17**, 594; (*c*) M. Funahashi and N. Tamaoki, *ChemPhysChem*, 2006, **7**, 1193.
12 (*a*) S. R. Farrar, A. E. A. Contoret, M. O'Neill, J. E. Nicholls, G. J. Richards and S. M. Kelly, *Phys. Rev. B*, 2002, **66**, 125107; (*b*) K. L. Woon, M. P. Aldred, P. Vlachos, G. H. Mehl, T. Stirner, S. M. Kelly and M. O'Neill, *Chem. Mater.*, 2006, **18**, 2311.
13 I. McCulloch, W. Zhang, M. Heeney, C. Bailey, M. Giles, D. Graham, M. Shkunov, D. Sparrowe and S. Tierney, *J. Mater. Chem.*, 2003, **13**, 2436.
14 T. Yasuda, K. Fujita, T. Tsutsui, Y. Geng, S. W. Culligan and S. H. Chen, *Chem. Mater.*, 2005, **17**, 264.
15 A. J. J. M. van Breemen, P. T. Herwig, C. H. T. Chlon, J. Sweelssen, H. F. M. Schoo, S. Setayesh, W. M. Hardeman, C. A. Martin, D. M. de Leeuw, J. J. P. Valeton, C. W. M. Bastiaansen, D. J. Broer, A. R. Popa-Merticaru and S. C. J. Meskers, *J. Am. Chem. Soc.*, 2006, **128**, 2336.
16 S. Gauza, C.-H. Wen, S.-T. Wu, N. Janarthanan and C.-S. Hsu, *Jpn. J. Appl. Phys., Part 2*, 2004, **43**, 7634.
17 K. L. Woon, M. O'Neill, P. Vlachos, M. P. Aldred and S. M. Kelly, *Liq. Cryst.*, 2005, **32**, 1191.
18 H. Zhang, S. Shiino, A. Shishido, A. Kanazawa, O. Tsutsumi, T. Shiono and T. Ikeda, *Adv. Mater.*, 2000, **12**, 1336.
19 H. Sirringhaus, R. J. Wilson, R. H. Friend, M. Inbasekaran, W. Wu, E. P. Woo, M. Grell and D. D. C. Bradley, *Appl. Phys. Lett.*, 2000, **77**, 406.
20 I. O. Shklyarevskiy, P. Jonkheijm, N. Stutzmann, D. Wasserberg, H. J. Wondergem, P. C. M. Christianen, A. P. H. J. Schenning, D. M. de Leeuw, Ž. Tomović, J. Wo, K. Müllen and J. C. Maan, *J. Am. Chem. Soc.*, 2005, **127**, 16233.
21 (*a*) T. Yatabe, A. Kaito and Y. Tanabe, *Chem. Lett.*, 1997, 799; (*b*) T. Yatabe, T. Kanaiwa, H. Sakurai, H. Okumoto, A. Kaito and Y. Tanabe, *Chem. Lett.*, 1998, 345; (*c*) T. Yatabe, N. Minami, H. Okumoto and K. Ueno, *Chem. Lett.*, 2000, 742.
22 (*a*) M. P. Aldred, A. J. Eastwood, S. M. Kelly, P. Vlachos, A. E. A. Contoret, S. R. Farrar, B. Mansoor, M. O'Neill and W. C. Tsoi, *Chem. Mater.*, 2004, **16**, 4928; (*b*) M. P. Aldred, A. J. Eastwood, S. P. Kitney, G. J. Richards, P. Vlachos, S. M. Kelly and M. O'Neill, *Liq. Cryst.*, 2005, **32**, 1251.
23 J. Simon, J.-J. André and A. Skoulios, *New J. Chem.*, 1986, **10**, 295.
24 (*a*) D. Demus, *Liq. Cryst.*, 1989, **5**, 75; (*b*) D. Demus, *Mol. Cryst. Liq. Cryst.*, 2001, **364**, 25.
25 P. Galda and M. Rehahn, *Synthesis*, 1996, 614.
26 L. Larios-López, D. Navarro-Rodríguez, E. M. Aris-Marín, I. Moggio, C. V. Reyes-Castañeda, B. Donnio, J. LeMoigne and D. Guillon, *Liq. Cryst.*, 2003, **30**, 423.
27 S. Lightowler and M. Hird, *Chem. Mater.*, 2005, **17**, 5538.
28 (*a*) Y. Geng, A. Trajkovska, D. Katsis, J. J. Ou, S. W. Culligan and S. H. Chen, *J. Am. Chem. Soc.*, 2002, **124**, 8337; (*b*) Q. Liu, W. Liu, B. Yao, H. Tian, Z. Xie, Y. Geng and F. Wang, *Macromolecules*, 2007, **40**, 1851.
29 R. Guntner, T. Farrell, U. Scherf, T. Miteva, A. Yasuda and G. Nelles, *J. Mater. Chem.*, 2004, **14**, 2622.
30 (*a*) J. Jo, C. Chi, S. Höger, G. Wegner and D. Y. Yoon, *Chem.–Eur. J.*, 2004, **10**, 2681; (*b*) C. Chi, G. Lieser, V. Enkelmann and G. Wegner, *Macromol. Chem. Phys.*, 2005, **206**, 1597.
31 R. E. Gill, A. Meetsma and G. Hadziioannou, *Adv. Mater.*, 1996, **8**, 212.
32 (*a*) T. Maddux, W. Li and L. Yu, *J. Am. Chem. Soc.*, 1997, **119**, 844; (*b*) W. Li, H. Wang, L. Yu, T. L. Morkved and H. M. Jaeger, *Macromolecules*, 1999, **32**, 3034.
33 A. P. H. J. Schenning, A. El-ghayoury, E. Peeters and E. M. Meijer, *Synth. Met.*, 2001, **121**, 1253.
34 H.-C. Lin, C.-M. Tsai, G.-H. Huang and J.-M. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 783.
35 P. Wautelet, M. Moroni, L. Oswald, J. Le Moigne, A. Pham, J.-Y. Bigot and S. Luzzati, *Macromolecules*, 1996, **29**, 446.

36 H. Barrientos, E. Arias, I. Moggio, J. Romero, O. Rodríguez, E. Giorgetti and T. Del Rosso, *Synth. Met.*, 2004, **147**, 267.
37 T. Geelhaar, *Liq. Cryst.*, 1998, **24**, 91.
38 (*a*) J. Malthête, M. Leclercq, M. Dvolaitzky, J. Gabard, J. Billard, V. Pontikis and J. Jacques, *Mol. Cryst. Liq. Cryst.*, 1973, **23**, 233; (*b*) J. Malthête, J. Canceill, J. Gabard and J. Jacques, *Tetrahedron Lett.*, 1981, **37**, 2815.
39 H. Takatsu, K. Takeuchi, Y. Tanaka and M. Sasaki, *Mol. Cryst. Liq. Cryst.*, 1986, **141**, 279.
40 G. W. Skelton, D. Dong, R. P. Tuffin and S. M. Kelly, *J. Mater. Chem.*, 2003, **13**, 450.
41 S.-T. Wu, C.-S. Hsu and K.-F. Shyu, *Appl. Phys. Lett.*, 1999, **74**, 344.
42 C. Sekine, K. Iwakura, N. Konya, M. Minai and K. Fujisawa, *Liq. Cryst.*, 2001, **28**, 1375.
43 C. Pugh and V. Percec, *Polym. Bull.*, 1990, **23**, 177.
44 A. R. A. Palmans, M. Eglin, A. Montali, C. Weder and P. Smith, *Chem. Mater.*, 2000, **12**, 472.
45 (*a*) S.-T. Wu, C.-S. Hsu and Y.-Y. Chuang, *Jpn. J. Appl. Phys., Part 2*, 1999, **38**, L286; (*b*) C.-S. Hsu, K.-F. Shyu, Y.-Y. Chuang and S.-T. Wu, *Liq. Cryst.*, 2000, **27**, 283.
46 C. Sekine, K. Fujisawa, K. Iwakura and M. Minai, *Mol. Cryst. Liq. Cryst.*, 2001, **364**, 711.
47 (*a*) H. Li, D. R. Powell, R. K. Hayashi and R. West, *Macromolecules*, 1998, **31**, 52; (*b*) H. Li, D. R. Powell, T. K. Firman and R. West, *Macromolecules*, 1998, **31**, 1093.
48 P. Samorí, V. Francke, V. Enkelmann, K. Müllen and J. P. Rabe, *Chem. Mater.*, 2003, **15**, 1032.
49 (*a*) J. S. Schumm, D. L. Pearson and J. M. Tour, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1360; (*b*) J. M. Tour, *Chem. Rev.*, 1996, **96**, 537; (*c*) L. Jones, II, J. S. Schumm and J. M. Tour, *J. Org. Chem.*, 1997, **62**, 1388.
50 (*a*) R. P. Hsung, C. E. D. Chidsey and L. R. Sita, *Organometallics*, 1995, **14**, 4808; (*b*) U. Ziener and A. Godt, *J. Org. Chem.*, 1997, **62**, 6137.
51 (*a*) O. Lavastre, L. Ollivier, P. H. Dixneuf and S. Sibandhit, *Tetrahedron*, 1996, **52**, 5495; (*b*) H. Kukula, S. Veit and A. Godt, *Eur. J. Org. Chem.*, 1999, 277.
52 (*a*) P. Samorí, V. Francke, K. Müllen and J. P. Rabe, *Chem.–Eur. J.*, 1999, **5**, 2312; (*b*) C.-Z. Zhou, T. Liu, J.-M. Xu and Z.-K. Chen, *Macromolecules*, 2003, **36**, 1457; (*c*) C. Xue and F.-T. Luo, *Tetrahedron*, 2004, **60**, 6285.
53 (*a*) K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467; (*b*) S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627; (*c*) K. Sonogashira, *J. Organomet. Chem.*, 2002, **653**, 46.
54 Since the backbone of oligomer **1** is composed of three phenylene-ethynylene units and one phenyl ring, we call **1** a trimer conveniently. For the same reason oligomers **2–4** are called a tetramer, a pentamer, and a hexamer, respectively.
55 (*a*) A. K. Flatt, Y. Yao, F. Maya and J. M. Tour, *J. Org. Chem.*, 2004, **69**, 1752; (*b*) J. M. Tour, A. M. Rawlett, M. Kozaki, Y. Yao, R. C. Jagessar, S. M. Dirk, D. W. Price, M. A. Reed, C.-W. Zhou, J. Chen, W. Wang and I. Campbell, *Chem.–Eur. J.*, 2001, **7**, 5118.
56 I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH, Weinheim, 2003.