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Nanophase segregated mesophase morphology in self-organized novel disc-rod oligomesogens

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Electronic supplementary information

Synthesis of novel disc-rod oligomers

The synthesis of disc-rod oligomesogens is outlined in Scheme 1. Compounds 1-5 and ω-bromo alkoxycyanobiphenyls (RBr) were prepared as reported. Powdered KOH (135 mg, 2.4 mmol) was mixed with DMSO (10 ml) at room temperature and stirred for 10 min. Hexaacetoxy-TCQ (66.8 mg, 0.1 mmol) followed by the appropriate ω-bromo alkoxycyanobiphenyl (2.4 mmol) was added and the reaction mixture was stirred at 55 °C for 24 h and then worked up by addition of ice-water and extracted with dichloromethane. The crude product was purified by column chromatography (silica gel, hexane-ethyl acetate 1:1 followed by dichloromethane) and then crystallized from acetone or precipitated with dichloromethane-ethyl acetate to afford pure yellow material in about 40% yield.

6a: 1H NMR (400 MHz; CDCl3; Me4Si) δH 7.71 (s, 3H, Ar-H from TCQ), 7.65 (d, 12H, J = 6.5 Hz, Ar-H from biphenyl), 7.59 (d, 12H, J = 6.5 Hz, Ar-H from biphenyl), 7.49 (d, 12H, J = 8.8 Hz, Ar-H from biphenyl), 6.96 (d, 12H, J = 8.9 Hz, Ar-H from biphenyl), 6.90 (s, 3H, Ar-H from TCQ), 4.2-4.1 (m, 12H, Ar-OCH2), 3.98-4.05 (m, 12H, Ar-OCH2), 2.0-1.91 (m, 12H, CH2), 1.89-1.82 (m, 12H, CH2), 1.65-1.60 (m, 24H, CH2). All other compounds give similar spectra except for more number of aliphatic methylene protons.
13C NMR (100 MHz, CDCl3, Me4Si) δC 159.7, 145.1, 132.6, 131.3, 128.3, 127.0, 119.1, 115.0, 110.1, 69.0, 67.9, 29.22, 28.9, 25.8. All other compounds give similar spectra.

FT-IR νmax(KBr)/cm⁻¹ 2922, 2854, 2224, 1620, 1601, 1541, 1506, 1491, 1456, 1377, 1338, 1295, 1251, 1221, 1178, 1105, 822, 721, 667. All other compounds give similar spectra.

Elemental analysis

6a, Found: C, 77.64; H, 6.00; N, 7.01. C135H126N10O12 requires C, 77.94; H, 6.10; N, 6.73%. 6b, Found: C, 78.20; H, 6.33; N, 5.81. C147H150N10O12 requires C, 78.51; H, 6.72; N, 6.23%. 6c, Found, C, 79.30; H, 7.21; N, 5.50. C159H174N10O12 requires C, 79.01; H, 7.26; N, 5.79%. 6d, Found: C, 78.90; H, 7.51; N, 5.80. C171H198N10O12 requires C, 79.44; H, 7.72; N, 5.42%.

Monotropic optically isotropic phase of compound 6a: The observation of an optically isotropic texture in a liquid crystalline compound between two birefringent phases, under the crossed polarized microscope, gives rise to possibilities like spontaneous homeotropic alignment of the compound or occurrence of a re-entrant isotropic phase. In our compound 6a we observe that the optically isotropic phase appears monotypically from the preceding Smectic phase of the compound with sharp and cornered phase boundaries of its domains (Fig.1). The transition to an amorphous solid state is unlikely because of the abrupt extinction of birefringence and first order phase transitions observed in the DSC thermogram and the existence of re-entrant isotropic can be ruled out by the observed high viscosity of the phase. The transition to a homeotropic alignment in this compound can be ruled out by taking into account the values of transition enthalpy and nature of phase transition. Moreover, our attempts to align the higher homologous homeotropically did not yield the desired alignment which precludes the spontaneous alignment of the lower homologue 6a. The monotropic (thermodynamically unstable) nature of the
optically isotropic phase excludes its characterization by X-ray diffraction studies which would have otherwise provided unequivocal assignment of the phase structure, its symmetry and detailed molecular organization in the phase. On the basis of POM and DSC we can assign the optically isotropic phase to a cubic phase although the symmetry and detailed molecular organization like bicontinuous cubic or micellar cubic could not be established by XRD. Furthermore, the existence of well characterized cubic phases with sharp and cornered phase boundaries of their domains while growing from other phases, as has been observed in this compound 6a, has been documented between crystalline phase and smectic phases.1-3

References


Fig.1. Transition to cubic phase from smectic A phase of compound 6a.
Fig. 2 Polarising optical micrograph of Cubic phase of compound 6a.

Fig. 3 Crystal growth from cubic phase of compound 6a.
**Fig. 4** DSC trace of compound 6a on heating and cooling (scan rate 5 °C/min).

**Fig. 5** X-ray diffraction pattern of compound 6d in the mesophase.
Fig. 6 XRD of compound 6b in the mesophase.

Fig. 7 XRD of compound 6c in the mesophase.