

Tunable Mesogens Based on Shape-Persistent Aromatic Oligoamides: From Lamellar, Columnar, to Nematic Liquid Crystalline Phase

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ABSTRACT



Crescent aromatic oligoamides are shown to form thermotropic lamellar columnar, rectangular columnar, and discotic nematic mesophases according to structural variation, demonstrating their capability to serve as a new class of diverse mesogens of liquid crystals.

Liquid crystals (LC) based on organic molecules with different shapes and large or extended cores, particularly discotic LC, have arrested increasing attention in the past decade.¹ Apart from the conventional rod-like and disk-

like shape of mesogenic molecules, a variety of novel molecular shapes such as cone,² bent-core,³ and ring⁴ have been reported to display LC behaviors. Shape-persistent molecules as defined by their noncollapsible framework are intriguing in terms of their well-defined structures and

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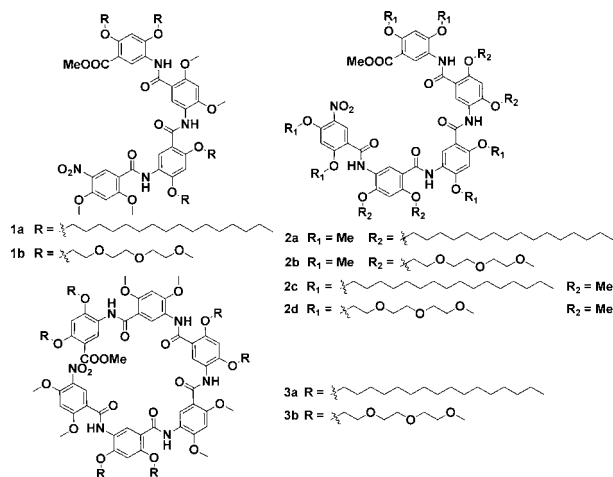
unique capability of forming mesophase.⁵ To date a number of liquid crystalline shape-persistent compounds have been generated such as phenylacetylene macrocycles,⁶ dendrimers,⁷ and V-shaped³ molecules containing five-membered heterocycles.

Aromatic oligoamides with backbones rigidified by intramolecular hydrogen bonds are attracting intense research interests in recent years.⁸ Among them, crescent aromatic oligoamides containing three-center hydrogen bonds reported by Gong et al.⁹ represent an interesting class of shape-persistent molecules due to their characteristic features in folded conformations⁹ and internal cavities for ion-complexation.^{9g} In particular, short oligomers consisting of less than six benzene residues take a flat, crescent conformation.^{9a,c,g} These molecules, along with their cyclic analogues as reported recently by us and the collaborators,¹⁰ have large aromatic surfaces favorable for π - π stacking and thus demonstrated a high propensity for

strong aggregation and self-assembly.^{9f,10a} It is reasoned that with flat stiff cores defined by the constitutional backbones and flexible peripheral side chains appropriately positioned, it would be possible for these oligoamide molecules to form well-organized mesophases. However, the mesomorphism for these interesting shape-persistent compounds has remained unknown since they were first described 10 years ago.^{9a}

Herein we report on our findings of diverse mesogenic phases of crescent oligoamides **1–3** (Scheme 1) and tuning of their LC mesophases via structural variation by extending the crescent molecular backbones and adjusting peripheral side chains. These compounds were shown to form thermotropic lamellar columnar (L_{CoI} for **1a**), rectangular columnar (CoI_r for **2c**, **2d** and **3a**), and discotic nematic (N_D for **3b**) mesophases.

Scheme 1. Molecular Structures of Aromatic Oligoamides **1–3**



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The key compounds for our investigation are oligoamides **1–3** with 4–6 long alkyl or triethylene glycol (TEG) chains attached to the backbones. They were synthesized according to the similar reported procedures.⁹ All compounds were characterized with NMR and mass spectroscopy.¹¹

Thermogravimetric analysis (TGA) of compounds **1–3** revealed no mass loss up to 270 °C, well above the isotropization temperature,¹¹ indicating thermal stability of the oligoamides. However, whether the intramolecular three-center hydrogen bonds are strong enough to endure the high temperature condition at which they were examined for DSC or high temperature XRD experiments is still not clear. Thus, **2b** was chosen as a representative example for variable temperature FTIR (VT FTIR) examination in solid state. The NH stretching frequency at 3347 cm^{-1} was found to experience almost no change upon cooling from 190 to 40 °C, and no new band pertinent to the NH amide was observed.¹¹ Since the change of hydrogen bonding is directly reflected in the change of stretching frequencies of amide NH groups,^{9b} these data showed that intramolecular

(11) See the Supporting Information for details.

hydrogen bonding was maintained in the temperature range examined, suggesting the persistence of crescent conformation at high temperature.

The thermotropic behavior of these compounds was then studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and variable temperature X-ray diffraction (VT XRD), and the results are summarized in Table 1.

Table 1. Phase Behaviors of Oligoamides **1**, **2**, and **3**

compounds	temp(°C) and ΔH (kJ mol ⁻¹) ^a
1a	Cr $\xrightarrow[31.5(-43.4)]{41.6(42.0)}$ L _{Col} $\xrightarrow[207.6(-37.8)]{218.3(33.4)}$ I
1b	Cr ₁ $\xrightarrow[76.8(-2.5)]{90.4(2.0)}$ Cr ₂ $\xrightarrow[153.2(-31.6)]{172.7(31.4)}$ I
2a	Cr $\xrightarrow[136.6(-22.3)]{168.8(25.5)}$ I
2b	Cr $\xrightarrow[150.2(-41.5)]{186.3(51.9)}$ I
2c	Cr $\xrightarrow[14.7(-46.4)]{28.9(45.1)}$ Col _r $\xrightarrow[185.7(-23.8)]{192.9(23.5)}$ I
2d	Cr $\xrightarrow[24.0(-3.9)]{38.5(2.1)}$ Col _r $\xrightarrow[94.7(-12.9)]{117.3(10.7)}$ I
3a	Cr $\xrightarrow[17.1(-30.5)]{30.3(25.4)}$ Col _r $\xrightarrow[110.9(-12.2)]{145.0(17.3)}$ I
3b	g $\xrightarrow[116.0(-3.9)]{52.9}$ N _D $\xrightarrow[116.0(-3.9)]{117.4(2.9)}$ I

^a The transition temperatures (°C) and enthalpies (listed in parentheses, kJ/mol) were determined by DSC at 10 °C/min. Cr = crystalline phase; L_{Col} = columnar lamellar mesophase; Col_r = rectangular columnar mesophase; g = glassy; N_D = discotic nematic mesophase; I = isotropic liquid.

The LC property was first noticed in tetramer **1a**. It melts at 41.6 °C and exhibits a broken fan-like texture at 200 °C upon cooling from isotropic phase (Figure 1a). The XRD pattern at 140 °C for the oriented sample revealed five reflections at 36.9, 19.1, 12.6, 9.5, and 7.6 Å in the low angle regime with the reciprocal spacing ratio of 1:¹/₂:¹/₃:¹/₄:¹/₅ assigned as the (001), (002), (003), (004), and (005) reflections, indicative of a layered phase with the periodicity of 36.9 Å (Figure 2a). In addition, the diffuse scattering halo at 4.4 Å corresponds to the mean distance between the fluid alkyl chains, and the diffraction at 3.5 Å has a value that is typical of the distance relating to the π - π interactions between aromatic cores, suggesting the formation of a highly ordered lamellar columnar mesophase (L_{Col}) as shown in the model proposed (Figure 2a, inset). The *d*-spacing at 14.7 Å in the middle-angle range agrees well with the value of 14.0 Å as observed in the crystal structure of similar tetramer derivatives,^{9c} which can be related to the width of the aromatic cores of the molecule **1a**.

The first observation of mesophase for **1a** is particularly interesting since its corresponding lower oligomers such as trimeric and dimeric analogues never indicated any sign of mesomorphism. Besides, the wide temperature range (> 170 °C) over which the L_{Col} phase is stable for **1a** is

striking. This result prompted us to probe the possibility of other oligoamides as mesogenic molecules. Thus, **1b**, which shares exactly the same backbone but differs in the polarity of side chains, was prepared and analyzed by DSC and POM. Unexpectedly, **1b** failed to indicate mesomorphic property but formed rectangular columnar lattice,¹¹ suggesting the great impact of polarity of side chains. It is known that polar TEG chains have more conformational flexibility compared to alkyl chains,¹² which could reduce capacity of packing and cause loss of LC property or forming a less ordered N_D phase;¹³ however, other factors may also determine the formation of mesophases.

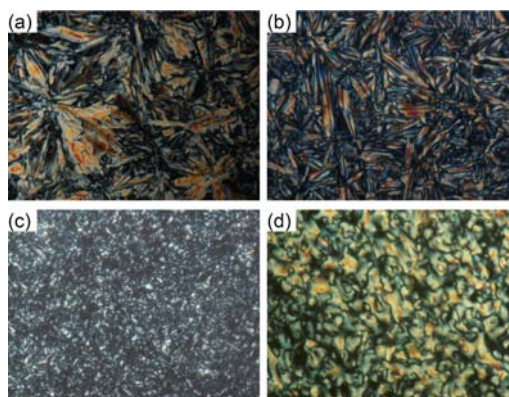


Figure 1. Polarized optical micrograph of (a) L_{Col} phase of **1a** at 200 °C; (b) Col_r phase of **2c** at 125 °C; (c) Col_r phase of **3a** at 100 °C; and (d) N_D phase of **3b** at 115 °C.

Allowing for the aromatic surface that is crucial for aggregation and intermolecular stacking,^{9f} further extension of the backbone should provide chances for the generation of LC properties. Thus, compound **2b**, which has one more added aromatic residue along the backbone than **1b**, was prepared. Unexpectedly, **2b** showed nonmesomorphic property.¹¹ The negative result made us decide to prepare pentamer **2a**, which resembles **1a** to a great extent in structures at one of the terminus and in the number of long alkyl side chains. Surprisingly, contrary to our expectation, **2a** failed to exhibit mesogenic phases.¹¹ We presume that increasing the surface area necessary for stacking interactions via extending the backbone alone does not help give rise to LC property, and it is likely that the balance between the core dimension and the flexible periphery is critical as observed in many other liquid crystalline molecules.^{6b,14}

Compounds **2c** and **2d**, which share the exact same backbone as **2a** and **2b** but bear six instead of four side chains, were designed accordingly. Indeed, both of them exhibit LC phases. For example, when **2c** is subjected to

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DSC analysis, it shows two enantiotropic phase transitions at 28.9 and 192.9 °C in the second heating circle. POM image shows a lancet texture¹⁵ (Figure 1b), which is often observed in rod-like mesogen, and attributed to smectic phase. However, the XRD pattern recorded at 187 °C shows five reflections at 32.9, 25.2, 16.9, 14.6, and 11.2 Å, which are indexed in sequence as (110, 200), (210), (220), (320), and (600) reflections, revealing a rectangular columnar (Col_r) phase with the cell parameter of $a = 65.8$ Å and $b = 38.0$ Å (Figure 2b). By substituting **2c** with TEG, the clearing point on cooling experienced a drastic reduction from 185.7 °C in **2c** to a much lower temperature of 94.2 °C in **2d**, disclosing the pronounced polarity effect of peripheral side chains upon the LC property. The presence of the mobile TEG chains possibly induces a large disturbance for the ordered packing and thus results in decreased clearing point.¹² The observation of a stable LC phase in **2c** and **2d**, which failed to be observed in **2a** and **2b**, clearly indicates that the number of side chains is crucial to the success of the designed LC molecules.

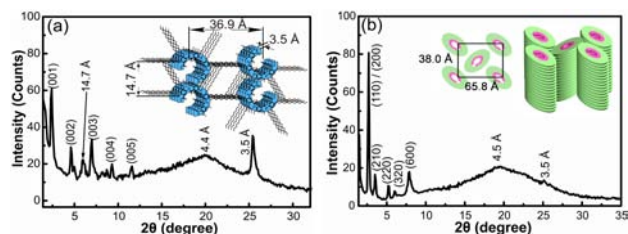


Figure 2. X-ray diffractograms for (a) the L_{Col} phase of **1a** at 140 °C and (b) the Col_r of **2c** at 178 °C, cooling from isotropic phase at 2 °C min⁻¹.

Further extension of the backbone based on **2c** and **2d** leads to hexamers **3a** and **3b**. Both of them showed fluidity and birefringence on POM (Figure 1c and d). Compound **3a** exhibits the schlieren texture. The XRD pattern recorded at 90 °C shows the reflections that all point to a Col_r mesophase. It is noteworthy that **3a** shows a broad melting transition at 30.3 °C, nearly room temperature and a wide temperature mesophase range (30.3 to 145.0 °C in the second heating), which is particularly intriguing in terms of applications. In the case of **3b** bearing polar side chains, the DSC profile exhibits a phase transition at 117.4 °C on heating with $\Delta H = 2.9$ kJ mol⁻¹, and the mesophase appears at 116 °C with $\Delta H = -3.9$ kJ mol⁻¹ on cooling. The enthalpy change falls within the range for the isotropic enthalpy of nematic phase (1–5 kJ mol⁻¹).^{1c} In addition, the VT XRD patterns persist in a wide temperature range (30–235 °C), embracing only one broad and diffuse peaks in wide-angle regime,¹¹ which supports the N_D phase. The observation that **3a** forms Col_r mesophase and **3b** produces

less ordering nematic phase is interesting since the optimized structure of **3** as indicated in molecular modeling shows a nonplanar conformation¹¹ compared to **2d** with a flat core. We speculate that side chain packing should function cooperatively with the less ordered aromatic packing in **3** due to the helical conformation to determine the final outcome of LC properties. The TEG chains in **3b** would interfere with the packing of the core and prevent the crescent molecules from efficient columnar packing, which is otherwise less likely to occur in **2d** having the alkyl chains and a flat core or in **3a** where the core packing is similar to **3b**, but alkyl chains dominate to assist intermolecular packing. Therefore, the presence of more flexible TEG chains favors the less ordered organization of the N_D phase in **3b**.^{13b} To our knowledge, so far few discotic systems could exhibit N_D phase in the low temperature range.^{1c}

In summary, a series of shape-persistent aromatic oligoamides including tetramers, pentamers, and hexamers shows liquid crystalline birefringence over a wide temperature range. Both the constitutional components of crescent oligoamides and side chains are crucial to the success of designed molecules to show LC properties. With their tunable crescent backbones, these compounds of various size exhibit rich mesomorphic properties ranging from lamellar, rectangular columnar, to discotic nematic mesophases, demonstrating their ability to serve as a new class of mesogens of liquid crystals. So far no examples of these crescent aromatic oligoamides have been found to exhibit liquid crystalline properties. It is expected that further structural modification and functionalization may provide versatile LC materials based on these crescent oligoamides with controlled change of mesophase patterns, thus enriching the family of LC materials with tailored new and special properties. Detailed studies on these aspects are currently being investigated in our laboratory and will be reported in due course.

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Supporting Information Available. General experimental methods, synthesis of compounds, NMR spectra, TGA, VT FTIR, DSC, POM, XRD, and ab initio molecular modeling of **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no competing financial interest.