Semiflexible Star-Shaped Mesogens as Nonconventional Columnar Liquid Crystals

Matthias Lehmann,*[,†,||] Raluca I. Gearba,[‡] Michel H. J. Koch,[§] and Dimitri A. Ivanov[‡]

Laboratoire de chimie des polymères, CP 206/1, and Laboratoire de physique des polymères, CP 223, Université Libre de Bruxelles, Boulevard du Triomphe, B-1050 Brussels, Belgium, and European Molecular Biology Laboratory, Hamburg Outstation, EMBL c/o DESY, Notkestrasse 85, D-22603, Hamburg, Germany

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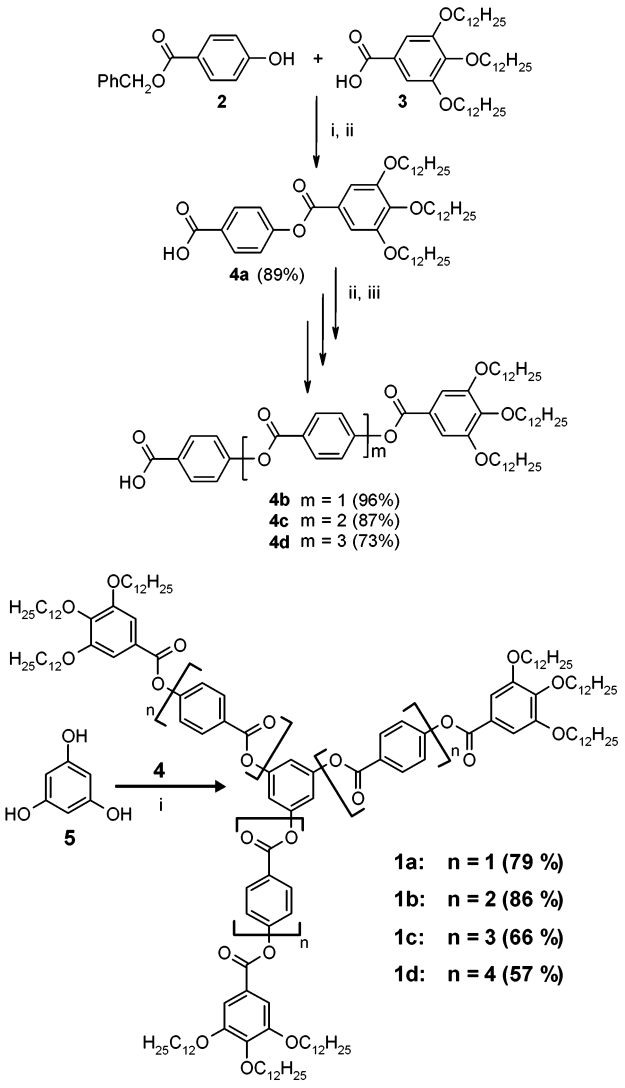
Nonconventional flexible mesogens forming columnar mesophases are currently of great interest due to their facile alignment and control of morphology.[1] They consist of physically or chemically different segments which can microsegregate into columnar assemblies.[2] Mesogenic or promesogenic units linked by flexible spacers to a center constitute star-shaped mesogens which frequently self-organize in layered structures by adopting suitable conformations.[3] Star-shaped molecules with three semi-flexible or rigid arms based on benzoyloxy-,[4−6] styryl-,[7,8] phenylethynyl-,[9,10] and diacetylene units[11] possess only restricted conformational freedom, but nevertheless, these mesogens have recently been shown to stack in columnar mesophases. Interestingly, if these arms are directing radially away from the center, such molecules should have cavities, where guests can be incorporated;[7a,12] thus, the question arises on how such systems can densely pack into columnar structures.

Scheme 1. Convergent Synthesis of Star-Shaped Mesogens 1



i: CH_2Cl_2, DPTS, DCC, rt; ii: H_2, Pd/C, Et_2O, rt; iii: **2**, CH_2Cl_2, DPTS, DCC, rt

The present work focuses on star-shaped molecules with a benzoyloxy scaffold **1**. For the parent molecule **1** (n = 0), only a monotropic liquid-crystal phase is obtained.[4] Molecules with elongated arms have recently been reported to form a Col_{hd} mesophase and a star-shaped conformation with interdigitation of lateral flexible chains has been proposed.[6] To gain more insights into columnar organization of star-shaped semiflexible mesogens based on benzoyl units **1**, a series of C_3 symmetrical oligomers were synthesized, with up to five benzoyloxy units in a single arm. These compounds are comparable with stilbenoid molecules, where the extension of the branches stabilizes the columnar mesophases.[6,7,12]

Synthesis was carried out following a convergent strategy outlined in Scheme 1. The readily available 4-hydroxy benzyl benzoate **2** was used as the extension unit.[13] Starting from the 3,4,5-tridodecyloxybenzoic acid **3**,[14] iterative esterification with **2** and reductive depro-

* To whom correspondence should be addressed. E-mail: matthias.lehmann@ulb.ac.be.
† Laboratoire de chimie des polymères, CP 206/1.
‡ Laboratoire de physique des polymères, CP 223, Université Libre de Bruxelles.
§ European Molecular Biology Laboratory, DESY.
|| Current address: Institute of Chemistry, Chemnitz University of Technology, Strasse der Nationen 62, D-09107 Chemnitz, Germany.

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Table 1. Phase Transitions of Molecules 1 and 4 as Determined by POM and DSC in the Second Heating Scan (Heating Rate: 10 °C/min)

compound	phase transition temperatures (onset) [°C]/transition enthalpies [kJ/mol][c]
4a[a]	Cr 87/56.9 I
4b	Cr 87/16.7 LC 114/2.2 I
4c	X 147/0.3 LC 197/1.8 I
4d[a]	Cr 85/57.7 LC_1 120/1.5 LC_2 128/4.5 LC_3 218/0.6 LC_4 241/1.2 LC_5 262/2.2 I (dec)
1a[b]	g T_g = 20 °C Col_{hd} 53/5.5 I after annealing at room temperature (2 days): Cr 13/64.5 Col 55/32.7 I
1b	Col_1 79/11.6 Col_2 98/3.0 I
1c	Col_1 170/10.1 Col_2 172/5.4 I[d]
1d[a]	Col_1 240/10.6 Col_2 249/5.8 I (dec)

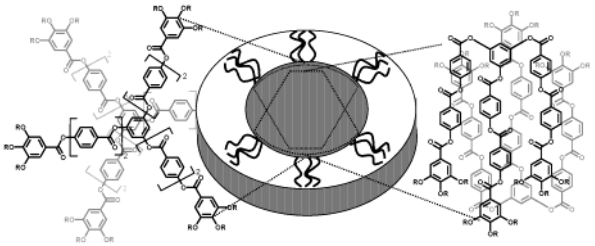
[a] Data for the first heating. [b] See ref 6. [c] g, glassy state; X, unidentified phase; LC, liquid-crystal phase; Col, columnar mesophase; Col_{hd}, hexagonal disordered columnar mesophase. [d] Slight decomposition is observed after annealing for several minutes in the isotropic phase.

tection of the benzyl ester yielded arms **4a**−**d**.[15] A last convergent coupling to the phloroglucinol core **5** provided the target molecules **1a**−**d**. High purity of all materials was achieved by simple recrystallization from acetone after each single step, which was proven by ^{1}H NMR and elemental analysis.[16]

The thermotropic behavior of the star-shaped molecules **1** and arms **4** was studied by means of differential scanning calorimetry (DSC) and polarized optical microscopy (POM) and data are collected in Table 1. Already the acids **4** show liquid-crystalline properties, if they are composed of three or more benzoyloxy units, which can be understood if phasmidic-like dimers are formed.[17]

The clearing temperature of compounds **1a**−**d** increases with the size of these molecules, similarly to the one of the corresponding arms **4a**−**d**. Except for **1a**, DSC measurements reveal for all compounds two enantiotropic mesophases. For **1d** no transition is observed during cooling from the isotropic liquid because the molecules decompose above the isotropization temperature (249 °C). This could explain the absence of characteristic textures of **1d** in POM micrographs. When cooling materials **1a**−**1c** from the isotropic phase to their high-temperature mesophase, a pseudo-focal-conic texture appears,[16] which provides evidence for a columnar structure.[18] At lower temperatures **1b**−**1d** organize in a second very highly viscous mesophase, which does not undergo further transitions and is stable at ambient temperature. Compound **1a** shows different behavior. Previously, we reported a crystalline phase at low temperature;[6] DSC reinvestigation with a larger sample weight gives evidence for a glass transition at T_g = 20 °C, similar to other derivatives of the same molecular size but different substitution.[6] As a consequence of this glass transition and the reduced molecular mobility, the columnar hexagonal phase can be frozen when kept below 20 °C. However, if annealed above T_g, the material undergoes a transition to another mesophase, Col (Table 1), which can be revealed by DSC[16] and the lower birefringence of the optical texture. Although the transition Col−I is characterized by a rather high enthalpy (32.7 kJ/mol), the phase is waxy, highly viscous, but still shearable. Consequently, the hexagonal phase of **1a** is only monotropic, as for the parent compound.[4]

Table 2. Star Shape versus E Shape: X-ray Data and Columnar Diameters Estimated from Possible Conformers of 1



compound	r_{core}[a] [Å]	$d_{calc,star}$[b] [Å]	$d_{calc,E}$[c] [Å]	d_{exp} [Å]	a[d] [Å]	ρ[e] [g/cm^3]
1a (35 °C)	15.2	42.7	42.5	36.8	42.5	0.58
1b (91 °C)	21.7	55.7	49.2	43.2	49.9	0.49
1c (171 °C)	28.2	68.6	55.5	49.6	57.4	0.41
1d (247 °C)	34.6	81.6	61.9	56.3	65.0	0.36

[a] Radii of the oligoester cores estimated for model compounds with CS Chem 3D software. [b] Diameters based on star-shaped molecules with interdigitated flexible chains obtained with $d_{calc,star} = 2 \times r_{core} + l_{flex,chain}$, $l_{flex,chain}$ = 12.4 Å. [c] Molecular diameter for E-shaped conformers calculated according to $d_{calc,E} = r_{core,E} + 2 \times l_{flex,chain}$, $r_{core,E}$ were obtained from model conformers. [d] $a = 2 \times d_{exp}/\sqrt{3}$. [e] $\rho = M/(N_A \times a^2 \times \sin 60° \times h)$ was calculated for a Col_{hd} phase with an estimated columnar slice thickness h = 4.5 Å and only one molecule in the unit cell; M is the molecular mass. The small values suggest that there are at least two molecules per unit cell, that is, per columnar slice.

Preliminary X-ray studies of mesogens **1** were performed with synchrotron radiation.[19,20] Table 2 summarizes the d spacings for the high-temperature mesophase of **1a**−**d**. Molecule **1a** has been recently described to self-assemble in a hexagonal columnar mesophase since three reflections with reciprocal distances with the ratio of 1:$\sqrt{3}$:2 have been detected.[6] Interdigitation of lateral chains has been proposed to account for the small intercolumnar distance. In the high-temperature mesophase, **1b** and **1c** have only a single reflection in the small-angle region and the larger, extended star-shaped molecule **1d** two reflections with the ratio 1:2. A broad halo at wide angles (4.5 Å) corresponds to the mean distance of the liquidlike side chains. Together with the typical pseudo-focal-conic texture, this points to a hexagonal symmetry of a two-

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dimensional lattice of columns for the phase Col_2. Further evidence can be obtained from calculation of columnar diameters based on the core radius estimated from molecular models of the star-shaped mesogens (Table 2, column 2) and the flexible length of the dodecyloxy chain (12.4 Å).[21] The values $d_{calc,star}$ for star-shaped molecules with fully interdigitated flexible dodecyloxy chains are much larger than the found experimental *d* spacings and only the columnar diameter of the smallest mesogen **1a** would fit the *a* parameter of a proposed hexagonal phase (see column 3 and 6, Table 2).[6] An overall star shape of the mesogens **1** should be expected, if only rotations around the single bonds between aromatic rings and carboxyl group would be realized. However, a synclinic conformation of aromatic rings has been suggested for phasmidic oligoesters.[22] Taking this into account, a possible conformer for **1** can be proposed, where two of the three arms are rotated around the CO single bond of the inner carboxyl group. In this way, an E-shaped molecule is obtained, in which nonpolar aliphatic chains are segregated from the polar aromatic core. A pair of mesogens can then build the columnar unit as shown in Table 2, which is supported by density estimations assuming a thickness of 4.5 Å for a columnar slice (see column 7, Table 2). The diameters corresponding to the E-shaped conformers fit satisfactorily the calculated parameters *a* of a hexagonal phase. The small deviation of the experimental data from theoretical diameters of the pairs can be explained by an imperfect stacking of the benzoyloxy scaffold. The mesogens are rather disordered along the columns since no additional reflection has been detected at wide angles.

The powder diffraction patterns of **1a** annealed at room temperature and the low-temperature mesophases of **1c**−**d** show several reflections in the small-angle region, which can be attributed to columnar phases of lower symmetry. Eight reflections are clearly distinguished for the annealed phase of **1a**.[16] They can be indexed according to a centered rectangular unit cell with $a = 76.1$ Å and $b = 35.2$ Å. The *cm* space group of the 2D lattice is confirmed by the absence of all reflections with $h + k = 2n + 1$. Only three reflections are found for the low-temperature phases of the larger molecules **1b**−**d**, which do not allow an unequivocal identification of their 2D structure. In the wide-angle region only a halo is detected for all compounds.

In summary, star-shaped oligoester mesogens **1** form columnar LC phases. X-ray results point to a stacking of conformers which do not have a star-shaped conformation as suggested by the molecular structure. Further studies by dilatometry, 2D X-ray, and solid-state NMR techniques are currently in progress to establish a more detailed model of the supramolecular columnar assemblies.

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Supporting Information Available: Experimental details, preparation procedures for **1** and **4** with analytical data (^1H and ^{13}C NMR, mass spectrometry, and elemental analysis), optical texture for **1b**, and X-ray graph and DSC curves for **1a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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