Liquid Crystals

Liquid Crystals with Complex Superstructures**

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The investigation of molecular self-organization is one of the most exciting areas of contemporary chemical research. Significant progress was recently achieved in the field of crystal engineering, especially with coordination polymers.[1] In contrast to these crystalline systems, which once formed are hard to modify, fluid self-organized structures can easily respond to external stimuli and change as a result of changed external conditions. This fundamental principle is used by all biological systems.[2] Liquid-crystalline (LC) systems combine order and mobility and therefore can be regarded as simple model systems in which the driving forces of self assembly can be studied in a systematic and controlled manner. However, the known self-organized structures of LC materials, though of great technological importance,[3] are relatively simple, and are restricted mostly to nematic layered (smectic = Sm) and columnar morphologies (Col).[4] More recently the formation of bicontinuous networks and spherelike aggregates was found to lead to new cubic and noncubic mesophase structures.[5–7] Based on the concept of competitive polyphilicity, elaborated in our laboratories,[8,9] it now seems possible to further increase the complexity of these self-organized fluid systems. This concept was successfully applied first to rodlike bolaamphiphiles with nonpolar lateral chains (see Figure 1), which form honeycomb-like arrays of cylinders and a series of novel layer structures.[8] However, facial amphiphiles, in which the molecular topology is reversed, that is, a polar group is attached to a lateral position on a rigid aromatic core and lipophilic chains are tethered at the termini (see Figure 1), have so far failed to give such complex structures.[10]

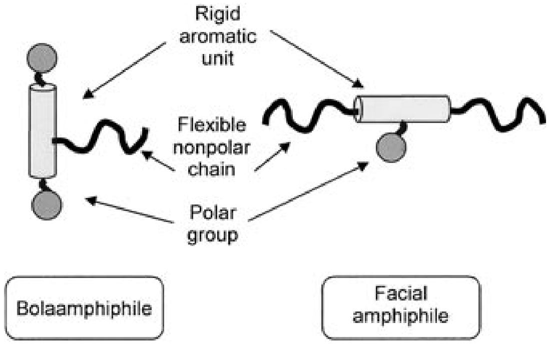

Figure 1. Schematic structures of ternary bolaamphiphiles and facial amphiphiles.

Herein we report successful generation of novel soft matter morphologies with facial polyphilic LC molecules of a new type, composed of three incompatible segments. The new LC phases comprise three distinct subspaces, each containing one of the three molecular parts. Two of the incompatible segments, aromatic and aliphatic, form alternating layers. The third segment, which incorporates an ionic group, forms closed spheroidic aggregates, which are distributed either randomly within the aromatic sublayers (filled random-mesh phase) or on an hexagonal net (rhombohedral 3D phase, Rho). These polar ionic groups can also coalesce into infinite columns, which penetrate the layer stacks leading to a completely new type of liquid-crystal organization, characterized by an orthogonal set of layers and columns in one structure, designated as channeled-layer phases (ChL). The first representative of such mesophases, the hexagonal channeled-layer phase (ChL_{hex}) is unambiguously proven by

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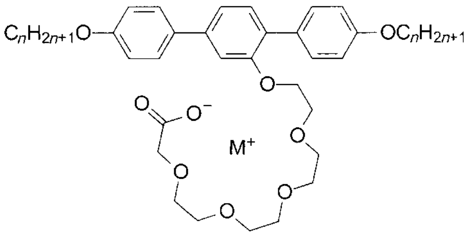
electron-density calculation based on high-resolution X-ray diffraction. It is also shown that the transitions between these three new types of LC organization can be tuned by molecular design and triggered by external stimuli.

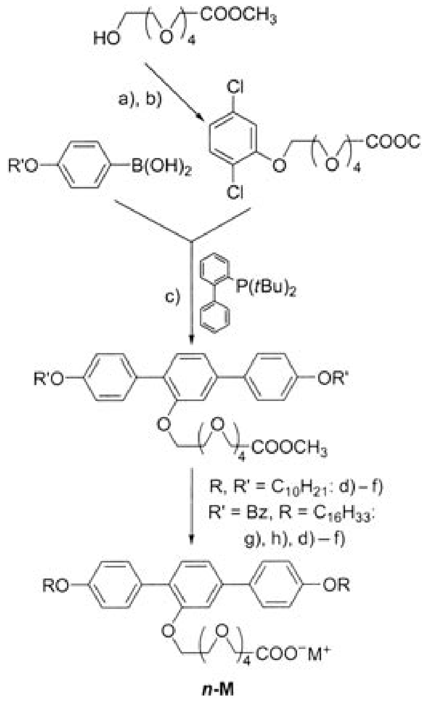
Table 1: Transition temperatures, corresponding enthalpy values, and lattice parameters of the LC phases of the compounds ***n*-M**.[a]



Complex	*n*	M	*T*/°C[b][Δ*H*/kJ mol^{-1}][b]	Lattice parameter/nm^{-1}[c]
16-Na	16	Na	Cr_1 37 [17.4] Cr_2 52[d] [42.7] Rho 60 [0.1] SmA_{frm} 108 [2.1] Iso	$d_1 = 4.0$ (90 °C), $a = 3.4$, $c = 12.8$ (50 °C)
16-Cs	16	Cs	Cr_1 37 [35.4] Cr_2 90[d] [14.9] ChL_{hex} 114 [2.0] Iso	$a = 3.9$, $c = 4.1$ (103 °C)
10-Li	10	Li	G 7[e] ChL_{hex} 99 [1.8] Iso	$a = 3.8$, $c = 3.6$ (75 °C)
10-Na	10	Na	G 17[e] ChL_{hex} 105 [1.7] Iso	$a = 3.9$, $c = 3.7$ (70 °C)
10-K	10	K	G 4[e] ChL_{hex} 123 [2.1] Iso	$a = 3.8$, $c = 3.6$ (115 °C)
10-Cs	10	Cs	Cr_1 51[d] [20.3]Cr_2 71[d] [3.3] (G-8) M1 120[f] [–] ChL_{hex} 127 [2.3] Iso	$a = 4.08$, $c = 3.72$ (80 °C)

[a] The analytical data and tables with X-ray data are provided in the Supporting Information; abbreviations: Cr = crystalline solid state; G = glassy state; Iso = isotropic liquid state; Rho = mesophase with a rhombohedral 3D lattice ($R\bar{3}m$), see Figure 3b; SmA_{frm} = filled random-mesh phase, see Figure 3a; ChL_{hex} = channeled-layer phase (*P6/mmm*), see Figure 3c; M1 = low-temperature mesophase. [b] Obtained by differential scanning calorimetry (DSC-7, Perkin Elmer, 10 K min^{-1}) during the second heating scan and confirmed by polarizing microscopy. [c] Obtained from the Guinier pattern, except the values of **10-Cs**, which were taken from the synchrotron small-angle diffraction experiments. [d] Observed only in the first heating scan. [e] Even after storage at 25 °C for about six months no crystallization could be observed. [f] Transition can only be detected in the X-ray diffraction pattern.

The compounds denoted **16-Na, 16-Cs** and **10-M** (M = Li, Na, K, Cs) were synthesized according to Scheme 1 and the mesophase properties are summarized in Table 1. The sodium salt **16**-Na forms two mesophases. Between 60 °C and the isotropization temperature at 107 °C the X-ray diffraction pattern is characterized by two orders of a meridional-layer reflection, which corresponds to a periodicity of $d_1 = 4.0$ nm (see Figure 2a). The diffuse wide-angle scattering is circular and has two clear maxima centered on the equator (see Figure 2b). This feature indicates a smectic A (SmA) liquid-crystal phase, with the molecules on average perpendicular to the layer plane, but without long-range positional order within the layer. As expected, d_1 is shorter than the length of the extended molecule ($L = 5.6$ nm), hence the alkyl chains from neighboring layers show some interdigitation. However, in contrast to the conventional SmA phase, even for a highly oriented sample, the diffuse wide angle scattering forms a closed ring (see Figure 2b), and the pattern contains an additional diffuse small angle equatorial maximum, which corresponds to an average distance of $d_2 = 3.2$ nm (see Figure 2a). This diffuse maximum indicates an additional short range periodicity in the layer plane. An explanation of this unique feature can be sought in the T-shaped triblock structure of the molecule. As in other SmA phases the aromatic cores and the alkyl chains are segregated into distinct sublayers. However, the polar groups, fixed to the centers of the terphenyl cores and yet strongly incompatible with them, are forced to cluster mainly within the terphenyl sublayers (see Figure 3a). These clusters are distributed randomly within the aromatic sublayers, with an average distance of $d_2 \approx 3.2$ nm. The polar groups are quite flexible and likely to be orientationally disordered within the aggregates, hence the circular shape of the diffuse wide-angle scattering.



***n*-M**

Scheme 1. Synthesis of compounds ***n*-M**. a) toluenesulfonyl chloride, pyridine; b) 2,5-dichlorophenol, K_2CO_3; c) $Pd(OAc)_2$, KF, THF;[11] d) NaOH, H_2O; e) HCl, H_2O, Et_2O; f) MOH or Cs_2CO_3 (M is Na–Cs); g) $Pd(OH)_2$, cyclohexene, MeOH; h) $C_{16}H_{33}Br$, K_2CO_3, Bu_4NI.

The layered LC phase can thus be described as a random-mesh phase, in which the holes are filled by the polar lateral groups, that is, by the third incompatible component (filled random-mesh phase, SmA_{frm}). In this respect the mesophase is new and different from conventional smectic phases and from the mesh phases known in lyotropic systems,[12] block copolymers,[13] and rod–coil molecules,[14] in which the holes or dimples within a sublayer are filled not by a third component but by excess material from the two adjacent sublayers.

The rhombohedral phase—a correlated filled hexagonal mesh phase—is described next. Upon cooling the SmA_{frm}

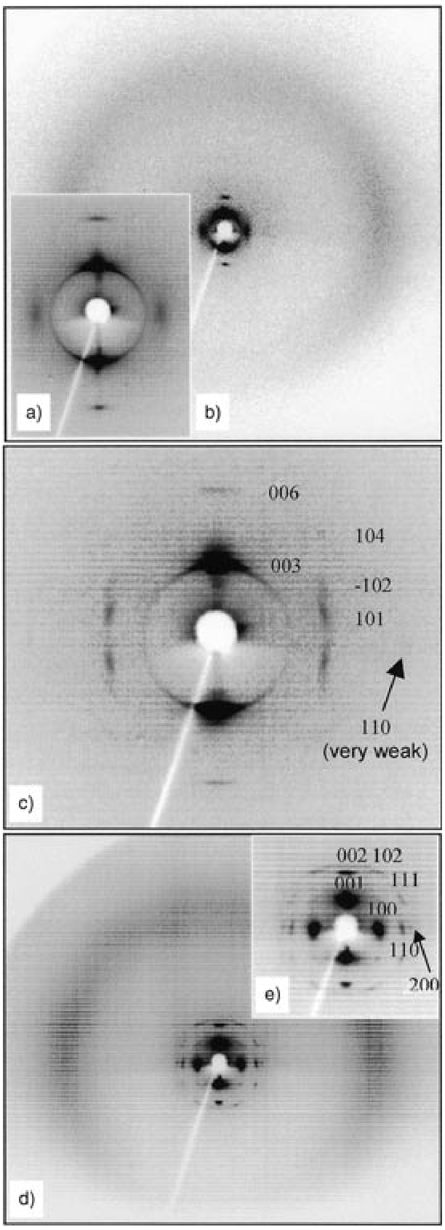


Figure 2. X-ray diffraction pattern of aligned samples of the mesophases. a) Filled random mesh phase ($\mathrm{SmA}_{\mathrm{frm}}$) of **16-Na** at 102 °C (small-angle region). b) Same as (a), but wide-angle region. c) Rhombohedral ($R\bar{3}m$) phase of **16-Na** at 50 °C (small-angle region). d) Wide-angle region of the $\mathrm{ChL}_{\mathrm{hex}}$ ($P6/mmm$) phase of **10-K** at 85 °C. e) Same as (d), but small-angle region. In all diffraction patterns the *c*-axis is vertical, perpendicular to the substrate and the X-ray beam. The samples are disordered around an ∞-fold axis perpendicular to the substrate (fiber geometry).

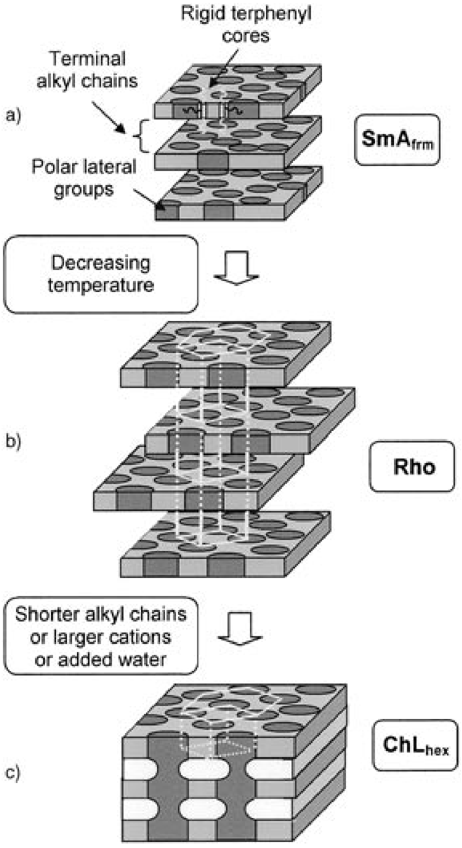


Figure 3. Organization of the facial amphiphiles ***n*-M** depending on the molecular structure and conditions. For clarity, the alkyl chains are not shown in the models and the centers of the unit cells of the 3D lattices are offset vertically from the inversion center by half a sublayer thickness.

phase in **16-Na** below 60 °C, the X-ray diffraction pattern changes significantly. The diffuse small-angle scattering on the equator splits and condenses into a series of row-line Bragg reflections (see Figure 2 c). This diffraction pattern can be indexed on a rhombohedral 3D lattice, space group $R\bar{3}m$, with the parameters $a = 3.4$ nm and $c = 12.8$ nm. No significant change can be observed at this phase transition under the polarizing microscope. The fanlike texture of the $\mathrm{SmA}_{\mathrm{frm}}$ phase remains and also the optically isotropic (homeotropically aligned) regions do not change.[15] Only a significant increase in viscosity is observed. This observation confirms that the mesophase is optically uniaxial, which is consistent with the proposed rhombohedral lattice. To understand the structure of the Rho phase it is reasonable to assume that at the $\mathrm{SmA}_{\mathrm{frm}} \rightarrow \mathrm{Rho}$ transition, the polar domains pack on a hexagonal 2D lattice within the aromatic sublayers (filled-hexagonal-mesh layers). The occurrence of this order within the layers is accompanied by long-range positional correlation between layers in an ABC fashion, thus leading to the 3D rhombohedral symmetry $R\bar{3}m$, as shown in Figure 3 b. In contrast to the small-angle scattering, the overall appearance of the wide-angle region of the X-ray diffraction pattern does not change at the phase transition, that is, the diffuse ring with distinct equatorial maxima remains. This is in line with the proposed model and indicates that the phase is indeed liquid crystalline with a 3D mesoscale lattice and that it belongs to correlated layer structures.[16] The structure is related to that of the $R\bar{3}m$ mesh phase in some other organized fluids,[12–14] but again unlike in those systems, the holes in the layers are filled with a distinct third component.

The third phase, described below, has a 3D hexagonal structure consisting of layers penetrated by continuous polar channels (channeled-layer phase, $\mathrm{ChL}_{\mathrm{hex}}$). It is found in compound **16-Cs**, in which the Na^+ ion of **16-Na** is replaced by

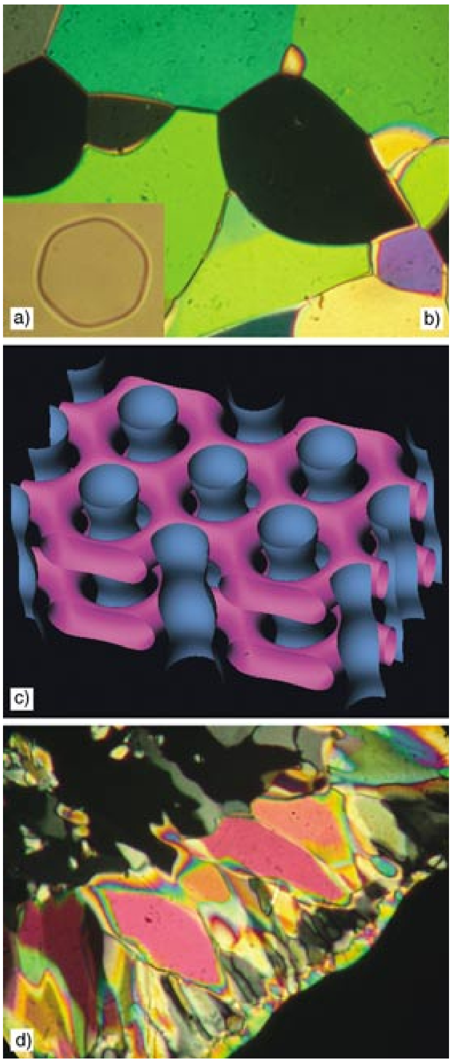


Figure 4. The channeled layer mesophase (ChL_{hex}). a) Growth of an optically isotropic hexagon of the ChL_{hex} phase from the isotropic liquid state at 127 °C. b) Texture of the ChL_{hex} phase of compound **10-Cs** as observed between crossed polarizers at 125 °C (the optically isotropic regions are homeotropically aligned regions). c) Reconstructed electron-density map of the ChL_{hex} mesophase of compound **10-Cs**; the blue isoelectron surfaces enclose the polar channellike domains (high electron density) and the pink surface encloses the low density, that is, aliphatic volume. Texture of the ChL_{hex} phase induced in the contact region between **16-Na** and 5.0 M aqueous NaCl solution at 95 °C. The dark area at the right is the NaCl solution, the dark areas at the left represent homeotropically aligned regions of the ChL_{hex} phase (layers parallel to the substrate).

the larger Cs^+, and also in the series of salts **10-M** (M = Li, Na, K, Cs), in which the length of the two terminal alkyl chains is reduced from hexadecyl to decyl. The common feature of all five compounds is the appearance of a mosaic-like texture with large optically isotropic regions (see Figure 4 b) at the transition from the isotropic liquid to the mesophase. The optically isotropic regions grow as rounded hexagons (see Figure 4 a). This growth pattern, the optical uniaxiality and the rather high viscosity of the mesophase, are preliminary indications of a 3D hexagonal structure, and such a structure was indeed confirmed by X-ray diffraction. The diffraction pattern of compound **10-K**, obtained with an aligned sample (see Figure 2 d and e) shows diffuse wide angle scattering with distinct equatorial maxima. This is very similar to the appearance of the Rho phase, but the positions of the Bragg reflections in the small-angle region are completely different. The reflections can be indexed on a 3D hexagonal lattice, space group $P6/mmm$, with the parameters $a = 3.8$ nm and $c = 3.6$ nm. Similar diffraction patterns were observed for the mesophases of all other **10-M** compounds as well as for **16-Cs**; the lattice parameters are collated in Table 1.

More detailed X-ray investigations were carried out for compound **10-Cs** by using a synchrotron source. Small-angle diffraction intensities were measured from high-resolution powder patterns. The corrected intensities and a description of the electron-density-reconstruction procedure are given in the Supporting Information. The electron-density map of the ChL_{hex} phase of compound **10-Cs** is shown in Figure 4 c. The blue surfaces enclose the polar domains (high electron density) and the pink surface encloses the low-density, that is, aliphatic volume. According to the map, the terphenyls are positioned perpendicular to the layer planes (as also indicated by the diffuse wide angle maxima on the equator), thus forming a perforated layer between the perforated alkyl layers. The polar domains form cylinders with undulated profile, arranged on a hexagonal 2D lattice and penetrating the layer structure. At lower temperature additional mesophases were found for the Cs-salt **10-Cs**, which require additional investigations.

From the comparison of compounds **10-Na** and **16-Na** the effect of the length of the terminal alkyl chains is evident. For long chains the aliphatic sublayers are too thick to allow fusion of the polar regions. For such compounds the ABC packing of the layers (Rho phase) allows optimal space filling. In the short-chain compounds the aliphatic sublayers are thinner and fusion of the polar regions is possible. The resulting reduction in interfacial area stabilizes the AAA stacking (ChL_{hex} structure), which allows the formation of continuous polar channels (see Figure 3 c). The same change from Rho to ChL_{hex} is observed when the Na^+ ions of **16-Na** are replaced by Cs^+ ions in **16-Cs**. This change could be interpreted in terms of the larger Cs^+ ions increasing the overall volume of polar domains and allowing them to fuse, even across the thick hexadecyl sublayer of **16-Cs**.

The mesophase type can also be influenced by solvents. For example, the addition of a 5.0 M sodium chloride solution to **16-Na** induces a ChL_{hex} phase as indicated by the very typical texture of this mesophase (see Figure 4 d). Similar to the effect of large cations, the added aqueous solution is thought to induce fusion of the polar domains by increasing their volume through the coordination of water molecules and/or additional Na^+ ions.

The above results show that competition of multiple-level microsegregation and anisotropic interaction of rodlike molecular segments presents a successful strategy for the design of new and exciting mesophase morphologies. The self-organized structures obtained with the molecules presented here are all quite distinct from conventional thermotropic and lyotropic liquid-crystalline phases of other compounds with low molecular weights and from the mesophases of some LC dendrimers[6,17] and main chain polymers.[18] The mesophases we report here represent combinations of spheroids or columns with layers. Hence, a higher-than-usual level of structural complexity is achieved through the presence of three incompatible molecular moieties, instead of two as in more conventional amphiphiles. Though there have been reports of several complex polymer morphologies in triblock copolymers[19] the present morphologies are different with regards to their structure and size. For example, "spheres-on-layer" morphologies were reported for linear ABC block copolymers, whereas the Rho phase represents a "spheres-in-layer" morphology. Similarly, in the $\mathrm{ChL}_{\mathrm{hex}}$ phase the cylinders are arranged perpendicular to the layer planes, whereas in the "cylinder-on-layer" polymer morphology the columns run parallel to the layers. Additionally, these ordered structures occur at a significantly smaller length scale (3–10 nm) than those of the block copolymers (10 to >100 nm).

In the $\mathrm{ChL}_{\mathrm{hex}}$ phase reported here, the polar regions represent well defined ion-carrying channels, which can be modified by molecular design and influenced by external stimuli. Hence, these or similar materials might be useful, for example, as components in ion-conducting nanodevices. One can also envisage their use as ion-triggered gate valves, opened ($\mathrm{ChL}_{\mathrm{hex}}$ phase) by a solution carrying large ions and closed (Rho phase) when small or no ions are present. The study of the current structures may also shed new light on ionic channels in biological systems and on transport across lipid membranes.[20] Being mechanically more robust than columnar liquid crystals and readily surface-aligned,[21] the 3D mesophases may also be used for encapsulating low-molecular and polymeric guests, such as drugs, and electroluminescent[22] or electronically conducting polymers[23] and biopolymers.[24]

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[1] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629 – 1658; S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276 – 288; C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem.* **2004**, *116*, 1490 – 1521, *Angew. Chem. Int. Ed.* **2004**, *43*, 1466 – 1496; S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388 – 2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334 – 2375; S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276 – 288.

[2] G. T. Steward, *Liq. Cryst.* **2004**, *31*, 443 – 471.

[3] P. Kirsch, M. Bremer, *Angew. Chem.* **2000**, *112*, 4384 – 4405; *Angew. Chem. Int. Ed.* **2000**, *39*, 4216 – 4235; D. Pauluth, K. Tarumi, *J. Mater. Chem.* **2004**, *14*, 1219 – 1227.

[4] D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill, *Handbook of Liquid Crystals, Vol. 1–3*, Wiley-VCH, Weinheim, **1998**.

[5] K. Borisch, S. Diele, P. Göring, H. Kresse, C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 529 – 543; C. Tschierske, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 69 – 80.

[6] G. Ungar, Y. Liu, X. Zeng, V. Percec, W.-D. Cho, *Science* **2003**, *299*, 1208 – 1211; X. Zeng, G. Ungar, Y. Liu, V. Percec, A. E. Dulcey J. K. Hobbs, *Nature* **2004**, *428*, 157 – 160. V. Percec, C. M. Mitchell, W.-D. Cho, S. Uchida, M. Glodde, G. Ungar, X. Zeng, Y. Liu, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.* **2004**, *126*, 6078 – 6094.

[7] Introduction of chirality is an alternative way to modify mesophase structures, especially of lamellar phases: H.-S. Kitzerow, C. Bahr, *Chirality in Liquid Crystals*, Springer, New York, **2001**.

[8] X. H. Cheng, M. K. Das, S. Diele, C. Tschierske, *Angew. Chem.* **2002**, *114*, 4203 – 4207; *Angew. Chem. Int. Ed.* **2002**, *41*, 4031 – 4035; X. H. Cheng, M. Prehm, M. K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume, C. Tschierske, *J. Am. Chem. Soc.* **2003**, *125*, 10977 – 10996; M. Prehm, S. Diele, M. K. Das, C. Tschierske, *J. Am. Chem. Soc.* **2003**, *125*, 614 – 615.

[9] C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 1485 – 1508; C. Tschierske, *J. Mater. Chem.* **2001**, *11*, 2647 – 2671; C. Tschierske, *Ann. Rep. Progr. Chem., Ser. C* **2001**, *97*, 191 – 268.

[10] F. Hildebrandt, J. A. Schröter, C. Tschierske, R. Festag, M. Wittenberg, J. H. Wendorff, *Adv. Mater.* **1997**, *9*, 564 – 567; J. A. Schröter, C. Tschierske, M. Wittenberg, J.-H. Wendorff, *Angew. Chem.* **1997**, *109*, 1160 – 1163; *Angew. Chem. Int. Ed. Engl.* **1997**, *36,* 1119 – 1121; R. Plehnert, J. A. Schröter, C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 2611 – 2626.

[11] J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 9550 – 9561.

[12] M. C. Holmes, *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 485 – 492.

[13] I. W. Hamley, *The Physics of Block-Copolymers*, Oxford University Press, Oxford, **1998**, pp. 24 – 130.

[14] M. Lee, B.-K. Cho, W.-C. Zin, *Chem. Rev.* **2001**, *101,* 3869 – 3892; J.-H. Ryu, N.-K. Oh, W.-C. Zin, M. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 3551 – 3558.

[15] The optical uniaxiality of this phase is consistent with the terphenyl units having an average orientation perpendicular to the layer planes.

[16] M. Prehm, S. Diele, M. K. Das, C. Tschierske, *J. Am. Chem. Soc.* **2003**, *125*, 614 – 615.

[17] L. Gehringer, C. Bourgogne, D. Guillon, B. Donnio, *J. Am. Chem. Soc.* **2004**, *126*, 3856 – 3867; M. Marcos, A. Omenat, J. L. Serrano, *C. R. Chim.* **2003**, *6,* 947 – 957.

[18] K. Fu, N. Sekine, M. Sone, M. Tokita, J. Watanabe, *Polym. J.* **2002**, *34*, 291 – 297.

[19] S. Sioula, N. Hadjichristidis, E. L. Thomas, *Macromolecules* **1998**, *31,* 5272 – 5277; V. Abetz in *Supramolecular Polymers*, (Ed.: A. Ciferri), Marcel Dekker, New York, **2000**, pp. 215 – 262; J. Beckmann, C. Auschra, R. Stadler, *Macromol. Rapid Commun.* **1994**, *15*, 67 – 72; H. Hückstädt, A. Göpfert, V. Abetz, *Macromol. Chem. Phys.* **2000**, *201*, 296 – 307.

[20] D. A. Doyle, J. M. Cabral, R. A. Pfuetzner, A. Kuo, J. M. Gulbis, S. L. Cohen, B. T. Chait, R. MacKinnon, *Science* **1998**, *280*, 69 – 77.

[21] Between glass substrates (microscope slides), a homeotropic alignment of the $\mathrm{ChL}_{\mathrm{hex}}$ phases (channels perpendicular to the substrate surfaces) is spontaneously formed by slow cooling from the isotropic melted state. This alignment is indicated by the optically isotropic appearance of the thin films obtained in this way. The homeotropic alignment is found over large areas (several square centimeters), only at the edges and around gas bubbles a birefringent texture (defects) can be found.

[22] Z. N. Bao, K. R. Amundson, A. J. Lovinger, *Macromolecules* **1998**, *31*, 8647 – 8649.

[23] V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudsonk, H. Duank, *Nature* **2002**, *419*, 384 – 387.

[24] I. Koltover, T. Salditt, J. O. Radler, C. R. Safinya, *Science* **1998**, *281*, 78 – 81.