Laterally Connected 'Trimesogens'

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Lateral fixing of three rod-like 4,4″-didecyloxy-*p*-terphenyl-units gives liquid crystalline materials with a broad smectic A-mesophase and a considerably increased stability with respect to the nematic phase of the parent 4,4″-didecyloxy-2′-methyl-*p*-terphenyl.

Most thermotropic liquid crystalline compounds consist of rodlike (calamitic) molecules. If these single molecules are introduced into a polymer chain or attached *via* an appropriate spacer to a polymeric backbone, liquid crystalline polymers result.

Dimers,[1] trimesogens,[2–4] tetramesogens[5] and larger oligomers with a well-defined molecular structure are intermediate between low molecular mass and polymeric liquid crystals. In most cases the calamic units are connected *via* their terminal chains. Only a few mesogenic polymers with rigid cores laterally attached to a polymeric backbone (type **A**),[6,7] some examples of main chain polymers with perpendicularly connected rigid cores (type **B**),[8] and Siamese twins[9] have been described. All these compounds give rise to the nematic mesophase in contrast to the end fixed liquid crystalline oligomers and polymers which are predominately smectogenic.

Herein we report the new compounds **3** and **6** in which three calamitic *p*-terphenyl rigid cores are laterally attached to each other by means of two different topologies. These oligomers differ from the existing polymers by the type of mesogenic units used and the structure of the linking units, but nevertheless, their structural features resemble some of those in polymers **A** and **B**.

These compounds were synthesized according to the Schemes 1 and 2 using a Pd⁰-catalysed cross coupling reaction as the key step.[10]†

Investigation of these new compounds by polarizing microscopy and calorimetric measurements have proven that both compounds have broad mesomorphic ranges with unexpected high clearing temperatures (see Table 1). By cooling from the isotropic melt at 124 °C (for **3**) and 155 °C (for **6**), the formation of batonnets that rapidly coalesce to a focal conic fan-like texture is observed, indicating a smectic A-type mesophase. In the case of compound **3** the S_A-phase could be supercooled down to room temperature without crystallization. At 8 °C the transition to the glassy state is observed. X-Ray investigations have further proven the smectic layer structure. The X-ray pattern shows a sharp reflection in the small angle region and a diffuse scattering in the wide angle region, supposing a smectic layer structure without order in the layers. The layer thickness (d) is 3.44 nm for **3** at 60 °C, and 3.60 nm for **6** at 60 °C. These d values are in the same order of magnitude as that of the 4,4″-didecyloxy-2′-methyl-*p*-terphenyl **7**[11] (d = 3.63 nm at 89 °C) which may be looked upon as a single calamitic unit of the trimesogens **3** and **6**.

Using CPK-models and assuming an all *trans* conformation of the alkyl chains, the molecular length (L) of compound **7** was determined to be 3.8 nm. Using this value, the d/L ratios given in Table 1 were determined. The thickness of the smectic layers of compounds **3** and **6** is only slightly smaller than the length of their single calamitic units. This is in agreement with our model in which the layers of the smectic phase of the trimesogens **3** and **6** are formed by the parallel arrangement of the calamitic single units.

If one compares the mesogenic properties of the compounds **3**, **6** and **7** (Table 1), it is obvious that the covalent fixing of three calamitic single molecules **7** *via* their lateral substituents gives rise to a considerable increase of the clearing temperature. It is especially remarkable, that this lateral fixation stabilizes the

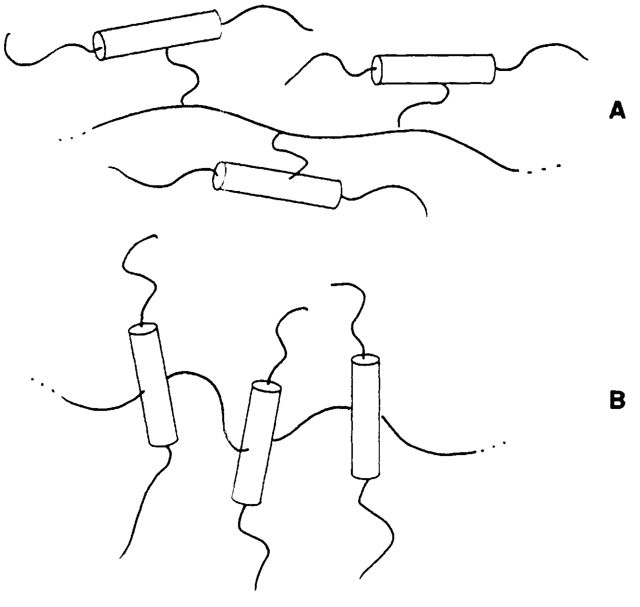
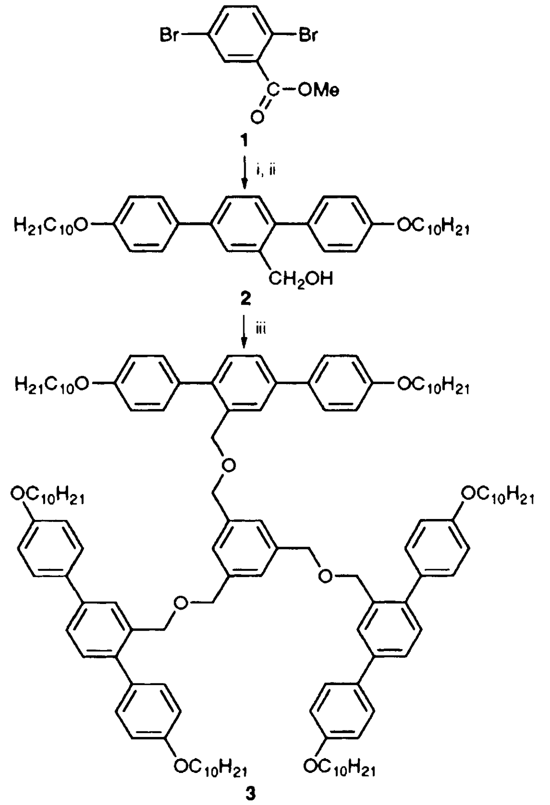
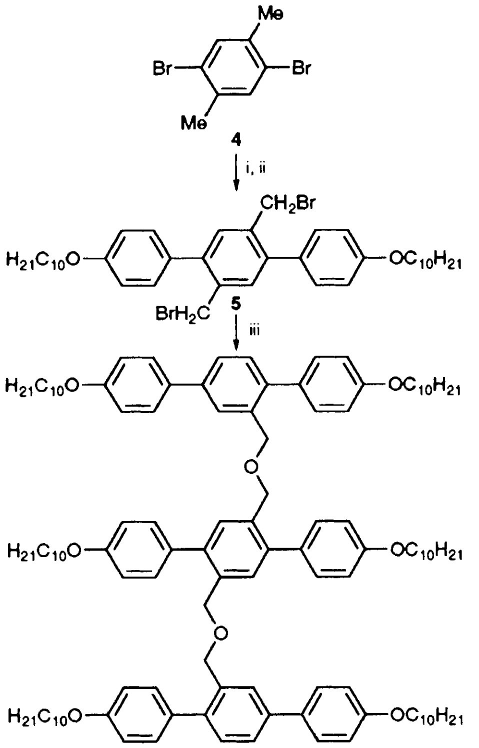


Fig. 1 Structural types of laterally fixed liquid crystalline polymers



Scheme 1 *Reagents and conditions*: i, 4-decyloxyphenylboronic acid, $Pd(PPh_3)_4$, glyme–aq. $NaHCO_3$, 5 h, 100 °C, 93%; ii, LAH, THF, 24 h, 20 °C, 90%; iii, 1,3,5-tris(bromomethyl)benzene, KH, cat. NBu_4I, THF, 48 h, 20 °C, 60%



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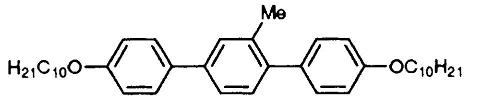
Scheme 2 *Reagents and conditions*: i, 4-decyloxyphenylboronic acid, Pd(PPh$_3$)$_4$, benzene–aq. Na$_2$CO$_3$, 5 h, reflux, 95%; ii, NBS, CCl$_4$, 2 h, reflux, 78%; iii, **2**, KH, cat. Bu$_4$NI, THF, 24 h, reflux, 74%

Table 1

Compound	Transition temperatures T/°C (transition enthalpies ΔH/kJ mol^{-1})^a	d/nm (T/°C)	d/L
3	cr 73 (g 8) S$_A$ 124 is (57.5) (19.7)	3.44 (60)	0.905
6	cr 36 S$_A$ 155 is (18.5) (11.5)	3.60 (60)	0.95
7	cr 72 S$_A$ 104 N 109 is	3.63 (89)	0.995

^{a} Abbreviations: cr = crystalline, S$_A$ = smectic A-phase, N = nematic phase, g = glass temperature, is = isotropic phase.



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S$_A$-layer structure with respect to the nematic mesophase of compound **7**, suggesting that the lateral fixation of calamitic units leads to an increase of the structural order.

These results indicate that the lateral fixation of calamitic mesogens is a powerful tool to obtain liquid crystalline materials with interesting physical properties. We have to conclude, that not only terminal but also lateral attachment of rod-like mesogenic groups can favour the smectic state.

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Footnotes

† Correct C, H analyses, and ^{1}H and ^{13}C NMR spectra were obtained *e.g.* for **3**: ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, Me$_4$Si) δ 0.87 (t, ^3J 6.3 Hz, 18 H; CH$_3$), 1.25 (m, 84 H; CH$_2$), 1.75 (m, 12 H; CH$_2$), 3.90 (dt, ^3J 6.4 Hz, 12 H; O–CH$_2$), 4.46 (s, 12 H; Ar–CH$_2$), 6.89–7.67 (m, 36 H; Ar–H); **6**: ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, Me$_4$Si) δ 0.86 (t, ^3J 6.2 Hz, 18 H; CH$_3$), 1.26 (m, 84 H; CH$_2$), 1.77 (m, 12 H; CH$_2$), 3.93 (dt, $^3J_{H,H}$ 7.5 Hz, 12 H; O–CH$_2$), 4.44 (s, 8 H; Ar–CH$_2$), 6.83–7.68 (m, 32 H; Ar–H).

References

1 P. J. Barnes, A. G. Douglass, S. K. Heeks and G. R. Luckhurst, *Liq. Cryst.*, 1993, **13**, 603.
2 G. S. A. Hard, A. G. Douglass, C. T. Imrie and L. Taylor, *Liq. Cryst.*, 1992, **11**, 779.
3 V. Bach, V. K. Beck, K. H. Etzbach, K. Siemensmeyer and G. Wagenblast, *Proceedings 21. Freiburger Arbeitstagung Flüssigkristalle*, 1992, P40.
4 K. Zab, O. Agert, D. Joachimi, B.Neumann and C. Tschierske, *Liq. Cryst.*, 1994, in the press.
5 R. Eidenschink, F. H. Kreuzer and W. H. De Jeu, *Liq. Cryst.*, 1990, **8**, 879.
6 F. Hessel and H. Finkelmann, *Polym. Bull (Berlin)*, 1985, **14**, 375.
7 G. W. Gray, J. S. Hill and D. Lacey, *Angew. Chem., Int. Ed. Engl. Adv. Mater*, 1989, **28**, 1120.
8 V. Krone, H. Ringsdorf, M. Ebert, H. Hirschmann and J. H. Wendorff, *Liq. Cryst.*, 1991, **9**, 165.
9 H. Dehne, A. Roger, D. Demus, S. Diele, H. Kresse, G. Pelzl, W. Wedler and W. Weissflog, *Liq. Cryst.*, 1989, **6**, 47.
10 M. Hird, G. W. Gray and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1991, **206**, 187.
11 C. Tschierske, F. Hilderbrandt, J. A. Schröter, R. Rietz, R. Kleppinger, L. Schneider and H. Wendorff, *Proceedings 22. Freiburger Arbeitstagung Flüssigkristalle*, 1993, 11.