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Model studies towards liquid crystalline dendrimers with mesogenic repeat units throughout the structure

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Abstract—Model studies towards liquid crystal dendrimers in which the mesogenic units are based on alkoxyalkylbiphenyls and repeat through the structure are described; the parent monomers show smectic mesophases demonstrating the suitability of the motifs.

The interplay between microscopic and macroscopic behaviour lies at the heart of molecular-based materials research and a superb example is provided by the field of liquid crystals. The dendrimeric molecular architecture has proved extremely fascinating, not least because the properties of dendrimers tend to be significantly different from traditional polymers based on related repeat units.[1] The dendrimeric architecture, in which branching repeat units radiate from a central core, contrasts directly with the parallel molecular ('unit') alignment in liquid crystal phases. Despite this apparent dichotomy, a number of liquid crystal dendrimers are known.[2] In most cases, these materials are prepared by substituting mesogenic units onto the termini of classical dendrimers (termed side-chain dendrimers[3] by analogy to side-chain polymers). Liquid crystal dendrimers in which the mesogenic units repeat through the structure (termed main-chain dendrimers[3]) are rare[3,4] and model studies towards such materials are described herein.

Biphenyl units, which can be considered as the archetypal liquid crystal cores,[5] were chosen as the basis for investigation. Perhaps the simplest biphenyl unit which could be used in dendrimer construction is 3,4′,5-trisubstituted biphenyl itself. This building block was briefly investigated but, as expected, model compounds of type **1** proved to be non-mesogenic. More elaborate bis-biphenyls were therefore targeted (Fig. 1). The molecular design was based on knowledge of the 'parent' biphenyl mesogens where it is known that alkoxyalkylbiphenyls are liquid crystalline[6] but bisalkoxy derivatives are not.[7]

The alkoxyalkylbiphenyl unit was therefore incorporated in the molecular design and the first targets (repeating units) were formulated as **2** and **3**. The synthesis of model monomers is shown in Scheme 1. Both syntheses follow similar routes and, in order to provide rapid access to key intermediates, rely on statistical

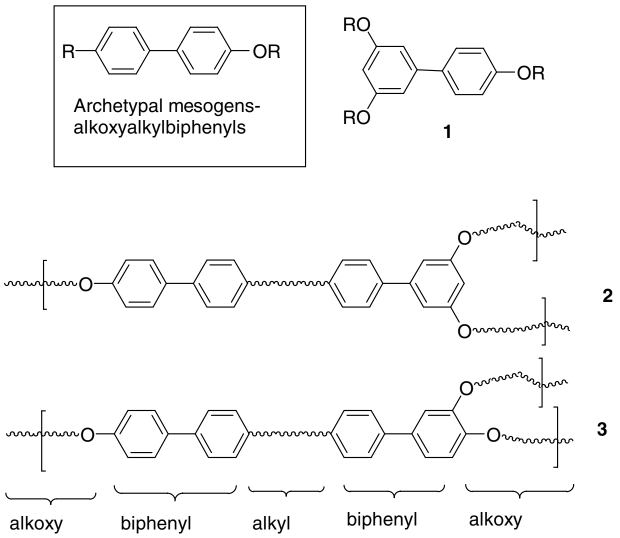

Figure 1. Dendrimer repeat units containing the alkoxyalkylbiphenyl motif.

Keywords: Dendrimers; Liquid crystals; Polycatenar.

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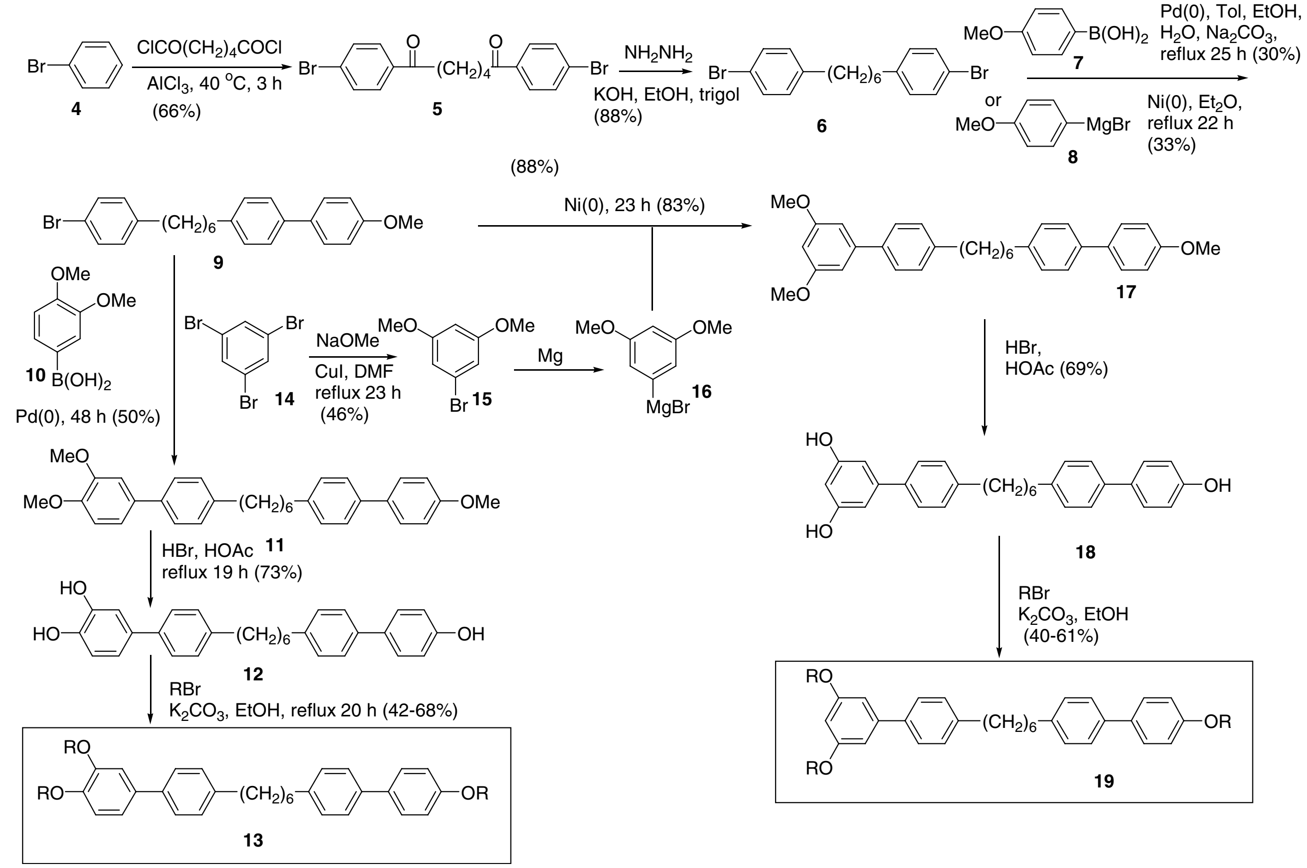

Scheme 1. Synthesis of model tricatenar monomers.

cross-coupling reactions for desymmetrisation. Friedel–Crafts reaction between bromobenzene (used as solvent) and adipoyl chloride[8,9] gave diketone **5**, which was reduced[8] using the Huang–Minlon modification of the Wolff–Kishner reaction. Suzuki coupling between dibromide **6** and 4-methoxyphenylboronic acid **7** gave an acceptable yield of singly coupled product **9** (unreacted starting material was recycled). Similar Suzuki coupling between **9** and **10** gave **11**, whereas isomer **17** was most conveniently prepared using a nickel-catalysed Kumada coupling employing the Grignard reagent formed from **15**. Trimethoxy intermediates **11** and **17** were demethylated using HBr/HOAc to give triols **12** and **18**. Realkylation gave the two series of model monomers **13** and **19**.

Liquid crystalline compounds, which present a structure which is a hybrid between rod-like and disc-like molecules, are termed 'polycatenar' liquid crystals[10] and **13** and **19** are therefore elaborated versions of tricatenar compounds. Their liquid crystalline behaviour was investigated using polarising optical microscopy (POM) and differential scanning calorimetry (DSC), and the results are summarised in Tables 1 and 2.

Both series of compounds show liquid crystal behaviour. Compounds in series **13** develop monotropic smectic phases on cooling, whereas those of series **19** show enantiotropic smectic phases. The phases were assigned as smectic A based on the textures observed under POM.

Table 1. Thermal properties of model monomers **19** on cooling

R	Transition temperatures (isotropic liquid–smectic mesophase) °C
n-Hexyl	51
n-Heptyl	40
n-Octyl	39
n-Decyl	39
n-Dodecyl	35
n-Octanoyl	47

All materials show a monotropic mesophase which persists to room temperature. A more detailed table is presented in Supplementary data.

Table 2. Thermal properties of model monomers **13** on cooling

R	Transition temperatures (isotropic liquid (I)–smectic mesophase (S) – crystal (Cr)) °C
n-Hexyl	I 109 S 84 Cr
n-Heptyl	I 108 S 84 Cr
n-Octyl	I 108 S 83 Cr
n-Decyl	I 104 S 70 Cr
n-Dodecyl	I 108 S 87 Cr

All materials show an enantiotropic mesophase. A more detailed table is presented in the Supplementary data.

It is worth noting that alkoxyalkylbiphenyls typically show smectic liquid crystal behaviour also.