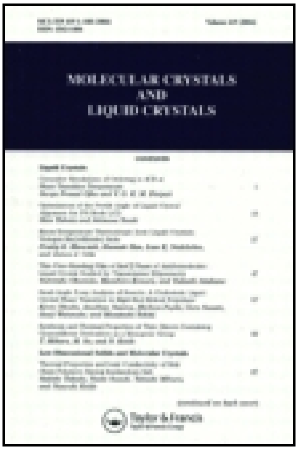

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Synthesis, Phase Behaviour and Structure of Liquid Crystalline Carbosilane Dendrimers with Methoxyphenyl Benzoate Terminal Mesogenic Groups

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Synthesis, Phase Behaviour and Structure of Liquid Crystalline Carbosilane Dendrimers with Methoxyphenyl Benzoate Terminal Mesogenic Groups

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For the first time a series of liquid crystalline dendrimers of generations 1 – 4 containing 8, 16, 32 and 64 terminal methoxyphenyl benzoate mesogenic groups respectively have been synthesised. Mesogenic groups were attached to the carbosilane dendritic matrices with terminal allyl groups through $-OOC-(CH_2)_{10}-Si(CH_3)_2OSi(CH_3)_2-$ spacer by a hydrosilylation reaction. Structure and purity of all new compounds were confirmed by ^{1}H-NMR spectroscopy and GPC analysis. Phase behaviour of LC dendrimers was investigated by means of polarising optical microscopy, DSC and X-ray methods. All LC dendrimers synthesised display mesophases of smectic types as well as crystalline phases over wide temperature region. Possible structure and arrangement of molecules of LC dendrimers in these mesophases are discussed.

Keywords: liquid crystal dendrimers; smectic mesophase; hydrosilylation

INTRODUCTION

A new direction in chemistry and physical chemistry of macromolecular compounds associated with the synthesis and study of highly branched polymers and oligomers, called dendrimers, has recently been actively developed [1]. Among dendritic compounds, a great scientific interest is the liquid crystalline (LC) dendrimers[2-11]. Their molecules combine structural units capable of LC mesophase formation (mesogenic groups) with dendritic or 'cascade' architecture.

This presentation deals with the carbosilane LC dendrimers with terminal mesogenic groups. Each superbranched molecule can be represented as a sort of a sphere, the internal part of which consists of non-mesogenic blocks (siloxane or silane type) and aliphatic spacers. This is a "soft" matrix of dendrimer. The rigid mesogens, being the molecules of liquid crystals, form the outside surface of the sphere. Three different constituents can be distinguished in such molecules: the internal dendritic core, the outer mesogenic groups and the spacers between the former and the latter. All of them have an influence on the size and the rigidity of these molecules and, as a result, on the properties of such compounds. Earlier we have synthesised five generations of LC dendrimers with cyanobiphenyl mesogenic groups[9]. This work presents synthesis, phase behaviour and structure of a series of new liquid crystalline dendrimers of generations 1 – 4 containing 8, 16, 32 and 64 terminal methoxyphenyl benzoate mesogenic groups.

EXPERIMENTAL

^{1}H-NMR spectra of the samples were recorded using Bruker WP-200 and WP-250 spectrometers in CCl_4 and $CDCl_3$ solutions. GPC analysis was performed in THF on Knauer set up equipped with Ultrastyragel 8×300 mm column (Waters) having pore size 10^3 Å, detectors – RI Waters R-410 and UV spectrometer Knauer. Waters 19×300 mm column fulfilled with Ultrastyragel 10^3 Å was used for preparative GPC. Phase transitions were studied by differential scanning calorimetry (DSC) with a Mettler TA-4000 thermosystem at a scanning rate of 10 K/min. The polarising microscopic investigations were performed using a Mettler FP-800 central processor equipped with a hot stage Mettler FP-82 and control unit in conjunction with a Lomo R-112 polarising microscope. X-ray diffraction measurements were made using CuK_α -radiation (λ = 1.542 Å) from 1.5kW sealed tube. Monochromatisation was done with a nickel filter and a graphite crystal. The diffraction patterns were collected using two dimensional position sensitive detector equipped with a computer. The samples for diffraction were pre-aligned by cooling from the isotropic phase in a 9.4 T magnetic field.

Synthesis

G-1(Und-MPhB)$_8$. Detailed synthesis was described elsewhere[4].

G-2(Und-MPhB)$_{16}$ was synthesized from carbosilane dendritic matrix G-2(All)$_{16}$ (0.23 g, 1.47 × 10^{-5} mol) and 4-methoxyphenyl 4'-[11-(tetramethyldisiloxy) undecanoyloxy] benzoate (H-Si-Und-MPhB, 2.08 g, 3.8 × 10^{-3} mol) according to the procedure for G-1(Und-MPhB)$_8$ described in [4]. Yield:

0.99 g (67%). Monodisperse compound was isolated by preparative GPC chromatography. ^{1}H-NMR data: (CCl_4, 200 MHz): δ=0.1 (s,36H), 0.2 (s, 192H), 0.7 (m, 112H), 1.4 (m, 268H); 1.8 (m, 32H); 2.6 (m, 32H); 3.9 (t, 48H); 7.0 (d, 32H); 7.2 (d, 32H); 7.3 (d, 32H); 8.3 (d, 32H).

G-3(Und-MPhB)$_{32}$. 25 ml of a dried toluene was added to the mixture of carbosilane dendritic matrix G-3(All)$_{32}$ (0.088 g, 2.52 × 10^{-5} mol) and H-Si-Und-MPhB (0.66 g, 1.2 × 10^{-3} mol). 15 ml of toluene was removed by evaporation. 3 μl of Pt-catalyst PC072 was added to the reaction mixture and it was stirred at the magnetic stirring for a week at 25°C. After evaporating *in vacuo* (133 Pa), the product was isolated from the excess of H-Si-Und-MPhB by multiple boiling with methanol. Yield: 0.43 g (85%). Monodisperse compound was isolated by preparative GPC chromatography. ^{1}H-NMR data: ($CDCl_3$, 250 MHz): δ= -0.08 (s, 84H), 0.03 (s, 384H), 0.54 (m, 240H), 1.28 (m, 568H), 1.73 (m, 64H), 2.55 (m, 64H), 3.79 (t, 96H), 6.90 (d, 64H), 7.09 (d, 64H), 7.19 (d, 64H), 8.18 (d, 64H).

G-4(Und-MPhB)$_{64}$ was synthesised from G-4(All)$_{64}$ (0.17 g, 2.19 × 10^{-5} mol) and H-Si-Und-MPhB (1.15 g, 2.1 × 10^{-3} mol) according to the procedure given for G-3(Und-MPhB)$_{32}$. Yield: 0.89 g (95 %). Monodisperse compound was isolated by preparative GPC chromatography. ^{1}H-NMR data: ($CDCl_3$, 250 MHz): δ= -0.08 (s, 180H), 0.03 (s, 768H), 0.54 (m, 624H), 1.27 (m, 268H), 1.72 (m, 128H), 2.54 (m, 128H), δ= 3.78 (t, 196H), 6.89 (d, 28H), 7.08 (d, 128H), 7.18 (d, 128H), 8.18 (d, 128H).

RESULTS AND DISCUSSION

General approach to the synthesis of LC dendrimers with terminal mesogenic groups was elaborated in our laboratory earlier[2,4]. In the case of carbosilane dendrimers it consists of 3 main steps[4]: 1) synthesis of carbosilane dendritic matrices with the terminal allylic groups; 2) modification of mesogens in such a way that they have methylene spacer and active terminal groups Si-H capable of reacting with the terminal allyl groups of carbosilane dendritic matrices; 3) coupling of mesogenic groups modified to the dendritic matrices synthesised.

Synthesis of initial carbosilane dendritic matrices with terminal allyl groups G-n(All)$_m$* (m=8,16,32,64 for n=1,2,3,4) was described in detail elsewhere[11]. Modification of methoxyphenyl benzoate mesogenic groups was performed according to the procedure described before[4]. Figure 1 illustrates the coupling of modified mesogenic groups H-Si-Und-MPhB to the dendritic matrices by the

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* In the formula G-n(X)$_m$: n is the generation number, m is the number of terminal groups X shown in the parentheses.

hydrosilylation reaction for LC dendrimer of generation 2 (n=2, m=16). LC dendrimers of other generations was synthesized by the same way. A 1.5-fold excess of mesogen-containing silane was used to guarantee complete binding of mesogenic groups to all allyl groups of the dendrimers. Reactions were continued till allyl groups have disappeared completely. It was controlled by ^{1}H-NMR spectra. High purity of these dendrimers was achieved by the method of preparative GPC.

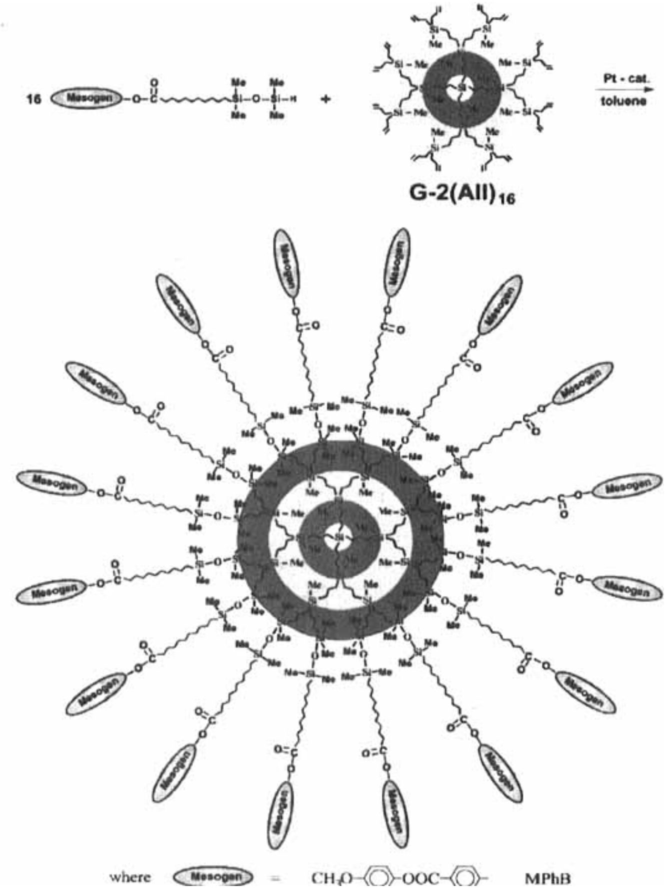


FIGURE 1. Synthesis of LC dendrimer G-2(Und-MPhB)$_{16}$.
(See Color Plate I at the back of this issue)

Purity and individuality of all LC dendrimers synthesised were approved by GPC analysis (Table I) and ^{1}H-NMR spectroscopy (Experimental part).

TABLE I. Molecular mass characteristics of LC dendrimers

Dendrimer	$MW_t^{\#}$	M_n (GPC)	M_w/M_n (GPC)	M_n(GPC)/ MW_t
G-1(Und-MPhB)$_8$	5052	5667	1.02	1.12
G-2(Und-MPhB)$_{16}$	10418	9437	1.02	0.91
G-3(Und-MPhB)$_{32}$	21148	14417	1.02	0.68
G-4(Und-MPhB)$_{64}$	42610	21068	1.02	0.49

$^{\#}MW_t$ - *theoretical molecular weight calculated from structural formula.*

With increasing of the generation number of dendrimers the molecular weights calculated from polystyrene standards diverts more and more from theoretical molecular weights calculated from structural formulas. These results are in agreement with the literature data for the similar systems[8,11]. It is well known that dendrimers possess less hydrodynamic volume than their linear analogues because of compact architecture of the later[1].

Thermal behaviour of LC dendrimers was investigated by means of polarising optical microscopy and DSC. The results are summarised in diagram shown in Figure 2.

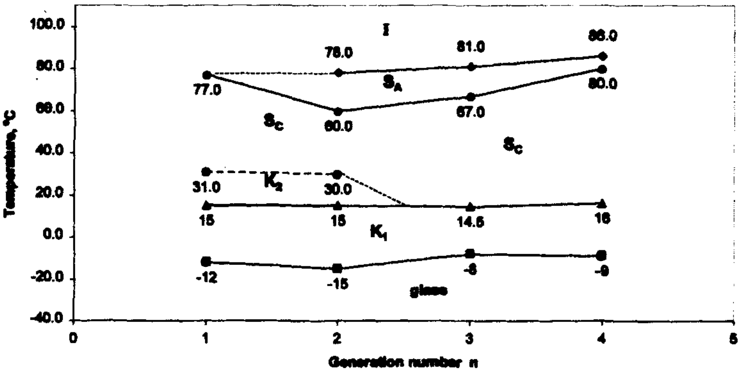
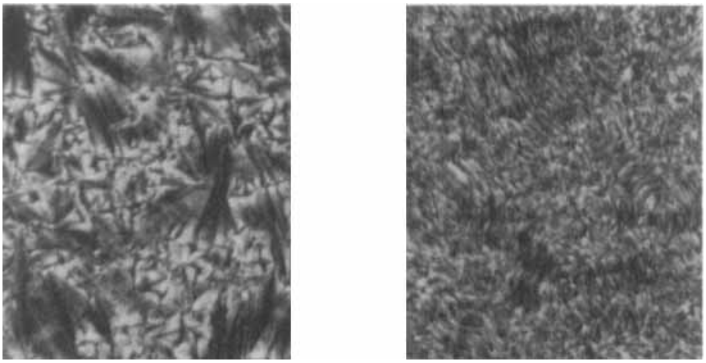


FIGURE 2. Phase diagram of LC dendrimers G-n(Und-MPhB)$_m$.

As can be seen from the phase diagram most of LC dendrimers with methoxyphenyl benzoate mesogenic groups has smectic A (S_A) and smectic C (S_C) mesophases as well as crystalline phase K_1. In addition LC dendrimers of generations 1 and 2 have another crystalline phase K_2. LC dendrimer of generation 1 G-1(Und-MPhB)$_8$ has no S_A mesophase. In cross polarisers S_A mesophase was characterised by a fan-shaped texture (Figure 3a), S_C mesophase was characterised by a broken fan-shaped texture (Figure 3b). Transition S_A - S_C was seen as breakage of fans and was fully reversible on heating and cooling.



(a) (b)

FIGURE 3. Optical polarising microphotographs of G-2(Und-MPhB)$_{16}$: a) fan-shaped texture (S_A, 69.5°C, magnification × 200), b) broken fan-shaped texture (S_C, 50.4°C, magnification × 200)
(See Color Plate II at the back of this issue)

DSC curves showed two first order phase transitions, corresponding $K - S_C$ and $S_A - I$, as well as glass transition temperature in the region of −10 °C. S_C - S_A transition does not seen on DSC curves. It is usual situation when it is second order phase transition or has extremely low enthalpy. Enthalpy of smectic A – isotropic melt transition decreases with the increase of generation number (Table II), while temperature of $S_A - I$ phase transition slightly increases (Figure 2). Total enthalpy of crystal – smectic C transition also decreases with the increase of generation number, while temperature of $K_1 - S_C$ phase transition is left almost unchanged. Thermal stability of crystal phase K_2 decreases with increase of generation number. It is stable for LC dendrimer G-1(Und-MPhB)$_8$ and metastable for G-2(Und-MPhB)$_{16}$. LC dendrimers G-3(Und-MPhB)$_{32}$ and G-4(Und-MPhB)$_{64}$ do not form it at all. All LC dendrimers synthesised crystallize including LC dendrimers of generation 4 bearing 64 methoxyphenyl benzoate mesogenic groups in the one molecule. This fact differs the series of LC dendrimers under consideration from the ones described before[2,4-6,11].

TABLE II. Enthalpies of phase transitions from second heating DSC curves and X-ray diffraction data of LC dendrimers

Dendrimer	Enthalpy of phase transition (J/g)			Layer spacings	
	$K_1 \rightarrow K_2$	$K_2 \rightarrow S_C$	$S_A \rightarrow I$	d (Å)	D (Å)
G-1(Und-MPhB)$_8$	15.9 (1.7)	1.9 (14.4)	8.6 (8.3)	40.5	4.85
G-2(Und-MPhB)$_{16}$	13.5 (11.7)	- (1.4)	6.6 (6.7)	42.7	4.89
G-3(Und-MPhB)$_{32}$	13.2 (13.4)	-	6.2 (6.2)	44.5	4.92
G-4(Und-MPhB)$_{64}$	12.0 (12.2)	-	5.7 (6.2)	46.6	4.94

Note: Enthalpies from first heating curves are shown in brackets.

Structure of LC dendrimers synthesised was investigated by means of X-ray diffraction measurements. WAXS results showed one diffuse peak with intermesogenic distance about 5 Å, that slightly raises with the increase of the generation number (D in Table II). SAXS measurements revealed two sharp reflections being first and second order from the layer spacings (d in the Table II). They also increase with the increasing of the generation number. These results suggest the existence of orthogonal disordered smectic A mesophase for all the compounds in question.

In order to confirm S_C - S_A transition, temperature dependent X-ray measurements were carried out on samples that were pre-aligned by a magnetic field. Neither sizeable sharp change of the layer spacings, nor large deviation from 90° in angle between the director and the smectic layers were observed at the transition points. This indicates that all the LC dendrimers possess a smectic A mesophase. Nevertheless, these data do not completely exclude the possibility of existence of low-tilted smectic C mesophase. In practice, a tilt of less than ~10° is not observable in the angle between the diffuse peak and the smectic layer because of the "fibre" distribution of the local domains.

As a result, we can conclude that all the LC dendrimers possess lamellar structure where the layers of mesogenic groups alternate with the layers of dendritic cores (Figure 4). Layer spacing rises with increasing of generation number which means the layers of dendritic cores are thickening. Methoxyphenyl benzoate mesogenic groups are either orthogonal to the layer or have low tilt angle. Since the layer spacing is about 14Å less than the mesogen tip to tip distance, the mesogenic units must overlap to form an interdigitated single-layer structure.

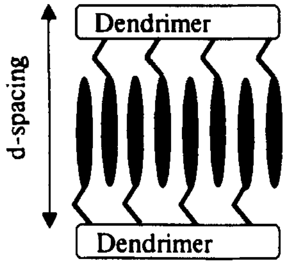


FIGURE 4. Schematic structure of layered mesophase of LC dendrimers

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