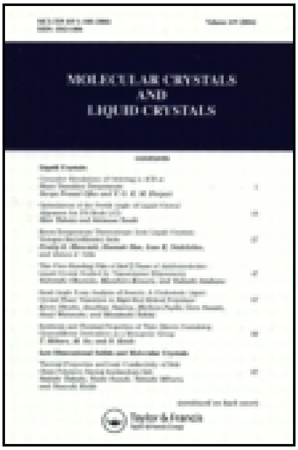

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[a] Chemistry Department, Moscow State University, 119899, Moscow, Russia

[b] ISPM RAS, 70 Profsoyuznaya st., Moscow, 117393, Russia

[c] HH Wills Physics Laboratory, University of Bristol, Bristol, BS8 1TS, UK

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Liquid Crystalline Carbosilane Dendrimers with Terminal Phenyl Benzoate Mesogenic Groups: Influence of Generation Number on Phase Behaviour

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[a]*Chemistry Department, Moscow State University, 119899 Moscow, Russia,* [b]*ISPM RAS, 70 Profsoyuznaya st., Moscow, 117393 Russia; and* [c]*HH Wills Physics Laboratory, University of Bristol, Bristol, BS8 1TS, UK*

The thermal behaviour of two series of liquid crystalline carbosilane dendrimers of generations 1 – 5 containing 8, 16, 32, 64 and 128 terminal phenyl benzoate mesogenic groups, respectively, was investigated by means of polarising optical microscopy, DSC and X-ray methods. Mesogenic groups on the base of methoxybenzoic (anisic) acid (Anis) and methoxyphenol (MPhB) were linked to the carbosilane dendritic matrices through $-OOC-(CH_2)_{10}-Si(CH_3)_2OSi(CH_3)_2-$ spacer. All LC dendrimers synthesised display smectic type mesophases and crystal phases over wide temperature region. LC dendrimers of fifth generation have more complex phase behaviour: heating the samples leads to transition from smectic to, most probably, columnar mesophases.

Keywords: carbosilane dendrimers; liquid crystals; phase behaviour

INTRODUCTION

In recent years dendrimers have attracted increased attention of researchers due to their regular highly branched molecular structure and possibilities for their use as novel materials.[1] LC dendrimers with terminal mesogenic groups are of great scientific interest due to their specific molecular structure combined flexible spherical dendritic architecture with rigid rod-like mesogenic groups capable of anisotropic LC mesophase formation. Contemporary synthetic techniques permit to create dendrimers with well-defined molecular mass and structure. Nowadays different LC dendrimers on the base of polyorganosiloxane[2,3], carbosilane[4,5], polyimine[6,7] and other dendritic structure were synthesized. Their molecules consist of the following structural units: dendritic matrices, aliphatic spacers and mesogenic groups. Each of them influence on the formation of LC mesophases and the type of their structure. However, the data available nowadays do not allow predicting the thermal properties for such systems of different structures.

Therefore the goal of this work is to compare the phase behaviour of two series of carbosilane LC dendrimers with the same dendritic matrices and aliphatic spacers but different mesogenic groups for evaluation of the influence of chemical nature of mesogenic groups on the phase behaviour of LC dendrimers of different generations.

EXPERIMENTAL

Phase behaviour was studied by differential scanning calorimetry (DSC) with a Mettler TA-4000 thermosystem at a scanning rate of 10 K/min. The polarizing 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 polarizing microscope. X-ray diffraction measurements were made using CuK$_\alpha$-radiation (λ = 1.542 Å) from 1.5 kW 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 study were prealigned by cooling from the isotropic phase in a 9.4 T magnetic field.

Materials.

The objects of investigations were two series of carbosilane LC dendrimers from first to five generations with 8, 16, 32, 64 and 128 terminal phenyl benzoate mesogenic groups for generations 1, 2, 3, 4 and 5, respectively. Their general formulae is shown in Fig. 1. Both series of LC dendrimers differ from each other by the chemical nature of terminal mesogenic groups: first of them have mesogenic groups on the base

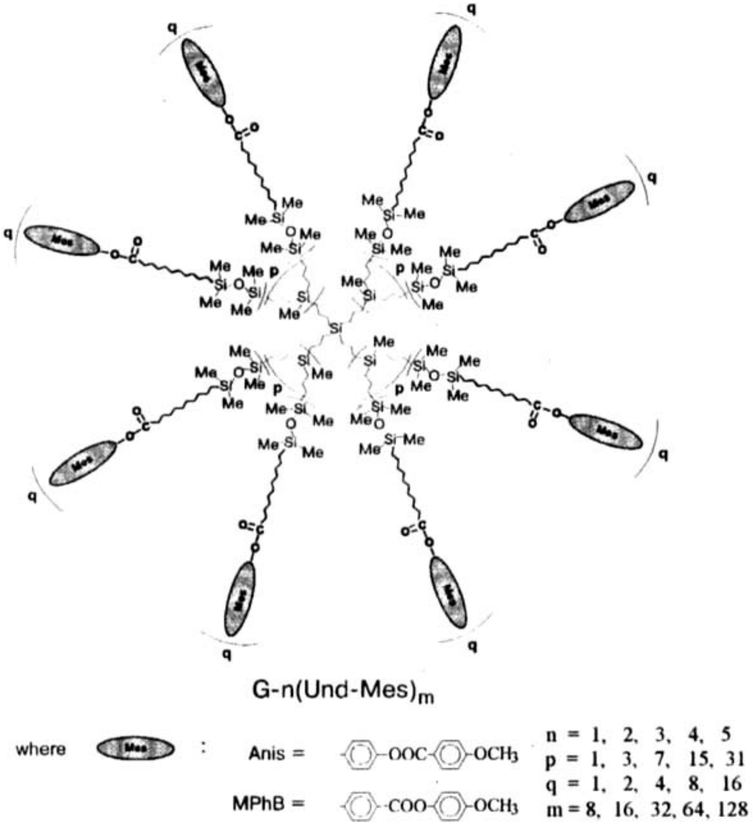

FIGURE 1. General structural formulae of LC dendrimers G-n(Und-Mes)$_n$, where n - generation number, m - the number of terminal mesogenic groups (Mes).

of methoxybenzoic (anisic) acid (Anis), the second - on the base of methoxyphenol (MPhB) derivatives. Both types of mesogenic groups were linked to carbosilane dendritic matrices through the same -OOC-$(CH_2)_{10}$-$Si(CH_3)_2OSi(CH_3)_2$- (Und) flexible spacer. The detailed synthesis of these LC dendrimers was described elsewhere.[8,9] Pure monodisperse compounds were isolated by preparative GPC. Their structure and purity were proved by H^1 NMR and GPC techniques.

RESULTS AND DISCUSSION

The results of investigations of thermal behaviour and structure of mesophases are summarized in the phase diagrams (Figure 2). Phase behaviour of LC dendrimers of generations 1-4 is similar for both series. All of them have smectic A (SmA) and smectic C (SmC) mesophases as well as crystalline phase K_1. Also LC dendrimers of generations 1 and 2 have another crystalline phase K_2. The exception is **G-1(Und-MPhB)$_8$**, which has no SmA mesophase.[4] In crossed polarisers of optical microscope the SmA mesophase was characterized by a fan-shaped texture. Transition SmA-SmC was seen as breakage of fans and was fully reversible under heating and cooling.

Most of the transitions shown in the phase diagrams are seen in DSC curves as the first order phase transitions excluding SmA-SmC one which is the second order phase transition. However it has the first order with the enthalpy of 2.0 J/g for LC dendrimer **G-4(Und-Anis)$_{64}$**.

There are some general trends for both series of LC dendrimers. First of all, thermal stability of LC mesophases increases, but thermal stability of crystal phase K_2 decreases with the generation number increasing. The K_2 phase is stable for **G-1** dendrimers, metastable for **G-2** dendrimers and it is not formed by LC dendrimers of 3-5 generations.

Also increasing the generation number leads to the growth of the clearing temperatures for both series of LC dendrimers. This effect was also observed for carbosilane LC dendrimers with terminal cyanobiphenyl mesogenic groups[10] and was explained by increasing of the cooperative interactions between mesogenic groups like it happens for LC oligomers and polymers. The enthalpies of the SmA - isotropic melt transitions decrease with generation number increasing. This dependence was observed for all carbosilane LC dendrimers investigated by now.[10,11] It means that the influence of isotropic dendritic matrix intensifies with the generation number increasing and opposes the formation of anisotropic mesophases.

There are some differences in the phase behaviour between two series under considerations. First of all, LC dendrimer **G-1(Und-Anis)$_8$** has low clearing temperature as compared with **G-1(Und-MPhB)$_8$**: 58°C versus 77°C (Fig. 2). However, crystallization temperature is almost the same for both LC dendrimers: about 30°C. It leads to considerable increase of temperature interval of the LC mesophase formation for **G-1(Und-MPhB)$_8$** as compared with **G-1(Und-Anis)$_8$**.

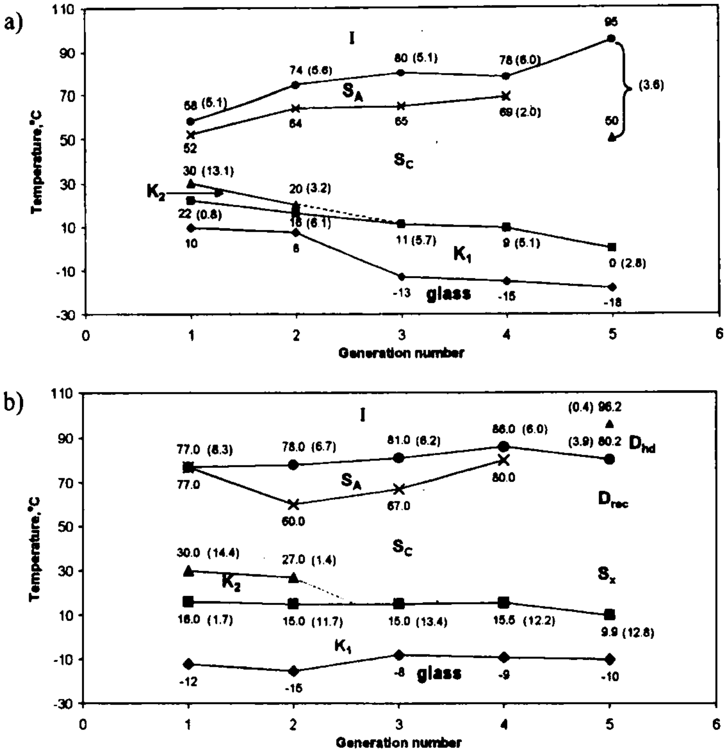

FIGURE 2. Phase diagrams for 2 series of LC dendrimers: a) G-n(Und-Anis)$_m$, b) G-n(Und-MPhB)$_m$. The numbers indicate temperatures of phase transitions (in °C), appropriate enthalpies of which are shown in the parenthesis (in J/g).

More significant difference observed for LC dendrimers of fifth generation **G-5(Und-Anis)$_{128}$** and **G-5(Und-MPhB)$_{128}$**.

DSC heating thermogram of **G-5(Und-MPhB)$_{128}$** shows three endothermal peaks at 10, 80 and 96°C with the enthalpies of 12.8, 3.9 and 0.4 J/g, respectively. Polarizing optical microscopy showed that this LC dendrimer forms only a non-characteristic (focal-conic) texture in the temperature interval from room temperature to 80°C, where birefringence disappears completely. In accordance with DSC data it should be attributed to formation of homeotropic texture rather than transition to isotropic melt. Actual transition to the isotropic melt occurs at 96°C, however it can not be seen in polarizing optical microscopy. It is well-known from the literature that homeotropic texture can be observed for smectic SmA or columnar D_{hd} mesophases.[10] Bearing in mind that very similar carbosilane LC dendrimer with cyanobiphenyl groups **G-5(Und-CB)$_{128}$** forms columnar D_{hd} mesophase at high temperature[12] it is reasonable to suppose that LC dendrimer **G-5(Und-MPhB)$_{128}$** also form columnar mesophase. It is confirmed by a similarity of DSC data of both LC dendrimers. For **G-5(Und-MPhB)$_{128}$** the enthalpy of phase transition at 80°C is an order of magnitude more then the isotropization enthalpy (3.9 and 0.4 J/g, respectively). The same situation was observed for **G-5(Und-CB)$_{128}$**, where $\Delta H(D_{rec} - D_{hd}) = 2.1$ J/g, while $\Delta H(D_{hd} - I) = 0.2$ J/g. Such difference in the enthalpies of phase transitions can be explained on the base of two levels of structural organization: one is anisotropic ordering of mesogenic groups leading to smectic layers[i] and another one is columnar arrangement of dendritic molecules as a whole. Distortion of smectic layers takes much more energy than distortion of columnar arrangement of dendritic molecules at least due to the fact that each molecule of LC dendrimer of fifth generation contains 128 mesogenic groups, which interact each other and with mesogenic groups from the other molecules.

In order to check these suggestions X-ray measurement were made for LC dendrimer **G-5(Und-MPhB)$_{128}$** at different temperatures (Fig.3). At 25°C 1st and 2nd order Bragg reflections are seen. Their intensities decrease with the temperature, while their positions, corresponding to the interlayer spacing 51.3 Å, does not change. This is consistent with the SmA mesophase. Starting from 55°C the layered structure begins to disappear and only one very wide peak with low intensity is seen higher then 75°C. Its position gradually changes with temperature to higher Q values and reaches Q=0.14 (d=44.9 Å) at about 92°C. Further heating does not lead to any changes in the diffraction pattern.

These data indicate that the shape of dendritic molecule changes from the strongly anisotropic at room temperature in smectic mesophase to almost isotropic in the upper weakly ordered mesophase. Nevertheless, they do not allow the type of this mesophase to be deter-

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[i] Smectic layers are constituent part of rectangular D_{rec} mesophase formed by the molecules of carbosilane LC dendrimers.[10]

mined due to the weak ordering. Similar gradual changes in the layer spacings was also observed for rectangular columnar mesophase of **G-5(Und-CB)$_{128}$**, however, D_{rec} phase was strongly birefringent showing mosaic texture in polarizing optical microscope.

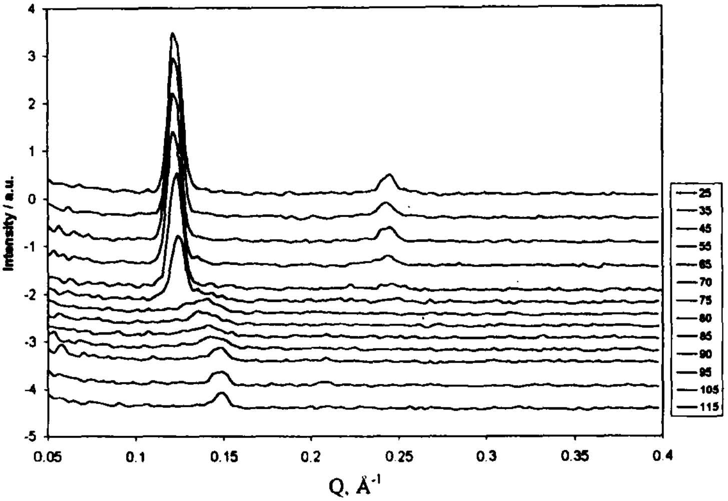

FIGURE 3. SAXS for LC dendrimer G-5(Und-MPhB)$_{128}$ at different temperatures shown each 5°C in the region of phase transitions (65 - 95°C) and each 10°C for the other regions.

The phase behaviour of **G-5(Und-Anis)$_{128}$** is different. On DSC curve as well as a glass transition at -18°C and crystallization at 0°C it shows a very wide peak from 50 to 95°C with the total enthalpy of 3.6 J/g under heating and cooling. It can only be explained as a gradual transition from one mesophase to another with subsequent isotropisation at 95°C. A similar gradual transition from SmA to D_{rec} mesophase in the temperature region of 40-121°C was observed for **G-5(Und-CB)$_{128}$** that was confirmed by SAXS results[12]; however it was not seen in DSC data, probably due to wide temperature interval of this transition. It is probable that the small interval of the transition for **G-5(Und-Anis)$_{128}$** lead to its being visible on the DSC curve. Similarity of phase behaviour of both LC dendrimers is in agreement with optical microscopy investigations, showing that **G-5(Und-Anis)$_{128}$** have strong birefringence till the isotropization at 95°C. However, it has a non-characteristic texture, which do not allow make any suggestion concerning the type of mesophases formed. SAXS measurements, which are in progress now, should allow to suggest structural model for mesophase formed by this LC dendrimer.

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