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X.-M. ZHU, N. I. BOIKO, E. A. REBROV†, A. M. MUZAFAROV†,
M. V. KOZLOVSKY‡, R. M. RICHARDSON§ and V. P. SHIBAEV*

Faculty of Chemistry, Moscow State University, Leninskie Gory, Moscow 119899,
Russia
†Institute of Synthetic Polymeric Materials, Russian Academy of Sciences,
Ul. Profsoyuznaja 70, Moscow 117393, Russia
‡Institute of Physical Chemistry, Darmstadt University of Technology,
Petersenstr. 20, D-64287 Darmstadt, Germany
§H. H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

This paper presents a systematic study of two series of carbosilane liquid crystalline (LC) dendrimers from first to fifth generations bearing 8, 16, 32, 64 and 128 terminal chiral mesogenic groups, respectively. All the LC dendrimers synthesized are characterized by the same glass transition temperature around −5°C. It has been shown that the LC dendrimers of the lower generations (G-1–G-3) form a ferroelectric SmC* phase over a very broad temperature range up to about 180°C, while the LC dendrimers of the higher generations (G-4 and G-5) display a rectangular columnar mesophase (Col$_r$). Schemes of packing in the SmC* and Col$_r$ mesophases formed by the LC dendrimers are suggested and discussed. Electrical measurements on the ferroelectric LC dendrimers have shown that an increase in generation number leads to a decrease in the value of the spontaneous polarization and an increase in switching time.

1. Introduction

In recent years liquid crystalline (LC) dendrimers, in particular, LC dendrimers with terminal mesogenic groups have become objects of great interest due to their unique superbranched structures. Molecules of these compounds contain on their periphery mesogenic groups that are capable of forming anisotropic structures, and the internal core consists of an amorphous superbranched dendritic matrix. The coexistence of both amorphous and mesogenic parts predetermines a microsegregation in such systems. In this sense, it is of great interest to investigate the structural organizations adopted by these compounds.

Up to now many LC dendrimers with terminal mesogenic groups of different chemical structures have been synthesized: polyorganosilanes [1, 2], carbosilanes [3–8], poly(propyleneimine)s [9, 10], and poly(amideamine)s [11]. Most of them exhibit the simplest smectic phases— SmA and SmC. It should be noted that among the various known smectic phases, the chiral smectic C (SmC*) phase is the most interesting, because it can show ferroelectric properties and very fast switching between two stable states of the mesogenic units [12, 13]. Low molar mass ferroelectric liquid crystals show great potential for electro-optical applications. The synthesis of ferroelectric LC polymers was achieved for the first time by Shibaev *et al.* [14] using comb-like polymers. Considering the significant scientific and technological interest in the SmC* phase, it was logical to synthesize chiral LC dendrimers capable of forming the SmC* phase in order to obtain ferroelectric liquid crystals with a unique dendritic structure. Preliminary data concerning the synthesis and investigation of chiral carbosilane LC dendrimers from first to third generation showing ferroelectric properties have been presented in our previous papers [15, 16]. The first information concerning the synthesis of a ferroelectric LC dendrimer of the third generation was published by Busson *et al.* in 1998 [17], but no values of spontaneous polarization (P$_s$) were mentioned.

It is well known that all the structural units of LC dendrimers, such as the internal core, the spacer length and the type of mesogenic group, influence their physicochemical behaviour [18]. The goals of this work are

*Author for correspondence;
e-mail: lcp@libro.genebee.msu.su

to reveal the influence of generation number and the nature of the terminal mesogenic groups on the phase behaviour, structure and ferroelectric properties of LC dendrimers with chiral mesogenic groups. Carbosilane LC dendrimers of the first to fifth generations with different terminal chiral mesogenic groups were chosen as the research materials (figure 1).
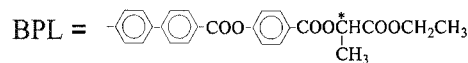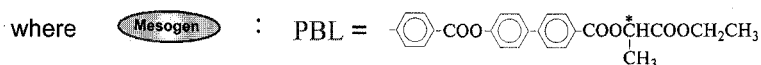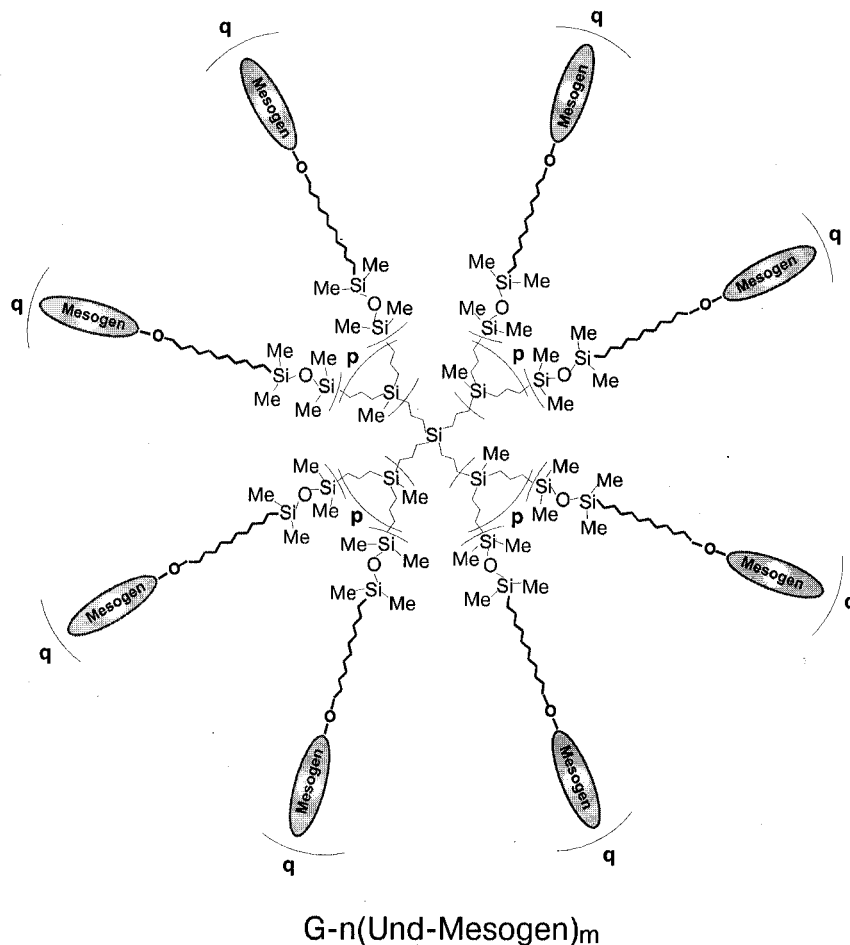
The terminal mesogenic units—ethyl (*S*)-lactate derivatives containing three benzene rings (PBL and BPL)—were coupled to the carbosilane dendritic matrix via an aliphatic spacer consisting of 11 methylene groups (Und = undecylene). It is well known that a combination of four factors—a long spacer, extended rigid fragments,

transverse dipole moments and chiral groups—leads to the formation of the SmC* phase in low molar mass and polymer systems.

2. Experimental

The synthesis and characterization of the carbosilane LC dendrimers with terminal chiral mesogenic groups was performed according to the method published elsewhere [19].

GPC analysis was performed using THF solutions on a Knauer set-up equipped with an Ultrastyralgel 8×300 mm column (Waters) having a pore size of 10^3 Å and a detector—UV spectrometer Knauer. All data were

$$\text{G-}n(\text{Und-Mesogen})_m$$

where [Mesogen] : PBL = ⬡-COO-⬡-⬡-COO$\overset{*}{\text{C}}$HCOOCH$_2$CH$_3$
                                                                         |
                                                                        CH$_3$

BPL = ⬡-⬡-COO-⬡-COO$\overset{*}{\text{C}}$HCOOCH$_2$CH$_3$
                                                           |
                                                          CH$_3$

Generation number ⟶ n = 1, 2, 3, 4, 5

p = 1, 3, 7, 15, 31

q = 1, 2, 4, 8, 16

Number of terminal groups ⟶ m = 8, 16, 32, 64, 128

Figure 1. General formula for the carbosilane LC dendrimers with terminal chiral mesogenic groups.

referenced to narrow polystyrene standards. A Waters $19 \times 300\,mm$ column filled with Ultrastyralgel, $10^3\,Å$, was used for preparative GPC. ^1H NMR spectra were recorded using a WP-250 spectrometer. All spectra were run using $CDCl_3$ solutions. Phase transitions were studied by differential scanning calorimetry (DSC) with a Mettler TA-4000 thermosystem at a scanning rate of $10°C\,min^{-1}$. Sample masses were typically chosen between 12 and 20 mg. The investigation of textures was carried out using a Mettler FP-800 central processor equipped with a Mettler FP-82 hot stage and control unit, in conjunction with a Lomo R-112 polarizing microscope. X-ray diffraction measurements were made using CuK_α radiation ($\lambda = 1.542\,Å$) from a 1.2 kW sealed tube. Monochromatization was obtained with a graphite crystal. Electrical measurements on ferroelectric compounds were performed using a repolarization method. The values of the spontaneous polarization were calculated directly from polarization hysteresis loops which were obtained by integration of the cell current. A sine-wave voltage (up to 120 V peak to peak, frequency range 10–100 Hz) was applied across a $10\,\mu m$ thick sample. The ohmic leakage was roughly compensated by an active resistance, and fine compensation was achieved by on-line loop calculations by a computer equipped with an analog to digital converter. Switching time was measured according to the scheme for measuring $\mathbf{P}_s$ using a 35 V amplitude rectangular voltage (frequency range 10–100 Hz). The response current was displayed on an oscilloscope. Switching time was calculated as the time for the charge of the reference condenser to change from 10% to 90% on applying the voltage.

3. Results and discussion

3.1. *Synthesis and characterization*

Synthetic details and characterization of carbosilane LC dendrimers of generations 1, 2, 3, 4 and 5 containing 8, 16, 32, 64 and 128 terminal chiral mesogenic groups, respectively, have been published [19]. The synthesis involved three steps:

(1) Synthesis of vinyl-terminated mesomorphic precursors

 Und-PBL

 Und-BPL
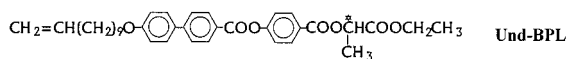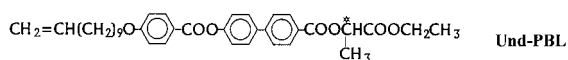
(2) Synthesis of mesogen-containing fragments with a reactive Si–H terminal group
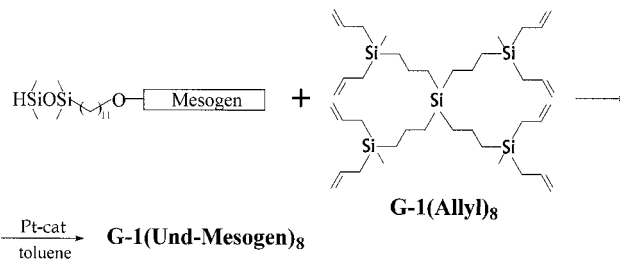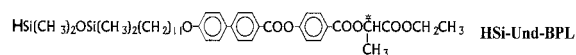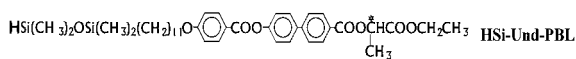
 HSi-Und-PBL

 HSi-Und-BPL

Figure 2. Scheme of coupling of mesogen-containing fragments to the carbosilane dendritic matrix of the first generation.

(3) Coupling of mesogen-containing fragments with a Si–H terminal group to carbosilane matrices with terminal allyl groups (figure 2).

All LC dendrimers were purified by preparative HPLC. The structures and purity of all the dendrimers were confirmed by ^1H NMR spectroscopy and GPC analysis. All LC dendrimers synthesized were monodisperse compounds having the ratio M_w/M_n equal to 1.02.

3.2. *The vinyl-terminated mesomorphic precursors and mesogen-containing fragments with a Si–H terminal group*

The phase behaviour and spontaneous polarization of the vinyl-terminated and siloxane-terminated precursors are given in table 1.

On heating from the crystal phase, the vinyl-terminated precursors Und-PBL and Und-BPL display the ferroelectric SmC* phase with high spontaneous polarizations, of the order of $100\,nC\,cm^{-2}$; they then transform into a high temperature SmA phase. The temperature ranges of the SmC* phases of the siloxane precursors with a terminal $Si(CH_3)_2{-}O{-}Si(CH_3)_2H$ group (HSi-Und-PBL and HSi-Und-BPL) are strongly extended in comparison with those of the vinyl compounds. In addition these precursors do not crystallize, transforming into a glassy state on cooling. On the contrary, the temperature range of the SmA phase for HSi-Und-BPL is strongly reduced and even non-existent for HSi-Und-PBL. As previously demonstrated [20],

Table 1. Characteristics of the vinyl and siloxane terminated monomeric precursors.

Compound	Phase sequence/°C	$\mathbf{P}_s$(max)/nC cm^{-2}
Und-PBL	Cr$_1$ 52 Cr$_2$ 66 SmC* 80 SmA 134 I	105
Und-BPL	Cr$_1$ 34 Cr$_2$ 53 SmC* 115 SmA 150 I	143
HSi-Und-PBL	g $\sim$ $-$10 SmC* 121 I	—
HSi-Und-BPL	g $\sim$ $-$10 SmC* 125 SmA 138 I	—

the terminal siloxane group acts as a molecular template for producing the ferroelectric SmC* phase because of the microseparation of the aromatic, paraffinic and siloxane moieties.

3.3. *Phase behaviour of the carbosilane LC dendrimers with terminal chiral mesogenic groups*

The scheme of phase transitions for all the chiral LC dendrimers synthesized is demonstrated schematically in figure 3. As can be seen from the data, the LC dendrimers from the first to the third generations form lamellar smectic phases (SmC* and SmA phases), while the LC dendrimers of the fourth and fifth generations display a rectangular columnar (Col$_r$) phase.

3.3.1. *LC dendrimers exhibiting lamellar smectic phases*

First, let us consider the thermal properties of the LC dendrimers of generations 1–3. For the LC dendrimers of the first series G-n(Und-PBL)$_m$ the SmC* phase is the only mesophase observed; all these dendrimers display a transition from the isotropic phase into the SmC*

phase and from the SmC* phase into a glassy state. Polarizing optical microscopy (POM) showed that all these dendrimers form the broken fan-shaped texture typical of the SmC* phase; see figure 4 (*a, b*).

Only one endothermic peak, which corresponds to the smectic–isotropic transition, is recorded on the DSC thermograms of these dendrimers on heating; see figure (5).

X-ray data for these dendrimers at wide and small angles confirmed the existence of a smectic phase with a disordered arrangement of mesogenic groups in layers. Two sharp reflections at small angles, corresponding to the first and second order Bragg reflections from smectic layers, and a diffuse maximum at wide angles are observed in the diffractograms (figure 6) from room temperature until the clearing point. However, the X-ray measurements did not allow the tilt angle of the mesogenic groups to be determined because we did not succeed in orienting the samples even using a high magnetic field (9.4 T). Nevertheless, the ferroelectric switching observed in thin electro-optical cells of these dendrimers, figure 4 (*c*), proved the formation of the tilted SmC* phase.

The LC dendrimers of the second series G-n(Und-BPL)$_m$ show a more complicated phase sequence. These dendrimers form not only a SmC* phase, but also a high temperature SmA phase. POM showed that on cooling a sample of G-1(Und-BPL)$_8$ below its clearing point, formation of a broken fan-shaped texture occurred, figure 4 (*d*). On heating, this texture transforms into a fan-shaped texture characteristic of the orthogonal SmA phase, figure 4 (*e*); then the isotropic phase is formed. Formation of the SmA phase is not observed on cooling, and this is probably explained by a tendency to supercooling and by the narrow temperature interval of this phase. The LC dendrimer of the second generation G-2(Und-BPL)$_{16}$ displays a SmC*–SmA transition both on heating and cooling as observed by POM. The LC dendrimer of the third generation G-3(Und-BPL)$_{32}$ forms only a non-characteristic texture, and we were not able to detect the SmC*–SmA transition by POM without an electric field. This transition was discovered only in the course of our electro-optical investigations. DSC showed the SmC*–SmA transition as an endothermic peak only for the LC dendrimer of the second generation G-2(Und-BPL)$_{16}$; see figure 5 (*b*). The absence of a peak on the DSC curves corresponding to this transition, for the dendrimers of the first and third generations, can probably be explained by either the narrowness of the temperature range of the SmA phase or a low transition enthalpy. SAXS data however confirmed the SmC*–SmA transition in the LC dendrimers of the second and third generations. As is seen from
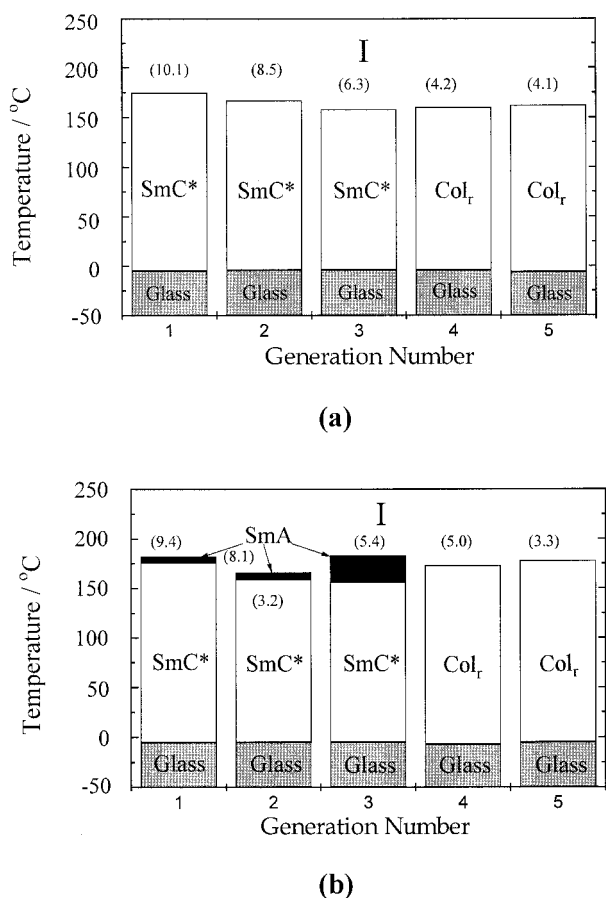
(a)

(b)

Figure 3.   Scheme of phase transitions for the chiral carbosilane LC dendrimers: (*a*) G-n(Und-PBL)$_m$, (*b*) G-n(Und-BPL)$_m$, with the transition enthalpies (J g^{-1}) in parentheses.
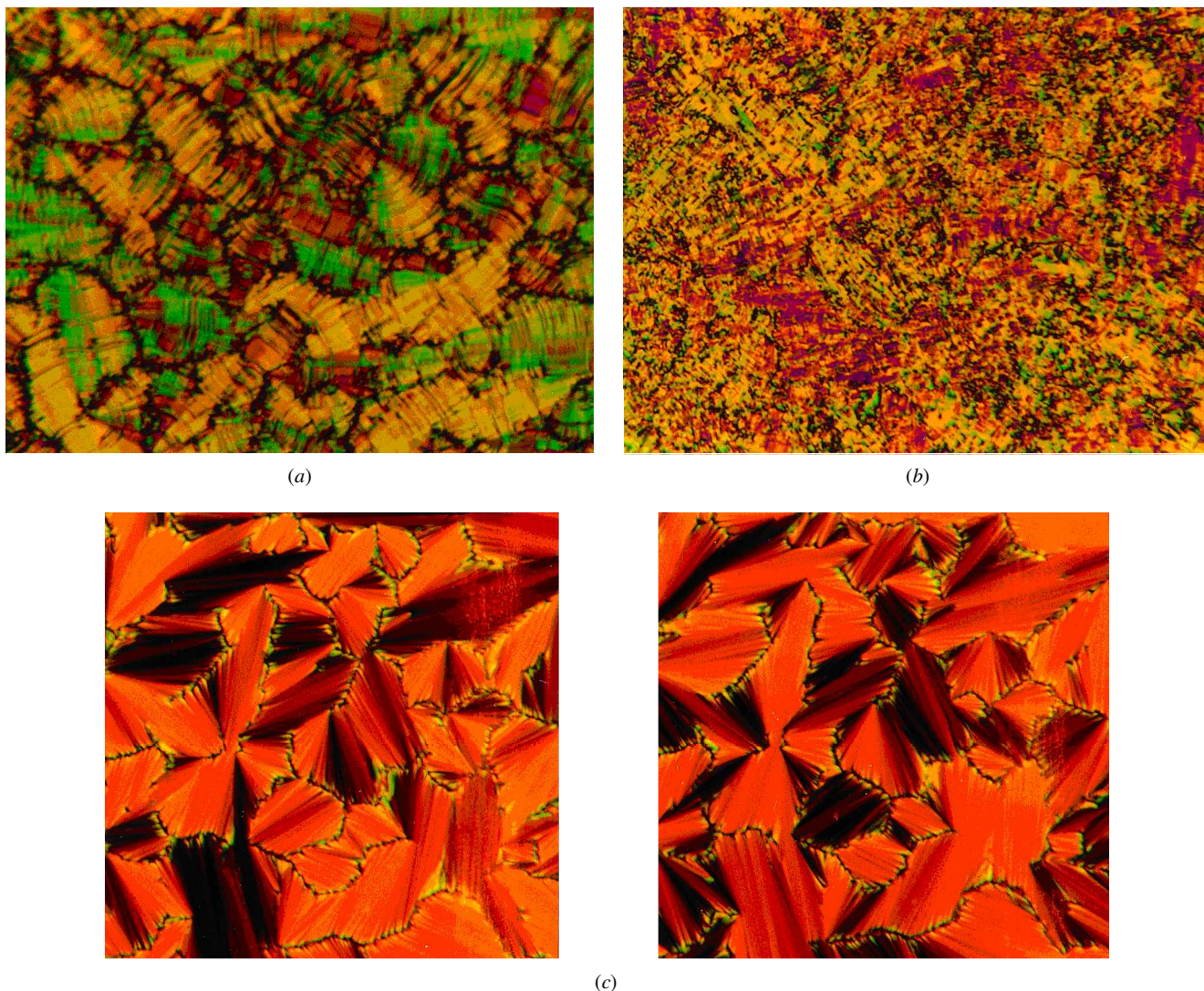
(a)

(b)

(c)

Figure 4. Textures of the smectic phases formed by LC dendrimers ($200\times$): (a) broken fan-shaped texture of dendrimer G-1(Und-PBL)$_8$ in the SmC* phase (150°C); (b) broken fan-shaped texture of dendrimer G-3(Und-PBL)$_{32}$ in the SmC* phase (140°C); (c) electro-optical switching effect for dendrimer G-1(Und-PBL)$_8$ in the SmC* phase (150°C); (d) broken fan-shaped texture of dendrimer G-1(Und-BPL)$_8$ in the SmC* phase (150°C); (e) fan-shaped texture of dendrimer G-1(Und-BPL)$_8$ in the SmA phase (174°C).

figure 7, a small increase and a subsequent decrease of the interlayer spacing d_{001} is observed in the region of the SmC*–SmA transition. The increase in d_{001} is caused by the decrease of the tilt angle; the subsequent decrease is due to the decrease in the order parameter in the SmA phase on heating. The dendrimer of the first generation displays a small increase in d_{001} in the region of the SmC*–SmA transition and the following decrease is not observed, perhaps because the temperature range of the SmA phase is too narrow. The dependence of the interlayer spacing d_{001} on generation number for the LC dendrimers of generations 1–3 is given in figure 8.

One can see that the d_{001} values increase from the first to the third generation. Based on the SAXS data and computer modelling, we suggest a one-layered packing model in the SmC* phase (figure 9).

It should also be noted that d_{001} of the LC dendrimers G-n(Und-PBL)$_m$ is always greater than that of the other series G-n(Und-BPL)$_m$. Perhaps, the tilt angle in G-n(Und-PBL)$_m$ is greater than that in G-n(Und-BPL)$_m$. It is well known from the literature that ferroelectric liquid crystals with a phase sequence SmC*–I are characterized by greater tilt angles (close to 45°C) than for those with a phase sequence SmC*–SmA [21].
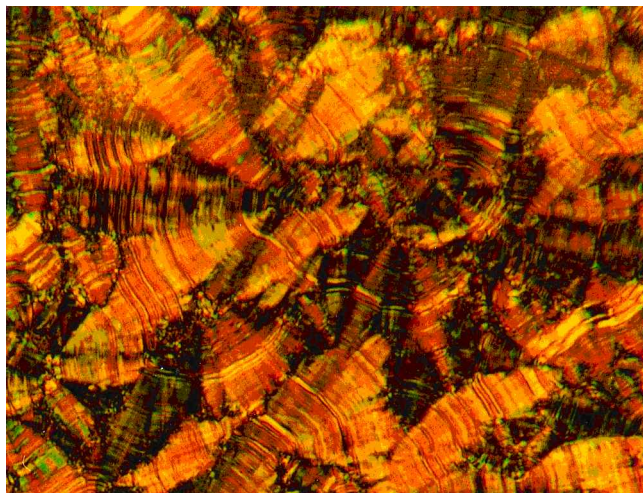
(*d*)
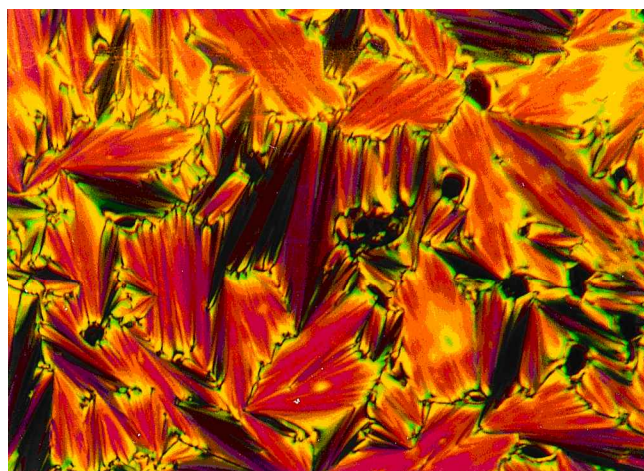
(*e*)

Figure 4.   (*continued*).

Thus, it has been shown that the amorphous super-branched part of the lower generation dendrimers does not hinder the formation of the ferroelectric SmC* phase. The phase sequence of these LC dendrimers is similar to that of their siloxane monomeric precursors, but the temperature range of the SmC* phase of the dendrimers is much broader.

3.3.2. *LC dendrimers of the fourth and fifth generations*

Now let us discuss the phase behaviour of the LC dendrimers of the fourth and fifth generations, which display a Col_r phase. POM showed that all these compounds display a weakly birefringent mosaic texture (figure 10) in the temperature range of the mesophase. Similar textures were observed for a hexagonal columnar phase [8, 21, 22] and the so-called M_x phase [23].

The DSC curves of these dendrimers show a first order phase transition (figure 5). X-ray study showed three Bragg reflections at small angles (figure 11) and one diffuse peak at wide angles. It should be noted that the peaks are broad and there is no long range translational order.

Analysis of the correlation between the Q values of the small angle reflections allowed us to suggest a rectangular columnar structure (Col_r) where $Q_I^2 + Q_{II}^2 = Q_{III}^2$. The reflections can be indexed as $(0\,0\,1)$, $(1\,0\,0)$ and $(1\,0\,1)$ from a 2D rectangular lattice. The positions of the reflections are temperature-independent for LC dendrimers of the fifth generation G-5(Und-PBL)$_{128}$ and G-5(Und-BPL)$_{128}$, and are slightly shifted to higher Q with increasing temperature (within 1 Å) for the analogous LC dendrimers of the fourth generation G-4(Und-PBL)$_{64}$ and G-4(Und-BPL)$_{64}$. The interlayer

distances d_{001}, d_{100}, d_{101} and the lattice parameters a, c of the 2D rectangular unit cell are given in table 2. The model of the rectangular columnar structure formed by these LC dendrimers of higher generation is shown in figure 12.

Each column consists of ellipsoidal discs of LC dendrimers, flattened towards the columnar axis in one direction and elongated perpendicular to that direction. The mesogenic groups are located entirely on the surfaces of the columns, while the inner part of the columns consists of the dendritic cores of the molecules of the LC dendrimers. The formation of the columnar phase has also been proved by atomic force microscopy (AFM), the data for which are to be published [24]. It should be noted that a rectangular columnar structure of dendrimers was found in the carbosilane LC dendrimer of the fifth generation with terminal cyanbiphenylyl mesogenic groups G-5(Und-CB)$_{128}$ [8], which on heating from room temperature displays a smooth transition SmA $\rightarrow$ Col$_r$. Further heating leads to a hexagonal columnar phase (Col$_{hd}$), and then to the transition to the isotropic melt.

Table 2.   Interlayer distances and lattice parameters of LC dendrimers of the fourth and fifth generations.

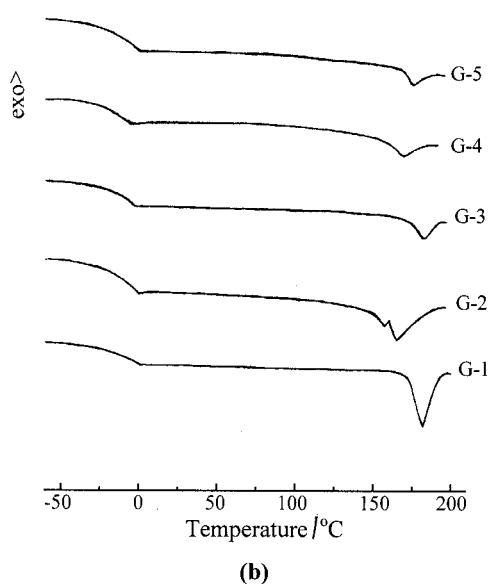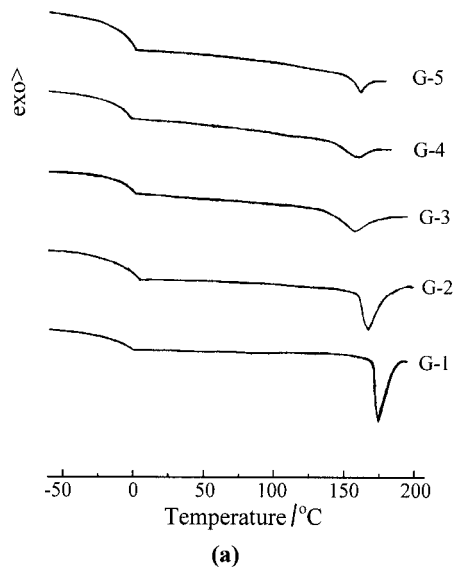| Dendrimer	Interlayer distances and lattice parameters/Å		
	$d_{001}(C)$	$d_{100}(a)$	d_{101}
G-4(Und-PBL)$_{64}$	47.7	27.4	23.9
G-5(Und-PBL)$_{128}$	49.8	30.6	25.4
G-4(Und-BPL)$_{64}$	45.8	27.4	23.6
G-5(Und-BPL)$_{128}$	50.3	31.7	26.9

(a)

(b)

Figure 5. DSC traces for chiral carbosilane LC dendrimers: (*a*) G-*n*(Und-PBL)$_m$, (*b*) G-*n*(Und-BPL)$_m$.

Meanwhile, the LC dendrimer of the fourth generation from this series G-4(Und-CB)$_{64}$ forms only a lamellar SmA phase.

3.4. *The influence of generation number on the phase behaviour*

Let us return to the phase diagrams of the LC dendrimers (figure 3). First, it should be noted that all the LC dendrimers are characterized by low glass transition temperatures ($\sim -5^\circ$C), which are practically independent of the generation number. Increase of the generation number of the LC dendrimers forming lamellar smectic phases results in a decrease in the clearing point, except for G-3(Und-BPL)$_{32}$, and a decrease
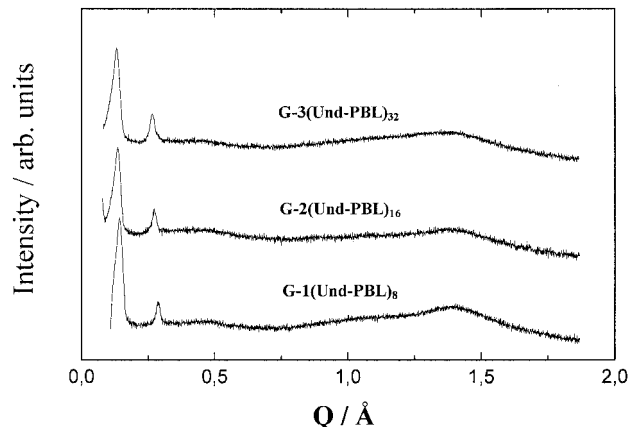

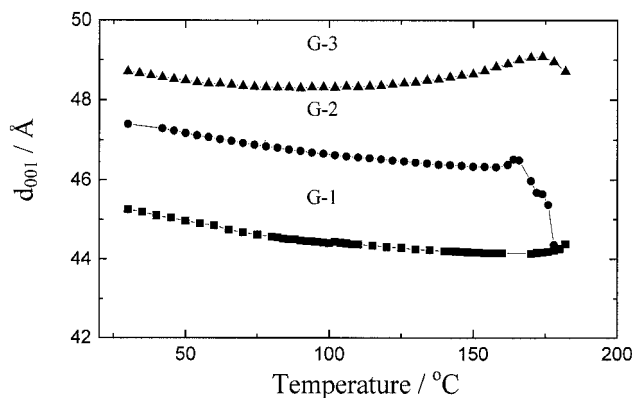Figure 6. X-ray diffractograms of LC dendrimers in the SmC* phase (30°C).

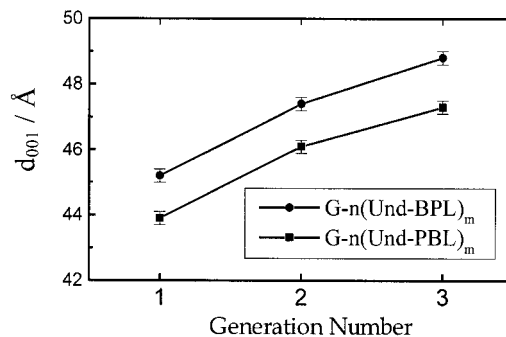Figure 7. Temperature dependence of interlayer spacing d_{001} for LC dendrimers G-*n*(Und-BPL)$_m$.

Figure 8. Dependence of interlayer spacing d_{001} on the generation number for LC dendrimers exhibiting smectic phases (30°C).

in enthalpy of the transition from smectic phase to isotropic melt. LC dendrimers are microsegregated systems, and there are two opposite factors influencing their phase behaviour. On the one hand, interaction of the mesogenic groups leads to formation of a smectic layered structure; on the other hand, the superbranched dendritic core has a tendency to take up an isotropic conformation.
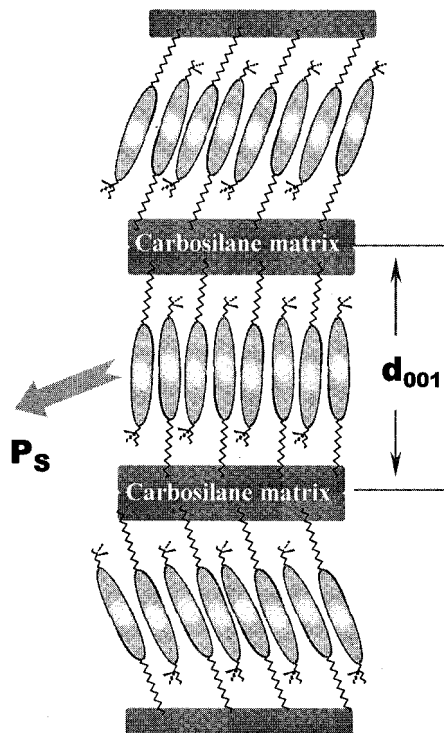
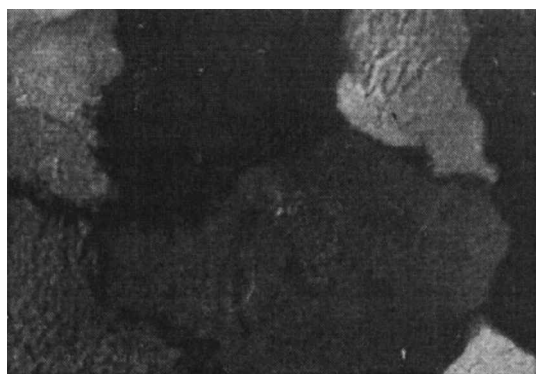Figure 9.   Model of the mesogenic group packing of LC dendrimers in the helical SmC* phase.

Figure 10.   Low birefringence mosaic texture of LC dendrimer G-4(Und-BPL)$_{64}$ in the Col$_r$ phase (100°C, 200×).
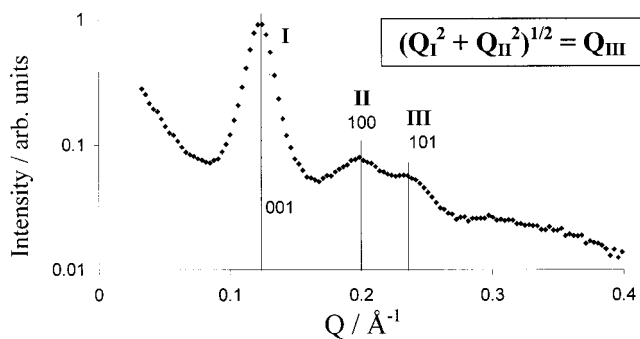

Figure 11.   Small angle X-ray diffractogram of LC dendrimer G-5(Und-BPL)$_{128}$ (from 40 to 160°C).
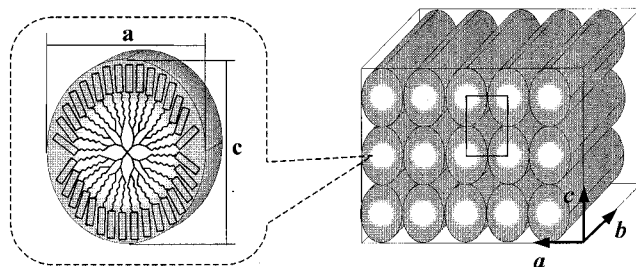

Figure 12.   Model of packing proposed for LC dendrimer molecules in the Col$_r$ phase, where $a = d_{100}$, $c = d_{001}$.

The dendritic matrices of low generations are easily deformed so that they can be tuned to the layered packing of the mesogenic groups. The higher the generation number, the more significant is the disordering influence of the dendritic matrix on the packing of the mesogenic groups. As a result, the temperature of isotropization, as well as the transition enthalpy decreases with increasing generation number. With further generation number increase (to the fourth and fifth generations), the influence of the dendritic matrix becomes more pronounced. In this case, lamellar smectic phases are not observed; instead, the LC dendrimers of the fourth and fifth generations form a rectangular columnar phase. With increasing generation number from the fourth to fifth, the phase sequence remains and a small increase in clearing point and decrease in the transition enthalpy are observed.

3.5. *Ferroelectric properties of LC dendrimers forming the SmC* phase*

As mentioned above, LC dendrimers of generations 1–3 form the SmC* phase, and this shows ferroelectric switching, figure 4(*c*). In this part of the work we will discuss the influence of generation number on the ferroelectric properties, such as the spontaneous polarization, $\mathbf{P}_s$ and the switching time, τ.

The values of $\mathbf{P}_s$ were measured by the repolarization method and calculated from polarization hysteresis loops. A typical hysteresis loop obtained for a ferroelectric LC dendrimer is shown in figure 13.

In order to study the influence of generation number on the ferroelectric properties, the measurements were made for the different materials at the same reduced temperature T_r given by

$$T_r = T - T_c$$

where T_c corresponds to the I–SmC* transition temperature for the series G-n(Und-PBL)$_m$, and to the SmA–SmC* transition temperature for the series of G-n(Und-BPL)$_m$. The temperature dependences of $\mathbf{P}_s$ for all the ferroelectric LC dendrimers and their siloxane monomeric precursors are shown in figure 13. As can be
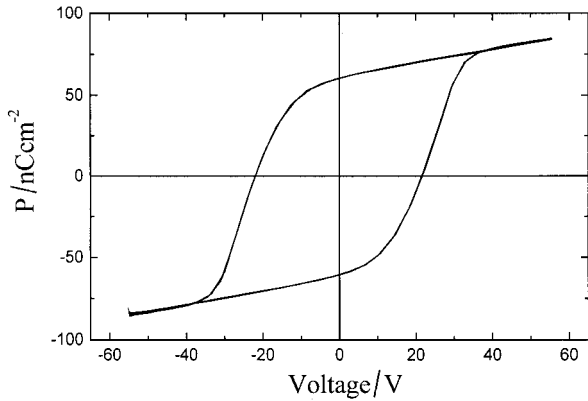
Figure 13. Hysteresis dependence of the polarization on the electric field, obtained for G-1(Und-BPL)$_8$ at 100°C, $f = 80$ Hz.

the dendritic matrices 'dilute' the dipole moment of the system. As mentioned in the previous section, the interlayer spacing d_{001} also increases with increasing generation number, and this means that the dipole moment of the system becomes even more diluted with increasing generation number. Apart from this, the higher the generation number, the more significant is the disordering influence of the dendritic matrix. Thus, the increase in generation number must increase disordering in the system and could lead to a decrease in the average tilt angle in the SmC* phase. It also might be one of the reasons for the decrease in P_s with increasing generation number.

Of most importance for technological applications is the switching time, τ. As shown in figure 15, the switching

seen from these data, the P_s values of the LC dendrimers are lower than those of their siloxane precursors, and decrease with increasing generation number. Apparently,
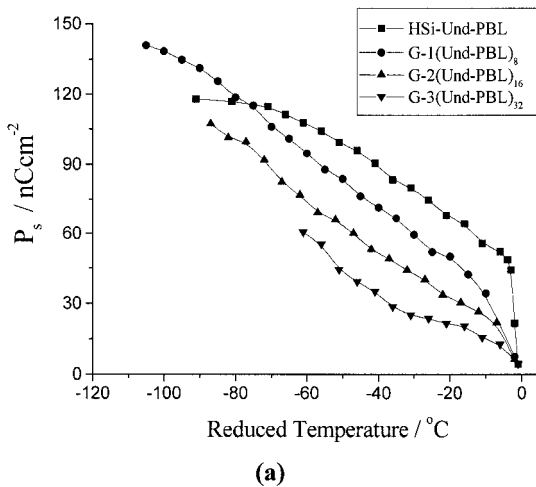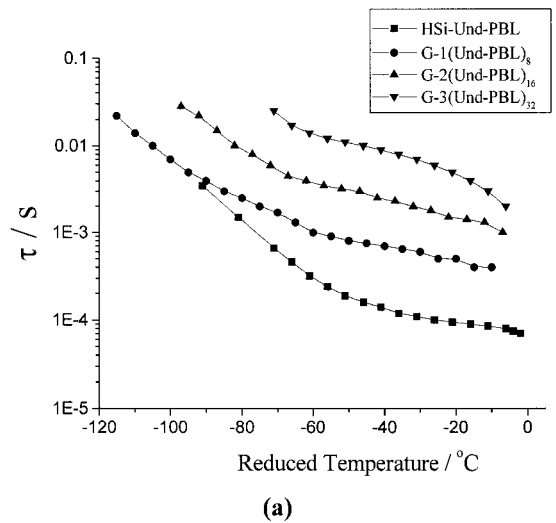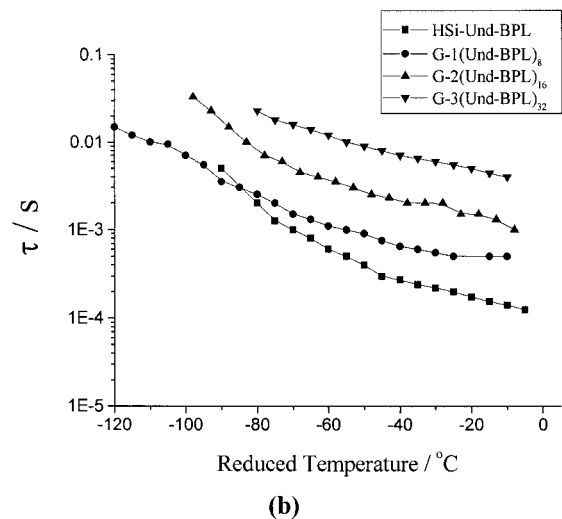

(a)
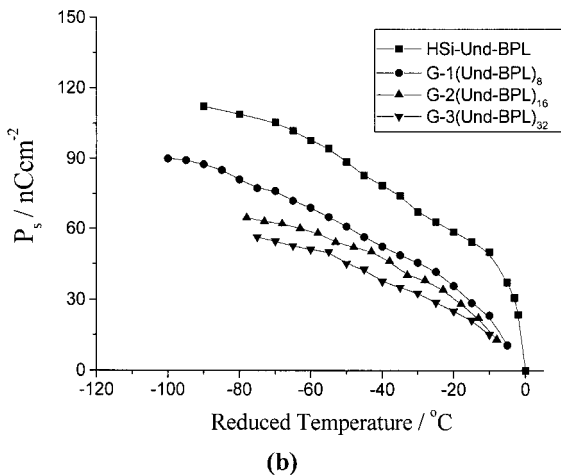
(b)

Figure 14. Temperature dependence of P_s for the ferroelectric LC dendrimers and their siloxane-terminated precursors.

(a)

(b)

Figure 15. Temperature dependence of the switching time for ferroelectric LC dendrimers and their siloxane-terminated precursors.

times for the LC dendrimers are much higher than those for the siloxane low molecular mass analogues. Increase in generation number also results in an increase in τ. The switching time of carbosilane ferroelectric LC dendrimers is in the range 1–10 ms, similar to that for side group ferroelectric LC polysiloxanes.

4. Conclusions

Phase behaviours and structures of the five generations of carbosilane LC dendrimers with terminal chiral mesogenic groups have been considered. It was shown that LC dendrimers of low generation (1–3) exhibit lamellar smectic phases (SmA and SmC*). The ferroelectric SmC* phase is observed over a very broad temperature range from the glass transition temperature ($\sim -5°C$) up to about 180°C. For the higher generations, the influence of the superbranched dendritic core becomes more pronounced and opposes smectic phase formation. In this case the formation of a rectangular columnar phase is observed. The ferroelectric properties of the LC dendrimers exhibiting the SmC* phase were studied. It was shown that increase in generation number leads to a decrease in spontaneous polarization and an increase in switching time.

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