Structure of carbosilane amphiphilic liquid-crystalline codendrimers in bulk and in thin (Langmuir) films

I. D. Leshchiner,[a] E. V. Agina,[a] N. I. Boiko,[a] R. Richardson,[b] and V. P. Shibaev[a]*

[a]Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 939 0174. E-mail: igleshch@yahoo.com
[b]H. H. Wills Physics Laboratory, University of Bristol,
Tyndall av., Bristol BS8 1TL, United Kingdom

Amphiphilic carbosilane liquid-crystalline codendrimers with terminal mesogenic butoxybenzoate and phenolic groups have been synthesized for the first time. The structures and compositions of the synthesized codendrimers were characterized by NMR spectroscopy. The data from polarization optical microscopy, differential scanning calorimetry, and small-angle X-ray scattering demonstrated that all codendrimers possessed mesomorphic properties. They form thin (Langmuir) films at the water—air interface. The surface pressure—surface area isotherms were plotted. The Langmuir—Blodgett films of different thicknesses were obtained by the vertical dipping method on the solid substrate. The film structures were studied by grazing incidence X-ray diffraction analysis.

Key words: dendrimers, codendrimers, carbosilane, liquid-crystalline, amphiphilic, Langmuir—Blodgett films.

The studies of liquid-crystalline (LC) dendrimers had long ago attracted attention of researchers working in the areas of both high-molecular-weight compounds and liquid crystals.[1—5] Unusual molecular topology of these systems that are prone to microsegregation and self-assembling with the formation of a complicated hierarchy of supramolecular structures evoked increased interest in studying the structure formation processes of these compounds in dilute solutions[6] and in the solid phase.[7] Undoubtedly, substantial information on the structure of LC dendrimers could be obtained by the study of their thin films prepared by the Langmuir—Blodgett method (LB films).

However, to use this procedure, one needs, as a rule, amphiphilic molecules capable of specific orientation on the water surface with the polar groups arranged in the aqueous phase and nonpolar groups, in the organic phase. Carbosilane dendrimers, which have been studied in detail in our previous works,[1,2,7] do not meet, unfortunately, these requirements. Therefore, we concentrated our attention on the synthesis of amphiphilic carbosilane LC codendrimers of the first, third, and fifth generations containing different ratios of hydrophilic (phenolic YOH) and hydrophobic (butoxybenzoate, Y´OBu) mesogenic groups (Fig. 1).

As can be seen from Fig. 1, a dendrite molecule with random distribution of mesogenic and phenolic terminal fragments, in essence, is a biphilic codendrimer in which heterogeneous terminal groups are chemically bound to the carbosilane matrix through the aliphatic spacers consisting of ten methylene units.

It should be mentioned that the number of previously synthesized and studied codendrimers is rather small, although many LC dendrimers were described.[8,9]

The following tasks were set in the present work:

(1) to develop a method for the synthesis of the LC codendrimers based on the carbosilane dendritic matrix;

(2) to study the influence of the composition and generation number of the synthesized codendrimers on the formation of the LC structures;

(3) to reveal the possibility of formation of the thin LB films from the synthesized LC codendrimers and to study their structures.

Results and Discussion

Synthesis of codendrimers. We have developed a general approach to the synthesis of amphiphilic carbosilane LC codendrimers, which includes the following main stages:

(1) synthesis of the reactive component (Scheme 1) containing the terminal reactive Si—H group, an aliphatic spacer, and a protected ester of *para*-hydroxybenzoic acid;

(2) attachment of the synthesized protected fragment to the carbosilane dendritic matrix with the terminal allyl groups followed by removal of methoxycarbonyl protecting groups (Scheme 2);

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2063—2072, October, 2008.

1066-5285/08/5710-2101 © 2008 Springer Science+Business Media, Inc.

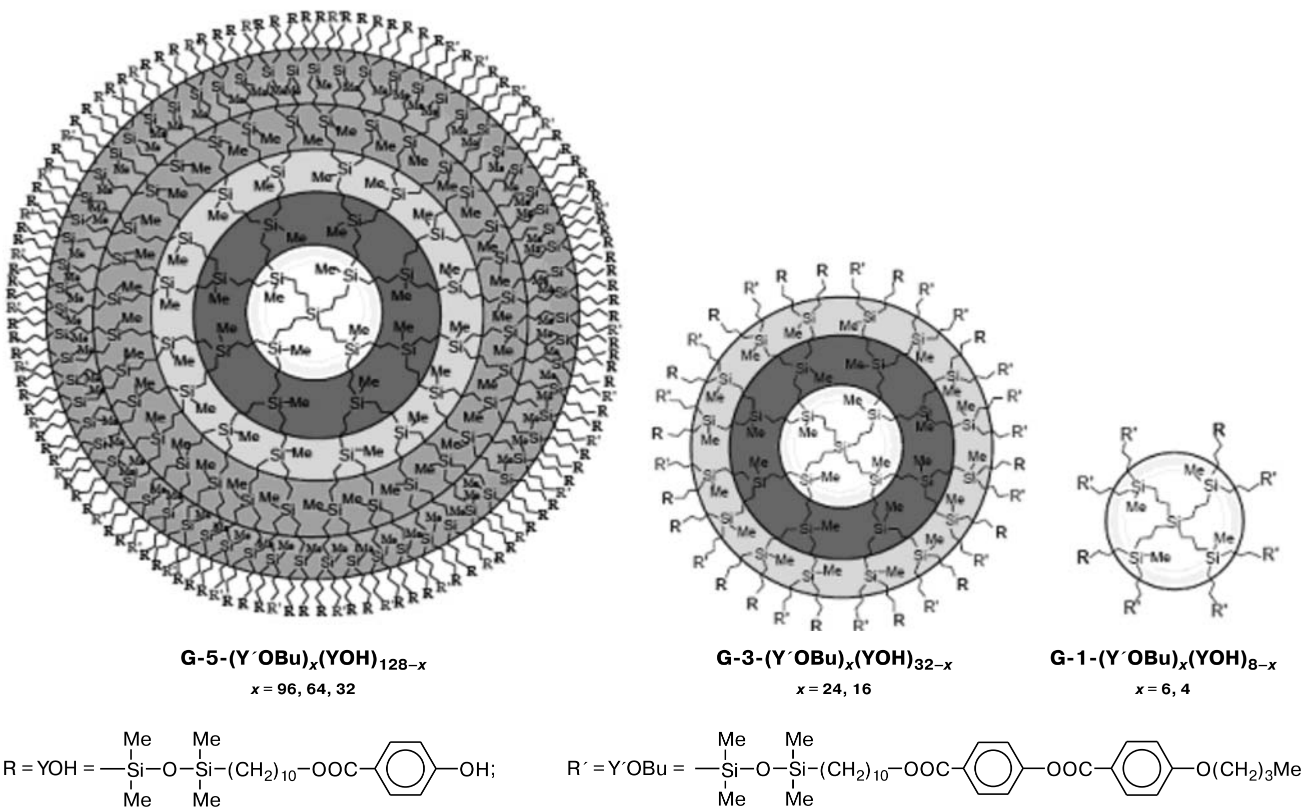


Fig. 1. Objects of the study: amphiphilic carbosilane codendrimers with terminal butoxyphenylbenzoate and phenolic groups.

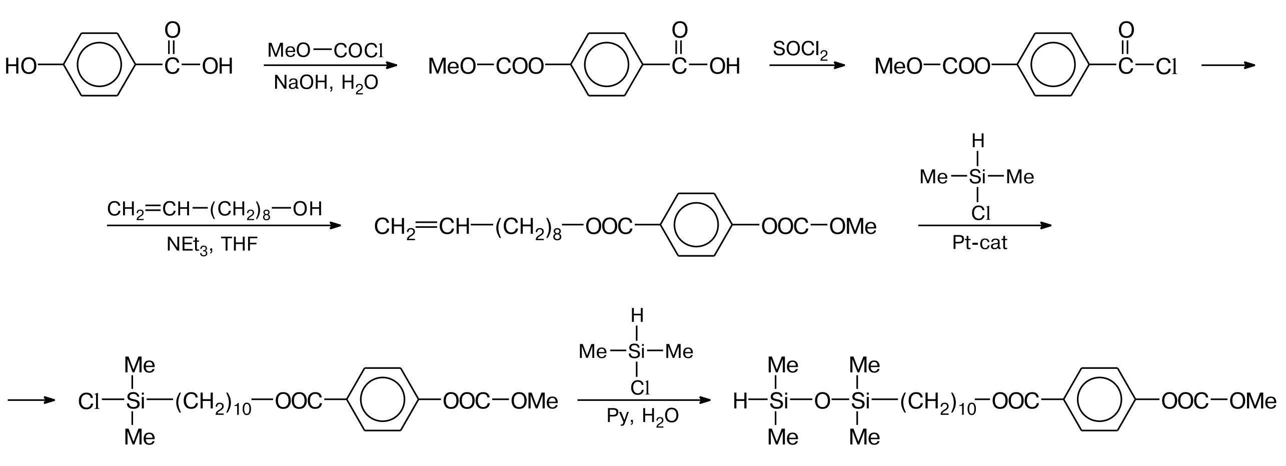
(3) synthesis of the codendrimer with the random distribution of phenolic and mesogenic terminal groups.

The reactive component was synthesized according to a known procedure[10,11,12] (Scheme 1).

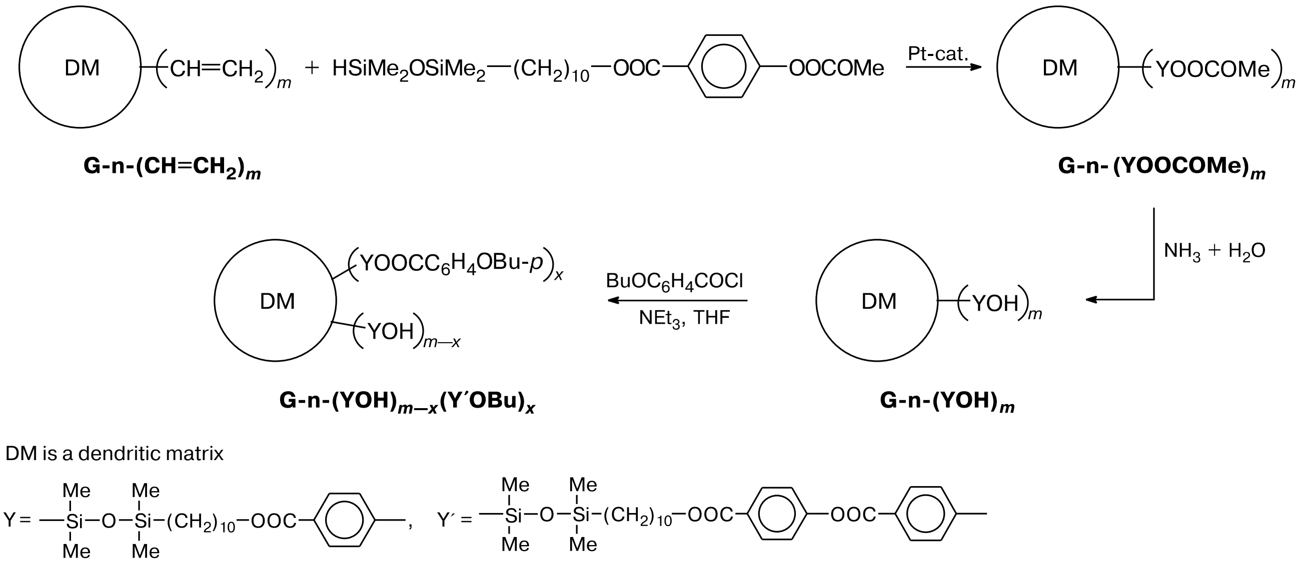
It was necessary to protect the initial phenolic group for carrying out consecutive reactions, especially the hydrosilylation reaction, which does not occur in the presence of the phenolic group. The acid was esterified with a higher ω-unsaturated alcohol to facilitate mesophase formation, and a hydrodisiloxane fragment with the terminal functional Si—H group capable of reacting with the "surface" groups of dendritic matrices was formed. Then the synthesized derivative was attached to the terminal allyl groups of the carbosilane matrices of different generations, and finally the protecting groups were removed (Scheme 2).

The codendrimers with the random distribution of the phenolic and mesogenic groups with different composi-

Scheme 1



Scheme 2



tion were synthesized from the corresponding carbosilane dendrimers with the terminal phenolic groups of the general formula **G-*n*(YOH)$_m$** by reaction with the stoichiometric amount of *para*-butoxybenzoyl chloride (see Scheme 2). The reaction was carried out in anhydrous THF in the presence of triethylamine, and the target compounds were isolated by preparative GPC. Random codendrimer **G-5-Y′OBu(75)** (Table 1) was synthesized by hydrosilylation using a mixture of mesogenic and protected silanes taken in the corresponding ratio, followed by purification from low-molecular-weight admixtures, deprotection, and repeated purification by GPC. The composition of the synthesized codendrimers was determined from the ^{1}H NMR spectra by calculating the ratio of integral intensities of signals for the protons corresponding to the substituted and unsubstituted phenolic groups (Fig. 2). The experimentally calculated degrees of substitution were very close to the stoichiometrically specified values (see Table 1).

Table 1. Experimental and calculated compositions of the synthesized codendrimers

Codendrimer	Formula	α* (%)	
		I	II
G-1-Y′OBu(50)	G-1-(Y′OBu)$_4$(YOH)$_4$	50	47
G-1-Y′OBu(75)	G-1-(Y′OBu)$_6$(YOH)$_2$	75	78.5
G-3-Y′OBu(50)	G-3-(Y′OBu)$_{16}$(YOH)$_{16}$	50	47
G-3-Y′OBu(75)	G-3-(Y′OBu)$_{24}$(YOH)$_8$	75	75
G-5-Y′OBu(25)	G-5-(Y′OBu)$_{32}$(YOH)$_{96}$	25	24.5
G-5-Y′OBu(50)	G-5-(Y′OBu)$_{64}$(YOH)$_{64}$	50	50.5
G-5-Y′OBu(75)	G-5-(Y′OBu)$_{96}$(YOH)$_{32}$	75	75

* α is the degree of substitution of R′ for R (see Fig. 1); I is calculation, and II is experimental.

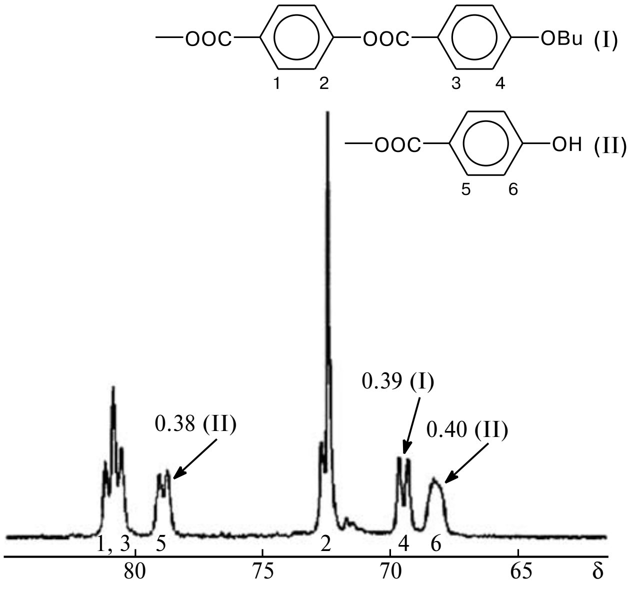


Fig. 2. Fragment of the ^{1}H NMR spectrum of codendrimer **G-3-Y′OBu(50)**.

The individual character and purity of all synthesized dendrimers were confirmed by GPC, and the structures were determined by ^{1}H NMR spectroscopy.

Phase behavior. The phase behavior of the synthesized codendrimers was studied by differential scanning calorimetry (DSC) (Fig. 3), polarization optical microscopy (POM), and X-ray diffraction analysis. It should be noted that the phase behavior of the codendrimers of the lower (first, third) and fifth generations differed substantially. The phase behavior of the codendrimers of the first and third generations was the same as regards the number and character of the phases, and only the enthalpies and tem-

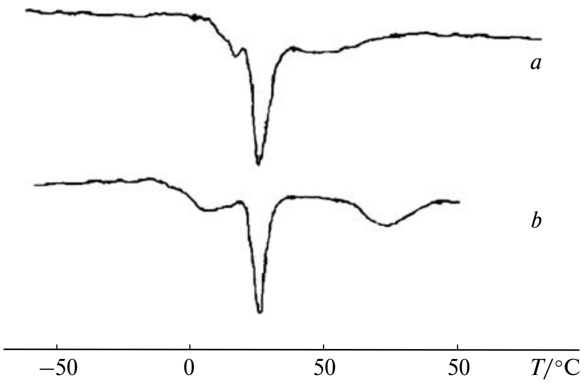


Fig. 3. DSC curves for codendrimers **G-1-Y′OBu(75)** (*a*) and **G-3-Y′OBu(75)** (*b*).

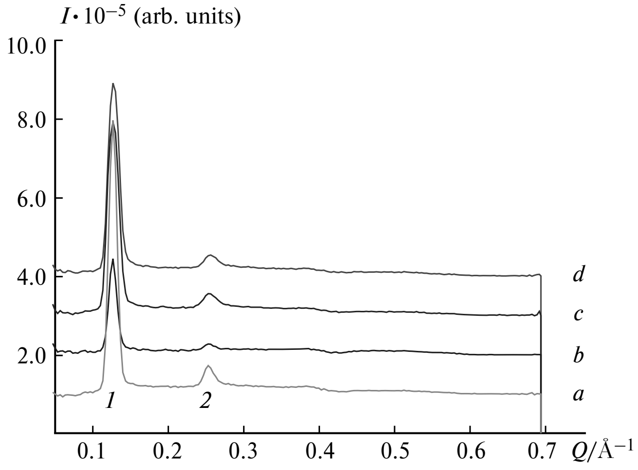


Fig. 4. Small-angle X-ray scattering patterns for codendrimer **G-3-Y′OBu(75)** at 20 (*a*), 25 (*b*), 35 (*c*), and 40 °C (*d*).

peratures of phase transitions were different (Table 2). The DSC curves for codendrimers **G-1-Y′OBu(75)** and **G-3-Y′OBu(75)** (see Fig. 3) exhibit two endothermic transitions corresponding to the consecutive melting of two low-temperature crystalline phases in the temperature interval from 0 to 25 °C. The comparison of the phase behavior of the codendrimers with that of the homodendrimer bearing the butoxyphenylbenzoate mesogenic groups[13] suggests that the second transition corresponds to melting of the butoxybenzoate domains, because the temperatures and heats of transitions of the homo- and codendrimers are close (see Table 2). The codendrimer differs from the homodendrimer only in the presence of some number of peripheral phenolic groups, and the first of the melting transitions (near 10 °C) is absent in the DSC curve of the homodendrimer. Therefore, the first transition can be ascribed to the melting of the phenolic domains. At temperatures above 25 °C the smectic A phase (SmA) is observed in the codendrimers, which is confirmed by the characteristic fan-like structure seen with a polarization microscope. However, the interval of the existence of the LC phase for the first generation is somewhat narrower than that for the third generation, which was also observed for the homodendrimers as the generation number decreased.[13]

Table 2. Temperatures and enthalpies of the phase transitions of the codendrimers based on the data from POM, DSC, and X-ray diffraction analysis

Codendrimer	Phase transitions, T/°C (E/J g^{-1})
G-1-Y′OBu(100)*	K 35.3 (16.5) SmC 101.6 (11.3) I
G-1-Y′OBu(75)	K_1 24.0 (2.8) K_2 27.6 (11.2) SmA 55.0 (5.2) I
G-1-Y′OBu(50)	K_6 (0.8) SmA 14.2 (0.9) I
G-3-Y′OBu(100)*	K 20.0 (8.2) SmC 108.3 (7.7) I
G-3-Y′OBu(75)	K_1 10.1 (4.7) K_2 25.7 (8.9) SmA 64.1 (4.9) I
G-5-Y′OBu(100)*	K 22.7 (5.8) Col_{rec} 90 Col_{hd} 124.3 (6.3) I
G-5-Y′OBu(75)	K 30 Col 95 I
G-5-Y′OBu(50)	K 30 Col 85 I
G-5-Y′OBu(25)	K 30 Col 59 I

Note. K is the crystalline phase, SmC is the smectic C mesophase, Col_{rec} is the orthogonal columnar mesophase, Col_{hd} is the hexagonal columnar mesophase, and I is the isotropic melt. The enthalpies of transition (E) are given in parentheses.

* Data for the phenylbenzoate homodendrimers.[13]

The study of the phase behavior of codendrimers **G-1-Y′OBu(50)** and **G-3-Y′OBu(50)** showed that a decrease in the number of mesogenic groups in the molecule resulted in the gradual degeneration of the phase transitions. The region of existence of the crystalline and LC phases of codendrimer **G-1-Y′OBu(50)** shifts to lower temperatures and the enthalpies of melting do not exceed 1 J g^{-1} (see Table 2). It is known that the enthalpies of transitions decrease with an increase in the number of generation of the LC dendrimers[13—15] and, hence, no significant transitions were detected for the codendrimer of a higher generation (**G-3-Y′OBu(50)**). In addition, the low temperatures of phase existence do not allow one to study the textures with a polarization optical microscope.

The X-ray studies were carried out to confirm that the codendrimers formed the smectic mesophase (Fig. 4).

The small-angle diffraction patterns of nonoriented codendrimer **G-3-Y′OBu(75)** exhibit the peaks corresponding to the first and second reflection orders from the smectic layers at $Q_1 = 0.127$ Å^{-1} and $Q_2 = 0.253$ Å^{-1} (peaks *1* and *2*). The calculated interplanar spacing for this codendrimer at room temperature is 50 Å. Based on these data and calculated lengths of the lateral groups (Y′OBu = 29 Å, YOH = 19 Å, see Fig. 1), one can propose the molecular packing of the codendrimer in the SmA phase presented in Fig. 5. The presence of the

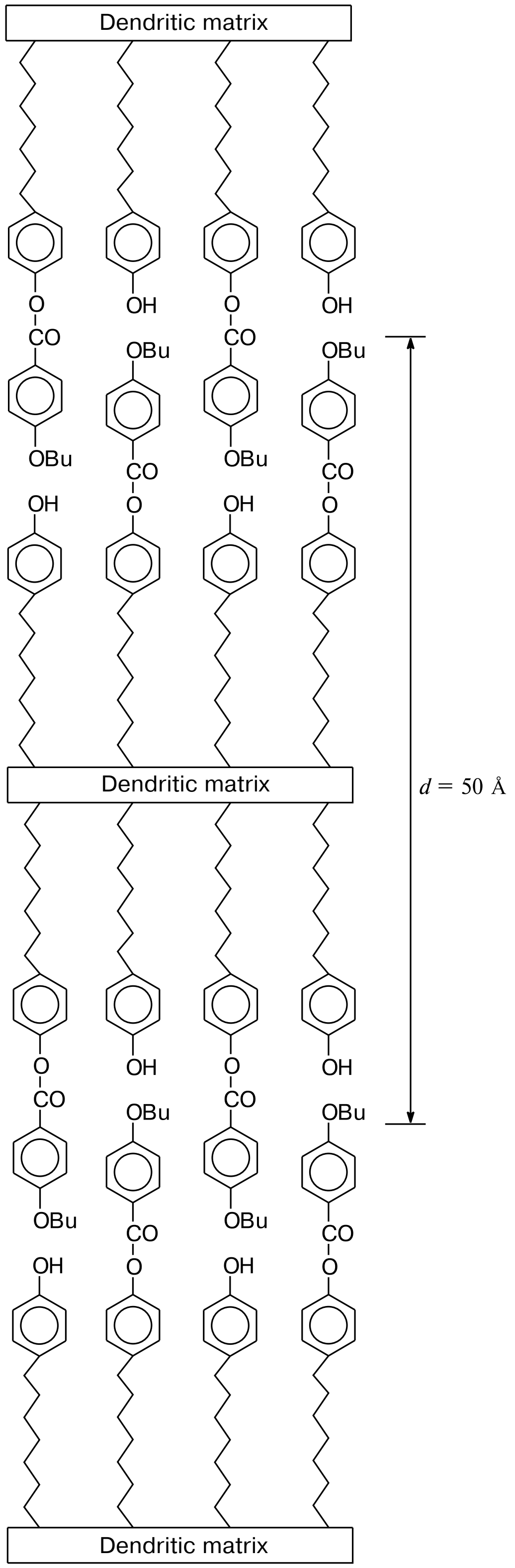


Fig. 5. Scheme of the proposed packing of LC codendrimer **G-3-Y′OBu(75)** in the smectic A mesophase.

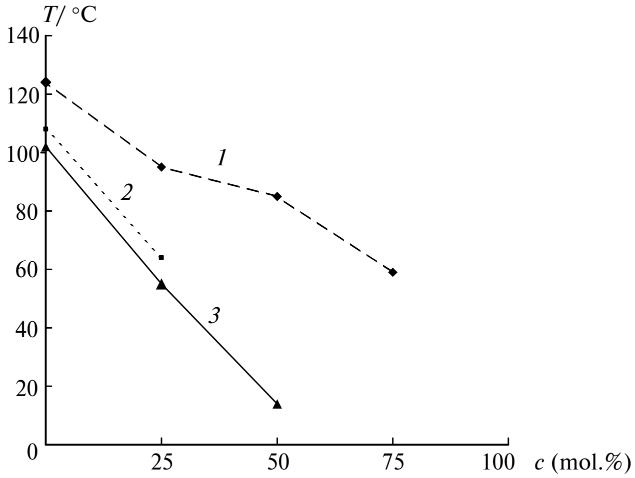


Fig. 6. Dependences of the temperatures of transitions from the LC phase to the isotropic state on the composition of the codendrimers: *1*, **G-5**; *2*, **G-3**; *3*, **G-1** (*c* is relative concentration of phenolic groups).

smectic phase for codendrimer **G-1-Y′OBu(75)**, whose X-ray pattern contains two reflections at $Q_1 = 0.140$ Å^{-1} and $Q_2 = 0.280$ Å^{-1}, is confirmed analogously.

The substantial change in the phase behavior is observed for the codendrimers of the fifth generation. According to the DSC and POM data, codendrimers **G-5-Y′OBu(25)**, **G-5-Y′OBu(50)**, and **G-5-Y′OBu(75)** presumably form the columnar phase. To determine the character of the structures formed, we intend to perform further detailed X-ray studies of oriented samples of the dendrimers.

Let us consider the thermal properties of the phases of the codendrimers synthesized. As can be seen from Fig. 6 presenting the temperatures of transitions from the LC phase to the isotropic state, the stability of the LC phase increases with an increase in the generation number (*i.e.*, molecular weight), which is consistent with published data for homodendrimers.[13] The same trend of the transition temperatures is observed with an increase in the number of mesogenic groups in the codendrimer. The increase in the overall number of mesogenic groups leads to a broader interval of existence of both the smectic (first and third generations) and columnar (fifth generation) mesophases.

Studies of the Langmuir and Langmuir—Blodgett films. First let us consider the behavior of the synthesized amphiphilic statistical codendrimers in monolayers at the water—air interface, and then we will consider their behavior in mono- and polylayers on a silicon support.

It should be noted that stable films formed for all compositions and all generations of the codendrimers under study. However, distinctions in the behavior of the dendrimers of different generations, *viz*., different hysteresis effects, in the compression—decompression process

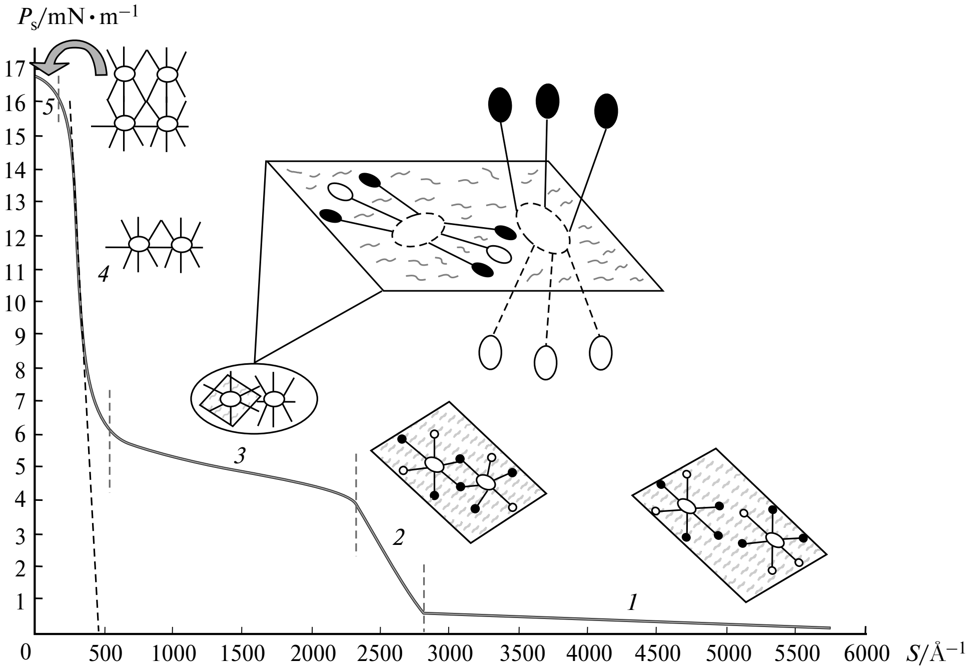


Fig. 7. Surface pressure—surface area isotherm for codenrimer **G-3-Y′OBu(75)** at 25 °C; S is the surface area per molecule.

should be emphasized. They indicate the different nature of the processes that occur at the interface with an increase in the rigidity of the matrix core.

Let us consider the behavior of the lower-generation codendrimers using the **G-3-Y′OBu(75)** codendrimer as an example. The compression isotherm of the codendrimer **G-3-Y′OBu(75)** film in the coordinates surface pressure—surface area is shown in Fig. 7. Five regions (*1—5*) are distinctly seen on the curve. The first region corresponds to the "two-dimensional gas": the dendrimer molecules are remote from each other and, probably, they lie flat on the interface with no interaction between them. Therefore, a decrease in the film surface area does not increase the surface pressure. The second region corresponds to the "two-dimensional liquid," where the dendrimer molecules still lie flat, but the interaction between them increases the surface pressure upon compression of the film (elastic deformation). The "phase transition" occurs, most likely, in the third region: the shape of the dendrimer changes: its molecules gradually acquire the vertical orientation. In this case, the hydrophilic phenolic groups are immersed into the subphase (water), and the hydrophobic phenyl benzoate groups remain on the surface. In the fourth region, the surface pressure increases sharply with a small decrease in the film surface area, which suggests the formation of a "two-dimensional solid" and the end of orientation of the surface groups of the dendritic molecule. Finally, the film collapses in the fifth region. The approximation of the isotherm in the fourth region to the zero value of the surface pressure allows one to calculate the surface area occupied by one molecule in the densest packing of

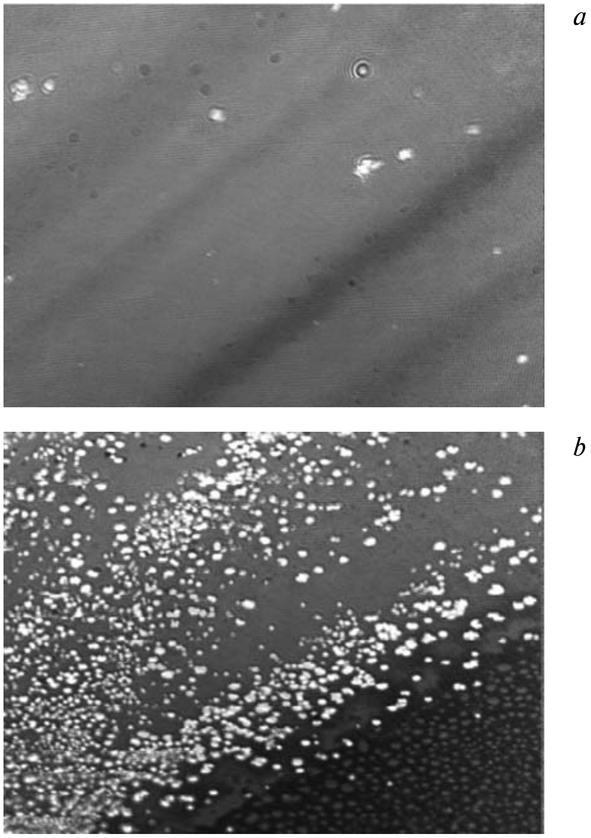


Fig. 8. The Brewster angle microscopic image of the film of codendrimer **G-3-Y′OBu(75)** under surface pressures of 4 (*a*) and 6 mN m^{-1} (*b*). Lighter areas correspond to the vertical orientation of the dendrimer molecules.

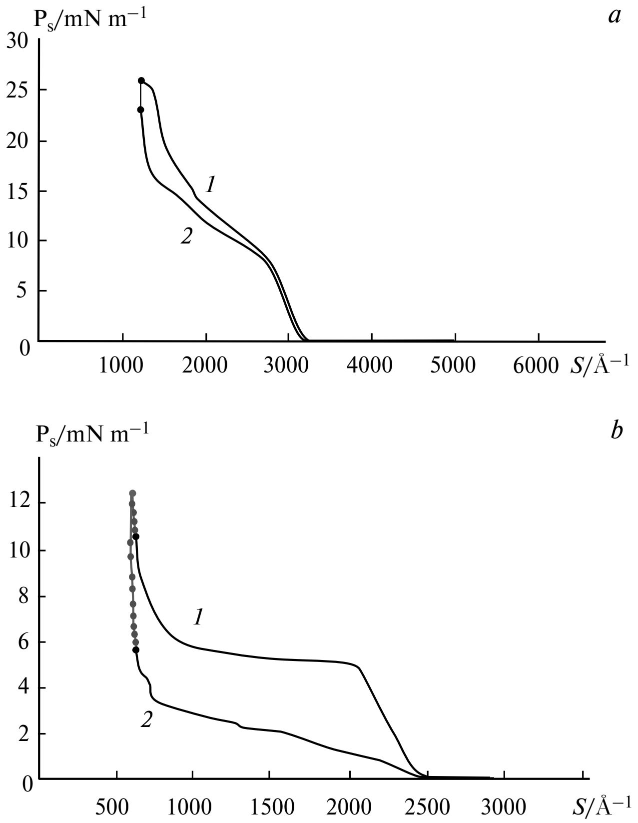


Fig. 9. Hysteresis during compression/decompression of the monolayer of codendrimers **G-5-Y′OBu(25)** (*a*) and **G-3-Y′OBu(75)** (*b*): *1*, compression; *2*, decompression.

dendrimers in the film. For codendrimer **G-3-Y′OBu(75)** this value is 470 Å^2 per molecule, which corresponds to the theoretical calculations (one mesogenic group occupies a surface area of 20 Å^2, and the number of hydrophobic groups in a molecule is 24, *i.e.*, the surface area occupied by a molecule should be 480 Å^2).

This behavior of the monolayer was confirmed using the Brewster angle microscopy (Fig. 8). Rather homogeneous film experiences a sharp change in the structure upon the formation of a new phase, during which the dendrimer molecules are oriented vertically. As can be seen from Fig. 8, on going from region *2* (the dendrimer molecules lie flat) to region *3* (the molecules transit to the vertical position), light islands corresponding to the vertically oriented molecules are formed. It is noteworthy that this transition is jumpwise, the molecules are rapidly oriented, and cavities of the unfilled surface are formed upon the rearrangement.

The behavior of the codendrimers of the fifth generation was virtually the same, but differed basically from that of the codendrimers of the lower generations. This distinction is well observed when the hysteresis in the compression—decompression curves is considered (Fig. 9). As can be seen from the data presented (see Fig. 9, *a*), the decompression curve for codendrimer **G-5-Y′OBu(25)** passes along the same route as the compression isotherm passes and demonstrates only small hysteresis. It can be assumed that no rearrangement of the molecules occurs during compression in this case. At the same time, codendrimer **G-3-Y′OBu(75)** exhibits considerable hysteresis related to the rearrangement of the molecules from the vertically oriented state back to the "flat" conformation (see Fig. 9, *b*).

The monolayer formation by the fifth generation codendrimers suggests that no rearrangement of the hydrophobic and hydrophilic groups occurs within the molecule. The poor deformability of the carbosilane core of the fifth generation codendrimer and steric hindrance on the surface of the molecule do not allow the terminal groups to move freely in space, which results only in the gradual compaction of molecules in the monolayer and a smooth growth of the curve up to the film collapse. In this case, the molecules behave as "elastic balls" (Fig. 10).

The prepared films were transferred by the vertical dipping method onto the solid support (a silicon plate), thicknesses of 2, 10, 14, and 24 layers were obtained. The films were transferred under a constant pressure corresponding to the densest packing of the dendritic molecules in the layer. It was shown that the coefficient of transfer of the substance to the support is inversely proportional to the number of transferred layers and varies from 85% for the bilayer film to 60% for the 24-layer film.

The structure of the films obtained on the support was studied by the grazing incidence X-ray diffraction method. The diffraction patterns were primarily recorded at the grazing incidence angle varied in such a way that the Q vector was always perpendicular to the support surface and the reflection (record) angle remained unchanged. The Q value relates to the incidence angle θ and wavelength λ as follows: $Q = 4\pi\sin\theta/\lambda$. The formation of lamellar structures was observed only for the codendrimers

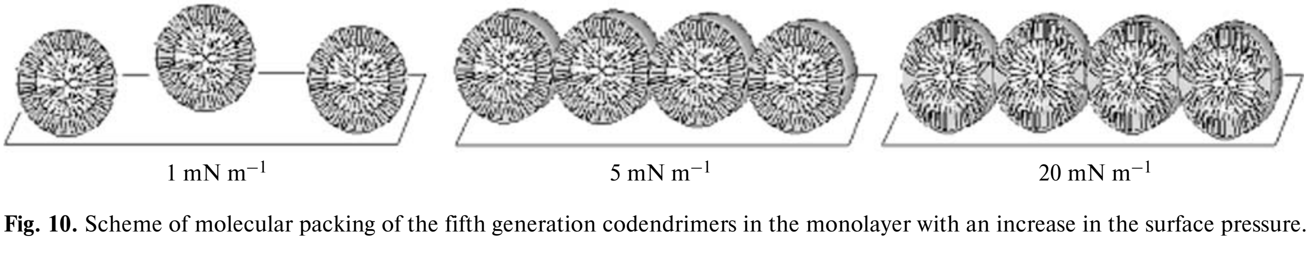


Fig. 10. Scheme of molecular packing of the fifth generation codendrimers in the monolayer with an increase in the surface pressure.

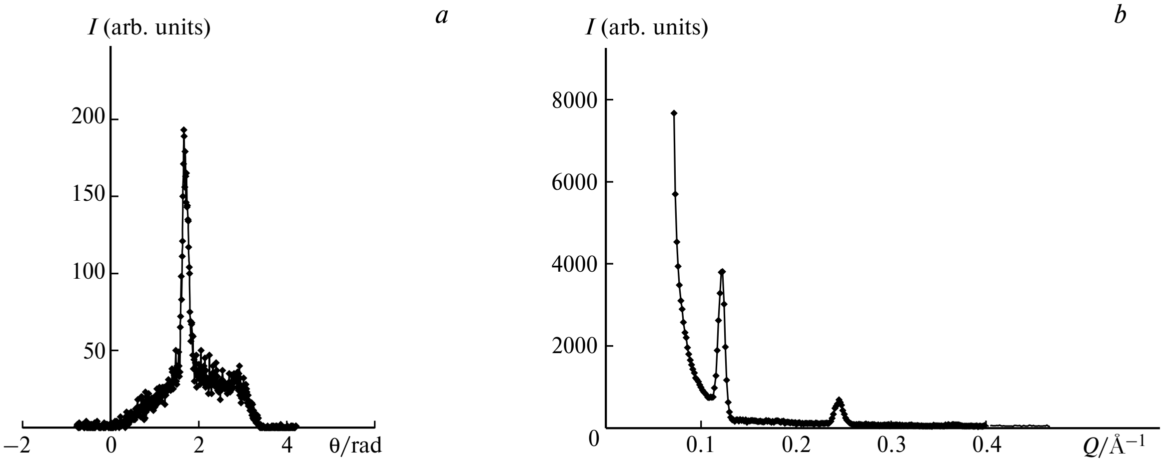


Fig. 11. Diffraction patterns of the 14-layer film of dendrimer **G-3-Y´OBu(75)** at the fixed (*a*) and variable X-ray radiation incident angles (*b*).

with the 75% substitution of the phenolic groups for the butoxybenzoate groups (Fig. 11, *a*). Further the measurements were carried out at a fixed incidence angle to determine the direction of layer ordering, and then the incidence angle was varied (see Fig. 11, *b*). The distinct Bragg peak (1.73°) indicates that the layers formed are parallel to the support.

The interlayer spacings calculated from the diffraction patterns for dendrimers **G-1-Y´OBu(75)** and **G-3-Y´OBu(75)** was equal to 47 and 51 Å, respectively, which are somewhat larger than the interlayer distances in the SmA mesophase for these codendrimers in block.

The diffraction patterns of other codendrimers exhibit no reflections, because these codendrimers form, most likely, structures ordered in the support plane (first generation) or columnar phases (fifth generation).

Thus, we synthesized for the first time the carbosilane codendrimers with the random distribution of the terminal hydrophilic and hydrophobic groups. The study of the phase behavior of the codendrimers synthesized showed that an increase in the generation number of the codendrimers, regardless of their composition, resulted in an increase in the isotropization temperatures and qualitative transition from the lamellar to columnar mesophases, whereas a decrease in the overall number of mesogenic groups in a codendrimer molecule led to the narrowing of the intervals of liquid-crystalline phase existence, a decrease in the clearing point, and degeneration of the phase transitions. The codendrimers synthesized form stable films at the water—air interface and on the solid support. An increase in the generation number of the codendrimers changes the mechanism of monolayer formation. The data obtained make it possible to consider the carbosilane codendrimers as promising materials for the modification of various surfaces.

Experimental

Physicochemical methods of investigation. The ^{1}H NMR spectra were recorded on a Bruker WP-250 instrument. Analytical and preparative GPC were carried out on a Knauer instrument on the Phenomenex column (19S300 mm) packed with Ultrastyrogel 1000 Å. The eluent was tetrahydrofuran, and a Waters R-410 refractometer and a Knauer UV spectrometer were used as detectors. The heats of phase transitions were determined by differential scanning calorimetry using a Mettler TA-4000 system. The scanning rate was 10 deg min^{-1}. Optical studies of the textures were carried out and the temperatures of phase transitions were determined in crossed polaroids of a LOMO R-112 optical polarization microscope equipped with a heating stage with a Mettler FP-800 microprocessor heating rate regulator. The X-ray diffraction studies of the samples in block were carried out on a specially designed diffractometer using the CuKα radiation. The Ni film was used for the radiation monochromatization, and the scattered radiation was measured using a two-dimensional detector connected with a computer for data analysis and collection. The sample—detector distance was 800 mm.

Thin Langmuir—Blodgett films were studied using a NIMA Langmuir trough (model 601S) and a NIMA PS4 surface pressure sensor. The NIMA software was used for the calculation of the isotherm parameters and transfer coefficients. The films were studied at the air—water interface, and ultrapure water was used as the subphase. Water was purified on a Purite Neptune ion-exchange system. A solution of a codendrimer in chloroform with a concentration of 1.00 g L^{-1} was used for film formation. The rate of film compression was 30 mm min^{-1}. The films were transferred onto the solid support (silicon plates) by the vertical dipping method.

The films were deposited layer by layer, the surface pressure was maintained corresponding to the maximum compressed state of the film (for example in case of **G-3-Y´OBu(75)** equal to 0.015 N m^{-1}), and the rate of support dipping was 14 mm min^{-1}. The thicknesses of the films were 2, 10, 14, and 24 layers.

The structures of the deposited films were studied by grazing incidence angle X-ray diffraction on an XPERT PRO diffractometer. The range of accessible Q values was 0.07—2.1 Å^{-1}.

Synthesis of codendrimers. The dendrimers with the phenolic periphery were synthesized according to a procedure known for the dendrimers of the first[10] and third generations.[11,12]

The ^{1}H NMR spectra were similar for all dendrimers (the only difference being the number of protons) and the assignment of the signals can be presented as follows, δ: –0.08 (s, Si—CH_3 matrix); 0.03 (s, Si—O—Si—CH_3); 0.4—0.7 (m, Si—CH_2); 1.2—1.4 (m, CH_3 of the Bu group); 1.67—1.77 (m, CH_2 spacers); 4.05 (t, OCH_2 of the Bu group); 4.30 (m, OCH_2 of the spacer); 6.85 (d, CH, YOH); 6.95 (d, CH, Y´OBu); 7.27 (d, CH_2, YO); 7.89 (d, CH, YOH); 8.06 (d, CH, Y´OBu); 8.11 (d, CH, YO).

Dendrimer G-3-Y´OBu(75). *para*-Butoxybenzoyl chloride (0.44 mmol, Sigma—Aldrich) was added to a solution of compound **G-3-(YOH)$_{32}$** (0.0178 mmol) (see Scheme 2) and Et_3N (0.44 mmol) in anhydrous THF (10 mL). The reaction mixture was stirred without cooling for 48 h, then the precipitate was filtered off, the filtrate was diluted with diethyl ether and three times washed with water. The organic layer was concentrated *in vacuo* to dryness. The chromatographically pure dendrimer was isolated by GPC in 58% yield. ^{1}H NMR ($CDCl_3$, 250 MHz), δ: –0.08 (s, 84 H); 0.03 (s, 384 H); 0.4—0.7 (m, 304 H); 1.2—1.4 (m, 312 H); 1.67—1.77 (m, 64 H); 4.05 (t, 48 H); 4.30 (m, 64 H); 6.85 (d, 16 H); 6.95 (d, 48 H); 7.27 (d, 48 H); 7.89 (d, 16 H); 8.06 (d, 48 H); 8.11 (d, 48 H).

Dendrimer G-3-ArOBu(50). The synthesis was carried out similarly to the procedure of the synthesis of compound **G-3-ArOBu(75)** from **G-3-(YOH)$_{32}$** (0.240 g, 0.0142 mmol), Py (18 mg, 0.228 mmol), and *para*-butoxybenzoyl chloride (48 mg, 0.228 mmol). The final purification of the product from admixtures was carried out by preparative GPC. The yield of the chromatographically pure dendrimer was 158 mg (56%). ^{1}H NMR ($CDCl_3$, 250 MHz), δ: –0.08 (s, 84 H); 0.03 (s, 384 H); 0.4—0.7 (m, 304 H); 1.2—1.4 (m, 568 H); 1.67—1.77 (m, 64 H); 4.05 (t, 32 H); 4.30 (m, 64 H); 6.85 (d, 32 H); 6.95 (d, 32 H); 7.27 (d, 32 H); 7.89 (d, 32 H); 8.06 (d, 32 H); 8.11 (d, 32 H).

Dendrimer G-1-Y´OBu(75). The synthesis was carried out similarly to the procedure for the preparation of compound **G-3-Y´OBu(75)** from compound **G-1-(YOH)$_8$** (0.263 g, 0.066 mmol), Py (31.2 mg, 0.396 mmol), and *para*-butoxybenzoyl chloride (84 mg, 0.396 mmol). The product was purified from admixtures by preparative GPC. The yield of the chromatographically pure dendrimer was 131 mg (39%). ^{1}H NMR ($CDCl_3$, 250 MHz), δ: –0.09 (s, 12 H); 0.012 (s, 96 H); 0.55 (m, 64 H); 1.2—1.4 (m, 136 H); 1.73 (m, 16 H); 4.05 (t, 12 H); 4.27 (m, 16 H); 6.85 (d, 4 H); 6.95 (d, 12 H); 7.27 (d, 12 H); 7.89 (d, 4 H); 8.06 (d, 12 H); 8.11 (d, 12 H).

Dendrimer G-1-Y´OBu(50). The synthesis was carried out similarly to the procedure for the preparation of compound **G-3-Y´OBu(75)** from compound **G-1-(YOH)$_8$** (0.100 g, 0.025 mmol), Py (8.1 mg, 0.103 mmol), and *para*-butoxybenzoyl chloride (22 mg, 0.103 mmol). The product was purified from admixtures by preparative GPC. The yield of the chromatographically pure dendrimer was 131 mg (39%). ^{1}H NMR ($CDCl_3$, 250 MHz), δ: –0.09 (s, 12 H); 0.012 (s, 96 H); 0.55 (m, 64 H); 1.2—1.4 (m, 136 H); 1.73 (m, 16 H); 4.05 (t, 8 H); 4.27 (m, 16 H); 6.85 (d, 8 H); 6.95 (d, 8 H); 7.27 (d, 8 H); 7.89 (d, 8 H); 8.06 (d, 8 H); 8.11 (d, 8 H).

Dendrimer G-5-Y´OBu(25). The synthesis was carried out similarly to the procedure for the preparation of compound **G-3-Y´OBu(75)** from compound **G-5-(10-YOH)$_{128}$** (0.200 g, 0.00292 mmol) and Py (24 mg, 0.280 mmol), which were dissolved in anhydrous THF (10 mL), and *para*-butoxybenzoyl chloride (63 mg, 0.280 mmol) was added. The product was purified by preparative GPC. The yield of the chromatographically pure dendrimer was 138 mg (64%). ^{1}H NMR (THF-d_8, 250 MHz), δ: –0.08 (s, 372 H); 0.03 (s, 1536 H); 0.4—0.7 (m, 1264 H); 1.2—1.4 (m, 2296 H); 1.67—1.77 (m, 256 H); 4.05 (t, 64 H); 4.30 (m, 256 H); 6.85 (d, 192 H); 6.95 (d, 64 H); 7.27 (d, 64 H); 7.89 (d, 192 H); 8.06 (d, 64 H); 8.11 (d, 64 H).

Dendrimer G-5-Y´OBu(50). The synthesis was carried out similarly to the procedure for the preparation of compound **G-3-Y´OBu(75)** from compound **G-5-(YOH)$_{128}$** (0.130 g, 0.00190 mmol) and Et_3N (49.5 mg, 0.490 mmol), which were dissolved in anhydrous THF (10 mL), and *para*-butoxybenzoyl chloride (24 mg, 0.490 mmol) was added. The product was finally purified from admixtures by preparative GPC. The yield of the chromatographically pure dendrimer was 111 mg (74%). ^{1}H NMR (THF-d_8, 250 MHz), δ: –0.08 (s, 372 H); 0.03 (s, 1536 H); 0.4—0.7 (m, 1264 H); 1.2—1.4 (m, 2296 H); 1.67—1.77 (m, 256 H); 4.05 (t, 128 H); 4.30 (m, 256 H); 6.85 (d, 128 H); 6.95 (d, 128 H); 7.27 (d, 128 H); 7.89 (d, 128 H); 8.06 (d, 128 H); 8.11 (d, 128 H).

Dendrimer G-5-Y´OBu(75). The reaction mixture consisting of the dendritic carbosilane matrix **G-5-(CH=CH$_2$)$_{128}$** (0.100 g, $6.31 \cdot 10^{-6}$ mol), 10-(1,1,3,3-tetramethyldisiloxanyl)decyl 4-[(methoxycarbonyl)oxy]benzoate (0.15 g, $0.30 \cdot 10^{-3}$ mol), 4-{[11-(1,1,3,3-tetramethyldisiloxanyl)undecyl]oxy}phenyl 4-butoxybenzoate (0.58 g, $0.91 \cdot 10^{-3}$ mol), a 3% solution (10 μL) of a Pt complex with divinyltetramethyldisiloxane in xylene (PC-072), and anhydrous toluene (10 mL) was magnetically stirred in a closed vessel under argon at 35 °C (in an oil bath) for 72 h. After the cessation of the reaction, the reaction mixture was passed through silica gel to deactivate the catalyst using THF as the eluent. Then a 25% aqueous solution of ammonia (10 mL) was added dropwise on cooling to a solution of the synthesized compound in an ethanol—THF (1 : 1) system (10 mL). The reaction mixture was stirred without cooling for 2 h and then poured into water, and the pH value was brought to 8 with acetic acid. The resulting suspension was extracted with diethyl ether three times. The ethereal fraction was washed with water three times and dried with anhydrous sodium sulfate. The obtained solution was concentrated *in vacuo* to dryness. The product was purified from high-molecular-weight admixtures by preparative GPC. The yield of the chromatographically pure dendrimer was 0.260 g (73%). ^{1}H NMR (THF-d_8, 250 MHz), δ: –0.08 (s, 372 H); 0.03 (s, 1536 H); 0.4—0.7 (m, 1264 H); 1.2—1.4 (m, 2296 H); 1.67—1.77 (m, 256 H); 4.05 (t, 192 H); 4.30 (m, 256 H); 6.85 (d, 64 H); 6.95 (d, 192 H); 7.27 (d, 192 H); 7.89 (d, 64 H); 8.06 (d, 192 H); 8.11 (d, 192 H).

The authors are grateful to A. M. Muzafarov and E. A. Rebrov (Institute of Synthetic Polymeric Materials, Russian Academy of Sciences) for the carbosilane dendrite matrices with terminal allyl groups kindly presented for the synthesis, as well as to the coworkers of the Institute of Synthetic Polymeric Materials (Russian Academy of Sciences) for NMR studies.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 07-03-01089), European Cooperation in Science and Technology (COST Program, Chemistry, Grant D35, WG13), and the Council on Grants at the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-5899.2006.3).

References

1. S. A. Ponomarenko, N. I. Boiko, V. P. Shibaev, *Vysokomol. Soedin.*, *Ser. A*, 2001, **43**, 1 [*Polym. Sci., Ser. A*, 2001, **43** (Engl. Transl.)].
2. R. M. Richardson, S. A. Ponomarenko, N. I. Boiko, V. P. Shibaev, *Liq. Cryst.*, 1999, **26**, 101.
3. I. M. Saez, J. W. Goodby, *Liq. Cryst.*, 1999, **26**, 7, 1101.
4. J. L. Serrano, M. Marcos, R. Martin, M. Gonzalez, J. Barbera, *Chem. Mater.*, 2003, **15**, 3866.
5. J. Barbera, R. Gimenez, M. Marcos, J. L. Serrano, *Liq. Cryst.*, 2002, **29**, 309.
6. A. V. Lezov, A. B. Mel´nikov, G. E. Polushina, E. A. Antonov, M. E. Novitskaya, N. I. Boiko, S. A. Ponomarenko, E. A. Rebrov, V. P. Shibaev, E. I. Ryumtsev, A. M. Muzafarov, *Dokl. Akad. Nauk*, 2001, **381**, 1, 69 [*Dokl. Chem.*, 2001, **381** (Engl. Transl.)].
7. S. A. Ponomarenko, N. I. Boiko, V. P. Shibaev, R. M. Richardson, I. J. Whitehouse, E. A. Rebrov, A. M. Muzafarov, *Macromolecules*, 2000, **33**, 5549.
8. J.-M. Rueff, J. Barbera, B. Donnio, D. Guillon, M. Marcos, J.-L. Serrano, *Macromolecules*, 2003, **36**, 8368.
9. M. Liebau, H. Janssen, K. Inoue, S. Shinkai, J. Huskens, R. Sijbesma, E. W. Meijer, D. Reinhoudt, *Langmuir*, 2002, **18**, 674.
10. N. Boiko, X. Zhu, A. Bobrovsky, V. Shibaev, *Chem. Mater.*, 2001, **13**, 1447.
11. I. D. Leshchiner, E. V. Agina, N. I. Boiko, V. P. Shibaev, R. M. Richardson, *Zhidkie kristally i ikh prakticheskoe ispol´zovanie* [*Liquid Crystals and Their Application*], Izd. Ivanovo Gos. Univ., 2004, **3—4**, 74 (in Russian).
12. K. L. Genson, J. Holzmueller, I. Leshchiner, E. Agina, N. Boiko, V. P. Shibaev, V. V. Tsukruk, *Macromolecules*, 2005, **38**, 8028.
13. E. V. Agina, N. I. Boiko, R. M. Richardson, B. I. Ostrovskii, V. P. Shibaev, E. A. Rebrov, A. M. Muzafarov, *Vysokomol. Soedin., Ser. A*, 2007, **49**, 1 [*Polym. Sci., Ser. A*, 2007, **49** (Engl. Transl.)].
14. M. V. Ryabkov, B. V. Lebedev, N. N. Smirnova, E. V. Agina, S. A. Ponomarenko, E. A. Makeev, N. I. Boiko, V. P. Shibaev, *Zh. Fiz. Khim.*, 2004, **78**, 1933 [*Russ. J. Phys. Chem.*, 2004, **78** (Engl. Transl.)].
15. B. V. Lebedev, N. N. Smirnova, M. V. Ryabkov, S. A. Ponomarenko, E. A. Makeev, N. I. Boiko, V. P. Shibaev, *Vysokomol. Soedin.*, *Ser. A*, 2001, **43**, 514 [*Polym. Sci., Ser. A*, 2001, **43** (Engl. Transl.)].

Received June 14, 2007;
in revised form March 20, 2008