ORIGINAL CONTRIBUTION

Synthesis and physical behavior of amphiphilic dendrimers with layered organization of hydrophilic and hydrophobic blocks

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Abstract Amphiphilic carbosilane dendrimers with novel architectural layout have been synthesized. These dendrimers contain peripheral groups consisting of covalently bound promesogenic fragments and hydrophilic (oligoethyleneglycolic) linkages which are connected to a carbosilane core in two distinct ways: as spacer or as tail arrangement. Such molecules have a block structure where the hydrophilic and hydrophobic blocks are distributed within the dendrimer forming layers of different polarity. The hydrophilic layer is either enclosed between two hydrophobic parts of the molecule or is situated on the periphery. The synthetic strategy for achieving these structures is described. The interfacial properties of the dendrimers were studied and the influence of the dendritic structure's organization on the Langmuir film formation process is assessed.

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Introduction

Studies of the structure and properties of amphiphilic polymers attract considerable attention of scientists when searching for new materials that can form self-assembling monolayers and Langmuir–Blodgett (LB) films or can modify the macroscopic properties of the surface and interface.

Supramolecular structures of such films, forming various functional surfaces had been intensively investigated in the last two decades due to the possibility of their applications in biomedics, sensing, catalysis, lithography, and many other fields [1–11].

Of special interest are amphiphilic dendrimers consisting of hydrophilic and hydrophobic fragments whose behavior is still insufficiently studied. At the same time, their molecular architecture, monodispersity, high content of terminal groups, and tendency to assemble into well-defined nanoscaled supramolecular structures definitely deserves special attention. Monomolecular Langmuir films of dendrimers with terminal groups of different functionality (electrosensitive, photosensitive, etc.) transferred layer-by layer on solid substrates (LB films) are very promising for opto- and microelectronics and could yield thin-film materials with programmed optical, waveguiding, pyroelectric, and other unusual properties. [1–5].

The preparation of Langmuir films from amphiphilic dendrimers or monodendrons has been investigated by several research groups [6–20]. Most of these studies have been done on the dendrimers consisting of a hydrophilic core and hydrophobic periphery. Only a few articles were devoted to dendrimers with hydrophobic core and hydrophilic terminal groups [21].

Among the amphiphilic dendrimers, special interest is attracted to a subclass of liquid crystalline (LC) dendrimers containing terminal mesogenic and amphiphilic groups. Such molecules contain units capable of forming mesophases (hydrophobic mesogenic groups) characterized by anisotropy of physical properties and hydrophilic fragments thus their organization and self-assembly in materials can be controlled by external fields. The first example of a study on LC amphiphilic dendrimers at an air–water interface has been demonstrated by us in [22]. Such dendrimers are composed of carbosilane cores with covalently attached separate (polar-phenolic and nonpolar-mesogenic) terminal groups. The hydrophilic/hydrophobic balance in these molecules was modified only by the change of the composition ratio of the terminal mesogenic and non-mesogenic groups. A choice of well-described carbosilane cores can prevail when considering practical applications since they possess similarity to popular platforms of silicon based nanoparticles, are stable at high temperatures and various environmental conditions.

It has been shown that spread films of first- and third generations of the dendrimers exhibit a structural change, forming a well-organized monolayer film, in which phenolic terminal groups are being immersed into the water while mesogenic groups are forced out of the water. The influence of composition and generation number on surface pressure surface area isotherms and film stability was studied. It is a general rule for low generations of LC dendrimers that the dendritic core is deformed and the mesogens dominate the structure of the mesophase, as for higher generations the geometrical requirements and crowding of the "dendritic arms" tend to drive the self-assembly behavior. When considering the design of the amphiphilic LC dendrimers it was supposed that we could control the hydrophilic–hydrophobic balance in the complex hybrid molecules and tailor their type of LC packing.

It is clear that changes and adjustments in the chemistry of the amphiphilic dendrimer's terminal groups effectively control both the structure of the Langmuir films and the nature of groups exposed at the outside surface. Unfortunately, the importance of chemical functionalities of different parts of the molecule still remains an open question.

This work provides valuable information on the role of molecular layout of various parts of the layered dendritic molecule in its molecular conformation at the air water interface. The co-existence of incompatible hydrophilic and hydrophobic fragments in a single molecule with mesogens and dendritic matrix allows for the rational design of new LC materials, including novel water soluble systems (Fig. 1).

Experimental

Materials Chemical compounds for synthesis were obtained from "Sigma-Aldrich Co.", "Merck" and "Chimmed" and used as received, exclusive of solvents which if required were left over molecular sieve or freshly distilled. 4-([undec-10-en-1-yl]oxy)benzoic acid, 4-butoxybenzoyl chloride and 4-[(metoxycarbonyl)oxy] benzoic acid where prepared according to standard techniques [23, 24] . For all catalytic hydrosilylation reactions, absolute toluene was used. Silica gel 40–60 mesh ("Merck") was used for column chromatography.

Synthesis Amphiphilic mesogen-containing dendrimers with layered organization of hydrophilic and hydrophobic blocks were synthesized according to the techniques described below.

Synthesis of siloxane-terminated reactive fragments Depending on the positions of the hydrophilic (oligoethyleneglycolic) layer (block) dendrimer precursors were obtained by following two routes (Fig. 2).

Fragments for dendrimers with hydrophilic periphery Detailed synthetic procedures, techniques and characterization for these compounds and precursors (P-x1 to P-x4) presented in the right scheme of Fig. 2 are available in the Electronic supplementary material (ESM).

Fragments for dendrimers with hydrophobic periphery To acquire this type of fragments the following synthetic procedures were used.

3,6,9,12-tetraoxapentadec-14-en-1-ol {tetraethyleneglycol monoallyl ether} (P-y1)

In a three-necked flask for 500 mL, equipped with a mechanical stirrer, drop funnel and thermometer, 200 mL of absolute THF and (10 mL, 11.24 g, 57.9 mmol) tetraethylene glycol was added. After that, small portions of sodium hydride (2.78 g 60 % dispersion in mineral oil, 69.5 mmol) in THF were added until hydrogen stopped evolving. Then, a solution of allylbromide (5.79 mL, 66.5 mmol) in THF was added and the reaction mixture was stirred for further 3 h. Subsequently, a small amount of ethanol followed by water was added and the mixture was evaporated under vacuum at low heat. The resulting mixture was dissolved in diethyl ether (400 mL) and washed with water two times (50 mL), the water was extracted with chloroform, the combined fractions were dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The resulting oil was purified by column chromatography over silica gel eluent dichloromethane/methanol (1:20 (v/v)), and then finally distilled in high vacuum (0.4 mmHg). Yield: 6.327 g (47 %) of colorless liquid. NMR ^{1}H (500 MHz, CDCl$_3$,

Fig. 1 Amphiphilic mesogen-containing dendrimers with hydrophilic and hydrophobic terminal blocks
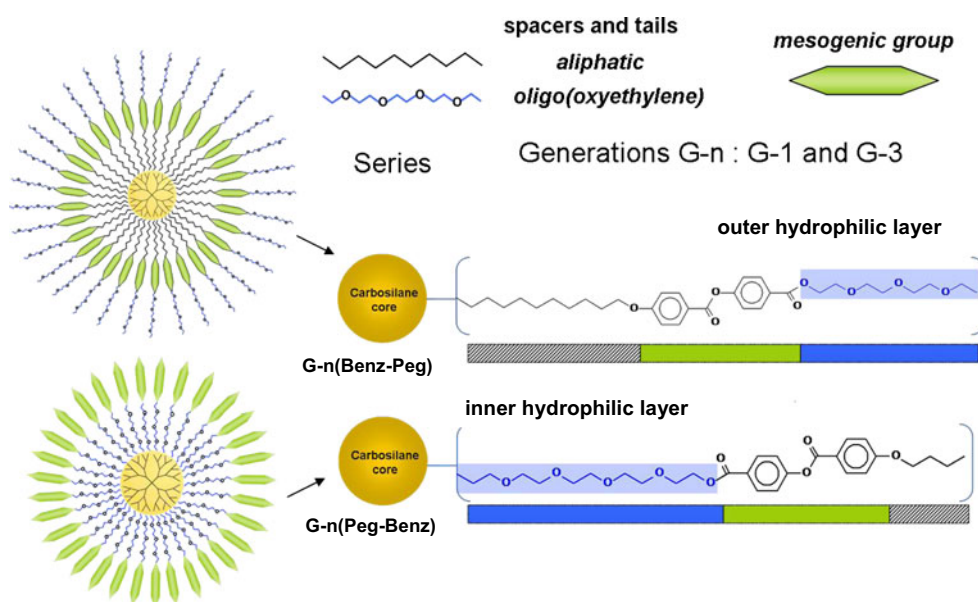
ppm): 3.59 (m, 4H), 3.65 (m, 10H), 3.70 (t, 2H, $J=4.4$ Hz), 4.00 (d, 2H, $J=5.7$ Hz), 5.16 (d, 1H, $J=10.4$ Hz), 5.25 (d, 1H, $J=17.3$ Hz), 5.89 (m, 1H). NMR ^{13}C (62.9 MHz, CDCl$_3$, ppm) 61.62, 69.30, 70.22, 70.48, 72.15, 72.50, 117.10, 134.56.

3,6,9,12-tetraoxapentadec-14-en-1-yl 4-[(methoxycarbonyl)oxy]benzoate (P-y2)

To the solution of compound *I* 5,707 g (29.1 mmol) in 15 mL thionyl chloride a drop of DMF was added. The mixture was
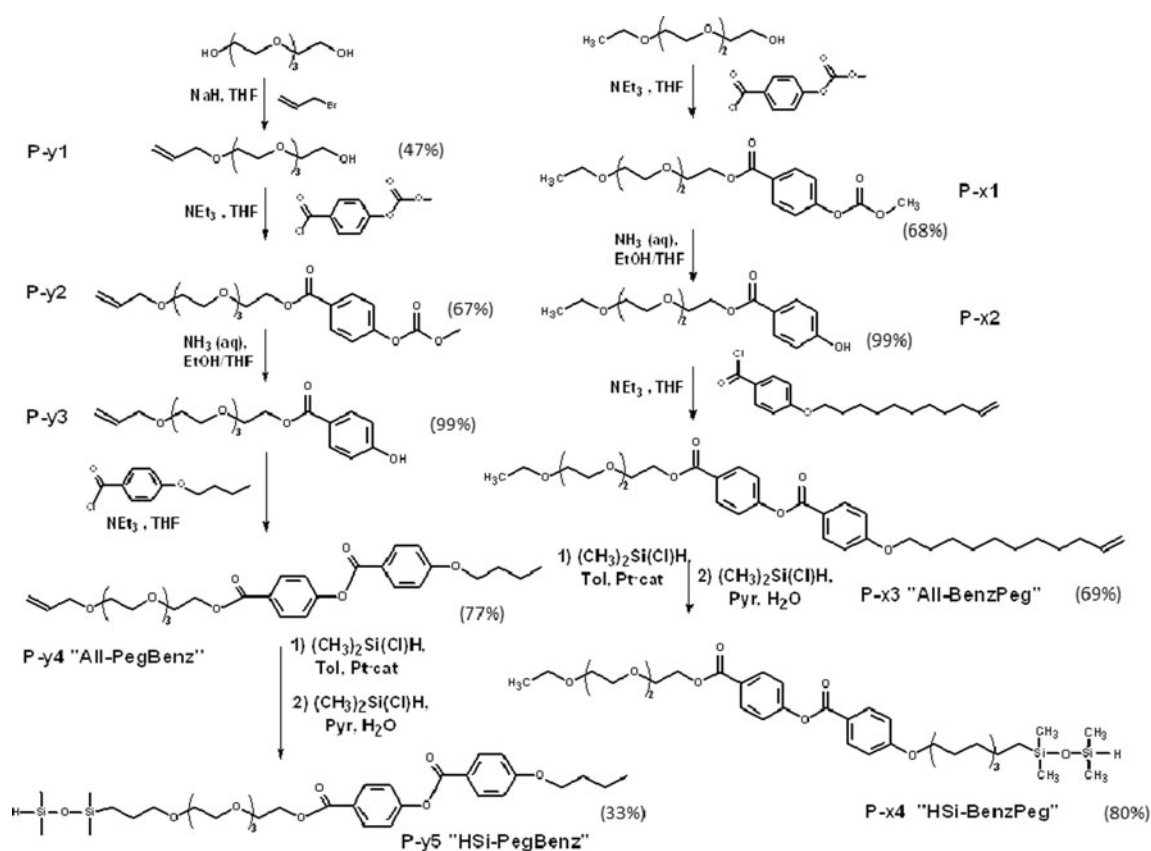

Fig. 2 Reaction pathways for obtaining siloxane-terminated reactive fragments (precursors)

left for 8 h without heating or stirring. Further, the excess thionyl chloride was removed under reduced pressure and moderate heating. Obtained crystals were dissolved in THF (30 mL) and added dropwise to a cooled solution of compound P-y1 5.6855 g (24.3 mmol) and NEt₃ (4.05 mL, 29.1 mmol) in THF (30 mL). The resulting mixture was stirred for 6 h at rt, filtered, and the solvent was removed at reduced pressure. The residue was dissolved in diethyl ether (200 mL), washed with water three times, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The resulting oil was purified by column chromatography over silica gel eluent hexane/ethyl acetate (1:1 (v/v)). Yield: 6.65 g (67 %) of colorless oil. NMR ^{1}H (500 MHz, CDCl₃, ppm): 3.58(t, 2H, J=4.9 Hz), 3.62–3.71 (m, 10H), 3.82 (t, 2H, J=4.9 Hz), 3.91 (s, 3H), 4.00 (d, 2H, J=5.7 Hz), 4.46 (t, 2H, J=4.9 Hz), 5.16 (d, 1H, J=10.4 Hz), 5.26 (d, 1H, J=17.1 Hz), 5.89 (m, 1H), 7.25 (d, 2H, J=8.8 Hz), 8.08 (d, 2H, J=8.8 Hz). NMR ^{13}C (125 MHz, CDCl₃, ppm): 55.49, 64.24, 69.14, 69.40, 70.60, 70.63, 70.67, 72.15, 116.94, 120.87, 127.88, 131.31, 134.76, 153.51, 154.58, 165.56.

3,6,9,12-tetraoxapentadec-14-en-1-yl 4-hydroxybenzoate (P-y3)

To a cooled solution of compound P-y2 (6.452 g, 15.6 mmol) in 10 mL of mixture ethanol–THF (1:1) 10 mL of 25 % aqueous ammonia solution was added dropwise. The reaction mixture was stirred for two additional hours and then poured into water; the pH was brought up to 8 with 1 N HCl. The resulting suspension was extracted with diethylether three times. Combined diethylether fractions were washed with water once and then dried over anhydrous sodium sulfate. The resulting solution was evaporated till dryness in vacuo. Yield was >99 %. The resulting oil was purified by column chromatography over silica gel eluent hexane/ethyl acetate (1:9 (v/v)). MALDI-TOF MS (2-(4-hydroxyphenylazo) benzoic acid, [M+Na]$^+$) m/z 376.82 exp. (377.16 theor.) NMR ^{1}H (500 MHz, CDCl₃, ppm): 3.56 (t, 2H, J=4.4 Hz), 3.60–3.71 (m, 10H), 3.80 (t, 2H, J=4.7 Hz), 3.98 (d, 2H, J=5.7 Hz), 4.41 (t, 2H, J=4.7 Hz), 4.85 (b, 1H), 5.14 (d, 1H, J=10.4 Hz), 5.24 (d, 1H, J=17.3 Hz), 5.87 (m, 1H), 6.83 (d, 2H, J=8.5 Hz), 7.87 (d, 2H, J=8.5 Hz). NMR ^{13}C (125 MHz, CDCl₃, ppm) 63.69, 69.30, 69.33, 70.50, 72.15, 115.25, 117.22, 121.65, 131.85, 134.51, 160.96, 166.54.

4-(2,5,8,11,14-pentaoxaheptadec-16-enoyl)phenyl 4-butoxybenzoate (P-y4)

To a cooled solution of compound P-y3 (5.6976 g, 16.1 mmol) and NEt₃ (2.24 mL, 16.1 mmol) in dry THF (30 mL) a solution of 4-butoxybenzoyl chloride (3.42 g, 16.1 mmol) in THF was added. The resulting mixture was further stirred for 6 h without cooling, and then filtered and evaporated under

vacuum. The residue was dissolved in diethylether (300 mL), washed three times with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure. Received viscous liquid was purified by column chromatography, eluent hexane/ethyl acetate (1:1 (v/v)). Yield: 6.58 g (77 %). MALDI-TOF MS (2-(4-hydroxyphenylazo) benzoic acid, [M+Na]$^+$) m/z 552.94 exp. (553.24 theor.) NMR ^{1}H (500 MHz, CDCl₃, ppm): 0.98 (t, 3H, J=7.4 Hz), 1.50 (m, 2H), 1.79 (m, 2H), 3.57 (t, 2H, J=4.7 Hz), 3.61–3.71 (m, 10H), 3.82 (t, 2H, J=4.9 Hz), 4.00 (d, 2H, J=5.7 Hz), 4.04 (t, 2H, J=6.6 Hz), 4.47 (t, 2H, J=4.9 Hz), 5.14 (d, 1H, J=10.4 Hz), 5.25 (d, 1 H, J=17.3 Hz), 5.89 (m, 1H), 6.96 (d, 2H, J=8.8 Hz), 7.28 (d, 2H, J=8.8 Hz), 8.11 (d, 4H, J=7.9 Hz). NMR ^{13}C (125 MHz, CDCl₃, ppm) 13.68, 19.07, 31.02, 64.13, 67.96, 69.12, 69.36, 70.56, 70.59, 70.64, 72.09, 114.32, 116.85, 121.00, 121.70, 127.45, 131.15, 132.26, 134.73, 154.82, 163.70, 164.22, 165.71.

4-(18,18,20-trimethyl-2,5,8,11,14,19-hexaoxa-18, 20-disilahenicosan-1-oyl)phenyl 4-butoxybenzoate (P-y5)

To the solution of compound P-y4 (4.3953 g, 8.28 mmol) and chlorodimethylsilane (4.59 mL, 41 mmol) in absolute toluene (4 mL) 20 μl of the Pt-catalyst (PC-072 divinyltetramethyldisiloxane platinum complex in xylene) was added. The resulted solution was stirred under argon for a week. The reaction was monitored by ^{1}H NMR until the extinction of the signals corresponding to the proton signals of the end double bond: $δ$=5.15 (m, 2H) и $δ$=5.91 (m, 1H). To the reaction mixture 32.1 mL (0.29 mol) of additional chlorodimethylsilane in 30 mL of dry THF was added and at 0 °C the solution of 20.1 mL (0.249 mol) pyridine and 5.96 mL (0.33 mol) of water in 30 mL of THF was added dropwise. The reaction mixture was stirred at rt for 30 min, after which 300 mL of chloroform and 50 mL of water was added. The chloroform layer was washed with water three times until a neutral pH. Chloroform solution was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The resulting compound was purified by column chromatography over silica gel, eluent hexane/ethyl acetate (1:1 (v/v)). Yield: 1.812 g (33 %) colorless oil. MALDI-TOF MS (2-(4-hydroxyphenylazo) benzoic acid, [M+Na]$^+$) m/z 687.19 exp. (687.30 theor.) NMR ^{1}H (500 MHz, CDCl₃, ppm): 0.06 (s, 6H), 0.14 (d, 6H, J=2.7 Hz), 0.50 (m, 2H), 0.99 (t, 3H, J=7.3 Hz), 1.52 (m, 2H), 1.60 (m, 2H), 1.81 (m, 2H), 3.40 (t, 2H, J=6.6 Hz), 3.57 (m, 2H), 3.61–3.71 (m, 10H), 3.83 (t, 2H, J=4.6 Hz), 4.05 (t, 2H, J=6.5 Hz), 4.47 (t, 2H, J=4.4 Hz), 4.66 (m, 1H), 6.96 (d, 2H, J=8.5 Hz), 7.28 (d, 2H, J=8.5 Hz), 8.12 (m, 4 H). NMR ^{13}C (125 MHz, CDCl₃, ppm) −0.06, 0.87, 13.77, 14.02, 19.17, 23.34, 31.12, 64.22, 68.07, 69.24, 70.02, 70.65, 70.70, 70.73, 74.14, 114.41, 121.11, 121.79, 127.55, 131.26, 132.36, 154.90, 163.79, 164.33, 165.82.
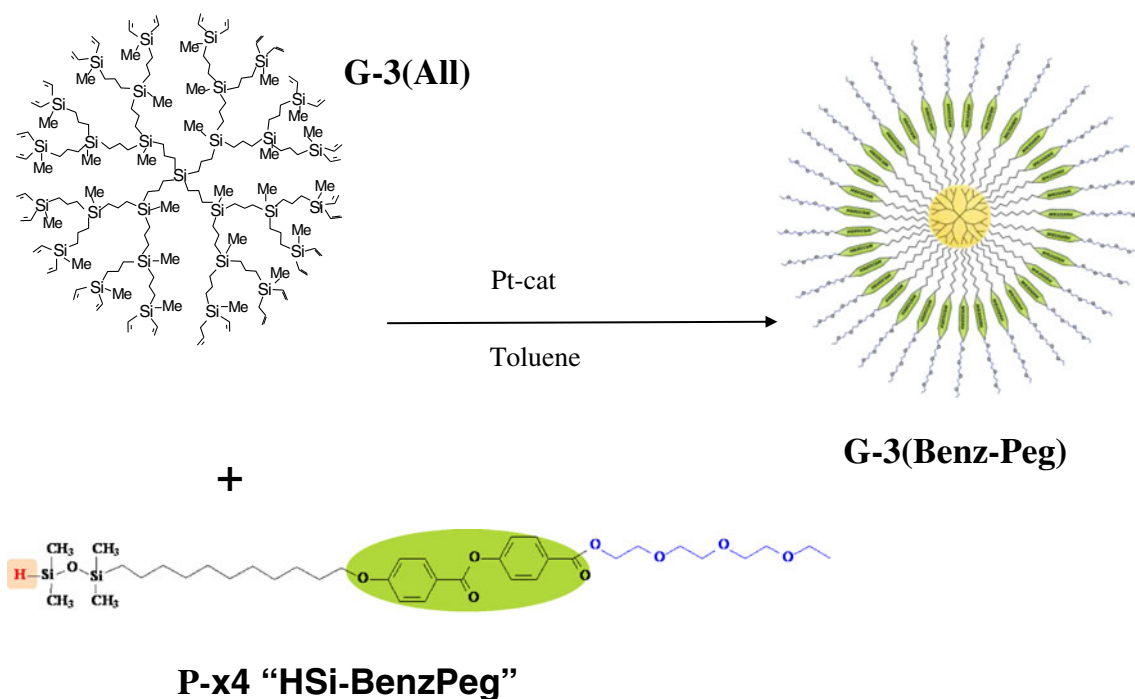
G-3(All)

+

P-x4 "HSi-BenzPeg"

G-3(Benz-Peg)

Pt-cat

Toluene

Fig. 3 Scheme of the synthesis of third generation amphiphilic dendrimers of the series G-n(Benz-Peg)

Synthesis of amphiphilic mesogen-containing dendrimers with hydrophilic and hydrophobic terminal blocks Amphiphilic dendrimers were synthesized using the obtained precursors from appropriate amounts of allyl-terminated carbosilane matrices (G-n(All), synthesis of which is described elsewhere [25]) according to the standard hydrosilylation procedures [26, 27] (Fig. 3). Techniques are presented with detail in the ESM.

Characterization All dendrimers were purified by semipreparative gel-permeation chromatography (GPC). The analytical GPC curves show that all products are highly monodisperse. The GPC experiments were preformed on Aquilon system equipped with Waters R-410 RI detector and Knauer UV-detector. Phenomenex columns with pore sizes of 1,000 Å were used. The dendrimers and precursors chemical composition was accessed by ^{1}H NMR, ^{13}C NMR and COSY (^{1}H, ^{1}H) and HSQC (^{1}H, ^{13}C), spectra taken from CDCl$_3$, CD$_2$Cl$_2$, DMSO-d6, THF-d8 solutions (see ESM). Spectra were registered on Bruker WP-250, Avance 250, 500DPX with a gradient probe. Structure of the precursors and dendrimers were also studied by MALDI-TOF MS using Micromass M@ldi (tm) instrument working in linear or reflectron mode. 10 mg/mL solutions of 2,5-dihydrobenzoic acid, 2-(4-hydroxyphenylazo)benzoic acid and 3-indolacrilic acid in THF where used for the matrix substance.

Thermal properties of the dendrimers were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 K/min. All experiments were performed using a

"Mettler TA-400" thermal analyzer. A LOMO P-112 polarization microscope equipped with a "Mettler FP-84" thermocell and a "Mettler FP-800" microprocessor temperature control was used for polarization optical microscopy. A "Linkam" liquid nitrogen cooled cell was utilized for low temperature studies.

Langmuir and LB Films The spreading solutions were prepared by dissolving the dendrimers or precursors in chloroform at 1.00 mg/mL concentrations. The solutions were spread on the water surface with a micro-syringe, and the film was then left to equilibrate before the
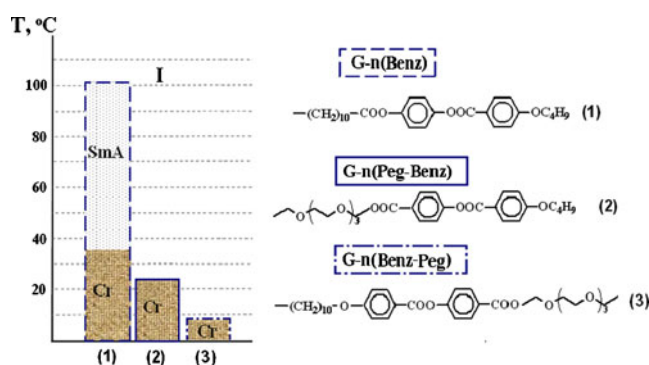

Fig. 4 Scheme of phase transitions for fully hydrophobic dendrimers G-n(Benz) and amphiphilic dendrimers G-n(Peg-Benz) and G-n(Benz-Peg) of the first generation. *Insert* shows the chemical structures of dendrimer terminal groups. *SmA* smectic mesophase, *Cr* crystal phase, *I* isotropic state
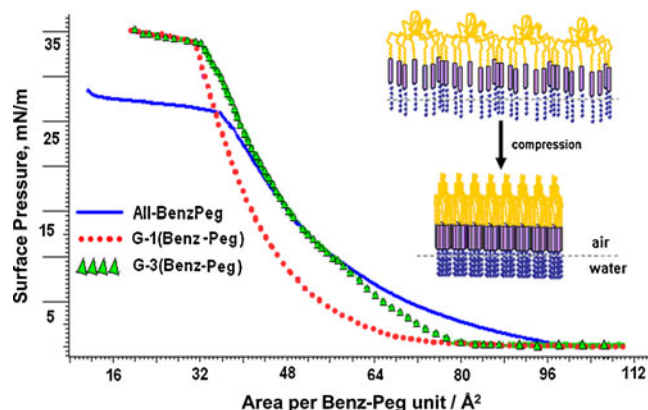
Fig. 5 Compression isotherms of lower molecular mass precursor P-x3 "All-BenzPeg" (analogue of the dendrimer terminal group) and dendrimers G-n(Benz-Peg) of the first and third generations at T= 25 °C. The inset shows the model of possible structural changes during compression of dendrimer film

compression started. Data was collected with a Nima 601S system using a Teflon trough and barriers in a dust-free environment. Ultrapure water was used for the subphase (72.8 mN/m, 18 MΩcm). The monolayers were compressed with speeds ranging from 5 to 70 mm/min, with almost no influence of the barrier velocity on the observed behavior. The phase transitions of the spread monolayer were observed using a Micro-BAM (Nima) fitted with a Teflon trough such that images of the air-solution interface could be taken by the CCD camera (image size 800×430 μm, ~×40 magn.). The image contrast consisted of 256 Gy levels. LB films were obtained by transfer on quartz slides or silicon wafers. The vertical dipping method with the dipping speed of 14 mm/min was used to obtain 2, 10, 14, and 24 layer films. Film transfers were performed at surface pressures close to the collapse point corresponding to most condensed phase in the monolayer. The X-ray diffraction studies of LB films were made on a

Panalytical XPERT PRO diffractometer. The scattering vector (Q) range was 0.07–2.1 Å^{-1}.

Results and Discussion

Synthesis Before obtaining dendrimers of various generations, synthesis of their precursors had to be carried out. Two types of mesogenic amphiphilic precursors H-Si-PegBenz and H-Si-BenzPeg were synthesized (Fig. 2). Stage-by-stage synthesis included bonding blocks of different polarity into one molecule in the desired order. Both of the functional groups of the tetraethylene glycol in P-y1 can react with allyl bromide. For this reason, the sodium hydride was taken as just one equivalent to form predominantly mono-substituted adduct. This reaction produces noticeable amounts of di-substituted and non-substituted tetraethylene glycol which are removed by column chromatography and high vacuum distillation. Different polarity blocks covalently bound into one molecule cause severe hindrance of the reactions due to solubility problems in a common organic solvent. Solubility and Pt-complexation issues prove to be vital when attempting hydrosilylation of the allyl-containing amphiphilic precursors in toluene and use of tetramethylsiloxane is preferred. Reactions and products were monitored by not only NMR but also MALDI-TOF MS, giving a versatile method to see if the proper hydrosilylation product is formed, while NMR is not always capable to show small structural differences of the possible byproducts.

Using the precursors, dendrimer series G-n(Peg-Benz) and G-n(Benz-Peg) were synthesized comprising of first- and third-generation dendrimers with amphiphilic terminal groups. Reactions were performed by standard hydrosilylation technique which allows one to attach precursor fragments onto an allyl-terminated carbosilane core [28]. Completeness of the reaction was monitored by ^{1}H NMR and then the purified dendrimers of lower generations were

Fig. 6 GIXRD of a multilayer LB film of dendrimer G-3 (Benz-Peg) with the calculated model that explains the observed d spacing
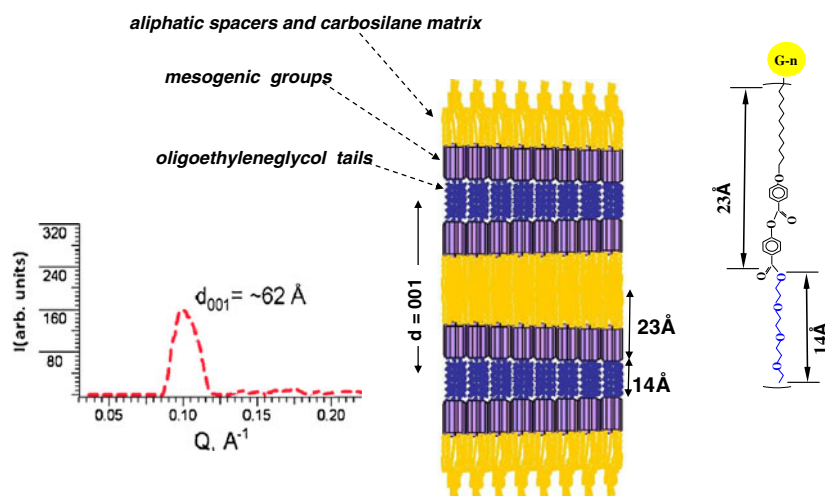
studied for possible undersubstitution [29–31] by MALDI-TOF MS. Typical results (see ESM) show that the group addition yield for some dendrimers was >95 % (which means the majority of the molecules in the samples have full substitution or one undersubstituted group). The full structure of the obtained precursors and dendrimers was proven by various 1D and 2D NMR techniques (ESM).

Phase behavior It was found that despite anticipation of LC properties in synthesized dendrimers, none of them formed mesophases. Thus, one can conclude that upon substitution of aliphatic spacer or tail in mesogen-containing butoxybenzoate terminal groups of the previously reported LC dendrimers [32] G-n(Benz) with oligoethyleneglycols, the phase behavior changes dramatically. Dendrimers and precursors lose their liquid crystallinity (smectic phase is not formed) and only crystallize below room temperatures above which they are in the isotropic state (Fig. 4 and S14–I5). For example, dendrimer G-1(Peg-Benz) crystallizes below 25 °C while the crystallization temperature of dendrimer G-1(Benz-Peg) is below 7 °C. Large values of phase transition enthalpy of the dendrimers also indicate the formation of crystalline phases. Thus, enthalpy of crystalline phase melting of the dendrimer G-1(Peg-Benz) is about 24 J/g which is more than two times higher than the melting of the smectic mesophase in the isotropic melt for the dendrimer G-1(Benz) [33].

These results show that the introduction of oligoethyleneglycolic fragments in the mesogen-containing terminal groups (spacer or tail) of the dendrimers has significant influence not only on their phase state but also on the isotropization temperatures.

Langmuir films One of the main questions that arise upon obtaining the amphiphilic dendrimers from monomer precursors is how the dendritic architecture of the molecules influences the behavior of thin films. Dendrimer's G-n(Benz-Peg) structure presented in Fig. 1 allows one to assume that, if dendrimer molecules are flexible enough, their individual branches can accept the conformation of separate monomer precursors (for example P-x3 "All-BenzPeg"). To compare the behavior of the thin film of the dendrimer and the monomer, the dendrimer isotherm's "Area per molecule" axis can be divided by the number of branches (terminal groups) on the dendrimer (i.e., 8 for G-1, 32 for G-3). And thus, not only the shape but the isotherm positions and area per molecule values can be compared (Fig. 5). As can be seen from Fig. 5, general shapes of all curves are almost identical—the isotherms display a gas phase with nearly zero surface pressure upon spreading, followed by a sharp rise in surface pressure at lower area, indicating the formation of stable monolayers. Interestingly, areas per terminal group of the dendrimer molecules are slightly shifted towards smaller values as compared to the low molecular weight analogue. All dendrimer curves were

reversible and reproducible which confirms the stability of the Langmuir monolayers.

The data obtained give evidence that terminal groups of dendrimers G-n(Benz-Peg) behave similarly to their analogue if applied to the interface. Nevertheless, the effect of dendritic structure is also clearly visible: the dendrimer film is less prone to collapse – surface pressures are ~10 mN/m more than those which break a monomolecular film of precursor molecules that are not covalently connected to each other. It means that stability of dendrimer's monomolecular film is greater when compared with low molecular mass analogues of dendrimer's terminal groups.

The area occupied by one terminal group of dendrimers at surface pressures close to the collapse point extrapolated to zero surface pressure is in the 52–60 Å² range. This is larger than the typical 20 Å² cross-sectional area for an alkyl spacer and the expected area for a terminal group, containing phenyl rings [34]. This means that the molecular area is not determined by just stacking of mesogen-containing groups, probably with oligoethylene glycol tails contributing to this through strong solvation forces. Also, it is noticeable that there is a dependence of these values on the generation number, presumably the dendritic matrix
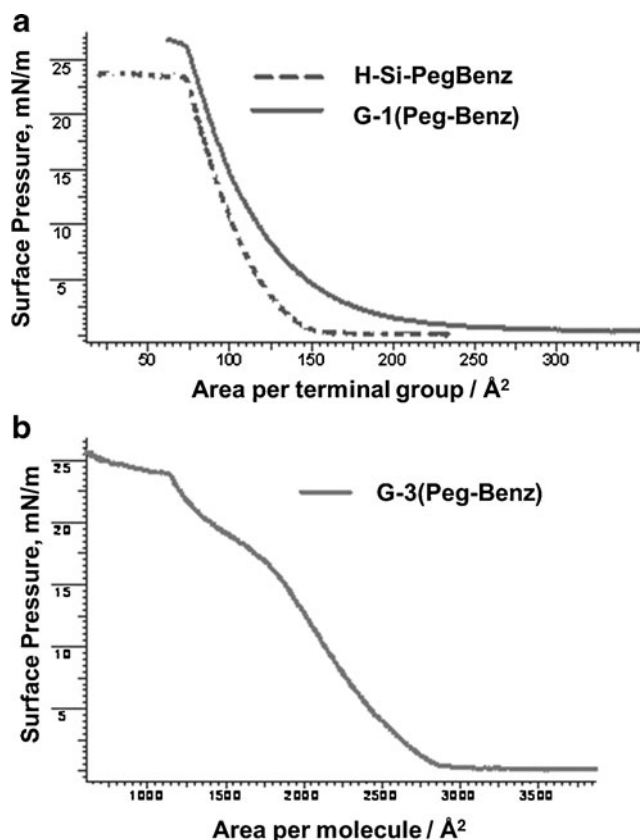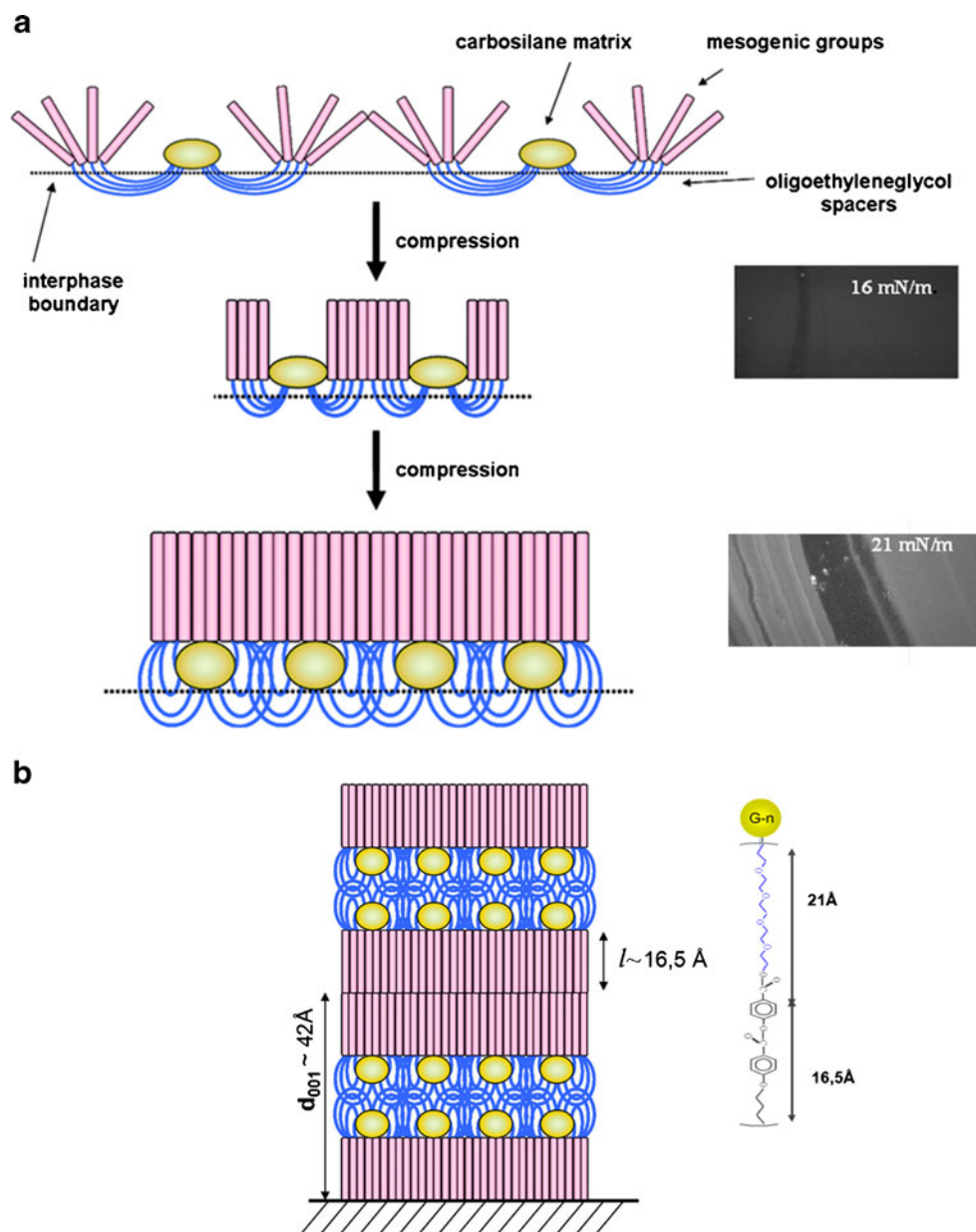

Fig. 7 Langmuir isotherms at $T=25$ °C **a** low molecular mass precursor P-y5 "All-PegBenz" (analogue of the dendrimer terminal group) and dendrimer G-1(Peg-Benz); **b** for dendrimer G-3(Peg-Benz)

playing a role in restricting the maximal compression
density.

Based on the obtained data, a model for the packing
structure in monolayers of the dendrimer G-n(Benz-Peg) at
the water–air interface can be proposed (Fig. 5). On com-
pression, hydrophilic tails of the dendrimer groups tend to
become immersed into water while the hydrophobic spacers
and matrixes align above the surface. Mesogenic fragments
in such model should form a lamella-type layer due to the
strong lateral interactions of their aromatic rings. It is most
likely that separation of some groups from the surface of water
due to steric hindrance caused by the dendritic structure of
molecules is observed as the film is further compressed near
collapsing. Further compression induces a collapse into a 3D
liquid film.

In order to examine the dendrimer films in the solid state,
the obtained monolayers were transferred onto solid substrates
and Grazing Incidence X-ray Diffraction (GIXRD) was used
to study properties of these thin films. It was found that neither
lower molecular mass compounds, nor first-generation den-
drimers G-1(Benz-Peg) form periodical structures—they yield
an isotropic "liquid" film.

At the same time, X-ray diffraction pattern of G-3(Benz-
Peg) LB films are characterized by the existence of a distinct
peak at $d=62$ Å (Fig. 6). Molecular modeling of the terminal
groups for these dendrimers supports a packing scheme
depicted in Fig. 6. The lengths of hydrophilic oligoethylene
glycol and hydrophobic fragments are in a good agreement
with the observed d spacing, assuming a lamellar structure in
which the hydrophobic (mesogenic and aliphatic) fragments

and hydrophilic fragments are packed into layers with periodicity equal to ~60 Å (23 Å×2+14 Å). Thus, the dendritic nature of the molecules actually stabilizes the layer structure, allowing "mesophase" formation in LB films compared to low molecule mass compounds of the same type (monomer precursors). This effect might be achieved by the influence of steric factors on alignment of terminal groups (they have less freedom and are held in proximity with each other).

Now, let us look at the behavior of dendrimers G-n(Peg-Benz) containing the inner hydrophilic fragments.

A comparison of two Langmuir isotherms belonging to dendrimer G-1(Peg-Benz) with hydrophobic periphery and its terminal group precursor (Fig. 7a) shows similarity in the isotherm shape and position. Meanwhile, the form of isotherm produced from the compression of G 3(Peg-Benz) differs significantly from the low molecular mass analogue (Fig. 7b). The curve is characterized by a rise at area 2700 $Å^2$ per molecule and a second steep rise around 1500 $Å^2$. Between these areas, a plateau-like feature was observed at 16–20 mN/m.

This observation is explainable since the hydrophilic part of the terminal group of the dendrimer is actually located between two hydrophobic parts: the mesogenic group and the carbosilane dendritic core. Such architecture prevents the groups from assuming a simple vertical position favored by the di-block nature of the amphiphilic precursor that lacks the second hydrophobic part (the carbosilane core). BAM microphotographs (S16) show that the dendrimer film exhibits a significant thickness change (long before collapsing) which explains the plateau-like feature on the Langmuir curve.

Possible model for the packing of dendrimer G-n(Peg-Benz) in the monolayer at the water–air interface can be offered as an explanation of observed behavior (Fig. 8). The first transition which is seen on the isotherm as a "step" around 10–15 mN/m (Fig. 7b) involves the orientation of lateral groups lying on the surface into a vertical position which is favored by strong lateral interactions of promesogenic fragments. While the second transition (Fig. 7b), which is clearly seen on the BAM microphotograph (S16) and involves the monolayer thickness increase, is explained by a conformational change of dendritic molecules within the monolayer because of the tendency of lateral groups to form a "continuous layer" by expelling carbosilane matrixes which form a separate layer below the surface. This may be favored by the fact that long oligoethyleneglycolic fragments surround the hydrophobic core allowing its partial submersion into water.

The area occupied by one terminal group of dendrimer at surface pressures close to the collapse point is in the range 62–70 $Å^2$. This value is comparable with that of the molecular area of the terminal group of dendrimers G 3(Benz-Peg). All curves were reversible (see S17) and repeatable that allows to speak about stability of the Langmuir monolayer and gives another argument against multilayer formation.

Obtained LB films had shown reflexes at ~42 Å for third generation (G-3(Benz-Peg)) under GIXRD. While first-generation dendrimer LB films once again showed lack of stability, third-generation dendrimer structures resemble a double-layered system, assuming a layered structure with layers of hydrophilic and hydrophobic fragments as it is depicted in the model (Fig. 8b). Mesogens form a bilayer structure while the carbosilane matrices and oligoethylene glycol spacers form a joint amorphous layer in between.

Conclusions

A novel class of dendritic compounds consisting of two series with layered organization of hydrophilic and hydrophobic blocks was designed and synthesized. Molecules of such class posses mesogenic fragments in their terminal groups and can potentially form thermotropic or lyotropic LC phases. An effect of dendritic architecture on the behavior of amphiphilic molecules was shown. It was demonstrated that connecting a number of separate amphiphilic molecules with a single branching center increases film stability which can lead to ordered and stable LB films. The manner in which the terminal groups are "tied" to a hydrophobic branching center (via the hydrophilic or the hydrophobic part) was shown to greatly impact the mechanism of film formation and the film's structure. Such novel surfactants and architecture principles may lead to the discovery of new self-assembling materials and the possibility of fabricating organized thin films from compounds lacking the ability to form structured nano-dimensional assemblies. It opens up new possibilities for industrial applications of such films in sensors, optical or biomedical devices. Also, such dendrimer platform containing olygoethylene glycol fragments and other functional groups can potentially be used to make materials for water-castable coatings, stimuli-responsive vehicles, nanoreactors or drug delivery agents.

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