Pergamon

TETRAHEDRON

Tetrahedron 58 (2002) 4031–4040

Cell membrane as a model for the design of semifluorinated ion-selective nanostructured supramolecular systems

Virgil Percec* and Tushar K. Bera

Department of Chemistry, Roy and Diana Vagelos Laboratories, University of Pennsylvania, Philadelphia, PA 19104-6323, USA

Received 7 November 2001; accepted 14 December 2001

Abstract—The synthesis and polymerization of two AB_3 tapered, self-assembling methacrylate monomers (**12** and **13**) based on a first generation semifluorinated alkyl-substituted monodendron (i.e. minidendron) are described. These monomers contain either a benzo-15-crown-5 derivative, which is incorporated via the esterification of 4′-hydroxymethyl-1,4,7,10,13-pentaoxabenzocyclopentadecane or a podant group, which is incorporated via the monoesterification of tetraethylene glycol at its focal point, and both bear polymerizable groups on their periphery. The corresponding polymers (**14–16**) self-assemble and subsequently self-organize into supramolecular networks, which form a 2-D hexagonal columnar lattice via the fluorophobic effect. These networks consist of a continuous phase, which is based on the semifluorinated, paraffinic barrier layer and which is perforated in a hexagonal array by ion-selective or ion-active channels constructed from the benzo crown-ether and tetraethylene glycol respectively. The replacement of alkyl groups from the periphery of the tapered monodendrons with semifluorinated ones induces the self-assembly and, subsequently, the self-organization into supramolecular networks. These networks form 2-D hexagonal columnar lattices with thermal stability in some cases of up to 110°C. The design of such functional supramolecular systems was inspired by the bilayer fluid mosaic structure of the cell membrane. The lipid bilayer of the cell membrane, which in its ordered state acts as a barrier to the passage of polar molecules, was replaced with the semifluorinated paraffinic barrier, while the protein-based ionic channels were replaced with benzo-15-crown-5 and tetraethylene glycol based channels. The resulting supramolecular material has the mechanical integrity required for both ion-active and ion-selective nanostructured supramolecular systems.

1. Introduction

The fluid mosaic model of the cell membrane[1,2] consists of a self-assembled lipid bilayer containing protein-based active elements that are co-assembled in the bilayer structure. In its ordered state, the lipid bilayer is an excellent barrier to polar molecules and, as a consequence, has the capability to partition discrete metabolic aqueous compartments. The impermeability of the lipid bilayer to polar or charged molecules allows the solute concentration on each of its sides to differ dramatically. The second function of the lipid bilayer is to accommodate proteins with various tertiary structures that are able to provide and control the transfer of energy and materials and also to act as catalysts. Simultaneously, the cell membrane has the ability to respond to changing external conditions that may demand that certain molecules and ion-pairs pass through the lipid bilayer (Fig. 1). The proteins that penetrate the bilayer structure are bound to the membrane mostly by hydrophobic interactions. In its disordered state, i.e. above the physiological temperature, the lipid bilayer loses its barrier and transport properties and therefore the cell membrane loses its fundamental functions.

A similar synthetic supramolecular system capable of being externally regulated could have immense technological implications for areas such as selective membranes, ionic, protonic and electronic conductors, enzyme-like catalysis, energy transfer and conversion, particularly if all these applications could be exhibited by one self-assembled unit. A synthetic system must not copy the cell membrane concept, but use its principles as a model to create a system that is adaptable to the current technological methods. Therefore, the lipid bilayer barrier may be replaced with an alternative barrier material that has the required combination of order and fluidity, at least during certain stages of its self-assembly and self-organization. Simultaneously, the membrane proteins may be replaced with currently available ion-selective or ion-active elements such as crown-ethers or polypodants. The latter should be equipped with the ability to spontaneously self-assemble into channels, which are incorporated in the barrier part of the material. By analogy with a protein-based ionic channel, this material should be able to flux energy and materials between various compartments. New synthetic mechanisms to externally regulate the *on* and *off* states of the channel should be discovered and/or designed. Therefore, bio-inspired design and synthesis are not necessarily expected to duplicate

---

Keywords: hexagonal columnar; dendritic monomer; semifluorinated alkyl group; cell membrane; polymerization; nanostructured supramolecular network.

* Corresponding author. Tel.: +1-215-573-5527; fax: +1-215-573-7888; e-mail: percec@sas.upenn.edu

0040–4020/02/$ - see front matter
PII: S0040-4020(02)00266-1

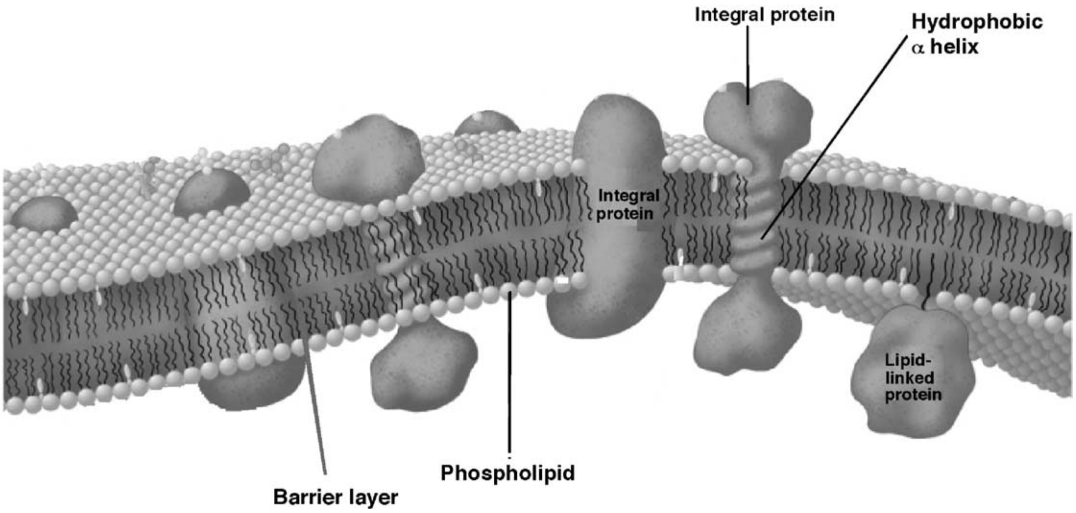


Figure 1. Schematic representation of the bilayer fluid mosaic model of the cell membrane. Integral proteins are embedded in the bilayer composed of phospholipids.

concepts from nature and may lead to new concepts suitable for related or different functions.

With the goal of creating ion-selective and ion-active self-regulated supramolecular systems we have pioneered the design and synthesis of conventional side-chain,[2] main-chain[3] and macrocyclic[4] liquid crystalline polymers and oligomers containing crown-ethers and polypodants as ion-active elements. In all cases, calamitic mesogenic groups have been employed to induce 1-D or 2-D liquid-like nematic and smectic order which is complemented by ionic activity. Polymerization has been used as the most frequent tool to enable mechanical integrity and provide a broad range of thermal stability in the liquid ordered state.[5,6]

A second and more efficient class of building blocks that self-assemble into ionic channels, and which subsequently self-organize in a 2-D hexagonal columnar lattice, has been studied in our laboratory. In this case the concept is based on tapered minidendritic units containing crown-ethers or oligo (ethylene oxide) units at their core (Fig. 2), leading to the development of both molecular[6] and macromolecular[7] ion-active systems. Enhanced conductivity along these ion-channels which are organized in a hexagonal columnar 2-D lattice was reported from our laboratory,[6a,c] and together with structural studies[6a,b,e,f] has demonstrated the structure of these assemblies. Subsequently, increased ionic conductivity in other liquid crystalline states was reported from other laboratories.[8]

Self-assembling tapered molecules containing crown-ethers were recently employed in a new concept for the design of functional nanoporous membranes known as gel template leaching.[9] The mono[10a,b] and multifunctionalization[11] of the periphery of these building blocks with polymerizable groups has been used in the design of self-organized soluble and insoluble nanostructured membranes. We believe that the self-assembling tapered groups containing active element(s) in their core and one or more polymerizable groups on their periphery can be developed for use in the generation of multifunctional membranes. Such membranes would possess many of the characteristics available in the fluid mosaic model of the cell membrane (Fig. 1). The aliphatic tails of the tapered groups (Fig. 2(b)) represent more than 80% of the entire supramolecular assembly and, therefore, provide an excellent and inexpensive barrier material. The functionalization of the tapered building blocks with a single polymerizable group on their periphery (Fig. 2(b)) provides, after polymerization, a soluble supramolecular network, which has multiple possibilities for the alignment of its active channels and may be processed in a variety of ways. In addition, the introduction in the core of the taper of more than one active element followed by incorporation into a suitable macromolecular architecture could yield membranes with multiple channel functionality useful for ionic, protonic and electronic transport, catalysis and for other functions. This architectural design contrasts with the one in which the polymerizable group is attached to the apex of the monodendron and the resulting polymer exhibits a cylindrical structure (Fig. 2(a)),[10c–i] rather than a network of cylinders. Last but not least, self-organized supramolecular structure of the synthetic nanostructured material described in Fig. 2(b) may provide access to features such as self-repair and external regulation.

One of the major requirements for such a nanostructured supramolecular system is that the 2-D self-organized structure should persist over a broad temperature range, thus providing sufficient thermal stability. Previously designed ion-selective and ion-active systems only self-assemble in a 2-D hexagonal columnar fluid lattice after complexation with metal salts.[10–12] Recently, we reported the design and synthesis of AB_3 tapered minidendritic benzyl ethers, which contain oligooxyethylene units with different chain length as ion-active elements in their core and a single polymerizable group on their periphery.[13] The polymers obtained from these AB_3 tapered minidendritic monomers form supramolecular networks with narrow thermal stability of their 2-D hexagonal columnar (ϕ_h) liquid crystalline phase. The 2-D hexagonal columnar lattice is responsible both for the barrier and transport properties of these new materials, therefore, an extension of its thermal stability is desirable.

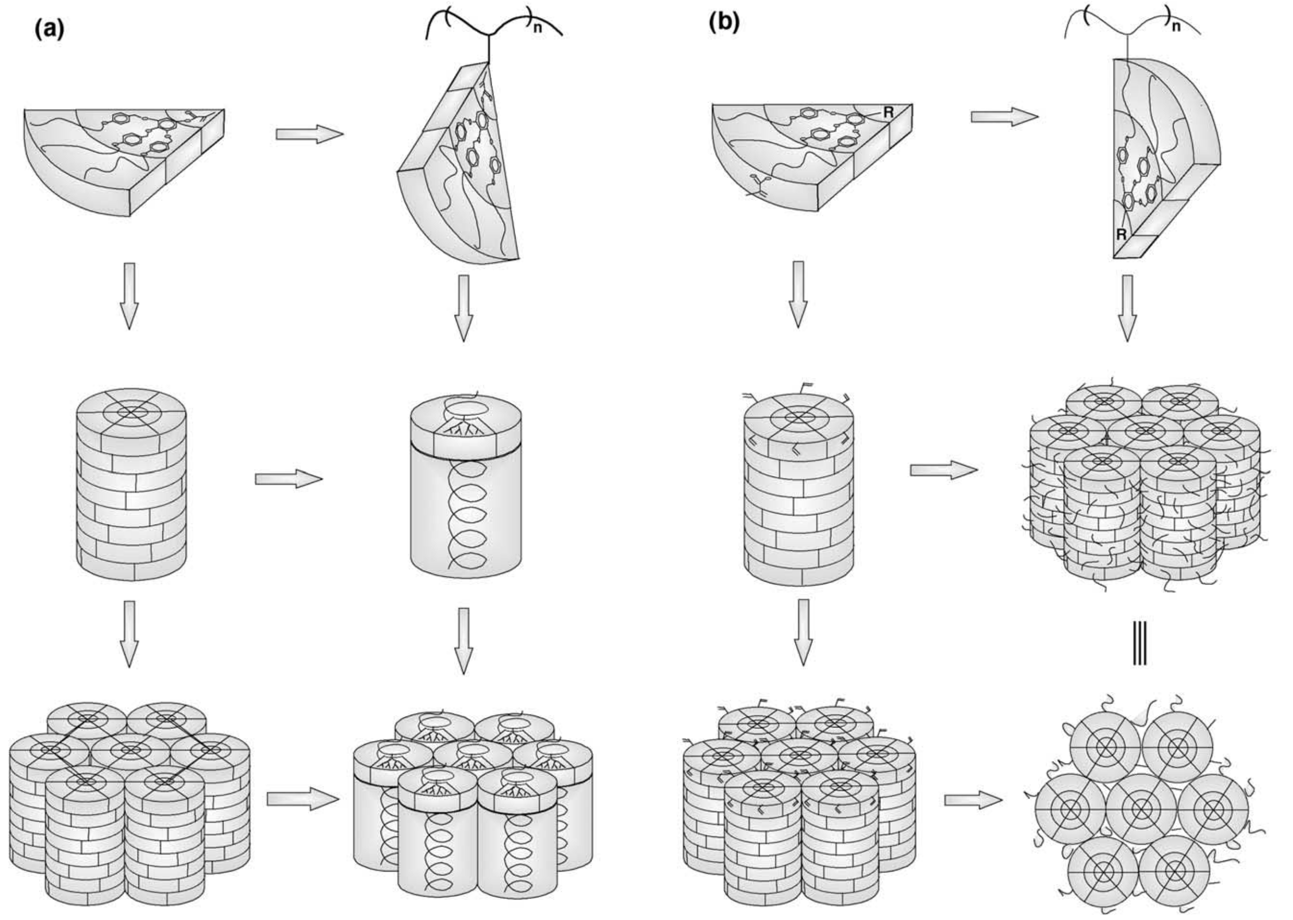


Figure 2. Self-assembly and self-organization followed by polymerization or polymerization followed by self-assembly and self-organization of tapered monodendrons containing a polymerizable group at the apex (a) or on the periphery of the taper (b). The R group in (b) represents the ionic, electronic or protonic active element.

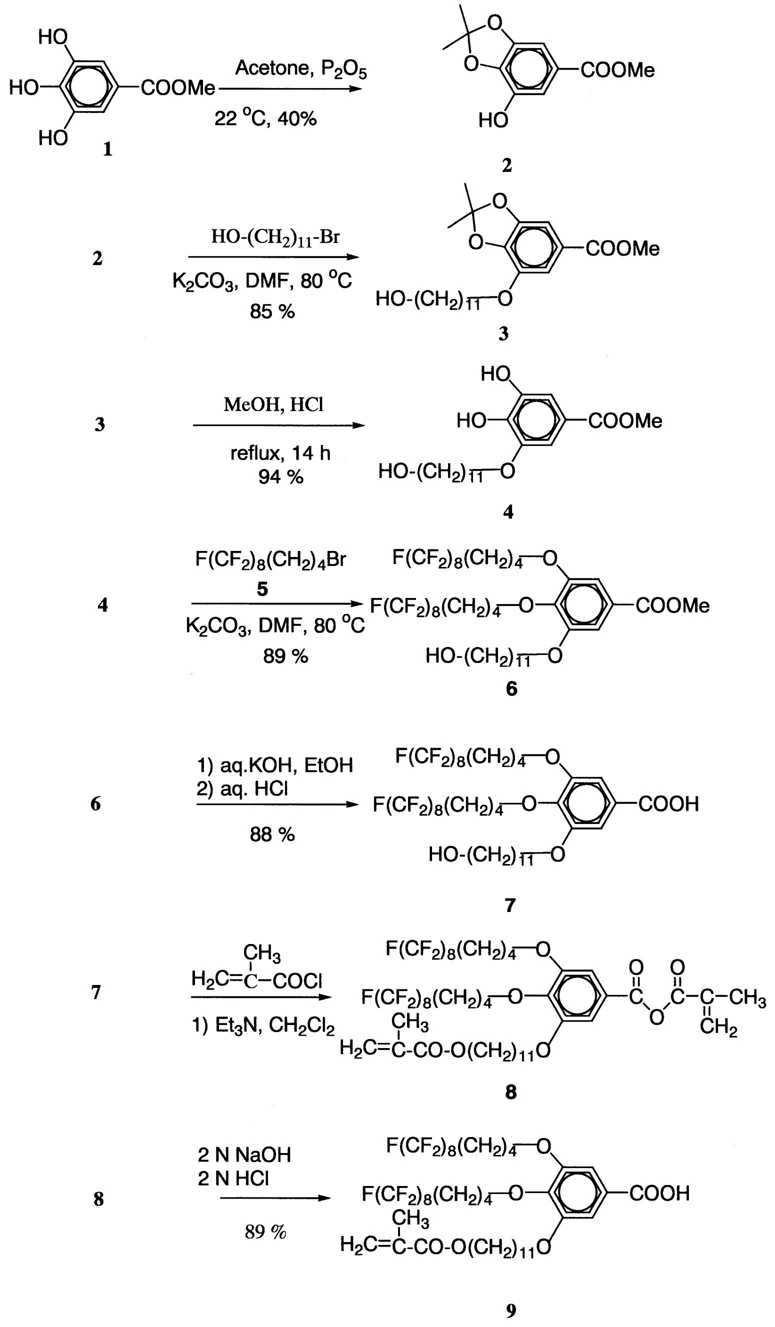
An approach towards this goal would be to design higher generation tapered dendritic monomers,[14] which have the potential to broaden the thermal stability of the resulting functional polymers. However, this requires extensive molecular design and synthetic effort and faces the permanent challenge of self-assembly in a 3-D cubic lattice[14] rather than a 2-D hexagonal columnar lattice. A second approach would be to replace the alkyl groups on the periphery of the tapered dendrons with semifluorinated ones. Previously, we have demonstrated that the fluorophobic effect induces self-assembly of semifluorinated monodendrons into supramolecular columnar dendrimers,[6e,7e,f] while their parent hydrogenated monodendrons do not self-assemble. Subsequently, it has been demonstrated that this effect plays a role in the field of rod-like liquid crystals[15] and, more recently, also in other self-assembled systems,[16] including the field of peptides.[17]

In this publication, we report the design and synthesis of semifluorinated AB_3 methacrylate monomers containing a polymerizable group on their periphery and a benzo-15-crown-5 group or a podant tetraethylene glycol at their core. After polymerization, supramolecular networks, which demonstrate suitable thermal stability for their 2-D hexagonal columnar liquid crystalline lattice, were achieved solely via the *fluorophobic* effect and without any additional ion-mediated interaction process.

2. Results and discussion

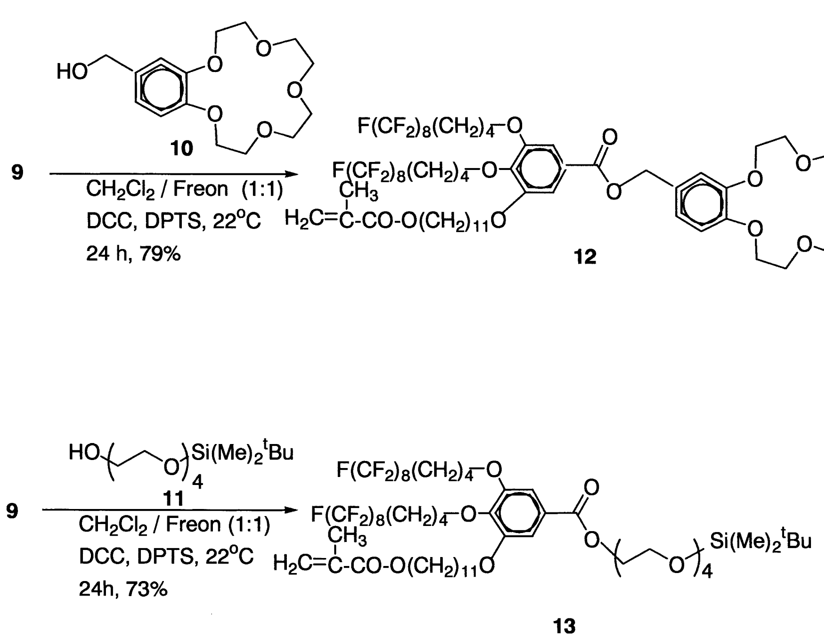
2.1. Synthesis of tapered semifluorinated monomers and polymers

The monomethacrylate-functionalized monodendrons such as 1,4,7,10,13-pentaoxabenzocyclopentadecane-2-ylmethyl-3-(11-methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluoro dodecan-1-yloxy) benzoate (**12**) and 2-{2-[2-(2-*tert*-butyl dimethyl siloxy ethoxy) ethoxy] ethoxy} ethyl-3-(11-methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluoro dodecan-1-yloxy) benzoate (**13**) were synthesized as outlined in Schemes 1 and 2. The synthetic strategy used here starts with the protection of two phenolic OH groups of 3,4,5 trihydroxy methyl benzoate (**1**). This was accomplished by reacting **1** with acetone in presence of the dehydrating agent P_2O_5 to obtain 3,4-isopropyliden-5-hydroxy methyl benzoate (**2**)[23] in 40% yield after 1 h at 22°C. The hydroxy group of **2** was alkylated with 1-bromoundecanol in DMF at 60°C, using K_2CO_3 as base, yielding **3** in 85% yield. The deprotection of the isopropylidene-protected group was accomplished in refluxing MeOH/HCl to produce **4** in 94% yield. The next step in the sequence of reactions involved the etherification of the two phenolic hydroxy groups of methyl 3,4-dihydroxy-5-(11-hydroxyundecyloxy) benzoate (**4**)[23] with 12,12,



Scheme 1.

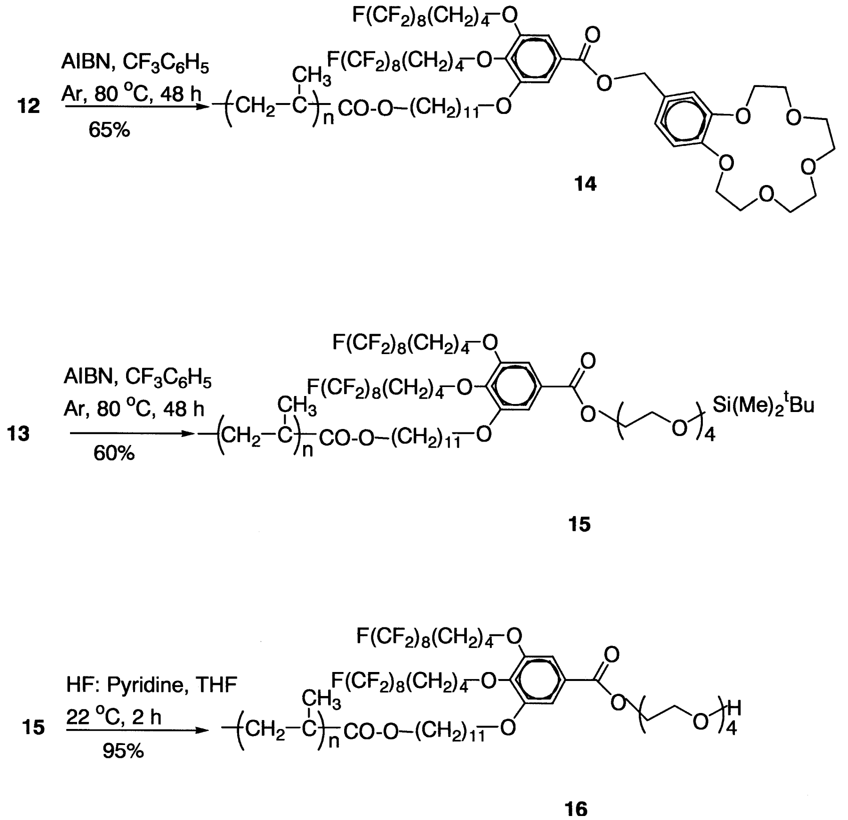
12,11,11,10,10,9,9,8,8,7,7,6,6,5,5, hepta decafluoro dodecyl bromide (**5**),[7f] using anhydrous K_2CO_3 in DMF at 70°C and yielding methyl 3-(11-hydroxyundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluoro dodecan-1-yloxy) benzoate (**6**) in 89% yield after recrystallization from acetone (Scheme 1). After saponification of the ester group of **6** with aqueous KOH in 90% EtOH at reflux, the corresponding acid **7** was obtained in 88% yield. Esterification of this hydroxy-functionalized acid **7** with methacrylic acid chloride using Et_3N in CH_2Cl_2 at 0–5°C yielded 3-(11-methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluoro dodecan-1-yloxy) benzoic acid (**9**) in 89% yield after the mixed benzoic methacryloyl anhydride (**8**) was hydrolyzed by basic work up (2N NaOH aqeous solution). In the last step, the acid was treated with either 4′-hydroxymethyl-[1,4,7,10,13-pentaoxabenzo cyclopenta decane] (**10**)[6a] or with 2-{2-(2-(2-(2-(*tert*-butyldimethylsiloxy) ethoxy) ethoxy) ethoxy) ethanol (**11**)[10f] under neutral reaction conditions (DCC/DPTS) to produce the methacrylate-functionalized monomers 1,4,7,10,13-pentaoxabenzocyclopentadecane-2-ylmethyl-3-(11-methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluoro dodecan-1-yloxy) benzoate (**12**) and 2-{2-[2-(2-*tert*-butyl dimethyl siloxy ethoxy) ethoxy] ethoxy} ethyl-3-(11-methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluoro dodecan-1-yloxy) benzoate (**13**) in 79 and 73% yields, respectively,



Scheme 2.

after purification by column chromatography (SiO_2, 10% EtOAc in hexanes) (Scheme 2).

Polymerization of the resulting methacrylates **12** and **13** was performed at 80°C in α,α,α-trifluoro toluene (50 wt%) using 1.0 wt% AIBN as radical initiator (Scheme 3). The resulting polymethacrylates **14** and **15** were obtained in 60–65% yields after purification by column chromatography (Al_2O_3, CH_2Cl_2 as eluent to remove unreacted monomer) (Scheme 3). The removal of the TBDMS group of **15** was conveniently performed using HF/Py in THF at 22°C to produce polymethacylate **16** in 95% yield. Polymethacrylate **16** is insoluble in common organic solvents but soluble in fluorinated ones, i.e. α,α,α-trifluoro toluene. The molecular



Scheme 3.

Table 1. Structural and thermal analysis of the polymers **14–16**

Polymer	Yield (%)	Mn (GPC)	Mw/Mn (GPC)	Thermal transitions (°C) and corresponding enthalpy changes (Kcal/mol)[a]	
				Heating	Cooling
14	65	20,000	1.30	g 30.0 k 55.7 (3.21) Φ_h 99.0 (0.31) i g 29.0 Φ_h 100.5 (0.22) i	i 90.5 (−0.24) Φ_h 25.5 g
15	60	33,491	1.47	g −1.0 Φ_h 38.0 (0.37) i g 2.0 Φ_h 36.4 (0.29) i	i 23.1 (0.32) Φ_h −0.9 g
16	–	–	–	g −0.0 Φ_h 111.0 (0.67) i k 19.0 (2.31) Φ_h 106.0 (0.60) i	i 95.3 (−0.62) Φ_h 9.0 (−2.35) k

[a] Data on the first line under heating were obtained during the first heating scan. Data on the second line under heating were obtained during second heating scan.

weights of polymethacrylates **14** and **15** relative to polystyrene standards (Mn) and their molecular weight distributions (Mw/Mn) are listed in Table 1.

2.2. Thermal and structural analysis of polymethacrylates 14–16

The thermal behavior and the structural analysis of polymethacrylates **14–16** were carried out by a combination of techniques that include differential scanning calorimetry (DSC), X-ray diffraction (XRD) and thermal optical polarized microscopy (TOPM) experiments according to standard procedures used in our laboratory.[2–4,6,7] Transition temperatures and the corresponding enthalpy changes are summarized in Table 1. Monomer **12** displays a monotropic hexagonal columnar (ϕ_h) liquid crystalline phase (see Section 4). However, the corresponding polymer (**14**) displays an enantiotropic liquid crystalline phase (Table 1). This transformation of **12** to **14** also enhances the thermal stability of the ϕ_h phase by up to 100°C, polymerization has been used often as a tool to increase the thermal stability of liquid crystalline states.[5,6] Polymers **15** and **16** also display an enantiotropic hexagonal columnar (ϕ_h) liquid crystalline (LC) phase, despite the fact that their monomeric precusor is liquid. The assignment of the mesophase was made by small and wide angle XRD experiments. The *d*-spacings of all reflections are presented in Table 2 together with their lattice parameter (*a*). Bragg diffraction peaks corresponding to a lattice spacing in a ratio of $1{:}1/\sqrt{3}{:}1/\sqrt{7}$, which are characteristic of a 2-D hexagonal columnar lattice,[18–22] are exhibited at small angles by **14–16**. The thermal stability of the ϕ_h phase of **16** increased by 70°C from that of **15** by removing the *tert*-butyl dimethyl silyl group from the core of **15**. This enhanced thermal stability of **16** is due to the H-bonding interactions of the tetraethylene glycol present in the core of the supramolecular column. However, the presence of *tert*-butyl dimethyl silyl group in the core of the supramolecular column of **15** contributed to an increased column diameter by 3 Å when compared with the column diameter of **16**. More detailed structural analysis[6a,b,e,f] and conductivity measurements[6a,c] reported previously from our laboratory have demonstrated that these supramolecular cylinders contain an ionic channel penetrating through their center.

Table 2. Structural analysis by X-ray diffraction of polymers **14–16**

Polymer	Temp. (°C)	d_{100} (Å)	d_{110} (Å)	d_{210} (Å)	$\langle d_{100}\rangle$[a]	a[b]
13	90	41.5	22.1	14.7	39.6	45.7
14	32	43.2	22.7	15.4	41.0	47.3
15	85	40.3	20.9	14.3	38.0	43.9

[a] $\langle d_{100}\rangle=(d_{100}+\sqrt{3}d_{110}+\sqrt{7}d_{210})/3$; $a=2\langle d_{100}\rangle/\sqrt{3}$.

[b] Lattice dimension.

It should be noted that the replacement of the alkyl groups on the periphery of the tapered dendrons with semifluorinated ones induces the self-assembly and the self-organization into supramolecular columnar networks, thereby forming a 2-D hexagonal columnar lattice with a broad range of thermal stability. The ϕ_h phase of **15** is stable until 38°C, while that of **16** persists until 111°C (Table 1). Therefore, this approach of replacing two alkyl chains with two semifluorinated ones alleviates the need for the extensive synthetic effort involved in the preparation of higher generations of tapered dendritic monomers which might similarly increase the thermal stability. The experiments described herein expand the synthetic applications of semifluorinated compounds at the interface between supramolecular[6e,f,7e,f,15] and macromolecular[2c,24] chemistry.

3. Conclusions

The synthesis and polymerization of two AB_3 self-assembling methacrylate monomers **12** and **13** based on the first generation semifluorinated alkyl substituted monodendrons (i.e. minidendrons) containing a benzo-15-crown-5 derivative, which is incorporated via the esterification of 4′-hydroxymethyl-1,4,7,10,13-pentaoxabenzocyclopentadecane or a podant which is incorporated via the monoesterification of tetraethylene glycol at its focal point and a polymerizable group on their periphery are described. The corresponding polymers **14–16** self-assemble and self-organize into supramolecular networks that form a 2-D hexagonal columnar lattice solely via the fluorophobic effect. By analogy with related structures,[6a,b,e,f] this network consists of a continuous phase, which is based on a semifluorinated, paraffinic barrier layers and which is perforated in a hexagonal array by ion-active channels constructed from the benzo-15-crown-5 and tetraethylene glycol, respectively. All polymers display an enantiotropic hexagonal columnar liquid crystalline phase. These polymers exhibit a range of thermal stability of their hexagonal columnar phase of up to 110°C. These experiments have demonstrated that the replacement of alkyl chains with semifluorinated ones alleviates the need for extensive synthetic effort when synthesizing higher generation dendritic monomers, which would have the potential to broaden the thermal stability of the 2-D hexagonal lattice of the resulting functional polymers. The enhancement of the thermal stability of the ϕ_h phase of **16** by up to 70°C is achieved by removal of the TBDMS protection group from the core of **15**.

4. Experimental

4.1. General

4-Dimethylamino pyridine (DMAP, 98%, Fluka), 1,3-dicyclohexyl carbodiimide (DCC, 99%, Aldrich), HCl (A.C.S. Reagents, Fisher Scientific), $MgSO_4$ (Fisher Scientific), $LiAlH_4$ (95%, Aldrich), α,α,α-trifluoro toluene (Aldrich, 99+%), 1,1,2-trichlorotrifluoroethane (Freon) (Aldrich, 99.8%) were used as received. THF (A.C.S. Reagents, Fisher Scientific) was dried over sodium/benzophenone ketyl and distilled before use. NEt_3 (99%, Aldrich) was dried over CaH_2 and distilled before use. DMF (A.C.S. Reagents, Fisher Scientific) was dried over CaH_2 and distilled under vacuum. CH_2Cl_2 (A.C.S. Reagents, Fisher Scientific) was dried over CaH_2 and distilled. Benzene (A.C.S., Fisher Scientific) was washed with 50 mL portions of H_2SO_4 until they remained relatively uncolored, washed with H_2O to neutral pH, dried over $MgSO_4$, filtered, dried over sodium/benzophenone ketyl and distilled before use. Azobisisobutyronitrile (AIBN, Fluka) was recrystallized from methanol below 40°C. Tetraethylene glycol (99%, Aldrich) was dried over sodium and distilled under vacuum before use. 4-Dimethylaminopyridinium-*p*-toluene sulfonate (DPTS),[6a] 12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5, hepta decafluoro dodecyl bromide (**5**),[7f] methyl-3-(11-hydroxy undecyloxy)-4,5-dihydroxy benzoate (**4**),[23] 4′-hydroxymethyl-[1,4,7,10,13-pentaoxabenzo cyclopenta decane] (**10**),[6a] 2-{2-(2-(2-(2-(*tert*-butyldimethylsiloxy) ethoxy) ethoxy) ethoxy) ethanol (**11**),[10f] were synthesized according to literature procedures. ^{1}H NMR, (200 MHz), ^{13}C NMR (50 MHz) and ^{19}F NMR (188 MHz) spectra were recorded on a Varian Gemini 200 spectrometer with tetramethylsilane (TMS) internal standard for ^{1}H NMR and ^{13}C and fluorotrichloromethane ($CFCl_3$) internal standard for ^{19}F. Chromatographic purification was conducted using 200–400 mesh silica gel obtained from Natland International Corporation, Morrisville, NC. Relative molecular weights were determined using a Perkin–Elmer Series 10 GPC equipped with a LC-100 column oven (40°C), Nelson Analytical 900 Series integrator data station, and two Polymer Laboratories PL gel columns of 5×10^2 and 10^4 Å, and THF as eluent at 1 mL/min. Detection was by UV absorbance at 254 nm. Relative weight average (Mw) and number average (Mn) molecular weights were calculated by using a calibration plot constructed from polystyrene standards. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument. Gas chromatography analysis (GC) was performed on a Hewlett–Packard 5890 gas chromatograph equipped with a packed column of 10% SP 2100 on 80/100 Supelcoport and a Hewlett–Packard 3392A integrator. Thermal transitions were determined on a Perkin–Elmer DSC-7 differential scanning calorimeter. In all cases the heating and cooling rates were 10°C/min. First order transitions were reported as the maxima or minima of the endothermic and exothermic peaks during the second heating and cooling scans. Glass transition temperatures (T_g) were measured as the middle point of the change in heat capacity. Zn and In were used as calibration standards. X-Ray diffraction experiments were performed using a multi-wire area detector (Siemens) with a Cu $K_{\alpha1}$ radiation obtained from a rotating anode (Nonius FR591) X-ray generator after passing through a set of mirrors and then a monochromator. The X-ray beam path is under low vacuum to reduce the background scattering from air. Powdered samples were held at constant temperature (±0.1°C) in a temperature-controlled cell. An Olympus BX-40 optical polarized microscope (100× magnification) equipped with a Mettler FP 82 hot stage and a Metler FP 80 central processor was used to verify thermal transitions and to characterize the anisotropic textures. The elemental analysis (C, H) of all new compounds were performed by M-H-W Laboratories, Phoenix, A.

4.1.1. Methyl-3-(11-hydroxyundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluorododecan-1-yloxy) bezoate (6). To a round bottom flask equipped with a nitrogen inlet–outlet, containing a degased stirring mixture of **4** (1.5 g, 4.23 mmol) and K_2CO_3 (5 g, 36.17 mmol) in 60 mL of DMF at 60°C, was added **5** (5.17 g, 9.31 mmol) in small portions over 10 min. After 24 h at 60°C, the reaction mixture was poured into a 500 mL of ice-water. The resulting solid was filtered and washed with water twice. After recrystallization from acetone, 4.9 g (89%) of white solid **6** was obtained. Purity: 99% (HPLC). Mp 57–58°C TLC: R_f=0.28 (2:1 hexanes/EtOAc). ^{1}H NMR (200 MHz, $CDCl_3$, 20°C): δ 1.1–1.2 (overlapped peaks, 26H), 2.2–2.3 (m, 4H), 3.4 (t, 2H, J=6.6 Hz), 3.9 (s, 3H), 4.1 (m, 6H), 7.3 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, 20°C): δ 17.2, 25.7–32.8 (m), 52.1, 62.9, 68.4, 69.1, 72.5, 107.8, 108.1, 125.1, 141.9, 152.5, 152.9, 166.8. Elemental analysis: calcd for $C_{43}H_{45}O_6F_{34}$: C, 39.61; H, 3.47. Found. C, 39.57; H, 3.45.

4.1.2. 3-(11-Hydroxyundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluorododecan-1-yloxy) benzoic acid (7). In a 250 mL round-bottom flask containing a Teflon coated magnetic stir bar was placed 4.8 g (3.68 mmol) of **6**, 40 mL of 90% EtOH, and 0.7 g (12.47 mmol) of KOH pellets. The mixture was refluxed under N_2 for 2 h. The reaction mixture was cooled to 22°C and the resulting solids were dissolved in 100 mL of hot THF with stirring. The solution was cooled to 0°C and acidified with conc. HCl. The solution was poured into 500 mL of ice-water and extracted with Et_2O (3×100 mL). The combined Et_2O extract was washed with water (2×200 mL), brine (2×200 mL) and dried over $MgSO_4$. The solution was filtered and the solvent was evaporated, resulting in 4.2 g (88%) of white crystals **7**. Mp 94–96°C. Purity: 99% (HPLC). TLC: R_f=0 (2:1 hexanes/EtOAc). ^{1}H NMR (200 MHz, $CDCl_3$, 20°C): δ 1.1–1.2 (overlapped m, 26H), 2.2–2.3 (m, 4H), 3.4 (t, 2H, J=6.7 Hz), 4.1 (m, 6H), 7.3 (s, 2H). ^{19}F NMR (188 MHz, CD_3COCD_3, $CFCl_3$, 20°C): δ −79.9 (s, 6F, CF_3), −113.1 (s, 4F, CH_2CF_2), −120.7 (s, 12F $(CF_2)_3$), −121.6 (s, 4F, $CF_2CF_2CH_2$),

-122.2 (s, 4F, $CF_3CF_2CF_2$), -125.1 (s, 4F, CF_3CF_2). ^{13}C NMR (50 MHz, $CDCl_3$, 20°C): δ 18.1, 26.8–34, 62.5, 69.2, 69.8, 73.2, 108.8, 109.1, 126.5, 141.3, 153.7, 152.9, 166.8. Elemental analysis: calcd for $C_{42}H_{43}O_6F_{34}$: C, 39.11; H, 3.35. Found. C, 38.87; H, 3.29.

4.1.3. 3-(11-Methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluorododecan-1-yloxy) benzoic acid (9). 1.6 g (15.3 mmol) freshly distilled methacryloyl chloride was slowly added to a cold (0°C) solution of **7** (4.0 g, 3.1 mmol) and Et_3N (1.54 g, 15.3 mmol) in 40 mL CH_2Cl_2 under N_2. The ice cooling was removed, and the reaction mixture was stirred at 22°C for 24 h. The reaction mixture was concentrated and diluted with 200 mL of Et_2O and washed with H_2O (2×100 mL), 2N NaOH (3×100 mL), 2N HCl (2×100 mL), H_2O (2×100 mL), and finally with brine (1×200 mL). The organic phase was dried over $MgSO_4$, and the solvent was removed in vacuo. After recrystallization from acetone, 3.74 g (89%) of white solid **9** was obtained. Purity: 98% (HPLC). TLC: R_f=0 (2:1 hexanes/EtOAc). ^1H NMR (200 MHz, $CDCl_3$, 20°C): δ 1.18–1.95 (overlapped m, 29H), 2.05–2.27 (m, 4H), 4.01–4.23 (m, 8H), 5.55 (s, 1H), 6.1 (s, 1H), 7.33–7.35 (d, 2H, J=4 Hz). ^{19}F NMR (188 MHz, CD_3COCD_3, $CFCl_3$ 20°C): δ -81.9 (s, 6F, CF_3), -115.2 (s, 4F, CH_2CF_2), -122.7 (s, 12F, $(CF_2)_3$), -123.5 (s, 4F, $CF_2CF_2CH_2$), -124.2 (s, 4F, $CF_3CF_2CF_2$), -127.1 (s, 4F, CF_3CF_2). ^{13}C NMR (50 MHz, $CDCl_3$, 20°C): δ 18.1, 26.8–34.0 (m), 62.5, 69.2, 69.8, 73.2, 108.8, 109.1, 126.5, 141.3, 153.7, 152.9, 166.8. Elemental analysis: calcd for $C_{46}H_{47}O_7F_{34}$: C, 40.69; H, 3.48. Found. C, 40.10; H, 3.52.

4.1.4. 1,4,7,10,13-Pentaoxabenzocyclopentadecane-2-ylmethyl-3-(11-methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluorododecan-1-yloxy) benzoate (12). To a well stirred solution of **9** (1.16 g, 0.85 mmol) and **10** (0.29 g, 0.97 mmol) in 20 mL dry CH_2Cl_2 and 10 mL 1,1,2-trichlorotrifluoroethane, DCC (0.61 g, 3.0 mmol) was added under N_2. DPTS (0.117 g, 0.4 mmol) was added last. The reaction mixture was stirred at 22°C for 24 h. The reaction mixture was diluted with hexanes (50 mL) and filtered. The solution was concentrated and precipitated in a large excess of methanol three times. The crude product was purified by column chromatography (SiO_2, 10% EtOAc in hexanes) to yield 1.1 g (79%) of white solid **12**. Purity: 99% (HPLC). TLC: R_f=0.46 (2:1 hexanes/EtOAC). ^1H NMR (200 MHz, $CDCl_3$, 20°C): δ 1.1–1.95 (overlapped m, 29H), 2.05–2.27 (m, 4H), 3.73 (m, 8H, OCH_2CH_2O, on benzo crown ether), 3.9 (m, 4H, $ArOCH_2CH_2$, on benzo crown ether), 4.08 (m, 4H, $ArOCH_2CH_2$, on benzo crown ether), 4.01–4.23 (m, 8H, $CH_2{=}C(CH_3)CO_2\mathit{CH_2}$, CH_2OAr), 5.18 (s, 2H, CO_2CH_2, on benzo crown ether), 5.47 (s, 1H), 6.03 (s, 1H), 6.8–6.9 (overlapped peaks, 3H, aromatic protons of benzo crown ether), 7.1–7.35 (m, 2H, ArH ortho to CO_2CH_2). ^{19}F NMR (188 MHz, CD_3COCD_3, $CFCl_3$ 20°C): δ -80.9 (s, 6F, CF_3), -114.2 (s, 4F, CH_2CF_2), -121.7 (s, 12F, $(CF_2)_3$), -121.2 (s, 4F, $CF_2CF_2CH_2$), -125.2 (s, 4F, $CF_3CF_2CF_2$), -128.1 (s, 4F, CF_3CF_2). ^{13}C NMR (50 MHz, $CDCl_3$, 20°C): δ 17.5, 18.2, 24.1, 26.1–31.05 (m), 64.7, 66.8, 68.4, 69.1, 69.5, 72.4, 107.8, 108., 113.7–114.6 (m), 121.8, 124.9 125.0, 129.0, 140.8, 149.1, 152.4–152.8 (m), 166.15, 168.44. Elemental analysis: calcd for $C_{61}H_{67}O_{12}F_{34}$: C, 44.72; H, 4.11. Found. C, 44.20; H, 4.30. DSC: 1st heating: k 45.71 k 67.11 i. 2nd heating: k 33.3 k 61.20 i. 1st cooling i 42.45 Φ_h (-5.72) -4.84 k.

4.1.5. 2-{2-[2-(2-*tert*-Butyl dimethyl siloxy ethoxy) ethoxy] ethoxy} ethyl-3-(11-methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9, 8,8,7,7,6,6,5,5-heptadecafluorododecan-1-yloxy) benzoate (13). To a well stirred solution of **9** (2.0 g, 1.47 mmol) and **11** (0.63 g, 2.04 mmol) in 25 mL dry CH_2Cl_2 and 15 mL dry 1,1,2-trichlorotrifluoroethane, DCC (0.9 g, 4.36 mmol) was added under N_2. DPTS (0.04 g, 0.13 mmol) was added last. The reaction mixture was stirred at 22°C for 24 h. The reaction mixture was diluted with 100 mL of hexanes and filtered. The raw product (viscous mass) was purified by column chromatography (SiO_2, 10% EtOAc in hexanes) to yield 1.76 g (73%) of **13** as a colorless viscous liquid. Purity: 99% (HPLC). TLC: R_f=0.44 (2:1 hexanes/EtOAc). ^1H NMR (200 MHz, $CDCl_3$, 20°C): δ 0.05 (s, 6H), 0.88 (s, 9H), 1.29–2.04 (m, 29H, 2.17–2.3 (m, 4H), 3.54 (t, 2H J=6.5 Hz), 3.64–3.83 (m, 12H), 4.02–4.16 (m, 8H), 4.46 (t, 2H, J=6.7 Hz), 5.53 (s, 1H), 6.09 (s, 1H), 7.27–7.29 (d, 2H, J=3.95 Hz). ^{19}F NMR (188 MHz, CD_3COCD_3, $CFCl_3$ 20°C): δ -80.1 (s, 6F, CF_3), -114.0 (s, 4F, CH_2CF_2), -120.9 (s, 12F, $(CF_2)_3$), -121.6 (s, 4F, $CF_2CF_2CH_2$), -125.2 (s, 4F, $CF_3CF_2CF_2$), -128.4 (s, 4F, CF_3CF_2). ^{13}C NMR (50 MHz, $CDCl_3$, 20°C): δ -5.09, 17.6, 18.4, 26.3, 28.8–31.4 (m), 63.01, 64.4, 65.0, 68.8, 69.5, 72.7, 108.3, 108.7, 125.1, 125.4, 137.2, 152.7–153.1 (m), 166.2. Elemental analysis: calcd for $C_{60}H_{77}O_{11}SiF_{34}$: C, 43.75; H, 4.70. Found. C, 43.96; H, 4.57.

4.2. Polymerization of monomers 12 and 13

Both monomers were polymerized as a 50% (w/v) solutions in α,α,α-trifluorotoluene under argon at 80°C for 48 h. AIBN (1% w/w) was used as radical initiator. The polymerization solution was degased by three freeze-pump-thaw cycles before polymerization. All polymers were separated from unreacted monomers by column chromatography (neutral alumina, CH_2Cl_2). The yield and molecular weight distributions and DSC of the polymers obtained are shown in Table 1.

4.2.1. Poly (1,4,7,10,13-pentaoxabenzocyclopentadecane-2-ylmethyl-3-(11-methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluoro dodecan-1-yloxy) benzoate) (14). ^1H NMR (200 MHz, $CDCl_3$, 20°C): δ 1.1–2.0 (br, 29H), 2.05–2.3 (br, 4H), 3.73 (br, 8H, OCH_2CH_2O, on benzo crown ether), 3.9 (br, 4H, $ArOCH_2CH_2$, on benzo crown ether), 4.08 (br, 4H, $ArOCH_2CH_2$, on benzo crown ether), 4.01–4.3 (m, 8H, $CH_2{=}C(CH_3)CO_2\mathit{CH_2}$, CH_2OAr), 5.2 (bs, 2H, CO_2CH_2, on benzo crown ether), 6.8–67.0 (br, 3H, aromatic protons of benzo crown ether), 7.1–7.4 (br, 2H, ArH ortho to CO_2CH_2).

4.2.2. Poly (2-{2-[2-(2-*tert*-butyl dimethyl siloxy ethoxy) ethoxy] ethoxy} ethyl-3-(11-methacryloylundecyloxy)-4,5-bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluorododecan-1-yloxy) benzoate) (15). ^1H NMR (200 MHz, $CDCl_3$, 20°C): δ 0.05 (bs, 6H), 0.88 (bs, 9H), 1.3–2.04 (br, 29H), 2.2–2.4 (br, 4H), 3.54 (br, 2H), 3.6–3.8 (br, 12H), 4.1–4.2 (br, 8H), 4.4 (br, 2H), 7.2–7.3 (br, 2H).

4.2.3. Poly (2-{2-[2-(2-hydroxyethoxy) ethoxy] ethoxy} ethyl-3-(11-methacryloylundecyloxy)-4,5 bis (12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-heptadecafluorododecan-1-yloxy) benzoate) (16). Elemental analysis calcd for $C_{54}H_{63}O_{11}F_{34}$: C, 42.28; H, 4.13. Found. C, 41.23; H, 3.97.

Acknowledgements

Financial support by Office of Naval Research and National Science Foundation is gratefully acknowledged.

References

1. (a) Singer, S. J.; Nicolson, G. L. *Science* **1972**, *175*, 720. (b) Voet, D.; Voet, J. G.; Pratt, C. W. *Fundamentals of Biochemistry*; Wiley: New York, 1999; p 239.
2. (a) Rodriguez, J. M. P.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 1363. (b) Percec, V.; Rodenhouse, R. *Macromolecules* **1989**, *22*, 4408. (c) Rodenhouse, R.; Percec, V.; Feiring, A. E. *J. Polym. Sci., Part C: Polym. Lett.* **1990**, *28*, 345. (d) Percec, V.; Hsu, C.-S. *Polym. Bull.* **1990**, *23*, 463. (e) Rodenhouse, R.; Percec, V. *Makromol. Chem.* **1991**, *192*, 1873. (f) Rodenhouse, R.; Percec, V. *Polym. Bull.* **1991**, *25*, 47. (g) Rodenhouse, R.; Percec, V. *Adv. Mater.* **1991**, *3*, 101. (h) Percec, V.; Rodenhouse, R. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 15. (i) Ungar, G.; Percec, V.; Rodenhouse, R. *Macromolecules* **1992**, *24*, 1996. (j) Percec, V.; Johanson, G.; Rodenhouse, R. *Macromolecules* **1992**, *25*, 2563. (k) Percec, V.; Tomazos, D. *J. Mater. Chem.* **1993**, *3*, 633. (l) Percec, V.; Tomazos, D. *J. Mater. Chem.* **1993**, *3*, 643.
3. (a) Shaffer, T. D.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 2755. (b) Percec, V.; Rodenhouse, R. *Macromolecules* **1989**, *22*, 2043.
4. Percec, V.; Turkaly, P. J.; Asandei, A. D. *Macromolecules* **1997**, *30*, 943.
5. Percec, V.; Keller, A. *Macromolecules* **1990**, *23*, 4347.
6. (a) Percec, V.; Johansson, G.; Heck, J.; Ungar, G.; Batty, S. V. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1411. (b) Johansson, G.; Percec, V.; Ungar, G.; Abramic, D. *J. Chem. Soc., Perkin Trans. 1* **1994**, 447. (c) Ungar, G.; Batty, S. V.; Percec, V.; Heck, J.; Johansson, G. *Adv. Mater. Opt. Electron.* **1994**, *4*, 303. (d) Tomazos, D.; Out, R.; Heck, J. A.; Johansson, G.; Percec, V.; Möller, M. *Liq. Cryst.* **1994**, *16*, 509. (e) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855. (f) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, *278*, 449.
7. (a) Percec, V.; Heck, J. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1992**, *33* (1), 217. (b) Percec, V.; Heck, J. H.; Tomazos, D.; Ungar, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2381. (c) Percec, V.; Heck, J.; Tomazos, D.; Fulkenberg, F.; Blackwell, H.; Ungar, G. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2799. (d) Percec, V.; Tomazos, D.; Heck, J.; Blackwell, H.; Ungar, G. *J. Chem. Soc., Perkin Trans. 2* **1994**, 31. (e) Percec, V.; Schlueter, .; Kwon, Y. K.; Blackwell, H.; Möller, M.; Slanger, P. J. *Macromolecules* **1995**, *28*, 8807. (f) Johansson, G.; Percec, V.; Ungar, G.; Zhou, J. P. *Macromolecules* **1996**, *29*, 646. (g) Percec, V.; Schlueter, D.; Ungar, G.; Cheng, S. Z. D.; Zhang, A. *Macromolecules* **1998**, *31*, 1745.
8. (a) McHattie, G. S.; Imrie, C. T.; Ingram, M. D. *Electrochim. Acta* **1998**, *43*, 1151. (b) Zheng, Y.; Chia, F.; Ungar, G.; Richardson, T. H.; Wright, P. V. *Electrochim. Acta* **2001**, *46*, 1397 and references cited therein.
9. Gankema, H.; Hampenius, M. A.; Möller, M.; Johansson, G.; Percec, V. *Macromol. Symp.* **1996**, *102*, 381.
10. (a) Percec, V.; Zipp, G.; Johansson, G.; Beginn, U.; Möller, M. *Macromol. Chem. Phys.* **1997**, *198*, 265. (b) Beginn, U.; Zipp, G.; Möller, M.; Johansson, G.; Percec, V. *Macromol. Chem. Phys.* **1997**, *198*, 2839. (c) Percec, V.; Heck, J. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 591. (d) Percec, V.; Schlueter, D.; Kwon, Y. K.; Blackwell, J.; Möller, M.; Slangen, J. P. *Macromolecules* **1995**, *28*, 8807. (e) Percec, V.; Schlueter, D. *Macromolecules* **1997**, *30*, 5783. (f) Percec, V.; Schlueter, D.; Ungar, G.; Cheng, S. Z. D.; Zhang, A. *Macromolecules* **1998**, *31*, 1745. (g) Percec, V.; Ahn, C.-H.; Cho, W.-D.; Jamieson, A. M.; Kim, J.; Leman, T.; Schmidt, M.; Gerle, M.; Möller, M.; Prokhorova, S. A.; Sheiko, S. S.; Cheng, S. Z. D.; Zhang, A.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 8619. (h) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161. (i) Percec, V.; Holerca, M. N. *Biomacromolecules* **2000**, *1*, 6. (j) Percec, V.; Holerca, M. N.; Magonov, S. N.; Yeardley, D. J. P.; Ungar, G.; Duan, H.; Hudson, S. D. *Biomacromolecules* **2001**, *2*, 706. (k) Percec, V.; Holerca, M. N.; Uchida, S.; Yeardley, D. J. P.; Ungar, G. *Biomacromolecules* **2001**, *2*, 729.
11. (a) Beginn, U.; Zipp, G.; Möller, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 631. (b) Beginn, U.; Zipp, G.; Möller, M. *Chem. Eur. J.* **2000**, *6*, 2016. (c) Beginn, U.; Zipp, G.; Mourran, A.; Welther, P.; Möller, M. *Adv. Mater.* **2000**, *12*, 513. (d) Beginn, U.; Zipp, G.; Möller, M. *Adv. Mater.* **2000**, *12*, 510.
12. Percec, V.; Zipp, G.; Johansson, G.; Beginn, U.; Möller, M. *Macromol. Chem. Phys.* **1997**, *198*, 265.
13. Percec, V.; Bera, T. K. *Biomacromolecules* **2002**, *3*, 167.
14. (a) Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yeardley, D. P. *J. Am. Chem. Soc.* **1998**, *120*, 11061. (b) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1598. (c) Percec, V.; Cho, W.-D.; Ungar, G. *J. Am. Chem. Soc.* **2000**, *122*, 10273. (d) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2001**, *123*, 1302.
15. Johanson, G.; Percec, V.; Ungar, G.; Smith, K. *Chem. Mater.* **1997**, *9*, 164.
16. Weck, M.; Dunn, A. R.; Matsumoto, K.; Coates, G. W.; Lobkovsky, E. B.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2741.
17. (a) Bilgicer, B.; Fichera, A.; Kumar, K. *J. Am. Chem. Soc.* **2001**, *123*, 4393. (b) Tang, Y.; Girlanda, G.; Vaidehi, N.; Kua, J.; Mainz, D. T.; Goddard, III, W. A.; DeGrado, W. F.; Tirrell, D. A. *Biochemistry* **2001**, *40*, 2790.
18. Percec, V.; Heck, J.; Lee, M.; Ungar, G.; Castillo, A-A. *J. Mater. Chem.* **1992**, *2*, 1033.
19. (a) Pershan, P. S. *Structure of Liquid Crystal Phases*, World Scientific: Singapore; 1998, p 3. (b) Helfrich, J. *Phys. Colloq.* **1979**, *40*, 3.
20. Helfrich, J. *Phys. Colloq.* **1993**, *34*, 2050.

21. Percec, V.; Heck, J.; Ungar, G. *Macromolecules* **1991**, *24*, 4957.
22. Ungar, G. *Polymer* **1993**, *34*, 2050.
23. Percec, V.; Ahn, C.-H.; Bera, T. K.; Ungar, G.; Yeardley, D. J. P. *Chem. Eur. J.* **1999**, *5*, 1070.
24. Feiring, A. E. In *Organofluorine Chemistry*, Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum: New York, 1994; p 339.