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Dramatic Stabilization of a Hexagonal Columnar Mesophase Generated from Supramolecular and Macromolecular Columns by the Semifluorination of the Alkyl Groups of Their Tapered Building Blocks

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ABSTRACT: The tapered building blocks 3,4,5-tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoic acid (**8-10/0**), 3,4,5-tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoic acid (**8-4/6**), 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate (**11-10/0**), 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate (**11-4/6**), 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris(*n*-decan-1-yloxy)benzoate (**18-10/0**), 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((5,5,6,6,7,7,-8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate (**18-4/6**), the methacrylates of **11-10/0** (**12-10/0**), **11-4/6** (**12-4/6**), **18-10/0** (**19-10/0**), and **18-4/6** (**19-4/6**), and the corresponding polymethacrylates **13-10/0, 13-4/6, 20-10/0**, and **20-4/6** were synthesized and characterized. With the exception of **8-10/0** which forms a smectic mesophase, all other building blocks and polymers self-assemble into tubular supramolecular architectures which generate hexagonal columnar (Φ_h) mesophases. The fluorination of six out of the ten methylene units of the alkyl tails of these compounds induces a dramatic stabilization of their Φ_h. In the case when the parent hydrogenated compound (**8-10/0**) forms a lamellar smectic mesophase or only a crystalline phase (**18-10/0**), fluorination generates a Φ_h mesophase.

Introduction

In a series of publications from our laboratory we have reported on the self-assembly of tapered building blocks containing various endo-receptors such as crown ethers, oligo(oxyethylene)s, H-bonding, etc., into tubular supramolecular architectures which in turn are responsible for the formation of a hexagonal columnar (Φ_h) liquid crystalline phase.[1-3] The replacement of the endo-receptor of these tapered building blocks with a covalently bonded polymer backbone, generates polymers which by analogy with their low molar mass homologues self-assemble into tubular architectures.[1-3] Although the mechanisms of self-assembly of both low molar mass and polymeric structures are far from being elucidated, in the case of polymers, most probably the tubular structure seems to be based on a single backbone surrounded by its own tapered side groups. By analogy with the case of the self-assembly of rod-like viruses, the random-coil configuration of the backbone should be distorted into a helical-like one.[2,3] The ability of a certain polymer backbone to distort its own conformation is determined mainly by the capability of its own tapered side group to overcome the entropy loss during self-assembly. Briefly, these tapered groups play the role of the bricks in the construction of a chimney. The wider and stronger they are the more stable is the resulting construction. Additional increase of its stability is provided by using a cement, its role in our particular case being played by the endo-receptor and also by the polymer backbone.

The tapered building blocks employed are constructed by using 3,4,5-trihydroxybenzoate derivatives such as 3,4,5-tris[(4-(*n*-alkan-1-yloxy)benzyl)oxy]benzoate and 3,4,5-tris(*n*-alkan-1-yloxy)benzoate, respectively.[1] The ability of these two classes of tapered side groups to generate a tubular supramolecular architecture is determined by the length of their *n*-alkan-1-yloxy groups.[1,2]

It is well-known that perfluorinated alkanes are more rigid and less miscible (fluorophobic effect) than the corresponding perhydrogenated alkanes.[4] As a consequence, the replacement of a perhydrogenated alkane with a perfluorinated one in the tail of a rod-like molecular liquid crystal enhances the thermal stability of the liquid crystalline phase.[5] At the same time the combination of perfluorinated and perhydrogenated segments within the same molecule produces a microsegregation at the molecular level, and this process can be alone responsible for the formation of lamellar thermotropic[6,7] and lyotropic mesophases.[8]

This paper will report the first series of experiments on the investigation of the influence of fluorination of the alkyl groups of tapered building blocks on their ability to self-assemble into supramolecular tubular architectures. The synthesis and characterization of 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate (**11-10/0**) and 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate (**11-4/6**), of their intermediary compounds **8-10/0** and **8-4/6**, of the corresponding polymethacrylates (**13-10/0, 13-4/6**), and of 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris(*n*-decan-1-yloxy)benzoate (**18-10/0**) and 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl-3,4,5-tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate (**18-4/6**) as well as of their corresponding polymethacrylates (**20-10/0, 20-4/6**) will be described. The replacement of six of the

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ten methylene units with perfluorinated ones transforms **11-10/0** from a building block which displays a very narrow temperature range Φ_h mesophase and **18-10/0** from a building block which displays a lamellar crystalline structure into **11-4/6** and **18-4/6**, tapered blocks which self-assemble into tubular supramolecular architectures which exhibit a Φ_h mesophase. Both **13-10/0** and **20-10/0** form tubular architectures. The thermal stabilities of the Φ_h mesophase of **13-4/6** and **20-4/6** are increased versus that of the perhydrogenated homologues by 129 and 78 deg, respectively.

Experimental Section

Materials. Methyl 3,4,5-trihydroxybenzoate (98%), methyl 4-hydroxybenzoate (98%), 1-bromodecane (98%), 1,3-dicyclohexylcarbodiimide (DCC, 99%), $LiAlH_4$ (95%), 4-(dimethylamino)pyridine (DMAP, 99%), *p*-toluenesulfonic acid (98.5%), basic and neutral chromatographic Al_2O_3 (all from Aldrich), 5% Pd on carbon (Lancaster Synthesis), 1-iodo-5,5,6,6,7,7,8,8,9,9,10,-10,10-tridecafluorodecane (96.4%, Hoechst), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), chromatographic SiO_2 (both from Fisher), SiO_2 thin layer chromatography sheets with fluorescent indicator (Kodak) and other conventional reagents were used as received. Tetraethylene glycol (99%, Aldrich) was stored over 4 Å molecular sieves for more than 24 h and then was vacuum distilled onto 4 Å molecular sieves, discarding the forerun. *N,N'*-Dimethylformamide (DMF) was dried over CaH_2, filtered, and distilled under vacuum. Et_2O was dried over sodium/benzophenone ketyl and distilled. Pyridine was dried over KOH, distilled, and stored over KOH. Et_3N was dried over KOH, distilled, and stored over KOH. CH_2Cl_2 was distilled from CaH_2. Methacryloyl chloride (99%, Fluka) was distilled under vacuum from *tert*-butylhydroquinone. Benzene was washed with H_2SO_4 until the washes were colorless and then with water to neutral pH, dried over $MgSO_4$, filtered, and then distilled from sodium/benzophenone ketyl under Ar. 2,2'-Azobis(isobutyronitrile) (AIBN, Kodak) was recrystallized from MeOH at 4 °C.

Techniques. ^1H, ^{19}F, and ^{13}C NMR (200, 188, and 50 MHz, respectively) spectra were recorded on a Varian Gemini 200 at 20 °C with tetramethylsilane (TMS) internal standard for ^1H and ^{13}C and fluorotrichloromethane ($CFCl_3$) internal standard for ^{19}F. IR spectra were recorded on a Perkin-Elmer 1320 spectrometer. Relative molecular weights of polymers were measured by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC pump equipped with an LC-100 column oven (40 °C), a UV detector, and a Nelson 900 series integrator data station. A set of two Polymer Laboratories PL gel columns of 5×10^2 and 10^4 Å and THF eluent at 1 mL min^{-1} were used. Polystyrene standards were used for calibration. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. 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. Differential scanning calorimetry (DSC) measurements were recorded on a Perkin-Elmer DSC-7. Indium and zinc were used as calibration standards. Heating and cooling rates were 10 °C min^{-1}. First-order transitions are reported as the maximum of endothermic and minimum of exothermic peaks, and glass transitions are recorded as the middle of the change in heat capacity. An Olympus BX40 optical polarized microscope equipped with a Mettler FP82 hot stage and a Mettler FP80 central processor was used to observe thermal transitions and analyze anisotropic textures. Molecular modeling was performed on CSC Chem3D from Cambridge Scientific Computing, Inc. X-ray diffraction patterns were recorded for single fibers on Kodak direct exposure film, using Ni-filtered Cu Kα radiation and pinhole or toroidal collimation. Fibers were drawn with tweezers from the homogeneous film of the polymer or low molar mass compound on a microscope slide at 60 °C, then cooled to room temperature, and stored at 4 °C for several days. The fiber specimens were mounted vertically and were perpendicular to the horizontal X-ray beam. The *d* spacings were measured from the film data using an Optronics P1000 scanning optical densitometer. The wide angle *d* spacings were calibrated using calcium fluoride. Small angle X-ray data were also recorded at room temperature (25 °C) using a Phillips PN 3550/10 diffractometer in the transmission mode, with a slit width of 0.033° and Cu Kα radiation. Data were recorded along the equatorial direction for a single oriented fiber. Density measurements were determined by flotation in $DMSO/H_2O$ (for **13-10/0** and **20-10/0**) and $DMSO/CCl_4$ (for **13-4/6** and **20-4/6**) at 25 °C.

Synthesis of Monomers and Polymers. 2-{2-[2-(2-(Allyloxy)ethoxy)ethoxy]ethoxy}ethanol (16)[9] **and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS)**[10] were prepared by literature procedures.

Methyl 4-(*n*-Decan-1-yloxy)benzoate (3-10/0). A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stirring bar was charged with 290 mL of DMF and 67.0 mL (0.323 mol) of 1-bromodecane (**1-10/0**). The mixture was sparged with Ar for 10 min and then 110 g (0.80 mol) of anhydrous K_2CO_3 and 58.4 g (0.384 mol) methyl 4-hydroxybenzoate (**2**) were added. The mixture was heated at 70 °C for 4 h with stirring under an Ar atmosphere, after which ^1H NMR analysis indicated complete reaction. The reaction was cooled to room temperature and the solids were filtered. The filtrate was diluted with $CHCl_3$ and transferred to a separatory funnel. The organic phase was washed three times with 500 mL portions of H_2O, twice with 200 mL portions of dilute HCl, and then twice with 500 mL portions of H_2O. The organic phase was dried over $MgSO_4$ and filtered and the solvent evaporated. The crude product was passed through a short column of neutral Al_2O_3 using 20:1 hexanes/ethyl acetate eluent. The resulting solid was recrystallized from hot EtOH, giving 79.5 g (85.0%) of white crystals. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 3H, CH_3, *J* 6.8 Hz), 1.27 [overlapped m, 14H, $(CH_2)_7$], 1.80 (m, 2H, CH_2CH_2OPh, *J* 6.7), 3.88 (s, 3H, CO_2CH_3), 4.00 (t, 2H, CH_2OPh, *J* 6.7), 6.90 (d, 2H, Ar*H* *ortho* to CH_2O, *J* 8.9), 7.98 (d, 2H, Ar*H* *ortho* to CO_2CH_3, *J* 8.9). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.0 (CH_3), 22.6 (CH_2CH_3), 25.9–29.5 [$(CH_2)_6$], 31.8 ($CH_2CH_2CH_3$), 51.7 (CO_2CH_3), 68.1 (CH_2-OPh), 114.0, 122.2, 131.5, 162.9 (aromatic), 166.8 ($PhCO_2CH_3$). IR, ν_{max} (cm^{-1}): 1710 (C=O). Mp: 47 °C. TLC: $R_f = 0.39$ (10:1 hexanes/ethyl acetate).

Methyl 4-((5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-*n*-decan-1-yl)oxy)benzoate (3-4/6). The etherification of 32.67 g (65.07 mmol) of 1-iodo-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecane (**1-4/6**) with 11.11 g (73.02 mol) of methyl 4-hydroxybenzoate (**2**) was performed as described in the synthesis of **3-10/0**, resulting in 29.9 g (87.4%) of white crystals. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [overlapped m, 4H, $(CH_2)_2$], 2.17 (overlapped m, 2H, $-CF_2CH_2$, *J* 8.8), 3.89 (s, 3H, $-CO_2CH_3$), 4.05 (t, 2H, $-CH_2OPh$, *J* 5.5), 6.90 (d, 2H, Ar*H* *ortho* to CH_2O, *J* 8.9), 7.99 (d, 2H, Ar*H* *ortho* to CO_2CH_3, *J* 8.9). ^{19}F NMR, δ ($CDCl_3$, $CFCl_3$, ppm): −81.40 (s, 3F, CF_3), −115.7 (m, 2F, CF_2CH_2, *J* 14.7), −122.6 (s, 2F, $CF_2CF_2CH_2$), −123.5 (s, 2F, $CF_2CF_2CF_2CH_2$), −124.1 (s, 2F, $CF_2CF_2CF_2CF_2$-CH_2), −126.1 (s, 2F, $CF_2CF_2CF_2CF_2CF_2CH_2$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.3 ($CF_2CH_2CH_2$), 28.6 ($CF_2CH_2CH_2CH_2$-CH_2O), 30.7 (CF_2CH_2, J_{C-F} 22.4), 51.9 ($PhCO_2CH_3$), 67.2 (CH_2-OPh), 100−130 [m, $CF_3(CF_2)_5$], 114.1, 122.8, 131.7, 162.6 (aromatic), 166.9 ($PhCO_2CH_3$). IR, ν_{max} (cm^{-1}): 1710 (C=O). Mp: 53−54 °C. TLC: $R_f = 0.55$ (CH_2Cl_2).

4-(*n*-Decan-1-yloxy)benzyl Alcohol (4-10/0). A 1 L round-bottomed flask containing a Teflon-coated magnetic stir bar and equipped with an addition funnel was charged with 200 mL of Et_2O and 15.5 g (0.408 mol) of $LiAlH_4$. The reaction flask was sealed with a $CaCl_2$ drying tube, and the solution was cooled in an ice bath. **3-10/0** (79.5 g, 0.272 mol) was dissolved in 250 mL of Et_2O and added dropwise to the $Et_2O/LiAlH_4$ slurry over a 1 h period. The ice bath was removed, and the reaction mixture was stirred for an additional hour, at which time the reaction was shown to be complete by ^1H NMR analysis. The reaction mixture was again cooled in an ice bath, and H_2O was added cautiously dropwise with stirring until hydrogen evolution ceased. Dilute HCl was then added until both phases were homogeneous. The two-phase reaction mixture was transferred to a separatory funnel, and the organic phase was washed three times with 150 mL portions of H_2O and once with 150 mL of saturated NaCl and then dried over $MgSO_4$. The mixture was filtered and the solvent evaporated, resulting in 69.9 g (97.3%) of white solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 3H, CH_3, *J* 6.8), 1.27 [overlapped m, 14H, $(CH_2)_7$], 1.78 (m, 2H, CH_2CH_2OPh, *J* 6.5), 3.95 (t, 2H, CH_2OPh, *J* 6.5), 4.62 (d, 2H, CH_2OH, *J* 5.6), 6.90 (d, 2H, Ar*H* *ortho* to CH_2O, *J* 8.6), 7.28 (d, 2H, Ar*H* *ortho* to CH_2OH, *J* 8.6). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.1 (CH_3), 22.7 (CH_2CH_3), 26.0–29.5 [$(CH_2)_6$], 31.9 ($CH_2CH_2CH_3$), 65.0 (CH_2OH), 68.0 (CH_2OPh), 114.5, 128.6, 132.9, 158.8 (aromatic). IR, ν_{max} (cm^{-1}): 3100–3500 (OH). Mp: 58 °C. TLC: $R_f = 0.34$ (3:1 hexanes/ethyl acetate).

4-((5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-*n*-decan-1-yl)oxy)benzyl Alcohol (4-4/6). The reduction of 29.9 g (56.8 mmol) of **3-4/6** was performed as described for **3-10/0**, yielding 25.1 g (88.7%) of white powder. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 1.57 (s, 1H, O*H*), 1.89 [overlapped m, 4H, $(CH_2)_2$], 2.16 (overlapped m, 2H, $-CF_2CH_2$, *J* 8.8), 4.00 (t, 2H, $-CH_2OPh$, *J* 5.6), 4.62 (d, 2H, $PhCH_2OH$, *J* 5.2), 6.88 (d, 2H, Ar*H* *ortho* to CH_2O, *J* 8.6), 7.29 (d, 2H, Ar*H* *ortho* to CH_2OH, *J* 8.6). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.2 ($CF_2CH_2CH_2$), 28.7 ($CF_2CH_2CH_2CH_2$), 30.6 (CF_2CH_2, J_{C-F} 22.4), 64.9 ($PhCH_2OH$), 67.2 (CH_2OPh), 100–130 [m, $CF_3(CF_2)_5$], 114.5, 128.6, 133.3, 158.4 (aromatic). IR, ν_{max} (cm^{-1}): 3200–3500 (OH). Mp: 65 °C. TLC: $R_f = 0.07$ (CH_2Cl_2).

4-(*n*-Decan-1-yloxy)benzyl Chloride (5-10/0). A 250 mL round-bottom flask equipped with an addition funnel and a Teflon-coated stir bar was charged with 22.0 g (83.3 mmol) of **4-10/0**, 100 mL of CH_2Cl_2, and 0.6 mL of DMF. The flask was flushed with Ar and closed with a $CaCl_2$ drying tube abd then cooled in an ice bath followed by dropwise addition of 7.0 mL (87 mmol) of $SOCl_2$ over 15 min. The ice bath was removed upon completion of the $SOCl_2$ addition, and the reaction mixture was stirred for an additional 45 min. ^1H NMR analysis indicated complete reaction. The solvent and excess $SOCl_2$ were evaporated and the product was dried under vacuum, resulting in 23.5 g (99.8%) of slightly yellow liquid which was used without any further purification. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 3H, CH_3, *J* 5.9), 1.27 [overlapped m, 14H, $(CH_2)_7$], 1.81 (m, 2H, CH_2CH_2OPh, *J* 6.7), 3.95 (t, 2H, CH_2OPh, *J* 6.7), 4.57 (s, 2H, CH_2Cl), 6.87 (d, 2H, Ar*H* *ortho* to CH_2O, *J* 8.6), 7.28 (d, 2H, Ar*H* *ortho* to CH_2Cl, *J* 8.6). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 13.9 (CH_3), 22.5 (CH_2CH_3), 25.8–29.4 [$(CH_2)_6$], 31.7 ($CH_2CH_2CH_3$), 46.2 (CH_2Cl), 67.9 (CH_2OPh), 114.5, 129.3, 129.9, 159.1 (aromatic). IR, ν_{max} (cm^{-1}): 1235 (CH_2Cl).

4-((5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-*n*-decan-1-yl)oxy)benzyl Chloride (5-4/6). The chlorination of 25.1 g (50.4 mmol) of **4-4/6** was performed as described for **4-10/0**, resulting in 25.5 g (97.9%) of white crystals. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [overlapped m, 4H, $(CH_2)_2$], 2.16 (overlapped m, 2H, $-CF_2CH_2$, *J* 8.8), 4.00 (t, 2H, $-CH_2OPh$, *J* 5.6), 4.57 (s, 2H, $PhCH_2Cl$), 6.87 (d, 2H, Ar*H* *ortho* to CH_2O, *J* 8.7), 7.31 (d, 2H, Ar*H* *ortho* to CH_2Cl, *J* 8.7). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.2 ($CF_2CH_2CH_2$), 28.6 ($CF_2CH_2CH_2CH_2$), 30.6 (CF_2CH_2, J_{C-F} 22.6), 46.3 ($PhCH_2Cl$), 67.2 (CH_2OPh), 100–130 [m, $CF_3(CF_2)_5$], 114.5, 128.6, 133.3, 159.0 (aromatic). IR, ν_{max} (cm^{-1}): 1240 (CH_2Cl). Mp: 41 °C.

Methyl 3,4,5-Tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate (7-10/0). A 500 mL round-bottom flask with Teflon-coated magnetic stirring bar was charged with 23.5 g (83.3 mmol) of **5-10/0** and 200 mL of DMF. The mixture was sparged thoroughly with Ar, and 4.78 g (26.0 mmol) of methyl 3,4,5-trihydroxybenzoate (**6**) and 22.4 g (162 mmol) of anhydrous K_2CO_3 were added. The mixture was heated at 70 °C for 12 h with stirring under an Ar atmosphere. ^1H NMR indicated complete consumption of the starting benzyl chloride. The reaction mixture was cooled to room temperature, filtered, and then diluted with Et_2O and transferred to a separatory funnel. The organic phase was washed with two 300 mL portions of H_2O, 100 mL of dilute HCl, 300 mL of H_2O and 100 mL of saturated NaCl. The organic phase was separated, dried over $MgSO_4$, and filtered, and the solvent was evaporated. The crude product was passed through a short basic Al_2O_3 column using CH_2Cl_2 eluent. The product was recrystallized from warm acetone, resulting in 19.6 g (81.7%) of white solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, *J* 6.7), 1.27 [overlapped m, 42H, $(CH_2)_7$], 1.82 (m, 6H, CH_2CH_2OPh, *J* 6.3), 3.88 (s, 3H, CO_2CH_3), 3.91–3.99 (overlapped t, 6H, CH_2OPh), 5.00–5.04 (overlapped s, 6H, $PhCH_2OPh$), 6.75 (d, 2H, Ar*H* *ortho* to CH_2OPh, *para* to $PhCO_2CH_3$, *J* 8.6), 6.89 (d, 4H, Ar*H* *ortho* to CH_2OPh, *meta* to $PhCO_2CH_3$, *J* 8.7), 7.24 (d, 2H, Ar*H* *meta* to CH_2OPh, *para* to $PhCO_2CH_3$, *J* 8.6), 7.33 (d, 4H, Ar*H* *meta* to CH_2OPh, *meta* to $PhCO_2CH_3$, *J* 8.7), 7.36 (s, 2H, Ar*H*CO_2CH_3). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.0 (CH_3), 22.6 (CH_2CH_3), 26.0–29.5 [$(CH_2)_6$], 31.8 ($CH_2CH_2CH_3$), 52.0 (CO_2CH_3), 67.9 (CH_2OPh), 71.0 ($PhCH_2OPh$ *meta* to CO_2CH_3), 74.6 ($PhCH_2OPh$ *para* to CO_2CH_3), 109.1, 114.0, 114.3, 124.9, 128.5, 129.2, 129.6, 130.1, 142.4, 152.6, 158.9 (aromatic), 166.6 ($PhCOCH_3$). IR, ν_{max} (cm^{-1}): 1705 (C=O). Mp: 65–66 °C. TLC: $R_f = 0.51$ (CH_2Cl_2). GPC: 99%.

Methyl 3,4,5-Tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate (7-4/6). Etherification of 25.5 g (49.4 mmol) of **5-4/6** with 2.83 g (15.4 mmol) of methyl 3,4,5-trihydroxybenzoate (**6**) was performed as described for **5-10/0**, yielding 19.3 g (77.1%) of white powder. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [overlapped m, 12H, $(CH_2)_2$], 2.16 (overlapped m, 6H, $-CF_2CH_2$), 3.88 (s, 3H, CO_2CH_3), 3.96–4.01 (overlapped t, 6H, CH_2OPh), 5.01 (s, 2H, $PhCH_2OPh$ *para* to CO_2CH_3), 5.05 (s, 4H, $PhCH_2OPh$ *meta* to CO_2CH_3), 6.74 (d, 2H, Ar*H* *ortho* to CH_2OPh, *para* to $PhCO_2CH_3$, *J* 8.7), 6.89 (d, 4H, Ar*H* *ortho* to CH_2OPh, *meta* to $PhCO_2CH_3$, *J* 8.7), 7.24 (d, 2H, Ar*H* *meta* to CH_2OPh, *para* to $PhCO_2CH_3$, *J* 8.6), 7.33 (d, 4H, Ar*H* *meta* to CH_2OPh, *meta* to $PhCO_2CH_3$, *J* 8.7), 7.37 (s, 2H, Ar*H*CO_2CH_3). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.3 ($CF_2CH_2CH_2$), 28.7 ($CF_2CH_2CH_2CH_2$), 30.6 (CF_2CH_2, J_{C-F} 22.6), 52.1 (CO_2CH_3), 67.2 (CH_2OPh), 71.0 ($PhCH_2OPh$ *meta* to CO_2CH_3), 74.7 ($PhCH_2OPh$ *para* to $PhCO_2CH_3$), 100–130 [m, $CF_3(CF_2)_5$], 109.1, 114.0, 114.4, 125.1, 129.0, 129.3, 129.9, 130.3, 142.4, 152.6, 158.7 (aromatic), 166.7 ($PhCOCH_3$). IR, ν_{max} (cm^{-1}): 1705 (C=O). DSC: heating, k 84, 91 (12.14) Φ_h 119 (2.90) i; cooling, i 110 (2.85) Φ_h 64 (7.21) k. GPC, 99%. TLC: $R_f = 0.60$ (CH_2Cl_2).

3,4,5-Tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoic Acid (8-10/0). In a 250 mL Erlenmeyer flask containing a Teflon-coated magnetic stirring bar was placed 8.58 g (9.30 mmol) of **7-10/0**, 3.53 g (63.0 mmol) of KOH, and 70 mL of 95% EtOH. The reaction mixture was heated to reflux temperature with stirring for 50 min. The reaction was judged complete by TLC analysis. The reaction mixture was then allowed to cool to room temperature, and the resulting precipitate was filtered, washed with EtOH, and then placed in a 250 mL Erlenmeyer flask with a Teflon-coated magnetic stirring bar. THF (100 mL) was added to the solid and 1 M HCl was added dropwise with stirring until pH = 1 was reached by pH paper. The THF solution was poured into 200 mL of Et_2O and washed twice with 100 mL portions of H_2O and then with 50 mL of saturated NaCl. The organic phase was separated and dried over $MgSO_4$. The mixture was filtered and the solvent evaporated. The product was recrystallized from warm hexanes, resulting in 7.37 g (83.2%) of white solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, *J* 6.6), 1.27 [overlapped m, 42H, $(CH_2)_7$], 1.79 (m, 6H, CH_2CH_2OPh, *J* 6.3), 3.92–4.00 (overlapped t, 6H, CH_2OPh), 5.00–5.04 (overlapped s, 6H, $PhCH_2OPh$), 6.76 (d, 2H, Ar*H* *ortho* to CH_2OPh, *para* to $PhCO_2H$, *J* 8.2), 6.90 (d, 4H, Ar*H* *ortho* to CH_2OPh, *meta* to $PhCO_2H$, *J* 8.6), 7.25 (d, 2H, Ar*H* *meta* to CH_2OPh, *para* to $PhCO_2H$, *J* 8.6), 7.34 (d, 4H, Ar*H* *meta* to CH_2OPh, *meta* to $PhCO_2H$, *J* 8.6), 7.41 (s, 2H, Ar*H*CO_2H). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.1 (CH_3), 22.6 (CH_2CH_3), 26.0–29.5 [$(CH_2)_6$], 31.9 ($CH_2CH_2CH_3$), 68.0 (CH_2OPh), 71.0 ($PhCH_2OPh$ *meta* to CO_2H), 74.7 ($PhCH_2OPh$ *para* to CO_2H), 109.6, 114.0, 114.4, 124.0, 128.4, 129.2, 130.2, 143.1, 152.6, 159.0 (aromatic), 171.8 ($PhCO_2H$). IR, ν_{max} (cm^{-1}): 1680 (C=O). TLC: $R_f = 0$ (CH_2Cl_2). Thermal transitions and corresponding enthalpy changes are listed in Table 1.

3,4,5-Tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoic Acid (8-4/6). The hydrolysis of 12.0 g (7.38 mmol) of **7-4/6** was performed as described for **7-10/0** and resulted in 9.74 g (82.0%) of white solid. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [m, 12H, $(CH_2)_2$], 2.16 (m, 6H, $-CF_2CH_2$), 3.96−4.01 (m, 6H, CH_2OPh), 5.04 (s, 2H, $PhCH_2OPh$ *para* to CO_2H), 5.07 (s, 4H, $PhCH_2OPh$ *meta* to CO_2H), 6.76 (d, 2H, Ar*H* *ortho* to CH_2OPh, *para* to $PhCO_2H$, *J* 9.3), 6.90 (d, 4H, Ar*H* *ortho* to CH_2OPh, *meta* to $PhCO_2H$, *J* 9.3), 7.24 (d, 2H, Ar*H* *meta* to CH_2OPh, *para* to $PhCO_2H$, *J* 9.3), 7.29 (d, 4H, Ar*H* *meta* to CH_2OPh, *meta* to $PhCO_2H$, *J* 9.3), 7.42 (s, 2H, $ArHCO_2H$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.3 ($CF_2CH_2CH_2$), 28.8 ($CF_2CH_2CH_2CH_2$), 30.7 (CF_2CH_2, J_{C-F} 22.6), 67.2 (CH_2OPh), 71.0 ($PhCH_2OPh$ *meta* to CO_2H), 74.7 ($PhCH_2OPh$ *para* to $PhCO_2H$), 109.7, 114.1, 114.5, 124.1, 128.9, 129.4, 129.8, 130.3, 143.3, 152.7, 158.8 (aromatic), 171.6 ($PhCO_2H$). IR, ν_{max} (cm^{-1}): 1690 (C=O). GPC, 99%. TLC: R_f = 0 (CH_2Cl_2). Thermal transitions and corresponding enthalpy changes are listed in Table 1.

2-{2-[2-(2-(Methacryloyloxy)ethoxy)ethoxy]ethoxy}-ethanol (10). A 100 mL round-bottom flask equipped with an addition funnel and a Teflon-coated magnetic stirring bar was charged with 56.3 g (0.289 mol) of tetraethylene glycol (**9**) and 8 mL (0.08 mol) of pyridine. The flask was flushed with Ar and cooled in an ice bath. Methacryloyl chloride (2.5 mL, 0.025 mol) was added dropwise with stirring over 10 min. The ice bath was removed and the mixture was stirred 30 min further. The reaction mixture was poured into 100 mL of $CHCl_3$ and extracted three times with 100 mL of H_2O, then three times with 100 mL of dilute HCl, and once with 100 mL of H_2O. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The crude product was chromatographed on neutral Al_2O_3 (ethyl acetate eluent), resulting in 1.8 g (28%) of colorless viscous liquid. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 1.94 [s, 3H, $-COC(CH_3)=CH_2$], 2.58 (s, 1H, O*H*), 3.65−3.79 [m, 14H, $(CH_2CH_2O)_3CH_2$], 4.29 [t, 2H, $CH_2OCOC(CH_3)=CH_2$, *J* 5.0], 5.58 [m, 1H, $COC(CH_3)=CH_2$], 6.14 (s, 1H, $COC(CH_3)=CH_2$). IR, ν_{max} (cm^{-1}): 3200−3600 (OH), 1710 (C=O), 1640 (C=C). TLC: R_f = 0.18 (ethyl acetate).

2-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-Tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate (11-10/0). A 100 mL round-bottom flask equipped with a Teflon-coated magnetic stirring bar was charged with 2.22 g (2.44 mmol) of **8-10/0**, 9.55 g (49.2 mmol) of tetraethylene glycol (**9**), 12 mL of CH_2Cl_2, 0.155 g (0.496 mmol) of DPTS, and 0.655 g (3.17 mmol) of DCC. The flask was flushed with Ar, and the reaction mixture was stirred for 33 h under Ar. ^{1}H NMR analysis indicated complete reaction. The reaction mixture was filtered, and the filtrate was diluted with 50 mL of CH_2Cl_2, then washed with three 50 mL portions of H_2O, and dried over $MgSO_4$. The solvent was evaporated, and the crude product was chromatographed on neutral Al_2O_3 using a 2:1 hexanes/ethyl acetate mobile phase, resulting in 0.83 g (31%) of colorless oil. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, *J* 6.7), 1.27 [overlapped m, 42H, $(CH_2)_7$], 1.79 (m, 6H, CH_2CH_2OPh), 3.65−3.69 [m, 12H, $(OCH_2CH_2)_3OH$], 3.85 (t, 2H, $PhCO_2CH_2CH_2$, *J* 4.9), 3.92−4.00 (m, 6H, CH_2OPh), 4.45 (t, 2H, $PhCO_2CH_2CH_2$, *J* 4.9), 5.00−5.04 (overlapped s, 6H, $PhCH_2OPh$), 6.74 (d, 2H, Ar*H* *ortho* to CH2OPh, *para* to $PhCO_2CH_2$, *J* 8.7), 6.89 (d, 4H, Ar*H* *ortho* to CH_2OPh, *meta* to $PhCO_2CH_2$, *J* 8.7), 7.25 (d, 2H, Ar*H* *meta* to CH_2OPh, *para* to $PhCO_2CH_2$, *J* 8.6), 7.33 (d, 4H, Ar*H* *meta* to CH_2OPh, *meta* to $PhCO_2CH_2$, *J* 8.7), 7.37 (s, 2H, $ArHCO_2CH_2$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.1 (CH_3), 22.6 (CH_2CH_3), 26.0−29.5 [$(CH_2)_6$], 31.8 ($CH_2CH_2CH_3$), 61.6 (CH_2OH), 64.1 ($PhCO_2CH_2$), 68.0 (CH_2OPh), 69.2−70.6, 72.5 [$CH_2O(CH_2CH_2O)_2CH_2$], 71.1 ($PhCH_2OPh$ *meta* to CO_2CH_2), 74.6 ($PhCH_2OPh$ *para* to CO_2CH_2), 109.3, 114.0, 114.4, 124.9, 128.5, 129.2, 129.6, 130.2, 142.9, 152.6, 159.0 (aromatic), 166.1 ($PhCO_2CH_2$). GPC: 99%. IR, ν_{max} (cm^{-1}): 3100−3600 (OH), 1700 (C=O). TLC, R_f = 0.5 (1:1 hexanes/ethyl acetate). Thermal transitions and corresponding enthalpy changes are listed in Table 1.

2-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-Tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate (11-4/6). The esterification of 5.02 g (3.10 mmol) of **8-4/6** and 12.45 g (64.10 mmol) of tetraethylene glycol (**9**) was perfomed as described for **8-10/0** in 2:1 CH_2Cl_2/Freon 113 solvent, resulting in 0.94 g (17%) of white solid. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [m, 12H, $(CH_2)_2$], 2.16 (m, 6H, $-CF_2CH_2$), 3.52−3.64 [m, 12H, $(OCH_2CH_2)_3OH$], 3.85 (t, 2H, $PhCO_2CH_2CH_2$, *J* 4.9), 3.92−4.00 (m, 6H, CH_2OPh), 4.46 (t, 2H, $PhCO_2CH_2CH_2$, *J* 4.9), 5.04 (s, 2H, $PhCH_2OPh$ *para* to CO_2CH_2), 5.07 (s, 4H, $PhCH_2OPh$ *meta* to CO_2CH_2), 6.76 (d, 2H, Ar*H* *ortho* to CH_2OPh, *para* to $PhCO_2CH_2$, *J* 9.3), 6.90 (d, 4H, Ar*H* *ortho* to CH_2OPh, *meta* to $PhCO_2CH_2$, *J* 9.3), 7.24 (d, 2H, Ar*H* *meta* to CH_2OPh, *para* to $PhCO_2CH_2$, *J* 9.3), 7.29 (d, 4H, Ar*H* *meta* to CH_2OPh, *meta* to $PhCO_2CH_2$, *J* 9.3), 7.38 (s, 2H, $ArHCO_2CH_2$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.3 ($CF_2CH_2CH_2$), 28.7 ($CF_2CH_2CH_2CH_2$), 30.6 (CF_2CH_2, J_{C-F} 22.4), 61.7 (CH_2OH), 64.1 ($PhCO_2CH_2$), 67.2 (CH_2OPh), 69.3−70.6, 72.5 [$CH_2O(CH_2CH_2O)_2CH_2$], 71.0 ($PhCH_2OPh$ *meta* to CO_2CH_2), 74.6 (CH_2OPh *para* to CO_2CH_2), 109.4, 114.1, 114.4, 125.0, 129.0, 129.3, 129.8, 130.2, 142.5, 152.6, 158.7 (aromatic), 166.2 ($PhCO_2CH_2$). IR, ν_{max} (cm^{-1}): 3100−3600 (OH), 1700 (C=O). GPC: 99%. TLC: R_f = 0.07 (1:1 hexanes/ethyl acetate). Thermal transitions and corresponding enthalpy changes are listed in Table 1.

2-{2-[2-(2-(Methacryloyloxy)ethoxy)ethoxy]ethoxy}-ethyl 3,4,5-Tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate (12-10/0). A 100 mL round-bottom flask equipped with Teflon-coated magnetic stirring bar was charged with 1.50 g (1.61 mmol) of **8-10/0**, 0.548 g (2.09 mmol) of **10**, 10 mL of CH_2Cl_2, 0.100 g (0.320 mmol) of DPTS, and 0.431 g (2.09 mmol) of DCC. The flask was flushed with Ar and stirred for 15 h, after which ^{1}H NMR analysis indicated complete reaction. The reaction mixture was filtered, and the filtrate solvent was evaporated. The residue was dissolved in hexanes and filtered again. The crude product was chromatographed on neutral Al_2O_3 (4:1 hexanes/ethyl acetate), resulting in 0.95 g (51%) of colorless oil. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3, *J* 6.2), 1.27 [overlapped m, 42H, $(CH_2)_7$], 1.79 (m, 6H, CH_2CH_2OPh), 1.94 [s, 3H, $-COC(CH_3)=CH_2$], 3.65−3.69 [m, 10H, $(OCH_2CH_2)_2OCH_2$], 3.85 (t, 2H, $PhCO_2CH_2CH_2$, *J* 5.1), 3.92−4.00 (overlapped t, 6H, CH_2OPh), 4.28 [t, 2H, $CH_2OCOC(CH_3)=CH_2$, *J* 5.0], 4.45 (t, 2H, $PhCO_2CH_2CH_2$, *J* 4.9), 5.00−5.04 (overlapped s, 6H, $PhCH_2OPh$), 5.56 (s, 1H, $COC(CH_3)=CH_2$), 6.12 (s, 1H, $COC(CH_3)=CH_2$), 6.75 (d, 2H, Ar*H* *ortho* to CH_2OPh, *para* to $PhCO_2CH_2$, *J* 8.6), 6.89 (d, 4H, Ar*H* *ortho* to CH_2OPh, *meta* to $PhCO_2CH_2$, *J* 8.6), 7.24 (d, 2H, Ar*H* *meta* to CH_2OPh, *para* to $PhCO_2CH_2$, *J* 8.5), 7.33 (d, 4H, Ar*H* *meta* to CH_2OPh, *meta* to $PhCO_2CH_2$, *J* 8.7), 7.37 (s, 2H, $ArHCO_2CH_2$).^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.1 (CH_3), 18.3 [$COC(CH_3)=CH_2$], 22.6 (CH_2CH_3), 26.0−29.5 [$(CH_2)_6$], 31.9 ($CH_2CH_2CH_3$), 63.8 [$CH_2OCOC(CH_3)=CH_2$], 64.1 ($PhCO_2CH_2$), 68.0 (CH_2OPh), 69.1−70.6, 72.5 [$CH_2O(CH_2CH_2O)_2CH_2$], 71.1 ($PhCH_2OPh$ *meta* to CO_2CH_2), 74.6 ($PhCH_2OPh$ *para* to CO_2CH_2), 109.3, 114.0, 114.4, 124.9, 125.7, 128.5, 129.2, 129.6, 130.2, 136.0, 142.5, 152.6, 159.0 (aromatic), 166.1 [$PhCO_2CH_2$, $COC(CH_3)=CH_2$]. IR, ν_{max} (cm^{-1}): 1710 (C=O), 1640 (C=C). GPC: 99%. TLC: R_f = 0.11 (3:1 hexanes/ethyl acetate).

2-{2-[2-(2-(Methacryloyloxy)ethoxy)ethoxy]ethoxy}-ethyl 3,4,5-Tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate (12-4/6). The esterification of 1.61 g (0.999 mmol) of **8-4/6** with 0.343 g (1.29 mmol) of **10** in 5:1 CH_2Cl_2/Freon 113 was performed as described for the synthesis of **12-10/0** and yielded 1.05 g (56.5%) of colorless viscous liquid. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [m, 12H, $(CH_2)_2$], 2.00−2.16 (overlapped m, 9H, CF_2CH_2, $COC(CH_3)=CH_2$), 3.62−3.74 [m, 10H, $(OCH_2CH_2)_2OCH_2$], 3.82 (t, 2H, $PhCO_2CH_2CH_2$, *J* 5.3), 3.93−4.04 (m, 6H, CH_2OPh), 4.28 (t, 2H, $CH_2OCOC(CH_3)=CH_2$, *J* 5.3], 4.45 (t, 2H, $PhCO_2CH_2CH_2$, *J* 5.3), 5.00 (s, 2H, $PhCH_2OPh$ *para* to CO_2CH_2), 5.05 (s, 4H, $PhCH_2OPh$ *meta* to CO_2CH_2), 5.55 (m, 1H, $COC(CH_3)=CH_2$), 6.12 (m, 1H, $COC(CH_3)=CH_2$), 6.74 (d, 2H, Ar*H* *ortho* to CH2OPh, *para* to $PhCO_2CH_2$, *J* 8.7), 6.89 (d, 4H, Ar*H* *ortho* to CH_2OPh, *meta* to $PhCO_2CH_2$, *J* 8.7), 7.25 (d, 2H, Ar*H* *meta* to CH_2OPh, *para* to $PhCO_2CH_2$, *J* 8.7), 7.34 (d, 4H, Ar*H* *meta* to CH_2OPh, *meta* to $PhCO_2CH_2$, *J* 8.7), 7.38 (s, 2H, $ArHCO_2CH_2$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.3 ($CF_2CH_2CH_2$), 18.4 [$COC(CH_3)=CH_2$], 28.7 ($CF_2CH_2CH_2CH_2$), 30.5 (CF_2CH_2, J_{C-F} 22.4), 63.8 [$CH_2OCOC(CH_3)=CH_2$], 64.1 ($PhCO_2CH_2$), 67.2 (CH_2OPh), 69.3−70.6, 72.5 [$CH_2O(CH_2CH_2O)_2CH_2$], 71.0 ($PhCH_2OPh$ *meta* to CO_2CH_2), 74.6 (CH_2OPh *para* to CO_2CH_2), 109.3, 114.0, 114.4, 125.0, 125.7, 129.0, 129.3, 129.8, 130.2, 136.0, 142.5, 152.6, 158.7 (aromatic), 166.2 [$\mathrm{Ph}\mathit{C}\mathrm{O_2CH_2}$, $\mathrm{CO}\mathit{C}\mathrm{(CH_3){=}CH_2}$]. IR, ν_{max} (cm^{-1}): 1710 (C=O), 1640 (C=C). GPC: 99%. TLC: $R_f = 0.07$ (1:1 hexanes/ethyl acetate). Thermal transitions and corresponding enthalpy changes are listed in Table 1.

Poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate) (13-10/0). A 25 mL Schlenk tube containing a Teflon-coated magnetic stir bar was charged with 0.80 g (0.69 mmol) of **12-10/0**, 2.7 mg (0.016 mmol) of AIBN, and 1 mL of benzene and sealed with a rubber septum. The solution was subjected to five freeze–pump–thaw cycles, sealed, and stirred at 60 °C for 23 h. The crude reaction mixture was passed through a short neutral Al_2O_3 column (hexanes eluent) to remove residual monomer, resulting in 0.66 g (83%) of polymeric solid. GPC: $M_n = 16\,900$, DP(n) = 15, $M_w/M_n = 1.6$. Thermal transitions and corresponding enthalpy changes are listed in Table 1.

Poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate) (13-4/6). The polymerization of 0.98 g (0.53 mmol) of **12-4/6** was performed as described for **12-10/0**. Purification by column chromatography (neutral Al_2O_3, Freon 113 mobile phase) resulted in 0.64 g (65%) of polymeric solid. GPC, $M_n = 22\,800$, DP(n) = 12, $M_w/M_n = 1.2$. Thermal transitions and corresponding enthalpy values are listed in Table 1.

Methyl 3,4,5-Tris(*n*-decan-1-yloxy)benzoate (14-10/0). A 250 mL round-bottom flask equipped with a Teflon-coated magnetic stirring bar was charged with 170 mL of DMF and 25 mL (0.12 mol) of 1-bromodecane (**1-10/0**). The mixture was sparged with argon, and then 25.5 g of anhydrous K_2CO_3 (0.184 mol) and 5.5 g (0.029 mol) of methyl 3,4,5-trihydroxybenzoate (**6**) were added as Ar sparging was continued. The mixture was heated at 80 °C for 5 h with stirring under an Ar atmosphere. The reaction was judged complete by ^1H NMR analysis. The reaction mixture was cooled to room temperature, and the solids were filtered. The filtrate was diluted with 400 mL of Et_2O and transferred to a separatory funnel. The organic phase was washed twice with 200 mL portions of H_2O, twice with 200 mL portions of dilute HCl, once with 100 mL of H_2O, and then with 50 mL of saturated NaCl. The organic phase was separated and dried over $MgSO_4$. The mixture was filtered, and the solvent was evaporated. The crude product was passed through a short column of basic Al_2O_3 using Et_2O eluent. The product was recrystallized from methanol, resulting in 11.8 g (65.0%) of white solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, $\mathrm{C}\mathit{H}_3$, *J* 6.7), 1.27 [overlapped m, 42H, $\mathrm{(C\mathit{H}_2)_7}$], 1.78 (m, 6H, $\mathrm{C\mathit{H}_2CH_2OPh}$), 3.89 (s, 3H, $\mathrm{PhCO_2C\mathit{H}_3}$), 4.01 (t, 6H, $\mathrm{C\mathit{H}_2OPh}$, *J* 6.2), 7.25 (s, 2H, $\mathrm{Ar\mathit{H}{-}CO_2CH_3}$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.0 ($\mathrm{\mathit{C}H_3}$), 22.6 ($\mathrm{\mathit{C}H_2CH_3}$), 26.0–30.3 [$\mathrm{(CH_2)_6}$], 31.9 ($\mathrm{\mathit{C}H_2CH_2CH_3}$), 52.1 ($\mathrm{CO_2\mathit{C}H_3}$), 69.1 ($\mathrm{\mathit{C}H_2OPh}$, *meta* to CO_2CH_3), 73.4 ($\mathrm{\mathit{C}H_2OPh}$, *para* to CO_2CH_3), 107.9, 124.6, 142.3, 152.7 (aromatic), 166.8 ($\mathrm{Ph\mathit{C}O_2CH_3}$). IR, ν_{max} (cm^{-1}): 1710 (C=O). Mp: 29 °C. TLC: $R_f = 0.40$ (15:1 hexane/ethyl acetate).

Methyl 3,4,5-Tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate (14-4/6). The etherification of 20.0 g (39.9 mmol) of 1-iodo-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecane (**1-4/6**) with 2.45 g (13.3 mmol) of methyl 3,4,5-trihydroxybenzoate (**6**) was performed as described for **14-10/0**, resulting in 12.5 g (72.3%) of white solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [overlapped m, 12H, $\mathrm{(C\mathit{H}_2)_2}$], 2.17 (m, 6H, $\mathrm{{-}CF_2C\mathit{H}_2}$, *J* 8.8), 3.89 (s, 3H, $\mathrm{{-}CO_2C\mathit{H}_3}$), 4.02 (m, 6H, $\mathrm{{-}C\mathit{H}_2OPh}$, *J* 5.2), 7.28 (s, 2H, $\mathrm{Ar\mathit{H}CO_2CH_3}$). ^{19}F NMR, δ ($CDCl_3$, $CFCl_3$, ppm): −81.40 (s, 3F, $\mathrm{C\mathit{F}_3}$), −115.7 (m, 2F, $\mathrm{C\mathit{F}_2CH_2}$, *J* 14.7), −122.6 (s, 2F, $\mathrm{C\mathit{F}_2CF_2CH_2}$), −123.5 (s, 2F, $\mathrm{C\mathit{F}_2CF_2CF_2CH_2}$), −124.1 (s, 2F, $\mathrm{C\mathit{F}_2CF_2CF_2CF_2CH_2}$), −126.1 (s, 2F, $\mathrm{C\mathit{F}_2CF_2CF_2CF_2CF_2CH_2}$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.3 ($\mathrm{CF_2CH_2\mathit{C}H_2}$), 28.7 ($\mathrm{CF_2CH_2CH_2\mathit{C}H_2CH_2O}$, *meta* to CO_2CH_3), 29.7 ($\mathrm{CF_2CH_2CH_2\mathit{C}H_2CH_2O}$, *para* to CO_2CH_3), 30.7 (t, $\mathrm{CF_2\mathit{C}H_2}$, J_{C-F} 22.4), 52.1 ($\mathrm{PhCO_2\mathit{C}H_3}$), 68.9 ($\mathrm{\mathit{C}H_2OPh}$, *meta* to CO_2CH_3), 72.6 ($\mathrm{\mathit{C}H_2OPh}$, *para* to CO_2CH_3), 100–130 [m, $\mathrm{\mathit{C}F_3(\mathit{C}F_2)_5}$], 108.0, 125.3, 141.8, 152.6 (aromatic), 166.6 ($\mathrm{Ph\mathit{C}O_2CH_3}$). IR, ν_{max} (cm^{-1}): 1700 (C=O). Mp: 55 °C.

3,4,5-Tris(*n*-decan-1-yloxy)benzoic Acid (15-10/0). In a 250 mL round-bottom flask equipped with a condenser and Teflon-coated magnetic stir bar was placed 11.81 g (19.52 mmol) of **14-10/0**, 78 mL of 95% ethanol, and 7.7 g (140 mmol) of KOH pellets. The mixture was heated at reflux temperature for 30 min with stirring. The reaction mixture was acidified with 6 M HCl to pH = 1 and then poured into 100 mL H_2O with stirring. The product was filtered, washed with H_2O, and recrystallized from 2-propanol, resulting in 9.49 g (82.3%) of white solid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3), 1.27 [overlapped m, 36H, $\mathrm{(C\mathit{H}_2)_6}$], 1.47 (m, 6H, $\mathrm{C\mathit{H}_2CH_2CH_2OPh}$), 1.79 (m, 6H, $\mathrm{C\mathit{H}_2CH_2OPh}$), 4.02 (m, 6H, $\mathrm{C\mathit{H}_2OPh}$), 7.32 (s, 2H, $\mathrm{Ar\mathit{H}CO_2H}$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.1 ($\mathrm{\mathit{C}H_3}$), 22.7 ($\mathrm{\mathit{C}H_2CH_3}$), 26.1–30.3 [$\mathrm{(CH_2)_6}$], 31.9 ($\mathrm{\mathit{C}H_2CH_2CH_3}$), 69.1 ($\mathrm{\mathit{C}H_2CH_2OPh}$, *meta* to CO_2H), 73.5 ($\mathrm{\mathit{C}H_2OPh}$, *para* to CO_2H), 108.6, 123.7, 143.1, 152.8 (aromatic), 172.2 ($\mathrm{Ph\mathit{C}O_2H}$). IR, ν_{max} (cm^{-1}): 1680 (C=O). Mp: 51 °C. TLC, $R_f = 0$ (CH_2Cl_2). Thermal transitions and corresponding enthalpy changes are listed in Table 1.

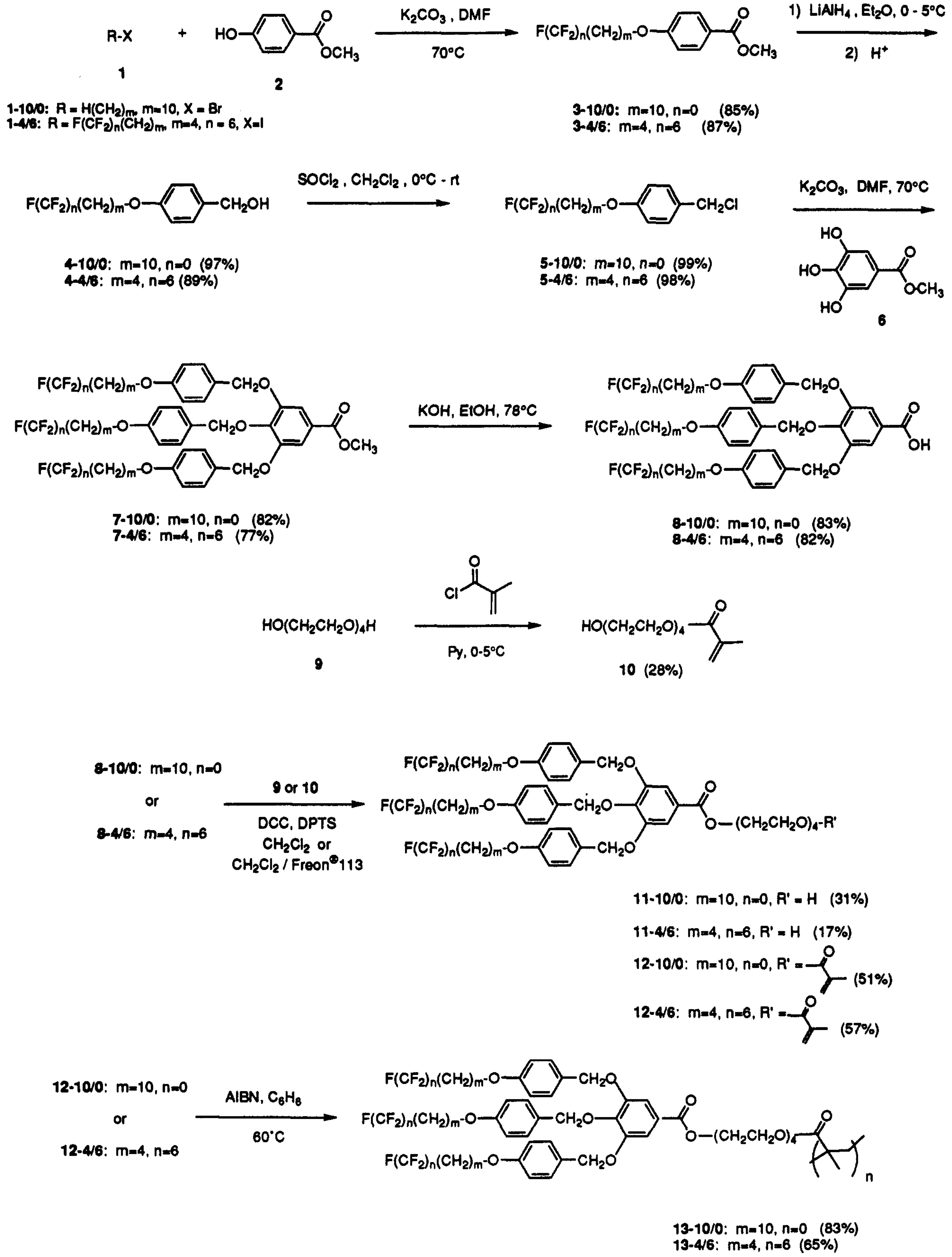
3,4,5-Tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoic Acid (15-4/6). Hydrolysis of 11.2 g (8.60 mmol) of **14-4/6** was performed as described for **14-10/0** to yield 10.8 g (97.7%) of white solid after recrystallization. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [overlapped m, 12H, $\mathrm{(C\mathit{H}_2)_2}$, *J* 6.7], 2.17 (m, 6H, $\mathrm{{-}CF_2C\mathit{H}_2}$, *J* 7.1), 4.09 (m, 6H, $\mathrm{{-}C\mathit{H}_2OPh}$, *J* 5.9), 7.34 (s, 2H, $\mathrm{Ar\mathit{H}CO_2H}$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.3 ($\mathrm{CF_2CH_2\mathit{C}H_2}$), 28.7 ($\mathrm{CF_2CH_2CH_2\mathit{C}H_2CH_2O}$, *meta* to CO_2H), 29.7 ($\mathrm{CF_2CH_2CH_2\mathit{C}H_2CH_2O}$, *para* to CO_2H), 30.6 (t, $\mathrm{CF_2\mathit{C}H_2}$, J_{C-F} 22.6), 68.4 ($\mathrm{\mathit{C}H_2OPh}$, *meta* to CO_2H), 72.7 ($\mathrm{\mathit{C}H_2OPh}$, *para* to CO_2H), 100–130 [m, $\mathrm{\mathit{C}F_3(\mathit{C}F_2)_5}$], 108.6, 124.2, 142.7, 152.6 (aromatic), 171.8 ($\mathrm{Ph\mathit{C}O_2H}$). IR, ν_{max} (cm^{-1}): 1690 (C=O). TLC, $R_f = 0$ (CH_2Cl_2). Thermal transitions and corresponding enthalpy changes are listed in Table 1.

2-{2-[2-(2-(Allyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-Tris(*n*-decan-1-yloxy)benzoate (17-10/0). A 100 mL round-bottom flask containing a Teflon-coated magnetic stir bar was charged with 1.51 g (2.54 mmol) of **15-10/0**, 0.761 g (3.05 mmol) of 2-{2-[2-(2-(allyloxy)ethoxy)ethoxy]ethoxy}ethanol (**16**), 10 mL of CH_2Cl_2, 0.16 g (0.51 mmol) of DPTS, and 0.68 g (3.3 mmol) of DCC. The mixture was stirred for 14 h at room temperature under Ar atmosphere. The crude mixture was filtered, and the filtrate solvent was removed by rotary evaporation. The residue was dissolved in hexanes and filtered again. The filtrate solvent was removed by rotary evaporator. The crude product was chromatographed on neutral Al_2O_3 (4:1 hexane/ethyl acetate eluent), resulting in 1.78 g (86.6%) of colorless liquid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, $\mathrm{C\mathit{H}_3}$), 1.27 [overlapped m, 42H, $\mathrm{(C\mathit{H}_2)_7}$], 1.74 (m, 6H, $\mathrm{C\mathit{H}_2CH_2OPh}$), 3.68 [overlapped m, 12H, $\mathrm{(OC\mathit{H}_2C\mathit{H}_2)_3}$], 3.82 (t, 2H, $\mathrm{PhCO_2CH_2C\mathit{H}_2O}$, *J* 5.0), 4.02 (overlapped m, 8H, $\mathrm{C\mathit{H}_2OPh}$, $\mathrm{C\mathit{H}_2CH{=}CH_2}$), 4.46 (t, 2H, $\mathrm{PhCO_2C\mathit{H}_2CH_2O}$, *J* 5.0), 5.05–5.30 (m, 2H, $\mathrm{CH_2CH{=}C\mathit{H}_2}$), 5.89 (m, 1H, $\mathrm{CH_2C\mathit{H}{=}CH_2}$), 7.26 (s, 2H, $\mathrm{Ar\mathit{H}CO_2CH_2}$). IR, ν_{max} (cm^{-1}): 1710 (C=O). TLC: $R_f = 0.28$ (2:1 hexane/ethyl acetate).

2-{2-[2-(2-(Allyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate (17-4/6). The esterification of 1.31 g (1.01 mmol) of **15-4/6** with 0.306 g (1.21 mmol) of 2-{2-[2-(2-(allyloxy)ethoxy)ethoxy]ethoxy}ethanol (**16**) was performed as described for **15-10/0** using 10:1 CH_2Cl_2/Freon 113 solvent to yield 1.32 g (84.8%) of colorless viscous liquid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [overlapped m, 12H, $\mathrm{(C\mathit{H}_2)_2}$], 2.17 (m, 6H, $\mathrm{{-}CF_2C\mathit{H}_2}$, *J* 8.8), 3.68 [overlapped m, 12H, $\mathrm{(C\mathit{H}_2C\mathit{H}_2O)_3}$], 3.83 (t, 2H, $\mathrm{PhCO_2CH_2C\mathit{H}_2O}$, *J* 4.9), 4.02 (overlapped m, 8H, $\mathrm{C\mathit{H}_2OPh}$, $\mathrm{C\mathit{H}_2CH{=}CH_2}$), 4.46 (t, 2H, $\mathrm{PhCO_2C\mathit{H}_2CH_2O}$, *J* 4.9), 5.05–5.30 (m, 2H, $\mathrm{CH_2CH{=}C\mathit{H}_2}$), 5.89 (m, 1H, $\mathrm{CH_2C\mathit{H}{=}CH_2}$), 7.29 (s, 2H, $\mathrm{Ar\mathit{H}CO_2CH_2}$). IR, ν_{max} (cm^{-1}): 1705 (C=O). TLC: $R_f = 0.3$ (1:1 hexanes/ethyl acetate).

2-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-Tris(*n*-decan-1-yloxy)benzoate (18-10/0). A 100 mL flask equipped with a condenser and a Teflon-coated magnetic stir bar was charged with 1.77 g (2.19 mmol) of **17-10/0**, 60 mL of MeOH, 0.215 g of 5% Pd on carbon, and 0.058 g (0.30 mmol) of *p*-toluenesulfonic acid. The reaction mixture was heated at 60 °C for 1.5 h. TLC analysis indicated complete depro-

Scheme 1. Synthesis of Poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate) (13-10/0) and Poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate) (13-4/6)



tection. The reaction mixture was filtered, and MeOH was removed by rotary evaporation. The residue was dissolved in $CHCl_3$ and washed three times with 100 mL portions of H_2O. The $CHCl_3$ solution was dried with $MgSO_4$. The mixture was filtered and the solvent evaporated, resulting in 1.36 g (80.8%) of colorless liquid. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, CH_3), 1.27 [overlapped m, 42H, $(CH_2)_7$], 1.77 (m, 6H, CH_2-CH_2OPh), 2.56 (br s, 1H, OH), 3.66 [overlapped m, 12H,

Table 1. Characterization of 8-*m*/*n*, 11-*m*/*n*, 12-*m*/*n*, 13-*m*/*n*, 15-*m*/*n*, 18-*m*/*n*, 19-*m*/*n*, and 20-*m*/*n*[a]

compd	yield (%)[b]	purity (HPLC) (%)	M_n (GPC)	M_w/M_n (GPC)	thermal transitions (°C) and enthalpy changes (kcal/mol or kcal/mru): heating	cooling
8-10/0	83	99			k_1 24, 33, 41 (2.12)[c] k_2 57 (0.08) k_3 80 (2.72) s 145 (2.96) i[d]	
8-4/6	82	99			k 80 (11.78) Φ_h 197 (4.30) i[d]	
11-10/0	31	99			k 24 (18.27) i[e] k 23 (18.04) i[e]	i 3 (17.12) k
11-4/6	17	99			k 34 (7.19) Φ_h 90 (1.06) i k 14 (3.96) Φ_h 89 (0.90) i	i 86 (0.85) Φ_h −2 (3.78) k
12-10/0	51	99			k 24 (12.59) i k 24 (13.09) i	i 7 (12.42) k
12-4/6	57	99			k_1 30 (10.19) k_2 41 (5.33) cu 61 (0.67) i k 6 (1.59) cu 61 (0.44) i	i 55 (0.48) cu −12 (1.53) k
13-10/0	83	100	16 900	1.6	g 3 Φ_h 66 (0.24) i g 2 Φ_h 66 (0.24) i	i 57 (0.23) Φ_h −7 g
13-4/6	65	100	22 800	1.2	g 14 Φ_h 200 (0.34) i g 13 Φ_h 195 (0.32) i	i 186 (0.33) Φ_h 6 g
15-10/0	82	99			k_1 7 (0.35) k_2 53 (13.03) i k_1 24 (−2.53) k_2 46 (10.31) i	i 2 (8.62) k
15-4/6	98	99			k 76 (28.15) Φ_h 79 (0.82) i k_1 30 (0.49) k_2 51 (1.99) Φ_h 79 (0.56) i	i 72 (0.57) Φ_h 43 (2.22) k
18-10/0	81	99			k 2 (11.39) i k 2 (11.41) i	i −16 (10.75) k
18-4/6	84	99			Φ_h 11 (0.20) i Φ_h 11 (0.21) i	i 3 (0.22) Φ_h
19-10/0	80	99			k_1 −8 (9.96) k_2 −2 (−12.19) k_3 14 (13.27) i[f]	
19-4/6	70	99			*g*	*g*
20-10/0	89	100	135 200	2.5	Φ_h 28 (0.14) i Φ_h 24 (0.14) i	i 15 (0.15) Φ_h
20-4/6	14	*h*	*h*	*h*	Φ_h 102 (0.42) i Φ_h 102 (0.19) i	i 83 (0.17) Φ_h

[a] Data collected from the first heating and cooling DSC scans are on the first line, and data from the second heating scan are on the second line (k = crystalline phase, s = smectic mesophase, Φ_h = hexagonal columnar mesophase, cu = cubic mesophase, i = isotropic phase). [b] Isolated. [c] Combined enthalpy. [c] Decomposition. [e] A narrow temperature range Φ_h phase is detectable above melting by optical microscopy and X-ray. [f] Polymerization. [g] Liquid to −30 °C. [h] Polymer insoluble in THF.

$\mathrm{OC}H_2\mathrm{C}H_2)_3\mathrm{OH}]$, 3.83 (t, 2H, $\mathrm{PhCO_2CH_2C}H_2\mathrm{O}$, *J* 5.0), 4.01 (m, 6H, $\mathrm{C}H_2\mathrm{OPh}$), 4.46 (t, 2H, $\mathrm{PhCO_2C}H_2\mathrm{CH_2O}$, *J* 5.1), 7.26 (s, 2H, $\mathrm{Ar}H\mathrm{CO_2CH_2}$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 14.1 ($\mathit{C}H_3$), 22.7 ($\mathit{C}\mathrm{H_2CH_3}$), 26.1−30.3 [$(\mathrm{CH_2})_6$], 31.9 ($\mathit{C}\mathrm{H_2CH_2CH_3}$), 61.8 ($\mathit{C}\mathrm{H_2OH}$), 64.0 ($\mathrm{PhCO_2}\mathit{C}\mathrm{H_2}$), 69.2 ($\mathit{C}\mathrm{H_2OPh}$, *meta* to $\mathrm{CO_2CH_2}$), 70.3−72.5 [$\mathrm{CH_2O(}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O)_2}\mathit{C}\mathrm{H_2}$], 73.5 ($\mathit{C}\mathrm{H_2OPh}$, *para* to $\mathrm{CO_2CH_2}$), 108.2, 124.6, 142.3, 152.8 (aromatic), 166.4 ($\mathrm{Ph}\mathit{C}\mathrm{O_2CH_2}$). IR, ν_{max} (cm^{-1}): 3200−3600 (OH), 1710 (C=O). GPC: 99%. TLC: R_f = 0.04 (2:1 hexane/ethyl acetate). Thermal transitions and corresponding enthalpy changes are listed in Table 1.

2-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate (18-4/6). The allyl ether deprotection was perfomed as described for **17-10/0**. From 1.32 g (0.865 mmol) of **17-4/6** was obtained 1.07 g (84.1%) of **18-4/6** as a colorless liquid. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [m, 12H, $(\mathrm{C}H_2)_2$, *J* 5.1], 2.17 (m, 6H, $-\mathrm{CF_2C}H_2$, *J* 8.8), 2.61 (broad s, 1H, $\mathrm{O}H$), 3.68 [overlapped m, 12H, $(\mathrm{C}H_2\mathrm{C}H_2\mathrm{O})_3$], 3.83 (t, 2H, $\mathrm{PhCO_2CH_2C}H_2\mathrm{O}$, *J* 5.6), 4.08 (overlapped m, 6H, $\mathrm{C}H_2\mathrm{OPh}$), 4.46 (t, 2H, $\mathrm{PhCO_2C}H_2\mathrm{CH_2O}$, *J* 5.4), 7.30 (s, 2H, $\mathrm{Ar}H\mathrm{CO_2CH_2}$). ^{13}C NMR, δ ($CDCl_3$, TMS, ppm): 17.3 (d, $\mathrm{CF_2CH_2}\mathit{C}\mathrm{H_2}$, *J* 3.2), 28.7 ($\mathrm{CF_2CH_2CH_2}\mathit{C}\mathrm{H_2CH_2O}$, *meta* to $\mathrm{CO_2CH_2}$), 29.7 ($\mathrm{CF_2CH_2CH_2}\mathit{C}\mathrm{H_2CH_2O}$, *para* to $\mathrm{CO_2CH_2}$), 30.6 (t, $\mathrm{CF_2}\mathit{C}\mathrm{H_2}$, J_{C-F} 22.5), 61.7 ($\mathit{C}\mathrm{H_2OH}$), 64.1 ($\mathrm{CO_2}\mathit{C}\mathrm{H_2}$), 68.4 ($\mathit{C}\mathrm{H_2OPh}$, *meta* to $\mathrm{CO_2CH_2}$), 69.3−72.5 [$\mathrm{CH_2(O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2)_2O}\mathit{C}\mathrm{H_2}$], 72.6 ($\mathit{C}\mathrm{H_2OPh}$, *para* to $\mathrm{CO_2CH_2}$), 100−130 [m, $\mathit{C}\mathrm{F_3(}\mathit{C}\mathrm{F_2)_5}$], 108.2, 125.2, 142.0, 152.5 (aromatic), 166.1 ($\mathrm{Ph}\mathit{C}\mathrm{O_2CH_2}$). IR, ν_{max} (cm^{-1}): 3200−3600 (OH), 1710 (C=O). GPC: 99%. TLC: R_f = 0.09 (1:1 hexanes/ethyl acetate). Thermal transitions and corresponding enthalpy values are listed in Table 1.

2-{2-[2-(2-(Methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-Tris(*n*-decan-1-yloxy)benzoate (19-10/0). A 25 mL three-neck round-bottomed flask containing a Teflon-coated magnetic stir bar was charged with 1.0 g (1.3 mmol) of **18-10/0**, 5 mL of CH_2Cl_2, and 0.3 mL of Et_3N. The flask was flushed with Ar and closed with an Ar inlet, rubber septum, and glass stopper. The reaction mixture was cooled in an ice bath and 0.15 mL (1.6 mmol) of methacryloyl chloride was added dropwise with a syringe. The ice bath was removed, and the reaction was stirred under an Ar atmosphere for 1.5 h. TLC analysis indicated complete reaction. The reaction mixture was diluted with 30 mL of CH_2Cl_2 and poured into 30 mL of H_2O. The organic phase was drawn off and washed with 30 mL of dilute HCl and with 30 mL of H_2O. The organic phase was dried with $MgSO_4$ and filtered and the solvent evaporated. The crude residue was chromatographed on neutral Al_2O_3 (3:1 hexanes/ethyl acetate eluent), resulting in 0.80 g (80%) of colorless liquid. ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 0.88 (t, 9H, $\mathrm{C}H_3$, *J* 7.1), 1.27 [overlapped m, 42H, $(\mathrm{C}H_2)_7$], 1.77 (m, 6H, $\mathrm{C}H_2\mathrm{CH_2OPh}$), 1.94 (s, 3H, $-\mathrm{COC(C}H_3\mathrm{)=CH_2}$), 3.65 [overlapped m, 10H, $(\mathrm{OC}H_2\mathrm{C}H_2)_2\mathrm{C}H_2$], 3.82 (t, 2H, $\mathrm{PhCO_2CH_2C}H_2\mathrm{O}$, *J* 5.1), 4.01 (t, 6H, $\mathrm{C}H_2\mathrm{OPh}$, *J* 6.0), 4.30 (t, 2H, $-\mathrm{C}H_2\mathrm{OCOC(CH_3)=CH_2}$, *J* 5.1), 4.46 (t, 2H, $\mathrm{PhCO_2C}H_2\mathrm{CH_2O}$, *J* 4.8), 5.57 (s, 1H, $\mathrm{COC(CH_3)=C}H_2$), 6.12 (s, 1H, $\mathrm{COC(CH_3)=C}H_2$), 7.26 (s, 2H, $\mathrm{Ar}H\mathrm{CO_2CH_2}$). IR, ν_{max} (cm^{-1}): 1705 (C=O), 1640 (C=C). GPC: 99%. TLC: R_f = 0.42 (1:1 hexane/ethyl acetate).

2-{2-[2-(2-(Methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-Tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate (19-4/6). The esterification of 1.0 g (0.68 mmol) of **18-4/6** and 0.08 mL (0.8 mmol) of methacryloyl chloride was performed as described for **18-10/0** to yield 0.73 g (70%) of colorless liquid after purification by column chromatography (neutral Al_2O_3, 2:1 hexanes/ethyl acetate). ^{1}H NMR, δ ($CDCl_3$, TMS, ppm): 1.89 [m, 12H, $(\mathrm{C}H_2)_2$, *J* 5.1], 1.95 [s, 3H, $\mathrm{COC(C}H_3\mathrm{)=CH_2}$], 2.17 (m, 6H, $-\mathrm{CF_2C}H_2$, *J* 8.8), 3.68 [overlapped m, 10H, $(\mathrm{C}H_2\mathrm{C}H_2\mathrm{O})_2\mathrm{C}H_2$], 3.82 (t, 2H, $\mathrm{PhCO_2CH_2C}H_2\mathrm{O}$, *J* 5.6), 4.08 (overlapped m, 6H, $\mathrm{C}H_2\mathrm{OPh}$), 4.30 (t, 2H, $-\mathrm{C}H_2\mathrm{OCOC(CH_3)=CH_2}$, *J* 5.1), 4.46 (t, 2H, $\mathrm{PhCO_2C}H_2\mathrm{CH_2O}$, *J* 4.6), 5.57 (s, 1H, $\mathrm{COC(CH_3)=C}H_2$), 6.12 (s, 1H, $\mathrm{COC(CH_3)=C}H_2$), 7.26 (s, 2H, $\mathrm{Ar}H\mathrm{CO_2CH_2}$). IR, ν_{max} (cm^{-1}): 1710 (C=O), 1640 (C=C). GPC: 99%. TLC: R_f = 0.35 (2:1 hexanes/ethyl acetate).

Poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris(*n*-decan-1-yloxy)benzoate) (20-10/0). A 25 mL Schlenk tube containing a Teflon-coated magnetic stir bar was charged with 0.64 g (0.77 mmol) of **19-10/0**, 1.9 mg (0.012 mmol) of AIBN, and 1.5 mL of benzene and sealed with rubber septum. The solution was subjected to five

Table 2. Characterization of 8-*m*/*n*, 11-*m*/*n*, 13-*m*/*n*, and 20-*m*/*n* by X-ray Diffraction Experiments

compd	T (°C)	d_{100} (Å)	$\langle d_{100}\rangle^a$ (Å)	d_{110} (Å)	d_{200} (Å)	a^b (Å)	R^b (Å)	S^b (Å)
8-10/0[e]	87	33.7			17.1	33.7[c]		
8-4/6[e]	89	37.9	37.8	21.8	18.9	43.6	21.8	25.2
11-10/0[e]	26	43.8	43.2[d]	24.6		49.9	24.9	28.8
11-4/6[e]	40	50.2	49.9	28.5	25.1	57.6	28.8	33.3
13-10/0[f]	23	49.4	50.1	29.1	25.3	57.9	28.9	33.4
13-4/6[g]	24	55.9	55.7	31.7	28.1	64.3	32.2	37.2
20-10/0[f]	24	40.2	40.2	22.9	20.3	46.4	23.2	26.8
20-4/6[f]	24	40.9	40.9	23.5	20.5	47.2	23.6	27.3

[a] $\langle d_{100}\rangle = [d_{100} + d_{110}(\sqrt{3}) + 2d_{200}]/3$. [b] $a = 2\langle d_{100}\rangle/\sqrt{3}$, $R = \langle d_{100}\rangle/\sqrt{3}$, $S = 2R/\sqrt{3}$. [c] Layer thickness. [d] $\langle d_{100}\rangle = [d_{100} + d_{110}(\sqrt{3})]/2$. [e] As received bulk. [f] Fiber. [g] Sheared film.

freeze–pump–thaw cycles, sealed, and stirred at 60 °C for 13 h. The crude reaction mixture was passed through a short neutral Al_2O_3 column to remove residual monomer, resulting in 0.57 g (89.4%) of polymeric solid. GPC: M_n = 135 200, DP(n) = 162, M_w/M_n = 2.5. ^1H NMR, δ ($CDCl_3$, TMS, ppm): 0.86 (br t, 9H, CH_3), 1.27 [overlapped m, 42H, $(CH_2)_7$], 1.77 (br m, 6H, CH_2CH_2OPh), 3.66 [overlapped m, 10H, $(OCH_2CH_2)_2CH_2$], 3.79 (t, 2H, $PhCO_2CH_2CH_2O$, *J* 6.6), 3.98 (t, 6H, CH_2OPh, *J* 4.8), 4.30 (br s, 2H, CH_2OCO), 4.42 (br s, 2H, $PhCO_2CH_2CH_2O$), 7.23 (s, 2H, $ArHCO_2CH_2$). Thermal transitions and corresponding enthalpy changes are listed in Table 1.

Poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate) (20-4/6). Radical polymerization of 0.67 g (0.84 mmol) of **19-4/6** was performed as described for **19-10/0**. Purification by column chromatography (neutral Al_2O_3, Freon 113) resulted in 0.09 g (14%) of polymeric solid. ^1H NMR, δ ($CDCl_3$/Freon 113, TMS, ppm): 1.89 [m, 12H, $(CH_2)_2$, *J* 5.1], 2.17 (m, 6H, $-CF_2CH_2$,), 3.68 [overlapped m, 10H, $(CH_2CH_2O)_2CH_2CH_2OCO$], 3.82 (br s, 2H, $PhCO_2CH_2CH_2O$), 4.08 (br s, 6H, CH_2OPh), 4.30 (br s, 2H, $-CH_2OCO$), 4.46 (br s, 2H, $PhCO_2CH_2CH_2O$), 7.26 (s, 2H, $ArHCO_2CH_2$). GPC: polymer was not soluble in THF. Thermal transitions and corresponding enthalpy changes are listed in Table 1.

Results and Discussion

Scheme 1 outlines the synthesis of **11-10/0** and **11-4/6**, of the corresponding methacrylates **12-10/0** and **12-4/6**, and of the polymethacrylates **13-10/0** and **13-4/6**. This sequence of reactions is almost similar to that reported previously for the preparation of the same series of compounds based on 3,4,5-tris[(*p*-(*n*-dodecan-1-yloxy)benzyl)oxy]benzoate.[1d] As in the previous case[1d] all reaction steps were accomplished in very high yields. The main difference from the present and previous procedure occurs in the synthesis of the methacrylates **12-10/0** and **12-4/6**. Previously,[1d] they were prepared by the esterification of the intermediary alcohols with methacryloyl chloride. In the present case we found that the synthesis of 2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethanol (**10**) from tetraethylene glycol and methacryloyl chloride followed by its esterification with **8-10/0** and **8-4/6** is more convenient for the preparation of methacrylates **12-10/0** and **12-4/6**. In addition, due to the insolubility of **8-4/6** in conventional solvents, its esterification with **10** was carried out in a 5:1 mixture of CH_2Cl_2/Freon 113. Radical polymerization of both **12-10/0** and **12-4/6** was performed in benzene at 60 °C. Both polymers were purified by column chromatography (Al_2O_3/hexane eluent for **13-10/0** and Al_2O_3/Freon 113 for **13-4/6**). Polymerization results are reported in Table 1.

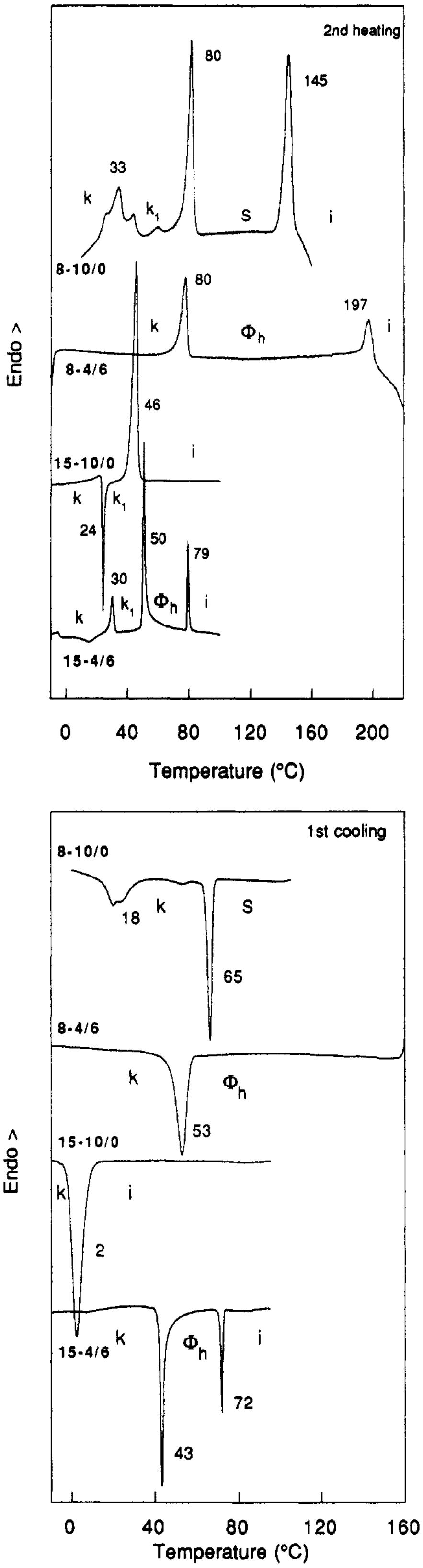


Figure 1. Second heating and first cooling DSC traces of 3,4,5-tris[[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoic acid (**8-10/0**), 3,4,5-tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoic acid (**8-4/6**), 3,4,5-tris(*n*-decan-1-yloxy)benzoic acid (**15-10/0**), and 3,4,5-tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoic acid (**15-4/6**).

The synthesis of **18-10/0**, **18-4/6**, **19-10/0**, **19-4/6**, **20-10/0**, and **20-4/6** is outlined in Scheme 2. It follows a modified reaction scheme which was used previously for the preparation of some related compounds with different *n*-alkyl tails.[1e] In the previous case[1e] the synthesis of compounds of type **18** was carried out by direct esterification of acids of type **15** with excess tetraeth-

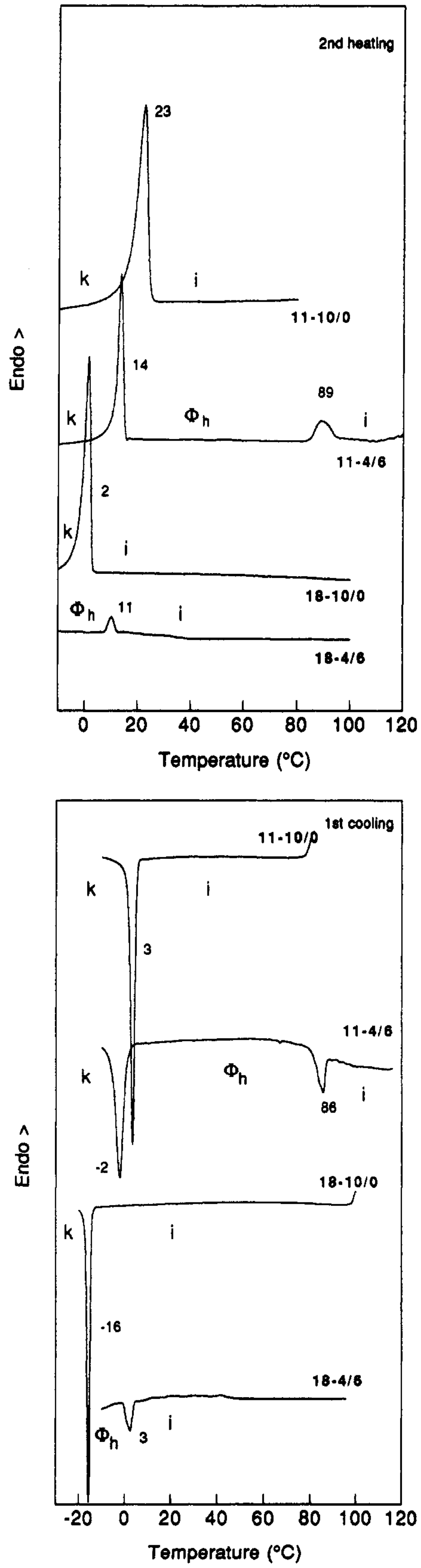


Figure 2. Second heating and first cooling DSC traces of 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate (**11-10/0**), 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate (**11–4/6**), 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris(*n*-decan-1-yloxy)benzoate (**18-10/0**), and 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate (**18-4/6**).

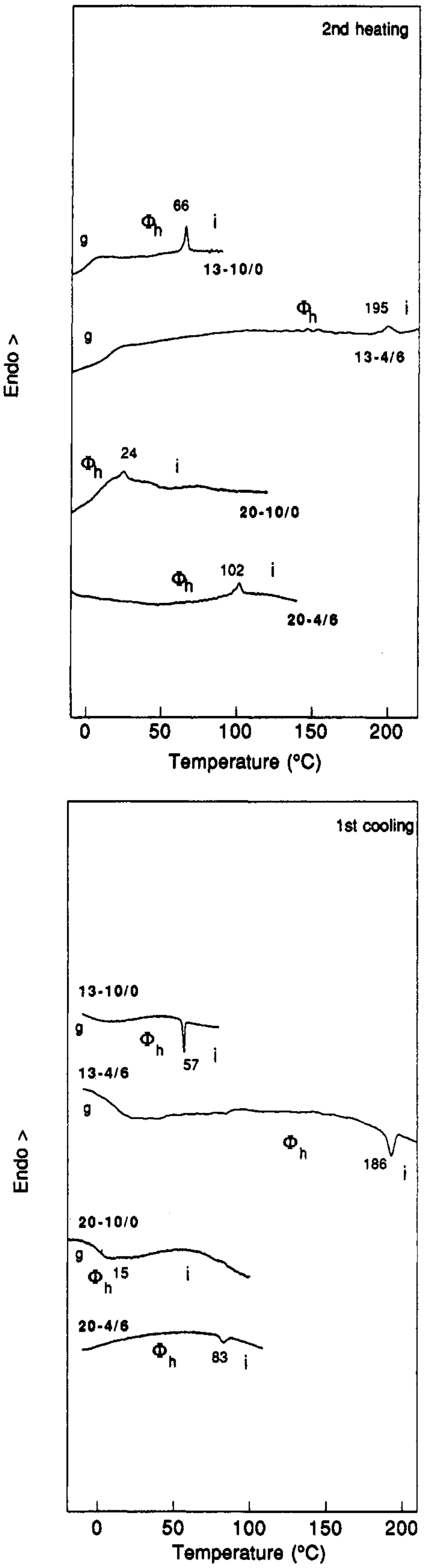
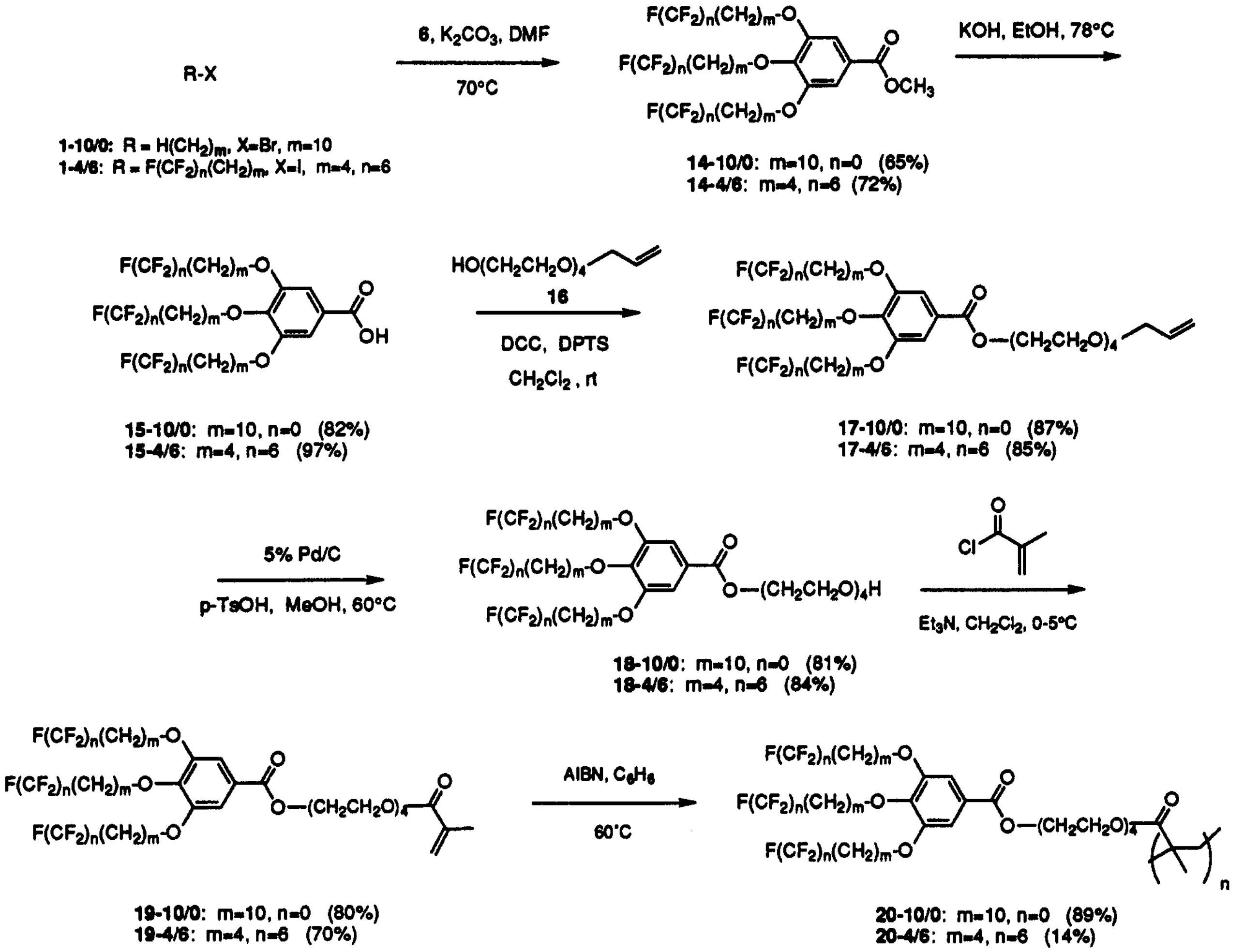


Figure 3. Second heating and first cooling DSC traces of poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate) (**13-10/0**), poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate) (**13-4/6**), poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris(*n*-decan-1-yloxy)benzoate) (**20-10/0**), and poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate) (**20-4/6**).

Scheme 2. Synthesis of Poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris(*n*-decan-1-yloxy)benzoate) (20-10/0) and Poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate) (20-4/6)



ylene glycol followed by extensive and tedious purification. In the present reaction scheme the acids **15-10/0** and **15-4/6** were esterified with **16**. The monoallyl ether of tetraethylene glycol can be conveniently prepared and purified.[9] The allyl ether protecting groups of **17-10/0** and **17-4/6** were easily cleaved by hydrogenolysis[11] to produce **18-10/0** and **18-4/6** in high yield. Monomers **19-10/0** and **19-4/6** were obtained by direct esterification of **18-10/0** and **18-4/6** with methacryloyl chloride. Radical polymerization of both monomers initiated with AIBN was performed in benzene at 60 °C. A very low yield of **20-4/6** was obtained due to the insolubility of the polymer in the polymerization solvent. Due to its insolubility in THF the molecular weight of **20-4/6** was not determined. The polymer structure and the absence of unreacted monomer was confirmed by ^{1}H NMR spectra recorded in a mixture of Freon 113/CDCl$_3$. The purities of all compounds presented in Schemes 1 and 2 are higher than 99% and are reported in Table 1.

All compounds were characterized by a combination of techniques consisting of differential scanning calorimetry (DSC), thermal optical polarized microsopy and X-ray diffraction experiments. The Φ_h phases of all these compounds exhibit fan-shape textures similar to those reported previously for related compounds.[1] Thermal transition temperatures were determined by DSC and the assignment of various phases of interest was done by X-ray diffraction and optical microscopy.

Figure 1 presents DSC second heating and first cooling traces of compounds **8** and **15**. Upon melting, **8-10/0** exhibits a smectic phase. The homologous acid containing *n*-dodecyl as alkyl tails exhibited a Φ_h mesophase.[1d] Replacing six of the ten methylene groups of the alkyl tails of **8-10/0** with perfluorinated groups yields **8-4/6**, which displays a Φ_h mesophase. The isotropization temperature of the Φ_h phase of **8-4/6** is 52 deg higher than that of the smectic phase of **8-10/0**. **15-10/0** is only crystalline, while **15-4/6** exhibits a Φ_h phase.

Figure 2 presents the DSC traces of compounds **11** and **18**. **11-10/0** is only crystalline. However, optical polarized microscopy and X-ray experiments show that **11-10/0** displays a very narrow temperature range Φ_h mesophase just above the melting temperature at 25 °C. The homologous compound with twelve methylene groups as alkyl tails exhibits a Φ_h phase.[1d] **11-4/6** exhibits a Φ_h phase which undergoes isotropization at 89 °C. **18-10/0** melts into an isotropic liquid at 2 °C, while its homologous compound **18-4/6** displays a Φ_h phase stable up to 11 °C.

Finally, the DSC traces of polymers **13** and **20** are presented in Figure 3. All polymers exhibit a Φ_h phase. The Φ_h phase of **13-10/0** undergoes isotropization at 66 °C, while the corresponding semifluorinated **13-4/6** does so at 195 °C. **20-10/0** shows a very narrow range for its Φ_h phase (isotropization at 24 °C). Upon fluorination, polymer **20-4/6** increases its isotropization to 102 °C.

All these DSC experiments demonstrate an extraordinary increase of the stability of a Φ_h phase of both

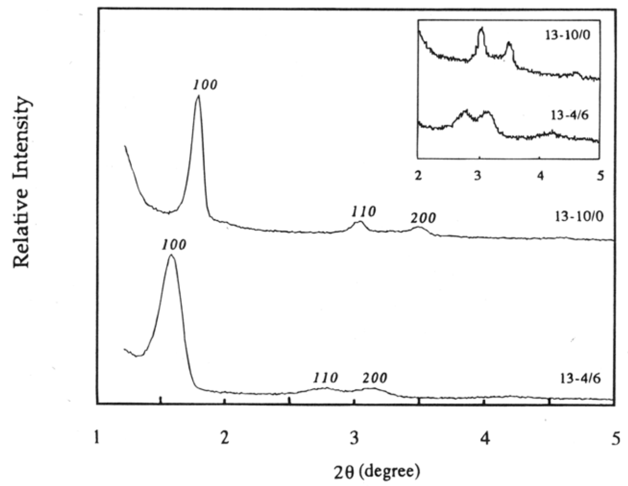


Figure 4. X-ray diffractograms of poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-(*n*-decan-1-yloxy)benzyl)oxy]benzoate) (**13-10/0**) and poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris[(4-((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzyl)oxy]benzoate) (**13-4/6**).

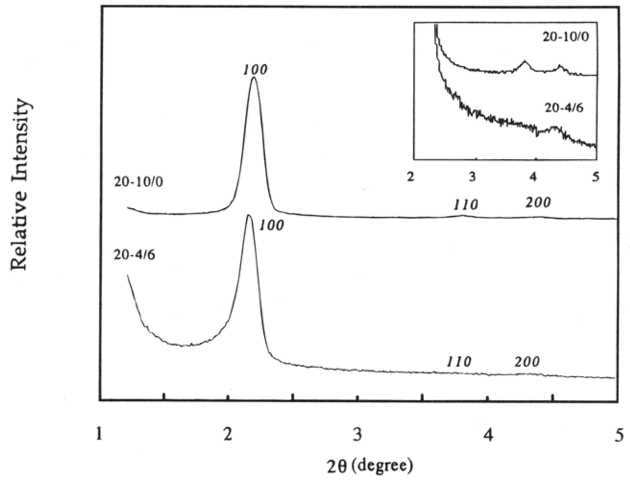


Figure 5. X-ray diffractograms of poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris(*n*-decan-1-yloxy)benzoate) (**20-10/0**) and poly(2-{2-[2-(2-(methacryloyloxy)ethoxy)ethoxy]ethoxy}ethyl 3,4,5-tris((5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-*n*-decan-1-yl)oxy)benzoate) (**20-4/6**).

monomers and polymers upon semifluorination of their alkyl tails. The thermal transitions and the corresponding assignments are summarized in Table 1. Interesting to mention is that monomer **12-4/6** exhibits a cubic mesophase followed by a polymerization process (Table 1). A complete characterization of this phase will be reported in a different publication.

The mesophases of these compounds were characterized by X-ray diffraction experiments, when possible on oriented samples, and the results are summarized in Table 2. Detailed discussions on the interpretation and calculation of various column parameters of Φ_h phases from X-ray results were presented elsewhere[1a,c,e] and will not be repeated here.

Figures 4 and 5 present two examples of X-ray diffraction patterns of Φ_h phases of homologous perhydrogenated and semifluorinated compounds. Besides the shift of their d spacings, a very significant difference exists in the enhanced intensity of the d_{200} diffraction after fluorination. Figure 4 compares the diffractograms of **13-10/0** and **13-4/6**, while Figure 5, those of **20-10/0** and **20-4/6**. Clear diffractions of d_{100}, d_{110}, and d_{200} in the expected ratios[1a,c,e] are observed. However, the ratio of the intensity $d_{110}/d_{200} > 1$ in **13-10/0** and **20-10/0** and <1 in **13-4/6** and **20-4/6**.

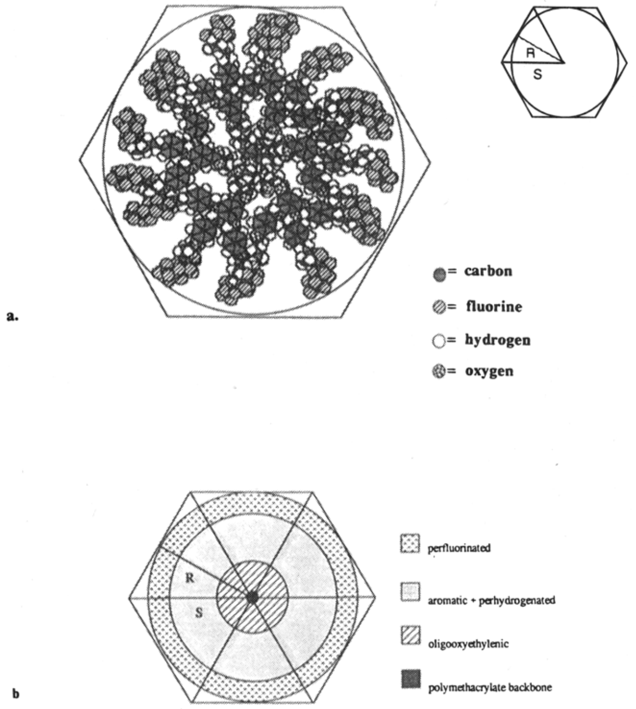


Figure 6. (a) Schematic representation of a top view of a column self-assembled from a polymer containing tapered side groups. (b) Schematic of a column cross-sectional area.

Table 2 summarizes the results of the characterization of all compounds in their smectic and Φ_h mesophases. Figure 6a presents a schematic of the top view of a column self-assembled from a polymer containing tapered side groups in the Φ_h phase. The polymer backbone penetrates through the center of the column and is surrounded by the oligo(oxyethylene) segment followed by the tapered side groups with their melted alkyl tails radiating toward the periphery of the column. The diameter (a), radius (R), and side (S) of the column are recorded in Figure 6a and reported in Table 2. An inspection of Tables 1 and 2 brings the following instructive information. The transition from **8-10/0** to **8-4/6** transforms the mesophase from smectic to Φ_h. This most probably means that **8-10/0** has a less tapered shape than **8-4/6**. The semifluorination of the alkyl tails of **11-10/0** and of the corresponding polymer **13-10/0** yields an increase of the column diameter. The diameter of the column resulting from polymer **13-4/6** is 6.4 Å larger than the diameter of the column resulting from **13-10/0**. The corresponding increase of the diameter of **11-4/6** is larger most probably due to the different temperature at which the values of **11-10/0** (26 °C) and **11-4/6** (40 °C) were recorded. It has been previously reported that an increase in temperature enhances the column diameter.[3c] The increase in the column diameter of compounds **11-4/6** and **13-4/6** may suggest that the dramatic enhancement of the stability of their Φ_h phase can be due to the enhanced stability of their tapered building blocks, which is induced by the higher rigidity of the semifluorinated segment which requires a higher melting temperature. At the same time the semifluorinated alkyl tail may generate a two-phase structure (fluorinated surface and hydrogenated core), as outlined in Figure 6b. A definitive explanation of this trend requires a systematic investigation of the thermal stability of the Φ_h phase as a function of the ratio between the perfluorinated and perhydrogenated lengths of the semifluorinated alkyl tail segments.

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