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Homeotropically Aligned Self-Organizing Dendronized Polymer

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Supporting Information

INTRODUCTION

Self-organizing dendronized polymers embody the bottom-up paradigm for the self-assembly of nanostructured materials.[1] The presence of a dendritic side chain on each repeat unit of the linear polymer backbone gives dendronized polymer chains a nanometer-sized diameter, and this dimension can be tailored though the generation number of the dendrons,[2] the peripheral groups on the dendrons,[3] or the branching number of the repeating unit in the dendrons. An additional degree of size and shape control is available by controlling the degree of polymerization of the dendronized polymer.[4] Short dendronized polymers can adopt a spherical shape or self-assemble to form larger cylindrical polymer objects, whereas long dendronized polymers are cylindrically shaped.[4a,5] Self-organization of these nanoscale molecular building blocks makes it possible to create ordered arrays over large areas.[6] Herein, we describe the synthesis and phase behavior of a dendronized polymer (Figure 1) that spontaneously orients perpendicular to the surface when sandwiched between glass slides.

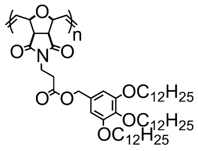

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Figure 1. Structure of the dendronized polymer **1**.

Thermotropic self-organization of dendronized polymers in bulk is a general phenomenon that has been demonstrated for a large number of different polymer backbones, but only with a narrow subset of dendrons. Percec and co-workers have meticulously investigated polymers dendronized with self-assembling benzyl ether-type dendrons.[2d,3−5,7] Mezzenga, Schlüter, and co-workers have demonstrated that complexes of anionic surfactants with cationic dendronized polymers form long-range liquid crystalline order in bulk.[8] Many of these dendrons exhibit liquid crystal mesomorphism in bulk based on phase segregation of peripheral hydrocarbon groups from the branched dendron.[9] Polymerization of these dendritic macromonomers stabilizes the liquid crystal mesophase through a molecular weight effect similar to that observed with side-chain liquid crystalline polymers.[5] Polymers dendronized with amphiphilic polyamide dendrons[10] or with amphiphilic poly(alkyl ether) dendrons[11] do not exhibit mesomorphism in bulk despite their apparent similarity to the examples noted above.

Dendronized polymer **1** was designed to investigate whether a mismatch between the size of the main-chain repeat unit and the size of the dendron will prevent dendronized polymers from self-organizing. We previously investigated the synthesis and bulk structure of poly(oxanorbornenedicarboximide)s dendronized with amphiphilic poly(alkyl ether) dendrons.[11] We polymerized dendritic macromonomers up to the third generation in a living manner and varied the length of the peripheral hydrocarbon chains from 10 to 22 carbons. All of the polymers are isotropic in the melt phase. Percec has reported dendronized poly(oxanorbornene)s that exhibit liquid crystalline phases based on amphiphilic benzyl ether-type dendrons.[5a,7a−c] We speculated that the number of dendrons attached to each repeat unit was a critical factor contributing to the marked difference in the phase behavior of Percec's dendronized polymers with two attached dendrons per repeat unit and ours with only one dendron per repeat unit. Dendronized polymer **1** retains the polymerizable group and linker from our previous study[11] and incorporates the first-generation dendron from Percec's seminal work[7a] on dendronized poly(oxanorbornene)s. Numerous polymers have been dendronized with the dendron in **1**, and in each case the dendronized polymers exhibit liquid crystalline phases.[2d,7a,12] The absence of a liquid crystalline phase in **1** would confirm that dense packing of the dendrons around the polymer backbone is critical to the emergent property of self-organization in dendronized polymers.

RESULTS AND DISCUSSION

The synthesis of dendronized polymer **1** is described in Figure 2. Anhydride **2** was obtained as a single diastereomer from the Diels−Alder reaction of furan and maleic anhydride.[13] In a two-step, one-pot sequence, anhydride **2** was reacted with β-alanine *tert*-butyl ester to afford **3** in 81% yield. Carboxylic acid **4** was obtained from **3** by TFA-catalyzed hydrolysis of the ester. We previously reported[11] that other routes[14] to prepare **4** were unsatisfactory in our hands, so we were pleased to obtain **4** in good overall yield. The first-generation dendritic alcohol **7** was prepared according to an established procedure.[4b] Williamson etherification of propyl gallate (**5**) with 1-bromododecane provided **6** in good yield. The alcohol was obtained by reduction of the ester with $LiAlH_4$. Carbodiimide-mediated condensation of alcohol **7** with carboxylic acid **4** proceeded smoothly, and the dendritic macromonomer **8** was obtained in good yield after purification by column chromatography. The identity and purity of the macromonomer were confirmed on

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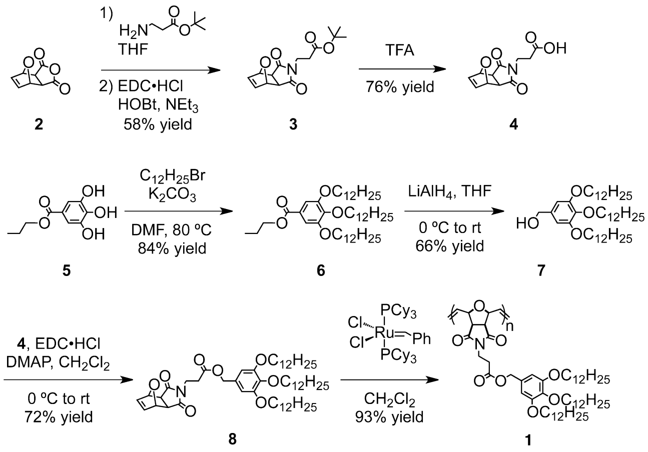

Figure 2. Synthesis and polymerization of dendritic macromonomer **8**.

the basis of ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, gel permeation chromatography (GPC), and elemental analysis.

Macromonomer **8** was subjected to ring-opening metathesis polymerization (ROMP) initiated with the first-generation Grubbs catalyst ($[M]_0/[I]_0 = 50$). The polymerization reaction was allowed to proceed until monomer was no longer observed in GPC of the reaction mixture and was then quenched by addition of ethyl vinyl ether. The polymerization reaction was complete after 5 h, and **1** was obtained in high yield. Dendronized polymer **1** was characterized by ^{1}H NMR spectroscopy to determine the ratio of *cis*:*trans* alkenes (33:77) and by GPC to confirm that the sample has a narrow distribution of molecular weights (M_n = 50 600, M_w/M_n = 1.06). The microstructure and molecular weight characteristics of the sample are similar to the polymers dendronized with poly(alkyl ether) dendrons previously reported by our group.[11]

Polymer **1** was characterized by observing the sample under polarized optical microscopy while heating the sample in a hot stage. When polymer **1** was sandwiched between a glass microscope slide and a glass coverslip, we observed the sample to undergo a melting transition from a birefringent solid to an isotropic liquid at 112 °C. Upon cooling to room temperature, the sample remained optically isotropic. Differential scanning calorimetry (DSC) experiments confirmed several first-order phase transitions up to the isotropization temperature (108 °C) in the first heating cycle and revealed two first-order phase transitions in subsequent cooling and heating cycles (Figure 3a). The DSC data are tabulated in Table 1, and these suggested that polymer **1** forms a mesophase that had been overlooked in our polarized optical microscopy experiments. To determine whether the optically isotropic appearance of polymer **1** was due to homeotropic alignment, we reexamined the sample sandwiched between a silanized glass microscope slide and coverslip. Indeed, the sample that was sandwiched between hydrophilic glass slides appears optically isotropic (Figure 3b) while the sample sandwiched between hydrophobic glass slides appears birefringent (Figure 3c). Planar alignment was also observed from a sample of polymer **1** prepared on a glass slide with no coverslip (see Supporting Information).[15] As is typical for liquid crystalline dendronized polymers, the birefringent texture did not contain any characteristic defects upon which to assign the phase. The difference between the appearances of polymer **1** in the two sample configurations suggests that the sample is homeotropically aligned.

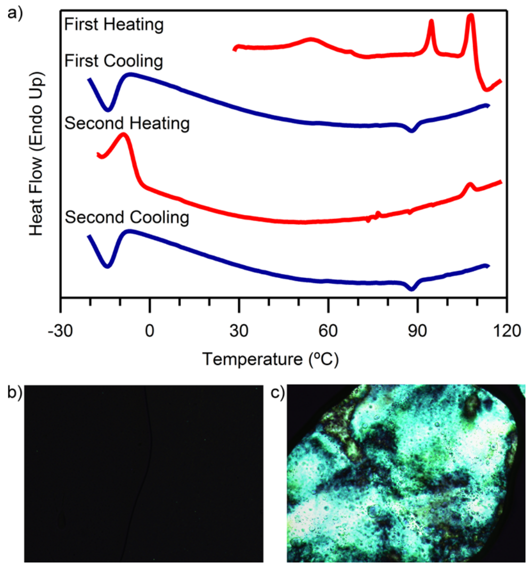

Figure 3. (a) DSC Thermograms from first and second heating–cooling cycles for dendronized polymer **1** (10 °C/min). Polarized optical micrographs of polymer **1** (b) sandwiched between glass slides and (c) sandwiched between silanized glass slides.

Table 1. Thermal Transition Temperatures (°C) and Corresponding Enthalpy Changes (kcal/mol)

cycle	
first heating	k 95 (0.27) k 108 (0.73) i
first cooling	k −14 (0.94) $\mathrm{Col_h}$ 88 (0.12) i
second heating	k −8.36 (1.11) $\mathrm{Col_h}$ 107 (0.10) i
second cooling	k −14 (0.92) $\mathrm{Col_h}$ 88 (0.12) i

Wide- and small-angle X-ray scattering studies of **1** were undertaken to confirm the presence of and assign the liquid crystalline phase. Data were acquired after cooling the sample from the isotropic melt phase to the liquid crystalline phase. A diffuse peak ($d = 2\pi/q \sim 0.455$ nm) corresponding to the melted peripheral alkyl chains was observed in the wide-angle scattering pattern. The small-angle scattering pattern contained one intense scattering peak and two weaker peaks in the ratio q_1:q_2:q_3 = 1:$\sqrt{3}$:2 (Figure 4a) from which we conclude that the dendronized polymer organizes in a hexagonal columnar lattice. The lattice parameter for polymer **1** at 80 °C was calculated to be 4.34 nm from eq 1.[16] The lattice parameter dimension is equivalent to the diameter of an individual column in the hexagonal lattice, so the diameter of a single chain of dendronized polymer **1** is 4.3 nm at this temperature (Figure 4b). The diameter of polymer **1** is similar to other polymers dendronized with the same first-generation dendron[2d,7a,12] including the poly(oxanorbornene) to which two of these dendrons are attached to each repeat unit.[7a] We calculated the end-to-end length for a molecular model of monomer **8** in an *all-trans* conformation to be 2.8 nm, so the diameter of the cylindrical polymer in the liquid crystalline phase is approximately twice the length of the dendronized polymer repeat unit. Tilting of the dendron relative to the column axis and *gauche* conformations in the alkyl chains would account for the difference between the calculated and observed column diameters (i.e., 5.6 nm vs 4.3 nm). The degree of tilting (∼50°) required to match the experimental column diameter has been observed in X-ray diffraction experiments with oriented fiber samples of dendronized polymers.[2d,3b,17] Close agreement

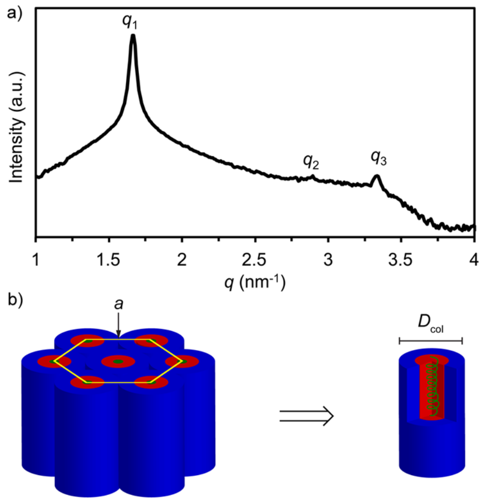

Figure 4. (a) Plot of the small-angle X-ray scattering intensity profile of polymer **1** at 80 °C. (b) Schematic diagram of hexagonally ordered cylindrical dendronized polymers in the liquid crystalline phase. The lattice parameter (a) calculated from the scattering data is equivalent to the diameter (D_{col}) of a dendronized polymer chain.

between the structure of the self-organized lattices of polymer **1** and the poly(oxanorbornene) with two dendrons attached to each repeat unit[7a] suggests that intramolecular self-assembly of the dendrons is able to overcome any mismatch between the size of the dendron and the size of the main chain repeat unit.

$$a = \frac{4\pi}{3\sqrt{3}}\left(\frac{1}{q_1} + \frac{\sqrt{3}}{q_2} + \frac{2}{q_3}\right) \tag{1}$$

A model for the hexagonal columnar lattice and core−shell structure of an individual cylindrical dendronized polymer is shown in Figure 4b. Such a model is intuitively reasonable based on the composition and shape of the dendrons. The peripheral alkyl chains constitute a majority of the repeat unit (f_{alkyl} = 0.80) and should make up the continuous domain of the mesophase. The tapered shape of the dendrons imposes a packing preference for the narrow apex of the dendron to form the core of the cylinder and the peripheral alkyl chains at the exterior of the cylinder[18] (i.e., an *exo*-recognition process[19]). The covalent connection between the dendron and the polymer backbone also restricts the arrangement of the dendrons and reinforces the packing of taper-shaped dendrons with the apex at the core of the cylinder.[18] Direct visualization through transmission electron microscopy experiments with self-assembling dendrons[9d] and polymers dendronized with self-assembling dendrons[20] has confirmed that the aromatic portion of the dendrons form the core of the cylinders and that the alkyl chains make up the continuous phase of the hexagonal lattice. It is worth noting that an alternative model in which alkyl chains comprise the cylinders and the dendronized polymers constitute the matrix of various columnar mesophases has been reported for self-organizing supramolecular complexes of dendronized polyelectrolytes with surfactants.[8c] Dendronized polymer **1** and other polymers dendronized with self-assembling dendrons are different from those supramolecular complexes because the arrangement of the alkyl chains in self-assembling benzyl ether-type dendrons is restricted by the conformations available to the dendron end groups. We conclude that the dendronized polymer **1** forms a hexagonally ordered two-dimensional lattice of cylinders that are each composed of a single poly(oxanorbornene) chain encapsulated by the self-assembling dendrons attached to each repeat unit.

Self-organization of polymer **1** is in marked contrast to the phase behavior of polymers dendronized with amphiphilic poly(alkyl ether) dendrons previously reported by us.[11] The diameter of polymer **1** in the liquid crystalline phase is similar to the diameters of the polymers dendronized with poly(alkyl ether) dendrons, so the poly(alkyl ether) dendrons are likely large enough to fully encapsulate the polymer backbone. A mismatch between the size of the polymer repeat unit and the size of the dendrons is an unlikely reason for why the amphiphilic poly(alkyl ether) dendrons did not endow the dendronized polymer with liquid crystalline properties. A plausible explanation for the difference between these dendronized polymers is that shape incompatibility between the branching groups and peripheral groups is critical to achieving phase segregation of the core and peripheral groups. The poly(alkyl ether) branching units are too similar to the peripheral alkyl groups, whereas the aromatic rings in polymer **1** segregate from the peripheral alkyl chains.

In the homeotropically aligned sample of dendronized polymer **1** the optically isotropic appearance of the sample results from the cylindrical polymers spontaneously orienting perpendicular to the glass surfaces. Self-assembling dendrons with semifluorinated peripheral groups[9b] and polymers dendronized via supramolecular interactions[6] with these dendrons have been reported to homeotropically align on glass surfaces. However, most derivatives of these semifluorinated dendrons[21] and covalently dendronized polymers with these semifluorinated dendrons[2d,7d] exhibit planar alignment rather than homeotropic alignment. There are no reports of dendronized polymers that spontaneously align perpendicular to the substrate surface. Dendronized polymer **1** is unique from other dendronized polymers because it exhibits homeotropic alignment.

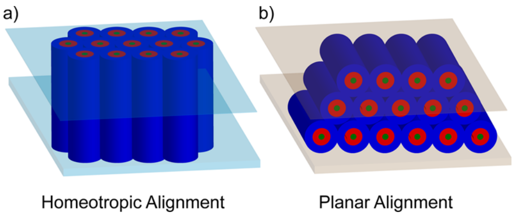

Figure 5. (a) Illustration of homeotropic alignment of dendronized polymer **1** between hydrophilic surfaces. (b) Illustration of planar alignment of dendronized polymer **1** between hydrophobic surfaces.

Homeotropic alignment of columnar mesophases on glass is attributed to interactions between polar functional groups in the mesogen with the polar surface.[22] We speculate that the polar functional groups of the poly(oxanorbornene-dicarboximide) backbone provide a similar driving force for homeotropic alignment. This is consistent with a model of the dendronized polymer in which the peripheral alkyl groups of the dendron make up the continuous domain of the mesophase. Increasing the number of dendrons covalently attached to the poly(oxanorbornene) backbone causes the self-organizing dendronized polymers to adopt a planar orientation parallel to the glass surface.[5a,7a] Self-organizing dendronized poly(oxanorbornene)s that exhibit planar alignment have a larger fraction of nonpolar functional groups than polymer **1**, and the polar interactions between the backbone and the surface contribute less to polymer−substrate interfacial energy.

■ CONCLUSION

Individual molecules and supramolecules that spontaneously produce functional nanostructured arrays are critical components to fulfill the vision of bottom-up self-assembly.[23] Self-organization into liquid crystalline lattices is an emergent property that can be exploited for simple processing of molecules into ordered nanostructures.[23] Dendronized polymers offer a combination of tunable structural features that can be exploited to endow these materials with desirable functions,[1] while only a narrow subset of dendronized polymers self-organize into lattices. We have identified from our unsuccessful attempt to observe self-organization in polymer dendronized with amphiphilic poly(alkyl ether) dendrons that shape incompatibility between the branching and peripheral groups is critical for creating self-organizing dendronized polymers. Furthermore, we have uncovered a unique example of a dendronized polymer that exhibits homeotropic alignment.

■ EXPERIMENTAL SECTION

Materials. Anhydrous tetrahydrofuran (THF, 99.9%), anhydrous dichloromethane (CH_2Cl_2, 98%), 4-(dimethylamino)pyridine (DMAP, 99%), trifluoroacetic acid (TFA, 99%), furan (≥99%), maleic anhydride (99%), β-alanine *tert*-butyl ester hydrochloride (98%), 2,5-dihydroxybenzoic acid (98%), ethyl vinyl ether (99%), and bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride (Grubbs catalyst, first generation, 97%) were used as received from Aldrich. Dichloromethane (CH_2Cl_2, A.C.S. reagent), chloroform ($CHCl_3$, A.C.S. reagent), *N*,*N*-dimethylformamide (DMF, 99.9%), and hydrogen chloride (HCl, A.C.S reagent) were used as received from EMD. Ethyl acetate (EtOAc, A.C.S. reagent), diethyl ether (Et_2O, A.C.S. reagent), acetone (A.C.S. reagent), and sodium hydroxide (NaOH, A.C.S. reagent) were used as received from Fisher. For the polymerization reactions, anhydrous CH_2Cl_2 was degassed by subjecting the solvent to three to four freeze−pump−thaw cycles. Sodium chloride (NaCl, A.C.S. reagent), anhydrous magnesium sulfate ($MgSO_4$, 99.9%), and potassium carbonate (K_2CO_3, A.C.S. reagent) were used as received from J.T. Baker. Triethylamine (NEt_3, 99%), 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 98%), lithium aluminum hydride powder ($LiAlH_4$, 97%), *n*-butyltrichlorosilane (97+%), and *n*-propyl gallate (**5**, 98%) were used as received from AlfaAesar. Hexanes (hex, A.C.S. reagent), methanol (MeOH, A.C.S. reagent), and tetrahydrofuran (THF, A.C.S. reagent) were used as received from BDH. 1-Bromododecane (98.0%) was used as received from TCI America. Chloroform-*d* with 0.03% v/v tetramethylsilane ($CDCl_3$, 99.8% D) and methanol-d_4 (CD_3OD, 99.9% D) were used as received from Cambridge Isotope Laboratories. 1-Hydroxybenzotriazole hydrate (HOBt) was used as received from Creosalus. Alumina basic powder (50−200 μm) was used as received from Dynamic Adsorbents. 4-(Dimethylamino)pyridinium tosylate (DPTS) was prepared according to a literature procedure.[24]

Techniques. Thin layer chromatography (TLC) was performed on 60 Å silica gel plates (250 μm, Whatman) and observed using a UV lamp (254 nm) or with $KMnO_4$ stain. Flash column chromatography was performed on a Teledyne Isco CombiFlash Rf with RediSep Rf Normal Phase disposable silica cartridges. NMR spectra were recorded on a Bruker NanoBay (^{1}H, 400 MHz; ^{13}C, 100 MHz) instrument or a Bruker AVANCE III instrument equipped with a Prodigy cold probe (^{1}H, 500 MHz; ^{13}C, 125 MHz). Peak multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, hept = heptet, sept = septet, and m = multiplet. Samples were dissolved in deuterated solvent, and chemical shifts (δ) are reported in ppm relative to tetramethylsilane signal at δ 0 ppm. Direct injection, low-resolution electrospray ionization mass spectrometry (ESI-MS) data were acquired in positive polarity mode on an Agilent LC-MSD with a G1956A single quadrupole mass spectrometer (accuracy ±0.1 amu). The MALDI-TOF data were recorded on a Bruker Autoflex II TOF/TOF workstation. MALDI-TOF samples (10 mg/mL) were prepared in THF with 2,5-dihydroxybenzoic acid as the matrix and silver trifluoroacetate as the ionizing species. Gel permeation chromatography (GPC) was performed on a LC-20AD liquid chromatography pump equipped with a DGU-20A5 degasser, CBM-20A controller, RID-10A RI detector, and CTO-20A column oven (all from Shimadzu) equipped with three American Polymer Standards AM GPC gel columns of 100 Å (5 μm), 500 Å (5 μm), and 10 000 Å (5 μm). Relative molecular weights and molecular weight distributions were determined according to a calibration made from narrow polydispersity polystyrene standards (American Polymer Standards). Polarized optical microscopy was performed on an Olympus BX43 optical microscope with a FP82HT hot stage and FP900 controller (both from Mettler Toledo). Melting point determinations were performed on a Thomas-Hoover Unimelt capillary melting point apparatus.

***exo*,*exo*-5,6-(Dicarboxylic anhydride)-7-oxabicyclo[2.2.1]-hept-2-ene (2).**[13] To a round-bottom flask, maleic anhydride (3.8432 g, 39.192 mmol), Et_2O (30 mL), and furan (4.4 mL, 61 mmol) were added. The mixture was refluxed for 16 h. The mixture was cooled, and the precipitate was collected by filtration and then rinsed three times with cold Et_2O. Compound **2** was obtained as a colorless solid (4.3131 g, 66%). TLC (CH_2Cl_2): R_f = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.59 (s, 2H), 5.47 (s, 2H), 3.20 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 169.9, 137.0, 82.2, 48.7. Spectral data agree with the literature.[25]

***N*-[2-(*tert*-Butoxycarbonyl)ethyl]-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo*,*exo*-dicarboxylic Imide (3).** A solution of **2** (4.2116 g, 25.351 mmol) and β-alanine *tert*-butyl ester hydrochloride (4.6437 g, 25.563 mmol) in dry THF (15 mL) was stirred for 7 h. To the solution, NEt_3 (3.6 mL), EDC·HCl (9.6940 g, 50.569 mmol), and HOBt (7.7942 g, 50.893 mmol) were added, and the mixture was stirred for 21 h. The solvent was removed *in vacuo*; the product was purified by column chromatography (SiO_2, hex to 1:1 hex/EtOAc) and then recrystallized from CH_2Cl_2 to give a solid weighing 6.01 g (81%). TLC (1:1 hex/EtOAc): R_f = 0.08. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.52 (s, 2H), 5.29 (s, 2H), 3.77 (t, J = 7.5 Hz, 2H), 2.87 (s, 2H), 2.07 (t, J = 7.5 Hz, 2H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 175.9, 169.8, 136.6, 80.9, 53.4, 47.4, 34.7, 33.2, 28.0.

***N*-[2-(Hydroxycarbonyl)ethyl]-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo*,*exo*-dicarboxylic Imide (4).** In a Schlenk tube, **3** (5.7142 g, 19.481 mmol) and cold TFA were combined. The solution was stirred for 2 h at room temperature. The product was precipitated into cold water, collected by filtration, rinsed with cold hexanes, and dried to obtain **4** as a colorless solid (3.5239 g, 76%). ^{1}H NMR (400 MHz, CD_3OD, δ): 6.56 (s, 2H), 5.17 (s, 2H, CH(O)), 3.72 (t, J = 7.8 Hz, 2H), 2.93 (s, 2H), 2.56 (t, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD, δ): 176.8, 172.8, 136.2, 80.8, 48.2, 34.1, 31.2. mp 135−136 °C (lit.[26] mp 132−134 °C). Spectral data agree with the literature.[26]

Propyl 3,4,5-Tris(*n*-dodecan-1-yloxy)benzoate (6).[7a] A solution of **5** (3.25 g, 15.3 mmol) in DMF (100 mL) was added dropwise to a solution of K_2CO_3 (18.72 g, 138.2 mmol) and 1-bromodecane (15.0 g, 60.2 mmol) in DMF (200 mL). The solution was stirred at 80 °C for 20 h. The reaction mixture was poured onto ice and filtered, and the resulting solid was dissolved in Et_2O and washed with water, dilute HCl, water, and saturated NaCl(aq). The organic layer was dried over $MgSO_4$. The solids were removed by filtration, and the volatiles were removed in vacuo. The resulting solid was purified by column chromatography (SiO_2, hex to 95:5 hex/EtOAc), giving **2** as a colorless solid (9.18 g, 84%). TLC (95:5 hex/EtOAc): R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.25 (s, 2H), 4.25 (t, J = 6.7 Hz, 2H), 4.01 (t, J = 6.5 Hz, 6H), 1.81 (m, 6H), 1.76 (m, 2H), 1.47 (m, 6H), 1.28 (overlapped m, 54H), 1.04 (t, J = 7.5 Hz, 3H), 0.90 (t, J = 6.8 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.5, 152.7, 142.3, 124.9, 107.9, 73.4, 69.1, 66.4, 31.8, 30.3, 29.7, 29.6, 29.5, 29.4, 29.3, 26.0, 22.6, 22.1, 14.1, 10.5. ESI−MS (m/z): $[M + H]^+$ calcd for $C_{46}H_{84}O_5$, 717.2; found, 717.6. GPC: M_n = 830, M_w/M_n = 1.06. The spectral data agree with literature.[7a]

3,4,5-Tris(*n*-dodecan-1-yloxy)benzyl Alcohol (7).[4b] A solution of **1** (9.75 g, 13.6 mmol) in dry THF (50 mL) was added dropwise to a suspension of $LiAlH_4$ (0.3 g, 8.5 mmol) in dry THF (125 mL) at 0 °C. The mixture was stirred at room temperature for 30 min. The reaction mixture was quenched with 0.3 mL of deionized water, 0.3 mL of 5% NaOH(aq), and 1 mL of deionized water and filtered to remove solids. Volatiles were removed in vacuo. The resulting solid was purified by column chromatography (SiO_2, 9:1 hex./EtOAc) and then recrystallized from acetone to give a colorless solid (5.95 g, 66%). TLC (9:1 hex/EtOAc): $R_f = 0.21$. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.58 (s, 2H), 4.61 (d, $J = 6.0$ Hz, 2H), 3.99 (m, 6H), 1.81 (m, 6H), 1.79 (t, $J = 6.0$ Hz, 1H), 1.47 (m, 6H), 1.29 (overlapped m, 48H), 0.90 (t, $J = 6.8$ Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 153.3, 137.6, 136.0, 105.4, 73.4, 69.1, 65.7, 31.9, 30.3, 29.8, 29.7, 29.4, 26.2, 26.1, 22.7, 14.1. ESI-MS (m/z): $[M + H]^+$ calcd for $C_{43}H_{80}O_4$, 661.1; found, 661.5. GPC: $M_n = 890$, $M_w/M_n = 1.05$. The spectral data agree with the literature.[4b]

***N*-[2-([3,4,5-Tris(*n*-dodecyloxy)benzyloxy]carbonyl)ethyl]-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo,exo*-dicarboxylic Imide (8).** A solution of **4** (0.3342 g, 1.409 mmol), **7** (0.5200 g, 1.513 mmol), and DTPS (0.0457 g, 0.1463 mmol) in anhydrous CH_2Cl_2 (5 mL) was cooled in an ice−water bath. To this solution, EDC·HCl (0.6158 g, 3.212 mmol) was added. After 5 min the solution was allowed to warm to room temperature, and stirring was continued for 22 h. The reaction solution was concentrated in vacuo. The resulting solid was purified by flash column chromatography (SiO_2, hex to 5:1 hex/EtOAc), which yielded **8** as a colorless solid (0.3994 g, 58%). TLC (5:1 hex/EtOAc): $R_f = 0.23$. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.56 (s, 2H), 6.53 (s, 2H), 5.27 (s, 2H), 5.01 (s, 2H), 3.97 (overlapped m, 6H), 3.83 (t, $J = 5.8$ Hz, 2H), 2.83 (s, 2H), 2.69 (t, $J = 5.9$ Hz, 2H), 1.80 (m, 6H), 1.50 (m, 6H) 1.29 (overlapped m, 48H), 0.90 (t, $J = 6.7$, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 175.8, 170.5, 153.2, 136.6, 130.4, 107.2, 80.9, 69.2, 67.1, 47.4, 34.6, 32.0, 29.7, 29.4, 26.1, 22.7, 14.1. MALDI-TOF (m/z): $[M + Na]^+$ calcd for $C_{54}H_{89}NNaO_8$, 902.65; found, 902.97. Anal. Calcd for $C_{54}H_{89}NO_8$: C, 73.68; H, 10.19; N, 1.59. Found: C, 73.80; H, 10.02; N, 1.47. GPC: $M_n = 1080$, $M_w/M_n = 1.06$.

Poly(*N*-[2-([3,4,5-tris(*n*-dodecyloxy)benzyloxy]carbonyl)-ethyl]-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo,exo*-dicarboxylic Imide) (1). A Schlenk tube was charged with a magnetic stir bar, first-generation Grubbs' catalyst (0.0019 g, 0.0023 mmol), and **8** (0.1008 g, 0.1145 mmol) and capped with a rubber septum. The tube was evacuated and filled with N_2 to degas. Degassed, anhydrous CH_2Cl_2 (2.4 mL) was added under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 4.5 h. Ethyl vinyl ether (1 mL) was added to the reaction vessel, and the reaction mixture was stirred for 5 min. The solution was precipitated into cold MeOH (60 mL), and the solid was collected by filtration. The product was taken up in 5:1 hex/EtOAc and passed through a column of basic Al_2O_3. The product was collected by filtration after precipitation into cold methanol (93.6 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.56 (s, 2H), 6.12 (s, 2H), 5.83 (s, 2H), 4.99 (s, 2H), 4.97 (s, 2H), 4.50 (s, 2H), 3.97 (overlapped m, 6H), 3.82 (s, 2H), 3.32 (s, 2H), 2.67 (s, 2H), 1.80 (overlapped m, 6H), 1.48 (overlapped m, 6H) 1.28 (overlapped m, 48H), 0.90 (t, $J = 6.7$ Hz, 9H). GPC: $M_n = 50\,600$, $M_w/M_n = 1.06$.

Preparation of Silanized Glass Slides. The glass microscope slide and coverslip were rinsed with acetone, washed with $CHCl_3$ by sonicating for 20 min, and then washed with CH_2Cl_2/water by sonicating for 20 min. Then, the glass and a beaker with 1 mL of *n*-butyltrichlorosilane were placed in a desiccator which was connected to a vacuum line. The desiccator was opened to vacuum until the silane boiled, and then the desiccator was closed and left overnight. After venting excess silane, the glass slides were baked for 12 h at 120 °C.

Differential Scanning Calorimetry (DSC). Thermal transitions were measured using a PerkinElmer Diamond thermogravimetric/differential thermal analysis module with a platinum−platinum rhodium 13% thermocouple in aluminum pans from PerkinElmer and analyzed using a Pyris software package. Calibration was with an indium reference. Samples were heated at 10 °C/min.

Wide- and Small-Angle X-ray Scattering. Wide- and small-angle X-ray scattering were obtained at the X27C beamline of the National Synchrotron Light Source, Brookhaven Naitonal Laboratory (Upton, NY). Scattering was detected from an X-ray wavelength of 0.137 nm with a Mar CCD 2-D area detector at temperatures controlled by an Instec temperature controller. Samples were sandwiched between Kapton tape in a steel washer which was loaded onto the hot stage. Scattering was measured for 10 s and was background corrected. The sample-to-detector distance for the wide-angle X-ray scattering measurements was 118 mm. The sample-to-detector distance for the small-angle X-ray scattering measurements was 801 mm. The data were analyzed in xPolar version 1.4.1.0 software from Precision Works NY.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional micrographs, comparison of core−shell models, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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