# Tubular Architectures from Polymers with Tapered Side Groups. Assembly of Side Groups *via* a Rigid Helical Chain Conformation and Flexible Helical Chain Conformation Induced *via* Assembly of Side Groups

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*Received August 23, 1995; Revised Manuscript Received December 7, 1995*[⊗]

ABSTRACT: Syntheses of *N*-[3,4,5-tris(*n*-dodecan-1-yloxy)phenyl]maleimide (**6**) and *exo,exo*-5,6-bis[[[3,4,5-tris(*n*-dodecan-1-yloxy)benzoyl]oxy]methyl]-7-oxabicyclo[2.2.1]hept-2-ene (**16**) and their polymerization by radical, anionic and ring opening metathesis polymerizations, respectively, to yield the corresponding polymers **7** and **17** are described. Regardless of the polymerization method by which it was synthesized, **7** produced a hexagonal columnar ($\Phi_h$) liquid crystalline phase generated from the tubular architecture of the rigid 7/2 helical chain conformation surrounded by its tapered side groups. **17** also produces a $\Phi_h$ phase. However, in this case, the assembly of tapered side groups of **17** into a tubular architecture induced a 3/1 helical chain conformation of its own flexible backbone. These two experiments support the model in which polymers containing tapered side groups form tubular supramolecular architectures by inducing a flexible helical chain conformation during the self-assembly of their own tapered side groups or by favoring the self-assembly of tapered side groups when a suitable rigid helical chain conformation is adopted by their own backbone.

## Introduction

We are designing tapered building blocks (*i.e.*, *exo*-receptors) containing *endo*-receptors and/or polymerizable groups that, after various complexation and/or polymerization processes, self-assemble into tubular supramolecular architectures.[1−4] The simplest tapered groups employed in our investigations are based on 3,4,5-tris[[(*n*-alkan-1-yloxy)benzyl]oxy]benzoic acid (*n*-ABG) and 3,4,5-tris(*n*-alkan-1-yloxy)benzoic acid (*n*-AG). In these self-assembling processes, the role of the tapered building block is similar to that of a brick in construction; through its shape it determines the final shape of the architecture generated, and through its size and surface smoothness it influences the stability of the construction. Additional stability is provided by the *endo*-receptor or by the polymer backbone (quasi *endo*-receptor), which plays a role similar to that of cement. For the preceding reasons, *n*-AG is the least efficient building block.

In the case of polymers containing *n*-ABG or *n*-AG tapered side groups attached directly or *via* an *endo*-receptor to their backbone, the supramolecular tubular architecture can be generated either by combining several relatively extended backbones within the center of a column or by a single backbone that adopts a helix-like conformation penetrating through the center of the column.[1−3] In both cases, the tapered side groups radiate towards the periphery of the column. For entropic reasons, the helix-like single-chain architectural model is preferred. The structural details of these columns are determined by analyzing the hexagonal columnar ($\Phi_h$) mesophase and/or the hexagonal crystalline phase generated by these supramolecular tubes by X-ray diffraction experiments.[1,3] We envision that an ideal combination between a rigid helical chain conformation and 12-AG type tapered side groups would favor the assembly of a tubular supramolecular architecture while a rigid linear chain would not. Alternatively, the attachment of 12-AG-based tapered side groups to a semiflexible backbone that has the ability to adopt a helical chain conformation will induce the helical conformation in the $\Phi_h$ phase. Experiments along this line would indirectly support the concept of a helical chain conformation rather than that based on a large number of extended chains penetrating through the center of the column for the formation of the supramolecular architecture.

It is well-known that poly(*N*-phenylmaleimide) is obtained with a predominantly *threo* diisotactic configuration, regardless of the polymerization mechanism.[5] It was suggested that the resulting backbone has a *3/1* helical conformation.[5,6] Also, *N*-phenylmaleimide polymerizes by a living anionic mechanism.[7] Molecular modeling experiments have indicated that if our suggested helical single-chain model is correct, poly[*N*-[3,4,5-tris(*n*-dodecan-1-yloxy)phenyl]maleimide] should generate a tubular supramolecular architecture that produces a $\Phi_h$ mesophase, in spite of its 12-AG tapered side groups being the least efficient in stabilizing the architecture. It has also been suggested that poly[*exo,*-*exo*-5,6-bis(disubstituted)-7-oxabicyclo[2.2.1]hept-2-ene] derivatives have (in solution) the ability to form a helical structure with all of the tetrahydrofuran oxygens facing into the interior of the *helix*.[8a,b] Even if a recent publication demonstrates that these polymers adopt a coil conformation in solution,[9] this does not demonstrate that they do not have the ability to form helical structures as originally suggested.[8a,b]

We became interested in 7-oxabicyclo[2.2.1]hept-2-ene-based monomers for several different reasons. Their

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

polymers are able to adopt various chain conformations with complexation capabilities. These monomers are easily functionalized and can be polymerized by various Ru-based catalysts that tolerate a large variety of functional groups,[8−10] such as those present in the structures of 12-ABG and 12-AG. Molecular models of the polymers based on the 7-oxabicylco[2.2.1]hept-2-ene derivative containing 12-AG groups have demonstrated that they produce a tubular architecture only when the backbone adopts a helical conformation. A positive result based on this hypothesis will be significant for at least two different reasons. First, it will demonstrate that this backbone does, as originally suggested,[8] have the ability to form helical structures. Second, it will support the concept that the tubular supramolecular architecture based on a single helical chain penetrating through the center of the column can induce helical chain conformations in flexible polymers *via* the assembly of their tapered side groups.

The goal of this paper is to report the syntheses of *N*-[3,4,5-tris(*n*-dodecan-1-yloxy)phenyl]maleimide and *exo*,*exo*-5,6-bis[[[3,4,5-tris(*n*-dodecan-1-yloxy)benzoyl]oxy]methyl]-7-oxabicyclo[2.2.1]hept-2-ene, their polymerization by radical, anionic and metathesis mechanisms, respectively, and the characterization of the resulting polymers. Both monomers produced polymers displaying $\Phi_h$ phases, which are generated from supramolecular columns derived from a helical single-chain conformation surrounded by tapered side groups.

## Experimental Section

**A. Materials.** 1,2,3-Trihydroxybenzene (99%), 1-bromododecane (98%), tetrabutylammonium bromide (TBAB) (99%), $NH_2NH_2 \cdot H_2O$ (98%), methyl 3,4,5-trihydroxybenzoate (98%), $LiAlH_4$ (95%), $RuCl_3 \cdot xH_2O$ (99%), and basic chromatographic $Al_2O_3$ (all from Aldrich) were used as received. Graphite powder, $HNO_3$ (ACS reagent), sodium acetate (NaOAc) (anhydrous, ACS reagent), $SiO_2$ gel (all from Fisher Scientific), $SiO_2$ thin layer chromatography sheets with fluorescent indicator (Kodak), and other conventional reagents were used as received. Benzene (thiophene free, Fisher Scientific) used for the free radical polymerizations was washed three times with concentrated $H_2SO_4$ and dried over $MgSO_4$. Benzene, $Et_2O$, and THF were dried by reflux over sodium/benzophenone ketyl under inert atmosphere and were freshly distilled before use. $HNO_3$ supported on silica gel ($HNO_3 \cdot SiO_2$) was prepared according to a literature procedure.[11] Silica gel (60−200 mesh, Fisher Scientific) was stirred with 8 N $HNO_3$ (840 mL, 6.7 mol). The $HNO_3 \cdot SiO_2$ was filtered, rinsed several times with water, and dried in air for 1 week. The acid content was determined by titration with a 0.1 N NaOH solution, using phenolphthalein as an indicator. Anhydrous *t*-BuOK was prepared in the following way. A Pyrex tube was charged with several grams of *t*-BuOK (Aldrich, 97%) and fitted to a Schlenk receiving tube equipped with a 45° angled neck. After *t*-BuOK was dried for 1 h at 100 °C under vacuum, the Schlenk tube was cooled in a dry ice/acetone bath and *t*-BuOK was sublimed by heating over an open flame under high vacuum. $SOCl_2$ (Aldrich, 97%) was distilled from quinoline. Pyridine was dried, distilled, and stored over KOH. $CH_2Cl_2$ was dried over $CaH_2$ and distilled. *N*,*N*′-dimethylformamide (Fisher) was dried over $CaH_2$, filtered, and distilled under vacuum. Furan (Aldrich, 99%) was washed twice with 5% KOH, dried over $Na_2SO_4$, filtered, and distilled from solid KOH under Ar. Maleic anhydride (Aldrich) was dissolved in $CHCl_3$, filtered through silica gel, and recrystallized from $CHCl_3$. $LiSO_3CF_3$ (Aldrich) was dried at 120 °C *in vacuo* overnight. $(Ph_3P)_2Cl_2Ru{=}CHCH{=}CPh_2$ was prepared by a literature procedure.[12]

**B. Techniques.** $^1H$ NMR (200 MHz) and $^{13}C$ NMR (50 MHz) spectra were recorded on a Varian Gemini 200 spectrometer at 20 °C with a tetramethylsilane (TMS) internal standard. IR spectra were recorded on a Perkin-Elmer 1320 spectrometer. Melting points were determined by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. The purity of products was determined by a combination of thin layer chromatography (TLC) on silica gel plates with a fluorescent indicator and high-pressure liquid chromatography (HPLC) using a Perkin-Elmer Series 10 high-pressure liquid chromatograph equipped with an LC-100 column oven (40 °C), a Nelson Analytical 900 Series integrator data station, and two Perkin-Elmer PL gel columns of $5 \times 10^2$ and $1 \times 10^4$ Å, using THF as eluent at 1 mL/min. Detection was by UV absorbance at 254 nm. Weight-average ($M_w$) and number-average ($M_n$) molecular weights were determined on the same instrument from a calibration plot constructed from polystyrene standards. Thermal transitions were measured on a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC). The heating and cooling rates were 10 °C min$^{-1}$ unless otherwise noted. First-order transition temperatures were reported as the maxima and minima of their endothermic and exothermic peaks. Glass transition temperatures ($T_g$) were read at the middle of the change in heat capacity. Indium and zinc were used as calibration standards. X-ray scattering patterns were recorded by using either a helium-filled, flat plate, wide angle (WAXS) camera or a pinhole-collimated, small angle (SAXS) camera and also by using an Image Plate area detector (MAR Research) with a graphite-monochromatized pinhole-collimated beam and a helium tent. The samples, in glass capillaries, were held in a temperature-controlled cell (±0.1 °C). Ni-filtered Cu Kα radiation was used. Densities ($\rho$) were determined by flotation in gradient columns. An Olympus BX-40 optical polarized microscope (100× magnification) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to verify thermal transitions and characterize anisotropic textures. Molecular modeling was performed on CSC Chem3D from Cambridge Scientific Computing, Inc.

**C. Syntheses. 1. 3,4,5-Tris(*n*-dodecan-1-yloxy)benzene (2).** To a round-bottom flask equipped with a $N_2$ inlet−outlet, containing a stirring mixture of 1,2,3-trihydroxybenzene (31.5 g, 0.25 mol) and $K_2CO_3$ (249 g, 1.20 mol) in 400 mL of DMF at 60 °C, was added 1-bromododecane (176.5 g, 0.600 mol) in small portions over 10 min, followed by the addition of TBAB (0.5 g, 0.3 mol %). After 4 h at 60 °C, the reaction mixture was poured into 2 L of vigorously stirring ice−water. The creamy, granular solid was filtered and washed with water. After two recrystallizations from a $CHCl_3$/MeOH (1:1) mixture, 94.8 g (75.1%) of a white solid was obtained: mp 39.5−40.5 °C; $R_f$ = 0.7 (19:1 hexanes/ethyl acetate); $^1H$ NMR ($CDCl_3$, TMS) $\delta$ 0.88 (t, 9H, $CH_3$), 1.26 (overlapped peaks, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.78 (m, 6H, $CH_2CH_2O$), 3.90 (overlapped t, 6H, $CH_2O$), 6.55 (d, 2H, 4,6-positions), 6.90 (d, 1H, 5-position); $^{13}C$ NMR ($CDCl_3$, TMS) $\delta$ 14.1 ($CH_3$), 22.7 ($CH_3CH_2$), 26.1 ($CH_2CH_2CH_2O$), 29.4 ($CH_3CH_2CH_2CH_2$), 29.5 ($CH_3CH_2CH_2CH_2(CH_2)_5$), 29.9 ($CH_2CH_2O$, 1,3-positions), 30.3 ($CH_2CH_2O$, 2-position), 31.9 ($CH_3CH_2CH_2$), 69.0 ($CH_2O$, 1,3-positions), 73.3 ($CH_2O$, 2-position), 106.7 (4,6-positions), 123.1 (5-position), 138.4 (2-position), 153.4 (1,3-positions). Anal. Found (calcd): C, 79.73 (79.93); H, 12.63 (12.46).

**2. 3,4,5-Tris(*n*-dodecan-1-yloxy)-1-nitrobenzene (3).** Compound **3** was synthesized by the nitration of **2** with $SiO_2 \cdot HNO_3$ according to a literature procedure.[11,13] Over a stirred suspension of $HNO_3$ (63 g, 0.25 mol, 25% on $SiO_2$) in 400 mL of $CH_2Cl_2$ was rapidly added **2** (31.6 g, 0.050 mol) in 100 mL of $CH_2Cl_2$. The resulting red solution was stirred at room temperature for 15 min, after which time the $SiO_2$ was filtered and washed several times with $CH_2Cl_2$. The solvent was evaporated on a rotary evaporator, and the resultant orange oil was dissolved in 50 mL of hexanes. Upon the addition of 600 mL of MeOH with vigorous shaking, the product separated as a yellow solid. The solid was filtered, washed with cold MeOH, and dried in air. Recrystallization from a $CHCl_3$/MeOH (1:1) mixture at −20 °C yielded 28.0 g (82.8%) of a white solid: mp 54.5−55.5 °C (lit. mp[14] 58−59 °C); $R_f$ = 0.5 (19:1 hexanes/ethyl acetate); $^1H$ NMR ($CDCl_3$, TMS) $\delta$,0.88 (t, 9H, $CH_3$), 1.26 (overlapped peaks, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.78 (m, 6H, $CH_2CH_2O$), 4.04 (overlapped t, 6H, $CH_2O$), 7.47 (s, 2H, Ar*H*); $^{13}C$ NMR ($CDCl_3$, TMS) $\delta$ 14.1 ($CH_3$), 22.7 ($CH_3CH_2$), 26.1 ($CH_2CH_2CH_2O$), 29.4 ($CH_3CH_2CH_2CH_2$), 29.5 ($\mathrm{CH_3CH_2CH_2CH_2(\mathit{C}H_2)_5}$), 29.9 ($\mathrm{\mathit{C}H_2CH_2O}$, 3,5-positions), 30.3 ($\mathrm{\mathit{C}H_2CH_2O}$, 4-position), 31.9 ($\mathrm{CH_3CH_3\mathit{C}H_2}$), 69.3 ($\mathrm{\mathit{C}H_2O}$, 3,5-positions), 73.7 ($\mathrm{\mathit{C}H_2O}$, 4-position), 101.9 (*ortho* to $\mathrm{NO_2}$), 143.0 (*ipso* to $\mathrm{NO_2}$), 144.0 (*para* to $\mathrm{NO_2}$), 152.6 (*meta* to $\mathrm{NO_2}$). Anal. Found (calcd): C, 74.24 (74.61); H, 11.88 (11.48); N, 2.02 (2.07).

**3. 3,4,5-Tris(*n*-dodecan-1-yloxy)-1-aminobenzene (4).** Compound **4** was synthesized by the reduction of **3** with $\mathrm{NH_2NH_2{\cdot}H_2O}$ over graphite powder.[13−15] Compound **3** (40.6 g, 0.600 mol), $\mathrm{NH_2NH_2{\cdot}H_2O}$ (15.0 g, 0.20 mol), and graphite (30 g) were heated in 400 mL of reluxing EtOH for 24 h under an Ar atmosphere. The cooled mixture was diluted with 400 mL of $\mathrm{CH_2Cl_2}$. Graphite was filtered and washed several times with $\mathrm{CH_2Cl_2}$. The colorless solution was concentrated in a rotary evaporator, and the resultant white solid was dissolved in 300 mL of $\mathrm{CH_2Cl_2}$. After precipitation in 2 L of MeOH, the white solid obtained was collected by filtration and washed with cold MeOH. After drying under vacuum over $\mathrm{P_2O_5}$, 36.0 g (92.8%) of a white powder was obtained: mp 71.5−72.5 °C (lit. mp[14] 75 °C); $R_f = 0.25$ (9:1 hexanes/ethyl acetate); IR (KBr, $\mathrm{cm^{-1}}$) 3414, 3335, 3210 (NH); $^{1}\mathrm{H}$ NMR ($\mathrm{CDCl_3}$, TMS) $\delta$ 0.88 (t, 9H, $\mathrm{C\mathit{H}_3}$), 1.26 (overlapped peaks, 48H, $\mathrm{CH_3(C\mathit{H}_2)_8}$), 1.46 (m, 6H, $\mathrm{C\mathit{H}_2(CH_2)_2O}$), 1.76 (m, 6H, $\mathrm{C\mathit{H}_2CH_2O}$), 3.46 (bs, 2H, $\mathrm{N\mathit{H}_2}$), 3.84 (t, 2H, $\mathrm{C\mathit{H}_2O}$ on 4-position), 3.91 (t, 4H, $\mathrm{C\mathit{H}_2O}$ on 3,5-positions), 5.91 (s, 2H, *ortho* to $\mathrm{NH_2}$); $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$, TMS) $\delta$ 14.1 ($\mathrm{\mathit{C}H_3}$), 22.7 ($\mathrm{CH_3\mathit{C}H_2}$), 26.1 ($\mathrm{CH_2\mathit{C}H_2CH_2O}$), 29.4 ($\mathrm{CH_3CH_2CH_2\mathit{C}H_2}$), 29.5 ($\mathrm{CH_3CH_2CH_2CH_2(\mathit{C}H_2)_5}$), 29.9 ($\mathrm{\mathit{C}H_2CH_2O}$, 3,5-positions), 30.3 ($\mathrm{\mathit{C}H_2CH_2O}$, 4-position), 31.9 ($\mathrm{CH_3CH_3\mathit{C}H_2}$), 68.8 ($\mathrm{\mathit{C}H_2O}$, 3,5-positions), 73.5 ($\mathrm{\mathit{C}H_2O}$, 4-position), 94.3 (*ortho* to $\mathrm{NH_2}$), 130.2 (*para* to $\mathrm{NH_2}$), 142.3 (*ipso* to $\mathrm{NH_2}$), 153.6 (*meta* to $\mathrm{NH_2}$). Anal. Found (calcd): C, 78.28 (78.07); H, 12.67 (12.33); N, 2.12 (2.17).

**4. *N*-[3,4,5-Tris(*n*-dodecan-1-yloxy)phenyl]maleamic acid (5).** Compound **5** was synthesized by the condensation of **4** with maleic anhydride.[16] To a solution of maleic anhydride (1.36 g, 14.0 mmol) in 40 mL aof cetic acid (AcOH) was slowly added **4** (6.46 g, 10.0 mmol) in 30 mL of $\mathrm{CHCl_3}$ at room temperature. The yellow suspension was stirred for 1 h, after which time 50 mL of MeOH was added. The mixture was filtered and the solid was washed with MeOH and dried in air. After recrystallization from 2-propanol, 6.10 g (81.0%) of a bright yellow solid was obtained: mp 131−132 °C; IR (KBr, $\mathrm{cm^{-1}}$) 3525 (OH), 1711 (COOH), 1694 (CONH); $^{1}\mathrm{H}$ NMR ($\mathrm{CDCl_3}$, TMS) $\delta$ 0.88 (t, 9H, $\mathrm{C\mathit{H}_3}$), 1.26 (overlapped peaks, 48H, $\mathrm{CH_3(C\mathit{H}_2)_8}$), 1.46 (m, 6H, $\mathrm{C\mathit{H}_2(CH_2)_2O}$), 1.76 (m, 6H, $\mathrm{C\mathit{H}_2CH_2O}$), 3.95 (t, 6H, $\mathrm{C\mathit{H}_2O}$), 6.40 (d, 1H, $\mathrm{NHCOC\mathit{H}{=}CHCO_2H}$, $J = 12.9$ Hz), 6.90 (s, 2H, Ar$H$), 8.84 (s, 1H, N$H$); $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$, TMS) $\delta$ 14.1 ($\mathrm{\mathit{C}H_3}$), 22.7 ($\mathrm{CH_3\mathit{C}H_2}$), 26.1 ($\mathrm{CH_2\mathit{C}H_2CH_2O}$), 29.3−29.7 ($\mathrm{CH_3CH_2CH_2(\mathit{C}H_2)_6}$), 29.9 ($\mathrm{\mathit{C}H_2CH_2O}$, 3,5-positions), 30.3 ($\mathrm{\mathit{C}H_2CH_2O}$, 4-position), 31.9 ($\mathrm{CH_3CH_3\mathit{C}H_2}$), 69.3 ($\mathrm{\mathit{C}H_2O}$, 3,5-positions), 73.7 ($\mathrm{\mathit{C}H_2O}$, 4-position), 100.2 (*ortho* to NH), 130.4 (*para* to NH), 131.9 (*ipso* to NH), 133.5 ($\mathrm{NHCO\mathit{C}H{=}CHCO_2H}$), 135.7 ($\mathrm{NHCOCH{=}\mathit{C}HCO_2H}$), 153.2 (*meta* to NH), 164.1 ($\mathrm{NH\mathit{C}OCH{=}CHCO_2H}$), 166.4 ($\mathrm{NHCOCH{=}CH\mathit{C}O_2H}$). Anal. Found (calcd): C, 74.19 (74.24); H, 11.41 (10.97); N, 1.86 (1.88).

**5. *N*-[3,4,5-Tris(*n*-dodecan-1-yloxy)phenyl]maleimide (6).** Compound **6** was synthesized by the cyclocondensation of **5**.[16] Maleamic acid **5** (6.50 g, 8.70 mmol) and NaOAc (0.82 g, 10 mmol) were heated at 90 °C in 50 mL of $\mathrm{Ac_2O}$. After 4 h, TLC analysis indicated complete reaction. The reaction mixture was poured into 500 mL of stirring ice−water, and the resultant yellow solid was filtered, dried, and recrystallized two times from 2-propanol to yield 5.0 g (79%) of pale yellow solid: mp 79−80 °C; $R_f = 0.6$ (8:2 hexanes/ethyl acetate); IR (KBr, $\mathrm{cm^{-1}}$) 1719 ($\mathrm{C{=}O}$); $^{1}\mathrm{H}$ NMR ($\mathrm{CDCl_3}$, TMS) $\delta$ 0.88 (t, 9H, $\mathrm{C\mathit{H}_3}$), 1.27 (overlapped peaks, 48H, $\mathrm{CH_3(C\mathit{H}_2)_8}$), 1.46 (m, 6H, $\mathrm{C\mathit{H}_2(CH_2)_2O}$), 1.76 (m, 6H, $\mathrm{C\mathit{H}_2CH_2O}$), 3.95 (t, 6H, $\mathrm{C\mathit{H}_2O}$, $J =$ 6.2 Hz), 6.50 (s, 4H, $\mathrm{C\mathit{H}{=}C\mathit{H}}$), 6.82 (s, 2H, *ortho* to N); $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$, TMS) $\delta$ 14.1 ($\mathrm{\mathit{C}H_3}$), 22.7 ($\mathrm{CH_3\mathit{C}H_2}$), 26.1 ($\mathrm{CH_2\mathit{C}H_2CH_2O}$), 29.3−29.7 ($\mathrm{CH_3CH_2CH_2(\mathit{C}H_2)_6}$), 29.6 ($\mathrm{\mathit{C}H_2CH_2O}$, 3,5-positions), 30.3 ($\mathrm{\mathit{C}H_2CH_2O}$, 4-position), 31.9 ($\mathrm{CH_3CH_3\mathit{C}H_2}$), 69.1 ($\mathrm{\mathit{C}H_2O}$, 3,5-positions), 73.5 ($\mathrm{\mathit{C}H_2O}$, 4-position), 105.2 (*ortho* to N), 126.1 (*ipso* to N), 134.1 ($\mathrm{CH{=}CH}$), 138.1 (*para* to N), 153.3 (*meta* to N), 169.6 ($\mathrm{\mathit{C}{=}O}$). Anal. Found (calcd): C, 75.96 (76.09%); H, 11.45 (10.97%); N, 1.89 (1.93%).

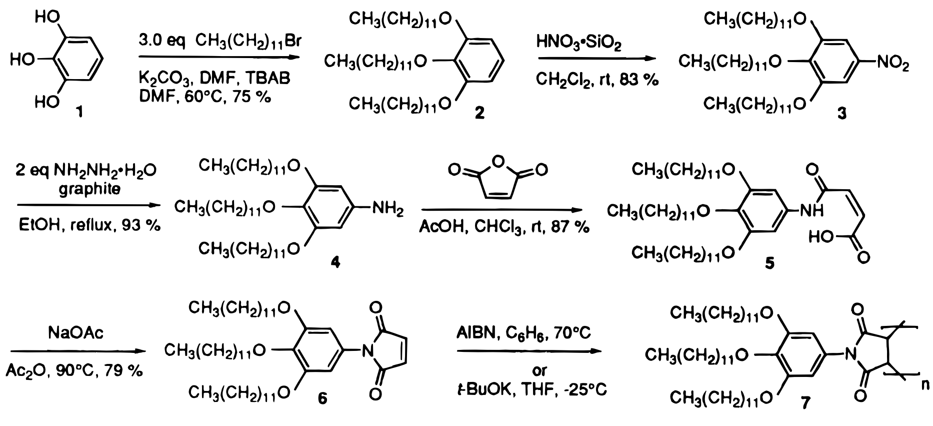
**6. *exo,exo*-7-Oxabicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Anhydride (10).** The synthesis of **10** was performed according to a literature procedure.[17] From 7.89 g (0.08 mol) of maleic anhydride (**9**) and 11.6 mL (0.16 mol) of furan (**8**) was obtained 9.34 g (70.3%) of a white powder. mp 118 °C (dec) (lit.[17] mp 125 °C; $^{1}\mathrm{H}$ NMR ($\mathrm{CD_3COCD_3}$, TMS) $\delta$ 3.38 (s, 2H, $\mathrm{CHC\mathit{H}COO}$), 5.38 (s, 2H, $\mathrm{OC\mathit{H}CHCOO}$), 6.65 (s, 2H, $\mathrm{{=}C\mathit{H}}$); $^{13}\mathrm{C}$ NMR ($\mathrm{CD_3COCD_3}$, TMS) $\delta$ 49.8 ($\mathrm{CH\mathit{C}HCOO}$), 83.0 ($\mathrm{O\mathit{C}HCHCOO}$), 137.6 ($\mathrm{{=}\mathit{C}H}$), 171.5 ($\mathrm{\mathit{C}O}$); IR (KBr, $\mathrm{cm^{-1}}$) 1770 ($\mathrm{C{=}O}$), 1655 ($\mathrm{C{=}C}$).

**7. *exo,exo*-5,6-Bis(hydroxymethyl)-7-oxabicyclo[2.2.1]-hept-2-ene (11).** The synthesis of **11** was performed according to a literature procedure.[18] From 9.04 g (54.2 mmol) of **10** was obtained 3.8 g (44.9%) of a colorless viscous liquid: $^{1}\mathrm{H}$ NMR ($\mathrm{CD_3COCD_3}$, TMS) $\delta$ 1.81 (m, 2H, $\mathrm{OCHC\mathit{H}CH_2OH}$, $J = 5.3$ Hz), 3.5−3.8 (m, 4H, $\mathrm{OCHCHC\mathit{H}_2OH}$), 4.08 (t, $\mathrm{O\mathit{H}}$, $J = 6.3$ Hz), 4.72 (t, 2H, $\mathrm{OC\mathit{H}CHCH_2OH}$, $J = 1.0$ Hz), 6.36 (t, 2H, $\mathrm{{=}CH}$, $J = 1.0$ Hz); $^{13}\mathrm{C}$ NMR ($\mathrm{CD_3SOCD_3}$, TMS) $\delta$ 42.1 ($\mathrm{OCH\mathit{C}HCH_2OH}$), 60.2 ($\mathrm{OCHCH\mathit{C}H_2OH}$), 79.7 ($\mathrm{O\mathit{C}HCHCH_2OH}$), 135.4 ($\mathrm{{=}\mathit{C}H}$); IR (KBr, $\mathrm{cm^{-1}}$) 3200−3600 (OH), 1690 ($\mathrm{C{=}C}$); TLC, $R_f = 0.36$ (10% methanol/ethyl acetate).

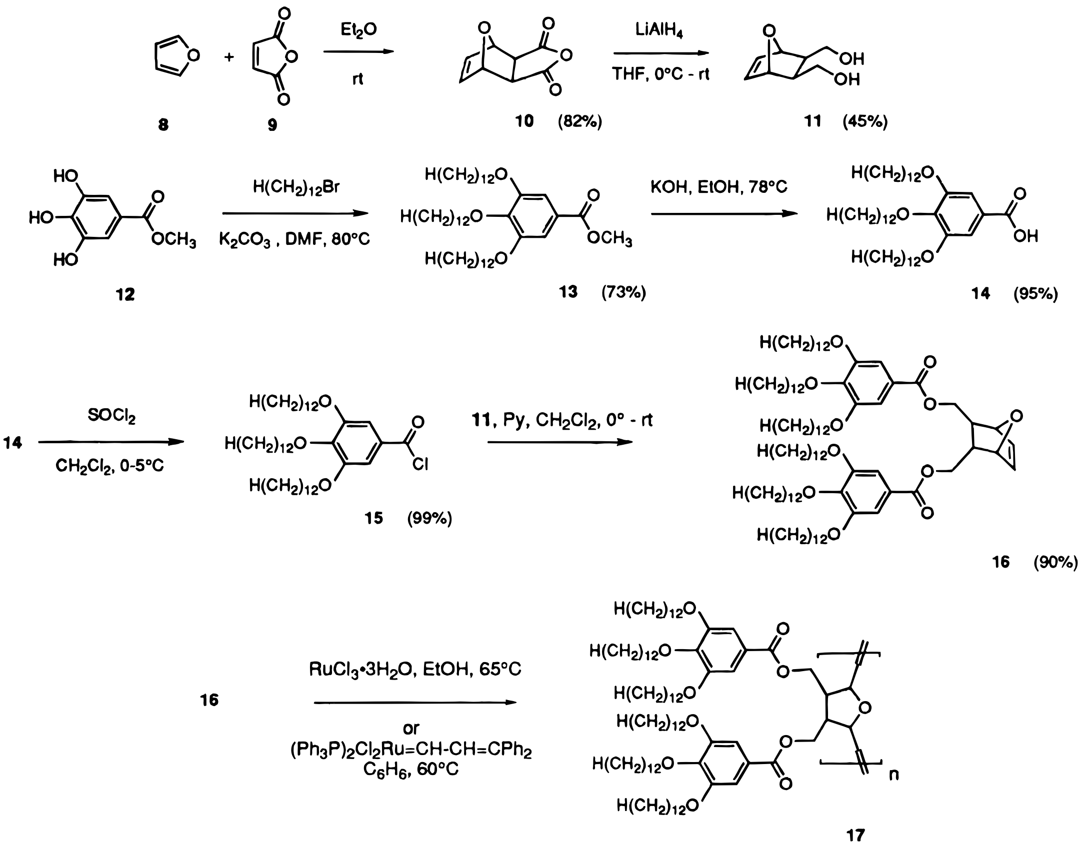
**8. Methyl 3,4,5-Tris(*n*-dodecan-1-yloxy)benzoate (13).** The synthesis of **6** was performed by using a modification of a literature procedure.[19] A 500 mL three-neck flask with a Teflon-coated magnetic stir bar was charged with 60.3 g (0.24 mol) of 1-bromododecane and 300 mL of DMF. The mixture was sparged with Ar, and then 51.0 g (0.36 mol) of $\mathrm{K_2CO_3}$ and 11.1 g (0.06 g) of methyl 3,4,5-trihydroxybenzoate (**12**) were added. The reaction mixture was heated at 80 °C for 8 h with stirring under an Ar atmosphere, and then it was cooled to room temperature and filtered. The filtrate was diluted with 400 mL of $\mathrm{Et_2O}$ and transferred to a separatory funnel. The organic phase was washed three times with 500 mL portions of $\mathrm{H_2O}$, once with 400 mL of dilute HCl, once with 200 mL of $\mathrm{H_2O}$, and then with 50 mL of saturated NaCl. The organic phase was separated and dried over $\mathrm{MgSO_4}$. The mixture was filtered and the solvent was evaporated. The crude product was passed through a short column of basic $\mathrm{Al_2O_3}$ using $\mathrm{Et_2O}$ as eluent. The product was recrystallized from acetone to yield 30.3 g (73.3%) of a white solid: mp 43 °C, (lit.[20] mp 39−42.5 °C); $^{1}\mathrm{H}$ NMR ($\mathrm{CDCl_3}$, TMS) $\delta$ 0.88 (t, 9H, $\mathrm{C\mathit{H}_3}$, $J = 6.3$ Hz), 1.27 (overlapped m, 54H, $\mathrm{(C\mathit{H}_2)_9}$), 1.78 (m, 6H, $\mathrm{C\mathit{H}_2CH_2OPh}$), 3.89 (s, 3H, $\mathrm{CO_2C\mathit{H}_3}$), 4.01 (m, 6H, $\mathrm{C\mathit{H}_2OPh}$, $J = 6.3$ Hz), 7.25 (s, 2H, $\mathrm{Ar\mathit{H}CO_2CH_3}$); $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$, TMS) $\delta$ 14.1 ($\mathrm{\mathit{C}H_3}$), 22.7 ($\mathrm{\mathit{C}H_2CH_3}$), 26.1−30.2 ($\mathrm{((CH_2)_7}$), 31.9 ($\mathrm{\mathit{C}H_2CH_2CH_3}$), 52.1 ($\mathrm{CO_2\mathit{C}H_3}$), 69.1 ($\mathrm{\mathit{C}H_2CH_2OPh}$), 73.4 ($\mathrm{\mathit{C}H_2OPh}$), 107.7 (*ortho* to $\mathrm{CO_2CH_3}$), 124.6 (*ipso* to $\mathrm{CO_2CH_3}$), 142.3 (*para* to $\mathrm{CO_2CH_3}$), 152.8 (*meta* to $\mathrm{CO_2CH_3}$), 166.9 ($\mathrm{Ph\mathit{C}O_2CH_3}$); IR (KBr, $\mathrm{cm^{-1}}$) 1710 ($\mathrm{C{=}O}$); GPC, 99%; TLC, $R_f = 0.56$ (10:1 hexanes/ethyl acetate).

**9. 3,4,5-Tris(*n*-dodecan-1-yloxy)benzoic acid (14).** The synthesis of **13** was performed by using a modification of a literature procedure.[19] In a 125 mL Erlenmeyer flask containing a Teflon-coated magnetic stir bar was placed 5.1 g (7.3 mmol) of **13**, 40 mL of 95% EtOH, and 2.9 g (51.1 mmol) of KOH pellets. The mixture was heated at 78 °C for 50 min with stirring, after which time hydrolysis was judged to be complete by TLC analysis. The reaction mixture was cooled to room temperature, and the resulting crystalline solid was filtered and washed with cold EtOH. The filtered solid was transferred to a 250 mL Erlenmeyer flask and dissolved in 100 mL of THF with stirring. The solution was acidified with dilute HCl until pH 1. The solution was poured into 150 mL of $\mathrm{Et_2O}$ and transferred to a separatory funnel. The organic phase was washed two times with 50 mL of $\mathrm{H_2O}$ and then once with saturated NaCl and was dried over $\mathrm{MgSO_4}$. The solution was filtered and the solvent was evaporated, resulting in 4.7 g (95.3%) of white crystals: mp 60 °C (lit.[19] mp 64 °C); $^{1}\mathrm{H}$ NMR ($\mathrm{CDCl_3}$, TMS) $\delta$ 0.88 (t, 9H, $\mathrm{CH_3}$, $J = 6.7$ Hz), 1.26 (overlapped m, 54H, $\mathrm{(CH_2)_9}$), 1.79 (m, 6H, $\mathrm{C\mathit{H}_2CH_2OPh}$), 4.02 (m, 6H, $\mathrm{C\mathit{H}_2OPh}$), 7.32 (s, 2H, $\mathrm{Ar\mathit{H}CO_2H}$); $^{13}\mathrm{C}$ NMR ($\mathrm{CDCl_3}$, TMS: $\delta$ 14.1 ($\mathrm{\mathit{C}H_3}$), 22.7 ($\mathrm{\mathit{C}H_2CH_3}$), 26.1−30.2 ($\mathrm{((CH_2)_7}$), 31.9 ($\mathrm{\mathit{C}H_2CH_2CH_3}$), 69.2 ($\mathrm{\mathit{C}H_2CH_2OPh}$), 73.6 ($\mathrm{\mathit{C}H_2OPh}$), 108.5 (*ortho* to $\mathrm{CO_2H}$), 123.7 (*ipso* to $\mathrm{CO_2H}$), 143.1 (*para* to $\mathrm{CO_2H}$), 152.9 (*meta* to $\mathrm{CO_2H}$), 172.2 ($\mathrm{Ph\mathit{C}O_2H}$); IR (KBr, $\mathrm{cm^{-1}}$) 1680 ($\mathrm{C{=}O}$); TLC, $R_f$ = 0 (10:1 hexanes/ethyl acetate).

**Scheme 1. Synthesis of 6 and Its Polymerization to 7.**



**Scheme 2. Synthesis of 16 and Its Polymerization to 17.**



**10. 3,4,5-Tris(*n*-dodecan-1-yloxy)benzoyl chloride (15).** A 50 mL two-neck round-bottom flask with a Teflon-coated magnetic stir bar was charged with 1.51 g (2.22 mmol) of **14**, 10 mL of $CH_2Cl_2$, and 0.1 mL of DMF. The reaction flask was flushed with Ar, sealed with a rubber septum, and cooled in an ice bath. $SOCl_2$ (0.2 mL, 2.44 mmol) was added dropwise to the chilled reaction mixture. The ice bath was removed and the reaction mixture was stirred for 1 h. The solvent was evaporated, and the resulting 1.52 g (99%) of a white solid was dried under vacuum: mp 42 °C (lit.[21] mp 38 °C); $^1$H NMR, ($CDCl_3$, TMS) $\delta$ 0.88 (t, 9H, $CH_3$, $J = 6.7$ Hz), 1.26 (overlapped m, 54H, $(CH_2)_9$), 1.79 (m, 6H, $CH_2CH_2OPh$, $J = 6.8$ Hz), 4.02 (m, 6H, $CH_2OPh$, $J = 6.4$ Hz), 7.33 (s, 2H, Ar*H*COCl); $^{13}$C NMR ($CDCl_3$, TMS) $\delta$ 14.1 ($CH_3$), 22.7 ($CH_2CH_3$), 26.1–30.2 ($(CH_2)_7$), 31.9 ($CH_2CH_2CH_3$), 69.3 ($CH_2CH_2OPh$), 73.7 ($CH_2OPh$), 110.0 (*ortho* to COCl), 127.3 (*ipso* to COCl), 144.7 (*para* to COCl), 152.9 (*meta* to COCl), 167.7 (Ph*C*OCl); IR (KBr, cm$^{-1}$) 1745 (C=O).

**11. *exo,exo*-5,6-Bis[[[3,4,5-tris(*n*-dodecyl-1-oxy)benzoyl]oxy]methyl]-7-oxabicyclo[2.2.1]hept-2-ene (16).** A 250 mL three-neck round-bottom flask with an addition funnel, argon inlet–outlet, and a Teflon-coated stir bar was charged with 1.15 g (7.4 mmol) of **11** and 70 mL of pyridine. The flask was cooled in an ice bath, and 10.26 g (14.8 mmol) of **15** dissolved in 30 mL of $CH_2Cl_2$ was added dropwise over a 20 min period. The ice bath was then removed and the reaction mixture was stirred for an additional 3 h. The reaction mixture was diluted with 150 mL of $CH_2Cl_2$ and washed three times with 100 mL portions of $H_2O$. The organic phase was dried over $Na_2SO_4$ and filtered, and the solvent was rotary evaporated. The crude product was chromatographed on $SiO_2$ using a hexanes/ethyl acetate (20:1) mobile phase, resulting in 6.38 g (58.3%) of a white solid: mp 53 °C; $^1$H NMR ($CDCl_3$, TMS) $\delta$ 0.88 (t, 18H, $CH_3$, $J = 6.9$ Hz), 1.26 (overlapped m, 108H, $(CH_2)_9$), 1.78 (m, 12H, $CH_2CH_2OPh$, $J = 6.6$ Hz), 2.20 (t, 2H, OCHC*H*$CH_2$OCO, $J = 5.7$ Hz), 4.02 (m, 12H, $CH_2OPh$, $J = 6.5$ Hz), 4.34–4.60 (m, 4H, $CHCH_2OCOPh$), 4.94 (s, 2H, OC*H*CH$CH_2$OCO), 6.42 (s, 2H, =C*H*), 7.28 (s, 4H, Ar*H*$CO_2$-$CH_2$); $^{13}$C NMR ($CDCl_3$, TMS) $\delta$ 14.1 ($CH_3$), 22.7 ($CH_2CH_3$), 26.1–30.3 ($(CH_2)_7$), 31.9 ($CH_2CH_2CH_3$), 39.6 (OCH*C*H$CH_2$-OCO), 64.3 (OCHCH$CH_2$OCO), 69.2 ($CH_2CH_2OPh$), 73.5 ($CH_2$-OPh), 80.6 (O*C*HCH$CH_2$OCO), 108.1 (*ortho* to $CO_2CH_2$), 124.5 (*ipso* to $CO_2CH_2$), 135.6 (=*C*H), 142.6 (*para* to $CO_2CH_2$), 152.9 (*meta* to $CO_2CH_2$), 166.1 (Ph*C*$O_2CH_2$); IR (KBr, cm$^{-1}$) 1705 (C=O), 1650 (C=C); GPC, 99%; TLC, $R_f = 0.24$ (10:1 hexane/ethyl acetate).

**Table 1. Characterization of 7 and 17 by GPC and DSC Analysis**[a]

| polymer | yield (%) | method | solvent | temp (°C) | time (h) | $[M]_0$ (mol/L) | $[M]_0/[I]_0$ (mol/mol) | $M_n \times 10^{-3}$ (GPC) | $M_w/M_n$ (GPC) | $LiSO_3CF_3$ (mol/mru) | thermal transitions (°C) and corresponding enthalpy changes (kcal/mru[e]) in parentheses | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | heating | cooling |
| 7 | 75 | A | $C_6H_6$ | 70 | 24 | 0.70 | 233 | 4.6 | 1.89 | | g 76 $\Phi_h$ 149 (0.37) i<br>g 89 $\Phi_h$ 156 (0.14) i | i 146[b] $\Phi_h$ |
| 7 | 95 | A | $C_6H_6$ | 70 | 24 | 4.0 | 10 | 16.3 | 2.32 | | g 115[b] $\Phi_h$ >290[b] i<br>g 115[b] $\Phi_h$ >290[b] i | i >290[b] $\Phi_h$ 110[b] g |
| 7 | 0 | B | THF | −78 | 2 | 0.010 | 20 | | | | | |
| 7 | 55 | B | THF | −25 | 1.5 | 0.005 | 10 | 14.4 | 1.6 | | g 68 $\Phi_h$ 215[b] i<br>$\Phi_h$ 217[b] i | i 205[b] $\Phi_h$ 60 g |
| 7 | 99 | B | THF | −60 | 2.5 | 0.010 | 5 | 7.73 | 1.38 | | g 75 $\Phi_h$ 156 (0.55) i<br>g 84 $\Phi_h$ 150[b] i | i 143[b] $\Phi_h$ 60 g |
| 17 | 62 | C | EtOH | 65 | 42 | 0.680 | 10 | 216.5 | 1.9 | | g 33 $\Phi_h$ 88 (0.16) i<br>g 30 $\Phi_h$ 86 (0.15) i | i 83 (0.08) $\Phi_h$ 23 g |
| 17 | 21 | D | $C_6H_6$ | 60 | 14 | 0.166 | 45.4 | 78.2 | 1.1 | | *c* | *c* |
| 17 | | C | | | | | | 216.5 | 1.9 | 1.24[d] | g 31 $\Phi_h$ 86 (0.11) i<br>g 31 $\Phi_h$ 84 (0.02) i | i 84 (0.01) $\Phi_h$ 26 g |

[a] Data on the first lines under heating were obtained during the first heating scan. Data on the second line under heating were obtained during the second heating scan. [b] Transition temperatures determined by optical polarized microscopy. [c] Polymer not isolated. [d] Salt complexes with 0.42 and 0.86 mol of $LiSO_3CF_3$ per mru of **17** displayed thermal behavior identical to that of uncomplexed **17**. [e] mru = moles of repeat units.

**Table 2. Characterization of Oriented Samples of Polymers 7 and 17 by X-ray Diffraction Experiments**

| polymer | temp (°C) | $\rho^a$ (g/cm$^3$) | $d_{100}$ (Å) | $d_{110}$ (Å) | $d_{200}$ (Å) | $d_{\text{intra,exp}}$ (Å) | $a^b$ (Å) | $R^c$ (Å) | $S^d$ (Å) | $\mu^e$ (Å) | $d_{\text{intra,calc}}$ (Å) | helical pitch |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **7** | 160 | 0.953 | 26.7 | 15.2 | 13.3 | 4.7 | 30.6 | 15.3 | 17.7 | 3.0 | 8.7<br>4.2 | 7/2<br>3/1 |
| **17** | 55 | 0.969 | 32.9 | 18.7 | 16.2 | 4.4 | 37.4 | 19.1 | 22.1 | 2.2 | 4.5<br>6.0 | 3/1<br>2/1 |
| **17**[f] | 71 | | 32.2 | 18.3 | 15.9 | | 36.6 | 18.6 | 21.5 | | | |

[a] Density at 22 °C. [b] $a = 2(d_{100})/\sqrt{3}$. [c] $R = d_{100}/\sqrt{3}$. [d] $S = 2R/\sqrt{3}$. [e] $\mu = [\rho(3\sqrt{3})N_A S^2 t]/2M$ = number of monomer units per column cross section with diameter *a* and a repeat unit along the column equal to $d_{\text{intra}}$. [f] Salt complex with 1.24 mol of $LiSO_3CF_3$ per mru of **17**.

**12. Free Radical Polymerization of 6 (Method A).** A typical procedure for the free radical polymerization of **6** is as follows. Compound **6** (0.454 g, 6.25 mmol, 5% w/v), AIBN (4.5 mg, 1% w/w), and 9 mL of benzene were sealed in a Schlenk tube. The solution was degassed by freeze−pump−thaw cycles, and the mixture was heated at 70 °C for 24 h under $N_2$ and then precipitated into MeOH. The yellow solid was filtered and reprecipitated from a benzene solution into acetone. The polymer was collected by vacuum filtration and dried on the filter to yield 0.34 g (75%) of a glassy yellow solid. The absence of residual monomer in the resultant polymers was verified by $^1H$ NMR and GPC. The yield and molecular weight distributions of the polymers obtained are shown in Table 1.

**13. Anionic Polymerization of 6 (Method B).** A typical procedure for the anionic polymerization of **6** is as follows.[7] In a Schlenk tube was dissolved **6** (0.22 g, 0.30 mmol) in 60 mL of anhydrous THF. The yellow solution was degassed by three freeze−pump−thaw cycles. The solution was then cooled to −25 °C in a dry ice/$CCl_4$ bath, and *t*-BuOK (0.60 mL of a 0.050 M solution in THF prepared from freshly sublimed *t*-BuOK, 0.030 mmol) was added *via* syringe. The solution turned orange. After 1.5 h, the polymerization was quenched with 2 mL of 10% HCl in MeOH. After warming to 10 °C, the reaction mixture was poured into MeOH. After a second precipitation in MeOH and drying on the filter, 0.120 g (54.5%) of a gummy yellow solid was obtained. The absence of residual monomer in the resultant polymers was verified by $^1H$ NMR and GPC analyses. Table 1 summarizes the polymerization results.

**14. Polymerization of 16 Initiated with $RuCl_3 \cdot xH_2O$ (Method C).** The polymerization of **16** was performed according to a literature procedure.[8] A 20 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with 1.01 g (0.68 mmol) of **16**. The flask was heated to 65 °C to melt the monomer, and then 1 mL of 95% EtOH was added, followed by 0.015 g (0.068 mmol) of $RuCl_3 \cdot xH_2O$. The mixture was stirred vigorously for 42 h at 65 °C in air. The crude polymer was dissolved in hexanes and passed through a short $SiO_2$ column. The resulting polymer was dissolved in THF and precipitated into methanol twice to yield 0.63 g (62.1%) of a white polymeric solid: GPC, $M_n = 216\,500$, $M_w/M_n = 1.9$; $^1H$ NMR ($CDCl_3$, TMS) $\delta$ 0.86 (br t, 18H, $CH_3$), 1.26 (overlapped m, 108H, $(CH_2)_9$), 1.70 (br s, 12H, $CH_2CH_2OPh$,), 2.58 (br s, 2H, $OCHCHCH_2OCO$), 3.85 (br s, 12H, $CH_2OPh$), 4.21, 4.41 (overlapped m, 6H, $OCHCHCH_2OCO$), 5.81 (br s, 2H, $=CH$), 7.02 (br s, 4H, $ArHCO_2CH_2$); $^{13}C$ NMR ($C_6D_6$, TMS) $\delta$ 13.9 ($CH_3$), 22.7 ($CH_2CH_3$), 26.4−30.8 ($(CH_2)_7$), 32.0 ($CH_2CH_2CH_3$), 46.3 ($OCHCHCH_2OCO$), 62.6 ($OCHCHCH_2OCO$), 68.8 ($CH_2CH_2OPh$), 73.0 ($CH_2OPh$), 77.3 ($CH{=}CHCHO$, *cis*), 81.1 ($CH{=}CHCHO$, *trans*), 107.9, 124.4 (aromatic), 133.1 ($=CH$), 142.7, 153.0 (aromatic), 165.7 ($PhCO_2CH_2$). From an inverse gated decoupling $^{13}C$ NMR experiment,[22] integration of *cis*-$CH{=}CHCHO$ (77.3 ppm) versus *trans*-$CH{=}CHCHO$ (88.1 ppm) yielded 37.3% *cis* and 62.7% *trans* sequences.

**15. Polymerization of 16 Initiated with $(Ph_3P)_2Cl_2Ru{=}CHCH{=}CPh_2$ (Method D).** A Schlenk tube containing a Teflon-coated stir bar was charged with 0.20 gof **16** and 0.8 mL of benzene. The solution was subjected to three freeze−pump−thaw cycles. A second Schlenk tube containing a Teflon-coated stir bar was charged with 0.003 g of $(Ph_3P)_2Cl_2Ru{=}CHCH{=}CPh_2$ and degassed. The monomer solution was transferred to the catalyst tube with a syringe and placed in a 60 °C oil bath. Within 1.5 h, GPC analysis revealed 2% polymer ($M_n$ = 78 200, $M_w/M_n$ = 1.1), 19% polymer ($M_n$ = 5900), and 79% unreacted monomer. After 14 h there was no substantial increase in the polymer conversion.

**16. Preparation of $LiSO_3CF_3$ Complexes of 17.** Complexes of **17** with $LiSO_3CF_3$ were prepared by the addition of a standard 0.10 M solution of $LiSO_3CF_3$ to **17**. The solvent was removed under vacuum, and the complex was dried under vacuum in a desiccator. The absence of uncomplexed $LiSO_3CF_3$ was verified by DSC and X-ray diffraction experiments.

## Results and Discussion

**Synthesis of Monomers 6 and 16.** Scheme 1 outlines the syntheses of *N*-[3,4,5-tris(*n*-dodecan-1-yloxy)phenyl]maleimide (**6**) and its corresponding polymer **7**. In the first step, 1,2,3-trihydroxybenzene (**1**) was alkylated with 1-bromododecane to produce 3,4,5-tris(*n*-dodecan-1-yloxy)benzene (**2**) in 75.1% yield after recrystallization from 1:1 $CHCl_3$/MeOH. Nitration of **2** was carried out with $HNO_3$ supported on $SiO_2$[11] at room temperature and a 15 min reaction time to yield

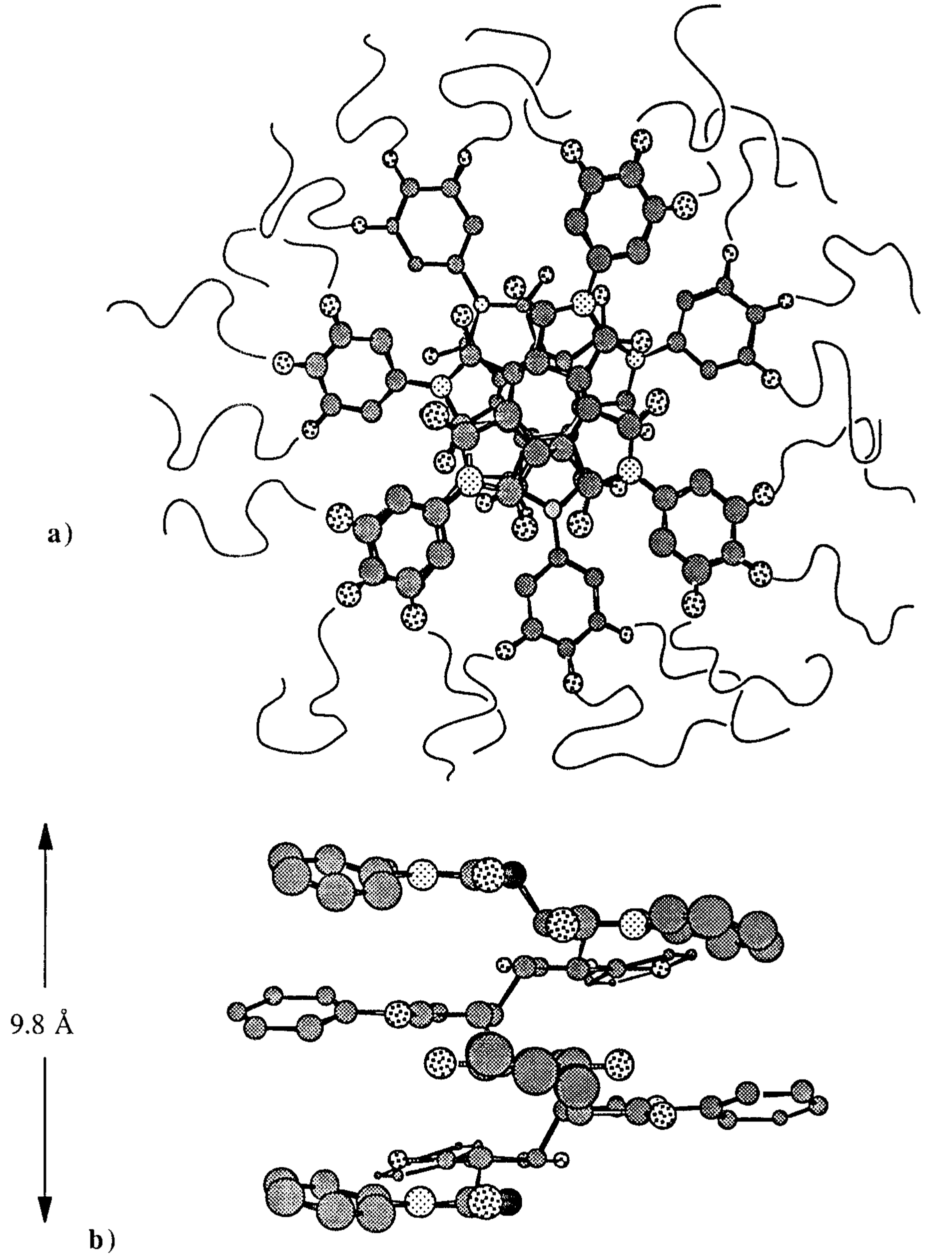


**Figure 1.** Molecular model of a single chain of **7** in (a) top view of the *threo* diisotactic or 7/2 helical chain conformation and (b) side view of the *threo* diisotactic 7/2 helical conformation. In the top view, the alkyl tails are represented schematically. In the side view, hydrogens, lone pairs, and alkyloxy tails have been hidden for clarity.

82.8% 3,4,5-tris(*n*-dodecan-1-yloxy)-1-nitrobenzene (recrystallized from 1:1 $CHCl_3$/MeOH) (**3**). This nitration reagent is very efficient and suppresses oxidative demethylation of **2** during the nitration process.[11] Reduction of **3** with $NH_2NH_2{\cdot}H_2O$ over graphite powder in ethanol produced 3,4,5-tris(*n*-dodecan-1-yloxy)-1-aminobenzene (**4**) in 92.8% yield. The maleamic acid **5** obtained from **4** and maleic anhydride in 81% yield was cyclized with NaOAc in $Ac_2O$[16] to produce monomer **6** in 79% yield.

Scheme 2 describes the synthesis of *exo,exo*-5,6-bis-[[[3,4,5-tris(*n*-dodecan-1-yloxy)benzoyl]oxy]methyl]-7-oxabicyclo[2.2.1]hept-2-ene (**16**) and its ring opening metathesis polymerization to **17**. Diels−Alder addition of maleic anhydride (**9**) to furan (**8**) in $Et_2O$ at room temperature produced the anhydride **10**[17] in 70.3% yield. The anhydride **10** was reduced with $LiAlH_4$ in THF at room temperature to generate **11**[18] in 45% yield. 3,4,5-Tris[*n*-dodecan-1-yloxy)benzoic acid (**14**) was synthesized by the alkylation of methyl 3,4,5-trihydroxybenzoate with 1-bromododecane[19] followed by the hydrolysis[20] of the resultant **13** with KOH in EtOH at 78 °C. Esterification of **11** with the acid chloride of **14** (*i.e.*, **15**)[21] yielded **16** (58.3% yield, after purification by column chromatography, $SiO_2$, 20:1 hexanes/ethyl acetate).

**Polymerization of Monomers 6 and 16.** *N*-Phenylmaleimide polymerizes by both radical (method A) and anionic (method B) mechanisms.[5−7] Radical polymerization of **6** initiated with AIBN was carried out in benzene at 70 °C (Table 1). Living anionic polymerization of *N*-phenylmaleimide was accomplished with *t*-BuOK in THF at −70 °C.[7] The lowest temperature at which monomer **6** is soluble in THF, even at a very low concentration, is −50 °C. At −78 °C the solution of **6** in THF forms a gel, and no polymerization in the presence of *t*-BuOK took place. Two polymerizations were performed with *t*-BuOK at −50 and −25 °C. Although a relatively low monomer concentration was required to maintain a homogeneous solution at these temperatures, good control of the polymer molecular weight and a narrow molecular weight distribution were obtained (Table 1).

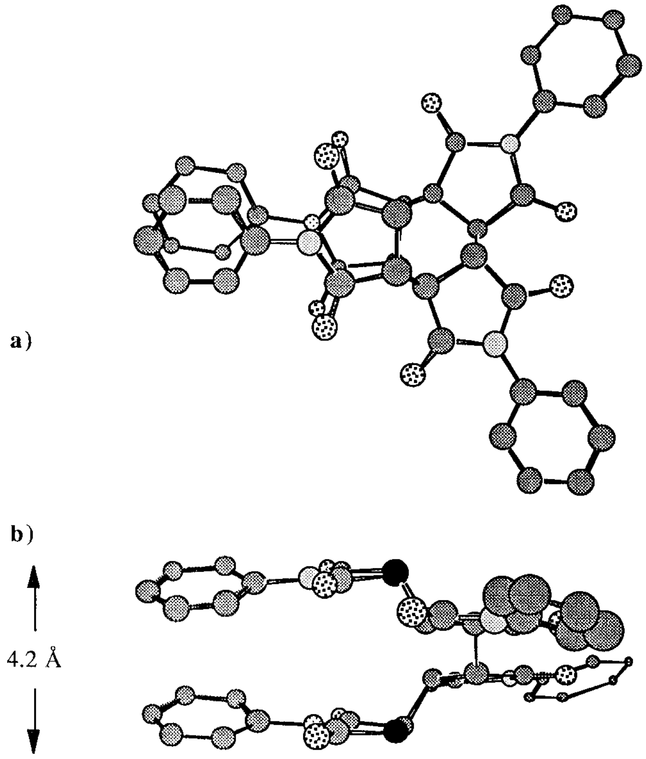


**Figure 2.** Molecular model of a single chain of **7** in (a) top view of the *threo* disyndiotactic 3/1 helical chain conformation and (b) side view of the *threo* diisotactic 3/1 helical conformation. Hydrogens, lone pairs, and alkyloxy tails have been omitted for clarity.

Two polymerization experiments were carried out with **16**. The first one, initiated with $RuCl_3 \cdot xH_2O$ (method C), was carried out in 95% EtOH at 65 °C in air.[8-10] After 42 h, a polymer with $M_n = 216\,500$ and $M_w/M_n = 1.9$ was obtained in 62.1% yield. The polymer backbone microstructure was analyzed by using an inverse gated decoupled $^{13}C$ NMR experiment.[22] Integration of *cis*-CH=CH*C*HO (77.3 ppm) versus *trans*-CH=CH*C*HO (88.1 ppm) yielded 37.3% *cis* and 62.7% *trans* sequences. The polymerization of **16** initiated with $(Ph_3P)_2Cl_2Ru{=}CHCH{=}CPh_2$[12] was less successful, and the resulting polymer was not separated from the reaction mixture (Table 1). Additional experiments with this and other metathesis initiators to generate a controlled polymerization of **16** are in progress.

**Thermal and Structural Characterization of Polymer 7.** Differential scanning calorimetric (DSC) traces of polymers **7** (obtained at 20 °C/min) with $M_n = 4.6 \times 10^3$, $7.73 \times 10^3$ and $14.4 \times 10^3$, exhibit a glass transition temperature ($T_g$), followed by a mesophase that undergoes isotropization ($T_i$) through a broad endotherm. The enthalpy change associated with this $T_i$ is very small and can be calculated only for polymers with $M_n < 10^4$. The $T_i$ increases dramatically at higher $M_n$ values, and above $10^4$ the enthalpy associated with this transition decreases. Therefore, for $M_n > 10^4$, the $T_i$ could be determined only by thermal optical polarized microscopy. The very sharp increase in $T_i$ with molecular weight is associated with a very rigid polymer backbone. Table 1 summarizes all characterization data for polymers **7**. The mesophase observed above $T_g$ was characterized by X-ray diffraction experiments and was assigned to a $\Phi_h$ LC phase (Table 2). On the optical polarized microscope, all polymers **7** become liquid-like above $T_g$ and form an anisotropic texture that does not develop into a characteristic texture even after annealing. Most probably, polymers **7** exhibit high $T_g$ values, which have a very low change in heat capacity and could only be observed by DSC with difficulty. The $T_g$ of poly(*N*-phenylmaleimide) is reported to be higher than 330 °C.[5a] Addition of three dodecyl groups to the structure of poly(*N*-phenyl maleimide) lowers the $T_g$, depending on the molecular weight, to about 100 °C.

X-ray diffraction experiments were carried out on both powder and oriented samples of **7**. An oriented film of **7** with $M_n = 16.3 \times 10^3$ or $14.4 \times 10^3$ was obtained by casting a film from a $CHCl_3$ solution onto a KBr plate. The film was sheared at 170 °C, cooled to room temperature, and the KBr plate was dissolved in water. Fibers were obtained from the same polymer samples at 170 °C. The X-ray diffraction data of **7** are identical regardless of the molecular weight of the sample and are summarized in Table 2. The expected ratio for a $\Phi_h$ phase is $d_{100}{:}d_{110}{:}d_{200} = 1{:}1/(3)^{1/2}{:}1/2$. This ratio agrees with the ratio of the experimental values from Table 2 and, therefore, demonstrates that the mesophase exhibited by polymers **7** above $T_g$ is $\Phi_h$. From the X-ray data presented in Table 2, the lattice parameter *a*, the radius of the column *R*, and the value *S* are calculated as explained in the footnote of the table and presented in detail in previous publications from our laboratory.[1] The number of monomer units ($\mu$) per column cross section with diameter *a* and height equal to the repeat unit along the column ($d_{intra} = 4.7$ Å) obtained for the supramolecular column of polymer **7** is $\mu = 3.0$. Molecular modeling of the *threo* diisotactic chain of polymer **7** yields an incomplete 3/1 helical chain conformation with a calculated value of $d_{intra(calc)} = 4.23$ Å. A complete turn can be obtained for a 7/2 helical chain conformation (Figure 1). This generates a value $d_{intra(calc)} = 9.8$ Å. Half of this value is 4.9 Å and is in closer agreement with the experimental $d_{intra} = 4.7$ Å than the 4.23 Å value obtained for the 3/1 helical chain conformation. On the basis of this discussion, we favor the 7/2 helical chain conformation for the polymer **7** in its $\Phi_h$ mesophase presented in Figure 1 over that of the 3/1 helical conformation presented in Figure 2.

**Thermal and Structural Characterization of Polymer 17.** Polymer **17** with $M_n = 216\,500$ was characterized by DSC and X-ray scattering experiments. In spite of its very high molecular weight, on the DSC curve **17** exhibits a well-defined $T_g$ at 33 °C and a $T_i$ at 88 °C (Table 1). The supercooling of the $T_i$ is only 5 °C which is extremely low for such a high molecular weight polymer and demonstrates that this phase transition is thermodynamically controlled. Due to its high molecular weight, the texture of this polymer did not develop into a very characteristic one, even after annealing. X-ray diffraction experiments performed on oriented fibers of **17** above its $T_g$ demonstrated a $\Phi_h$ mesophase and a $d_{intra} = 4.4$ Å along the column (Table 2). Up to 1.2 mol of $LiSO_3CF_3$ per repeat unit of **17** can be dissolved in this supramolecular tubular architecture. The DSC traces and the X-ray diffraction pattern of these complexes are not very different from those of the uncomplexed polymer **17**. A 5 °C decrease in the $T_i$ is observed after complexation (Table 1). However, within experimental error no change in the column diameter could be observed by X-ray experiments (Table 2).

Molecular modeling experiments on **17** indicate that it can adopt a range of helical conformations due to the stereochemistry of the polymer backbone. To decide on a most probable conformation, we must remember both the concentration of 62.7% *trans* repeat units and the $LiSO_3CF_3$ complexation experiments when applying the X-ray data to our model. The most straightforward conformation for **17** is a zig-zag (*i.e.*, a 2/1 helix). This implies a fully extended backbone that contains no center cavity, which allows cooperation between furanyl

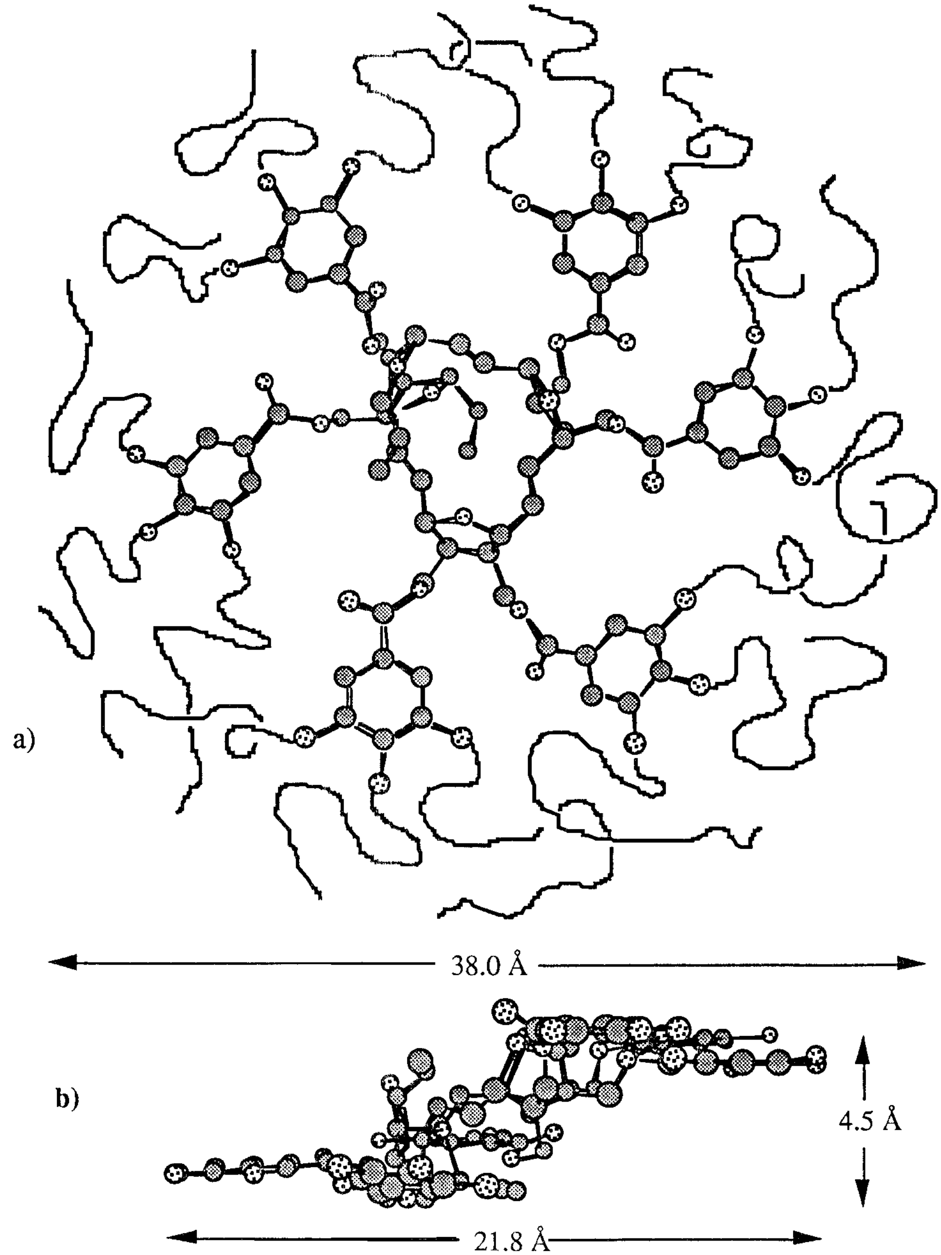


**Figure 3.** Molecular model of a single chain of **17** in (a) top view of the 3/1 helical chain conformation and (b) side view of the 3/1 helical conformation. In the top view, the alkyl tails are represented schematically. In the side view, hydrogens, lone pairs, and alkyloxy tails have been hidden for clarity.

oxygens during the ion complexation. From molecular modeling of an energy-minimized *trans*-linked extended dimer, the repeat was 6.0 Å. This value is significantly larger than the experimental $d_{\text{intra}} = 4.4$ Å. An energy-minimized *cis*-linked extended dimer has a repeat of 4.4 Å, which matches the experimental $d_{\text{intra}}$ value. Therefore, our model $d_{\text{intra}}$ falls between these values, being closer to 6.0 Å if it contains only *trans* extended conformations and closer to 4.4 Å if it contains only *cis* extended conformations.

The number of monomer units ($\mu$) per column cross section with diameter $a$ and height equal to the repeat unit along the column ($d_{\text{intra}} = 4.7$ Å) obtained for polymer **17** in the $\Phi_h$ phase is $\mu = 2.2$. This value suggests a helical conformation intermediate between a 2/1 zig-zag and a 3/1 helix. For space filling reasons, the 2/1 zig-zag conformation derived from only the *trans* units cannot generate a columnar structure from one single chain. It requires two repeat units from two different chains to come in close proximity in such a way that they form a disklike cross section of the column. This implies a double-helix conformation, which is not probable for a chain containing a combination of *trans* and *cis* units. The *cis* units make one chain traverse from one double helix to another double helix and thus generate a network of columns. The formation of a $\Phi_h$ structure like this requires a kinetically controlled process, which is not observed in the case of **17**. Therefore, the double-helix suggestion seems unlikely as there is no apparent driving force or sufficiently pure chain stereochemistry that could lead to the formation of such a complex architecture. In addition, a supramolecular column generated from a double helix is more rigid and, therefore, implies more kinetic control during the formation of the $\Phi_h$ phase.

Figures 3 and 4 present the supramolecular column generated from the 3/1 helical conformation of **17** and the channel created in the core. The alkyl tails of the 12-AG groups are melted as in the previous systems.[2] From molecular modeling (Figures 3 and 4), the dimensions of a 3/1 helix of **17** using two *trans* and one *cis* linkages best fits the X-ray data ($d_{\text{intra,calc}} = 4.5$ Å, $a_{\text{calc}} = 38.0$ Å) and permits all of the furanyl oxygens to

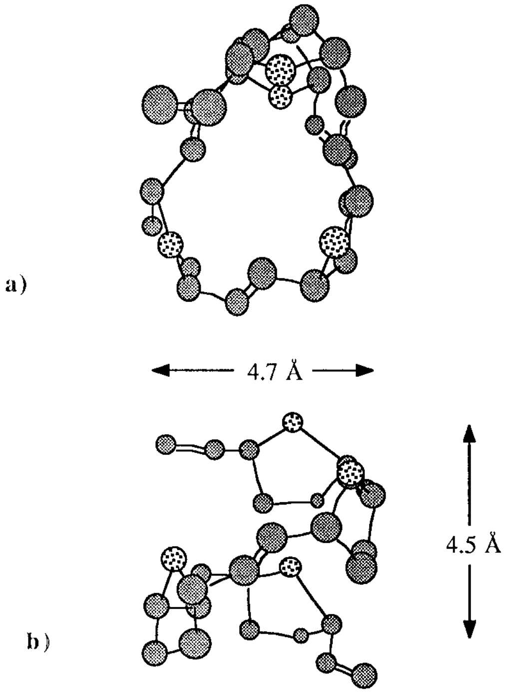


**Figure 4.** Molecular model of the polymer backbone of **17** in (a) top view of the 3/1 helical chain conformation and (b) side view of the 3/1 helical chain conformation. The taper-shaped side groups, hydrogens, and lone pairs have been hidden for clarity.

remain in the helix interior, opening the possibility for the observed cooperation between the furanyl oxygens in ion complexation. However, this model implies a $\mu = 3$, which leads us to also consider a helix with a lower pitch, such as 5/2 or 9/4. Presently we do not know the distribution of *cis* and *trans* sequences in **17**. If **17** has a block type microstructure, *trans* units would form the supramolecular columns or disks on the basis of 3/1 helical chains, which are interconnected *via* less ordered segments of *cis* units. This structure generates a lower overall polymer density than the one of the pure *trans* columnar sequences and explains the discrepancy between experimental $\mu = 2.2$ and theoretical $\mu = 3.0$ in a 3/1 helical conformation. The fact that the polymer complexes ions provides additional evidence of a helical structure. On the basis of these arguments, we can conclude that a 3/1 helical chain conformation generated from the taper units of **17** provides a reasonable structure for the supramolecular columns of the $\Phi_h$ mesophase of **17**.

## Conclusions

We believe that the present experimental data available for the $\Phi_h$ phases generated by polymers **7** and **17** support the hypothesis for the supramolecular column based on single-chain helicity. In the case of **7**, the rigid helical chain conformation favors the formation of the column by optimum filling of the space together with its own tapered side groups. In the case of **17**, the arrangement of the tapered side groups in a columnar structure requires that their own flexible backbone adopts a helical conformation.

**Acknowledgment.** Financial support by the National Science Foundation (DMR-92-06781) (USA) the Engineering and Physical Science Research Council (UK), and NATO (traveling grant) is gratefully acknowledged. An IBM and a Sicka graduate fellowship to G.J. are also acknowledged.

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MA951244K