Synthesis of Functionalized Side-Chain Liquid Crystal Polymers: Polyphenolic Combs

Satya B. Sastri[†] and Samuel I. Stupp*

Departments of Materials Science and Engineering and Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

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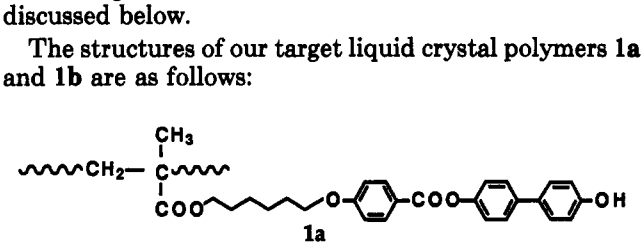
ABSTRACT: This work studied the synthesis of self-ordering comb polymers containing functionalized side chains. The target polymers in the study had methacrylate backbones with hydroxy-functionalized side chains containing phenolic groups at their termini. The synthesis of the targeted polymers was accomplished in seven steps and involved identifying suitable protecting groups for the phenolic monomers before free-radical polymerization. The various protecting groups explored for this purpose were dimethylthexylsilyl ether (OΣ), benzyl carbonate (OCOOBn), trimethylsilyl ether (OTMS), triethylsilyl ether (OTES), diphenylmethylsilyl ether (ODPMS), and tetrahydropyranyl ether (OTHP) groups. Our studies show that ODPMS and OTHP ether groups are best suited to synthesize the functionalized polymers. Deprotection of polymers protected with these groups after free-radical polymerization could be quantitatively accomplished under relatively mild conditions. One of the target polymers and its corresponding functionalized monomer were found to melt into liquid crystalline fluids which exhibited isotropization transitions at higher temperatures. The synthesis of these polymers is significant in the context that mesomorphic behavior is not considered common in organic molecules with functions that can form intermolecular hydrogen bonds. Also these comb polymers may exhibit interesting behavior at interfaces with solid surfaces given the presence of reactive or hydrogen-bond-forming functions in their self-assembling side chains. One example would be their behavior as coupling agents at a composite material interface.

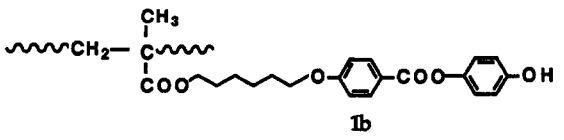
Introduction

The concept of functionalized liquid crystal polymers (LCPs) has not been extensively investigated, and hence information on the subject is limited. There are many reasons why it is interesting to introduce chemical functions in self-ordering macromolecules. The phenomena that can be studied with such polymers include chemical reactions in ordered media, the behavior of self-ordering interphases that bond to surfaces at phase boundaries, and the ordering of chemical functions on surfaces. There are both synthetic and structural barriers to the formation of functionalized self-ordering polymers. From a synthetic point of view chemical functions can interfere with polymerization reactions or may not survive them. Structural barriers are often encountered because chemical functions that engage in strong interactions such as hydrogen bonding can make liquid crystalline phases thermodynamically unstable. One reason is that melting points of crystals are often raised significantly by hydrogen bonding. Some specific examples of hydrogen bonds interfering with the occurrence of mesomorphism are discussed below.

The structures of our target liquid crystal polymers **1a** and **1b** are as follows:



1a



1b

[†] Present address: Materials Chemistry Branch, Naval Research Laboratory, Washington, DC 20375.

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The literature contains examples of small molecules in which hydrogen bonding interferes with liquid crystallinity or stabilizes the mesomorphic state.[1–5] Interference may arise due to high melting points or the nonlinear arrangement of interacting molecules. An example of hydrogen bonding stabilizing mesophases is the dimerization of carboxylic acids which preserves linearity and increases the aspect ratio. Among the many small-molecule liquid crystals that have been synthesized to date, only a few have the phenolic functionality of **1a** and **1b**.[6,7] To our knowledge, polyphenolic main-chain or side-chain polymeric liquid crystals had not been reported in the literature at the time of our first report on the subject.[8]

The choice of the functional group was based primarily on the potential ability of these phenolic groups to interact with surfaces containing polar groups. Specifically, phenolic side chains were viewed as moieties that could interact strongly or react with oxidized surfaces and thus be useful in studies of self-ordering macromolecules at an interface. The choice of aromatic moieties, the hexamethylene spacer, and the methacrylate backbone was based on the numerous similar structures known to form side-chain LCPs.[9,10] Many polymers with the skeletal structure of **1b** are also known to show mesomorphic behavior.[11,12] All compounds **b** correspond to intermediates in the synthesis of **1b** while those for biphenyl compounds are labeled with the suffix **a**. The placement of hydroxyl groups in the mesogenic units themselves had the objective of coupling the ordering of functional groups to the ordering of mesogenic units in these polymers. Such an organized array of functional groups may very well influence, for example, chemical reactivity at a phase boundary. We report in this paper the synthetic pathway to the targeted phenolic monomers and polymers. Subsequent papers from our group will focus on the properties of the various monomers and polymers, including their behavior on fiber surfaces and Langmuir–Blodgett films.

Results and Discussion

Stepwise Construction of the Functionalized Monomer. Synthesis of the monomer proceeded with the

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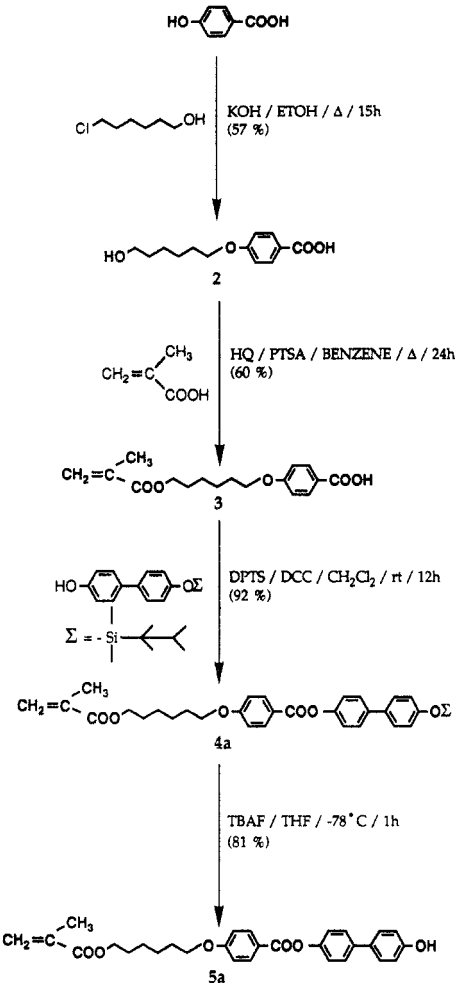
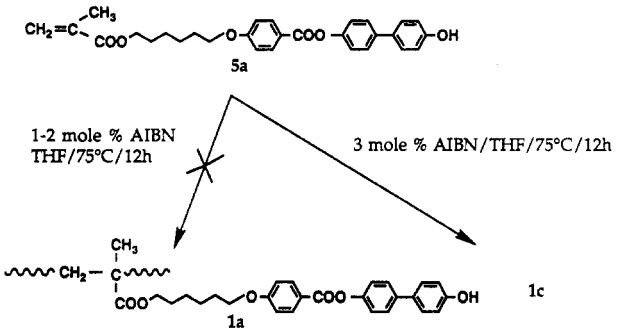
Scheme I



reactions outlined in Scheme I. First, a flexible spacer was introduced by an etherification reaction of *p*-hydroxybenzoic acid with 6-chlorohexanol to obtain **2**.[13] Analytically pure **2** was obtained by recrystallization from ethanol in 57% yield. Next, the polymerizable double bond was incorporated by azeotropic esterification of **2** with a 4-fold excess of methacrylic acid in benzene with *p*-toluenesulfonic acid (PTSA) as a catalyst and hydroquinone as the polymerization inhibitor.[14] Purification of product **3** could be achieved in 60% yield by recrystallization either with isopropyl alcohol or with an ethanol–hexane mixture. In both cases recrystallization was very slow and the appearance of crystals required refrigeration for 3–4 days. Esterification of compound **3** with the biphenylic fragment was attempted by carbodiimide chemistry.[15,16] Initial conditions involving the acid, 1.1 equiv of 1,3-dicyclohexylcarbodiimide (DCC), and 0.2 equiv of 4-(dimethylamino)pyridine (DMAP) as catalyst afforded the product in only 50% yield after chromatographic purification, the major impurity being *N*-acylurea. It was recently discovered in our laboratory that 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) is an effective polyesterification catalyst.[17] Use of this methodology improved the yield of the pure ester to 90%. Thus DPTS was first synthesized by mixing a benzene solution of anhydrous PTSA with an equimolar solution of DMAP, and the crude product was recrystallized from dry dichloroethane. Protected monomer **4** was then desilylated with *n*-tetrabutylammonium fluoride (TBAF) at −78 °C in tetrahydrofuran (THF). After this reaction analytically pure functionalized monomers, **5a** and **5b**, were isolated by chromatographic purification with silica gel followed by

Scheme II

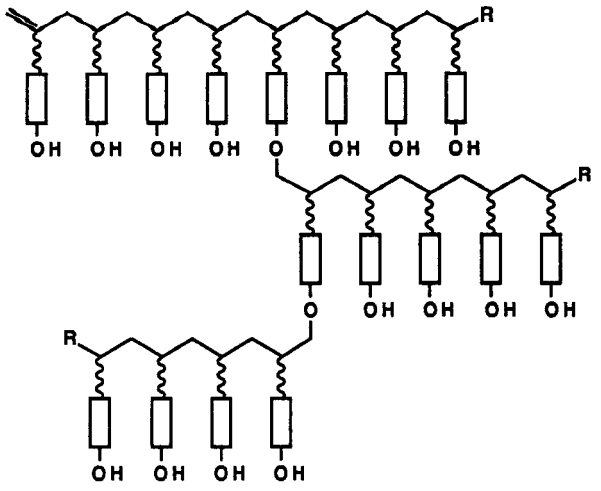


recrystallization from heptane in 81% and 84% yields, respectively. Both vinyl proton peaks (δ 5.50–6.00) and the phenolic proton peak (δ 9.70–9.80) are observed in ^{1}H-NMR spectra of monomers **5a** and **5b**.

Polymerization. Target polymers **1a** and **1b** should be obtainable through conventional addition polymerization mechanisms from the corresponding methacrylic monomers. To date, however, only a few methods are known for the preparation of functionalized polymers with free phenolic groups, the most common one being free-radical polymerization of the acetylated monomers followed by deprotection by alkaline hydrolysis.[18] This approach is, however, restricted to simple monomers that are stable in alkaline media and therefore not applicable in the present case. Direct free-radical polymerization (as shown in Scheme II) of the phenolic monomers using an initiator was only partially successful. The polymerization reaction itself failed when 1–2 mol % azobis(isobutyronitrile) (AIBN) initiator was employed and the starting material was recovered in quantitative yield. On the other hand, 3 mol % AIBN afforded a polymeric residue that was insoluble in most organic solvents and was only sparingly soluble in dimethylformamide (DMF) (this solvent was later identified to be the best solvent for the target polymers). ^{1}H-NMR analysis in deuterated DMF and elemental analysis identified the product to be the polymer of **5a**. Characterization of this material by optical microscopy and differential scanning calorimetry (DSC) indicated the product was an infusible solid.

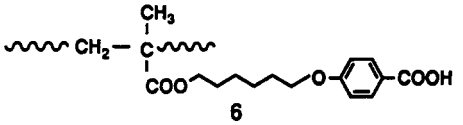
Earlier investigations on polymerization reactions involving phenolic monomers by free-radical initiation are somewhat contradictory. While some investigators observed no effect of the phenolic group on polymerization,[19] others reported total inhibition.[20,21] The nature of aromatic substituents on phenolic groups is thought to play an important role in the course of polymerization. For instance, it has been observed that the presence of electron-donating groups such as alkyl and alkoxy groups facilitates inhibition,[20] presumably because hydrogen abstraction generates stable phenoxy radicals. On the other hand, the presence of electron-withdrawing groups such as carboxyls in the aromatic ring has the opposite effect, and monomers such as 5-vinylsalicylic acid undergo polymerization without difficulty.[21] In the present case, isolation of an insoluble and infusible product with high initiator concentrations suggests the formation of phenoxy radicals and light cross-linking of the system as shown in **1c**.

It was clear that the use of protecting groups had to be explored for the synthesis of the target polymers. We first considered the possibility of polymerizing the dimethylthexylsilyl ether protected monomer, **4a**, followed by deprotection of the polymeric product. Polymerization of monomer **4a** using general polymerization conditions of 2 mol % AIBN and THF as solvent afforded polymer



1c

with side chains protected with dimethylthexylsilyl groups. This product was further purified by dissolving in chloroform and precipitating into methanol to obtain an 88% yield of the protected polymer. Deprotection of the silyl ether gorups either by TBAF or by acetic acid and water mixtures proved to be a difficult task due to the poor solubility of the polymer in the reaction medium. While significant amounts of aromatic ester cleavage products were isolated with TBAF reagent (such as 6), acidic medium hydrolysis yielded partially deprotected polymers which later proved to be interesting materials.[22]



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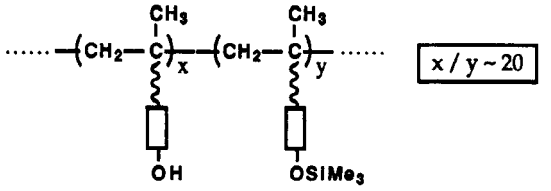
Monomers with carbonylbenzoxy groups as protecting groups were successfully synthesized using appropriate intermediates and polymerized under standard conditions. Deprotection reactions were attempted by the catalytic hydrogenation technique with Pd/C as catalyst. However, the removal of catalyst particles from the polymeric product was not possible presumably due to strong adsorption on carbon surfaces. Nonetheless, complete deprotection of the polymer did occur based on ^{1}H-NMR experiments.

Trimethyl ether protecting groups were also used given their facile removal under mild conditions, and this methodology was partially successful in the synthesis of phenolic polymer **1a**. Due to the instability of the protected monomer to purification by silica gel chromatography, polymerization was attempted without further purification of the monomer prepared from **5a** using 1.1 equiv of chlorotrimethylsilane and 1.1 equiv of trimethylamine in THF (replacing the trimethyl groups on Si by triethyl groups also posed a similar problem). The resultant polymer was purified by precipitation into cold methanol, redissolving in chloroform, and reprecipitating in the same solvent. Interestingly, the ^{1}H-NMR spectrum of this polymer revealed a sharp peak around δ 9.70 and only a small peak around δ 0.20 corresponding respectively to the phenolic and the trimethylsilyl ether protons. Based on the integral heights of the two peaks, we infer that, on average, approximately 1 out of every 20 side chains retained a protecting group. Therefore, the structure of the polymeric product is that of a protected–deprotected copolymer as shown in **1d**. As will be discussed in a subsequent paper, this copolymer revealed interesting



1d

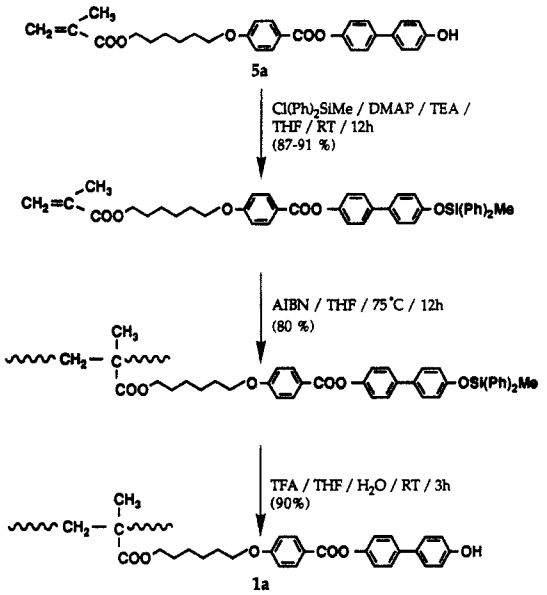
properties different from those of the fully deprotected polymer.[22] Complete deprotection of **1d** was easily accomplished by stirring a solution of **1d** in THF with an acetic acid and water mixture for 4 h at room temperature. ^{1}H-NMR and elemental analysis identified the polymer to be **1a**. Furthermore, based on the nitrogen content of the polymer, the degree of polymerization (dp) of this polymer should be *ca.* 50. Unfortunately the reproducibility of this reaction proved to be difficult even when stringent reaction conditions were maintained, and thus two other alternatives were considered.

One additional protecting group tested was diphenylmethylsilyl (DPMS) ether since it could combine stability to acidic silica gel chromatography with deprotection under mild conditions. The selection of this group was suggested by Sommer's classic work on the rates of acidic and basic hydrolysis of silyl ether as a function of the ligands on silicon.[23] Sommer found that, under basic hydrolysis conditions, steric and electronic effects oppose one another. The net result is that larger alkyl groups slow down hydrolysis ($Me_3Si \gg Et_3Si$) while phenyl groups have little effect ($Me_3Si \approx Ph_3Si$). On the other hand, under acidic conditions, steric and electronic effects both slow down hydrolysis but the rate is more strongly influenced by electronic effects ($Me_3Si = 400 \times Ph_3Si$) than by steric effects ($Me_3Si = 60 \times Et_3Si$). In accordance with these findings, Denmark et al.[24] observed that DPMS groups had the same base lability as Me_3Si but a much greater acid stability, thereby enabling purification with acidic silica gel. Thus, the protected monomer was conveniently prepared with 1.1 equiv of chlorodiphenylmethylsilane in the presence of 1.1 equiv of base as shown in Scheme III. Purification was achieved by flash chromatography, yielding 84% of a white crystalline product. The corresponding polymers with phenyl and biphenyl side chains having approximate degrees of polymerization (dp's) of 100 and 80, respectively, were prepared using general polymerization conditions in 75–80% yield.

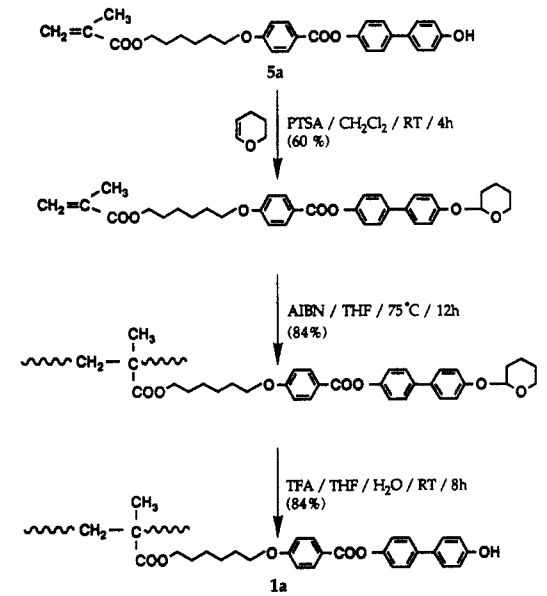
Even though deprotection of DPMS ether groups on many small organic molecules could be quantitatively accomplished in 1 min or less with TBAF, poor solubility of the polymer posed problems. Heterogeneous reaction mixtures resulted when deprotection conditions involving THF–acetic acid–H_2O mixtures or aqueous methanolic solutions were employed. However, THF–TFA–H_2O mixtures containing low concentrations of water (10:7.5:1) produced a homogeneous reaction mixture that led to complete deprotection of the polymer in approximately 3 h. On the basis of ^{1}H-NMR spectra in DMF-d_7, pure polyphenolic functionalized comb polymers were obtained and the yields were in the range of 82–90%.

The final protecting group investigated was tetrahydropyranyl (THP) ether (Scheme IV). It was anticipated that in polar solvents polymers protected with THP groups would show better solubility than those containing silyl ether groups. Protected monomer **12** was prepared using 1.5 equiv of 3,4-dihydropyran and PTSA as the catalyst in methylene chloride. Purification by flash chromatography followed by recrystallization from heptane afforded a 60% yield of pure protected monomer. Standard

Scheme III



Scheme IV



conditions were employed to obtain the polymer of dp *ca.* 200 in 84% yield. Deprotection of the polymer could be accomplished under conditions similar to those employed for the diphenylmethylsilyl ether protected polymer except that longer reaction times (8–10 h) were needed to observe 100% deprotection. As expected, however, it was easy to maintain a homogeneous solution throughout the course of deprotection. The polymer isolated by this route in 86% yield was identical to that obtained via Scheme III.

Characterization of the phenolic monomers and target polymers by polarized optical microscopy revealed liquid crystallinity in monomer **5a** and in its corresponding polymer **1a** but not in **5b** and **1b**. The liquid crystalline monomer and polymer melted at 128 and 158 °C, respectively, into birefringent liquids and also revealed isotropization transitions at 176 and 262 °C. The polyphenolic comb polymers may exhibit interesting behavior at interfaces with solid surfaces given the combination of properties in their side chains, namely, a self-assembling nature and the presence of strongly interactive chemical functions. A more detailed analysis of phase transitions and other physical properties in these systems are described in a subsequent paper.

Conclusions

The synthesis of hydroxy-functionalized self-ordering comb polymers was successfully accomplished. Free-radical polymerization of the unprotected phenolic monomers used in the synthesis either failed or resulted in the formation of a cross-linked polymer. A successful synthesis required a protection–polymerization–deprotection sequence to obtain the polyphenolic polymer. Among several protecting groups investigated, diphenylmethylsilyl and tetrahydropyranyl ether groups gave the best results. One of the target polymers and its corresponding unprotected monomer melt into liquid crystalline fluids and exhibit isotropization transitions. The polyphenolic comb polymers synthesized may behave interestingly at interfaces with solid surfaces given the self-assembling and strongly interactive nature of their side chains. One example would be their behavior as coupling agents at a composite material interface.

Experimental Section

General Information. All glassware was oven dried overnight at 145–155 °C. Solvents were dried by refluxing 3–5 h over an appropriate drying agent, fractionally distilled through a 10-cm Vigreau column, and stored over 4-Å molecular sieves. Drying agents used were phosphorus pentoxide for methylene chloride, calcium hydride for DMF and triethylamine, and sodium over benzophenone for THF. All other reagents and solvents were used as received. Analytical and preparative TLC utilized Merck silica gel plates with a QF-254 indicator. Silica gel chromatography was performed by the method of Still[25] using Woelm 32–63-μm silica gel.

^{1}H- and ^{13}C-NMR analyses were carried out at 300 and 75 MHz, respectively, on a General Electric QE 300 instrument. Carbon–hydrogen substitution patterns were determined by either the attached proton test (APT) or distortionless enhancement by polarization transfer (DEPT) pulse sequences. Electron ionization (EI) mass spectra were recorded on a Varian MAT CH-5 spectrometer with ionization voltages of 10 and 70 eV, and infrared spectra were recorded on a Beckman 4240 spectrometer. EI data were presented in the form m/z with intensities relative to a base peak of 100 units. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory, and melting points were determined with a Perkin-Elmer DSC 4 at a heating rate of 20–40 °C min^{-1}. Optical microscopy utilized a Leitz Laborlux 12-pol polarizing microscope equipped with a Leitz Laborlux hot stage and a Micristar thermocontroller.

Synthesis. Details of the experimental procedures employed for the synthesis of monomer **5a** and its polymer **1a** are described below. Identical procedures were utilized to synthesize polymer **1b** from its corresponding monomer **5b**. The synthesis of monoprotected hydroquinone and bisphenol used in Scheme I followed previous preparations for monocarbonates,[14] silyl ethers,[15] and selective deprotection of the carbonylbenzoxy group.[15–18]

Monomer Synthesis. 4-[(6-Hydroxyhexyl)oxy]benzoic Acid (2). A three-necked, 300-mL flask equipped with a stirbar, an addition funnel, and a condenser was charged with 4-hydroxybenzoic acid (46.000 g, 0.333 mol), KI, (20.0 mg), ethanol (120 mL), and KOH solution (50.000 g in 50 mL of water). To the resulting yellow solution was added 6-chlorohexanol (50.090 g, 0.068 mol) dropwise through the addition funnel. The mixture was heated to reflux for 15 h using an oil bath maintained at 110 °C. Subsequently, the reaction mixture was cooled to room temperature, stirred with water (100 mL), and acidified with aqueous concentrated HCl. The solid product was collected by suction filtration, washed thoroughly with water, and purified by recrystallization from ethanol.

Yield: 57%. Mp: 87–88 °C. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.50; H, 7.70. ^{1}H NMR (300 MHz, acetone-d_6): δ 1.41 (m, 4 H), 1.76 (m, 2 H), 2.01 (m, 2 H), 3.50 (t, J = 6.36 Hz, 2 H), 4.05 (t, J = 6.47 Hz, 2 H), 6.98 (d, J = 8.92 Hz, 2 H), 7.94 (d, J = 8.88 Hz, 2 H). ^{13}C NMR (75 MHz, DMF-d_7): δ 25.92 (CH_2), 26.00 (CH_2), 29.32 (CH_2), 33.05 (CH_2), 61.67 (CH_2), 68.27 (CH_2), 114.38 (CH), 123.39 (C), 131.81 (CH), 163.03

(C), 167.53 (C). MS (70 eV): m/z 238 (14, M^+), 138 (100), 121 (52), 82 (50), 65 (22), 55 (99), 41 (51).

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid (3). A 1-L, single-neck flask was charged with **2** (23.300 g, 0.097 mol), 4-toluenesulfonic acid monohydrate (11.680 g, 0.061 mol), hydroquinone (3.886 g, 0.035 mol), methacrylic acid (33.500 g, 0.389 mol), and benzene (600 mL). A Dean-Stark apparatus fitted with a condenser and drying tube was connected to the reaction flask, and the whole assembly was immersed in an oil bath. The temperature of the bath was slowly raised to 120 °C and maintained at that temperature for 24 h. The contents were cooled to room temperature and taken up in 2 L of ether. The ether extract was washed twice with water and then with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Recrystallization from isopropyl alcohol yielded analytically pure sample.

Yield: 60%. Mp: 56–58 °C. Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.33; H, 7.19. ^{1}H NMR ($CDCl_3$): δ 1.46 (m, 4 H), 1.70 (m, J = 6.63 Hz, 2 H), 1.81 (m, J = 6.58 Hz, 2 H), 1.87 (s, 3 H), 4.01 (t, J = 6.26 Hz, 2 H), 4.14 (t, J = 6.54 Hz, 2 H), 5.50 (s, 1 H), 6.10 (s, 1 H), 6.91 (d, J = 8.53 Hz, 2 H), 8.04 (d, J = 8.46 Hz, 2 H). ^{13}C NMR DMSO-d_6): δ 18.11 (CH_3), 25.41 (CH_2), 25.49 (CH_2), 28.28 (CH_2), 28.73 (CH_2), 64.38 (CH_2), 67.80 (CH_2), 114.16 (CH), 123.13 (CH_2), 125.40 (C), 131.54 (CH), 136.21 (C), 162.49 (C), 167.31 (C). MS (70 eV): m/e 306 (8, M^+), 138 (42), 87 (55), 83 (70), 41 (100).

4-(Dimethylamino)pyridinium 4′-Toluenesulfonate (DPTS). Hydrated PTSA was dried by azeotropic distillation of a benzene solution using a Dean-Stark trap. An equimolar solution of DMAP in warm benzene was then added to the anhydrous solution of PTSA. After thorough mixing, the resulting suspension was cooled to room temperature, and the solid product was collected by suction filtration. The crude product was purified by recrystallization from dry dichloroethane, yielding white needles.

Yield: 75%. Mp: 165–166 °C. Anal. Calcd for $C_{14}H_{18}N_2SO_3$: C, 57.12; H, 6.16; N, 9.52. Found: C, 57.08; H, 6.26; N, 9.69. ^{1}H NMR ($CDCl_3$): δ 2.27 (s, 3 H), 3.16 (s, 6 H), 6.95 (d, J = 7.71 Hz, 2 H), 7.09 (d, J = 8.15 Hz, 2 H), 7.46 (d, J = 8.03 Hz, 2 H), 8.19 (d, J = 7.69 Hz, 2 H).

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4′-[(Dimethylthexylsilyl)oxy]-1,1′-biphenyl-4-yl Ester (4a). A single-neck, 250-mL, round-bottom flask containing a stirbar and fitted with a Claisen adapter connected to a septum and a nitrogen inlet was assembled hot and flushed thoroughly with nitrogen. The Claisen adapter was briefly removed and replaced with a powder funnel through which was added **3** (12.290 g, 0.040 mol), 4-[4′-(dimethylthexylsiloxy)phenyl]-phenol (14.500 g, 0.044 mol), DPTS (2.300 g, 0.008 mol), and 1,3-dicyclohexylcarbodiimide (12.380 g, 0.060 mol). The Claisen adapter was returned, and the system was again flushed with nitrogen. Dry dichloromethane (200 mL) was added *via* syringe, and the contents were stirred at room temperature. Within 15 min, urea precipitated from solution. Stirring continued under a nitrogen atmosphere for an additional 12 h at room temperature, and urea was then filtered off and the solution concentrated to obtain a viscous oil. A slow-crystallizing product was obtained after purification by column chromatography in three batches of 8.000 g each (silica, 15% acetone in petroleum ether).

Yield: 92%. Mp: 61–62 °C. Anal. Calcd for $C_{37}H_{48}O_6Si$: C, 72.05; H, 7.84. Found: C, 72.16; H, 7.91. ^{1}H-NMR ($CDCl_3$): δ 0.22 (s, 6 H), 0.92 (d, J = 6.84 Hz, 6 H), 0.94 (s, 6 H), 1.46 (m, 4 H), 1.70 (m, J = 6.63 Hz, 2 H), 1.76 (m, 1 H), 1.81 (m, J = 6.58 Hz, 2 H), 1.87 (s, 3 H), 3.93 (t, J = 6.56 Hz, 2 H), 4.09 (m, J = 6.56 Hz, 2 H), 5.48 (s, 1 H), 6.06 (s, 1 H), 6.83 (d, J = 8.55 Hz, 2 H), 6.88 (d, J = 8.90 Hz, 2 H), 7.17 (d, J = 8.59 Hz, 2 H), 7.38 (d, J = 8.56 Hz, 2 H), 7.49 (d, J = 8.58 Hz, 2 H), 8.08 (d, J = 8.80 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ −22.79 (CH_3), 17.94 (CH_3), 18.23 (CH_3), 19.81 (CH_3), 24.68 (c), 25.33 (CH_2), 25.43 (CH_2), 28.64 (CH_2), 33.83 (CH), 64.13 (CH_2), 67.65 (CH_2), 113.88 (CH), 120.03 (CH), 121.25 (C), 121.60 (CH), 124.76 (C), 127.17 (CH), 127.62 (CH), 131.85 (CH), 133.06 (CH), 136.08 (C), 138.01 (C), 149.70 (C), 154.75 (C), 163.05 (C), 164.35 (C). MS (70 eV): m/z 616 (10, M^+), 288 (100), 121 (67), 69 (18), 73 (11).

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4-[(Dimethylthexylsilyl)oxy]phenyl Ester (4b). Yield: 83%. Anal. Calcd for $C_{31}H_{44}O_6Si$: C, 69.96; H, 8.29. Found: C, 69.29; H, 8.37. ^{1}H NMR ($CDCl_3$): δ 0.23 (s, 6 H), 0.93 (d, J = 6.86 Hz, 6 H), 0.94 (s, 6 H), 1.41 (m, 4 H), 1.62 (m, 2 H), 1.73 (m, 2 H), 1.74 (m, 1 H), 1.87 (s, 3 H), 4.04 (t, J = 6.97 Hz, 2 H), 4.14 (t, J = 7.01 Hz, 2 H), 5.55 (s, 1 H), 6.10 (s, 1 H), 6.83 (d, J = 7.01 Hz, 2 H), 6.94 (d, J = 8.9 Hz, 2 H), 7.31 (d, J = 8.85 Hz, 2 H), 8.10 (d, J = 8.84 Hz, 2 H).

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4′-Hydroxy-1,1′-biphenyl-4-yl Ester (5a). A dry, 250-mL, single-neck flask fitted with a Claisen adapter connected to a nitrogen inlet and a septum was charged with **4a** (11.000 g, 0.018 mol) and dry THF (100 mL). The solution was cooled to −78 °C, and *n*-tetrabutylammonium fluoride (26.7 mL of a 1 N solution in THF; 0.027 mol) was added dropwise through a syringe. After stirring the resulting pale yellow solution at −78 °C for 1 h, a small quantity of the reaction mixture was removed and extracted with ether and washed with 1 N HCl. TLC analysis (developed with 35% acetone in petroleum ether) of the ether layer showed that no starting material remained. At this point, a solution of acetic acid (5 mL) in ether (50 mL) was added in one portion to the flask at −78 °C, and the mixture was transferred to a separatory funnel containing ether (200 mL) and saturated sodium bicarbonate (300 mL). The layers were separated, and the organic phase was washed with water (3 × 200), dried (Na_2SO_4), and concentrated. Purification was achieved by flash chromatography (silica, 35% acetone in petroleum ether) followed by recrystallization from a mixture of heptane and isopropyl alcohol (2:1).

Yield: 81%. Mp: 129–130 °C. Anal. Calcd for $C_{29}H_{30}O_6$: C, 73.46; H, 6.36. Found: C, 73.52; H, 6.41. ^{1}H NMR (DMSO-b_6): δ 1.43 (m, 4 H), 1.62 (m, J = 6.72 Hz, 2 H), 1.75 (m, J = 6.57 Hz, 2 H), 1.87 (s, 3 H), 4.06 (2 t, J = 6.67 Hz, 4 H), 5.65 (s, 1 H), 6.01 (s, 1 H), 6.83 (d, J = 8.62 Hz, 2 H), 7.09 (d, J = 8.98 Hz, 2 H), 7.26 (d, J = 8.68 Hz, 2 H), 7.48 (d, J = 8.67 Hz, 2 H), 7.61 (d, J = 8.72 Hz, 2 H), 7.64 (d, J = 8.91 Hz, 2 H), 9.58 (s, 1 H). ^{13}C NMR (DMSO-d_6): δ 17.69 (CH_3), 24.91 (CH_3), 25.02 (CH_2), 27.87 (CH_2), 28.24 (CH_2), 64.00 (CH_2), 67.76 (CH_2), 114.41 (CH), 115.63 (CH), 120.84 (CH_2), 121.87 (CH), 124.98 (C), 126.66 (CH), 127.48 (CH), 130.04 (C), 131.74 (C), 135.91 (C), 137.74 (C), 149.33 (C), 157.07 (C), 163.02 (C), 164.02 (C), 166.35 (C). MS (70 eV): m/e 474 (m, M^+), 290 (34), 289 (100), 185 (11), 121 (79). IR (KBr disc): 3309, 2443, 2858, 1886, 1731, 1682, 1604, 1562, 1506, 1435, 1302, 1252, 1196, 1154, 1055, 985, 942, 872, 844, 794, 752.

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4-Hydroxyphenyl Ester (5b). Yield: 84%. Mp: 96–97 °C. Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.33; H, 6.58. ^{1}H NMR (DMSO-d_6): δ 1.41 (m, 4 H), 1.61 (m, J = 6.77 Hz, 2 H), 1.72 (m, J = 6.63 Hz, 2 H), 1.86 (s, 3 H), 4.05 (2 t, J = 7.07 Hz, 4 H), 5.65 (s, 1 H), 6.01 (s, 1 H), 6.77 (d, J = 8.87 Hz, 2 H), 7.00 (d, J = 8.86 Hz, 2 H), 7.06 (d, J = 8.91 Hz, 2 H), 8.01 (d, J = 8.9 Hz, 2 H), 9.46 (s, 1 H). ^{13}C NMR (DMSO-d_6): δ 18.02 (CH_3), 25.21 (CH_2), 25.31 (CH_2), 28.11 (CH_2), 28.51 (CH_2), 64.26 (CH_2), 67.86 (CH_2), 114.46 (CH), 115.63 (CH), 121.17 (CH_2), 122.56 (CH), 125.40 (C), 131.86 (CH), 136.05 (C), 142.89 (C), 155.18 (C), 163.06 (C), 164.60 (C), 166.53 (C). MS (70 eV): m/e 398 (14, M^+), 290 (100), 219 (12), 203 (32), 133 (21), 122 (59), 120 (57). IR (KBr disk): 3380, 2929, 2858, 1724, 1682, 1590, 1506, 1464, 1433, 1309, 1252, 1182, 1161, 1062, 992, 928, 837 cm^{-1}.

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4′-[(Methyldiphenylsilyl)oxy]-1,1′-biphenyl-4-yl Ester. The reaction procedure was identical to that described for the synthesis of benzyl[4-[4′-(dimethylthexylsiloxy)phenyl]-phenyl]carbonate employing **5a** (7.700 g, 0.013 mol), 4-DMAP (0.339 g, 0.003 mol), dry THF (100 mL), dry triethylamine (1.938 mL, 0.014 mol), and chlorodiphenylmethylsilane (2.30 mL, 0.014 mol).

Yield: 87–91%. Mp: 56–58 °C. Anal. Calcd for $C_{42}H_{42}O_6Si$: C, 75.19; H, 6.31. Found: C, 74.99; H, 6.23. ^{1}H NMR ($CDCl_3$): δ 0.75 (s, 3 H), 1.46 (m, 4 H), 1.69 (m, J = 7.03 Hz, 2 H), 1.78 (m, J = 7.08 Hz, 2 H), 1.90 (s, 3 H), 4.03 (t, J = 6.4 Hz, 2 H), 4.10 (t, J = 6.59 Hz, 2 H), 5.51 (s, 1 H), 6.06 (s, 1 H), 6.85 (d, J = 8.64 Hz, 2 H), 6.91 (d, J = 8.92 Hz, 2 H), 7.16 (d, J = 8.64 Hz, 2 H), 7.37 (m, 10 H), 7.48 (d, J = 8.63 Hz, 2 H), 7.62 (d, J = 9.01 Hz, 2 H), 8.09 (d, J = 8.92 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ −2.64 (CH_3), 18.12 (CH_3), 25.57 (CH_2), 25.65 (CH_2), 28.43 (CH_2), 28.87 (CH_2), 64.67 (CH_2), 67.97 (CH_2), 114.21 (CH), 120.16 (CH), 121.57 (CH_2), 121.83 (CH), 125.10 (C), 127.54 (CH), 127.72 (CH), 127.90

(CH), 130.07 (CH), 132.16 (CH), 133.72 (C), 134.26 (CH), 135.25 (C), 136.28 (C), 138.24 (C), 150.00 (C), 154.61 (C), 163.34 (C), 164.79 (C), 167.34 (C). MS (70 eV): *m/e* 670 (12, M^+), 290 (18), 289 (100), 197 (14), 121 (68), 69 (16).

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4-[(Methyldiphenylsilyl)oxy]phenyl Ester. Yield: 84%. Anal. Calcd for $C_{36}H_{38}O_6Si$: C, 72.70; H, 6.44. Found: C, 72.79; H, 6.35. ^1H NMR ($CDCl_3$): δ 0.77 (s, 3 H), 1.49 (m, 1 H), 1.71 (m, J = 6.99 Hz, 2 H), 1.81 (m, J = 7.16 Hz, 2 H), 1.94 (s, 3 H), 4.02 (t, J = 6.39 Hz, 2 H), 4.15 (t, J = 6.58 Hz, 2 H), 5.50 (s, 1 H), 6.10 (s, 1 H), 6.84 (d, J = 8.75 Hz, 2 H), 6.98 (d, J = 8.97 Hz, 2 H), 7.40 (m, 10 H), 7.65 (d, J = 9.06 Hz, 2 H), 8.09 (d, J = 8.86 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ -3.02 (CH_3), 18.01 (CH_3), 25.31 (CH_2), 25.40 (CH_2), 28.17 (CH_2), 28.60 (CH_2), 64.25 (CH_2), 67.64 (CH_2), 113.90 (CH), 120.13 (CH), 125.25 (CH_2), 122.19 (CH), 125.03 (C), 127.72 (CH), 129.90 (CH), 131.84 (CH), 134.00 (CH), 134.82 (C), 136.04 (C), 144.89 (C), 152.21 (C), 163.02 (C), 164.67 (C), 167.05 (C). MS (70 eV): *m/e* 594 (32, M^+), 374 (11), 290 (100), 214 (14), 203 (30), 199 (45).

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4′-[(Tetrahydropyranyl)oxy]-1,1′-biphenyl-4-yl Ester. A 100-mL single-neck flask equipped with a stirbar and a Claisen adapter connected to a nitrogen inlet and a septum was charged with **5a** (1.000 g, 2.107 mmol) and PTSA (50 mg, 0.263 mmol). The flask was thoroughly flushed with nitrogen, and the contents were dissolved in dry dichloromethane (25 mL). 3,4-Dihydropyran (0.288 mL, 3.157 mmol) was added *via* syringe, and the contents were stirred at ambient temperature for 4 h. After ensuring by TLC that no starting material remained unreacted (developed with 15% acetone in petroleum ether), the solution was transferred to a separatory funnel containing 100 mL of ether. The ether layer was washed with water (3 × 100) and brine (1 × 100) and dried over Na_2SO_4. Concentration yielded a light yellow solid which was first purified by flash chromatography (silica, 30% acetone in petroleum ether) and then followed by recrystallization from heptane.

Yield: 60%. Mp: 96–97 °C. Anal. Calcd for $C_{34}H_{38}O_4$: C, 73.09; H, 6.86. Found: C, 73.02; H, 6.98. ^1H NMR ($CDCl_3$): δ 1.49 (m, 4 H), 1.61 (m, 4 H), 1.72 (m, 8 H), 1.92 (s, 3 H), 3.58 (m, 1 H), 3.91 (m, 1 H), 4.05 (t, J = 7.07 Hz, 2 H), 4.19 (t, J = 6.98 Hz, 2 H), 5.48 (t, 1 H), 5.65 (s, 1 H), 6.01 (s, 1 H), 6.98 (d, J = 8.87 Hz, 2 H), 7.19 (d, J = 8.89 Hz, 2 H), 7.24 (d, J = 8.86 Hz, 2 H), 7.51 (d, J = 8.91 Hz, 2 H), 7.60 (d, J = 8.93 Hz, 2 H), 8.21 (d, J = 8.93 Hz, 2 H). MS (70 eV): *m/e* 558 (12, M^+), 474 (57), 290 (100), 289 (100), 203 (15), 186 (32), 185 (25).

Polymer Synthesis. General Polymerization Procedure. A single-neck flask containing a stirbar was fitted with a Claisen adapter. One end of the adapter was connected to a septum, and the other end was attached to a reflux condenser with an argon inlet. The whole setup was assembled hot, flame dried, and flushed thoroughly with argon. Two 15-mL, pear-shaped flasks were connected to septa while hot and allowed to cool under an argon atmosphere. Into one of the flasks was transferred the preweighed monomer by momentarily removing the septum, and into the other was transferred AIBN (1–2 mol %). The monomer was dissolved in freshly dried THF (0.8–1 mL per 100 mg of monomer) and was transferred to the polymerization flask *via* syringe. The initiator was dissolved in THF (0.003 g in 0.2–0.3 mL) and added to the monomer solution. The polymerization flask was placed in an oil bath, and the temperature was gradually increased to 75 °C and maintained at that temperature for 12 h. The solution was then cooled to room temperature, concentrated, and redissolved in chloroform. The solution was filtered under gravity, concentrated to near dryness, and precipitated with a large excess of methanol. This procedure yielded analytically pure polymer in most cases. For some polymers, further purification was achieved by redissolution in $CHCl_3$ followed by reprecipitation with ether or pentane or a mixture of both the solvents. The resultant precipitate was refrigerated for 4 h, collected by suction filtration, and dried at 60 °C for 18 h *in vacuo*.

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4′-[(Methyldiphenylsilyl)oxy]-1,1′-biphenyl-4-yl Ester Homopolymer. Yield: 80%. Dp: *ca.* 100. Anal. Calcd for $(C_{42}H_{42}O_6Si)_n$: C, 75.19; H, 6.31. Found: C, 75.42; H, 6.33; N, <0.06. ^1H NMR ($CDCl_3$): δ 0.73 (s, 3 H), b, 2 H), 1.04 (b, 2 H), 1.43 (b, 4 H), 1.55 (b, 2 H), 1.76 (b, 3 H), 3.94 (b, 4 H), 6.85 (2 d, J = 8.25 Hz, 4 H), 7.09 (d, J = 8.41 Hz, 2 H), 7.36 (m, 10 H), 7.62 (2 d, J = 8.24 Hz, 4 H), 8.03 (d, J = 8.88 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ -2.65 (CH_3), 18.01 (CH_3), 20.22 (CH_3), 25.70 (CH_2), 25.87 (CH_2), 28.03 (CH_2), 28.09 (CH_2), 28.93 (CH_2), 64.98 (CH_2), 67.96 (CH_2), 114.14 (CH), 120.16 (CH), 121.56 (CH), 121.85 (CH), 127.46 (C), 127.54 (CH), 127.83 (C), 127.95 (CH), 130.11 (C), 132.19 (CH), 133.58 (C), 134.27 (CH), 135.19 (C), 138.24 (C), 149.84 (C), 154.58 (C), 163.25 (C), 164.73 (C), 164.79 (C).

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4-[(Methyldiphenylsilyl)oxy]phenyl Ester Homopolymer. Yield: 74%. Dp: *ca.* 80. Anal. Calcd for $(C_{36}H_{38}O_6Si)_n$: C, 72.70; H, 6.44. Found: C, 72.93; H, 6.54; N, 0.09. ^1H NMR ($CDCl_3$): δ 0.71 (s, 3 H), 0.88 (b, 2 H), 1.03 (b, 2 H), 1.41 (b, 4 H), 1.60 (b, 2 H), 1.73 (b, 3 H), 3.91 (b, 4 H), 6.77 (d, J = 8.69 Hz, 2 H), 6.86 (d, J = 8.69 Hz, 2 H), 7.36 (m, 10 H), 7.60 (2d, J = 8.92 Hz, 4 H).

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4′-[(Tetrahydropyranyl)oxy]-1,1′-biphenyl-4-yl Ester Homopolymer. Yield: 84%. Dp: *ca.* 200. Mp: 134–138 °C. Anal. Calcd for $(C_{34}H_{38}O_7)_n$: C, 73.09; H, 6.89. Found: C, 73.58; H, 6.93; N, <0.03. ^1H NMR ($CDCl_3$): δ 0.92 (b, 2 H), 1.06 (b, 2 H), 1.45 (b, 4 H), 1.60 (b, 4 H), 1.64 (b, 4 H), 1.77 (b, 3 H), 3.59 (b, 1 H), 3.94 (b, 5 H), 5.41 (b, 1 H), 6.88 (d, J = 8.60 Hz, 2 H), 7.04 (d, J = 8.80 Hz, 2 H), 7.13 (d, J = 8.91 Hz, 2 H), 7.40 (2d, J = 8.84 Hz, 4 H), 8.05 (d, J = 8.89 Hz, 2 H).

Deprotection of Polymers. A 100-mL, single-neck flask containing a stirbar was charged with 4-[[6-[(2-methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic acid 4′-[(methyldiphenylsilyl)oxy]-1,1′-biphenyl-4-yl ester homopolymer (0.575 g 0.857 mmol of functional groups). THF (30 mL) was added *via* syringe, and the contents were stirred at room temperature until a clear solution was obtained (*ca.* 15 min). To the resultant homogeneous solution was added *via* syringe trifluoroacetic acid (7.66 mL, 99.430 mmol) followed by water (1.20 mL, 66.666 mmol). The reaction flask was stoppered, and the contents were stirred at room temperature. Within 10 min, the solution became turbid and additional THF was added at regular intervals to maintain a clear solution throughout the reaction time. After 3 h of stirring the solution was concentrated and precipitated into excess ether. The resultant suspension was refrigerated for 2 h, and the polymer was then collected by suction filtration and dried *in vacuo* at 60 °C for 20 h.

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4′-Hydroxy-1,1′-biphenyl-4-yl Ester Homopolymer (1a). Yield: 90%. Dp: *ca.* 100. Mp: 145–164 °C. Anal. Calcd for $(C_{29}H_{30}O_6)_n$: C, 73.46; H, 6.36. Found: C, 73.88; H, 6.34. ^1H NMR (DMF-d_7): δ 0.96 (b, 2 H), 1.00 (b, 2 H), 1.45 (b, 4 H), 1.65 (b, 4 H), 1.76 (b, 3 H), 4.02 (b, 4 H), 6.89 (d, J = 8.41 Hz, 2 H), 7.04 (b, 2 H), 7.23 (b, 2 H), 7.45 (b, 2 H), 7.56 (b, 2 H), 8.06 (b, 2 H); 9.78 (s, 1 H). ^{13}C NMR (DMF-d_7): δ 18.81 (CH_3), 19.91 (CH_3), 26.24 (CH_2), 26.56 (CH_2), 28.18 (CH_2), 29.39 (CH_2), 31.06 (CH_2), 65.44 (CH_2), 69.00 (CH_2), 1.537 (CH), 116.56 (CH), 122.31 (C), 122.83 (CH), 127.67 (CH), 128.52 (CH), 131.49 (C), 132.74 (CH), 139.05 (C), 150.69 (C), 158.45 (C), 162.88 (C), 162.94 (C), 164.30 (C), 165.11 (C). IR (KBr disk): 3410, 2942, 2850, 1734, 1705, 1604, 1582, 1511, 1500, 1468, 1442, 1420, 1401, 1263, 1216, 1165, 1079, 1002, 846, 820, 742 cm^{-1}.

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic Acid 4-Hydroxyphenyl Ester Homopolymer (1b). Yield: 82%. Dp: *ca.* 80. Anal. Calcd for $(C_{23}H_{26}O_6)_n$: C, 69.33, H 6.58. Found: C, 68.92; H, 6.54. ^1H NMR (DMF-d_7): δ 0.94 (b, 2 H), 1.08 (b, 2 H), 1.46 (b, 4 H), 1.65 (b, 2 H), 1.77 (b, 3 H), 4.05 (b, 4 H), 6.85 (d, J = 8.54 Hz, 2 H), 7.04 (2d, J = 8.81 Hz, 4 H), 8.04 (d, J = 8.80 Hz, 2 H), 9.67 (s, 1 H). IR (KBr disk): 3430, 2942, 2854, 1728, 1704, 1606, 1577, 1512, 1457, 1448, 1420, 1387, 1354, 1312, 1257, 1166, 1072, 1007, 873, 845, 822, 803, 762 cm^{-1}.

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Appendix

This appendix contains the analysis of some intermediates synthesized as precursors for the hydroxy-functionalized polymers. The properties of these monomers and polymers are discussed in a subsequent paper.

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]-benzoic Acid 4'-[(Dimethylthexylsilyl)oxy]-1,1'-biphenyl-4-yl Ester Homopolymer. Yield: 88%. Dp: *ca.* 200. Anal. Calcd for $C_{37}H_{48}O_6Si$: C, 69.96; H, 8.29. Found: C, 69.20; H, 8.06; N, <0.03. ^1H NMR ($CDCl_3$): δ 0.22 (b, 6 H), 0.91 (b, 2 H), 1.08 (b, 2 H), 1.44 (b, 4 H), 1.66 (b, 2 H), 1.80 (s, 3 H), 4.01 (b, 4 H), 6.86 (d, J = 8.50 Hz, 2 H), 7.20 (d, J = 8.70 Hz, 2 H), 7.38 (b, 2 H), 8.10 (d, J = 8.80 Hz, 2 H).

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]-benzoic Acid 4'-[[(Phenylmethoxy)carbonyl]oxy]-1,1'-biphenyl-4-yl Ester. Yield: 50%. Mp: 70–71 °C. Anal. Calcd for $C_{37}H_{36}O_8$: C, 73.01; H, 5.96. Found: C, 72.98; H, 6.08. ^1H NMR ($CDCl_3$): δ 1.40 (m, J = 6.18 Hz, 4 H), 1.62 (m, J = 6.72 Hz, 2 H), 1.73 (m, J = 6.94 Hz, 2 H), 1.87 (s, 3 H), 4.06 (m, J = 6.41 Hz, 4 H), 5.29 (s, 2 H), 5.65 (s, 1 H), 6.01 (s, 1 H), 7.09 (d, J = 8.9 Hz, 2 H), 7.33 (2d, J = 8.62 Hz, 4 H), 7.40 (m, 5 H), 7.72 (2d, J = 8.64 Hz, 4 H), 8.06 (d, J = 8.83 Hz, 2 H). ^{13}C NMR (DMSO-d_6): δ 17.97 (CH_3), 25.72 (CH_2), 25.38 (CH_2), 28.12 (CH_2), 28.57 (CH_2), 64.15 (CH_2), 67.63 (CH_2), 69.90 (CH_2), 113.90 (CH), 120.97 (CH), 121.05 (CH_2), 121.81 (CH), 124.88 (C), 127.59 (CH), 127.63 (CH), 128.08 (CH), 128.27 (CH), 128.32 (CH), 131.88 (CH), 134.40 (C), 136.03 (C), 137.13 (C), 150.17 (C), 150.24 (C), 153.14 (C), 163.05 (C), 164.30 (C), 166.89 (C). MS (70 eV): m/e 608 (14, M^+), 291 (41), 290 (100), 219 (15), 204 (33). IR (KBr disk): 2929, 2844, 1772, 1590, 1492, 1449, 1379, 1252, 1196, 1154, 1062, 992 cm^{-1}.

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]-benzoic Acid 4-[[(Phenylmethoxy)carbonyl]oxy]-phenyl Ester. Yield: 60%. Mp: 85–86 °C. Anal. Calcd for $C_{31}H_{32}O_8$: C, 69.91; H, 6.06. Found: C, 69.78; H, 6.11. ^1H NMR (DMSO-d_6): δ 1.35 (m, 4 H), 1.55 (m, J = 6.64 Hz, 2 H), 1.66 (m, J = 6.54 Hz, 2 H), 1.80 (s, 3 H), 4.01 (m, J = 6.43 Hz, 4 H), 5.21 (s, 2 H), 5.58 (s, 1 H), 5.94 (s, 1 H), 7.02 (d, J = 8.62 Hz, 2 H), 7.26 (m, 5 H), 7.32 (2d, J = 8.62 Hz, 4 H), 7.98 (d, J = 8.81 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 18.16 (CH_3), 25.48 (CH_2), 25.57 (CH_2), 28.33 (CH_2), 28.76 (CH_2), 64.37 (CH_2), 67.76 (CH_2), 70.19 (CH_2), 114.09 (CH), 121.08 (CH_2), 121.71 (CH), 122.52 (CH), 125.09 (C), 128.34 (CH), 128.49 (CH), 128.58 (CH), 132.09 (CH), 134.50 (C), 136.24 (C), 148.20 (C), 148.38 (C), 152.28 (C), 163.30 (C), 164.44 (C), 167.22 (C). MS (70 eV): m/e 533 (30, M^+), 425 (40), 323 (40), 289 (100), 221 (68), 155 (40), 121 (100). IR (KBr disk): 2929, 2858, 1752, 1724, 1604, 1506, 1379, 1316, 1259, 1189, 1154, 1062, 1006, 935, 837 cm^{-1}.

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]-benzoic Acid 4'-[[(Phenylmethoxy)carbonyl]oxy]-1,1'-biphenyl-4-yl Ester Homopolymer. Yield: 88%. Dp: *ca.* 150. Mp: 134–142 °C. Anal. Calcd for $C_{37}H_{36}O_8$: C, 73.01; H, 5.96. Found: C, 72.96; H, 5.94; N, <0.04. ^1H NMR ($CDCl_3$): δ 0.89 (b, 2 H), 1.08 (b, 2 H), 1.45 (b, 4 H), 1.60 (b, 2 H), 1.77 (b, 3 H), 3.92 (b, 4 H), 5.28 (b, 2 H), 6.81 (d, J = 8.79 Hz, 2 H), 7.21 (2d, J = 8.81 Hz, 4 H), 7.29 (b, 14 H), 8.03 (b, 2 H). IR (KBr disk): 2929, 1717, 1591, 1485, 1379, 1252, 1189, 1154, 1062, 999, 837 cm^{-1}.

4-[[6-[(2-Methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]-benzoic Acid 4-[[(Phenylmethoxy)carbonyl]oxy]-phenyl Ester Homopolymer. Yield: 75%. Dp: *ca.* 150. Mp: 82–87 °C. ^1H NMR ($CDCl_3$): δ 0.91 (b, 2 H), 1.18 (b, 2 H), 1.46 (b, 4 H), 1.68 (b, 2 H), 1.81 (b, 3 H), 3.84 (b, 4 H), 5.25 (b, 2 H), 6.89 (d, J = 8.80 Hz, 2 H), 7.20 (2d, J = 8.84 Hz, 4 H), 7.31 (b, 5 H), 8.01 (b, 2 H). IR (KBr disk): 2929, 1724, 1597, 1499, 1372, 1252, 1154, 1048, 999, 837, 759 cm^{-1}.

Polymer 1d. Yield: 75%. Dp: *ca.* 50. ^1H NMR (DMF-d_7): δ 0.73 (s, $^1/_2$H), 0.96 (b, 2 H), 1.00 (b, 2 H), 1.45 (b, 4 H), 1.65 (b, 2 H), 1.76 (b, 3 H), 4.02 (b, 2 H), 6.89 (b, J = 8.41 Hz, 2 H), 7.09 (b, 2 H), 7.44 (b, 2 H), 7.56 (b, 2 H), 8.06 (b, 2 H), 9.77 (s, 1 H).

Supplementary Material Available: Detailed procedures (including Scheme I) and analytical data for the preparation of benzyl [4-(4'-hydroxyphenyl)phenyl]carbonate, benzyl (4-hydroxyphenyl)carbonate, benzyl [4-[4'-(dimethylthexylsiloxy)-phenyl]phenyl]carbonate, benzyl [4-(dimethylthexylsiloxy)-phenyl]carbonate, 4-[4'-(dimethylthexylsiloxy)phenyl]phenol, and 4-(dimethylthexylsiloxy)phenol (5 pages). Ordering information is given on any current masthead page.

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