Triphenylene-Based Discotic-Liquid-Crystalline Polymers: A Universal, Rational Synthesis

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Abstract: A simple, regiospecific synthesis of main-chain, triphenylene-based discotic-liquid-crystalline polymers is described in which the key step is the assembly of the triphenylene nucleus through the oxidative coupling of phenyl and biphenyl residues. Hence, treatment of a mixture of 3,3′-bis(hexyloxy)-4,4′-dimethoxybiphenyl and 1,2-bis(hexyloxy)benzene with ferric chloride in dichloromethane followed by a reductive, methanol workup gives 2,7-dimethoxy-3,6,10,11-tetrakis(hexyloxy)triphenylene, **7**. The 2,7-linked main-chain polymer **8** is produced by demethylation and condensation with 1,11-dibromoundecane, has average molecular weight 24 000, and D_h mesophase range of 98–118 °C. The 3,6- and 2,3-linked polymers were prepared in a similar manner.

Introduction

The importance of liquid crystal polymers (LCP's) based on the self-organizing behavior of rodlike moieties (polymeric calamitic liquid crystals) is well-established.[1] Indeed, it has continued to expand since the 1960s when their unique properties and industrial relevance were first recognized. LCP's based on the self-organizing properties of disklike moieties (polymeric discotic liquid crystals) were discovered much more recently.[2,3] Their supramolecular organization is illustrated in Figure 1. The unique properties of these materials are also expected to lead to industrial applications. In contrast to calamitic LCP's, no satisfactory, flexible synthesis yet exists for the production of reasonable quantities of structurally homogeneous discotic LCP's. The pioneering synthesis of Ringsdorf and co-workers[2,3] produces a mixture of products, is limited by scale, and, more importantly, produces a mixture of inseparable isomers of ill-defined structure.

Clearly the development of the science and applications of discotic LCP's is dependent on the establishment of new, efficient synthetic strategies for the multigram production of regiospecific/single-isomer materials. With future applications in mind, we have targeted main-chain polyether-linked triphenylene discogens. These should also prove more thermally and chemically stable than the ester-linked polymers prepared previously by other groups.[3,4] In this paper we report the development of a universal, regiospecific synthesis for the production of such polymers.

Results

Most of the discotic polyesters prepared to date have been made by a route in which the key reaction is the partial hydrolysis/alkylation of triphenylene hexaacetate **1** as shown in Scheme 1.[2] This route requires extensive chromatographic separation of products, and so the scale on which these polymers have been prepared is small. Furthermore, the fact that only a mixture of diacetates can be isolated means that any main-chain polymers produced are structurally inhomogeneous.[3]

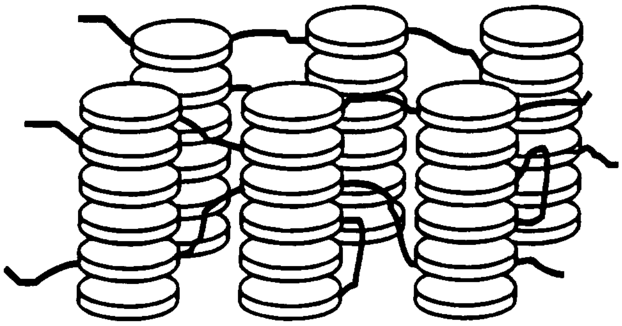

Figure 1. Schematic representation of the structure of an hexagonal mesophase (D_h) of a discotic LCP. The disks represent the central cores of the discogens. The intercolumnar space is filled by (hydrocarbon) side chains which, with the exception of the core–core linkages, have been omitted for clarity.

We have developed a rational, universal synthesis aqllowing the production of polymers of unique, defined structure on a multigram scale. The key step of this synthesis, shown in Scheme 2, is the oxidative coupling of biphenyl **6** with a 1,2-dialkoxybenzene using iron(III) chloride, followed by a methanol reductive-workup procedure, to yield the unsymmetrically substituted triphenylene **7**.[5] The methanol has a dual function. It acts as a reductant for the initially formed triphenylene cation (formaldehyde is liberated) and also precipitates the desired triphenylene from solution. Subsequent demethylation with lithium diphenylphosphide[6] gives the diphenol, and the polymer is obtained by reaction of its dicesium salt with an α,ω-dibromoalkane in *N*-methylpyrrollidone (NMP). In a similar manner, we have prepared the other isomeric polymers as shown in Scheme 3. The synthesis of dimethoxytriphenylene **9** was wholly analogous to that of **7**, whereas compound **13** was available from a previously published mixed trimerization route.[7]

Each of the polymers was purified by reprecipitation (dichloromethane/ethanol) which gave off-white solids. These gave "clean" high-field NMR spectra and elemental analyses consistent with the assigned structures. Typical average molecular weights obtained were **8** (24 000), **10** (8000), and **14** (7000)

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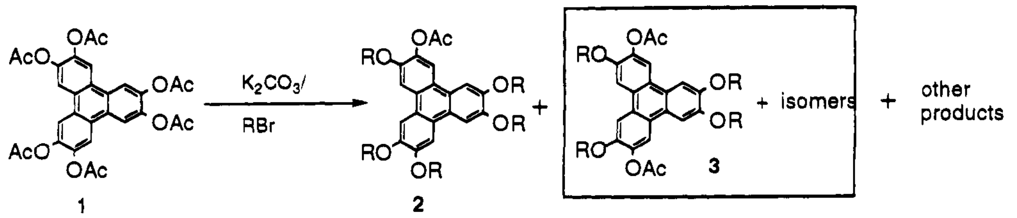
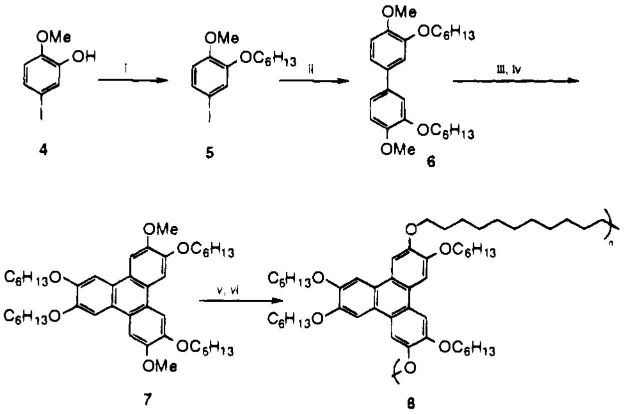
Scheme 1. Synthesis of Polymeric Discotic-Liquid-Crystal Precursors Based on the Partial Hydrolysis of Hexaacetate 1[a]



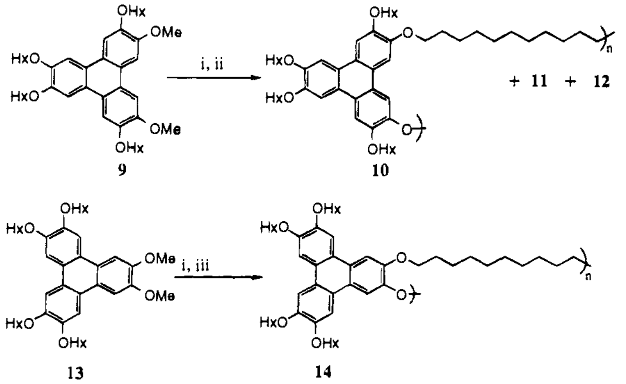
[a] Further elaboration of the monoacetate has led to side-chain liquid-crystal polymers,[2] whereas elaboration of the mixture of diacetates has led to main-chain liquid-crystal polymers, albeit of incompletely defined structure.[3]

Scheme 2. Synthesis of the 2,7-Linked Discotic Polymer[a]



[a] Reagents: (i) n-$C_6H_{13}Br$, K_2CO_3, ethanol, reflux; (ii) Cu, Δ; (iii) 1,2-bis(hexyloxy)benzene, $FeCl_3$; (iv) MeOH; (v) $LiPPh_2$, THF; (vi) Cs_2CO_3, $Br(CH_2)_{11}Br$, NMP.

Scheme 3. Synthesis of the 3,6- and 2,3-Isomers[a]



[a] Reagents: (i) $LiPPh_2$, THF; (ii) Cs_2CO_3, $Br(CH_2)_{11}Br$, NMP; (iii) Cs_2CO_3, $Br(CH_2)_{10}Br$, NMP.

(as determined by size-exclusion chromatography calibrated against polystyrene standards). In the case of polymer **10**, formation of cyclic oligomers was a competing process: Figure 2b clearly shows the presence of two low-molecular-weight components. These have been isolated and identified as cyclic monomer **11** and dimer **12**. Cyclic oligomer formation may also, in part, account for the low average molecular weight of polymer **14** (Figure 2c also indicates the presence of low-molecular-weight components). However, in this case, the higher sensitivity of the phenolic intermediate to decomposition under the reaction conditions may be a more significant factor.

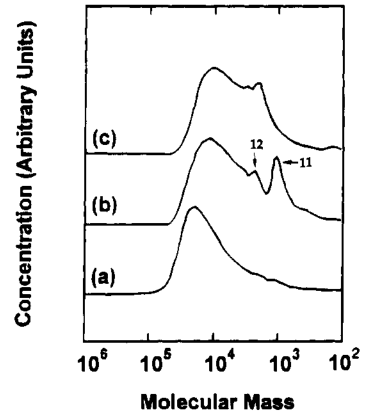


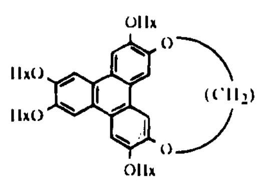
Figure 2. Size-exclusion chromatograms of the three discotic polymers (crude): (a) 2,7-isomer **8**. (b) 3,6-isomer **10**. (c) 2,3-isomer **14**.

Table 1. Mesophase Ranges of the New Discotic Polymers

polymer	T_D (°C)	T_I (°C)
8	98	118
10	93	120
14	100	115

The thermochemical behavior of the three polymers (Table 1) was analyzed by polarizing microscopy and DTA. All three polymers have similar properties and give a single DTA peak corresponding to the liquid crystal/isotropic liquid transition (T_I). No other peaks are observed on cooling down to room temperature. Similarly, the texture of the polymers, as observed by polarizing microscopy, remains unchanged on cooling the mesophase down to room temperature, but below a temperature T_D the sample could no longer be sheared. Both transition temperatures are reversible and reproducible over many cycles.

Polymer **8** was further characterized by low-angle X-ray diffraction. The photograph at 112 °C shows a diffraction pattern where the two inner rings correspond to spacings in the ratio of $1:\sqrt{3}$, characteristic of hexagonal structure (D_h mesophase), and remains essentially unchanged down to room



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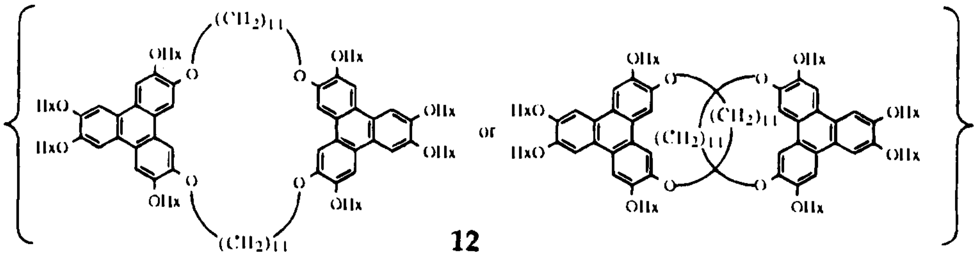

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temperature. The X-ray diffraction peaks correspond to an intracolumnar distance of 3.5 Å and an intercolumnar distance of 17.3 Å, and can be compared with distances of 3.5 Å and 19.5 Å for the hexakis(hexyloxy) monomer in its mesophase.[8] The full mesophase characterization of the polymers will appear elsewhere.[9]

Conclusions

The phenyl/biphenyl oxidative coupling reaction provides a simple, regiospecific route to hexaalkoxytriphenylenes of the type shown in Schemes 2 and 3. More elaborate schemes have been explored,[10,11] but for polymer precursors, this simple, one-pot methodology has clear advantages. Most notably, it allows single-isomer, main-chain, polymeric discotic liquid crystals to be prepared on an unprecedented scale, enabling the potential of these exciting new materials to be explored and exploited.

Experimental Section

General Information. ^{1}H NMR measurements were obtained on a General Electric 300 MHz spectrometer. Polarizing microscopy and DTA were performed using a Mettler FP90 processor with FP82 and FP84 stages. X-ray scattering experiments were conducted with a simple pinhole camera, consisting of a Phillips generator and tubes, nickel-filtered Cu Kα radiation of wavelength $\lambda = 0.154$ nm, Linderman sample tube (0.7 mm i.d.) to plate distance 112.8 mm.

2-(Hexyloxy)phenol, 15. A mixture of catechol (50 g, 0.45 mol), bromohexane (75 g, 0.45 mol), and potassium carbonate (100 g) was stirred in refluxing ethanol (250 mL) for 12 h. The mixture was cooled and dichloromethane (250 mL) added. The solid was filtered off and the filtrate concentrated *in vacuo*. Distillation at 150–160 °C (14 mmHg) afforded **15** (60 g, 69%) as a colorless oil. Anal. Found (Calcd for C_6H_{12}): C, 73.95 (74.19; H, 9.3 (9.34). ^{1}H NMR 6.95–6.79 (m, 4H, ArH), 5.79 (br s, 1H, OH), 3.95 (t, 2H, $J = 7$ Hz, OCH_2), 1.82 (m, 2H, $J = 7$ Hz, OCH_2CH_2), 1.44–1.26 (m, 6H, CH_2), 0.87 (t, 3H, $J = 7$ Hz, CH_3).

2-(Hexyloxy)phenyl Acetate, 16. Acetyl chloride (35 g, 0.45 mol) was added to **15** (65 g, 0.34 mol) with stirring over 1 h and the mixture stirred for a further 24 h. Dichloromethane (200 mL) was added and the solution washed with dilute potassium carbonate until the aqueous layer was basic. The organic solution was dried ($MgSO_4$) and the solvent removed *in vacuo*. Distillation of the residue at 100–106 °C at 0.8 mmHg afforded **16** as a colorless oil (75 g, 94%). ^{1}H NMR 7.12–6.80 (m, 4H, ArH), 3.87 (t, 2H, $J = 7$ Hz, OCH_2), 2.20 (s, 3H, $COCH_3$), 1.70 (m, 2H, $J = 7$ Hz, OCH_2CH_2), 1.44–1.26 (m, 6H, CH_2), 0.89 (t, 3H, $J = 7$ Hz, CH_3).

2-(Hexyloxy)-5-iodophenol, 17. **16** (24 g, 0.10 mol) was dissolved in chloroform (150 mL) and cooled to 8 °C. Iodine monochloride (20 g, 0.12 mol) in chloroform (50 mL) was added dropwise, maintaining the reaction temperature between 8 and 13 °C. The mixture was stirred at room temperature overnight and washed with sodium metabisulfite until the iodine color disappeared and then with water. The organic solution was separated and the solvent removed *in vacuo*. The residual red/brown oil was dissolved in ethanol (20 mL) and a solution of sodium hydroxide (35 g, 0.86 mol) in ethanol (50 mL) and water (40 mL) was added. The solution was refluxed for 1 h, allowed to cool, and carefully acidified with 40% sulfuric acid. The mixture was extracted with dichloromethane (2 × 150 mL) and the organic solutions were dried ($MgSO_4$). Removal of solvent *in vacuo* followed by distillation of the residue at 140–145 °C at (1.2 mmHg) gave a yellow oil which crystallized overnight. Recrystallization from light petroleum afforded **17** (20.5 g, 64%), mp 29–30 °C. ^{1}H NMR 7.23 (s, 1H, ArH), 7.14 (d, 1H, $J = 8$ Hz, ArH), 6.57 (d, 1H, $J = 8$ Hz, ArH), 5.63 (s, 1H, OH), 3.99 (t, 2H, $J = 7$ Hz, OCH_2), 1.79 (m, 2H, $J = 7$ Hz, OCH_2CH_2), 1.45–1.32 (m, 6H, CH_2), 0.91 (t, 3H, $J = 7$ Hz, CH_3).

2-(Hexyloxy)-5-iodoanisole, 18. **17** (15.1 g, 0.047 mol) and sodium hydroxide (2 g, 0.05 mol) were stirred in ethanol (100 mL) for 10 min. Methyl iodide (10 g, 0.07 mol) was added and the solution was stirred at room temperature for 3 days. The mixture was acidified with dilute sulfuric acid and extracted with dichloromethane (2 × 100 mL). The solvents were removed *in vacuo* and the residue was crystallized from ethanol to give **18** (12.2 g, 78%), mp 44–44.5 °C. Anal. Found (Calcd for $C_{13}H_{19}IO_2$): C, 46.9 (46.72); H, 5.95 (5.95); I, 37.95 (37.97). ^{1}H NMR 7.20 (d, 1H, $J = 8.5$ Hz, ArH), 7.12 (s, 1H, ArH), 6.62 (d, 1H, $J = 8.5$ Hz, ArH), 3.97 (t, 2H, $J = 7$ Hz, OCH_2), 3.84 (s, 3H, OCH_3), 1.83 (m, 2H, $J = 7$ Hz, OCH_2CH_2), 1.47–1.31 (m, 6H, CH_2), 0.90 (t, 3H, $J = 7$ Hz, CH_3).

4,4′-Bis(hexyloxy)-3,3′-dimethoxybiphenyl, 19. **18** (15 g, 0.45 mol) was mixed intimately with copper powder (17 g). The mixture was heated carefully to 270 °C where an exothermic reaction took place causing the temperature to rise to 320 °C. After cooling the mixture was extracted repeatedly with dichloromethane (~350 mL). The solvent was removed *in vacuo* and the residue crystallized from methanol to give **19** (6.1 g, 66%), mp 82.5–83 °C. Anal. Found (Calcd for $C_{26}H_{38}O_4$): C, 75.4 (75.32); H, 9.45 (9.24). ^{1}H NMR 7.08–7.06 (m, 4H, ArH), 6.92 (d, 2H, $J = 9$ Hz, ArH), 4.04 (t, 4H, $J = 7$ Hz, OCH_2), 3.93 (s, 6H, OCH_3), 1.86 (m, 4H, $J = 7$ Hz, OCH_2CH_2), 1.50–1.33 (m, 12H, CH_2), 0.90 (t, 6H, $J = 7$ Hz, CH_3).

3,6-Dimethoxy-2,7,10,11-tetrakis(hexyloxy)triphenylene, 9. **19** (3.6 g, 8.7 mmol) and 1,2-di(hexyloxy)benzene (7.25 g, 26 mmol) were stirred in dichloromethane (50 mL) and iron(III) chloride (18 g, 111 mmol) was added. After stirring for 1 h the mixture was poured onto methanol (100 mL) and the resulting solid immediately filtered off and dried in a desiccator. Purification by column chromatography (silica, benzene/light petroleum 4:1) afforded **9** (4.6 g, 77%), mp 116.5 °C. Anal. Found (Calcd for $C_{44}H_{64}O_6$): C, 76.85 (76.70); H, 9.5 (9.36). ^{1}H NMR 7.80 (s, 2H, ArH), 7.79 (s, 2H, ArH), 7.78 (s, 2H, ArH), 4.24–4.17 (m, 8H, OCH_2), 4.06 (s, 6H, OCH_3), 2.18–1.96 (m, 8H, OCH_2CH_2), 1.55–1.34 (m, 24H, CH_2), 0.90 (t, 12H, $J = 7$ Hz, CH_3).

3,6-Dihydroxy-2,7,10,11-tetrakis(hexyloxy)triphenylene 20. Diphenylphosphine 1.7 g, 9.2 mmol) was dissolved in dry THF (60 mL) and cooled in an ice bath under argon. Butyllithium (2.5 M in hexanes, 5 mL, 12.5 mmol) was added over 10 min. Solid **9** (1.7 g, 2.5 mmol) was added and the solution magnetically stirred at 50–60 °C for 4 h and at room temperature overnight. The mixture was poured onto dilute sulfuric acid and extracted with ethyl acetate (3 × 70 mL). The solvent was removed *in vacuo* and the residue precipitated from dichloromethane with methanol. The precipitate was filtered off, dried, and purified by column chromatography (silica, benzene) to give **20** (1.2 g, 74%), mp 105 °C. Anal. Found (Calcd for $C_{42}H_{60}O_6$): C, 76.15 (76.32); H, 9.1 (9.15). ^{1}H NMR 7.95 (s, 2H, ArH), 7.79 (s, 2H, ArH), 7.72 (s, 2H, ArH), 4.25–4.18 (m, 8H, OCH_2), 1.99–1.85 (m, 8H, OCH_2CH_2), 1.62–1.30 (m, 24H, CH_2), 0.90 (t, 12H, $J = 7$ Hz, CH_3).

Polymerization of 2,7,10,11-Tetrakis(hexyloxy)-3,6-dihydroxytriphenylene. **20** (0.576 g, 0.872 mmol) was stirred in *N*-methylpyrrolidone (NMP) (2 mL) and degassed with argon. Cesium carbonate (0.5 g) was added and the mixture stirred for 5 min. 1,11-Dibromoundecane (274 mg, 0.872 mmol) in *N*-methylpyrrolidone (0.5 mL) was added and the flask immediately immersed in an oil bath at 85 °C. A two-phase mixture was immediately formed which was stirred at 85 °C for 2 days and poured onto water. The solid was filtered, reprecipitated from dichloromethane with ethanol, and separated by column chromatography (silica, benzene, then dichloromethane) to give monomer **11** (60 mg), mp 73 °C. M^+(FAB) = 812 ($C_{53}H_{80}O_6 = 812$): ^{1}H NMR 7.91 (s, 2H, ArH), 7.84 (s, 4H, ArH), 4.21–4.35 (m, 12H, OCH_2), 1.98 (m, 12H, $J = 7$ Hz, OCH_2CH_2), 1.65–1.35 (m, 38H, CH_2), 0.93 (t, 12H, $J = 7$ Hz, CH_3); dimer **12** (35 mg), K-D 130 °C D-I 140 °C, M^+(FAB) = 1625 ($C_{106}H_{160}O_{12} = 1624$), ^{1}H NMR 7.81 (m, 6H, ArH), 4.24 (t, 12H, $J = 7$ Hz, OCH_2), 1.91 (t, 12H, $J = 7$ Hz, OCH_2CH_2), 1.65–1.35 (m, 38H, CH_2), 0.93 (t, 12H, $J = 7$ Hz, CH_3); polymer **10** (450 mg), M_w ~9000, K-D 93 °C, D-I 120 °C. Anal. Found (Calcd for $(C_{53}H_{80}O_6)_n$): C, 78.45 (78.28); H, 9.75 (9.92). ^{1}H NMR 7.81 (s, 6H, ArH), 4.24 (t, 12H, $J = 7$ Hz, OCH_2), 1.91 (m, 12H, $J = 7$ Hz, OCH_2CH_2), 1.65–1.35 (m, 38H, CH_2), 0.93 (t, 12H, $J = 7$ Hz, CH_3). Note that the ^{1}H NMR of **12** is virtually identical to that of polymer **10** but distinct from that of the monomer **11**. This may suggest that the macrocyclic structure is more likely than the catenane.

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4-Iodo-2-(hexyloxy)anisole, 5. **4** (50 g, 0.2 mol) (prepared from guaiacol *via* a route analogous to 2-(hexyloxy)-5-iodophenol), hexyl bromide (38 g, 0.23 mol), and potassium carbonate (42 g) were stirred in refluxing ethanol (150 mL) for 6 h. Light petroleum ether was added to the cooled mixture and the solid filtered off and washed with light petroleum ether. The organic solvents were removed *in vacuo* and the residual oil distilled at 130−132 °C (0.75 mmHg) to yield **5** (58 g, 87%). Anal. Found (Calcd for $C_{13}H_{19}IO_2$): C, 46.45 (46.72); H, 5.9 (5.95); I, 37.95 (37.97). ^{1}H NMR 7.21 (d, 1H, *J* = 8 Hz, ArH), 7.12 (s, 1H, ArH), 6.61 (d, 1H, *J* = 8 Hz, ArH), 3.97 (t, 2H, *J* = 7 Hz, OCH_2), 3.81 (s, 3H, OCH_3), 1.83 (m, 2H, *J* = 7 Hz, $OCH_2C\mathit{H}_2$), 1.49−1.30 (m, 6H, CH_2), 0.90 (t, 3H, *J* = 7 Hz, CH_3).

3,3′-Bis(hexyloxy)-4,4′-dimethoxybiphenyl, 6. **5** (20 g, 0.06 mol) and copper powder (20 g) were thoroughly mixed together and heated to 270 °C for 10 min. The mixture was cooled and extracted repeatedly with chloroform. The solvent was removed *in vacuo* and the residue crystallized from ethanol to afford **6** (5.9 g, 48%), mp 75.5−76.5 °C. Anal. Found (Calcd for $C_{26}H_{38}O_4$): C, 75.3 (75.32); H, 9.1 (9.24). ^{1}H NMR 7.08−7.06 (m, 4H, ArH), 6.93 (d, 2H, *J* = 9 Hz, ArH), 4.08 (t, 4H, *J* = 7 Hz, OCH_2), 3.90 (s, 6H, OCH_3), 1.74 (m, 4H, *J* = 7 Hz, $OCH_2C\mathit{H}_2$), 1.50−1.30 (m, 12H, CH_2), 0.90 (t, 6H, *J* = 7 Hz, CH_3).

2,7-Dimethoxy-3,6,10,11-tetrakis(hexyloxy)triphenylene 7. A mixture of iron(III) chloride (45 g, 0.29 mol), concentrated sulfuric acid (0.5 mL), **6** (8 g, 0.019 mol), and 1,2-bis(hexyloxy)benzene (22.8 g, 0.082 mol) was stirred in dichloromethane (150 mL) for 1 h. The reaction mixture was carefully poured onto methanol (500 mL), and after cooling in ice the resulting solid was filtered off and washed with methanol. Separation on silica (benzene eluant) afforded **7** (6 g, 45%), mp 98 °C. Anal. Found (Calcd for $C_{44}H_{64}O_6$): C, 76.7 (76.70); H, 9.35 (9.36). ^{1}H NMR 7.85 (s, 2H, ArH), 7.81 (s, 4H, ArH), 4.27−4.21 (m, 8H, OCH_2), 4.10 (s, 6H, OCH_3), 1.97−1.91 (m, 8H, $OCH_2C\mathit{H}_2$), 1.60−1.55 (m, 24H, CH_2), 0.93 (t, 12H, *J* = 7 Hz, CH_3).

2,7-Dihydroxy-3,6,10,11-tetrakis(hexyloxy)triphenylene, 21. By use of a similar procedure to that used in the preparation of **20**, **21** was obtained in 73% yield, mp 186 °C. Anal. Found (Calcd for $C_{42}H_{60}O_6$): C, 76.25 (76.32); H, 9.1 (9.15). ^{1}H NMR 7.95 (s, 2H, ArH), 7.80 (s, 2H, ArH), 7.69 (s, 2H, ArH), 4.26−4.17 (m, 8H, OCH_2), 1.95−1.90 (m, 8H, $OCH_2C\mathit{H}_2$), 1.60−1.38 (m, 24H, CH_2), 0.94 (t, 12H, *J* = 7 Hz, CH_3).

Polymerization of 2,7-Dihydroxy-3,6,10,11-tetrakis(hexyloxy)-triphenylene. **21** (400 mg, 6.06×10^{-4} mol) and cesium carbonate (390 mg, 1.2×10^{-4} mol) were dissolved in NMP (1.3 mL). 1,11-Dibromoundecane (190 mg, 6.05×10^{-3} mol) in NMP (1 mL) was added and the mixture immediately submerged in an oil bath at 110 °C. The mixture was stirred for 1 h at 110 °C and cooled. Water was added and the resulting solid repeatedly washed with water and ethanol. Reprecipitation from dichloromethane with ethanol afforded the polymer **8** as an off-white solid (280 mg), $M_w \sim 24\,000$, K-D 98 °C, D-I 118 °C. Anal. Found (Calcd for $(C_{53}H_{80}O_6)_n$): C, 78.3 (78.28); H, 10.2 (9.92). ^{1}H NMR 7.81 (s, 6H, ArH), 4.22 (t, 12H, *J* = 7 Hz, OCH_2), 1.92 (m, 12H, *J* = 7 Hz, $OCH_2C\mathit{H}_2$), 1.65−1.30 (m, 38H, CH_2), 0.93 (t, 12H, *J* = 7 Hz, CH_3).

2,3-Dihydroxy-6,7,10,11-tetrakis(hexyloxy)triphenylene, 22. By use of a similar procedure to that used for the preparation of **20**, **22** was obtained in 77% yield as a white solid which rapidly darkened in air. ^{1}H NMR 7.91 (s, 2H, ArH), 7.77 (s, 2H, ArH), 7.72 (s, 2H, ArH), 4.19 (t, 4H, *J* = 7 Hz, OCH_2), 4.03 (t, 4H, *J* = 7 Hz, OCH_2), 1.99−1.73 (m, 8H, $OCH_2C\mathit{H}_2$), 1.57−31 (m, 24H, CH_2), 0.92 (t, 12H, *J* = 7 Hz, CH_3).

Polymerization of 2,3-Dihydroxy-6,7,10,11-tetrakis(hexyloxy)-triphenylene. **22** (1.565 g, 2.38×10^{-3} mol) was stirred in degassed NMP (5 mL) with cesium carbonate (2 g) under argon. 1,10-Dibromodecane (0.709 g, 2.42×10^{-3} mol) in NMP was added and the flask immediately submerged in an oil bath at 110 °C. The mixture was stirred at 110 °C for 24 h and cooled and water (20 mL) was added. The solid was filtered off, washed with water and ethanol, and reprecipitated from dichloromethane with ethanol to give the polymer **14** (1.6 g), $M_w \sim 7000$. K-D 100 °C, D-I 115 °C. Anal. Found (Calcd for $(C_{52}H_{78}O_6)_n$): C, 77.4 (78.15); H, 10.2 (9.84). ^{1}H NMR 7.83 (s, 6H, ArH), 4.23 (t, 12H, *J* = 7 Hz, OCH_2), 1.89 (m, 12H, *J* = 7 Hz, $OCH_2C\mathit{H}_2$), 1.71−1.40 (m, 36H, CH_2), 0.91 (t, 12H, *J* = 7 Hz, CH_3).

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