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Design of Side Chain and Main Chain Liquid Crystalline Polymers Containing Supramolecular Quasi-Rigid-Rodlike Mesogens Obtained from Collapsed Main Chain Macrocyclics

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ABSTRACT: The synthesis of the AB_2 mesogenic group 13-hydroxy-1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)tridecane (TPT′-OH, **11**) and its use in the preparation of 1,12,33,44-tetraoxa-25-[(methacryloyloxy)undecanyl]-57-ethyl[12.0.2.12.0.2]paracyclophane (**17**), 1,12,33,44,65,76-hexaoxa-25-[(methacryoyloxy)undecanyl]-57,89-diethyl[12.0.2.12.0.2.12.0.2]paracyclophane (**24**), and 1,12,33,44,65,76,97,108-octaoxa-25-[(methacryloyloxy)undecanyl]-57,89,121-triethyl[12.0.2.12.0.2.12.0.2.12.0.2]paracyclophane (**30**) and of the corresponding polymethacrylates **18**, **25**, and **31** are described. Monomers **17**, **24**, and **30** are the main chain cyclic dimer, trimer, and tetramer, respectively, of 1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)butane (TPB′, **13**) with **11** and 1,10-dibromodecane and, therefore, are attached to the methacryloyl group through a spacer containing 11 methylenic units. The collapsed conformation of these macrocyclics combined with their degree of oligomerization places these quasi-rigid-rodlike mesogens side-on in **18**, end-on in **25**, and in between side-on and end-on in **31**. The synthesis of the biselectrophilic macrocyclic main chain dimers 1,7,28,34-tetraoxa-20,47-bis(bromohexyl)[7.0.2.7.0.2]paracyclophane (**40**) from 8-hydroxy-1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)octane (TPO-OH, **36**) and 1,5-dibromopentane and 1,12,39,50-tetraoxa-32,70-bis(bromoundecanyl)[12.0.0.2.12.0.0.2]paracyclophane (**46**) from 13-hydroxy-1-(4-hydroxyphenyl)-2-(4-hydroxy-4″-terphenylyl)tridecane (TPT-OH, **42**) and 1,10-dibromodecane is also presented. Their phase transfer-catalyzed polyetherification with TPB′ produced the main chain polyethers **41** and **47**. The mesomorphic behavior of these first examples of side chain and main chain polymers containing macrocyclic mesogens is discussed. In spite of the long spacer used in the design of these polymers, they do not crystallize and also do not display smectic phases. **25**, **31**, and **47** exhibit an enantiotropic nematic phase, while **18** and **41** are amorphous. The use of the spacer in the construction of both the macrocyclic mesogen and the corresponding main chain and side chain liquid crystalline polymers provides the highest degree of conformational disorder from all known polymers exhibiting a nematic mesophase.

Introduction

In 1975, de Gennes[1] suggested that main chain thermotropic liquid crystalline polymers (LCP) might be prepared by incorporating mesogenic groups and flexible spacers in the main chain of a polymer. In the same year Roviello and Sirigu[2] provided the first examples of thermotropic main chain LCPs based on the spacer concept. In 1978, Finkelmann, Ringsdorf, et al.[3] advanced the flexible spacer concept to decouple the motion of the main chain and mesogenic side groups in side chain LCPs. Although conceptually more complex[4−6] than originally conceived, the spacer concept was responsible for the very fast developement of the field of LCPs. In addition, the complexity of the spacer concept generated a tremendous research interest and enthusiasm in the field of main chain and side chain LCPs with flexible spacers.

We are concerned with two main problems in which the spacer concept plays a dominant role. The first one is the elaboration of model polymers and polymerization reactions that facilitate the understanding of the simplest classes of main chain and side chain LCPs.[4,5] The second one is the molecular design of novel classes of molecular and macromolecular liquid crystals with complex architecture such as cyclic,[7,10] hyperbranched,[8,10b,c] and dendrimers.[9,10d] Cyclics based on main chain polymers containing flexible spacers and mesogenic units based on conformational isomerism produce in the LC phase a collapsed quasi-rigid-rodlike conformation.[7h,10d] The proper combination between the structure of mesogen and length of the flexible spacer has been shown to generate cyclic LCs exhibiting mesophases that are more stable than those of the corresponding low and high molecular weight linear polymers (Figure 1).[7h,10d] Therefore, contrary to what has been considered for over 100 years, cyclic and not linear is the ideal structure which yields liquid crystallinity for structures based on both conformationally flexible[7a−m,10d] or rigid[7n] rodlike groups and flexible spacers. Consequently, these collapsed macrocyclics represent the ideal "mesogenic" unit.

An interesting feature of rodlike mesogens based on collapsed cyclics is that in spite of their high rigidity,[7l] in the LC phase they tolerate a much higher conformational entropy than the corresponding linear compounds.[10d] This permits the molecular design of both conventional main chain and side chain LCPs as well as of more complex architectures with extremely rigid,[7d,h,l] but at the same time soluble, mesogens. The recent elaboration of a simple stepwise synthesis of cyclic LC compounds in high yield[7m] allowed for the first time an entry into the new field of LCPs based on supramolecular rigid-rodlike mesogens obtained from collapsed macrocyclics. This novel class of LCPs provides the most complex exploitation of the spacer concept. The goal of this publication is to report the rational design, synthesis, and characterization of the first examples of side chain and main chain LCPs containing supramo-

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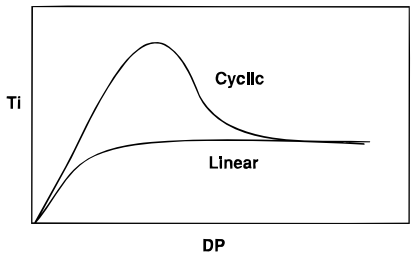


Figure 1. Theoretical and experimental dependence of the isotropization temperature (T_i) of cyclic and linear main chain LCPs on their degree of polymerization (DP). Both T_i and DP are in arbitrary units.

lecular quasi-rigid-rodlike mesogens obtained from collapsed macrocyclics.

Experimental Section

Materials. 1,5-Dibromopentane (97%), 1,10-dibromodecane (97%), 6-chloro-1-hexanol (95%), 11-bromo-1-undecanol (97%), tetrabutylammonium hydrogen sulfate (TBAH, 97%), PPh_3 (99%), CBr_4 (99%), Al_2O_3, (all from Aldrich), tetrapentylammonium iodide (97%) (Eastman Organic Chemicals), anhydrous $AlCl_3$ (99%), Mg (both from Fluka), $LiAlH_4$ (99%), CH_3I (99%), CH_3COOH, SiO_2 (from Fisher), 5% Pd on carbon (Lancaster Synthesis), and Cs_2CO_3 (Alpha) were used as received. Methacryloyl chloride (Fluka) was distilled under vacuum; azobis(isobutyronitrile) (AIBN; Kodak) was recrystallized from MeOH. Et_2O was dried by refluxing over $LiAlH_4$. DMF, CH_2Cl_2, and $CHCl_3$ were dried by refluxing over CaH_2. Benzene used as solvent in radical polymerizations was washed with H_2SO_4 and water, dried over $MgSO_4$, and distilled from Na/benzophenone. All dried solvents were freshly distilled before each use. *o*-Dichlorobenzene (*o*-DCB) was distilled under reduced pressure. 4-Methoxybiphenyl (**1**), 4-acetoxybiphenyl (**2**), 4-methoxy-4′-biphenylyl methyl ketone (**3**), (4-methoxy-4-biphenylyl)acetic acid (**5**), 1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)ethanone (**8**), and 1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)butane (TPB′, **13**) were synthesized as previously reported.[11] 1-[4-[(Bromodecanyl)oxy]phenyl]-2-[4-[(bromodecanyl)oxy]-4′-biphenylyl]butane (**14**), 1-(4-hydroxyphenyl)-2-[4-(benzyloxy)-4′-biphenylyl]butane (**19**), 1-[4-(bromodecanoxy)phenyl]-2-[4-(benzyloxy)-4′-biphenylyl]butane (**20**), 1-[4-[[4-[2-[4-(benzyloxy)-4′-biphenylyl]butyl]phenoxy]decanoxy]-phenyl]-2-[2-[4-(benzyloxy)-4′-biphenylyl]butyl]phenoxy]decanoxy]-4′-biphenylyl]butane (**26**), 1-[4-[[4-[2-(4-hydroxy-4′-biphenylyl)butyl]phenoxy]decanoxy]phenyl]-2-[4-[[4-[2-(4-hydroxy-4′-biphenylyl)butyl]phenoxy]decanoxy]-4′-biphenylyl]butane (**27**), and 1-[4-[[4-[2-[4-(bromodecanoxy)-4′-biphenylyl]butyl]phenoxy]-decanoxy]phenyl]-2-[4-[[4-[2-[4-(bromodecanoxy)-4′-biphenylyl]-butyl]phenoxy]decanoxy]-4′-biphenylyl]butane (**28**) were prepared as previously described.[7m] The synthesis of 13-hydroxy-1-(4-hydroxyphenyl)-2-(4-hydroxy-4″-terphenylyl)tridecane (TPT-OH, **42**) was reported elsewhere.[9] All other chemicals were commercially available and used as received.

Techniques. A Varian Gemini 200 spectrometer was used to record the ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra at 20 °C. TMS was used as internal standard. Relative molecular weights and purities were determined on a Perkin-Elmer Series 10LC GPC/HPLC instrument, equipped with a LC-100 column oven, a Nelson Analytical 900 Series data station, and a UV detector. The measurements were done using THF as solvent (1 mL/min, 40 °C) and two PL gel columns of 5×10^2 and 10^4 Å. A calibration plot constructed with polystyrene standards was used for the determination of the relative molecular weights. The purity of the compounds was also supported by thin layer chromatography (TLC) obtained on silica gel plates (Kodak) with fluorescent indicator. A Perkin-Elmer PC Series DSC-7 differential scanning calorimeter equipped with a TAC7/DX thermal analysis controller was used to record the first-order thermal transitions which were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transitions were measured as the middle of the change in heat capacity. The instrument was calibrated with In and Zn standards. Scanning rates were 20 °C/min in all cases. All heating and cooling scans were perfectly reproducible after the first heating scan. The first heating scan could be reobtained after proper annealing. An Olympus BX40 optical polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to analyze the anisotropic textures. Molecular modeling was performed on a Silicon Graphics computer on the MacroModel software (version 5, Columbia University) using the MM3 force field for energy minimization.

Synthesis of 13-Hydroxy-1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)tridecanone (9). To a mixture of **8** (13.9 g, 42 mmol), THF (150 mL), NaOH (10 N, 150 mL), and TBAH (2.8 g, 8 mmol) was added dropwise $Br(CH_2)_{11}OH$ (12.6 g, 50 mmol). The mixture was stirred vigorously at 40 °C for 10 h; then CH_2Cl_2 (200 mL) was added. The organic phase was washed with water, dilute HCl, and water and dried over $MgSO_4$. The solvents were evaporated, and the solid was recrystallized from MeOH. The yield was 14.7 g (72%) of white crystals, mp = 55−56 °C, purity (HPLC), >99%. ^{1}H-NMR (δ, ppm, $CDCl_3$, TMS): 1.24 (m, 16H, -$CH_2(CH_2)_8(CH_2)$OH), 1.55 (m, 2H, -CH_2CH_2OH), 1.85 (q, 1H, -$CH_2(CH_2)_{10}$OH), 2.16 (q, 1H, -$CH_2(CH_2)_{10}$OH), 3.63 (t, 2H, -CH_2OH, J = 6.6 Hz), 3.83 (s, 6H, -OCH_3), 4.52 (t, 1H, -CHCO-, J = 7.2 Hz), 6.88 (d, 2H, *ortho* to -OCH_3 on the monophenyl ring, J = 8.9 Hz), 6.91 (d, 2H, *ortho* to -OCH_3 on the biphenyl ring, J = 8.74 Hz), 7.34 (d, 2H, *ortho* to -CHCO- on the biphenyl ring, J = 8.26 Hz), 7.46 (d, 2H, *meta* to -CHCO- on the biphenyl ring, J = 8.18 Hz), 7.48 (d, 2H, *meta* to -OCH_3 on the biphenyl ring, J = 8.8 Hz), 7.99 (d, 2H, *ortho* to -CHCO- on the monophenyl ring, J = 8.92 Hz).

Synthesis of 13-Hydroxy-1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)tridecane (10). An $AlCl_3$·Et_2O complex[12] prepared by the slow addition of $AlCl_3$ (23 g, 0.17 mol) to dry Et_2O (100 mL) at −10 °C under N_2 was added to a mixture of $LiAlH_4$ (3.3 g, 0.09 mol) and dry Et_2O (100 mL) followed by a solution of **9** (14.5 g, 0.03 mol) in dry $CHCl_3$ (80 mL). After 0.5 h of stirring, the reaction was quenched by the slow addition of dilute HCl (200 mL). The organic layer was separated, washed with water, and dried over $MgSO_4$. The solvent was evaporated, and the product was purified by flash column chromatography (ethyl acetate/hexane = 1/3) to yield 11.4 g (83%) of white crystals, mp = 55−57 °C, purity (HPLC), 99%. ^{1}H-NMR (δ, ppm, $CDCl_3$, TMS): 1.2 (m, 16H, -$CH_2(CH_2)_8(CH_2)_2$OH), 1.6 (m, 4H, -$CH_2(CH_2)_8CH_2CH_2$OH), 2.84 (m, 3H, -$C_6H_4C_6H_4CHCH_2C_6H_4$-), 3.59 (t, 3H, -CH_2OH, J = 6.62 Hz), 3.76 (s, 3H, -OCH_3 on the monophenyl ring), 3.85 (s, 3H, -OCH_3 on the biphenyl ring), 6.75 (d, 2H, *ortho* to -OCH_3 on the monophenyl ring, J = 8.5 Hz), 6.96 (d, 4H; 2H *ortho* to -OCH_3 on the biphenyl ring; 2H *meta* to -OCH_3 on the monophenyl ring, J = 8.4 Hz), 7.14 (d, 2H, *ortho* to -$CHCH_2$- on the biphenyl ring, J = 8.06 Hz), 7.45 (d, 2H, *meta* to -$CHCH_2$- on the biphenyl ring, J = 8.06 Hz), 7.53 (d, 2H, *meta* to -OCH_3 on the biphenyl ring, J = 8.72 Hz).

Synthesis of 13-Hydroxy-1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)tridecane (11, TPT′-OH). To a mixture of Mg (5.75 g, 0.23 mol) and dry Et_2O (80 mL) was added CH_3I[13] (33 g, 0.23 mol) dropwise under N_2 at 5 °C. To the resulting solution was added **10** (7.7 g, 0.015 mol). The temperature was increased to 40 °C, Et_2O was distilled, and then the mixture was heated to 150 °C, and the melt was stirred for 5 h. After cooling to 0 °C, Et_2O (100 mL) was added followed by the slow addition of dilute HCl. The organic layer was washed with water and dilute $NaHCO_3$ followed by dilute $Na_2S_2O_3$. The colorless organic phase was dried over $MgSO_4$, and the solvent was evaporated to yield an oil that crystallized on standing. The solid was washed with cold toluene to yield 5.9 g (86%) of white crystals, mp = 144−146 °C, purity (HPLC), >99%. ^{1}H-NMR (δ, ppm, $CDCl_3$, TMS): 1.2 (m, 16H, -$CH_2(CH_2)_8(CH_2)_2$OH), 1.6 (m, 4H, -$CH_2(CH_2)_8CH_2CH_2$OH), 2.79 (m, 3H, -$C_6H_4C_6H_4CHCH_2C_6H_4$-), 3.65 (t, 2H, -CH_2OH, J = 6.6 Hz), 5 (s, 1H, -C_6H_4O*H*), 5.03 (s, 1H, -$C_6H_4C_6H_4$O*H*), 6.68 (d, 2H, *ortho* to -OH on the monophenyl ring, J = 8.6 Hz), 6.88 (d, 2H, *ortho* to the -OH on the biphenyl ring, J = 8.7 Hz), 6.91 (d, 2H, *meta* to -OH on the monophenyl ring, J = 8.6 Hz), 7.14 (d, 2H, *ortho* to -$CHCH_2$- on the biphenyl ring, J = 8.26 Hz),

Table 1. Characterization of the Macrocyclic Intermediary Compounds, Monomers, and Corresponding Polymers

macrocycle	separated yield (%)	purity (HPLC) (%)	molecular weight (GPC) exptl	molecular weight (GPC) calcd	thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses: second heating	thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses: first cooling
TPB′-(c)10(2)^{7m}	4.5	98.8	1116	912	g 18 k 64 (−3.67) k 113 (3.94) i	i 12 g
TPB′-TPT′-(c)10(2)OAc (**15**)	35	99	1440	1096	g −7 i	i −13 g
TPB′-TPT′-(c)10(2)OH (**16**)	80	98.9	1396	1051	g 11 i	i 0 g
TPB′-TPT′-(c)10(2)MA (**17**)	87	99	1410	1119	g −10 i	i −17 g
TPB′-TPT′-(c)10(2)PMA (**18**)	60		M_n = 64 000	M_w/M_n = 2.54	g 52 i	i 45 g
TPB′-(c)10(3)^{7m}	45.5	99	1928	1368	g 33 s^A 64 (0.12) n 80 (0.28) i	i 75 (0.28) n 57 (0.12) s_A 27 g
(TPB′)$_2$-TPT′-(c)10(3)OH (**23**)	25	99	2080	1512	g 15 s_A 45 (0.13) n 55 (0.29) i	i 49 (0.30) n 40 (0.11) s_A 10 g
(TPB′)$_2$-TPT′-(c)10(3)MA (**24**)	90	98.8	2110	1580	g −1 s_A 23 (0.08) n 33 (0.21) i	i 26 (0.20) n 14 (0.09) s_A −10 g
(TPB′)$_2$-TPT′-(c)10(3)PMA (**25**)	28		M_n = 11 000	M_w/M_n = 1.4	g 36 n 53 (0.13) i	i 37 (0.12) n 23 g
TPB′-(c)10(4)^{7m}	10.8	98.7	2692	1824	g 31 n 123 (1.28) i	i 117 (1.25) n 23 g
(TPB′)$_3$-TPT′-(c)10(4)OH (**29**)	35	99	2945	1964	g 25 n 89 (1.23) i	i 84 (1.25) n 19 g
(TPB′)$_3$-TPT′-(c)10(4)MA (**30**)	84	99	3053	2032	g 15 n 86 (1.10) i	i 81 (1.08) n 6 g
(TPB′)$_3$-TPT′-(c)10(4)PMA (**31**)	32		M_n = 75 00	M_w/M_n = 1.7	g 33 n 63 (0.73) i	i 59 (0.69) n 18 g
TPO-(c)5(2)OH (**39**)	23	99	1180	916	g 47 i	i 41 g
TPO-(c)5(2)Br (**40**)	83	98.9	1213	1042	g 43 k 125 (−6.97) k 159 i	i 35 g
poly[TPO-(c)5(2)-*co*-TPB′] (**41**)	86		M_n = 9000	M_w/M_n = 1.5	g 76 i	i 67 g
TPT-(c)10(2)OH (**45**)	19	99	1488	1348	k 150 (4.88) i	i 123 (0.59) n 102 (2.92) k 94 g
TPT-(c)10(2)Br (**46**)	81	99	1507	1474	k 85 (−2.33) k 122 (1.8) k 132 (0.4) k 144 (0.4) i	i 127 (0.7) n 52 k 5 g
poly[TPT-(c)10(2)-*co*-TPB′] (**47**)	88		M_n = 40 000	M_w/M_n = 2.1	g 69 n 143 (0.56) i	i 134 (0.55) n 61 g

7.43 (d, 2H, *meta* to the -OH on the biphenyl ring, J = 8.7 Hz), 7.47 (d, 2H, meta to -CHCH$_2$- on the biphenyl ring, J = 8.3 Hz).

Synthesis of 13-Acetoxy-1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)tridecane (12, TPT′-OAc). A solution of **11** (5.38 g, 0.011 mol) in CH_3COOH (150 mL) was stirred at 100 °C for 10 h. The solution was filtered, and excess CH_3COOH was distilled. The solid was dissolved in CH_2Cl_2 (200 mL), and the solution was washed with water, dilute $NaHCO_3$, and water. The solvent was evaporated to give an oil that crystallized on standing. The solid was washed with hexane to yield 5.42 g (92%) of white crystals, mp = 112−114 °C, purity (HPLC), >99%. ^{1}H-NMR (δ, ppm, $CDCl_3$, TMS): 1.2 (m, 16H, -CH$_2$(*CH*$_2$)$_8$(CH$_2$)$_2$OH), 1.6 (m, 4H, -C*H*$_2$(CH$_2$)$_8$C*H*$_2$-CH$_2$OH), 2.05 (s, 3H, -OCOC*H*$_3$), 2.8 (m, 3H, -C$_6$H$_4$C$_6$H$_4$C*H*CH$_2$C$_6$H$_4$-), 4.06 (t, 2H, -C*H*$_2$OCOCH$_3$, J = 6.72 Hz), 4.71 (s, 1H, -C$_6$H$_4$O*H*), 4.82 (s, 1H, -C$_6$H$_4$C$_6$H$_4$O*H*), 6.68 (d, 2H, *ortho* to -OH on the monophenyl ring, J = 8.6 Hz), 6.88 (d, 2H, *ortho* to the -OH on the biphenyl ring, J = 8.7 Hz), 6.91 (d, 2H, *meta* to -OH on the monophenyl ring, J = 8.6 Hz), 7.14 (d, 2H, *ortho* to -CHCH$_2$- on the biphenyl ring, J = 8.26 Hz), 7.43 (d, 2H, *meta* to -OH on the biphenyl ring, J = 8.7 Hz), 7.47 (d, 2H, meta to -CHCH$_2$- on the biphenyl ring, J = 8.3 Hz).

Synthesis of 1,12,33,44-Tetraoxa-25-(acetoxyundecanyl)-57-ethyl[12.0.2.12.0.2]paracyclophane (15, TPB′-TPT′-(c)10(2)OAc). To a 5 L 3-neck flask equipped with a mechanical stirrer, containing DMF (4 L) and Cs_2CO_3 (1.3 g, 4 mmol) was added a solution of **13** (0.66 g, 1.32 mmol) and **14** (1 g, 1.32 mmol) in DMF (100 mL) was added dropwise under N_2 *via* a syringe pump. The mixture was stirred at 80 °C for 4 days. DMF was distilled, and CH_2Cl_2 was added. The organic phase was washed with water, dilute HCl, and water and dried over $MgSO_4$. The solvent was evaporated, and the solid was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1/15) to yield 480 mg (35%) of a white crystalline solid, purity (HPLC), >99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.87 (t, 3H, -CH$_2$C*H*$_3$, J = 7.32 Hz), 1.3 (m, 42H; 24H, -O(CH$_2$)$_2$-(C*H*$_2$)$_6$(CH$_2$)$_2$O-, 18H, -CH(C*H*$_2$)$_9$(CH$_2$)$_2$OCOCH$_3$), 1.73 (m, 10H; 8H, -OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O-, 2H, -(CH$_2$)$_9$C*H*$_2$CH$_2$OCOCH$_3$), 2.04 (s, 3H, -OCOC*H*$_3$), 2.75 (m, 4H, -C$_6$H$_4$CHC*H*$_2$C$_6$H$_4$-), 2.95 (m, 2H, -C$_6$H$_4$C*H*CH$_2$C$_6$H$_4$-), 3.85 (t, 4H, -CH$_2$C$_6$H$_4$OC*H*$_2$-, J = 6 Hz), 4.01 (m, 6H; 4H, -C*H*$_2$OC$_6$H$_4$C$_6$H$_4$-, 2H, -C*H*$_2$-OCOCH$_3$), 6.65 (d, 4H, *ortho* to -CH$_2$O- on the monophenyl, J = 8.06 Hz), 6.78 (d, 4H, *ortho* to -CH$_2$O- on the biphenyl, J = 8.42 Hz), 6.94 (d, 4H, *meta* to -OCH$_2$- on the monophenyl, J = 8.06 Hz), 7.02 (d, 4H, *ortho* to -CHCH$_2$- on the biphenyl, J = 7.68 Hz), 7.39 (d, 4H, *meta* to -CHCH$_2$ on the biphenyl, J = 7.7 Hz), 7.49 (d, 4H, *meta* to -CH$_2$O- on the biphenyl, J = 8.72 Hz).

Synthesis of 1,12,33,44-Tetraoxa-25-(hydroxyundecanyl)-57-ethyl[12.0.2.12.0.2]paracyclophane (16, TPB′-TPT′-(c)10(2)OH). A mixture of **15** (460 mg, 0.42 mmol), THF (10 mL), and NaOH (10 N, 10 mL) was stirred at 70 °C for 10 h. CH_2Cl_2 was added, and and the organic phase was washed with water, dilute HCl, and water and dried over $MgSO_4$. The solution was concentrated, and the product was purified by flash column chromatography (SiO_2, CH_2Cl_2). The yield was 355 mg (80%), purity (HPLC), >99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.87 (t, 3H, -C*H*$_3$, J = 7.4 Hz), 1.3 (m, 42H; 24H, -O(CH$_2$)$_2$(C*H*$_2$)$_6$-(CH$_2$)$_2$O-, 18H, -CH-(C*H*$_2$)$_9$(CH$_2$)$_2$OCOCH$_3$), 1.7 (m, 10H; 8H, -OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O-, 2H, -(CH$_2$)$_9$C*H*$_2$CH$_2$OCOCH$_3$), 2.75 (m, 4H, -C$_6$H$_4$CHC*H*$_2$C$_6$H$_4$-), 2.95 (m, 2H, -C$_6$H$_4$C*H*CH$_2$C$_6$H$_4$-), 3.63 (t, 2H, -C*H*$_2$OH, J = 6.54 Hz), 3.85 (t, 4H, -CH$_2$C$_6$H$_4$-OC*H*$_2$-, J = 6 Hz), 3.98 (t, 4H, -C*H*$_2$OC$_6$H$_4$C$_6$H$_4$-, J = 6.54 Hz), 6.65 (d, 4H, *ortho* to -CH$_2$O- on the monophenyl, J = 8.7 Hz), 6.78 (d, 4H, *ortho* to -CH$_2$O- on the biphenyl, J = 8.43 Hz), 6.93 (d, 4H, *meta* to -OCH$_2$- on the monophenyl, J = 8.78 Hz), 7.02 (d, 4H, *ortho* to -CHCH$_2$- on the biphenyl, J = 7.3 Hz), 7.38 (d, 4H, *meta* to -CHCH$_2$ on the biphenyl, J = 8.34 Hz), 7.49 (d, 4H, *meta* to -CH$_2$O- on the biphenyl, J = 8.72 Hz).

Synthesis of 1,12,33,44-Tetraoxa-25-[(methacryloyloxy)undecanyl]-57-ethyl[12.0.2.12.0.2]paracyclophane (17, TPB′-TPT′-(c)10(2)MA). To a solution of **16** (0.35 g, 0.3 mmol) and NEt_3 (52 mg, 0.5 mmol) in dry CH_2Cl_2 (4 mL) was added methacryloyl chloride (43 mg, 0.4 mmol under N_2 at 0 °C. The mixture was stirred for 5 h and then charged on top of a column packed with Al_2O_3 and eluted with CH_2Cl_2. The yield was 0.32 g (87%), purity (HPLC), 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.87 (t, 3H, -CH$_2$C*H*$_3$, J = 7.4 Hz), 1.3 (m, 42H; 24H, -O(CH$_2$)$_2$(C*H*$_2$)$_6$(CH$_2$)$_2$O-, 18H, -CH(C*H*$_2$)$_9$(CH$_2$)$_2$OCOCH$_3$), 1.72 (m, 10H; 8H, -OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O-, 2H, -(CH$_2$)$_9$C*H*$_2$CH$_2$-OCOCH$_3$), 1.93 (m, 3H, -C(C*H*$_3$)═CH2), 2.74 (m, 4H, -C$_6$H$_4$-CHC*H*$_2$C$_6$H$_4$-), 2.95 (m, 2H, -C$_6$H$_4$C*H*CH$_2$C$_6$H$_4$-), 3.85 (t, 4H, -CH$_2$C$_6$H$_4$OC*H*$_2$-, J = 6 Hz), 3.98 (t, 4H, -C*H*$_2$OC$_6$H$_4$C$_6$H$_4$-, J = 6.54 Hz), 4.13 (t, 3H, -C*H*$_2$OCOCH$_3$, J = 6.63 Hz), 5.53 (m, 1H, -OCOC(CH$_3$)═C*H*$_2$, *cis* to -CH$_3$), 6.09 (m, 1H, -OCOC-(CH$_3$)═C*H*$_2$, *trans* to -CH$_3$), 6.65 (d, 4H, *ortho* to -CH$_2$O- on the monophenyl, J = 8.72 Hz), 6.78 (d, 4H, *ortho* to -CH$_2$O-

on the biphenyl, $J = 8.43$ Hz), 6.93 (d, 4H, *meta* to -OCH_2- on the monophenyl, $J = 8.78$ Hz), 7.02 (d, 4H, *ortho* to -$CHCH_2$- on the biphenyl, $J = 7.34$ Hz), 7.39 (d, 4H, *meta* to -$CHCH_2$ on the biphenyl, $J = 8.2$ Hz), 7.49 (d, 4H, *meta* to -CH_2O- on the biphenyl, $J = 8.76$ Hz).

Synthesis of Poly{1,12,33,44-tetraoxa-25-[(methacryloyloxy)undecanyl]-57-ethyl[12.0.2.12.0.2]paracyclophane} (18, TPB′-TPT′-(c)10(2)PMA). A 10 mL flask containing **17** (320 mg, 0.28 mmol), AIBN (10 mg, 0.06 mmol), and dry C_6H_6 (1 mL) was sealed under Ar and then was subjected to five freeze−pump−thaw cycles. After stirring at 60 °C for 15 h, the mixture was precipitated into MeOH and then from CH_2Cl_2 into acetone to yield 190 mg (60%) of **18**. $M_n = 6.4 \times 10^4$; $M_w/M_n = 2.5$. Thermal transitions are reported in Table1.

Synthesis of 13-Acetoxy-1-[4-[[4-[2-[4-(benzyloxy)-4′-biphenylyl]butyl]phenoxy]decanoxy]phenyl]-2-[4-[[4-[2-[4-[(benzyloxy)-4-biphenylyl]butyl]phenoxy]decanoxy]-4′-biphenylyl]tridecane (21). A mixture of **20** (3.79 g, 6 mmol), **12** (1.51 g, 3 mmol), K_2CO_3 (4.2 g, 30 mmol), and DMF (100 mL) was stirred under N_2 at 80 °C for 10 h. The mixture was poured into water, acidified with dilute HCl, and extracted with CH_2Cl_2 (100 mL, 4 times). The organic phase was dried over $MgSO_4$, and the solvent was evaporated. The product was purified by column chromatography (SiO_2, ethyl acetate/hexanes = 1/8) to yield 3.1 g (65%) of a white solid, purity (HPLC), 98.8%. Thermal transitions (DSC): first heating k 59 i, cooling i 50 n 47 k 1 g, second heating g 6 k 55 n 58 i. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.78 (t, 6H, -C*H*$_3$, $J = 7.3$ Hz), 1.2 (m, 16H, -CH_2(C*H*$_2$)$_8$(CH_2)$_2$OCOCH_3), 1.34 (m, 24H, -O(CH_2)$_2$(C*H*$_2$)$_6$(CH_2)$_2$O-), 1.75 (m, 16H; 4H, -C*H*$_2$(CH_2)$_8$$CH_2$-$CH_2$OCOC$H_3$, 8H, -OC$H_2$C*H*$_2$($CH_2$)$_6$C*H*$_2$$CH_2$O-, 4H, -C*H*$_2$$CH_3$), 2.04 (s, 3H, OCOC*H*$_3$), 2.7 (m, 3H, -$C_6H_4$C*H*$CH_2C_6H_4$-), 2.84 (m, 6H, -$C_6H_4CHCH_2C_6H_4$-), 3.89 (t, 4H, -$CH_2C_6H_4OCH_2$($CH_2$)$_8$-$CH_2OC_6H_4$-, $J = 6.5$ Hz), 4.03 (m, 6H; 4H, -$C_6H_4C_6H_4$-OC*H*$_2$(CH_2)$_8$C*H*$_2$OC_6H_4-, 2H, -C*H*$_2$OCOCH_3), 5.01 (s, 2H, -$CH_2C_6H_4OCH_2C_6H_5$), 5.11 (s, 2H, -$C_6H_4C_6H_4OCH_2C_6H_5$), 6.76 (d, 6H, *ortho* to -OCH_2 on the monophenyl ring, $J = 8.5$ Hz), 6.83 (d, 4H, *ortho* to the benzyloxy on the monophenyl ring, $J = 8$ Hz), 6.95 (d, 6H, *meta* to -O(CH_2)$_{10}$O- on the monophenyl ring, $J = 8.3$ Hz), 7.03 (d, 4H, *ortho* to the benzyloxy of the biphenyl ring, $J = 8.7$ Hz), 7.14 (d, 6H, *ortho* to -$CHCH_2$- on the biphenyl, $J = 8.14$ Hz), 7.4 (m, 20H; 6H *meta* to the benzyloxy on the biphenyl, 6H, *meta* to -$CHCH_2$- on the biphenyl, 10H of the two benzyl groups).

Synthesis of 13-Acetoxy-1-[4-[[4-[2-(4-hydroxy-4′-biphenylyl)butyl]phenoxy]decanoxy]phenyl]-2-[4-[[4-[2-(4-hydroxy-4′-biphenylyl)butyl]phenoxy]decanoxy]-4′-biphenylyl]tridecane (22). A mixture of **21** (2.6 g, 1.6 mmol), Pd/C (0.2 g), and CH_3COOH (60 mL) was repeatedly vacuumed and flushed with H_2 and then stirred under H_2 at 60 °C for 10 h. The solution was filtered, and CH_3COOH was distilled. CH_2Cl_2 and water were added, and the organic phase was washed with water, dilute $NaHCO_3$, and water. The solvent was evaporated, and the product was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1/3) to yield 1.87 g (81%) of a white solid, purity (HPLC), 99%. Thermal transitions (DSC): heating g 5 n 20 i, cooling i 8 n −5 g. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.78 (t, 6H,-CH_2C*H*$_3$, $J = 7.4$ Hz), 1.17 (m,16H, -CH_2(C*H*$_2$)$_8$(CH_2)$_2$OCOCH_3), 1.33 (m, 24H, -O(CH_2)$_2$(CH_2)$_6$(CH_2)$_2$O-), 1.76 (m, 16H; 8H, -OCH_2C*H*$_2$(CH_2)$_6$-CH_2CH_2O-, 4H, -C*H*$_2$$CH_3$, 4H, -C*H*$_2$($CH_2$)$_8$C*H*$_2$$CH_2$OCOC$H_3$), 2.03 (s, 3H, -OCOC*H*$_3$), 2.71 (m, 3H, -$C_6H_4$C*H*$CH_2C_6H_4$-), 2.82 (m, 6H, -$C_6H_4CHCH_2C_6H_4$), 3.88 (t, 4H, -$CH_2C_6H_4OCH_2$-), 4.02 (m, 6H; 4H, -$C_6H_4C_6H_4OCH_2$-, 2H, -C*H*$_2$OCOC$H_3$), 4.58 (s, 1H, -$CH_2C_6H_4OH$), 4.84 (s, 1H, -$C_6H_4C_6H_4OH$), 6.68 (d, 4H, *ortho* to the OH on the monophenyl ring, $J = 8$ Hz), 6.74 (d, 6H, *ortho* to -OCH_2- on the monophenyl, $J = 8.06$ Hz), 6.88 (d, 6H *ortho* to -OCH_2-, *ortho* to the OH on the biphenyl, $J = 8$ Hz), 6.95 (d, 6H, *meta* to -OCH_2- on the monophenyl, $J = 7.78$ Hz), 7.14 (d, 6H, *ortho* to -$CHCH_2$- on the biphenyl, $J = 7.98$ Hz), 7.44 (d, 6H, *meta* to -$CHCH_2$- on the biphenyl, $J = 8$ Hz), 7.5 (d, 6H, *meta* to -OCH_2, *meta* to OH on the biphenyl ring, $J = 8.2$ Hz).

Synthesis of 1,12,33,44,65,76-Hexaoxa-25-(hydroxyundecanyl)-57,89-diethyl[12.0.2.12.0.2.12.0.2]paracyclophane (23, (TPB′)$_2$-TPT′-(c)10(3)OH). To a 5 L 3-neck flask equipped with a mechanical stirrer, containing DMF (4 L) and Cs_2CO_3 (0.2 g, 0.6 mmol) was added a solution of **22** (0.29 g, 0.2 mmol), and Br(CH_2)$_{10}$Br (61 mg, 0.2 mmol) in DMF (50 mL) dropwise *via* a syringe pump over 5 h. The mixture was stirred under N_2 at 80 °C for 4 days. DMF was distilled, the product was extracted in CH_2Cl_2, and the organic phase was washed with water. The solvent was evaporated, and the solid was dissolved in THF (30 mL) and stirred with NaOH (10 N, 30 mL) at reflux for 10 h. The reaction mixture was extracted with CH_2Cl_2, and the organic phase was washed with water, dilute HCl, and water, and dried over $MgSO_4$. The solvent was evaporated, and the product was purified by column chromatography (SiO_2, ethyl acetate/hexanes = 1/6) to yield 75 mg (25%) of a white solid, purity (HPLC), 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.81 (t, 6H, -CH_2C*H*$_3$, $J = 7.16$ Hz), 1.19 (m, 16H, -CH_2(C*H*$_2$)$_8$(CH_2)$_2$OH), 1.32 (m, 36H, -O(CH_2)$_2$(C*H*$_2$)$_6$-(CH_2)$_2$O-), 1.75 (m, 20H; 12H, -OCH_2C*H*$_2$(CH_2)$_6$C*H*$_2$$CH_2$O-, 4H, -C*H*$_2$($CH_2$)$_8$C*H*$_2$$CH_2$OH, 4H, -C*H*$_2$$CH_3$), 2.81 (m, 9H, -$C_6H_4$-C*H*$CH_2C_6H_4$-), 3.61 (q, 2H, -C*H*$_2$OH, $J = 5.42$ Hz), 3.90 (t, 6H, -C_6H_4OC*H*$_2$-, $J = 6.6$ Hz), 3.97 (t, 6H, -$C_6H_4C_6H_4$OC*H*$_2$-, $J = 6.2$ Hz), 6.69 (d, 6H, *ortho* to -OCH_2- on the monophenyl ring, $J = 8.6$ Hz), 6.88 (d, 6H, *meta* to -OCH_2- on the monophenyl ring, $J = 8.7$ Hz), 6.93 (d, 6H, *ortho* to -OCH_2- on the biphenyl ring, $J = 8.48$ Hz), 7.09 (d, 6H, *ortho* to -$CHCH_2$- on the biphenyl ring, $J = 8.14$ Hz), 7.42 (=d, 6H, *meta* to -$CHCH_2$- on the biphenyl ring, $J = 8.10$ Hz), 7.49 (d, 6H, *meta* to -CH_2O- on the biphenyl ring, $J = 8.7$ Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.26 and14.13 (-*C*H$_3$), 22.71−35.91 (-(CH_2)$_{10}$, and -OCH_2(*C*H$_2$)$_8$$CH_2$O-), 42.47 (-CH*C*H$_2$-), 49.68 (-*C*H$CH_2$-), 63.09 (-*C*H$_2$OH), 67.87 (-O*C*H$_2$- on the monophenyl), 68.03 (-O*C*H$_2$- on the biphenyl), 114.01 (*ortho* to -OCH_2- on the monophenyl), 114.75 (*ortho* to -OCH_2- on the biphenyl), 126.25 (*ortho* to -$CHCH_2$- on the biphenyl), 126.25 (*ortho* to -$CHCH_2$- on the biphenyl), 127.82 (*meta* to -$CHCH_2$- on the biphenyl), 128.25 (*meta* to -OCH_2- on the biphenyl), 130.01 (*meta* to -OCH_2- on the monophenyl), 132.65 (*para* to -OCH_2- on the biphenyl), 133.44 (*para* to -OCH_2- on the monophenyl), 138.26 (*para* to -$CHCH_2$- on the biphenyl), 143.36 (*ipso* to -$CHCH_2$- on the biphenyl), 157.17 (*ipso* to -OCH_2- on the monophenyl), 158.45 (*ipso* to -OCH_2- on the biphenyl).

Synthesis of 1,12,33,44,65,76-Hexaoxa-25-[(methacryloyloxy)undecanyl]-57,89-diethyl[12.0.2.12.0.2.12.0.2]paracyclophane (24, (TPB′)$_2$-TPT′-(c)10(3)MA). To a solution of **23** (70 mg, 0.05 mmol) and NEt_3 (6.5 mg, 0.06 mmol) in dry CH_2Cl_2 (4 mL) was added methacryloyl chloride (5.85 mg, 0.05 mmol) was added under N_2 at 0 °C. The mixture was stirred for 5 h and then charged on the top of an Al_2O_3 column and eluted with CH_2Cl_2 to yield 71 mg (90%) of **24**, purity (HPLC), 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.81 (t, 6H, -CH_2C*H*$_3$, $J = 7.06$ Hz), 1.2 (m, 16H, -CH_2(C*H*$_2$)$_8$(CH_2)$_2$OCOC-(CH_3)=CH_2), 1.32 (m, 36H, -O(CH_2)$_2$(C*H*$_2$)$_6$(CH_2)$_2$O-), 1.75 (m, 20H; 12H, -OCH_2C*H*$_2$(CH_2)$_6$C*H*$_2$$CH_2$O-, 4H, -C*H*$_2$$CH_3$, 4H, -C*H*$_2$($CH_2$)$_8$C*H*$_2$$CH_2$OCOC($CH_3$)=$CH_2$), 1.93 (s, 3H, -C(C*H*$_3$)=$CH_2$), 2.81 (m, 9H, -C*H*C*H*$_2$-), 3.87 (t, 6H, -C_6H_4-OC*H*$_2$-, $J = 5.86$ Hz), 3.98 (t, 6H, -$C_6H_4C_6H_4$OC*H*$_2$-, $J = 6.1$ Hz), 4.12 (t, 2H, -C*H*$_2$OCO-, $J = 6.6$ Hz), 5.53 (m, 1H, -C(CH_3)=C*H*$_2$, *cis* to -CH_3), 6.09 (m, 1H, -C(CH_3)=C*H*$_2$, *trans* to -CH_3), 6.70 (d, 6H, *ortho* to -OCH_2- on the monophenyl), 6.87 (d, 6H, *meta* to -OCH_2- on the monophenyl, $J = 8.5$ Hz), 6.94 (d, 6H, *ortho* to -OCH_2- on the biphenyl ring, $J = 8.72$ Hz), 7.10 (d, 6H, *ortho* to -$CHCH_2$- on the biphenyl, $J = 7.98$ Hz), 7.42 (d, 6H, *meta* to -$CHCH_2$- on the biphenyl, $J = 7.4$ Hz), 7.50 (d, 6H, *meta* to -OCH_2- on the biphenyl, $J = 8.7$ Hz).

Synthesis of Poly{1,12,33,44,65,76-hexaoxa-25-[(methacryloyloxy)undecanyl]-57,89-diethyl[12.0.2.12.0.2.12.0.2]paracyclophane} (25, (TPB′)$_2$-TPT′-(c)10(3)PMA}). A 10 mL flask containg **24** (70 mg, 0.04 mmol), AIBN (3.5 mg, 0.02 mmol), and dry C_6H_6 (0.8 mL) was sealed with a rubber septum under Ar, and the mixture was subjected to five freeze−pump−thaw cycles. After stirring at 60 °C for 15 h, the solution was precipitated into CH_3OH. The solid was charged on the top of a column with SiO_2 and eluted with ethyl acetate/hexanes = 1/5 to yield 20 mg (28%) of **25**. $M_n = 11\,000$; $M_w/M_n = 1.4$.

Thermal transitions are reported in Table 1.

Synthesis of 1,12,33,44,65,76,97,108-Octaoxa-25-(hydroxyundecanyl)-57,89,121-triethyl[12.0.2.12.0.-2.12.0.2.12.0.2]paracyclophane (29, (TPB′)$_3$-TPT′-(c)10(4)-OH). To a 5 L 3-neck flask equipped with a mechanical stirrer and containing DMF (4 L) and Cs_2CO_3 (0.6 g, 1.8 mmol) was added a solution of **28** (0.32 g, 0.19 mmol) and **12** (0.096 g, 0.19 mmol) in DMF (50 mL) dropwise over 5 h *via* a syringe pump. After 4 days of stirring at 80 °C under N_2, DMF was distilled; the product was dissolved in CH_2Cl_2 and washed with water. The solvent was evaporated; the solid was dissolved in THF (20 mL) and stirred with NaOH (10 N, 20 mL) at reflux for 10 h. The mixture was extracted with CH_2Cl_2, washed with water, dilute HCl, and water, and dried over $MgSO_4$. The product was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1/4) to yield 130 mg (35%) of **29**, purity (HPLC), 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.79 (t, 9H, -CH_2CH_3, J = 7.32 Hz), 1.19 (m, 16H, -$CH_2(CH_2)_8(CH_2)_2$OH), 1.32 (m, 48H, -$O(CH_2)_2(CH_2)_6(CH_2)_2$O-), 1.75 (m, 26H; 16H, -OCH_2CH_2-$(CH_2)_6CH_2CH_2$O-, 6H, -CH_2CH_3, 4H, -$CH_2(CH_2)_8CH_2CH_2$OH), 2.7 (m, 4H, -$CHCH_2$-), 2.82 (m, 8H, -$CHCH_2$-), 3.61 (t, 2H, -CH_2-OH, J = 6.58 Hz), 3.87 (t, 8H, -$C_6H_4OCH_2$-, J = 6.6 Hz), 3.98 (t, 8H, -$C_6H_4C_6H_4OCH_2$-, J = 6.6 Hz), 6.71 (d, 8H, *ortho* to -OCH_2- on the monophenyl ring, J = 8.58 Hz), 6.90 (d, 8H, *ortho* to -OCH_2- on the biphenyl, J = 8 Hz), 6.93 (d, 8H, *meta* to -OCH_2- on the monophenyl, J = 8.58 Hz), 7.10 (d, 8H, *ortho* to -$CHCH_2$- on the biphenyl, J = 8.06 Hz), 7.43 (d, 8H, *meta* to -$CHCH_2$- on the biphenyl, J = 8.22 Hz), 7.49 (d, 8H, *meta* to -OCH_2- on the biphenyl, J = 8.72 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.23 (-CH_3), 26.02−35.72 (-$(CH_2)_{10}$, -$OCH_2(CH_2)_8CH_2$O-), 42.88 (-$CHCH_2$), 47.85 (-$CHCH_2$-), 63.08 (-CH_2-OH), 67.87 (-OCH_2- on the monophenyl), 68.02 (-OCH_2- on the biphenyl), 114.02 (*ortho* to -OCH_2- on the monophenyl), 114.73 (*ortho* to -OCH_2- on the biphenyl), 126.29 (*ortho* to -$CHCH_2$- on the biphenyl), 127.83 (*meta* to -$CHCH_2$- on the biphenyl), 128.22 (*meta* to -OCH_2- on the biphenyl), 130.01 (*meta* to -OCH_2- on the monophenyl), 132.68 (*para* to -OCH_2- on the biphenyl), 133.42 (*para* to -OCH_2- on the monophenyl), 138.29 (*para* to -$CHCH_2$- on the biphenyl), 143.49 (*ipso* to -$CHCH_2$- on the biphenyl), 157.20 (*ipso* to -OCH_2- on the monophenyl), 158.45 (*ipso* to -OCH_2- on the biphenyl).

Synthesis of 1,12,33,44,65,76,97,108-Octaoxa-25-[(methacryloyloxy)undecanyl]-57,89,121-triethyl[12.0.2.-12.0.2.12.0.2.12.0.2]paracyclophane (30, (TPB′)$_3$-TPT′-(c)-10(4)MA). To a solution of **29** (100 mg, 0.05 mmol) and NEt_3 (9.2 mg, 0.92 mmol) in dry CH_2Cl_2 (6 mL) was added methacryloyl chloride (8 mg, 0.07 mmol) under N_2 at 0 °C. The mixture was stirred for 5 h and then charged on a column with Al_2O_3 and eluted with CH_2Cl_2 to yield 85 mg (84%) of **30**, purity (HPLC), 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.79 (t, 9H, -CH_2CH_3, J = 7.38 Hz), 1.19 (m, 16H, -$CH_2(CH_2)_8(CH_2)_2C(CH_3)$=$CH_2$), 1.32 (m, 48H, -$O(CH_2)_2(CH_2)_6(CH_2)_2$O-), 1.75 (m, 26H; 16H, -$OCH_2CH_2(CH_2)_6CH_2CH_2$O-, 6H, -$CH_2CH_3$, 4H, -$CH_2(CH_2)_8CH_2$-$CH_2$OH), 1.93 (s, 3H, -$C(CH_3)$=$CH_2$), 2.71 (m, 4H, -$CHCH_2$-), 2.82 (m, 8H, -$CHCH_2$-), 3.88 (t, 8H, -$C_6H_4OCH_2$-, J = 6.52 Hz), 3.98 (t, 8H, -$C_6H_4C_6H_4OCH_2$-, J = 6.6 Hz), 4.12 (t, 2H, -CH_2-$OCOC(CH_3)$=CH_2, J = 6.64 Hz), 5.53 (m, 1H, -$C(CH_3)$=CH_2, -CH_3), 6.08 (m, 1H, -$C(CH_3)$=CH_2 *trans* to -CH_3), 6.72 (d, 8H, *ortho* to -OCH_2- on the monophenyl, J = 8.52 Hz), 6.90 (d, 8H, *ortho* to -OCH_2- on the biphenyl, J = 8 Hz), 6.94 (d, 8H, *meta* to -OCH_2- on the monophenyl, J = 8.7 Hz), 7.10 (d, 8H, *meta* to -$CHCH_2$- on the biphenyl, J = 8.06 Hz), 7.43 (d, 8H, *meta* to -$CHCH_2$- on the biphenyl, J = 8.26 Hz), 7.49 (d, 8H, *meta* to -OCH_2- on the biphenyl, J = 8.8 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.74 (-CH_3), 26.01−35.76 (-$(CH_2)_{10}$-, -$OCH_2(CH_2)_8CH_2$O-), 42.87 (-$CHCH_2$-), 49.61 (-$CHCH_2$-), 64.84 (-CH_2-OCO-), 67.86 (-OCH_2- on the monophenyl), 68.01 (-OCH_2- on the biphenyl), 113.78 (*ortho* to -OCH_2- on the monophenyl), 114.71 (*ortho* to -OCH_2- on the biphenyl), 125.69 (CH_2=), 126.29 (*ortho* to to -$CHCH_2$- on the biphenyl), 127.83 (*meta* to -$CHCH_2$- on the biphenyl), 128.22 (*meta* to -OCH_2- on the biphenyl), 130.02 (*meta* to -OCH_2- on the monophenyl), 132.68 (*para* to -OCH_2 on the biphenyl), 133.42 (*para* to -OCH_2- on the monophenyl), 138.29 (*para* to -$CHCH_2$- on the biphenyl), 140.58 (-$(CH_3)C(CO)$=CH_2), 143.74 (*ipso* to -$CHCH_2$- on the biphenyl), 157.19 (*ipso* to -OCH_2- on the monophenyl), 158.45 (*ipso* to -OCH_2- on the biphenyl), 163.32 (*C*=O).

Synthesis of Poly{1,12,33,44,65,76,97,108-octaoxa-25-[(methacryloyloxy)undecanyl]-57,89,121-triethyl-[12.0.2.12.0.2.12.0.2.12.0.2]paracyclophane} (31, (TPB′)$_3$-TPT′-(c)10(4)PMA). A 10 mL flask containing **30** (82 mg, 0.04 mmol), AIBN (3.5 mg, 0.02 mmol), and dry C_6H_6 (0.8 mL) was sealed with a rubber septum under Ar, and the mixture was subjected to five freeze−pump−thaw cycles. After stirring at 60 °C for 15 h, the mixture was precipitated in CH_3OH, and the solid was purified by column chromatography (SiO_2, ethyl acetate/hexanes = 1/9) to yield 26 mg (32%) of **31**. M_n = 7500; M_w/M_n = 1.87. Thermal transitions are reported in Table 1.

Synthesis of 6-Iodo-1-hexanol (33). A mixture of Cl-$(CH_2)_6$OH (32 g, 0.23 mol), NaI (60 g, 0.56 mol), $(CH_3(CH_2)_4)_4$-NI (1 g, 0.02 mmol), and acetone (200 mL) was stirred at reflux for 12 h. The reaction mixture was filtered, extracted with CH_2Cl_2, washed with water, dilute $Na_2S_2O_3$, and water, and dried over $MgSO_4$. The solvent was evaporated, and the product was distilled under reduced pressure to yield 50 g (95%) of a colorless oil. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.41 (m, 4H, $I(CH_2)_2(CH_2)_2(CH_2)_2$OH), 1.58 (m, 2H, -$CH_2CH_2$OH), 1.84 (m, 2H, -$CH_2CH_2$I), 3.20 (t, 2H, -$CH_2$I, J = 6.96 Hz), 3.64 (t, 2H, -CH_2OH, J = 6.44 Hz).

Synthesis of 8-Hydroxy-1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)octanone (34). A mixture of **8** (23 g, 0.69 mmol), $HO(CH_2)_6$I (19 g, 0.85 mmol), THF (250 mL), NaOH (10 N, 250 mL), and TBAH (4.5 g, 0.014 mmol) was stirred at 30 °C for 10 h under N_2. The reaction mixture was extracted with CH_2Cl_2 (200 mL), washed with water, dilute HCl, and water, and dried over $MgSO_4$. The solvent was evaporated, and the product was purified first by column chromatography (SiO_2, ethyl acetate/hexanes = 1/9) and then by recrystallization from hexanes/toluene = 3/1 to yield 23.5 g (78%) of white crystals, mp = 76−78 °C, purity (HPLC), 98.7%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.34 (m, 6H, -$CH_2(CH_2)_3(CH_2)_2$OH), 1.55 (m, 2H, -CH_2CH_2OH), 1.88 (m, 1H, -$CH(CH_2(CH_2)_5OH)$-CH_2-), 2.21 (m, 1H, -$CH(CH_2(CH_2)_5OH)CO$-), 3.60 (t, 2H, -CH_2-OH, J = 6.5 Hz), 3.81 (s, 6H, -OCH_3), 4.50 (t, 1H, -Ph$CH((CH_2)_6$-OH)CO-, J = 7.28 Hz), 6.68 (d, 2H, *ortho* to -OCH_3 on the monophenyl, J = 8.98 Hz), 6.94 (d, 2H, *ortho* to -OCH_3 on the biphenyl, J = 8.82 Hz), 7.34 (d, 2H, *ortho* to CHCO on the biphenyl, J = 8.41 Hz), 7.46 (d, 2H, *meta* to CHCO on the biphenyl, J = 8.32 Hz), 7.48 (d, 2H, *meta* to -OCH_3 on the biphenyl, J = 8.96 Hz), 7.99 (d, 2H, *ortho* to CO on the monophenyl, J = 8.94 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 25.41−33.84 (-$(CH_2)_5$-), 52.69 (CH_3O- on the monophenyl), 55.23 (CH_3O- on the biphenyl), 62.67 (-CH_2OH), 113.57 (*ortho* to -OCH_3 on the monophenyl), 114.02 (*ortho* to -OCH_3 on the biphenyl), 126.89 (*ortho* to -CHCO- on the biphenyl), 127.79 (*meta* to -CHCO- on the biphenyl), 128.34 (*meta* to -OCH_3 on the biphenyl), 129.74 (*para* to -OCH_3 on the monophenyl ring), 130.83 (*meta* to -OCH_3 on the monophenyl), 133.01 (*para* to -OCH_3 on the biphenyl), 138.45 (*para* to -CHCO- on the biphenyl), 139.15 (*ipso* to -CHCO- on the biphenyl), 158.92 (*ipso* to -OCH_3 on the monophenyl), 163.14 (*ipso* to -OCH_3 on the biphenyl), 198.53 (*C*=O).

Synthesis of 8-Hydroxy-1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)octane (35). An $AlCl_3$ (23.8 g, 0.18 mmol)·-Et_2O (dry, 100 mL) complex[12] was added to a slurry of $LiAlH_4$ (3.4 g, 0.09 mmol) in dry Et_2O (100 mL) at −20 °C under N_2. A solution of **34** (13 g, 0.03 mol) in dry $CHCl_3$ (70 mL) was added dropwise, and the mixture was stirred at −20 °C for 0.5 h. Dilute HCl (100 mL) was added, and the organic phase was washed with water and dried over $MgSO_4$. Purification by column chromatography (SiO_2, ethyl acetate/hexanes = 1/3) followed by recrystallization from hexanes/toluene = 3/1 yielded 10.5 g (85%) of white crystals, mp = 64−66 °C, purity (HPLC), 98.8%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.23 (m, 6H, -$CH_2(CH_2)_3(CH_2)_2$OH), 1.62 (m, 4H, -$CH_2(CH_2)_4CH_2CH_2$OH), 2.82 (m, 3H, -Ph$CHCH_2$Ph-), 3.58 (t, 2H, -CH_2OH, J = 6.6 Hz), 3.76 (s, 3H, -CH_2PhOCH_3), 3.85 (s, 3H, -Ph$PhOCH_3$), 6.75 (d, 2H, *ortho* to OCH_3 on the monophenyl, J = 8.76 Hz), 6.81 (d,

4H; 2H, *meta* to OCH_3 on the monophenyl, 2H, *ortho* to OCH_3 on the biphenyl, $J = 8.84$ Hz), 7.14 (d, 2H, *ortho* to -$CHCH_2$- on the biphenyl, $J = 8.30$ Hz), 7.49 (d, 2H, *meta* to -$CHCH_2$- on the biphenyl, $J = 8.26$ Hz), 7.56 (d, 2H, *meta* to -OCH_3 on the biphenyl, $J = 8.81$ Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 25.62−35.37 (-(CH_2)$_5$), 42.95 (-$CHCH_2$-), 47.81 (-$CHCH_2$-), 55.12 (CH_3O- on the monophenyl), 55.27 (CH_3O- on the biphenyl), 62.91 (-CH_2OH), 113.38 (*ortho* to -OCH_3 on the monophenyl), 114.08 (*ortho* to -OCH_3 on the biphenyl), 126.34 (*ortho* to -$CHCH_2$- on the biphenyl), 127.84 (*meta* to -OCH_3 on the biphenyl), 128.06 (*meta* to -OCH_3 on the biphenyl), 129.99 (*meta* to -OCH_3 on the monophenyl), 132.82 (*para* to -OCH_3 on the biphenyl), 133.56 (*para* to -OCH_3 on the monophenyl), 138.22 (*para* to -$CHCH_2$ on the biphenyl), 143.81 (*ipso* to -$CHCH_2$- on the biphenyl), 157.61 (*ipso* to -OCH_3 on the monophenyl), 158.85 (*ipso* to -OCH_3 on the biphenyl).

Synthesis of 8-Hydroxy-1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)octane (TPO-OH, 36). To a mixture of Mg (8.72 g, 0.35 mol) and dry Et_2O (100 mL) was added CH_3I[13] (51 g, 0.35 mol) dropwise at 5 °C under N_2. To the resulting solution was added **35** (10 g, 0.25 mol). The mixture was stirred at 40 °C for 1 h allowing most of the Et_2O to distill and then at 150 °C for 5 h. The melt was cooled to 0 °C, and Et_2O (100 mL) followed by dilute HCl was added. The organic phase was washed with water, dilute $NaHCO_3$, dilute $Na_2S_2O_3$, and water and dried over $MgSO_4$. Recrystallization from CH_2Cl_2 yielded 7.8 g (88%) of fine white crystals, mp = 87−89 °C, purity (HPLC), 99%. ^{1}H-NMR ($(CD_3)_2CO$, TMS, δ, ppm): 1.26 (m, 6H, -$CH_2(CH_2)_3(CH_2)_2OH$), 1.42 (m, 2H, -$CH_2(CH_2)_5OH$), 1.67 (m, 2H, -$(CH_2)_4CH_2CH_2OH$), 2.84 (m, 3H, -PhC*H*CH_2Ph-), 3.58 (t, 2H, -CH_2OH, $J = 6.6$ Hz), 4.57 (s, 1H, -PhO*H*), 4.80 (s, 1H, -PhPhO*H*), 6.68 (d, 2H, *ortho* to OH on the monophenyl, $J = 8.44$ Hz), 6.91 (d, 2H, *meta* to OH on the monophenyl, $J = 8.44$ Hz), 6.93 (d, 2H, *ortho* to OH on the biphenyl, $J = 8.36$ Hz), 7.21 (d, 2H, *ortho* to -$CHCH_2$- on the biphenyl, $J = 8.06$ Hz), 7.43 (d, 2H, *meta* to -$CHCH_2$- on the biphenyl, $J = 8.20$ Hz), 7.47 (d, 2H, *ortho* to OH on the biphenyl, $J = 8.42$ Hz). ^{13}C-NMR ($(CD_3)_2CO$, TMS, δ, ppm): 23.97−33.78 (-(CH_2)$_5$-), 40.91 (-$CHCH_2$-), 45.95 (-$CHCH_2$-), 59.76 (-CH_2OH), 113.12 (*ortho* to OH on the monophenyl), 113.98 (*ortho* to OH on the biphenyl), 124.22 (*meta* to -$CHCH_2$- on the the biphenyl), 125.94 (*ortho* to -$CHCH_2$- on the biphenyl), 126.54 (*meta* to OH on the biphenyl), 128.27 (*meta* to OH on the biphenyl), 129.68 (*para* to -$CHCH_2$- on the biphenyl), 136.73 (*para* to OH on the monophenyl), 142.12 (*ipso* to -$CHCH_2$- on the biphenyl), 153.67 (*ipso* to OH on the monophenyl), 155.24 (*ipso* to OH on the biphenyl).

Synthesis of 8-Acetoxy-1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)octane (37, TPO-OAc). A mixture of **36** (5.4 g, 12.9) and CH_3COOH (200 mL) was stirred at 100 °C for 10 h. Excess CH_3COOH was distilled; the product was dissolved in CH_2Cl_2, washed with water and dilute $NaHCO_3$, and dried over $MgSO_4$. The solvent was evaporated, and the product was purified by column chromatography (SiO_2, ethyl acetate/hexane = 2/1) and recrystallized from toluene to yield 5.35 g (87%) of white crystals, mp = 96−98 °C, purity (HPLC), 99%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.23 (m, 6H, -$CH_2(CH_2)_3(CH_2)_2OH$), 1.55 (m, 4H, -$CH_2(CH_2)_3CH_2CH_2OCOCH_3$), 2.03 (s, 3H, -$COCH_3$), 2.80 (m, 3H, PhC*H*C$H_2$Ph-), 4.01 (t, 2H, -$CH_2OCOCH_3$), 6.68 (d, 2H, *ortho* to OH on the monophenyl, $J = 8.44$ Hz), 6.91 (d, 2H, *meta* to OH on the monophenyl, $J = 8.44$ Hz), 6.93 (d, 2H, *ortho* to the OH on the biphenyl, $J = 8.36$ Hz), 7.21 (d, 2H, *ortho* to -$CHCH_2$- on the biphenyl, $J = 8.06$ Hz), 7.43 (d, 2H, *meta* to -$CHCH_2$- on the biphenyl, $J = 8.20$ Hz), 7.47 (d, 2H, *ortho* to OH, on the biphenyl, $J = 8.42$ Hz). ^{13}C-MNR ($CDCl_3$, TMS, δ, ppm): 21.02 (CH_3), 25.72−35.22 (-(CH_2)$_5$-), 42.92 (-$CHCH_2$-), 47.76 (-$CHCH_2$-), 64.65 (-CH_2-OAc), 114.92 (*ortho* to OH on the monophenyl), 115.58 (*ortho* to OH on the biphenyl), 126.37 (*meta* to -$CHCH_2$- on the biphenyl), 127.80 (*ortho* to -$CHCH_2$- on the biphenyl), 128.10 (*meta* to OH on the biphenyl), 130.22 (*meta* to OH on the monophenyl), 138.26 (*para* to OH on the monophenyl), 143.80 (*ipso* to -$CHCH_2$- on the biphenyl), 153.58 (*ipso* to OH on the monophenyl), 154.90 (*ipso* to OH on the biphenyl), 172.35 (*C*=O).

Synthesis of 8-Acetoxy-1-[4-(bromopentoxy)phenyl]-2-[4-(bromopentoxy)-4′-biphenylyl]octane (38). A mixture of **37** (2.5 g, 0.5 mmol), $Br(CH_2)_5Br$ (25 g, 0.1 mol), and K_2CO_3 (2.9 g, 21 mmol) was stirred at 60 °C under N_2 for 12 h. CH_2Cl_2 was added, and the organic phase was washed with water, dilute HCl, and again water and dried over $MgSO_4$. The solvent and excess $Br(CH_2)_5Br$ were distilled, and the product was purified by column chromatography (SiO_2, ethyl acetate/hexanes = 1/9) to yield 2.28 g (63%) of a colorless oil, purity (HPLC), 99%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.23 (m, 6H, -$CH_2(CH_2)_3(CH_2)_2OCOCH_3$), 1.64 (m, 8H; 4H, -$CH_2(CH_2)_2CH_2$-$CH_2OCOCH_3$, 4H, -$O(CH_2)_2CH_2(CH_2)_2Br$), 1.97 (m, 8H, -$OCH_2$-$CH_2CH_2CH_2CH_2Br$), 2.03 (s, 3H, -$COCH_3$), 2.81 (m, 3H, -PhC*H*C$H_2$Ph-), 3.46 (t, 2H, -$CH_2Br$, $J = 6.42$ Hz), 3.98 (t, 2H, -$CH_2C_6H_4OCH_2$-, $J = 6.14$ Hz), 4.02 (m, 4H; 2H, -$C_6H_4C_6H_4$-OCH_2-, 2H, -CH_2OCOCH_3), 6.74 (d, 2H, *ortho* to -OCH_2 on the monophenyl, $J = 8.71$ Hz), 6.95 (d, 4H; 2H, *ortho* to -OCH_2- on the biphenyl, 2H, *meta* to -OCH_2- on the monophenyl, $J = 8.88$ Hz), 7.14 (d, 2H, *ortho* to -$CHCH_2$- on the biphenyl, $J = 8.36$ Hz), 7.46 (d, 2H, *meta* to -$CHCH_2$- on the biphenyl, $J = 8.28$ Hz), 7.52 (d, 2H, *meta* to -OCH_2- on the biphenyl, $J = 8.74$ Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 22.74 (-CH_3), 24.66−32.09 (-(CH_2)$_5$, -$OCH_2(CH_2)_3CH_2Br$), 32.31 (-CH_2Br on the monophenyl ring), 33.34 (-CH_2Br on the biphenyl ring), 42.74 (-$CHCH_2$-), 47.55 (-$CHCH_2$-), 64.28 (-CH_2-OAc), 67.19 (-CH_2-Ph-OCH_2-), 67.37 (-Ph-Ph-OCH_2-), 113.83 (*ortho* to -OCH_3 on the monophenyl), 114.50 (*ortho* to -OCH_2- on the biphenyl), 126.13 (*ortho* to -$CHCH_2$- on the biphenyl), 127.60 (*meta* to -$CHCH_2$- on the biphenyl), 127.92 (*meta* to -OCH_2- on the biphenyl), 132.52 (*para* to -OCH_2- on the biphenyl), 133.24 (*para* to -OCH_2- on the monophenyl), 138.04 (*para* to -$CHCH_2$- on the biphenyl), 143.56 (*ipso* to -$CHCH_2$- on the biphenyl), 156.91 (*ipso* to -OCH_2-), 158.14 (*ipso* to -OCH_2-), 170.79 (-$COCH_3$).

Synthesis of 1,7,28,34-Tetraoxa-20,47-bis(hydroxyhexyl)[7.0.2.7.0.2]paracyclophane (39, TPO-(c)5(2)OH). To a 5 L 3-neck flask equipped with mechanical stirrer and containing DMF (4 L) and Cs_2CO_3 (2 g, 6.1 mmol) was added a solution of **37** (0.5 g, 1.15 mmol) and **38** (0.84 g, 1.15 mmol) dropwise over 5 h *via* a syringe pump. The mixture was stirred at 80 °C under N_2 for 4 days. DMF was distilled, and the product was dissolved in CH_2Cl_2 and washed with water. The solvent was evaporated, THF (20 mL), and NaOH (10 N, 20 mL) were added, and the mixture was stirred at reflux for 10 h. The reaction mixture was extracted with CH_2Cl_2, washed with water, dilute HCl, and again water, and dried over $MgSO_4$. Purification by column chromatography (SiO_2, ethyl acetate/hexanes = 1/1) yielded 220 mg (23%) of white crystals, mp (DSC) = 160 °C. Thermal transitions are reported in Table 1, purity (HPLC), 99%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.31 (m, 12H, -$CH_2(CH_2)_3(CH_2)_2OH$), 1.52 (m, 4H, -CH_2-CH_2OH), 1.73 (m, 16H; 8H, -OCH_2CH_2-, 4H, -$CH_2(CH_2)_3CH_2$-CH_2OH, 4H, -$O(CH_2)_2CH_2(CH_2)_2O$-), 2.71 (m, 4H, -PhCHCH_2-Ph-), 3.97 (m, 2H, -PhC*H*CH_2Ph-), 6.58 and 6.73 (overlapping doublets, 4H, *ortho* to -OCH_2 on the monophenyl, $J = 8.68$ Hz), 6.65 (d, 4H, *meta* to -OCH_2 on the monophenyl, $J = 8.2$ Hz), 6.92 (d, 4H, *ortho* to -OCH_2- on the biphenyl, $J = 8.66$ Hz), 6.96 (d, 4H, *ortho* to -$CHCH_2$- on the biphenyl, $J = 7.98$ Hz), 7.34 and 7.37 (overlapping doublets, 4H, *meta* to -$CHCH_2$- on the biphenyl ring, $J = 8$ Hz), 7.45 and 7.48 (overlapping doublets, 4H, *meta* to -OCH_2 on the biphenyl, $J = 8.60$ Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 22.72−36.71 (-(CH_2)$_5$-, -$OCH_2(CH_2)_3CH_2O$-), 42.64 (-$CHCH_2$-), 48.11 (-$CHCH_2$-), 63.06 (-CH_2OH), 67.64 (-OCH_2- on the monophenyl), 67.88 (-OCH_2- on the biphenyl), 113.74 (*ortho* to -OCH_2- on the monophenyl), 114.85 (*ortho* to -OCH_2- on the biphenyl), 126.08 (*ortho* to -$CHCH_2$- on the biphenyl), 127.72 (*meta* to -$CHCH_2$- on the biphenyl), 128.41 (*meta* to -OCH_2- on the biphenyl), 132.84 (*para* to -$CHCH_2$- on the biphenyl), 138.09 (*para* to -$CHCH_2$- on the monophenyl) 142.91 (*ipso* to -$CHCH_2$- on the biphenyl), 157.04 (*ipso* to -OCH_2- on the monophenyl), 158.60 (*ipso* to -OCH_2- on the biphenyl).

Synthesis of 1,7,28,34-Tetraoxa-20,47-bis(bromohexyl)-[7.0.2.7.0.2]paracyclophane (40, TPO-(c)5(2)Br). To a

solution of **39** (190 mg, 0.2 mmol) and CBr_4 (86 mg, 0.26 mmol) in dry THF (15 mL) was added PPh_3 (68 mg, 026 mmol) in dry THF (4 mL) dropwise, and the mixture was stirred at 30 °C for 10 h. CH_2Cl_2 was added, and the organic phase was washed with water, dilute HCl, and water and dried over $MgSO_4$. Purification by column chromatography (SiO_2, ethyl acetate/hexanes = 1/9) yielded 170 mg (83%) of white crystals, mp = 158−160 °C. Thermal transitions are reported in Table 1, purity (HPLC), 98.9%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.34 (m, 12H, -$CH_2(CH_2)_3(CH_2)_2$Br), 1.82 (m, 20H; 12H, -$OCH_2(CH_2)_3$-CH_2O-, 8H, -$CH_2(CH_2)_3CH_2CH_2$Br), 2.72 (m, 4H, -PhCHCH_2-Ph-), 2.97 (m, 2H, -PhCHCH$_2$Ph-), 3.38 (t, 4H, -CH_2Br, J = 6.8 Hz), 3.87 (m, 4H, -PhOCH_2-), 3.99 (m, 4H, -PhPhOCH_2-), 6.59 and 6.74 (overlapping doublets, 4H, *ortho* to -OCH_2 on the monophenyl, J = 8.65 Hz), 6.66 (d, 4H, *meta* to -OCH_2 on the biphenyl, J = 8.78 Hz), 6.74 and 6.90 (overlapping doublets, 4H, *ortho* to -OCH_2- on the monophenyl, J = 8.70 Hz), 6.94 (d, 4H, *ortho* to -$CHCH_2$- on the biphenyl, J = 8.5 Hz), 7.35 and 7.38 (overlapping doublets, 4H, *meta* to -$CHCH_2$- on the biphenyl, J = 8.17 Hz), 7.46 and 7.49 (overlapping doublets, 4H, *meta* to -OCH_2- on the biphenyl, J = 8.74 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 22.69−32.74 (-(CH_2), -$OCH_2(CH_2)_3CH_2$O-), 33.92 (-CH_2Br), 42.81 (-CHCH_2-), 48.04 (-CHCH$_2$-), 67.57 (-OCH_2- on the monophenyl), 67.82 (-OCH_2- on the biphenyl), 113.72 (*ortho* to -OCH_2- on the monophenyl), 114.92 (*ortho* to -OCH_2- on the biphenyl), 126.07 (*ortho* to -$CHCH_2$- on the biphenyl), 127.74 (*meta* to -$CHCH_2$- on the biphenyl), 128.38 (*meta* to -OCH_2- on the biphenyl), 130.02 (*meta* to -OCH_2- on the monophenyl), 132.28 (*para* to -OCH_2- on the biphenyl), 133.41 (*para* to -OCH_2- on the monophenyl), 138.06 (*para* to -$CHCH_2$- on the biphenyl), 142.60 (*ipso* to -$CHCH_2$- on the biphenyl), 142.78 (*ipso* to -$CHCH_2$- on the biphenyl), 157.02 (*ipso* to -OCH_2- on the monophenyl), 158.40 (*ipso* to -OCH_2- on the biphenyl).

Synthesis of Poly{1,7,28,34-tetraoxa-20,47-bis[[4-[2-(4-oxy-4′-biphenylyl)butyl]phenoxy]hexyl][7.0.2.7.0.2]-paracyclophane} (41, Poly{TPO-(c)5(2)-*co*-TPB′}). A mixture of **40** (93 mg, 0.09 mmol), **13** (28 mg, 0.09 mmol), TBAH (12 mg, 0.03 mmol), NaOH (10 N, 0.2 mL), and *o*-DCB (0.2 mL) was stirred under N_2 at 80 °C for 6 h. CH_2Cl_2 was added, and the organic phase was washed with water, dilute HCl, and water. The polymer was precipitated from CH_2Cl_2 in CH_3-OH followed by precipitation from CH_2Cl_2 in acetone. The yield was 92 mg (86%). $M_n = 9 \times 10^3$; $M_w/M_n = 1.5$. Thermal transitions are reported in Table1.

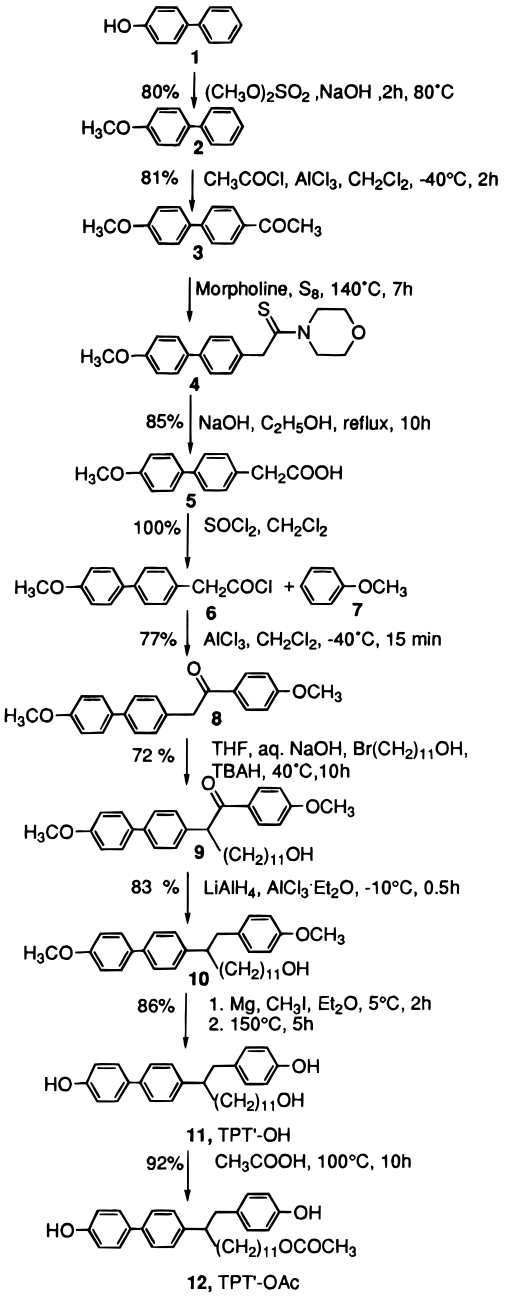
Synthesis of 13-Acetoxy-1-(4-hydroxyphenyl)-2-(4-hydroxy-4″-terphenylyl)tridecane (43, TPT-OAc). A mixture of **42** (4 g, 7.4 mmol) and CH_3COOH (100 mL) was stirred at 100 °C for 12 h. The solution was filtered and excess CH_3-COOH was distilled. The product was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1/3) and recrystallized from hexane/toluene = 1/1 to yield 3.8 g (89%) of white crystals, mp (DSC) = 168 °C, purity (HPLC), 98.7%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.2 (m, 16H, -$CH_2(CH_2)_8(CH_2)_2$-$OCOCH_3$), 1.6 (m, 4H, -$CH_2(CH_2)_8CH_2CH_2OCOCH_3$), 2.06 (s, 3H, -COC$H_3$), 2.82 (m, 3H, -PhC$HCH_2$PH-), 4.07 (t, 2H, -C$H_2$-$OCOCH_3$, J = 6.58 Hz), 6.71 (d, 2H, *ortho* to OH on the monophenyl, J = 8.58 Hz), 6.93 (d, 2H, *meta* to OH on the monophenyl, J = 8.54 Hz), 6.95 (d, 2H, *ortho* to OH on the terphenyl, J = 8.74 Hz), 7.20 (d, 2H, *ortho* to -$CHCH_2$- on the terphenyl, J = 8.38 Hz), 7.56 (d, 4H; 2H, *meta* to OH on the terphenyl, 2H, *meta* to -$CHCH_2$- on the terphenyl, J = 8.64 Hz), 7.65 (d, 4H, middle ring of the terphenyl group).

Synthesis of 13-Acetoxy-1-[4-(bromodecanoxy)phenyl]-2-[4-(bromodecanoxy)-4″-terphenylyl]tridecane (44). A mixture of **43** (2.1 g, 3.63 mmol), $Br(CH_2)_{10}Br$ (5.5 g, 18.6 mmol), DMF (5 mL), and K_2CO_3 (4 g, 30 mmol) was stirred for 5 h at 60 °C under N_2. CH_2Cl_2 was added, and the organic phase was washed with water, dilute HCl, and water, and dried over $MgSO_4$. Purification by column chromatography (SiO_2, ethyl acetate/hexanes = 1/5) followed by recrystallization from hexanes/toluene = 1/1 afforded 2.43 g (66%) of white crystals, mp (DSC) = 67 °C, purity (HPLC), 98.2%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.2 (m, 16H, -$CH_2(CH_2)_8(CH_2)_2$-$OCOCH_3$), 1.32 (m, 24H, -$O(CH_2)_2(CH_2)_6(CH_2)_2$Br), 1.6 (m, 4H, -$CH_2(CH_2)_8CH_2CH_2OCOCH_3$), 1.8 (m, 8H, -$OCH_2CH_2(CH_2)_6CH_2$-$CH_2$Br), 2.06 (s, 3H, -COC$H_3$), 2.82 (m, 3H, -PhC$HCH_2$Ph-), 3,41 (t, 4H, -C$H_2$Br, J = 6.68 Hz), 3.88 (t, 2H, -PhOCH_2-, J = 6.2 Hz), 4.03 (m, 4H; 2H, -PhPhPhOCH_2-, 2H, -CH_2OCOCH$_3$), 6.74 (d, 2H, *ortho* to -OCH_2 on the monophenyl, J = 8.34 Hz), 6.94 (overlapped doublet, 2H, *meta* to -OCH_2 on the monophenyl, J = 8.06 Hz), 6.98 (overlapped doublet, 2H, *ortho* to -OCH_2 on the terphenyl, J = 7.98 Hz), 7.17 (d, 2H, *ortho* to -$CHCH_2$- on the terphenyl, J = 8.06 Hz), 7.53 (overlapped doublet, 2H, *meta* to -$CHCH_2$- on the terphenyl, J = 7.25 Hz), 7.56 (overlapped doublet, 2H, *meta* to -OCH_2- on the terphenyl, J = 7.7 Hz), 7.56 (m, 4H, middle ring of the terphenyl group).

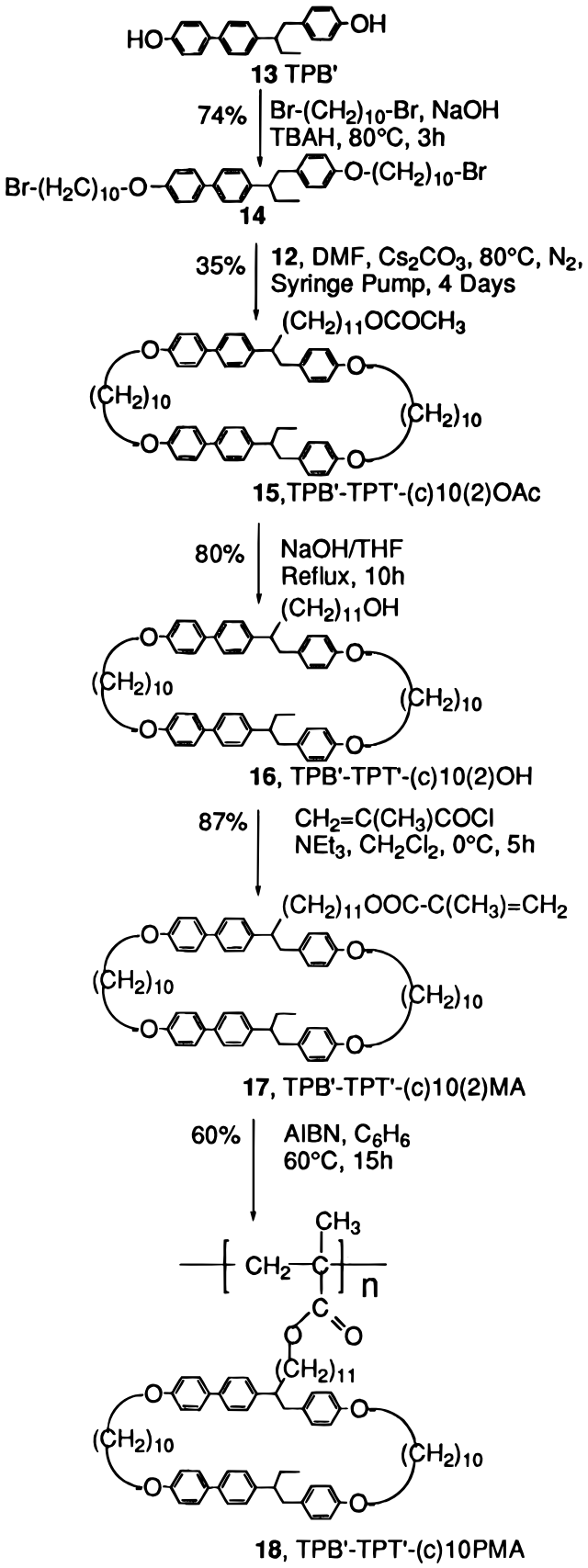
Synthesis of 1,12,39,50-Tetraoxa-32,70-bis(hydroxyundecanyl)[12.0.0.2.12.0.0.2]paracyclophane (45, TPT-(c)-10(2)OH). To a 5 L 3-neck flask equipped with mechanical stirrer and containing DMF (4 L) and Cs_2CO_3 (2.45 g, 7.5 mmol) was added a solution of **43** (0.84 g, 1.46 mmol) and **44** (1.48 g, 1.46 mmol) in DMF (30 mL)/THF (20 mL) dropwise over 5 h *via* a syringe pump. The mixture was stirred under N_2 at 80 °C for 4 days. DMF was distilled; the product was extracted with CH_2Cl_2 and washed with water. The solvent was evaporated, and the product was stirred with a mixture of THF (25 mL)/NaOH (10 N, 25 mL) at reflux for 10 h. The CH_2Cl_2-extracted phase was washed with water, dilute HCl, and water and dried over $MgSO_4$. Purification by column chromatography (SiO_2, ethyl acetate/hexanes = 1/2) followed by recrystallization from hexanes yielded 0.35 g (19%) of white crystals, purity (HPLC), 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.23−1.47 (m, 56H; 24H, -$O(CH_2)_2(CH_2)_6(CH_2)_2$O-, 32H, -$CH_2(CH_2)_8(CH_2)_2$-OH), 2.76 (m, 4H, -PhCHCH_2Ph-), 2.92 (m, 2H, -PhCHCH$_2$-Ph-), 3.62 (t, 2H, -CH_2OH, J = 6.58), 3.86 (t, 4H, -PhOCH_2-, J = 6.4 Hz), 3.99 (t, 4H, -PhPhPhOCH_2-, J = 6.35 Hz), 6.65 (d, 4H, *ortho* to -OCH_2- on the monophenyl, J = 8.68 Hz), 6.79 (d, 4H, *meta* to -OCH_2- on the monophenyl, J = 8.72 Hz), 6.97 (d, 4H, *ortho* to -OCH_2- on the terphenyl, J = 8.78 Hz), 7.05 (d, 4H, *ortho* to -$CHCH_2$- on the terphenyl, J = 8.14 Hz), 7.47 (d, 4H, *meta* to -$CHCH_2$- on the terphenyl, J = 8.18 Hz), 7.54 (d, 4H, *meta* to -OCH_2- on the terphenyl, J = 8.68 Hz), 7.60 (m, 4H, middle ring of the terphenyl group). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 25.75−36.40 (-$(CH_2)_{10}$-, -OCH_2-$(CH_2)_8CH_2$O-), 42.78 (-CH$_2$CH-), 48.09 (-CH$_2$CH-), 63.11 (-CH$_2$OH), 67.09 (-OCH_2- on the monophenyl), 68.00 (-OCH_2- on the terphenyl), 113.95 (*ortho* to -OCH_2- on the terphenyl), 114.95 (*ortho* to -OCH_2- on the monophenyl), 126.45 (*ortho* to -OPh- on the middle terphenyl ring), 126.92 (*meta* to -OPh- on middle terphenyl ring), 127.14 (*meta* to -CH_2CH- on the terphenyl ring), 129.95 (*meta* to -OCH_2- on the monophenyl ring), 128.43 (*meta* to -OCH_2- on the terphenyl ring), 130.04 (*ortho* to -CH_2-CH- on the terphenyl ring), 132.48 (*para* to -OCH_2- on the terphenyl ring), 133.08 (*para* to -CH_2CH- on the terphenyl ring), 136.93 (*ortho* to -OPh- on the terphenyl ring), 137.99 (*para* to -CH_2O- on the terphenyl ring), 138.15 (*para* to -OPh- on the middle terphenyl ring), 139.30 (*para* to -OCH_2- on the monophenyl ring), 144.10 (*ipso* to -CH_2CH- on the terphenyl), 151.79, 157.16 (*ipso* to -OCH_2- on the monophenyl), 158.77 (*ipso* to -OCH_2- on the terphenyl).

Synthesis of 1,12,39,50-Tetraoxa-32,70-bis(bromoundecanyl)[12.0.0.2.12.0.0.2]paracyclophane (46, TPT-(c)10-(2)Br). To a solution of **45** (0.35 g, 0.26 mmol) and CBr_4 (0.34 g, 1.04 mmol) in dry THF (15 mL) was added a solution of PPh_3 in dry THF (5 mL). The mixture was stirred under N_2 for 12 h at 30 °C. The CH_2Cl_2-extracted phase was washed with water, dilute HCl, and water and dried over $MgSO_4$. Purification by column chromatography (SiO_2, ethyl acetate/hexane = 1/25) followed by recrystallization from hexanes yielded 0.3 g (81%) of white crystals. Thermal transitions are reported in Table 1, purity (HPLC), 99%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.23−1.47 (m, 56H; 24H, -$O(CH_2)_2(CH_2)_6$-(CH_2)O-, 32H, -$CH_2(CH_2)_8(CH_2)_2$Br), 1.8 (m, 16H; 8H, -$OCH_2CH_2(CH_2)_6CH_2CH_2$O-, 8H, -$CH_2(CH_2)_8CH_2CH_2$Br), 2.76 (m, 4H, -PhCHC$H_2$PH-), 2.92 (m, 2H, -PhC$HCH_2$Ph-), 3.4 (t, 4H, -C$H_2$Br, J = 6.62 Hz), 3.86 (t, 4H, -PhOCH_2-, J = 6.4 Hz), 3.99 (t, 4H, -PhPhPhOCH_2-, J = 6.35 Hz), 6.65 (d, 4H, *ortho* to -OCH_2- on the monophenyl, J = 8.68 Hz), 6.79 (d, 4H, *meta* to -OCH_2- on the monophenyl, J = 8.72 Hz), 6.97 (d, 4H, *ortho* to -OCH_2- on the terphenyl, J = 8.78 Hz), 7.05 (d, 4H, *ortho* to

Scheme 1. Synthesis of TPT′ (12)



Scheme 2. Stepwise Synthesis of TPB′-TPT′-(c)10(2)PMA (18)



-$CHCH_2$- on the terphenyl, $J = 8.14$ Hz), 7.47 (d, 4H, *meta* to -$CHCH_2$- on the terphenyl, $J = 8.18$ Hz), 7.54 (d, 4H, *meta* to -OCH_2- on the terphenyl, $J = 8.68$ Hz), 7.60 (m, 4H, middle ring of the terphenyl group).

Synthesis of Poly{1,12,39,50-tetraoxa-32,70-bis[[[4-[2-(4-oxyphenyl)butyl]-4′-biphenylyl]oxy]undecanyl]-[12.0.0.2.12.0.0.2]paracyclophane} (47, Poly{TPT-(c)10(2)-*co*-TPB′}). A solution of **46** (92 mg, 0.06 mmol), **13** (19.9 mg, 0.06 mmol), TBAH (8.5 mg, 0.02 mmol), *o*-DCB (0.15 mL), and NaOH (10 N, 0.15 mL) was stirred at 80 °C under N_2 for 6 h. The reaction mixture was diluted with CH_2Cl_2, and the solution was precipitated first into CH_3OH and then from CH_2Cl_2 into acetone. The yield was 90 mg (88%). $M_n = 4 \times 10^4$; $M_w/M_n = 2.1$. Thermal transitions are reported in Table 1.

Results and Discussion

Synthesis and Characterization of Side Chain LCPs. Scheme 1 outlines the synthesis of the monomer TPT′-OH (**11**) and the protection of its alcohol group as acetate (TPT′-OAc, **12**). A detailed description of the sequence of reactions from **1** to **8** will be published elsewhere.[11] C-alkylation with 1-bromoundecan-11-ol yielded **9** (72% yield). The keto group of **9** was reduced with $AlCl_3 \cdot Et_2O$[12] to produce **10** in 83% yield. Demethylation of **10** under nucleophilic conditions with CH_3MgI at 150 °C[13] afforded monomer TPT′-OH (**11**) in 86%

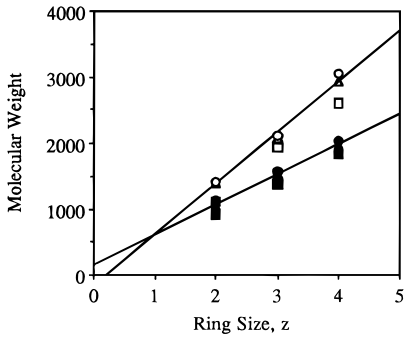


Figure 2. Dependence of the theoretical and experimental molecular weights of TPB′-(c)10(2), TPB′-(c)10(3), TPB′-(c)10-(4), ($M_{n_{th}}$ = ■, $M_{n_{exp}}$ = □); TPB′-TPT′-(c)10(2)OH (**16**), (TPB′)$_2$-TPT′-(c)10(3)OH (**23**), and (TPB′)$_3$-TPT′-(c)10(4)OH (**29**) ($M_{n_{th}}$ = ▲, $M_{n_{exp}}$ = △); and TPB′- TPT′-(c)10(2)MA (**17**), (TPB′)$_2$-TPT′-(c)10(3)MA (**24**), and (TPB′)$_3$-TPT′-(c)10(4)MA (**30**) ($M_{n_{th}}$ = ●, $M_{n_{exp}}$ = ○) on the ring size and functionality. Calculated values, closed symbols; experimental values, open symbols.

yield. Since in the next reaction step the two phenolic groups of **11** required alkylation under mild basic conditions, the alcohol group of **11** was protected as its acetate by direct esterification with CH_3COOH. TPT′-OAc was obtained in 92% yield.

Scheme 2 describes the preparation of monomer TPB′-TPT′-(c)10(2)MA (**17**) and the corresponding polymer TPB′-TPT′-(c)10(2)PMA (**18**). The detailed synthesis of TPB′(**13**)[11] and its biselectrophilic derivative **14**[7m] are described elsewhere. The cyclization of **14** with **13** was performed under high dilution,[7m] in DMF, using Cs_2CO_3 as base. Under these reaction conditions, the acetate group of **12** is stable. **15** was obtained in 35% yield. The cleavage of the acetate group of **15** was performed with NaOH and THF to produce **16** in 87% yield. Esterification of the alcohol group of **16** with methacryloyl chloride under conventional conditions yielded the methacrylate monomer **17**. The corresponding polymethacrylate **18** was synthesized by radical-initiated polymerization of **17**.

Figure 2 plots the dependence of the theoretical and experimental molecular weights as a function of ring size (z) for all series of cyclic compounds reported in this publication. The experimental molecular weights were obtained by GPC calibrated with polystyrene standards. These plots show a linear dependence between the hydrodynamic volume of these compounds and their size and therefore demonstrate the cyclic structure and the correct size of these compounds.[7] The transition temperatures of compounds TPB′-(c)10(2)[7m] and **15**−**18** are reported in Table 1. With the exception of TPB′-(c)10-(2) which is crystalline, all other compounds exhibit only a glass transition temperature (T_g). It is well recognized that polymerization of nonliquid crystalline monomers most frequently yields polymers which display LC phases. This trend is known as the "polymer effect".[4] Therefore, at first sight, it may look surprising that the polymerization of monomer **17** does not yield a LC polymer (**18**). Theoretical considerations[14] of the "polymer effect" require however that the polymerizable nonliquid crystalline monomer should display a virtual mesophase in order to generate a polymer exhibiting a monotropic or enantiotropic mesophase. A virtual mesophase is usually covered by a crystalline phase. Monomer **17** is liquid at room temperature, and on cooling it forms a glass (Table 1). Therefore, the potential mesophase of this compound if it exists is kinetically prohibited by its T_g. After polymerization T_g of monomer **17** increases by 62 °C. However, no

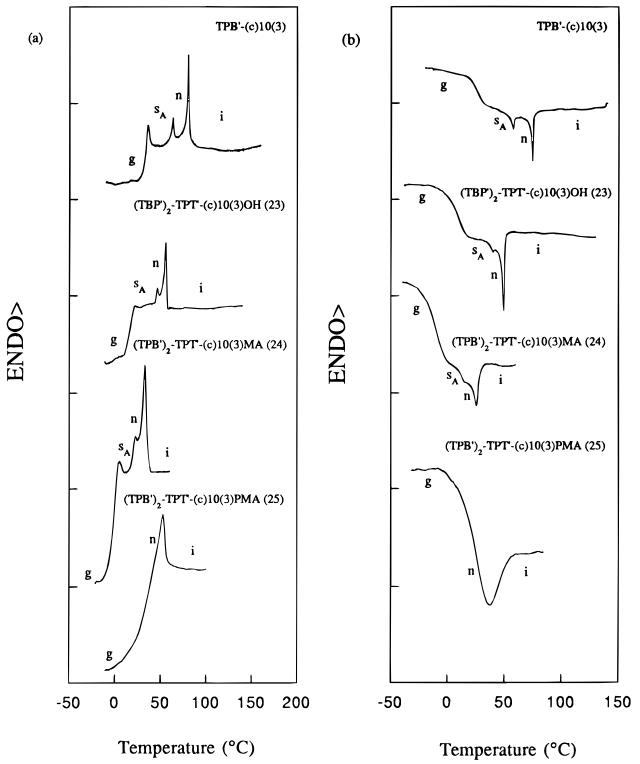


Figure 3. DSC traces of TPB′-(c)10(3), (TPB′)$_2$-TPT′-(c)10(3)-OH (**23**), (TBP′)$_2$-TPT′-(c)10(3)MA (**24**), and (TPB′)$_2$-TPT′-(c)-10(3)PMA (**25**): (a) second heating scan and (b) first cooling scan.

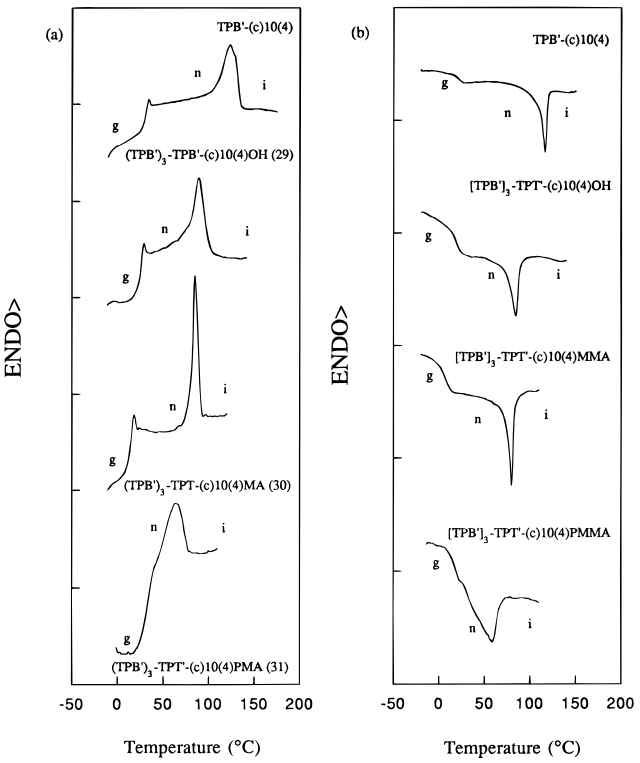
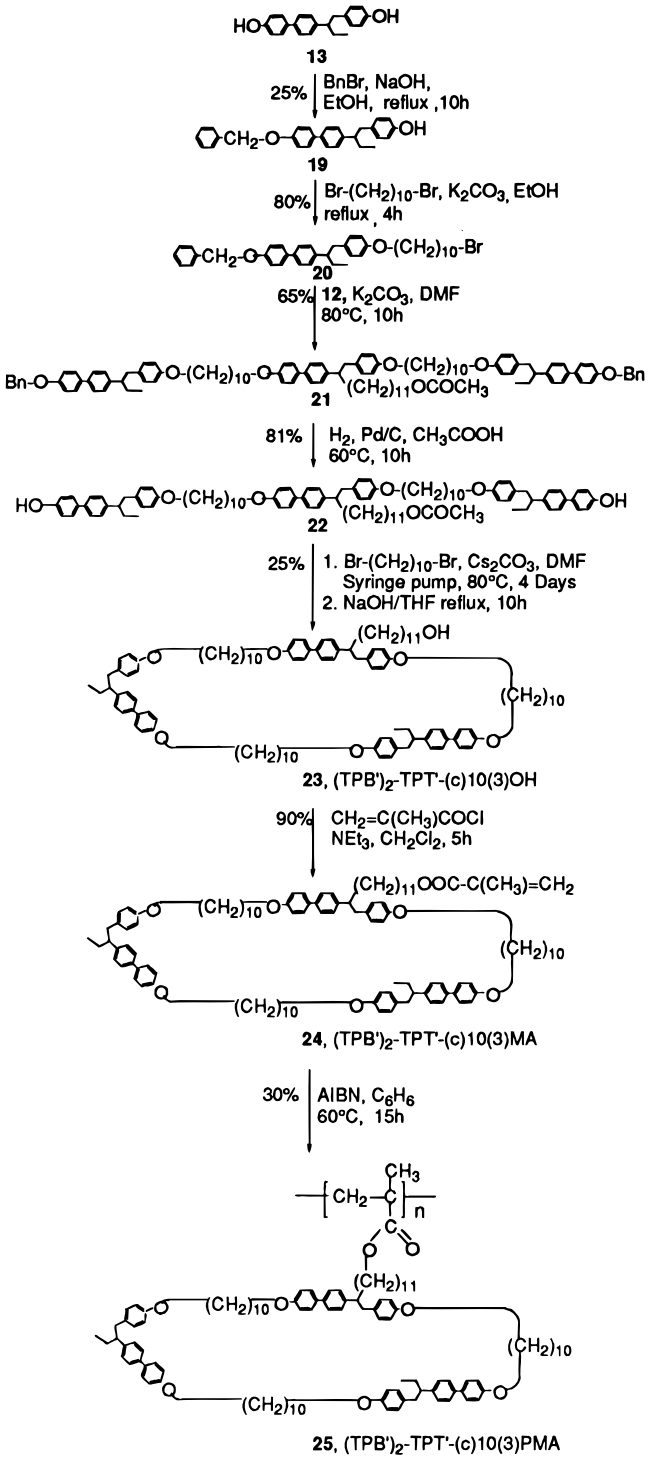


Figure 4. DSC traces of TPB′-(c)10(4), (TPB′)$_3$-TPT′-(c)10(4)-OH (**29**), (TBP′)$_3$-TPT′-(c)10(4)MA (**30**), and (TPB′)$_3$-TPT′-(c)-10(4)PMA (**31**): (a) second heating scan and (b) first cooling scan.

mesophase forms, most probably because the increase in the kinetically prohibited mesophase as a function of the degree of polymerization has a lower slope than that of the increase in T_g.[14]

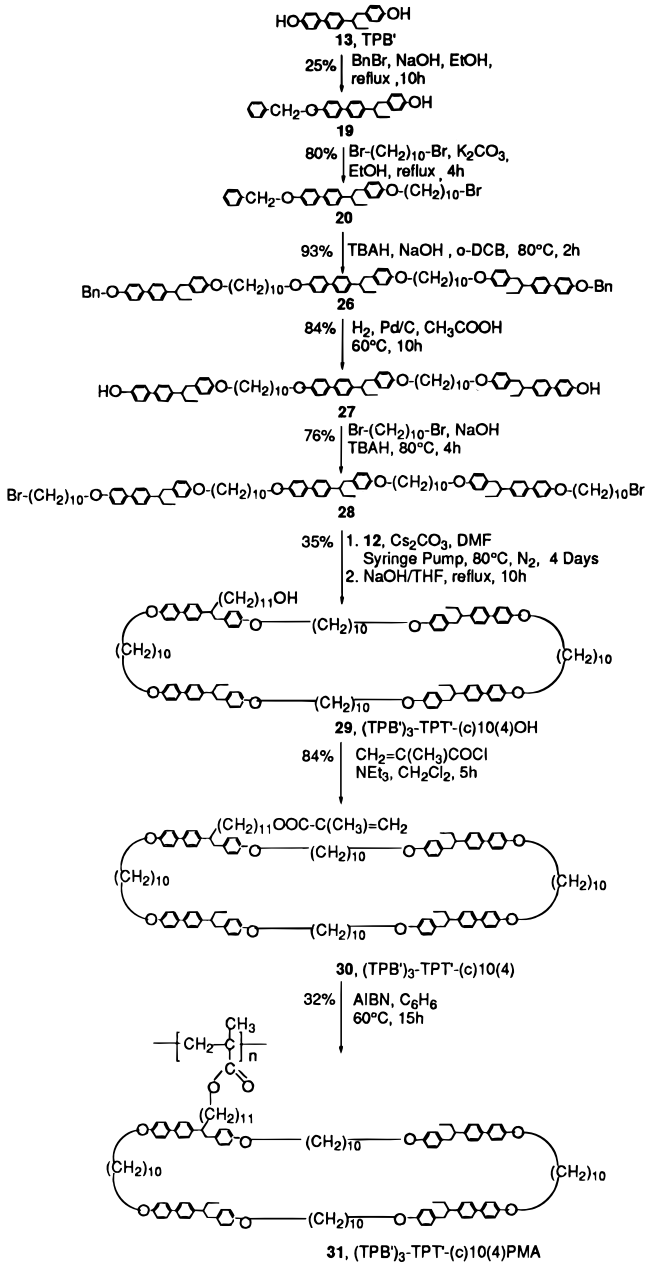
Scheme 3. Stepwise Synthesis of $(TPB')_2$-TPT′-(c)10(3)PMA (25)



All cyclic dimers based on 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB)[7a−m] and TPB′ [7m] and flexible spacers are crystalline or amorphous. However, larger cyclics such as trimers, tetramers, and pentamers based on the same mesogenic group and a suitable length of the flexible spacer display mesophases that undergo isotropization at higher temperatures than the corresponding linear polymers. Consequently, we decided to synthesize monomer **24** which is based on the cyclic trimer of TPB′ and 1,10-dibromodecane (TPB′-(c)-10(3)). TPB′-(c)10(3) exhibits enantiotropic s_A and nematic phases.[7m]

Scheme 3 describes the synthesis of monomer $(TPB')_2$-TPT′-(c)10(3)MA (**24**) and the corresponding polymer

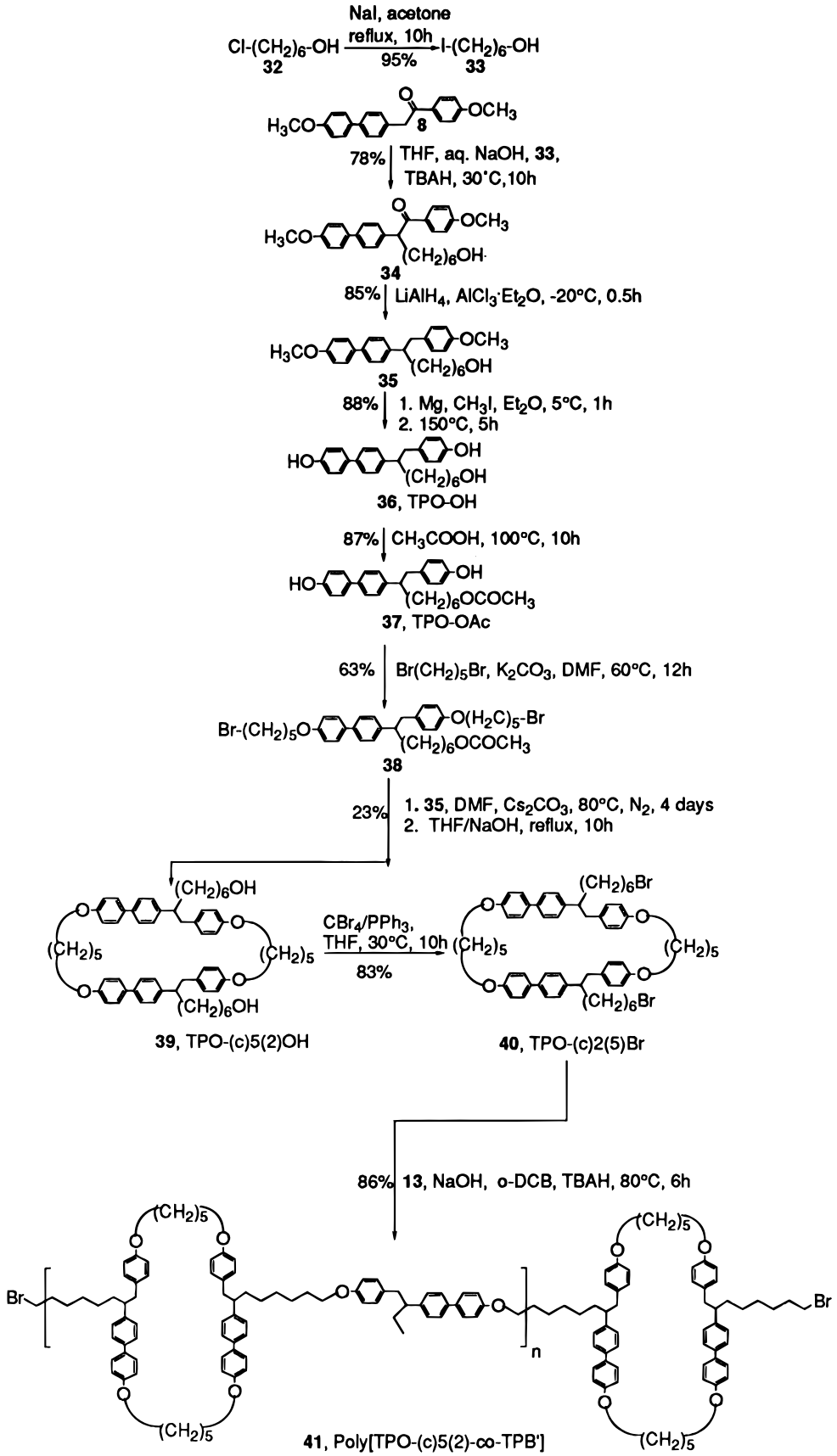
Scheme 4. Stepwise Synthesis of $(TPB')_3$-TPT′-(c)10(4)PMA (31)



$(TPB')_2$-TPT′-(c)10(3)PMA (**25**). The preparation of compounds **19** and **20** was reported elsewhere.[7m] The alkylation of **12** with 2 mol of **20** in DMF using K_2CO_3 as base yielded **21** in 65% yield. Hydrogenolysis of **21** with Pd/C in CH_3COOH produced **22** (81% yield). Cyclization of **22** with 1,10-dibromodecane under similar conditions as those used for the synthesis of **15** followed by the cleavage of the acetate group produced **23** in 25% yield. Esterification of **23** with methacryloyl chloride produced **24** which was polymerized to **25** *via* radical initiation.

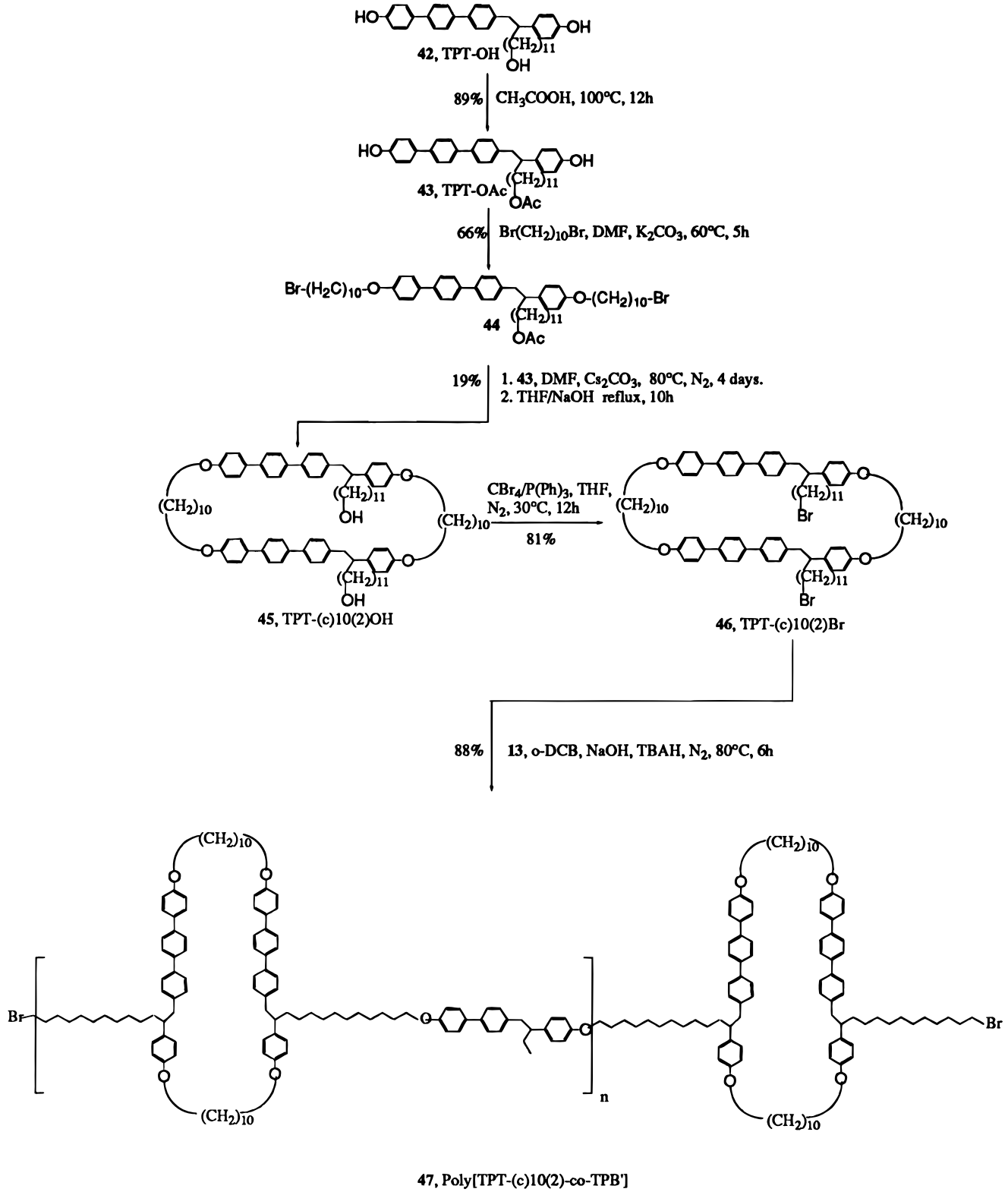
Figure 3 shows heating and cooling DSC traces of TPB′-(c)10(3), $(TPB')_2$-TPT′-(c)10(3)OH (**23**), $(TPB')_2$-TPT′-(c)10(3)MA (**24**), and the corresponding linear polymer **25.** The corresponding thermal transitions are presented in Table 1. The cyclic model compound TPB′-(c)10(3), the intermediary compound **23**, and the monomer **24** exhibit enantiotropic s_A and nematic (n) phases. These were assigned by the focal conic fan shape and respectively schlieren textures displayed by these compounds on the optical polarized microscope. These

Scheme 5. Stepwise Synthesis of Poly[TPO-(c)5(2)-*co*-TPB′] (41)



mesophases are in agreement with those displayed by the parent unsubstituted cyclic trimers.[7h,m] The transition temperatures associated with these phases decrease with the increase of the size of the substituent attached to the cyclic compound, *i.e.*, in the order TPB′-(c)10(3) > **23** > **24**. The resulting polymer **25** displays only an enantiotropic nematic mesophase which overlaps its T_g. The isotropization temperature (T_i) of the polymer **25** is 20 °C higher than that of the corresponding monomer **24**, while T_g is 37 °C higher. Therefore, due the lower increase in the LC transition temperatures versus that of T_g, the s_A phase observed in **24** is surpassed by T_g.

Scheme 6. Stepwise Synthesis of Poly[TPT-(c)10(2)-*co*-TPB′] (45)



Consequently, in **25**, the s_A phase becomes kinetically controlled.

Scheme 4 describes the synthesis of the methacrylate **30** and the corresponding polymethacrylate **31** which contains the cyclic tetramer of TPB′, *i.e.*, TPB′-(c)10(4), as mesogenic group, connected to the polymer backbone with a spacer containing 11 methylenic units. The synthesis of intermediary compounds **26**−**28** was described elsewhere.[7m] Cyclization of **28** with **12** under conditions similar to those used for the preparation of **15** and **23** followed by the cleavage of the acetate protecting group produced **29** in 35% yield. Esterification of **29** with methacryloyl chloride generated **30** which was polymerized radically to yield **31**. The DSC traces of the model compound TPB′-(c)10(4) and **29**−**31** are shown in Figure 4. All compounds exhibit an enantiotropic nematic phase. By analogy with the case of the cyclic trimer (Figure 3), T_i decreases by increasing the size of the substituent attached to the cyclic compound, *i.e.*, the order is TPB′-(c)10(4) > **29** > **30** > **31**.

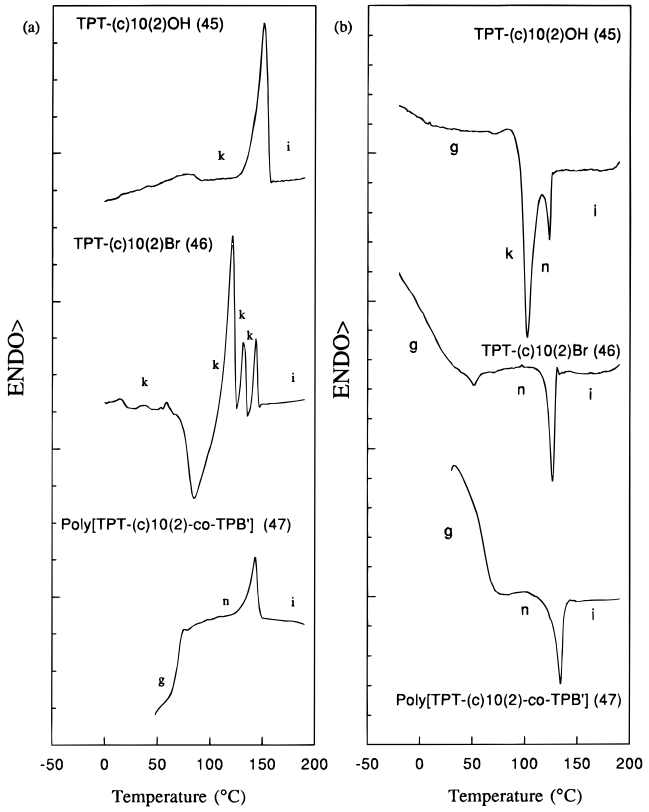


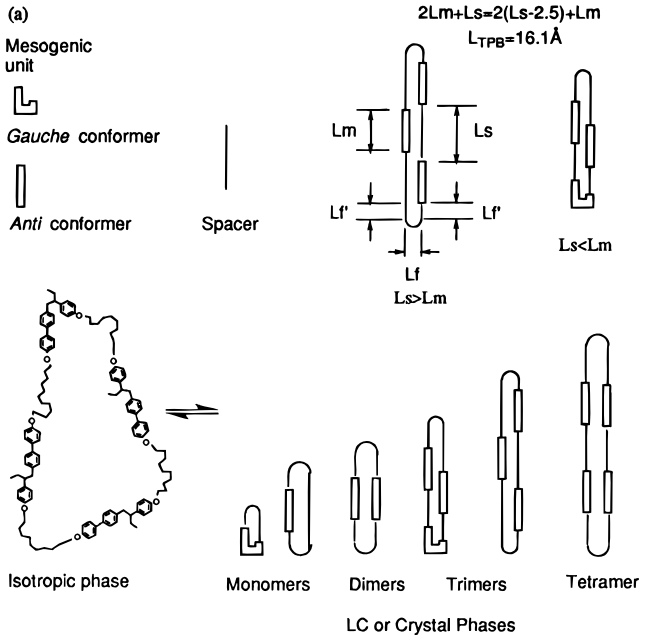
Figure 5. DSC traces of TPT-(c)10(2)OH (**45**), TPT-(c)10(2)-Br (**46**), and poly[TPT-(c)10(2)-*co*-TPB′]: (a) second heating scan and (b) first cooling scan.

The main difference between this system and the one outlined in Scheme 3 and Figure 3 consists in a decrease of T_i of the monomer **30** after polymerization. T_i of **30** is larger than that of **31** (Figure 4, Table 1). This difference will be explained later.

Synthesis and Characterization of Main Chain LCPs. Schemes 5 and 6 outline the synthesis of the first examples of main chain polymers containing cyclic mesogens. These reaction schemes required the preparation of the biselectrophilic cyclic dimers TPO-(c)5(2)-Br (**40**) and TPT-(c)10(2)Br (**46**). As described in Scheme 5, the first step in their synthesis consists in the C-alkylation of **8** with 1-iodohexan-6-ol to produce **34** which was reduced with $AlCl_3 \cdot Et_2O/LiAlH_4$[12] to **35**. The demethylation of the methoxy groups of **35** under nucleophilic conditions[13] produced **36**. The alcohol group of **36** was protected as acetate (**37**). Alkylation of **37** with a large excess of 1,5-dibromopentane yielded **38**. Cyclization of **38** with **37** under high dilution produced **39** in 23% yield. The bromination of the alcohol groups of **39** with CBr_4/PPh_3[15] yielded the required monomer TPO-(c)5(2)Br (**40**). Phase transfer-catalyzed polyetherification of **40** with **13** produced the copolymer poly[TPO-(c)5(2)-*co*-TPB′] (**41**) which contains a combination of linear and macrocyclic mesogens. Charaterization of **39** by DSC showed only $T_g = 76$ °C (Table 1).

Scheme 6 describes the successful synthesis of the first example of a main chain LCP containing cyclic and linear mesogens. The cyclic biselectrophilic mesogen TPT-(c)10(2)Br (**46**) was prepared in four steps starting from TPT′-OH. The synthesis of TPT′-OH was reported previously.[9] The alcohol group of **42** was first protected as acetate by esterification with CH_3COOH to yield **43** (89% yield), which was alkylated with an excess of 1,-10-dibromodecane to produce **44** (66% yield). Cyclization of **43** with **44** yielded **45** (19% yield). Bromination of the alcohol groups of **45** with CBr_4/PPh_3[15] produced monomer TPT-(c)10(2)Br (**46**). The synthesis of the copolymer poly[TPT-(c)10(2)-*co*-TPB′] was accomplished by the phase transfer-catalyzed polyetherification of **46** with **13**.

Scheme 7. (a) Dependence between Spacer Length, Size of Macrocyclic, and Conformation of the Resulting Supramolecular Quasi-Rigid-Rodlike Collapsed Structure in the LC Phase and (b) Structural Models for LCPs Based on Macrocyclic Mesogens That Adopt Various Collapsed Attachments Determined by Their Structural Design



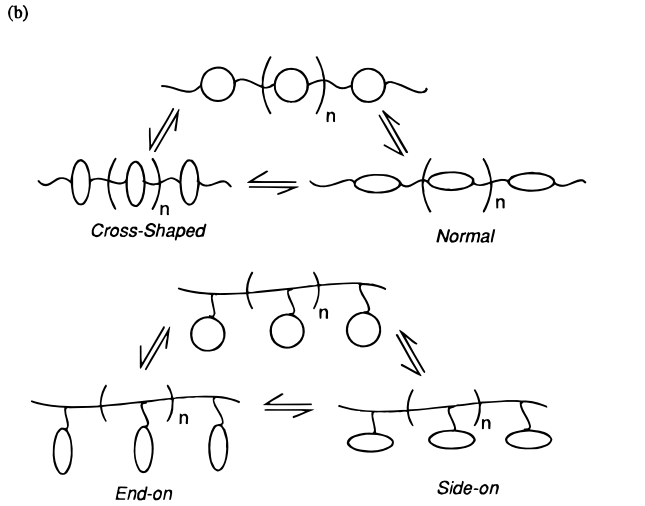
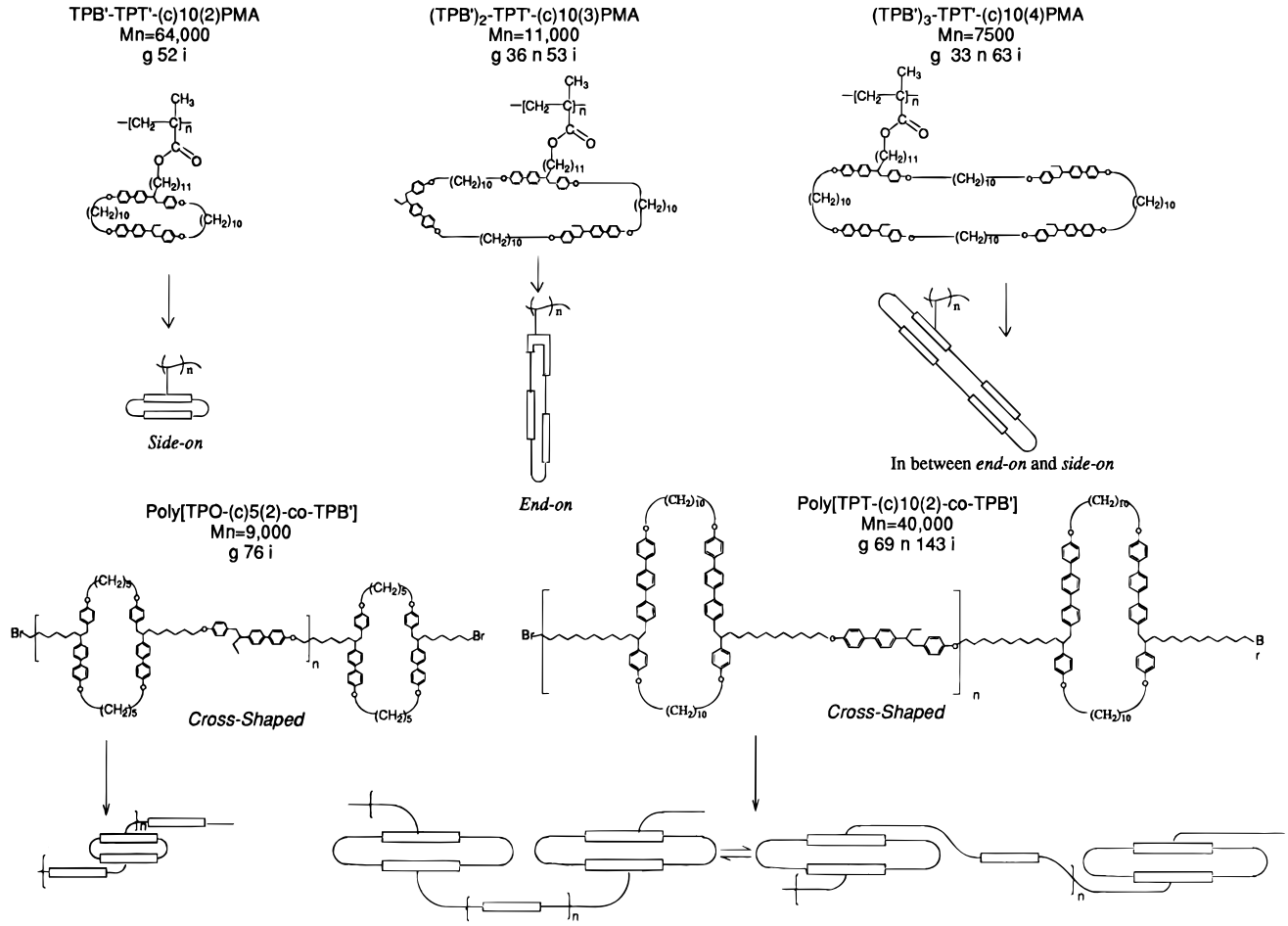


Figure 5 presents the DSC traces of **45**−**47**. Thermal transitions collected from these DSC traces are summarized in Table 1. Both **45** and **46** exhibit a monotropic nematic phase. T_i of **46** is higher than that of **45**, while the crystallization tendency of **46** is lower than that of **45**. Polymer **47** exhibits an enantiotropic nematic mesophase which undergoes isotropization at a higer temperature than the precursor monomer **46**.

Structural Models for Side Chain and Main Chain LCPs Containing Collapsed Macrocyclic Mesogens. Scheme 7a outlines the dependence between the spacer length, the length of the mesogen, and the collapsed rodlike conformation of the macrocyclic

Scheme 8



compounds as a function of ring size.[7h,10d] As we observe from this figure in the even sizes of macrocyclics, the conformation of the conformationally flexible mesogen (*i.e.*, TPB or TPB′) is always *anti* regardless of spacer length. However, in the odd sizes of macrocyclics, when the length of the spacer is shorter than that of the TPB or TPB′ mesogen, the collapsed macrocyclic contains one TPB or TPB′ unit as part of the fold, and this unit has a *gauche* conformation. This dependence was established by X-ray diffraction experiments.[7h,10d] The length of TPB and TPB′ compound becomes equal to that of the spacer when the spacer contains 12 methylenic units. Therefore in the LC phase the macrocyclic monomer **24** from Scheme 3 collapses into a quasi-rigid-rodlike conformation which places the mesogen, from which the flexible spacer is attached, in the fold. As a consequence, the polymer derived from monomer **24** has an end-on attached collapsed mesogen. Alternatively, polymer **18** has side-on attached collapsed macrocyclic mesogens. This brief discussion is generalized in Scheme 7b which outlines the concept of producing main chain and side chain LCPs containing macrocyclic mesogens which, depending on their design, "know" how to collapse into cross-shaped, normal, end-on and side-on, respectively, attachments.

Scheme 8 outlines the mechanism and the structural models which explain the formation of the LC phases and the phase behavior of side chain polymers **18**, **25**, and **31** and main chain polymers **41** and **47**.

In all cases, depending on the ring size and the relationship between the length of the mesogenic group and the length of the spacer, the combination of *anti* and *gauche* conformers of the conformationally flexible mesogen and the extended or folded spacers is responsible for the ultimate shape of the quasi-rigid-rodlike mesogen obtained from the collapsed macrocyclic.[7h,10d] In the case of side chain LCPs, the mesogen can be attached in a side-on or end-on mode through its flexible spacer to the backbone.[4a,16,17] In our present experiments the spacer is always attached from the flexible part of the mesogen. On the basis of detailed structural considerations presented in previous publications[7h,10d] when the length of the mesogen is shorter than that of the spacer (as is the case of TPB′ and -$(CH_2)_{10}$-), cyclics with *even* degrees of polymerization have the structures outlined for compounds **18**, **31**, **41**, and **47** in Scheme 8, *i.e.*, the spacer is in the fold, and the mesogen is in its *anti* conformation. For similar cyclic mesogens with *odd* degrees of polymerization, one of the mesogens is in the fold (**25**, Scheme 8). In this last case the side chain LCP **25** has the mesogenic group attached in an end-on mode. Consequently, the side chain polymer **18** has a side-on nonmesogenic group, while **25** an end-on attached mesogenic group. The mesogenic group in **31** is attached in an intermediary fashion between end-on and side-on. In the case of end-on attached mesogens, there is a sharp increase in T_i with the increase in the degree of polymerization,[4a,b] and this is indeed the case for polymer **25**. Side-on polymers exhibit a much lower increase in their T_i versus the degree of polymerization.[4a,16] On the basis of this discussion, it seems that the macrocyclic dimer present as a side group in the polymer **18** is not mesogenic. This could be due to its lower axial ratio, $x = L/d$: $x = 1.89$ (for the collapsed cyclic dimer) versus $x = 6.19$ for the collapsed cyclic trimer. In the case of **31** the attachement of the

mesogen is between side-on and end-on. This is the least favorable architecture which in the case of conventional side chain LCPs destabilizes both side chain crystallization and the formation of the mesophase.[17] Although the cyclic tetramer attached as a side group in **31** is a very efficient mesogen ($x = 6.7$, Table 1), its unsuitable attachment to the polymer backbone does not stabilize the mesophase upon polymerization. Finally the bottom of Scheme 8 illustrates the structures of main chain polymers **41** and **47.** In order to generate a nematic mesophase, the collapsed cross-shaped cyclic and the linear mesogens should align in a parallel way. The collapsed rodlike cyclic groups of **41** can not accommodate this conformation since the spacer length containig five methylenic units is too short to permit the alignment of the two mesogens ($x = 1.65$). In the case of polymer **47**, the cyclic monomer displays a nematic phase due to its more efficient collapsed macrocyclic mesogen ($x = 3.44$). At the same time the spacer length containing 11 methylenic units permits the organization of the two mesogens in a linear extended conformation which is responsible for the formation of the nematic phase of this polymer.

We believe that the experiments described in this paper demonstrate both the complexity and the synthetic capabilities of the spacer concept. There are several very interesting features displayed by these polymers. First, although the main chain and the side chain polymers contain a spacer based on 11 methylenic units, they do not crystallize and do not exhibit smectic phases. We are not aware of examples of side chain LCPs containing such a long spacer and an end-on attached mesogen, which display only nematic mesophases. Second, the nematic mesophases exhibited by these polymes have a large chance to be biaxial, since some of these macrocyclic mesogens have shown to display a biaxial nematic mesophase.[7i,k] Third, the combination of spacers used in the architecture of the macrocyclic mesogens and the corresponding polymers provides the highest degree of conformational disorder from all known main chain and side chain LC polymers exhibiting a nematic mesophase. This is due to the much lower entropy of isotropization of the supramolecular quasi-rigid-rodlike mesogens attached from collapsed macrocyclics than that of their linear homologues.[7h,10d] Last, but not least, the ability of these polymers to change the structure of their macrocyclic building blocks from mesogenic to nonmesogenic opens many new synthetic capabilities and new potential physical properties.

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