Toward "Willowlike" Thermotropic Dendrimers

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ABSTRACT: The synthesis and characterization of the AB_2 monomers 6-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)hexane (8 or TPH-b), 13-bromo-1-(4-hydroxyphenyl)-2-[4-(6-hydroxy-2-naphthalenylyl)-phenyl]tridecane (22 or BPNT-b), and 13-bromo-1-(4-hydroxyphenyl)-2-(4-hydroxy-4″-*p*-terphenylyl)tridecane (30 or TPT-b) are described. The phase-transfer-catalyzed polyetherification of all monomers followed by in situ alkylation of their phenolate chain ends with bromoalkanes, benzyl chloride, or allyl chloride led to the soluble hyperbranched polymers TPH-b-X, BPNT-b-X, and TPT-b-X (where X refers to the nature of their chain ends, for example, when X = Bz = benzyl, X = All = allyl, and, when X = numeral, it represents the number of carbons in the alkyl chain end). The minimum energy conformations of the flexible branching points of these polymers are anti and gauche. The gauche conformer leads to a hyperbranched polymer with a conventional treelike architecture. By analogy with the behavior of the corresponding linear polymers, above their glass transition temperature, these hyperbranched polymers are considered to minimize their free energy by lowering their free volume via a conventional nematic mesophase which is generated by the conformational change of their structural units from gauche to anti. The overall change in the architecture of these hyperbranched polymers via the anti–gauche conformational change of their structural units resembles that of a willow. Regardless of the nature of X, TPH-b-X and BPNT-b-X display only a very narrow enantiotropic nematic mesophase. TPT-b-8 with M_n = 11 800 and M_w/M_n = 2.42 exhibits an enantiotropic nematic mesophase over a range of 82 °C. The degree of branching of TPT-b-All is 0.82. Thus TPT-b is of extreme interest for further investigations on this novel class of hyperbranched polymers and for the synthesis of thermotropic liquid crystalline dendrimers.

Introduction

Dendrite, arborol, and branched are synonyms of Greek, Latin, and English origin respectively, for branched structures resembling treelike architectures. Synthetic dendrimers, arborols, or hyperbranched compounds are, therefore, oligomers or polymers resembling a tree in structure and subsequently containing a branching point in each structural unit. This very active area of research was reviewed,[1-4] and the proceedings of a recent symposium describe the most recent developments in this field.[5] As any other synthetic macromolecule, dendrimers, arborols, or hyperbranched architectures can be synthesized with broad or uniform molecular weight distributions. Dendrimers with broad molecular weight distributions are prepared by conventional chain or step polymerizations of AB_2 monomers and are frequently named hyperbranched polymers. Hyperbranched polymers with uniform molecular weight distributions are prepared via multistep synthetic sequences using a divergent[1,6] or convergent approach,[1,7] have a branching point in each structural unit except those from their chain ends, and are frequently named dendrimers or arborols. Regardless of their molecular weight uniformity, this novel class of hyperbranched macromolecules should generate architectures which resemble, depending on the rigidity of their structural units, just like in the case of natural trees, various treelike architectures.

Synthetic methods were developed for the preparation of dendrimers and hyperbranched polymers based on most classes of linear polymers. *Nevertheless, all dendrimers and hyperbranched polymers synthesized to date, although may display various treelike shapes, provide in the melt phase only a disordered liquid phase.*[1-5]

Recently, we have initiated a program to design dendrimers and hyperbranched polymers which exhibit order in one or more than one dimension in the melt phase.[8] The first example reported was a hyperbranched polymer which displays a conventional thermotropic uniaxial nematic mesophase.[8a] Almost simultaneously, a hyperbranched polymer displaying a lyotropic mesophase was reported from a different laboratory.[9] A dendrimer synthesized from the structural units of our hyperbranched polymer should, in principle, provide access to a unimolecular liquid crystalline phase obtained from a single polymer surrounded by its own melted chain ends. *Therefore, this concept can be exploited to design unimolecular nematic droplets dispersed into an isotropic liquid which is generated by the melted paraffinic chain ends of the dendrimer.* The trivial question to be asked first is, will the structural transition from a hyperbranched to a dendrimer architecture maintain the thermotropic liquid crystalline phase of the former structure? Regardless of the answer to this question, liquid crystalline phases obtained from branched architectures should exhibit sufficiently different structures, dynamics, and properties from those of the corresponding linear polymers to deserve investigation. In addition, we can foresee some of the technologically important property weaknesses of main-chain liquid crystalline polymers being overcome by hyperbranched architectures. Our synthetic approach used in the molecular design of this dendrimer is based on that of the "willow" tree. That is, our dendrimer has branching points which are conformationally flexible. The two most stable conformers of these branching units display well-defined geometries (i.e., anti and gauche) which are useful both during the synthesis process and in the generation of the liquid crystalline nematic mesophase. This conformationally flexible AB_2 structural unit was elaborated as a preparative application of our research on thermotropic liquid crystalline polymers based on conformational isomerism.[10,11] Recently this concept was used for the synthesis of other liquid crystals with complex architecture such as macrocyclics.[12] The "willow tree" strategy used in the design of the liquid crystalline hyperbranched polymers can be envisioned if we consider

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the structure generated when we lay down on the ground a willow tree. Due to their flexibility, its branches will change their conformation and align almost parallel to each other in order to minimize the free volume occupied by the tree. Certainly a synthetic willow tree should act in a similar manner. Our first example of a liquid crystalline hyperbranched polymer exhibited a nematic mesophase only in a very narrow range of temperature which was almost overlapping its glass transition temperature.[8] We are interested in the design of hyperbranched polymers and dendrimers which will display a nematic mesophase within a sufficiently broader range of temperature to be accessible for physical investigations.

The goal of this paper is to select the AB_2 monomer suitable for the preparation of dendrimers with a broad range of temperatures of their nematic mesophase. Therefore, first we will report the synthesis and polymerization of various AB_2 monomers which are at the same time mesogenic units based on conformational isomerism. The characterization of the resulting hyperbranched polymers will also be discussed. These results will provide directions toward the most suitable structural requirements which are necessary for the molecular design of dendrimers displaying a nematic mesophase within a broad range of temperatures.

Experimental Section

Materials. BBr_3 (1.0 M in CH_2Cl_2), $SOCl_2$ (97%), $LiAlH_4$ (95+%), $(CH_3)_2SO_4$ (99%), PPh_3 (99%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), (4-methoxyphenyl)acetic acid (99%), 8-bromooctanoic acid (97%), 11-bromoundecanoic acid (97%), 1-bromooctane (99%), CBr_4 (99%), butyllithium (2.5 M in hexane), trimethyl borate (99%), borane–tetrahydrofuran complex (1.0 M in THF), benzyl chloride (97%), 1-bromohexane (98%), 1-bromooctane (99%), 4-phenylphenol (98%), triethylsilane (99%) (all from Aldrich), $AlCl_3$ (anhydrous powder), Br_2 (reagent ACS), $Na_2S_2O_3$, CF_3COOH (peptide synthesis grade) (all from Fisher Scientific), 1-bromobutane (98%) (Pfaltz & Bauer), NaI (Matheson Coleman & Bell), and 6-bromo-2-naphthol (97%) (from Lancaster) were used as received. Et_2O was dried by refluxing over $LiAlH_4$ followed by distillation. CH_2Cl_2 was refluxed over CaH_2 and distilled before use. Acetone was refluxed over CaH_2 and distilled before use. NaI was dried at 110 °C under vacuum overnight. *o*-Dichlorobenzene (*o*-DCB) was distilled under reduced pressure. *N,N*-Dimethylformamide (DMF) was dried over CaH_2 and distilled under reduced pressure. All other chemicals were commercially available and were used as received. Tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] was synthesized according to a literature procedure.[13]

Synthesis of 1-(4-Biphenyloxy)-4-bromobutane (3). 3 was prepared by the etherification of 4-phenylphenol (1) with excess 1,4-dibromobutane (2). 1 (17.0 g, 0.10 mol) was dissolved in 200 mL of absolute EtOH in a 500-mL one-neck flask equipped with a reflux condenser and a N_2 inlet–outlet. Anhydrous K_2CO_3 (13.8 g, 0.10 mol) was added, and the reaction mixture was stirred at reflux for 2.5 h under a nitrogen atmosphere. 2 (32.4 g, 0.15 mol) was then added, and the reaction mixture was stirred at reflux temperature for 16 h. After EtOH was distilled off in a rotary evaporator, the remaining solid was dissolved in 200 mL of $CHCl_3$. The $CHCl_3$ solution was washed with water, dilute HCl, and water successively and dried over $MgSO_4$. After filtration, the solvent was evaporated to give a solid which was subsequently dissolved in hot EtOH. The insoluble part [i.e., 1,4-bis(4-biphenyloxy)-butane] was removed by filtration. The soluble product was *recrystallized from 95% EtOH to yield 11.6 g* (38.0%) of fine crystals. Purity (HPLC): 99%. Mp: 75–76 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.03 (m, 4H, $BrCH_2(CH_2)_2$–), 3.51 (t, 2H, $BrCH_2$–, J = 6.4 Hz), 4.04 (t, 2H, –CH_2O–, J = 5.4 Hz), 6.97 (d, 2H, ortho to the ether of the biphenyl ring, J = 9.1 Hz), 7.31 (overlapped peak, 2H, meta to the phenyl ring of the monosubstituted phenyl ring), 7.43 (overlapped peak, 1H, para to the phenyl ring of the monosubstituted phenyl ring), 7.54 (m, 4H, meta to the ether of the phenyl ring and ortho to the phenyl ring of the monosubstituted phenyl ring).

Synthesis of 1-(4-Biphenyloxy)-4-iodobutane (4). 1-(4-Biphenyloxy)-4-bromobutane (3); 11.6 g, 0.038 mol) and anhydrous NaI (8.52 g, 0.057 mol) were dissolved in 50 mL of dry acetone in a 100-mL one-neck flask equipped with a condenser. The reaction mixture was stirred at room temperature for 21 h. After evaporation of the solvent the solid was dissolved in 200 mL of $CHCl_3$, washed two times with 200 mL of water, once with a 5% Na_2SO_3 solution, and once with water, and dried over $MgSO_4$. The solvent was evaporated to give a solid which was crystallized from 200 mL of 95% EtOH to yield 11.2 g (84.1%) of white crystals. Purity (HPLC): 98.7%. Mp: 89–90 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.98 (m, 4H, $ICH_2(CH_2)_2$–), 3.27 (t, 2H, $1CH_2$–, J = 6.7 Hz), 4.02 (t, 2H, –CH_2O–, J = 5.6 Hz), 6.95 (d, 2H, ortho to the ether of the biphenyl ring, J = 8.5 Hz), 7.29 (overlapped peak, 2H, meta to the phenyl ring of the monosubstituted phenyl ring), 7.41 (overlapped peak, 1H, para to the phenyl ring of the monosubstituted phenyl ring), 7.53 (m, 4H, meta to the ether of the phenyl ring and ortho to the phenyl ring of the monosubstituted phenyl ring.

Synthesis of 1-(4-Methoxy-4′-biphenylyl)-2-(4-methoxyphenyl)ethanone (5). 5 was synthesized as was reported previously.[8a] Purity (HPLC): 98%. Mp: 197–199 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.80 (s, 3H, CH_3O–monophenyl), 3.86 (s, 3H, CH_3O–biphenyl), 4.24 (s, 2H, –CH_2–), 6.88 (d, 2H, ortho to the methoxy of the monophenyl ring, J = 8.2 Hz), 7.00 (d, 2H, ortho to the methoxy of the biphenyl ring, J = 9.3 Hz), 7.22 (d, 2H, meta to the methoxy of the monophenyl ring, J = 8.2 Hz), 7.58 (d, 2H, meta to the methoxy of the biphenyl ring, J = 9.3 Hz), 7.64 (d, 2H, meta to the carbonyl of the biphenyl ring, J = 8.0 Hz), 8.06 (d, 2H, ortho to the carbonyl of the biphenyl ring, J = 8.0 Hz).

Synthesis of 6-(4-Biphenyloxy)-1-(4-methoxy-4′-biphenylyl)-2-(4-methoxyphenyl)hexanone (6). To a 1000-mL three-neck flask equipped with a reflux condenser and a magnetic stirrer were successively added 5 (13.3 g, 40 mmol), 150 mL of toluene, 4 (14.1 g, 40 mmol), TBAH (1.36 g, 4.0 mmol), and 100 mL of 50% (w/w) NaOH. A balloon filled with nitrogen was placed at the top of the condenser. The reaction mixture was stirred vigorously at 60 °C for 2 h. During this time, the color of the solution changed from yellow to almost white and a product precipitated. The reaction mixture was diluted with 500 mL of water and filtered. The solid product was suspended in THF and treated with 20% HCl to cleave the acetal linkage of the O-alkylated product. The mixture was filtered, washed with water and then with methanol, and dried under vacuum. The obtained white solid was recrystallized from 400 mL of toluene to yield 16.3 g (73.1%) of fine crystals. Purity (HPLC): >99%. Mp: 181–182 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.49 (m, 2H, $PhCHCH_2CH_2$–), 1.85 (m, 3H, –OCH_2CH_2– and $PhCH_aCH_b(H_c)$–), 2.24 (m, 1H, $PhCH_aCH_b(H_c)$–), 3.76 (s, 3H, CH_3O–monophenyl), 3.85 (s, 3H, CH_3O–biphenyl), 3.97 (t, 2H, –OCH_2–, J = 6.4 Hz), 4.56 (t, 1H, –COCH–, J = 6.9 Hz), 6.85 (d, 2H, ortho to the methoxy of the monophenyl ring, J = 8.3 Hz), 6.93 and 6.97 (d, 2H, ortho to the methoxy of the biphenyl ring, J = 8.3 Hz), 6.97 (d, 2H, ortho to the ether of the biphenyl ring, J = 8.3 Hz), 7.26 (d, 2H, meta to the methoxy of the monophenyl ring, J = 8.3 Hz), 7.41–7.54 (m, 11H, protons of the monosubstituted phenyl ring, meta to the ether, meta to the carbonyl, and meta to the methoxy of the biphenyl rings), 8.02 (d, 2H, ortho to the carbonyl of the biphenyl ring, J = 9.0 Hz).

Synthesis of 6-(4-Biphenyloxy)-1-(4-methoxy-4′-biphenylyl)-2-(4-methoxyphenyl)hexane (7). To a 250-mL three-neck flask equipped with a reflux condenser and a dropping funnel were added 6 (8.35 g, 15 mmol) and 110 mL of CF_3COOH.[14] 6 did not dissolve completely. After heating to reflux temperature, triethylsilane (3.84 g, 33 mmol) was added dropwise and the reaction mixture was stirred at reflux for 50 min, after which time the reaction was allowed to cool to room temperature. The product was precipitated in 300 mL of MeOH, and the precipitate was filtered and washed with methanol. The product was dried under vacuum to yield 7.63 g (93.7%) of a fine white powder. Purity (HPLC): >99%. Mp: 150–151 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.33 (m, 2H, $PhCHCH_2CH_2$–), 1.73 (m, 4H, $-OCH_2CH_2$– and $PhCHCH_2$–), 2.87 (m, 3H, $PhCHCH_2Ph$), 3.79

(s, 3H, CH_3O–monophenyl), 3.83 (s, 3H, CH_3O–biphenyl), 3.89 (t, 2H, $-OCH_2-$, J = 6.4 Hz), 6.83 (d, 2H, ortho to the methoxy of the monophenyl ring, J = 8.5 Hz), 6.90 (d, 2H, ortho to the methoxy of the biphenyl rings, J = 8.3 Hz), 6.95 (d, 2H, ortho to the ether of the biphenyl ring, J = 8.9 Hz), 7.07 (d, 2H, meta to the methoxy of the monophenyl ring, J = 8.5 Hz), 7.07 (d, 2H, ortho to the methylene of the biphenyl ring, J = 8.2 Hz), 7.30–7.55 (m, 11H, protons of the monosubstituted phenyl ring, meta to the metoxy and meta to the ether of the biphenyl rings and meta to the methylene of the biphenyl ring).

Synthesis of 6-Bromo-1-(4-hydroxy-4'-biphenylyl)-2-(4-hydroxyphenyl)hexane (8). 7 (7.33 g, 13.5 mmol) was dissolved in 200 mL of dry CH_2Cl_2 in the three-neck flask equipped with a dropping funnel and a nitrogen inlet–outlet. The flask was cooled in a dry ice–acetone bath, and BBr_3 (1.0 M in CH_2Cl_2, 60 mL, 0.06 mol) was added dropwise to the suspension. The color of the solution changed from orange to red. The reaction mixture was stirred at room temperature overnight after which 100 mL of water was added slowly. The reaction product was extracted with 300 mL of Et_2O, washed three times with water, and dried over $MgSO_4$. After evaporation of the solvent, the resulting viscous solid was purified by silica gel column chromatography (hexane–Et_2O gradient, 2/1 to 1/1). After evaporation of the solvent, the resulting solid was recrystallized from toluene/hexanes (30/10) to yield 2.97 g (63.7%) of white crystals. Purity (HPLC): ≥99%. Mp: 103–110 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.27 (m, 2H, $PhCHCH_2CH_2-$), 1.74 (m, 2H, $BrCH_2CH_2-$), 1.77 (m, 2H, $PhCHCH_2-$), 2.78 (m, 1H, $PhCHCH_2Ph$), 2.84 (m, 2H, $PhCHCH_2Ph$), 3.30 (t, 2H, $BrCH_2-$, J = 7.0 Hz), 4.64 (s, 1H, HO–), 4.80 (s, 1H, HO–), 6.74 (d, 2H, ortho to the hydroxy of the monophenyl ring, J = 8.5 Hz), 6.88 (d, 2H, ortho to the hydroxy of the biphenyl ring, J = 7.8 Hz), 6.99 (d, 2H, meta to the hydroxy of the monophenyl ring, J = 8.5 Hz), 7.05 (d, 2H, ortho to the methylene of the biphenyl ring, J = 8.1 Hz), 7.39 (d, 2H, meta to the methylene of the biphenyl ring, J = 8.1 Hz), 7.45 (d, 2H, meta to the hydroxy of the biphenyl ring, J = 7.8 Hz).

Synthesis of 11-Bromoundecan-1-ol (10). 10 was prepared by the reduction of 11-bromoundecanoic acid (9) with borane–THF.[15] A three-neck flask equipped with a dropping funnel and a N_2 inlet–outlet and containing BH_3–THF (225 mL, 0.225 mol) was cooled to −78 °C (dry ice–acetone bath). 9 (40 g, 0.15 mol) in 210 mL of THF was added dropwise. After addition, the reaction mixture was allowed to reach room temperature and was stirred for 10 h. Distilled water (50 mL) was added dropwise, followed by 120 mL of saturated K_2CO_3. The aqueous layer was extracted with 400 mL of Et_2O, then washed with 100 mL of water, and dried over $MgSO_4$ to yield a white solid which was recrystallized from 150 mL of not hexanes to yield 34.8 g (91.8%) of white needlelike crystals. Mp: 44.5–46.5 °C (lit.[16] mp 46–49 °C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.24 (m, 14H, $-CH_2(CH_2)_7CH_2-$), 1.50 (m, 2H, $-CH_2CH_2OH$), 1.80 (m, 2H, $-CH_2CH_2Br$), 3.34 (t, 2H, $-CH_2Br$, J = 7.0 Hz), 3.58 (t, 2H, $-CH_2OH$, J = 7.0 Hz).

Synthesis of 11-Iodoundecan-1-ol (11). 10 (30 g, 0.12 mol), dried NaI (50 g, 0.333 mol), and 250 mL of anhydrous acetone were combined in a 500-mL one-neck round-bottomed flask equipped with a condenser containing a drying agent ($MgSO_4$) on top, and the resulting mixture was stirred for 16 h.[17] The solvent was evaporated to give a yellow solid which was recrystallized from 300 mL of *n*-hexane to yield 34.2 g (96%) of light yellow crystals. Purity (HPLC): 99.5%. Mp: 41–42 °C. ^{1}H-NMMR ($CDCl_3$, TMS, δ, ppm): 1.29 (m, 14H, $-CH_2(CH_2)_7CH_2-$), 1.60 (m, 2H, $-CH_2CH_2OH$), 1.82 (t, 2H, $-CH_2CH_2I$, J = 7.0 Hz), 3.66 (m, 2H, $-CH_2OH$).

Synthesis of 1-(4-Methoxyphenyl)-2-(4-bromophenyl)-ethanone (14). 14 was prepared by Friedel–Crafts acylation of anisole with (4-bromophenyl)acetyl chloride. (4-Bromophenyl)-acetic acid (12; 45 g, 0.21 mol) and $SOCl_2$ (22.7 mL, 0.31 mol) were placed in a 250-mL three-neck flask equipped with a nitrogen inlet–outlet. After adding a few drops of DMF, the reaction mixture was stirred at room temperature for 3 h. Excess $SOCl_2$ was removed under reduced pressure to produce a yellow solid which was used directly in the acylation reaction. 13 (49 g, 0.21 mol) was dissolved in 150 mL of CH_2Cl_2 in a 500-mL three-neck flask equipped with a nitrogen inlet–outlet, thermometer, and dropping funnel. The solution was cooled below 10 °C with an ice–water bath, after which time anhydrous $AlCl_3$ (42 g, 0.31 mol) was added. Then (4-bromophenyl)acetyl chloride (12'; 49 g, 0.21 mol) dissolved in 200 mL of anhydrous CH_2Cl_2 was added dropwise, maintaining the reaction temperature below 10 °C. After the addition, the solution changed from orange to red and was stirred at 0–10 °C for 3 h. The reaction mixture was poured into a solution of 50 mL of concentrated HCl, 200 mL of ice water, and 300 mL of $CHCl_3$. The organic layer was separated and washed twice with 400 mL of water, dried over $MgSO_4$, and filtered and the solvent was removed on a rotary evaporator. The product was recrystallized from 800 mL of 95% EtOH to yield 46 g (72%) of white crystals. Purity (HPLC): 96%. Mp: 140–141 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.86 (s, 3H, CH_3O-), 4.18 (s, 2H, $-CH_2CO-$), 6.93 (d, 2H, ortho to the methoxy of the substituted phenyl ring, J = 10.0 Hz), 7.12 (d, 2H, meta to the bromo of the substituted phenyl ring, J = 8.0 Hz), 7.43 (d, 2H, ortho to the bromo of the substituted phenyl ring, J = 8.0 Hz), 7.97 (d, 2H, meta to the methoxy of the substituted phenyl ring, J = 10.0 Hz).

Synthesis of 13-Hydroxy-1-(4-methoxyphenyl)-2-(4-bromophenyl)tridecanone (15). 15 was prepared by the alkylation of 14 with 11. 14 (26.3 g, 0.086 mol), 11 (27 g, 0.91 mol), TBAH (1.46 g, 0.0043 mol), and 250 mL of THF were mixed in a 1000-mL one-neck flask. Then 50% NaOH (132 mL) was added dropwise. After addition, the reaction mixture was stirred for 12 h, after which time NMR analysis indicated complete conversion. The aqueous layer was extracted once with $CHCl_3$. The organic extract was washed once with dilute HCl and twice with water and dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. The product was purified by column chromatography (hexane/Et_2O gradient, from 10/1 to 1/1) to yield 43.6 g (97.6%) of a light yellow transparent liquid. Purity (HPLC): 95%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.23 (m, 14H, $-CH_2CH_2(CH_2)_7CH_2CH_2-$), 1.55 (m, 2H, $-CH_2CH_2OH$), 1.75 (m, 2H, $-CHCH_2CH_2-$), 2.10 (m, 2H, $-CHCH_2-$), 3.64 (t, 2H, $-CH_2-$OH, J = 6.0 Hz), 3.84 (s, 3H, $-OCH_3$), 4.46 (t, 1H, $-CHCO-$, J = 8.0 Hz), 6.89 (d, 2H, ortho to the methoxy of the substituted phenyl ring, J = 8.0 Hz), 7.19 (d, 2H, meta to the bromo of the substituted phenyl ring, J = 8.0 Hz), 7.41 (d, 2H, ortho to the bromo of the substituted phenyl ring, J = 8.0 Hz), 7.94 (d, 2H, meta to the methoxy of the substituted phenyl ring, J = 8.0 Hz).

Synthesis of 2-Bromo-6-methoxynaphthalene (17). 17 was prepared by the methylation of 2-bromo-6-naphthol (16). 16 (30 g, 0.14 mol), NaOH (6.6 g, 0.17 mol), and 90 mL of water were combined in a 500-mL three-neck flask equipped with a dropping funnel and stirred for 30 min to generate the sodium phenolate. $(CH_3)_2SO_4$ (26 mL, 0.16 mol) was added dropwise to the red solution at 70 °C, after which time it was stirred for 3 h. The reaction mixture was extracted with 500 mL of $CHCl_3$, washed two times with 30 mL of dilute HCl and three times with 60 mL of water, dried over $MgSO_4$, and filtered, and the solvent was evaporated to yield 31.3 g (90.8%) of a light brown solid. Purity (HPLC): 87.95%. Mp: 122–125 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.90 (s, 3H, CH_3O-), 7.07 (s, 1H, ortho to the methoxy of the substituted naphthalene), 7.14 (d, 1H, meta to the methoxy of the substituted naphthalene, J = 10.0 Hz), 7.47 (d, 1H, ortho to the methoxy of the substituted naphthalene, J = 10.0 Hz), 7.54 (d, 1H, ortho to the bromo of the substituted naphthalene, J = 8.0 Hz), 7.62 (d, 1H, meta to the bromo of the substituted naphthalene, J = 8.0 Hz), 7.88 (s, 1H, ortho to the bromo of the substituted naphthalene).

Synthesis of 6-Methoxynaphthalene-2-boronic Acid (18). 18 was prepared by a general method used for the synthesis of arylboronic acids.[18] 17 (26 g, 0.11 mol) was dissolved in 270 mL of anhydrous THF in a 500-mL three-neck flask equipped with a dropping funnel, thermometer, and nitrogen inlet–outlet. The solution was cooled to −78 °C with a dry ice–acetone bath. *n*-BuLi (1.6 M in hexanes, 90 mL, 0.14 mol) was added to the stirring mixture dropwise, maintaining the temperature below −65 °C. $B(OCH_3)_3$ (28 mL, 0.25 mol) in 50 mL of anhydrous THF was added dropwise, maintaining the temperature below −65 °C. The reaction mixture was subsequently warmed to room temperature and stirred overnight. Dilute HCl (10%, 100 mL) was added dropwise, and the mixture was stirred for 1 h. The solution was extracted two times with Et_2O, washed with water, dried over $MgSO_4$, and filtered, and the solvent was evaporated to yield a

light brown solid. The brown powder was dissolved in THF, precipitated in hexanes, and filtered to yield 23 g (98%) of a light brown powder which was used in the next step without further purification. Mp: 211–216 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.89 (s, 3H, CH_3O–), 4.80 (s, 2H, HO–), 7.11 (d, 1H, ortho to the methoxy of the substituted naphthalene, J = 8.8 Hz), 7.20 (s, 1H, ortho to the methoxy of the substituted naphthalene), 7.86 (d, 1H, meta to the methoxy of the substituted naphthalene, J = 8.8 Hz), 7.97 (d, 1H, meta to the boronic acid of the substituted naphthalene, J = 8.0 Hz), 8.26 (d, 1H, ortho to the boronic acid of the substituted naphthalene, J = 8.0 Hz), 8.75 (s, 1H, ortho to the boronic acid of the substitued naphthalene).

Synthesis of 13-Hydroxy-1-(4-methoxyphenyl)-2-[4-(6-methoxy-2-naphthalenylyl)phenyl]tridecanone (19). 19 was prepared by a Pd(0)-catalyzed cross-coupling reaction of aryl bromide 15 with aryl boronic acid 18.[19] 15 (10 g, 0.049 mol), $Pd(PPh_3)_4$ (1.57 g, 0.001 mol), 2 N $NaCO_3$ (85 mL), and 105 mL of toluene were added to a 250-mL three-neck flask under a nitrogen atmosphere. 18 (8.38 g, 0.037 mol) dissolved in EtOH (73 mL, 95%) was added dropwise at 100 °C. After addition, the reaction mixture was stirred at 100 °C for 8 h. The reaction mixture was cooled to room temperature and diluted with chloroform and water to separate the two phases. The organic layer was separated, dried over $MgSO_4$, and filtered, and the solvent was distilled in a rotary evaporator. The resulting product was purified by column chromatography (silica gel, CH_2Cl_2/hexane gradient) to yield 15.5 g (63%) of a deep brown liquid. Purity (HPLC): 98.7%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.24 (m, 14H, $-(CH_2)_7CH_2CH_2OH$), 1.54 (m, 2H, $-CH_2CH_2OH$), 1.66 (s, 1H, –OH), 1.88 (m, 2H, $-CH_2(CH_2)_9OH$), 2.18 (m, 2H, $-CH_2(CH_2)_{10}OH$), 3.62 (t, 2H, $-CH_2OH$, J = 6.0 Hz), 3.82 (s, 3H, CH_3O–monophenyl), 3.92 (s, 3H, CH_3O–naphthalene biphenyl), 4.56 (t, 1H, –CHCO–, J = 7.0 Hz), 6.90 (d, 2H, ortho to the methoxy of the monophenyl ring J = 8.0 Hz), 7.16 (d, 1H, ortho to the phenyl of the naphthalene ring, J = 8.0 Hz), 7.16 (d, 1H, ortho to the methoxy of the naphthalene ring, J = 8.0 Hz), 7.41 (d, 2H, ortho to the methane of the phenyl ring, J = 8.0 Hz), 7.62 (d, 2H, meta to the methane of the phenyl ring, J = 8.0 Hz), 7.68 (s, 1H, ortho to the methoxy of the naphthalene ring), 7.78 (d, 1H, meta to the phenyl of the naphthalene ring, J = 8.0 Hz), 7.78 (d, 1H, meta to the methoxy of the naphthalene ring, J = 8.0 Hz), 7.92 (s, 1H, ortho to the phenyl of the naphthalene ring), 8.01 (d, 2H, meta to the methoxy of the monophenyl ring, J = 8.0 Hz).

Synthesis of 13-Hydroxy-1-(4-methoxyphenyl)-2-[4-(6-methoxy-2-naphthalenylyl)phenyl]tridecane (20). 20 was prepared by the reduction of 19 with a $LiAlH_4/AlCl_3{\cdot}Et_2O$ complex.[20] $AlCl_3$ (17 g, 0.12 mol) was placed in a 100-mL three-neck flask equipped with a dropping funnel and a nitrogen inlet–outlet. The mixture was cooled in an ice–water bath to 0 °C, after which time 60 mL of anhydrous Et_2O was added dropwise. $LiAlH_4$ (1.834 g, 0.056 mol) was placed in a 250-mL three-neck flask equipped with a nitrogen inlet–outlet and cooled in an ice–water bath. To the flask containing $LiAlH_4$ was added successively 60 mL of anhydrous Et_2O, 60 mL of a $AlCl_3{\cdot}Et_2O$ solution in Et_2O, 60 mL of anhydrous $CHCl_3$, and 19 (12 g, 0.02 mol) dissolved in 60 mL of anhydrous $CHCl_3$ at 0 °C. The reaction mixture was stirred at room temperature for 10 h. Dilute HCl (220 mL, 25%) was added dropwise with stirring to decompose the $LiAlH_4/AlCl_3{\cdot}Et_2O$ complex. The product was extracted with 200 mL of $CHCl_3$, washed with 100 mL of 5% $NaHCO_3$ and 200 mL of water, dried over $MgSO_4$, and filtered, and the solvent was evaporated. After purification by column chromatography (silica gel, CH_2Cl_2), 10.5 g (81.6%) of a yellow solid was obtained. Purity (HPLC): 99.5%. Mp: 62–64 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.20 (m, 16H, $-(CH_2)_8CH_2CH_2OH$), 1.53 (m, 2H, $-CH_2CH_2OH$), 1.65 (m, 2H, $-CH_2(CH_2)_{10}OH$), 2.69–2.84 (m, 3H, $-CHCH_2$–monophenyl), 3.60 (t, 2H, $-CH_2OH$, J = 7.0 Hz), 3.75 (s, 3H, CH_3O–monophenyl), 3.92 (s, 3H, CH_3O–naphthalene phenyl), 6.81 (d, 2H, ortho to the methoxy of the monophenyl ring, J = 8.0 Hz), 6.97 (d, 2H, meta to the methoxy of the monophenyl ring, J = 8.0 Hz), 7.16 (d, 2H, ortho to the methane of the phenyl ring, J = 8.0 Hz), 7.16 (d, 1H, ortho to the phenyl of the naphthalene ring, J = 8.0 Hz), 7.16 (d, 1H, ortho to the methoxy of the naphthalene ring, J = 8.0 Hz), 7.21 (s, 1H, ortho to the methoxy of the naphthalene ring), 7.60 (d, 2H, meta to the methine of the phenyl ring, J = 8.0 Hz), 7.77 (d, 1H, meta to the methoxy of the naphthalene ring, J = 8.0 Hz), 7.77 (d, 1H, meta to the phenyl of the naphthalene ring, J = 8.0 Hz), 7.97 (s, 1H, ortho to the phenyl of the naphthalene ring).

Synthesis of 13-Bromo-1-(4-methoxyphenyl)-2-[4-(6-methoxy-2-naphthalenylyl)phenyl]tridecane (21). 21 was prepared by the bromination of 20 with CBr_4/PPh_3.[21] To a 250-mL three-neck flask equipped with an addition funnel and a nitrogen inlet–outlet were added 20 (10 g, 0.0185 mol), CBr_4 (8.7 g, 0.026 mol), and 50 mL of anhydrous THF. PPh_3 (6.88 g, 0.026 mol) dissolved in 50 mL of anhydrous THF was added dropwise at 0–5 °C. After the addition, the reaction mixture was stirred for 6 h, after which time it was filtered and the solvent was distilled in a rotary evaporator. Purification by column chromatography (silica gel, CH_2Cl_2:hexanes = 1:1) yielded 10 g (98%) of a light yellow solid. Purity (HPLC): 99.5%. Mp: 67–69 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.20 (m, 16H, $-(CH_2)_8CH_2CH_2Br$), 1.66 (m, 2H, $-CH_2(CH_2)_{10}Br$), 1.82 (m, 2H, $-CH_2CH_2Br$), 2.73–2.84 (m, 3H, $-CHCH_2$–monophenyl), 3.38 (t, 2H, $-CH_2Br$, J = 7.0 Hz), 3.76 (s, 3H, CH_3O–monophenyl), 3.93 (s, 3H, CH_3O–naphthalene phenyl), 6.76 (d, 2H, ortho to the methoxy of the monophenyl ring, J = 8.0 Hz), 6.98 (d, 2H, meta to the methoxy of the monophenyl ring, J = 8.0 Hz), 7.17 (d, 2H, ortho to the methine of the phenyl ring, J = 8.0 Hz), 7.17 (d, 1H, ortho to the phenyl of the naphthalene ring, J = 8.0 Hz), 7.17 (d, 1H, ortho to the methoxy of the naphthalene ring, J = 8.0 Hz), 7.21 (s, 1H, ortho to the methoxy of the naphthalene ring), 7.62 (d, 2H, meta to the methine of the phenyl ring, J = 8.0 Hz), 7.76 (d, 1H, meta to the methoxy of the naphthalene ring, J = 8.0 Hz), 7.76 (d, 1H, meta to the phenyl of the naphthalene ring, J = 8.0 Hz), 7.97 (s, 1H, ortho to the phenyl of the naphthalene ring).

Synthesis of 13-Bromo-1-(4-hydroxyphenyl)-2-[4-(6-hydroxy-2-naphthalenylyl)phenyl]tridecane (22). 22 was prepared by the demethylation of 21 with BBr_3.[22] To 40 mL of anhydrous CH_2Cl_2 cooled to −78 °C in a 500-mL three-neck flask equipped with a dropping funnel and a nitrogen inlet–outlet was added dropwise BBr_3 (solution 1.0 M in CH_2Cl_2, 50 mL, 0.049 mol) followed by 21 (9.07 g, 0.016 mol) dissolved in 80 mL of anhydrous CH_2Cl_2. The reaction mixture was stirred for 10 h at room temperature, after which time 51 mL of H_2O was added dropwise. Et_2O (300 mL) was added, the organic layer was separated, washed with 100 mL of water, dried over $MgSO_4$, and filtered, and the solvent was evaporated. The product was purified by column chromatography (silica gel, CH_2Cl_2) to yield 4.5 g (52%) of light pink crystals. Purity (HPLC): 99.5%. Mp: 67–69 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.20 (m, 16H, $-(CH_2)_8CH_2CH_2Br$), 1.60 (m, 2H $-CH_2(CH_2)_{10}Br$), 1.82 (m, 2H, $-CH_2CH_2Br$), 2.83 (m, 3H, $-CHCH_2$–monophenyl), 3.39 (t, 2H, $-CH_2Br$, 4J = 7.0 Hz), 4.58 (s, 1H, HO–monophenyl), 5.01 (s, 1H, HO–naphthalene biphenyl), 6.69 (d, 2H, ortho to the hydroxy of the monophenyl ring, J = 8.0 Hz), 6.93 (d, 2H, meta to the hydroxy of the monophenyl ring, J = 8.0 Hz), 7.17 (d, 2H, ortho to the methine of the phenyl ring, J = 8.0 Hz), 7.17 (d, 1H, ortho to the phenyl of the naphthalene ring, J = 8.0 Hz), 7.17 (d, 1H, meta to the methoxy of the naphthalene ring, J = 8.0 Hz), 7.21 (s, 1H, ortho to the methoxy of the naphthalene ring), 7.60 (d, 2H, meta to the methine of the phenyl ring, J = 8.0 Hz), 7.77 (d, 1H, meta to the hydroxy of the naphthalene ring, J = 8.0 Hz), 7.77 (d, 1H, meta to the phenyl of the naphthalene ring, J = 8.0 Hz), 7.97 (s, 1H, ortho to the phenyl of the naphthalene ring).

Synthesis of 4-Acetoxybiphenyl (23). 23 was prepared from 1 (80 g, 0.47 mol) and acetic anhydride (67 mL, 0.70 mol) according to a literature procedure.[10d] The product was recrystallized from 95% EtOH to yield 95 g (89%) of white crystals. Purity (HPLC): 99.5%. Mp: 86–88 °C (lit.[23] mp 86–87 °C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.32 (s, 3H, CH_3–), 7.16 (d, 2H, ortho to the acetoxy of the substituted phenyl ring, J – 8.0 Hz), 7.44 (m, 3H, meta and para of the unsubstituted phenyl ring), 7.56 (d, 2H, meta to the acetoxy of the unsubstituted phenyl ring, J = 8.0 Hz), 7.59 (d, 2H, ortho of the unsubstituted phenyl ring, J = 8.0 Hz).

Synthesis of 4-Acetoxy-4'-bromobiphenyl (24). 24 was prepared by the bromination of 23 (50 g, 0.24 mol) with Br_2 (18 mL, 0.33 mol) and anhydrous Na_2CO_3 (75 g, 0.71 mol) in 180 mL of anhydrous $ClCH_2CH_2Cl$. The synthesis and purification of 24 was described previously.[24] The product was recrystallized from 200 mL of toluene to yield 75 g (60.7%) of white crystals. Purity

(HPLC): 99.5%. Mp: 129–131 °C (lit.[23] mp 128–130 °C). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.32 (s, 3H, CH_3–), 7.16 (d, 2H, ortho to the acetoxy of the substituted phenyl ring, J = 8.7 Hz), 7.42 (d, 2H, ortho to the bromine of the substituted phenyl ring, J = 8.0 Hz), 7.56 (d, 2H, meta to the bromine of the substituted phenyl ring, J = 8.0 Hz), 7.57 (d, 2H, meta to the acetoxy of the substituted phenyl ring, J = 8.7 Hz).

Synthesis of 4-Bromo-4′-methoxybiphenyl (25). **25** was prepared by the hydrolysis and subsequent methylation of **24**. **24** (40 g, 0.14 mol) was hydrolyzed by refluxing with 250 mL of EtOH and NaOH (12.4 g, 0.31 mol) for 3 h. EtOH was distilled, and 150 mL of water was added to dissolve the sodium salt of 4-hydroxy-4′-bromobiphenyl. $(CH_3)_2SO_4$ (43 g, 0.34 mol) was added dropwise at 70 °C, and the reaction mixture was stirred overnight. Then it was cooled to room temperature, and the precipitated product was filtered, washed once with dilute HCl and twice with water, and recrystallized from 95% EtOH to yield 25.8 g (70.5%) of white crystals. Purity (HPLC): 99.5%. Mp: 144–145 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.83 (s, 3H, CH_3O–) 6.96 (d, 2H, ortho to the methoxy of the substituted phenyl ring, J = 8.0 Hz), 7.39 (d, 2H, meta to the methoxy of the substituted phenyl ring, J = 8.0 Hz), 7.43 (d, 2H, ortho to the bromine of the substituted phenyl ring, J = 10.0 Hz), 7.52 (d, 2H, ortho to the bromine of the substituted phenyl ring, J = 10.0 Hz).

Synthesis of 4-Methoxy-4′-biphenylboronic Acid (26). **26** was synthesized according to the general procedure described for the preparation of **18** starting from **25** (20 g, 0.076 mol) with n-BuLi (2.5 M in hexanes, 37 mL, 0.091 mol) and trimethyl borate (19 mL, 0.17 mol) in 220 mL of anhydrous THF.[18] After filtration, 15 g (90%) of a white powder was obtained and used in the next reaction step without further purification. Mp: 175–183 °C; ^{1}H-NMR (acetone-d_6, TMS, δ, ppm): 3.85 (s, 3H, CH_3O–), 5.81 (s, 2H, HO–), 7.02 (d, 2H, ortho to the methoxy of the substituted phenyl ring, J = 8.3 Hz), 7.61 (d, 2H, meta to the methoxy of the substituted phenyl ring, J = 8.3 Hz), 7.63 (d, 2H, meta to the boronic acid of the substituted phenyl ring, J = 9.3 Hz), 7.95 (d, 2H, ortho to the boronic acid of the substituted phenyl ring, J = 9.3 Hz).

Synthesis of 13-Hydroxy-1-(4-methoxyphenyl)-2-(4-methoxy-4″-*p*-terphenylyl)tridecanone (27). **27** was prepared by the Pd(0)-catalyzed (1.16 g, 0.001 mol) cross-coupling of **15** (15.9 g, 0.033 mol) with **26** (8.4 g, 0.04 mol) in 2N Na_2CO_3 (57 mL, 0.2 mol), 75 mL of toluene, and 53 mL of EtOH.[19] A method similar to the general one described for the preparation of **19** was used. After purification by column chromatography (silica gel, CH_2Cl_2/hexanes gradient), 14.4 g (74.5%) of yellow solid was obtained. Purity (HPLC): 99.5%. Mp: 72–74 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.24 (m, 14H, $-(CH_2)_7CH_2CH_2OH$), 1.54 (m, 2H, $-CH_2CH_2OH$), 1.63 (s, 1H, $-OH$), 1.85 (m, 2H, $-CH_2(CH_2)_9OH$), 2.19 (m, 2H, $-CH_2(CH_2)_{10}OH$), 3.63 (t, 2H, $-CH_2OH$, J = 7.0 Hz), 3.82 (s, 3H, CH_3O–monophenyl), 3.85 (s, 3H, CH_3O–terphenyl, 2s), 4.55 (t, 1H, $-CH-$, J = 8.0 Hz), 6.89 (d, 2H, ortho to the methoxy of the monophenyl ring, J = 9.0 Hz), 6.98 (d, 2H, ortho to the methoxy of the terphenyl ring, J = 8.0 Hz), 7.39 (d, 2H, ortho to the methine of the terphenyl ring, J = 8.0 Hz), 7.56 (d, 2H, meta to the methoxy of the terphenyl ring, J = 8.0 Hz), 7.56 (d, 2H, meta to the methine of the terphenyl ring, J = 8.0 Hz), 7.60 (s, 4H, second phenyl of the terphenyl ring), 8.01 (d, 2H, ortho to the carbonyl of the monophenyl ring, J = 9.0 Hz).

Synthesis of 13-Hydroxy-1-(4-methoxyphenyl)-2-(4-methoxy-4″-*p*-terphenylyl)tridecane (28). **28** was prepared by the reduction of **27** (12 g, 0.021 mol) with $LiAlH_4$ (1.83 g, 0.056 mol) and $AlCl_3$ (16.1 g, 0.12 mol) in 120 mL of anhydrous Et_2O and 120 mL of anhydrous $CHCl_3$. The general procedure described for the synthesis of **20** was used. After purification by column chromatography (silica gel, $CHCl_2$) and subsequent recrystallization from 95% EtOH, 9.6 g (82%) of white needlelike crystals was obtained. Purity (HPLC): 99.5%. Mp: 117–119 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.19 (m, 16H, $-(CH_2)_8CH_2CH_2OH$), 1.51–1.64 (m, 2H, $-CH_2CH_2OH$), 1.51–1.64 (m, 2H, $-CH_2CHCH_2$–monophenyl), 2.73–2.83 (m, 3H, $-CHCH_2$–monophenyl), 2.73–2.83 (s, 1H, $-OH$), 3.61 (t, 2H, $-CH_2OH$, J = 7.0 Hz), 3.74 (s, 3H, CH_3O–monophenyl), 3.84 (s, 3H, CH_3O–terphenyl), 6.74 (2H, d, ortho to the methoxy of the monophenyl ring, J = 9.0 Hz), 6.95 (d, 2H, ortho to the methoxy of the terphenyl ring, J = 8.0 Hz), 6.99 (d, 2H, meta to the methoxy of the monophenyl ring, J = 9.0 Hz), 7.16 (d, 2H, ortho to the methine of the terphenyl ring, J = 8.0 Hz), 7.53 (d, 2H, meta to the methoxy of the terphenyl ring, J = 8.0 Hz), 7.57 (d, 2H, meta to the methine of the terphenyl ring, J = 8.0 Hz), 7.62 (s, 4H, second phenyl of the terphenyl ring).

Synthesis of 13-Bromo-1-(4-methoxyphenyl)-2-(4-methoxy-4″-*p*-terphenylyl)tridecane (29). **29** was prepared by the bromination of **28** (8.5 g, 0.015 mol) with CBr_4 (7.08 g, 0.02 mol) and PPh_3 (5.6 g, 0.02 mol) in 50 mL of anhydrous THF according to the general method described for the synthesis of **21**.[21] After purification by column chromatography (silica gel, CH_2Cl_2), the resulting **29** was recrystallized from 95% EtOH to yield 9.0 g (95%) of white crystals. Purity (HPLC): 99.5%. Mp: 110–111 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.20 (m, 16H, $-(CH_2)_8CH_2CH_2Br$), 1.69 (m, 2H, $-CH_2(CH_2)_{10}Br$), 1.83 (m, 2H, $-CH_2CH_2Br$), 2.76–2.83 (m, 3H, $-CHCH_2$–monophenyl), 3.40 (t, 2H, $-CH_2Br$, J = 6.0 Hz), 3.77 (s, 3H, CH_3O–monophenyl), 3.87 (s, 3H, CH_3O–terphenyl), 6.76 (d, 2H, ortho to the methoxy of the monophenyl ring, J = 8.0 Hz), 6.97 (d, 2H, ortho to the methoxy of the terphenyl ring, J = 8.0 Hz), 7.01 (d, 2H, meta to the methoxy of the terphenyl ring, J = 8.0 Hz), 7.18 (d, 2H, meta to the methine of the terphenyl ring, J = 8.0 Hz), 7.55 (d, 2H, meta to the methoxy of the terphenyl ring, J = 8.0 Hz), 7.59 (d, 2H, meta to the methine of the terphenyl ring, J = 8.0 Hz), 7.65 (s, 4H, second phenyl of the terphenyl ring).

Synthesis of 13-Bromo-1-(4-hydroxyphenyl)-2-(4-hydroxy-4″-*p*-terphenylyl)tridecane (30). **30** was prepared by the demethylation of **29** (7.45 g, 0.012 mol) with BBr_3 (35 mL, 0.03 mol) in 35 mL of anhydrous CH_2Cl_2 according to the general procedure described for the synthesis of **22**. After purification by column chromatography (silica gel, CH_2Cl_2 solvent), **30** was recrystallized from toluene/hexanes to yield 6.5 g (97.29%) of white crystals. Purity (HPLC): 99.5%. Mp: 146–147 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.20 (m, 16H, $-(CH_2)_8CH_2CH_2Br$), 1.61 (m, 2H, $-CH_2(CH_2)_{10}Br$), 1.83 (m, 2H, $-CH_2CH_2Br$), 2.76–2.83 (m, 3H, $-CHCH_2$–monophenyl), 3.39 (t, 2H, $-CH_2Br$, J = 8.0 Hz), 4.58 (s, 1H, HO–monophenyl), 4.85 (s, 1H, HO–terphenyl), 6.68 (d, 2H, ortho to the hydroxy of the monophenyl ring, J = 8.0 Hz), 6.92 (d, 2H, ortho to the hydroxy of the terphenyl ring, J = 8.0 Hz), 6.93 (d, 2H, ortho to the methylene of the monophenyl ring, J = 8.0 Hz), 7.17 (d, 2H, ortho to the methine of the terphenyl ring, J = 8.0 Hz), 7.53 (d, 2H, meta to the hydroxy of the terphenyl ring, J = 8.0 Hz), 7.53 (d, 2H, meta to the methine of the terphenyl ring, J = 8.0 Hz), 7.63 (d, 4H, second phenyl of the terphenyl ring, J = 4.0 Hz).

Synthesis of Hyperbranched Polyethers. Scheme 4 outlines the synthesis of the hyperbranched polyethers. Conventional liquid–liquid two-phase (organic solvent–aqueous NaOH solution) phase-transfer-catalyzed polyetherification conditions were used for the polymerization of the AB_2 monomers **8**, **22**, and **30**.[8a] These polyetherifications were performed under a N_2 atmosphere at 80 °C in an o-dichlorobenzene–10 N NaOH two-phase system (10 times molar excess of NaOH versus phenol groups) in the presence of various amounts of TBAH as a phase-transfer catalyst followed by the alkylation of free phenolate chain ends with an alkyl bromide or with benzyl chloride. An example of the polyetherification is as follows.

To a 25-mL one-neck flask equipped with a condenser and a N_2 inlet–outlet were successively added **30** (0.1499 g, 0.25 mmol), 10 N NaOH (0.5 mL, 5 mmol), o-dichlorobenzene (0.5 mL), and TBAH (0.1698 g, 0.50 mmol, 100 mol % of phenol groups). The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80 °C under N_2 for 30 min. 1-Bromooctane (0.0531 g, 0.275 mmol) in o-dichlorobenzene (0.5 mL) was added to the reaction mixture which was stirred for an additional 30 min at 80 °C under N_2. The reaction mixture was diluted with $CHCl_3$ and water, and the organic layer was washed once with water, once with dilute HCl, and three times with water. The polymer solution was precipitated into MeOH to yield 0.134 g (79.9%) of a fine white polymer powder. The polymer was further purified by precipitation from a $CHCl_3$ solution into acetone, followed by two precipitations from a THF solution into water.

Synthesis of TPT-b-All and Separation of the TPT-b-(c)-All. To a 25-mL one-neck flask equipped with a condenser and a N_2 inlet–outlet were successively added **30** (0.3598 g, 0.6 mmol), 10 N NaOH (1.2 mL, 12 mmol), o-dichlorobenzene (1.2

mL), and TBAH (0.4075 g, 1.2 mmol, 100 mol % of phenol groups). The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80 °C under N_2 for 45 min. Allyl chloride (0.0918 g, 1.2 mmol) in *o*-dichlorobenzene (1.2 mL) was added to the reaction mixture which was stirred for an additional 45 min at 80 °C under N_2. The reaction mixture was diluted with $CHCl_3$ and water, and the organic layer was washed once with water, once with dilute HCl, and three times with water. The polymer solution was precipitated into MeOH to yield 0.2930 g (81.40%) of a fine white polymer powder. GPC analyses showed the presence of an oligomer and of the hyperbranched polymer. The polymer was separated by precipitation from a $CHCl_3$ solution into acetone twice followed by two precipitation from a THF solution into water to yield 0.2004 g (55.67%). At this time, GPC showed no oligomer residue in the hyperbranched TPT-b-All. This TPT-b-All polymer was used to calculate the degree of branching by ^{1}H-NMR spectroscopy. The acetone of the acetone solution was distilled, and the GPC and TLC showed that it contained several oligomers. The lowest molecular weight oligomer was separated by column chromatography (silica gel, CH_2Cl_2:hexanes = 1:1.5 as eluent) to yield 0.0156 g (4.65%) of monodisperse product. Its characterization by ^{1}H-NMR spectroscopy demonstrated that this product is obtained by intramolecular self-etherification of TPT-b followed by etherification with allyl chloride. Its structure (TPT-b(c)-All) will be discussed in detail in the Results and Discussion section.

Techniques. ^{1}H-NMR (200 MHz) spectra were recorded on Varian XL-200 and Gemini spectrometers with TMS as the internal standard and $CDCl_3$ or acetone-d_6 as the solvent. The purity of the products was determined by a combination of thin layer chromatography (TLC) on silica gel plates (Kodak) with a fluorescent indicator and high-pressure liquid chromatography (HPLC). Relative molecular weights of the hyperbranched polyethers were determined by gel permeation chromatography (GPC). HPLC and GPC analyses were accomplished with a Perkin-Elmer Series 10 LC equipped with an LC-100 column oven and a Nelson Analytical 900 Series data station. The measurements were made by using a UV detector, $CHCl_3$ or THF as the solvent (1 mL/min, 40 °C), two PL gel columns of 5×10^2 and 10^4 Å, and a calibration plot constructed with polystyrene standards.

A Perkin-Elmer DSC-7 differential scanning calorimeter was used to measure the thermal transitions. Heating and cooling rates were 20 °C/min in all cases. First-order transitions (crystal–crystal, crystal–liquid crystal, liquid crystal–isotropic, etc.) were read at the maxima and minima of the endothermic and exothermic peaks, respectively. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. All heating and cooling scans after the first heating scan were identical.

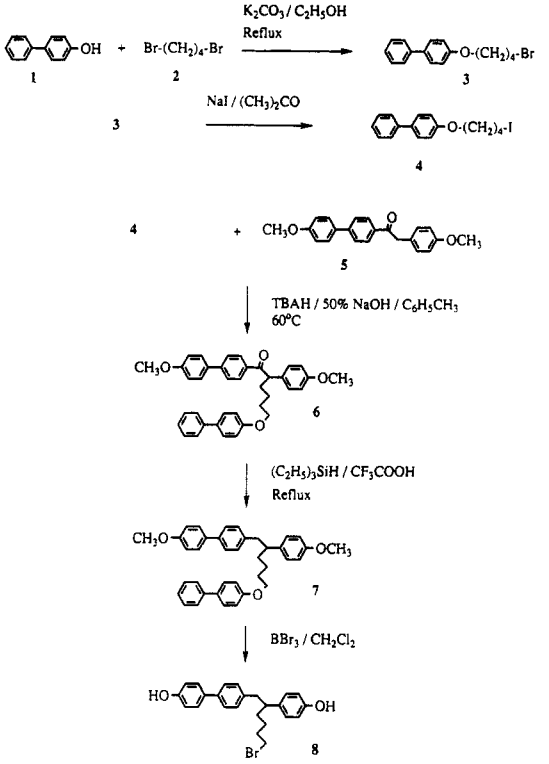
A Carl-Zeiss optical polarized microscope (magnification 100×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to verify the anisotropic textures.

Results and Discussion

Synthesis and Polymerization of AB_2 Monomers. Various examples of dendrimeric and hyperbranched polyethers were reported in the literature. Dendrimeric poly(benzyl ether)s with uniform molecular weight distributions were synthesized by a stepwise convergent[7] approach, while the corresponding hyperbranched polymers with broad molecular weight distributions were prepared by the polyetherification of AB_2 monomers.[25] Dendrimeric aliphatic polyethers were synthesized by a divergent approach.[26] Aromatic hyperbranched polyethers with broad molecular weight distributions were synthesized by the aromatic nucleophilic substitution polyetherification of AB_2 monomers,[27,28] while a stepwise convergent approach was used for the preparation of a poly(ether ketone) dendrimer with uniform molecular weight distribution.[29]

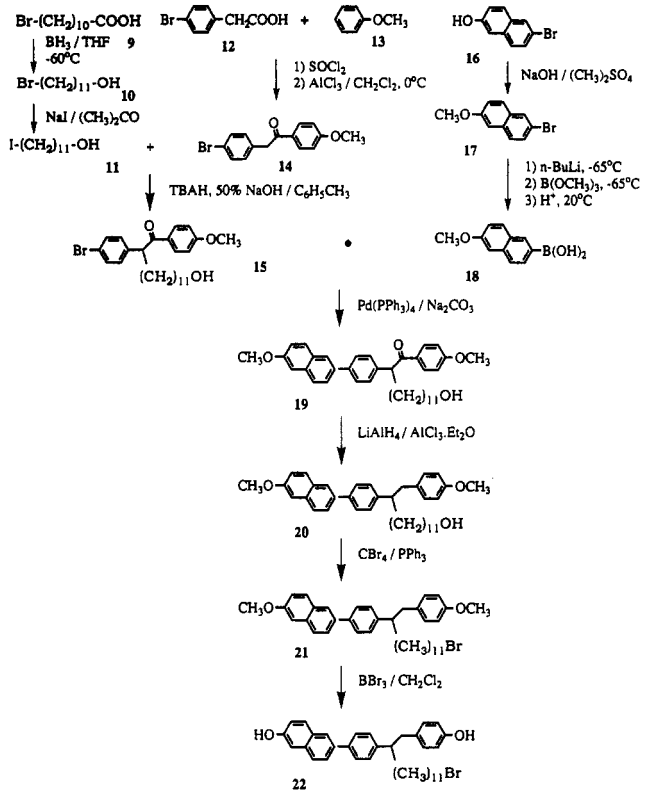
The first examples of thermotropic liquid crystalline hyperbranched polymers with broad molecular weight distributions were obtained from AB_2 monomers via two different synthetic routes which lead to polymers containing either rodlike[8a] or disklike[8b] mesogenic units. The hyperbranched polymer based on rodlike mesogenic units was synthesized by a phase-transfer-catalyzed polyetherification and displays a nematic mesophase over a very narrow range of temperature.[8a] The hyperbranched polymer containing disclike mesogens was prepared via an electrophilic cyclotetramerization reaction which generates the disklike cyclotetraveratrilene units during the polymerzation reaction and exhibits a columnar hexagonal mesophase.[8b]

Scheme 1. *Synthesis* of 6-Bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)hexane (8 or TPH-b)

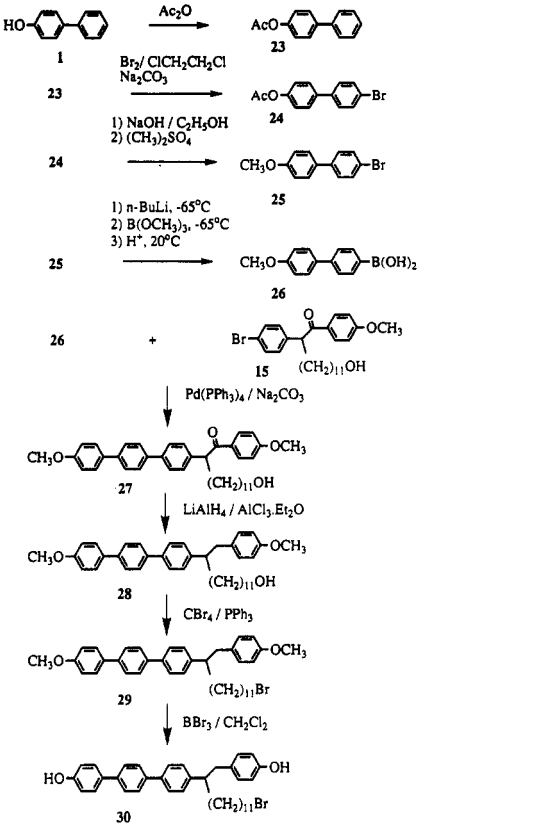


The goal of this paper is to describe the synthesis of three novel AB_2 monomers which are mesogenic units based on conformational isomerism and are suitable for the preparation of hyperbranched polymers containing rodlike mesogenic units. Scheme 1 outlines the synthesis of 6-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)hexane (8). 8 was prepared by a synthetic route related to the one described previously for the synthesis of 10-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)-decane.[8a] We decided to prepare 8 since it has a shorter spacer than the previously reported 10-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane. Model linear polymers with alkyl side groups suggested that a shorter spacer in the AB_2 monomer might increase the isotropization temperature of the nematic mesophase of the previously reported hyperbranched polymer.[8a] The C-alkylation of 1-(4-methoxy-4′-biphenylyl)-2-(4-methoxyphenyl)ethanone (5) was performed with 1-(4-biphenyloxy)-4-iodobutane (4). 5 was synthesized as reported previously.[8a] Direct alkylation of 5 with 4-bromobutan-1-ol did not work, most probably due to its intramolecular etherification to yield tetrahydrofuran. In the alkylation of 5 we used 4 rather than 3 since it is well established that the iodide living group favors C- versus O-alkylation reactions.[30] Compound 6 precipitates from the reaction mixture as a solid together with the corresponding

Scheme 2. Synthesis of 13-Bromo-1-(4-hydroxyphenyl)-2-[4-(6-hydroxy-2-naphthalenylyl)phenyl]tridecane (22 or BPNT-b)



Scheme 3. Synthesis of 13-Bromo-1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-*p*-terphenylyl)tridecane (30 or TPT-b)



O-alkylated product of **5**. The acetal linkage of the O-alkylated product of **5** was cleaved with HCl, and the resulting **5** was easily separated from **6** by washing with methanol followed by recrystallization from toluene. The reduction of the keto group of **6** to **7** was performed with $(C_2H_5)_3SiH$ in CF_3COOH.[14] Dealkylation of **7** with BBr_3 in CH_2Cl_2 leads directly to **8** since in the deprotection step the bromination of the –OH group takes place. The alkylation of **5** with **4** also facilitated the separation of the C- and O-alkylated products. In the synthesis of 10-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane which was reported previously,[8a] we used 8-iodooctan-1-ol in the alkylation step of **5**, and the separation of the C- and O-alkylated products was more difficult than in the present case.

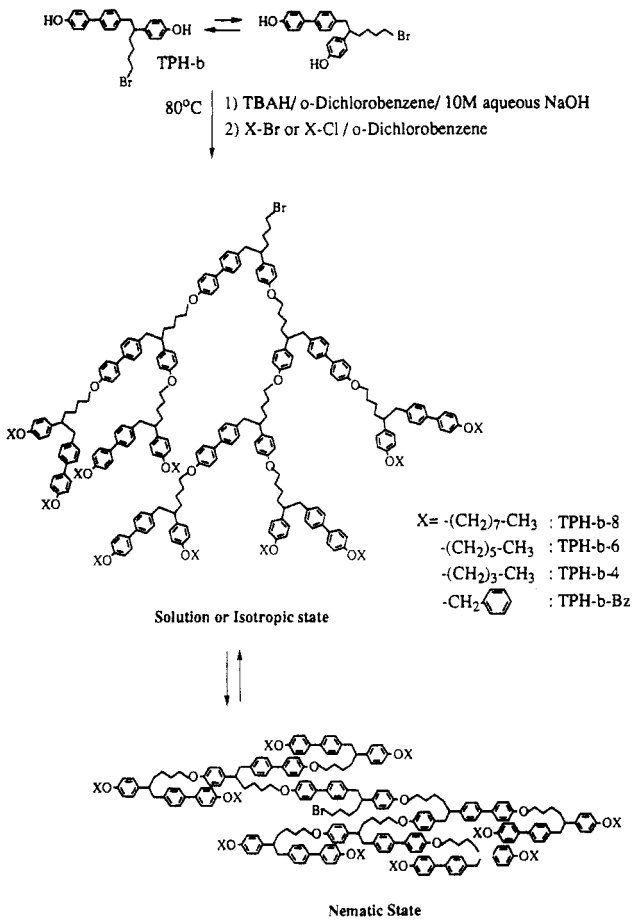
The second approach to the generation of a hyperbranched polymer with a broader mesophase was based on the enlargement of the 4-hydroxy-4′-biphenylyl unit of 10-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane first to 4-(6-hydroxy-2-naphthalenylyl)phenyl and then to 4-hydroxy-4′-*p*-terphenylyl to generate the new monomers 13-bromo-1-(4-hydroxyphenyl)-2-[4-(6-hydroxy-2-naphthalenylyl)phenyl]tridecane (**22**) and 13-bromo-1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-*p*-terphenylyl)-tridecane (**30**). The syntheses of these two monomers are outlined in Schemes 2 and 3. An inspection of the structures of monomers **8**, **22**, and **30** from Schemes 1–3 shows that they have different spacer lengths and hydroxyaryl structural units. At the same time the flexible group of **8** is a constitutional isomer of the flexible group of **22** and **30**. For example, in the case of **8** the 4-hydroxyphenyl group is attached to position 2 of the 1,2-disubstituted 8-bromohexane, while in the case of monomers **22** and **30**, the 4-hydroxyphenyl group is placed in position 1 of the 1,2-disubstituted 13-bromotridecane.

As illustrated in Scheme 2, the most important step in the synthesis of **22** consists of the Pd(0)-catalyzed cross-coupling of 13-hydroxy-1-(4-methoxyphenyl)-2-(4-bromophenyl)tridecanone (**15**) with 6-methoxynaphthalene-2-boronic acid (**18**) by a Suzuki reaction.[19] This reaction tolerates the unprotected alcohol group of **15**. **15** was obtained in high yield by the sequence of reactions consisting of Friedel–Crafts acylation of anisole with (4-bromophenyl)acetic acid to yield 1-(4-methoxyphenyl)-2-(4-bromophenyl)ethanone (**14**) which was C-alkylated with 11-iodoundecan-1-ol. **18** was synthesized from 6-bromo-2-hydroxynaphthalene (**16**) by methylation followed by lithiation with BuLi and subsequent reaction with $B(OCH_3)_3$. **19** was transformed into **22** first by reduction of its keto group with a $LiAlH_4/AlCl_3{\cdot}Et_2O$ complex[20] to yield **20**. The alcohol group of **20** was brominated with CBr_4/PPh_3[21] to yield **21**. **21** was demethylated with BBr_3[22] in CH_2Cl_2 to yield **22**.

The detailed synthesis of **30** is presented in Scheme 3. In this reaction scheme, the main step is the Suzuki cross-coupling of **15** with 4-methoxy-4′-biphenylboronic acid (**26**). **26** was synthesized by the esterification of 4-phenylphenol (**1**) with acetic anhydride followed by bromination, hydrolysis, and methylation to yield 4-bromo-4′-methoxybiphenyl (**25**). **25** was lithiated and subsequently reacted with $B(OCH_3)_3$ to yield **26**. **27** was transformed into **30** by a sequence of reactions similar to that used for the preparation of **22**. All new monomers **8**, **22**, and **30** were obtained with purities higher than 99%.

Monomers **8**, **22**, and **30** were polyetherified by using conventional liquid–liquid two-phase conditions (*o*-dichlorobenzene as organic solvent–10 N NaOH aqueous solution) in the presence of 100 mol % of TBAH (versus the initial phenol groups) as phase-transfer catalyst at 80 °C under a N_2 atmosphere, followed by the in situ alkylation of the phenolate chain ends of the hyperbranched polymer with an alkyl bromide, benzyl chloride, or allyl chloride. Schemes 4 and 5 outline the polymerization reactions and the structures of the resulting

Scheme 4. Synthesis of Hyperbranched Polyethers Based on TPH-b (TPH-b-X) and the Schematic Representation of the Transformation between Their Nematic and Isotropic Phases



hyperbranched polymers. All polymers are soluble in *o*-dichlorobenzene as long as their phenolate chain ends are paired with tetrabutylammonium counterions. The polymers containing free phenol or alkali-metal phenolate chain ends are insoluble in organic solvents. However, the polymers containing phenolate chain ends are soluble in water. Therefore, in order to isolate soluble hyperbranched polymers, their phenolate chain ends were alkylated in situ. The resulting polymers are soluble in a large variety of aromatic and aliphatic halogenated solvents such as *o*-dichlorobenzene, chlorobenzene, chloroform, and methylene chloride and also in THF and aromatic hydrocarbons. The end-capped hyperbranched polymers are labeled with short names which were developed based on the same rules as those used for the similar examples of polymers reported previously.[8a] These notations are summarized in Schemes 4 and 5. In all short names the capital letters refer to the short name of the AB_2 monomer, i.e., TPH-b = 8, BPNT-b = 22, and TPT-b = 30. In the case of polymers, X stands for the group used in the alkylation of their phenol chain ends. When X is a numeral, it represents the number of carbon atoms of the alkyl tail, while X = Bz stands from benzyl and X = All = allyl.

Table 1 summarizes some representative polyetherification results together with the thermal characterization of the resulting hyperbranched polymers. No special efforts were made to optimize the polymerization conditions. However, comparing polyetherification experiments performed under similar conditions, we can observe that the number-average molecular weights of the hyperbranched polyethers are much lower than those of the corresponding linear polyethers.[8a,10] As in the previously reported experiments,[8a] we could hardly detect the $-CH_2Br$ and $-CH_2OH$ polymer chain ends by 200-MHz ^{1}H-NMR spectroscopy. Figures 1 and 2 present representative examples of the NMR spectra of monomer **22** and BPNT-b-8, and monomer **30** and TPT-b-9, respectively. The assignments of all chemical shifts are reported on both figures. Three important observations are obtained from these spectra. The triplet g which is due to the $-CH_2Br$ group of monomers **22** and **30** (Figures 1a and 2a) is completely absent in the resulting hyperbranched polymers (Figures 1b and 2b). The ratios of the signals j to d ($-CH_2OAr$) in both polymers (Figures 1b and 2b) are equal. No $-CH_2Br$, $-CH_2OH$, or $-CH{=}CH_2$ resonances which are expected for the polymer chain ends[8a] are observed. These results suggested that both the phenol and the $-CH_2Br$ chain ends were completely consumed during this polymerization. The phenol chain end is expected to be consumed via the sequence of reactions outlined in Schemes 4 and 5. Nevertheless, the absence of the $-CH_2Br$ chain end can be explained only by an intramolecular alkylation reaction which produced a cyclic structural unit. This cyclic structural unit terminates the polymerization process and, therefore, limits the molecular weight of the hyperbranched polymers prepared by the direct polyetherification of the AB_2 monomers **22** and **30**. This reaction will be demonstrated for the polymerization of **30** in the next section.

Figure 3 presents a representative 20-MHz ^{1}H-NMR spectrum of TPH-b-4 together with its protonic assignments which show the presence of small peaks corresponding to an olefin and a methylenic group attached to a hydroxy group. This spectrum demonstrates that, in the polymerization of **8**, not only intramolecular etherification of the electrophilic chain end but also side reactions such as elimination and hydrolysis of the bromine take place. This is most probably due to the fact the nucleophilic attack of the phenolate anion on the methylenic group is more sterically hindered in monomer **8** than in monomers **22** and **30** due to the shorter spacer length, and, therefore, elimination and displacement by a smaller nucleophile or base such as OH^- are favored. Consequently, the molecular weights of TPH-b-X reported in Table 1 are lower than those of the other hyperbranched polymers due to a combination of side reactions which include intramolecular cyclization, elimination, and displacement of the electrophilic group of monomer **8**.

Structural Characterization of TPT-b-All Hyperbranched Polymers, TPT-b(c)-All, and Degree of Branching. In order to provide a more comprehensive structural characterization of these hyperbranched polyethers and of the side reactions taking place during their preparation, an allyl-terminated TPT-b-X, i.e., TPT-b-All, was synthesized and characterized. It was expected that the allyl chain ends would show different chemical shifts for their $-CH_2CH{=}CH_2$ methylenic units attached to the hydroxyphenylene and hydroxyterphenylene groups and this would provide a quantitative access to the determination both of the side reactions and of the degree of branching. Chart 1 outlines the most representative structural units expected to result from the polyetherification of TPT-b into the hyperbranched TPT-b-All. The structure from the left side of Chart 1 shows examples of dendritic and linear internal units, terminal units containing bromoalkyl and hydroxyalkyl groups, and terminal units with allyl ether groups. The structure on the right side of Chart 1 shows the terminal group obtained via the intramolecular cyclization of the hydroxyphenylene unit of TPT-b with its own bromoalkane group.

Scheme 5. Synthesis of Hyperbranched Polyethers Based on BPNT-b (BPNT-b-8) and TPT-b (TPT-b-8) and the Schematic Representation of the Transformation between Their Nematic and Isotropic Phases

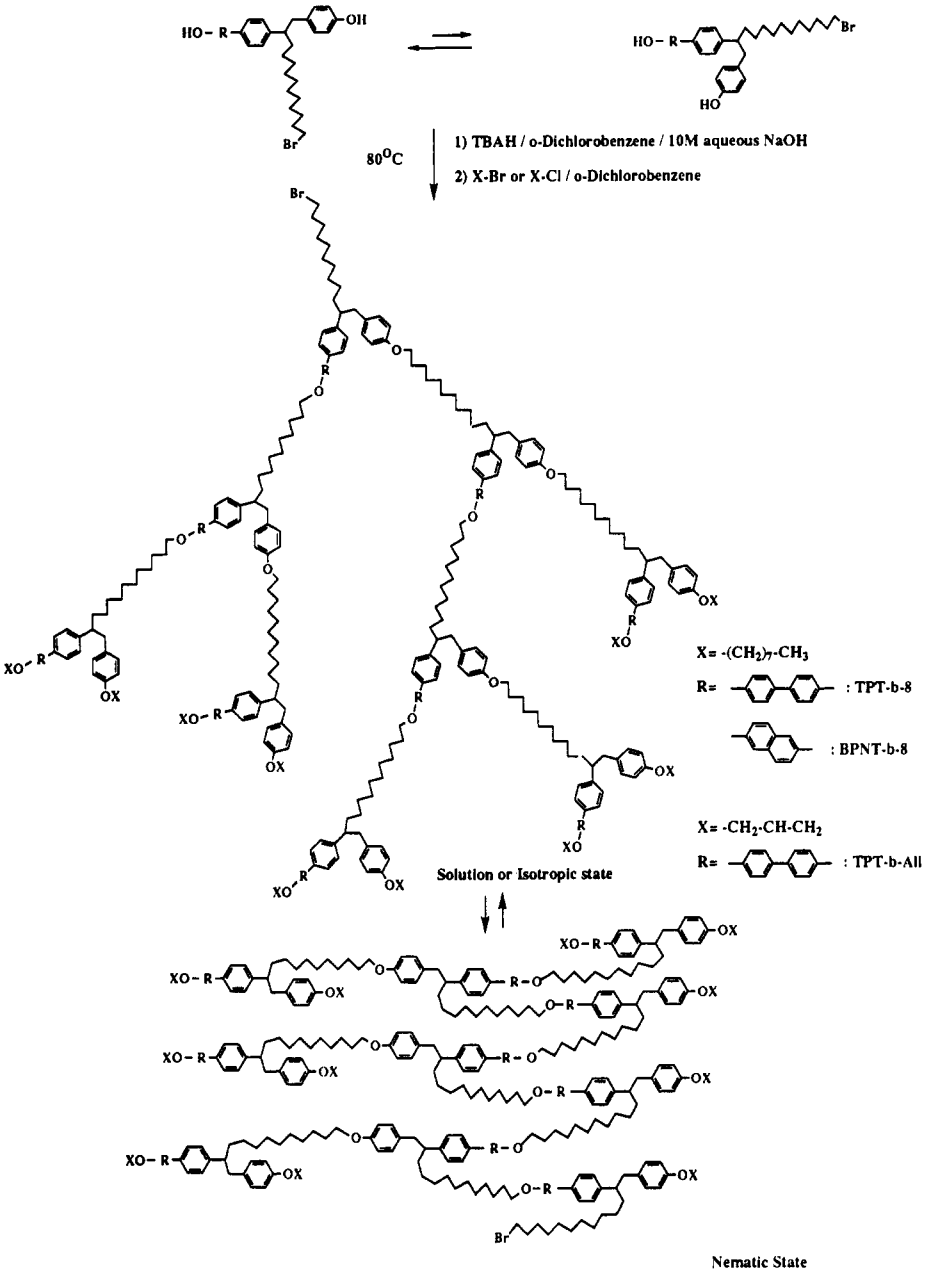


Table 1. Synthesis and Characterization of Hyperbranched Polymers and Comparison of Their Phase Behavior with That of the Linear Model Polyether (TPD-8)[a]

				thermal transitions (°C) and corresponding enthalpy changes (kJ/mru, in parentheses)	
polymer	yield (%)	M_n (GPC)	M_w/M_n (GPC)	heating	cooling
TPD-b-8[b]	80.0	7900	2.60	g 19 n 37 (2.41) i	i 25 (-2.17) n 10 g
TPH-b-Bz[c]	94.1	2520	1.69	g 47 i	i 39 g
TPH-b-4	71.9	3140	1.51	g 42 n 48 (0.12) i	i 33 g
TPH-b-6	65.1	3170	1.57	g 29 n 40 (0.20) i	i 33 (-0.08) n 22 g
TPH-b-8	75.7	3220	1.58	g 24 n 41 (1.85) i	i 30 (-1.82) n 15 g
BPNT-b-8[d]	71.5	8640	2.49	g 27 n 59 (1.89) i	i 49 (-2.51) n 18 g
TPT-b-8[e]	79.9	11800	2.42	g 50 n 132 (2.96) i	i 125 (-2.88) n 38 g
TPT-b-All	81.4	8333	1.90	k 126 (7.59) n 155 (3.46)	i 149 (-2.90) n 166 (-6.98) k
TPD-8[f]	92.2	27500	2.00	g 19 n 60 (6.61) i	i 47 (-6.61) n 13 g

[a] Yields are after precipitation in methanol. Molecular weights and thermal transitions are after precipitation in acetone. All thermal data are collected from second heating and first cooling DSC scans. [b] TPD-b-X = short name for the polymer derived from 10-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (see ref 8a). [c] TPH-b-X = polymer derived from 8. [d] BPNT-b-X = polymer derived from 22. [e] TPT-b-X = polymer derived from 30. [f] TPD-8 = linear polymer from 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane and 1,8-dibromooctane (see ref 8a).

Figure 4a presents a representative GPC trace of the hyperbranched TPT-b-All before precipitation in acetone. In addition to the elution peak of the hyperbranched polymer, a peak at higher elution volume and lower molecular weight is always present in these hyperbranched polymers. Upon precipitation of the hyperbranched

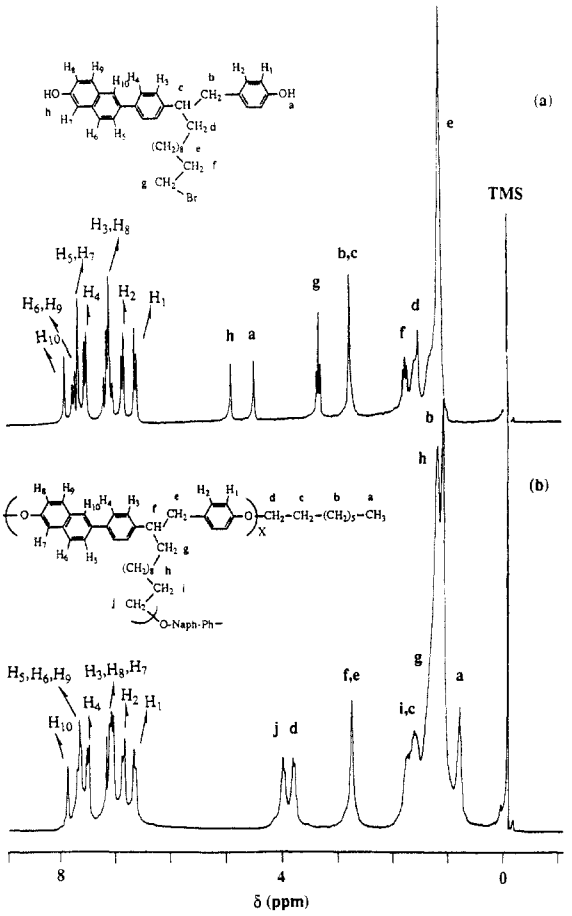


Figure 1. 200-MHz ^{1}H-NMR spectra ($CDCl_3$, TMS, 20 °C) and the protonic assignments of (a) BPNT-b and (b) BPNT-b-8.

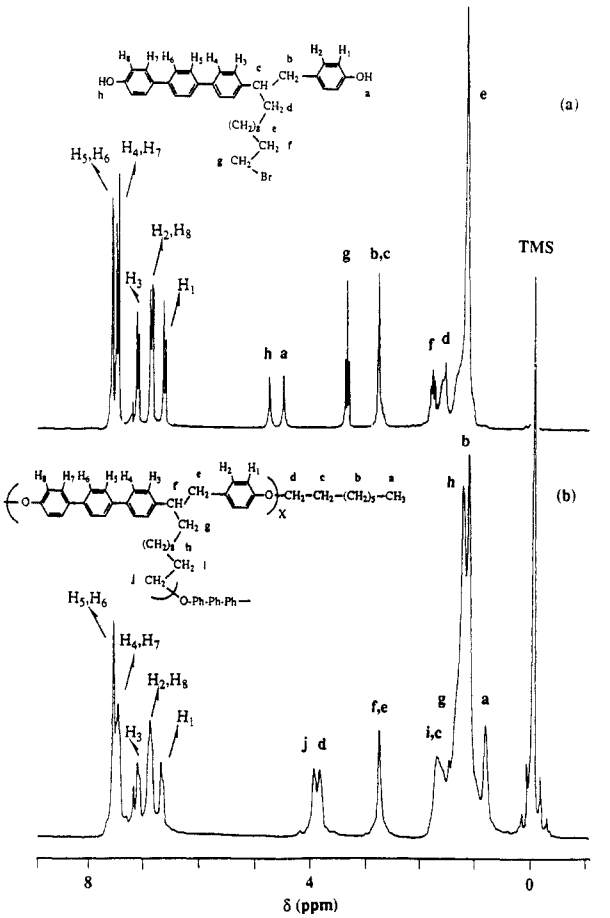


Figure 2. 200-MHz ^{1}H-NMR spectra ($CDCl_3$, TMS, 20 °C) and the protonic assignments of (a) TPT-b and (b) TPT-b-8.

polymer in acetone, the product with low molecular weight remains in the acetone fraction. Figure 4b shows the GPC trace of the acetone-insoluble fraction of TPT-b-All. The solvent of the acetone-soluble fraction was evaporated, and the pure low molecular weight product, TPT-b(c)-All, was separated by column chromatography as described in the experimental part. Its GPC trace is shown in Figure 4c.

Figure 5 presents the 200-MHz ^{1}H-NMR spectrum of the cyclic low molecular weight compound, TPT-b(c)-All, together with its structure and the assignment of its protonic resonances. Partial decoupling experiments were carried out in order to make these assignments. Intramolecular etherification of the hydroxyphenylenic unit by its own bromoalkane followed by etherification with allyl chloride yields the product at the top of Figure 4. This sequence of reactions is expected. The hydroxyphenylenic unit is more reactive than the hydroxyterphenylenic unit and at the same time this intramolecular cyclization is favored for kinetic and steric reasons. This intramolecular cyclization takes place during the polymerization of all AB_2 monomers described in this paper. Their phase behavior was characterized after the low molecular weight cyclic product was separated by precipitation in acetone.

Figure 6 shows the structure of the hyperbranched TPT-b-All together with its protonic assignments. Besides the expected resonances we see in this figure the signals c(c), m, n, and n′ which are due to the resonances of the protons from the cyclic chain end shown in Figure 5 and Chart 1. Extensive purification of the hyperbranched TPT-b-All could not remove these signals. This demonstrates as shown in Chart 1 that this cyclic unit is present in small concentrations as a chain end of the hyperbranched TPT-b-All. The integration of the ratio between the cyclic,

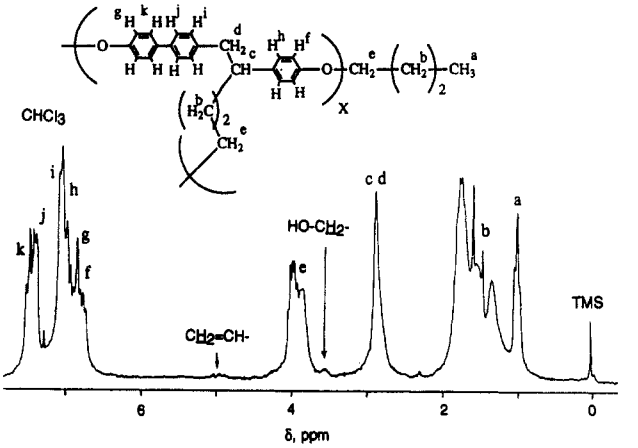
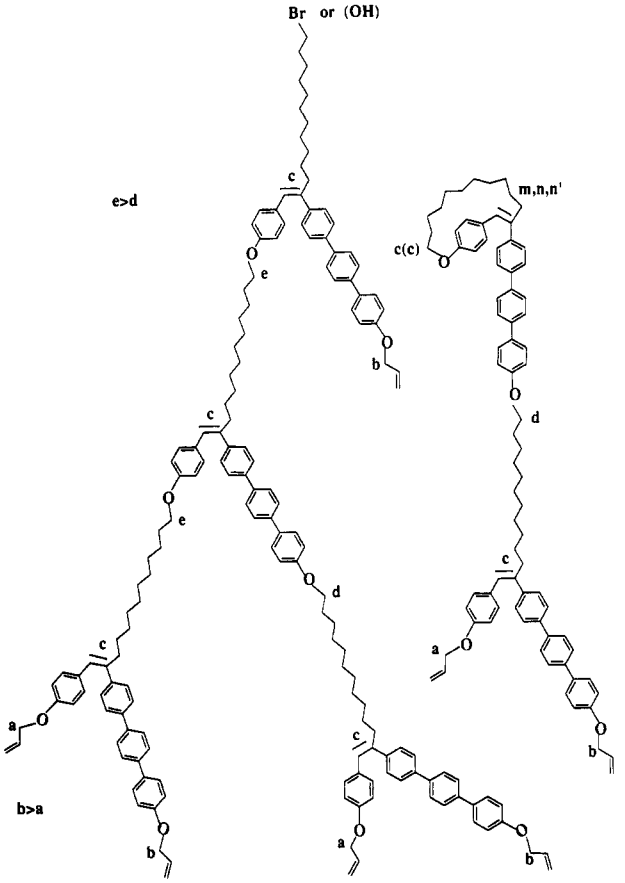


Figure 3. 200-MHz ^{1}H-NMR spectrum ($CDCl_3$, TMS, 20 °C) and the protonic assignments of TPH-b-8.

$-CH_2OH$, and $-CH_2Br$ chain ends from Figure 6 leads to the conclusion that TPT-b(c)-All contains these chain ends in the following molar concentrations: 0.56, 0.15, and 0.29, respectively. Very instructive information is obtained from Figure 6. The chemical shifts of the resonances a and b which are due to $-CH_2CH{=}CH_2$ in the phenylenic and terphenylenic ether chain ends, respectively, have different chemical shifts. The ratio between these two integrals shows that there is a larger concentration of allyl ether chain ends attached to hydroxyterphenyl than hydroxyphenyl units (b/a = 1.57). This is expected since the higher reactivity of the hydroxyphenyl groups promotes their faster consumption during the polyetherification process. The higher ratio between the signals b/a is in agreement with the higher ratio of the signals e/d and

Chart 1. The Most Representative Structural Units of the Hyperbranched *Polymer* TPT-b-All[a]



[a] Letters indicate the chemical shifts from Figures 5 and 6.

demonstrates a higher concentration of structural units derived from the hydroxyphenyl group in the internal structural units of the hyperbranched polymer.

The degree of branching of a hyperbranched polymer can be determined by the following formula:[31]

$$DB = \frac{\text{no. of dendritic units + no. of terminal units}}{\text{no. of total units}}$$

$$\% \text{ Branching} = (DB) \times 100$$

$$\text{no. of total units} = \frac{c + m + n + n'}{3} + \frac{c(c)}{2} = 46.93$$

$$\text{no. of chain ends (except cyclic)} = \frac{a}{2} = 17.35$$

$$\text{no. of singular structural units} = \frac{b-a}{2} = 8.4$$

$$\text{no. of cyclic ends} = \frac{c(c)}{2} = 1.3$$

no. of dendrimeric units - no. total units -[no. of chain ends (except cyclic) + no. of singular units + no of cyclic ends] = 46.93 - 27.05 = 19.88

$$DB = \frac{\text{no. of dendritic units + no. of chain ends (except cyclic) + no. of cyclic ends}}{\text{no. of total units}}$$

$$DB = \frac{19.88 + 17.35 + 1.3}{46.93} = 0.821$$

% Branching = 82.1

The degree of branching of TPT-b-All is higher than the degrees of branching reported for hyperbranched polyesters synthesized from AB_2 monomers.[31,32] These last values are from 0.50 to 0.60 and are explained by the steric inhibition generated during the polymerization process. The two phenolate groups of TPT-b are much less affected by steric hindrance effects, and the degree of branching is mostly determined by the difference

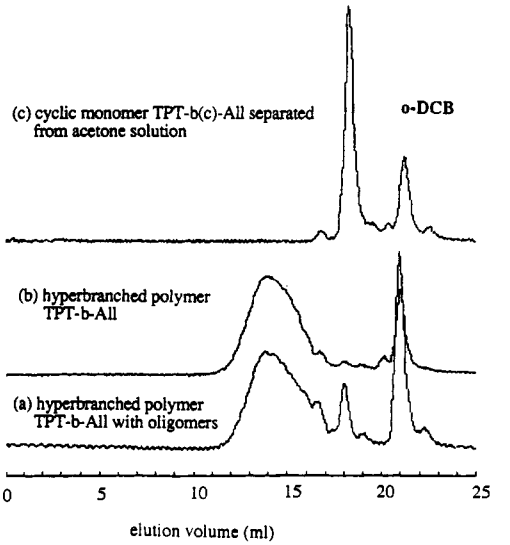


Figure 4. GPC traces of the hyperbranched TPT-b-All obtained (a) after precipitation in methanol and (b) after precipitation in acetone and of the cyclic monomer TPT-b-All (c) (see Figure 5 for its structure).

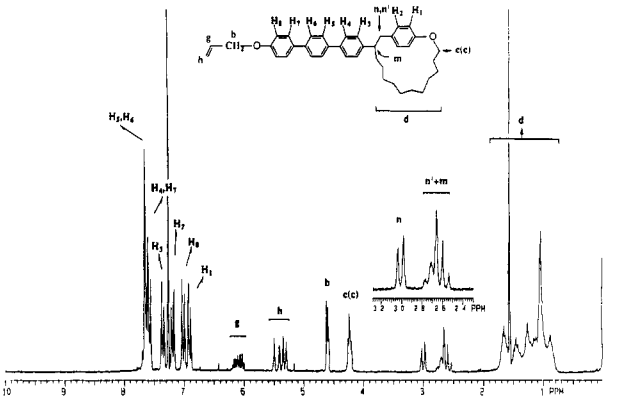


Figure 5. 200-MHz ^{1}H-NMR ($CDCl_3$, TMS, 20 °C) spectrum of TPT-b(c)-All.

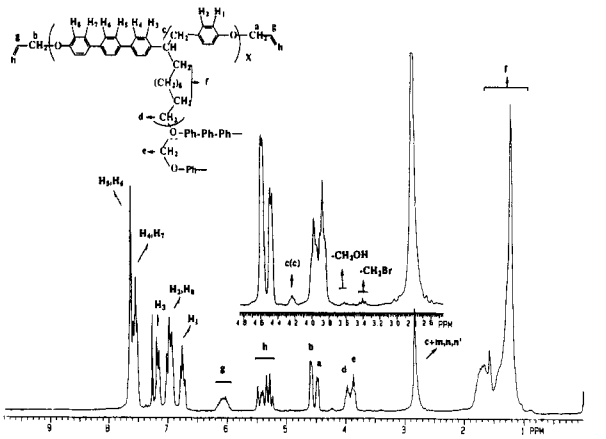


Figure 6. 200-MHz ^{1}H-NMR ($CDCl_3$, TMS, 20 °C) spectrum of TPT-b-All after precipitation in acetone.

between the reactivity of the two phenolate groups. More detailed investigations on the influence of reaction conditions and the degree of polymerization of these hyperbranched polymers on their degree of branching will be discussed elsewhere.

Thermal Characterization of the Hyperbranched Polyethers. The second heating and first cooling DSC traces of TPH-b-X polymers are presented in Figure 7. The DSC traces of the first heating scan are identical with those of the second heating scan except that they present an endothermic peak which starts at the onset of the glass

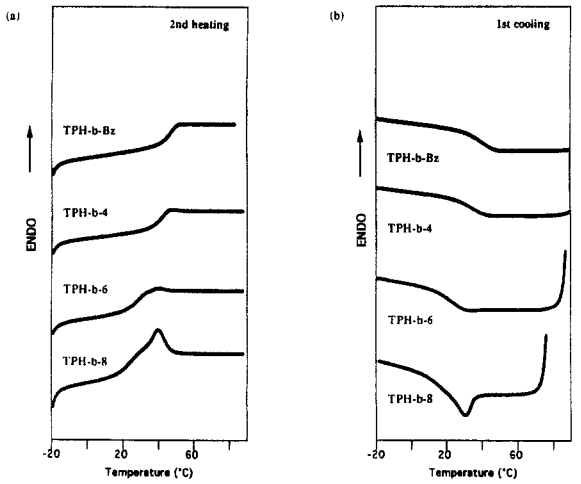


Figure 7. Representative DSC thermograms (20 °C/min) of hyperbranched polyethers based on TPH-b and alkyl bromide or benzyl chloride derived chain ends (TPH-b-X, where X is the structure of the chain end groups, i.e., Bz = benzyl, 4 = butyl, 6 = hexyl, and 8 = octyl): (a) second heating scan; (b) first cooling scan.

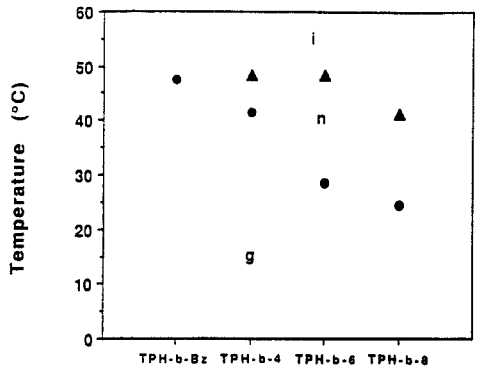


Figure 8. Transition temperatures of TPH-b-X as a function of X: (●) T_g; (▲) T_i (both data are from the second heating scan).

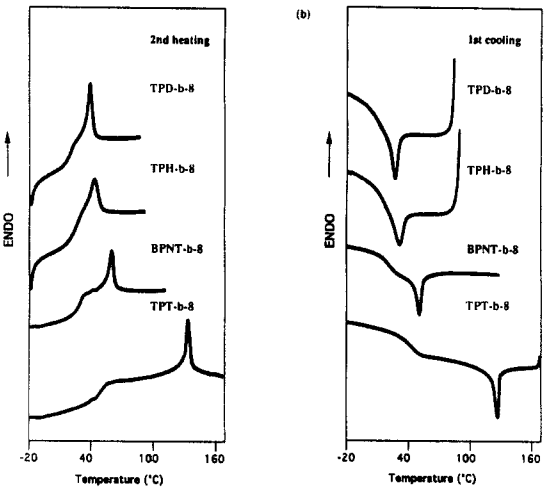


Figure 9. Representative DSC thermograms (20 °C/min) of hyperbranched polyethers TPH-b-8 BPNT-b-8, and TPT-b-8 and of linear polyether TPD-8: (a) second heating scan; (b) first cooling scan.

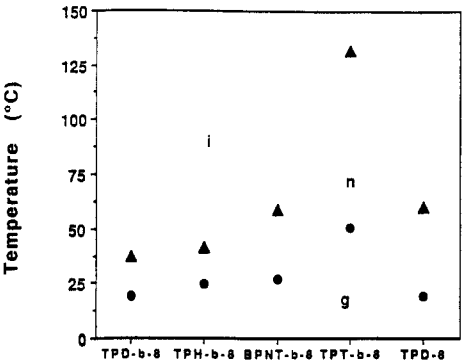


Figure 10. Transition temperatures of TPH-b-8, BPNT-b-8, and TPT-b-8 and their comparison with the corresponding parameters of the linear model TPD-8 polymer: (●) T_g; (▲) T_i (both data are collected from the second heating scan).

transition temperature. The change in the heat capacity at the glass transition does not change from the first to the second heating scan. Therefore, this peak is due to excess heat capacity. During the second heating and first cooling scans, TPH-b-X exhibits only a glass transition temperature. TPH-b-4m TPH-b-6, and TPH-b-8 display a nematic mesophase over a very narrow range of temperature. In all three polymers during heating the isotropization temperatures are a few degrees higher than their glass transition temperature and on cooling overlap the glass transition temperature (Table 1). An inspection of the data from Table 1 shown that the isotropization temperatures of TPH-b-4, TPH-b-6, and TPH-b-8 are almost independent of X. However, their glass transition temperatures are decreasing with the increase of the length of their alkyl chain ends. As a consequence of this trend the monotropic mesophase of TPH-b-4 becomes enantiotropic in TPH-b-6 and TPH-b-8. The plot from Figure 8 demonstrates this trend. These results are in agreement with those reported previously on TPD-b-X.[8a] The transition temperatures of TPD-b-8 are also reported in Table 1 and demonstrate that they are very close to those of TPH-b-8.

Figure 9 compares representative DSC traces of the second heating and first cooling scans of TPD-b-8, TPH-b-8, BPNT-b-8, and TPT-b-8. On increasing the length of the rigid part of the AB_2 mesogen from TPD-b-8 and TPH-b-6 to BPNT-b-8 and TPT-b-8, both the glass transition temperatures and the isotropization temperatures increase. Nevertheless, the increase in the isotropization temperature is much larger than that of the glass transition (Table 1). The largest increase in the isotropization temperature occurs at the transition from BPNT-b-8 to TPT-b-8. TPT-b-8 displays an enantiotropic nematic mesophase which is thermodynamically stable within a very reasonable range of temperatures (i.e., from 50 to 132 °C). Therefore, monomer **30** provides an extremely valuable AB_2 compound for the synthesis of liquid crystalline dendrimers. TPT-b-All presents an even higher isotropization transition than TPT-b-8 and a crystalline phase (Table 1). This is most probably due to the high rigidity of the allyl chain ends of TPT-b-All. Figure 10 plots the glass transition and isotropication temperatures versus molecular structure for this novel class of hyperbranched polymers and compares it with that of the linear model polymer TPD-8.

Finally Figure 11 presents representative textures of the nematic mesophase of BPNT-b-8 and TPT-b-8. The transition from isotropic to nematic and the most probable conformations of these hyperbranched polymers in isotropic and nematic phases are illustrated in Schemes 4 and 5. We believe that the proper molecular design of the structural units of these willowlike hyperbranched polymers minimizes their free energy in the liquid and in the melt phase by lowering their free volume via a conventional nematic mesophase which is generated by the conformational change of their structural units from gauche to anti. This is a well-established fact in the case of linear liquid crystalline polyethers based on conformational isomerism.[10,11] Recently, the gauche–anti conformational change

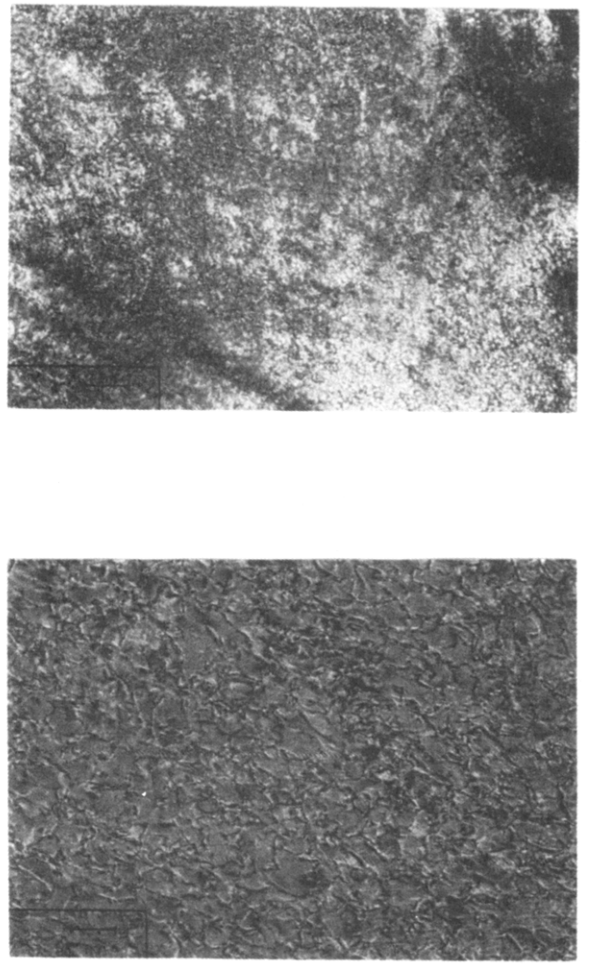


Figure 11. Representative textures of the nematic phase observed under an optical polarized microscope (100×) of (a) BPNT-b-8 after annealing at 30 °C for 45 min and (b) TPT-b-8 after annealing at 126.8 °C for 1.5 h.

was evidenced by ^{13}C-NMR spectroscopy.[33] Nevertheless, spectroscopic studies on these hyperbranched polymers are required to confirm that the gauche–anti conformational change suggested indeed occurs in these hyperbranched stuctures at the isotropic–nematic phase transition.

Research on the synthesis of the dendrimers based on TPT-6 and on the detailed structural and dynamic characterization of these hyperbranched and dendrimeric liquid crystals is in progress.

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