Synthesis and Characterization of a Thermotropic Nematic Liquid Crystalline Dendrimeric Polymer[†]

Virgil Percec* and Masaya Kawasumi

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106

Received December 30, 1991; Revised Manuscript Received April 16, 1992

ABSTRACT: The synthesis and characterization of 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (TPD) and of 10-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (TPD-b) are described. Polyetherification of TPD with α,ω-dibromoalkanes containing from 6 to 10 methylene units leads to the model polyethers TPD-X (where X = 6–10 and represents the number of methylene units in the flexible spacer). TPD-X with X = 6, 8, and 10 exhibit an enantiotropic nematic mesophase, while those with X = 7 and 9 are glassy. Homopolymerization of TPD-b followed by in situ alkylation of the phenol chain ends leads to the TPD-b-X dendrimeric polymers (X is the structure of the alkylated phenol chain ends, i.e., Bz = benzyl, 4 = butyl, 6 = hexyl, 8 = octyl). TPD-b-X with X = Bz, 6, and 8 represent the first examples of dendrimeric polymers which exhibit a thermotropic enantiotropic nematic mesophase. The isotropization temperature of the TPD-b-X is lower than that of their linear model TPD-8.

Introduction

In the past decade there has been an increased interest in the synthesis and characterization of polymers exhibiting complex architectures. Such a novel class of macromolecules was provided by *dendrimers* or *hyperbranched polymers*, i.e., *polymers containing a branching point in each structural unit.*[1–12] Dendrimers display a treelike architecture and are not expected to display liquid crystallinity. For example, dendritic aromatic polyesters,[7e,11b] polyphenylenes,[6,11a] and poly(benzyl ethers)[7a,b] were reported and they do not exhibit liquid crystallinity although their linear homologues do. A dendrimer was used as solvent to generate a nonaqueous lamellar liquid crystal from octanoic acid.[13] A lyotropic liquid crystalline dendritic aromatic polyamide was prepared in parallel with our work reported here,[14] and a thermotropic hyperbranched polymer containing disklike mesogens and displaying a columnar hexagonal mesophase was recently reported from our laboratory.[15]

This paper will present the synthesis and characterization of the first thermotropic liquid crystalline dendrimer exhibiting a nematic mesophase. Its synthesis was accomplished by the phase-transfer-catalyzed polyetherification of the AB$_2$ monomer 10-bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (TPD-b). This monomer represents a mesogenic unit based on conformational isomerism.[16,17] The phase behavior of the resulting dendrimer with different chain ends (TPD-b-X, whose X indicates the structure of the chain end) will be compared to that of its linear model compounds synthesized by the polyetherification of 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (TPD) with α,ω-dibromoalkanes containing an X number of methylene units (TPD-X, where X = 6–10).

Experimental Section

Materials. Boron tribromide (1.0 M in CH$_2$Cl$_2$), thionyl chloride, lithium aluminum hydride (95+%), dimethyl sulfate (99%), triphenylphosphine (99%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), (4-methoxyphenyl)acetic acid (99%), 8-bromooctanoic acid (97%), 1-iodooctane (98%), benzyl chloride (97%), 1-bromohexane (98%), 1-bromooctane (99%) (all from Aldrich), aluminum chloride, bromine (both from Fisher Scientific), and 1-bromobutane (Pfaltz & Bauer) were used as received.

1,6-Dibromohexane (97%), 1,7-dibromoheptane (97%), 1,8-dibromooctane (98%), 1,9-dibromononane (97%), and 1,10-dibromodecane (97%) (all from Aldrich) were purified by vacuum distillation. Diethyl ether (Et$_2$O) was dried by refluxing over LiAlH$_4$ followed by distillation. Methylene chloride was refluxed over CaH$_2$ and then distilled from CaH$_2$. *o*-Dichlorobenzene was distilled under reduced pressure. Dimethylformamide (DMF) was dried over calcium hydride and distilled under reduced pressure. All other chemicals were commercially available and were used as received.

(4-Hydroxyphenyl)acetic acid (4), (4-acetoxyphenyl)acetic acid (5), 4-acetoxybiphenyl (2), and 1-(4-acetoxy-4′-biphenylyl)-2-(4-acetoxyphenyl)ethanone (7), all of purity >99% (HPLC), were synthesized and characterized as described previously.[17]

The syntheses of TPD and TPD-b are outlined in Schemes I and II.

1-(4-(Octyloxy)-4′-biphenylyl)-2-(4-(octyloxy)phenyl)decanone (8). 1-(4-Acetoxy-4′-biphenylyl)-2-(4-acetoxyphenyl)ethanone (7)[17] (19.4 g, 50 mmol) was dissolved in 300 mL of THF in a 1-L three-neck flask equipped with a reflux condenser and a magnetic stirrer. To this solution were successively added 1-iodooctane (32.5 mL, 180 mmol), TBAH (5.1 g, 15 mmol), and 300 mL of 50% (wt/wt) NaOH–water solution. The reaction mixture was stirred vigorously at 60 °C. After 7 and 14 h, 9 mL (7 h) and 4.2 mL (14 h) of 1-iodooctane and 1.7 g (for both times) of TBAH were added. After 30 h the water layer was diluted with 400 mL of water, and the organic layer was separated. The water layer was extracted with 250 mL of CHCl$_3$. The combined organic layer was washed twice with 300 mL of water. To this organic layer was added a mixture of 100 mL of concentrated HCl and 200 mL of water. Then the mixture was stirred for 30 min and the organic layer was separated, washed twice with 300 mL of water, and dried over anhydrous MgSO$_4$. The solvents were removed in vacuo to give a yellow liquid, which was dissolved in 100 mL of THF in a one-neck flask equipped with a magnetic stirrer. To this solution were successively added 1-iodooctane (9.0 mL, 50 mmol), TBAH (2.0 g, 5 mmol), and 100 mL of 50% NaOH–water solution. The reaction mixture was stirred vigorously at 25 °C. After 4 h the product was extracted with 300 mL of CHCl$_3$ and 300 mL of water. The organic layer was separated and washed sequentially with 300 mL of water, then with a mixture of 100 mL of concentrated hydrochloric acid and 200 mL of water, and finally two times with 300 mL of water. Then it was dried over anhydrous MgSO$_4$ and filtered, and the solvents were removed in vacuo. The resulting liquid was crystallized from EtOH and then further purified by silica gel column chromatography. First only hexanes were used as eluent

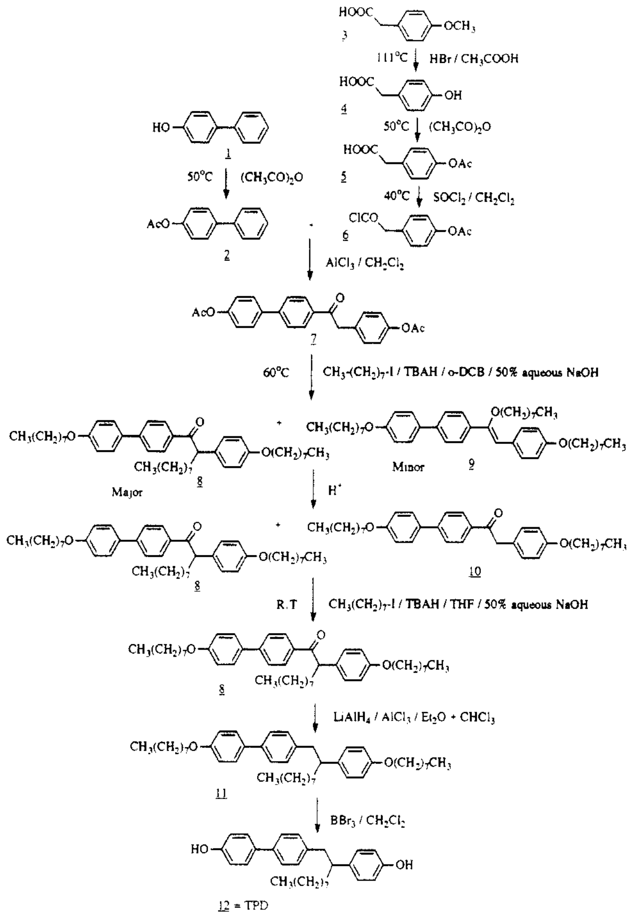
---

* To whom correspondence should be addressed.

[†] Part 23 of "Liquid Crystalline Polyethers Based on Conformational Isomerism". Part 22: ref 16e.

0024-9297/92/2225-3843$03.00/0

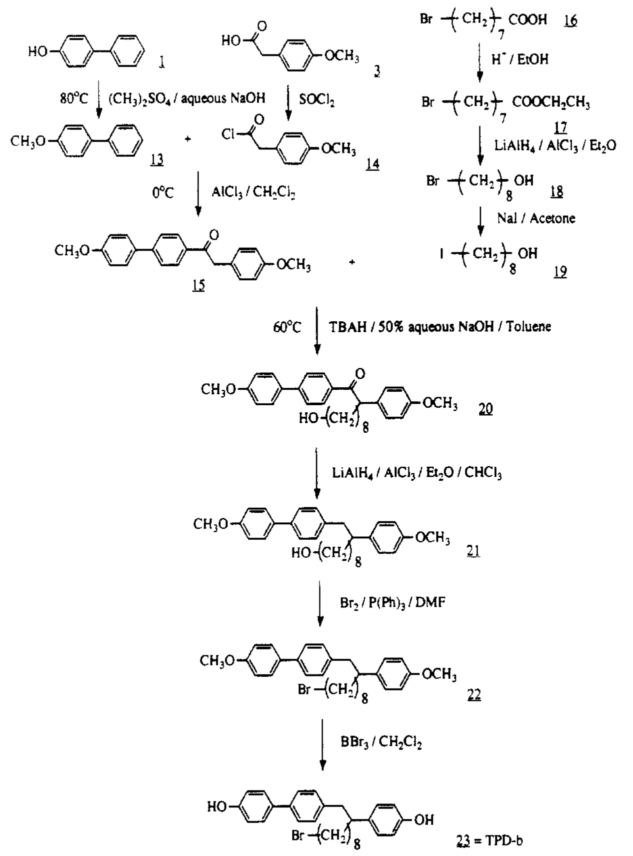
Scheme I
Synthesis of 1-(4-Hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (TPD)



to remove the excess 1-iodooctane. Then Et_2O was gradually increased from 0 to 16% of the total amount of eluent to elute the desired compound. After the evaporation of the solvent 13.8 g (43.1%) of a colorless liquid 8 was obtained. This liquid crystallized on standing. Purity (HPLC), 97%. Mp 55–57 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ): 0.89 (9 H, CH_3, m), 1.23–1.28 (32 H, $CH_3(CH_2)_5CH_2CH_2O$ and $CH_3(CH_2)_6CH_2CHCO$, m), 1.76 (5 H, OCH_2CH_2 and one of $COCHCH_2$, m), 2.13 (1 proton, the other one of $COCHCH_2$, m), 3.89 and 3.99 (4 H, OCH_2, 2 t, J = 6.7 Hz and J = 6.2 Hz), 4.50 (1 H, $COCH$, t, J = 7.1 Hz), 6.83 (2 H, ortho to octyloxy of the monophenyl ring, d, J = 8.4 Hz), 6.96 (2 H, ortho to octyloxy of the biphenyl ring, d, J = 8.9 Hz), 7.23 (2 H, meta to octyloxy of the monophenyl ring, d, J = 7.8 Hz), 7.52 and 7.57 (4 H, meta to octyloxy of the biphenyl ring and meta to acyl of the biphenyl ring, 2 d, J = 9.3 Hz and J = 9.3 Hz), 8.02 (2 H, ortho to acyl of the biphenyl ring, d, J = 7.8 Hz).

1-(4-(Octyloxy)-4′-biphenylyl)-2-(4-(octyloxy)phenyl)decane (11). This compound was prepared by the reduction of 1-(4-(octyloxy)-4′-biphenylyl)-2-(4-(octyloxy)phenyl)butanone (8) with $LiAlH_4/AlCl_3$.[18] $AlCl_3$ (15.7 g, 117 mmol) was placed in a 100-mL three-neck flask equipped with a dropping funnel, a nitrogen inlet–outlet, and a magnetic stirrer and cooled in an ice water bath, after which dry Et_2O (50 mL) was added dropwise under nitrogen. $LiAlH_4$ (2.04 g, 54 mmol) was placed in a 500-mL three-neck flask equipped with a dropping funnel, a nitrogen inlet–outlet, and a magnetic stirrer and cooled in an ice water bath. To the flask containing $LiAlH_4$ were added successively 50 mL of dry Et_2O and the solution of the $AlCl_3{\cdot}Et_2O$ complex prepared as above. A solution of 8 (12.8 g, 20 mmol) in 100 mL of dry Et_2O was added dropwise to the reducing agent solution maintained at 0 °C. The resulting reaction mixture was stirred at 25 °C for 4 h. To this mixture were added dropwise a solution of 53 mL of concentrated HCl and 66 mL of water. After the reaction mixture was stirred for a while, 300 mL of Et_2O was added. The organic layer was separated, washed two times with 300 mL of water, and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated to give a colorless liquid.

Scheme II
Synthesis of 10-Bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (TPD-b)



The solid was recrystallized from 1-butanol to yield 9.4 g (74.6%) of 11 as white fine crystals. Purity (HPLC), >99%. Mp 50–51 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ): 0.89 (9 H, CH_3, m), 1.19–1.30 (32 H, $CH_3(CH_2)_5CH_2CH_2O$ and $CH_3(CH_2)_6CH_2CH$-phenyl, m), 1.57–1.77 (6 H, OCH_2CH_2 and phenyl-$CHCH_2CH_2$, m), 2.76 (1 H, CH-monophenyl, m), 2.85 (2 H, biphenyl-CH_2, d, J = 6.9 Hz), 3.92 and 3.98 (4 H, OCH_2, 2 t, J = 6.4 Hz and J = 6.0 Hz), 6.80 (2 H, ortho to octyloxy of the monophenyl ring, d, J = 8.5 Hz), 6.94 (2 H, ortho to octyloxy of the biphenyl ring, d, J = 7.9 Hz), 7.03 and 7.06 (4 H, meta to octyloxy of the monophenyl ring and ortho to methylene of the biphenyl ring, 2 d, J = 6.9 Hz and J = 6.4 Hz), 7.39 (2 H, meta to methylene of the biphenyl ring, d, J = 7.8 Hz), 7.49 (2 H, meta to octyloxy of the biphenyl ring, d, J = 8.0 Hz). The ^{1}H-NMR spectrum showed that 11 is free of unreacted ketone 8.

1-(4-Hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (12). A 250-mL three-neck flask equipped with a dropping funnel, a nitrogen inlet–outlet, and a magnetic stirrer was cooled in a dry ice–acetone bath. To this flask were added 33 mL of dry CH_2Cl_2 and 33 mL of 1.0 M BBr_3 solution in CH_2Cl_2 (33 mmol).[20] A solution of 11 (8.2 g, 13 mmol) in 65 mL of dry CH_2Cl_2 was added dropwise to the BBr_3 solution. After the addition, the mixture was stirred at 25 °C for 25 h. Then it was cooled by an ice water bath, and 35 mL of water was added slowly. The mixture was extracted with 300 mL of Et_2O and 200 mL of water. The organic layer was separated, washed two times with 100 mL of water, and dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to produce a white solid which was column chromatographed (SiO_2). First a mixture of hexanes and Et_2O (1:1 v/v) was used to remove the 1-bromooctane which was produced in the reaction. Then Et_2O was used to flush out the product which was recrystallized from 70 mL of toluene to yield 3.4 g (65.0%) of fine white crystals. Purity (HPLC), >99%. Mp 124–127 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ): 0.85 (3 H, CH_3, t, J = 6.8 Hz), 1.19 (12 H, $CH_3(CH_2)_6$, m), 1.65 (2 H, $CH_3(CH_2)_6CH_2$, m), 2.77 (1 H, CH-monophenyl, m), 2.83 (2 H, biphenyl-CH_2, m), 4.67–4.80 (2 H, CH-phenylene-OH and HO-biphenyl, 2 br s), 6.73 (2 H, ortho to hydroxy of the monophenyl ring, d, J = 7.0 Hz), 6.88 (2 H, ortho to hydroxy of the biphenyl ring, d, J = 9.4

Hz), 6.99 (2 H, meta to hydroxy of the monophenyl ring, d, J = 8.8 Hz), 7.04 (2 H, ortho to methylene of the biphenyl ring, d, J = 8.3 Hz), 7.38 (2 H, meta to methylene of the biphenyl ring, d, J = 8.0 Hz), 7.45 (2 H, meta to hydroxy of the biphenyl ring, d, J = 8.4 Hz).

4-Methoxybiphenyl (13). 4-Phenylphenol (1) (68.0 g, 0.40 mol) was dissolved in a NaOH (16.0 g, 0.40 mol)–water (240 mL) solution in a 500-mL Erlenmeyer flask equipped with a magnetic stirrer at 80 °C. Me_2SO_4 was added to this solution slowly via a syringe, and the reaction mixture was stirred for 15 min. Then it was cooled to 25 °C to give a solid, which was washed with 10% NaOH–water solution and water, and recrystallized from 95% EtOH to give 58.8 g (79.8%) of white crystals. Purity (HPLC), >99%. Mp 86–88 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ): 3.84 (3 H, CH_3, s), 6.98 (2 H, ortho to methoxy of the substituted phenyl ring, d, J = 9.1 Hz), 7.30–7.57 (7 H, 5 protons of the unsubstituted phenyl ring and 2 protons meta to methoxy of the substituted phenyl ring, m).

1-(4-Methoxy-4′-biphenylyl)-2-(4-methoxyphenyl)ethanone (15). 3 (33.24 g, 0.20 mol), $SOCl_2$ (17.5 mL, 0.24 mol), and a few drops of DMF were placed in a 250-mL three-neck flask equipped with a nitrogen inlet–outlet and a magnetic stirrer and the mixture was stirred for 4 h. The excess $SOCl_2$ was removed in vacuo to produce a pale yellow liquid, which was used directly in the acylation reaction.

13 (40.0 g, 0.22 mol) was dissolved in 300 mL of dry CH_2Cl_2 in a 1-L three-neck flask equipped with a nitrogen inlet–outlet, a thermometer, a dropping funnel, and a magnetic stirrer. The solution was cooled to below 10 °C in an ice water bath after which 82.7 g (0.62 mol) of anhydrous $AlCl_3$ was added. 14 was dissolved in 200 mL of dry CH_2Cl_2. This solution was added dropwise to the solution of 13 so that the reaction temperature did not rise above 10 °C. After the addition, the solution was stirred below 10 °C for 5.5 h. Then it was poured into a mixture of 100 mL of concentrated HCl, 600 mL of ice water, and 300 mL of $CHCl_3$. The resulting compound was not very soluble in the organic layer. The organic solvents were evaporated in vacuo to give a solid, which was separated and washed twice each time with 1.5 L of water. It was dried, recrystallized first from $CHCl_3$ and subsequently from toluene, and dried to yield 26.1 g (39.3%) of fine crystals. The product was recovered from $CHCl_3$ solution and then recrystallized first from $CHCl_3$ and then from toluene to yield 8.70 g of crystals. The combined yield was 34.8 g (52.3%). Purity (HPLC), 98%. Mp 197–199 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ): 3.80 (3 H, CH_3O-monophenyl, s), 3.86 (3 H, CH_3O-biphenyl, s), 4.24 (2 H, CH_2, s), 6.88 (2 H, ortho to methoxy of the monophenyl ring, d, J = 9.3 Hz), 7.00 (2 H, ortho to methoxy of the biphenyl ring, d, J = 9.3 Hz), 7.22 (2 H, meta to methoxy of the monophenyl ring, d, J = 7.4 Hz), 7.58 (2 H, meta to methoxy of the biphenyl ring, d, J = 9.3 Hz), 7.64 (2 H, meta to acyl, d, J = 7.9 Hz), 8.06 (2 H, ortho to acyl, d, J = 7.9 Hz).

8-Bromooctan-1-ol (18). 8-Bromooctanoic acid (16) (27.0 g, 0.121 mol) was dissolved in absolute EtOH (180 mL) in a single-neck flask equipped with a reflux condenser and a magnetic stirrer. A few drops of sulfuric acid were added and the solution was refluxed for 21 h. The reaction mixture was cooled to 25 °C, and the EtOH was evaporated in vacuo to give an orange liquid, which was mixed with Et_2O. The resulting solution was washed with water, 10% $NaHCO_3$–water solution, and water three times and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated to give the ester 17 as a liquid. The ester 17 was reduced without further purification. The ^{1}H-NMR spectrum showed complete esterification. ^{1}H-NMR (CDCL$_3$, TMS, δ): 1.25 (3 H, CH_3CH_2O, t, J = 6.9 Hz), 1.33 (6 H, $(CH_2)_3(CH_2)_2Br$, m), 1.63 (2 H, $EtOCOCH_2CH_2$, m), 1.85 (2 H, CH_2CH_2Br, m), 2.29 (2 H, $EtOCOCH_2$, t, J = 7.4 Hz), 3.41 (2 H, CH_2Br, t, J = 7.1 Hz), 4.13 (2 H, CH_3CH_2O, q, J = 7.2 Hz).

$AlCl_3$ (32.3 g, 0.242 mol) was placed in a 250-mL three-necks flask equipped with a dropping funnel, a nitrogen inlet–outlet, and a magnetic stirrer and cooled in an ice water bath, after which dry Et_2O was added dropwise under nitrogen. $LiAlH_4$ (9.2 g, 0.24 mol) was placed in a 1-L three-neck flask equipped with a dropping funnel, a nitrogen inlet–outlet, and a magnetic stirrer and cooled in an ice water bath. To the flask containing $LiAlH_4$ were added successively 120 mL of dry Et_2O and the solution of $AlCl_3\cdot Et_2O$ complex prepared as above. A solution of 17 (30.4 g, 0.121 mmol) in 120 mL of dry Et_2O was added dropwise to the reducing agent solution maintained at 0 °C. The resulting reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was cooled by an ice water bath, and to this mixture were added successively a mixture of 40 mL of MeOH and 40 mL of Et_2O and a mixture of 100 mL of concentrated HCl and 120 mL of water. After the mixture was stirred for several hours, 300 mL of Et_2O and 300 mL of water were added. The organic layer was separated, washed three times with 300 mL of water, and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated to yield 21.4 g (84.6%) of alcohol 18 as a liquid. ^{1}H-NMR ($CDCl_3$, TMS, δ): 1.34 (8 H, $(CH_2)_4(CH_2)_2Br$, m), 1.55 (2 H, $HOCH_2CH_2$, m), 1.85 (2 H, CH_2CH_2Br, m), 2.38 (1 H, $HOCH_2$, s), 3.41 (2 H, CH_2Br, t, J = 6.5 Hz), 3.61 (2 H, $HOCH_2$, t, J = 7.0 Hz).

8-Iodooctan-1-ol (19). 18 (21.4 g, 0.102 mol) and anhydrous NaI (45.9 g, 0.306 mol) were dissolved in acetone (250 mL) in a 500-mL single-neck flask equipped with a condenser and a magnetic stirrer. The reaction mixture was stirred at 25 °C for 66 h. Then the solvent was evaporated. The obtained reaction mixture was extracted with 200 mL of Et_2O and 200 mL of water. The organic layer was washed three times with water and dried over anhydrous $MgSO_4$. The solvent was evaporated to give brown liquid which was column chromatographed (SiO_2) with a mixture of Et_2O and hexanes (1:2 v/v) as eluent to yield 19 as a colorless liquid, 23.0 g (88.2%). ^{1}H-NMR ($CDCl_3$, TMS, δ): 1.34 (8 H, $(CH_2)_4(CH_2)_2I$, m), 1.56 (2 H, $HOCH_2CH_2$, m), 1.59 (1 H, $HOCH_2$, s), 1.82 (2 H, CH_2CH_2I, m), 3.19 (2 H, CH_2I, t, J = 7.4 Hz), 3.64 (2 H, $HOCH_2$, t, J = 6.4 Hz).

10-Hydroxy-1-(4-methoxy-4′-biphenylyl)-2-(4-methoxyphenyl)decanone (20). A mixture of 15 (26.1 g, 79 mmol), toluene (280 mL), 8-iodooctanol (19) (22.2 g, 86 mmol), TBAH (1.34 g, 3.9 mmol), and 50% (wt/wt) NaOH–water solution was placed in a 1-L three-neck flask equipped with a reflux condenser and a magnetic stirrer. A balloon filled with N_2 was placed at the top of the reflux condenser. The reaction mixture was stirred vigorously at 60 °C for 4 h. During the reaction the color of the solution changed from yellow to orange. The organic and aqueous layers were diluted with 600 mL of water and 300 mL of $CHCl_3$, respectively, after which the organic layer was separated and washed with 300 mL of water. To this organic layer was added a mixture of 200 mL of concentrated HCl and 400 mL of water. Then the mixture was stirred for 2 h and the organic layer was separated, washed with 600 mL of water twice, and dried over anhydrous $MgSO_4$. After filtration, the solvents were removed in vacuo to give a solid which was dissolved in MeOH at reflux temperature. The insoluble part, which was ketone 15, was removed by filtration, and the solution was cooled in a refrigerator to give white crystals. These crystals were recrystallized from 95% EtOH to yield 13.4 g (36.9%) of white crystals. The product was recovered from the EtOH solution and recrystallized from EtOH to give 7.9 g of crystals as a second crop. The combined yield was 21.4 g (58.8%). Purity (HPLC), 98%. Mp 78–80 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ): 1.28 (10 H, $(CH_2)_5CH_2CH_2OH$, m), 1.53 (2 H, CH_2CH_2OH, m), 1.79 and 2.13 (2 H, $COCHCH_2$, 2 m), 3.62 (2 H, CH_2OH, t, J = 6.7 Hz), 3.75 and 3.84 (6 H, CH_3O-monophenyl and CH_3O-biphenyl, 2 s), 4.51 (1 H, COCH, t, J = 7.4 Hz), 6.84 (2 H, ortho to methoxy of the monophenyl ring, d, J = 8.3 Hz), 6.97 (2 H, ortho to methoxy of the biphenyl ring, d, J = 8.9 Hz), 7.25 (2 H, meta to methoxy of the monophenyl ring, d, J = 8.8 Hz), 7.53 (2 H, meta to methoxy of the biphenyl ring, d, J = 9.3 Hz), 7.57 (2 H, meta to acyl of the biphenyl ring, d, J = 8.0 Hz), 8.02 (2 H, ortho to acyl of the biphenyl ring, d, J = 8.3 Hz).

10-Hydroxy-1-(4-methoxy-4′-biphenylyl)-2-(4-methoxyphenyl)decane (21). $AlCl_3$ (33.3 g, 0.25 mol) was placed in a 250-mL three-neck flask equipped with a dropping funnel, a nitrogen inlet–outlet, and a magnetic stirrer and cooled in an ice water bath, after which dry Et_2O was added dropwise under nitrogen. $LiAlH_4$ (1.63 g, 43 mmol) was placed in a 250-mL three-neck flask equipped with a dropping funnel, a nitrogen inlet–outlet, and a magnetic stirrer and cooled in an ice water bath. To the flask containing $LiAlH_4$ were added successively 60 mL of dry Et_2O, the solution of $AlCl_3\cdot Et_2O$ complex[18] prepared in the first flask, and 60 mL of dry $CHCl_3$. A solution of 20 (11.5 g, 25 mmol) in 60 mL of dry $CHCl_3$ was added dropwise to the reducing agent solution maintained at 0 °C. The resulting reaction mixture was stirred at 25 °C for 12 h and then cooled with an ice water bath, and a mixture of 80 mL of concentrated HCl and 100 mL of water was added dropwise. After the mixture was stirred for 5 h, the organic layer was separated, washed two times with 200 mL of water, and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated to give a colorless liquid. The liquid was column chromatographed (SiO_2, flash) with $CHCl_3$ as eluent. The obtained liquid crystallized on standing. Purity (HPLC), 99%. Mp 56–59 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ): 1.20 (10 H, $(CH_2)_5CH_2CH_2OH$, m), 1.51 (4 H, CH_2CH_2OH and biphenyl-CH_2CHCH_2, m), 2.78 (1 H, CH-monophenyl, m), 2.86 (2 H, biphenyl-CH_2CH, d, J = 5.8 Hz), 3.60 (2 H, CH_2OH, t, J = 6.7 Hz), 3.79 and 3.84 (6 H, CH_3O-monophenyl and CH_3O-biphenyl, 2 s), 6.82 (2 H, ortho to methoxy of the monophenyl ring, d, J = 8.9 Hz), 2.96 (2 H, ortho to methoxy of the biphenyl ring, d, J = 8.3 Hz), 7.05 (2 H, meta to methoxy of the monophenyl ring, d, J = 9.9 Hz), 7.06 (2 H, ortho to methylene of the biphenyl ring, d, J = 7.9 Hz), 7.40 (2 H, meta to methylene of the biphenyl ring, d, J = 8.0 Hz), 7.50 (2 H, meta to methoxy of the biphenyl ring, d, J = 9.2 Hz). The ^{1}H-NMR spectrum showed that **21** is free of unreacted ketone **20**.

10-Bromo-1-(4-methoxy-4′-biphenylyl)-2-(4-methoxyphenyl)decane (22). Triphenylphosphine (4.13 g, 15.7 mmol) was dissolved in dry DMF (30 mL) in a 100-mL three-neck flask equipped with a dropping funnel, a nitrogen inlet–outlet, and a magnetic stirrer. Bromine (2.62 g, 16.4 mmol) was added dropwise to the solution cooled by an ice water bath. To the resulting $P(C_6H_5)_3 \cdot Br_2$ complex was added dropwise a solution of **21** in 30 mL of dry DMF.[19] The reaction mixture was stirred for 12 h at 25 °C after which DMF was evaporated in vacuo. The obtained liquid was extracted four times with 125 mL of hexanes, followed by evaporation of the hexanes to give the crude product as a liquid. The crude product, was column chromatographed (SiO_2), eluting with a mixture of petroleum ether and Et_2O (19:1 v/v) to yield 3.1 g (61%) of a colorless liquid. Purity (HPLC), >99%. ^{1}H-NMR ($CDCl_3$, TMS, δ): 1.19 and 1.35 (10 H, $CH_2(CH_2)_5CH_2CH_2Br$, m), 1.61 (2 H, $CHCH_2(CH_2)_7Br$, m), 1.80 (2 H, CH_2CH_2Br, m), 2.76 (1 H, CH-monophenyl, m), 2.86 (2 H, biphenyl-CH_2, d, J = 6.2 Hz), 3.37 (2 H, CH_2Br, t, J = 6.8 Hz), 3.78 and 3.84 (6 H, CH_3O-phenylene-CH and CH_3O-biphenyl, 2 s), 6.81 (2 H, ortho to methoxy of the monophenyl ring, d, J = 8.5 Hz), 6.96 (2 H, ortho to methoxy of the biphenyl ring, d, J = 8.8 Hz), 7.04 (2 H, meta to methoxy of the monophenyl ring, d, J = 8.7 Hz), 7.06 (2 H, ortho to methylene of the biphenyl ring, d, J = 8.3 Hz), 7.40 (2 H, meta to methylene of the biphenyl ring, d, J = 7.9 Hz), 7.50 (2 H, meta to methoxy of the biphenyl ring, d, J = 9.4 Hz).

10-Bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (23). A 100-mL three-neck flask equipped with a dropping funnel, a nitrogen inlet–outlet, and a magnetic stirrer was cooled in a dry ice–acetone bath. To this flask were added 15 mL of dry CH_2Cl_2 and 15 mL of 1.0 M BBr_3 solution in CH_2Cl_2.[20] A solution of **22** (3.1 g, 6.1 mmol) in 30 mL of dry CH_2Cl_2 was added dropwise to the BBr_3 solution. After the addition, the mixture was stirred at 25 °C for 5 h. To this reaction mixture were added slowly 15 mL of water, 200 mL of Et_2O, and 100 mL of water. The organic layer was separated, washed three times with 100 mL of water, and dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo to produce a white solid which was recrystallized from toluene to yield 1.9 g (64%) of fine crystals. Purity (HPLC) >99%. Mp 115–117 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ): 1.18 and 1.35 (10 H, $CH_2(CH_2)_5CH_2CH_2Br$, m), 1.64 (2 H, $CHCH_2(CH_2)_7Br$, m), 1.80 (2 H, CH_2CH_2Br, m), 2.76 (1 H, CH-monophenyl, m), 2.82 (2 H, biphenyl-CH_2, m), 3.36 (2 H, CH_2Br, t, J = 6.7 Hz), 4.62 and 4.82 (2 H, HO-phenylene-CH and HO-biphenyl, 2 s), 6.72 (2 H, ortho to hydroxy of the monophenyl ring, d, J = 8.2 Hz), 6.84 (2 H, ortho to hydroxy of the biphenyl ring, d, J = 8.4 Hz), 6.97 (2 H, meta to hydroxy of the monophenyl ring, d, J = 8.3 Hz), 7.03 (2 H, ortho to methylene of the biphenyl ring, d, J = 7.7 Hz), 7.37 (2 H, meta to methylene of the biphenyl ring, d, J = 8.4 Hz), 7.44 (2 H, meta to hydroxy of the biphenyl ring, d, J = 8.6 Hz).

Synthesis of Linear Polyethers. Conventional liquid–liquid two-phase (organic solvent–aqueous NaOH solution) phase-transfer-catalyzed polyetherification conditions were used for the preparation of linear polyethers. The polyetherifications were carried out under a nitrogen atmosphere at 80 °C in an *o*-dichlorobenzene–10 N NaOH solution (10-fold molar excess of NaOH versus phenol groups) in the presence of TBAH as phase-transfer catalyst. The molar ratio of nucleophilic to electrophilic monomers was in every case 1.0/1.0. An example of polyetherification is as follows.

To a 25-mL single-neck flask equipped with a condenser and a nitrogen inlet–outlet were successively added 0.201 g (0.500 mmol) of TPD (**12**), 1.0 mL of *o*-dichlorobenzene, 0.136 g (0.500 mmol) of 1,8-dibromooctane, 1.0 mL of 10 N NaOH, and 0.0814 g (0.240 mmol, 20 mol % of phenol groups) of TBAH. The ratio between the volume of *o*-dichlorobenzene and the total moles of monomers was maintained constant in all polymerizations. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80 °C under nitrogen. After 2 h of reaction, the organic and aqueous layers were diluted with $CHCl_3$ and water, respectively, and the aqueous layer was separated. The organic layer was washed with water, followed by dilute hydrochloric acid, and again three times with water. The polymer was separated by the precipitation of its solution into MeOH. The remaining salt was eliminated by precipitation from THF solution into water to yield 0.236 g (92%) of a white precipitate. The polymer was further purified by three successive precipitations from THF solution into water, from $CHCl_3$ solution into acetone, and then from $CHCl_3$ solution into MeOH.

Synthesis of Dendritic Polyethers. Conventional liquid–liquid two-phase (organic solvent–aqueous NaOH solution) phase-transfer-catalyzed polyetherification conditions were used for the preparation of dendritic polyethers. The polyetherification of the AB_2 type monomer **23** was carried out under a nitrogen atmosphere at 80 °C in an *o*-dichlorobenzene–10 N NaOH solution (10-fold molar excess of NaOH versus phenol groups) in the presence of TBAH followed by the alkylation of unreacted phenolate chain ends with alkyl bromide or benzyl chloride. An example of the polyetherification is as follows.

To a 25-mL single-neck flask equipped with a condenser and a nitrogen inlet–outlet were successively added **23** (0.144 g, 0.300 mmol), 10 N NaOH (0.6 mL), *o*-dichlorobenzene (0.6 mL), and TBAH (0.204 g, 0.600 mmol, 100 mol % of phenol groups). The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80 °C under nitrogen for 30 min. Then benzyl chloride (0.0418 g, 0.33 mmol) and *o*-dichlorobenzene (0.6 mL) were added to the reaction mixture. After 30 min of reaction at 80 °C, the organic and aqueous layers were diluted with $CHCl_3$ and water, respectively, and the aqueous layer was separated. The organic layer was washed with water, followed by dilute HCl, and again three times with water. The polymer was separated by the precipitation of its solution into MeOH to obtain 0.116 g (79%) of a white precipitate. The polymer was further purified by two successive precipitations from THF solution into water and dried in vacuo.

Techniques. ^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as an internal standard.

Relative molecular weights were determined by gel permeation chromatography (GPC). High-pressure liquid chromatography (HPLC) and GPC analysis were carried out 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 the UV detector, $CHCl_3$ as 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-4 differential scanning calorimeter equipped with a TADS data station Model 3600 was used to determine the thermal transitions. Heating and cooling rates were 20 °C/min in all cases. First-order transitions (liquid crystalline–isotropic etc.) were read at the maximum or minimum of the endothermic or exothermic peaks. 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 produced perfectly reproducible data. We will report the transitions collected from second or subsequent heating scans and from the first cooling scan.

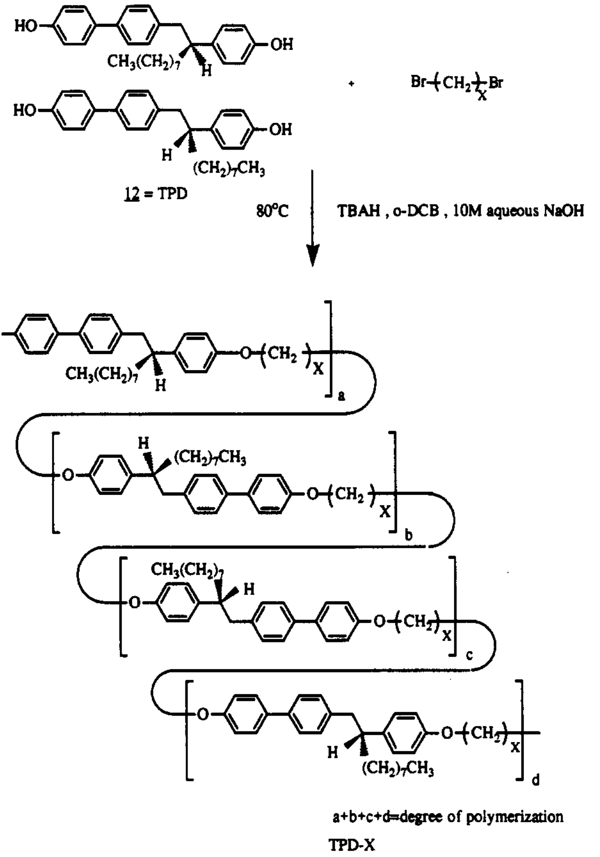
A Carl Zeiss optical polarizing microscope (magnification 100×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800

Table I
Characterization of Linear Polyethers (TPD-*X*) with Different Spacers (*X*) and of Dendritic Polyethers (TPD-b-*X*) with Different Chain Ends (*X*)[a]

polymer	*X*	yield (%)	M_n(GPC)	M_w/M_n(GPC)	thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses: heating	cooling
TPD-6	hexane	84.8	29800	1.6	g 31 n 71 (1.40) i	i 58 (1.51) n 24 g
TPD-7	heptane	94.1	27900	1.8	g 21 i	i 17 g
TPD-8	octane	92.2	27500	2.0	g 19 n 60 (1.58) i	i 47 (1.58) n 13 g
TPD-9	nonane	96.8	41800	2.0	g 17 i	i 10 g
TPD-10	decane	90.1	30800	1.8	g 15 n 55 (1.63) i	i 42 (1.70) n 8 g
TPD-b-Bz	benzyl	79.2	4700	3.8	g 48 n 60 (0.10) i	i 53 (0.15) n 43 g
TPD-b-4	butyl	70.3	4400	3.5	g 40 i	i 34 g
TPD-b-6	hexyl	82.2	4700	3.9	g 24 n 39 (0.15) i	i 30 (0.18) n 18 g
TPD-b-8	octyl	80.0	7900	2.6	g 20 n 40 (0.75) i	i 30 (0.70) n 15 g

[a] Data collected from second heating and first cooling DSC scans.

Scheme III
Synthesis of Linear Polyethers Based on 1-(4-Hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane and α,ω-Dibromoalkanes Containing *X* Methylene Units (TPD-*X*)



central processor was used to observe the thermal transitions and to analyze the textures.[21]

Results and Discussion

The synthesis of monomer **12** (TPD) is outlined in Scheme I and that of monomer **23** (TPD-b) in Scheme II. TPD was used to synthesize linear polyethers which are models of the dendritic polymers synthesized from monomer TPD-b. The decision for the synthesis of the AB_2 monomer TPD-b was made based on the phase behavior of polymers TPD-*X*. The phase behavior of both linear and dendritic polyethers was characterized by a combination of techniques consisting of differential scanning calorimetry and thermal optical polarized microscopy.

Scheme III outlines the polyetherification of TPD with α,ω-dibromoalkanes containing from six to ten methylene units. As shown in Scheme III, TPD has a stereocenter and, therefore, since we use the racemic mixture of its two enantiomers, upon polyetherification with α,ω-dibromoalkanes we generate a copolymer (TPD-*X*) containing all four constitutional isomers and stereoisomers of TPD. The results on the synthesis and characterization of TPD-*X* with *X* = 6–10 are summarized in Table I. The relative number-average molecular weights of all TPD-*X* polymers are close to or higher than 30 000. The DSC traces of their second heating and first cooling scans are presented in Figure 1. First, second, and subsequent DSC heating scans are almost identical. First and subsequent DSC cooling scans are also identical. As observed from these DSC traces, polymers TPD-6, TPD-8, and TPD-10 display an enantiotropic mesophase which exhibits on the optical

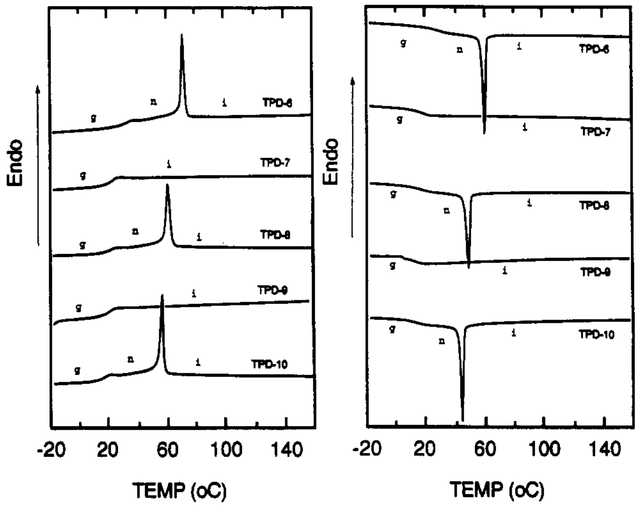


Figure 1. Second heating (a, left) and first cooling (b, right) DSC thermograms (20 °C/min) of linear polyethers based on TPD and α,ω-dibromoalkanes containing *X* methylene units (TPD-*X*).

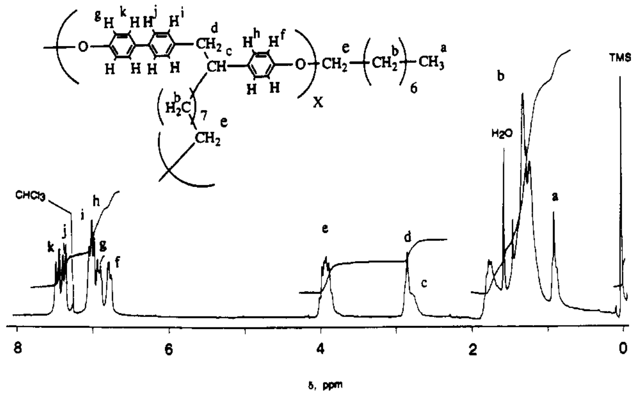
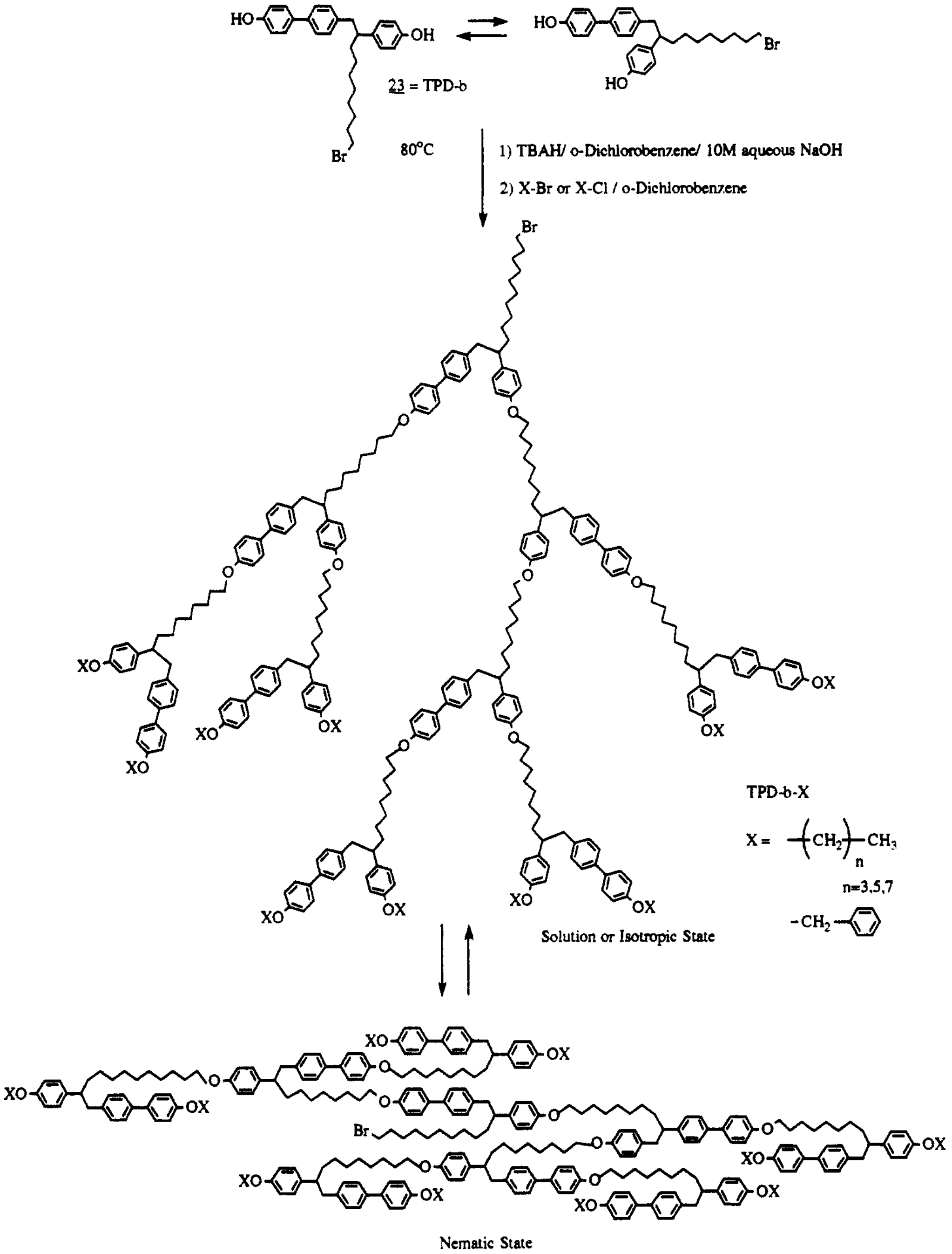


Figure 2. 200-MHz ^{1}H-NMR spectrum of TPD-b-8 ($CDCl_3$).

Scheme IV

Synthesis of Dendrimeric Polyethers Based on 10-Bromo-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)decane (TPD-b-*X*) and the Schematic Representation of the Transformation between Nematic and Isotropic Phases



polarized microscope a classic nematic texture, and, therefore, this phase is nematic. TPD-7 and TPD-9 are glassy polymers. This behavior can be understood by analogy with the phase behavior of the polyethers based on 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane and α,ω-dibromoalkanes.[17] Due to the odd–even effect of the isotropization transition temperatures, the isotropization values of the TPD-*X* with odd values of *X* are much lower than those of the polymers with even values of *X* and, therefore, are either located in close proximity of the glass transition temperature or below it. Consequently, the formation of the mesophase is kinetically prohibited for the case of the polymers with *X* = 7 and 9. These experiments have demonstrated that the most suitable AB_2 monomer for the preparation of a dendritic thermotropic nematic liquid crystalline polymer is TPD-b or similar monomers containing a lower but even number of methylene units in their bromoalkyl group. On the basis of the experimental results described above, monomers AB_2 with even and longer bromoalkyl groups than bromooctyl would generate dendrimers with lower isotropization transition temperatures, while similar monomers with an odd number of carbons in their bromoalkyl spacer would generate amorphous polymers.

Scheme IV outlines the synthesis of the TPD-b-*X* (where *X* is the structure of the chain ends) dendrimers by the homopolyetherification of TPD-b, which is a mesogenic monomer based on conformational isomerism.[16,17] The gauche conformer of TPD-b favors the synthesis of the dendritic architecture, while its anti conformer favors the formation of a conventional nematic liquid crystalline phase.

The results of the homopolyetherification of TPD-b are summarized in Table I. The homopolymer with *X* = H, i.e., the polymer containing phenol chain ends, could not be characterized because it is insoluble in halogenated

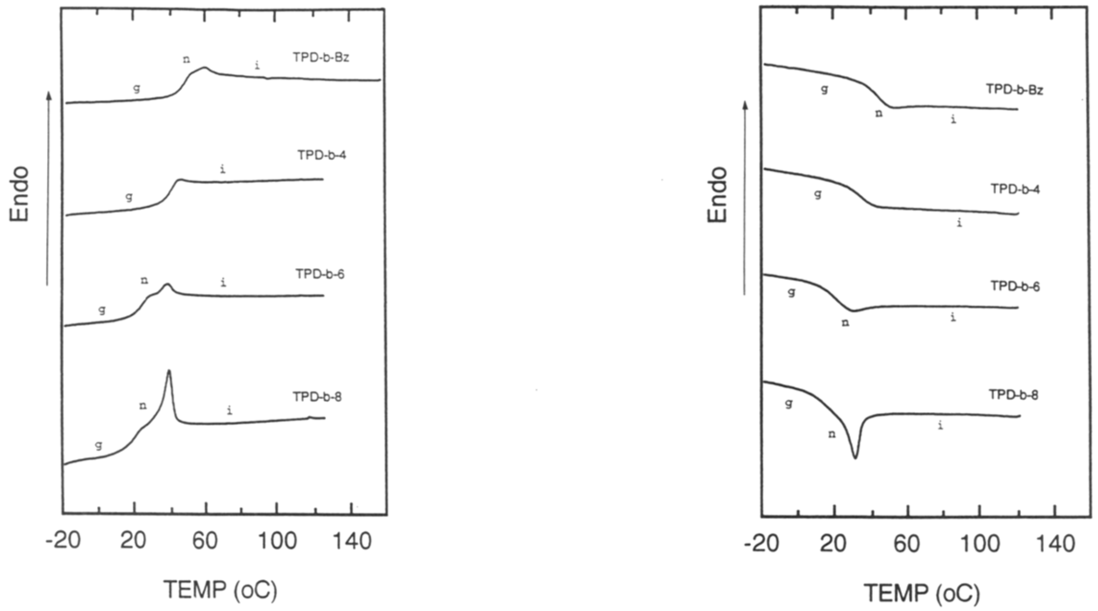


Figure 3. Second heating (a, left) and first cooling (b, right) DSC thermograms (20 °C/min) of dendrimeric polyethers based on TPD-b and alkyl bromide or benzyl chloride (TPD-b-*X*; *X* is the structure of the chain end groups, i.e., Bz = benzyl, 4 = butyl, 6 = hexyl, and 8 = octyl).

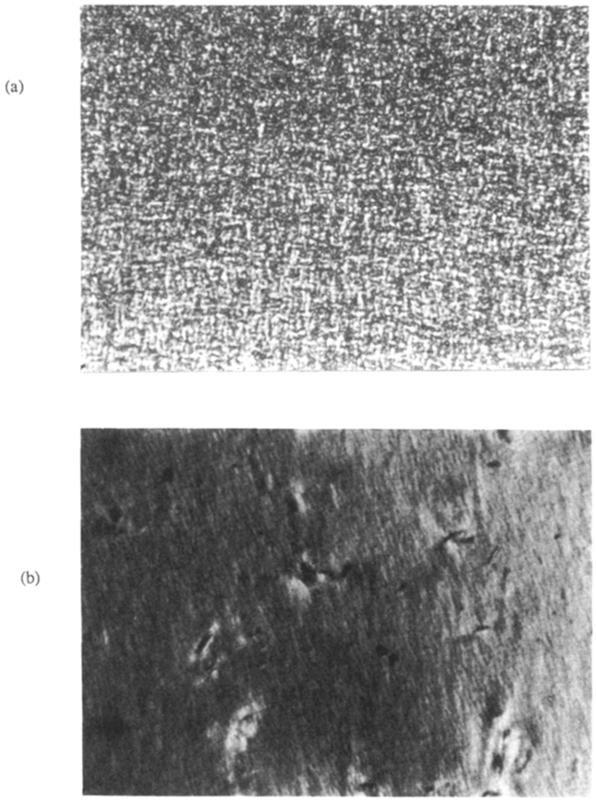


Figure 4. Optical polarized micrographs (300×) of (a) TPD-10 after annealing for 20 min at 43 °C and (b) TPD-b-8 after annealing for 1.5 h at 36 °C. The micrographs have been reduced to 55% of their original size for publication purposes.

and aromatic solvents, and in its deprotonated form it is soluble only in water. Therefore, at the end of the polymerization, the phenol chain ends of the TPD-b-*X* dendrimer were endcapped in the same reaction flask and the resulting polymers were characterized (Table I). The phenol chain ends of TPD-b-*X* were reacted with benzyl chloride (TPD-b-Bz), 1-butyl bromide (TPD-b-4), 1-hexyl bromide (TPD-b-6), and 1-octyl bromide (TPD-b-8), respectively. The characterization of TPD-b-*X* polymers is summarized in Table I. As we can observe from Table I, the molecular weights of the dendrimer are lower than those of the corresponding model linear polymers TPD-*X*. This is most probably due to an intramolecular alkylation of a phenol group by the alkyl bromide chain end of TPD-b. This reaction represents a chain termination and, therefore, limits the molecular weight of the polymer. For the range of molecular weights of TPD-b-*X* from Table I we did expect to observe the CH_2Br chain end of the polymer. Figure 2 shows a representative 200-MHz ^1H-NMR spectrum of TBD-b-8 together with its protonic assignments, which demonstrates the absence of the CH_2Br chain end.

The second heating and first cooling DSC traces of TPD-b-*X* dendrimers are presented in Figure 3. First, second, and subsequent heating DSC traces are almost identical. First and subsequent cooling DSC traces are also identical. As we can observe from Figure 3 and Table I, the nature of the polymer chain ends affects the glass transition temperature of the dendrimer. When the alkyl length of the chain end increases from butyl to octyl, the glass transition temperature of the dendrimer decreases from 40 to 20 °C. As a consequence, TPD-b-4 is only glassy, while TPD-b-6 and TPD-b-8 display enantiotropic nematic mesophases. The isotropization temperatures of TPD-b-6 and TPD-b-8 are identical and therefore are not affected by the nature of the polymer chain ends. The breadth of the temperature range of the mesophase is therefore determined by the glass transition temperature of the dendrimer. This result can be easily explained if we recall that, in the liquid crystalline phase of the liquid crystalline polymers with flexible spacers, the spacers intercalated between two mesogens are extended while the spacers from the polymer chain end are melted.[22] Consequently, the spacers between mesogens are determining the thermodynamic stability of the mesophase while the aliphatic chain ends being melted are lowering the glass transition temperature of the polymer. The TPD-b-*X* dendrimers have always the same spacer length between the mesogenic groups but different aliphatic chain ends. Therefore, the isotropization temperature should always be the same, while the glass transition should be affected dramatically by the nature of the chain ends. An exception is provided by the dendrimer with benzyl ether chain ends (TPD-b-

Bz), which exhibits a very narrow enantiotropic mesophase which undergoes isotropization at a higher temperature than that of the other TPD-b-*X* polymers. At the same time its glass transition temperature is also higher than those of the other TPD-b-*X* dendrimers. This behavior also can be explained if we consider that the benzyl ether chain end increases the length of the mesogenic unit and, therefore, has an opposite effect from that of the aliphatic chain ends. That is, it increases both the glass transition and the isotropization temperature of the dendrimer. All TPD-b-*X* dendrimers exhibit a lower isotropization transition temperature than that of their linear model TPD-8 (Table I). This is most probably due to the fact that the number of trans methylene units of the flexible spacer of TPD-b-*X* is lower than that of the trans methylene units of the flexible spacer of TPD-8. Also the molecular weights of the TPD-b-*X* dendrimers are lower than that of the linear model TPD-8, and this also contributes to the lower isotropization temperature of the dendrimers as compared to that of their linear models.

Scheme IV outlines the mechanism responsible for the formation of the conventional nematic mesophase exhibited by the TPD-b-*X* dendrimers. In solution and in the isotropic phase the TPD-b mesogenic unit of the dendrimers is most probably in its gauche conformer or in a dynamic equilibrium between the gauche and anti conformers and, therefore, generates the conventional architecture characteristic for dendrimers. On lowering the temperature of the isotropic melt, the TPD-b mesogen displays mostly or only the anti conformer.[16,17,22b,23] This conformational change transforms the architecture of the dendritic polymer from a treelike form into the compact form shown at the bottom of Scheme IV. This last architecture is expected based on simple thermodynamic considerations, since it lowers the free volume and, subsequently, the free energy of the system. Since long-range order can not be envisioned for a polymer architecture like this, it generates only a noncrystallizable uniaxial nematic mesophase. On the optical polarized microscope, TPD-b-*X* with *X* = Bz, 6, and 8 display a classic nematic texture. Representative examples of textures exhibited by the linear polymer TPD-10 and the dendrimer TPD-b-8 are presented in Figure 4.

These results have demonstrated the ability to synthesize dendrimers which exhibit thermotropic nematic liquid crystalline mesophases by using a suitable selection of their structural unit. We think this is a very rewarding result since it generates both a novel class of thermotropic nematic liquid crystalline polymers and a novel phase exhibited by dendritic polymers. Therefore, these results open new synthetic and theoretical opportunities in the areas of both liquid crystalline polymers and dendrimeric polymers.

Acknowledgment. Financial support by the National Science Foundation, Polymers Program (Grant DMR-86-19724), and Toyota Central Research & Development Laboratories, Nagoya, Japan, is gratefully acknowledged.

References and Notes

(1) (a) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *12*, 117. (b) For a review on dendrimers, see: Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(2) (a) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2004. (b) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849. (c) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176. (d) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Saunders, M. J.; Grossman, S. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1178. (e) Newkome, G. R.; Behera, R. K.; Moorefield, C. N.; Baker, G. R. *J. Org. Chem.* **1991**, *56*, 7162.

(3) (a) Padias, A. B.; Hall, H. K., Jr.; Tomalia, D. A.; McConnel, J. R. *J. Org. Chem.* **1987**, *52*, 5305. (b) Hall, H. K., Jr.; Polis, D. W. *Polym. Bull.* **1987**, *17*, 409. (c) Hall, H. K., Jr. *J. Macromol. Sci., Chem.* **1988**, *A25*, 729.

(4) (a) Shirota, Y.; Kobata, T.; Noma, N. *Chem. Lett.* **1989**, 1145. (b) Higuchi, A.; Inada, H.; Kobata, T.; Shirota, Y. *Adv. Mater.* **1991**, *3*, 549.

(5) (a) Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 7136. (b) Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1990**, *112*, 3687.

(6) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592.

(7) (a) Hawker, C.; Frecht, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010. (b) Wooley, K. L.; Hawker, C. J.; Frecht, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1059. (c) Hauker, C. J.; Frechet, J. M. J. *Macromolecules* **1990**, *23*, 4726. sen: (d) Wooley, K. L.; Hawker, J. C.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583. (e) Hawker, J. C.; Lee, R.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252. (f) Uhrich, K. E.; Boegeman, S.; Frechet, J. M. J.; Turner, R. S. *Polym. Bull.* **1991**, *25*, 551.

(8) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7077.

(9) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1991**, *24*, 3469.

(10) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043.

(11) (a) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346. (b) Kwock, E. W.; Neenan, T. X.; Miller, T. M. *Chem. Mater.* **1991**, *3*, 775.

(12) Moore, J. S.; Xu, Z. *Macromolecules* **1991**, *24*, 5893.

(13) Friberg, S. E.; Podzimek, M.; Tomalia, D. A.; Hedstrand, D. M. *Mol. Cryst. Liq. Cryst.* **1988**, *164*, 157.

(14) Kim, Y. H. *J. Am. Chem. Soc.*, in press and personal communication.

(15) Percec, V.; Cho, C. G.; Pugh, C.; Tomazos, D. *Macromolecules* **1992**, *25*, 1164.

(16) (a) Percec, V.; Yourd, R. *Macromolecules* **1989**, *22*, 524. (b) Percec, V.; Yourd, R. *Macromolecules* **1989**, *22*, 3229. (c) Percec, V.; Tsuda, Y. *Macromolecules* **1990**, *23*, 5. (d) Percec, V.; Tsuda, Y. *Macromolecules* **1990**, *23*, 3520. (e) Percec, V.; Zuber, M.; Cheng, S. Z. D.; Zhang, A. Q. *J. Mater. Chem.* **1992**, *2*, 407.

(17) Percec, V.; Kawasumi, M. *Macromolecules* **1991**, *24*, 6318.

(18) (a) Nystrom, R. F.; Berger, C. R. *J. Am. Chem. Soc.* **1958**, *80*, 2896. (b) Albrecht, W. L.; Gustafson, D. H.; Horgan, S. W. *J. Org. Chem.* **1972**, *37*, 3355.

(19) (a) Schwarz, M.; Oliver, J. E.; Sonnet, P. E. *J. Org. Chem.* **1975**, *40*, 16. (b) Anderson, A. G.; Jr.; Freenor, F. J. *J. Org. Chem.* **1972**, *37*, 626. (c) Horner, L.; Oediger, H.; Hoffman, H. *Justus Liebigs Ann. Chem.* **1959**, *626*, 26.

(20) McOmie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289.

(21) (a) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, 1978. (b) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals. Textures and Structures*; Heyden and Son Inc.: Philadelphia, 1984.

(22) (a) Yoon, D. Y.; Flory, P. J. *Mater. Res. Soc. Symp. Proc.* **1989**, *134*, 11. (b) Yoon, D. Y.; Sigaud, G.; Sherwood, M.; Wade, C.; Percec, V.; Kawasumi, M., to be published. (c) Sigaud, G. In *Phase Transitions in Liquid Crystals*, Proceedings of NATO Advanced Study Institute, to be published.

(23) (a) Percec, V.; Zuber, M. *Polym. Bull.* **1991**, *25*, 695. (b) Petraccone, V.; Pirozzi, B. *Macromolecules* **1991**, *24*, 6470. (c) Yandrasits, M. A.; Cheng, S. Z. D.; Zhang, A.; Cheng, J.; Wunderlich, B.; Percec, V. *Macromolecules* **1992**, *25*, 2112.

Registry No. **1**, 92-69-3; **3**, 104-01-8; **7**, 136089-74-2; **8**, 141848-14-8; **11**, 141848-15-9; **12**, 141848-16-0; **13**, 613-37-6; **14**, 4693-91-8; **15**, 141848-17-1; **16**, 17696-11-6; **17**, 29823-21-0; **18**, 50816-19-8; **19**, 79918-35-7; **20**, 141848-18-2; **21**, 141848-19-3; **22**, 141848-20-6; **23**, 141848-21-7; TPD-6, 141848-22-8; TPD-7, 141848-23-9; TPD-8, 141848-24-0; TPD-9, 141848-25-1; TPD-10, 141848-26-2; $CH_3(CH_2)_7I$, 629-27-6.