Liquid-Crystalline Polyethers Based on Conformational Isomerism. 18.[†] Polyethers Based on a Combined Mesogenic Unit Containing Rigid and Flexible Groups: 1-(4-Hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane

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ABSTRACT: The synthesis of the racemic mesogenic unit 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)-butane (TPB) which represents a combination based on rigid and flexible groups is presented. The "polyethers" based on TPB and α,ω-dibromoalkanes (TPB-X) containing from 4 to 20 methylenic units (X) were synthesized by phase-transfer-catalyzed polyetherification and characterized by a combination of differential scanning calorimetry and thermal optical polarized microscopy. All polymers are soluble in conventional solvents at room temperature. TPB-X polyethers are copolymers containing four different constitutional isomeric structural units derived from the two enantiomers of TPB. TPB-5 is glassy. TPB-4 to TPB-10 exhibit only an enantiotropic nematic mesophase. TPB-11 to TPB-15 and TPB-17 exhibit a crystalline and an enantiotropic nematic mesophase and TPB-16 a crystalline phase and a monotropic nematic mesophase, while TPB-18 to TPB-20 are only crystalline. The phase behavior of TPB-X was explained by analyzing the various trends of the dependences of the glass transition, nematic–isotropic, isotropic–nematic, melting, and crystallization temperatures as a function of X.

Introduction

The traditional synthetic procedure employed in the preparation of main-chain and side-chain liquid-crystalline polymers is based on the use of the concept of the rigid-rodlike mesogenic unit.[1–10] Additional classes of mesogenic groups were recently reviewed.[11]

In the previous publications from this series we have advanced the concept of the flexible rodlike mesogenic unit or rodlike mesogenic unit based on conformational isomerism. This concept was already used to synthesize main-chain liquid-crystalline polyethers based on conformational isomerism without[12] and with[13,14] flexible spacers. Recently we discussed critically the similarities and differences between flexible, semiflexible, and rigid-rodlike mesogens.[15] It has been demonstrated that these polymers can be used to tailor-make nematic,[13,14,16] smectic,[17a] and hexagonal columnar[17b] mesophases. The first examples of polymers exhibiting two nematic mesophases were also provided by these polymers.[14b] Additional examples of liquid-crystalline polymers based on conformational isomerism were reported from other laboratories.[18–21] So far the experiments reported from our laboratory were performed with polyethers and copolymers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE)[13,14] or 1,2-bis(4-hydroxyphenyl)ethane (BPE)[17] and α,ω-dibromoalkanes. Most of the polyethers based on MBPE exhibited virtual mesophases[14b] which were determined by using a copolymerization technique elaborated in our laboratory.[13,14]

Recently we reported a thermodynamic scheme which correlates the thermodynamic stabilities of liquid-crystalline (i.e., virtual, monotropic, and enantiotropic) and crystalline phases.[22,23] The definition of virtual, monotropic, and enantiotropic mesophases and their interconversion was also discussed previously.[22] According to this scheme,[22,23] the transformation of a virtual and monotropic mesophase into an enantiotropic mesophase can be accomplished by increasing both the rigidity (i.e., by decreasing the entropy of the mesophase, by increasing the free energy of the isotropic phase, and, therefore, by increasing the isotropization temperature) and the disorder (i.e., by decreasing the perfection of the crystalline phase which increases its free energy and therefore decreases the melting temperature) of the molecule. Additional details on this manipulation of the phase transitions are available.[22,23] The goal of this paper is to demonstrate this concept. The previously used flexible mesogens were based on substituted or unsubstituted BPE. We will increase the rigidity of this mesogen by substituting a phenyl unit with a biphenyl unit and will increase its disorder by substituting the 1,2-ethane unit with a 1,2-butane unit. The replacement of 1,2-ethane with 1,2-butane adds a lateral ethyl substituent to the BPE mesogen. This lateral substituent decreases the order of the mesogen in the crystalline phase and, therefore, lowers its melting point. In addition, as will be discussed in more detail later, this new mesogen increases the number of constitutional isomeric structural units of the resulting polymer, from one to four, and this decreases even more the degree of order of the polymer chains in the crystalline phase. The resulting mesogenic unit is 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB). The synthesis and phase behavior of polyethers based on this mesogen and α,ω-dibromoalkanes containing X number of methylenic units (TPB-X, X = 4–20) will be described.

Experimental Section

Materials. 1,4-Dibromobutane (99%), 1,6-dibromohexane (97%), 1,7-dibromoheptane (97%), 1,8-dibromooctane (98%), 1,9-dibromononane (97%), 1,10-dibromodecane (97%), and 1,11-dibromoundecane (98%) (all from Aldrich) were used as received. 1,5-Dibromopentane (97%, Aldrich) was fractionated by vacuum distillation. 1,12-Dibromododecane (technical, Aldrich) was purified by recrystallization from methanol. 1,16-Dibromohexadecane (Pfaltz and Bauer) and 1,18-dibromooctadecane (K and K Laboratories) were used as received. 1,13-Dibromotridecane, 1,14-dibromotetradecane, 1,15-dibromopentadecane, 1,17-dibromoheptadecane, 1,19-dibromononadecane, and 1,20-dibromoeicosane were synthesized as described

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in a previous publication and papers cited therein.[14b] All other chemicals were commercially available and were used as received.

Synthesis of (4-Hydroxyphenyl)acetic Acid (4). 4 was prepared by the demethylation of (4-methoxyphenyl)acetic acid (3). (4-Methoxyphenyl)acetic acid (49.9 g, 0.30 mol) was dissolved in a mixture of 48% hydrobromic acid (113 mL, 1.0 mol) and acetic acid (400 mL) in a 1-L round-bottom flask equipped with reflux condenser and magnetic stirrer. The resulting solution was heated to reflux for 12 h (reflux temperature, 111 °C) after which the reaction mixture was cooled to room temperature. The excess of hydrobromic acid and acetic acid was removed under reduced pressure in the presence of an appropriate amount of water to avoid esterification. White crystals separated from the solution. They were separated by filtration and recrystallized from water (100 mL) to yield 42.7 g (93.6%) of large needlelike crystals. Mp: 146–152 °C (lit.[24] mp 148 °C). ^{1}H NMR (acetone-d_6, TMS): δ 3.51 (2 protons, $-CH_2-$, s), 6.80 (2 protons, ortho to the hydroxy of the phenyl ring, d, J = 8.8 Hz), 7.11 (2 protons, meta to the hydroxy of the phenyl ring, d, J = 6.9 Hz). The ^{1}H NMR spectrum showed that the resulting 4 is free of unreacted methoxy groups.

Synthesis of (4-Acetoxyphenyl)acetic Acid (5). (4-Acetoxyphenyl)acetic acid (5) was prepared by the acetylation of (4-hydroxyphenyl)acetic acid (4). (4-Hydroxyphenyl)acetic acid (4; 42.7 g, 0.281 mol) and acetic anhydride (53 mL, 0.562 mol) were placed in a 250-mL round-bottom flask equipped with reflux condenser and magnetic stirrer. A few drops of sulfuric acid was added, and the reaction mixture was stirred at 50 °C for 2 h. Then it was allowed to cool to room temperature. A total of 150 mL of water was added, and the mixture was stirred to produce a white precipitate. The precipitate was separated by filtration, washed with water, and dried to yield 37.2 g (68%) of white fine crystals. Mp: 105–108 °C (lit.[25] mp 108–110 °C). ^{1}H NMR ($CDCl_3$, TMS): δ 2.29 (3 protons, CH_3-, s), 3.59 (2 protons, $-CH_2-$, s), 7.08 (2 protons, ortho to the acetoxy of the phenyl ring, d, J = 8.3 Hz), 7.32 (2 protons, meta to the acetoxy of the phenyl ring, d, J = 8.3 Hz).

Synthesis of 4-Acetoxybiphenyl (2). 4-Acetoxybiphenyl (2) was prepared by the acetylation of 4-phenylphenol (1). 4-Phenylphenol (1); 51.1 g, 0.30 mol) and acetic anhydride (42 mL, 0.45 mol) were placed in a 250-mL round-bottom flask equipped with reflux condenser and magnetic stirrer. After the addition of a few drops of sulfuric acid, the reaction mixture was stirred at 60 °C for 2 h. Then it was cooled to room temperature, 200 mL of water was added, and the mixture was stirred until a white solid separated. The precipitate was washed with water and recrystallized from 95% ethanol to give 57.2 g (89.8%) of white crystals. Purity (HPLC): 100%. Mp: 86–88 °C (lit.[26] mp 86–87 °C). ^{1}H NMR ($CDCl_3$, TMS): δ 2.32 (3 protons, CH_3-, s), 7.19 (2 protons, ortho to the acetoxy of the substituted phenyl ring, d, J = 8.8 Hz), 7.45 (3 protons, meta and para of the unsubstituted phenyl ring, m), 7.55 (2 protons, meta to acetoxy of the substituted phenyl ring, d, J = 7.4 Hz), 7.57 (2 protons, ortho of the unsubstituted phenyl ring, d, J = 8.7 Hz).

Synthesis of 1-(4-Acetoxy-4′-biphenyl)-2-(4-acetoxyphenyl)ethanone (7). (4-Acetoxyphenyl)acetic acid (5; 29.1 g, 150 mmol) was dissolved in 150 mL of dry methylene chloride in a 500-mL three-necked flask equipped with a dropping funnel, nitrogen inlet–outlet, and magnetic stirrer. Thionyl chloride (16.4 mL, 225 mmol) was added dropwise to this solution. The resulting mixture was refluxed for 16 h after which methylene chloride and excess thionyl chloride were removed under reduced pressure to produce a yellow liquid which was used directly in the acylation reaction. 4-Acetoxybiphenyl (2; 38.2 g, 180 mmol) was dissolved in 150 mL of methylene chloride in a 500-mL three-necked flask equipped with a nitrogen inlet–outlet, thermometer, dropping funnel, and magnetic stirrer. The solution was cooled to below 10 °C in an ice–water bath after which 72.0 (540 mmol) of anhydrous $AlCl_3$ was added. (4-Acetoxyphenyl)acetyl chloride (6) was dissolved in 150 mL of dry methylene chloride. This solution was added dropwise to the solution of 4-acetoxybiphenyl so that the reaction temperature did not rise above 10 °C. After the addition, the deep red solution was stirred at room temperature for 3 h. Then it was poured into a mixture of 75 mL of concentrated HCl, 600 mL of ice–water, and 300 mL of chloroform. The organic layer was separated and washed twice each time with 500 mL of water, after which it was dried over anhydrous $MgSO_4$ and filtered and the solvents were removed in a rotary evaporator to produce an orange solid. The solid was washed twice each time with 200 mL of hot 95% ethanol and dried to yield 48.4 g (83.1%) of crystals. After recrystallization from 1.3 L of toluene, 40.4 g (69.3%) of white crystals was obtained. Purity (HPLC): 92.7%. Mp: 195–198 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 2.29 (3 protons, $CH_3COOPhCH_2-$, s), 2.33 (3 protons, CH_3COO-biphenyl, s), 4.30 (2 protons, $-CH_2-$, s), 7.09 (2 protons, ortho to the acetoxy of the monophenyl ring, d, J = 9.3 Hz), 7.22 (2 protons, ortho to the acetoxy of the biphenyl ring, d, J = 7.9 Hz), 7.28 (2 protons, meta to the acetoxy of the monophenyl ring, d, J = 8.8 Hz), 7.64 (4 protons, meta to the acetoxy of the biphenyl ring and meta to the acyl, dd, J = 8.0 Hz, J = 8.9 Hz), 8.06 (2 protons, para to the acyl, d, J = 9.3 Hz).

Synthesis of 1-(4-Ethoxy-4′-biphenyl)-2-(4-ethoxyphenyl)butanone (8). 1-(4-Acetoxy-4′-biphenyl)-2-(4-acetoxyphenyl)ethanone (7; 10.5 g, 97 mmol) was dissolved in 160 mL of tetrahydrofuran in a 1-L three-necked flask equipped with reflux condenser and magnetic stirrer. To this solution was successively added iodoethane (15.2 g, 97 mmol), tetrabutylammonium hydrogen sulfate (3.2 g, 9.4 mmol), and 160 mL of a 50% (w/w) NaOH–water solution. The reaction mixture was stirred vigorously at 60 °C for 10 h. During the reaction the color of the solution changed from orange to slight yellow. The organic and aqueous layers were diluted with 400 mL of water and 400 mL of chloroform, respectively, after which the organic layer was separated and washed with 200 mL of water. To this organic layer was added a mixture of 100 mL of concentrated HCl and 200 mL of water. Then it was stirred for 30 min, and the organic layer was separated, washed with 300 mL of water, and dried over magnesium sulfate. The solvents were removed in a rotary evaporator to give a yellow solid which was dissolved in 60 mL of tetrahydrofuran in a one-necked flask equipped with magnetic stirrer. To this solution were successively added iodoethane (4.21 g, 27 mmol), tetrabutylammonium hydrogen sulfate (1.08 g, 3.2 mmol), and 60 mL of a 50% NaOH–water solution. The reaction mixture was stirred vigorously at room temperature. After 1 h the product was extracted with 200 mL of chloroform and 200 mL of water. The organic layer was separated and washed sequentially with 200 mL of water, a mixture of 40 mL of concentrated hydrochloric acid, and 160 mL of water and two times with 200 mL of water. Then it was dried over magnesium sulfate and filtered, and the solvents were removed on a rotary evaporator. The resulting white solid was recrystallized from 200 mL of methanol to yield 6.21 g (59.1%) of white crystals. Purity (HPLC): 97.3%. Mp: 123–125 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 0.87 (3 protons, $-CHCH_2CH_3$, t, J = 7.1 Hz), 1.40 (6 protons, $-OCH_2CH_3$, tt, J = 6.9 Hz and J = 6.9 Hz), 2.01 (2 protons, $-CHCH_2CH_3$, m), 4.02 (4 protons, $-OCH_2CH_3$, qq, J = 6.8 Hz and J = 6.7 Hz), 4.41 (1 proton, $-CHC{=}O$, t, J = 7.2 Hz), 6.85 (2 protons, ortho to the ethoxy of the monophenyl ring, d, J = 8.2 Hz), 6.99 (2 protons, ortho to the ethoxy of the biphenyl ring, d, J = 8.4 Hz), 7.21 (2 protons, meta to the ethoxy of the monophenyl ring, d, J = 7.9 Hz), 7.55 (4 protons, meta to the ethoxy of the biphenyl ring and meta to the acyl of the biphenyl ring, 2d, J = 9.8 Hz and J = 9.3 Hz), 7.99 (2 protons, ortho to the acyl of the biphenyl ring, d, J = 8.4 Hz).

Synthesis of 1-(4-Ethoxy-4′-biphenyl)-2-(4-ethoxyphenyl)butane (11). 11 was prepared by the reduction of 1-(4-ethoxy-4′-biphenyl)-2-(4-ethoxyphenyl)butanone (8) with $LiAlH_4$–$AlCl_3$.[27,28] $AlCl_3$ (12.5 g, 94 mmol) was placed in a 100-mL three-necked flask equipped with a dropping funnel, nitrogen inlet–outlet, and magnetic stirrer and cooled in an ice–water bath, after which dry diethyl ether was added dropwise under nitrogen. $LiAlH_4$ (1.63 g, 43 mmol) was placed in a 250-mL three-necked flask equipped with a dropping funnel, nitrogen inlet–outlet, and magnetic stirrer and cooled in an ice–water bath. To the flask containing $LiAlH_4$ were added successively 35 mL of dry diethyl ether, the solution of the $AlCl_3$ diethyl ether complex, and 35 mL of dry chloroform. A solution of 8 (6.21 g, 16 mmol) in 35 mL of dry chloroform was dropwise to the reducing agent solution maintained at 0 °C. The resulting reaction mixture was stirred at room temperature for 3 h. To this mixture was added dropwise a solution of 40 mL of concentrated HCl and 50 mL of water. After the reaction mixture was stirred for 5 h, the product was extracted with 200 mL of chloroform. The organic layer was separated, washed two times with 300 mL of water, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to give a white solid. The solid was recrystallized from 500 mL of methanol to yield 4.70 g (78.4%) of white needlelike crystals. Purity (HPLC): 99.8%. Mp: 107–109 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ 0.77 (3 protons, $-\mathrm{CHCH_2C}H_3$, t, *J* = 7.3 Hz), 1.39 (6 protons, $-\mathrm{OCH_2C}H_3$, tt, *J* = 6.9 Hz), 1.64 (2 protons, $-\mathrm{CHC}H_2\mathrm{CH_3}$, m), 2.67 (1 proton, $-\mathrm{C}H-$, m), 2.86 (2 protons, $\mathrm{PhC}H_2\mathrm{CH}-$, d, *J* = 7.0 Hz), 4.03 (4 protons, $-\mathrm{OC}H_2\mathrm{CH_3}$, qq, *J* = 7.4 Hz), 6.83 (2 protons, ortho to the ethoxy of the monophenyl ring, d, *J* = 8.9 Hz), 6.96 (2 protons, ortho to the ethoxy of the biphenyl ring, d, *J* = 9.4 Hz), 7.05 (4 protons, ortho to the methylene of the biphenyl ring and meta to the ethoxy of the monophenyl ring, dd, *J* = 7.9 Hz and *J* = 8.9 Hz), 7.37 (2 protons, meta to the ethoxy of the biphenyl ring, d, *J* = 7.8 Hz), 7.46 (2 protons, meta to the methylene of the biphenyl ring, d, *J* = 8.8 Hz). The ^{1}H NMR spectrum showed that 11 is 100% pure and therefore free of unreacted ketone 8.

Synthesis of 1-(4-Hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (12). A 250-mL three-necked flask equipped with a dropping funnel, nitrogen inlet–outlet, and magnetic stirrer was cooled in a dry ice–acetone bath. To this flask were added 30 mL of dry methylene chloride and 30 mL of 1.0 M $\mathrm{BBr_3}$ solution in methylene chloride (30 mmol).[29] A solution of 11 (4.70 g, 12.5 mmol) in 60 mL of dry methylene chloride was added dropwise to the $\mathrm{BBr_3}$ solution. After the addition, the mixture was stirred at room temperature for 16 h. To this reaction mixture were added slowly 30 mL of water and 200 mL of diethyl ether. The organic layer was separated, washed two times with 100 mL of water, and dried over anhydrous magnesium sulfate. The solvent was evaporated on a rotary evaporator to produce a white solid which was recrystallized two times from 100 mL of toluene to yield 3.11 g (78.1%) of white needlelike crystals. Purity (HPLC): >99.8%. Mp: 145–146 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ 0.77 (3 protons, $-\mathrm{C}H_3$, t, *J* = 7.1 Hz), 1.69 (2 protons, $\mathrm{CH_3C}H_2-$, m), 2.68 (1 protons, $-\mathrm{C}H-$, m), 2.85 (2 protons, $\mathrm{PhC}H_2\mathrm{CH}-$, d of d, *J* = 5.8 Hz and 8.3 Hz), 4.62 (1 proton, $-\mathrm{CHPhO}H$, s), 4.82 (1 proton, *H*O-biphenyl, s), 6.77 (2 protons, ortho to the hydroxy of the monophenyl ring, d, *J* = 8.5 Hz), 6.91 (2 proton, ortho to the hydroxy of the biphenyl ring, d, *J* = 9.3 Hz), 6.98 (2 proton, meta to the hydroxy of the monophenyl ring, d, *J* = 8.8 Hz), 7.09 (s protons, ortho to the methylene of the biphenyl ring, d, *J* = 8.9 Hz), 7.37 (2 protons, meta to the hydroxy of the biphenyl ring, d, *J* = 7.7 Hz), 7.43 (2 protons, meta to the methylene of the biphenyl ring, d, *J* = 8.6 Hz).

Synthesis of Polyethers. Conventional liquid–liquid two-phase (organic solvent–aqueous NaOH solution) phase-transfer-catalyzed polyetherification conditions were used for the preparation of polyethers.[13] The polyetherifications were carried out under a nitrogen atmosphere at 80 °C in an *o*-dichlorobenzene–10 N NaOH–water solution (10 times the molar excess of NaOH versus phenol groups) in the presence of tetrabutylammonium hydrogen sulfate (TBAH) as phase-transfer catalyst. The molar ratio of nucleophilic to electrophilic monomers was in every case 1.0/1.0. An example of copolyetherification is as follows.

To a 25-mL single-necked flask equipped with a condenser and nitrogen inlet–outlet were successively added 0.191 g (0.600 mmol) of 12, 1.2 mL of *o*-dichlorobenzene, 0.163 g (0.600 mmol) of 1,8-dibromooctane, 1.2 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 6 h of reaction, the organic and aqueous layers were diluted with chloroform and water, respectively, and the aqueous layer was separated. The organic layer was washed with water, followed by dilute hydrochloric acid, and again with water three times. The polymer was separated by precipitation of its solution into methanol to obtain 0.251 g (98%) of white fibrous precipitate. The polymer was further purified by two successive precipitations from chloroform solution first into acetone and then into methanol.

Techniques. ^{1}H NMR (200-MHz) spectra were recorded on a Varian XL-200 spectrometer.

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, chloroform 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 (crystalline–crystalline, crystalline–liquid crystalline, 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. A detailed discussion on the influence of the thermal history of the sample on phase transitions of polyethers based on MBPE was presented in a previous publication.[14] We will report the transitions collected from first and second or subsequent heating scans and from the first cooling scan.

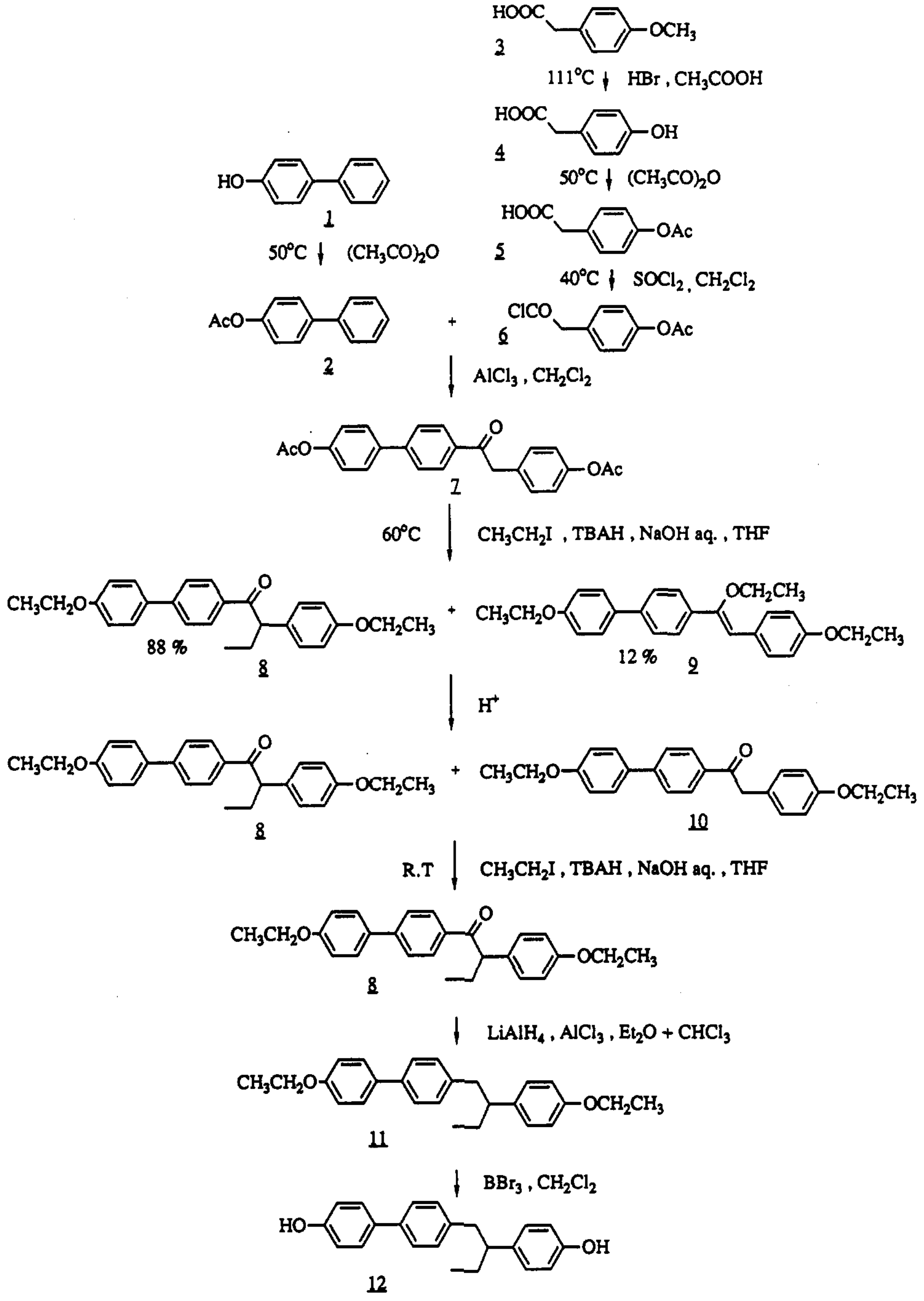
A Carl Zeiss optical polarizing microscope (magnification 100×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the textures.[30,31]

Results and Discussion

Scheme I outlines the synthesis of 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (12). Monomer 12 has a chiral center (Scheme II). However, its synthesis by the sequence of the reactions from Scheme I results in a racemic mixture. There are only a few experimental details concerning the synthesis of 12 which we would like to mention. Although 4 is commerically available, we prefer to prepare it from 3 since this route is less expensive. The alkylation of 7 with ethyl iodide was performed under various reaction conditions. A high yield of C-alkylated product 8 (88%) was obtained under the experimental conditions described in the Experimental Section. By decreasing the reaction temperature from 60 to 25 °C the yield of the C-alkylated product increases to 94%. However, at this temperature the etherification of the phenol groups is very slow and therefore we prefer to perform the reaction at 60 °C. The rest of the alkylated product obtained at 60 °C (12%) results from the O-alkylation of the carbonyl group 7 and is 9. During this alkylation step the cleavage of the acetyl groups of 7 takes place and the resulting phenol groups are alkylated to produce 8 and 9. Since the separation of 9 from 8 was very difficult, we cleaved the ethyl vinyl ether group of 9 from the mixture containing both 9 and 8 to produce a mixture containing 8 and 10. The mixture of 8 and 10 was realkylated to produce almost pure 8. After recrystallization from methanol, 8 was separated in 97.3% purity. It is very important that the keto group of 8 is reduced quantitatively to $-\mathrm{CH_2}-$. This was accomplished by using a $\mathrm{LiAlH_4}$–$\mathrm{AlCl_3{\cdot}Et_2O}$ reducing system,[40,41] in $\mathrm{CHCl_3}$. Compound 12 was obtained by the deethylation of 11 with $\mathrm{BBr_3}$ in $\mathrm{CH_2Cl_2}$.[42] When 12 contains a small amount of unreacted keto groups, it leads to cross-linked polymers. This is due to the additional C alkylation of the –CH– unit activated by the C═O group. Therefore, it is essential that 12 does not contain any product with unreduced C═O groups.

Table I presents the yields and the molecular weights of polyethers (TPB-*X*) obtained by the phase-transfer-catalyzed polyetherification of 12 with α,ω-dibromoalkanes containing from 4 to 20 methylenic units (*X*). According to our[32] and others[33-35] results, the number-average molecular weights of TPB-*X* are higher than those below

Scheme I
Synthesis of 1-(4-Hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane (TPB)



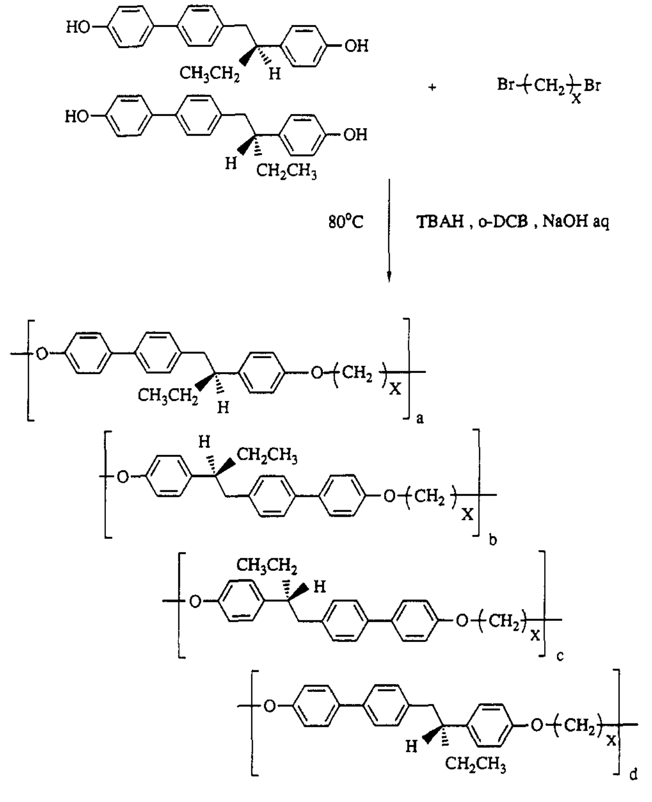
which phase-transition temperatures are molecular weight dependent. Therefore, we can compare the phase-transition temperatures of various TPB-*X* as a function of the number of carbons in the flexible spacer *X*.

Regardless of the spacer length, both TPB-*X* containing odd and even numbers of methylenic units in the spacer are soluble at room temperature in solvents like chloroform, tetrahydrofuran, chlorobenzene, *o*-dichlorobenzene, methylene chloride, etc. This is in contrast to polyethers and copolyethers based on α,ω-dibromalkanes and 4,4′-dihydroxybiphenyl which exhibit a very low solubility even at high temperature.[36] Also, polyethers based on MBPE and α,ω-dibromoalkanes containing low numbers of even methylenic units and high numbers of both odd and even methylenic units are soluble only at high temperatures.[14b] However, the solubility of copolyethers both of 4,4′-dihydroxybiphenyl[36] and of MBPE[14a] containing two or more than two flexible spacers increases versus that of the parent homopolymers. This effect is due to an increased entropy which decreases the ability of the polymer to crystallize.[22,23]

An inspection of Scheme II can easily explain the high solubility of the "homopolyethers" TPB-*X*. Since the monomer 12 represents in fact a racemic mixture of two enantiomers, the resulting "homopolymers" are in fact copolymers containing four different constitutional isomeric structural units. Such a structure has a high configuration entropy and should lead to TPB-*X* with low crystallization tendency and, therefore, high solubility. The rigidity of monomer 12 is higher than that of MBPE. However, since the homopolymers of 12 are quaternary copolymers while the homopolymers of MBPE are binary copolymers of constitutional isomeric structural units, the solubility of TPB-*X* is higher than that of MBPE-*X*.

Figure 1a presents the second heating while Figure 1b presents the first cooling DSC scans of TPB-*X*. With the exception of TPB-9 and TPB-10 the first DSC heating

Scheme II Synthesis of Polyethers Based on 1-(4-Hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane and α,ω-Dibromoalkanes Containing X Methylenic Units (TPB-X)



scans are almost identical with the second and subsequent DSC scans. TPB-5 exhibits only a glass transition temperature. The other polymers from TPB-4 to TPB-10 exhibit an enantiotropic nematic mesophase. The nematic mesophase of TPB-7 is kinetically controlled since its isotropization temperature is very close to T_g. Therefore, both the temperature and the enthalpy associated with the isotropization of the nematic phase of TPB-7 are affected by the thermal history of the sample and are not as reliable as those of the other polymers. TPB-4 to TPB-10 do not crystallize on the second and subsequent heating scans and on the first and subsequent cooling scans. TPB-9 and TPB-10 exhibit a melting transition only on the first heating scan (Table I). Since these crystalline phases are located in the close proximity of the glass transition temperature, they are kinetically controlled and do not appear on subsequent DSC scans. Polymers with more than 10 methylenic units in the flexible spacer crystallize. Thus TPB-11 to TPB-15 and TPB-17 present an enantiotropic nematic mesophase, while TPB-18 to TPB-20 are only crystalline. The nematic mesophase of all these polymers was identified by thermal optical-polarized microscopy[30,31] and by X-ray diffraction experiments.[37] After proper annealing on the optical-polarized microscope all polymers exhibit a schlieren nematic texture.

The thermal transition temperatures and the corresponding enthalpy changes of TPB-X collected from second heating and first cooling scans are summarized in Table I. Data from the first heating scans are tabulated only for TPB-9 and TPB-10. The first and second DSC heating scans of the other polymers are almost identical. Some slight differences appear only for the enthalpy changes associated with the melting transitions.

Figure 2a presents the dependence of the glass transition (T_g), melting (T_m), and nematic to isotropic (T_{ni}) transition temperatures versus the number of methylenic units of the flexible spacer (X) of TPB-X. T_m and T_{ni} refer to data collected from the second DSC heating scan (Table I). The T_g values of TPB-4 to TPB-10 plotted in Figure 2a were determined from the second DSC heating scan while those of the polymers with longer spacers from the first heating scan. This is due to the fact that the T_g of glassy polymers are more accurate when determined from the second heating scan. However, TPB-11 to TPB-20 are crystalline polymers, and when separated by precipitation from solution, therefore, when characterized during the first DSC scans, they have a lower degree of crystallinity than after heating and cooling scans. Therefore, for crystallizable polymers the T_g values determined from the first DSC heating scan seem to be more accurate than those determined from the second DSC heating scan.

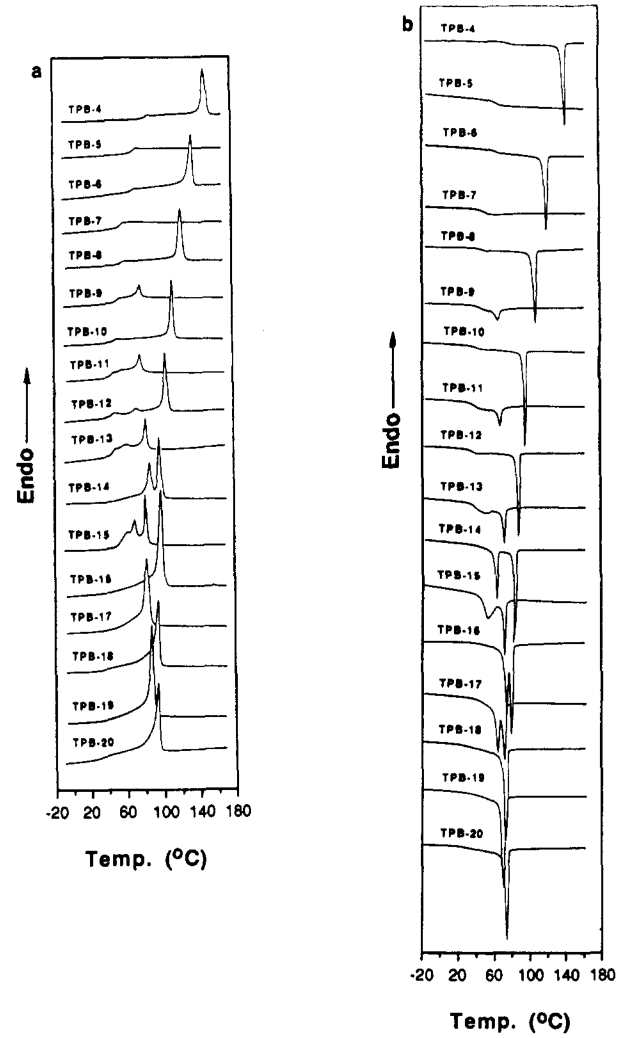


Figure 1. Second heating (a) and first cooling (b) DSC thermograms (20 °C/min) of polyethers based on TPB and α,ω-dibromoalkanes containing X methylenic units (TPB-X).

The dependences of T_{ni} and T_{in} versus X of TPB-X follow a similar trend as the corresponding virtual data reported for MBPE-X.[14b] That is, in addition to the odd–even dependence of T_{ni} and T_{in}, there is a continuous decrease of the transition temperatures for the polymers containing an even X and a continuous increase for the polymers containing an odd X (Figure 2a,b). This opposite trend provides a vanishing of the odd–even dependence at long flexible spacers. The same trend was observed for the series of polyethers based on 1-(4-hydroxyphenyl)-2-(2-chloro-4-hydroxyphenyl)ethane and α,ω-dibromoalkanes (ClBPE-X).[38] A discussion of the dependence of

Table I
Characterization of Polyethers Based on TPB and α,ω-Dibromoalkanes (TPB-X) with Different Numbers of Methylenic Units (X). Data Collected from Second Heating and First Cooling DSC Scans

				thermal transitions (°C) and corresponding enthalpy changes (K·cal/mru) in parentheses	
X	yield, %	$(M_n)_{GPC}$	$(M_w/M_n)_{GPC}$	heating	cooling
4	80.1	14 700	1.82	g 82 n 154 (2.04) i	i 142 (2.10) n 75 g
5	87.3	15 400	2.89	g 67 i	i 62 g
6	94.6	32 300	2.10	g 67 n 137 (2.16) i	i 122 (2.22) n 59 g
7	95.0	20 500	2.07	g 53 n 72 (0.05) i	i 60 (0.095) n 48 g
8	97.5	30 300	2.13	g 52 n 123 (2.43) i	i 107 (2.45) n 43 g
9	99.6	39 300	2.29	g 43 k 52 n 74 (0.78) i[a]	
				g 47 n 74 (0.78) i	i 62 (0.77) n 39 g
10	99.0	37 700	2.22	g 42 k 48 n 112 (2.54) i[a]	
				g 43 n 112 (2.54) i	i 96 (2.61) n 35 g
11	91.1	19 800	2.12	g 40 k 54 (0.24) n 74 (1.08) i	i 64 (1.09) n 47 (0.15) k 34 g
12	99.9	42 600	2.38	g 39 k 69 n 104 (2.56) i	i 88 (2.69) n 31 g
13	99.0	32 900	2.08	g 41 k 47 (0.39) n 79 (1.48) i	i 70 (1.52) n 47 (0.38) k 32 g
14	92.4	30 200	2.16	g 49 k 85 (1.83) n 96 (2.57) i	i 83 (2.71) n 60 (1.85) k 43 g
15	89.5	29 900	2.12	g 45 k 67 (2.21) n 80 (1.99) i	i 70 (2.14) n 50 (1.89) k 40 g
16	93.5	33 900	2.22	g 54 k 97 (6.50) i	i 79 (3.17) n 72 (3.13) k 41 g
17	99.4	38 000	2.60	g 47 k 79 n 81 i	i 70 (2.46) n 61 (2.59) k 40 g
18	95.5	37 100	3.88	g 37 k 91 (5.81) i	i 72 (5.61) k 35 g
19	89.1	36 700	2.22	g 40 k 86 (6.66) i	i 69 (6.48) k 36 g
20	98.5	39 200	2.45	g 36 k 93 (6.11) i	i 74 (5.44) k 27 g

[a] Data from first heating scan.

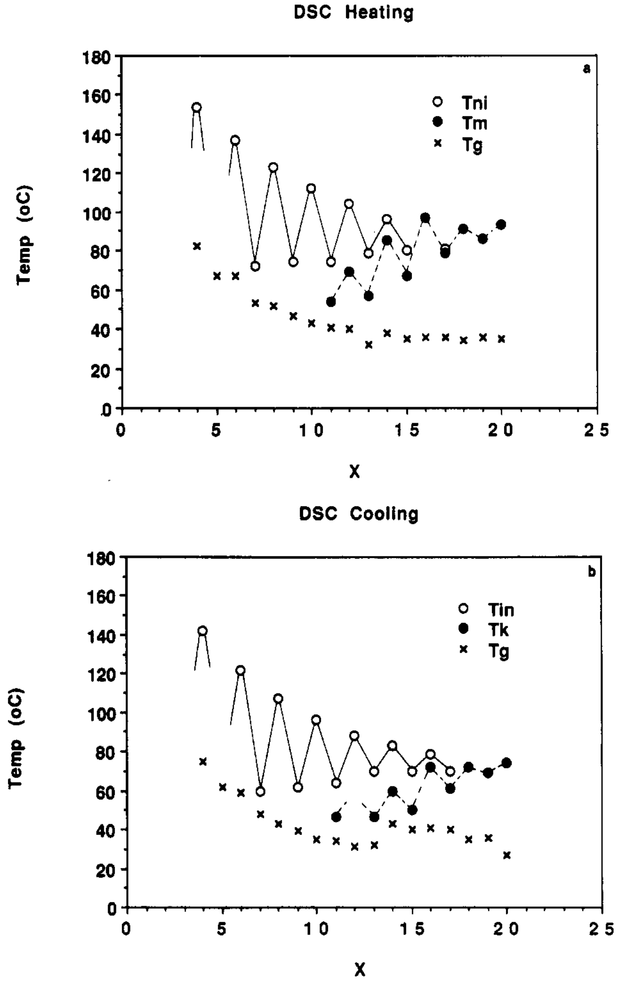


Figure 2. Dependence of phase-transition temperatures of TPB-X on the number of methylenic units in the flexible spacer (X): (a) data from the second heating scan (T_g data of TPB-11 to TPB-20 are from the first heating scan); (b) data from the first cooling scan.

T_{ni} versus spacer length for both model compounds and other polymers reported in the literature was presented previously.[14b] Both T_m and T_k of TPB-X are increasing with the increase of X (Figure 2a,b). At a certain value of X T_m and T_k values are higher than the T_{ni} (at X = 16) and T_{in} values (at X = 18). Consequently, with the exception of TPB-5 which is glassy the polymers from TPB-4 to TPB-15 and TPB-17 exhibit an enantiotropic mesophase. TPB-16 displays only a monotropic mesophase, and TPB-18 to TPB-20 are crystalline and therefore exhibit only virtual mesophases. In conclusion, the opposite trends of the dependences T_m, T_k versus those of T_{ni}, T_{in} as a function of X can easily explain the difference between the thermodynamic stability of the mesophase (i.e., enantiotropic, monotropic, and virtual) versus that of the crystalline phase at various spacer lengths.

As expected, the T_g of all polymers decreases by increasing the value of X (Figure 2a,b). This trend is opposite to that of T_{ni} and T_{in} of the polymers with odd spacers and of T_m and T_k of polymers with both odd and even spacers. As a consequence, at a certain value of X there is an intercept of the dependences T_{ni} and T_{in} (of polymers containing odd spacers) versus X with that of the dependence T_g versus X. At this intercept the T_{ni} and T_{in} values are below T_g and, therefore, the corresponding polymer does not exhibit a mesophase since its formation is prohibited by the lack of motion of the glassy phase. This is the case of TPB-5 which is amorphous and therefore exhibits only a glass transition temperature (Figures 1 and 2 and Table I). TPB-7 exhibits a nematic mesophase which is kinetically controlled since it is located in the close proximity of T_g (Figures 1 and 2). When T_m and T_k values are lower than the T_g values, the corresponding polymers cannot crystallize and, therefore, they should provide noncrystallizable nematic polymers. This is the case of TPB-4 and TPB-6 to TPB-8 which display an enantiotropic nematic mesophase and are noncrystallizable because their T_k values are lower than their T_g values. TPB-9 and TPB-10 exhibit a melting transition only in the first DSC heating scans (Table I). Since their T_m values are in the close proximity of their glass transition temperatures, these polymers cannot crystallize from the melt and, therefore, on the second and subsequent heating scan they exhibit only an enantiotropic nematic mesophase (Figures 1 and 2 and Table I). However, during precipitation from solution and drying at room temperature they crystallize again.

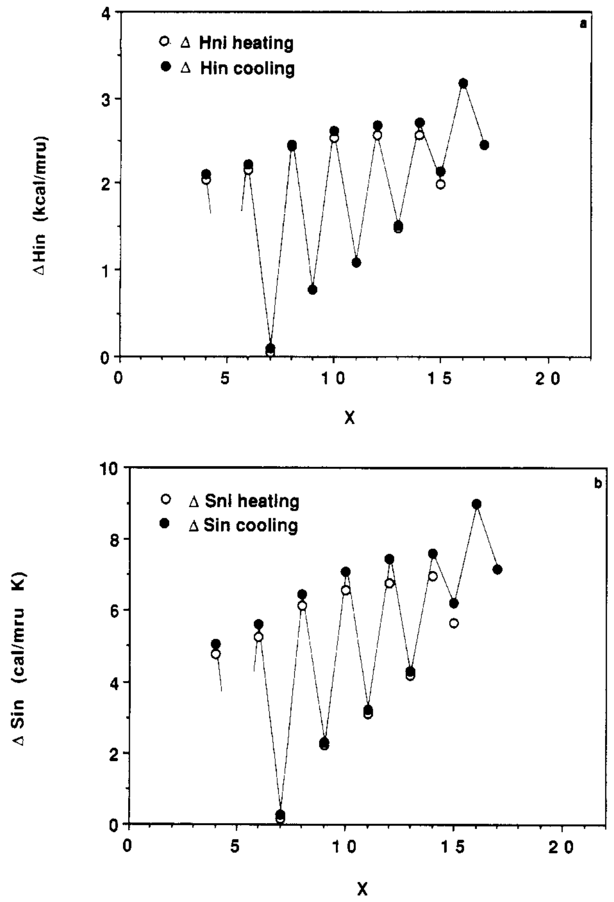


Figure 3. Dependence of the enthalpy change (a) and the entropy change (b) associated with the nematic–isotropic transitions on the number of methylenic units in the flexible spacer (X) of TPB-X.

The different dependences of T_g, T_m, and T_{ni} versus X from Figure 2a,b provide a clear picture on how their trends affect the difference between the various thermodynamic stabilities of the nematic mesophase of TPB-X as a function of spacer length. According to Figure 2a,b, noncrystallizable enantiotropic nematic polymers of TPB-X can be obtained when the melting temperature is below the glass transition temperature. This is the case of TPB-4 and TPB-6 to TPB-10.

Figure 3a plots the enthalpy changes associated with the nematic-isotropic (ΔH_{ni}) and isotropic–nematic (ΔH_{in}) phase transitions as a function of X. The corresponding entropy changes (ΔS_{ni} and ΔS_{in}) are plotted in Figure 3b. Both plots resemble the trends observed for the similar thermodynamic parameters reported for MBPE-X^{14b} and ClBPE-X.[38] A final interpretation of the thermodynamic parameters of TPB-X requires the determination of these parameters of the monotropic nematic mesophase exhibited by TPB-16 and of the virtual nematic mesophases exhibited by TPB-19 and TPB-20.

The synthetic route elaborated for the preparation of TPB allows the preparation of additional novel mesogens with multiple functionalities.

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