Polymer Vol. 37 No. 17, pp. 3889–3897, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
S0032-3861(96)00206-6
0032-3861/96/$15.00+0.00

# TPB′: a constitutional isomeric mesogen based on conformational isomerism which generates pairs of completely isomorphic polyethers

**V. Percec*, A. D. Asandei and M. Zhao**
*The W. M. Keck Laboratories for Organic Synthesis, Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106-7202, USA*

*(Received 14 August 1995)*

The synthesis and characterization of 1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)butane (TPB′) which is the constitutional isomer of 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB) and of the corresponding polyethers with $\alpha,\omega$-dibromoalkanes (TPB′-X with $X = 4$–19, where X = number of methylenic groups in the spacer) are described. The phase behaviour of TPB′-X is similar to that of TPB-X previously reported from our laboratory (*Macromolecules* 1991, **24**, 6318), except that both the crystalline melting and the nematic–isotropic temperatures of TPB′-X are higher than those of TPB-X. Since the increase of the isotropization temperature is larger than that of the melting temperature, at long spacers virtual mesophases of TPB-X became monotropic for TPB′-X. This is explained by the difference between the axial ratio ($x = L/d$) of these two constitutional isomers, i.e., $x = 1.46$ for TPB and $x = 2.01$ for TPB′. TPB-X and TPB′-X are isomorphic within their nematic and crystalline phases. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: constitutional isomerism; axial ratio; nematic isomorphism)**

## INTRODUCTION

The concept of main chain liquid crystalline polymers (LCPs) based on conformational isomerism was elaborated in our laboratory[1a] and allowed the molecular engineering of main chain LCPs displaying virtual, monotropic and enantiotropic uniaxial nematic[1a–c], smectic[1e], hexagonal columnar[1f,g] and two uniaxial nematic[1h,i] mesophases. This concept received synthetic[2a–e], experimental[2f] and theoretical[2g–i] interest in other laboratories. The interconversion between virtual, monotropic and enantiotropic mesophases can be manipulated via various molecular and macromolecular parameters using some thermodynamic schemes elaborated in our laboratory[3]. Well-defined linear main chain LCPs based on conformational isomerism provided models for the investigation and elucidation of some of the most fundamental problems of the field of LCPs such as chain conformation by D-n.m.r.[4a,b] and SANS[4c] experiments, structure and dynamics of disclinations by electron microscopy[4d,e] viscoelastic and chain conformation properties by dynamic light scattering[4f–k] and rheology of the nematic and isotropic phases[4e]. Several brief reviews describing mostly synthetic and structural aspects of this class of polymers are available[5]. Mesogenic monomers based on conformational isomerism were also designed for the preparation of new classes of main chain LCPs with complex architecture such as macrocyclic[6], hyperbranched[7] and dendrimeric[8]. A short review on this novel class of LCPs is also available[9].

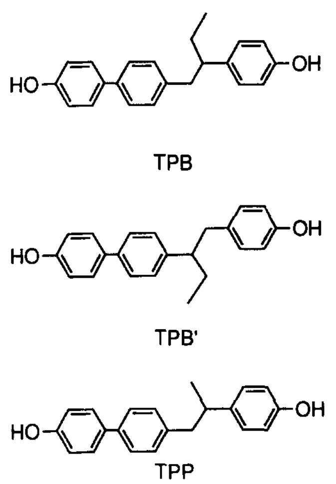
While we are concerned with the design of new and complex classes of LCPs, the elaboration of simple, linear main chain LCPs which are invaluable for physical investigations maintains the same priority in our laboratory.

The polyethers based on 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB)[1d] (*Scheme 1*) and $\alpha,\omega$-dibromoalkanes (TPB-X where X is the number of methylenic units in the flexible spacer) have generated the most extensively investigated and the best elucidated nematic linear[4] and macrocyclic[6] main chain LCPs. The replacement of 1,2-disubstituted butane of TPB by 1,2-disubstituted propane produced 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)propane[10a] (TPP) (*Scheme 1*). TPP-X[10a–c] exhibit both nematic and smectic mesophases and rational copolymerization experiments have generated for the first time the isotropic–nematic–hexagonal columnar–crystalline phase transition sequence[5c].

The goal of this paper is to report the synthesis and characterization of 1-(4-hydroxy-4′-biphenylyl)butane (TPB′) and of its polyethers based on $\alpha,\omega$-dibromoalkanes (TPB′-X). TPB′ is the constitutional isomer of TPB (*Scheme 1*). TPB′-X and TPB-X display an almost identical phase behaviour except that the transition temperatures and the corresponding thermodynamic parameters of TPB′-X are higher than those of TPB-X. This was attributed to the larger axial ratio of TPB′ and therefore higher rigidity of the TPB′-X polyethers. Unexpectedly, these two series of polyethers are isomorphic within both their crystalline and liquid crystalline phases. Therefore the TPB-X/TPB′-X pair of polyethers becomes

---

*To whom correspondence should be addressed



**Scheme 1** Structures of TPB, TPB′ and TPP mesogenic groups based on conformational isomerism

extremely valuable for the physical investigation of various fundamental aspects of the nematic phase since the rigidity of this system can be tuned up in a rational way by copolymerization and/or blending experiments without affecting the chemical structure of the system under investigation.

## EXPERIMENTAL

### *Materials*

1,4-Dibromobutane (99%), 1,5-dibromopentane (97%), 1,6-dibromohexane (97%), 1,7-dibromoheptane (97%), 1,8-dibromononane (97%), 1,10-dibromodecane (97%), 1,11-dibromoundecane (98%), acetyl chloride (97%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), anhydrous $AlCl_3$ (99%) (from Fluka, Ronkonkoma, NY), $LiAlH_4$ (99%), $S_8$ sublimed (both from Fisher, Pittsburgh, PA) and morpholine (from Baker Chemicals, Philipsburg, NJ) were used as received. 1,12-Dibromoundecane (Technical, Aldrich, Milwaukee, WI) was recrystallized from methanol. 1,16-Dibromohexadecane (Pfaltz and Bauer, Watersburg, CT) as well as 1,18-dibromooctadecane (K and K Laboratories, Plainview, NY) were used as received. 1,19-Dibromononadecane was synthesized as previously described[1b]. $Et_2O$ was dried by refluxing over $LiAlH_4$. Both $CH_2Cl_2$ and $CHCl_3$ were dried by refluxing over $CaH_2$. All dried solvents were freshly distilled before each use. *o*-Dichlorobenzene (*o*-DCB) was distilled under reduced pressure. All other chemicals were commercially available and were used as received.

### *Techniques*

A 200 MHz Varian Gemini 200 spectrometer was used to record the $^1H$-n.m.r. spectra at 20°C. TMS was used as internal standard. Relative molecular weights and purities were determined on a Perkin–Elmer Series 10LC GPC/HPLC instrument, equipped with a LC-100 column oven, a Nelson Analytical 900 Series data station, and a u.v. detector. The measurements were done using THF as solvent, (1 ml $min^{-1}$, 40°C) and two PL gel columns of $5 \times 10^2$ and $10^4$ Å. A calibration plot constructed with polystyrene standards was used for the determination of the relative molecular weights. A Perkin–Elmer PC Series DSC-7 d.s.c. equipped with a TAC7/DX thermal analysis controller was used to record the first-order thermal transitions which were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transitions were measured at the middle point of the change in heat capacity. The instrument was calibrated with In and Zn standards. Scanning rates were 20°C $min^{-1}$ in all cases. All heating and cooling scans were perfectly reproducible after the first heating scan. The first heating scan could be reobtained after proper annealing. An Olympus BX40 optical polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor, was used to analyse the anisotropic textures.

*Synthesis of 4-methoxybiphenyl* **2**. 4-Methoxybiphenyl (**2**), was prepared by the methylation of 4-phenylphenol (**1**), (200 g, 1.18 mol) dissolved in 800 ml of a 1.6 N NaOH solution to which $(CH_3O)_2SO_2$ (311 g, 2.47 mol) was added dropwise at 80°C. After 2 h, the reaction mixture was cooled to 20°C, the resulting precipitate was filtered, washed with dilute (10%) NaOH solution, water, and recrystallized from 95% EtOH to yield 173 g (80%) of white crystals. Purity (h.p.l.c.):>99%, m.p.: 86–88°C (lit.[11] m.p. = 87 – 85.5°C). $^1H$ n.m.r. ($\delta$, ppm, TMS, $CDCl_3$): 3.86 (s, 3H,-$OCH_3$), 6.99 (d, 2H, *ortho* to the metoxy of the substituted ring, $J = 8.72$ Hz), 7.33 (d, 1H, *para* to $CH_3$–O–$C_6H_4$–, $J = 7.4$ Hz), 7.43 (t, 2H, *meta* to $CH_3$–O–$C_6H_4$–, $J = 7.4$ Hz), 7.54 (d, 2H, *meta* to $CH_3$–O–, $J = 8.7$ Hz), 7.56 (d, 2H, *ortho* to $CH_3$–O–$C_6H_4$–, $J = 7$ Hz).

*Synthesis of 4-methoxy-4′-biphenylyl methyl ketone* **3**. 4-Methoxybiphenyl (**2**) (163 g, 0.7 mol) was dissolved in 900 ml of dry $CH_2Cl_2$ and the solution was cooled to −40°C with a dry ice–acetone bath. Anhydrous $AlCl_3$, (140 g, 1.04 mol) was added slowly to produce a green solution to which acetyl chloride (82 g, 1.04 mol) was added dropwise. After the addition was complete, the reaction mixture was allowed to reach room temperature, and then was refluxed for 2 h. After cooling to −10°C, cold conc. HCl (500 ml), was slowly added to decompose the yellow green complex. The organic layer was separated and $CH_2Cl_2$ was distilled under reduced pressure to yield a greenish white precipitate which was washed with water. The isomeric 3-acetyl-4′-methoxybiphenyl was removed by extracting the solid three times with $Et_2O$. Recrystallization from toluene afforded 134 g (81%) of white shiny flakes. Purity (h.p.l.c.): >99%, m.p.: 153–155°C (lit.[11] m.p. = 153 – 154°C). $^1H$ n.m.r. ($CDCl_3$, TMS, $\delta$, ppm): 2.63 (s, 3H,-$COCH_3$), 3.86 (s, 3H,-$OCH_3$), 7.00 (d, 2H *ortho* to the methoxy, $J = 8.4$ Hz), 7.58 (d, 2H, *meta* to the $CH_3CO$–, $J = 8.6$ Hz), 7.65 (d, 2H, *meta* to the metoxy, $J = 8.4$ Hz), 8.02 (d, 2H, *ortho* to the $CH_3CO$–, $J = 8.2$ Hz).

*Synthesis of 4-methoxy-4′-biphenylylacetic acid* **5**. Compound **5** was synthesized from **3** by the Wilgerodt–Kindler reaction[12]. A mixture of **3** (123 g, 0.54 mol), $S_8$ (26.12 g, 0.82 mol) and morpholine (71 g, 0.82 mol) was stirred at 100°C for 2 h, allowing most of the $H_2S$ to evolve, and then was refluxed at 140°C for 6 h. The reaction mixture was poured into water and the yellow brown solid was filtered and washed with water. The crude thiomorpholide (**4**) was hydrolysed by refluxing for 10 h with ethanolic NaOH (1200 ml). $C_2H_5OH$ was distilled under reduced pressure, and the acid was refluxed for 1 h with a 10% NaOH solution (500 ml). The brown reddish solid which separated was filtered. The resulting solution was acidified to precipitate the acid as white flakes. After recrystallization from $C_2H_5OH$, 111 g (85%) of white crystals were obtained. Purity (h.p.l.c.): 98.8%, m.p.: 181–184°C. $^1H$ n.m.r. ($\delta$, ppm, $CDCl_3$, TMS): 3.69 (s, 2H-$CH_2$-COOH), 3.85 (s, 3H, -$OCH_3$), 6.97 (d, 2H, *ortho* to the methoxy, $J = 8.4$ Hz), 7.34 (d, *ortho* to -$CH_2$COOH, $J = 7.9$ Hz), 7.51 (m, 4H, 2H *meta* to -$OCH_3$, 2H *meta* to -$CH_2$ COOH).

*Synthesis of 1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)ethanone* ***8***. To a solution of **5** (69 g, 0.29 mol) in 100 ml of dry $CH_2Cl_2$, $SOCl_2$ (44 g, 0.38 mol) was added dropwise and the mixture was stirred for 3 h at room temperature. $CH_2Cl_2$ and the excess $SOCl_2$ were distilled under reduced pressure to give the intermediary 4-methoxy-4′-biphenylyl acetyl chloride (**6**) (3.18 ppm, s, –$CH_2$COCl) as a yellow brownish solid. Dry $CH_2Cl_2$ (300 ml) was added to redissolve **6**, the flask was cooled to −40°C with a dry ice–acetone bath, and anisole (**7**) (46.85 g, 0.44 mol) was added. Anhydrous $AlCl_3$ (58 g, 0.43 mol) was added slowly and stirring was maintained for 15 min. The deep red solution was poured into 500 ml of a 10% HCl. The resulting solid was filtered, washed with water and recrystallized twice from toluene to yield 74 g (77%) of white, mica-like crystals. Purity (h.p.l.c.): >99%, m.p.: 190–193°C. $^1H$ n.m.r. ($\delta$, ppm, $CDCl_3$, TMS): 3.84 (s, 3H, –$OCH_3$ of the monophenyl ring), 3.87 (s, 3H, –$OCH_3$ of the biphenyl), 4.27 (s, 2H, –$CH_2$CO–), 6.94 (d, 2H, *ortho* to the methoxy of the monophenyl ring, $J = 8.7$ Hz), 6.96 (d, 2H, *ortho* to the methoxy of the biphenyl ring, $J = 8.5$ Hz), 7.32 (d, 2H, *ortho* to the –$CH_2$CO– of the biphenyl, $J = 8.1$ Hz), 7.51 (d, 4H; 2H *meta* to the methoxy of the biphenyl, 2H *meta* to the –$CH_2$CO– of the biphenyl, $J = 8.4$ Hz), 8.03 (d, 2H, *meta* to the methoxy of the monophenyl ring, $J = 8.6$ Hz).

*Synthesis of 1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)butanone* ***9***. To a mixture of **8** (73 g, 0.22 mol), THF (600 ml), NaOH (400 ml, 50% wt/wt in water) and TBAH (7.47 g, 0.24 mol), $C_2H_5I$[1d] (37 g, 0.24 mol) was added dropwise. The yellow–orange solution was stirred vigorously at 40°C for 10 h then THF was distilled under reduced pressure and $CHCl_3$ (300 ml) was added. The organic layer was washed with water followed by dil. HCl to yield a clear yellow solution which was dried over $MgSO_4$. After the solvent was evaporated, the remaining solid was dissolved in hot $CH_3OH$ and the solution was filtered. The solvent was distilled and the solid was recrystallized twice from EtOH to yield 54 g (74%) of white crystals. Purity (h.p.l.c.): 98.9%, m.p. = 99–102°C. $^1H$ n.m.r. ($\delta$, ppm, $CDCl_3$, TMS): 0.93 (t, 3H, –$CH_2CH_3$, $J = 7.3$ Hz), 1.90 (q, 1H, –$CH_2$–$CH_3$, $J = 7.3$ Hz), 2.22 (q, 1H, –$CH_2$–$CH_3$, $J = 7.3$ Hz), 3.82 (s, 3H, –$OCH_3$ of the monophenyl ring), 3.83 (s, 3H, –O–$CH_3$ of the biphenyl), 4.43 (t, 1H, –CH(Et)–CO, $J = 7.24$ Hz), 6.88 (d, 2H, *ortho* to the methoxy of the monophenyl ring, $J = 8.9$ Hz), 6.93 (d, 2H, *ortho* to the methoxy of the biphenyl, $J = 8.8$ Hz), 7.33 (d, 2H, *ortho* to the –CH–CO– of the biphenyl, $J = 8.2$ Hz), 7.47 (d, 4H, 2H *meta* to the methoxy of the biphenyl and 2H *meta* to the –CH–CO– of the biphenyl, $J = 8.8$ Hz), 7.98 (d, 2H, *meta* to the methoxy of the monophenyl ring, $J = 8.9$ Hz).

*Synthesis of 1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)butanone* ***10***. An $AlCl_3$·$Et_2O$ complex[13] was prepared by adding slowly $AlCl_3$ (106 g, 0.8 mol) to dry $Et_2O$ (400 ml) at −10°C under nitrogen. To a mixture of $LiAlH_4$ (15 g, 0.4 mol) and dry $Et_2O$ (150 ml) were added dropwise first the $AlCl_3$·$Et_2O$ complex and then a solution of **9** (48 g, 0.13 mol) in 200 ml of dry $CHCl_3$. After the addition was complete the reaction was stirred for 0.5 h and then was quenched by slowly adding 500 ml of dil. HCl. The organic layer was separated, washed with water and dried over $MgSO_4$. The solvent was distilled and the remaining solid was purified by recrystallization from methanol to afford 44 g (91%) of white crystals. Purity (h.p.l.c.): >99%, m.p.: 116–119°C. $^1H$ n.m.r. ($\delta$, ppm, $CDCl_3$, TMS): 0.79 (t, 3H, $CH_3$–$CH_2$, $J = 7.3$ Hz), 1.64, (m, 2H, $CH_3CH_2$), 2.72 (m, 1H, –CH–$CH_2$–), 2.86 (d, 2H, –CH–$CH_2$–, $J = 7$ Hz), 3.76 (s, 3H, –$OCH_3$ of the monophenyl ring), 3.85 (s, 3H, O–$CH_3$ of the biphenyl ring), 6.76 (d, 2H, *ortho* to the methoxy of the monophenyl ring, $J = 8.4$ Hz), 6.97 (d, 4H; 2H *ortho* to the methoxy of the biphenyl ring, 2H *meta* to the methoxy of the monophenyl ring, $J = 8.4$ Hz), 7.15 (d, 2H, *ortho* to –CH(Et)–$CH_2$– of the biphenyl ring $J = 8.1$ Hz), 7.46 (d, 2H, *meta* to the –CH(Et)–$CH_2$– of the biphenyl ring, $J = 8.1$ Hz), 7.54 (d, 2H, *meta* to the methoxy on the biphenyl ring $J = 8.5$ Hz). The n.m.r. spectra showed that **10** was completely free of unreduced ketone **9**.

*Synthesis of 1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)butanone* ***11***. A solution of **10** (43 g, 0.13 mol), HBr (aq. 48%, 180 ml) and $CH_3COOH$[14] (400 ml) was refluxed at 111°C for 10 h then the excess of HBr and $CH_3COOH$ was distilled under reduced pressure and the resulting solid was washed with water. Recrystallization from a 1/1 (v/v) mixture of $CH_3OH$ and $H_2O$ afforded 32 g (79.6%) of white fluffy crystals. Purity (h.p.l.c.): >99%, m.p.: 165–168°C. $^1H$ n.m.r. ($\delta$, ppm, $CDCl_3$, TMS): 0.79 (t, 3H, –$CH_3$, $J = 7.2$ Hz), 1.7 (m, 2H, $CH_3$–$CH_2$–), 2.73 (q, 1H, –CH(Et)–$CH_2$–, $J = 5$ Hz), 2.84 (d, 2H, –CH(Et)–$CH_2$, $J = 7.3$ Hz), 4.54 (s, 1H, –OH of the monophenyl ring), 4.75 (s, 1H, –OH of the biphenyl), 6.68 (d, 2H, *ortho* to the hydroxy of the monophenyl ring, $J = 8.4$ Hz), 6.89 (d, 2H, *ortho* to the OH of the biphenyl, $J = 8.1$ Hz), 6.92 (d, 2H, *meta* to the hydroxy of the monophenyl ring, $J = 8.2$ Hz), 7.14 (d, 2H *ortho* to the –CH–$CH_2$– of the biphenyl, $J = 8.1$ Hz), 7.44 (d, 2H, *meta* to the hydroxy of the biphenyl, $J = 7.9$ Hz), 7.48 (d, 2H *meta* to the –CH–$CH_2$ of the biphenyl, $J = 8.1$ Hz).

### *Synthesis of polyethers*

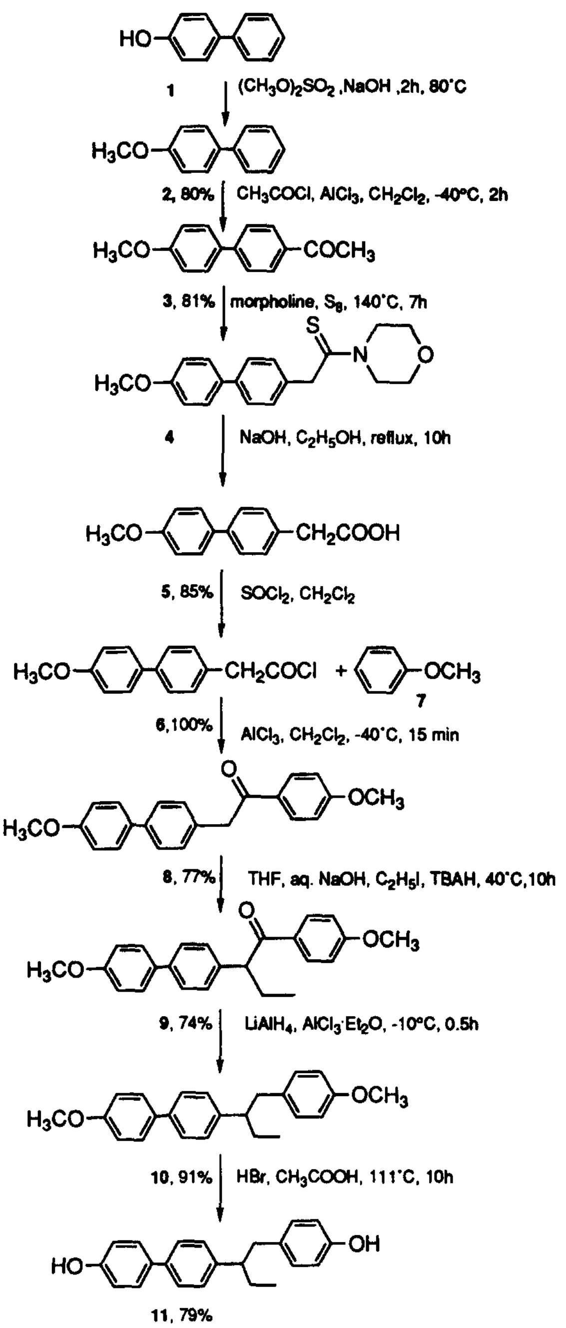
Conventional liquid–liquid two phase (organic solvent–aqueous NaOH solution) phase transfer catalysed polyetherification conditions[1d] were used in the synthesis of the polyethers. The reaction was carried out under nitrogen atmosphere, at 80°C in an *o*-dichlorobenzene–10 N NaOH aqueous solution (10 times the molar excees of NaOH *versus* the phenol groups), in the presence of TBAH, as phase transfer catalyst. In all cases the ratio between the electrophilic and nucleophilic monomers was 1 : 1. An example is provided below: To a 25 ml one neck round bottom flask equipped with magnetic stirrer and condenser were added **11** (0.159 g, 0.5 mmol), NaOH (1 ml, 10 N) and the mixture was stirred at room temperature for 10 min after which 1,8-dibromooctane (0.135 g, 0.5 mmol), *o*-DCB (1 mL) and TBAH (0.0678 g, 0.2 mmol, 20 mol% *versus* the phenol groups) were successively added. A balloon filled with nitrogen was placed on the top of the condenser, and the reaction mixture was stirred with 1100 rpm at 80°C for 6 h, after which the organic and aqueous layers were diluted with $CHCl_3$ and water respectively. The organic layer was separated, washed with water followed by dil. HCl and again with water several times. After its $CHCl_3$ solution was filtered, the polymer was separated by precipitation into $CH_3OH$ to give 0.201 g (94%) of a white fibrous solid. The polymer was further purified by reprecipitation first from $CHCl_3$ solution into acetone and then from THF solution into water.

*Preparation of the TPB′-X/TPB-X blends*

Both TPB-10/TPB′-10 and TPB-13/TPB′-13 blends were prepared by dissolving the weighted amounts of the components in $CHCl_3$ under stirring until complete homogenization of the solution. The solvent was then evaporated, and the sample was dried under vacuum.

## RESULTS AND DISCUSSION

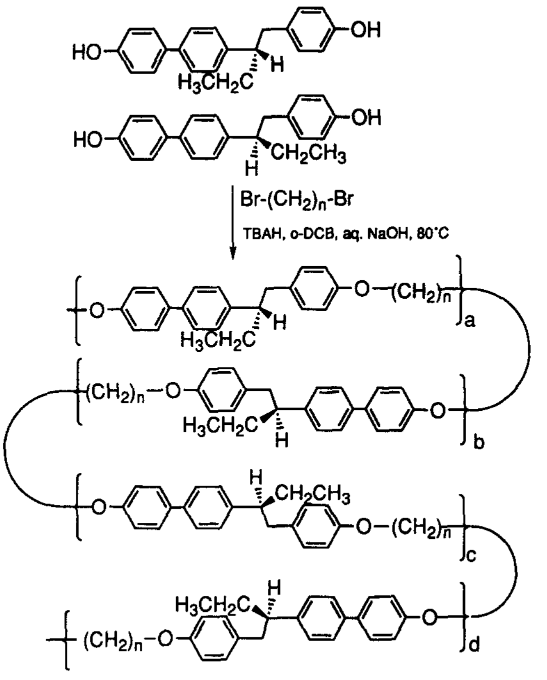
*Scheme 2* outlines the synthesis of 1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-byphenylyl)butane (**11**, TPB′). The reaction sequence adopted is less expensive and consists of fewer steps than the one previously reported for the preparation of TPB[1d]. 4-Methoxybiphenyl (**2**) was obtained by the methylation of the inexpensive 4-phenylphenol with $(CH_3O)_2SO_2$ in 80% yield. Friedel–Crafts acylation of **2** with acetyl chloride produced **3** in 81% yield. 4-Methoxy-4′-biphenylylacetic acid (**5**) was obtained in 85% yield after the hydrolysis with NaOH in ethanol of the intermediary thiomorpholide (**4**) generated by the Wilgerodt–Kindler reaction of **3** with $S_8$ and morpholine. The 4-methoxy-4′-biphenylylacetic acid (**5**) was converted to the corresponding acid chloride **6** with $SOCl_2$. **6** was used without purification in the Friedel-Crafts acylation of anisole to yield 1-(4-methoxyphenyl)-2-(4-methoxy-4′-biphenylyl)ethanone (**8**) in 77% yield. It is essential that this reaction is carried out at very low temperature and in a very short reaction time. Alternatively self acylation of **6** leads to a large amount of side products. Therefore, the transformations of **3** into **5** and of **5** into **8** were both carried out as one pot two step reactions. The phase transfer catalysed C alkylation of **8** with $C_2H_5I$ was performed as previously described in the synthesis of TPB[1d]. In the present case, after the O alkylated side product was cleaved with HCl, hot filtration of the methanol solution followed by recrystallization afforded the more soluble **9** in 74% yield. In the case of TPB[1d], realkylation was required in order to separate the product from the cleaved O alkylated compound. Reduction of the keto group of **9** was accomplished using the $LiAlH_4/AlCl_3{\cdot}Et_2O$[13] complex. This reaction was completed in 0.5 h and **10** was obtained in 91% yield after recrystallization from methanol. The demethylation of **10** was performed with HBr in $CH_3COOH$[14] and afforded **11** in 79% yield. The overall number of one pot reaction steps used in the synthesis of TPB′ is seven versus ten used in the synthesis of TPB[1d].



**Scheme 2** Synthesis of 1-(4-hydroxyphenyl)-2-(4-hydroxy-4′-biphenylyl)butane (TPB′)

*Scheme 3* outlines the synthesis of the polyethers based on TPB′ and $\alpha,\omega$-dibromoalkanes (TPB′-X). They were prepared via the phase transfer catalysed procedure elaborated for the synthesis of TPB-X[1d]. Since TPB′ has a stereogenic center, TPB′-X are regioirregular copolymers of the two constitutional isomeric repeat units of TPB′ and of the two enantiomers of each of them. The microstructure of this chain has a high constitutional and configurational entropy which explains its low crystallization tendency and high solubility.

*Table 1* summarizes the relative molecular weights of these polymers as determined by g.p.c. calibrated with polystyrene standards, their polydispersities and the yields. In the case of TPB-X an absolute calibration



**Scheme 3** Synthesis of polyethers based on TPB′ and $\alpha,\omega$-dibromoalkanes (TPB′-X)

was obtained by using oligomeric model compounds[6c]. This calibration showed that Mn obtained by g.p.c. with polystyrene standards is 1.6 times higher than the absolute values and we expect a comparable difference for the TPB′-X polymers. However the relative molecular weights of the two sets of polyethers are similar and much higher than the values at which we expect the phase transition temperatures to be dependent on molecular weight. Therefore, the transition temperatures of TPB′-X and TPB-X can be compared in a quantitative way.

Thermal characterization of TPB′-X was carried out by a combination of techniques consisting of d.s.c. and thermal optical polarized microscopy. Second heating and first cooling d.s.c. traces of TPB′-X are presented in *Figure 1*. The information obtained from these d.s.c. curves together with that from the first heating and subsequent heating and cooling scans which are not shown in *Figure 1* are summarized in *Table 1*. We will discuss these results and compare them with those obtained for TPB-X[1d].

At the first sight the d.s.c. traces of TPB′-X and TPB-X look almost identical. However a close inspection reveals beside similarities a series of remarkable differences, TPB′-4 exhibits a crystalline melting on the heating scan and a monotropic nematic phase upon cooling while TPB-4 displays an enatiotropic nematic mesophase. The isotropization transition of TPB′-4 is higher than that of TPB-4. At the same time TPB′-4 has a much higher crystallization tendency than TPB-4. Due to the very close proximity between the isotropization and the glass transition temperatures both TPB-5 and TPB′-5 are amorphous. Both TPB′-X and TPB-X with X = 6–8 exhibit a noncrystallizable enantiotropic nematic mesophase. The isotropization temperature of TPB′-X is

**Table 1** Characterization of polyethers based on TPB′ and $\alpha,\omega$-dibromoalkanes (TPB′-X). Data collected from the first heating and first cooling d.s.c. scans are on the first line. Data collected from the second heating d.s.c. scans are on the second line

| X | Yield (%) | $M_n$ | $M_W/M_n$ | Thermal transitions (°C) and corresponding enthalpy changes (kcal $mru^{-1}$) in parentheses | |
|---|---|---|---|---|---|
| | | (g.p.c.) | | Heating | Cooling |
| 4 | 84.4 | 26300 | 1.98 | g 88 k 130 (-0.80) k 183 (3.68) i<br>g 88 k 182 (3.68) i | i 148 (2.67) n 79 g |
| 5 | 83.3 | 21100 | 2.05 | g 68 i<br>g 69 i | i 60 g |
| 6 | 91.1 | 42100 | 2.39 | g 69 n 145 (2.90) i<br>g 68 n 145 (2.89) i | i 124 (2.85) n 59 g |
| 7 | 92.3 | 38800 | 2.26 | g 55 n 86 (0.60) i<br>g 56 n 88 (0.055) i | i 74 (0.05) n 49 g |
| 8 | 93.7 | 24100 | 2.13 | g 52 n 127 (3.32) i<br>g 51 n 127 (3.36) i | i 111 (3.16) n 42 g |
| 9 | 94.2 | 35300 | 2.12 | g 43 k 51 (0.10) n 79 (1.27) i<br>g 45 n 79 (1.29) i | i 65 (1.16) n 35 g |
| 10 | 93.8 | 48400 | 2.02 | g 42 k 47 (0.22) n 118 (3.52) i<br>g 42 n 118 (3.48) i | i 101 (3.24) n 33 g |
| 11 | 95.1 | 31700 | 1.92 | g 40 k 44 (0.24) k 59 (0.34) n 77 (1.54) i<br>g 39 k 59 (0.4) n 79 (1.56) i | i 68 (1.54) n 48 (0.38) k 31 g |
| 12 | 91.3 | 43100 | 2.08 | g 33 k 40 (0.24) k 68 (0.38) n 108 (3.3) i<br>g 36 k 69 (0.37) n 108 (3.32) i | i 90 (3.24) n 53 (0.28) k 30 g |
| 13 | 92.4 | 53200 | 2.07 | g 40 k 45 (0.28) k 61 (0.34) n 82 (1.98) i<br>g 34 k 62 (0.34) n 82 (1.97) i | i 68 (1.93) n 49 (0.29) k 28 g |
| 16 | 93.3 | 32200 | 1.95 | g 44 k 47 k 87 k 94 (2.88) k 102 (1.8) i<br>g 33 k 87 (2.52) k 94 (2.88) k 102 (1.80) i | i 82 (3.87) n 62 (2.9) k 27 g |
| 18 | 90.8 | 31800 | 2.77 | g 43 k 77 (0.27) k 93 (6.80) i<br>g 32 k 93 (6.85) i | i 70 (3.52) n 63 (2.93) k 25 g |
| 19 | 94.7 | 30700 | 2.13 | g 41 k 53 (0.30) k 84 (7.40) i<br>g 31 k 85 (7.37) i | i 69 (3.40) n 64 (3.54) k 23 g |

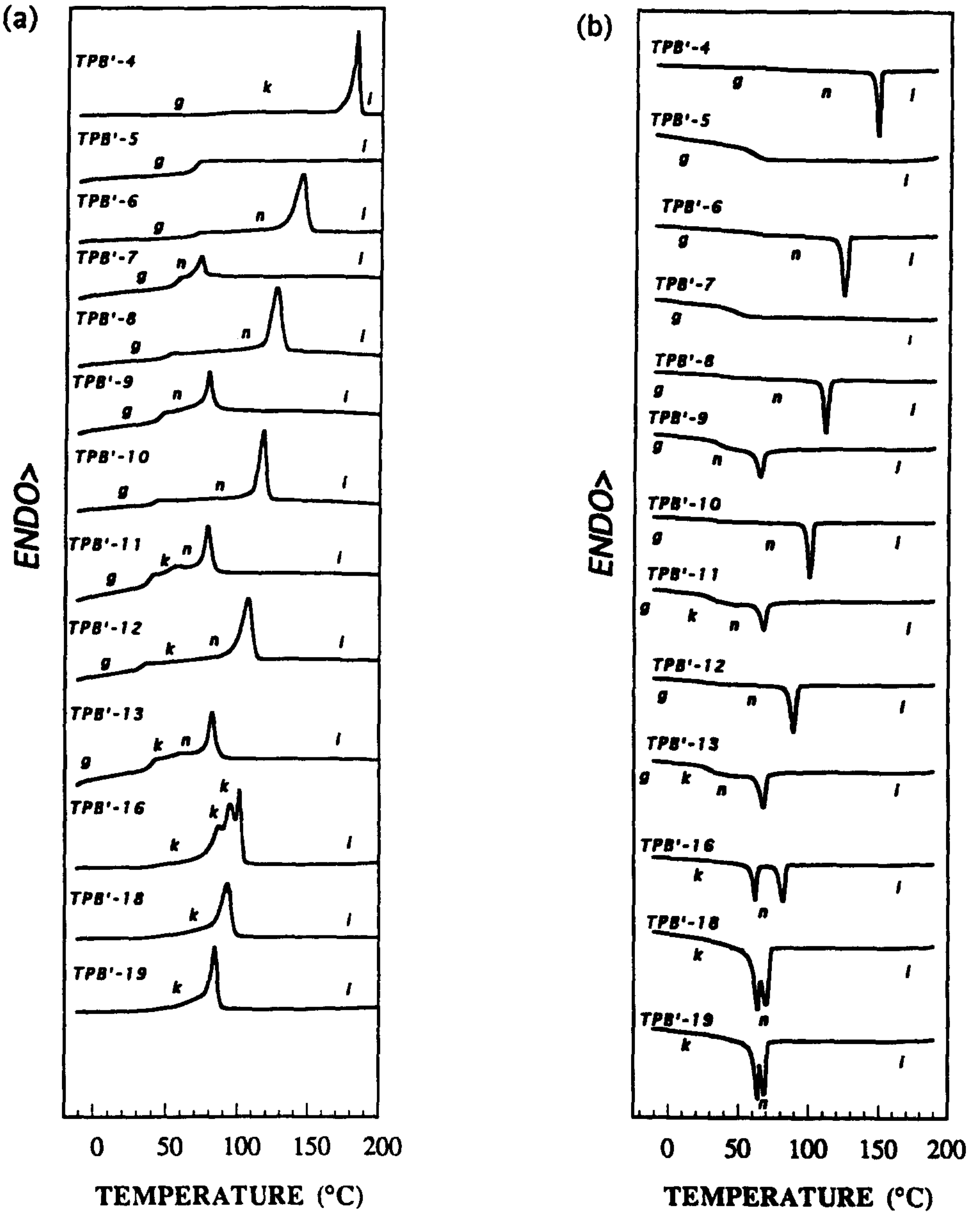


**Figure 1** D.s.c. traces of TPB′-X polyethers: (a) second heating scan, (b) first cooling scan

higher than that of TPB-X. TPB′-X and TPB-X with X = 9–13 exhibit a crystalline phase followed by an enantiotropic nematic mesophase. TPB′-X with X = 16, 18 and 19 display a monotropic nematic phase. However, TPB-18 and TPB-19 are only crystalline. *Figure 2* plots the transition temperatures of TPB′-X as a function of X on heating (a) and cooling (b). They are very similar to those of TPB-X[1d], except that the isotropization temperatures are consistently higher for TPB′-X. The other major difference between the two polymers is the higher crystallization tendency of TPB′-4 *versus* TPB-4, and of TPB-18 and TPB-19 *versus* TPB′-18 and TPB′-19. As a consequence TPB′-4 displays a monotropic nematic phase while TPB-4 an enatiotropic nematic phase *Figure 3*. At the same time TPB′-18 and TPB′-19 exhibit monotropic nematic phases whereas TPB-18 and TPB-19 are both only crystalline. *Figure 4a* plots the enthalpy changes associated with the isotropic–nematic transition ($\Delta H_{\mathrm{i-n}}$) while *Figure 4b* the corresponding entropy changes ($\Delta S_{\mathrm{i-n}}$) for both TPB′-X and TPB-X. These results definitively demonstrate that the nematic phase of TPB′-X is more ordered than that of TPB-X.

Where is the difference between TPB′-X and TPB-X arising from? *Figure 5* shows the molecular models of the TPB and TPB′ mesogens. The diameter of TPB′ is $d$ = 8 Å, that of TPB is $d$ = 11 Å, while their length ($L$) is 16.1 Å. Therefore the structural change from one constitutional isomer (TPB) to the other (TPB′) increases the axial ratio $x = L/d$ from 1.46 for TPB to 2.01 for TPB′. As a consequence, the Kuhn's segment of TPB′-X is longer than that of TPB-X. This difference is sufficient to make the TPB′-X polymers more rigid and exhibit a higher isotropization temperature than TPB-X. This is a remarkable result which agrees with the theoretical predictions on the dependence of the isotropization temperature on the axial ratio[15]. Moreover, it shows how sensitive is the dependence of a nematic phase on subtle changes in the molecular structure like the one between TPB to TPB′. The increase in axial ratio of TPB′ *versus* that of TPB leads to an increase in both the crystalline melting as well as in the nematic to isotropic transition temperatures. However, the two phases are affected by the structural variation to a different extent. At longer spacers the increase in the isotropization temperature is

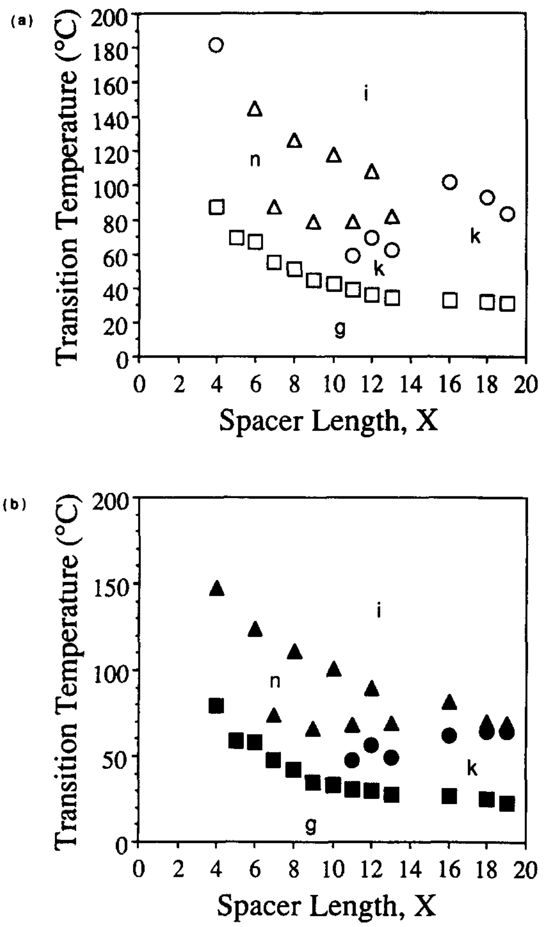


**Figure 2** The dependence of the phase transition temperatures of TPB′-X polyethers on the number of methylenic groups in the spacer, X. (a) Data collected from the second heating d.s.c. scan ($T_g$ = □, $T_{n-i}$ = △, $T_{k-i}$ or $T_{k-n}$ = ○), (b) Data collected from the first cooling d.s.c. scan ($T_g$ = ■, $T_{n-k}$ = ●, $T_{i-n}$ = ▲)

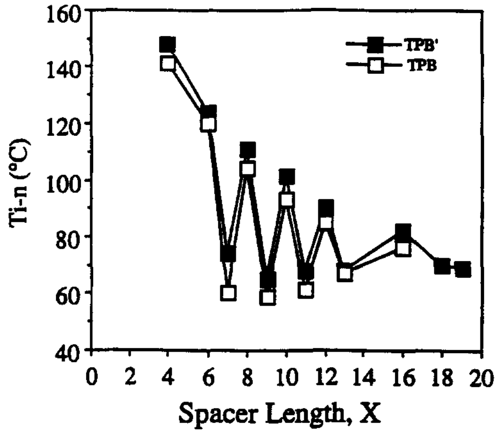


**Figure 3** The dependence of the isotropic to nematic ($T_{i-n(TPB-X)}$ = □, $T_{i-n(TPB'-X)}$ = ■) transition temperatures of TPB-X and TPB′-X as a function of X

consistently at least 10°C higher than the crystalline melting, demonstrating that the change in the axial ratio affects more strongly the nematic phase than the crystalline phase. As a consequence, at very long spacers we can uncover virtual mesophases of TPB-X and convert them into monotropic mesophases of TPB′-X. At very short spacers the effect is reversed. TPB′-4 exhibits a much higher crystallization tendency than TPB-4. Solubility experiments carried out both in nematic and in isotropic solvents have shown that TPB′-X are less soluble than TPB-X.

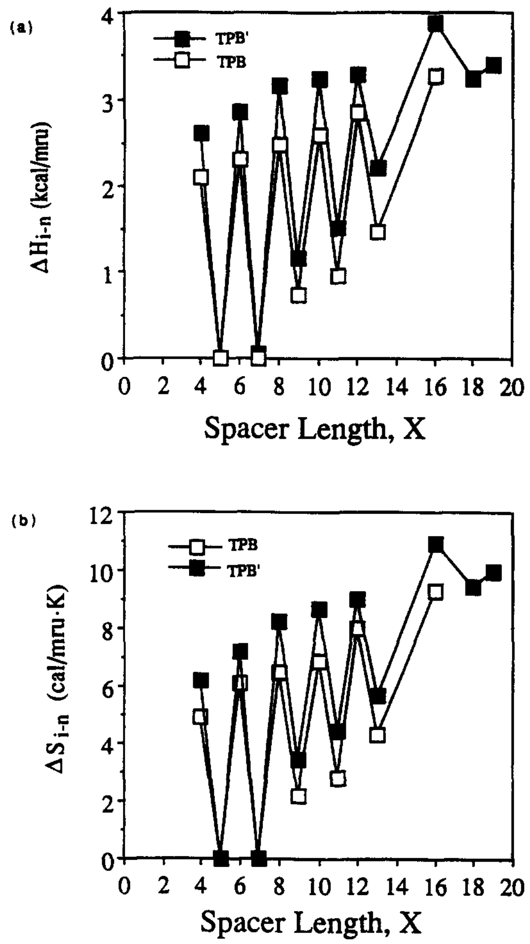


**Figure 4** The dependence of (a) enthalpy ($\Delta H_{i-n(TPB-X)}$ = □, $\Delta H_{i-n(TPB'-X)}$ = ■) and (b) entropy ($\Delta S_{i-n(TPB-X)}$ = □, $\Delta S_{i-n(TPB'-X)}$ = ■) changes associated with the isotropic nematic transition of TPB-X and TPB′-X as a function of X

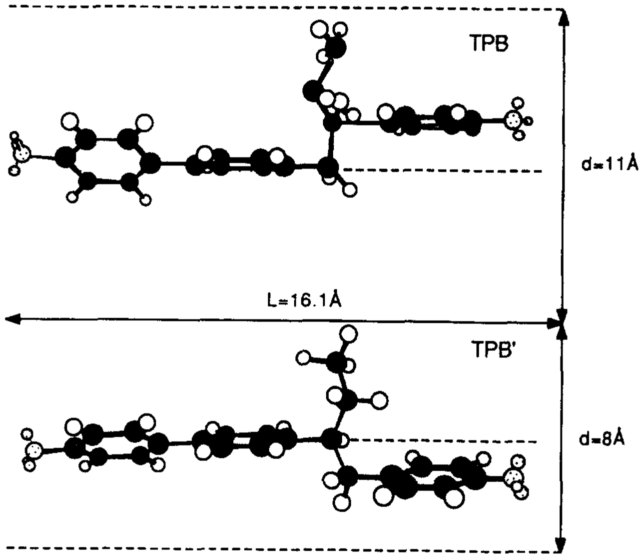


**Figure 5** Molecular models of the TPB and TPB′ mesogenic groups

The miscibility and isomorphism of the TPB-10/TPB′-10

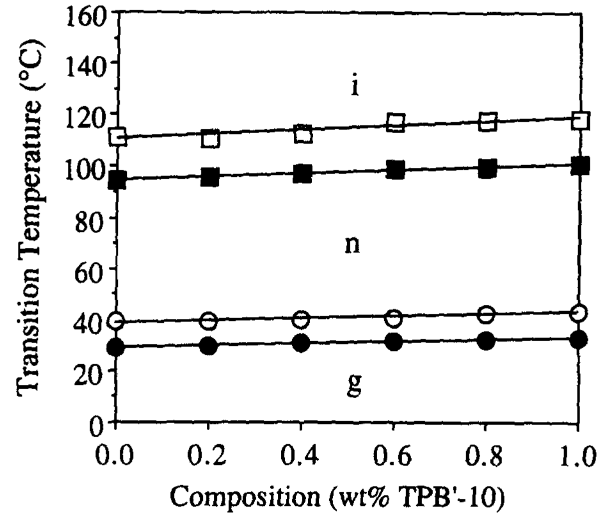


**Figure 6** The dependence of $T_{n-i}$ (□), $T_{i-n}$ (■), $T_{g-n}$ (○) and $T_{n-g}$ (●) on the composition of TPB-10/TPB′-10 blends. Data collected from the second heating (open symbols) and first cooling (closed symbols) d.s.c. scans

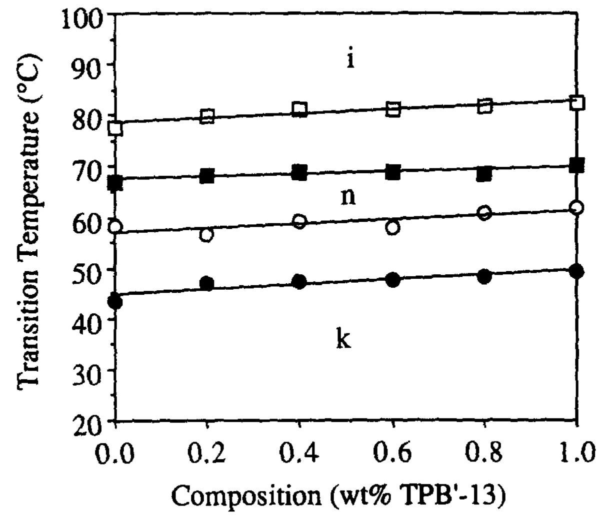


**Figure 7** The dependence of $T_{n-i}$ (□), $T_{i-n}$ (■), $T_{k-n}$ (○) and $T_{n-k}$ (●) on the composition of TPB-13/TPB′-13 blends. Data collected from the second heating (open symbols) and first cooling (closed symbols) d.s.c. scans

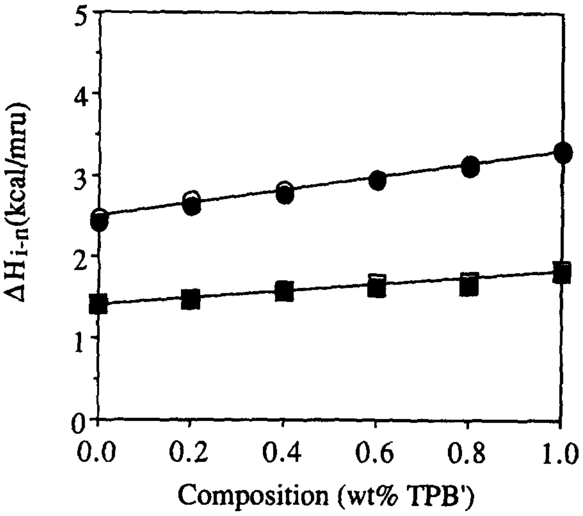


**Figure 8** The dependence of the enthalpy changes associated with the nematic–isotropic ($\Delta H_{n-i}$ = ○ for TPB-10/TPB′-10 blends and $\Delta H_{n-i}$ = □ for TPB-13/TPB′-13 blends) and isotropic–nematic ($\Delta H_{i-n}$ = ● for TPB-10/TPB′10 blends and $\Delta H_{i-n}$ = ■ for TPB-13/TPB′-13 blends) transitions of the TPB-10/TPB′-10 and TPB-13/TPB′-13 blends. Data collected from the second heating (open symbols) and first cooling (closed symbols) d.s.c. scans

and TPB-13/TPB′-13 pairs were investigated by characterizing their blends by d.s.c. and optical polarized microscopy in all their phases. *Figure 6* plots the glass transition and the isotropization temperatures of TPB-10/TPB′-10 obtained from heating and cooling d.s.c. scans. Complete miscibility is observed in the glassy phase and isomorphism in the nematic phase of these two polymers. *Figure 7* plots the transition temperatures of the TPB-13/TPB′-13 blends. The results from *Figure 7* show that these two polymers are isomorphic in both their nematic and crystalline phases. Supporting evidence for this statement is obtained from *Figure 8* which plots the corresponding enthalpy changes associated with the transition temperatures from *Figures 6* and *7*.

The isomorphism in various phases of LC polymers and copolymers was discussed in great detail in a previous publication from our laboratory[16]. There are very few cases in which pairs of homopolymers are miscible and therefore isomorphic in their liquid crystalline phases. The fact that the pairs of TPB-X and TPB′-X are miscible in both their crystalline and liquid crystalline phases is quite unique. This behaviour allows the molecular engineering of the degree of order in the nematic phase via a rational combination of copolymerization[17] and blending experiments[16].

## CONCLUSION

The synthesis and characterization of TPB′, the constitutional isomer of TPB and of the corresponding polyethers TPB′-X with X = 4–19 were presented. The phase behaviour of TPB′-X is similar to that of TPB-X[1d]. However, the crystalline melting and the nematic–isotropic temperatures of TPB′-X are higher than those of TPB-X. Also, the solubility of TPB′-X is lower than that of TPB-X. Since the increase of the isotropization temperature is larger than that of the melting temperature, at long spacers virtual mesophases of TPB-X became monotropic for TPB′-X. These results conclude that both the nematic and crystalline phases of TPB′-X are more ordered than those of the corresponding constitutional isomeric TPB-X. This difference was explained by the difference between the axial ratio ($x = L/d$) of these two constitutional isomers: $x = 1.46$ for TPB and $x = 2.01$ for TPB′.

The miscibility between selected pairs of blends of TPB′-X with TPB-X was also investigated. It was found that these pairs of constitutional isomeric polyethers are miscible both in their nematic and crystalline phases and therefore are completely isomorphic. This unique behaviour of TPB-X and TPB′-X provides access to the molecular engineering of the degree of order in the nematic phase via a rational combination of copolymerization and blending experiments. TPB-10 is presently the most suitable model for physical investigations of the thermotropic nematic mesophase[4]. The complementarity between TPB′-X and TPB-X will broaden the scope of these investigations.

## ACKNOWLEDGEMENT

Financial support by the National Science Foundation (DMR-91-22227) is gratefully acknowledged.

## REFERENCES

1 For selected publications from our laboratory on main LCP based on conformational isomerism exhibiting *a uniaxial nematic phase*: (a) Percec, V. and Yourd, R. *Macromolecules* 1988, **21**, 3379; (b) Percec, V. and Tsuda, Y. *Macromolecules* 1990, **23**, 3509; (c) Ungar, G., Feijoo, J. L., Keller, A., Yourd, R. and Percec, V. *Macromolecules* 1990, **23**, 3411; (d) Percec, V. and Kawasumi, M. *Macromolecules* 1991, **24**, 6318; *smectic phase*: (e) Ungar, G., Feijoo, J. L., Percec, V. and Yourd, R. *Macromolecules* 1991, **24**, 1168; *hexagonal columnar phase*; (f) Ungar, G., Feijoo, J. L., Yourd, R. and Percec, V. *Macromolecules* 1991, **24**, 953; (g) Percec, V., Zuber, M., Ungar, G. and Alvarez-Castillo, A. *Macromolecules* 1992, **25**, 1193; *two uniaxial nematic phases* (h) Ungar, G., Percec, V. and Zuber, M. *Macromolecules 1992*, **25**, 75 (i) Ungar, G., Percec, V. and Zuber, M. *Polym. Bull.* 1994, **32**, 325

2 For selected publications from other laboratories on main chain LCPs based on conformational isomerism see: (a) Jonsson, H., Werner, P., Gedde, U. W. and Hult, A. *Macromolecules* 1989, **22**, 1683; (b) Jonsson, H., Walgren, E., Hult, A. and Gedde, U. W. *Macromolecules* 1990, **23**, 1041; (c) Irvin, R. S., Sweeny, W., Gardner, K. H., Gochanour, C. R. and Weinberg, M. *Macromolecules* 1989, **22**, 1065; (d) Bilibin, A. Y., Tenkovtsev, A. V. and Piraner, O. N. *Makromol. Chem.* 1989, **190**, 3013; (e) Carpeneto, L., Costa, G., Marsano, E., Morinelli, S., Piombo, V. and Valenti, B. *Polym. Adv. Tech.* 1994, **5**, 416; (f) Cheng, J., Jin, Y., Chen, W., Wunderlich, B., Jonsson, H., Hult, A. and Gedde, U. W. *J. Polym. Sci: Part B: Poly. Phys.* 1994, **32**, 721. For the theoretical confirmation of the excluded *anti* extended conformation in the mesophase see: (g) Petraccone, Y. and Pirozzi, B. *Macromolecules* 1991, **24**, 6470. For the theoretical explanation of the two uniaxial nematic phases reported in ref. 1h and 1i see: (h) Ferrarini, A., Luckhurst, G. R., Nordio, P. L. and Roskilly, S. J. *Chem. Phys. Lett.* 1993, **214**, 409; (i) Luckhurst, G. R., *Macromol. Symp.* 1995, **96**, 1.

3 For thermodynamic schemes which explain the dependence of liquid crystalline transitions on molecular and macromolecular parameters see: (a) Percec, V. and Keller, A. *Macromolecules* 1990, **23**, 4347; (b) Keller, A., Ungar, G. and Percec, V. 'Advances in Liquid Crystalline Polymers' (Eds R. A. Weiss and C. K. Ober), ACS Symposium Series, **435**, Washington DC, 1990, p. 308

4 *Chain conformation by D-n.m.r.*: (a) Sherwood, M. H., Sigaud, G., Yoon, D. Y., Wade, C. G., Kawasumi, M. and Percec, V. *Mol. Cryst. Liq. Cryst.* 1994, **254**, 455; (b) Leisen, J., Boeffel, C., Spiess, H. W., Yoon, D Y., Sherwood, M. H., Kawasumi, M. and Percec, V. *Macromolecules* 195, **28**, 6937; *chain conformation by SANS experiments*: (c) Hardouin, F., Sigaud, G., Archard, M. F., Brulet, A., Cotton, J. P., Yoon, D. Y., Percec, V. and Kawasumi, M. *Macromolecules* 1995, **28**, 5427; *structure and dynamics of disclinations by electron microscopy*: (d) Zhang, A., Yandrasits, M. A., Cheng, S. Z. D. and Percec, V. *Makromol. chem.* 1993, **194**, 3135; (e) Ding, D. K., Thomas, E. V. and Percec, V. *Macromolecules* (in press); *viscoelastic and chain conformation properties by dynamic light scattering*: (f) Gu, G. F., Jamieson, A. M., Lee, M., Kawasumi, M. and Percec, V. *Liq. Cryst.* 1992, **12**, 961; (g) Gu, G. F., Jamieson, A. M., Kawasumi, M., Lee, M. and Percec, V. *Macromolecules* 1992, **25**, 2151; (h) Chen, F. L. and Jamieson, A. M. *Macromolecules* 1993, **26**, 6576; (i) Chen, F. L. and Jamieson, A. M. *Macromolecules* 1994, **27**, 1943 and 4691; (j) Gu, D. F. and Jamieson, A. M. *Macromolecules* 1994, **27**, 337; (k) Chen, F. L., Jamieson, A. M., Kawasumi, M. and Percec, V. *J. Polym. Sci: Part B: Polym. Phys.* 1995, **33**, 1213; *rheology in the nematic and isotropic phases*: (l) Heberer, D. P., Odel, J. A. and Percec, V. *J. Mater. Sci.* 1994, **29**, 3477.

5 For few brief reviews which include also main chain LCPs based on conformational isomerism see: (a) Percec, V. and Tomazos, D. 'Comprehensive Polymer Science', First Suppl. (Ed. G. Allen), Pergamon Press, Oxford, 1992, p. 299; (b) Percec, V. 'Handbook of Liquid Crystal Research' (Eds P. J. Collings and J. S. Patel), Oxford, Univ. Press, Oxford, (in press); (c) Ungar, G., Zhou, J., Percec, V. and Chu, P. *Macromol. Symp.* 1995, **98**, 951

6 For selected publications from our laboratory on macrocyclic main chain LCPs see: (a) Percec, V., Kawasumi, M., Rinaldi, P. L. and Litmann, V. L. *Macromolecules* 1992, **25**, 3851; (b) Percec, V. and Kawasumi, M. *Adv. Mater.* 1992, **4**, 572; (c) Percec, V. and Kawasumi, M. *Macromolecules* 1993, **26**, 3663 and 3917; (d) Percec, V. and Kawasumi, M. *Chem. Mater.* 1993, **5**, 826; (e) Percec, V. and Kawasumi, M. *J. Chem. Soc. Perkin Trans. 1* 1993, 1319; (f) Li, J. F., Percec, V. and Rosenblatt, C. *Phys. Rev. E* 1993, **48**, R1; (g) Percec, V. and Kawasumi, M. *Liq. Cryst.* 1993, **13**, 83; (h) Percec, V. and Kawasumi, M. *J. Mater. Chem.* 1993, **3**, 725; (i) Percec, V. and Kawasumi, M. *Mol. Cryst. Liq. Cryst.* 1994, **238**, 21; (j) Li, J. F., Percec, V., Rosenblatt, C. and Lavrentovich, O. *Europhys. Lett.* 1994, **25**, 199

7 Hyperbranced structures: (a) Percec, V. and Kawasumi, M. *Macromolecules* 1992, **25**, 3843; (b) Percec, V., Chu, P. and Kawasumi, M. *Macromolecules* 1994, **27**, 4441.

8 Dendrimeric main chain LCPs: Percec, V., Chu, P., Ungar, G. and Zhou, J. *J. Am. Chem. Soc.* 1995, **117**, 11441

9 Percec, V. *Pure. Appl. Chem.* 1995, **12**, 2031

10 (a) Percec, V., Chu, P., Ungar, G., Cheng, S. Z. D. and Yoon, Y. *J. Mater. Chem.* 1994, **4**, 719; (b) Cheng, S. Z. D., Yoon, Y., Zhang, A. Savitski, E. P., Park, J. Y., Percec, V. and Chu, P. *Macromol. Rapid Commun.* 1995, **16**, 533; (c) Yoon, Y., Zhang, A., Ho, R. -M., Cheng, Z. S. D., Percec, V. and Chu, P. *Macromolecules* 1996, **29**, 3421

11 Percec, V., Zheng, Q. and Lee, M. *J. Mater. Chem.* 1991, **1**, 611

12 (a) For a review on the Wilgerodt reaction see: Brown, E. V. *Synthesis* 1975, 358; (b) for the use of various variants of the Wilgerodt reaction see: Percec, V. and Zuber, M. *J. Polym. Sci: Part A: Polym. Chem.* 1992, **30**, 997

13 Albrecht, W. L., Gustafson, D. H. and Horgan, S. W. *J. Org. Chem.* 1972, **37**, 3355

14 Bhatt, M. W. and Kulkarni, S. U. *Synthesis* 1983, 249

15 Sigaud, G. 'Phase Transitions in Liquid Crystals' (Eds S. Martelluci and A. N. Chester), NATO ASI Series, Series B, Physics, Vol. 290, Plenum Press, New York, 1992, p. 375

16 Percec, V. and Tsuda, Y. *Polymer* 1991, **32**, 661

17 Percec, V. and Tsuda, Y. *Polymer* 1991, **32**, 673