Liquid-Crystalline Polyethers Based on Conformational Isomerism Part 33: Thermotropic Polyethers Based on a Mesogenic Group Containing Rigid and Flexible Units: 1-(4'-Hydroxybiphenyl-4-yl)-2-(4-Hydroxyphenyl)propane

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The synthesis of a mesogenic group containing rigid and flexible units: 1-(4'-hydroxybiphenyl-4-yl)-2-(4-hydroxyphenyl)propane (TPP) is presented. TPP was polyetherified under phase-transfer catalysed conditions with \( x_{10} \)-dibromoalkanes containing 4–20 methylenic units. The resulting polyethers, TPP-x (where \( x \) = number of methylenic groups in the spacer), were characterized by a combination of techniques consisting of differential scanning calorimetry, thermal optical polarized microscopy and small- and wide-angle X-ray scattering experiments. All TPP-x polyethers displayed multiple crystalline phases whose nature was determined by the spacer length. TPP-x with \( x \) of less than 9 exhibited crystalline phases in which the mesogenic and spacer were intermeshed. Polymers with longer spacers displayed crystalline phases in which the mesogen and spacer were separated in separate layers of different electron densities. TPP-x with \( x = 5, 7, 9 \) and 11 also exhibited a nematic mesophase.

The traditional pathway used in the synthesis of molecular and macromolecular liquid crystals is based on the concept of a rigid-rod-like mesogenic unit. In 1988 we advanced the concept of a flexible rod-like mesogenic unit or rod-like mesogenic unit based on conformational isomerism. This concept was used to synthesize main-chain liquid-crystalline polymers based on conformational isomerism without and with flexible spacers. It has been demonstrated that this synthetic strategy can be employed to tailor-make linear polymers exhibiting one or two uniaxial nematic, smectic and columnar hexagonal mesophases.

Polyethers based on very flexible mesogenic groups such as 1,2-bis(4-hydroxyphenyl)ethane (BPE), and 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and \( x_{10} \)-dibromoalkanes display mostly virtual, but also monotropic and even enantiotropic mesophases. Transformation of virtual or monotropic mesophases into enantiotropic mesophases can be accomplished by copolymerization. Copolymerization experiments can also be used to determine thermal transitions and thermodynamic parameters of the virtual mesophases of the homopolymers. Thermodynamic schemes that explain the interconversion between virtual, monotropic and enantiotropic mesophases have been elaborated. These schemes suggest that the transformation of a virtual mesophase into an enantiotropic mesophase can also be accomplished by increasing the rigidity and decreasing the degree of order of the macromolecule or of its structural units or by a combination of both. Increased rigidity and decreased degree of order (i.e. increased conformational flexibility) have been used to design the mesogenic unit 1-(4'-hydroxybiphenyl-4-yl)-2-(4-hydroxyphenyl)butane (TPB), which, by polyetherification with \( x_{10} \)-dibromoalkanes, leads to soluble polyethers displaying only nematic mesophases.

Polyethers based on TPB and flexible spacers are presently employed as models for main-chain liquid-crystalline polymers in a variety of physical investigations. At the same time, TPB and its architectural variants are used in molecular engineering of molecular and macromolecular liquid crystals with complex architecture such as macrocycles and dendrimers. Some of these developments have recently been reviewed. The polyethers based on TPB and flexible spacers are soluble in conventional solvents and exhibit only nematic mesophases. We are also interested in the design of soluble, main-chain polyethers with more ordered mesophases than the nematic one. In principle, this can be accomplished by increasing the cylindrical shape of the TPB-like mesogen. The first aim of this paper is to report the synthesis of such a novel mesogenic unit, this is achieved by replacing the 1,2-substituted butane group of TPB by 1,2-substituted propane, i.e. 1-(4'-hydroxybiphenyl-4-yl)-2-(4-hydroxyphenyl)propane (TPP). The second aim of this paper is to describe the synthesis and characterization of polyethers based on TPP and \( x_{10} \)-dibromoalkanes containing 4–20 methylenic groups.
by gel permeation chromatography (GPC). HPLC and GPC analyses 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 a UV detector, CHCl₃ or THF as solvent (1 ml min⁻¹, 40 °C), two PL gel columns of 5 x 10⁻² and 1 x 10⁻² Å and a calibration plot constructed with polystyrene standards.

A Perkin-Elmer DSC-7 differential scanning calorimeter was used to measure the thermal transitions. Heating and cooling rates were always 20 °C min⁻¹. Indium was used as a calibration standard. First-order transitions (crystal-crystal, crystal-liquid-crystal, liquid crystal-isotropic, etc.) were read at the maxima or minima of the endothermic or exothermic peaks. Glass transition temperatures (Tₓ) were read at the middle of the change in the heat capacity. All heating and cooling scans after the first heating scan were identical.

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

X-Ray scattering patterns were recorded using a flat-plate wide-angle (WAXS) vacuum camera (at room temperature and elevated temperatures) or a helium-filled flat-film pinhole-collimated small-angle (SAXS) camera (at room temperature). Ni-filtered Cu-Kα radiation was used. The samples were either in the form of prepared polymers, free-standing powders, fibres or bulk samples in Lindemann thin-walled 1 mm capillaries cooled from the melt. The temperature stability of the X-ray heating cell was ±0.1 °C. WAXS experiments were also carried out with a Rigaku X-ray generator. The point-focused beam was monochromatized with a graphite crystal (Cu-Kα radiation). Diffractograms were recorded as a function of temperature (±0.5 °C cell stability) from polymer films obtained upon melting.

Synthesis of 4-Acetoxyphenylacetic Acid, 5

Compound 5 was prepared by the esterification of 4-methoxyphenol (80 g, 0.47 mol) with acetic anhydride (67 ml, 0.70 mol). The product was recrystallized from 95% ethanol to yield 90 g (89%) of white crystals. Purity (HPLC) 99.5%; mp 86–87 °C (lit. 86 °C), 1H NMR (CDCl₃, TMS): δ 2.29 (3 H, s, CH₃CO-biphenyl), 4.30 (2 H, s, -CH,-), 7.07 (2 H, d, ortho to acetoxy of the substituted phenyl ring, J 8.0 Hz), 7.44 (3 H, m, meta and para of the substituted phenyl ring), 7.56 (2 H, d, meta to acetoxy of the substituted phenyl ring, J 8.0 Hz), 7.59 (2 H, d, ortho of the unsubstituted phenyl ring, J 8.0 Hz).

Synthesis of 4-Hydroxyphenylacetic Acid, 4

Compound 4 was prepared by the demethylation of 4-methoxyphenylacetic acid (30 g, 0.30 mol) with hydrobromic acid (181 ml, 0.99 mol) in 400 ml acetic acid. The product was recrystallized from 100 ml water to yield 68 g (93.5%) of white, needle-like crystals. Mp 146–152 °C (lit. 150 °C), mp 148 °C); 1H NMR ([D₆]acetone, TMS)δ: 3.50 (2 H, s, -CH₂-), 6.79 (2 H, d, ortho to hydroxy of the phenyl ring, J 8.0 Hz), 7.13 (2 H, d, meta to hydroxy of the phenyl ring, J 8.0 Hz). The 1H NMR spectrum showed that 4 is free of unresolved methoxy groups.

Synthesis of 4-Hydroxyphenylacetic Acid, 5

Compound 5 was prepared by the esterification of 4 (75 g, 0.49 mol) with acetic anhydride (93 ml, 0.74 mol) according to the procedure described for the synthesis of 2. After washing with water several times and filtration, 76 g (80%) of a fine white powder was obtained. This was used in the next reaction step without further purification. Mp 105–108 °C (lit. 106 °C); 1H NMR (CDCl₃, TMS): δ 2.29 (3 H, s, CH₃-), 3.64 (2 H, s, -CH₂-), 7.06 (2 H, d, ortho to acetoxy of the phenyl ring, J 10.0 Hz), 7.31 (2 H, d, meta to acetoxy of the phenyl ring, J 10.0 Hz).

Synthesis of 1-(4-Acetoxybiphenyl-4-yl)-2-(4-acetoxyphenyl) ethane, 7

Compound 7 was prepared by the Friedel–Crafts acylation of 2 with 6. Compound 5 (45 g, 0.23 mol) and SOCl₂ (25 ml, 0.35 mol) were placed in a 250 ml three-necked flask equipped with a nitrogen inlet-outlet. After adding a few drops of N,N-dimethylformamide (DMF), the reaction mixture was stirred at room temperature for 2 h, and excess SOCl₂ was removed under reduced pressure to produce a yellow solid, which was used directly in the acylation reaction. The conversion was checked by NMR (CHCl₃ shift from 3.59 to 4.10). Compound 2 (59 g, 0.28 mol) was dissolved in 250 ml CH₂Cl₂ in a 1000 ml three-necked flask equipped with a nitrogen inlet-outlet, a thermometer and a dropping funnel. The solution was cooled to below 10 °C using an ice–water bath after which time anhydrous AlCl₃ (110 g, 0.83 mol) was added. 4-Acetoxyphenylacetyl chloride (6) dissolved in 200 ml anhydrous CH₂Cl₂ was added dropwise maintaining the reaction temperature below 10 °C. After completing the addition, the deep-red solution was stirred at the same temperature for 3 h. The reaction mixture was poured into a mixture containing 120 ml concentrated HCl, 1000 ml iced water and 600 ml CH₂Cl₂. The organic layer was separated and washed twice with 500 ml water, dried over MgSO₄, filtered and the solvent was removed on a rotary evaporator. The product was recrystallized from 1000 ml toluene to yield 63 g (70%) white crystals. Purity (HPLC) 99.5%; mp 196–198 °C; 1H NMR (CDCl₃, TMS)δ: 2.29 (3 H, s, CH₃CO-Ph-CH₂-), 2.33 (3 H, s, CH₃COO-biphenyl), 4.30 (2 H, s, -CH₂-), 7.07 (2 H, d, ortho to acetoxy of the monophenyl ring, J 8.0 Hz), 7.20 (2 H, d, ortho to acetoxy of the biphenyl ring, J 8.0 Hz), 7.31 (2 H, d, meta to acetoxy of the monophenyl ring, J 8.0 Hz), 7.65 (2 H, d, meta to acetoxy of the biphenyl ring, J 8.8 Hz), 7.65 (2 H, d, meta to carbonyl of the biphenyl ring, J 8.0 Hz), 8.08 (2 H, d, ortho to carbonyl of the biphenyl ring, J 8.0 Hz).

Synthesis of 1-(4'-Methoxybiphenyl-4-yl)-2-(4'-methoxyphenyl) propane, 8

Compound 8 (20 g, 0.052 mol) was dissolved in 10 ml 10% HCl. Ethanol (34 g, 0.35 mol) and excess SOCl₂ was added to the stirred solution at room temperature to produce a yellow solution. The mixture was filtered and the solvent was removed by evaporation. The residue was recrystallized from 80 ml ethanol to yield 32 g (78%) of white crystals. Purity (HPLC) 99.5%; mp 128–132 °C; 1H NMR (CDCl₃, TMS)δ: 1.52 (3 H, s, CH₃-), 3.85 (3 H, s, CH₃O-biphenyl), 4.66 (1 H, q, CH₂-CH-), 6.84 (2 H, d, ortho to hydroxy of the monophenyl ring, J 8.4 Hz), 6.97 (2 H, d, ortho to hydroxy of the biphenyl ring, J 8.8 Hz), 7.23 (2 H, d, meta to hydroxy of the monophenyl ring, J 8.4 Hz), 7.31 (2 H, d, meta to hydroxy of the biphenyl ring, J 8.8 Hz).
7.55 (2 H, d, meta to methoxy of the biphenyl ring, J 8.8 Hz),
7.55 (2 H, d, meta to carbonyl of the biphenyl ring, J 8.4 Hz).

Synthesis of 1-(4-Methoxybiphenyl-4-yl) propylene

Compound 9 was prepared by the reduction of 8 with LiAlH$_4$-AlCl$_3$ (35 g, 0.26 mol) was placed in a 250 ml three-necked flask equipped with a dropping funnel and a nitrogen inlet-outlet, and cooled in an ice-water bath, after which time 95 ml anhydrous diethyl ether was added dropwise. LiAlH$_4$ (40 g, 0.12 mol) was placed in a 250 ml three-necked flask equipped with a dropping funnel and a nitrogen inlet-outlet, and cooled in an ice-water bath. The flask containing LiAlH$_4$ was added successively 95 ml anhydrous diethyl ether, AlCl$_3$-diethyl ether complex solution, 95 ml containing LiAlH$_4$ were added successively 95 ml anhydrous CHCl$_3$ and then the solution of 8 in 95 ml anhydrous CHCl$_3$ was added dropwise to the reducing agent solution at 0 °C. The reaction mixture was stirred at room temperature for 5 h, after which time 30% HCl (290 ml) was added dropwise with stirring to decompose the LiAlH$_4$-AlCl$_3$ complex. The product was extracted with 400 ml CHCl$_3$, washed twice with 100 ml water and dried over MgSO$_4$. After filtration, the solvent was evaporated off to yield a light-yellow solid, which was recrystallized from 1100 ml ethanol to produce 13 g (88%) of white, needle-like crystals. Purity (HPLC) 99.5%; mp 128-129 °C; $^1$H NMR (CDCl$_3$, TMS) δH: 1.24 (3 H, d, CH$_3$-CH-, J 7.2 Hz), 2.67-2.94 (3 H, m, CH$_2$-CH$_2$-CH$_3$), 3.79 (3 H, s, CH$_3$O-Ph), 3.85 (3 H, s, CH$_3$O-biphenyl), 6.83 (2 H, d, ortho to methoxy of the monophenyl ring, J 9.1 Hz), 7.06 (2 H, d, ortho to methoxy of the biphenyl ring, J 9.2 Hz), 7.12 (2 H, d, ortho to methylene of the biphenyl ring, J 8.7 Hz), 7.12 (2 H, d, meta to methoxy of the monophenyl ring, J 9.1 Hz), 7.42 (2 H, d, meta to methoxy of the biphenyl ring, J 9.2 Hz), 7.51 (2 H, d, meta to methylene of the biphenyl ring, J 8.7 Hz).

Synthesis of Polyethers

Conventional liquid-liquid two-phase (organic solvent-aqueous NaOH solution) phase-transfer-catalysed polyetherification conditions were used for the preparation of polyethers. The polyetherifications were accomplished under a nitrogen atmosphere at 80 °C in an o-dichlorobenzene-10 mol 1$^{-1}$ NaOH two-phase system (10-fold molar excess of NaOH versus phenol groups) in the presence of TBAH as phase-transfer catalyst. The molar ratio of nucleophile to electrophilic monomers was always 10:1.0. An example of the polyetherification is as follows.

To a 25 ml single-necked flask equipped with a condenser and a nitrogen inlet-outlet were successively added 0.60 mmol (0.1826 g) of monomer TPP (10), 1.2 ml of o-dichlorobenzene, 0.60 mmol (0.1632 g) of 1,8-dibromooctane, 1.2 ml of 10 mol 1$^{-1}$ NaOH and 1.24 mmol (0.0815 g) of TBAH. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80 °C. After 3 h of reaction the organic and aqueous layers were diluted with CHCl$_3$ and water and the aqueous layer separated off. The organic layer was washed once with water, once with dilute HCl and three times with water. The polymer solution was precipitated into methanol to yield 0.2412 g (97%) of white fibrous material. The polymer was further purified by four successive precipitations from CHCl$_3$ solution into acetone, then once from CHCl$_3$ solution into methanol and finally twice from THF solution into water.

Results and Discussion

Scheme 1 presents the synthesis of racemic TPP (10). The synthesis of TPP was accomplished via a synthetic route similar to that employed in the preparation of TBP. As illustrated in Scheme 2, TPP has a stereocentre. However, the sequence of reactions outlined in Scheme 1 leads to the racemic mixture of the two enantiomers of TPP. The individual enantiomers of TPP can be prepared via the same procedure as that used in the synthesis of the two enantiomers of TBP.

There are a few details for the preparation of TPP that we should mention here. Although 4 is commercially available, we prefer to prepare it from 3 since this route is less expensive. The alkylation of 7 with ethyl iodide leads to a mixture of C- and O-alkylated products. Their separation was difficult. The O-alkylated product was cleaved in situ and then was realkylated with ethyl iodide to increase the overall yield of the C-alkylated product. In the alkylation of 7 with ethyl iodide only low amounts of O-alkylated and C-dialkylated products are obtained. The pure compound 8 can be separated from the C-dimethylated and O-methylated products by recrystallization from 95% ethanol. The reduction of 8 to 9 was performed with LiAlH$_4$-AlCl$_3$Et$_2$O in CHCl$_3$. The synthesis of the polyethers of TPP with $\alpha,\omega$-dibromooalkanes (TPP-x) was performed under phase-transfer catalysed polyetherification conditions developed in our laboratory (Scheme 2). As illustrated in Scheme 2 the resulting TPP-x polyethers are in fact copolymers derived from the four constitutional and stereoisomers of TPP. TPP-x containing even number $x$ is soluble only at high temperature in chlorobenzene, THF or chloroform. TPP-x with odd number $x$ is soluble at room temperature. TPP-x with $x=4, 6$ and 8 is so sparingly soluble that the molecular weight could not be determined byGPC. TPP-x with both odd and even $x$ is very soluble even at room temperature.
Table 1 summarizes the yields, molecular weights and phase-transition temperatures together with the corresponding thermodynamic parameters of all TPP-x. Although the molecular weights reported are only relative to polystyrene standards, they are all larger than the values below which they become molecular-weight dependent.\(^8\)

DSC traces of the first, second and subsequent heating scans are shown in Fig. 1(a), (b) and (c). The phase-transition temperatures reported in Table 1 were collected from the DSC traces of Fig. 1 and were assigned by a combination of thermal optical polarized microscopy and X-ray scattering experiments. Both these experiments will be discussed in a later section of this paper. The DSC traces from Fig. 1 demonstrate that TPP-x presents multiple phase transitions during both heating and cooling. All TPP-x are crystalline polymers with polymorphic crystalline phases. Only TPP-x with \(x = 5, 7, 9\) and 11 exhibit above their highest crystalline melting transition also an enantiotropic nematic mesophase. The highest phase-transition temperatures of TPP-x present an odd–even dependence on spacer length regardless of whether this transition refers to the melting of a crystal or of a liquid-crystalline phase into an isotropic liquid [Fig. 2(b)]. With increasing spacer length this dependence disappears. The second highest melting temperature is almost independent of spacer length [Fig. 2(a)]. Fig. 2(b) shows a plot of the highest transition (i.e., isotropization) and the nematic–crystalline transition temperatures for TPP-x with odd number \(x\). There is a continuous increase of the nematic–crystalline and a continuous decrease of the isotropization transition temperatures. At \(x = 13\) these two dependences intercept each other and therefore, for \(x > 13\) the nematic mesophase of TPP-x disappears.

Table 1

<table>
<thead>
<tr>
<th>(x)</th>
<th>Yield</th>
<th>Molecular Weight</th>
<th>Transition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X-Ray Characterization of TPP-x Polymers

In agreement with the DSC data, the X-ray diffraction experiments showed a clear difference in the behaviour of TPP-x polymers with \(x = \) even and \(x = \) odd. As was expected, this difference was most pronounced in polymers with short spacers. With increasing spacer length the phase behaviours of even and odd polymers gradually converged. This trend was in agreement with that observed by using DSC [Fig. 2(a)].

Polymers With Odd-numbered Spacers \(x \leq 9\)

X-ray scattering experiments confirmed that TPP-x (\(x = \) odd) polymers with short spacers, i.e., TPP-5, TPP-7 and TPP-9, are crystalline with a nematic phase at higher temperatures. The two main DSC peaks (Fig. 1) were thus identified as crystal–nematic (N) and nematic–isotropic (I) transitions, respectively. The powder pattern of the crystalline state is dominated by two intense, closely spaced reflections in the wide-angle range and no clear diffraction features at lower angles. For TPP-5 the Bragg spacings corresponded to the two wide-angle reflections 4.77 and 4.54 Å, at room temperature. On slow cooling from the nematic melt and after further annealing, additional weak diffraction features appeared. At 123 °C, i.e., between the temperatures of melting from the first DSC scan [i.e. 53 °C; see Table 1 and Fig. 1(a)] and the small DSC endotherm at 148 °C, the pattern thus recorded had the same global appearance as that at room temperature prior to annealing, with the two strong reflections corresponding to 4.80 and 4.63 Å. However, in addition there were two weak reflections at 4.98 and 5.11 Å. Upon cooling below the weak solid–solid transition the distribution of the satellite reflections on the low-angle side of the main wide-angle doublet changed into a short series of equidistant lines. In addition a very weak diffraction feature developed at lower angles, corresponding to 20.5 Å. The position of the dominant wide-angle doublet did not seem to change discontinuously at the solid–solid transition.

The main features of the fibre pattern of TPP-5 are shown schematically in Fig. 3. The two dominant reflections are seen to be on the same row line, one of the reflections being equatorial. The maximum annealing temperature was only 80 °C, which did not produce resolvable satellite reflections.
Scheme 2 Synthesis of polyethers based on 1-(4'-hydroxybiphenyl-4-yl)-2-(4-hydroxyphenyl) propane and α,ω-dibromoalkanes containing x methylenic units (TPP-x)

Table 1 Characterization of polyethers based on TPP and α,ω-dibromoalkanes (TPP-x) with different numbers of methylenic units (x). Data collected from first heating, cooling (both on first line) and second heating DSC (on the second line) scans

<table>
<thead>
<tr>
<th>x</th>
<th>yield (%)</th>
<th>$\langle M_d \rangle$ GPC</th>
<th>$\langle M_w/M_d \rangle$ GPC</th>
<th>thermal transitions/°C and corresponding enthalpy changes/kJ mru$^{-1}$ in parentheses$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>97.7</td>
<td>—</td>
<td>—</td>
<td>heating: K 65(0.5) K 144(2.68) K 280(21.77) I K 127(18.7) K 134(3.22) K 34 G</td>
</tr>
<tr>
<td>5</td>
<td>94.8</td>
<td>11,200</td>
<td>2.53</td>
<td>K 53(0.35) K 148(3.57) N 183(7.52) I K 173(4.76) N 108(-3.05) K 39 G</td>
</tr>
<tr>
<td>6</td>
<td>93.3</td>
<td>—</td>
<td>—</td>
<td>K 59(1.25) K 126(2.22) K 249(20.35) I K 234(19.36) K 121(0.44) K</td>
</tr>
<tr>
<td>7</td>
<td>97.5</td>
<td>25,000</td>
<td>2.60</td>
<td>K 49(0.48) K 150(5.0) N 178(5.88) I K 167(-5.81) N 126(-4.08) K 33 G</td>
</tr>
<tr>
<td>8</td>
<td>97.5</td>
<td>—</td>
<td>—</td>
<td>K 55(0.33) K 141(2.16) K 221(19.51) I K 167(-5.81) N 126(-4.08) K 33 G</td>
</tr>
<tr>
<td>9</td>
<td>99.0</td>
<td>29,500</td>
<td>2.30</td>
<td>K 48(0.56) K 154(7.43) N 173(6.69) I K 161(-7.32) N 133(-5.36) K 27 G</td>
</tr>
<tr>
<td>10</td>
<td>91.2</td>
<td>19,700</td>
<td>3.32</td>
<td>K 52(0.5) K 145(12.19) K 204(20.51) I K 186(-21.94) K 120(-12.67) K</td>
</tr>
<tr>
<td>11</td>
<td>91.3</td>
<td>31,800</td>
<td>1.68</td>
<td>K 49(0.5) K 111(9.75) K 155(8.7) N 165(6.2) I K 111(9.75) K 155(8.7) N 165(6.2) I</td>
</tr>
<tr>
<td>12</td>
<td>90.2</td>
<td>18,300</td>
<td>2.90</td>
<td>K 51(0.6) K 144(12.78) K 187(19.54) I K 156(-8.0) N 136(-6.7) K 95(-9.27) K</td>
</tr>
<tr>
<td>13</td>
<td>97.5</td>
<td>29,200</td>
<td>2.00</td>
<td>K 50(1.1) K 108(15.48) K 162(18.25) I K 147(-7.0) K 140(-10.3) K 97(-14.14) K 28 G</td>
</tr>
<tr>
<td>14</td>
<td>92.3</td>
<td>16,500</td>
<td>2.03</td>
<td>K 49(0.5) K 134(17.12) K 176(21.56) I K 161(-21.92) K 132(-18.49) K 32 G</td>
</tr>
<tr>
<td>15</td>
<td>93.3</td>
<td>20,900</td>
<td>2.02</td>
<td>K 49(0.66) K 118(19.93) K 158(20.41) I K 151(-21.67) K 129(-22.41) K 32 G</td>
</tr>
<tr>
<td>16</td>
<td>93.1</td>
<td>28,700</td>
<td>3.42</td>
<td>K 47(0.65) K 121(22.81) K 154(23.84) I K 137(-23.31) K 108(-24.91) K 21 G</td>
</tr>
<tr>
<td>17</td>
<td>95.2</td>
<td>34,500</td>
<td>1.89</td>
<td>K 47(0.65) K 121(22.81) K 154(23.84) I K 137(-23.31) K 108(-24.91) K 21 G</td>
</tr>
<tr>
<td>18</td>
<td>96.7</td>
<td>23,500</td>
<td>2.92</td>
<td>K 47(0.73) K 119(23.98) K 156(23.86) I K 137(-23.0) K 108(-25.05) K 23 G</td>
</tr>
<tr>
<td>19</td>
<td>89.4</td>
<td>23,100</td>
<td>2.01</td>
<td>K 47(0.73) K 119(23.98) K 156(23.86) I K 137(-23.0) K 108(-25.05) K 23 G</td>
</tr>
<tr>
<td>20</td>
<td>92.0</td>
<td>37,300</td>
<td>2.28</td>
<td>K 50(1.14) K 135(23.54) K 156(23.76) I K 139(-22.66) K 126(-28.06) K 31 G</td>
</tr>
</tbody>
</table>

$^a$mru = molecular repeat unit.
or the 20.5 Å feature. A sharp layer-line streak was present with the meridional spacing of 6.0 Å (indicated in Fig. 3). This was attributed to a maximum in the molecular structure factor.

A summary interpretation of the diffraction data on TPP-5 is that the crystal structure is based on a distorted hexagonal packing of tilted chains, with initially poor interchain transitional correlation. This correlation greatly improves on slow melt crystallization. The 20.5 Å periodicity which thus develops corresponds reasonably well with the calculated extended monomer length of 23.5 Å. The solid–solid transition at 143 °C appears to be associated with axial shift between neighbouring chains.
temperatures-of TPP-x as a function of x. Data collected from second heating scans.

In TPP-5 the departure from the hexagonal chain cross-section remained approximately constant with temperature, as judged by the constant splitting of the dominant, wide-angle reflection. In some TPP-x (x = odd) homopolymers with larger x, as well as in some copolymers of TPP with two different spacers (which will be described in a subsequent paper), the splitting decreased with temperature. This is illustrated in Fig. 4 for TPP-9. Here, with increasing temperature the cross-section of the unit cell perpendicular to the chain direction became progressively closer to the hexagonal. This may be associated with a reduction in the chain tilt.

Polymers With Odd-numbered Spacers x ≥ 11
TPP-x homopolymers with x ≥ 13 behaved quite differently from those described above, with TPP-11 being an intermediately case. The x ≥ 13 polymers did not exhibit the nematic phase although, as the thermograms showed, they underwent a strong transition below the final isotropization temperature. This, however, was a crystal-crystal transition and the polymers did not show a liquid-crystal phase at all (Figs. 1 and 2). Neither of the two crystal forms was isomorphous with those described above. For illustration, Fig. 5 shows the temperature evolution of the diffractogram of TPP-13. The low-temperature form was characterized by a number of intense Bragg peaks in the wide-angle region and by three orders of layer reflections at lower angles. The structure was clearly of lower symmetry than those described so far.

On the other hand, the scattering pattern of the high-temperature form was rather simple and was dominated at wide angles by a strong maximum with a medium-intensity reflection on either side of it. The strong low-angle fundamental was retained, but the higher orders were weakened, compared with the low-temperature form. The lowest angle reflection in both forms closely corresponded to the monomer spacings calculated for the extended monomer units. The considerable intensity was in contrast with the extremely weak or non-existent low-angle diffraction intensity of the TPP-x polymers with 5 ≤ x < 9. A strong layer reflection in the long spacer polymers suggested that aromatic mesogens and aliphatic spacers were segregated into separate layers of different electron densities. On the other hand, the absence of strong reflections in the low-angle region, as in polymers with 5 ≤ x ≤ 9, signified full or partial intermeshing.

Polymers TPP-15, TPP-17, TPP-19 and TPP-20 displayed
polymers with $x \leq 8$ the low-temperature transition endotherm was small whereas for polymers with $x \geq 10$ it was considerably larger (Fig. 1, Table 1).

X-Ray diffraction patterns of TPP-6 and TPP-8 were recorded as a function of temperature. Both the low- and the high-temperature phases were characterized by a strong sharp diffraction peak at 4.6 Å. The low-temperature phase had additional weak reflections on the high-angle side and one reflection at lower angles, corresponding to approximately half the monomer repeat: 12 Å ($= 24/2$ Å) for TPP-8, as compared with the extended monomer length of 27 Å. The observed reflections for TPP-8 could be indexed on a hexagonal unit cell with $a = 5.31$ Å and $c = 21$ Å, as shown in Table 2. The discrepancy between the measured (12.0) $d_{h00}$ spacing is not understood. Attempts at producing well oriented fibres were unsuccessful.

A significant feature of the low-temperature phase is the absence of the 001 reflection, indicating the existence of a glide plane parallel to the chain axis. Thus neighbouring chains are translated by half the monomer length with respect to each other. This seems to be a rather general feature of the main-chain polymers with shorter spacers and also parallels the behaviour of the TPP-$x$ ($x = \text{odd}$) polymers.

In the high-temperature phase only the strong sharp 100 hexagonal reflection remains. At lower angles two very weak diffraction features were observed, which correspond to 11.5 and 14.8 Å. As in the low-temperature form, no reflection was observed in the 20–30 Å region, which would correspond to monomer periodicity. Had it not been for the two weak reflections, the high-temperature phase would have been described as hexagonal columnar. It may be that these were not true Bragg reflections but rather sharp molecular transformation maxima, in which case the description of the phase as columnar would have been valid. Further attempts to prepare well oriented fibres of TPP-8 and TPP-6 are planned, with a view to resolving this question.

**Table 2 Observed reflections of TPP-8**

<table>
<thead>
<tr>
<th>reflection</th>
<th>measured (Å)</th>
<th>calculated (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.60</td>
<td>4.60</td>
</tr>
<tr>
<td>104</td>
<td>4.48</td>
<td>4.49</td>
</tr>
<tr>
<td>103</td>
<td>3.86</td>
<td>3.84</td>
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<tr>
<td>104</td>
<td>3.43</td>
<td>3.46</td>
</tr>
<tr>
<td>002</td>
<td>12.0</td>
<td>10.5</td>
</tr>
</tbody>
</table>

**Polymers with Even-numbered Spacers $x \geq 10$**

The main feature of the powder diffractions of the low-temperature phase of the polymers with longer even-numbered spacers was common to the whole series from TPP-10 to TPP-18. There were a number of strong reflections at wide angles, indicating low crystal symmetry (see Fig. 5). In addition, there was always a reasonably strong low-angle reflection corresponding closely to monomer periodicity, as well as its second- and sometimes third-order. For example, for TPP-12 the observed reflections corresponded to 26.3 and 26.5/2 Å, respectively, compared with the calculated extended monomer length of 32.2 Å. The appearance of the strong reflection in the region of the full monomer repeat suggests that mesogens and spacers form separate layers, in contrast to the observation with shorter-length spacer TPP polymers. The overall situation was similar to the odd-numbered spacer TPP series, except that the actual crystal structure was different in the two series.

With increasing temperature some diffraction peaks shifted...
conceivably, leading to merging of certain reflections [Fig. 6(d) and (e)]. This was associated with a heat capacity anomaly, which became apparent as a broad shoulder in the DSC traces of some of the polymers in the present group, e.g. in TPP-16 at ca. 100 °C.

Above the main transition, associated by the lower of the two large DSC endotherms (Fig. 1), the powder pattern was greatly simplified, leaving one dominant wide-angle reflection at 4.70 Å and a weaker reflection on either side; these corresponded to 5.16 and 4.23 Å (data for TPP-12). In addition, two orders of low-angle reflections remained, although they were shifted to somewhat smaller fundamental spacing. For TPP-12 the shift was from 26.4 to 24.2 Å. Thus, the high-temperature phase in TPP-N polymers with long, even-numbered spacers x ≥ 10 was isomorphous with the high-temperature form of the polymers having long odd-numbered spacers with x ≥ 13.

It was not surprising that the convergence of the structures of x = even- and x = odd-numbered polymers should occur for long spacers and at high temperatures. Increasing both spacer length and temperature reduced the probability of finding the spacer in its minimum-energy conformation. The fact that the spacers were conformationally disordered in the high-temperature phase was suggested by the above-mentioned average monomer shrinkage of more than 2 Å upon the transition from the low-temperature form to the high-temperature form. For a long disordered spacer, orientational correlation between its terminal bonds became too low for the even-odd variation to determine mutual orientation of successive mesogens and hence influence crystal structure. The nematic mesophase of TPP-x polymers with x = 5, 7, 9 and 11 exhibited characteristic schlieren textures.

![Fig. 6 X-Ray diffractograms of TPP-18 (powder) as a function of temperature. Temperature of each thermogram °C: (a) 30; (b) 40; (c) 60; (d) 80; (e) 100; (f) 110; (g) 120; (h) 130; (i) 140; (j) 150; (k) 160; (l) 170; (m) 180; (n) 190; (o) 200; (p) 210; (q) 220.](image)

**Conclusions**

The TPP-x polymers described in this paper provided a very complex and comprehensive system in which the structure of the polymers was strongly influenced by their spacer length. This system contrasted with the TPB-x polymers, which showed only a nematic and/or a nematic and a crystalline phase. Since some of the phases of TPP-x polymers exhibited various hexagonal or distorted hexagonal crystalline phases, they could be of great potential for the molecular design of polymers displaying a columnar hexagonal liquid-crystalline phase by suitable copolymerization experiments.

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**References**


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