Mesomorphic properties of copolyesters of 3,6-linked triphenylene-based units and polymethylene spacers

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Main chain discotic liquid crystalline polymers consisting of triphenylene-based units and alkyl spacers (C8, C10 and C12), connected by ester linkages in the 3- and 6-positions of triphenylene, have been synthesized and their mesomorphic properties were studied by DSC, polarizing optical microscopy and X-ray diffraction. It was found that these polymers exhibit a hexagonal columnar (Col_h) mesophase with intracolumnar order over a wide temperature range. The clearing temperature decreases on increasing the spacer length. It was found that the clearing temperatures are rather higher than that of the corresponding triphenylene monomer having six hexyloxy chains. These polymers form an ordered columnar mesophase, while the corresponding monomeric mesogen shows a disordered columnar phase. In the polymeric system, the fluctuations of the disc-like units in the mesophase are restricted by the connection of the mesogenic units, which stabilizes the columnar mesophase.

1. Introduction

Liquid crystalline polymers are an interesting class of materials with unique properties. For example, macroscopic reorientation in magnetic fields [1, 2] and by mechanical forces [3] can be realized, and functional properties such as extremely high modulus, high strength and high heat resistance have been successfully obtained [4–6]. These anisotropic properties have not been realized in low molecular mass liquid crystals. In addition, at temperatures below the glass transition temperature highly ordered anisotropic glasses are obtained and these structures, having electronic and photonic properties, may be conveniently fabricated for applications such as imaging technology, non-linear optics, and telecommunications [7, 8].

Recent studies of discotic mesogens have also included new materials showing photoconductive and semi-conductive properties, and having application potential in electronic devices [9, 10]. These follow the discovery of fast hole mobility ($10^{-1} cm^2 V^{-1} s^{-1}$) in a plastic columnar mesophase for a triphenylene mesogen with six peripheral pentylthio chains [11]. This value is almost comparable to the mobility found in organic single crystals and amorphous Si semiconductor ($1 cm^2 V^{-1} s^{-1}$) and is larger

than those of amorphous polymers ($10^{-3} cm^2 V^{-1} s^{-1}$) used in commercial Xerography and laser-printer applications [12–14].

However, only a relatively small number of liquid crystalline polymers containing disk-like mesogens, either as side groups or within the main chain, have been reported [15–18], while liquid crystalline polymers having rod-shaped mesogens have been extensively studied for more than two decades [19, 20]. In particular, triphenylene is a well known disc-shaped molecule incorporated into a wide diversity of mesogen structures. In recent years, Ringsdorf et al. and Boden et al. have reported the synthesis of structurally asymmetrical triphenylene derivatives [21–23]; also some types of side chain and main chain discotic liquid crystalline polymers containing triphenylene mesogenic units have been synthesized to reveal mesomorphic properties [24–27].

It is well recognized that disc-shaped molecules consisting of a flat rigid core, such as triphenylene containing peripherally attached aliphatic chains, have a tendency to exhibit discotic mesophases. These molecules tend to stack into columns to form a variety of columnar mesophases and show translational and rotational disordering along and around the columnar axis, respectively. Therefore, the mesomorphism of polymeric mesogens is thought to be different from that of the corresponding monomeric mesogens.

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In this work, new alternating copolyesters consisting of triphenylene-based mesogenic units and methylene spacers were synthesized and their mesomorphic properties were investigated; the discs were connected by ester linkages at the 3- and 6-positions, see the scheme.

2. Experimental

2.1. *Characterization*

The identification of synthetic products was carried out by ^{1}H NMR and IR spectroscopy, and by elemental analysis. ^{1}H NMR spectra were recorded on a JEOL
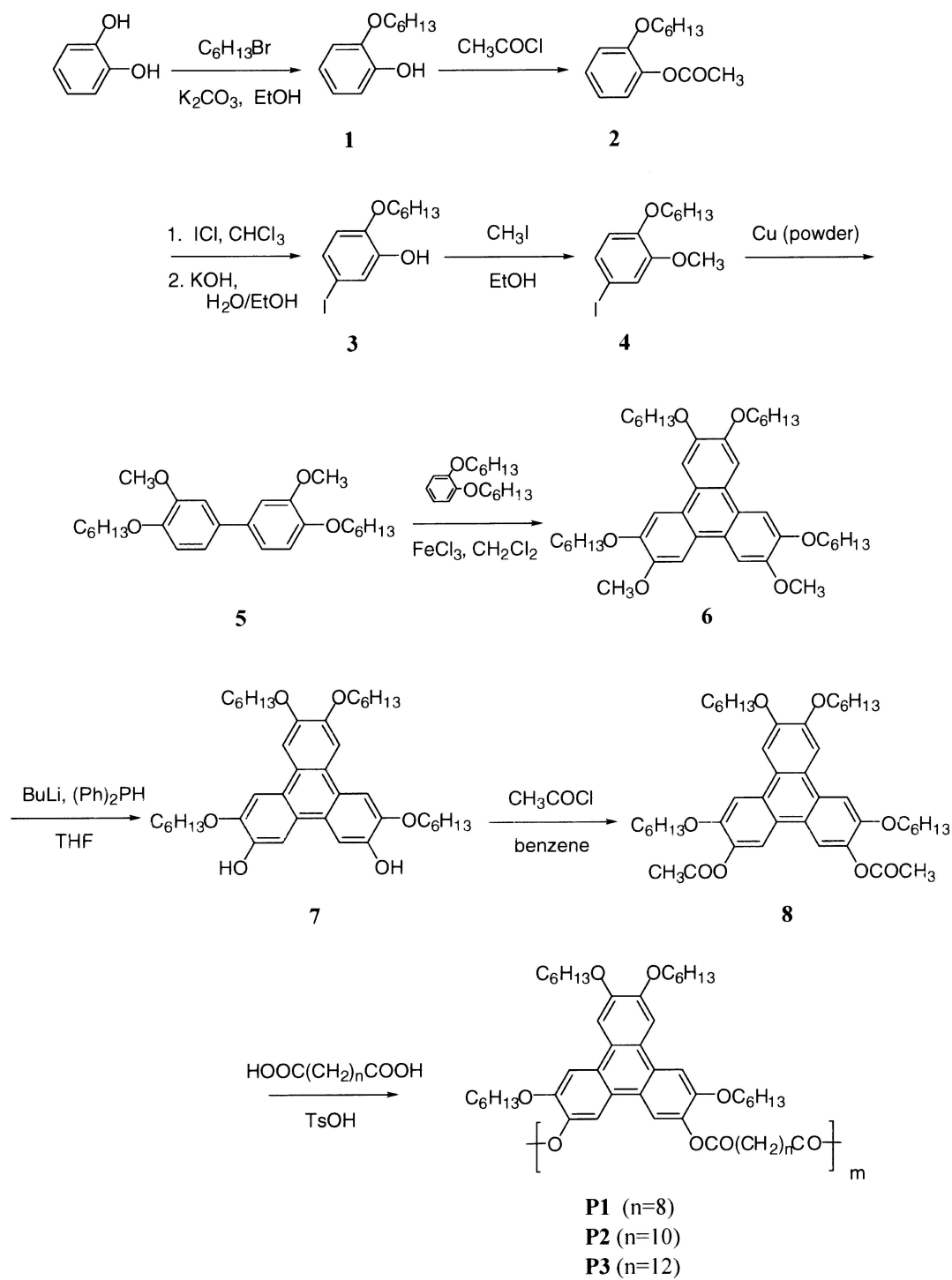
Scheme.

JNM-Alpha-500 spectrometer using Me₄Si as an internal standard. IR spectra were obtained with KBr pellets using a Perkin Elmer Pergon 1000 FTIR spectrometer. The elemental analysis was performed with a Perkin Elmer CHNS/O analyser 2400. Gel permeation chromatography (GPC) measurements ($CHCl_3$ as eluent) was used to measure the average molecular mass of polymers and calibrated using polystyrene standards.

The phase transition temperatures and enthalpies were measured using differential scanning calorimetry (DSC) (TA Instrument, 2920 MDSC) and the textures of the mesophases were observed using a polarizing optical microscopy (POM) (Olympus, BH-2), with a hot stage (Mettler, FP80HT) and controller (Mettler, FP80). X-ray diffraction (XRD) studies were carried out using a Rigaku Geigerflex X-ray diffractometer (CuK_α) with a custom-built hot stage.

2.2. *Monomer synthesis*

The synthetic route used to prepare the main chain discotic liquid crystalline polymers is outlined in the scheme. An asymmetrical triphenylene derivative **6** was prepared using an iron(III) chloride mediated oxidative coupling of 4,4′-bis(hexyloxy)-3,3′-dimethoxybiphenyl and 1,2-di(hexyloxy) benzene followed by a reductive methanol work-up [28]. The reaction of diester **8** and three homologues of α, ω-alkanedioic acid $HOOC(CH_2)_nCOOH$, with 8, 10 and 12 methylene groups, gave three copolymers under a melt condensation method using *p*-toluene-sulphonic acid as catalyst. The resulting polymers were purified by several times precipitation: the THF solution of the polymers was dropped into excess hexane with vigorous stirring.

2.2.1. *2-Hexyloxyphenol (1)*

A butanone solution of catechol (30.0 g, 273 mmol), potassium carbonate (55.0 g, 400 mmol) and bromohexane (45.0 g, 273 mmol) was heated under reflux for 24 h. The mixture was poured into 300 ml of distilled water and extracted with dichloromethane (200 ml). After drying over MgSO₄, the solvent was removed *in vacuo* and the residue distilled to give compound **1** (39.5 g, 74.7%, 140°C, 3 mm Hg). ¹H NMR ($CDCl_3$) δ/ppm: 6.97–6.80 (m, 4H, Ar–<u>H</u>), 5.82 (s, 1H, O<u>H</u>), 3.98 (t, 2H, O<u>CH</u>₂), 1.85 (m, 2H, OCH₂<u>CH</u>₂), 1.46–1.25 (m, 6H, (<u>CH</u>₂)₃), 0.91 (t, 3H, <u>CH</u>₃). IR (KBr), v_{max}/cm⁻¹: 3350 (O–H, str), 1617, 1518s (C=C, in-plane, str), 1260, 1171s (C–O, str).

2.2.2. *2-Hexyloxyphenyl acetate (2)*

Acetyl chloride (13.0 g, 165 mmol) was added to 20.0 g (100 mmol) of **1** and the mixture stirred until the reaction was complete. 300 ml of $CHCl_3$ was added and the solution was washed with aqueous potassium carbonate and then distilled water. The organic layer was dried over MgSO₄ and the solvent removed *in vacuo*. The remaining product **2** (18.5 g) was used in the next reaction without further purification. ¹H NMR ($CDCl_3$) δ/ppm: 7.15–6.81 (m, 4H, Ar–<u>H</u>), 3.87 (t, 2H, O<u>CH</u>₂), 2.25 (s, 3H, CO<u>CH</u>₃), 1.70 (m, 2H, OCH₂<u>CH</u>₂), 1.43–1.26 (m, 6H, (<u>CH</u>₂)₃), 0.90 (t, 3H, <u>CH</u>₃). IR (KBr), v_{max}/cm⁻¹: 1736s (C=O, str), 1617, 1518s (C=C, in-plane, str), 1260, 1171s (C–O, str).

2.2.3. *2-Hexyloxy-5-iodophenol (3)*

Compound **2** (18.5 g, 78.4 mmol) was dissolved in $CHCl_3$ (100 ml) and the solution cooled to room temperature. Iodine monochloride (20.0 g, 123 mmol) in $CHCl_3$ (30 ml) was added dropwise; the mixture was then stirred at room temperature overnight and washed with sodium metabisulfite. The solution was dried over MgSO₄ and the solvent removed *in vacuo*. The residue was dissolved in a mixture of ethanol (20 ml) and 50 ml of a solution of KOH (20.0 g, 357 mmol in 50 ml of water). After heating at reflux for 2 h, the solution was acidified with dilute aqueous HCl, and the mixture extracted with $CHCl_3$ and the organic solution dried over MgSO₄. The solvent was removed and the fraction distillating at (5 mm Hg, 180°C) was recrystallized from petroleum ether to give compound **3** (11.4 g, 82.7%). ¹H NMR ($CDCl_3$) δ/ppm: 7.23 (s, 1H, Ar–<u>H</u>), 7.14 (d, 1H, Ar–<u>H</u>), 6.57 (d, 1H, Ar–<u>H</u>), 5.63 (s, 1H, O–<u>H</u>), 4.00 (t, 2H, O<u>CH</u>₂), 1.79 (m, 2H, OCH₂<u>CH</u>₂), 1.45–1.30 (m, 6H, (<u>CH</u>₂)₃), 0.91 (t, 3H, <u>CH</u>₃). IR (KBr), v_{max}/cm⁻¹: 3350s (O–H, str), 1617, 1518s (C=C, in-plane, str), 1260, 1171s (C–O, str).

2.2.4. *2-Hexyloxy-5-iodoanisole (4)*

Compound **3** (11.0 g, 34.4 mmol) and KOH (2.0 g, 35.7 mmol) were stirred in ethanol (80 ml) for 20 min. Methyl iodide (10.0 g, 71.5 mmol) was added and the solution stirred at room temperature for 4 days. The mixture was acidified with dilute aqueous HCl and the products were extracted into $CHCl_3$. The solvent was removed *in vacuo* and the residue recrystallized from ethanol to give compound **4** (7.4 g, 68.1%, m.p. 44°C). ¹H NMR ($CDCl_3$) δ/ppm: 7.20 (d, 1H, Ar–<u>H</u>), 7.12 (s, 1H, Ar–<u>H</u>), 6.62 (d, 1H, Ar–<u>H</u>), 3.97 (t, 2H, O<u>CH</u>₂), 3.82 (s, 3H, O<u>CH</u>₃), 1.83 (m, 2H, OCH₂<u>CH</u>₂), 1.47–1.31 (m, 6H, (<u>CH</u>₂)₃), 0.90 (t, 3H, <u>CH</u>₃). IR (KBr), v_{max}/cm⁻¹: 1618, 1518s (C=C, in-plane, str), 1260, 1170s (C–O, str).

2.2.5. *4,4′-Bis(hexyloxy)-3,3′-dimethoxybiphenyl (5)*

Compound **4** (7.0 g, 21.9 mmol) was mixed with copper powder (20 g, 310 mmol), and the mixture heated slowly to 270°C. After cooling at room temperature, the mixture was extracted with $CHCl_3$. The residue, after removal of the solvent, was recrystallized from ethanol to give

compound **5** (2.1 g, 51.2%, m.p. 83.0°C). ^{1}H NMR (CDCl$_3$) δ/ppm: 7.08–7.05 (m, 4H, Ar–$\underline{H}$), 6.90 (d, 2H, Ar–$\underline{H}$), 4.04 (t, 4H, O$\underline{CH}_2$), 3.93 (s, 6H, O$\underline{CH}_3$), 3.93 (s, 6H, O$\underline{CH}_3$), 1.86 (m, 4H, OCH$_2\underline{CH}_2$), 1.50–1.31 (m, 12H, $(\underline{CH}_2)_3$), 0.90 (t, 6H, $\underline{CH}_3$). IR (KBr), v_{max}/cm^{-1}: 1617, 1518s (C=C, in-plane, str), 1261, 1171s (C–O, str).

2.2.6. *3,6-Dimethoxy-2,7,10,11-tetrahexyloxy-triphenylene (6)*

Compound **5** (2.0 g, 4.8 mmol) and 1,2-dihexyloxy-benzene (4.0 g, 14.3 mmol) were stirred in 30 ml of CH$_2$Cl$_2$, and iron(III) chloride (8.0 g, 49.2 mmol) was added. After further stirring for 3 h, the mixture was poured into 70 ml of CH$_3$OH and the resulting solid was filtered and dried. Purification by column chromatography (silica gel, CH$_2$Cl$_2$ as eluent) gave compound **6** (2.3 g, 69.1%, m.p. 116.5°C). Elemental analysis (C$_{44}$H$_{64}$O$_6$): found C 76.67, H 9.44; required C 76.70, H 9.36%. ^{1}H NMR (CDCl$_3$) δ/ppm: 7.80 (m, 6H, Ar–$\underline{H}$), 4.24 (m, 8H, O$\underline{CH}_2$), 4.06 (s, 6H, O$\underline{CH}_3$), 1.93–1.84 (m, 8H, OCH$_2\underline{CH}_2$), 1.55–1.35 (m, 36H, $(\underline{CH}_2)_3$), 0.90 (t, 12H, $\underline{CH}_3$). IR (KBr), v_{max}/cm^{-1}: 1617, 1518s (C=C, in-plane, str), 1260, 1171s (C–O, str), 834s (C=C, out-of-plane, m).

2.2.7. *3,6-Dihydroxy-2,7,10,11-tetrahexyl-oxytriphenylene (7)*

Diphenylphosphine (5.1 g, 27.6 mmol) was dissolved in 100 ml of dried THF and the solution cooled in an ice bath under N$_2$. Butyllithium (30 ml, 1.6M in hexane) was added slowly to this solution. Compound **6** (5.0 g, 7.3 mmol) was added and the mixture heated at reflux for 12 h. Dilute aqueous HCl was added to the reaction mixture and the organic layer extracted with AcOEt. The solvent was distilled *in vacuo* and precipitation of a CH$_2$Cl$_2$ solution with CH$_3$OH gave a white solid. This was filtered off and further purified by column chromatography (silica gel, benzene as eluent) to give compound **7** (3.1 g, 58%, m.p. 105°C). Elemental analysis (C$_{42}$H$_{60}$O$_6$0: found C 76.67, H 9.44; required C 76.32, H 9.15%. ^{1}H NMR (CDCl$_3$) δ/ppm: 7.92 (s, 2H, Ar–$\underline{H}$), 7.80 (s, 2H, Ar–$\underline{H}$), 7.75 (s, 2H, Ar–$\underline{H}$), 5.85 (s, 2H, O–$\underline{H}$), 4.28 (t, 4H, O$\underline{CH}_2$), 4.23 (t, 4H, O$\underline{CH}_2$), 1.99–1.85 (m, 8H, OCH$_2\underline{CH}_2$), 1.62–1.35 (m, 24H, $(\underline{CH}_2)_3$), 0.90 (t, 12H, $\underline{CH}_3$). IR (KBr), v_{max}/cm^{-1}: 3350s (O–H, str), 1617, 1518s (C=C, in-plane, str), 1260, 1171s (C–O, str), 834s (C=C, out-of-plane, m).

2.2.8. *3,6-Acetyloxy-2,7,10,11-tetrahexyloxy-triphenylene (8)*

A mixture of acetyl chloride (2.0 g, 25.5 mmol), compound **7** (0.28 g, 0.42 mmol) and K$_2$CO$_3$ (2.0 g, 14.5 mmol) in CH$_2$Cl$_2$ (50 ml) was heated at reflux for 12 h. The mixture was washed with KOH until the

aqueous portion became basic. After distillation of the solvent, the residue was recrystallized from MeOH to give compound **8** (0.12 g, 38.0%, m.p. 139°C). Elemental analysis (C$_{46}$H$_{64}$O$_8$): found C 73.87, H 8.81; required C 74.16, H 8.66%. ^{1}H NMR (CDCl$_3$) δ/ppm: 8.03 (s, 2H, Ar–$\underline{H}$), 7.83 (s, 4H, Ar–$\underline{H}$), 4.22 (m, 8H, O$\underline{CH}_2$), 2.39 (s, 6H, OC$\underline{CH}_3$), 1.99–1.85 (m, 8H, OCH$_2\underline{CH}_2$), 1.62–1.35 (m, 24H, $(\underline{CH}_2)_3$), 0.90 (t, 12H, $\underline{CH}_3$). IR (KBr), v_{max}/cm^{-1}: 1753s (C=O, str), 1620, 1514s (C=C, in-plane, str), 1266, 1178s (C–O, str), 839s (C=C, out-of-plane, m).

No mesophase was found for the precursor triphenylene derivatives (**7**, **8** and **9**) by POM. DSC measurements showed only one peak on both heating and cooling runs.

2.3. *Polymer preparations*

Equimolar amounts of monomer **8** and α,ω-alkanedioic acid, HOOC(CH$_2$)$_n$COOH were mixed in a poly-condensation tube; a 1% molar ratio of *p*-toluene-sulphonic acid was added as catalyst. The mixture was heated at 170°C with stirring for 3 h under reduced pressure (*c*. 30 mm Hg); the temperature was then elevated to 200°C and the pressure further decreased to *c*. 3 mm Hg. The mixture was continuously stirred for 3 h. After cooling to room temperature, the reaction mixture was dissolved in 5 ml of THF and precipitated three times from hexane (50 ml). The solid was filtered and dried *in vacuo* at room temperature. For **P1** ($n = 8$), elemental analysis (C$_{52}$H$_{74}$O$_8$)$_n$: found C 75.19, H 9.04; required C 75.51, H 8.96%. ^{1}H NMR (CDCl$_3$) δ/ppm: 8.0–7.6 (br, 6H, Ar–$\underline{H}$), 4.2 (br, 8H, O$\underline{CH}_2$), 2.60 (br, 4H, CO$\underline{CH}_2$), 1.99–1.85 (m, 8H, OCH$_2\underline{CH}_2$), 1.62–1.35 (m, 36H, $(\underline{CH}_2)_3$), 0.92 (br, 12H, $\underline{CH}_3$). IR (KBr), v_{max}/cm^{-1}: 1756s (C=O, str), 1619, 1513s (C=C, in-plane, str), 1267, 1177s (C–O, str), 840s (C=C, out-of-plane, m). The analytical data for **P2** and **P3** corresponded to that for **P1**. The molecular masses for these polymers are summarized in table 1.

3. Results and discussion

The DSC thermograms for **P1**, **P2** and **P3** show endothermic peaks at 211°C, 198°C, and 162°C on heating, respectively. These clearing temperatures are much higher than that of the corresponding monomeric triphenylene derivative, 2,3,6,7,10,11-hexahexyloxytriphenylene (HHTP). On subsequent cooling at 10°C min^{-1}, an exothermic peak was found. A glass transition temperature was observed for all three polymers, and appeared to be dependent on the length of the spacer. Figure 1 shows the DSC curves of **P3** on first heating and cooling as typical examples. The enthalpies of the clearing transition are comparable with those (10–20 J g^{-1}) for discotic main chain liquid crystalline polymers having similar structures [15, 29]. The phase transition temperatures and molecular masses of **P1**, **P2** and **P3** are summarized

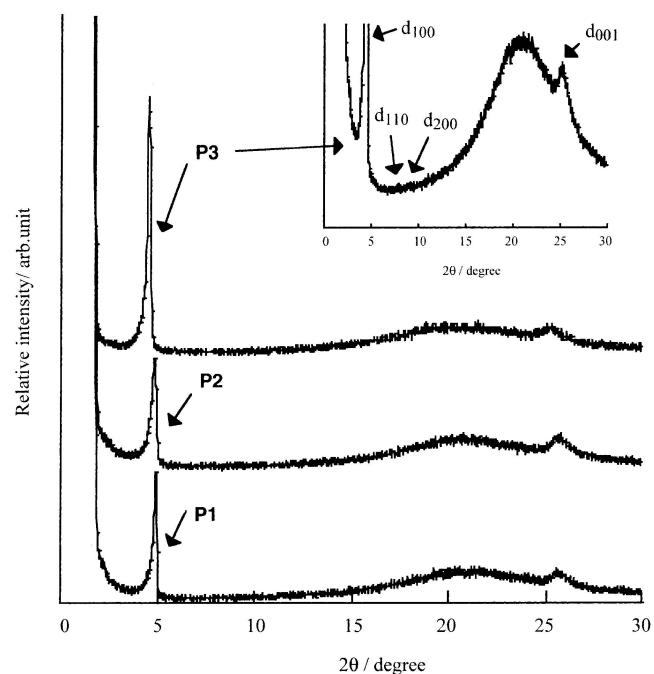Table 1. Phase transition temperatures, enthalpies and molecular masses for **P1**, **P2** and **P3**.

Polymer	Transition temperature/°C	ΔH/J g^{-1}	Molecular mass		
			M_n	M_w	M_w/M_n
P1	g (56) Col$_{ho}$ (211) Iso	20.9	8,303	39,797	4.8
P2	g (40) Col$_{ho}$ (198) Iso	18.7	6,041	9,659	1.6
P3	g (25) Col$_{ho}$ (162) Iso	8.9	5,415	8,818	1.7
HHTP	Cr (68) Col$_{hd}$ (100) Iso				
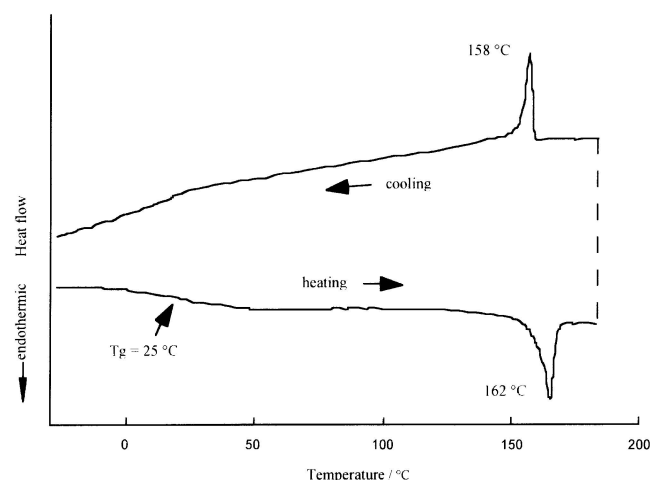
Figure 1. DSC thermograms of **P3** on heating and cooling (10°C min^{-1}).

Figure 2. X-ray diffraction patterns for **P1**, **P2** and **P3** at 100°C.

in table 1. Observations by POM revealed a texture with fine domains as often seen for liquid crystalline polymers.

It is found that not only the clearing and glass transition temperatures, but also the clearing enthalpies decrease with increasing spacer length. No change in either the microscopic textures or the XRD patterns were detected when the polymers were frozen at T_g.

XRD measurements of **P1**, **P2** and **P3** were performed between room temperature and a temperature 30°C above the clearing point. Figure 2 shows the XRD patterns for these polymers at 100°C. They are typical for a hexagonal columnar (Col$_h$) mesophase. As shown in the magnified pattern of **P3** in figure 2, a set of reflections corresponding to d_{100}, d_{110} and d_{200} having a spacing ratio of $1:1\sqrt{3}:1/2$ was observed and this supports the existence of hexagonal arrays of columns. A contact technique was performed to reveal that **P2** and hexapentyloxytriphenylene, which exhibits the Col$_h$ mesophase with intracolumnar ordering, showed miscibility in the mesophase. Two additional reflections were observed at *c.* 4.5 Å (broad halo) and *c.* 3.5 Å (weak peak), which are assigned to the average distance of the molten alkyl chains and intracolumnar order, respectively. It has been reported that a simple XRD pattern is obtained for untreated low molecular mass discotic liquid crystals in

the Col$_h$ mesophase [30–32], and these patterns for the polymers are comparable with those. However, it is interesting that the sharp reflection at *c.* 3.5 Å strongly indicates an ordered columnar phase, even though the corresponding HHTP forms only a disordered columnar mesophase [21]. Polymers with similar chemical structures were also reported to show Col$_h$ mesophases with ordered columns, although they were prepared from a mixture of unseparable isomers [33]. These data indicate that some restriction of the molecular mobility in the columnar mesophase takes place for polymeric systems and this should be related to the spacer length. In fact, the thermal stability of the Col$_h$ mesophase for **P1**–**P3** decreases on increasing the spacer length. Additionally, the viscosity of **P1**, **P2** and **P3** seemed to be higher than that of HHTP, as detected by pushing the cover slip during the textural observation through the microscope. The results of the XRD measurements are summarized in table 2.

The lattice constant α_{hex} for **P1**, **P2** and **P3** were calculated to be 20.8, 21.3, and 22.5 Å, respectively, and

Table 2.   XRD results for **P1**, **P2** and **P3** at 100°C.

Polymer	α_{hex}/Å	h k l	d/Å
P1	20.8	1 0 0	18.1
		1 1 0	10.4
		2 0 0	9.0
			4.5
		0 1	3.4
P2	21.3	1 0 0	18.4
		1 1 0	10.5
		2 0 0	9.1
			4.5
		0 0 1	3.4
P3	22.5	1 0 0	19.5
		1 1 0	11.3
		2 0 0	9.7
			4.5
		0 0 1	3.5

increases as the spacer lengthens. These values are very similar to that for the Col_h mesophase of HHTP (21 Å) [21], which is much smaller than the estimated diameter of a fully extended HHTP molecule (29 Å). The intra-columnar periodicity increases slightly as the spacer length is elongated. These results indicate that the shorter spacer length may lead to a shrinking of the lattice of hexagonal arrays of columns to form a more rigid columnar structure while the longer spacer causes the formation of an extended lattice which disrupts the columnar structure and the array. Figure 3 shows a schematic representation of this relationship between the spacer length and the two-dimensional molecular pack-ing of columns for **P1**, **P2** and **P3**. The inner and outer circles indicate the observed diameters of the columns and the fully extended HHTP molecule, respectively. This figure suggests that the shorter spacer in **P1** readily allows the hexagonal packing of the columns in a normal way as seen in HHTP, whereas the longer spacer in **P3** prevents such packing.

In a disordered Col_h phase consisting of monomeric discotic liquid crystals, there is, in general, no lateral correlation between the molecules in neighbouring columns. The molecules can slide freely in the trans-lational direction and freely fluctuate in rotation about the columnar axis. However, the spacer units connecting the discotic triphenylene mesogens in the polymers help build a tight network when a columnar structure is formed, as illustrated in figure 4. Therefore, it is reason-able to propose that the single mesogenic triphenylenes will not be so mobile in the translational direction and will only rotate around the columnar axis within a restricted angular range. The higher thermal stability of the Col_h mesophase in these copolymers, compared
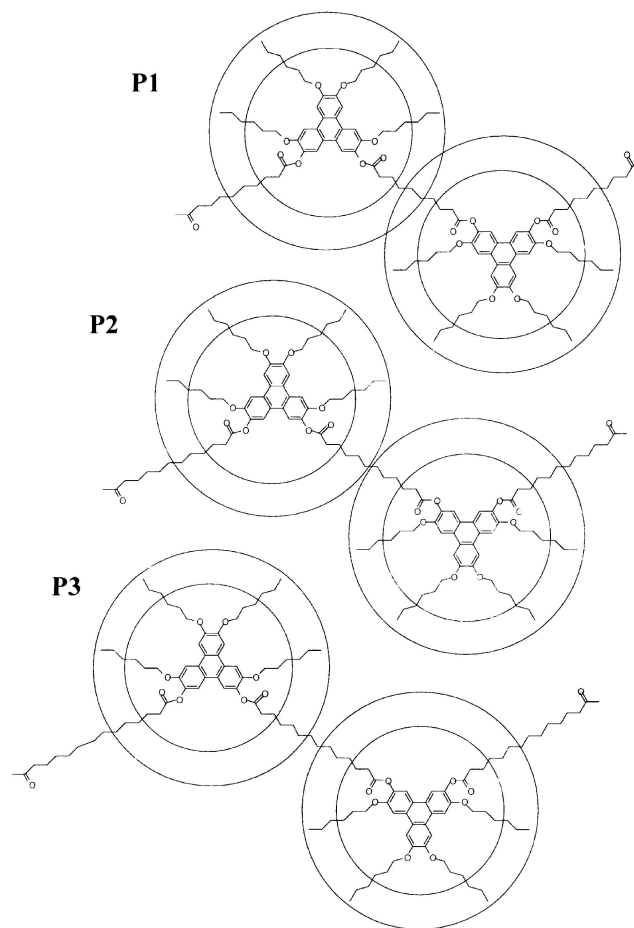

Figure 3.   Schematic representation of the spacer length dependent columnar structures.

with the corresponding monomeric mesogen, is probably due to the reduced fluctuations of the disc-like units, and this is consistent with HHTP showing a disordered Col_h phase. Therefore, these results imply that, in a well designed polymeric system, the order and fluctuations of the disc-like units may be modified in the columnar mesophase, and that one might be able to control the related properties such as charge migration. As for the possible structural variations, the attachment site of the spacers on the triphenylenes, the structure of the connecting links as well as the spacer lengths should now be considered.

Finally, it was also shown that **P1**, **P2** and **P3** form liquid crystal glasses and the glass transition temper-atures, T, decrease as the spacer length increases. In addition it was found that the XRD patterns of the polymers do not change at room temperature, even a few months after the first measurement. These are also characteristic and useful properties of polymeric systems having application potential as functional materials and in devices.
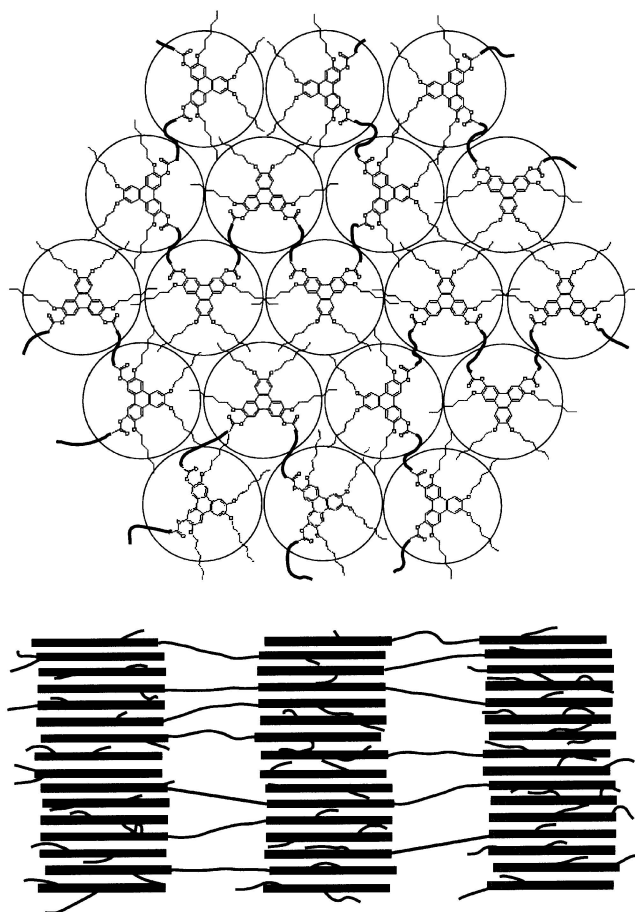
Figure 4. A schematic representation of the Col$_{ho}$ mesophase of the copolymers with a 3D network.

4. Conclusion

Three triphenylene-methylene copolymers, **P1**, **P2** and **P3** were prepared and their mesomorphic properties investigated. DSC and XRD measurements along with texture observations using a polarizing microscope showed that all the polymers form a very stable Col$_h$ mesophase with ordered columns over a broad temperature range and exhibit a liquid crystal glass at room temperature. It was also revealed that the inter- and intra-columnar ordering of the Col$_h$ phase is affected by the length of the methylene spacer. These results strongly indicate that an appropriate polymeric structure containing disc-shaped mesogens stabilizes the mesophase by restricting the mobility of the disc-like units due to inter- and intra-columnar connections.

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