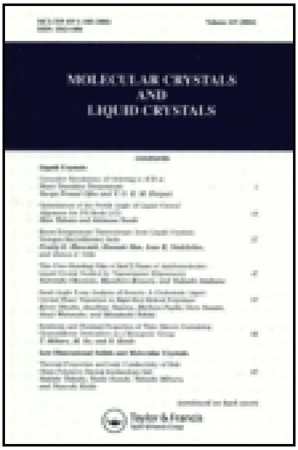

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Discotic Liquid Crystalline Block Copolymers 1: Side-Chain Discotic Liquid Crystalline Diblock Copolymers

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Discotic Liquid Crystalline Block Copolymers 1: Side-Chain Discotic Liquid Crystalline Diblock Copolymers

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In this paper we describe the synthesis of *diblock* copolymers based on a polystyrene backbone and containing one *side-chain* discotic liquid crystalline block. Evidence for the desired microphase separation and long-range ordering of the microphase separated structures in these polymers is less clear than it is for the *di- and triblock* copolymers with one *main-chain*discotic block described in the accompanying paper. However, when HAT4 or HAT6 is added to the copolymers homogeneous textures are observed by polarising microscopy and both DSC and low angle X-ray show the presence of separated liquid crystalline columnar discotic domains.

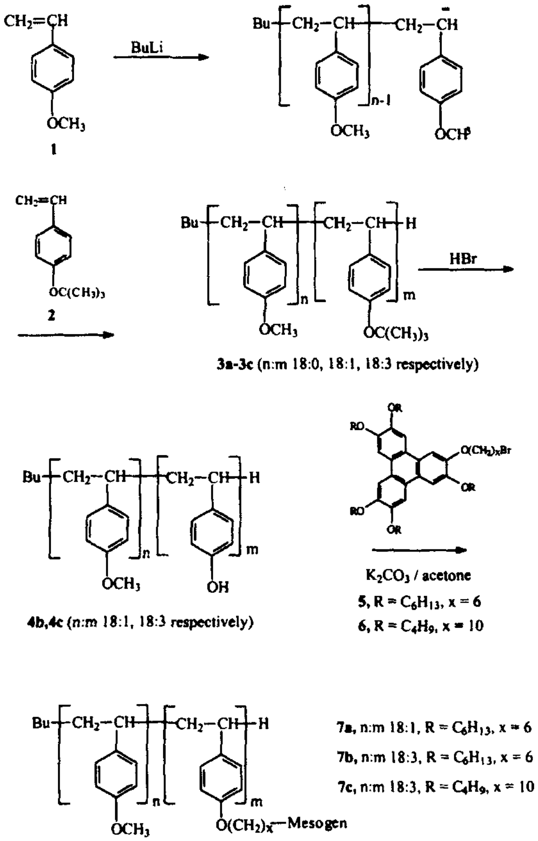
Keywords: discotic liquid crystalline polymers; diblock copolymers

INTRODUCTION

Some applications that have been suggested for discotic liquid crystals require films which are mechanically robust. This has been part of the motivation behind syntheses of both main-chain[1] and side-chain[2] discotic liquid crystalline homopolymers. Another way of producing films with good mechanical properties mignt be to make diblock copolymers in which just one of the blocks is a discotic liquid crystalline polymer and in which the other block can be engineered or varied in some way. However, there is another reason for interest in such polymers. Since the 1960's it has been known that (provided the segments A_n and B_m are immiscible) many diblock copolymers A_n-B_m are themselves 'liquid crystalline'. They undergo microscopic phase separation and form a range of ordered self-assembled superstructures analogous to those of conventional lyotropic liquid crystals. The microphase separated mesogenic units in diblock copolymers (like those in lyotropic systems) can be rod-like, disk-like or spherical. In diblock copolymers of the type described in this paper, in which one of these microphase separated units is itself based on a discotic liquid crystal, there should be some interplay between the discotic liquid crystal and 'diblock liquid crystal' properties. For example, one might argue that the underlying columnar architecture will mean that only rod-like microphase separated regions could be produced and that we should observe hexagonal but not lamellar superstructures within the polymer.[3] In this paper we describe an approach to the preparation of *diblock* copolymers containing one *side-chain* discotic block and in the accompanying paper *di- and triblock* copolymers with one *main-chain* discotic block.

SYNTHESIS

p-tert-Butoxystyrene **2** was prepared from bromobenzene by a Friedel-Crafts reaction with acetyl chloride, reduction to *p*-bromophenymethylcarbinol, dehydration, conversion to the Grignard reagent and reaction with *tert*-butyl perbenzoate.[4] This was used to prepare the functional diblock copolymers, poly[(*p*-methoxystyrene)-b-(*p*-hydroxystyrene)] **3b** and **3c** by sequential anionic polymerisation of *p*-methoxystyrene **1** and *p-tert*-butoxystyrene **2** followed by removal of the *tert*-butoxy group using hydrobromic acid as shown in Scheme 1.[4],[5]. NMR and elemental analyses showed that the composition of each poly[(*p*-methoxystyrene)-b-(*p-tert*-butoxystyrene)] copolymer **4b, 4c** accurately reflected the molar ratio of the two monomers. (*p*-methoxystyrene : *p*-*tert*-butoxystyrene used. 18:1 and 18:3 for **4b** and **4c** respectively). These block copolymers were then alkylated using the ω–bromo-terminated alkyloxytriphenylenes **5** and **6** / potassium carbonate / acetone. Whereas these alkylation reactions were clean, attempts to alkylate poly[(styrene)-b-(*p*-hydroxystyrene)] led to no (or very incomplete) alkylation.[4]



SCHEME 1. Synthesis of diblock discotic copolymers

CHARACTERISATION

Based on the NMR spectra, the alkylation reactions in this series were clean and went to completion. Other analytical and GPC data for the diblock copolymers is summarised in Table 1.

TABLE 1. Combustion analysis and GPC results for the block copolymers

	Found		Requires			
Copolymers	C	H	C	H	M_n X 10^{-3}	M_w/M_n
3a (18:0)	-	-	-	-	75	1.32
3b (18:1)	80.4	7.7	80.7	7.6	17	1.38
4b (18:1)	80.3	7.7	80.5	7.5	16	1.39
7a (18:1 **4b+5**)	79.6	8.1	80.0	8.1	24	1.45
3c (18:3)	80.6	7.8	80.8	7.8	13	2.31
4c (18:3)	80.2	7.6	80.5	7.4	-	-
7b (18:3 **4b+5**)	76.6	8.3	79.5	8.6	-	-
7c (18:3 **4b+6**)	78.3	8.9	79.2	8.3	21	2.40

GPC showed about the expected changes in molecular weights at each stage in the synthesis and that the polymers were free of low molar mass impurities. For example the calculated M_n for **7a** is 22 X 10^3 based on a value of M_n of 17 X 10^3 for **3b**. Although the NMR spectra were clean, higher M_n/M_w and poorer combustion analyses were obtained for the '18:3 series' perhaps suggesting that alkylation was not quite complete and this certainly proved a problem in attempts to prepare polymers n:m 18:9.[4] Table 2 summarises the DSC, polarising microscopy and low angle X-ray results for the polymers **3a, 7a, 7b** and **7c.** We were hoping to see evidence of microphase separation, of columnar liquid crystal-like behaviour within the

TABLE 2. Thermal behaviour of the polymers and their mixtures with HAT6 and HAT4.

Sample	DSC[1] onset (ΔH/ Jg^{-1})	X-ray[5]	polarising microscopy[6]
3a	110°C (T_g)	-	-
3a+3.5%w/w HAT6[2]	1st heating: 83°C (2.5) 2nd heating: 92°C (T_g)	diffuse (98°C)	macroscopic phase separation
3a+12%w/w HAT4[3]	1st heating: 86°C (2.9) 2nd heating: 82°C (T_g)	16.7 Å, weak, sharp (135°C)	-
3c	99 °C (T_g)	-	-
4c	106 °C (T_g)	-	-
7a (18:1 **4b**+**5**)	-	>18 Å, diffuse (98°C)	a few birefringent streaks appeared 85-95°C, broad clearing range above140°C[7]
7a + 2 % w/w HAT6[2]	96°C (T_g)	>18 Å, diffuse (98°C)	birefringent streaks appeared 85-95°C, softening ca 110 °C, very broad clearing range above140 °C[7]
7b (18:3 4b+5)	no apparent transitions	>18 Å, weak, diffuse (98°C)	birefringent streaks appeared 85-95°C, very broad clearing range above140 °C[7]
7b + 5 % w/w HAT6[2]	39°C (0.68)	>18 Å, strong, diffuse (98°C)	birefringent streaks at 20°C, softening ca 65°C, very broad clearing range above140°C[7]
7b + 13 % w/w HAT6[2]	37.0°C (0.85)	ca 19 Å, weak, broad (98 °C)	-
7c (18:3 **4b**+**6**)	60.9°C (0.87), 92°C (T_g)	>16 Å weak, diffuse (75 and 135°C)	birefringent streaks appeared 85-95 °C, very broad clearing range above 140°C[7]
7c + 11 % w/w HAT4[3]	53.9°C (1.7)	ca 16.5 Å, broad (75 and 135°C)	softening ca 65°C, birefringent streaks appeared 90-100°C, very broad clearing range above140°C[7]
7c + 24 % w/w HAT4[3]	39.4 °C (3.7), 99°C (T_g), ca 108.6°C (ca 2.6)[4]	16.6 Å, sharp (75 and 135°C)	softening ca 45°C, transition into a LC-phase (sandy texture and some parts with mosaic-like texture) 85-95°C, clearing 115-125°C

[1] Heating/cooling rate of 10°C/min. [2] HAT6 = 2,3,6,7,10,11-hexahexyloxytriphenylene K 70°C D_h 100°C I. [3] HAT4 - 2,3,6,7,10,11-hexabutoxy triphenylene K 89°C D_p 146°C I. [4] Glass transition and following first order transition are not baseline separated. [5] Samples were subject at least one complete heat/cool cycle before measurements were made. [6] Heating/cooling rate of 5°C/min. [7] The clearing range is strongly depending on the heating rate.

'discotic' domains and of long-range ordering of the microphase separated structures. For the pure copolymers, the evidence even for microphase separation is not very strong. There is weak birefringence and the presence of a glass transition at 96°C for **7a** could be interpreted in terms of the presence of phase separated regions of poly-*p*-methoxystyrene (T_g 110°C) but there was no X-ray evidence for the ca 20 Å repeat characteristic of phase separated D_h columnar regions. A possible reason for the failure to observe the desired ordered structures (at least for for **7a** and **7b**), may be the high glass transition temperature of the polystyrene backbone. To try to overcome these difficulties some HAT6 and HAT4 were added to the polymers with the hope that (i) this would lower T_g and (ii) that this would increase the extent of the 'discotic' domains. The results of these experiments are also presented in Table 2. They show that T_g is indeed depressed (for example the effect on **3a**) and that there now is much clearer evidence of phase separation and liquid crystal properties. It is particularly noteworthy that the HATn/diblock copolymer mixtures gave apparently homogeneous materials whereas HATn/homopolymer mixtures were phase separated on a scale that could be clearly observed with the optical microscope.

CONCLUSIONS

This paper describes an approach to the preparation of *diblock* copolymers containing one *side-chain* discotic liquid crystalline polymer block. One aspect of the design of these systems which we initially overlooked was the need to operate above the glass transition of the polymer backbone which, for these styrene derivatives is relatively high. In the case of the HAT6 derivatives, the mesophase is expected between about 70 and 100 °C and this is below the glass transition so our failure in these cases is hardly surprising. With 'HAT4-based' systems and when HAT4/HAT6 is added to the polymers, it is clear that liquid crystalline regions are generated which are smaller than can be observed by optical microscopy but the evidence for the desired microphase separation and of long-range ordering of the microphase separated structures is less clear than it is for the *di- and triblock* copolymers with one *main-chain* discotic block which are described in the accompanying paper.

EXPERIMENTAL

General ^{1}H NMR spectra were recorded on Bruker GE QE 300 instrument using $CDCl_3$ or CD_3COCD_3 as solvent. Phase behaviour was studied using an Olympus BH-2 optical polarizing microscope with a Mettler FP82 HT hot stage and a Perkin Elmer 7 thermal analysis system (cooling and heating rate, 10°C/min). Small angle X-ray diffraction experiments were conducted with a pinhole camera consisting of a Phillips generator and tubes, nickel filtered Cu K_α radiation of wavelength $\lambda = 0.154$ nm, and a Lindemann sample tube (1.5 mm i.d.) to plate distance of 120.0 mm. Gel permeation chromatography was performed on two mixed bed columns (Polymer Laboratories Ltd.) using a Merk L-6000 pump and a Varex light-scattering detector and an Optilab DSP interferometric refractometer (cell temp. 40°C, wave length 633 nm). Tetrahydrofuran was used as an eluent at a flow rate of 1 mL/min. Molecular weight were also calculated relative to polystyrene standards. For the mixture of polymer and triphenylene, both compounds were weighed into a flask, dissolved in an minimum of THF and evaporated in vacuum (10^{-2} bar) at 20°C.

2-(6-Bromohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene **5**

The mixture of 3,3',4,4'-tetrahexyloxybiphenyl (5.54 g, 10.0 mmol), ferric chloride (3.60 g, 22 mmol) in dichloromethane (50 ml) was stirred at 0°C for half an hour, then 2-(6-bromohexyloxy)-1-hexyloxybenzene (5.71 g, 16 mmol, prepared in a similar manner to 2-(10-bromodecyloxy)-1-

butoxybenzene described below) and more ferric chloride (3.60 g) was added. The mixture was stirred at room temperature (monitored by TLC). After the reaction had finished, the solution was carefully poured onto methanol (300 ml), cooled to 0°C, the crude product was filtered off and purified by column chromatography (silica gel eluting with dichloromethane: petroleum ether 1:1) and recrystallised from ethanol to give a white solid **5** (6.08 g, 67%, mp 50°C). ^{1}H-NMR: δ_H ($CDCl_3$) 0.93 (15H, t, J = 6.8 Hz, $O(CH_2)_5\mathit{CH_3}$), 1.10-1.70 (34H, m, $OCH_2CH_2(\mathit{CH_2})_3$ and $BrCH_2CH_2(\mathit{CH_2})_3$), 1.75-2.05 (14H, m, $OCH_2\mathit{CH_2}$ and $BrCH_2\mathit{CH_2}$), 3.40 (2H, t, J = 6.80 Hz, $Br\mathit{CH_2}$), 4.23 (12H, t, J = 6.5 Hz, $O\mathit{CH_2}$), 7.84 (6H, s, Ar*H*).

2-(10-Bromodecyloxy)-1-butoxybenzene

The mixture of catechol (5.5 g, 0.05 mol), 1-bromobutane (6.8 g, 0.05 mol) and potassium carbonate (13.8 g, 0.10 mol) in ethanol (25 ml) was heated under reflux for 24 hours. After the reaction had finished, the reaction mixture was filtered, extracted with dichloromethane (2 x 25 ml), washed with water, concentrated *in vacuo* to give 2-butoxyphenol (6.5 g, 72%) as a colourless oil which was used without further purification for next reaction step. ^{1}H-NMR: δ_H ($CDCl_3$) 0.98 (3H, t, J = 7.5 Hz, $OCH_2CH_2CH_2\mathit{CH_3}$), 1.52 (2H, m, $OCH_2CH_2\mathit{CH_2}$), 1.80 (2H, m, $OCH_2\mathit{CH_2}$), 3.98 (2H, t, J = 6.6 Hz, $O\mathit{CH_2}$), 6.85-6.98 (4H, m, ArH). The mixture of 2-butoxyphenol (3.32 g, 20 mmol), 1,10-dibromodecane (7.5 g, 25 mmol, 1.25 equiv.) and potassium carbonate (6.8 g, 50 mmol, 4.0 equiv.) in ethanol (25 ml) was heated under reflux for 24 hours. After the reaction had finished, it was filtered, extracted with dichloromethane (2 x 25 ml), concentrated *in vacuo*, purified by column chromatography (silica gel eluting with dichloromethane: petroleum ether 1:2) to give 2-(10-bromodecyloxy)-1-butoxybenzene as a colourless liquid (6.16 g, 80%). ^{1}H-NMR: δ_H ($CDCl_3$) 0.98 (3H, t, J = 7.5 Hz, $OCH_2CH_2CH_2\mathit{CH_3}$), 1.10-1.70 (14H, m, $BrCH_2CH_2(\mathit{CH_2})_6$ and

$OCH_2CH_2\mathit{CH_2}$), 1.75~2.05 (6H, m, $OCH_2\mathit{CH_2}$ and $BrCH_2\mathit{CH_2}$), 3.40 (2H, t, J = 6.90 Hz, $Br\mathit{CH_2}$), 3.96 (4H, 2xt, J = 6.7 Hz, $O\mathit{CH_2}$), 6.88 (4H, s, Ar*H*).

2-(10-Bromodecyloxy)-3,6,7,10,11-pentabutoxytriphenylene **6**

The mixture of 3,3',4,4'-tetrabutoxybiphenyl (1.77 g, 4 mmol), ferric chloride (1.0 g, 6.1 mmol) in dichloromethane (20 ml) was stirred at 0°C for half an hour, then 2-(10-bromodecyloxy)-1-butoxybenzene (3.85 g, 10 mmol) and more ferric chloride (1.0 g) was added. The mixture was stirred at room temperature (monitored by TLC). After the reaction had finished, the reaction mixture was carefully poured onto methanol (300 ml), cooled to 0°C, the crude product was filtered off and purified by column chromatography (silica gel eluting with dichloromethane: petroleum ether 1:1) and recrystallised from ethanol to give 2-(10-bromodecyloxy)-3,6,7,10,11-pentabutoxytriphenylene **6** as a white solid (1.82 g, 55%, mp 55.5 - 56.5°C). Elemental Analysis: C, 70.1; H 8.8; Br, 9.6. $C_{48}H_{71}BrO_6$ requires: C, 70.0; H, 8.7; Br, 9.7. Mass Spectrum: m/z (FAB) 824 (M^+, 95%); 822 (M^+, 86%); 778 ($[M - C_4H_9]^+$, 32.42%); 744 ($[M - Br]^+$, 12.7%); 57 ($[C_4H_9]^+$, 100%). ^{1}H-NMR: δ_H ($CDCl_3$) 1.05 (15H, t, J = 7.4 Hz, $O(CH_2)_3\mathit{CH_3}$), 1.10-1.70 (22H, m, $OCH_2CH_2\mathit{CH_2}$ and $BrCH_2CH_2\mathit{(CH_2)_5}$), 1.75-2.05 (14H, m, $OCH_2\mathit{CH_2}$ and $BrCH_2\mathit{CH_2}$), 3.40 (2H, t, J = 6.7 Hz, $Br\mathit{CH_2}$), 4.24 (12H, t, J = 6.5 Hz, $O\mathit{CH_2}$), 7.84 (6H, s, *ArH*).

Anionic copolymerisation of p-methoxystyrene **1** *with p-tert-butoxystyrene* **2**

A typical procedure is as follows: Using butyl lithium as an initiator, tetrahydrofuran as solvent, sequential copolymerisation of *p*-methoxystyrene **1** (1.34 g) and *p-tert*-butoxystyrene **2** (0.3 g) at –78 °C under argon yielded poly[(*p*-methoxystyrene)-b-(*p-tert*-butoxystyrene)] **3b** (1.63 g). ^{1}H-NMR: δ_H ($CDCl_3$) 0.8-2.2 ($\mathit{-CH_2-CH-}$ and $\mathit{CH_3}$), 3.65-3.85($Ar-O\mathit{CH_3}$), 6.2-7.2 (Ar*H*). The integration corresponds to a molar ratio *p*-methoxystyrene: *p-tert*-butoxystyrene (^{1}H-NMR) of 18:3. Analytical data is given in Table 1.

Poly[(p-methoxystyrene)-b-(p-hydroxystyrene)] **4b** and **4c**

A typical procedure is as follows: Poly[(*p*-methoxystyrene)-b-(*p-tert*-butoxystyrene)] **3b** (0.9 g) was dissolved in 1,4-dioxane (20 ml), and hydrobromic acid (0.42 ml, 5.0 equiv.) was added. The mixture was allowed to stir at room temperature for 24 hours. The reaction mixture was poured into water to precipitate, filtered and dried to give **4b** as a white solid (0.7 g). ^{1}H-NMR: δ_H (d_6-acetone): 1.2-2.2 (*-CH₂-CH-*), 3.75-4.00 (Ar-O*CH₃*), 6.4-7.2 (A*rH*), the peak at 1.27 ppm representing $C(CH_3)_3$ disappeared. The integration corresponds to a molar ratio *p*-methoxystyrene: *p-tert*-butoxystyrene (^{1}H-NMR) of 18:3. Analytical data is given in Table 1.

Reaction of poly[(p-methoxystyrene)-b-(p-hydroxystyrene)] **4b** and **4c** *with ω-bromo-terminated alkoxytriphenylenes* **5** and **6**

A typical procedure is as follows. The mixture of poly[(*p*-methoxystyrene)-b-(*p*-hydroxystyrene)] **4c** (0.2 g), 2-(6-bromohexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene **6** (0.60 g, excess), potassium carbonate (1.0 g) and a little drop of hydriodic acid in acetone (10 ml) was heated under reflux for 96h. After the reaction had completed, the mixture was concentrated *in vacuo*, dichloromethane (2 ml) was added, then poured into methanol. The crude diblock copolymer **7b** was filtered off, purified by soxhlet extraction (first extracted with ethanol to remove the unreacted *ω*–bromo-terminatedtriphenylene, then extracted with chloroform to remove inorganic salt). Methanol was added to the chloroform extract to precipitate the polymer which was reprecipitated from chloroform/methanol to give the solid product **7b** (0.25g). ^{1}H-NMR: $\delta_H(CDCl_3)$ 0.7~2.3 (*-CH₂-CH-*, *-CH₃* and *-CH₂-*), 3.60~4.00(benzene, Ar-O*CH₃* and Ar-O*CH₂*), 4.0~4.4(triphenylene, Ar-O*CH₂*), 6.1~6.9(benzene, *ArH*), 7.7~8.0 (triphenylene, *ArH*). The integration corresponds to a molar ratio *p*-methoxystyrene: *p*-tert-butoxystyrene (^{1}H-NMR) of 18:3. Analytical data is given in Table 1.

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