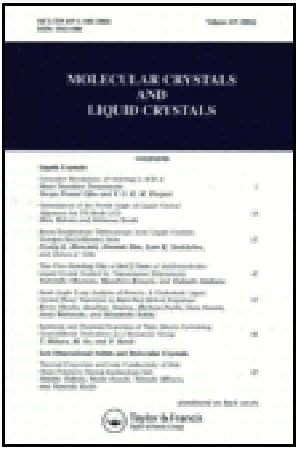

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Discotic Liquid Crystalline Block Copolymers 2: Main-Chain Discotic Liquid Crystalline Diblock and Triblock Copolymers

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In this paper we describe the synthesis of *diblock* and *triblock* copolymers containing one *main-chain* discotic liquid crystalline block and one or two polyethyleneoxy blocks, respectively. Evidence for the desired microphase separation is provided by DSC and both polarising microscopy and low angle X-ray show the presence of separated liquid crystalline columnar discotic domains.

Keywords: discotic liquid crystalline polymers; block copolymers

INTRODUCTION

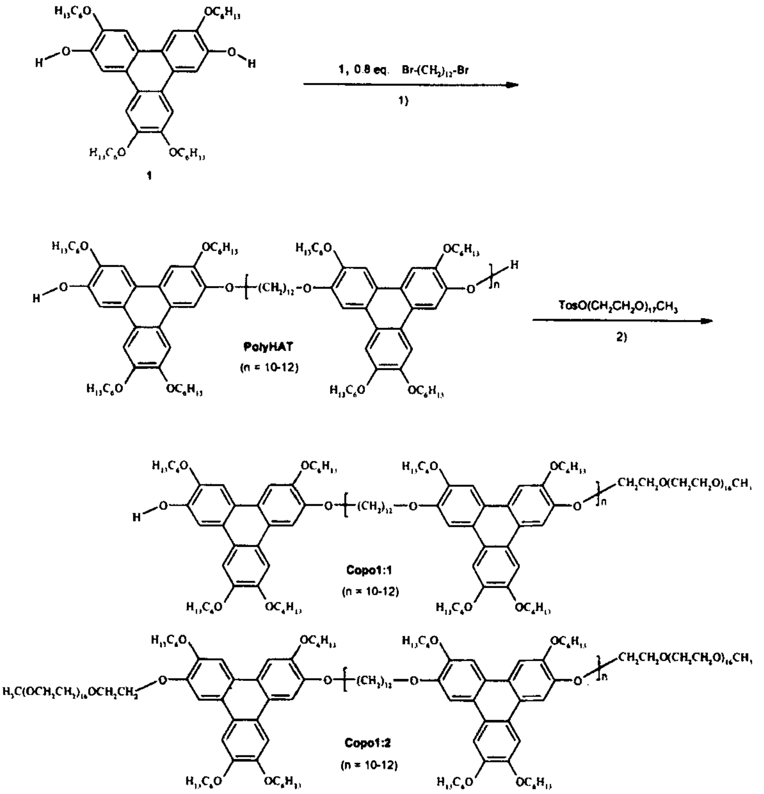
The preceding paper described the preparation and characterisation of diblock side-chain discotic liquid crystalline polymers based on a polystyrene backbone.[1] However, evidence for the desired microphase separation and long-range ordering of the microphase separated structures in these polymers is not very strong. One possible reason for this is that the polystyrene backbone has a high T_g - comparable with the temperatures at which the mesophase should be observed. The block copolymers described in this paper are based on main-chain discotic liquid crystal and polyethyleneoxy components and these show the desired micophase separation and liquid crystal properties.

SYNTHESIS

The triphenylene-based main chain polymer block **PolyHAT** was synthesised by reacting 2,7-dihydroxy-3,6,10,11-tetrakis(hexyloxy)triphenylene **1** with 1,12-dibromododecane using a molar ratio of 1:0.8, to ensure a termination of the polymer block by triphenylenic hydroxy groups (Scheme 1).[2] The mixture of polymers obtained was not isolated but reacted *in situ* with 2-methoxypoly(ethyleneoxy)ethyl tosylate (M_W = 750 g mol^{-1}). Simple flash chromatography of the crude product mixture on silica gave the diblock polymer **Copol:1**, the triblock copolymer **Copol:2** and unreacted **PolyHAT** as pure fractions.

CHARACTERIZATION

Integration of the ^{1}H-NMR signals at 7.83 ppm (aromatic protons), 4.22 ppm (OCH_2 linked to the triphenylene), 3.63 ppm (OCH_2 of the poly(oxyethylene)) and 3.37 ppm (OCH_3 of the poly(oxyethylene)) proved the diblock structure of **Copol:1** and the triblock structure of **Copol:2**. The integration corresponded to an average of 11 triphenylene units in the **PolyHAT** block, since the molecular



SCHEME 1 Synthesis of an extended diblock and triblock copolymers
1) NMP/CsCO$_3$/110 °C, 2) NMP/NaOH/80 °C

weight of the commercially available poly(oxyethylene) block **PEG750** is 750 g mol^{-1} (about 17 ethylene oxide units). A value of 11 triphenylene units was also confirmed by GPC measurements which revealed a molecular weight of 10^4 (±15 %) g mol^{-1} (M_W/M_n = 1.1) for both of the block copolymers and **PolyHAT**. An accurate distinction between the molecular weights of the three discotic polymers was not possible. However, the retention volumes of **Copol:1** and **Copol:2** were slightly higher than that of **PolyHAT**. Impurities of much higher or lower molecular weight (such as **PEG750**) were not detected.

TABLE 1. OPM, DSC and X-ray results for the two block copolymers

Block copolymers	OPM[1]	DSC[2]	X-ray[3]
Copol:1	sandy texture, no evidence of crystallization at 20 °C	37.4 °C (6.13 Jg^{-1}) LC→I 86.5 °C (1.32 Jg^{-1})	19.0 Å, 4.8 Å (halo), 3.7 Å
Copol:2	sandy texture, no evidence of crystallization at 20 °C	35.9 °C (11.86 Jg^{-1}) LC→I 66.4 °C (0.56 Jg^{-1})	19.0 Å, 4.8 Å (halo), 3.7 Å
mixture[4]	-	19.3 °C (0.55 Jg^{-1}) LC→I 103.1 °C (5.33 Jg^{-1})	-

[1]Both copolymers are already birefringent and ductile at 20 °C and the clearing temperature range is consistent with the DSC results. However, a uniform texture was only observed on cooling from the isotropic state. [2]The onset temperatures (ΔH) of the transitions are given for the second and subsequent heating runs at a rate of 10 °C/min. [3]All measurements were performed at 20 °C and 60 °C and gave identical results within the range of accuracy. [4]13:1 w/w mixture (ratio of **Copol:1**) of **PolyHAT** and **PEG750**, respectively.

Both block copolymers, **Copol:1** and **Copol:2**, showed an enantiotropic D_h mesophase between <20 °C and 86 °C or 66 °C, respectively, as proved by optical polarizing microscopy (OPM), differential scanning calorimetry (DSC) and X-ray measurements (Table 1). The observed sandy textures and the values of the X-ray diffraction peaks are very similar to the results reported for the analogous discotic homopolymers.[2] This already strongly suggests a fully phase separated discotic block. However, periodic superstructures of sufficient length are not present, since no further X-ray peaks were detected in the small angle regime. Two distinct melting transitions were observed in the DSC curves of **Copol:1** and **Copol:2** (Figure 1). A rather sharp melting of the **PEG750** block(s) was found at about 35 °C and the discotic block cleared in a very broad temperature range between 80-100 °C (**Copol:1**) and 60-80 °C (**Copol:2**). Therefore, a phase separation of the two immiscible blocks is evident. The enthalpy of the melting transition of the **PEG750** is roughly twice as big for the triblock copolymer **Copol:2** as for the diblock copolymer **Copol:1**, which is a further proof of the composition.

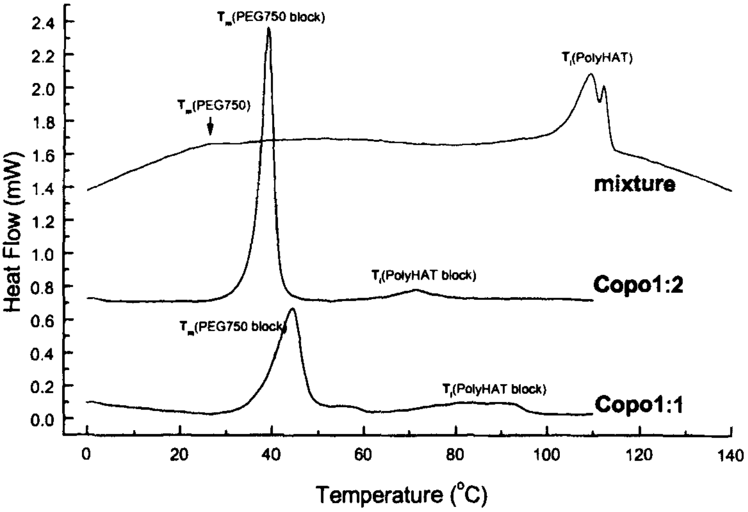


FIGURE 1. DSC curves of the block copolymers and a 13:1 w/w mixture of **PolyHAT** and **PEG750**

The thermal behaviour of the block copolymers is considerably different to that of the discotic homopolymer and to the physical mixture of **PolyHAT** and

PEG750 (molar ratios of **Copol:1**). Clearing temperatures and enthalpies of the discotic block within the block copolymers decreased by about 20 °C for each coupled **PEG750** block, whereas the addition of the same quantity of **PEG750** to **PolyHAT** did not show much effect. Also, the temperature range of the clearing process was drastically broadened to about 20 °C (**Copol:2**) or 30 °C (**Copol:1**) in comparison to a range of about 10 °C for the mixture. In contrast, the melting transitions of the **PEG750** blocks within the copolymer are sharper and shifted towards higher temperatures by about 20-30 °C compared with the mixture and the homopolymer **PEG750**.

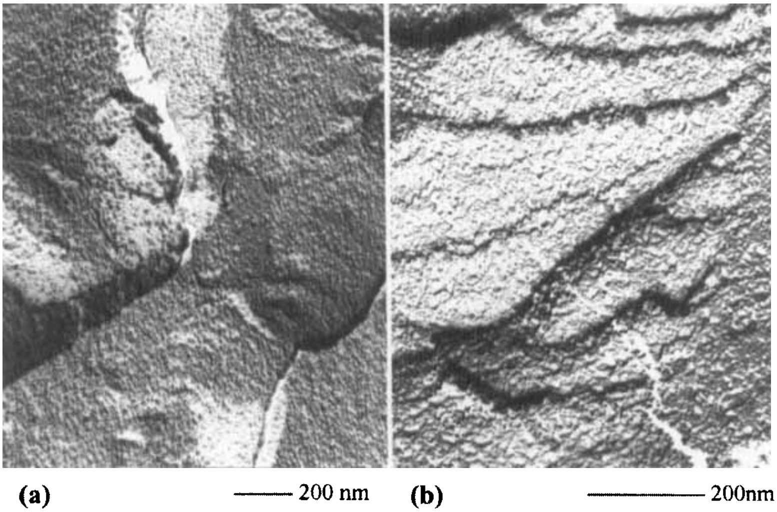


FIGURE 2. Freeze-fracture micrographs of **Copol:1** quenched from 40 °C showing aligned structures (a) and lamination (b)

An effect of the crystallizing **PEG750** block on the microscopic texture or X-ray pattern was not observed, which might be due to the expected very small domain size of the microphase separated blocks. The estimated length of the elongated discotic block is about 20 nm and that of the coiled **PEG750** block about 1.9 nm.

Transmission electron microscopy (TEM) images obtained from replicas of freeze-fractured **Copol:1** show evidence of aligned structures and lamination as shown in Figure 2a and 2b, respectively. Alignment and lamination support the formation of an ordered microphase separated structure, although no sufficiently ordered superstructure was found by small angle X-ray diffraction. Further samples are currently investigated.

CONCLUSIONS

A relatively simple and versatile synthetic approach to the preparation of diblock and triblock copolymers containing one main-chain discotic block and one or two poly(oxyethylene) blocks has been presented. Both block copolymers display enantiotropic liquid crystalline phases and all the analytical data presented are consistent with the microphase separation of the immiscible blocks. However, a final proof of the microphase separation and a determination of the domain structure is still to be made.

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 three columns (Polymer Laboratories Ltd. Plgel 10^3 Å, 500 Å and 100 Å) using a Merk L-6000 pump and a Mini Dawn light-scattering detector (Wyatt Technology) 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 polymer mixture of **PolyHAT** and **PEG750**, both compounds were weighed into a flask, dissolved in an minimum of THF and evaporated in vacuum (10^{-2} bar) at 20°C. The samples for freeze-fracture TEM were heated up to 85 °C (isotropic phase), slowly cooled to 40 °C and then quenched with liquid nitrogen. The specimens were freeze-fractured in vacuum ($3x10^{-7}$ Torr) at -150 °C using a Cressington CFE-50 freeze-fracture unit, coated with 1.8 nm of platinum at a 45 degree angle and finally with 12 nm of carbon at a 90 degree angle. The replicas were cleaned with chloroform, collected onto copper grids and examined using a Jeol 1200 EX transmission electron microscope operated at 80 kV.

2-Methoxypoly(ethyleneoxy)ethyl tosylate

Poly(ethylene oxide) monomethyl ether (M_w = 750, 15.7 g, 20.9 mmol) was dissolved in dry pyridine (5 ml) under argon. A solution of toluene-p-sulfonyl chloride (4.4 g, 23 mmol) in dry pyridine (5 ml) was then added dropwise to the mixture. The reaction mixture was stirred at room temperature under argon overnight. The resulting solution was poured into water and extracted with dichloromethane. The extract was washed with water, dried over anhydrous magnesium sulphate, concentrated *in vacuo*, purified by column chromatography (silica gel eluting with dichloromethane) to yield the product as a colourless oil (13.0 g, 68.8%). ^{1}H-NMR: δ_H ($CDCl_3$) 2.37 (3H, s, Ar-*CH₃*), 3.31 (3H, s, O*CH₃*), 3.55-4.10 (64H, m, O*CH₂*), 7.28 (2H, d, *J* = 8.2 Hz, *ArH*), 7.72 (2H, d, *J* = 8.2 Hz, *ArH*).

Copolymers **Copol:1** and **Copol:2**

2,7-dihydroxy-3,6,10,11-tetrahexyloxytriphenylene **1**[2] (0.66 g, 1.0 mmol), caesium carbonate (0.769 g, 4 mmol) and 1,12-dibromododecane (0.262 g, 0.80 mmol) were dissolved in N-methyl-2-pyrrolidinone (5 ml), and then immediately submerged in an oil bath at 110 °C for one day. The solution of 2-methyloxypoly(ethyleneoxy)ethyl tosylate (1.13 g, 1.2 mmol) in N-methyl-2-pyrrolidinone was added. The mixture was heated at 80 °C for two days. After the reaction had finished, the reaction mixture was poured into water, and extracted with dichloromethane (20 ml). The extract was washed with water, and the product precipitated by the addition of methanol. Reprecipitation from chloroform/methanol gave a crude mixture of homopolymer as well as diblock and triblock copolymers (0.32 g). The brown mixture was dissolved in a minimum of toluene and subject to chromatographic separation on silica. First toluene was used as eluent in order to remove starting materials and non polar impurities. Unreacted discotic homopolymer (**PolyHAT**) was eluted with toluene/isopropyl ether 1/1 (67 mg), **Copol:1** with toluene/THF 1/1 (52 mg) and **Copol:2** with toluene/THF 1/3 (49 mg). The fractions were concentrated, filtered (0.45 μm), and the beige polymers finally precipitated by the addition of methanol or methanol/water in case of **Copol:2**.

^{1}H-NMR: δ_H ($CDCl_3$) 0.93 (t, J = 6.8 Hz, $O(CH_2)_5\mathit{CH_3}$), 1.10-1.70 (m, $OCH_2CH_2(\mathit{CH_2})_3$), 1.93 (m, HAT-$OCH_2\mathit{CH_2}$), 3.38 (s, PEG-$O\mathit{CH_3}$), 3.55-3.75 (m, PEG-$O\mathit{CH_2}$), 3.82 (t, J = 5.0 Hz, PEG-$O\mathit{CH_2}$), 4.00 (2H, t, J = 5.0 Hz, PEG-$O\mathit{CH_2}$), 4.23 (t, J = 6.5 Hz, HAT-$O\mathit{CH_2}$), 4.40 (t, J = 5.0 Hz, PEG-$O\mathit{CH_2}$), 7.83 (s, *ArH*), 7.89 (s, *ArH*).

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