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Ordered Langmuir–Blodgett films derived from a mesogenic polymer amphiphile

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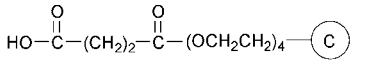
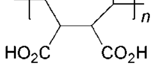
The synthesis of a novel side-chain liquid crystalline polymer in which cholesterol mesogenic units are linked to a styrene backbone by a tris(ethyleneoxy) spacer is described. This amphiphilic polymer displays an unusual discontinuity in its monolayer behaviour at the air–water interface. This behaviour appears to be associated with the attainment of a closely-packed arrangement of the cholesterol units at higher values of surface pressure. Glancing angle X-ray diffraction shows that a well-ordered Y-type film is obtained if deposition is performed at a surface pressure above that of the apparent rearrangement.

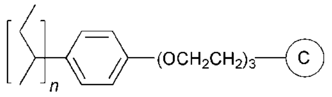
The fabrication of thin organic films is an important area of research which underpins a number of existing and emerging technologies.[1,2] Although many recent advances involve films with active functionality (*e.g.* electroluminescence) there is still a requirement for highly uniform organic films which can act as robust passive layers. For example, electronic biosensors are often designed to mimic the lipid bilayer found in cellular membranes by embedding a receptor in a thin, defect-free insulating layer so that a clear electronic signal is observed in the presence of an analyte.[3] In addition, uniform passive thin films are of great importance as spacers in various optical and electronic devices.[4] The highly ordered films prepared from amphiphilic molecules (*e.g.* long-chained alkanoic acids) by the Langmuir–Blodgett technique are particularly attractive for this purpose, although they suffer from a severe lack of thermal and mechanical stability. As compared to low molar mass amphiphiles, preformed polymeric amphiphiles generally produce LB films with enhanced mechanical and thermal resilience—but at the cost of a less ordered structure.[5–8]

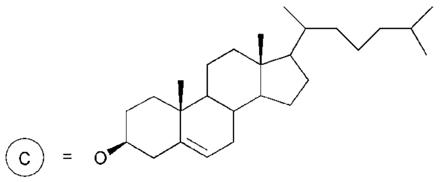
Cholesterol, a rigid component of many natural lipid bilayers,[9] continues to play an important role in the field of self-organising organic systems since the liquid crystalline state of matter was first discovered in some of its ester derivatives in the 1880s.[10] For example, it has been a component of model membrane systems, liposomes, chiral liquid crystals and polymeric liquid crystals.[9,11–13] An interesting amphiphilic cholesteric derivative **1**, described by Decher and Ringsdorf, was found to exhibit both thermotropic (temperature induced) and aqueous lyotropic (solvent dependent) liquid crystallinity.[14] It also forms micellar aggregates and an ordered monolayer film at the air–water interface. However, it cannot be deposited as a multilayer LB film. More recently, Hodge *et al.* prepared LB films derived from amphiphilic cholesterol-containing polymers based on a hydrophilic poly(maleic acid) backbone (*e.g.* **2**).[15] It was shown that reasonably well ordered LB films can be prepared from mesogen-containing poly(maleic acid). For example, the LB film derived from amphiphilic polymer **2** displays four orders of X-ray diffraction corresponding to the repeat bilayer spacing.

1 =


$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-(OCH_2CH_2)_4-\textcircled{C}$$

2 =


3 =




This paper describes the self-ordering and film-forming properties of a polystyrene derivative **3** in which the repeat unit contains a pendant mesogen, closely related to the amphiphilic compound **1**. Of particular interest is the compatibility of the hydrophobic polymer backbone with the formation of an ordered LB film.

Experimental

Material synthesis

High resolution (500 MHz) ^1H NMR spectra were recorded using a Varian Unity 500 spectrometer. IR spectra were recorded on an ATI Mattson Genesis Series FTIR (KBr/Germanium beam splitter). Elemental analyses were obtained using a Carlo Erba Instruments CHNS-O EA 108 Elemental Analyser. Routine low resolution chemical ionisation (CI) and electron ionisation (EI) were obtained using a Fisons Instruments Trio 2000. All solvents were dried and purified as

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described in Perrin and Armarego.[16] Silica gel (60 Merck 9385) was used in the separation and purification of compounds by column chromatography. All materials were heated at 100 °C under vacuum for 18 hours as the final step of purification. Molar mass was determined using gel permeation chromatography (GPC) using 3x PL Gel-Mixed B analytical columns (Polymer Laboratories) calibrated against polystyrene standards and using THF as eluant.

8-Cholesteryloxy-3,6-dioxaoctyl toluene-*p*-sulfonate 4

To a solution of cholesterol (6.04 g, 15.6 mmol) and triethylene glycol di-*p*-tosylate (21.52 g, 46.9 mmol) in anhydrous THF (75 ml) was added sodium hydride (0.8 g, 32 mmol) and the mixture stirred under nitrogen for 72 h at 50 °C. Water was added (20 ml) and the mixture extracted with ethyl acetate (3 × 60 ml), washed with water (2 × 50 ml) and dried over anhydrous magnesium sulfate. The solvent was removed and the crude product purified by column chromatography using an eluent of ethyl acetate–petroleum ether (1 : 5) to give **4** as a viscous, opaque and colourless oil (4.45 g, 42%), transition temperature; $T_g = -26$ °C, smectic A–isotropic = 55.6 °C (Found C, 71.28; H, 9.71; S, 4.96%; $C_{40}H_{64}SO_6$ requires C, 71.31; H, 9.59; S, 4.76%); δ_H (500 MHz, $CDCl_3$): 0.65–2.42 (46H, m, steroid nucleus and Ts CH_3), 3.10–3.16 (1H, m), 3.52–3.62 (8H, m), 3.66 (2H, t, *J* 7), 4.15 (2H, t, *J* 7), 5.28–5.31 (1H, m), 7.32 (2H, d, *J* 10), 7.79 (2H, d, *J* 10); *m*/*z* (EI) 368 ($M^+ - C_{13}H_{19}SO_6$), 303 ($M^+ - C_{27}H_{46}$).

4-(8′-Cholesteryloxy-3′,6′-dioxaoctyloxy)benzaldehyde 5

To a suspension of anhydrous potassium carbonate (1.46 g) in dry THF (40 ml) was added 4-hydroxybenzaldehyde (1.14 g, 9.3 mmol). After stirring the mixture at 20 °C for 1 h, a solution of **4** (4.42 g, 6.6 mmol) in THF (10 ml) was added dropwise. The mixture was stirred at reflux for 72 h and then washed with aq. NaOH solution (2 M, 25 ml) and the product extracted with ethyl acetate (60 ml × 3). The organic layer was washed with aq. NaOH (2 M, 25 ml × 2) and water (20 ml × 3) then dried over anhydrous magnesium sulfate. On removal of the solvent, **5** was obtained as a viscous, opaque and colourless oil (3.96 g, 97%) which was used in the next step without further purification. δ_H (500 MHz, $CDCl_3$): 0.65–2.42 (43H, m, steroid nucleus), 3.10–3.18 (1H, m), 3.58–3.62 (4H, m), 3.68 (2H, t, *J* 7), 3.74 (2H, t, *J* 7), 3.82 (2H, t, *J* 7), 4.20 (2H, t, *J* 7), 5.28–5.31 (1H, m), 6.99 (2H, d, *J* 10), 7.80 (2H, d, *J* 10), 9.84 (1H, s); *m*/*z* (EI) 623 ($M^+ + H^+$), 369 ($M^+ - C_{13}H_{17}O_5$), 255 ($M^+ - C_{27}H_{46}$).

4-(8′-Cholesteryloxy-3′,6′-dioxaoctyloxy)styrene 6

To a suspension of methyltriphenylphosphonium bromide (3.40 g, 9.5 mmol) in dry THF (25 ml) was added potassium *tert*-butoxide (1.08 g, 9.6 mmol). The resulting yellow suspension was added dropwise to a stirred solution of **5** (3.94 g, 6.3 mmol) over a period of 0.5 h and the reaction was stirred for a further 3 h. Water (20 ml) was added, the THF was removed under vacuum and the mixture extracted with ethyl acetate (40 ml × 2). The organic layer was washed with water (20 ml × 3), dried over anhydrous potassium carbonate and the solvent was removed under vacuum. The crude product was purified by column chromatography using an eluent of ethyl acetate–petroleum ether (1 : 5) to give **6** as a viscous, colourless oil (3.30 g, 80.5%), transition temperatures; $T_g = -29$ °C, smectic A–chiral nematic = 18.0 °C, chiral nematic–isotropic = 20.4 °C (Found C, 79.00; H, 10.30%; $C_{41}H_{64}O_4$ requires C, 79.18; H, 10.53%); δ_H (500 MHz, $CDCl_3$): 0.65–2.42 (43H, m, steroid nucleus), 3.10–3.18 (1H, m), 3.58–3.62 (4H, m), 3.68 (2H, t, *J* 7), 3.74 (2H, t, *J* 7), 3.84 (2H, t, *J* 7), 4.12 (2H, t, *J* 7), 5.06 (1H, d, *J* 11), 5.28–5.31 (1H, m), 5.59 (1H, d, *J* 18), 6.58 (1H, dd, *J* 11,18), 6.82 (2H, d, *J* 9), 7.29 (2H, d, *J* 9); *m*/*z* (EI) 621 ($M^+ + H^+$), 369 ($M^+ - C_{14}H_{19}O_4$), 253 ($M^+ - C_{27}H_{46}$).

Poly(4-[8′-cholesteryloxy-3′,6′-dioxaoctyloxy]styrene) 3

A solution of **6** (0.68 g, 1.1 mmol) and AIBN (1.5 mg, 0.009 mmol) in toluene (0.5 ml) was sealed in an ampoule under vacuum. The solution was heated at 80 °C for 3 h. Upon cooling, THF (10 ml) was added to the reaction mixture and the solution added dropwise to chilled methanol (0 °C). The resultant solid was collected by centrifugation and purified by reprecipitation (× 2) from THF solution into methanol to yield **3** as a white waxy solid (0.46 g, 68%), transition temperatures; $T_g = 16.7$ °C, smectic A–isotropic = 135.9 °C (Found C, 79.41; H, 10.40%; $C_{41}H_{64}O_4$ requires C, 79.18; H, 10.53%); δ_H (500 MHz, $CDCl_3$): 0.65–2.45 (46H, m, steroid nucleus and polystyrene Hs), 3.10–3.17 (1H, m), 3.58–3.62 (4H, m), 3.66–3.74 (4H, br m), 3.79 (2H, br s), 4.00 (2H, br s), 5.28–5.31 (1H, m), 6.10–6.60 (4H, br m).

Liquid crystal characterisation

Differential scanning calorimetry measurements were made on a Seiko DSC 220C machine and calibrated using an indium standard. Optical microscopy observations were made on a Nikon Optiphot-2 microscope with a Mettler FP80 HT Hot Stage. Low resolution X-ray diffraction from powder samples were recorded using Cu-Kα radiation ($\lambda = 1.54$ Å) from a Philips PW1130/00 generator with a nickel filter. The samples were contained in glass capillaries (Hilgenberg 0.01 mm thick glass, 1.0 mm outside diameter X-ray capillaries) and placed in the beam in an aluminium heating block. The temperature was regulated by a Control Techniques Process Instruments 453 Plus Thermal Controller. The diffracted X-rays were detected with a flat-plate photographic camera using Agfa-Gevaert Osray M3 X-ray film. The system was calibrated using sodium chloride.

LB Film fabrication and characterisation

Isotherm behaviour was measured for monolayers, spread from chloroform (Aldrich, HPLC grade) solution, on pure water at pH 5.5 with no added ions using the apparatus and procedures described previously.[6] Multilayer film formation was performed on clean glass slides treated with an atmosphere containing 1,1,1,3,3,3-hexamethyldisilazane to provide a hydrophobic surface. Glancing angle X-ray diffraction from the films was recorded using Cu-Kα radiation in a Philips PW1050 X-ray Diffractometer using a rotating intensity detector.

Results and discussion

Material synthesis

Polystyrene **3** was prepared using the route outlined in Scheme 1. Previously, mesogen-containing polystyrenes have been prepared by grafting the mesogenic unit onto preformed poly(*p*-hydroxystyrene).[17,18] More recently, mesogenic styrene monomers have been prepared to determine their utility for photo-initiated *in situ* polymerisation.[19–21] The chosen route, *via* the styrene monomer **6**, was anticipated to ensure a homogeneous sample of **3**. The synthesis of **6** was achieved using a Wittig reaction between the benzaldehyde derivative **5** and methyltriphenylphosphonium bromide, using work by Fréchet as precedence.[22] Free radical polymerisation of **4** in deaerated toluene solution using AIBN as initiator gave **3** in 68% yield.[23] High resolution ^1H NMR showed that the repeated reprecipitation of **3** from THF into methanol had successfully removed any unreacted monomer. GPC analysis of **3** indicated a number average molar mass of 26×10^3 amu (polydispersity = 2.4) relative to polystyrene standards and confirmed the absence of non-polymeric contaminants.

Thermal behaviour

Thermal analysis of polymer **3** by DSC reveals a reproducible and reversible glass transition commencing at 20.3 °C on heating, although on the initial heating cycle this transition is observed at 35 °C. The latter value is consistent with the observation that **3** is obtained as a waxy solid at room temperature on precipitation from methanol. A very sharp first order endotherm is observed at 135.9 °C (enthalpy of transition = 5.5 mJ mg^{-1}), on heating, which polarising optical microscopy shows to be associated with a liquid crystal to isotropic liquid transition. On cooling slowly from the isotropic melt, a largely homeotropic optical texture is observed with fine focal conic defects consistent with the formation of a smectic A mesophase. A powder X-ray analysis of the mesophase (at 80 °C) shows strong lamellar ordering with three orders of diffraction corresponding to a smectic layer spacing of 53 Å. This figure is significantly larger than the estimated length of the side chain unit ($\sim$32 Å) which indicates that the mesophase possesses a bilayer structure. It is interesting to compare the large thermal range of the liquid crystal phase of polymer **3** with the thermal behaviour of its monomer **6** which has a narrow chiral nematic phase between 18.0 and 20.4 °C with a smectic A phase at lower temperatures. This represents an extreme example of the well documented enhancement in the thermal stability of the smectic phase caused by the ordering effect of the polymer backbone.[24]

Monolayer properties

A small quantity of **3** was adsorbed at the air–water interface by carefully placing a few drops of dilute chloroform solution onto the surface of ultra-pure water contained in a Langmuir trough and allowing the solvent to evaporate. On compression of the adsorbed layer, the relationship between surface pressure (π/mN m^{-1}) and the area occupied per repeat unit (A/Å^2) was recorded. The π–A isotherm of **3** is given in Fig. 1, together with those of compound **1** and polymer **2** taken directly from the literature.[14,15] All three isotherms were recorded under similar conditions (20 °C, pH of subphase $\sim$5.5). It is apparent that the general appearance of the π–A isotherm of **3** differs from that of **1** and **2**. Specifically, at low values of π the area per repeat unit of **3** is significantly greater but at $\pi = 38$ mN m^{-1} there is a reversible and highly reproducible discontinuity so that at higher surface pressures (40–50 mN m^{-1}) the π–A curves of all three materials are very similar. Such a discontinuity on a π–A isotherm is associated with either a molecular rearrangement within the adsorbed monolayer, resulting in a lower area per repeat unit, or the destruction of the monolayer—usually the latter is not reversible whereas the monolayer of **3** only becomes irreversible at values of surface pressures approaching the collapse pressure which is in excess of 50 mN m^{-1}.

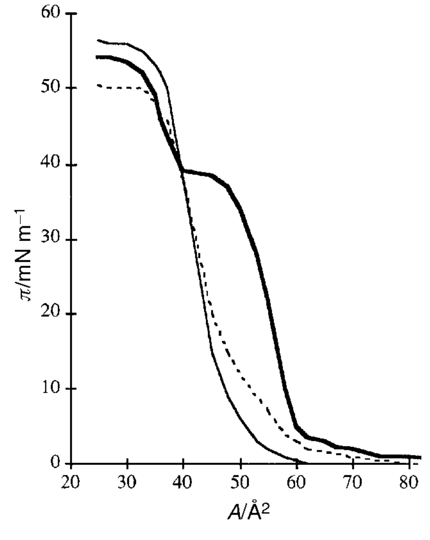


Fig. 1 The surface pressure, π/mN m^{-1} *versus* area per repeat unit, A/Å^2 isotherms for **1** (dashed line), **2** (thin solid line) and **3** (thick solid line) recorded on an aqueous subphase at 20 °C, pH = 5.5, compression speed = 1 mm s^{-1}. The data for **1** were taken from ref. 14 and that of **2** from ref. 15.

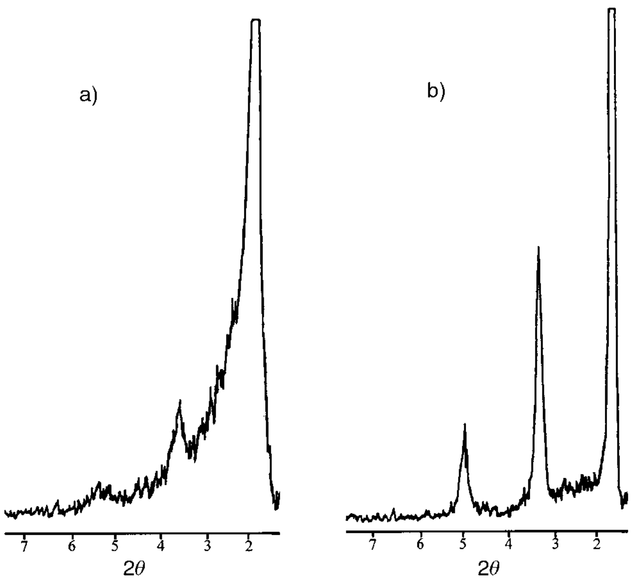
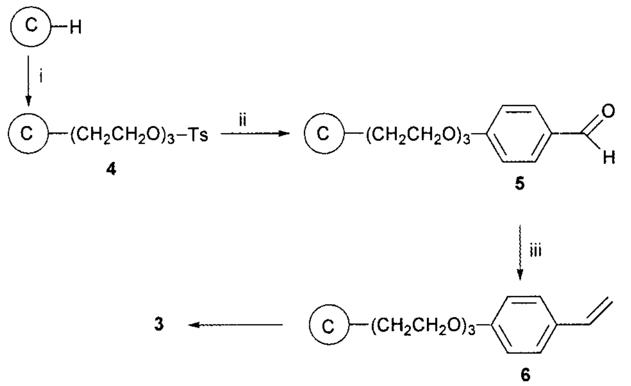


Fig. 2 Glancing angle X-ray diffractograms of Y-type LB films composed of 100 monolayers of polymer **3** deposited onto a hydrophobic substrate: a) deposition at 30 mN m^{-1} (relative intensity of first order peak = 249 counts s^{-1}, second order peak = 43 counts s^{-1}); b) deposition at 42 mN m^{-1} (relative intensity of first order peak = 422 counts s^{-1}, second order peak = 93 counts s^{-1}).

LB film formation

Deposition of polymer **3** onto a hydrophobic substrate was successful using the vertical deposition technique both on the upward and downward motion of the substrate through the monolayer to give a Y-type multilayer film. In both directions the transfer ratios approached unity. LB films were prepared from monolayers held at a surface pressure of 30 mN m^{-1}, a conventional value for film deposition, and at 42 mN m^{-1}—a value just above the unusual discontinuity in the π–A isotherm. Both types of film were highly uniform in appearance with a gold lustre. However, glancing angle X-ray diffraction analysis (Fig. 2) showed that there is a profound difference between the degree of order within films prepared at these two surface



Scheme 1

pressures. Surprisingly, the film with the higher degree of order was derived from the monolayer held at 42 mN m^{-1} which indicates that the discontinuity in the π–A isotherm of **3** is not associated with collapse of the monolayer. This film displays at least three orders of diffraction which correspond to a repeat layer spacing (d) of 53.8 Å. The lamellar spacing obtained from this film is almost identical to that observed from the powder diffraction analysis of the smectic mesophase of **3**. The d-spacing is again significantly larger than the estimated length of the side chain unit (~32 Å) and indicates a bilayer structure, as would be expected for a Y-type LB film. Some degree of intercalation or tilting of the side-chains is inferred from the smaller observed lamella spacing as compared to the estimated bilayer width (~64 Å). In contrast, the film deposited at a surface pressure of 30 mN m^{-1} shows only two distinct orders of diffraction (d = 52.6 Å) which are only half as intense as the corresponding reflections from the film prepared at 42 mN m^{-1}. There is also diffuse diffraction due to scattering from regions of ill-defined structure including a broad, weak diffraction which may be associated with third order diffraction from the layered structure.

A reasonable conclusion from these results is that the discontinuity in the π–A curve of **3** is associated with the transition between a disordered monolayer arrangement at lower values of π to a more ordered, closely-packed monolayer at higher values of π. The greater area per repeat unit at 30 mN m^{-1} (52 Å^2) than at 42 mN m^{-1} (40 Å^2) may be associated with the hydrophobic polystyrene backbone disturbing the packing of the cholesterol units. The area per repeat unit at 42 mN m^{-1} is consistent with that expected for a close packed arrangement of the cholesterol units similar to that obtained for **1** and **2**. Thus at high values of π , it appears that the hydrophobic repulsion of the polymer backbone to the aqueous subphase is overcome by the need to adopt a more space efficient arrangement within the monolayer.

Conclusions

Although many pre-formed polymers have been used for the fabrication of LB films, there are far fewer examples which show a convincing layered structure by glancing angle XRD. Generally, these are based on a hydrophilic polymer, for example poly(maleic anhydride),[5–8] poly(ethyleneoxy)[25] or poly(acrylamide),[26] with hydrophobic side-chains. The present work demonstrates that it is possible to obtain an *ordered* LB film from a hydrophobic polymer containing an appropriate side-chain. The importance of the hydrophilic oligo(ethyleneoxy) spacer is apparent by our failure to form a stable monolayer at the air–water interface derived from a similar polymer to **3** but containing an alkyl (undecyl) spacer. In addition, it is likely that the success of **3** as a film forming material is due to the extreme hydrophobicity and excellent self-ordering characteristics of the cholesterol unit. The role of the polymer chain in stabilising the monolayer is also apparent from the failure of monomer **6** to form a monolayer at the air–water interface. It is possible to envisage other LB film-forming polymer amphiphiles in which the spacer unit of the side-chain acts as the hydrophilic group.

Acknowledgements

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References

1 R. H. Tredgold, *Order in Thin Organic Films*, Cambridge University Press, Cambridge, 1994.
2 A. Ulman, *Introduction to Ultrathin Organic Films*, Academic Press, San Diego, 1991.
3 P. N. Bartlett, K. Bruce, E. J. Calvo and R. Etchenique, *J. Mater. Chem.*, 2000, **10**, 149 and references therein..
4 For example: M. Jin and G. Wang, *Jpn. J. Appl. Phys.*, 1997, **36**, L30.
5 P. Hodge, F. Davies and R. H. Tredgold, *Philos. Trans. R. Soc., London*, 1990, **330**, 153.
6 F. Davies, P. Hodge, C. R. Towns and Z. Ali-Adib, *Macromolecules*, 1991, **24**, 5695.
7 F. Davies, P. Hodge, X.-H. Lui and Z. Ali-Adib, *Macromolecules*, 1994, **27**, 1957.
8 I. P. Aspin, P. Hodge, C. R. Towns and Z. Ali-Adib, *Polymer*, 1995, **36**, 1707.
9 G. F. Gibbons, K. A. Mitropoulos and N. B. Myant, *The Biochemistry of Cholesterol*, Elsevier Biomedical Press, New York, 1982.
10 F. Reinitzer, *Monatsh Chem.*, 1888, **9**, 421.
11 H. Brockerhoff and L. S. Ramsammy, *Biochem. Biophys. Acta*, 1982, **691**, 227.
12 Y. S. Freidzon, A. V. Kharitonov, V. P. Shibaev and N. A. Platé, *Mol. Cryst. Liq. Cryst.*, 1982, **88**, 87.
13 S. K. Abid and D. C. Sherrington, *Polym. Commun.*, 1987, **28**, 16.
14 G. Decher and H. Ringsdorf, *Liq. Cryst.*, 1993, **13**, 57.
15 Z. Ali-Adib, A. Bomben, F. Davies, P. Hodge, P. Tundo and L. Valli, *J. Mater. Chem.*, 1996, **6**, 15.
16 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd edn., Pergamon, Oxford, 1988.
17 J. V. Crivello, M. Deptolla and H. Ringsdorf, *Liq. Cryst.*, 1988, **3**, 235.
18 G. S. Attard, C. T. Imrie and F. E. Karasz, *Macromolecules*, 1993, **26**, 3803.
19 H. Andersson, M. Trollsas, U. W. Gedde and A. Hult, *Macromol. Chem. Phys.*, 1995, **196**, 3667.
20 S. E. Williamson, D. Kang and C. E. Hoyle, *Macromolecules*, 1996, **29**, 8656.
21 A. Cook, S. Badriya, S. Greenfield and N. B. McKeown, *J. Mater. Chem.*, 2000, submitted.
22 J. M. J. Fréchet, E. Eichler, H. Ito and G. Wilson, *Polymer*, 1983, **24**, 995.
23 Monomer **6** is an isotropic liquid at room temperature which gradually solidifies as a result of polymerisation. However the compound is stable if kept as a solid in a refrigerator or at room temperature if a small amount of inhibitor (*e.g.* 2,6-di-*tert*-butyl-4-methylphenol) is added.
24 C. B. McArdle, *Side Chain Liquid Crystal Polymers*, Blackie, Glasgow, 1989.
25 R. C. Hall, G. A. Lindsay, B. Anderson, S. T. Kowel, B. G. Higgins and P. Stroeve, *Mater. Res. Soc. Symp. Proc.*, 1988, **109**, 351.
26 T. Miyashita, Y. Mizuta and M. Matsuda, *Br. Polym. J.*, 1990, **22**, 327.