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Convenient synthesis of a discotic side group liquid crystal polymer

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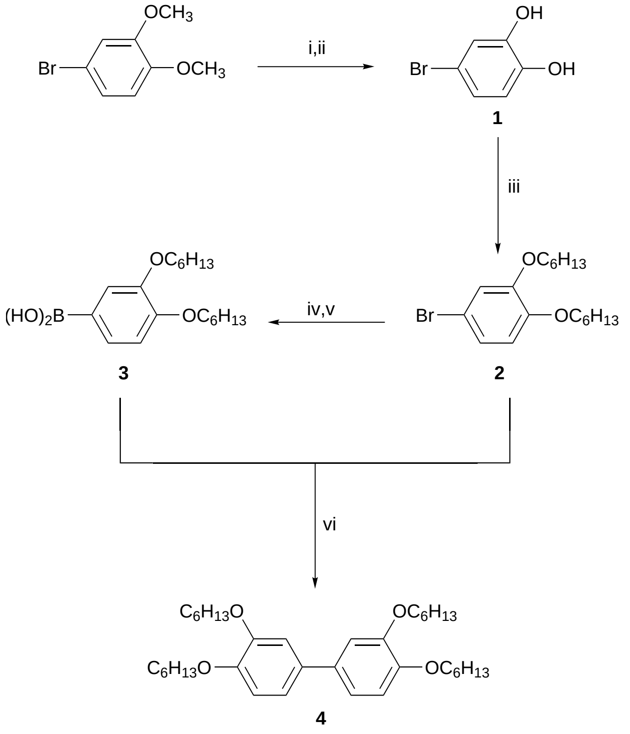
The synthesis of a discotic side group liquid crystal polymer based on poly(methyl methacrylate) is reported. This involves the oxidative coupling of 3,3′,4,4′-tetrakis(hexyloxy)biphenyl with 1-hexyloxy-2-methoxybenzene to yield the unsymmetrical triphenylene nucleus, 2-methoxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene. Subsequent demethylation followed by reactions first with 1,11-dibromoundecane and then with the potassium salt of methacrylic acid yielded the polymerisable monomer, 11-[3,6,7,10,11-pentakis(hexyloxy)-2-oxytriphenylene]undecyl methacrylate. This was polymerised in benzene using azoisobutyronitrile as the initiator. The thermal properties of the resulting polymer are described.

Side group liquid crystal polymers (SGLCP) consist of three distinct structural components: a polymer backbone, a liquid crystal group and connecting these, a flexible spacer which is most commonly an alkyl spacer.[1–3] The role of the flexible spacer is to decouple, to some extent, the opposing tendencies of the polymer backbone to adopt a random coil conformation from those of the liquid crystal groups to self-assemble into an ordered mesophase. This decoupling endows the polymers with a unique duality of properties; they exhibit macromolecular characteristics such as ease of processibility and glassy behaviour combined with, for example, the electro-optic properties of conventional low molar mass mesogens. This combination of polymeric and low molar mass mesogenic properties is the basis of the considerable application potential of SGLCPs in a range of advanced electro-optic technologies.[4–6] The intensive research interest in SGLCPs is not exclusively a result of this application potential, however, but also because they provide a demanding challenge to our understanding of the molecular factors that promote self-assembly in polymeric systems.

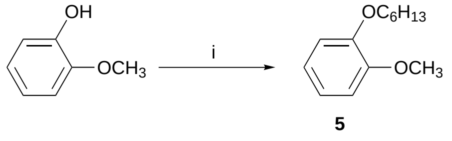
The overwhelming majority of SGLCPs reported in the literature contain rod-like or calamitic mesogenic groups. Indeed, there are surprisingly few reports of SGLCPs in which discotic mesogenic moieties are attached.[7–10] This situation stems largely from the synthetic difficulties in obtaining well-defined and monodisperse polymerisable monomers containing a discotic mesogenic unit. Indeed, the methods reported in the literature are based around laborious separation procedures involving several isomers of the triphenylene-based core. In recent years, however, there have been many advances in the synthesis of triphenylene-based compounds and in particular the pioneering work of Boden, Bushby, Cammidge and their co-workers[11–14] has now made it possible to obtain large quantities of monodisperse triphenylene-containing monomers. In this paper we describe a convenient synthetic route by which to prepare discotic SGLCPs based on poly(methyl methacrylate) and containing hexasubstituted triphenylene.

Results and Discussion

Reaction Schemes 1–4 outline the synthetic approach used to prepare the discotic SGLCP **10** in Scheme 4. At the heart of this methodology lies the fact that the synthesis of a discotic SGLCP *via* the polymerisation of a triphenylene-based monomer necessarily involves the preparation of an unsymmetrically hexasubstituted triphenylene nucleus. The preferred approach to such compounds involves coupling a 3,3′,4,4′-tetrakis(alkyloxy)biphenyl with a 1,2-dialkyloxybenzene.[12,15] This general strategy was adopted here (see Scheme 3) and hence, requires the synthesis of the appropriately substituted biphenyl and benzene derivatives.



Scheme 1 *Reagents and conditions*: i, BBr_3, CH_2Cl_2; ii, H_2O; iii, $C_6H_{13}Br$, K_2CO_3, DMF; iv, BuLi; v, $(PrO)_3B$; vi, $Pd(PPh_3)_4$, Na_2CO_3



Scheme 2 *Reagents and conditions*: i, $C_6H_{13}Br$, K_2CO_3, DMF

3,3′,4,4′-Tetrakis(hexyloxy)biphenyl (**4** in Scheme 1) was prepared by the tetrakis(triphenylphosphine)palladium(0)-catalysed coupling of 3,4-bis(hexyloxy)phenylboronic acid, **3**, with 3,4-bis(hexyloxy)bromobenzene, **2**, according to the procedure described by Gray *et al.*[16] Compound **2** was obtained in two

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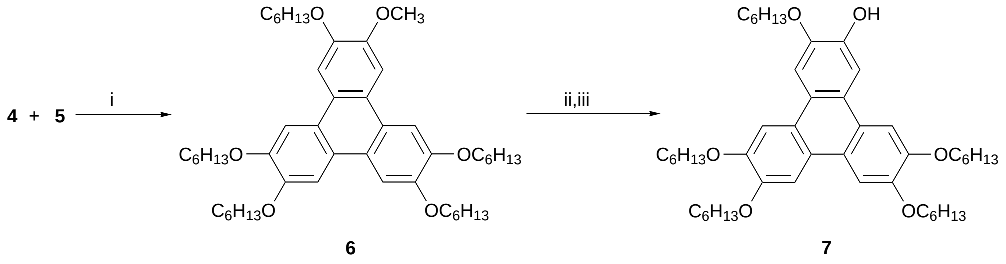
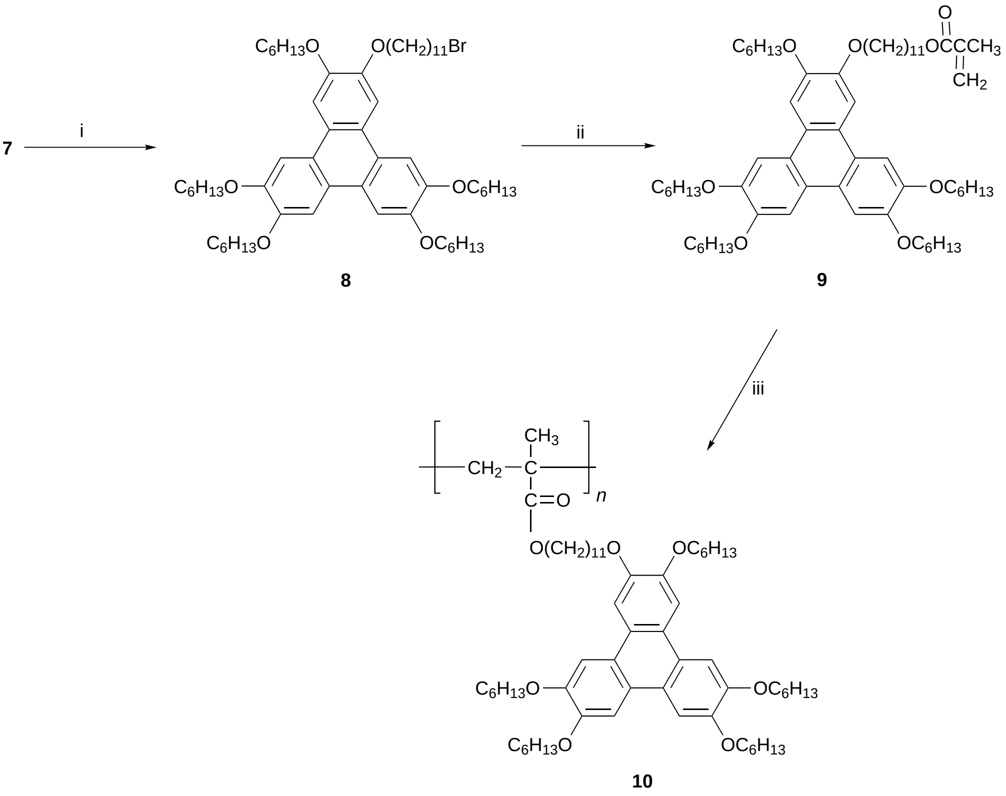


Scheme 3 *Reagents and conditions*: i, $FeCl_3$, CH_2Cl_2; ii, Ph_2PH, BuLi; iii, HCl



Scheme 4 *Reagents and conditions*: i, $Br(CH_2)_{11}Br$, K_2CO_3, acetone; ii, methacrylic acid, $KHCO_3$, DMF; iii, AIBN, benzene

steps (see Scheme 1): 3,4-dimethoxybromobenzene (4-bromoveratrole) was demethylated using boron tribromide[17] followed by the alkylation of the resulting 3,4-dihydroxybromobenzene using bromohexane to give **2**. Compound **3** was obtained *via* the reaction of **2** first with butyllithium to yield the lithium salt and subsequent conversion to the borate ester using triisopropyl borate which was hydrolysed *in situ* using hydrochloric acid to give **3**.[16] 1-Hexyloxy-2-methoxybenzene **5** was obtained readily by the alkylation of 2-methoxyphenol (guaiacol) using bromohexane (see Scheme 2).

The oxidative coupling of **4** with **5** (see Scheme 3) was achieved using iron(III) chloride[12,14,15] to give the unsymmetrical triphenylene nucleus **6**. As with previous reports, we found no evidence that detectable quantities of the triphenylene based on **5** were produced during the coupling reaction.

Demethylation of **6** using lithium diphenylphosphide[18] yielded the phenol **7** (see Scheme 3) which was reacted with a tenfold excess of 1,11-dibromoundecane[19] to give the monofunctionalised triphenylene nucleus **8** (see Scheme 4). This in turn was reacted with the potassium salt of methacrylic acid[20] yielding the methyl methacrylate-based monomer **9**. The polymerisation of **9** was performed in benzene using azoisobutyronitrile (AIBN) as the initiator.

The estimated weight average molar mass derived from gel permeation chromatography (GPC) for **10** is 61 000 g mol^{-1} and the number average molar mass is 9000 g mol^{-1}; the polydispersity of **10** is, therefore, high, 6.8. This can be attributed to the presence of a significant high molar mass fraction. We should note that these values for the molecular masses are at best approximations given the large differences in the hydrodynamic volumes of **10** and the polystyrene standards used to calibrate the GPC. For calamitic SGLCPs, however, these molar masses would ensure that not only does the polymer's thermal properties lie outside the molar mass dependent regime[21] but also that polydispersity did not influence the transitional behaviour.[22] It is not known whether the molar mass dependence of the thermal properties of discotic SGLCPs mirror those of calamitic systems and hence, it is unclear if the thermal behaviour of **10** is still molar mass dependent. We will return to this issue below.

The DSC trace obtained on the initial heating of **10** contains two transitions (see Fig. 1): a weak step in the baseline is observed at 2 °C and an endothermic peak is seen at 45 °C. On cooling from the isotropic phase, a birefringent texture begins to develop at *ca.* 45 °C and the phase is fluid albeit highly viscous. In consequence this is identified as a liquid crystal phase. The optical texture, however, is rather poorly defined and even after annealing for several days does not develop into a clear, characteristic texture in which a phase assignment is possible. The texture remains unchanged to below the second transition and thus, this is assigned as the glass transition. The entropy change associated with the

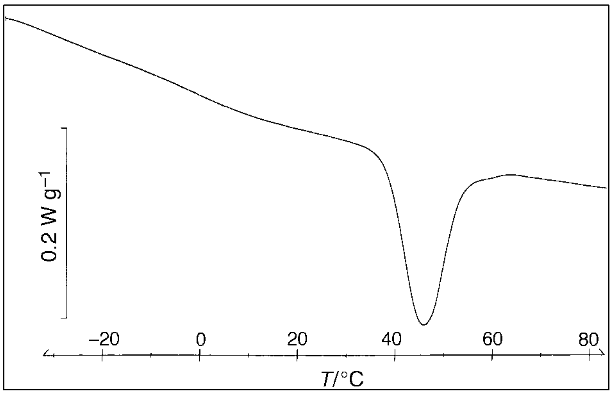


Fig. 1 DSC trace obtained on heating **10**

clearing transition expressed as the dimensionless quantity $\Delta S/R$ is 3.55. This relatively high value indicates that the phase possesses at least medium range ordering and given the structure of the polymer, is presumably columnar in nature. On cooling at 10 °C min^{-1} the isotropic phase is quenched into the glassy state and only on reheating is the mesophase observed. Similar behaviour has been observed for other discotic SGLCPs containing relatively rigid backbones.[9]

The monomeric analogue of the side-chain attached in polymer **10**, *i.e.* 2-undecyloxy-3,6,7,10,11-pentakis(hexyloxy)-triphenylene, has not been reported in the literature. The symmetric hexakis(hexyloxy)triphenylene has a clearing transition at 97 °C[23] and by analogy with other unsymmetrically substituted triphenylenes[15] this may be expected to fall by *ca.* 30 °C on replacing one hexyloxy chain by an undecyloxy chain. Thus it would appear that attaching the discotic monomer to the polymer backbone has reduced its clearing temperature. This is in stark contrast to the behaviour observed for calamitic SGLCPs for which attachment of the monomer significantly increases its clearing temperature.[1–3] This latter observation reflects that the attachment of the mesogenic units to the polymer chain increases the orientational correlations between the groups and hence, enhances the clearing temperature.[24]

The decrease in the clearing temperature of discotic monomers on attachment to a polymer backbone has also been observed for other systems and has been interpreted in terms of the polymer backbone acting as a diluent which reduces the ability of the columns to pack efficiently so reducing the clearing temperature.[9] The backbones must also traverse differing columns which again will have a destabilising effect on the arrangement of the columns. In addition, the attachment of the discs to the backbone hinders the axial motions of the discs within a column, which are known to occur in low molar systems,[8,25] so reducing the intra-column orientational correlations between the mesogenic groups. The possible effect of the end-groups on the thermal behaviour of **10** should not be neglected. A columnar arrangement will clearly be destabilised by the presence of bulky end-groups to a greater extent than a calamitic smectic phase in which the backbone is accommodated, at least to some extent, between the smectic layers.[26] Thus, the properties of discotic SGLCPs may remain molar mass dependent to higher degrees of polymerisation than calamitic SGLCPs and this now requires further investigation.

Conclusions

A convenient route for the preparation of discotic SGLCPs has been described. Structure–property relationships in discotic SGLCPs appear to be quite different to those established for calamitic systems although only a very limited number of discotic materials have been studied. The synthetic methodology described, however, will allow for the synthesis of a wider range of materials to test these initial findings.

Experimental

3,4-Dihydroxybromobenzene, 1

Compound **1** was prepared using the method described by McOmie *et al.*[17] Boron tribromide (20 ml, 0.2115 mol) was dissolved in dried dichloromethane (DCM) (100 ml) at −80 °C. A solution of 4-bromoveratrole (14 g, 0.0645 mol) in DCM (100 ml) was added dropwise. The resulting mixture was allowed to warm slowly to room temp. and stirred under a positive pressure of argon for 96 h. Water (50 ml) was added very slowly and the reaction mixture extracted using diethyl ether. The organic extract was washed twice with water and dried over magnesium sulfate. The diethyl ether was removed under reduced pressure to yield a crystalline solid which did not require purification. Yield 85%. δ_H ($CDCl_3$) 6.8–7.0 (m, aromatic, 3H); 4.4–5.8 (brs, OH, 2H). Mp 85–86 °C.

3,4-Bis(hexyloxy)bromobenzene, 2

A mixture of **1** (10.1 g, 53.4 mmol), bromohexane (36.3 g, 220 mmol) and potassium carbonate (41.2 g, 299 mmol) in dimethylformamide (DMF; 200 ml) was heated with stirring at 120 °C overnight. The mixture was allowed to cool and poured into cold water (*ca.* 1 l). This was extracted using chloroform and the organic extracts washed several times using water, twice using sodium hydroxide solution (5% w/v) and twice using water. The organic layer was dried over magnesium sulfate and the chloroform removed under reduced pressure. The oily residue was distilled from calcium hydride using a Kugelröhr apparatus. Yield 63%. δ_H ($CDCl_3$) 6.7–7.1 (m, aromatic, 3H); 4.0 (m, OCH_2, 4H); 1.8 (m, OCH_2CH_2, 4H); 0.9–1.7 [m, $O(CH_2)_2(CH_2)_3CH_3$, 18H].

3,4-Bis(hexyloxy)phenylboronic acid, 3

The acid **3** was prepared using the method described by Gray *et al.*[16] Thus, **2** (4 g, 11.2 mmol) was degassed under high vacuum using the freeze–pump–thaw method and tetrahydrofuran (40 ml) was distilled into the flask from sodium–benzophenone. This was stirred under a positive over pressure of argon for *ca.* 15 min and cooled to *ca.* −80 °C. A 10.0 M solution of *n*-butyllithium (1.5 ml) was injected into the flask and the resulting mixture stirred for a further *ca.* 2.5 h. Triisopropyl borate (8 ml) was added and the mixture allowed to warm to room temp. with stirring overnight. 3.0 M Hydrochloric acid (80 ml) was added, the mixture stirred for *ca.* 1 h and then extracted twice using diethyl ether. The combined organic extracts were washed several times using water and dried over magnesium sulfate. The diethyl ether was removed under reduced pressure and the crude product recrystallised from aqueous ethanol. Mp 96–97 °C. Yield 93%. δ_H ($CDCl_3$) 6.7–7.9 (m, aromatic, 3H); 3.9–4.2 (m, OCH_2, 4H); 0.8–2.0 [m, $OCH_2(CH_2)_4CH_3$, 22H]. The location of the acidic H is uncertain due to rapid exchange with small amounts of H_2O in the solvent.

3,3′,4,4′-Tetrakis(hexyloxy)biphenyl, 4

The biphenyl **4** was prepared using the method described by Gray *et al.*[16] A solution of **3** (2.7 g, 8.4 mmol) in ethanol (30 ml) was added to a stirred mixture of **2** (2.6 g, 7.3 mmol) and sodium carbonate (3.5 g, 33 mmol) in water (30 ml) under a positive over pressure of argon. A solution of tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.216 mmol) in benzene (30 ml) was added and the resulting mixture stirred under argon for *ca.* 24 h. This was allowed to cool and extracted using diethyl ether. The organic extracts were washed twice using brine and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product recrystallised with hot filtration from ethanol. Yield 62%. δ_H ($CDCl_3$) 6.9–7.1 (m, aromatic, 6H); 4.0 (m, OCH_2, 8H); 1.8 (m, OCH_2CH_2, 8H); 1.4, 1.6 (m, CH_2, 24H); 0.9 (t, CH_3, 12H, *J* 7.0) (*J* values in H_z throughout). Mp 75–76 °C.

1-Hexyloxy-2-methoxybenzene, 5

A mixture of 2-methoxyphenol (guaiacol, 20.8 g, 168 mmol), bromohexane (29.4 g, 178 mmol), potassium carbonate (35.2 g, 255 mmol) and DMF (200 ml) was heated at 120 °C with stirring overnight. The reaction mixture was allowed to cool and poured into cold water (*ca.* 1 l). The isolation and purification of the product was identical to that described for **2**. Yield 55%. δ_H ($CDCl_3$) 6.8 (m, aromatic, 6H); 4.1 (t, $ArOCH_2$, 2H, *J* 6.9); 4.0 (s, $ArOCH_3$, 3H); 1.9 (m, OCH_2CH_2, 2H); 1.3–1.6 [m, $O(CH_2)_2(CH_2)_2$, 4H]; 1.0 (t, CH_3, 3H, *J* 7.0).

2-Methoxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene, 6

Iron(III) chloride (0.89 g, 5.5 mmol) was added to a stirred solution of **4** (2.92 g, 5.27 mmol) in dichloromethane (70 ml) at 0 °C. The resulting mixture was stirred for a further *ca.* 10 min at 0 °C and **5** (1.65 g, 7.93 mmol) was added. This was stirred for *ca.* 15 min at 0 °C and a second portion of iron(III) chloride (1.32 g, 8.14 mmol) added. The reaction mixture was allowed to stir at 0 °C for 3 h and a second batch of **5** added (1.65 g, 7.93 mmol). After a further 10 min additional iron(III) chloride was added (0.89 g, 5.5 mmol). The resulting mixture was stirred at 0 °C for 1 h and subsequently allowed to warm to room temp. (*ca.* 30 min). The reaction mixture was poured into methanol at 0 °C and stored at *ca.* −20 °C overnight. The resulting precipitate was collected by filtration and this crude product was found to be a mixture of **4** and **6**. **6** was obtained by column chromatography using silica as the stationary phase and a 10% v/v diethyl ether–light petroleum (bp 40–60 °C) mixture as the eluent. The unreacted **4** eluted first from the column and was recovered. **6** was recrystallised from ethanol and dried under vacuum. The transitional behaviour of **6** is in good agreement with that reported in the literature.[23] Yield 55%. δ_H ($CDCl_3$) 7.8 (m, aromatic, 6H); 4.2 (t, $ArOCH_2$, 10H, *J* 6.4); 4.1 (s, $ArOCH_3$, 3H); 1.1–2.1 [m, $OCH_2(CH_2)_4$, 40H]; 1.0 (t, CH_3, 15H, *J* 6.9). Crystal–crystal 53 °C; crystal–mesophase 69 °C; mesophase–isotropic 78 °C.

2-Hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene, 7

Compound **7** was prepared using a method described by Ireland and Walba.[18] Thus, tetrahydrofuran (20 ml) was distilled from Na–benzophenone into a two-necked round bottomed flask on a high vacuum line. This was cooled to 0 °C and while stirring with an argon over pressure, diphenylphosphine (1.5 ml, 8.7 mmol) followed by *n*-butyllithium (1 ml of a 10 M solution) were injected into the flask. This mixture was allowed to warm to room temp. (*ca.* 30 min) and a solution of **6** (2.1 g, 2.77 mmol) in THF (30 ml) was injected into the flask. The resulting solution was allowed to stir at room temp. under a positive argon pressure overnight. 3 M Hydrochloric acid was added (100 ml) and after stirring for a further 30 min, the reaction mixture was extracted using chloroform. The organic layer was washed several times with water, once with 5% sodium hydroxide solution and finally twice more with water. The organic extracts were dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. The crude product was recrystallised from ethanol with hot filtration and dried under vacuum. Yield 1.85 g (90%). δ_H ($CDCl_3$) 7.6–8.0 (m, aromatic, 6H); 4.2 (m, $ArOCH_2$, 10H); 0.9–2.0 [m, $O(CH_2)_2(CH_2)_2CH_3$, 55H]. Mp 45–46 °C.

2-(11-bromoundecyloxy)-3,6,7,10,11-pentakis(hexyloxy)triphenylene, 8

Compound **8** was prepared using the method described by Attard *et al.*[19] Thus, a mixture of **7** (2 g, 2.69 mmol), 1,11-dibromoundecane (8.5 g, 27 mmol), potassium carbonate (4 g, 28 mmol) and acetone (200 ml) was refluxed with stirring overnight. The reaction mixture was filtered hot to remove the insoluble inorganic material and the acetone removed under reduced pressure. The excess 1,11-dibromoundecane was removed using a Kügelrohr apparatus. The residue was recrystallised from ethanol with hot filtration and dried under vacuum. Yield 2.1 g (80%). δ_H ($CDCl_3$) 7.8 (s, aromatic, 6H); 4.2 (t, $ArOCH_2$, 12H, *J* 6.4); 3.4 (t, CH_2Br, 2H, *J* 6.7); 0.9–2.0 [m, $(CH_2)_4CH_3$, $(CH_2)_9CH_2Br$, 73H]. Mp 46 °C.

11-[3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-yloxy]-undecyl methacrylate, 9

The methacrylate **9** was prepared using the method described by Craig and Imrie.[20] Methacrylic acid (1.1 g, 12.8 mmol) was dropped onto potassium hydrogen carbonate (1.0 g, 10.0 mmol) to form the potassium salt of methacrylic acid. This was stirred for *ca.* 10 min prior to the addition of a solution of **8** (2.1 g, 2.15 mmol) in DMF (30 ml) and a trace amount of hydroquinone. The resulting mixture was stirred at 120 °C for 24 h. After cooling, the mixture was poured into ice cold water (1 l) and the resulting precipitate collected by filtration and dissolved in chloroform. This solution was washed twice with 5% sodium hydroxide solution and twice with water. The organic extracts were dried over anhydrous magnesium sulfate and the chloroform removed under reduced pressure. The product was purified by recrystallisation twice from ethanol. Yield 80%. δ_H ($CDCl_3$) 7.8 (s, aromatic, 6H); 5.5, 6.1 (m, $C{=}CH_2$, 2H); 4.2 (t, $ArOCH_2$, 12H, *J* 6.4); 4.1 [t, $CH_2OC(O)$, 2H, *J* 6.6]; 1.81 (m, OCH_2CH_2, 14H); 1.2–1.7 (m, CH2, 44H); 0.9 (m, CH_3, 18H). Mp 35 °C.

Polymerisation of 9

Monomer **9** (0.7 g, 0.86 mmol) was dissolved in dry benzene (25 ml), and AIBN (5.74 mg, 0.034 mmol) was added as initiator. The reaction mixture was degassed twice using the freeze–pump–thaw method and subsequently flushed with argon for 15 min. The polymerisation flask was placed in a water bath at 60 °C to initiate polymerisation. After 72 h the polymer was precipitated in a large amount of methanol. The polymer was then redissolved in chloroform and reprecipitated into methanol. The removal of **9** from the polymer was monitored spectroscopically; specifically, the alkene stretch at 1637 cm^{-1} in the IR spectra of the monomer and the peaks associated with the alkene protons at 5.5 and 6.1 ppm in the ^1H NMR spectra. Repeated precipitations failed to completely remove traces of monomer, however, and instead, the polymer was purified by Soxhlet extraction using methanol for up to 72 h. Spectroscopic analysis confirmed the removal of monomer within the detection limits. δ_H ($CDCl_3$) 7.2, 7.8 m, aromatic, 6H); 4.2 [m, $ArOCH_2$, $CH_2OC(O)$, 14H]; 1.9, 1.6, 1.3 (m, CH_2, 60H); 0.9 (m, CH_3, 18H).

Characterisation

The proposed structures of all the compounds were verified using ^1H NMR and IR spectroscopy. ^1H NMR spectra were measured in $CDCl_3$ on a Bruker AC-F 250 MHz NMR spectrometer. IR spectra were recorded using a Nicolet 205 FTIR spectrometer. The purities of all the intermediates were verified using thin layer chromatography. The molar masses of the polymers were measured by gel permeation chromatography (GPC) using a Knauer Instruments chromatograph equipped with two PL gel 10 mm mixed columns and controlled by Polymer Laboratories GPC SEC V5.1 Software.

THF was used as the eluent. A calibration curve was obtained using polystyrene standards.

Thermal properties were determined by differential scanning calorimetry (DSC) using a Mettler-Toledo DSC 820 system equipped with an intracooler accessory and calibrated using an indium standard. The heating and cooling rates in all cases were 10 °C min^{-1}. Phase identification was performed by polarised light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and TMS 91 control unit.

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