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Polymerizable liquid crystalline twin molecules: synthesis and thermotropic properties

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The synthesis of 14 novel low molar mass liquid crystalline twin molecules is described and experimental details are given. The twin monomers contain two mesogenic units which are connected by a flexible spacer. Two terminal acrylate groups make these twins suitable for photopolymerization. The insertion of lateral groups into the mesogen leads to glass-forming properties. We tested several substituents ($-OCH_3$, $-CH_3$) in different positions of the mesogenic unit and investigated their thermotropic properties as well as their crystallization behaviour by polarizing microscopy and DSC experiments. Some of the novel twin molecules with lateral substituents in the mesogenic core have unusually broad mesophases of about 150°C. Below T_g stable LC glasses are formed. At room temperature a slow, kinetically hindered crystallization starts after about three hours. The broad mesophases of the twin molecules allow investigations of the photopolymerization kinetics over a wide temperature range. The addition of chiral non-liquid crystalline comonomers and subsequent photopolymerization leads to cholesteric networks with interesting optical properties. Last but not least, the twins are suitable mixing agents which suppress the crystallization of classical mono-rods.

1. Introduction

Low molar mass glass-forming nematics have recently attracted special interest as materials for optical applications, e.g. polarizers [1, 2] and IR reflectors, as well for cholesteric effect colours [3–6]. Such coatings are nowadays made from cholesteric pigments. A nematic host and a chiral dopant, which are both functionalized with polymerizable groups, are mixed with a photoinitiator, heated into the cholesteric mesophase and subsequently photopolymerized with UV light. Thereby the monomers are permanently fixed into a densely cross-linked network. Networks on the basis of acrylates [7–10], vinyl ethers [11], epoxides [12, 13] and thiolenes [14, 15] have been described in the literature. Recently we have also prepared networks from non-conjugated dienes by photoinitiated radical cyclopolymerization [16].

In the next process step, cholesteric polymer films obtained by photopolymerization are milled to form cholesteric pigments. The production of pigments, however, is not straightforward. One alternative, avoiding this pigment step, is the use of monomers which do not crystallize upon cooling and which are in their liquid crystalline state at room temperature. In the past, several synthetic approaches to low molar mass glass-forming monomers have been made, e.g. the synthesis of cholesteric cyclosiloxanes [3–5], mixtures of different mesogenic bisacrylates [17], bismethacrylates with three mesogenic units [18], hybrid monomers with two different polymerizable groups [19] and liquid crystalline derivatives of cyclohexane-1,3,5-carboxylic acid [20–22].

In this paper we describe another route to low molar mass liquid crystals which vitrify upon cooling, the synthesis of twin molecules. Such liquid crystals in which two mesogenic units are linked by a flexible spacer are also known as liquid crystal dimers or as bismesogens [23]. The first liquid crystalline twins were even mentioned by Vorländer about 70 years ago [24]. In recent years, growing attention has been paid to twin molecules, because they can be regarded as model compounds for LC main chain [25–27] and side group polymers [28, 29]. Twin molecules have molecular masses in the range of oligomers, but are still molecularly uniform materials. They combine properties typical of oligomers and polymers (like glass formation) with those of low molar mass monomers, such as facile orientation of the molecules in the mesophase.

Two principal architectures of twin molecules have been described in the literature (figure 1). The two mesogenic units can be connected by a flexible spacer either terminally, figure 1 (*a*) [25, 30, 31], or laterally, figure 1 (*b*) [32–34].

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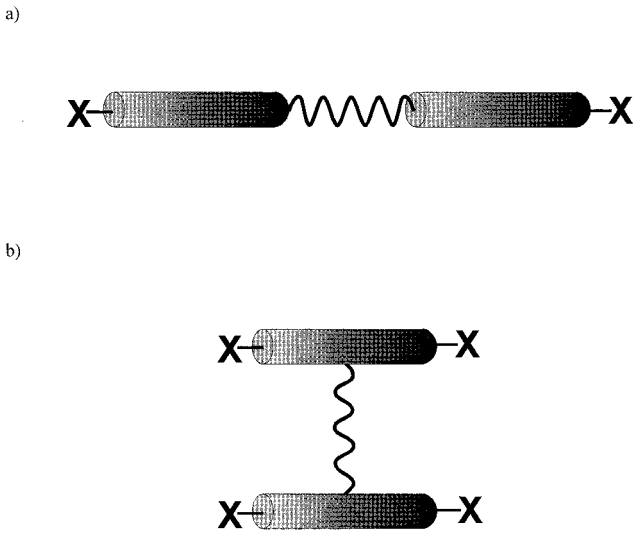


Figure 1. Schematic drawing of twin molecules with (*a*) terminal and (*b*) lateral connection of the mesogen units (*X*: end group, e.g. CH_3, OCH_3, CN, OC_nH_{2n+1}).

Terminally coupled liquid crystal dimers derived from 1-aminopyrene have been shown to form glasses by Imrie [35, 36]. The crystallization of these dimers is strongly depressed and glasses with a T_g well above room temperature are obtained.

In laterally coupled mesogens, a reduced crystallization tendency is also observed in some cases. The first glass-forming twin molecules were reported by Weissflog *et al.* [37], who synthesized three-core mesogens laterally connected by a spacer. These compounds show glass transitions by DSC, but start to crystallize upon storing above their T_g values. These twin molecules have no polymerizable groups necessary for photopolymerization. The first twin molecules with polymerizable end groups were recently reported by Shiota and Ober. These twin monomers have terminal vinyl or epoxide groups and form smectic network structures upon heating with different diamines [38–40].

In this paper we present a number of twin molecules with polymerizable acrylate groups. Several of these twin molecules do not crystallize upon cooling, but vitrify to LC glasses. We have synthesized several series of twins with lateral substituents ($-OCH_3$, $-CH_3$) in the mesogenic core. In these compounds, both the mesophase behaviour and the crystallization tendency strongly depend on the number and the position of the substituents in the molecules, and this will be discussed in detail.

2. Experimental

2.1. *Methods of characterization*

NMR spectra were obtained on solutions using a Bruker AC-250 spectrometer (250 MHz for ^1H NMR and 62.5 MHz for ^{13}C NMR). Thermal transitions were investigated with a Leitz Laborlux Pol-12 polarizing microscope equipped with a Mettler FP 82 hot stage and FP 80 processing unit (heating and cooling rate 10 K min^{-1}). Transition temperatures and enthalpies were recorded with a Perkin Elmer DSC 7 differential scanning calorimeter (heating and cooling rate 10 K min^{-1}). To avoid thermal polymerization of the acrylate groups, 1 wt % of sulphur was added to the monomers. The samples for DSC measurements were freeze dried from 1,4-dioxan solution.

2.2. *Synthesis*

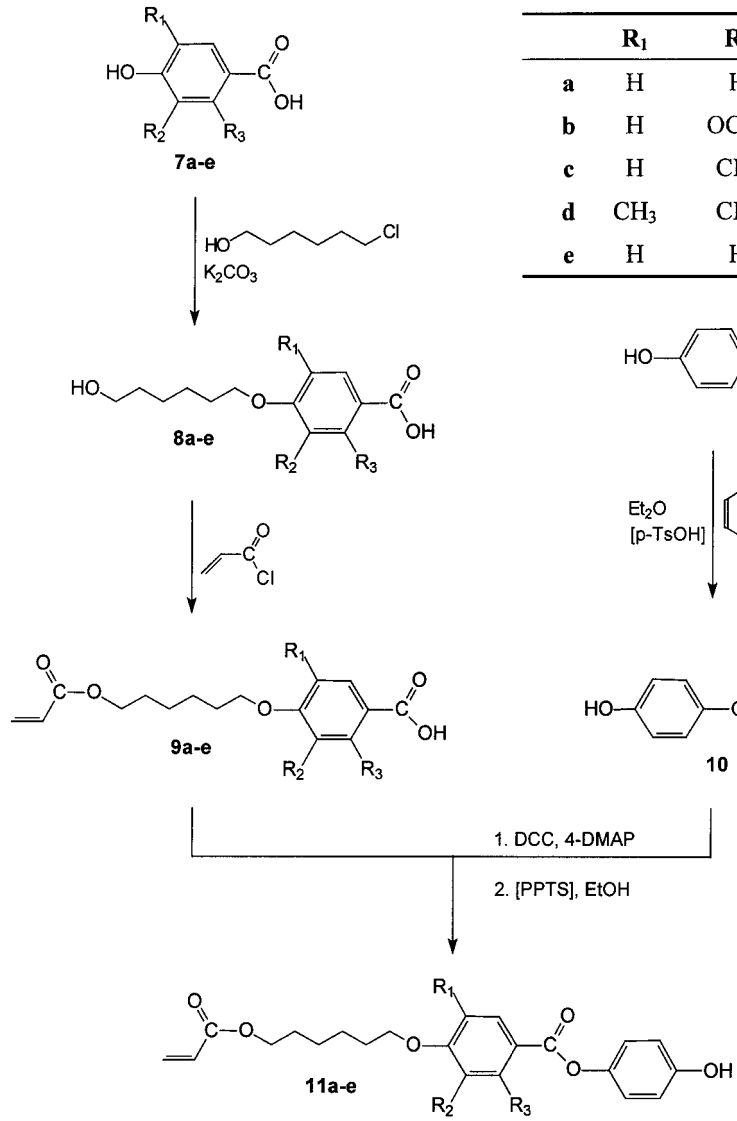
The synthetic pathway to the twin molecules is presented in schemes 1–3. Experimental details are not given for all compounds, but can be found in [41]. The synthesis of the substituted 4-hydroxybenzoic acids **7c–e** was carried out according to [42–46]; for details see also [41].

All reactions were carried out in an argon atmosphere. The data for the melting points were taken from 2nd heating runs (polarizing microscopy, heating rate 10 K min^{-1}).

2.2.1. *Preparation of the unsubstituted twin molecule* ***1***

2.2.1.1. *4-(6-Hydroxyhexyloxy)benzoic acid* ***8a***. 33.24 g (0.20 mol) of ethyl 4-hydroxybenzoate, 32.4 ml (0.24 mol) of 6-chlorohexanol, 55.28 g (0.40 mol) of K_2CO_3 and 3.00 g of KI in 300 ml of cyclohexanone were heated at reflux under vigorous stirring for 16 h. The excess of K_2CO_3 was hot filtered and washed with cyclohexanone. After evaporation of the solvent, the resulting oil was dissolved in 300 ml of methanol and, after addition of 44.90 g (0.80 mol) of KOH in 50 ml of water, heated at reflux for 16 h. The solvent was evaporated under vacuum and the residue dissolved in ice water. **8a** was obtained as a white precipitate by adding conc. HCl, and further purified by recrystallization from ethanol. Yield: 44.68 g (94%), m.p. 140–141°C.

2.2.1.2. *4-(6-Acryloyloxyhexyloxy)benzoic acid* ***9a***. 23.84 g (0.10 mol) of 4-(6-hydroxyhexyloxy)benzoic acid **8a**, 13.0 ml (0.11 mol) of *N*,*N*′-dimethylaniline and 0.30 g of 2,6-di-*tert*-butyl-*p*-cresol (DBPC) in 150 ml of dry 1,4-dioxan were heated to 60°C. At 60°C 9.8 ml (0.12 mol) of acryloyl chloride were added dropwise, so that the temperature did not exceed 65°C. For completion of reaction the mixture was stirred for 2 h at 60°C. After cooling, the clear solution was poured into ice water, giving a white precipitate. This was filtered off, washed with water, recrystallized twice from 2-propanol and dried at room temperature under vacuum. 26.89 g (92%) of **9a** were obtained as a white solid. Thermal behaviour: Cr 85 N 110 I.



	R_1	R_2	R_3
a	H	H	H
b	H	OCH_3	H
c	H	CH_3	H
d	CH_3	CH_3	H
e	H	H	CH_3

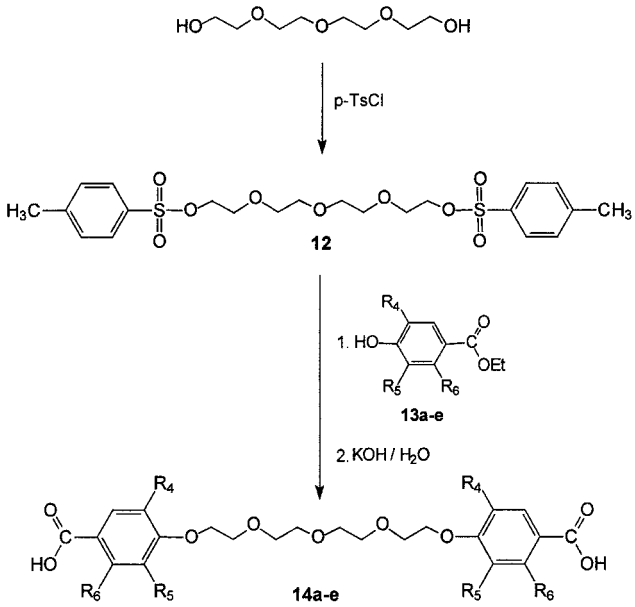
Scheme 1. Synthetic pathway to the mesogenic unit.

2.2.1.3. *4-(2-Tetrahydropyranyloxy)phenol* ***10***. Compound **10** was synthesized according to [13].

2.2.1.4. *4-[4-(6-Acryloyloxyhexyloxy)benzoyloxy]phenol* ***11a***. 2.92 g (10 mmol) of 4-(6-acryloyloxyhexyloxy)-benzoic acid **9a** and 2.8 ml (20 mmol) of triethylamine were dissolved in 40 ml of 1,2-dimethoxyethane and cooled to − 30°C. At − 30°C 0.78 ml (10 mmol) of mesyl chloride were added dropwise so that the temperature did not exceed − 25°C. After stirring for 1 h, 1.94 g (10 mmol) of 4-(2-tetrahydropyranyloxy)phenol **10**, 0.12 g (1 mmol) of 4-dimethylaminopyridine (4-DMAP) and 0.05 g of DBPC were added and the whole mixture stirred for another 3 h at 5°C. The precipitate was filtered off, washed twice with 1,2-dimethoxyethane and the filtrate evaporated. The resulting oil was dissolved in 150 ml of ethanol and after adding 0.25 g (1 mmol) of pyridinium *p*-toluenesulphonate (PPTS) and 0.05 g of DBPC stirred for 3 h at 60°C giving a clear solution. The solvent was evaporated under vacuum and the residue reprecipitated from 10 ml of tetrahydrofuran (THF) into ice water. 3.68 g (96%) of **11a** were obtained as a white powder, m.p. 83–89°C.

A different synthetic route to **11a**, with *N,N′*-dicyclohexylcarbodiimide (DCC) as activating agent, is described in [47].

2.2.1.5. *Tetraethylene glycol-1,13-ditosylate* ***12*** [48]. 19.42 g (0.10 mol) of tetraethylene glycol were dissolved in 50 ml of dry pyridine. At 0°C, 41.94 g (0.22 mol) of *p*-tosyl chloride were added in small portions to the solution so that a temperature of 10°C was not exceeded. After stirring for 1 h the mixture was stored in a refrigerator overnight. Then 100 ml of water were added



	R_4	R_5	R_6
a	H	H	H
b	H	OCH_3	H
c	H	CH_3	H
d	CH_3	CH_3	H
e	H	H	CH_3

Scheme 2. Synthetic pathway to the middle spacer.

and the suspension was three times extracted with 60 ml of chloroform. The combined organic layers were washed three times with 60 ml of 2M HCl, with 60 ml of 2M Na_2CO_3 and with 60 ml of water and then dried over Na_2SO_4. Evaporation of the solvent yielded **12** (46.47 g, 93%) as a yellow oil, which was used without further purification.

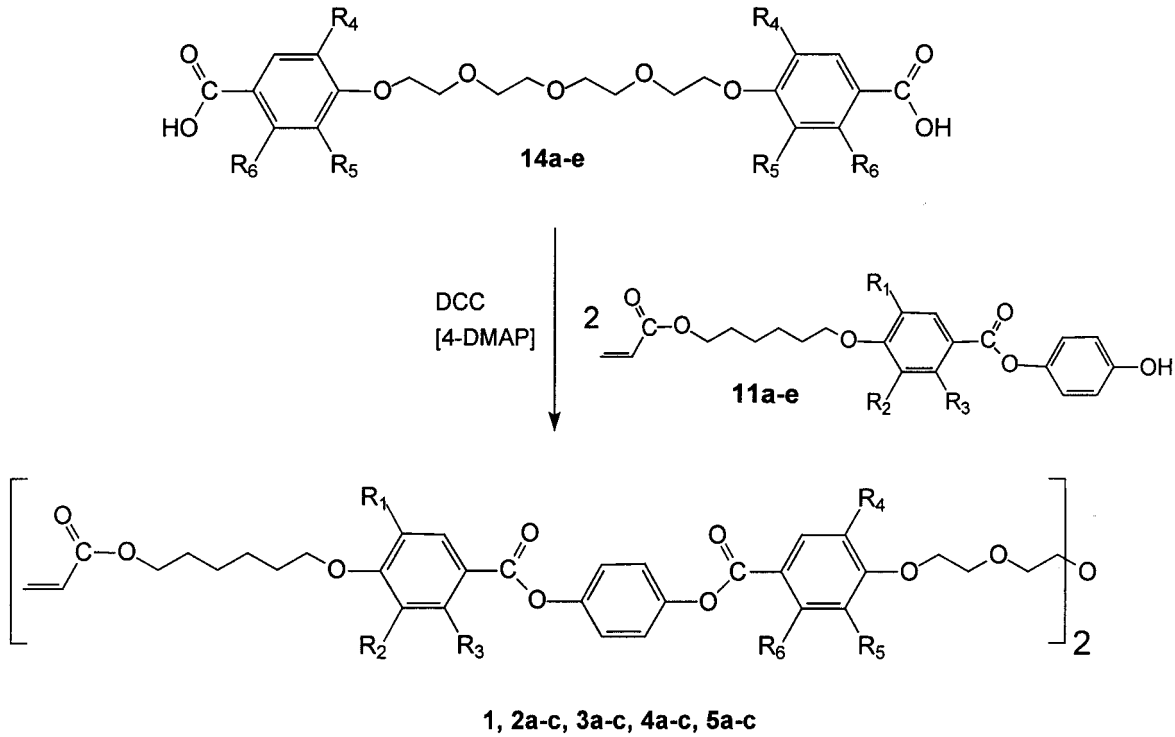
2.2.1.6. *Tetraethylene glycol-1,13-bis(4-benzoic acid)* ***14a***. 18.28 g (0.11 mol) of ethyl 4-hydroxybenzoate were dissolved in 300 ml of 2-butanone and saturated during 10 min with argon. After adding 55.28 g (0.40 mol) of K_2CO_3 and 3.00 g of KI the mixture was stirred vigorously for 2 h under reflux (T = 90°C). Then 25.13 g (0.05 mol) of tetraethylene glycol-1,13-ditosylate **12** in 30 ml of 2-butanone were added dropwise over a period of 30 min and the whole mixture heated at reflux for 16 h. The excess of K_2CO_3 was filtered off from the hot solution and washed twice with 2-butanone. After evaporation of the solvent, the resulting oil was dissolved in 300 ml of methanol, 22.44 g (0.40 mol) of KOH in 30 ml of water were added, and the mixture was heated at reflux for 16 h (T = 90°C). The solvent was evaporated again, the residue dissolved in ice water and acidified with conc. HCl. The precipitate was filtered off, washed with water and and recrystallized from ethanol to yield 18.78 g (86%) of **14a** as a white powder, m.p. 183–186°C.

2.2.1.7. *Monomer* ***1***. 1.30 g (3 mmol) of the bisbenzoic acid **14a** and 1.7 ml (12 mmol) of triethylamine in 100 ml of 1,2-dimethoxyethane were cooled to − 30°C. At − 30°C, 0.47 ml (6 mmol) of mesyl chloride were added dropwise and the mixture was stirred for 1 h. After adding 2.54 g (6.6 mmol) of the mesogen **11a**, 0.081 g (0.66 mmol) of 4-DMAP and 0.05 g of DBPC the mixture was stirred for another 3 h at 5°C. The precipitate was filtered off and washed twice with solvent. The filtrate was evaporated under vacuum and the residue purified by column chromatography (eluent: chloroform/ethyl acetate 1:2). 1.79 g (51%) of **1** were obtained as a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.50 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.75 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.85 (m, 4H, alkoxy−C$\underline{H}_2$−), 3.70 (m, 8H, −O−C$\underline{H}_2$−), 3.90 (t, 4H, ar−OCH_2C$\underline{H}_2$−O−), 4.05 (t, 4H, ar−O−C$\underline{H}_2$CH_2−), 4.20 20 (t, 4H, −COO−C$\underline{H}_2$−), 4.25 (t, 4H, ar−OC$\underline{H}_2$CH_2−O−), 5.85 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.15 (dd, 2H, −C$\underline{H}$=CH_2), 6.40 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.95 (d, 4H, arom.), 7.00 (d, 4H, arom.), 7.25 (s, 8H, arom.), 8.15 (d, 8H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 25.6, 28.4, 28.9 (−$\underline{C}$H$_2$−); 64.4 (−COO−$\underline{C}$H$_2$−); 67.6, 68.0 (ar−O−$\underline{C}$H$_2$−); 70.6, 70.8 (−O−$\underline{C}$H$_2$−); 114.2, 114.4, 121.4, 121.7, 122.5 (arom.); 128.5 (−$\underline{C}$H=CH$_2$); 130.5 (−CH=$\underline{C}$H$_2$); 132.2, 148.3, 163.1, 163.4 (arom.); 164.6, 164.7 (ar−$\underline{C}$OO−); 166.2 (−$\underline{C}$OO−).

2.2.2. *Preparation of the methoxy-substituted twin molecules* ***2a–c***

2.2.2.1. *4-(6-Hydroxyhexyloxy)-3-methoxybenzoic acid* ***8b***. 33.63 g (0.2 mol) of vanillic acid **7b** were dissolved in 500 ml of cyclohexanone. After adding 67 ml (0.5 mol) of 6-chlorohexanol, 82.93 g (0.6 mol) of K_2CO_3 and 5.00 g of KI the mixture was heated at reflux under vigorous stirring at 160°C for 16 h. The excess of K_2CO_3 was hot filtered and washed twice with cyclohexanone. The solvent was evaporated and the resulting oil dissolved in 300 ml of methanol. 44.8 g of KOH in 50 ml of water were added and the mixture was again stirred at 90°C for 3 h. After evaporation of the solvent, 300 ml of a 0.4M aqueous NaOH were added. The water phase was washed three times with diethyl ether and acidified with conc. HCl with cooling. The precipitate was filtered off, washed with water and recrystallized from 2-propanol. Yield: 48.3 g (90%) of a yellowish powder, m.p. 129–130°C.



Scheme 3. Synthetic pathway to the twin molecule (for R_1–R_6 see figure 2).

2.2.2.2. *4-(6-Acryloyl oxyhexylox y)-3-methoxybenz oic acid* ***9b***. Compound **9b** was synthesized in the same way as that described for **9a**, starting from 20.12 g (0.075 mol) of 4-(6-hydroxyhexyloxy)-3-methoxybenzoi c acid **8b**, 11.4 ml (0.09 mol) of *N*,*N*′-dimethylaniline, 0.20 g of 2,6-di-*tert*-butyl-*p*-cresol, 150 ml of dry 1,4-dioxan and 8.0 ml (0.098 mol) of acryloyl chloride. Purification was by recrystallizatio n from 2-propanol. Yield: 18.08 g (75%) of **9b** as a white solid, m.p. 117–118°C.

2.2.2.3. *4-[4-(6-Acryloylo xyhexylox y)-3-methoxybenzoyl - oxy]phenol* ***11b***. Compound **11b** was synthesized in the same way as **11a**, starting from 4-(6-acryloyloxyh exyloxy)-3-methoxybenzoic acid **9b**. Yield: 84% as a white solid, m.p. 100–102°C.

2.2.2.4. *Tetraethylene glycol-1,13-bis[4-(3-methoxy)-benzoic acid)* ***14b***. 1.15 g (0.048 mol) of sodium hydride were suspended in 60 ml of dimethylformamide (DMF). At 0°C, 8.63 g (0.044 mol) of ethyl vanillate in 20 ml of DMF were added carefully to the suspension. After stirring for 1 h, 10.02 g (0.02 mol) of tetraethylene glycol-1,13-ditosylate **12** in 20 ml of DMF were added and the whole suspension was stirred for 16 h at 60°C. Then the solvent was evaporated at 100°C under vacuum, together with 30 ml of xylene. The residue was extracted in a soxhlet with chloroform for 4 h. The solvent was again evaporated and the resulting oil heated at reflux in a mixture of 150 ml of methanol and 8.98 g (0.16 mol) of KOH in 20 ml of water for 16 h. After removing the solvent, the residue was dissolved in ice water and acidified with conc. HCl. The white precipitate of **14b** was further purified by recrystallization from ethanol. Yield: 3.00 g (30%), m.p. 164–166°C.

2.2.2.5. *Monomer* ***2a***. 0.87 g (2 mmol) of the bisbenzoic acid **14a**, 1.66 g (4 mmol) of the mesogen **11b**, 0.059 g (0.48 mmol) of 4-DMAP and 0.05 g of DBPC were dissolved in 50 ml of dry methylene chloride. At 0°C, 0.99 g (4.8 mmol) of DCC were added and the whole suspension was stirred for 30 min. The mixture was allowed to warm to room temperature and stirred for another 16 h. The precipitate of dicyclohexyl urea was filtered off and washed with solvent; the filtrate was reduced in volume. After adding 50 ml of methylene chloride more dicyclohexyl urea precipitates, and this was also filtered off. The filtrate was then washed twice with 30 ml of 2M HCl and 30 ml of saturated aqueous NaCl, dried over Na_2SO_4 and evaporated under vacuum. Further purification by column chromatograph y (eluent: chloroform/ethyl acetate 1 : 2) and recrystallization from 2-butanol yielded 1.13 g (46%) of monomer **2a** as a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.50 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.72 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.90 (m, 4H, alkoxy−C$\underline{H}_2$−), 3.72 and 3.73 (m, 8H, −O−C$\underline{H}_2$−), 3.89

(t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 3.93 (s, 6H, ar−OC$\underline{H}_3$), 4.10 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.17 (m, 8H, −COO−C$\underline{H}_2$−, ar−OC$\underline{H}_2$CH$_2$−O−), 5.81 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.12 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.39 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.92 (d, 2H, arom.), 6.98 (d, 4H, arom.), 7.24 (s, 8H, arom.), 7.66 (s, 2H, arom.), 7.82 (dd, 2H, arom.), 7.13 (d, 4H, arom.). ^{13}C NMR (CDCl$_3$): δ (ppm) = 25.55, 25.64, 28.43, 28.79 (−$\underline{C}$H$_2$−); 56.04 (ar−O$\underline{C}$H$_3$); 64.37 (−COO−$\underline{C}$H$_2$−); 67.61, 68.76 (ar−O−$\underline{C}$H$_2$CH$_2$−); 69.45, 70.61, 70.82 (−O−$\underline{C}$H$_2$−); 111.42, 112.64, 114.36, 121.44, 121.72, 122.56, 124.30 (arom.); 128.48 (−$\underline{C}$H=CH$_2$); 130.45 (−CH=$\underline{C}$H$_2$); 132.16, 148.32, 148.95, 153.12, 163.10 (arom.); 164.63, 164.76 (ar−$\underline{C}$OO−); 166.17 (−$\underline{C}$OO−).

2.2.2.6. *Monomer* ***2b***. Monomer **2b** was synthesized similarly to monomer **2a**, starting from mesogen **11a** and bisbenzoic acid **14b**. Purification was by column chromatography (eluent: chloroform/ethyl acetate 1:3) and recrystallization from 2-butanol. Yield: 53% as a white solid.

^{1}H NMR (CDCl$_3$): δ (ppm) = 1.52 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.75 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.87 (m, 4H, alkoxy−C$\underline{H}_2$−), 3.70 and 3.72 (m, 8H, −O−C$\underline{H}_2$−), 4.00 (m, 6H, ar−OC$\underline{H}_3$; 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 4.05 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.18 (t, 4H, −COO−C$\underline{H}_2$−), 4.25 (t, 4H, ar−OC$\underline{H}_2$CH$_2$−O−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.12 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.95 (d, 2H, arom.), 6.98 (d, 2H, arom.), 7.24 (s, 8H, arom.), 7.66 (d, 2H, arom.), 7.82 (dd, 2H, arom.), 8.13 (d, 2H, arom.). ^{13}C NMR (CDCl$_3$): δ (ppm) = 25.58, 25.61, 28.44, 28.87 (−$\underline{C}$H$_2$−); 55.96 (ar−O$\underline{C}$H$_3$); 64.33 (−COO−$\underline{C}$H$_2$−); 67.97, 68.36 (ar−O−$\underline{C}$H$_2$−); 69.34, 70.57, 70.82 (−O−$\underline{C}$H$_2$−); 111.97, 112.71, 114.19, 121.35, 121.86, 122.51, 124.17 (arom.); 128.45 (−$\underline{C}$H=CH$_2$); 130.44 (−CH=$\underline{C}$H$_2$); 132.18, 148.26, 149.03, 152.90, 163.37 (arom.); 164.65, 164.67 (ar−$\underline{C}$OO−); 166.16 (−$\underline{C}$OO−).

2.2.2.7. *Monomer* ***2c***. Monomer **2c** was synthesized similarly to monomer **2a**, starting from mesogen **11b** and bisbenzoic acid **14b**. Purification was by column chromatography (eluent: chloroform/ethyl acetate 1:2) and recrystallization from 2-butanol. Yield: 57% as a white solid.

^{1}H NMR (CDCl$_3$): δ (ppm) = 1.52 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.72 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.90 (m, 4H, alkoxy−C$\underline{H}_2$−), 3.70 and 3.75 (m, 8H, −O−C$\underline{H}_2$−), 3.83–4.00 (m, 4H, ar−OCH$_2$C$\underline{H}_2$−O−; 12H, ar−OC$\underline{H}_3$), 4.12 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.19 (t, 4H, −COO−C$\underline{H}_2$−), 4.30 (t, 4H, ar−OC$\underline{H}_2$CH$_2$−O−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.12 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.95 (d, 2H, arom.), 7.00 (d, 2H, arom.), 7.25 (s, 8H, arom.), 7.56 (d, 4H, arom.), 7.82 (dd, 4H, arom.). ^{13}C NMR (CDCl$_3$): δ (ppm) = 25.36, 25.47, 28.24, 28.61 (−$\underline{C}$H$_2$−); 55.76, 55.82 (ar−O$\underline{C}$H$_3$); 64.16 (−COO−$\underline{C}$H$_2$−); 68.20, 68.56 (ar−O−$\underline{C}$H$_2$−); 69.16, 70.39, 70.64 (−O−$\underline{C}$H$_2$−); 111.26, 111.79, 112.44, 112.53, 121.21, 121.64, 122.40, 124.00, 124.10 (arom.); 128.96 (−$\underline{C}$H=CH$_2$); 130.27 (−CH=$\underline{C}$H$_2$); 148.14, 148.68, 152.77, 152.96, 164.47 (arom.); 164.52 (ar−$\underline{C}$OO−); 165.94 (−$\underline{C}$OO−).

2.2.3. *Preparation of the methyl-substituted twin molecules* ***3a–c***

2.2.3.1. *4-(6-Hydroxyhexyloxy)-3-methylbenzoic acid* ***8c***. Compound **8c** was synthesized in the same way as that described for **8b**, starting from 4-hydroxy-3-methylbenzoic acid **7c**. Purification was by recrystallization from methanol. Yield: 82% of a white powder, m.p. 105–108°C.

2.2.3.2. *4-(6-Acryloyloxyhexyloxy)-3-methylbenzoic acid* ***9c***. Compound **9c** was synthesized in the same way as that described for **9b**. Purification was by recrystallization from a 1:1 mixture of water and methanol. Yield: 92% of a white powder, m.p. 83–87°C.

2.2.3.3. *4-[4-(6-Acryloyloxyhexyloxy)-3-methylbenzoyloxy]phenol* ***11c***. 4.60 g (15 mmol) of 4-(6-acryloyloxyhexyloxy)-3-methylbenzoic acid **9c**, 3.11 g (15 mmol) of 4-(2-tetrahydropyranyloxy)phenol **10**, 0.20 g (1.6 mmol) of 4-DMAP and 0.10 g of DBPC were dissolved in 60 ml of methylene chloride. At 0°C 3.71 g (18 mmol) of DCC were added and the mixture was stirred for 30 min, whereon a precipitate was formed. The mixture was allowed to warm to room temperature and stirred for another 16 h. The precipitate was filtered off and washed twice with solvent. The filtrate was reduced in volume under vacuum and poured over a 1 cm layer of silica. After evaporation of the solvent, the oil was dissolved in 100 ml of ethanol, 0.28 g (1.1 mmol) of PPTS and 0.10 g of DBPC were added and the whole mixture was stirred for 3 h at 60°C. When the reaction was complete (thin layer chromatography) the solvent was evaporated, the oil was dissolved in 10 ml of THF and the product precipitated into ice water. The yield was 4.48 g (100%) of a white solid, m.p. 70–71°C (1st heating; the sample forms a glass upon cooling).

2.2.3.4. *Ethyl 4-hydroxy-3-methylbenzoate* ***13c***. Compound **13c** was synthesized according to [45]. Yield: 67% as a white solid, m.p. 98–99°C.

2.2.3.5. *Tetraethylene glycol-1,13-bis[4-(3-methyl)benzoic acid]* ***14c***. Bisbenzoic acid **14c** was synthesized in the same way as **14a**. Purification was by recrystallization from a mixture of ethanol/water 2:1. Yield: 68% of a light beige powder, m.p. 156–161°C.

2.2.3.6. *Monomer **3a***. Monomer **3a** was synthesized similarly to **2a**, starting from mesogen **11c** and the bisbenzoic acid **14a**. Purification was by recrystallization from 2-butanol, column chromatography (eluent: chloroform/ethyl acetate 4:1) and reprecipitation from chloroform into hexane at −30°C. Yield: 53% of a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.48 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.71 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.87 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.28 (s, 6H, ar−C$\underline{H}_3$), 3.73 and 3.74 (m, 8H, −O−C$\underline{H}_2$−), 3.90 (t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 4.06 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.19 (m, 4H, −COO−C$\underline{H}_2$−), 4.22 (m, 4H, ar−OC$\underline{H}_2$CH$_2$−O−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.12 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.87 (d, 2H, arom.), 7.00 (d, 2H, arom.), 7.25 (s, 8H, arom.), 7.98 (s, 2H, arom.), 8.02 (d, 2H, arom.), 8.14 (d, 4H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 16.08 (ar−$\underline{C}$H$_3$); 25.58, 25.64, 28.42, 28.88 (−$\underline{C}$H$_2$−); 64.30 (−COO−$\underline{C}$H$_2$−); 67.55, 67.86 (ar−O−$\underline{C}$H$_2$−); 69.38, 70.53, 70.55 (−O−$\underline{C}$H$_2$−); 109.99, 114.30, 120.66, 121.67, 122.45, 126.83 (arom.); 128.41 (−$\underline{C}$H=CH$_2$); 129.96 (arom.); 130.41 (−CH=$\underline{C}$H$_2$); 132.12, 148.17, 148.33, 161.49, 163.03 (arom.); 164.56, 164.86 (ar−$\underline{C}$OO−); 166.12 (−$\underline{C}$OO−).

2.2.3.7. *Monomer **3b***. Monomer **3b** was synthesized in a similar way to **2a**, starting from mesogen **11a** and the bisbenzoic acid **14c**. Purification was by recrystallization from 2-butanol, column chromatography (eluent: chloroform/ethyl acetate 4:1) and reprecipitation from chloroform into hexane at −30°C. Yield: 60% of **3b** as a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.51 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.70 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.82 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.29 (s, 6H, ar−C$\underline{H}_3$), 3.65 −3.80 (m, 8H, −O−C$\underline{H}_2$−), 3.92 (t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 4.05 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.15–4.30 (m, 8H, −COO−C$\underline{H}_2$−, ar−OC$\underline{H}_2$CH$_2$−O−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.13 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.42 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.89 (d, 2H, arom.), 6.97 (d, 4H, arom.), 7.25 (s, 8H, arom.), 7.98 (s, 2H, arom.), 8.02 (dd, 2H, arom.), 8.14 (d, 4H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 16.21 (ar−$\underline{C}$H$_3$); 25.62, 25.65, 28.47, 28.91 (−$\underline{C}$H$_2$−); 64.38 (−COO−$\underline{C}$H$_2$−); 67.83, 68.01 (ar−O−$\underline{C}$H$_2$−); 69.58, 70.69, 70.97 (−O−$\underline{C}$H$_2$−); 110.30, 114.22, 121.18, 122.55, 127.04 (arom.); 128.49 (−$\underline{C}$H=CH$_2$); 129.99 (arom.); 130.47 (−CH=$\underline{C}$H$_2$); 132.54, 148.30, 148.36, 161.32, 163.40 (arom.); 164.72, 164.90 (ar−$\underline{C}$OO−); 166.22 (−$\underline{C}$OO−).

2.2.3.8. *Monomer **3c***. Monomer **3c** was synthesized in a similar way to **2a**, starting from mesogen **11c** and the bisbenzoic acid **14c**. Purification was by recrystallization from 2-butanol, column chromatography (eluent: chloroform/ethyl acetate 4:1) and reprecipitation from chloroform into hexane at −30°C. Yield: 57% of a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.53 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.74 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.87 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.27 (s, 3H, ar−C$\underline{H}_3$), 2.29 (s, 3H, ar−C$\underline{H}_3$), 3.65–3.85 (m, 8H, −O−C$\underline{H}_2$−), 3.92 (t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 4.06 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.15–4.30 (m, 8H, −COO−C$\underline{H}_2$−, ar−OC$\underline{H}_2$CH$_2$−O−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.12 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.86 (d, 2H, arom.), 6.90 (d, 2H, arom.), 7.24 (s, 8H, arom.), 7.98 (s, 4H, arom.), 8.02 (dd, 4H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 16.08 (ar−$\underline{C}$H$_3$); 25.63, 25.81, 28.42, 28.87 (−$\underline{C}$H$_2$−); 64.29 (−COO−$\underline{C}$H$_2$−); 67.75, 67.84 (ar−O−$\underline{C}$H$_2$−); 69.48, 70.60, 70.87 (−O−$\underline{C}$H$_2$−); 109.99, 110.24, 120.67, 122.46, 126.82, 126.95 (arom.); 128.40 (−$\underline{C}$H=CH$_2$); 129.89, 129.95 (arom.); 130.37 (−CH=$\underline{C}$H$_2$); 132.34, 132.43, 148.23, 161.24, 161.46 (arom.); 164.76, 164.82 (ar−$\underline{C}$OO−); 166.10 (−$\underline{C}$OO−).

2.2.4. *Preparation of the 3,5-dimethyl-substituted twin molecules **4a–c***

2.2.4.1. *3,5-Dimethyl-4-(6-hydroxyhexyloxy)benzoic acid **8d***. Compound **8d** was synthesized in the same way as that described for **8b**, starting from 3,5-dimethyl-4-hydroxybenzoic acid **7d**. Yield: 95% of a white powder, m.p. 122–125°C.

2.2.4.2. *3,5-Dimethyl-4-(6-acryloyloxyhexyloxy)benzoic acid **9d***. Compound **9d** was synthesized as described for **9b**. Purification was by reprecipitation from THF into ice water. Yield: 94% of a white powder, m.p. 67–71°C.

2.2.4.3. *4-[4-(6-Acryloyloxyhexyloxy)-3,5-dimethylbenzoyloxy]phenol **11d***. Compound **11d** was synthesized in the same way as that described for **11c**. Purification was by reprecipitation from THF into ice water, whereby **11d** was obtained as an oil. Crystallization starts after approximately 1 week in a refrigerator. Yield: 49% of a white powder, m.p. 65–66°C (1st heating, the sample forms a glass upon cooling).

2.2.4.4. *Ethyl 3,5-dimethyl-4-hydroxybenzoate **13d***. Compound **13d** was synthesized according to [45]. Purification was by recrystallization from water. Yield: 95% of a white solid, m.p. 110–113°C.

2.2.4.5. *Tetraethylene glycol-1,13-bis[4-(3,5-dimethyl)-benzoic acid] **14d***. Bisbenzoic acid **14d** was synthesized in the same way as **14a**. Purification was by column chromatography (eluent: ethyl acetate). Yield: 32% as a white powder, m.p. 123–127°C (1st heating; **14d** forms a glass upon cooling).

2.2.4.6. *Monomer **4a***. Monomer **4a** was synthesized similarly to monomer **2a**, starting from mesogen **11d** and the bisbenzoic acid **14a**. Purification was by recrystallization from 2-butanol, column chromatography (eluent: chloroform/ethyl acetate 4:1) and reprecipitation from chloroform into hexane at − 25°C. Yield: 51% of **4a** as a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.52 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.75 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.86 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.34 (s, 6H, ar−C$\underline{H}_3$), 3.73 and 3.74 (m, 8H, −O−C$\underline{H}_2$−), 3.83 (t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 3.91 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.20 (t, 4H, −COO−C$\underline{H}_2$−), 4.22 (t, 4H, ar−OC$\underline{H}_2$CH$_2$−O−), 5.83 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.13 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.42 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 7.00 (d, 4H, arom.), 7.25 (s, 8H, arom.), 7.87 (s, 4H, arom.), 8.14 (d, 4H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 16.32 (ar−$\underline{C}$H$_3$); 25.69, 25.80, 28.51, 30.19 (−$\underline{C}$H$_2$−); 64.40 (−COO−$\underline{C}$H$_2$−); 67.61, 69.45 (ar−O−$\underline{C}$H$_2$−); 70.60, 70.83, 72.12 (−O−$\underline{C}$H$_2$−); 114.36, 121.73, 122.52, 122.56, 124.29 (arom.); 128.49 (−$\underline{C}$H=CH$_2$); 130.46 (−CH=$\underline{C}$H$_2$); 130.99, 131.33, 132.18, 148.31, 160.74, 163.09 (arom.); 164.61, 164.85 (ar−$\underline{C}$OO−); 166.10 (−$\underline{C}$OO−).

2.2.4.7. *Monomer **4b***. Monomer **4b** was synthesized in a similar manner to monomer **2a**, starting from mesogen **11a** and the bisbenzoic acid **14d**. Purification was by recrystallization from 2-butanol, column chromatography (eluent: chloroform/ethyl acetate 8:1) and reprecipitation from chloroform into hexane at − 25°C. Yield: 52% of **4b** as a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.51 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.73 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.85 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.37 (s, 6H, ar−C$\underline{H}_3$), 3.76 (m, 8H, −O−C$\underline{H}_2$−), 3.86 (t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 4.03 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.05 (t, 4H, −COO−C$\underline{H}_2$−), 4.19 (t, 4H, ar−OC$\underline{H}_2$CH$_2$−O−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.13 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.97 (d, 4H, arom.), 7.25 (s, 8H, arom.), 7.87 (s, 4H, arom.), 8.14 (d, 4H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 16.30 (ar−$\underline{C}$H$_3$); 25.58, 25.61, 28.43, 28.87 (−$\underline{C}$H$_2$−); 64.34 (−COO−$\underline{C}$H$_2$−); 67.98, 70.36 (ar−O−$\underline{C}$H$_2$−); 70.68, 70.81, 71.51 (−O−$\underline{C}$H$_2$−); 114.19, 121.35, 122.49, 122.56, 124.46 (arom.); 128.46 (−$\underline{C}$H=CH$_2$); 130.45 (−CH=$\underline{C}$H$_2$); 130.98, 131.34, 132.19, 148.25, 160.46, 163.38 (arom.); 164.38, 164.81 (ar−$\underline{C}$OO−); 166.17 (−$\underline{C}$OO−).

2.2.4.8. *Monomer **4c***. Monomer **4c** was synthesized as for monomer **2a**, starting from mesogen **11d** and the bisbenzoic acid **14d**. Purification was by recrystallization from 2-butanol, column chromatography (eluent: chloroform/ethyl acetate 8:1) and reprecipitation from chloroform into hexane at − 25°C. Yield: 64% of **4c** as a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.51 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.72 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.86 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.34 (s, 6H, ar−C$\underline{H}_3$), 2.37 (s, 6H, ar−C$\underline{H}_3$), 3.76 (m, 8H, −O−C$\underline{H}_2$−), 3.79–3.91 (m, 8H, ar−OCH$_2$C$\underline{H}_2$−O−, ar−O−C$\underline{H}_2$CH$_2$−), 4.03 (t, 4H, −COO−C$\underline{H}_2$−), 4.19 (t, 4H, ar−OC$\underline{H}_2$CH$_2$−O−), 5.83 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.13 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 7.24 (s, 8H, arom.), 7.87 (s, 8H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 16.29 (ar−$\underline{C}$H$_3$); 25.66, 25.77, 28.48, 30.16 (−$\underline{C}$H$_2$−); 64.37 (−COO−$\underline{C}$H$_2$−); 70.34, 70.66 (ar−O−$\underline{C}$H$_2$−); 70.80, 71.50, 72.09 (−O−$\underline{C}$H$_2$−); 122.50, 124.25 (arom.); 128.46 (−$\underline{C}$H=CH$_2$); 130.42 (−CH=$\underline{C}$H$_2$); 130.96, 131.33, 148.30, 160.46, 160.73 (arom.); 164.78, 164.81 (ar−$\underline{C}$OO−); 166.16 (−$\underline{C}$OO−).

2.2.5. *Preparation of the methyl-substituted twin molecules **5a–c***

2.2.5.1. *4-(6-Hydroxyhexyloxy)-2-methylbenzoic acid **8e***. Compound **8e** was synthesized in the same way as that described for **8b**, starting from 4-hydroxy-2-methylbenzoic acid **7e**. Purification was by recrystallization from a mixture of water/ethanol 2:1. Yield: 76% of a white powder, m.p. 78–83°C.

2.2.5.2. *4-(6-Acryloyloxyhexyloxy)-2-methylbenzoic acid **9e***. Compound **9e** was synthesized in the same way as that for **9b**. Purification was by reprecipitation from THF into ice water. Yield: 95% of a white powder, m.p. 74–80°C.

2.2.5.3. *4-[4-(6-Acryloyloxyhexyloxy)-2-methylbenzoyloxy]phenol **11e***. Compound **11e** was synthesized in the same way as that described for **11c**. Purification was by reprecipitation from THF into ice water. Yield: 79% of a slightly yellow solid, m.p. 66–70°C (1st heating, the sample forms a glass upon cooling).

2.2.5.4. *Ethyl 4-hydroxy-2-methylbenzoate **13e***. Compound **13e** was synthesized as described in [45]. Yield: 85% of a white solid, m.p. 94–98°C.

2.2.5.5. *Tetraethylene glycol-1,13-bis[4-(2-methyl)benzoic acid) **14e***. Bisbenzoic acid **14e** was synthesized in the same way as that for **14a**. Purification was by recrystallization from a mixture of ethanol/water 4:3. Yield: 75% of a white powder, m.p. 142°C (1st heating, the sample forms a glass upon cooling).

2.2.5.6. *Monomer **5a***. Monomer **5a** was synthesized similarly to **2a**, starting from mesogen **11e** and the bisbenzoic acid **14a**. Purification was by column chromatography (eluent: chloroform/ethyl acetate 3:1) and

reprecipitation from chloroform into hexane at − 30°C. Yield: 50% of a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.50 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.73 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.80 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.66 (s, 6H, ar−C$\underline{H}_3$), 3.74 and 3.75 (m, 8H, −O−C$\underline{H}_2$−), 3.90 (t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 4.03 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.18 (m, 4H, −COO−C$\underline{H}_2$−), 4.21 (m, 4H, ar−OC$\underline{H}_2$CH$_2$−O−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.13 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.75 −6.82 (m, 4H, arom.), 7.00 (d, 4H, arom.), 7.24 (s, 8H, arom.), 8.14 (d, 4H, arom.), 8.16 (d, 4H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 22.46 (ar−$\underline{C}$H$_3$); 25.61, 25.64, 28.46, 28.92 (−$\underline{C}$H$_2$−); 64.38 (−COO−$\underline{C}$H$_2$−); 67.61, 67.81 (ar−O−$\underline{C}$H$_2$−); 69.46, 70.61, 70.82 (−O−$\underline{C}$H$_2$−); 111.51, 114.35, 117.64, 120.17, 121.77, 122.53, 122.70 (arom.); 128.49 (−$\underline{C}$H=CH$_2$); 130.47 (−CH=$\underline{C}$H$_2$); 132.19, 133.59, 144.27, 148.23, 162.42, 163.08 (arom.); 164.65, 165.06 (ar−$\underline{C}$OO−); 166.21 (−$\underline{C}$OO−).

2.2.5.7. *Monomer* ***5b***. Monomer **5b** was synthesized in the same way as monomer **2a**, starting from mesogen **11a** and the bisbenzoic acid **14e**. Purification was by column chromatography (eluent: chloroform/ethyl acetate 5:2) and reprecipitation from chloroform into hexane at − 30°C. Yield: 50% of a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.51 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.73 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.85 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.65 (s, 6H, ar−C$\underline{H}_3$), 3.73 and 3.74 (m, 8H, −O−C$\underline{H}_2$−), 3.87 (t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 4.05 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.15–4.24 (m, 8H, −COO−C$\underline{H}_2$−, ar−OC$\underline{H}_2$CH$_2$−O−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.13 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.79–6.87 (m, 4H, arom.), 6.97 (d, 4H, arom.), 7.24 (s, 8H, arom.), 8.14 (d, 4H, arom.), 8.16 (d, 4H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 22.43 (ar−$\underline{C}$H$_3$); 25.59, 25.62, 28.44, 28.88 (−$\underline{C}$H$_2$−); 64.36 (−COO−$\underline{C}$H$_2$−); 67.41, 67.98 (ar−O−$\underline{C}$H$_2$−); 69.46, 70.79, 70.79 (−O−$\underline{C}$H$_2$−); 111.62, 114.19, 117.75, 120.49, 121.38, 122.53, 122.66 (arom.); 128.45 (−$\underline{C}$H=CH$_2$); 130.48 (−CH=$\underline{C}$H$_2$); 132.20, 133.53, 144.22, 148.23, 162.09, 163.37 (arom.); 164.70, 165.00 (ar−$\underline{C}$OO−); 166.20 (−$\underline{C}$OO−).

2.2.5.8. *Monomer* ***5c***. Monomer **5c** was synthesized similarly to monomer **2a**, starting from mesogen **11e** and the bisbenzoic acid **14e**. Purification was by column chromatography (eluent: chloroform/ethyl acetate 3:1) and reprecipitation from chloroform into hexane at − 30°C. Yield: 50% of a white solid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.52 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.73 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.83 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.66 (s, 12H, ar−C$\underline{H}_3$), 3.73 and 3.74 (m, 8H, −O−C$\underline{H}_2$−), 4.90 (t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 4.03 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.15 −4.28 (m, 8H, −COO−C$\underline{H}_2$−, ar−O−C$\underline{H}_2$CH$_2$−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.13 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.81 (d, 4H, arom.), 6.82 (s, 4H, arom.), 7.23 (s, 8H, arom.), 8.16 (d, 4H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 22.40 (ar−$\underline{C}$H$_3$); 25.55, 25.58, 28.40, 28.87 (−$\underline{C}$H$_2$−); 64.33 (−COO−$\underline{C}$H$_2$−); 67.37, 67.75 (ar−O−$\underline{C}$H$_2$−); 69.41, 70.55, 70.75 (−O−$\underline{C}$H$_2$−); 111.58, 117.59, 120.12, 120.47, 122.64 (arom.); 128.42 (−$\underline{C}$H=CH$_2$); 130.43 (−CH=$\underline{C}$H$_2$); 133.50, 144.16, 148.15, 162.03, 162.36 (arom.); 164.97, 165.00 (ar−$\underline{C}$OO−); 166.16 (−$\underline{C}$OO−).

2.2.6. *Preparation of the methyl-substituted twin molecule* ***6***

2.2.6.1. *Methyl-4-(2-tetrahydropyranyloxy)phenol (1:1 mixture of the 2-methyl- and 3-methyl isomers)*. The methyl-4-(2-tetrahydropyranyloxy)phenols were synthesized as described in [13], starting from 2-methylhydroquinone. A different procedure is outlined in [15]. Yield: 31% of a slightly beige solid, m.p. 38–42°C (1st heating; the sample forms a glass upon cooling).

2.2.6.2. *4-[4-(6-Acryloyloxyhexyloxy)methylbenzoyloxy]-phenols*. The 4-[4-(6-acryloyloxy-hexyloxy)methylbenzoyloxy]phenols were synthesized in the same way as that described for **11c**. Purification was by reprecipitation from THF into ice water. First a brown oil was obtained, starting to crystallize after approximately 1 week. Yield: 58% of a slightly beige solid, m.p. 69–75°C (1st heating; the sample forms a glass upon cooling).

2.2.6.3. *Monomer* ***6***. Monomer **6** was synthesized similarly to monomer **2a**, starting from the 4-[4-(6-acryloyloxy-hexyloxy)methylbenzoyloxy]phenols and the bisbenzoic acid **14a**. Purification was by column chromatography (eluent: chloroform/ethyl acetate 7:1) and reprecipitation from chloroform into hexane at − 30°C. Yield: 60% of a white solid.

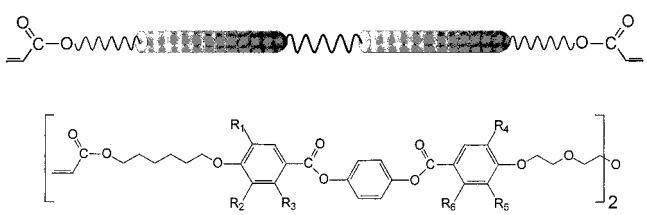
^{1}H NMR ($CDCl_3$): δ (ppm) = 1.51 (m, 8H, alkoxy−C$\underline{H}_2$−), 1.71 (m, 4H, alkoxy−C$\underline{H}_2$−), 1.85 (m, 4H, alkoxy−C$\underline{H}_2$−), 2.24 (s, 3H, ar−C$\underline{H}_3$), 3.74 and 3.75 (m, 8H, −O−C$\underline{H}_2$−), 3.91 (t, 4H, ar−OCH$_2$C$\underline{H}_2$−O−), 4.06 (t, 4H, ar−O−C$\underline{H}_2$CH$_2$−), 4.19 (t, 4H, −COO−C$\underline{H}_2$−), 4.21 (t, 4H, ar−OC$\underline{H}_2$CH$_2$−O−), 5.82 (dd, 2H, −CH=C$\underline{H}_2$ *cis*), 6.13 (dd, 2H, −C$\underline{H}$=CH$_2$), 6.41 (dd, 2H, −CH=C$\underline{H}_2$ *trans*), 6.94 −7.21 (m, 14H, arom.), 8.13 (d, 4H, arom.), 8.17 (d, 4H, arom.). ^{13}C NMR ($CDCl_3$): δ (ppm) = 16.29 (ar−$\underline{C}$H$_3$); 25.51, 28.33, 28.75 (−$\underline{C}$H$_2$−); 64.23 (−COO−$\underline{C}$H$_2$−); 67.51, 67.87 (ar−O−$\underline{C}$H$_2$−); 69.30, 70.48, 70.66 (−O−$\underline{C}$H$_2$−); 114.09, 114.15, 114.24, 114.30, 119.82, 121.15, 121.34, 121.67, 122.67, 123.88 (arom.); 128.37 (−$\underline{C}$H=CH$_2$); 130.34 (arom.); 131.53 (−CH=$\underline{C}$H$_2$); 132.04 146.78, 146.84, 148.17, 162.94, 163.00, 163.25 (arom.); 164.19, 164.25, 164.55, 164.61 (ar−$\underline{C}$OO−); 166.04 (−$\underline{C}$OO−).

3. Results and discussion

3.1. *Synthesis of twin molecules*

The chemical structures of the twin molecules are shown in figure 2. All monomers possess two mesogenic units connected by a flexible tetraethylene glycol spacer. This type of spacer was chosen because it is known that compared with alkyl chains, ethylene oxide spacers are more flexible and this leads to an improved solubility of the monomers [49]. The mesogenic units consist of three phenyl rings linked by ester bonds. Two polymerizable acrylate groups per monomer, which are connected to the mesogens by C6-spacers, guarantee a high network density after photopolymerization.

We have synthesized several series of twin molecules with and without lateral substituents in the mesogenic core. In contrast to twin **1** with no lateral substituent, the monomers of series **2** have methoxy substituents in the 3-position to the ester group. Twin **2a** has its substituent in the outer phenyl ring, twin **2b** in the inner phenyl ring and twin **2c** has two methoxy groups per mesogenic unit. Among the monomers of series **3** the methoxy substituent is replaced by the smaller and less polar methyl group, also in the 3-position to the ester group. Series **4** contains two methyl groups per substituted phenyl ring in the 3- and 5-positions, and series **5** has one methyl group per substituted ring, but in the 2-position to the ester group. The twin molecules **2–5** therefore carry substituents either in the outermost or innermost phenyl rings of the mesogen. Twin molecule **6**, however, has a methyl group in the central hydroquinone ring of each mesogenic unit.



Compound	R_1	R_2	R_3	R_4	R_5	R_6
1	H	H	H	H	H	H
2a	H	OCH_3	H	H	H	H
2b	H	H	H	H	OCH_3	H
2c	H	OCH_3	H	H	OCH_3	H
3a	H	CH_3	H	H	H	H
3b	H	H	H	H	CH_3	H
3c	H	CH_3	H	H	CH_3	H
4a	CH_3	CH_3	H	H	H	H
4b	H	H	H	CH_3	CH_3	H
4c	CH_3	CH_3	H	CH_3	CH_3	H
5a	H	H	CH_3	H	H	H
5b	H	H	H	H	H	CH_3
5c	H	H	CH_3	H	H	CH_3

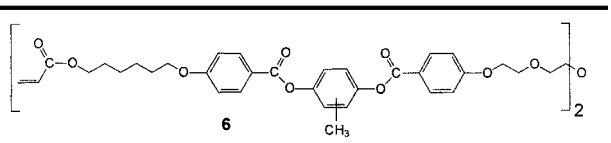


Figure 2. Chemical structure of the novel twin molecules.

The synthesis of the monomers involves three steps, the preparation of the mesogenic unit, the preparation of the middle spacer and the final esterification step in which the twin molecule is obtained. The preparation of the unsubstituted mesogen **11a** has already been reported by Broer *et al.* [9, 13, 47] (scheme 1). The key step in the synthesis of the mesogens **11a–e** is the non-symmetric esterification of the monoprotected hydroquinone **10** with the 4-(6-acryloyloxyhexyloxy)benzoic acids **9a–e**. We used a similar route for the substituted mesogens starting from vanillic acid **7b** for mesogen **11b**, from 3-methylbenzoic acid **7c** for **11c**, from 3,5-dimethylbenzoic acid **7d** for **11d** and from 2-methylbenzoic acid **7e** for **11e**. Vanillic acid is the only commercially available substituted 4-hydroxybenzoic acid. The benzoic acids **7c–e** were synthesized according to [42–46].

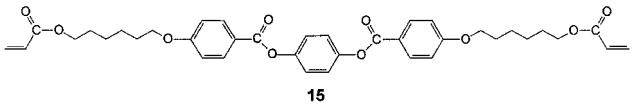
We used a modification of Broer's method [9, 13, 47] for the etherification of the 4-hydroxybenzoic acids **7** with 6-chlorohexanol (K_2CO_3, cyclohexanone) and a modified esterification of the 4-(6-hydroxyhexyloxy)-benzoic acids **8** with acryloyl chloride. The coupling of **9a–e** with the protected hydroquinone **10** was carried out with DCC instead of mesyl chloride as activating agent. All these modifications led to higher yields compared with those given in [9, 13].

The synthesis of the central part of the twin molecules (scheme 2) involves tosylation of tetraethylene glycol and subsequent esterification with the ethyl 4-hydroxybenzoates **13a–e**. In this case we used the ethyl benzoates instead of the benzoic acids to avoid condensation reactions. Because the tosylate is sensitive to heat, 2-butanone was used as solvent instead of cyclohexanone. A subsequent ester cleavage yields the tetraethylene glycol-1,13-bisbenzoic acids **14a–e**.

The last step in the synthesis of the twin molecules is the esterification of the mesogenic units **11a–e** with the middle spacers **14a–e** which was carried out by the DCC-method (scheme 3).

3.2. *Thermal behaviour and crystallization tendency*

The mesophase behaviour and the crystallization tendency of the liquid crystalline twin molecules was investigated by DSC and polarizing optical microscopy. Compared with the classical mesogenic diacrylate **15** (mono-rod, figure 3) synthesized by Broer and Lub [9]



15

Figure 3. Chemical structure of the classical diacrylate for *in situ* photopolymerization [9].

the mesophase range of twin **1** with no substituents in the mesogenic core is about 23°C broader and no monotropic smectic phase is observed upon cooling (table 1).

Because twin **1** shows a mesophase at temperatures higher than 100°C, it is necessary to stabilize the sample for the DSC investigations, since acrylates tend to polymerize thermally. As stabilizer we used small amounts of sulphur, which is an effective radical scavanger and has only a small influence on the transition temperatures [41, 50].

Table 1. Transition temperatures and enthalpies (in brackets) of twin **1** without lateral groups and the mono-rod **15**.

	Phase transition temperatures (°C) and enthalpies (kJ mol^{-1})	
Monomer	2nd heating	2nd cooling
Mono **15**	Cr 107 N 156 I[a] (65.2) (0.7)	I 153 N 85 Sm 73 Cr[a] (− 0.7) (− 0.7) (− 54.8)
Twin **1**	Cr 106 N 178 I[b] (26.0) (1.9)	I 176 N 80 Cr[b] (− 1.1) (− 23.6)

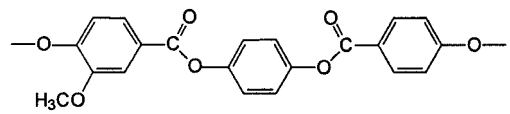
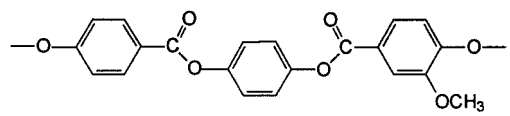
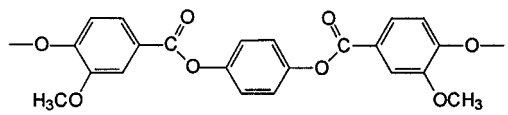
[a] DSC 10 K min^{-1}, 1 wt % sulphur (ref. [9]: Cr 108 (SmC 88) 155 I).
[b] DSC, 10 K min^{-1}, 2 wt % sulphur.

The phase behaviour of twin **1** shows, however, that connecting two mesogen units to give a twin molecule leads to a broad range mesophase, but is not efficient enough to suppress crystallization. For that reason we have varied the structure model of the 'twin molecules'. Structural variations have been made in all parts of the molecule, the middle spacer, the flexible terminal chain and the mesogenic unit and are illustrated in [41]. We found that only the insertion of lateral substituents in the mesogenic core leads to glass-forming materials. In this paper we will discuss this topic in detail.

The influence of the kind of substituent and the substitution pattern on the ability of a compound to vitrify to a LC glass, as well as on the mesophase behaviour of a liquid crystal are difficult to predict, as exemplified in several publications [51, 52]. Only trends can be given [53].

The first substituent we chose for the modification of our twin molecules was the methoxy group. It is known from the literature that methoxy groups decrease the crystallization tendency of aromatic main chain poly(ester)s and poly(ester amide)s and improve their solubility [54, 55]. Figure 2 shows the structure of the three different twin molecules with methoxy substituents in the mesogenic core (**2a–c**) and table 2 gives the corresponding transition temperatures. All compounds show melting peaks in the first heating run because the materials are able to crystallize when they are freeze-dried from a 1,4-dioxan solution. The thermal behaviour of the twin molecules **2a–c** strongly depends on the number and the position of the methoxy groups in the mesogenic unit.

Table 2. Transition temperatures and enthalpies (in brackets) of the twin molecules **2a–c** with methoxy groups in the 3-position to the ester group.

		Phase transition temperatures (°C)[a] and enthalpies (kJ mol^{-1})	
Monomer	Mesogenic unit	2nd heating	2nd cooling
2a		g − 3 N 117 I[b] (2.6) [c](1.2)	I 115 N − 7 g (− 1.5) (− 0.5)[c]
2b		Cr 93 N 126 I (43.4) (1.7)	I 121 N 53 Cr (− 1.6) (− 38.5)
2c		g 8 N 50 I[b] (0.7) (1.2)	I 46 N 0 g (− 1.2) (− 0.6)[c]

[a] DSC 10 K min^{-1}, 1 wt % sulphur.
[b] Glassy state stable at $T < T_g$; slow recrystallization at room temperature.
[c] Δc_p in kJ K^{-1} mol^{-1}.

Compared with twin **1**, the mesophase of twin **2c** with two methoxy groups per mesogen is drastically disturbed by the substituents and crystallization is suppressed. A glassy material with a nematic phase between 8 and 50°C is obtained. Below the T_g the glass is stable for several weeks. At room temperature, however, the compound starts to crystallize slowly. If the mesogenic unit contains only one methoxy group its position is important. Twin **2b** with the methoxy group in the inner phenyl ring melts at 93°C and shows a nematic phase up to 126°C. As expected the mesophase range of **2b** is smaller than that of the unsubstituted twin **1**. Upon cooling, **2b** can be supercooled strongly, but recrystallizes at 53°C. With the methoxy group in the outer phenyl ring (**2a**), a completely different behaviour is observed. The first heating run on DSC shows multiple melting peaks between 76°C and 88°C for **2a** and a nematic phase up to 117°C. In the following cooling run an exothermic peak at 115°C and a glass transition at − 7°C are observed (figure 4).

The small peak at 88°C in the second DSC heating run has a transition enthalpy of 1.57 kJ mol^{-1} which is in the range of a mesophase transition, but investigations by polarizing microscopy did not give any support for this. Therefore we did a DSC annealing experiment. Twin **2a** was stored for 1 h at 70°C and cooled down rapidly to − 30°C. In the next heating run, the T_g at − 3°C disappeared and a new melting point appeared at 88°C (figure 5).

To summarize the results, it was shown with the monomers **2a** and **2c** that twin molecules exhibit broad mesophase ranges and tend to vitrify upon cooling if lateral substituents are introduced in the mesogenic core. Below the T_g, the twin molecules form stable LC glasses. Annealing within the nematic phase at room temperature, however, leads to a slow, kinetically hindered crystallization.

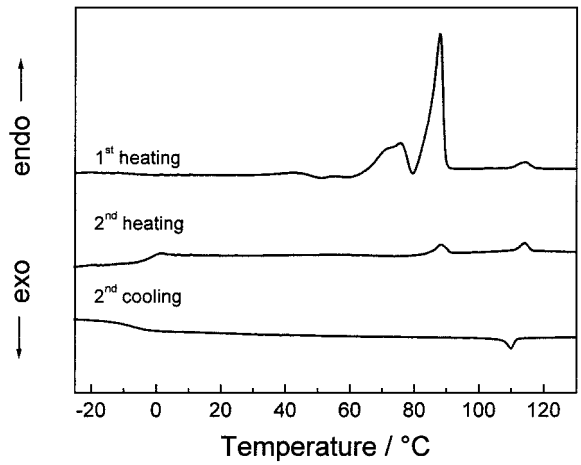


Figure 4. DSC experiment with twin **2a** (heating and cooling rate 10 K min^{-1}).

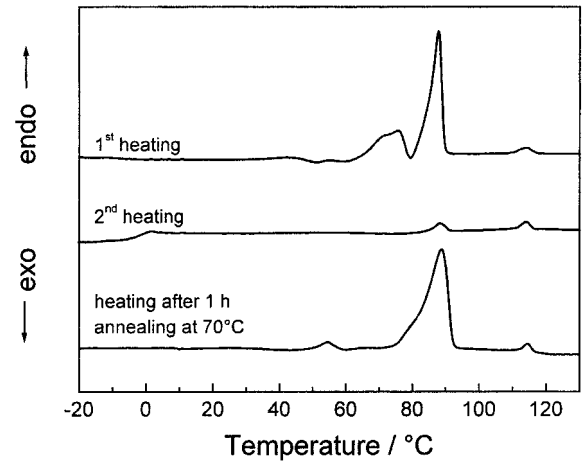


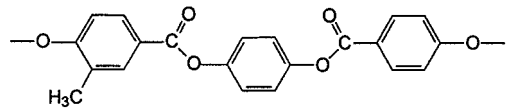
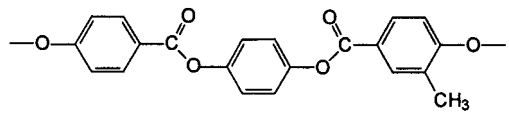
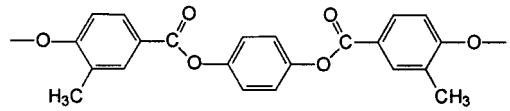
Figure 5. DSC annealing experiment with twin **2a** (heating rate 10 K min^{-1}).

To obtain more information about glass formation and mesophase behaviour in laterally substituted twin molecules we synthesized another series in which the methoxy groups are replaced by smaller and less polar methyl groups also in the 3-position to the ester group. Table 3 shows the transition temperatures of the three monomers **3a–c**.

In contrast to the monomers of the methoxy substituted series **2**, all compounds of series **3** crystallize. The melting points are in the same range as for the unsubstituted twin **1**, but the clearing points are lower due to the disturbance of the mesophase by the lateral groups. Glass formation is not observed in all three cases, independent of the substitution pattern. Only twin **3b** with the methyl group in the inner phenyl ring and twin **3c** with two methyl groups can be supercooled.

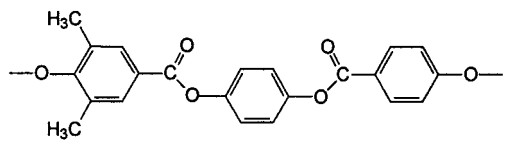
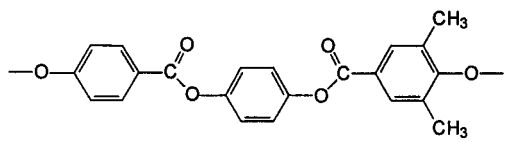
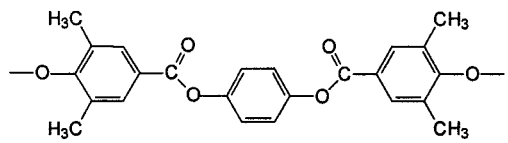
The second series with methyl substituents (monomers **4a–c**) contains two methyl groups per 4-hydroxybenzoic acid unit in the 3- and 5-positions to the ester group. Therefore, two or four lateral groups are in the mesogenic unit depending on the substitution pattern. Table 4 shows the structure and the mesophase behaviour of the twin molecules **4a–c**. The data from table 4 make it evident that the crystallization tendency cannot be predicted. From the results for the 3-methoxy (**2**) and the 3-methyl series (**3**), it might be expected that the insertion of a second methyl group would prevent crystallization and lead to glassy materials. In fact only twin **4b** with two methyl groups in the inner phenyl ring vitrifies and forms a LC glass. In the DSC experiment, two melting points at 68 and 76°C, as well as a nematic–isotropic transition at 97°C are observed during the first heating run. Upon cooling, the nematic phase remains and is frozen into a glass at − 18°C. The second heating shows the glass transition again, but the compound starts to recrystallize at 41°C. Compared with twin **3a** with only

Table 3. Transition temperatures and enthalpies (in brackets) of the twin molecules **3a–c** with methyl groups in the 3-position to the ester group.

Monomer	Mesogenic unit	Phase transition temperatures (°C)[a] and enthalpies (kJ mol^{-1}) 2nd heating	2nd cooling
3a		Cr 114 N 150 I (46.0) (1.3)	I 147 N 93 Cr (− 1.3) (− 45.4)
3b		Cr 110 N 156 I (49.3) (1.5)	I 152 N 66 Cr (− 0.9) (− 26.9)
3c		Cr 108 N 122 I (48.2) (1.1)	I 118 N 78 Cr (− 1.2) (− 40.3)

[a] DSC 10 K min^{-1}, 1 wt % sulphur.

Table 4. Transition temperatures and enthalpies (in brackets) of the twin molecules **4a–c** with methyl groups in the 3- and 5-positions to the ester group.

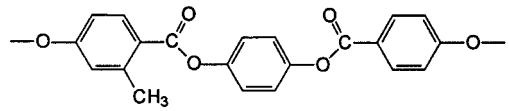
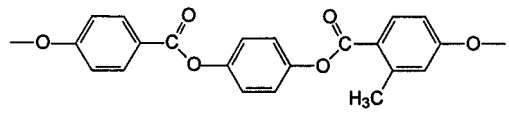
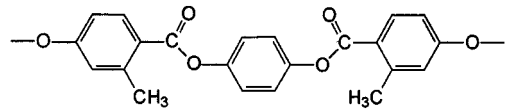
Monomer	Mesogenic unit	Phase transition temperatures (°C)[a] and enthalpies (kJ mol^{-1}) 2nd heating	2nd cooling
4a		Cr 95 N 117 I (70.7) (0.9)	I 113 N 53 Cr (− 1.0) (− 50.0)
4b		g − 14 ($T_{cryst.}$ 41)[b] (0.42)[c] (38.6) Cr_1 68 Cr_2 76 N 97 I (26.6) (33.1) (0.9)	I 93 N − 18 g (− 1.0) (− 0.4)[c]
4c		Cr 86 I (33.7)	I 42 Cr (− 6.5)

[a] DSC 10 K min^{-1}, 1 wt % sulphur.
[b] T_{cryst}: recrystallization temperature.
[c] Δc_p in kJ K^{-1} mol^{-1}.

one methyl group in the outer phenyl ring, the mesophase of twin **4a** is much more destabilized and no glass formation occurs. In twin **4c**, the destabilization is already so strong that liquid crystallinity is completely suppressed and only a melting point at 86°C is observed.

The last series of methyl substituted twin molecules has one methyl group per 4-hydroxybenzoic acid unit in the *ortho*-position to the ester group (**5a–c**). Table 5 gives the structures and the transition temperatures of the monomers. In this case a completely different mesophase behaviour and crystallization tendency is observed compared to the monomers **3a–c** with the methyl group in the *meta*-position. The methyl group in the 2-position leads to glass formation and broad mesophase ranges for all three monomers, and it is irrelevant whether the substituent is in the outer (**5a**) or inner phenyl ring (**5b**).

Table 5. Transition temperatures and enthalpies (in brackets) of the twin molecules **5a–c** with methyl groups in the 2-position to the ester group.

Monomer	Mesogenic unit	Phase transition temperatures (°C)[a] and enthalpies (kJ mol^{-1}) 2nd heating	2nd cooling
5a		g − 18 N 135 I (0.5)[b] (1.1)	I 131 N − 23 g (− 1.3) (− 0.6)[b]
5b		g − 15 N 129 I (0.4)[b] (1.1)	I 123 N − 20 g (− 1.2) (− 0.5)[b]
5c		g − 21 N 66 I (0.6)[b] (1.2)	I 61 N − 26 g (− 0.3) (− 0.6)[b]

[a] DSC 10 K min^{-1}, 1 wt % sulphur.
[b] Δc_p in kJ K^{-1} mol^{-1}.

As expected, twin **5c** with two methyl groups per mesogen has a smaller LC phase range than the monosubstituted twins.

Twin monomer **5a** exhibits the broadest mesophase range and the highest tendency to glass formation. Initially, **5a** is crystalline due to the work-up from solution, and a melting point is observed at 54°C during the first heating on DSC (figure 6). Upon cooling no crystallization occurs. Also during the next heating run only the T_g at − 18°C and the clearing point at 135°C are observed.

Below the glass transition temperature, twin **5a** forms a stable glass for several weeks. If an application of twin molecules as the nematic host for cholesteric mixtures is taken into account, the stability of the LC phase at room temperature is important. Therefore we carried out DSC annealing experiments at room temperature; the results are shown in figure 7. If a sample of **5a** is heated directly after a cooling cycle, only the glass transition at − 18°C and the clearing point at 135°C are detected. After storing at 25°C for one day, the sample has crystallized completely and multiple melting and recrystallization peaks are observed between 43 and 61°C. To determine the start of crystallization we chose a shorter annealing time of 3 h at 25°C. In this case the T_g can still be seen, but additionally small melting peaks

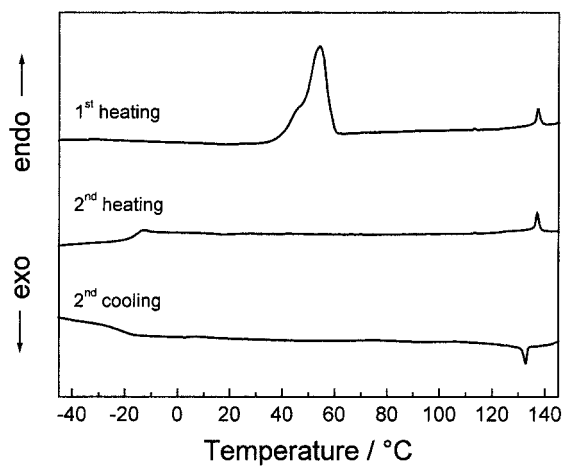


Figure 6. DSC experiment with twin **5a** (heating and cooling rate 10 K min^{-1}).

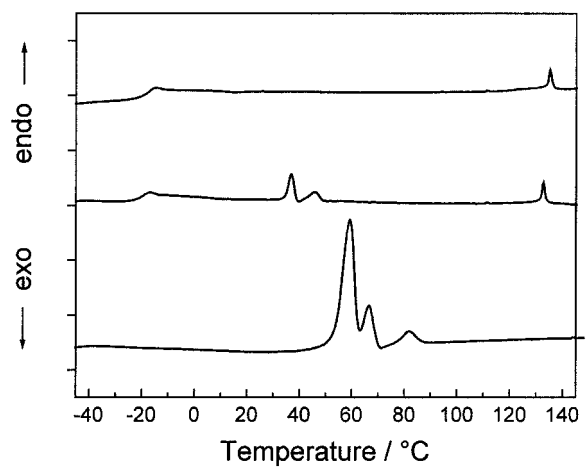


Figure 7. DSC annealing experiment with twin **5a** (top: second heating directly after cooling; middle: heating after 3 h annealing at 25°C; bottom: heating after 24 h annealing at 25°C; heating and cooling rate 10 K min^{-1}).

at 30 and 48°C had become visible. This result was also confirmed by polarizing optical microscopy. After 3 h small crystals are formed and start to grow very slowly.

We also synthesized a fourth type of methyl substituted twin molecule. In monomer **6**, the methyl group is not in the phenyl rings of the 4-hydroxybenzoic unit, but in the central phenyl ring of the mesogen. The synthesis of the mesogen was carried out following scheme 1, starting from 2-methylhydroquinone instead of hydroquinone. Thereby, a 1 : 1 mixture of the 2-methyl and the 3-methyl isomers of the THP-protected hydroquinone is obtained. Because of the reaction pathway (§ 3.1), a mixture of three isomers with different positions of the methyl group in the central phenyl ring is obtained. The mesophase behaviour of **6** is given in table 6.

Upon the first heating on DSC, a melting point at 89°C is detected. This is higher than the melting points of the monomers **5a** (54°C) and **5b** (49°C). The nematic–isotropic transition, however, is at 132°C which is comparable to the values for the monomers **5a** and **5b**. Subsequent cooling and heating runs showed no crystallization. Whether the substitution pattern or the mixture of three different isomers is responsible for the glass-forming properties could not be clarified.

3.3. *Kinetic investigations of twin molecules by photo-DSC measurements*

Twin molecules with two polymerizable acrylate groups can be permanently fixed in a network by *in situ* photopolymerization [6]. To obtain information about the photopolymerization kinetics, we carried out photo-DSC investigations. Twin molecule **5a** with an unusually broad nematic mesophase range between − 18 and 135°C allows these investigations over a wide temperature range. We made mixtures of **5a** with 1 wt % of photoinitiator (Irgacure 651, Ciba Geigy). These samples were irradiated with UV light in the photo-DSC. From the heat of polymerization, the conversion of acrylate groups was calculated at temperatures between zero and 135°C. Figure 8 shows a plot of the final conversion vs. the polymerization temperature.

The final conversion of the acrylate groups strongly depends on the polymerization temperature. In the case of twin **5a**, we obtained densely crosslinked networks with a conversion of more than 90% at polymerization temperatures higher than 80°C. Decreasing the polymerization temperature leads to a decrease in the final conversion. Two effects are responsible for this behaviour. First, at low temperatures (0°C) the viscosity of the monomer mixture is too high; the acrylate groups have insufficient mobility to react and a final conversion of only 3% is detected. Additionally the glass temperature of the network increases during photopolymerization from − 18°C in the monomer to 44°C in the network. Thereby residual acrylate groups are immobilized in the glassy state. For a detailed discussion of the photopolymerization behaviour see [41, 56].

3.4. *Cholesteric polymer networks with twin molecules forming the nematic host*

Nematic twin molecules are an ideal host for cholesteric mixtures because they exhibit broad mesophase ranges

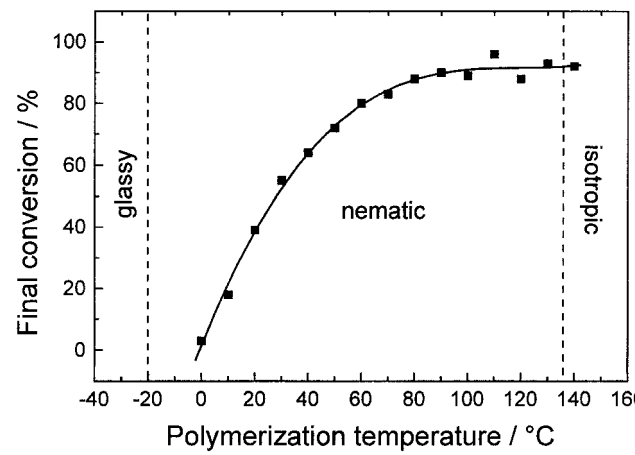
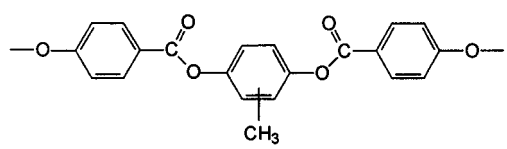


Figure 8. Photopolymerization of twin **5a**: final conversion vs. polymerization temperature.

Table 6. Transition temperatures and enthalpies (in brackets) of mixed twin isomers **6** with a methyl group in the central hydroquinone ring.

		Phase transition temperatures (°C)[a] and enthalpies (kJ mol^{-1})	
Monomer	Mesogenic unit	2nd heating	2nd cooling
6		g − 12 N 132 I (0.52) (1.2)	I 126 N − 18 g (− 1.2) (− 0.6)[b]

[a] DSC 10 K min^{-1}, 1 wt % sulphur.
[b] Δc_p in kJ K^{-1} mol^{-1}.

and glass-forming properties [6]. We prepared cholesteric mixtures from twin **2a** with a methoxy group in the outer phenyl ring and a chiral sorbitol derivative **16** [57], which also contains two polymerizable acrylate groups (figure 9). In this way, a high crosslink density is ensured after photopolymerization.

Mixtures containing up to 25 mol % of the chiral compound **16** exhibit broad mesophases and glass forming properties. Because **16** is not liquid crystalline itself, a higher content destroys the mesophase. Reflection in the visible range of the spectrum is observed in samples between 10 and 20 mol % of **16**. By *in situ* photopolymerization, the cholesteric mesophase can be permanently fixed in the network. To investigate the dependence of the reflection wavelength λ_R stemming from the content of chiral monomer, we recorded UV/Vis spectra of the cholesteric networks. In figure 10 the inverse reflection wavelength is plotted as a function of the content of **16** for polymerization temperatures of 25 and 65°C. From the slope, HTP values of about 20 μm^{-1} are calculated for both polymerization temperatures. If the higher molecular mass of twin molecules is taken into account, the helical twist of the twins induced by the chiral dopant **16** is in the same range as for classical mono-rods [6].

3.5. *Twin molecules as mixing agents for classical mono-rods*

Our novel twin molecules are able to form stable LC glasses if they have lateral substituents in the mesogenic core. The synthesis of twins, however, includes several steps and is more complex than the synthesis of comparable mono-rods like **15** (figure 3). Therefore we tested whether small amounts of twin molecules can suppress or prevent the crystallization of classical mono-rods. Figure 11 shows the phase diagram of nematic mixtures from twin **5a** and mono-rod **15**.

By mixing twin and mono-rod, a broad range nematic mesophase is formed. While the clearing point is almost constant, the T_g is shifted to lower temperatures by an increasing amount of mono-rod. Mixtures with more than 15 mol % of the twin **5a** do not show any recrystallization on DSC. An increasing amount of **15** in the mixture, however, leads to recrystallization and a melting point is observed.

4. Conclusions

In this paper we have described the synthesis and the thermotropic properties of 14 novel twin molecules. Such twin molecules are interesting for applications as nematic hosts in cholesteric mixtures because they do not crystallize, but vitrify and form LC glasses upon cooling. Further processing of these mixtures, e.g. *in situ* photopolymerization of the oriented mesophase, leads to cholesteric effect colours. For LC glasses, a special architecture of the monomers is required. We introduced lateral substituents in the mesogenic core of the twin molecules, and established that the kind of substituent, their number and their position are crucial to the mesophase behaviour and the crystallization tendency. If methyl groups are inserted into the outer phenyl ring of the mesogen in the *ortho*-position to the ester group an exceptionally broad range nematic phase between − 18 and 135°C was observed, as well as glass formation. At room temperature the LC phase is stable for about 3 h, before a slow, kinetically hindered crystallization starts.

The broad mesophase ranges of the twin molecules allow kinetic investigations of their photopolymerization over a wide temperature range, as well as the formation of cholesteric networks with a chiral non-liquid crystalline

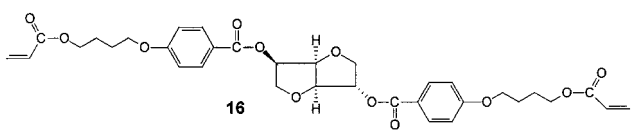


Figure 9. Structure of the chiral sorbitol derivative [57].

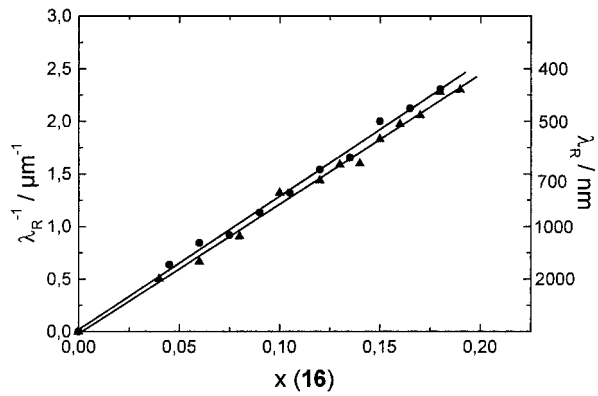


Figure 10. Inverse reflection wavelength λ_R^{-1} vs. the content of the chiral monomer **16** (T_{poly} = 65°C [●], T_{poly} = 25°C [▲]).

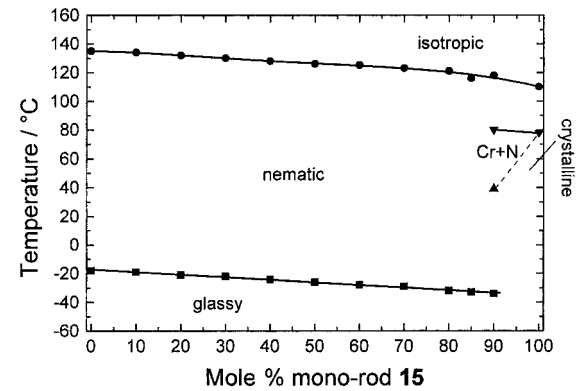


Figure 11. Phase diagram of nematic mixtures from twin **5a** and mono-rod **15**; T_g [■], T_c [●], $T_{cryst.}$ [▲], T_m [▼] (data taken from DSC runs; second heating, heating rate 10 K min^{-1}).

comonomer. By mixing small amounts of twin molecules with classical mono-rods the crystallization of the mono-rods can be suppressed.

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