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Vitrifying star-shaped liquid crystals: synthesis and application in cholesteric polymer networks

THOMAS PFEUFFER, DORIS HANFT and PETER STROHRIEGL*

Makromolekulare Chemie I and Bayreuther Institut für Makromolekülforschung (BIMF), Universität Bayreuth, 95440 Bayreuth, Germany

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In this paper, the formation of glass-forming reactive mesogens, that do not crystallize upon cooling, but vitrify and form supercooled LC phases, is described. These molecules exhibit broad range LC phases and enable us to carry out photopolymerization in a broad range of temperatures. From such reactive mesogens densely crosslinked networks in which the liquid crystalline order is permanently fixed are formed by photopolymerization. For this purpose eight novel low molecular mass LC materials with photopolymerizable acrylate groups have been synthesized and the detailed experimental procedures are given. The molecules have a star-shaped topology with three and four arms. The mesogenic units were varied by the addition of lateral groups in different positions. Comparing the twin molecules which we have described before with the novel three- and four-armed stars, we found that the supercooled LC phase in the three-armed stars has a stability superior to that in both twin molecules and four-armed stars. In the three-armed star triple-4 with a suitable substituent pattern, the supercooled nematic phase is stable at room temperature for at least nine months. Photo-DSC experiments show that the final conversion after 10 min of UV-irradiation for the three-armed star molecule triple-4 is as high as for the smaller molecules twin-4 and mono-4 over the whole temperature range. Doped with a suitable chiral molecule the novel nematics formed cholesteric phases which were used to make cholesteric polymer networks by photopolymerization.

1. Introduction

In the last decade the use of polymer films with a stable cholesteric order has attracted much interest in optical applications, e.g. colour filters in projection systems [1], reflective polarizers [2] or colour-effect pigments for cars [3]. Such films can be produced either by cooling vitrifying cholesteric materials below their glass transition temperature or by *in-situ* photopolymerization in the LC state.

Glass-forming LC materials can be divided into polymers [4–6] and low molecular mass compounds [7–10]. The main advantage of low molecular mass compounds compared with polymers is the lower viscosity [11] and therefore a fast and good orientation.

An attractive method for the production of polymer films with a stable cholesteric order is the photopolymerization of LC monomers [12]. Hereby small molecules are oriented rapidly and almost defect-free in their LC phase. After crosslinking via photopolymerization a polymer network is achieved which is thermally stable up to its decomposition temperature.

*Author for correspondence;
e-mail: peter.strohriegl@uni-bayreuth.de

For several years we have been synthesizing vitrifying materials with photopolymerizable groups in order to prevent crystallization and to allow photopolymerization at moderate temperatures. Our first approach towards a vitrifying photocrosslinkable LC material was the development of twin molecules [13]. These are molecules with two mesogenic units connected by a flexible spacer. At both ends of the mesogenic units acrylate moieties which enable photocrosslinking are connected via flexible chains. The chemical structures of some twin molecules are shown in figure 1.

By addition of different lateral side groups to the mesogenic units (R^1, R^2 and R^3 in figure 1), compounds could be prepared that do not crystallize in a DSC experiment during cooling from the isotropic melt, but rather vitrify and form a supercooled nematic state. Also, during the following heating the compounds do not show signs of crystallization. With their high clearing points and low glass transition temperatures, the compounds possess broad range nematic phases. The twin molecules with the highest tendency for glass formation are shown in table 1. However, the nematic state of the best twin molecules is stable at room temperature only for a few hours, before crystallization starts. In this

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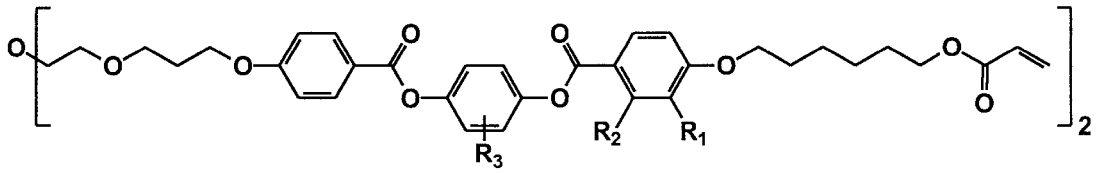


Figure 1. Chemical structure of twin molecules [13]. R^1, R^2 and R^3 are given in table 1.

paper we make use of that knowledge and describe the synthesis of star-shaped molecules with polymerizable acrylate units which have been designed to further increase the stability of the vitrified nematic phases. Mixing the star shaped monomers with a chiral sorbitol derivative and subsequent photopolymerization of the acrylate groups leads to densely crosslinked networks in which the cholesteric (N*) phase is permanently fixed.

2. Results and discussion

2.1. *Synthesis of the three- and four-armed star-shaped molecules*

In order to increase the stability of the liquid crystalline phase with respect to recrystallization, three- and four-armed star molecules were synthesized with a chemical structure similar to that of the twin molecules. Because it is well known that, due to steric effects, the crystallization of star-shaped molecules is hindered, we expected that a stable glassy state can be achieved with such molecules. In the following text, the three-armed star molecules are called triple and the four-armed star molecules are called tetra (see figure 2).

Additionally, the substitution patterns of the mesogenic units of the glass-forming twin molecules (twin-2, twin-3, twin-4) have been transferred to the star-shaped molecules, in order to suppress crystallization further. The chemical structures and the acronyms of all the novel star-shaped molecules are presented in figure 3.

The synthetic pathway to the molecules triple-1–triple-4 is presented in the scheme.

For the central parts of the star-shaped molecules a new synthesis was developed. The starting material was 1,1,1-tris(hydroxymethyl)propane for the triple compounds; for the tetra molecules the starting compound was

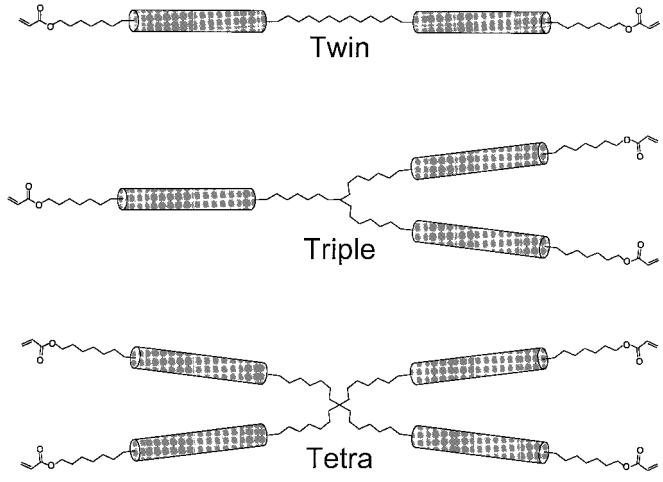


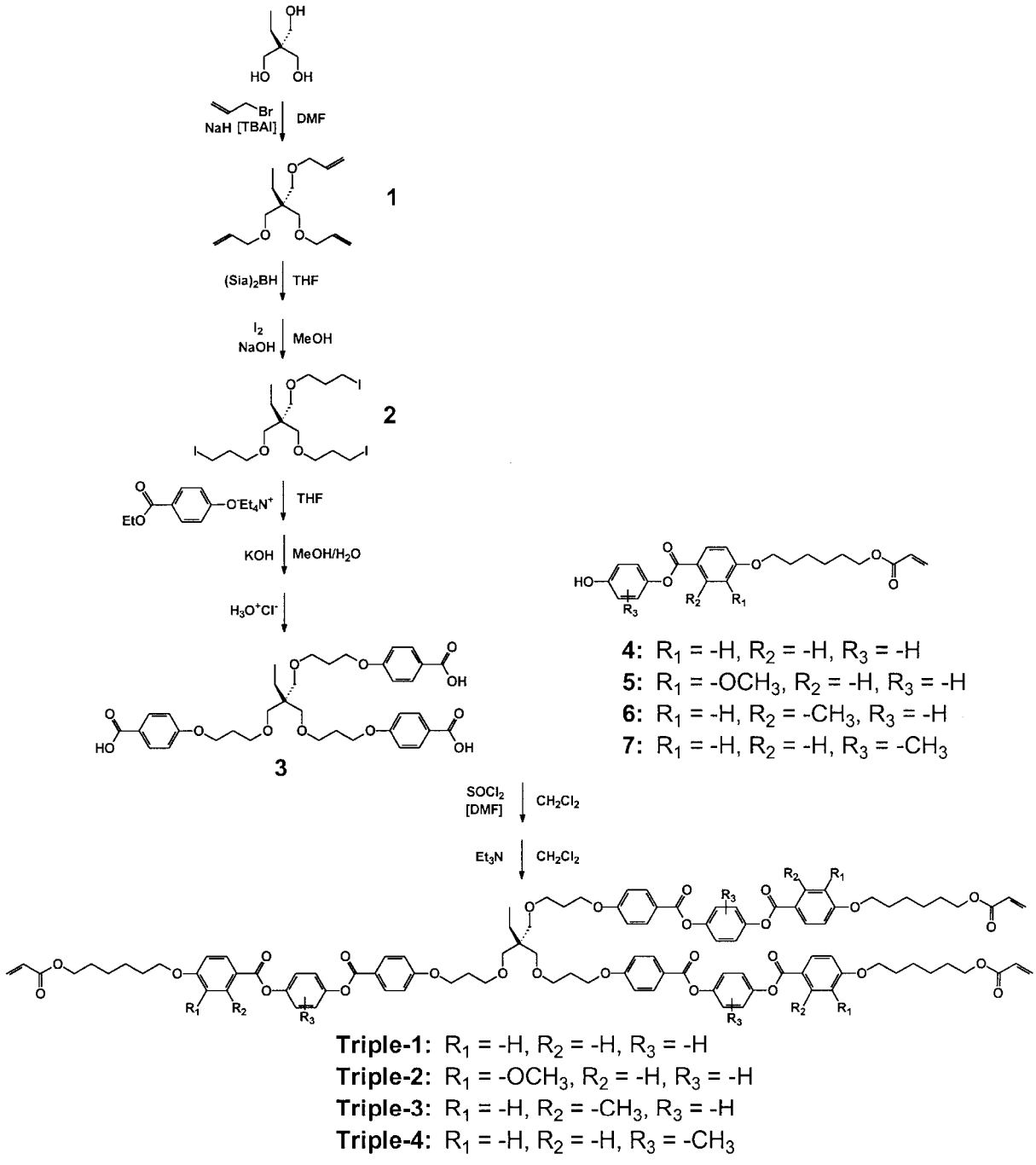
Figure 2. Schematic structures of twin, triple and tetra molecules.

2,2-bis(hydroxymethyl)1,3-propanediol (pentaerythritol). The hydroxy groups were etherified with allyl bromide and sodium hydride in DMF using tetrabutylammonium iodide (TBAI) as catalyst. The iodination of the terminal C-atoms of **1** (or **1a** for the tetra-molecules) was achieved by hydroboration with diisoamylborane—$(Sia)_2BH$ in the scheme—in THF followed by addition of iodine and NaOH. The etherification of **2** (or **2a** for the tetra-molecules) with the ethyl ester of 4-hydroxybenzoic acid was successful using the tetraethylammonium salt which is partially soluble in THF. Hydrolysis with KOH led to **3** (or **3a** for the tetra-molecules). The synthesis of the acrylate-containing mesogenic units **4**–**7** for the arms of the star-shaped molecules has already been described in detail and was carried out according to the procedures given in [13].

Table 1. Acronyms and thermal properties of twin molecules derived from DSC data [13]. Cr = crystalline, g = glassy, N = nematic, I = isotropic.

				Phase transition temperatures/°C		
Compound	R^1	R^2	R^3	2nd heating	2nd cooling	stability[a]
twin-1	H	H	H	Cr 106 N 178 I	I 176 N 80 Cr	—
twin-2	OCH_3	H	H	g −3 N 117 I	I 115 N −7 g	<1 h
twin-3	H	CH_3	H	g −18 N 135 I	I 131 N −23 g	3 h
twin-4	H	H	CH_3	g −12 N 132 I	I 126 N −18 g	6 h

[a] Time before crystallization starts.



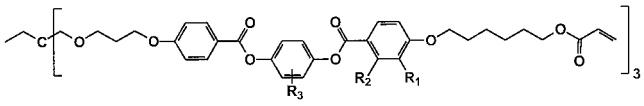
Scheme. Synthetic pathway to the triple molecules.

The final esterification was carried out on the acid chloride with triethylamine as base. All three-armed star-shaped molecules triple-1–triple-4 and four-armed star molecules tetra-1–tetra-4 shown in figure 3 were obtained by this procedure.

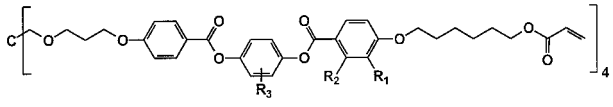
2.2. *Thermal properties*

The thermal properties of the novel star-shaped molecules are summarized in table 2.

The star-shaped architecture of the molecules alone, without lateral substituents at the mesogenic units (triple-1 and tetra-1), is not sufficient to suppress crystallization during cooling. In both cases the substances crystallize like the similar twin-1 compounds. However, triple-1 differs clearly from tetra-1 and twin-1 with respect to the degree of supercooling, i.e. the difference between the melting point and the recrystallization temperature. This difference taken from DSC experiments is



Compound	R_1	R_2	R_3
triple-1	H	H	H
triple-2	OCH_3	H	H
triple-3	H	CH_3	H
triple-4	H	H	CH_3



Compound	R_1	R_2	R_3
tetra-1	H	H	H
tetra-2	OCH_3	H	H
tetra-3	H	CH_3	H
tetra-4	H	H	CH_3

Figure 3. Chemical structures and acronyms of the novel triple (above) and tetra (below) molecules.

51°C in the case of triple-1, 26°C in the case of twin-1 and 22°C in the case of tetra-1. Thus crystallization of triple-1 is less favourable compared with twin-1 and tetra-1.

For the molecules with one lateral methoxy group per mesogenic unit, the differences between twin-2, triple-2 and tetra-2 are particulary strong. The molecular order of tetra-2 is so large that below a very narrow nematic phase, a SmA phase is formed. Upon further cooling the compound starts to crystallize. In contrast, twin-2 and triple-2 do not crystallize during cooling; instead the LC architecture vitrifies into a glassy state. However, the supercooled state of twin-2 is not very stable; reheating this glass produces a small melting peak [13]. Triple-2 shows a small amount of crystallinity only after storage for 17 h at room temperature.

By the introduction of a methyl group into the outer benzoic acid units, the supercooled nematic state is stable for 3 h in the case of twin-3 [13] and for more than a week in the case of triple-3, before recrystallization starts. Tetra-3 does not crystallize during cooling, but shows both recrystallization and subsequent melting in the following heating cycle.

The molecules with one lateral methyl group at each of the aromatic rings in the centre consist of isomeric mixtures, because the methyl group can be located in two different positions due to the synthesis procedure. In the case of the four-armed star-shaped molecule tetra-4, the supercooled nematic state is stable after storage for 24 h at room temperature, but after three days a small melting peak can be detected (see figure 4). Thus the stability exceeds that of twin-4, which shows the first signs of crystallization after 10 h at room temperature. Triple-4 possesses the highest stability in the glassy state. No crystallization was observed even after nine months of storage at room temperature; the DSC curves are shown in figure 5.

Thus, triple-4 forms an extremely stable supercooled nematic phase at room temperature. Due to the three acrylate groups in the molecule, the nematic phase can be permanently fixed into a densely crosslinked polymer network by photopolymerization.

Table 2. Transition temperatures and enthalpies (in brackets) of triple- and tetra-molecules.

	Phase transition temperatures/°C[a] and enthalpies/kJ mol^{-1}		
Compound	2nd heating	1st cooling	stability[c]
triple-1	Cr 132 (59.5) N 194 (3.2) I	I 190 (−3.0) N 81 (−35.9) Cr	—
tetra-1	Cr 173 (86.0) N 214 (4.2) I	I 208 (−4.4) N 151 (−82.9) Cr	—
triple-2	g 10 (0.7)[b] N 116 (2.5) I	I 114 (−2.4) N 5 (−0.8)[b] g	6 h
tetra-2	Cr 106 (54.2) SmA[d] 138 (1.3) N 143 (2.4) I	I 138 (−2.4) N 133 (−1.2) SmA 74 (−46.1) Cr	—
triple-3	g −13 (0.5)[b] N 124 (2.2) I	I 122 (−2.2) N −15 (−0.8)[b] g	1 week
tetra-3	g −4 (0.5)[b] Cr 106 (76.1) N 154 (3.2) I	I 150 (−3.1) N −6 (−1.2)[b] g	—
triple-4	g −22 (0.4)[b] N 101 (2.2) I	I 100 (−2.4) N −26 (−0.5)[b] g	>9 months
tetra-4	g 0 (0.5)[b] N 158 (4.0) I	I 155 (−3.8) N −3 (−0.6)[b] g	24 h

[a] DSC, 10 K min^{-1}, 1 wt % sulphur.
[b] Δ_{cp} in kJ K^{-1} mol^{-1}.
[c] Time before crystallization starts at room temperature.
[d] Layer distance determined by small angle X-ray measurement at 125°C: 60 Å.

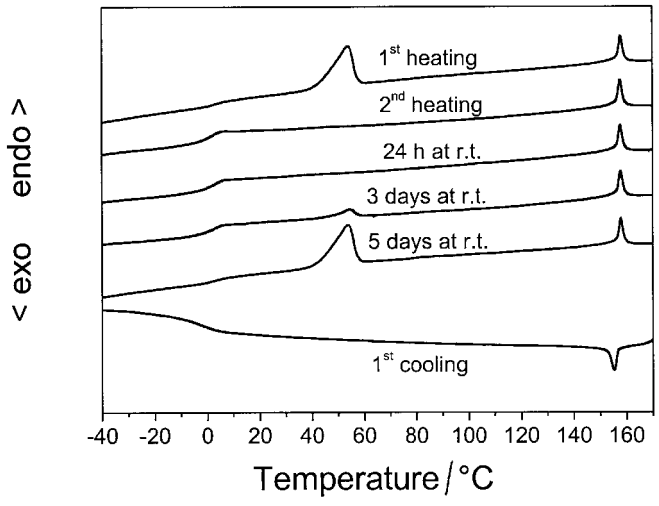


Figure 4. DSC curves of tetra-4 after different storage times at room temperature (r.t.), heating rate 10 K min^{-1}.

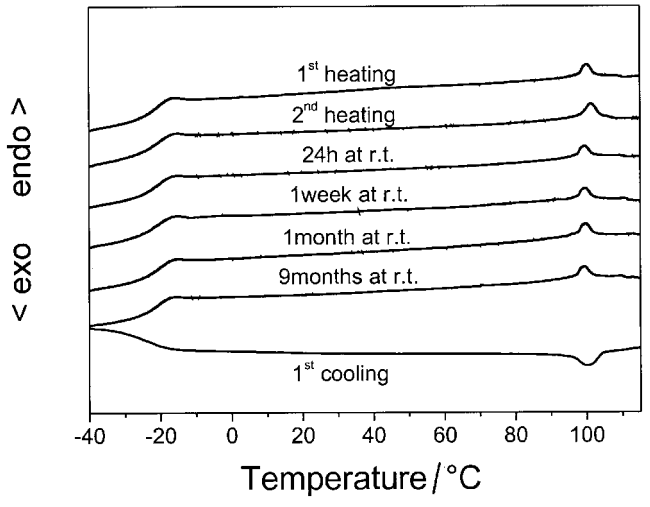


Figure 5. DSC curves of triple-4 after different storage times at room temperature (r.t.), heating rate 10 K min^{-1}.

From earlier experiments described in [13], it can be expected that the addition of a second monomer like the chiral sorbitol bisacrylate **8** would further increase the stability of the glassy state in the star-shaped nematic monomers described above.

2.3. *Photopolymerization behaviour*

The investigation of the photopolymerization kinetics of the four compounds with a lateral methyl group on the centre aromatic rings, mono-4, twin-4, triple-4 and tetra-4 (abbreviated in the following as **X-4**), was carried out by means of photo-DSC measurements. Mono-4 is the well known compound [14] with only one mesogenic unit shown in figure 6.

In figure 7 the final conversions after 10 min of irradiation are plotted versus the polymerization temperatures for the four **X-4** compounds. For all the **X-4** compounds the conversion is almost complete after 30 s of light exposure. Only at low polymerization temperatures, e.g. 20°C, is the final conversion achieved after a few minutes.

While the conversions of mono-4, twin-4 and triple-4 are very similar, the values of tetra-4 are shifted about 10°C to higher temperatures. The final conversion of the photopolymerization depends on the mobility of the molecules, particularly the acrylate groups, and therefore on the viscosity, which is temperature dependent. The viscosity increases as the temperature decreases and rises significantly at the glass transition temperature. The large star-shaped molecules are less mobile than the smaller ones (e.g. mono and twin), but they possess more acrylate groups per molecule. Thus the possibility that a star-shaped molecule is fixed into the network is larger compared with the mono or twin molecules, which possess only two acrylate groups. These two opposing effects (distance to the glass transition temperature and molecule size and functionality) compensate for twin-4 and triple-4. The lower mobility dominates in the case of tetra-4 resulting in a lower degree of conversion.

A conversion of approx. 80%, which guarantees the high network density necessary for applications, is achieved with twin-4 and triple-4 at a polymerization temperature of 60°C as well as with mono-4. For the same conversion of 80%, a polymerization temperature of 80°C is required for tetra-4. Note that at the same degree of final conversion, the statistical probability that free monomers are present in the network is smaller for triple-4 with the three acrylate groups per molecule, than for twin-4 with two acrylate groups. Therefore we assume that the photopolymerization of triple-4 at room

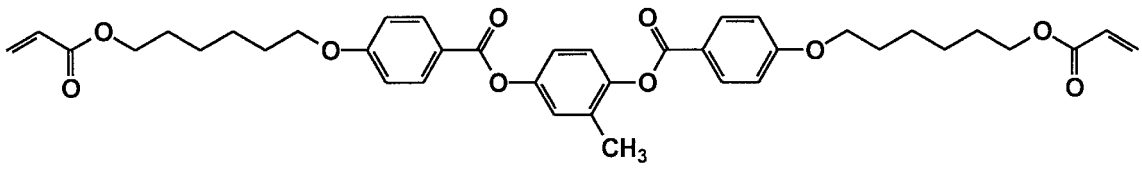


Figure 6. Chemical structure of mono-4.

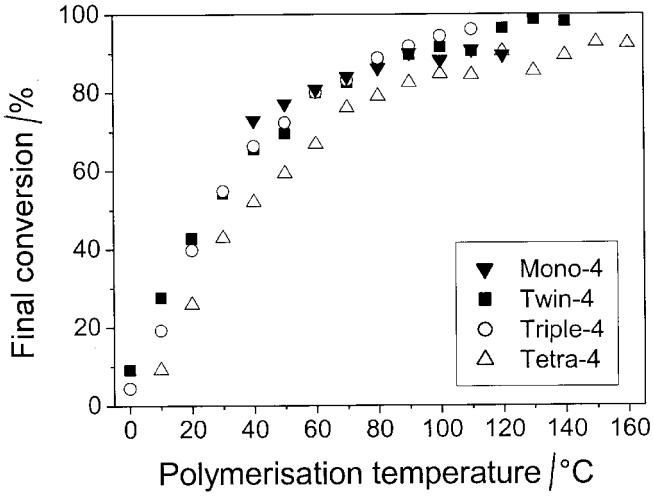


Figure 7. Final conversion at different polymerization temperatures for mono-4, twin-4, triple-4 and tetra-4 from photo-DSC measurements (1% photoinitiator Irgacure 651, 10 min of irradiation with 0.7 mW cm^{-2} at 365 nm).

temperature (50% conversion of acrylate groups) may lead to polymer networks in which the crosslink density is high enough for technical applications.

2.4. *Cholesteric polymer networks*

To prepare cholesteric (N*) polymer networks from the nematic star molecules, the chiral sorbitol bisacrylate **8** (provided by BASF AG) shown in figure 8, with a high helical twisting power (HTP), was used.

Using the **X-4** molecules with the methyl groups on the centre aromatic rings, it is possible to compare the HTP as a function of the topology and the number of mesogenic units—from one mesogenic unit (mono-4) to four mesogenic units (tetra-4). The classical HTP determination for **8** on a molar basis clearly shows that the HTP values differ significantly (see figure 9).

With increasing molecular size, an increasing molar amount of **8** is necessary to achieve the same reflection wavelength. However, the plot of the reciprocal wavelength versus the amount by weight of **8** shows that the values for mono-4, twin-4 and triple-4 are on the same straight line (see figure 10). This means, that in order to obtain the same reflection wavelength the same amount by weight of **8** is necessary for all three compounds.

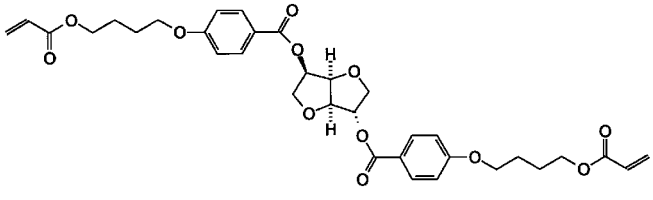


Figure 8. Chemical structure of the sorbitol bisacrylate **8** (BASF AG).

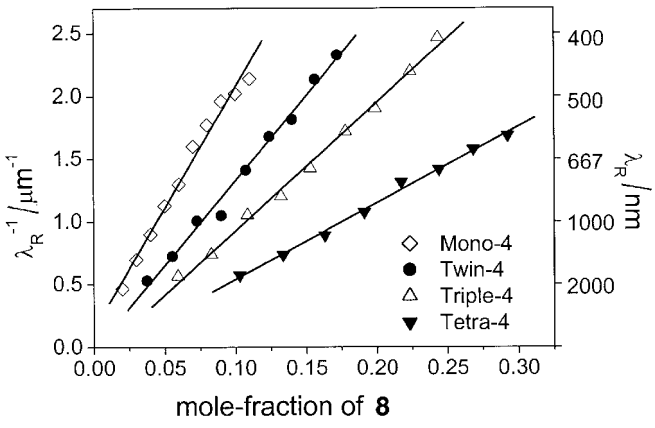


Figure 9. HTP/$\bar{n}$-determination of polymer networks from **8** and mono-4, twin-4, triple-4 or tetra-4 based on the molar amount of **8** (1% photoinitiator Irgacure 651, polymerization temperature 75°C). HTP-values for $\bar{n} = 1.6$ [15]: mono-4 +32.0 µm^{-1}, twin-4 +21.6 µm^{-1}, triple-4 +10.2 µm^{-1}, tetra-4 +6.1 µm^{-1}.

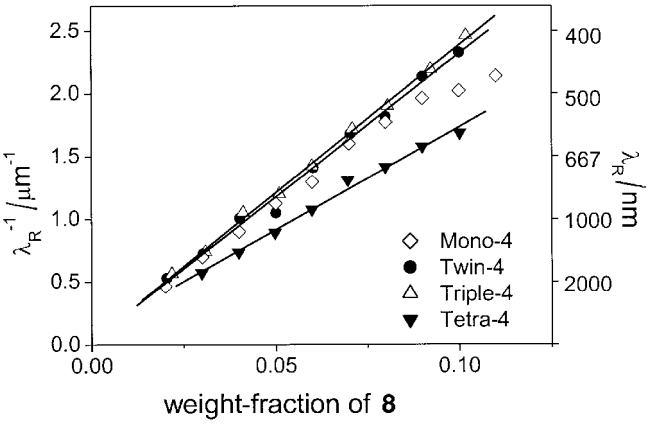


Figure 10. Plot of the reciprocal reflection wavelength versus the amount by weight of **8** in photocrosslinked cholesteric films of **8** and mono-4, twin-4, triple-4 or tetra-4 (polymerization temperature 75°C).

Since the weight standardization corresponds well with a standardization based on the number of mesogenic units, this result means that in twin-4 and triple-4 the mesogenic units are twisted as easily as in mono-4. Tetra-4 is less twisted and we explain the behaviour by the higher order of the four-armed molecules which has to be overcome by the chiral compound. This high degree of order can be rationalized by the large difference between the polymerization temperature (75°C) and the clearing point (pure tetra-4: 158°C), implying that the interactions between the mesogenic units are very high at 75°C. The higher degree of order in the tetra-compounds can also be seen in the occurrence of a SmA phase for tetra-2 and in the rapid recrystallization of tetra-3 upon cooling.

3. Experimental

3.1. *Methods of characterization*

NMR spectra were recorded in solution using a Bruker AC 250 spectrometer. Melting points, thermal transitions and the mesophase behaviour were obtained using 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-dioxane solution. The small angle X-ray investigations were carried out with a Huber Guinier Goniometer 600 and a Huber Quartz monochromator 611, using $CuK_{\alpha 1}$ radiation and a screen system, beam catcher and oven developed at the University of Bayreuth. The purity of the star-shaped molecules was checked by GPC measurements using an oligomer column set.

3.2. *Preparation of core materials for the triple molecule*

All reactions were carried out under an argon atmosphere.

3.2.1. *1,1,1-Tris(allyloxymethyl)propane* **1**

13.4 g (0.1 mol) of 1,1,1-tris(hydroxymethyl)propane were dissolved in 500 ml of dry DMF. 10.8 g of (0.45 mol) NaH and 3.7 g (0.01 mol) of TBAI as catalyst were added. At 0°C, 64.9 ml (0.75 mol) of allyl bromide were slowly dropped into the solution. After 16 h stirring at r.t. the excess of NaH was destroyed by addition of a small amount of methanol. The excess of allyl bromide and the solvent were removed *in vacuo*. After addition of 100 ml of H_2O, the aqueous solution was shaken three times with 100 ml of diethyl ether. The combined organic phases were washed twice with 100 ml of water. After removing the solvent *in vacuo*, the crude product was purified by column chromatography (hexane/ethyl acetate = 10/1). Yield: 22.5 g (88%) of a colourless liquid. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.86 (t, 3H, $CH_2{-}C\underline{H}_3$), 1.44 (q, 2H, $C{-}C\underline{H}_2{-}CH_3$), 3.33 (s, 6H, $C{-}C\underline{H}_2{-}O$), 3.93 (dd, 6H, $O{-}C\underline{H}_2{-}CH{=}C\underline{H}_2$), 5.18 (m, 6H, $CH{=}C\underline{H}_2$), 5.89 (m, 3H, $C\underline{H}{=}CH_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) 7.7 ($CH_2{-}\underline{C}H_3$); 23.0 ($\underline{C}H_2{-}CH_3$); 43.1 ($\underline{C}$); 70.7, 72.1 ($O{-}\underline{C}H_2$); 116.0 ($CH{=}\underline{C}H_2$); 135.3 ($\underline{C}H{=}CH_2$).

3.2.2. *1,1,1-Tris(3-iodo-propyloxymethyl)propane* **2**

At −10°C 31.8 ml (0.3 mol) of 2-methyl-2-butene were slowly added to 150 ml (0.15 mol) of a 1M BH_3-THF solution. After stirring the solution for 2 h at r.t. the mixture was cooled to 0°C and then 10.17 g (0.04 mol) of compound **1** were added dropwise. After stirring for an additional 2 h at r.t. the excess of borane was destroyed by a small amount of methanol. For the iodination, 38.1 g (0.15 mol) of iodine, 8.0 g (0.2 mol) of NaOH and 100 ml of methanol were added while cooling the reaction mixture with ice-water. After stirring the solution for 16 h at r.t. the mixture was discolourized by the addition of aqueous 1M $Na_2S_2O_3$. For the oxidation of the side product, diisoamyl boronic acid 4.8 g (0.12 mol) and NaOH in 40 ml of H_2O were added to the mixture and 24.5 ml of 30% aqueous H_2O_2 were carefully added at a temperature below 30°C. After stirring for one more hour at r.t., the organic solvents were removed *in vacuo* and the aqueous solution was shaken three times with 100 ml of diethyl ether. The combined organic phases were washed with 100 ml of brine and dried with Na_2SO_4. The solvent was removed *in vacuo* and the crude product purified by column chromatography (CH_2Cl_2). Yield: 15.0 g (59%) of a slightly yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.85 (t, 3H, $CH_2{-}C\underline{H}_3$), 1.38 (q, 2H, $C{-}C\underline{H}_2{-}CH_3$), 2.04 (quintet, 6H, $CH_2{-}C\underline{H}_2{-}CH_2$), 3.27 (t, 6H, $CH_2{-}C\underline{H}_2{-}I$), 3.27 (s, 6H, $C{-}C\underline{H}_2{-}O$), 3.44 (t, 6H, $O{-}C\underline{H}_2{-}CH_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) 3.8 ($-\underline{C}H_2{-}I$); 7.7 ($CH_2{-}\underline{C}H_3$); 23.0 ($-\underline{C}H_2{-}CH_3$); 33.5 ($CH_2{-}\underline{C}H_2{-}CH_2$); 43.3 ($\underline{C}$); 70.4, 71.1 ($O{-}\underline{C}H_2{-}$).

3.2.3. *Triple benzoic acid* **3**

7.98 g (0.048 mol) of ethyl 4-hydroxybenzoate were dissolved in 35.34 g (0.048 mol) of 20% aqueous tetraethylammonium hydroxide and the water was subsequently removed *in vacuo*. Then 150 ml of THF and 7.64 g (0.012 mol) of compound **2** were added and boiled for 16 h. The solid was filtered off and the solvent removed *in vacuo*. Then 150 ml of diethyl ether were added and the solution was shaken three times with 100 ml of 2M NaOH and once with 100 ml of H_2O. After drying with Na_2SO_4 the solvent was removed *in vacuo*. The ethyl ester was purified by column chromatography ($CHCl_3$/ethyl acetate = 10/1). For the hydrolysis of the ester groups, the material was dissolved in 300 ml methanol and 11.22 g (0.2 mol) of KOH in 30 ml of H_2O were added. After boiling for 16 h the methanol was removed. 100 ml of water were added and the solution was acidified with conc. HCl. The solid was filtered off and purified by recrystallization from methanol. Yield: 6.13 g (76%) of a white solid, m.p. 203–204°C. ^{1}H NMR (DMSO-d_6): δ (ppm) 0.73 (t, 3H, $CH_2{-}C\underline{H}_3$), 1.27 (q, 2H, $-C\underline{H}_2{-}CH_3$), 1.88 (quintet, 6H, $CH_2{-}C\underline{H}_2{-}CH_2$), 3.20 (s, 6H, $C{-}C\underline{H}_2{-}O$), 3.42 (t, 6H, $O{-}C\underline{H}_2{-}$), 4.03 (t, 6H, $O{-}C\underline{H}_2{-}$), 6.97 (d, 6H, $H_{arom.}$), 7.88 (d, 6H, $H_{arom.}$), 12.60 (s, 3H, $COO\underline{H}$). ^{13}C NMR (DMSO-d_6): δ (ppm) 7.7 ($CH_2{-}\underline{C}H_3$); 23.0 ($-\underline{C}H_2{-}CH_3$); 29.1 ($CH_2{-}\underline{C}H_2{-}CH_2$); 43.1 ($\underline{C}$); 65.0, 67.2, 70.7 ($O{-}\underline{C}H_2{-}$); 114.4, 123.2, 131.7, 162.5 ($C_{arom.}$); 167.3 ($-\underline{C}OOH$).

3.3. *Preparation of the core materials for the tetra-molecules*

All reactions were carried out under argon.

3.3.1. *Tetra-O-allyl-pentaerythritol* ***1a***

This was synthesized similarly to 1,1,1-tris(allyloxymethyl)propane **1** with 6.8 g (0.05 mol) of 2,2-bis(hydroxymethyl)-1,3-propanediol (pentaerythritol) as starting material, 8.0 g (0.3 mol) of NaH, 1.8 g (0.005 mol) of TBAI as catalyst and 42.3 ml (0.5 mol) of allyl bromide. The crude product was purified by column chromatography (hexane/ethyl acetate = 10/1). Yield: 13.4 g (90%) of a colourless liquid. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.46 (s, 8H, $C^-C\underline{H}_2{}^-O$), 3.95 (d, 8H, $O^-C\underline{H}_2{}^-CH^=CH_2$), 5.18 (m, 8H, $CH_2{}^-CH^=C\underline{H}_2$), 5.88 (m, 4H, $CH_2{}^-C\underline{H}^=CH_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) 45.3 ($\underline{C}$); 69.2, 72.2 ($O^-\underline{C}H_2$); 116.0 ($CH^=\underline{C}H_2$); 135.1 ($^-\underline{C}H^=CH_2$).

3.3.2. *Tetra-O-(3-iodo-propyl)pentaerythritol* ***2a***

This was synthesized similarly to 1,1,1-tris-(3-iodopropyloxymethyl)propane **2** from 4.45 g (0.015 mol) of compound **1a** with 12.7 ml (0.12 mol) of 2-methyl-2-butene and 60 ml (0.06 mol) of a 1M BH_3-THF solution for the hydroboration. For the iodation 19.0 g (0.075 mol) of iodine, 4.0 g (0.1 mol) of NaOH and 50 ml of methanol were used. The oxidation was carried out with 2.4 g (0.06 mol) of NaOH in 20 ml of H_2O and 12.3 ml of 30% aqueous H_2O_2. The crude product was purified by column chromatography (CH_2Cl_2). Yield: 6.5 g (54%) of a yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.04 (quintet, 8H, $CH_2{}^-C\underline{H}_2{}^-CH_2$), 3.27 (t, 8H, $CH_2{}^-C\underline{H}_2{}^-I$), 3.37 (s, 8H, $C^-C\underline{H}_2{}^-O$), 3.45 (t, 8H, $O^-C\underline{H}_2{}^-CH_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) 3.7 ($^-\underline{C}H_2{}^-I$); 33.5 ($CH_2{}^-\underline{C}H_2{}^-CH_2$); 45.5 ($\underline{C}$); 69.5, 70.5 ($O^-\underline{C}H_2{}^-$).

3.3.3. *Tetra benzoic acid* ***3a***

This was synthesized similarly to triple benzoic acid **3** from 4.85 g (0.006 mol) of compound **2a** with 5.00 g (0.03 mol) of ethyl 4-hydroxybenzoate and 22.01 g (0.03 mol) of 20% aqueous tetraethylammonium hydroxide. The product was purified by washing with a hot methanol/isopropanol (1/1) mixture. Yield: 3.62 g (71%) of a white solid, m.p. 254–255°C. ^{1}H NMR (DMSO-d_6): δ (ppm) 1.85 (quintet, 8H, $CH_2{}^-C\underline{H}_2{}^-CH_2$), 3.27 (s, 8H, $C^-C\underline{H}_2{}^-O$), 3.40 (t, 8H, $O^-C\underline{H}_2{}^-$), 4.00 (t, 8H, $O^-C\underline{H}_2{}^-$), 6.96 (d, 8H, $H_{arom.}$), 7.88 (d, 8H, $H_{arom.}$), 12.60 (s, 4H, $COO\underline{H}$). ^{13}C NMR (DMSO-d_6): δ (ppm) 28.7 ($CH_2{}^-\underline{C}H_2{}^-CH_2$); 45.1 ($\underline{C}$); 64.6, 67.0, 68.9 ($O^-\underline{C}H_2{}^-$); 114.1, 122.9, 131.3, 162.2 ($C_{arom.}$); 167.0 ($^-\underline{C}OOH$).

3.4. *Preparation of the acrylate-containing mesogens*

The synthesis of the four acrylate-containing mesogens **4**–**7** was carried out according to the detailed procedures given in [13].

3.5. *Preparation of the triple and tetra molecules*

Again all reactions were carried out under argon.

3.5.1. *Triple-1*

1.34 g (2 mmol) of triple benzoic acid **3** were stirred in 20 ml of dry CH_2Cl_2. Then 0.66 ml (9 mmol) of thionyl chloride and 10 drops of DMF as catalyst were added. The solution was heated at reflux for 3 h whereby a clear solution was obtained. The solvent and the excess of thionyl chloride were removed *in vacuo* and the acid chloride dried *in vacuo* for 1 h. For the esterification, the acid chloride was dissolved in 50 ml of dry CH_2Cl_2 and 2.54 g (6.6 mmol) of 4-[4-(6-acryloyloxyhexyloxy)-benzoyloxy]phenol **4** and 50 mg of 2,6-di-*tert*-butyl-*p*-cresol (DBPC) as inhibitor were added. To this solution 1.66 ml (12 mmol) of triethylamine were added slowly. After stirring for 16 h at r.t. 50 ml of CH_2Cl_2 were added and the organic phase was shaken twice with 50 ml of 2M HCl and once with 50 ml of H_2O. After drying with Na_2SO_4, the solvent was removed *in vacuo*. The crude product was purified by recrystallization (ethyl acetate). Yield: 3.02 g (85%) of a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.82 (t, 3H, $CH_2{}^-C\underline{H}_3$), 1.35–1.65 (m, 14H, $CH_2{}^-C\underline{H}_2{}^-CH_2$, $^-C\underline{H}_2{}^-CH_3$), 1.65–1.95 (2m, 12H, $O^-CH_2{}^-C\underline{H}_2{}^-CH_2$), 2.02 (quintet, 6H, $O^-CH_2{}^-C\underline{H}_2{}^-CH_2{}^-O$), 3.30 (s, 6H, $C^-C\underline{H}_2{}^-O$), 3.54 (t, 6H, $O^-C\underline{H}_2{}^-CH_2$), 4.00–4.21 (m, 18H, $O^-C\underline{H}_2{}^-CH_2$), 5.82 (dd, 3H, $C\underline{H}_2{}^=CH$ *cis*), 6.12 (dd, 3H, $CH_2{}^=C\underline{H}^-$), 6.42 (dd, 3H, $C\underline{H}_2{}^=CH$ *trans*), 6.96 (dd, 12H, $H_{arom.}$), 7.24 (s, 12H, $H_{arom.}$), 8.14 (d, 12H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ (ppm) 7.6 ($CH_2{}^-\underline{C}H_3$); 23.1 ($\underline{C}H_2{}^-CH_3$), 25.7, 28.5, 28.9, 29.4 ($CH_2{}^-\underline{C}H_2{}^-CH_2$); 43.2 ($\underline{C}$); 64.4, 65.1, 67.4, 68.0, 71.1 ($O^-\underline{C}H_2{}^-CH_2$); 114.2, 121.5, 122.6 ($C_{arom.}$); 128.5 ($^-\underline{C}H^=CH_2$); 130.5 ($^-CH^=\underline{C}H_2$); 132.2, 148.3, 163.4 ($C_{arom.}$); 164.7, 166.2 ($^-\underline{C}OO^-$).

3.5.2. *Triple-2*

This was synthesized similarly to triple-1 with 4-[4-(6-acryloyloxyhexyloxy)-3-methoxybenzoyloxy]-phenol **5** as the mesogenic unit. The product was purified by column chromatography (CH_2Cl_2/ethyl acetate = 10/1) and recrystallization (ethyl acetate). Yield: 67% of a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.82 (t, 3H, $CH_2{}^-C\underline{H}_3$), 1.35–1.65 (m, 14H, $CH_2{}^-C\underline{H}_2{}^-CH_2$, $^-C\underline{H}_2{}^-CH_3$), 1.65–1.95 (2m, 12H, $O^-CH_2{}^-C\underline{H}_2{}^-CH_2{}^-CH_2$), 2.03 (quintet, 6H, $O^-CH_2{}^-C\underline{H}_2{}^-CH_2{}^-O$), 3.31 (s, 6H, $C^-C\underline{H}_2{}^-O$), 3.54 (t, 6H, $O^-C\underline{H}_2{}^-CH_2$), 3.94 (s, 9H, $O^-C\underline{H}_3$), 4.16 (m, 18H, $O^-C\underline{H}_2{}^-CH_2$), 5.82 (dd, 3H, $C\underline{H}_2{}^=CH$ *cis*), 6.12 (dd, 3H, $CH_2{}^=C\underline{H}^-$), 6.44 (dd, 3H, $C\underline{H}_2{}^=CH$ *trans*), 6.95 (m, 9H, $H_{arom.}$), 7.25 (s, 12H, $H_{arom.}$), 7.67 (s, 3H, $H_{arom.}$), 7.83 (dd, 3H, $H_{arom.}$), 8.14 (d, 6H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ (ppm) 7.6 ($CH_2{}^-\underline{C}H_3$); 23.1 ($\underline{C}H_2{}^-CH_3$), 25.6, 25.7, 28.5, 28.8, 29.4 ($CH_2{}^-\underline{C}H_2{}^-CH_2$); 43.2 ($\underline{C}$); 56.1 ($O^-\underline{C}H_3$); 64.4, 65.1,

67.4, 68.8, 71.1 ($O^-\underline{C}H_2^-CH_2$); 111.4, 112.7, 114.2, 121.5, 122.6, 124.3 ($C_{arom.}$); 128.5 ($^-\underline{C}H^=CH_2$); 130.5 ($^-CH^=\underline{C}H_2$); 132.3, 148.4, 149.0, 153.2, 163.4 ($C_{arom.}$); 164.7, 164.8, 166.2 ($^-\underline{C}OO^-$).

3.5.3. Triple-3

This was synthesized similarly to triple-1 with 4-[4-(6-acryloyloxyhexyloxy)-2-methylbenzoyloxy]-phenol **6** as the mesogenic unit. The product was purified by column chromatography (CH_2Cl_2/ethyl acetate = 20/1) and reprecipitation from ethyl acetate solution into methanol. Yield: 72% of a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.82 (t, 3H, $CH_2^-C\underline{H}_3$), 1.35–1.65 (m, 14H, $CH_2^-C\underline{H}_2^-CH_2$, $^-C\underline{H}_2^-CH_3$), 1.65–1.95 (2m, 12H, $O^-CH_2^-C\underline{H}_2^-CH_2$), 2.03 (quintet, 6H, $O^-CH_2^-C\underline{H}_2^-CH_2^-O$), 2.65 (s, 9H, $Ar^-C\underline{H}_3$), 3.30 (s, 6H, $C^-C\underline{H}_2^-O$), 3.53 (t, 6H, $O^-C\underline{H}_2^-CH_2$), 4.00–4.21 (3t, 18H, $O^-C\underline{H}_2^-CH_2$), 5.82 (dd, 3H, $C\underline{H}_2^=CH$ *cis*), 6.12 (dd, 3H, $CH_2^=C\underline{H}^-$), 6.41 (dd, 3H, $C\underline{H}_2^=CH$ *trans*), 6.79 (m, 6H, $H_{arom.}$), 6.97 (d, 6H, $H_{arom.}$), 7.23 (s, 12H, $H_{arom.}$), 8.15 (m, 9H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ (ppm) 7.6 ($CH_2^-\underline{C}H_3$); 22.5 ($Ar^-\underline{C}H_3$); 23.1 ($\underline{C}H_2^-CH_3$), 25.7, 28.5, 29.0, 29.4 ($CH_2^-\underline{C}H_2^-CH_2$); 43.2 ($\underline{C}$); 64.4, 65.1, 67.4, 67.8, 71.2 ($O^-\underline{C}H_2^-CH_2$); 111.5, 114.2, 117.7, 120.2, 121.5, 122.6, 122.7 ($C_{arom.}$); 128.5 ($^-\underline{C}H^=CH_2$); 130.5 ($^-CH^=\underline{C}H_2$); 132.3, 133.6, 144.3, 148.2, 148.3, 162.5, 163.4 ($C_{arom.}$); 164.7, 165.1, 166.2 ($^-\underline{C}OO^-$).

3.5.4. *Triple-4*

This was synthesized similarly to triple-1 with 4-[4-(6-acryloyloxyhexyloxy) benzoyloxy] methylphenol **7** as the mesogenic unit. The product was purified by column chromatography (CH_2Cl_2/ethyl acetate = 10/1). Yield: 72% of a viscous, turbid oil. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.82 (t, 3H, $CH_2^-C\underline{H}_3$), 1.35–1.65 (m, 14H, $CH_2^-C\underline{H}_2^-CH_2$, $^-C\underline{H}_2^-CH_3$), 1.65–1.95 (2m, 12H, $O^-CH_2^-C\underline{H}_2^-CH_2$), 2.03 (m, 6H, $O^-CH_2^-C\underline{H}_2^-CH_2^-O$), 2.23 (s, 9H, $Ar^-C\underline{H}_3$), 3.31 (s, 6H, $C^-C\underline{H}_2^-O$), 3.54 (t, 6H, $O^-C\underline{H}_2^-CH_2$), 4.02–4.21 (m, 18H, $O^-C\underline{H}_2^-CH_2$), 5.82 (dd, 3H, $C\underline{H}_2^=CH$ *cis*), 6.12 (dd, 3H, $CH_2^=C\underline{H}^-$), 6.41 (dd, 3H, $C\underline{H}_2^=CH$ *trans*), 6.99 (m, 12H, $H_{arom.}$), 7.15 (m, 9H, $H_{arom.}$), 8.15 (m, 12H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ (ppm) 8.1 ($CH_2^-\underline{C}H_3$); 16.8 ($Ar^-\underline{C}H_3$); 23.5 ($\underline{C}H_2^-CH_3$), 26.1, 26.1, 28.9, 29.4, 29.8 ($CH_2^-\underline{C}H_2^-CH_2$); 43.7 ($\underline{C}$); 64.8, 65.6, 67.8, 68.5, 71.6 ($O^-\underline{C}H_2^-$); 114.6, 114.7, 120.4, 121.8, 121.9, 122.0, 122.1, 123.3, 124.5 ($C_{arom.}$); 128.9 ($^-\underline{C}H^=CH_2$); 130.9 ($^-CH^=\underline{C}H_2$); 132.1, 132.2, 132.7, 147.3, 147.4, 148.7, 148.8, 163.8, 163.9 ($C_{arom.}$); 164.9, 165.2, 165.3, 166.7 ($^-\underline{C}OO^-$).

3.5.5. *Tetra-1*

0.85 g (1 mmol) of tetra-benzoic acid **3a** were stirred in 20 ml of dry CH_2Cl_2. Then 0.73 ml (10 mmol) of thionyl chloride and 10 drops of DMF as catalyst were added. The solution was heated at reflux for 3 h whereby a clear solution was obtained. The solvent and the excess of thionyl chloride were removed *in vacuo* and the acid chloride dried *in vacuo* for 1 h. For the esterification, the acid chloride was dissolved in 50 ml of dry CH_2Cl_2 and 1.69 g (4.4 mmol) of 4-[4-(6-acryloyloxyhexyloxy)-benzoyloxy] phenol **4** and 20 mg of 2,6-di-*tert*-butyl-*p*-cresol (DBPC) as inhibitor were added. To this solution 1.11 ml (8 mmol) of triethylamine were added slowly. After stirring for 16 h at r.t. 50 ml of CH_2Cl_2 were added and the organic phase was shaken twice with 50 ml of 2M HCl and once with 50 ml of H_2O. After drying with Na_2SO_4 the solvent was removed *in vacuo*. The crude product was purified by column chromatography (CH_2Cl_2/ethyl acetate = 10/1). Yield: 1.30 g (56%) of a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.50 (m, 16H, $CH_2^-C\underline{H}_2^-CH_2$), 1.65–1.90 (2m, 16H, $O^-CH_2^-C\underline{H}_2^-CH_2^-CH_2$), 2.02 (m, 8H, $O^-CH_2^-C\underline{H}_2^-CH_2^-O$), 3.41 (s, 8H, $C^-C\underline{H}_2^-O$), 3.53 (t, 8H, $O^-C\underline{H}_2^-CH_2$), 4.01–4.21 (m, 24H, $O^-C\underline{H}_2^-CH_2$), 5.82 (dd, 4H, $C\underline{H}_2^=CH$ *cis*), 6.12 (dd, 4H, $CH_2^=C\underline{H}^-$), 6.41 (dd, 4H, $C\underline{H}_2^=CH$ *trans*), 6.96 (d, 16H, $H_{arom.}$), 7.23 (s, 16H, $H_{arom.}$), 8.13 (d, 16H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.7, 28.5, 29.0, 29.4 ($CH_2^-\underline{C}H_2^-CH_2$); 45.6 ($\underline{C}$); 64.4, 65.1, 67.5, 68.1, 69.7 ($O^-\underline{C}H_2^-$); 114.3, 121.5, 122.6 ($C_{arom.}$); 128.6 ($^-\underline{C}H^=CH_2$); 130.5 ($^-CH^=\underline{C}H_2$); 132.3, 148.3, 148.4, 163.3, 163.4 ($C_{arom.}$); 164.7, 166.3 ($^-\underline{C}OO^-$).

3.5.6. *Tetra-2*

This was synthesized similarly to tetra-1 with 4-[4-(6-acryloyloxyhexyloxy)-3-methoxybenzoyloxy]-phenol **5** as the mesogenic unit. The product was purified by column chromatography (CH_2Cl_2/ethyl acetate = 8/1). Yield: 62% of a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.51 (m, 16H, $CH_2^-C\underline{H}_2^-CH_2$), 1.65–1.95 (2m, 16H, $O^-CH_2^-C\underline{H}_2^-CH_2^-CH_2$), 2.01 (m, 8H, $O^-CH_2^-C\underline{H}_2^-CH_2^-O$), 3.41 (s, 8H, $C^-C\underline{H}_2^-O$), 3.53 (t, 8H, $O^-C\underline{H}_2^-CH_2$), 3.94 (s, 12H, $O^-C\underline{H}_3$), 4.07–4.21 (m, 24H, $O^-C\underline{H}_2^-CH_2$), 5.82 (dd, 4H, $C\underline{H}_2^=CH$ *cis*), 6.12 (dd, 4H, $CH_2^=C\underline{H}^-$), 6.40 (dd, 4H, $C\underline{H}_2^=CH$ *trans*), 6.95 (dd, 12H, $H_{arom.}$), 7.24 (s, 16H, $H_{arom.}$), 7.66 (d, 4H, $H_{arom.}$), 7.84 (dd, 4H, $H_{arom.}$), 8.14 (d, 8H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ (ppm) 26.1, 26.2, 29.0, 29.4, 29.9 ($CH_2^-\underline{C}H_2^-CH_2$); 46.1 ($\underline{C}$); 56.6 ($O^-\underline{C}H_3$); 65.0, 65.6, 68.0, 69.4, 70.2 ($O^-\underline{C}H_2^-$); 112.0, 113.2, 114.7, 122.0, 122.1, 123.1, 124.8 ($C_{arom.}$); 129.1 ($^-\underline{C}H^=CH_2$); 131.0 ($^-CH^=\underline{C}H_2$); 132.8, 148.9, 149.5, 153.7, 163.9 ($C_{arom.}$); 165.2, 165.3, 166.8 ($^-\underline{C}OO^-$).

3.5.7. *Tetra-3*

This was synthesized similarly to tetra-1 with 4-[4-(6-acryloyloxyhexyloxy)-2-methylbenzoyloxy]-phenol **6** as mesogenic unit. The product was purified

by column chromatography (CH_2Cl_2/ethyl acetate = 10/1). Yield: 53% of a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.49 (m, 16H, $CH_2{-}\underline{CH_2}{-}CH_2$), 1.65–1.90 (2m, 16H, $O{-}CH_2{-}\underline{CH_2}{-}CH_2{-}CH_2$), 2.01 (m, 8H, $O{-}CH_2{-}\underline{CH_2}{-}CH_2{-}O$), 2.65 (s, 12H, $Ar{-}\underline{CH_3}$), 3.41 (s, 8H, $C{-}\underline{CH_2}{-}O$), 3.53 (t, 8H, $O{-}\underline{CH_2}{-}CH_2$), 4.00–4.21 (3t, 24H, $O{-}\underline{CH_2}{-}CH_2$), 5.82 (dd, 4H, $\underline{CH_2}{=}CH$ *cis*), 6.12 (dd, 4H, $CH_2{=}\underline{CH}{-}$), 6.41 (dd, 4H, $\underline{CH_2}{=}CH$ *trans*), 6.78 (m, 8H, $H_{arom.}$), 6.96 (d, 8H, $H_{arom.}$), 7.23 (s, 16H, $H_{arom.}$), 8.14 (m, 12H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ (ppm) 22.5 ($Ar{-}\underline{C}H_3$); 25.7, 28.5, 29.0, 29.4 ($CH_2{-}\underline{C}H_2{-}CH_2$); 45.6 ($\underline{C}$); 64.4, 65.1, 67.5, 67.9, 69.7 ($O{-}C\underline{C}_2{-}$); 111.5, 114.2, 117.7, 120.3, 121.6, 122.6, 122.8 ($C_{arom.}$); 128.6 ($-\underline{C}H{=}CH_2$); 130.5 ($-CH{=}\underline{C}C_2$); 132.3, 133.6, 148.4, 162.5, 163.4 ($C_{arom.}$); 164.7, 165.1 ($-\underline{C}OO-$).

3.5.8. *Tetra-4*

This was synthesized similarly to tetra-1 with 4-[4-(6-acryloyloxyhexyloxy)-benzoyloxy] methylphenol **7** as the mesogenic unit. The product was purified by column chromatography (CH_2Cl_2/ethyl acetate = 10/1). Yield: 49% of a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.51 (m, 16H, $CH_2{-}\underline{CH_2}{-}CH_2$), 1.65–1.90 (2m, 16H, $O{-}CH_2{-}\underline{CH_2}{-}CH_2{-}CH_2$), 2.01 (m, 8H, $O{-}CH_2{-}\underline{CH_2}{-}CH_2{-}O$), 2.23 (s, 12H, $Ar{-}\underline{CH_3}$), 3.42 (s, 8H, $C{-}\underline{CH_2}{-}O$), 3.53 (t, 8H, $O{-}\underline{CH_2}{-}CH_2$), 4.02–4.21 (m, 24H, $O{-}\underline{CH_2}{-}CH_2$), 5.82 (dd, 4H, $\underline{CH_2}{=}CH$ *cis*), 6.12 (dd, 4H, $CH_2{=}\underline{CH}{-}$), 6.41 (dd, 4H, $\underline{CH_2}{=}CH$ *trans*), 7.00 (m, 16H, $H_{arom.}$), 7.12 (m, 12H, $H_{arom.}$), 8.14 (m, 16H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ (ppm) 16.4 ($Ar{-}\underline{C}H_3$); 25.7, 28.6, 29.0, 29.4 ($CH_2{-}\underline{C}H_2{-}CH_2$); 45.6 ($\underline{C}$); 64.5, 65.1, 67.5, 68.0, 69.7 ($O{-}\underline{C}H_2{-}$); 114.3, 120.0, 120.1, 121.4, 121.5, 121.6, 121.7, 122.9, 124.0, 124.1, 125.5 ($C_{arom.}$); 128.6 ($-\underline{C}H{=}CH_2$); 130.6 ($-CH{=}\underline{C}H_2$); 131.7, 131.8, 132.4, 147.0, 148.3, 148.4, 163.4 ($C_{arom.}$); 164.5, 164.8, 164.9, 166.3 ($-\underline{C}OO-$).

4. Conclusions

We have described the synthesis and the properties of four novel three-armed star-shaped molecules (triple) and four four-armed stars (tetra). These molecules were prepared for applications as the nematic host in cholesteric mixtures because they do not crystallize on cooling, but vitrify and form stable supercooled LC phases. The star-shaped molecules exhibit very broad range LC phases at moderate temperatures. A significant increase in the stability of the supercooled nematic state at room temperature, in comparison with the twin molecules described earlier, was achieved with the three-armed star molecules. Notably in triple-4, with one lateral methyl substituent at each centre ring of the mesogenic units, the nematic phase is stable for at least nine months at room temperature. The long term stability of the supercooled LC state in the four-armed star-molecules is much smaller. Photo-DSC experiments show that the final conversion of photopolymerization for the three-armed star molecule triple-4, after 10 min of UV irradiation, is as high as that for the smaller molecules twin-4 and mono-4 over the whole temperature range. Cholesteric polymer networks have been made from mono-4 and twin-4, as well as from the star-shaped triple-4 and tetra-4, by addition of a chiral sorbitol derivative and subsequent photopolymerization. Based on the amount by weight of the nematic matrix, the helical twisting power is almost the same for the mono, twin and triple molecule and a little smaller for the four-armed star.

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