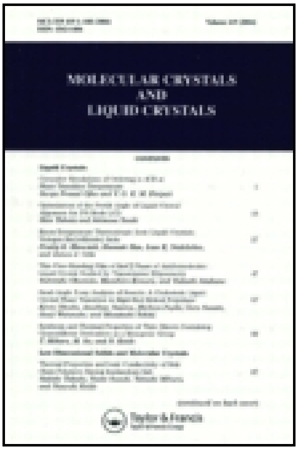

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Nematic Twin Molecules and their Application in Cholesteric Polymer Networks

Kathrin Kürschner [a] & Peter Strohriegl [a]

[a] Makromolekulare Chemie I and Bayreuther Institut für Makromolekülforschung (BIMF), Universität Bayreuth, D-95440, Bayreuth

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Nematic Twin Molecules and their Application in Cholesteric Polymer Networks

KATHRIN KÜRSCHNER and PETER STROHRIEGL

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

The synthesis of some novel nematic twin molecules is described. The insertion of lateral substituents into the mesogenic core leads to glass forming materials. Cholesteric mixtures of nematic twins and a highly twisting sorbitol derivative were crosslinked by in-situ photopolymerization, whereby the LC-structure of the monomers is permanently fixed in the network. UV/VIS spectra of the networks were recorded to investigate the dependence of the reflection wavelength from the content of chiral monomer and from the polymerization temperature.

Keywords: twin molecules; LC-glasses; in-situ photopolymerization; cholesteric polymer networks

INTRODUCTION

Cholesteric polymer networks (CPNs) have attracted special interest in recent years because of their unique optical properties, particular the selective reflection of circular polarized light and the angular dependence of the reflected wavelength[1,2,3]. The helical structure of the cholesteric mesophase is responsible for this effect. Thereby the wavelength of the reflected light is related to the helical pitch by the relation

$$\lambda_R = \bar{n} p \qquad (1)$$

where λ_R is the wavelength of the reflected light, n the average refractive index of the cholesteric phase and p the pitch of the helix. If λ_R is in the visible, cholesteric phases appear colored.

We obtain CPNs by in-situ photopolymerization of a monomer mixture containing a nematic host and small amounts of a chiral compound. Both monomers possess two polymerizable acrylate groups to ensure a high network density. In these networks the cholesteric structure of the monomers is permanently froozen-in. Typical applications for CPNs are polarizers[4] and effect pigments[5].

For applications of CPNs it is interesting to have monomers which do not crystallize upon cooling. Because of their low viscosity, such low molar mass glass forming materials guarantee a good orientation of the monomers in contrast to side chain LCs. In the past, such materials have been described on the basis of cyclic siloxanes[6,7], mixtures of different mesogenic bisacrylates[8], bismethacrylates with three mesogenic units[9] and hybrid monomers with two different polymerizable groups[10].

In this paper, we describe the synthesis of twin molecules. The typical structure of the twins is given in figure 1. Two classic mesogens in which three phenyl rings are linked by ester bonds, are connected by a flexible tetraethylene glycol spacer. Lateral substituents in the mesogenic core lead to glass forming materials.

We have synthesized two series with different substituents to investigate the influence of the substitution pattern on mesophase behavior and crystallization tendency.

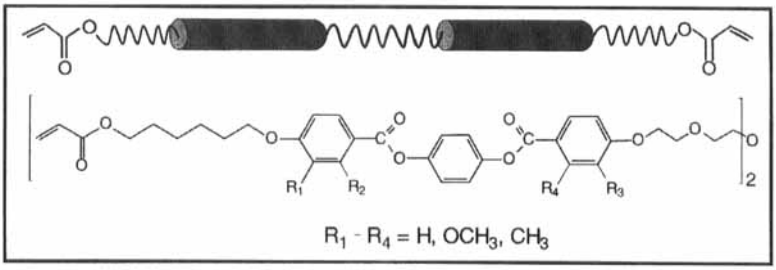


FIGURE 1 Schematic representation of twin monomers

EXPERIMENTAL

Cholesteric networks were prepared by adding 2 wt-% of 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba Geigy) as photoinitiator to a monomer mixture dissolved in chloroform. The solution was cast on the top of a glass slide and the solvent allowed to evaporate. The sample was heated into the isotropic state, cooled down into the mesophase and oriented with a second glass slide until a uniform Grandjean texture is achieved. Photopolymerization was initiated with a xenon high pressure lamp. The photopolymerization is described in more details in ref. 10.

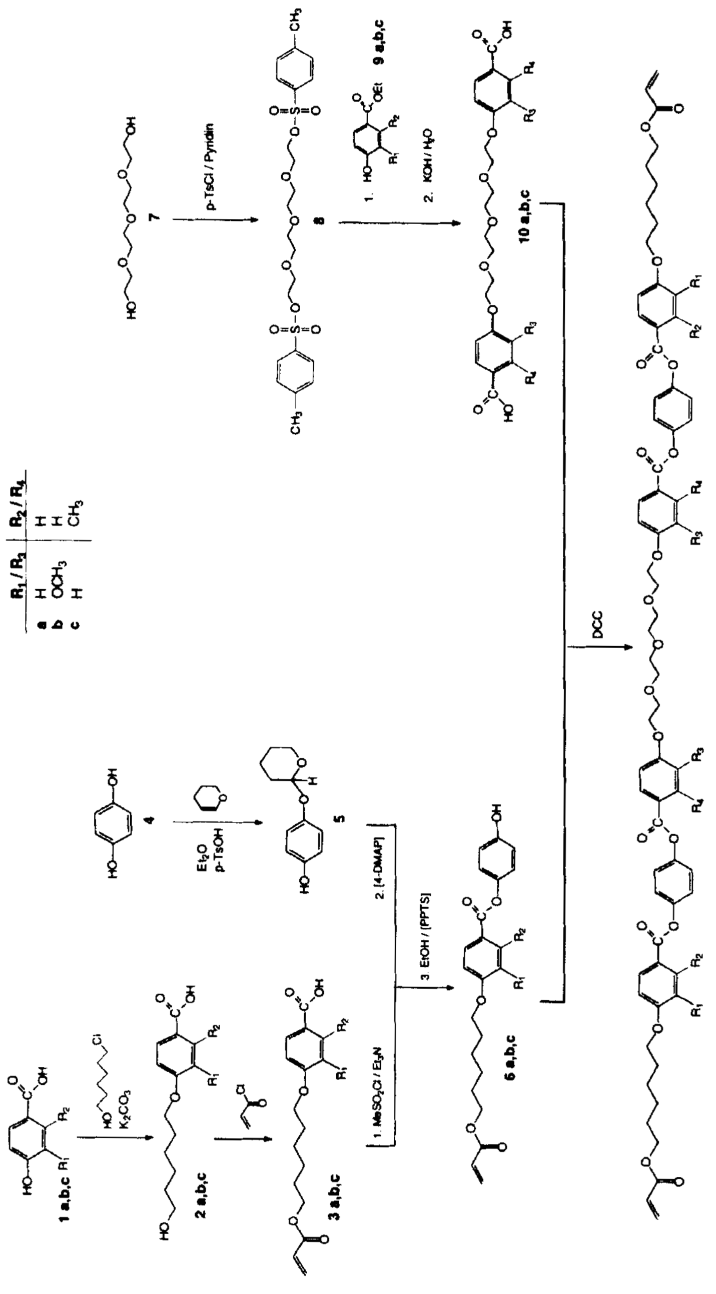
RESULTS AND DISCUSSION

Monomer synthesis

The chemical structure of nematic twin molecules is shown in scheme 1. Synthesis involves three steps.

The preparation of the mesogen **6 a** has been reported by Broer et al.[11,12]. The key step is the esterification of the monoprotected hydrochinone **5** with 4-(6-acryloyloxy-hexyloxy)benzoic acid **3 a**. We used the same pathway for **6 b** and **6 c** starting from vanillic acid **1 b** and 4-hydroxy-2-methyl-benzoic acid **1 c**. The flexible unit was prepared from tetraethylene glycol by tosylation, etherification with the substituted 4-hydroxy-ethyl-benzoates **9 a,b,c** and subsequent ester cleavage.

Two series of twin monomers have been prepared by DCC-esterification of the mesogens **6 a,b,c** with the flexible unit **10 a,b,c**. The first series contains methoxy groups in different positions of the mesogenic core and the second series contains methyl groups. Table 1 shows the compositions of the monomers. The details of the synthesis will be published elsewhere.



SCHEME 1 Synthetic pathway to nematic twin molecules

Thermal behavior

The thermal behavior of the different monomers was investigated by DSC and polarisation microscopy measurements. Table 1 represents the results.

TABLE 1: Thermal properties of the twin monomers

	R_1	R_2	R_3	R_4	Transition temperature [C°]
11	H	H	H	H	k 106 n 178 i [1)]
12	OCH_3	H	H	H	g -2 n 114 i [2)]
13	H	H	OCH_3	H	k 93 n 126 i [2)]
14	OCH_3	H	OCH_3	H	g -8 n 50 i [2)]
15	H	CH_3	H	H	g -18 n 135 i [2)]
16	H	H	H	CH_3	g -15 n 129 i [2)]
17	H	CH_3	H	CH_3	g -21 n 66 i [2)]

[1)] DSC, 2nd heating, 10 K/min, 2 wt-% sulfur
[2)] DSC, 2nd heating, 10 K/min, 1 wt-% sulfur

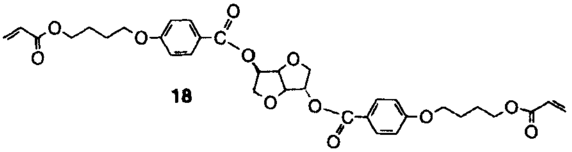
Compound **11** without any lateral groups in the mesogenic core exhibits a nematic phase between 106°C and 178°C. This is much broader than in classic rodlike bisacrylates[13]. The insertion of lateral substituents suppresses crystallization partially. Both the transition temperatures and crystallization tendency are strongly dependant on the structure, the number and the position of the substituents.

Twin **14** with four methoxy groups in the molecule is a glassy material with a T_G at -8°C and a clearing point at 50°C. If only two methoxy groups are present (**12**, **13**) their position in the mesogenic unit is crucially important. **13** with a methoxy group at the inner phenyl ring shows a nematic phase between 93°C and 126°C. Upon cooling **13** recrystallizes at 53°C. In contrast compound **12** with the methoxy group at the outer phenyl ring exhibits almost the same clearing temperature at 114°C but does not recrystallize upon cooling and shows a T_G at -2°C.

The second series with the methyl groups in 2-position shows a different thermal behavior. All three twin molecules (**15**, **16**, **17**) do not crystallize upon cooling. The mesophases are broader compared to the twins with the methoxy group in 3-position. In this series the compounds with the methyl groups at the outer (**15**) and inner (**16**) phenyl ring both have similar glass transitions and clearing points.

In-situ photopolymerization of cholesteric monomer mixtures

Cholesteric monomer mixtures were prepared from the twin molecule **12** with the methoxy group in the outer phenyl ring and the highly twisting sorbitol derivative **18**[14].



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The sorbitol derivative contains two acrylate groups which ensures a high crosslink density after polymerization.

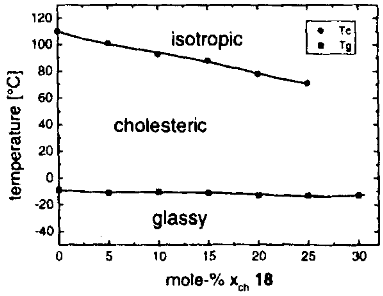

FIGURE 2 Phase diagram of mixtures of twin **12** and different amounts of the chiral compound **18** (DSC, 2nd cooling, 0.5 wt-% sulfur)

The phase diagram (Fig. 2) shows that all mixtures up to 25 mole-% of the sorbitol compound exhibit a broad cholesteric mesophase. Larger amounts of the non-mesogenic chiral compount are not miscible with twin **12**. All mixtures do not crystallize in the DSC experiment. The T_G-values are below 0°C, what allows polymerization at room temperature. Because of the high viscosity of the cholesteric mesophase at 25°C all samples were oriented between two glass slides at a reduced temperature of 0,95 ($T_{orientation}$ [°C] = $0.95*T_{clear}$ [°C]). A second series was oriented and crosslinked at 65°C. The polymerization was initiated by UV irradiation. By this procedure densely crosslinked networks are obtained, in which the helical structure is permanently froozen-in.

Optical characterization

UV/VIS spectra of the networks were recorded to investigate the dependence of the reflection wavelength λ_R from the content of chiral monomer. Therefore three series of networks were prepared with the twin molecule **12**, the mono-rod **19** and the chiral sorbitol derivative **18** to compare the twisting tendency.

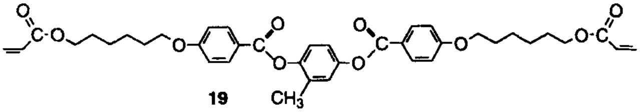

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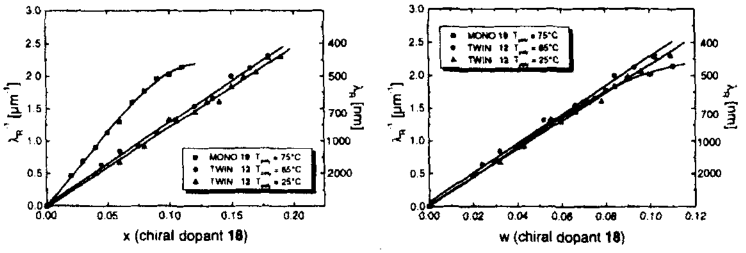
Table 2 summarizes the composition of the networks, polymerization temperatures and HTP-values.

TABLE 2 Cholesteric polymer networks

Network	**Nematic compound**	T_{poly} **[°C]**	**HTP/n̄ [µm⁻¹]**
NW 1	Twin **12**	25	12.3
NW 2	Twin **12**	65	12.7
NW 3	Mono **19**	75	20.0

In figure 3 the inverse reflection wavelength λ_R^{-1} is plotted as a function of the content of chiral compound.



a) b)

FIGURE 3 Reflection wavelength versus content of chiral compount **18** (a: mole-%, b: weight-%)

In all network types a blue shift of λ_R is observed with increasing content of the chiral compound. From the slope of the λ_R^{-1} curve the HTP-values have been calculated and are listed in table 2. As can be seen from fig. 3 the HTP-values of mono-rods and twins are in the same range, if the higher molecular weight of twins is taken into account.

To investigate the temperature dependence in our systems we polymerized three mixtures (red / 10.5 mole-% **18**, green / 13.5 mole-% **18**, blue / 16.5 mole-% **18**) at different temperatures and recorded UV/VIS spectra of the polymer films. The results are shown in figure 4. In contrast to other systems[10] all mixtures exhibit only a weak temperature dependence. λ_R is shifted by 50 nm for the red, 45 nm for the green and 35 nm for the blue sample if the polymerization temperature is changed from 30°C to 85°C.

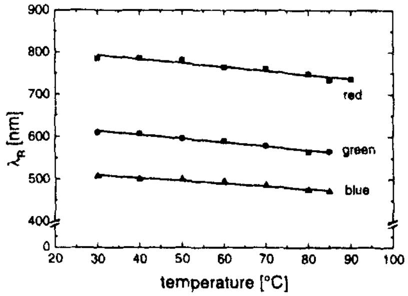


FIGURE 4 Dependence of λ_R from the polymerization temperature

Conclusion

Twin molecules with lateral groups in the mesogenic core are able to form glassy materials. Thereby the position of the substituent plays an important role concerning mesophase behavior and crystallization tendency. Mixtures of glassy twins with a highly twisting sorbitol derivative exhibit a broad cholesteric range and allow photopolymerization at room temperature. The temperature dependence of the reflection color is relatively weak.

Acknowledgement

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