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New liquid-crystalline polymers with chiral phases

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Liquid-crystalline polyesters with cholesteric and probably chiral smectic C* phases were prepared using combined liquid-crystalline polymers (that is polymers with the mesogenic groups in the main chain as well as in the side groups). Copolyesters of these polymers and polymers with olefinic double bonds could be cross-linked retaining the liquid-crystalline phases. This resulted in cross-linked polymers with elastic properties.

1. Introduction

Chiral liquid-crystalline phases, namely cholesteric and smectic C*, are of great interest today, the cholesteric phases because of their optical properties [1] and the chiral smectic C* phases because of their ferro-electric properties as well as the absence of a centre of symmetry [2] (of importance for non-linear optics). Low molar mass liquid crystals form these phases and liquid-crystalline side group polymers with chiral smectic C* phases have also been described [3, 4]. The new combined liquid-crystalline polymers [5] (that is polymers with the mesogenic groups in the main chain as well as in the side groups) seem especially interesting in order to synthesize polymers with chiral smectic C* phases, because they normally form different smectic phases [5] and it is easy to modify them chemically.

This paper describes the synthesis of a series of combined liquid-crystalline polymers which form cholesteric and probably chiral smectic C phases. Copolyesters with olefinic double bonds could be cross-linked in a second step, while retaining the liquid-crystalline phases by analogy to achiral polymers [6, 7]. These networks with elastic properties may be especially interesting in order to orient the liquid-crystalline phases mechanically and possibly to unwind the helix of the cholesteric and chiral smectic C* phase.

2. General part

The polymers 3-9 were prepared by a melt polycondensation (polymers 3-7, see table 1) or copolycondensation (polymers 8 and 9, see table 2) of the diols 1a-c and the diesters 2a-b according to procedures described elsewhere [5] (see the reaction scheme). The diesters 2a and 2b were synthesized in two steps. First the mono-ethers were prepared from 4,4'-dihydroxybiphenyl or 4,4'-dihydroxyazobenzene and the tosylate of (-)-2-methyl(*d*)-1-butanol. These mono-ethers were then reacted with diethyl 6-bromohexylmalonate (see §3).

The identification of the liquid-crystalline phases was done by D.S.C. measurements, polarizing microscopy and X-ray scattering. The results are summarized in tables 1 and 2. A typical D.S.C. scan is shown in figure 1. For all polymers no glass

REACTION SCHEME

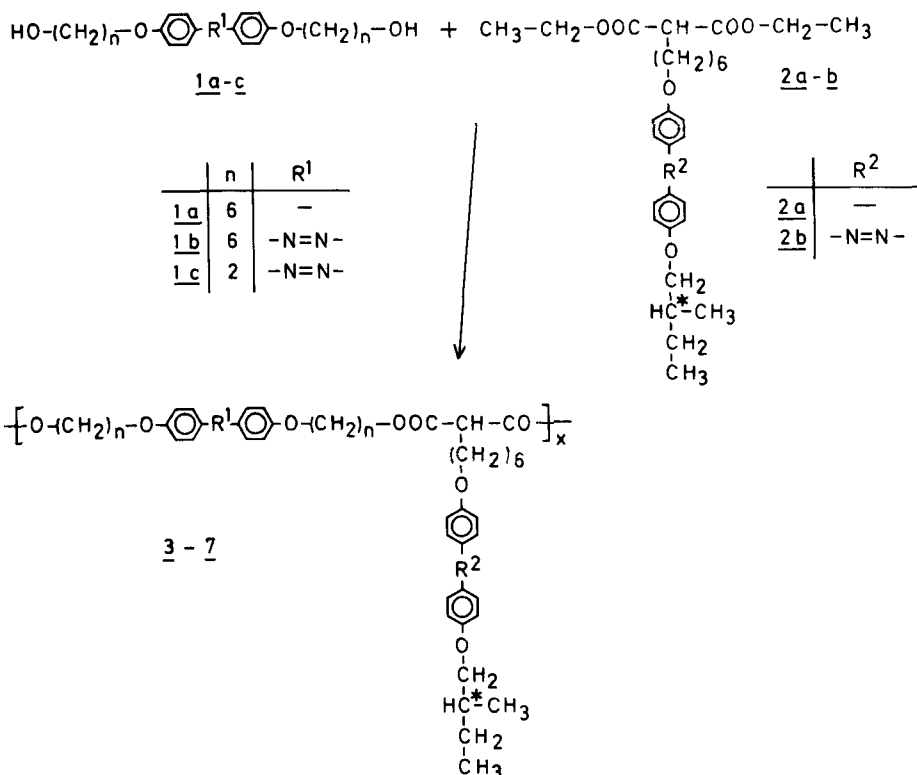


Table 1. Combined liquid-crystalline polymers 3–7 with chiral phases and their characterization.

No.	R^1	n	R^2	Molecular weight†	Phase transition temperatures‡ in °C
3	—	6	—	56000	K_1 151 K_2 154 I
4	—N=N—	6	—	3200	K 108 S_C^* 115 N^* 128 I
5	—N=N—	2	—	21000	K 150 I§
6	—	6	—N=N—	30000	K 130 S_C^* 136 I
7	—N=N—	6	—N=N—	36000	K 107 S_C^* 111 N^* 137 I

† Determined by G.P.C. in comparison to polystyrene standards.

‡ K_1 , K_2 or K: crystalline or ordered smectic phases not identified further. S_C^* : chiral smectic C, N^* : cholesteric.

§ Monotropic S_A or S_C phase not identified further.

transition temperature could be determined, due to the restricted mobility in the highly ordered smectic or crystalline phases (see figure 3) at low temperatures. Polarizing microscopy shows a biphasic region of about 5°C around the transition from the liquid-crystalline to the isotropic phase. Typical textures in the cholesteric and smectic phases are shown in figure 2. In the cholesteric phase oily streaks are observed (see figure 2(a)). In the smectic phase a broken fan-shaped texture, a schlieren texture or a lined texture [11] are observed (see figure 2(b) and (c)).

In the polymers 4 and 6–9 the long axes of the mesogenic groups (the mesogenic

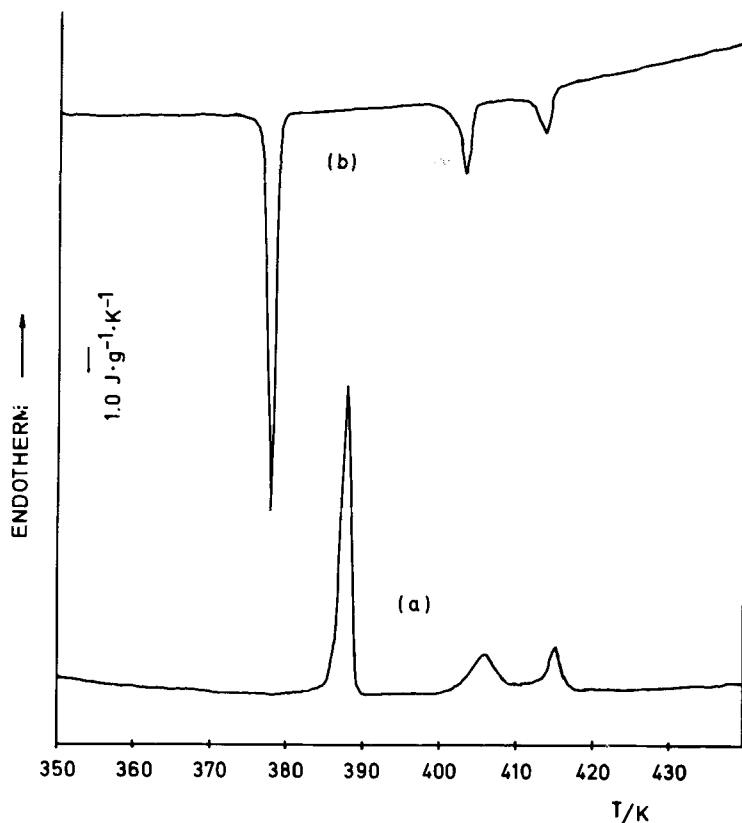


Figure 1. D.S.C. measurements of polymer **9** (see table 2); (a) heating rate $10^\circ\text{C}/\text{min}$ (b) or cooling rate $10^\circ\text{C}/\text{min}$.

groups in the main chains and in the side groups probably orient parallel to each other) are tilted with respect to the layer normal at room temperature in the crystalline or highly ordered smectic phase. This was confirmed by X-ray measurements of melt drawn fibres at room temperature (see figure 3). They show a series of small angle reflections at the meridian and wide angle reflections corresponding to two Bragg spacings. Therefore the order is better than in smectic G phases. The absence of additional reflections and the broadening of the wide angle reflections (relative to perfect crystals) also show that higher ordered smectic phases may be possible (smectic H). X-ray measurements of unoriented powder samples in the smectic A or C phase show only one sharp reflection at low angles (associated with the smectic layers) and a broad reflection at wide angles (associated with the lateral packing). For the polymers **6** and **7** the thickness of the smectic layers remains nearly unchanged at the transition from the crystalline to the smectic phase. For the copolyesters **8** and **9** however, the layer thickness increases for about 2 \AA . The combination of optical textures and X-ray measurements (a smectic phase with liquid-like layers, tilted structures at room temperature) gives strong evidence for chiral smectic C^* phases. Temperature dependent X-ray measurements of oriented samples of the polymers **4**, **6** and **7** to determine the smectic C^* phases unambiguously are in progress [8]. In order to prepare cross-linked polymers with chiral phases, copolyesters with olefinic double bonds were synthesized (see table 2). As an achiral but cross-linkable repeating



Figure 2. Textures of polymer **9** (crossed polarizers) at (a) 140°C in the cholesteric phase, and (b) at 130°C in the smectic phase; polymer **6** (c) at 134°C in the smectic phase.

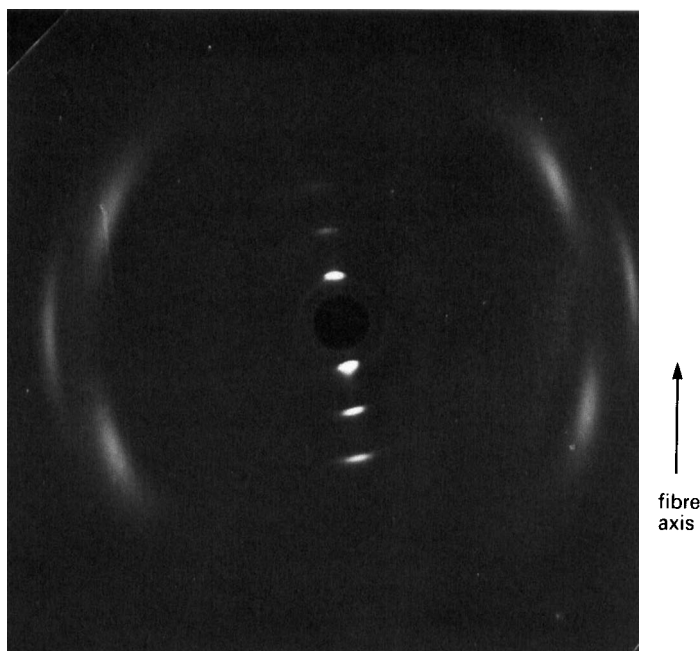


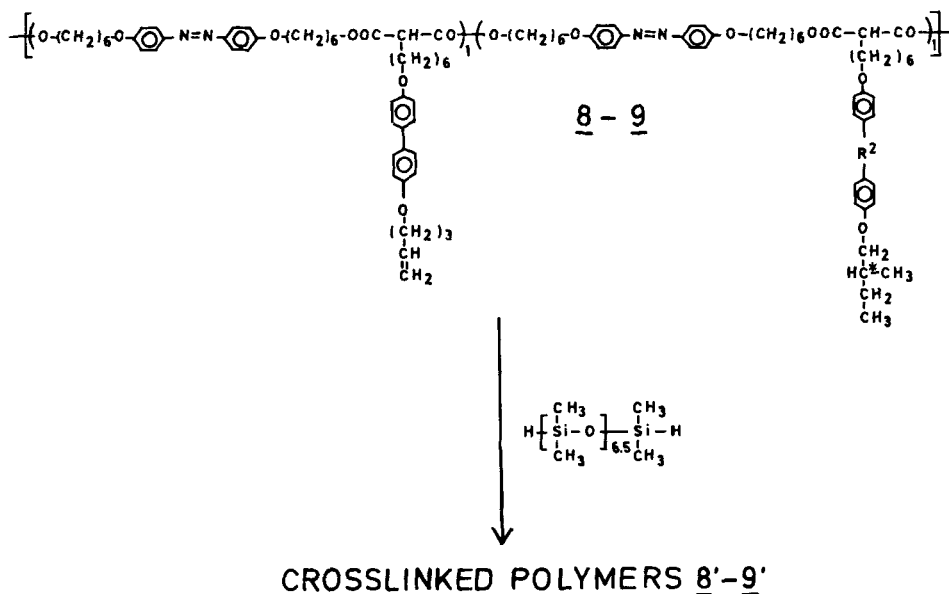
Figure 3. Fibre pattern of polymer **9'** at room temperature; distance from the sample to the film 94 mm; fibre axis vertical; the reflections correspond to Bragg-spacings of 24 Å (layers); 4.5 Å and 4.0 Å.

unit, the repeating unit on the left side of the structural formula of table 2 was chosen. A homopolymer built up from this repeating unit (polymer **12**) is described in [6]. The Si-H groups of the α -dimethylsilyl, ω -hydrogen-oligo (dimethylsiloxane) **10** (see table 2) can react by addition to the double bonds of the pentenyloxy end groups [9]. Thus, by reaction of some of the double bonds with Si-H bonds, cross-linked polymers (**8'** and **9'**) are prepared. After cross-linking the phase transition temperatures are reduced due to the presence of the non-mesogenic cross-linking agent **10**. This effect was also observed for achiral liquid crystalline polymers [6, 7].

3. Experimental part

4,4'-bis(6-hydroxyhexyl-oxy)biphenyl **1a** (m.p. 169°C), 4,4'-bis(6-hydroxyhexyl-oxy)azobenzene **1b** (m.p. 148°C) and 4,4'-bis(2-hydroxyethoxy)azobenzene **1c** (m.p. 202°C) were prepared as described in the literature [5]. The synthesis of the chiral mesogenic malonates **2** started with the conversion of (–)-2-methyl(*d*)-1-butanol ($[\alpha]_D^{20} = -5.90$; undiluted) into the corresponding tosylate (b.p.^{0.2}: 125°C) by analogy with known procedures [10]. 4-hydroxy(4'(2-methyl)butyloxy)biphenyl (m.p. 186°C, yield 43 per cent, $[\alpha]_D^{20} = 12.0$ in acetone) and 4-hydroxy(4'(2-methyl)butyloxy)azobenzene (m.p. 83°C, yield 30 per cent, $[\alpha]_D^{20} = 12.9$ in CH₂Cl₂) were prepared in the following manner: 0.1 mole of 4,4'-dihydroxybiphenyl or 4,4'-dihydroxyazobenzene were dissolved in a mixture of 25 g KOH, 70 ml ethanol and 35 ml of water. 24.3 g (0.1 mole) of 2-methyl(*d*)-1-butyl-*p*-toluene sulphonate in 10 ml of ethanol were added slowly and the mixture was refluxed for 6 hours. On cooling the di-ether precipitates. The filtrate was poured into cold 2 N NaOH in water. Immediately or after dilution with more water the mono-ether precipitates. It is purified by washing with 2 N NaOH and recrystallization from ethanol.

Table 2. Linear (**8** and **9**) and cross-linked (**8'** and **9'**) combined liquid-crystalline polymers and their characterization. Temperature dependent X-ray measurements of oriented fibres of the cross-linked polymers **8'** and **9'**, performed during the course of this publication, showed that the smectic phases are probably of the smectic A type. Originally chiral smectic C phases were expected. Since the layer thickness increases ($\approx 2 \text{ \AA}$) at the transition from the crystalline to the smectic phase for unoriented samples of the polymers **8** and **9**, this implies that also the uncross-linked polymers form smectic A phases.



No.	R^2	Molecular weight†	Mole per cent of cross-linking agent	Phase transition temperatures in °C
8	—	19000	—	K 116 S _A 135 I
8'	—	—	20	K 108 S _A 125 I
9	—N=N—	35000	—	K 115 S _A 133 N* 142 I
9'	—N=N—	—	20	K 101 S _A 135 I‡

† Determined by G.P.C. in comparison to polystyrene standards.

‡ The transition S_A-N and N-isotropic are broad and not resolved.

Diethyl 6-(4-(2-methyl-butyl-oxo)biphenyl-oxo) hexylmalonate **2a** (m.p. 65°C yield 30 per cent, $[\alpha]_D^{20} = +6.6$ in methylenedichloride) and diethyl 6-(4-(2-methyl-butyl-oxo)phenylazophenoxy)hexylmalonate **2b** (m.p. 61°C, yield 80 per cent, $[\alpha]_D^{20} = 7.5$ in methylenedichloride) were prepared according to [5]. All products were characterized by I.R. and $^1\text{H-N.M.R.}$ spectroscopy.

The melt polycondensation or copolycondensation was done according to [5]; the temperature did not exceed 180°C. Afterwards the polymers were dissolved in methylenedichloride and precipitated from diethylether. They were characterized by $^1\text{H-N.M.R.}$ spectroscopy and G.P.C. The optical rotation was determined with a Perkin-Elmer 241 instrument at four wavelengths and extrapolated to the sodium D line. All substances with an azo group have an absorption in the wavelength region

(360–570 nm) used for this extrapolation. Therefore the optical rotation for these polymers is less accurate. The results for the polymers in methylenedichloride are

$$\begin{array}{ll} \text{polymer 3: } [\alpha]_{\text{D}}^{20} = -3.88, & \text{polymer 4: } [\alpha]_{\text{D}}^{20} = -1.44, \\ \text{polymer 5: } [\alpha]_{\text{D}}^{20} = -25.7, & \text{polymer 6: } [\alpha]_{\text{D}}^{20} = -8.6, \\ \text{polymer 7: } [\alpha]_{\text{D}}^{20} = +3.27, & \text{polymer 8: } [\alpha]_{\text{D}}^{20} = +1.9, \\ \text{polymer 9: } [\alpha]_{\text{D}}^{20} = +2.25. & \end{array}$$

The cross-linking was done in dioxane with the α -dimethylsilyl, ω -hydrogen-oligo(dimethylsiloxane) **10** catalysed by dichlorodicyclopentadienyl-platinum [6]. The number average of the molecular weight of the cross-linking agent **10** was determined by $^1\text{H-N.M.R.}$

The liquid-crystalline phases of the linear and cross-linked polymers were studied by a Perkin-Elmer D.S.C.-2c differential scanning calorimeter (peak maxima) and by polarizing microscopy (microscope POL-BK II, Leitz in combination with a Mettler FB 2 hot stage). The X-ray experiments were performed with nickel filtered $\text{Cu K}\alpha$ radiation with a flat-plate camera.

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