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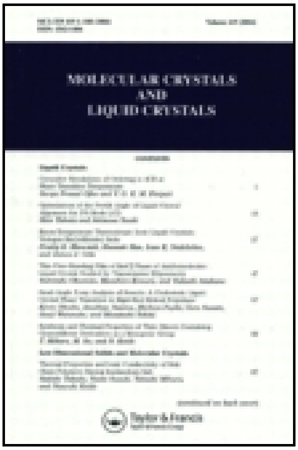

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Orientability of Crosslinked and of Chiral Liquid Crystalline Polymers

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ORIENTABILITY OF CROSSLINKED AND OF CHIRAL LIQUID CRYSTALLINE POLYMERS

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Abstract Crosslinked liquid crystalline (l.c.) polymers can be reversibly oriented in the l.c. phase by small mechanical strains. This property makes it very interesting to investigate chiral l.c. phases with a helical superstructure (cholesteric and chiral smectic C*). These phases can e.g. be realized with new combined main chain / side group polymers. In order to give a high spontaneous polarization to the polymers in the chiral smectic C* phase , polymers with a dipole moment at the chiral center were synthesized.

INTRODUCTION

Liquid crystalline (l.c.) polymers have been studied intensively during the recent years [1]. Most of the interest in these polymers results from their good orientability. Therefore we decided to investigate the strain induced orientation in different types of crosslinked l.c. polymers in more detail. The observed ease of this orientation made it interesting to synthesize also crosslinked l.c. polymers with chiral phases (cholesteric and chiral smectic C*). This paper describes investigations of the strain induced orientation in crosslinked l.c. polymers, X-ray measurements for their phase assignment and the synthesis of some new chiral l.c. polymers.

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STRAIN INDUCED ORIENTATION IN CROSSLINKED LIQUID CRYSTALLINE POLYMERS

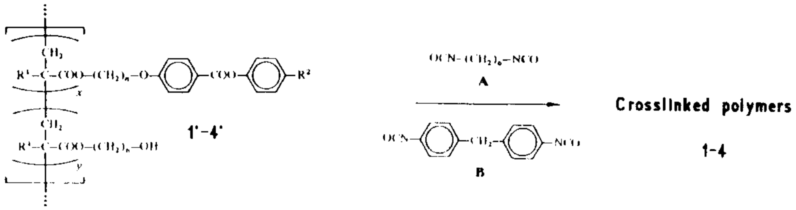
Starting from the first crosslinked liquid crystalline polysiloxanes [2], a variety of crosslinked liquid crystalline polymers has been synthesized during the recent years. These polymers include liquid crystalline side group polymers (polyacrylates, see Table I), main chain polymers (polymalonates, see Table II) and combined main chain / side group polymers (see Table III). The synthesis [3] and the phase assignment [4,5] (X-ray) of the polymers 1 -7 is already described elsewhere.
The synthesis of the new polymers 8 -9 was done in complete analogy to polymer 7 (see ref.[3]). The phase assignment was done as described in ref.[5] for the polymers 5-7. The results of temperature dependent X-ray measurements, which gives strong evidence for a smectic C phase in polymer 9, are presented in Figure 1. They show an increase of the smectic layer spacing with temperature in the s_C phase.

X-ray measurements

Most of the interest in liquid crystals results from the possibility of preparing well oriented samples in a simple way, Therefore, temperature dependent X-ray measurements were performed on stretched samples of the crosslinked polymers 1-7. It was the aim of these investigations, to determine the strain dependence of the orientation in the different liquid crystalline phases, and to compare them with the orientation in the isotropic phase at identical strains. The experimental set up for these investigations has already been described in ref.[5].

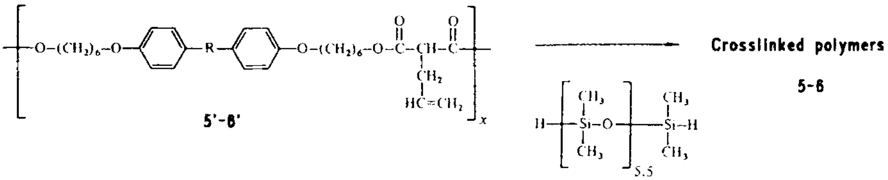
Starting with unoriented opaque samples of the crosslinked polymers, strains of more than 20% in the liquid crystalline phase resulted in well oriented samples (see Figures 2 and 3). The crosslinked polymers with nematic

TABLE I: Linear (1'-4') and crosslinked (1-4) liquid crystalline side group polymers



No	R¹	n	R²	Molecular weight	Amount of crosslinking agent(mol %)	Phase transitions in °C
1'	H	6	OCH_3	45000	-	g26 s_A82 n110 i
1	H	6	OCH_3	---	2.5(B)	g31 s_A80 n111 i
2'	H	2	OCH_3	100000	-	g56 n95 i
2	H	2	OCH_3	---	2.5(B)	g63 n 101
3'	CH_3	6	OCH_3	100000	-	g40 n106 i
3	CH_3	6	OCH_3	---	1.0(A)	g45 n107 i
4'	CH_3	6	OC_4H_9	100000	-	g45 s_A102 n106 i
4	CH_3	6	OC_4H_9	---	2.0(A)	g42 s_A104 n109 i

TABLE II: Linear (5'-6') and crosslinked (5-6) liquid crystalline main chain polymers



No	R	Molecular weight	Amount of crosslinking agent (mol %)	Phase transitions in °C
5'	-	80000	-	k61 s_B95 s_A113 i
5	-	---	5	k58 s_B87 s_A106 i
6'	-N=N-	20000	-	k34 s_A132 i
6	-N=N-	---	10	k31 s_A128 i

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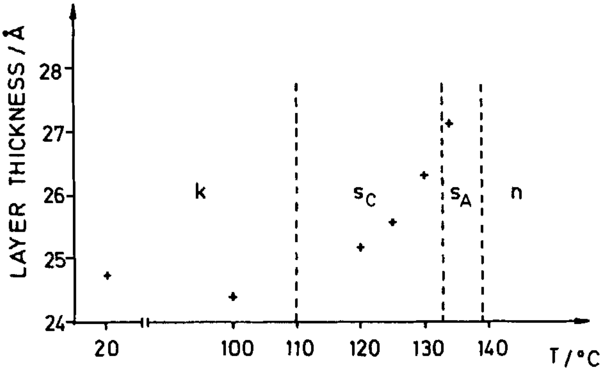
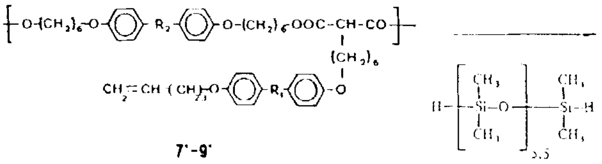


FIGURE 1: Thickness of the smectic layers in polymer 9' as function of temperature

TABLE III: Linear (7'-9') and crosslinked (7-9) combined main chain / side group polymers



7'-9'

Crosslinked polymers

7-9

No	R₂	R₁	Molecular weight	Amount of crosslinking agent (mol %)	Phase transitions in °C
7'	-N=N-	-	80000	-	k124 s_C150 s_A154 i
7	-N=N-	-	---	10	k119 s_C148 i[a]
8'		-N=N-	60000	-	k105 s_A149 i
8	--	-N=N-	---	20	k94 s_A137 i
9'	-N=N-	-N=N-	45000	-	k110s_C132s_A138n159i
9	-N=N-	-N=N-	---	10	k106s_C124[a] n151 i

[a] The transitions s_C to s_A are not resolved

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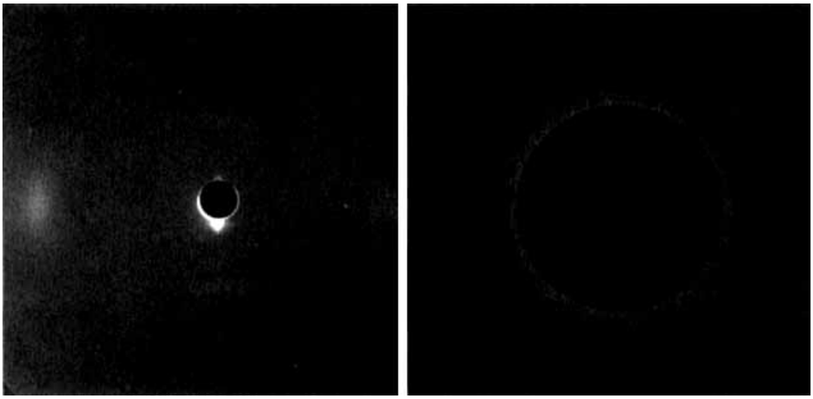
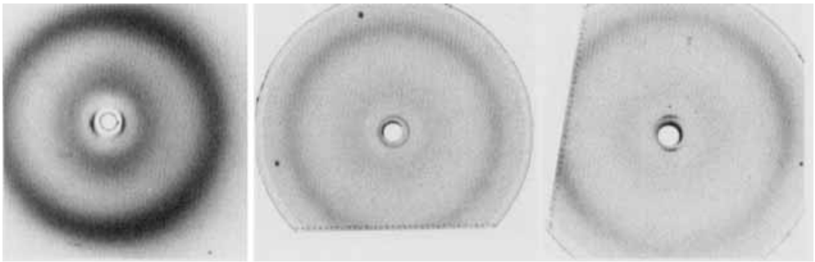


a) b)

FIGURE 2: Fiber pattern of polymer **6** at a strain of 50 % (fiber axis vertical); a) s_A-phase at 59°C, b) isotropic phase at 150°C; different distances sample - film were used; wide angle reflection: 4,3 Å, small angle reflection: 33 Å



a) b) c)

FIGURE 3: Fiber pattern of polymer **4** at room temperature in the s_A-phase; a) after a strain of 40 % in vertical direction, b) after relaxation in the isotropic phase, c) after a new strain of 40 % in horizontal direction (in this case the sample was cooled very quickly after the application of stress); wide angle reflection: 4,4 Å, small angle reflection: 28 Å

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phases became transparent during orientation. Higher stretching, up to 60 -80 % had no additional effects on the fiber pattern. That means, small strains are sufficient to obtain l.c. monodomains.

This strain dependence of the orientation is in agreement with the observations of other scientists on crosslinked l.c. side group polymers [6,7]. However no spontaneous orientation is observered in the stress free state, as reported for some crosslinked polysiloxanes [8], and the fiber pattern of uncrosslinked and crosslinked polymers are nearly identical [4,5].

The results of the side group polymers **1-4** are in complete agreement with earlier investigations [4]. In these investigations the same polymers had been stretched in the l.c. phase, but the X-ray measurements were performed afterwards in the glassy state. This correspondence proves that in fact equilibrium properties had been determined [4]. Again the mesogenic groups are oriented parallel to the direction of strain for the polyacrylates **1-2**, and perpendicular to the axis of strain for the polymethacrylates **3-4**.

In contrast to the l.c. phase, strains up to 80% had no measurable effect (X-ray) on the orientation in the isotropic phase, as shown in Figure 2 for the crosslinked main chain polymer **6**. This is analogous to the results of Finkelmann et al.[8] for crosslinked polysiloxanes.

If oriented samples are heated -free of stress- to the isotropic phase and are allowed to relax for some minutes, they return to their original unoriented state in the l.c. phase. Afterwards they can again be oriented in another direction by mechanical strains. This is shown in Figure 3 for the crosslinked side group polymer **4**.

Mechanical properties

The effects of the strain induced orientation (l.c. phase) and relaxation (isotropic phase) on the mechanical

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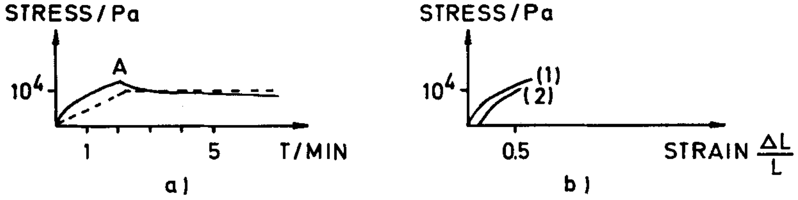

FIGURE 4:Stress-strain measurements on polymer 3 (strain rate:5 mm/min); a) the strain starts at 0 and stops at A ,(....)$^{\Delta l}/_{l}$:0.7, isotropic phase (110°C),(____)$^{\Delta l}/_{l}$:0.7, nematic phase (84°C), b) measurements at 84 °C in the nematic phase (1) first measurements on unoriented samples (2) repeated measurements on oriented samples

properties were investigated by stress-strain measurements for the crosslinked polymers **3-4** (see Figure 4). In the isotropic phase a normal elastic behavior is observed. In the l.c. phase, however, the stretching of a previously unoriented sample leads first to a macroscopic orientation and simultaneously to a stress relaxation. Afterwards, the oriented sample has changed dimensions in the stress free state. This strain induced orientation hardly relaxes, while the sample is in the l.c. phase. Therefore, the first measurement cannot be repeated directly. This can be done, however, if the sample is allowed to relax in the isotropic phase and then is cooled to the l.c. phase again (see Figure 4).

LIQUID CRYSTALLINE POLYMERS WITH CHIRAL PHASES

The results described above, show that it is easy to orient crosslinked l.c. polymers by application of mechanical strains. Therefore, it is interesting to look for l.c. phases, which show distinct changes of their properties during orientation. This should be especially interesting for polymers, which have the cholesteric and the chiral smectic C* phases. If it is possible to untwist the helical superstructure in these phases by mechanical forces, then a change of the selective reflection (cholesteric) or an electrical response (sc*) should result. This means, that the sample should itself act as a device which transforms a mechanical signal into an optical or an electrical signal.

The synthesis of the first uncrosslinked and crosslinked polymers, which form these phases has been described elsewhere [9]. But these polymers do not possess strong lateral dipole moments. Therefore no strong ferroelectric polarization can be expected in the chiral smectic C* phase.

Chiral polymers with dipole moments at the chiral center

Since it would be very interesting to prepare crosslinked polymers with strong ferroelectric polarizations resulting from the smectic C* phase, polymers are needed, which possess strong dipole moments close to the chiral center. For this purpose we prepared the combined main chain/ side group polymers **10** – **12** with chiral chloro-alcohols as end groups. These chloro-alcohols were prepared from amino acids [10]. The phase transition temperatures of the polymers **10** – **12** are summarized in Table IV. Their phase assignment was done in analogy to that of polymers **5** – **9**. The details of the synthesis and the phase assignment of these polymers will be published elsewhere [11].

EXPERIMENTAL PART

The synthesis of the polymers **8-9** was done in analogy to the procedures of ref.[3]. The X-ray measurements were performed as described in ref.[6].

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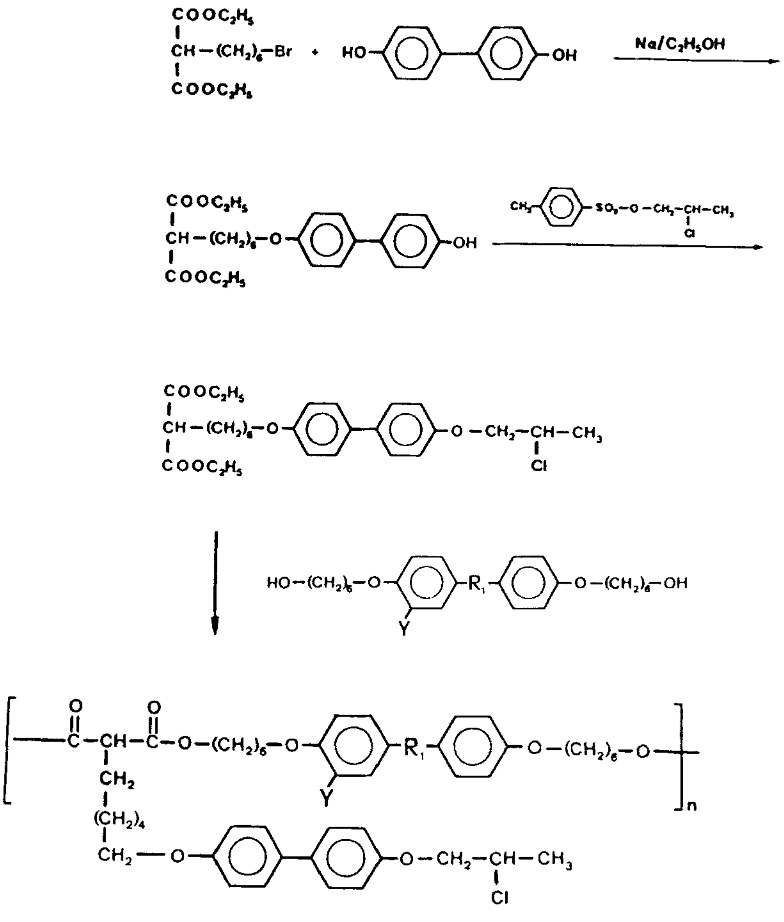
TABLE IV: Uncrosslinked combined main chain/ side group polymers (10-12) with chiral constituents



10-12

No	R1	Y	Phase transitions in °C
10	--	Br	k 45 n* 111 i
11	-N=N-	--	k 109 sc 149 i
12	-N=N(O)-	--	k 57 sc 140 sA 149 i

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