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## Liquid Crystals

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### Shape variation of cross-linked liquid-crystalline polymers by electric fields

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## Shape variation of cross-linked liquid-crystalline polymers by electric fields

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First experiments show that cross-linked liquid-crystalline polymers, which are swollen with nematic low molar mass liquid crystals and freely dispersed in this liquid crystal, change their shape if an electric field is applied. This shape variation depends on the degree of swelling.

Low molar mass liquid crystals [1] as well as polymeric liquid crystals [2-5] can be oriented in electric fields. Cross-linked networks prepared from the same polymers however behave differently. In first attempts to orient cross-linked liquid-crystalline polysiloxanes in electric or magnetic fields between glass plates or in N.M.R. tubes [6] no field effects were observed. This is probably because of the following reasons. An orientation of the mesogenic groups leads to a small but distinct orientation of the polymer chains [7-9] (prolate or oblate polymer coils). If the orientation of the mesogenic groups is changed by an electric field, the polymer chains must rearrange. In networks where all the polymer chains are linked covalently, this is difficult because the netpoints are fixed and because entanglements cause additional problems. In addition a reorientation of the polymer chains should lead to a change of the shape of the sample, because elastic forces try to change the position of the netpoints relative to each other (see figure 1). As the geometry of the sample is kept constant by mechanical forces (the surrounding glass plates), the preservation of the previous anisotropy of the polymer coils counteracts the tendency of the mesogenic groups to change their orientation in an electrical field.

The intention of this work was to use small pieces of cross-linked liquid-crystalline polymers swollen in a low molar mass nematic mixture to increase the tendency towards orientation in electric fields (only some mesogens are fixed to the polymer chains, but all try to orient). In addition these polymers were freely dispersed in the same nematic mixture to allow shape variations during the orientation of the mesogenic groups.

Two liquid-crystalline side group polymers with polyacrylate (polymer 1) and polymethacrylate chains (polymer 2) were used. Besides this they differed in the cross-linking density. The cross-linked polymers are specified in the table; their synthesis and characterization is described elsewhere [10, 11]. The pure uncross-linked polymer 1' orients homeotropically in electric fields [5]. Small pieces of the cross-linked polymers (10-100  $\mu\text{m}$ ) were prepared from larger samples by cutting with a microtome (polymer 1, thickness 2  $\mu\text{m}$ ) or simple grinding (polymer 2). These samples

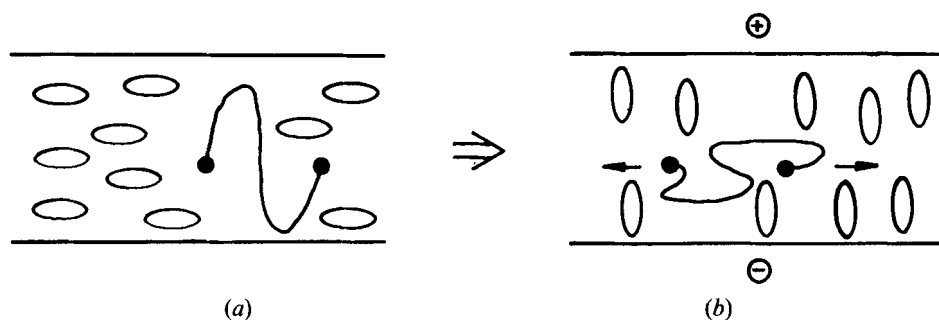
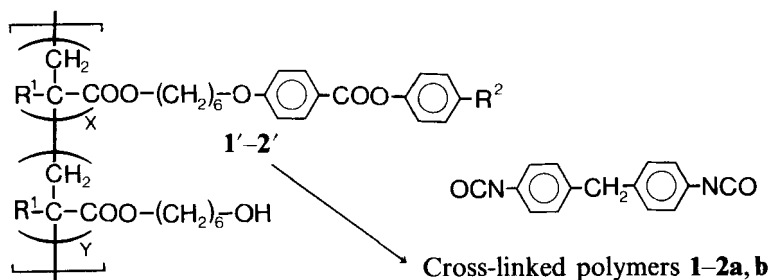


Figure 1. Schematic representation of the effect of reorientation of the mesogenic groups ( $\circ$ ) on the position of the netpoints ( $\bullet$ ) in a system with an anisotropic shape of the polymer chains ( $\sim$ ). Before the application of an electric field (a) a polymer chain, that tends to orient perpendicular to the long axes of the mesogenic groups, links two netpoints. The application of an electric field (b) leads to a reorientation of the mesogenic groups and to the corresponding reorientation of the polymer chain between the netpoints. However now the polymer chain is much too long and tries to increase the distance between the netpoints. This leads to a macroscopic shape variation.

Linear (1' and 2') and cross-linked (1 and 2a, b) liquid-crystalline side group polymers; the cross-linked polymers 1 and 2a, b were prepared from the polymers 1' and 2' respectively by reaction with diphenylmethane di-isocyanate (A).



No.	R <sup>1</sup>	R <sup>2</sup>	X: Y	Molecular weight (GPC)	Mole % of cross-linking agent	Degree of swelling† in wt %	Phase transition‡ temperatures
1'	H	CN	1:0.08	22000	—	—	g 29°C N 116°C I
1a	H	CN	1:0.08	—	2.0 (A)	140	g 27°C N 116°C I
2'	CH <sub>3</sub>	OCH <sub>3</sub>	1:0.05	> 100000	—	—	g 40°C N 106°C I
2a	CH <sub>3</sub>	OCH <sub>3</sub>	1:0.05	—	2.5 (A)	300	g 45°C N 106°C I
2b	CH <sub>3</sub>	OCH <sub>3</sub>	1:0.05	—	1.0 (A)	630	g 43°C N 107°C I

† Degree of swelling (toluene) in wt % at room temperature referred to the extracted polymer

‡ g, glassy liquid crystal; N, nematic; I, isotropic melt.

Figure 2. The effect of an electric field on a small particle (approximately  $120 \times 60 \mu\text{m}$ ) of polymer 2a at 72°C; (a) without electric field, (b) after application of an electric field of 30 V.

Figure 3. The effect of an electric field on particles (approximately  $70 \times 60 \mu\text{m}$  for the small particle on the right) of polymer 2b at 70°C; (a) without an electric field, (b) after application of an electric field of 30 V.



Figure 2 (b)

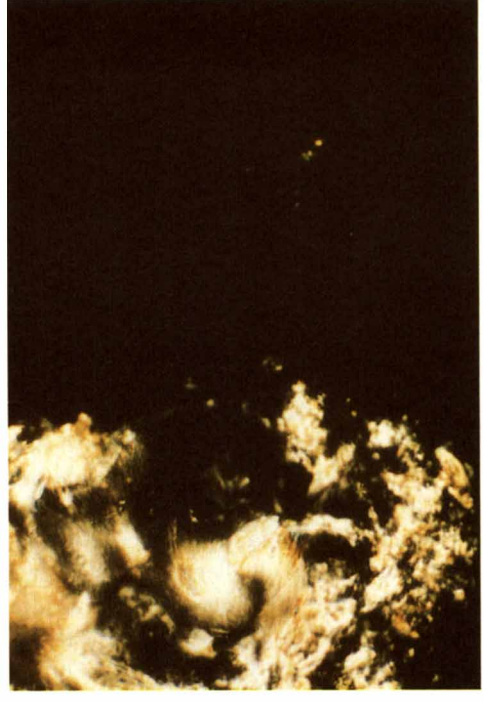


Figure 3 (b)



Figure 2 (a)

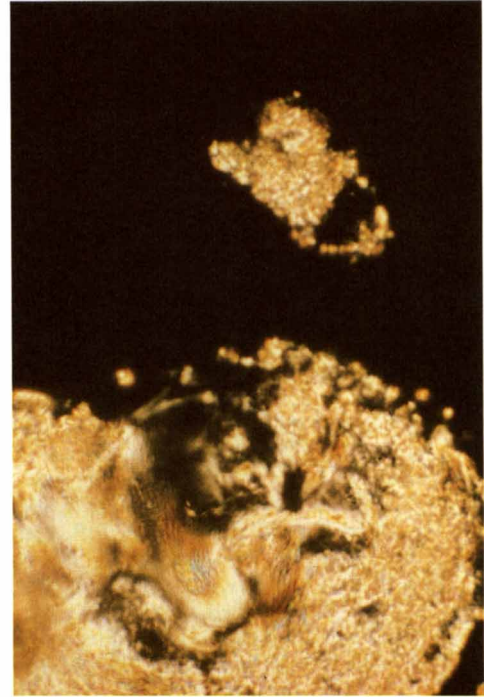


Figure 3 (a)

were dispersed in the nematic mixture 1132 TNC from Merck, Darmstadt (it is a phenyl-cyclohexane mixture), with a clearing point of 69°C. This dispersion was investigated in a liquid crystal display built up from two electrically conducting glass slides and a teflon spacer of 50  $\mu\text{m}$  thickness. It was thermostated at 60–70°C for several hours to allow swelling of the polymer samples. During the swelling, the volume of the cross-linked particles increased strongly. If they just fitted in between the two glass slides at the beginning, they became compressed at the end. Thereafter the clearing points of the cross-linked polymers were reduced in comparison to the pure polymers, but still some degrees higher than the clearing points of the nematic mixture 1132 TNC (69°C). The investigations were then performed in the biphasic region (1132 TNC: isotropic, swollen polymers: nematic).

The experiments gave the following results. If the swollen polymers **1** and **2a** are freely suspended, the application of an electric field ( $\approx 30$  V) leads to a rapid shape variation (faster than 1 s) as shown in figure 2. This shape variation is completely reversible; but the polymers do not orient homeotropically up to 60 V. Although the samples were free to change their shape, the steric restrictions due to the netpoints and entanglements do not allow a complete reorientation in the higher cross-linked polymers **1** and **2a**. No principle difference is observed between these two polymers, although in the swollen polymer **2a**, which has no strong dipole moments parallel to the long axes of the mesogenic groups, only the low molar mass nematic mixture enables the orientation. Contrary to this no electric field effect is observed up to 60 V, if the swollen polymers **1** and **2a** are compressed between the two glass slides. This corresponds to the effects described previously, that the conservation of the polymer geometry by the glass slides prevents the orientation of the mesogenic groups.

In the weaker cross-linked and higher swollen polymer **2b** application of an electric field leads to at least a partial homeotropic orientation of the sample (see figure 3). The regions that do not orient are probably highly pressed between the glass slides. Obviously the steric restrictions due to the netpoints and entanglements are less pronounced in the higher swollen networks. If the samples are not fixed between the glass slides, they change their shapes. These results confirm the working hypothesis, that a reorientation of the mesogenic groups leads to a reorientation of the polymer chains and consequently in cross-linked polymers to a shape variation. However other reasons for the observed effects such as changes in the surface tension or ionic currents cannot be excluded at this stage.

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