

The future of ceramics in Europe requires a joint (international) effort. This does not mean that the ceramists want to stay in an isolated position and are not interested in developments in other fields of materials science. On the contrary, in some areas there is so much overlap of interests that a cooperation with for instance, metallurgists or polymer chemists is certainly necessary and fruitful. For ceramists this is not new, since ceramics has always been an interdisciplinary science practised by chemists, physicists and metallurgists and now, as a result, the European Society

is always open for discussions with other societies or for bilateral meetings.

In this respect cooperation in education should be encouraged in order that European materials science and technology will in the future hold a strong position in the world of advanced materials. The ECerS is ready to contribute and participate.

[1] For a Conference Report see R. J. Brook, *Adv. Mater.* 1989 No. 11; *Angew. Chem. Int. Ed. Engl. Adv. Mater.* 28 (1989) No. 11; *Angew. Chem. Adv. Mater.* 101 (1989) No. 11.

Liquid Crystalline Elastomers

By Rudolf Zentel *

Crosslinkable Polymers
Chiral Phases
Piezo Electric Effects
Mechanical Orientability
Rubber-Like Elasticity

Today, material science is directed towards the development of multifunctional and oriented structures. One example of such supramolecular systems are liquid crystalline (LC) elastomers which combine the properties of LC phases (the combination of order and mobility) with rubber elasticity, one of the most typical polymer properties. Their most outstanding characteristic is their mechanical orientability; strains as small as 20 % are enough to obtain a perfectly oriented LC monodomain. This orientability, if LC elastomers with chiral phases are used, leads, for example, to elastomers with chiral smectic C* phases which are likely to show piezo-electric behavior.

1. Introduction

LC Phases combine the long range order of crystals with the mobility of liquids. Their formation from molecules with anisotropic forms, the so called "mesogenic" groups, has long been known for low molar mass compounds and structure-property relationships are well established.^[1, 2] These LC Phases are thermodynamically stable phases that exist in a temperature range between the crystalline phase and the isotropic melt. For rod-like mesogenic groups, these phases can be subdivided into the nematic phase, for which the long range order is only caused by the — more or less — parallel orientation of the mesogenic groups, and into different smectic phases, in which the molecules are additionally arranged in layers. Different orientations of the mesogenic groups with respect to the layers, which can be perpendicular or tilted, are the basis for a further discrimination between smectic A and smectic C phases (Fig. 1). The transitions among the different phases can be detected by, for example,

differential scanning calorimetry (DSC) which measures the latent heat associated with the phase transitions. The most prominent property of these phases is their orientability in electric and magnetic fields.

LC Polymers^[3-5] combine the self organization of the mesogenic groups into the ordered structure of LC phases with some typical polymer properties, such as the freezing of the disorder of the polymer chain at the glass transition temperature. Thus, in most cases, the LC phases also freeze glassy on cooling. In addition, an induced orientation can be frozen-in. LC Polymers can be prepared by incorporating the anisotropic mesogenic groups into polymeric systems. Three different ways (Fig. 2) to do this will be discussed, the first two of which are most commonly used. First, the mesogenic groups can be linked to the polymer chain as side groups, to produce LC side group polymers. Second, they

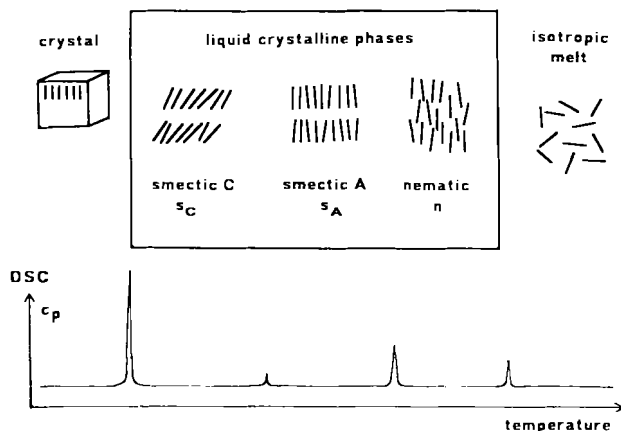


Fig. 1. Schematic representation of different LC phases that exist at temperatures between the crystalline and the isotropic phase. The transitions between these phases show up as peaks in Differential Scanning Calorimetry (DSC) measurements (C_p vs. temperature).

[*] Priv. Doz. Dr. R. Zentel
Institut für Organische Chemie
Universität Mainz, J.-J. Becher-Weg 18-20
D-6500 Mainz (FRG)

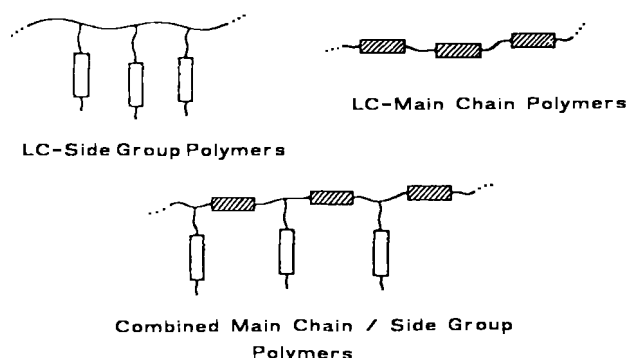


Fig. 2. Different types of LC polymers [5].

can be incorporated into the polymer chain, to obtain LC main chain polymers. Third, both structural principles can be combined, to prepare combined main chain/side group polymers ("combined" LC polymers).^[5]

LC Elastomers (Fig. 3) combine the properties already discussed, with rubber elasticity. In these systems a macro-

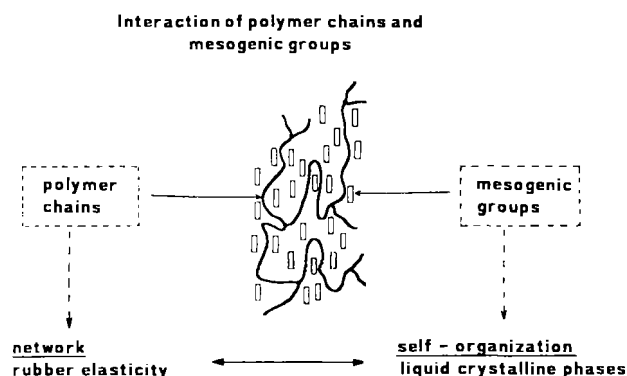


Fig. 3. Schematic representation of a crosslinked LC elastomer. The linkage between polymer chains and mesogenic groups is not yet specified.

scopic deformation of the crosslinked sample (above the glass transition temperature) leads to a corresponding equilibrium deformation of the polymer chains. Different degrees of orientation of the polymer chains can be achieved by stretching the macroscopic sample to different degrees. Afterwards an orientation of the mesogenic groups, which results due to interactions of polymer chains and mesogenic groups, can be determined under equilibrium conditions. In

uncrosslinked LC polymers however, non equilibrium orientations resulting from flow above the glass transition temperature have to be frozen-in below T_g . Therefore LC elastomers seem to be ideal systems in which to investigate the interaction of the orientation of the polymer chains (induced by mechanical fields) and that of the mesogenic groups (induced by electric fields). As polymer networks, which are not liquid crystalline, cannot be swollen with mesogenic groups in the LC phase due to incompatibility,^[6] the mesogenic groups must be linked covalently to the polymer chains (Fig. 4) to prevent a demixing.

In the following, ways to prepare differently structured LC elastomers (see Section 2.1.), as well as their properties, will be discussed. This will be done for achiral LC elastomers (see Section 2.2.) which have been studied most intensively, and then for the new elastomers with chiral LC phases (see Section 2.3.) which are interesting because of their optical and electrical properties.

2. Liquid Crystalline Elastomers

2.1. Structural Variation of Achiral Elastomers

Densely crosslinked thermosets with a liquid crystalline structure that remains unchanged up to the decomposition temperature of the polymer have been known for some time.^[7,8] Slightly crosslinked LC polymers, however, which show reversible phase transitions on heating and cooling and which show elastic properties, are relatively new. The first to be prepared were based on crosslinked side-group polymers (Fig. 4) with a polysiloxane backbone.^[9-12] This work has been summarized by Finkelmann et al.^[13] Shortly afterwards the work on LC elastomers was extended to crosslinked side group polymers with polyacrylate and polymethacrylate backbones^[14-18] and also to slightly crosslinked main chain polymers and "combined" polymers (Fig. 4).^[14,19,20] A comparative investigation of LC elastomers of these different structures is interesting because the behavior of the two "subsystems" (network of the polymer chains—mesogenic groups) in each case should be different. Thus the coupling between the orientation of polymer chains and mesogenic groups should differ significantly for the different types (Fig. 4). For crosslinked side group polymers the orientation



Rudolf Zentel (born 1953) studied chemistry at the University of Mainz, FRG, obtaining his Diploma in 1980 and his Ph.D. in 1983 after working with Professors G. Strobl and H. Ringsdorf. After this, he spent one year as a post-doctoral fellow at the University of Freiburg with Professor H.-J. Cantow, and then returned to Mainz in 1984 to start work on "Liquid Crystalline Elastomers". In April 1989 he finished his Habilitation and obtained the "Venia Legendi" in Organic Chemistry. Since July 1989 he has been at the IBM Almaden Research Center in San Jose (USA) as a Visiting Scientist working on materials for optical data storage. He has published 27 papers on various topics in polymer chemistry.

of the mesogenic groups is relatively free with respect to the polymer chain, since they are decoupled by a flexible spacer. In crosslinked main chain polymers, however, the mesogenic groups are directly incorporated into the polymer chains. Crosslinked "combined" polymers may behave in an intermediate manner because one half of the mesogenic groups are incorporated into the polymer chains, while the other half are linked to the polymer backbone as side groups via a flexible spacer. Both types of mesogens must, however, interact cooperatively to form an LC phase (both types of mesogens orient parallel to each other (Fig. 4)).^[19]

Crosslinked Side-Group Polymers

Main-Chain Polymers

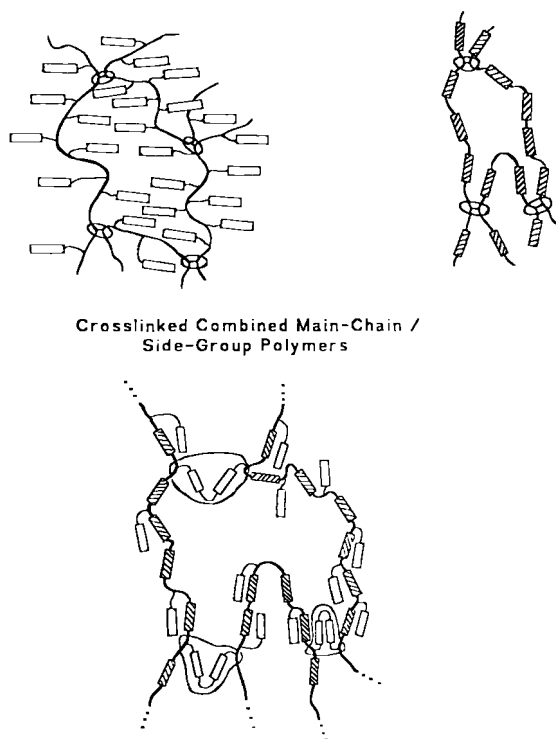
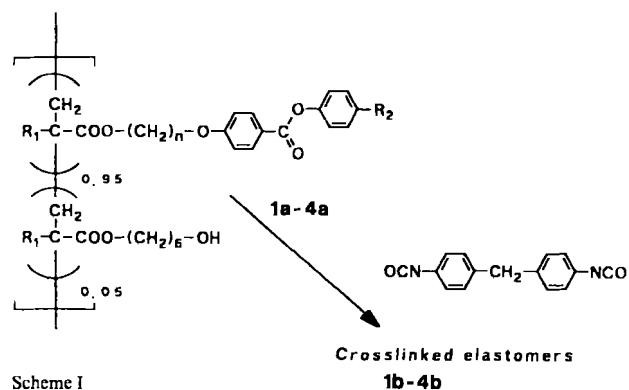


Fig. 4. Schematic representation of different types of LC elastomers.

Some of the LC elastomers derived from side group polymers are presented in Scheme I and Table 1. Due to the use



Scheme I

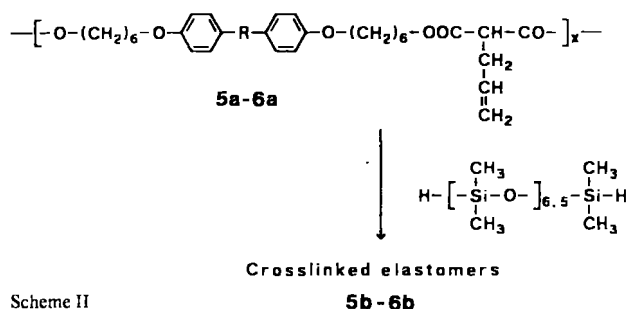
Table 1. Phase transitions of uncrosslinked (a) and crosslinked (b) LC side group polymers [14, 17] (see Scheme I).

No.	R ₁	n	R ₂	Molecular weight (GPC)	Cross linker (mol.-%)	Phase transitions ^[a] /K
1a	CH ₃	6	OCH ₃	> 100 000	—	g313 n379 i
1b	CH ₃	6	OCH ₃	—	0.5	g315 n379 i
2a	CH ₃	6	O-(CH ₂) ₃ CH ₃	> 100 000	—	g318 s _A 375 n379 i
2b	CH ₃	6	O-(CH ₂) ₃ CH ₃	—	3.5	g318 s _A 377 n382 i
3a	H	6	OCH ₃	45 000	—	g299 s _A 355 n383 i
3b	H	6	OCH ₃	—	2.5	g304 s _A 353 n384 i
4a	H	2	OCH ₃	> 100 000	—	g329 n368 i
4b	H	2	OCH ₃	—	2.5	g336 n376 i

[a] g: glassy frozen liquid crystal, s_A: smectic A, n: nematic, i: isotropic melt.

of functionalized polymethacrylates (**1a–2a**) and polyacrylates (**3a–4a**) of a high molecular weight, small amounts of diisocyanates are sufficient to prepare crosslinked samples (**1b–4b**). For the preparation of crosslinked polysiloxanes, however,^[9–12] much higher amounts of crosslinker are necessary, due to the lower molecular weight of the precursor polymers.

Some of the LC elastomers derived from main chain polymers are presented in Scheme II and Table 2. In this case the



Scheme II

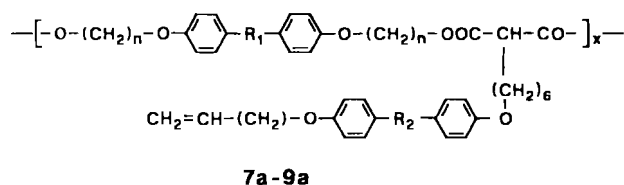
Table 2. Phase transitions of uncrosslinked (a) and crosslinked (b) LC main chain polymers [14, 19] (see Scheme II).

No.	R	Molecular weight (GPC)	Cross-linker (mol.-%)	Phase transitions ^[a] /K
5a	—	> 80 000	—	c334 s _B 368 s _A 386 i
5b	—	—	5	c329 s _B 368 s _A 389 i
6a	—N=N—	20 000	—	c307 s _A 405 i
6b	—N=N—	—	10	c304 s _A 401 i

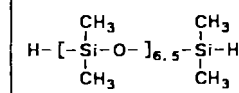
[a] c: crystalline, s_A: smectic A, s_B: smectic B, i: isotropic melt

crosslinking is performed by reaction of some of the olefinic double bonds of the polymer with the Si-H groups of an α, ω difunctionalized oligosiloxane.^[14, 20] Thus crosslinked polymers with different smectic phases can be obtained.

In Scheme III and Table 3 some of the LC elastomers derived from "combined" polymers are presented. Again the



7a-9a



Crosslinked elastomers

7b-9b

Scheme III

Table 3. Phase transitions of uncrosslinked (a) and crosslinked (b) combined LC polymers [14, 19, 20] (see Scheme III).

No.	R ₁	R ₂	Molecular weight (GPC)	Cross linker (mol.-%)	Phase transitions ^[a] /K
7a	-N=N-	-	> 80 000	-	c397 s _c 423 s _A 427 i
7b	-N=N-	-	-	10	c392 s _c 421 i ^[b]
8a	-N=N-	-N=N-	45 000	-	c383 s _c 405 s _A 411 n433 i
8b	-N=N-	-N=N-	-	10	c379 s _c 397 n424 i ^[b]
9a	-N(O)=N-	-N=N-	52 000	-	g293 s _c 399 s _A 407 n437 i
9b	-N(O)=N-	-N=N-	-	10	g293 s _c 395 s _A 403 n434 i

[a] c: crystalline or highly ordered smectic phase, s_c: smectic C, s_A: smectic A, n: nematic, i: isotropic melt. [b] the transitions s_c-s_A and s_A-n or i are not resolved.

crosslinking is done by a hydrosilylation reaction between the Si-H groups of the oligosiloxane and some of the double bonds at the end of the mesogenic side groups.^[14, 19, 20] The "combined" LC polymers show a strong polymorphism (Tab. 3, see also^[5b]) which means that different LC phases are often found for one polymer at different temperatures.

2.2. Properties of Achiral LC Elastomers

The basic properties of LC elastomers—such as: phase behavior, elasticity and orientability—are independent of their molecular structure (see Scheme I–III and Fig. 4).

The LC phase is retained for the crosslinked elastomers. X-Ray measurements performed with the uncrosslinked and the slightly crosslinked polymers (see Tab. 1–3) show the same LC phases.^[14, 17–20] Only for higher crosslinking densities are changes of the X-ray pattern sometimes observed.^[12] Thus the crosslinking reaction, which transforms a soluble polymer into a soft solid and prevents diffusion of the polymer chains, does not influence the LC order.

As long as the crosslinking density is low, the phase transition temperatures are not shifted significantly.^[9, 13–17] Only a slight increase or decrease (± 5 K) is observed (see Tab. 1–3 and Fig. 5) by DSC-measurements. A decrease of the phase transition temperature derives from the presence

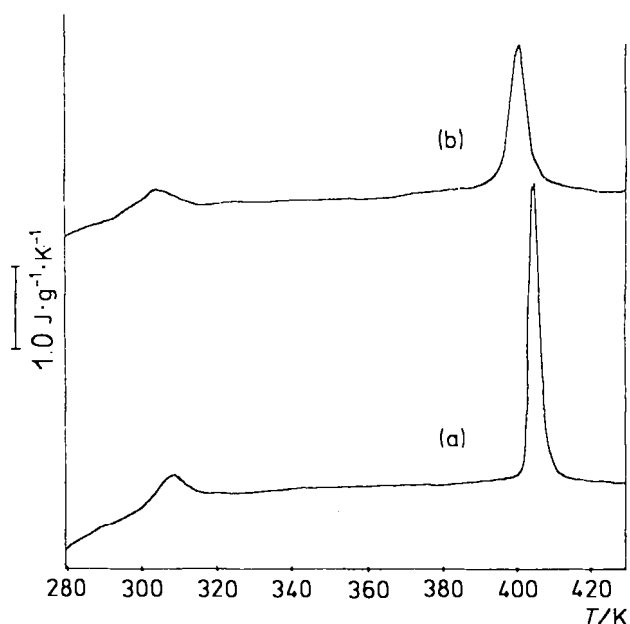


Fig. 5. DSC-measurements of the uncrosslinked main chain polymer 6a (a) and the crosslinked elastomer 6b (b) (Tab. 2), figure taken from ref. [14].

of the crosslinking molecules (diisocyanates or oligosiloxanes) at the netpoints, which are not mesogenic by themselves and disturb the LC order. An increase of the phase transition temperature may result from an increase of the molecular weight associated with the crosslinking reaction (an increase of the molecular weight increases the phase transition temperatures for uncrosslinked polymers).^[21] Theory further predicts that the state of order during the crosslinking reaction (LC or isotropic phase) should influence the phase transition temperatures of the final network,^[22] because the distribution of the netpoints should stabilize the state of order experienced during the crosslinking reaction.

All slightly crosslinked LC polymers show elastic properties (LC elastomers) both in the isotropic and in the LC phase. This is shown for one crosslinked side group polymer with a polymethacrylate chain by the mechanical-dynamical measurements shown in Figure 6^[23] (the results of the crosslinked polysiloxanes are described elsewhere).^[10, 12, 13, 24, 25] This behavior is also found for crosslinked main chain and "combined" polymers.^[23, 26]

In the isotropic phase a "normal" rubber-like behavior is observed.^[12, 13, 23–26] This is evident from the (rubber)-plateau in the real part of the compliance (J') at low frequencies (Fig. 6a). The plateau compliance is the same as that of slightly crosslinked elastomers that are not liquid crystalline. The decrease of J' at high frequencies, which is associated with a maximum in J'' , is due to the dynamic glass process and the slippage of entanglements. The presence of LC phases at lower temperatures only shows up in a strong increase of the stress optical coefficient^[10–13] at temperatures close to the transition into the nematic phase (pretransitional effects).

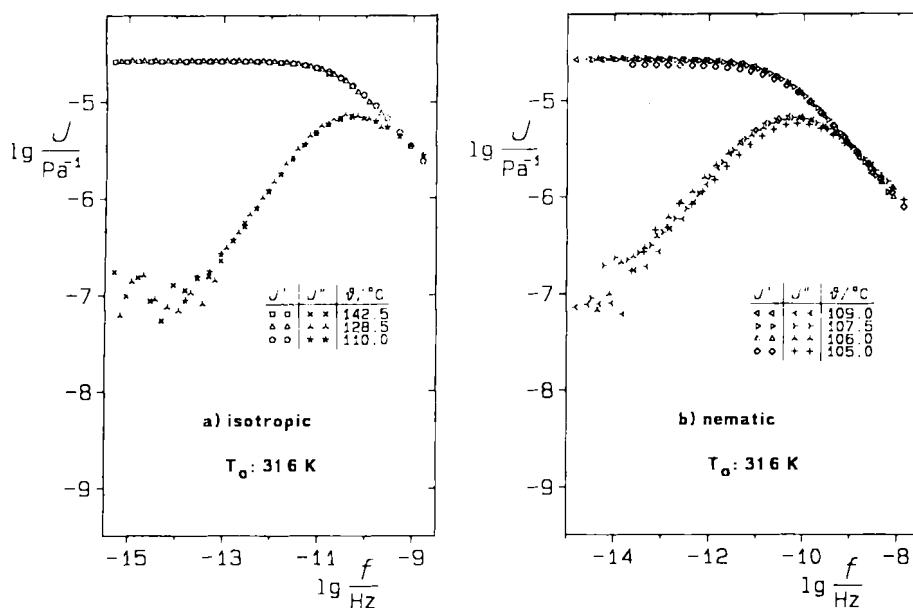


Fig. 6. Mastercurve obtained for the LC side group elastomer **2b** (Tab. 1). The real (J') and the imaginary (J'') part of the complex mechanical compliance is plotted. The measurements were performed in the isotropic (a) and in the unoriented nematic (b) phase (frequencies between 10^{-6} – 10^{-2} Hz) and shifted to a reference temperature of 316 K. Measurement performed by Hanus and Pechhold [23].

In the nematic phase the plateau compliance is the same as in the isotropic phase (see Fig. 6b). This proves that the chain conformation is not significantly changed at the transition to the nematic phase.^[27] This result is consistent with the results obtained by neutron scattering of uncrosslinked LC polymers of a similar structure,^[28] which show that the radius of gyration is slightly anisotropic in the nematic phase, but the averaged value is the same as in the isotropic phase. At the transition into the smectic A phase (layer structure), the plateau compliance is reduced, but the material remains elastic.

Care has to be taken in interpreting the mechanical measurements in the LC phase, because different properties are found for macroscopically unoriented samples (this corresponds more to the isotropic phase) and for LC monodomains (anisotropic elastic properties). These monodomains show—in addition—changed dimensions in the stress-free state,^[12, 25, 29] leading to a stress relaxation during formation. They can be produced—quite accidentally—by small strains during the measurement^[10–14, 17–19, 24–26, 29] and sometimes they form spontaneously^[12, 24] in highly crosslinked networks.

The mechanical orientability is the most prominent property of LC elastomers.^[10–14, 17–19, 24–26, 29] If the network does not orient spontaneously in the LC phase (that means, if the ground state is macroscopically unoriented), then small strains (about 20%) are enough for the reversible formation of an LC monodomain (Fig. 8).^[13, 25, 29] This orientation is achieved under equilibrium conditions far above the glass transition temperature. It is not necessary to freeze-in an orientation induced by flow, as in uncrosslinked LC polymers. Schätzle et al. were able to determine a threshold stress^[25] for the reversible orientation of LC elastomers. Also a small shift of the phase transition temperatures of about 2 K can be induced by stretching^[13, 25] and has been

theoretically explained.^[22, 30] The orientation induced by the same strain is orders of magnitude smaller if the elastomer is in the isotropic phase. This corresponds to the situation in non LC elastomers, for which strains up to 1000% are necessary to obtain a very well oriented sample. Such behavior is found for all types of LC elastomers (Fig. 4) independent of their molecular structure.^[29] Differences that are expected e.g. between crosslinked side group and main chain polymers (Fig. 4), may be hidden behind differences in the crosslinking density and the network topology.

The measurement of the strain induced orientation is done with the help of birefringence measurements^[10, 12, 25] (only isotropic phase), measurements of the IR-dichroism^[11, 25] and X-ray measurements^[17–19, 29] (isotropic and LC phase). In this way X-ray measurements, as presented in Figure 7 (polymer **3b** of Tab. 1) were obtained. This X-ray pattern can be used for an accurate assignment of the LC

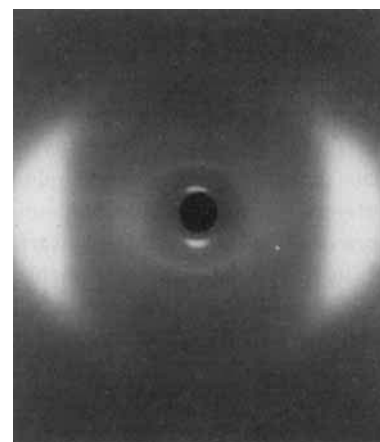


Fig. 7. Fiber pattern of elastomer **3b** (Tab. 1) in the smectic A phase (room temp.), strain $\Delta l/l_0 = 0.73$, fiber axis vertical, figure taken from ref. [17].

phases and, in addition, for a determination of the macroscopic orientation of the sample, as done by Mitchell et al.^[18] for a similar elastomer (Fig. 8). The orientation, which is reached at an extension ratio of 1.3, corresponds to a monodomain of a nematic polymer. It can be frozen-in below the glass transition temperature.

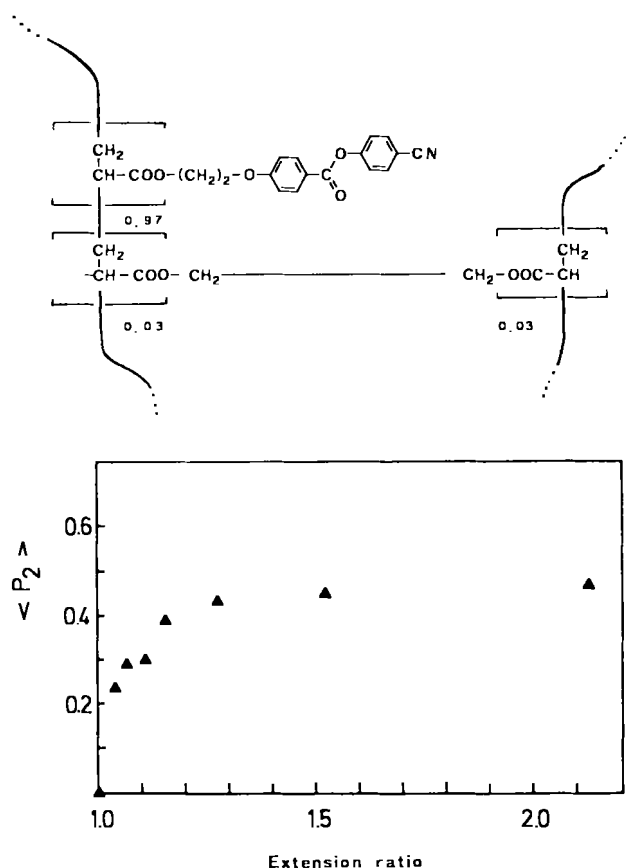


Fig. 8. A plot of the orientation parameter $\langle P_2 \rangle$ for the LC elastomer presented above; the ordinate corresponds to the extension applied. Figure taken from ref. [18] (Mitchell et al.).

The mechanical orientability of the LC elastomers is presumably due to the anisotropic conformation, which the polymer chains adopt in the LC phase^[28] (Fig. 3). Therefore the average distance between two crosslinks in a network does not only depend on the chain length between them, but also on the orientation relative to the long axis of the mesogenic groups. This leads to a coupling of the preferred orientation of polymer chains and mesogenic groups, which has been described theoretically by various authors.^[22, 30]

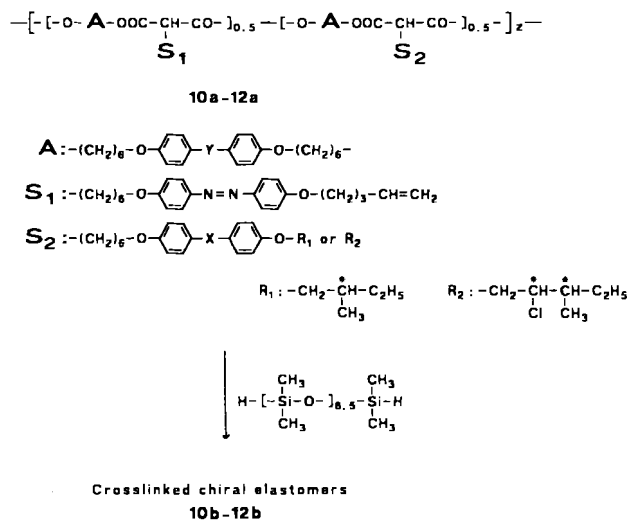
The reversible mechanical orientability of LC elastomers is of considerable interest for the following reasons: For most applications LC phases must be well aligned. LC elastomers thus offer a simple way to do this under equilibrium conditions. The aligned samples can then be used e.g. for an accurate phase assignment by X-ray measurements (Fig. 7),^[19, 26] for the determination of the orientation of polymer chains and mesogenic groups with respect to each

other^[10, 12, 17] or because of their optical properties. Their application as wave guides seems possible,^[31] because the local orientation and thus the birefringence can be changed by local strains. In addition, the orientation of an unoriented LC sample into a monodomain transforms reversibly a highly turbid sample into a transparent one. Therefore applications as mechanical-optical switches may be considered.

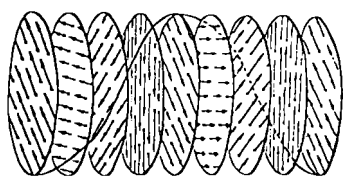
The anisotropic dielectric properties should also be considered. The stretching of a sample leads to orientation and changes the effective dielectric constant. This can be detected dielectrically. In turn, the action of electric fields on the material can lead to shape variations of the sample,^[15] because the elastomers (soft solids) try to orient the axis of their maximal dielectric constant parallel to the electric field.

2.3. Chiral LC Elastomers

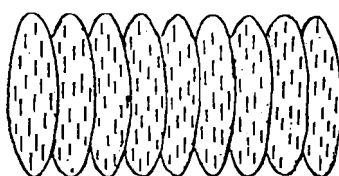
Bearing in mind the mechanical orientability of LC elastomers, it seems interesting to look for elastomers which show very drastic changes of their properties during orientation. In this context LC elastomers which combine the properties already discussed with the properties of chiral phases (cholesteric or chiral smectic C* phases) are of considerable interest. These phases, prepared from chiral mesogens, are the chiral modifications of the nematic and the smectic C phase. They possess very special properties, which are: selective reflection of light (cholesteric phase)^[1, 2, 32] and ferroelectric properties (chiral smectic C* phase)^[33] (see Fig. 9). Besides low molar mass liquid crystals, polymers with the same phases^[34, 35] have also been prepared. Since these properties are linked to the helical superstructure of the phases (Fig. 9a and c) it can be asked if it is possible to use a typical elastomer property—the orientability by stretching (mechanical field)—to untwist the helix (repeating distance: 0.2–2 μm). Such a possibility has been predicted theoretically.^[30] In low molar mass liquid crystals^[32, 33] the helical



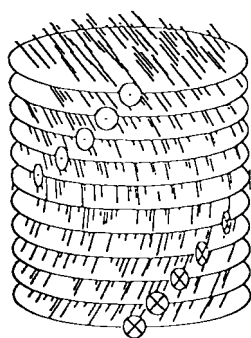
Scheme IV

cholesteric phase

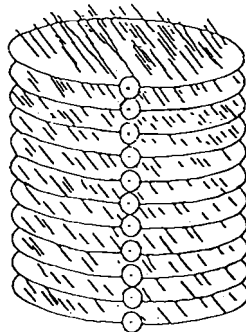
a) helical superstructure
(ground state)
selective reflection



b) nematic arrangement
no selective reflection

chiral smectic C* phase

c) helical superstructure
(ground state)
no macroscopic polarization



d) smectic C-like arrangement
macroscopic polarization

Fig. 9. Schematic representation of the cholesteric (a) and the chiral smectic C* (c) phase. Both phases have a helical superstructure in the ground state. The nematic arrangement (b) or the smectic C like arrangement (d) (untwisted states) can be induced by electric or magnetic fields or by stretching (LC elastomer).

structure can be untwisted by strong electric or magnetic fields, thus transforming the helical cholesteric phase (with selective reflection) into a nematic structure (without selective reflection, Fig. 9a and b) or the chiral smectic C* phase (without a macroscopic polarization) into a smectic C like structure (with a macroscopic polarization, Fig. 9c and d).

In order to investigate elastomers with these properties, a series of chiral crosslinkable polymers have been prepared (Tab. 4 and Scheme IV).^[36, 37] For this purpose combined polymers were selected because they form broad smectic and nematic phases (see Tab. 3) if they are achiral, and cholesteric and chiral smectic C* phases^[38] if they are chiral. The polymers thus prepared show cholesteric and chiral smectic C* phases in the uncrosslinked and crosslinked state (Tab. 4).

The phase assignment of these polymers was done by polarizing microscopy and by X-ray measurements,^[37] proving

Table 4. Phase transitions of uncrosslinked (a) and crosslinked (b) chiral combined polymers [37] (see Scheme IV).

No.	Y	X ₁	X ₂	R	Mole- cular weight	Cross- linker (mol.-%)	Phase transitions ^[a] /K
10a	-N=N-	-N=N-	-N=N-	R ₁	60 000	-	c382 s _c *397 n*422 i
10b	-N=N-	-N=N-	-N=N-	R ₁	-	10	c372 s _c *387 n*414 i
11a	-N(O)=N-	-N=N-	-N=N-	R ₁	47 000	-	g297 s _c *388 n*422 i
11b	-N(O)=N-	-N=N-	-N=N-	R ₁	-	10	g298 s _c *383 n*420 i
12a	-N(O)=N-	-	-	R ₂	17 000	-	g293 s _c *397 n*403 i
12b	-N(O)=N-	-	-	R ₂	-	20	g292 s _c *383 n*396 i

[a] c: crystalline or highly ordered smectic phase, g: glassy frozen phase, s_c*: chiral smectic C*, n*: cholesteric phase, i: isotropic melt

that cholesteric and different smectic phases were present. The ferroelectric properties of the chiral smectic C* phase

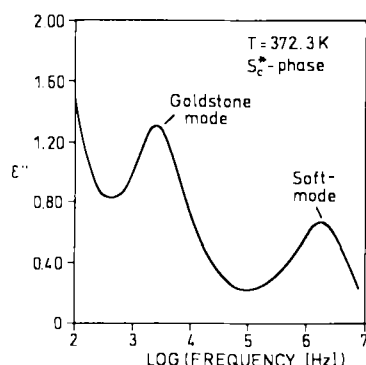


Fig. 10. A plot of the dielectric loss ϵ'' versus frequency for a thin (10 μm) and aligned sample of polymer **12a** (Tab. 4) measurement performed by Vallerien and Kremer [40].

can be determined by dielectric relaxation measurements.^[39] The results obtained from polymer **12a** are presented in Figure 10.^[40] In the chiral smectic C^* phase, two very intensive dielectric loss processes are found, which are not present in the isotropic phase. Due to their high intensity and their temperature dependence, they cannot be local relaxation processes.^[39] In analogy to low molar mass liquid crystals, these dielectric loss processes can be assigned as the soft mode and the Goldstone mode,^[41] which are typical for chiral smectic C^* phases (Fig. 9c). They correspond to fluctuations of the spontaneous electric polarization due to changes of the tilt angle (soft mode) or due to changes of the tilt direction at constant tilt angle (Goldstone mode, distortion of the helical structure).

The first X-ray measurements performed on the chiral elastomers prove that the helical superstructure in the cholesteric and chiral smectic C^* phase can be untwisted by stretching.^[37] This is presented in Figure 11 for the chiral smectic C^* phase of elastomer **11b**. For small strains, a fiber pattern as presented in Figure 11a is obtained. They correspond to an oriented chiral smectic C^* phase with a helical superstructure (Fig. 9c). For higher strains (about 400%) fiber pattern as presented in Figure 11b could be obtained. In this case it was necessary to cool the stretched sample down to the glass transition temperature in order to prevent a tearing of the sample during the measurement. These fiber patterns correspond to a smectic C like monodomain (Fig. 9d) without a helical superstructure. Therefore the sample should not have a macroscopic polarization for small strains (Fig. 9c and 11a) due to its helical superstructure, but it should have a macroscopic electric polarization (Fig. 9d and 11b) if it is highly strained.

Most of the work on chiral LC elastomers still remains to be done. For the future it is necessary to prepare e.g. elastomers with a still higher spontaneous polarization in the chiral smectic C^* phase. In addition it should be possible to stretch the elastomers more highly (> 400%) and to obtain in this way a uniform orientation over the whole sample^[37] (otherwise the polarizations arising from differently oriented domains will compensate each other). Despite these limita-

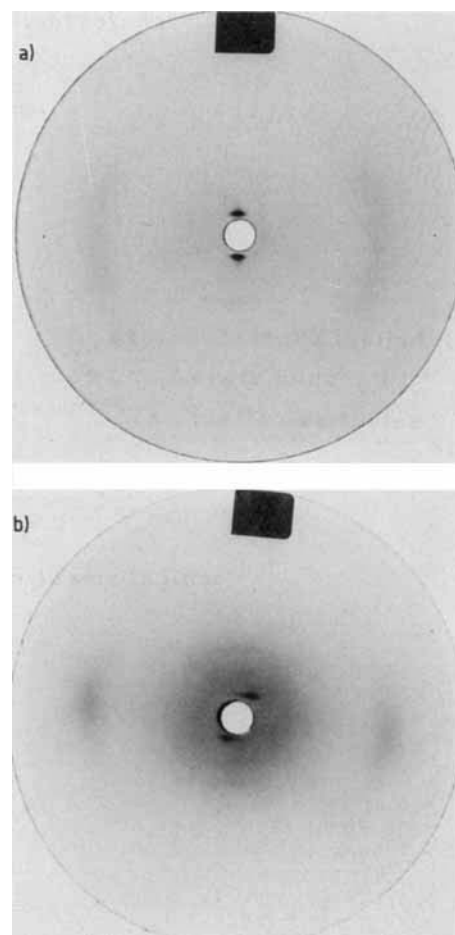


Fig. 11. X-Ray fiber pattern of the chiral elastomer **11b** (Tab. 4) in the chiral smectic C^* phase [37], fiber axis vertical. a) a strain of 300% applied, temperature 363 K. b) a strain of more than 400% was applied at 360–370 K, the measurement was performed at room temperature. The wide angle reflections correspond to 4.4 Å and the small angle reflections correspond to 26–27 Å.

tions the results of the X-ray measurements show that the chiral LC elastomers have the potential to act like a device that transforms a mechanical signal (the strain) into an optical signal (cholesteric phase, Fig. 9a and b) or an electrical signal (chiral smectic C^* phase, Fig. 9c and d). In the last case (chiral smectic C^* phase) the elastomer should behave like a piezo-element.

3. Summary and Outlook

Starting from a search for a detailed understanding of “classical” materials, such as liquid crystals, polymers and rubbers, material science today is directed to the investigation of more complex systems that combine different properties and functions with ordered structures. The interest in these more complex systems is twofold. On one hand new properties are expected, and on the other hand the study of the interaction of the different subsystems (e.g. polymer chains and mesogenic groups) is fascinating.

LC elastomers belong to this group of materials. They combine a wide variety of properties such as: i) the mechanical orientability of rubbers, ii) the ordered structure and the mobility of LC phases and iii) the possibility as in polymers to freeze-in an induced orientation below T_g .

LC elastomers with different molecular structures can be prepared by crosslinking LC polymers, while retaining the LC phases. Their elasticity is comparable to "classical" networks. While the understanding of the interaction of the liquid crystalline and the rubber properties in LC elastomers is still at an early stage their mechanical orientability makes them interesting for academic research (phase assignment, structure investigation) and also for applications such as optical switches (turbid—clear) or as wave guides.

The combination of these properties with chiral phases (chiral LC elastomers) yields materials that transform mechanical strain into optical or electrical signals and elastomers with chiral smectic C* phases are likely to show piezo electric properties.

Received May 17, 1989

- [1] P. G. de Gennes: *The Physics of Liquid Crystals*. Clarendon Press, Oxford 1975.
- [2] R. Steinsträßer, H. Krüger in E. Bartholomé et al. (Eds.): *Ullmanns Encyklopädie Technischer Chemie, 4. Aufl. 11*, Verlag Chemie 1976, p. 657.
- [3] H. J. Cantow (Ed.): *Adv. Polym. Sci.* 59–61 (1984).
- [4] H. Finkelmann, *Angew. Chem. Int. Ed. Engl.* 26 (1987) 816; *Angew. Chem.* 99 (1987) 840.
- [5] a) H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 113; *Angew. Chem.* 100 (1988) 117. b) B. Reck, H. Ringsdorf, *Makromol. Chem. Rapid Commun.* 6 (1985) 291.
- [6] F. Brochard, *J. Phys. (Les Ulis, Fr.)* 40 (1979) 1049.
- [7] Strzelecki, L. Liebert, *Bull. Soc. Chim. Fr.* (1973) 597.
- [8] S. N. Bhadani, D. G. Gray, *Mol. Cryst. Liq. Cryst. Lett.* 120 (1984) 255.
- [9] H. Finkelmann, H.-J. Kock, G. Rehage, *Makromol. Chem. Rapid Commun.* 2 (1981) 317.
- [10] H. Finkelmann, H.-J. Kock, W. Gleim, G. Rehage, *Makromol. Chem. Rapid Commun.* 5 (1984) 287.
- [11] J. Schätzle, H. Finkelmann, *Mol. Cryst. Liq. Cryst.* 142 (1987) 85.
- [12] W. Gleim, H. Finkelmann, *Makromol. Chem.* 188 (1987) 1489.
- [13] W. Gleim, H. Finkelmann in C. B. McArdle (Ed.): *Side Chain Liquid Crystal Polymers*, Blackie & Son, Glasgow 1989, p. 287.
- [14] R. Zentel, G. Reckert, *Makromol. Chem.* 187 (1986) 1915.
- [15] R. Zentel, *Liq. Cryst.* 1 (1986) 589.
- [16] F. J. Davis, A. Gilbert, J. Mann, G. R. Mitchell, *J. Chem. Soc., Chem. Commun.* (1986) 1333.
- [17] R. Zentel, M. Benalia, *Makromol. Chem.* 188 (1987) 665.
- [18] G. R. Mitchell, F. J. Davis, A. Ashman, *Polymer* 28 (1987) 639.
- [19] R. Zentel, G. F. Schmidt, J. Meyer, M. Benalia, *Liq. Cryst.* 2 (1987) 651.
- [20] S. Bualek, R. Zentel, *Makromol. Chem.* 189 (1988) 791.
- [21] V. Percec, C. Pugh in C. B. McArdle (Ed.): *Side Chain Liquid Crystal Polymers*, Blackie & Son, Glasgow 1989, p. 30; H. Finkelmann, G. Rehage, in ref. [3], p. 99; V. P. Shibaev, N. A. Platé, in ref. [3], p. 173.
- [22] M. Warner, K. P. Gelling, T. A. Vilgis, *J. Chem. Phys.* 88 (1988) 4008.
- [23] K.-H. Hanus, *Ph. D. thesis*, University of Ulm, FR-Germany 1989; K.-H. Hanus, B. Stoll, W. Pechhold, University of Ulm, FR-Germany in cooperation with R. Zentel, unpublished.
- [24] W. Oppermann, K. Braatz, H. Finkelmann, W. Gleim, H.-J. Kock, G. Rehage, *Rheol. Acta* 21 (1982) 423.
- [25] J. Schätzle, *Ph. D. Thesis*, University of Freiburg, FR-Germany 1989; J. Schätzle, W. Kaufhold, H. Finkelmann, *Makromol. Chem.* (1989) submitted.
- [26] K.-H. Hanus, W. Pechhold, F. Soergel, B. Stoll, R. Zentel, *Coll. & Polym. Sci.* (1989) submitted.
- [27] L. R. G. Treloar: *The Physics of Rubber Elasticity*. Clarendon Press, Oxford 1975.
- [28] R. G. Kirste, H. G. Ohm, *Makromol. Chem. Rapid Commun.* 6 (1985) 179; F. Moussa, J. P. Cotton, F. Hardouin, P. Keller, M. Lambert, G. Peppy, M. Mouzak, H. Richard, *J. Phys. (Les Ulis, Fr.)* 48 (1987) 1079.
- [29] S. Bualek, H. Kapitza, J. Meyer, G. F. Schmidt, R. Zentel, *Mol. Cryst. Liq. Cryst.* 155 (1988) 47.
- [30] H. Brand, *Makromol. Chem. Rapid Commun.* 10 (1989) 57.
- [31] H. Finkelmann, J. Schätzle, W. Kaufhold, L. Pohl, 18. *Freiburger Arbeitstagung Flüssigkristalle*, 15.–17. März 1989, Abstracts of Communications.
- [32] S. Chandrasekhar: *Liquid Crystals*, Cambridge University Press, Cambridge 1977.
- [33] J. W. Goodby, T. M. Leslie, *Mol. Cryst. Liq. Cryst.* 110 (1984) 175.
- [34] N. A. Platé, R. V. Talroze, Ya. S. Freidzon, V. P. Shibaev, *Polymer J.* 19 (1987) 135; H. Finkelmann, G. Rehage, in ref. [3], p. 99.
- [35] P. LeBarry, J. C. Dubois in C. B. McArdle (Ed.): *Side Chain Liquid Crystal Polymers*, Blackie & Son, Glasgow 1989, p. 130.
- [36] R. Zentel, G. Reckert, B. Reck, *Liq. Cryst.* 2 (1987) 83.
- [37] R. Zentel, *Liq. Cryst.* 3 (1988) 531; R. Zentel, G. Reckert, S. Bualek, H. Kapitza, *Makromol. Chem.* (1989) in press.
- [38] H. Kapitza, R. Zentel, *Makromol. Chem.* 189 (1988) 1793.
- [39] S. U. Vallerien, R. Zentel, F. Kremer, H. Kapitza, E. W. Fischer, *Makromol. Chem. Rapid Commun.* (1989) in press.
- [40] S. U. Vallerien, F. Kremer, MPI- für Polymerforschung, Mainz, FR-Germany, in cooperation with R. Zentel, unpublished.
- [41] J. Musevic, R. Blinc, B. Zeks, C. Filipic, M. Copic, A. Seppen, P. Wyder, A. Levanyuk, *Phys. Rev. Lett.* 60 (1988) 1530; S. U. Vallerien, F. Kremer, H. Kapitza, R. Zentel, W. Frank, *Phys. Lett. A* 138 (1989) 219.

The following review articles will be published in future issues:

H. Sixl et al.: Polymer Systems for Optoelectronics.

F. Aldinger, J. Huber et al.: High Performance Silicon Nitride Materials.

R. D. Miller: Substituted Silane Polymers—A New Look at Some Old Materials.

H. Eckert: Structural Characterization of Non-Oxide Chalcogenide Glasses Using Modern Solid State NMR Techniques.

K. Bange, T. Gambke: Electrochromic Materials for Optical Switching Devices.