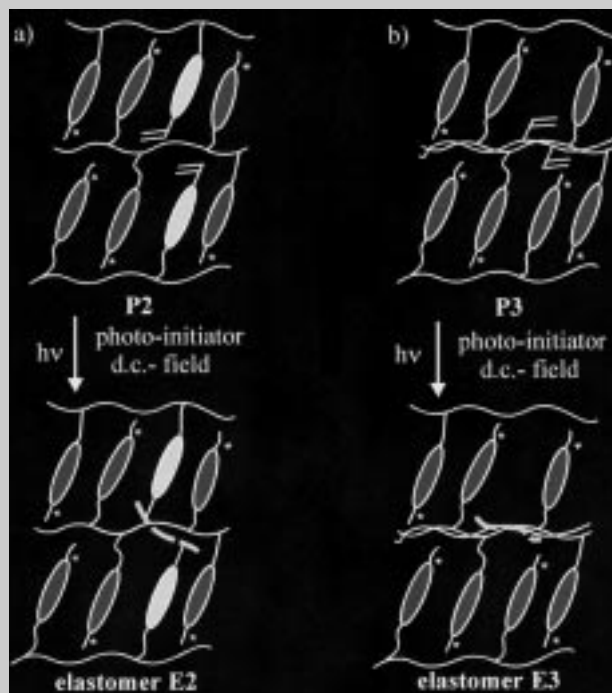


Full Paper: In order to evaluate structure-property relations in ferroelectric LC-elastomers concerning netpoint topology and netpoint density, three different elastomers were investigated. As far as the netpoint topology is concerned systems with a crosslinking within the smectic layers (intra-layer) and between different layers (inter-layers) behave differently. Only the inter-layer systems (elastomer **E2**) are able to stabilize the polar order of the smectic-C* phase. Increasing the crosslinking density by stepwise crosslinking leads to a continuous shift of the ferroelectric hysteresis. Two switching times with and against the elastic field of the network are observed. The difference between these switching times increases with increasing crosslinking density. From this difference an electric field can be calculated, which is necessary for a compensation of the elastic field of the network. Crosslinking of elastomer **E2** in the smectic A-phase leads to a stabilization of a macroscopically untilted state. If a tilt is induced in the crosslinked smectic A-phase by application of an electric field (electroclinic effect) the network keeps a memory of the polar state present during crosslinking.



Schematic representation of the different network topologies realized in the smectic-C* elastomers **E2** and **E3**, which preferably show inter-layer (**E2**) or intra-layer (**E3**) crosslinking

Ferroelectric liquid crystalline elastomers, 1

Variation of network topology and orientation

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1. Introduction

Slightly crosslinked liquid crystalline (LC) polymers that combine the properties of liquid crystalline phases (e.g. the self-organization of mesogens) and the elastic properties and formstability of polymeric networks are known as “liquid crystalline elastomers”^{1–3}. Especially smectic-C* elastomers and smectic-C* networks are of widespread interest as they show remarkable electromechanical effects like piezoelectricity. For that reason this class of material is taken into account to substitute the usual inor-

ganic piezoceramics and classical piezoelectric polymers such as poly(vinylidene difluoride) (PVDF) especially in micro-dimensions in the field of sensor-technology.

The experimental proof of piezoelectricity in chiral smectic-C* phases of LC elastomers was demonstrated in 1990 for the first time⁴. As the crosslinking of the combined main-chain/side-group polymers was done in the isotropic phase (using thermally activated polymerization of acrylate groups) a multidomain sample with no uniform director orientation was used for the first piezoelec-

tric measurements. In the meantime measurements of the direct and the inverse piezoelectric effect are published using mechanically oriented⁵⁾ or poled⁶⁾ smectic-C* elastomers. The macroscopic spontaneous polarization as a characteristic parameter of the ferroelectric smectic-C* phase in these systems is accessible by pyroelectric measurements. An alternative approach to piezoelectric networks is managed by polymerization of oriented low molar mass ferroelectric blends consisting of liquid crystalline diacrylates and non-reactive chiral compounds⁷⁾, or chiral acrylates, respectively⁸⁾. The value of the piezocoefficient in these systems is strongly dependent on the orientation and geometry of the smectic layers (bookshelf or chevron). High crosslinking densities in the systems result in solids that are no longer able to switch in electric a.c.-fields^{8, 9, 10)}.

Our successful approach to create smectic-C* elastomers that show piezoelectric effects, too, starts with an orientation of photo-crosslinkable ferroelectric polymers in the electric field. In a second step the stabilization of one ferroelectric switching state is managed by UV-irradiation that transfers the smectic-C* polymer into a smectic-C* elastomer¹¹⁾. Our systems still show as specialities – even in the crosslinked state – an asymmetric ferroelectric switching and a piezoeffect in the smectic-C* phase as well as in the smectic-A phase. The network formation stabilizes the tilt of the smectic-C* phase even in the high temperature smectic-A phase and in analogy to the “electroclinic effect” for these systems the notion of a “mechanoclinic effect” in the smectic-A phase was introduced^{12, 13)}.

Nowadays our investigations on liquid crystalline elastomers deal with structure-property relations like variations of the network-density, the netpoint topology and the ferroelectric polarization on the interplay between ferroelectric switching and network elasticity. This paper describes variations of the network density by step-wise crosslinking and variation of netpoint topology using different chemical structures and compositions of crosslinkable systems. Additionally this paper reports a closer look on the variation of director orientation during the radical photo-crosslinking reaction as the crosslinking is performed either in the smectic-C* or smectic-A phase. A second paper¹⁴⁾ deals with variations of the crosslinking density and the ferroelectric polarization by using different elastomer systems.

2. Experimental part

The synthesis of the polymers (see Scheme 1) has already been published^{11, 15, 16)}. ¹H NMR-spectra were recorded using a Bruker AC 200 FT-NMR spectrometer. IR spectra were recorded using a Jasco IR-Report 100 spectrometer or a Bruker IFS 48 FT-IR-spectrometer. GPC measurements were performed using a Waters Liquid Chromatograph (with UV

detector) with a column combination of 10³ Å (ultrastyrigel) and 10⁴ Å (PL-gel).

To get a homogeneous blend (**P4**) of copolysiloxane **P1** and crosslinkable oligosiloxane PS 901.5 (ABCR, P_n 4.35 as determined by GPC measurements against polystyrene standards) the two components were dissolved in CHCl₃ and the solvent was evaporated. The polymer/initiator-mixtures were prepared by dissolving **P2**, **P3** or **P4** together with 1 wt.-% photoinitiator [α,α -dimethoxy- α -phenylacetophenone (Ciba Geigy)] in chloroform. After evaporation of the solvent the mixture was filled into a commercially available liquid crystal-cell (EHC, Japan) using a Kofler hot-stage.

The phase transition temperatures were determined by optical polarizing microscopy using an Olympus BH-2 microscope and differential scanning calorimetry using a Perkin-Elmer DSC 7 (heating/cooling-rate of 10 °C/min).

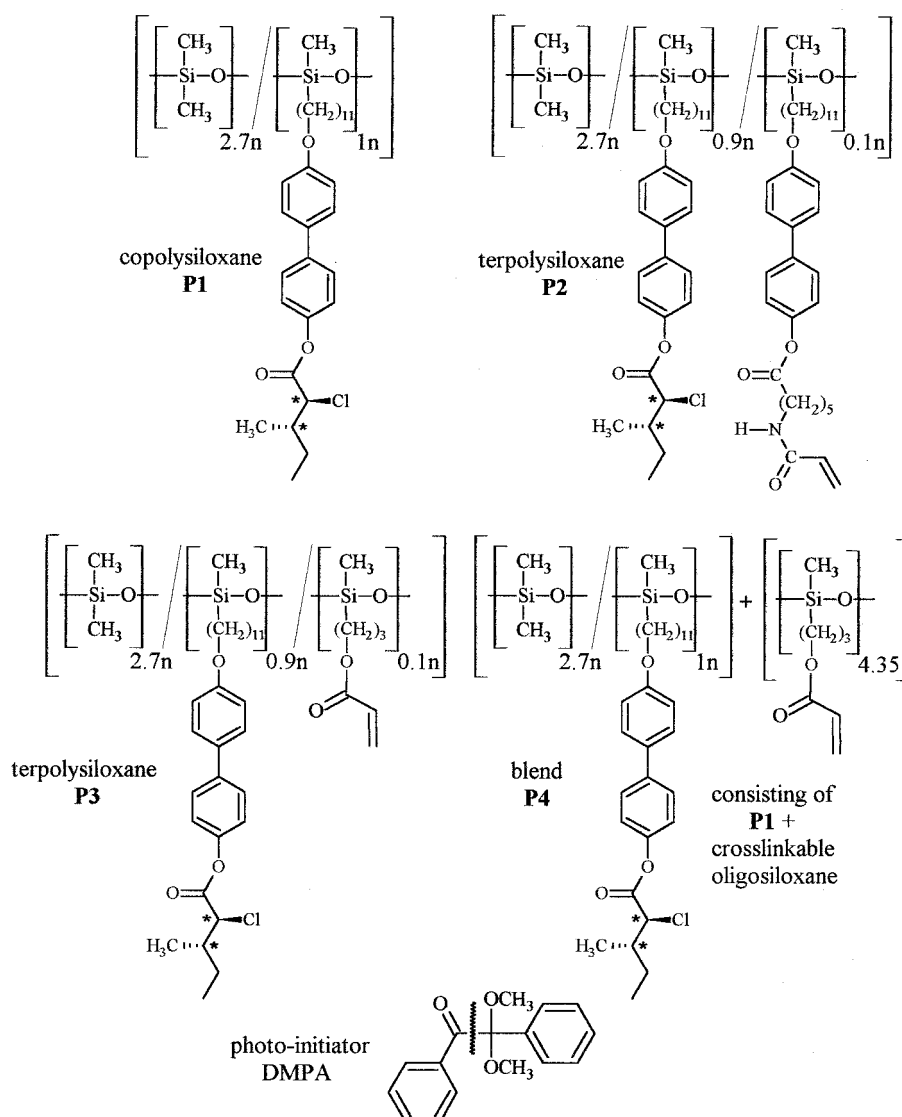
The electro-optical characterization of the polymers and the polymer/initiator-systems, respectively were performed with an Olympus BH-2 microscope, equipped with a 35 mm camera Olympus SC 35 or a photodiode BPW 34. Temperature dependent observations were possible using a Linkam THMS 600 hot-stage controlled by a Linkam TP 91. The driving voltage was supplied by a function generator HP 33120 A together with a KEPCO bipolar amplifier BOP 500 M. The current, which was measured over a Burster 1406 resistor decade (R = 10 kW), and the optical response were followed using a HP 54601 A oscilloscope. The measurement of the spontaneous polarization was performed using the “triangular-wave-method”^{17, 18)}. The switching-times were determined as time between $U_{\min}(t)$ and $U_{\max}(t)$ transition change (between 0% and 100% transmission) using the photo-voltage of the photodiode.

To create the elastomers commercially available cells were used consisting of two transparent ITO-electrodes (area 0.16 mm²) with an electrode distance of 10 μ m. To orient the liquid crystal to an almost perfect planar texture inside the cell several heating/cooling-cycles around the Curie-temperature with increasing field strength of the applied voltage were necessary. A crosslinking was performed in the liquid crystalline phase (smectic-C* or smectic-A), with or without applied d.c.-field, by using a high-pressure Xe-lamp (150 W, AMKO) with a light intensity of 10 mW/cm² (as measured in distance sample-light source). A 365 nm filter was put into the light beam during UV-irradiation to prevent side-reactions.

3. Results and discussion

3.1 Synthesis and characterization of the ferroelectric crosslinkable systems

The syntheses of the copolysiloxane **P1** and the terpolysiloxanes **P2–3** (see Scheme 1 for molecular structures) were done according to known procedures^{11, 15, 16)}. The resulting polymers and the content of crosslinkable groups were characterized by spectroscopic measurements (IR and ¹H NMR). The average molecular weight was determined by GPC measurements against polysty-

Scheme 1: Molecular structure of the systems **P1–4** and of the photo-initiator α,α -dimethoxy- α -phenylacetophenone (Ciba Geigy)Tab. 1. Average molecular weight of **P1–3** as determined by GPC against polystyrene standards, solvent CHCl_3

System	\bar{M}_n /(g/mol)	\bar{M}_w /(g/mol)
P1	12 700	21 200
P2	10 200	15 200
P3	10 800	22 200
P4	–	–

rene standards (solvent chloroform) (Tab. 1). In order to study the crosslinking topology in detail blend **P4** was mixed, consisting of copolysiloxane **P1** and a low molecular weight oligosiloxane PS 901.5 (ABCR) in the molar ratio of (9:1). So the same ratio of chiral to crosslinkable mesogens as in **P2–3** is guaranteed for **P4**.

As photo-initiator 1 wt.-% of α,α -dimethoxy- α -phenylacetophenone (Ciba Geigy) was mixed with the crosslink-

able polymers, respectively the crosslinkable blend, prior to the crosslinking experiments. Tab. 2 shows the liquid crystalline phase transition temperatures for the four systems (without and with photo-initiator). As the initiator acts as an “impurity” to the liquid crystalline system, it lowers the clearing points and phase transition temperatures of the pure compounds slightly.

Fig. 1 shows the schematic representation of two different network topologies realized by crosslinking of **P2** and **P3**^{11,16}. For liquid crystalline side chain polysiloxanes a microphase separation between the siloxane chains and the mesogens due to partial immiscibility was proposed^{19,20}. Whereas polymer **P2** has 10 mol-% crosslinkable acrylamide groups at the end of the mesogens, in polymer **P3** the crosslinkable acrylate groups are positioned very close to the copolysiloxane backbone. In blend **P4** the copolymer **P1** is mixed with an isotropic

Tab. 2. Mesophases of **P1–4** (pure and with admixture of photo-initiator) as determined by DSC, optical microscopy and electro-optical experiments

System	Molar ratio P1/oligosiloxane	Phase transitions (°C) without initiator	Phase transitions (°C) with 1 wt.-% initiator
P1	–	s_X 29/30 s_C^* 61 s_A 89 i	–
P2	–	s_X 29 s_C^* 57 s_A 84 i	s_X 29 s_C^* 52 s_A 75 i
P3	–	s_X 32 s_C^* 59 s_A 82 i	s_X 30/31 s_C^* 56 s_A 76/77 i
P4	(9:1)	s_X 29/30 s_C^* 55 s_A 74 i	s_X 30 s_C^* 50 s_A 68–70 i

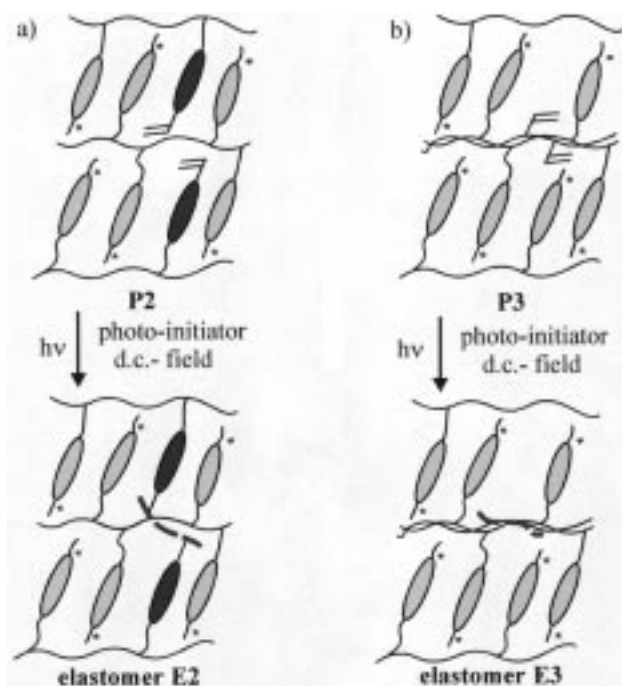


Fig. 1. Schematic representation of the different network topologies realized in the smectic- C^* elastomers **E2** and **E3**, which preferably show inter-layer (**E2**) or intra-layer (**E3**) crosslinking

crosslinkable oligosiloxane, which will preferably dissolve within the siloxane sublayers. After achieving a planar orientation of the polymer/initiator-mixtures by orienting the liquid crystal in an electric field, a radical photo-crosslinking in a liquid crystalline phase is started by UV-irradiation of the samples. This procedure transfers the polymers **P2** and **P3** into the corresponding elastomers **E2** and **E3** (Fig. 1). For the blend **P4** a structure with intra-layer crosslinking similar to **E3** must result.

3.2 Stepwise crosslinking of terpolysiloxane P2 in the smectic C^* -phase

Previous studies on the elastomers of terpolymer **P2** show a successful stabilization of one ferroelectric switching state, when the crosslinking reaction takes place in the smectic- C^* phase with applied d.c.-field^{11,12}. Afterwards a switching of the mesogens in the second, unfavored

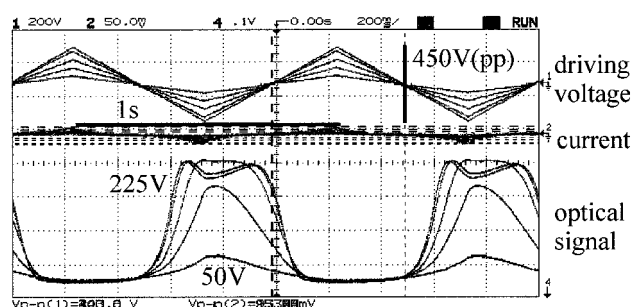


Fig. 2. Oscilloscope traces of the smectic- C^* elastomer **E2** after 2.45 min UV irradiation (completely irradiated LC cell), 100–450 V triangular wave, frequency 1 Hz, temperature 42 °C (10 °C below T_C)

switching-state is still possible. If the electric field is switched off, the network tugs the mesogens back into the state the crosslinking took place in. The entropy elasticity of the polymer network is the cause of the counterforce of the polymer network. The stabilization in the field-free state by the mechanical field of the network takes the role of an applied d.c.-field. In the smectic-A phase the mechanical field induces a tilt in analogy to the “electroclinic effect”. This interpretation is supported by the appearance of a piezoelectric-effect^{11,12} and a stabilized tilt-angle (as proven in 2D-FT-IR-measurements using static electric fields²²) in the smectic-A phase.

To have a closer look at the role of the netpoint density a stepwise crosslinking of polymer **P2** in the smectic- C^* phase at 42 °C [10 °C reduced temperature ($T_C - T$)] was performed. It shows a strengthening of the asymmetric ferroelectric switching process with increasing irradiation time. The oscilloscope-traces of the final state of **E2** are illustrated in Fig. 2. The optical signal of the cell is plotted against the applied driving voltage [100–450 V(pp)]. A bistable, asymmetric switching can be observed when at least 300 V(pp) are applied. Following the optical signal in Fig. 2 a stabilization of the “lower” switching state can be observed.

Simultaneously the ferroelectric optical hysteresis shows a stronger asymmetric loop concerning the zero point of the driving-voltage with increasing irradiation time. The final hysteresis of elastomer **E2** is represented in Fig. 3 for an applied driving-voltage of 400 V(pp) triangular wave and a frequency of 1 Hz at 7 °C reduced

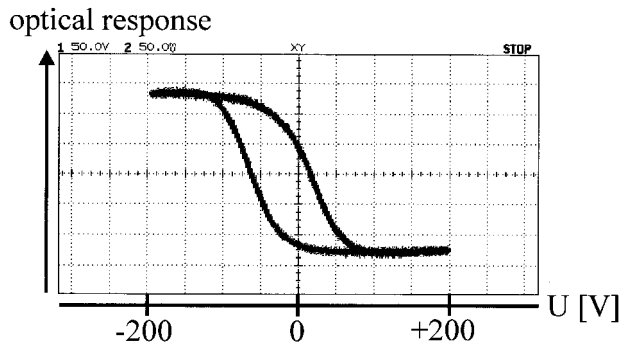


Fig. 3. Ferroelectric hysteresis of the smectic-C* elastomer **E2**, $U = 400$ V, $f = 1$ Hz, $T = 45$ °C, after 2.45 min UV irradiation

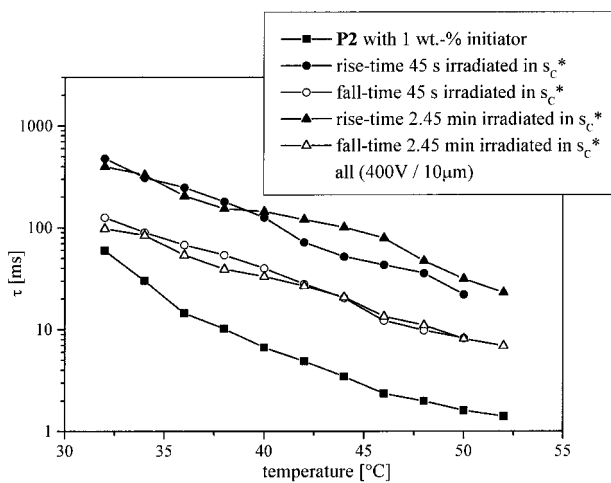


Fig. 4. Temperature dependent switching times for the uncrosslinked **P2**/initiator-mixture and the smectic-C* elastomer **E2** after 45 s and 2.45 min UV irradiation time

temperature (for the **P2**/initiator-mixture). A change in the width of the hysteresis compared to the uncrosslinked state was not observed.

The effect of stepwise crosslinking can be followed in the best way by measuring the switching times after each single irradiation of the same sample. The results are plotted in Fig. 4. After irradiation two switching times, the so called rise- and decay-time, are observed. They are no longer identical. There is one *slow* switching time, that is contributed to the switching *out* of the stabilized state (switching “*against*” the elastic force of the polymer network) and one *fast* switching time *into* the stabilized state (switching “*with*” the polymer network). The switching times show a difference of almost a factor of 5. The original switching times have to be multiplied with a factor of 4, respectively a factor of 19. With increasing irradiation time and crosslinking density of **E2** the difference of the two switching times is increasing. So both, the shift of the ferroelectric hysteresis and the difference in the ferroelectric switching times, can be used as a measure of the crosslinking density in a smectic-C* elastomer.

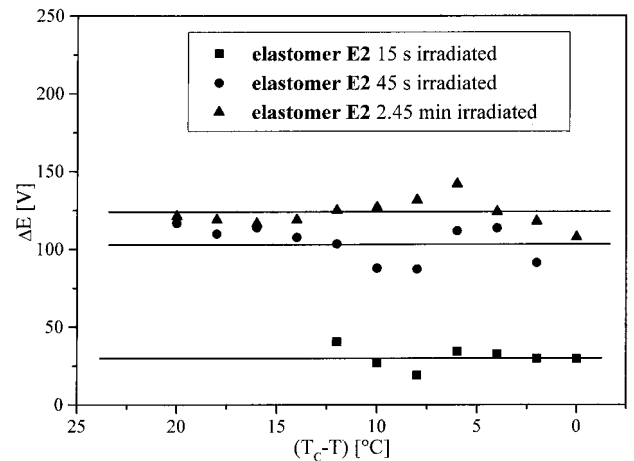


Fig. 5. Calculated “induced” bias-field due to network formation in the smectic-C* switching state for the smectic-C* elastomer **E2** for three different crosslinking densities

The network formation in one ferroelectric switching state acts like an external electric d.c.-field¹²⁾. Considering Eq. (1) for the ferroelectric switching time τ ²³⁾, the two different switching times of the crosslinked system are the result of two different “effective electric fields” ($E_{\text{eff}} = E \pm \Delta E$)

$$\tau \propto \frac{\gamma \cdot \sin \theta}{P_s \cdot E_{\text{eff}}} = \frac{\gamma \cdot \sin \theta}{P_s (E + \Delta E)} \quad (1)$$

with τ = switching time

γ = rotational viscosity

θ = tilt angle

P_s = spontaneous polarization

E_{eff} = effective electric field strength ($E_{\text{eff}} = E \pm \Delta E$)

Correcting the rise and the decay for an effective electric field by ΔE the same reduced switching time should result. The value for this external bias-field ΔE is a measure for the crosslinking density in the elastomeric system.

Fig. 5 shows the calculated external d.c.-fields for three different crosslinking densities of elastomer **E2**. Voltages of $\Delta E = 25$ V, 100 V and 125 V are obtained for irradiation times of 15 s, 45 s and 2.45 min.

The calculated values of ΔE are following the trend of the stepwise shift of the ferroelectric optical hysteresis with increasing irradiation time, but the two effects are not identical in the absolute values of the voltages. Generally the shift of the ferroelectric hysteresis (e.g. 40 V at 1 Hz in Fig. 5) determined for slower frequencies is smaller than the ΔE determined from switching experiments.

3.3 Crosslinking of terpolysiloxane **P2** in the smectic-A phase (without applied d.c.-field)

In order to stabilize the structure of the field-free smectic A phase of terpolymer **P2** the crosslinking reaction is per-

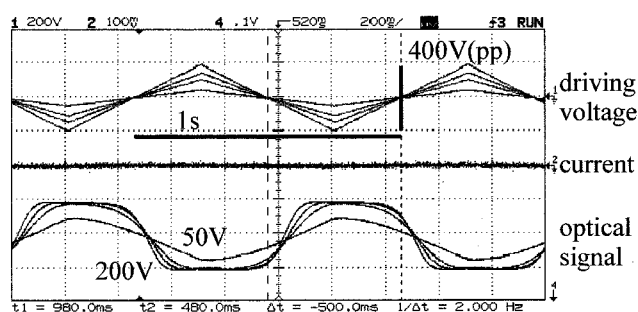


Fig. 6. Oscilloscope traces of the smectic-A elastomer **E2** (crosslinked without applied d.c.-field), 100–400 V triangular wave, frequency 1 Hz, temperature 46 °C (6 °C below T_C)

formed at 58 °C [(-6 °C) reduced temperature ($T_C - T$)] in the smectic-A phase. Contrary to the tilted smectic-C* phase the director of the mesogens in the smectic-A phase is oriented parallel to the smectic layer normal. After complete irradiation of polymer **P2** and cooling down into the smectic-C* phase again, a completely different switching behaviour is observed for the smectic-A elastomer **E2** compared to the smectic-C* elastomer **E2** (see Fig. 2). Fig. 6 shows the optical signal of the smectic-A elastomer in dependence of the driving-voltage [100–400 V(pp) triangular wave] recorded in the smectic-C* phase at 46 °C. The switching of the smectic-A elastomer **E2** is still symmetric as in the uncrosslinked state, but it needs high driving voltages (100 to 150 V compared to 20–30 V for the uncrosslinked polymer) to reach the two polar switching states. Obviously the mesogens prefer the overall untilted orientation even in the smectic-C* phase. From our optical observations we cannot differentiate between an untilted structure in the field free state (smectic-A like) or a structure with local tilts in different directions.

The temperature dependent ferroelectric optical hysteresis loops are shown in Fig. 7a) (uncrosslinked **P2**/initiator-mixture) and Fig. 7b) (smectic-A elastomer **E2**). Although the width of the hysteresis loops of the uncrosslinked **P2**/initiator-mixture and the crosslinked elastomer **E2** cannot be compared due to the different field strengths of the driving-voltages, it is obvious that the hysteresis loops show a different dependence of their shape on temperature variation. The loops in Fig. 7a) show the expected behaviour of a ferroelectric liquid crystal with a Curie temperature at 52 °C. At T_C the ferroelectric loop changes into an electroclinic response. The hysteresis loops of the smectic-A elastomer **E2** (Fig. 7b) always show – even at lower temperatures and higher driving voltages – the bended shapes of the high-temperature smectic-A phase of **P2**. The hysteresis of the crosslinked polymer shows a non-preference of both ferroelectric switching states.

The switching times show no difference between rise and decay and were measured as average. Compared to

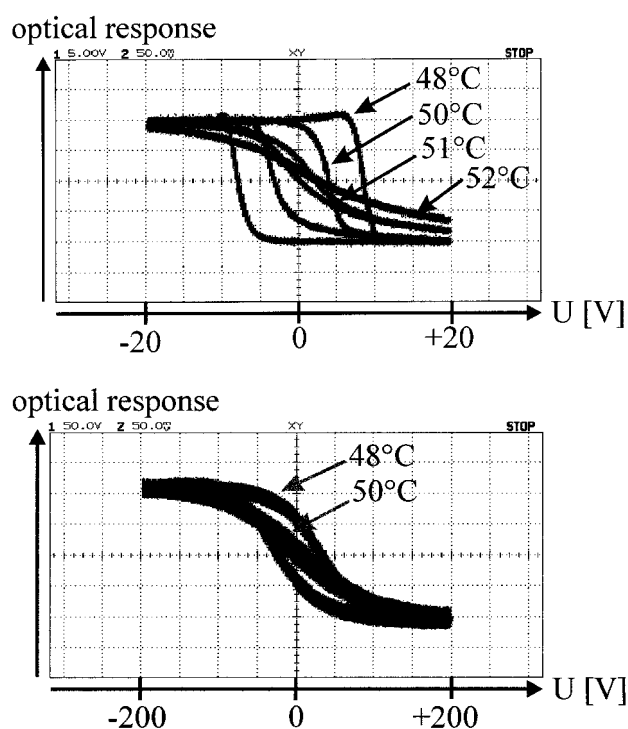


Fig. 7. (a) Temperature dependent hystereses at the smectic-C* smectic-A phase transition of the uncrosslinked **P2**/initiator-mixture at 48 °C, 50 °C, 51 °C and 52 °C before crosslinking, $f = 1$ Hz, $U = 40$ V(pp) triangular wave; (b) temperature dependent hystereses for the smectic-A elastomer **E2** (crosslinked without applied d.c.-field) at 48 °C and 52 °C, $U = 400$ V(pp) triangular wave, $f = 1$ Hz

the uncrosslinked **P2**/initiator-mixture the switching times of the smectic-A elastomer **E2** are increased by factor of 4. If the same network density as in the smectic-C* elastomer **E2** is assumed, the ferroelectric switching times are faster than expected in the resulting smectic-A elastomer **E2**.

3.4 Crosslinking of terpolysiloxane **P2** in the smectic-A phase (with applied d.c.-field)

If an electric d.c.-field is applied to a ferroelectric polymer in the smectic-A phase, a tilt angle θ_{ind} is induced in the polymer (“electroclinic effect”). This tilt angle is proportional to the applied field strength and transforms the originally orthogonal and unpolar smectic-A phase into a tilted and polar phase. A crosslinking in the smectic-A phase with applied d.c.-field should therefore lead to a stabilization of one ferroelectric switching state, analogous to the crosslinking in the smectic-C* phase with applied d.c.-field. A complete irradiation of the **P2**/initiator-mixture at 56 °C [(-4 °C) reduced temperature ($T_C - T$)] in the smectic-A phase with an applied d.c.-field of 100 V/10 μm showed again a stabilization of one ferroelectric switching state after cooling of the crosslinked

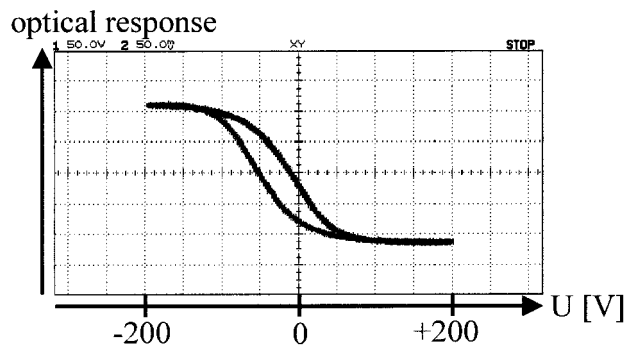


Fig. 8. Ferroelectric optical hysteresis of the smectic A-elastomer **E2** (crosslinked with applied bias-field in the smectic-A phase), $U = 400$ V, $f = 1$ Hz

sample into the smectic-C* phase. An asymmetric ferroelectric switching and a small shift of the ferroelectric optical hysteresis loop (Fig. 8) were observed. Compared to the hysteresis loop of the smectic-C* elastomer **E2** (as shown in Fig. 3) a narrowing of the loop has been found for the smectic-A elastomer **E2** with induced tilt angle (Fig. 8). We consider a smaller hysteresis for the smectic-A elastomer – compared to the smectic-C* elastomer – logical as the electroclinic tilt angle was smaller than the tilt angle in the smectic-C* phase. The smectic A-elastomer **E2** without induced tilt angle (Fig. 7b) shows at the same temperature (48 °C), same field strength of driving-voltage und frequency a broader optical hysteresis loop than the smectic A-elastomer **E2** with induced tilt angle (Fig. 8).

Generally the entropy elasticity of the polymer network that stabilizes the orientation present during crosslinking can be figuratively presented as a spring (Fig. 9a). An increasing counterforce of the network due to an increasing crosslinking density in the smectic-C* elastomer **E2** is shown as increasing number of entropy elastic springs (Fig. 9b).

The stabilization of the unpolar structure of the smectic-A phase, can be illustrated again with the picture of an entropic spring (Fig. 9c). A crosslinking of the polymer **P2** with the director oriented parallel to the smectic layer normal ($\theta = 0^\circ$) leads to a mechanical deformation of the network when the temperature is lowered into the smectic-C* phase. Both ferroelectric switching states are unfavored. The switching process stays symmetric but it needs high voltages to reach the polar, uniformly tilted states.

3.5 Variation of network topology in terpolysiloxane **P3** and blend **P4**

Terpolysiloxane **P3** contains 10 mol-% crosslinkable groups attached directly to the polysiloxane backbone (Scheme 1). Its crosslinking should lead preferably to

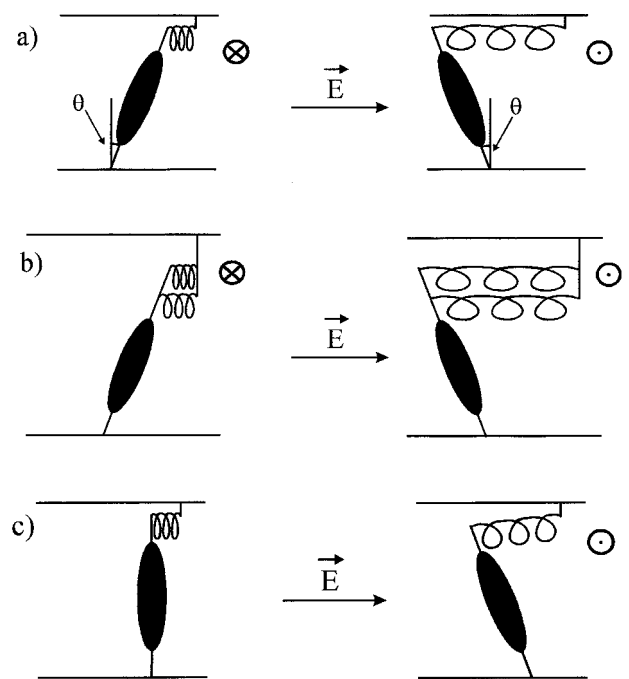


Fig. 9. Schematic illustration of the different crosslinking densities in the smectic-C* elastomer **E2**. The entropy elasticity is figuratively presented as a spring. (a) Weak crosslinking density: counterforce of polymer network weak, (b) high crosslinking density: increased counterforce of polymer network, (c) schematic representation of the crosslinking in the smectic A-elastomer **E2**. \otimes/\odot direction of the polarization vector in/out of plane of paper

intra layer crosslinks. A **P3**/initiator-mixture (in an oriented LC-cell) was crosslinked in the smectic-C* phase at 46 °C [10°C reduced temperature ($T_c - T$)] with an applied d.c.-field of 50 V/10 μm . In opposition to the smectic-C* elastomer **E2** the elastomer **E3** shows almost no difference in the switching behaviour compared to the uncrosslinked **P3**/initiator-mixture. A polar switching state could never be stabilized. Measurements of the spontaneous polarization revealed P_s -values of 75% of the original values. Measurements of the switching-times show almost no difference compared to polymer **P3**. There is no difference between rise and fall for elastomer **E3**. Obviously the coupling between the polymer network and the tilt direction of the mesogens is very weak in this case.

Alternatively blend **P4** and the resulting, heterogeneous elastomer **E4** were investigated. They gave almost the same results as the experiments for the polymer **P3**/elastomer **E3**-system. Both the blend and the elastomer give an optically completely homogeneous (not biphasic) picture. The switching times for the **P4**-system are illustrated in Fig. 10. After crosslinking the switching times for elastomer **E4** in the smectic-C* phase have to be multiplied by a factor of 2 compared to the uncrosslinked **P4**/initiator-mixture.

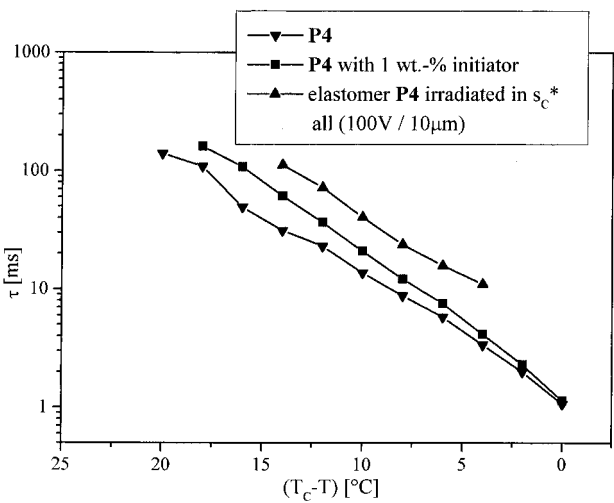


Fig. 10. Ferroelectric switching times of blend **P4**, the **P4**/initiator mixture and the resulting elastomer **E4**

To get information about the homogeneity of the cross-linked blend **E4** the birefringence in the isotropic phase was investigated. Heating the elastomer **E4** a few degrees over the clearing point of the uncrosslinked sample, a melting of the polymeric liquid crystal sets in. Some birefringent areas remain obviously due to a stress induced birefringence of areas rich in crosslinker (Fig. 11 b). Therefore the network formation in elastomer **E4** is heterogeneous.

Elastomer **E2** and elastomer **E3** – on the other hand – show a continuously decreasing brightness of birefringence when the clearing point is passed (Fig. 11 a). A homogeneous brown-grey area remains that indicates a homogeneous stress induced birefringence in the isotropic phase.

Finally the situation in elastomer **E3** and its interpretation has to be discussed. Concerning its homogeneity it is close to elastomer **E2**, concerning its switching characteristics it resembles elastomer **E4**. Temperature dependent

AFM measurements²⁴⁾ of thin films of elastomer **E3** show a stabilization of the smectic morphology, even in the isotropic phase. Steps on the surface (thickness one smectic layer) are preserved after crosslinking, even in the isotropic phase. Thus crosslinking to **E3** stabilizes the smectic layer structure effectively. During stretching elastomer **E2** (inter layer crosslinking) and **E3** (intra layer crosslinking) behave, however, very differently²⁵⁾.

The effect of crosslinking of **P3** to **E3** depends thus strongly on the properties investigated. This is a consequence of the predominant intra layer crosslinking. A fixation of the position of the smectic layers stabilizes optical textures and hinders the smectic layer rotation (the hindrance of smectic layer rotation has been investigated in detail²⁶⁾ for polymer stabilized ferroelectrics similar to **E4**). For the fixation of the polar axis it is, however, not enough to stabilize the smectic layers. Mesogens have to be incorporated into the network to determine the tilt direction of the director.

4. Conclusion

Concerning structure-property relations in ferroelectric LC-elastomers the following results were obtained:

- I. The coupling between the elastic forces of the polymer network and the director reorientation (ferroelectric switching) depends strongly on the network topology. If the netpoints are located – preferably – within the siloxane sublayer (intra layer crosslinking), then the coupling is very weak. It is not possible to stabilize a polar state in the smectic-C* phase. In addition the switching times are only slightly increased. This situation is realized in elastomers **E3** and **E4**. If the crosslinking happens between the siloxane sublayer and includes mesogens (inter-layer, elastomer **E2**), then the coupling becomes very strong. In this case it is possible to stabilize a polar state in the smectic-C* phase.

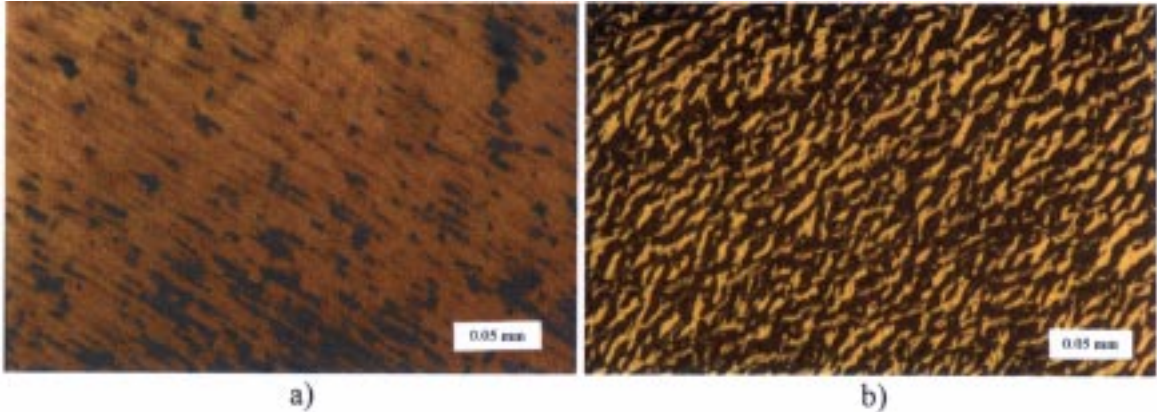


Fig. 11. Polarizing micrographs of (a) the smectic-C* elastomer **E2**, (b) the smectic-C* elastomer **E4** after heating several degrees into the isotropic phase of the uncrosslinked samples

- II. Crosslinking of elastomer **E2** in the smectic-C* phase leads to a shift of the ferroelectric hysteresis and two switching times with (fall-time) and against (rise-time) the elastic field of the network. Increasing the crosslinking density leads to an increasing asymmetry of the ferroelectric hysteresis and increases the difference between rise and fall. From both effects an electric field can be calculated, which is necessary to compensate the elastic field of the network. This field increases during stepwise crosslinking.
- III. Crosslinking of elastomer **E2** in the smectic-A phase leads – after cooling to the smectic-C* phase – to a stabilization of an macroscopically untilted state. Applying an d.c.-voltage in the smectic-A phase before crosslinking (electroclinic effect) leads again to a stabilization of the polar (tilted) state present during crosslinking.

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