Liquid Crystals

Publication details, including instructions for authors and subscription information:
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To cite this Article Gebhard, Elisabeth(1999) 'Preliminary communication of network formation on the soft-mode in ferroelectric LC elastomers', Liquid Crystals, 26: 2, 299 — 302

To link to this Article: DOI: 10.1080/026782999205452

URL: http://dx.doi.org/10.1080/026782999205452

LIQUID CRYSTALS, 1999, VOL. 26, NO. 2, 299–302

Preliminary communication

Influence of network formation on the soft-mode in ferroelectric LC elastomers

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(*Received 15 June 1998; in final form 14 September 1998 accepted 28 September 1998*)

The frequency and temperature dependence of the complex dielectric constant ε^* was measured for the smectic C*–smectic A phase transition for a crosslinkable ferroelectric polysiloxane. A stepwise crosslinking shifts the soft-mode absorption to lower frequencies, while an increase in relaxation strength and a broadening of the transition occurs. Whereas the shift of the soft-mode can be simply explained by an increase of viscosity in the resulting elastomer, the other two effects indicate an increase in the cooperativity of the soft-mode fluctuations due to the coupling of dipoles in the network even far from the phase transition.

LC elastomers are formed by crosslinking of LC polymers in such a way that long chain segments between the netpoints are unaffected [1–3]. As for elastomers in general, their microbrownian motions (local motions and the dynamic glass transition) are unaffected by the crosslinking as long as the distance between the netpoints is large. Only the macrobrownian motion, i.e. macroscopic flow, is prohibited. Motions which require a macroscopic reorientation of the LC director are, however, strongly slowed down [4–6] (ferroelectric systems) or are completely suppressed [7] (nematic systems). In addition it has been shown recently that the network couples the positional fluctuations between smectic layers and creates thereby a material with a real one dimensional long range order [8].

Measurements of the collective modes in the chiral smectic C* phase, i.e. the soft-mode and the Goldstone-mode [9–11], should allow a study of the influence of the polymer network on the director and tilt fluctuations. Such measurements have been made intensively for low molar mass and polymeric ferroelectric liquid crystals [12–14]. They have, however, not yet been reported for ferroelectric elastomers, simply because the network formation decreases the frequency of these modes and increases the ionic conductivity. These modes are therefore normally hidden under the conductivity contributions [15]. We have now been able to purify a ferroelectric LC polymer to such an extent that we could follow the soft-mode (tilt angle fluctuation) during the stepwise photochemical crosslinking.

For the results reported we used polymer **P1** (see the scheme). The phase transition temperatures were determined by optical polarizing microscopy and differential scanning calorimetry. The molecular mass $\bar{M}_w$ was determined by GPC as 9400 g mol^{-1} with a polydispersity D of 1.34 (against polystyrene standards/$CHCl_3$). The synthesis was done using polymer analogous reactions (polysiloxane backbone available from ABCR) and has already been described [4, 16]. In order to remove ionic impurities, polymer **P1** was purified several times by chromatography (neutral-Al_2O_3/CH_2Cl_2 p.a.). Polymer **P1** can be crosslinked to elastomer **E1** by a radical polymerization of the acrylate groups initiated by the photocleavage of a photoinitiator. As photoinitiator, 1 wt % of α, α-dimethoxy-α-phenylacetophenone (Ciba Geigy) was mixed with the polymer prior to the crosslinking experiments.

Before crosslinking, **P1** has a polarization up to 110 nC cm^{-2} (at saturation) and switching times of 1.4 ms (10 degrees below the SmA–SmC* transition temperature, T_C). After crosslinking, the switching times are increased by a factor of about six and the polarization drops to 80 nC cm^{-2}. In contrast to published results for related systems (see [4] and [6] for a detailed discussion), the orientation present during crosslinking is not stabilized due to the low amount of crosslinkable groups attached to the siloxane network.

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Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
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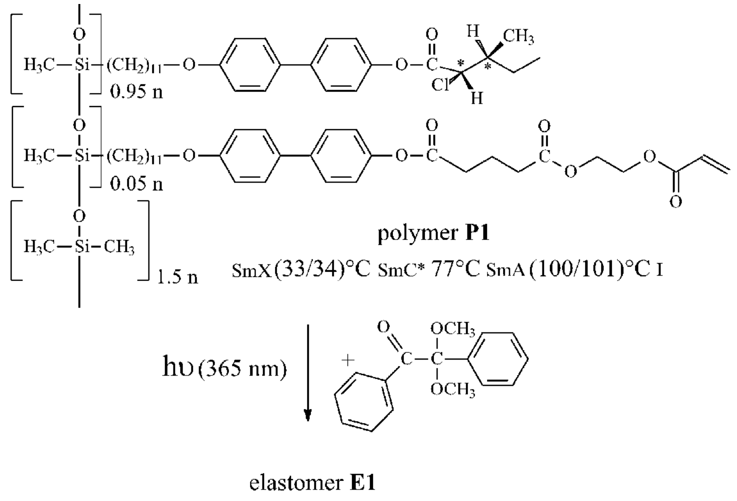


Scheme. Chemical structure and phase transition temperatures for the ferroelectric polysiloxane **P1** that is photocrosslinked to elastomer **E1** using a photoinitiator and UV light.

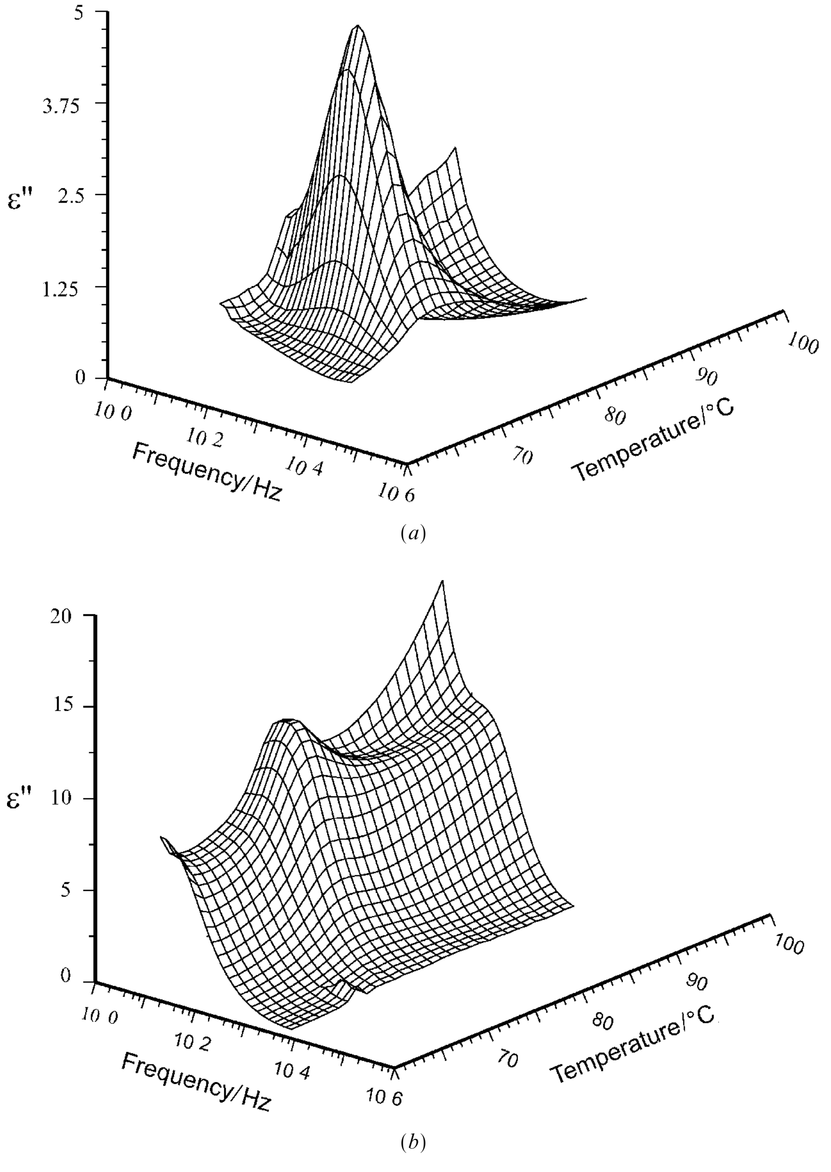
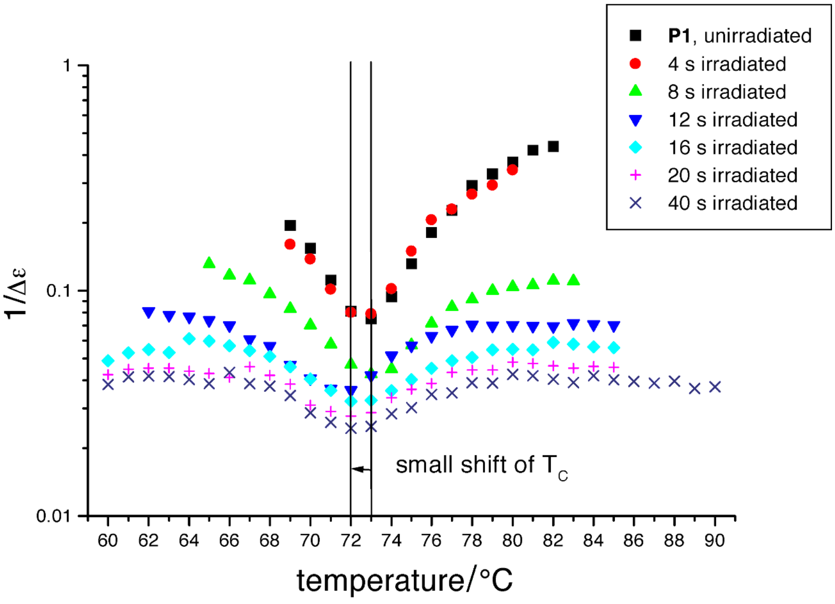


Figure 1. Dielectric loss ε'' of the soft-mode relaxation as a function of temperature and frequency (d.c. field 10 V). (*a*) Polymer **P1** mixed with photoinitiator before irradiation, showing the Curie temperature T_C (SmA–SmC*) at 73°C; (*b*) elastomer **E1** (= polymer **P1** after irradiation), T_C = 72°C.

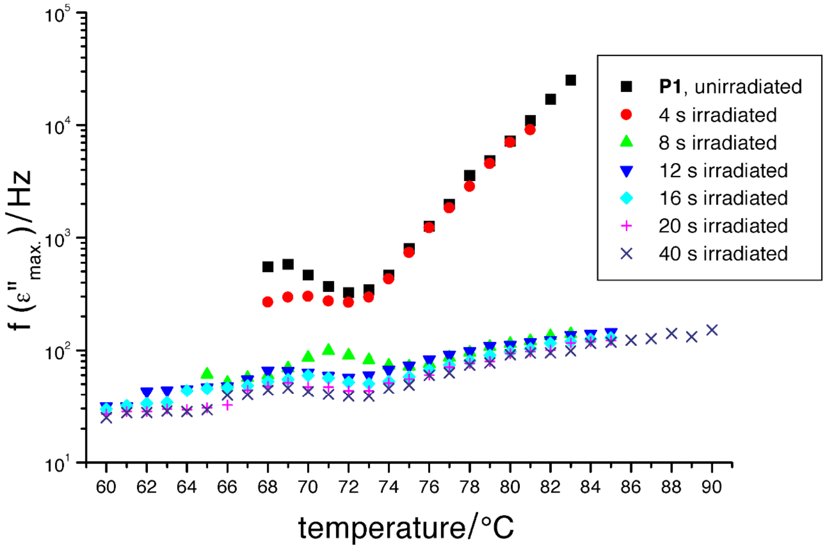
Dielectric measurements were performed using commercial EHC cells with samples oriented in the bookshelf geometry (these cells show a cell resonance above 10^5 Hz). The rubbed, polyimide coated electrodes were separated by spacers of 10 μm thickness. For measurements of the soft-mode dynamics, a HP 4284A impedance analyser was used covering the frequency range from 20 to 10^6 Hz. The measuring voltage was chosen as 1 V a.c. The temperature was controlled by a Cryosystem from Novocontrol (Quatro), the temperature interval was chosen to be ≈ 15°C around the Curie temperature. A d.c. bias of 10 V per 10 μm was applied to suppress the Goldstone-mode in the smectic C* phase. The dielectric strengths, as well as the corresponding relaxation frequencies of the the soft-mode, were determined by fitting the relaxations using the Havriliak–Negami function [17, 18].

The stepwise crosslinking of the polymer **P1** to **E1** was effected by irradiating the LC cell with UV light using a high pressure Xe-lamp (AMKO) and a 365 nm filter. At each step, a complete dielectric characterization (frequency and temperature scan) was made. For the two extreme cases (uncrosslinked **P1** and completely crosslinked **E1**) the results are shown in figure 1.

Three things are noteworthy on comparing figures 1 (*a*) and 1 (*b*). First the frequency of the soft-mode decreases after crosslinking as expected. Secondly, the



(*a*)



(*b*)

Figure 2. 'Critical slowing down' of (*a*) the inverse dielectric strength 1/Δε and (*b*) of the corresponding relaxation frequencies $f(\tilde{\varepsilon}_{\text{max.}})$ as functions of temperature.

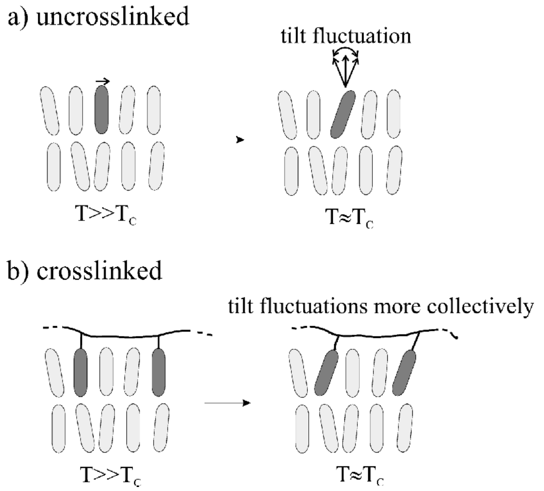


Figure 3. Schematic illustration of the tilt fluctuations of the ferroelectric mesogenic moieties on cooling from smectic A to chiral smectic C phase. (*a*) Uncrosslinked polymer **P1**: independence of tilt fluctuations for each mesogenic unit; (*b*) elastomer **E1**: long-range order induced by the network leads to higher cooperativity of tilt flucuations.

relaxation strength increases from values of about 5 to 15 for ε''. Thirdly, the temperature dependence of the soft-mode broadens. In order to discuss the change of the soft-mode during crosslinking more quantitatively, the maximum of the soft-mode was extracted from these measurements. In figure 2 a plot of the inverse relaxation strength, 2 (*a*), and of the frequency of the soft-mode maximum, 2 (*b*), is given.

Figure 2 shows the expected increase of the relaxation strength and the 'critical slowing down' at the phase transition for the uncrosslinked polymer **P1**. This is in accordance with [12–14]. Upon stepwise crosslinking, the frequency of the soft-mode decreases continuously. At the same time the temperature dependence broadens, figure 2 (*b*). Figure 2 (*a*) shows the increase of the relaxation strength, while the temperature dependence decreases again. In addition a small shift of the Curie temperature (transition smectic A to C*) of one degree is observed.

While the general decrease of the soft-mode frequency is expected, the increase of the relaxation strength and the broadening of the transition needs some explanation. We suggest that the increase of the relaxation strength could be described straight forwardly by an increase in the cooperativity of the soft-mode fluctuations. The broadening of the transition for the ferroelectric elastomers would then mean that the cooperativity of the fluctuations is large even far from the phase transition. This requires a mechanism which increases the cooperativity independently of the phase transition. This could be done by the polymer network, which couples mesogenic groups over large distances. The scenario is then as follows: For the uncrosslinked polymer **P1** the individual mesogen units tilt (more or less) individually. Their tilt couples to that of their neighbours by nearest neighbour interactions, see figure 3 (*a*). The magnitude of this coupling is dominated by the temperature dependent liquid crystalline potential. After crosslinking (**E1**), a temperature independent coupling via the network is added, because the tilting of one mesogen unit stretches the network and so induces a tilting of other mesogen units in the same direction, see figure 3 (*b*). Further investigations—varying crosslinking density and topology—are necessary to prove this interpretation finally and to show structure–property relations.

Financial support by the DFG is greatly appreciated.

References

[1] Zentel, R., 1989, *Angew. Chem. adv. Mat.*, **101,** 1437.
[2] Davis, F. J., 1993, *J. mater. Chem.*, **3,** 551.
[3] Gleim, W., and Finkelmann, H., 1989, *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Glasgow and London: Blackie), p. 287.
[4] Brehmer, M., Zentel, R., Wagenblast, G., and Siemensmeyer, K., 1994, *Macromol. Chem. Phys.*, **195,** 1891.
[5] Brehmer, M., and Zentel, R., 1995, *Macromol. Chem. rapid Commun.*, **16,** 659.
[6] Brehmer, M., Zentel, R., Gießelmann, F., Germer, R., and Zugenmaier, P., 1996, *Liq. Cryst.*, **21,** 589.
[7] Zentel, R., 1986, *Liq. Cryst.*, **1,** 589.
[8] Wong, G. C. L., de Jeu, W., Shao, H., Liang, K. S., and Zentel, R., 1997, *Nature*, **389,** 576.
[9] Blinc, R., and Zekš, B., 1978, *Phys. Rev. A*, **18,** 740.
[10] Levstik, A., Carlsson, T., Filipic, C. C., Levstik, I., and Zekš, B., 1987, *Phys. Rev. A*, **35,** 3527.
[11] Filipic, C., Carlsson, T., Levstik, A., Zekš, B., Blinc, R., Gouda, F., Lagerwall, S. T., and Skarp, K., 1988, *Phys. Rev. A*, **38,** 5833.
[12] Schönfeld, A., Kremer, F., and Zentel, R., 1993, *Liq. Cryst.*, **13,** 403.
[13] Schönfeld, A., Kremer, F., Poths, H., and Zentel, R., 1994, *Mol. Cryst. liq. Cryst.*, **254,** 49.
[14] Poths, H., Wischerhoff, E., Zentel, R., Schönfeld, A., Henn, G., and Kremer, F., 1995, *Liq. Cryst.*, **18,** 811.
[15] Gattinger, P., 1994, *Diploma thesis*, Universität Mainz, Germany.
[16] Gebhard, E., and Zentel, R., 1998, poster presentation in *27th Freiburger Arbeitstagung Flüssigkristalle*, March 1998, Freiburg.
[17] Havriliak, S., and Negami, S., 1966, *J. polym. Sci.*, **C14,** 89.
[18] Havriliak, S., and Negami, S., 1967, *Polymer*, **8,** 161.