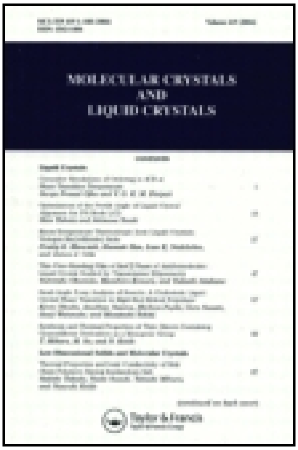

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Electroclinic Effect in Some Side-Chain Polysiloxane Liquid Crystals

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Version of record first published: 24 Sep 2006.

To cite this article: K. Flatischler , L. Komitov , K. Skarp & P. Keller (1991): Electroclinic Effect in Some Side-Chain Polysiloxane Liquid Crystals, Molecular Crystals and Liquid Crystals, 209:1, 109-115

To link to this article: http://dx.doi.org/10.1080/00268949108036184

Mol. Cryst. Liq. Cryst., 1991, Vol. 209, pp. 109–115
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Printed in the United States of America

Electroclinic Effect in Some Side-Chain Polysiloxane Liquid Crystals

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(Received July 26, 1990)

The electroclinic effect in the chiral smectic A phase has been investigated in side-chain polysiloxane liquid crystals. The amplitude of the electro-optical response in the smectic C* phase was studied, and the tilt angle determined by studying the response at very low frequency. The electroclinic effect shows the same general behaviour as in low-molecular weight systems, with a divergent electroclinic coefficient near T_c and a field-independent response time of about 10 microseconds a few degrees from T_c.

Keywords: electroclinic effect, polymeric liquid crystal, polysiloxane LC

INTRODUCTION

The electroclinic effect[1] in the chiral smectic A (A*) phase has recently received increased attention due to its application potential.[2,3] In the paraelectric A* phase, the soft-mode response shows a typical Curie-Weiss behaviour, with a divergent susceptibility at the transition to the ferroelectric chiral C (C*) phase. The amplitude of the soft-mode decreases steeply when entering the C* phase, hence the electroclinic effect, which in smectic phases is a soft-mode excitation, is of particular interest in the A* phase and other orthogonal smectic phases. The effect is studied in thin cells (usually a few micrometers thick) with the smectic layers perpendicular to the confining glass substrates (bookshelf geometry). An applied electric field E across the cell (along the smectic layers) will induce a molecular tilt θ, which is a linear function of the field. In the low-molecular weight materials studied so far, the largest induced tilt angles are around 10–12 degrees at temperatures not too far from the A*–C* transition. In the present paper we present measurements on a side-chain polysiloxane liquid crystal, exhibiting chiral smectic A and C phases. In the A* phase, a good bookshelf alignment could be obtained, and the electroclinic effect could be studied in detail. The alignment deteriorated when going into

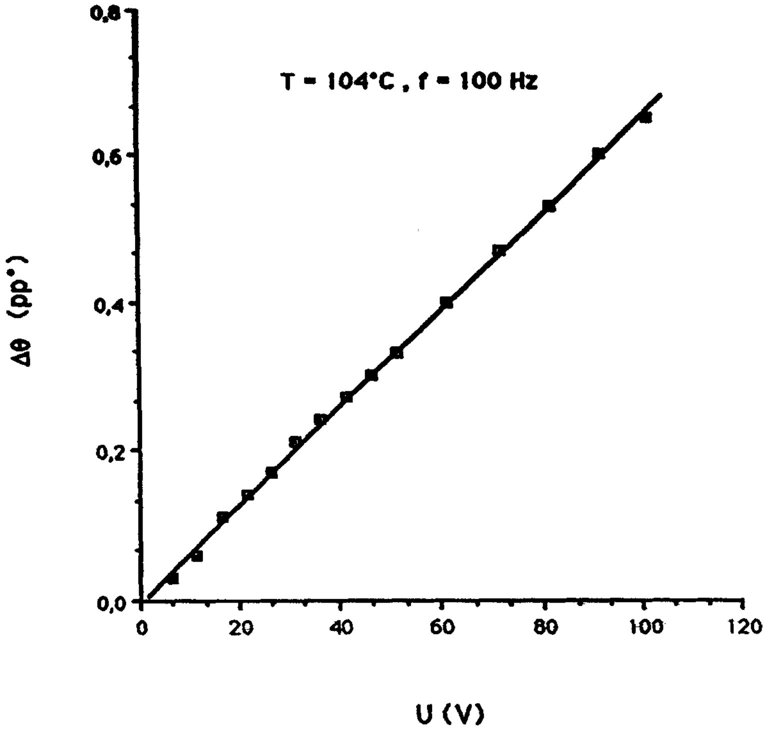
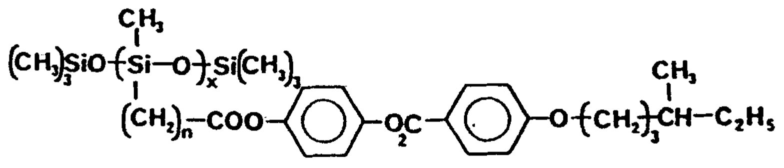


FIGURE 1 The dependence of the peak to peak induced tilt angle vs. peak to peak applied voltage V at T = 104°C for the investigated polymer.

the C* phase, especially at lower temperatures, which made measurements of polarization and other parameters difficult. However, applying a very low frequency signal, the tilt angle in the C* phase could be deduced from the amplitude of the optical response.

EXPERIMENTAL

Several new liquid crystalline side-chain polysiloxanes were synthesized by Keller.[4] From these polymers, we investigated compounds of the general form



The studies were concentrated on polymers with spacer length n = 10 and an average degree of polymerization x equal to 36. The transition temperatures are found to be (82.9°C) C* (101.9°C) A* (123.0°C) Isotropic, obtained from polarizing microscopy and DSC investigations.

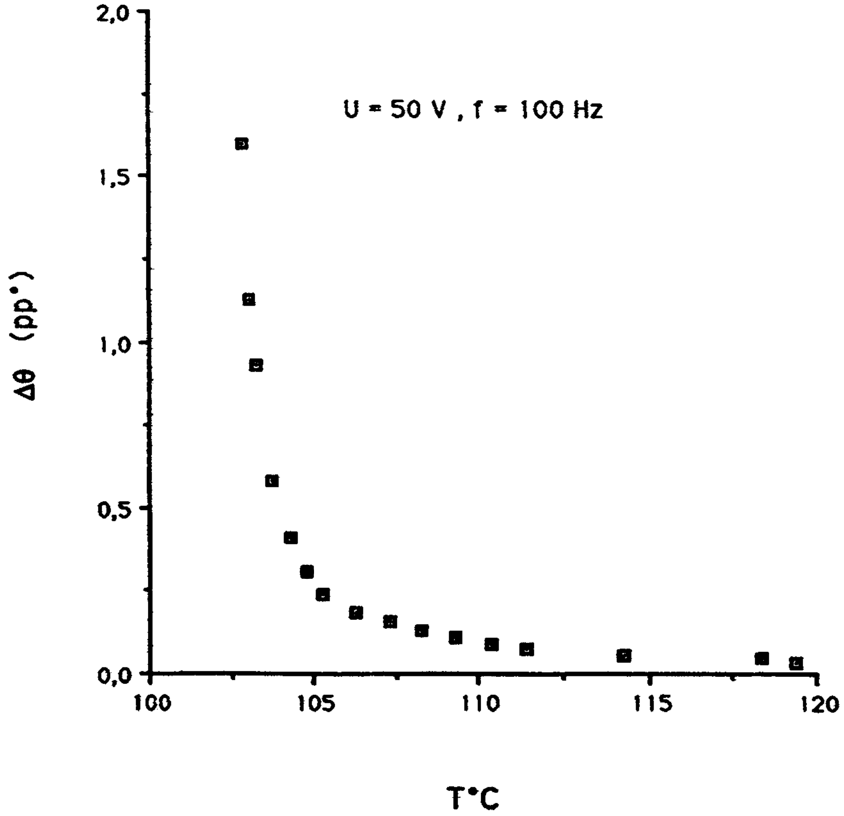


FIGURE 2 The temperature-dependence of the peak to peak induced tilt angle for an applied field of 50 V peak to peak amplitude and frequency 100 Hz.

The polymer was investigated in a standard set-up[5] for electro-optical and polarization measurements on ferroelectric smectics. Spacers of 2 micrometer thickness were evaporated on the lower glass plate. The cells were coated with siliconmonoxide, evaporated perpendicular to the plates, and the bookshelf alignment was obtained by shearing the upper plate in the A* phase. The polymer was introduced into the cell in the isotropic phase in a vacuum filling chamber.

In the chiral A phase, the bookshelf alignment is fairly easily obtained with the shearing technique, although care has to be taken to avoid the sample from going into the homeotropic alignment. In the C* phase, domains with different preferred directions are formed, and the alignment is distorted into a sandy texture. Using the standard set-up, the electroclinic effect in the A* phase could be readily characterized, but the measurements in the C* phase were difficult due to the poor alignment.

RESULTS

The characteristic features of the electroclinic effect may be deduced from a simple phenomenological description.[6] The result for the field-induced tilt angle θ is

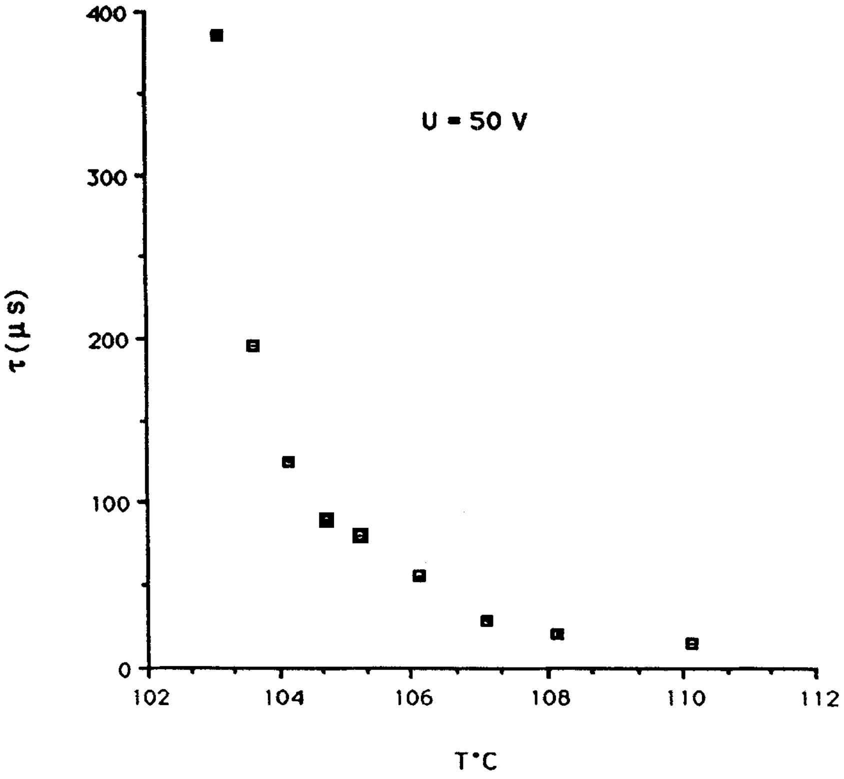


FIGURE 3 The temperature-dependence of the response time with the same applied field as in Figure 2.

$$\theta = e_c\, E \text{ where } e_e = \frac{d\theta}{dE} = \frac{\mu}{\alpha(T - T_c)}$$

The constants μ and α are coefficients in the Landau free-energy expansion,[6] and e_c is the electroclinic coefficient, which is seen to diverge at T_C. Far from the transition, on the other hand, e_c shows only a weak temperature dependence. In Figure 1 is shown the linear field-dependence of the induced tilt angle for the studied polymer, and in Figure 2 the divergence of e_c near the transition is demonstrated. The induced tilt angles are only a few tenths of a degree, which is almost two orders of magnitude less than what is achievable in low-molecular weight liquid crystals.

The electroclinic response time can be written as[6]

$$\tau = \frac{\gamma_\theta}{\alpha(T - T_c)}$$

where γ_θ is the soft-mode viscosity. The characteristic critical slowing-down when approaching T_C is evident from Figure 3. The feature of a field-independent re-

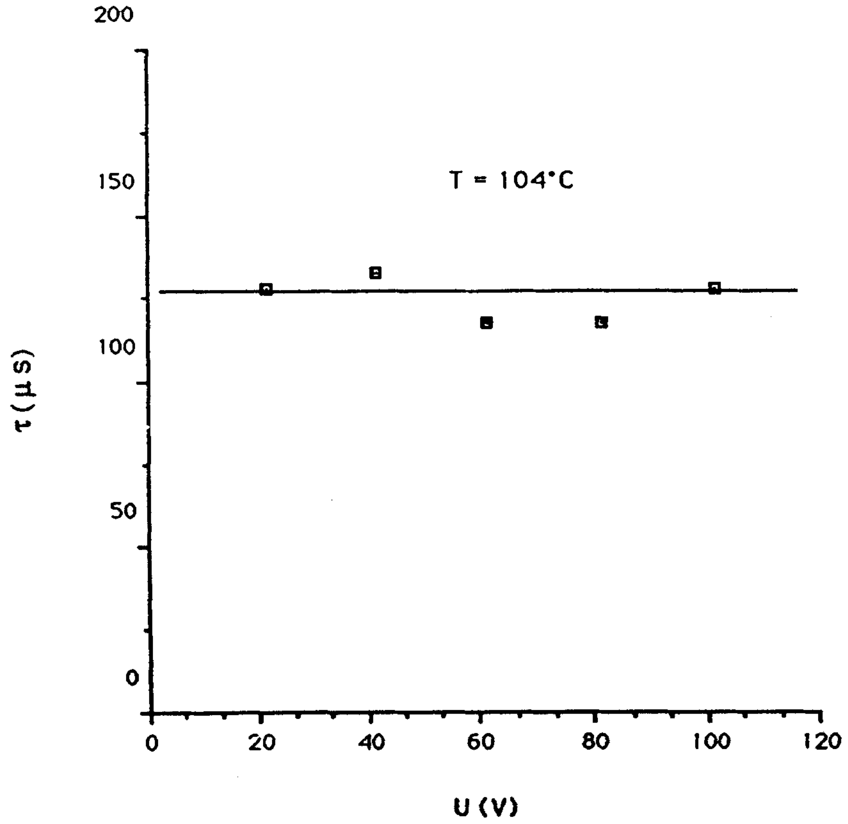


FIGURE 4 Response time versus applied electric field at $T = 104°C$.

sponse time, which distinguishes the electroclinic switching from both the ferroelectric and the dielectric response, is displayed in Figure 4. This measurement, giving $\tau = 125$ μs, was made not very far (2 degrees) from the transition. Further away from T_C the response time decreases to about 10 μs, which is about one order of magnitude larger than in low molecular weight systems. The response time shown in Figure 4 agrees with the frequency of the soft-mode relaxation, occurring at about 8 kHz at the same temperature (Figure 5).

When going from the A* phase to the ferroelectric C* phase, the texture of the polymer sample changes, and becomes irregular deep into the C* phase. It was not possible to measure the spontaneous polarization of the polymer, presumably because of the very high viscosity and ionic conductivity. The slow switching in the C* phase made it necessary to use a very low frequency when performing the tilt angle measurements. In the results shown in Figure 6, the frequency of the driving voltage was 0.08 Hz. A saturation in the measured tilt values was noticed above about 60 V for this frequency. The electro-optic switching times are comparatively much larger than for low molecular weight chiral C systems, lying in the 50–100 ms region.

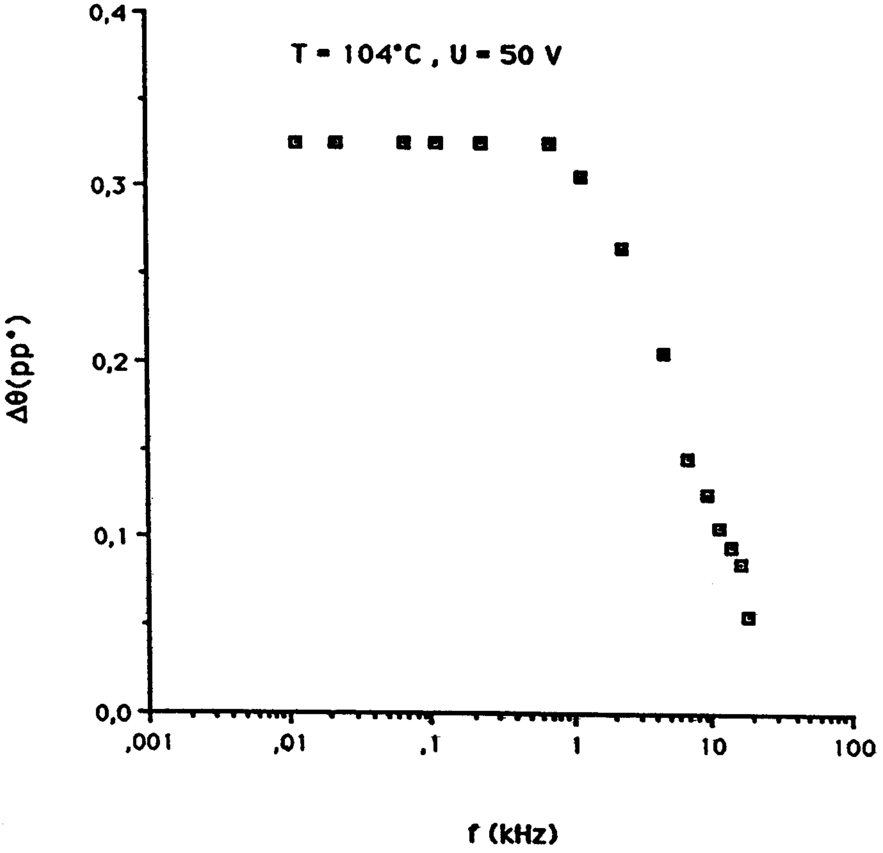


FIGURE 5 The frequency characteristics of the peak to peak electroclinic response Δ at T = 104°C. The soft-mode relaxation time is approximately 8 kHz.

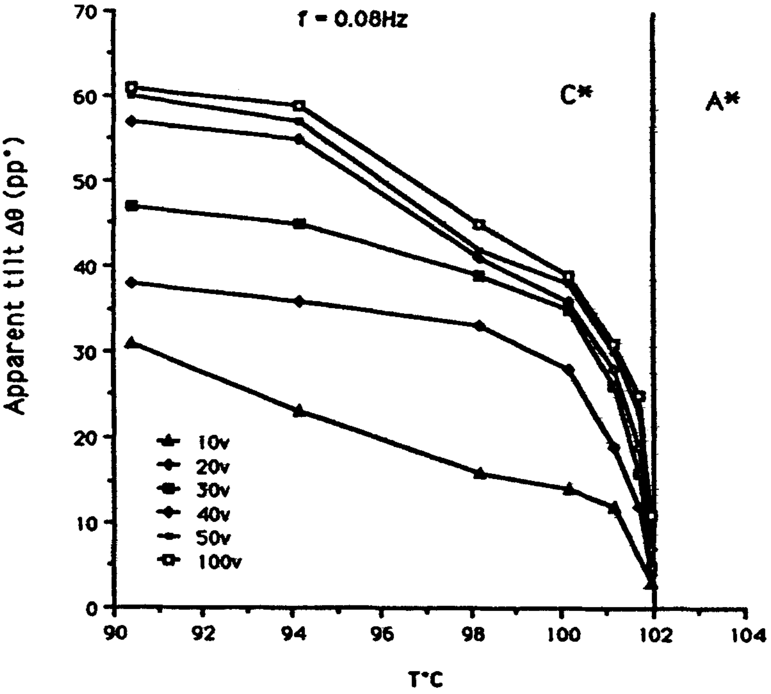


FIGURE 6 The apparent peak to peak tilt angle in the smectic C* phase of the polymer. The measured tilt angle values show a field dependence, with a saturation at about 60 V peak to peak. The field-dependence is presumably due to field-induced alignment effects on both the smectic layers and the director.

Acknowledgment

Work supported by the National Swedish Board for Technical Development under Grant No. 84-3693, and the Swedish Natural Science Research Council under Grant No. F-FU 3361.

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