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From monomeric to polymeric ferroelectric liquid crystals A comparative study of ferroelectric properties

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From monomeric to polymeric ferroelectric liquid crystals
A comparative study of ferroelectric properties

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Two new ferroelectric oligosiloxanes, a cyclic tetramer and a twin, have been synthesized. By a comparative study with their corresponding monomer and side chain polysiloxanes, the influence of oligo- and polymerization on the liquid crystalline and ferroelectric properties have been investigated. Polymerization leads to a stabilization of LC phases through increase of the clearing temperatures and suppression of crystallization. Oligomerization also leads to mesophase broadening, but, due to the low degree of polymerization, the effect is inferior to the linear polysiloxanes. The low viscosity of the oligosiloxanes ensures response times in the microsecond region, thus being comparable with their monomer and conventional LMWFLCs. It is found that polymerization increases the spontaneous polarization P_S. This is attributed to the density increase after polymerization, enhancing the inter-mesogenic interactions. The collective and local dynamics of the OFLCs are influenced differently with respect to their molecular structures. Each oligomer is already a good model for its corresponding polymer concerning the soft mode dynamics. For the local β-relaxation a similar temperature dependence of the relaxation times τ for the cyclic tetramer and for the side chain polysiloxanes is observed. The long axial rotation of the twin, having a very efficient decoupling, is significantly faster, thus resembling the monomer.

1. Introduction

Since the discovery of ferroelectricity in chiral C* smectics [1], low molecular weight ferroelectric liquid crystals (LMWFLCs) have been widely investigated with respect to their potential applications in the fast switching bistable displays [2, 3]. Also, polymeric ferroelectric liquid crystals (PLFCs) exhibiting S_C^* phases have now been studied for more than a decade with respect to their ferroelectric properties [4]. However, the fixation of mesogenic cores to a polymer backbone increases the phase transition temperatures and viscosities, and this results in unfavourably slow response times. Until now, apart from only a few publications [5, 6] almost no attention has been paid to oligomeric ferroelectric liquid crystals (OFLCs). As key intermediates, oligomeric ferroelectric liquid crystals combine the low viscosities (thus short response times) of LMFLC with the mechanical stability of PFLCs, leading to an interesting property profile [7]. Moreover, the absence of any polydispersity in some oligomers, which is by contrast an inherent property of polymers (except LC polymers prepared [8, 9] by living polymerization techniques), facilitates the reproducibility of LC and FLC properties.

To this end, we have synthesized two new OFLCs **2** and **3** (see scheme 1) with different molecular topologies and studied the influence of polymerization upon their liquid crystalline and ferroelectric properties (including molecular and collective dynamics) by comparative study with the corresponding monomer **1** and the linear polysiloxanes **4** and **5** (scheme 1). Organosilicon oligomers were chosen, because they are commercially available on a large scale and it had been proven for ferroelectric polysiloxanes [10] that the low viscosity of the backbone and the formation of a microphase-separated structure lead to a pronounced decrease in response times and improved alignment behaviour.

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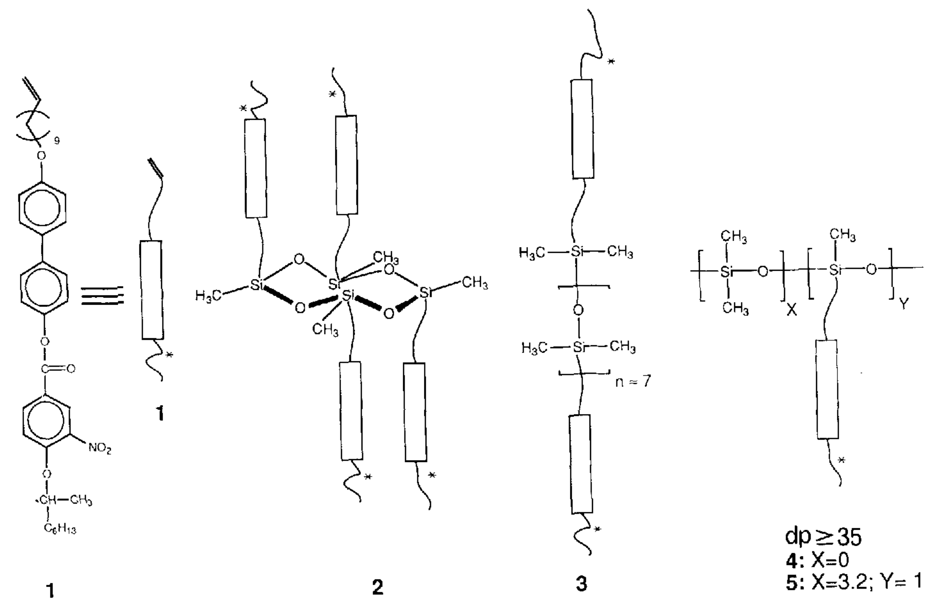


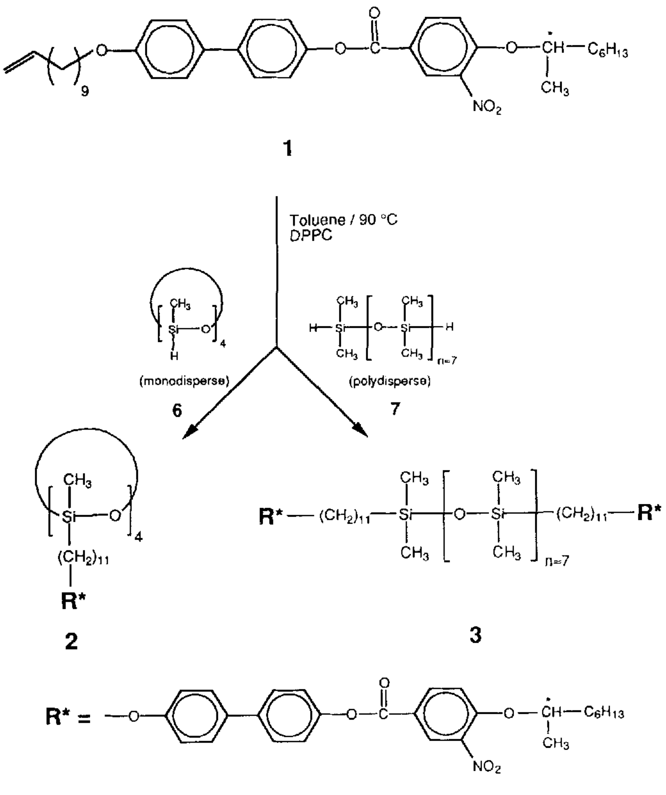
Scheme 1.

2. Synthesis and characterization

The oligomeric ferroelectric liquid crystals **2** and **3** were prepared through a classical hydrosilylation [11, 12] between the oligomeric precursor siloxane **6** or **7** and 4-(*R*-1-methylheptyloxy)-3-nitrobenzoic acid 4′-(undec-10-enyloxy)biphenyl-4-yl ester **1** [10] in the presence of dicyclopentadienylplatinium dichloride (DPPC) [13] as catalyst (see scheme 2). Only one possible conformation (atactic) of the cyclic tetramer **2** is presented in scheme 2. Triad analysis by ^{29}Si NMR of the cyclic siloxane **6** shows 50 per cent of heterotactic triads and 25 per cent each of syndio- and iso-tactic triads [14]. Assuming a Bernoulli distribution, a 50 per cent probability of meso-diads is expected.

For the cyclic tetramer **2** with one mesogenic moiety per siloxane unit, a similarity of its thermal and ferroelectric properties with its linear analogue **4** is expected. For the dimeric OFLC **3**, with a low average degree of polymerization (dp ≈ 8), the high amount of flexible siloxane units should firstly significantly reduce the viscosity and lead secondly to a suppression of the crystallization. Moreover, since the ratio of chiral mesogenic moieties to siloxane units in dimer **3** is comparable to that of the 'diluted' copolysiloxane **5**, some of its ferroelectric properties should also be similar.

To clarify these points, all compounds were investigated concerning their liquid crystalline properties by optical polarizing microscopy using a Leitz Ortolux II-Pol BK microscope equipped with a Mettler FP 5 hot stage in conjunction with a Mettler FP 50 thermal controller. Calorimetric measurements were performed with a (Perkin–Elmer) DSC-7 with a heating or cooling rate of ± 10°C. Peak maxima from the second heating were taken for the determination of the phase transition temperatures. The low enthalpy S_C^*–S_C^* transition was detected by the occurrence of pitch lines observed on microscopic observations. Temperature dependent powder X-ray measurements were performed with a Siemens TT-500



Scheme 2.

Phase transitions, spontaneous polarization P_s, tilt Θ and response time τ for compounds **1–5**.

Compound	Phase transitions/°C Transition enthalpies kJ mol^{-1} mol^{-1}	P_s†/nC cm^{-2}	Θ†/°	τ§/ms
1	CrK 61 S_C^* 80 S_A 88 I 20·8 0·2 3·1	184	27	0·1
2	Cr 81 S_X‡ 116 S_C^* 140 S_A^* 151 I 10 — 0·8 5·0	183	29	0·4
3	g −22 S_C^* 82 S_A^* 114 I — 4·2	112	32	0·1
4	g 21 S_X 57 S_C^* 156 S_A^* 183 I 0·74 3·1 2·72	211	29	17·3
5	g 0 S_X 46 S_C^* 98 S_A^* 144 I 10·3 — 4·2	104	26	3·9

† 10°C below the upper temperature limit of the S_C^* phase.

‡ Switchable higher ordered smectic phase; presumably S_F^* or S_I^*.

§ 10°C below the upper temperature limit of the S_C^* phase; applied field: 10 $V_{pp}/\mu m$.

instrument, with a home made oven, *in vacuo*, with Ni-filtered Cu_{K_α} radiation. The spontaneous polarizations, tilt angles and response times were measured according to procedures described in detail in [10]. Commercially prepared sample cells for E.H.C. company, Ltd. Japan, with rubbed polyimide coatings, were used with a thickness of 4 or 10 μm and an active electrode area of 0·16 cm^2. They were filled on a Kofler hot bench using the isotropic phase and capillary forces. Good planar alignments were obtained for all samples using heating and cooling cycles through the S_A^*–S_C^*-transition regime, while applying a low frequency square wave of a few Hertz and a voltage of 10 $V_{pp}/\mu m$.

Dielectric spectroscopy was performed with two different measurement systems in order to cover the entire frequency range from 10^{-1} to 10^9 Hz: (i) a frequency response analyser (Schlumberger 1260); (ii) a coaxial line reflectometer (HP 4191 A). Rubbed, polyimide coated electrodes diameter (5 mm, spacing 20 μm) were developed and could be used over the entire frequency regime [15].

Synthetic procedures and the data on the liquid crystalline and ferroelectric properties of compounds **1**, **4** and **5** are taken from [10]. The synthesis of the dimesogenic siloxanes **3** will be published elsewhere [16].

3. Results and discussion

3.1. *Mesophase behaviour*

The data relating to the phase transitions and some ferroelectric properties (P_s, Θ and τ) are compiled in the table. All compounds show broad chiral smectic C* and smectic A phases. Comparing the phase transition temperatures of **1** and the corresponding linear polysiloxanes **4** and **5**, a conventional behaviour of polymerized LCs is observed-stabilization of the LC phases through an increase of the clearing temperature and a suppression of crystallization. The polymer fixation increases the phase transition temperatures, is most pronounced for compounds (**2** and **4**) where all siloxane units are modified with mesogenic groups. The partial substitution of mesogenic siloxane units by non-mesogenic dimethylsiloxane units ('dilution;) [10] (compounds **3** and **5**) leads to a less pronounced increase in the transition temperatures. The OFLCs **2** and **3** show intermediate mesophase behaviour. The oligomerization also leads here to mesophase broadening, but nevertheless—because of the low degree of polymerization—the effect is smaller than for the linear polysiloxanes. The chiral smectic C* phase is limited in range for the cyclic tetramer **2** in the lower temperature regime, by an increased melting point and by the occurrence of a higher ordered smectic phase (denoted here as S_X). The existence of the latter could be confirmed by calorimetric detection of a very small endothermic transition to the S_C^* phase (10 times smaller than for the corresponding order S_C^*–S_A transition), suggesting a strong structural similarity between the two phases (presumably the phase is S_F^* or S_I^*). From microscopic observations, as well as dielectric and electro-optic measurements (see below), the S_X phase could be clearly detected. The crystallization of OFLC **3** is suppressed due to its polydispersity, yielding a low viscosity material with a room temperature switchable S_C^* phase.

The characterization of the smectic mesophase was also carried out by temperature-controlled X-ray diffraction of powder samples. An example, the X-ray diffraction patterns for OFLC **2** are displayed in figure 1. As is typical for microphase segregated LC polysiloxanes [10], the cyclic tetramer **2**, over the whole temperature regime of the LC phases, exhibit well-pronounced Bragg peaks (up to fifth order) in the small angle region, indicating a very good layer ordering. The 002 reflection in the S_C^* and S_X

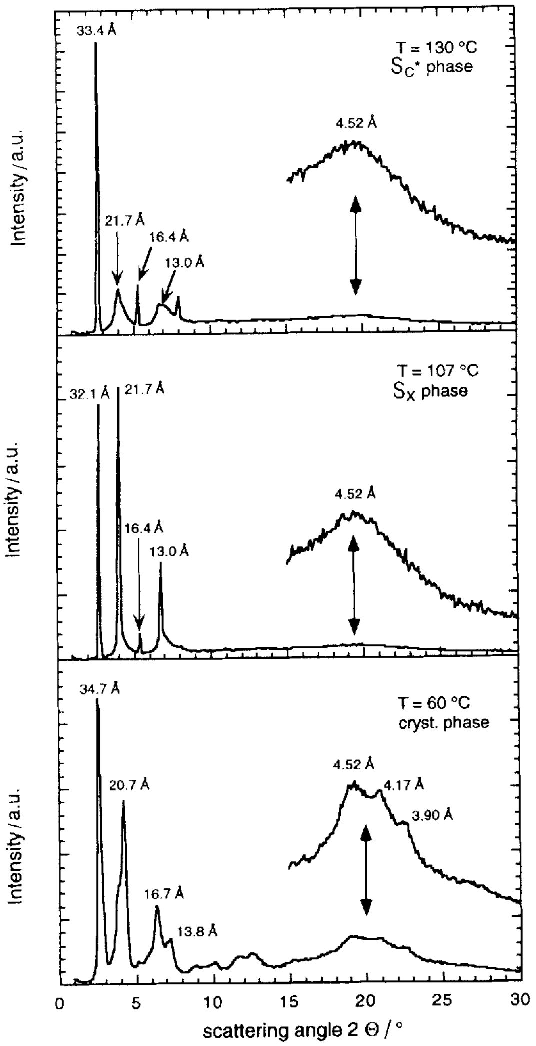
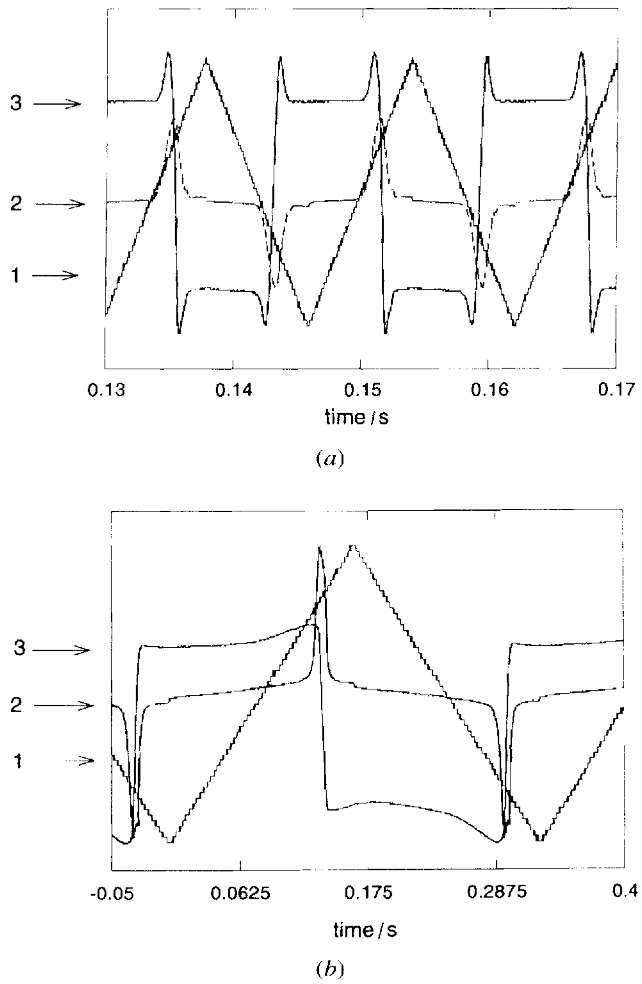


Figure 1. Temperature dependent X-ray data for powder samples of OFLC **2**.

phase of 33·4 Å and 32·1 Å, respectively, corresponds to the length of a tilted monolayer, whereas the 001 reflection (bilayer) could not be resolved with the experimental set-up used. In the S_C^* phase ($T = 130°C$, see figure 1) the wide angle region shows a halo, which is characteristic for a fluid-like packing of the mesogenic units. Cooling into the ferroelectric S_X phase gave no change in the wide angle region other than a sharpening and an intensity increase of the Bragg peaks, indicating a higher in-layer-ordering. This underlines once more the structural similarity between the S_X and the S_C^* phases. Well-aligned samples would be useful here to study the organization of this ferroelectric phase. The crystalline phase ($T = 80°C$, see figure 1, bottom) could be clearly detected by a splitting of the halo into several reflections (4·52 Å, 4·17 Å and 3·90 Å), representing an additional ordering within each smectic layer.

3.2. *Ferroelectric properties*

Figure 2 shows oscilloscope traces of the bistable ferroelectric switching of OFLC **2** in the S_C^* and S_X phases. The transition between these two phases could be detected by a marked slowing down of the polarization reversal current (coinciding with a pronounced viscosity increase) on passing into the S_X phase. In order to obtain saturation of the polarization, the frequency had to be reduced from 62 Hz in the S_C^* phase to 3 Hz in the S_X phase, while increasing simultaneously the applied electrical field. Response time measurements for OFLC **2** reveal the higher ordered organization of the S_X phase by a remarkable increase in the switching times (see figure 3). In the S_C^* phase, response times as short as 400 μs at 130°C (7·5 $V_{pp}/\mu m$) were measured, which are comparable to those for monomer **1** (see table 1). The low viscosity of the



(*a*)

(*b*)

Figure 2. Current (trace 2) and optical response (trace 3) of the cyclic tetramer **2** in 10 μm EHC cell. Trace 1 = applied voltage; measuring resistance: 10 kΩ. Note the different time axes. (*a*) S_C^* phase ($T = 130°C$): $P_s = 183\ nC\ cm^{-2}$, ($f = 62$ Hz; 67 V_{pp}); (*b*) S_X phase ($T = 105°C$): $P_s = 250\ nC\ cm^{-2}$, ($f = 3$ Hz, 82 V_{pp}).

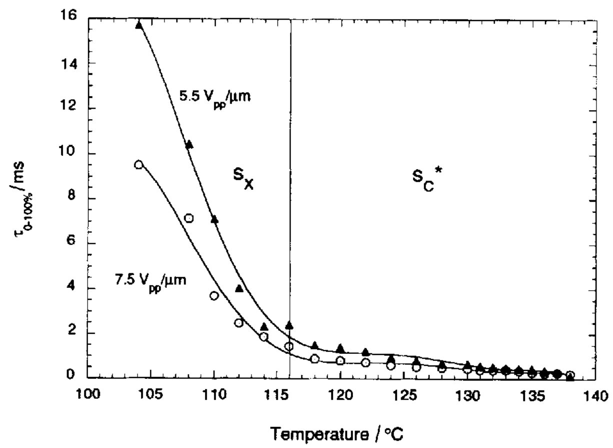


Figure 3. Response times $\tau_{0\text{-}100\ \text{per cent}}$ versus temperature for OFLC **2** (1 Hz square wave).

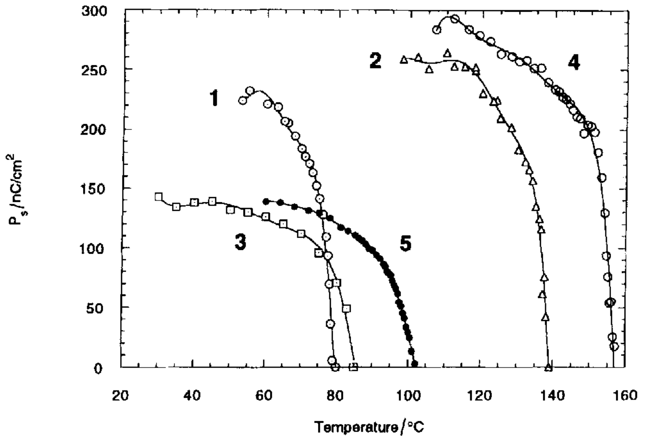


Figure 4. Temperature dependence of the spontaneous polarization P_s for compounds **1–5** (see scheme 1).

oligomeric FLCs presented here is proved by a simple, but nevertheless noteworthy observation: the filling of the LC test cells by capillary forces using the isotropic phase was finished within less than half an hour, whereas several hours were needed for the polymers. In this context it should be pointed out, that the dimesogenic OFLC **3** is, at room temperature, a waxy solid, which is switchable at room temperature with response times of 37 ms for 2 V_{pp}/μm at 30°C.

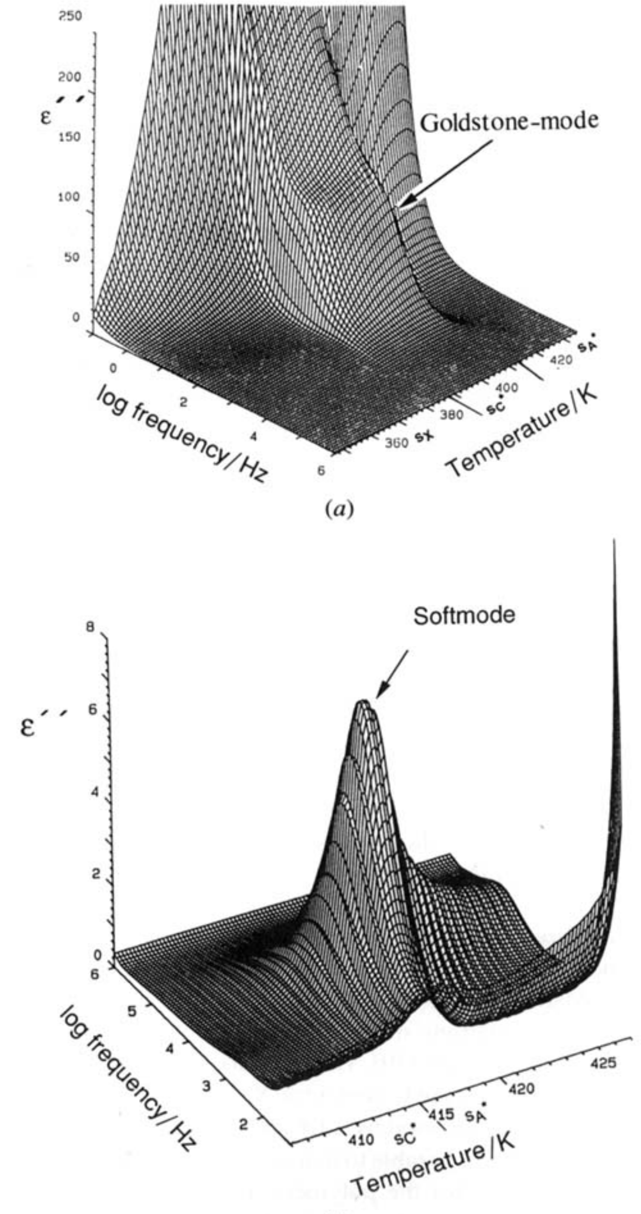
The temperature dependence of the spontaneous polarization P_s is shown in figure 4 for compounds **1–5**. From this, the influence of oligo- or poly-merization, respectively on the S_C^*–S_A^* phase transition temperature and on P_s can be summarized as follows. The polymer fixation of monomer **1** increases the S_C^*–S_A^* phase transition temperature for all compounds. The effect is most pronounced for homopolymer **4**, whereas the OFLCs **2** and **3** show an intermediate behaviour. Polymerization increases P_s. This follows from a comparison of monomer **1** with its corresponding homopolymer **4**. While the tilt angles vary only slightly (see table 1), the enhanced inter-mesogen interactions, caused by a density increase after polymerization [17], have to be responsible for this effect. The spontaneous polarization P_s of the cyclic tetramer **2** is comparable to that of monomer **1**. Here the low degree of polymerization (dp = 4) results in a density increase that is not too high. Moreover, the steric geometry of the cyclic siloxane core may perhaps interfere with a adoption of a conformation which is most suitable for high P_s values. The spontaneous polarization P_s for the 'diluted' compounds **3** and **5** are significantly lower than for the 'undiluted' compounds **2** and **4**. In these microphase separated systems [10, 18], the siloxane sub-layers do not contribute to P_s [10]. Since the mesogen concentration of OFLC **3** is not too different from that of copolysiloxane **5**, similar P_s values are measured.

3.3. *Dielectric properties—molecular and collective dynamics*

Broad-band dielectric spectroscopy was used in order to measure the Goldstone and soft mode dynamics, as well as the high frequency β-relaxation [19]. In the first part of the following chapter, a broad-band dielectric characterization of the cyclic tetramer **2** from 10^{-1} Hz–10^9 Hz is presented. The influence of oligo- or poly-merization on the molecular and collective dynamics of compounds **1–5** is presented in the second part.

3.3.1. *Broad-band dielectric characterization of OFLC* **2**

The relaxation spectrum below 1 MHz is dominated by the Goldstone mode (see figure 5 (*a*)), which is attributed to phase fluctuations of the polarization vectors of the helical superstructure [19]. The Goldstone mode is limited to the existence of the ferroelectric S_C^* phase and could be continuously suppressed by a DC bias field. Its frequency dependence is comparable to that of monomer **1**, but is 1–2 times faster than for the polymeric homologues **4** and **5** [20]. In the higher ordered ferroelectric S_X phase, it is presumably masked by the ionic conductivity, because the higher viscosity (here: Goldstone mode viscosity γ_G) leads to a decrease of the relaxation frequency. By applying a d.c. bias voltage of 30 V, the soft mode could be clearly detected as a strong dielectric loss ε'' in the temperature region of the S_C^*–S_A^* transition (see figure 5 (*b*)). This second collective process is assigned to tilt angle fluctuations of the helical superstructure [19]. The frequency of the maximum dielectric loss $f_{\max \varepsilon''}$ was found to be 2·5 kHz at the S_C^*–S_A^* transition. Two-dimensional representation of $f_{\max \varepsilon''}$ and of the inverse dielectric strength $1/\Delta\varepsilon$ versus temperature show the critical slowing down which is similarly found for conventional LMWFLCs [19]. In the high frequency range (10^6 Hz to 10^9 Hz), one local relaxation process is found for the cyclic



(*a*)

(*b*)

Figure 5. (*a*) Dielectric loss ε'' of the Goldstone mode as function of frequency and temperature for the cyclic tetramer **2** (sample thickness = 20 μm, sample diameter = 5 mm). (*b*) Dielectric loss ε'' of the soft mode as function of frequency and temperature for the cyclic tetramer **2** (DC-bias voltage: 30 V, sample thickness = 20 μm, sample diameter = 5 mm).

tetramer **2** (see figure 6). This so-called β-relaxation is assigned to the hindered long axial rotation of the mesogen units ('libration') [15]. The steps in ε'' in figure 6 are caused by the various LC phases, with different ordering of the dipoles, interacting with the external electric field. At the I–S_A^* transition, the improved alignment of the sample on cooling is responsible for the increase of $\Delta\varepsilon$. The tilting of the mesogenic units into a bookshelf geometry and the occurrence of a macroscopic polarization give rise to the second step at the S_C^*–S_A^* transition, because the aspect angle of the dipole moment, interacting with the external electrical field, changes. The better ordering of the ferroelectric dipoles in the higher ordered S_X phase results in the third step ε''. This increase correlates well with the sharpening of the polarization peaks in the switching experiments (see figure 2 (*b*)).

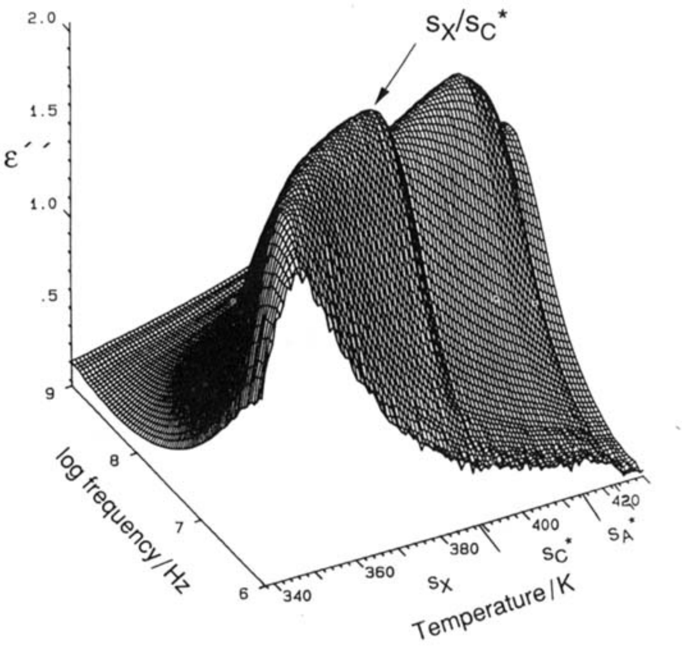


Figure 6. High frequency relaxation for the cyclic tetramer **2** (sample thicknesses = 20 μm, sample diameter = 5 mm).

3.3.2. *From monomer to polymer-collective and local dynamics*

The influence of oligo- or poly-merization on the soft mode dynamics and the high frequency relaxation is discussed in the following section.

The critical slowing down (visible as strong decrease in $f_{\max\varepsilon''}$) of the soft mode frequency $f_{\max\varepsilon''}$ is displayed in figure 7 as a function of T–T_C ($T_c = S_C^*$–S_A transition temperature). This is attributed to the growing collectivity (for example, domain size) of tilt fluctuations in the vicinity of the ferroelectric and paraelectric phase transition. It is most pronounced for monomer **1** and is weakest for 'diluted' copolysiloxane **5**. In relation to the latter, a ten times stronger critical slowing down is found for homopolymer **4**. The 'dilution' of mesogenic siloxane units with non-mesogenic dimethylsiloxane units seems to decrease the temperature dependence of the soft mode [21]. In this regard, the intermediate behaviour of OFLCs **2** and **3** should be pointed out. The soft mode behaviour of the cyclic tetramer **2** is already close to that of

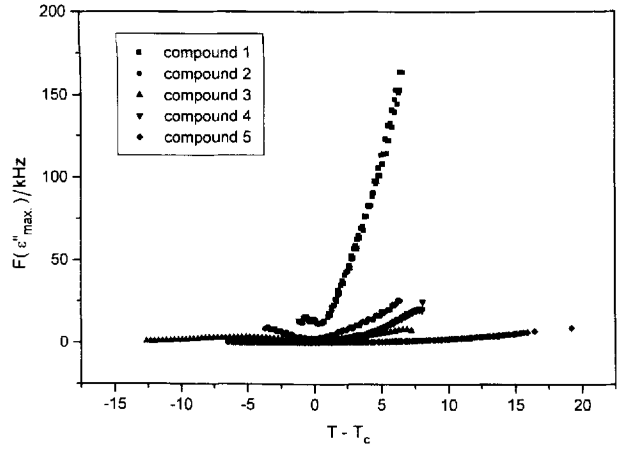


Figure 7. Comparison of the critical slowing down of the soft mode for compounds **1–5**.

homopolymer **4**, whereas for OFLC **3** it is closer to that of the 'diluted' copolysiloxane **5**. The question to be answered is: why is the increase of the soft mode frequency in the smectic A* phase so small for the polymers? A possible explanation involves taking the mobility of the polysiloxane chains into consideration. The fluctuation of the tilt of the mesogenic units (soft mode) decreases the smectic layer thickness, but increases its lateral extension (concerning constant density). Therefore the soft mode must be coupled to an extension of the siloxane sub-layers in the layer plane and thereby to the viscosity of the polymer chains.

In the high frequency regime, all samples show the β-relaxation, which is attributed—as already explained above—to the hindered long axial rotation of the mesogenic units. The relaxation times τ, obtained from Havriliak–Negami fits [22], are plotted in figure 8 as a function of the inverse temperature, $1/T$. Over the entire temperature range of the LC phases, the relaxation times τ of monomer **1** are approximately half a decade smaller than for the copolysiloxane **5**. The fixation of the mesogen units to a polymer backbone obviously hinders or slows down the long axial rotation. The oligomeric compounds **2** and **3** show an intermediate behaviour. However for the local β-relaxation, the situation is reversed in comparison to the soft mode dynamics (see figure 7), underlining the very different nature of these processes. The dynamics of the β-relaxation of the cyclic tetramer **2** is close to that of the polysiloxanes **4** and **5**, whereas the dimesogenic compound **3** is closer in behaviour to monomer **1**. At this point it is worthwhile to recall the molecular structures of these compounds. For the cyclic tetramer **2**, every siloxane unit is attached to a mesogenic group. The dimesogenic material **3** consists of short polymer chains with a low average degree of polymerization of about 8, where only two siloxane units are modified with mesogenic moieties. The rest of the molecule consists of flexible dimethylsiloxane (DMS) units (see scheme 1). Evidently, the short siloxane chains lead to an efficient decoupling of the mesogens, thereby not hindering the long axial rotation to much. A variation of the copolymer composition (polymers **4** and **5**), keeping the degree of polymerization longer than 35, has however no significant effect on the β-relaxation [21].

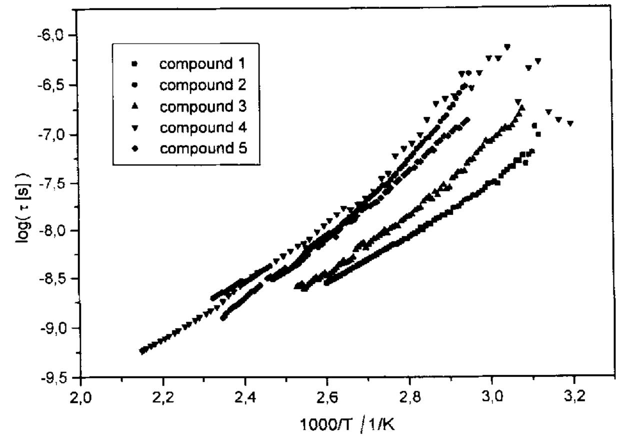


Figure 8. Activation plot for the high frequency relaxation for compounds **1–5**.

4. Conclusions

Summarizing the results outlined above, an intermediate behaviour of the oligomeric FLCs **2** and **3** is found. The question whether the OFLCs are good model compounds for FLC polymers strictly depends on their molecular structure and on the properties upon which one is focused.

Concerning the spontaneous polarization, the dimesogenic OFLC **3** is a good model compound for 'the diluted' polysiloxane **5**, because both systems, having an approximately equivalent ratio of mesogen units to dimethylsiloxane units, are microphase separated. As a result of the low degree of polymerization, the low viscosity of OFLCs **2** and **3** ensures rise-times in the sub-millisecond range. They are comparable with monomer **1** and conventional LMWFLCs. The polydispersity of the dimesogenic compound **3** prevents crystallization and preserves a room temperature switchable S_C^* phase.

The collective and local dynamics of the OFLCs are influenced differently with respect to their molecular structure. Each oligomer is a good model for its corresponding polymer concerning the soft mode dynamics. Thus, the soft mode of OFLC **3** is comparable to that of copolysiloxane **5**. The soft mode of the tetramer **2** is only slightly faster than for homopolymer **4**. For the local β-relaxation, a similar temperature dependence of the relaxation times τ for the cyclic tetramer **2** and for polymers **4** and **5** is observed. The long axial rotation of the dimesogenic siloxane **3**, having a very efficient decoupling, is significantly faster, and so it resembles the monomer.

5. Experimental

5.1. *Materials*

The oligomeric siloxanes **6** (from ABCR) and **7** (from Wacker) were used as received. Toluene was boiled over potassium and distilled under nitrogen. As a typical example the synthesis of OFLC **2** is presented below.

5.2. *Syntheseis of the cyclic tetramer* **2**

To a solution of 65 mg (1·06 mmol) of 1,3,5,7-methylhydrogen-cyclotetrasiloxane **6** and 0·798 mg (1·26 mmol) of monomer **1** [10] in 10 ml of dry toluene, were added 90 μl of a solution of 2 mg of dichloropentadienylplatinum (DPPC) [13] in 2 ml of dry toluene. The reaction mixture was stirred at 90°C in a nitrogen atmosphere for 24 h; then another portion of the catalyst solution (90 μl) was added and the mixture stirred for another 24 h. The solvent was removed and the crude product purified by flash chromatography (Merck, silica gel 60 Å). The excess of monomer **1** separated first using a petroleum ether/ethyl acetate mixture (vol. ratio 2 : 1). The cyclic tetramer **2** was finally eluated with chloroform. The solution collected was filtered through a PTFE filter (pore size = 25 μm) and the product precipitated from 150 ml methanol. Centrifugation and drying for 12 h at 45°C *in vacuo* yielded the pure tetramer **2**. Yield: 0·5 g (70 per cent); phase transitions see the table. $[\alpha]_D^{22}$: $-4{\cdot}8°$ ($c = 0{\cdot}43$, $CHCl_3$). $C_{39}H_{53}NO_7Si$ (675·95) calculated C, 69·29; H, 7·90; N, 2·07; found C, 69·13; H, 7·94; N, 2·09 per cent. ^{1}H NMR (200 MHz; $CDCl_3$): δ(ppm) = 8·86 [s, 1 $H_{arom.}$, $\mathbf{H}_2$-nitrobenzoate], 8·28–8·32 [m, 1 $H_{arom.}$ $\mathbf{H}_6$-nitrobenzoate, $^3J = 9$ Hz]; 7·46–7·59 [m, 4 $H_{arom.}$, $\mathbf{H}_{2,2',6,6'}$-biphenyl], 7·12–7·25 [m, $CDCl_3$ + 3 $H_{arom.}$, $\mathbf{H}_{3',5'}$-biphenyl + $\mathbf{H}_5$-nitrobenzoate], 6·93–6·97 [d, 2 $H_{arom.}$, $\mathbf{H}_{3,5}$-biphenyl, $^3J = 8$ Hz], 4·00–4·65 [m, 1 H, O–$\mathbf{CH}$*–C_6H_{13}], 3·94–3·97 [t, 2 H, –$\mathbf{CH}_2$–O–biphenyl, $^3J = 6$ Hz], 1·28–1·82 [m, 31 H, Si–CH_2–$(\mathbf{CH}_2)_9$–CH_2–O, $\mathbf{CH}_3$–CH*–O, –$(\mathbf{CH}_2)_5$–], 0·84–0·88 [t, 3 H, O–CH*–$(CH_2)_5$–$\mathbf{CH}_3$], 0·48–0·51 [m, 2 H, Si–$\mathbf{CH}_2$–], 0·06 [s, 3 H, $\mathbf{CH}_3$–Si–].

5.3. *Measurements*

^{1}H NMR measurements were conducted with a 200 MHz or 400 MHz. NMR FT-NMR spectrometer (Bruker). Specific rotations were measured using a polarimeter 241 (Perkin–Elmer) using a micro quartz cell (1 dm) and chloroform as solvent.

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