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Polar liquid crystalline monomers with two or three lactate groups for the preparation of side chain polysiloxanes

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Two new chiral liquid crystalline monomers with bilactate or trilactate chiral units were synthesized and studied. The monomers show the paraelectric SmA and ferroelectric SmC* phases. The antiferroelectric SmC_A* phase was detected only for the monomer possessing the bilactate unit. The temperature dependences of the spontaneous polarization and spontaneous tilt angle were measured. Real and imaginary parts of the complex permittivity were studied as a function of frequency and temperature. The synthesized monomers contain a double bond at the end of the achiral terminal chain, and were used to prepare liquid crystalline polysiloxanes.

1. Introduction

The existence of polar properties in liquid crystalline polymers [1] offers the possibility of controlling and changing their properties as required for application demands. However, the first ferroelectric polymers reported were difficult to align and not electro-optically active. Since then, several new structures have been reported [2–7], side chain polysiloxanes in particular showing smectic A or even polar phases [8–11]. However, several basic questions are still open, and in particular concerning main chain–side chain interactions, the connection between chemical structure, mesophase behaviour and the properties of the polar mesophases. The investigation of the structure–property relationships in side chain polymers is still of great significance for further progress in an understanding their basic properties and their practical use for technical applications.

In our previous work [12–14], new liquid crystalline (LC) materials, with various three-phenyl-ring mesogenic cores and bilactate or trilactate groups inserted as the chiral centres, showing stable and broad temperature range polar mesophases, were synthesized and studied. It seems reasonable to apply such structures in the preparation of chiral monomers to be used as the side chain groups in polysiloxanes.

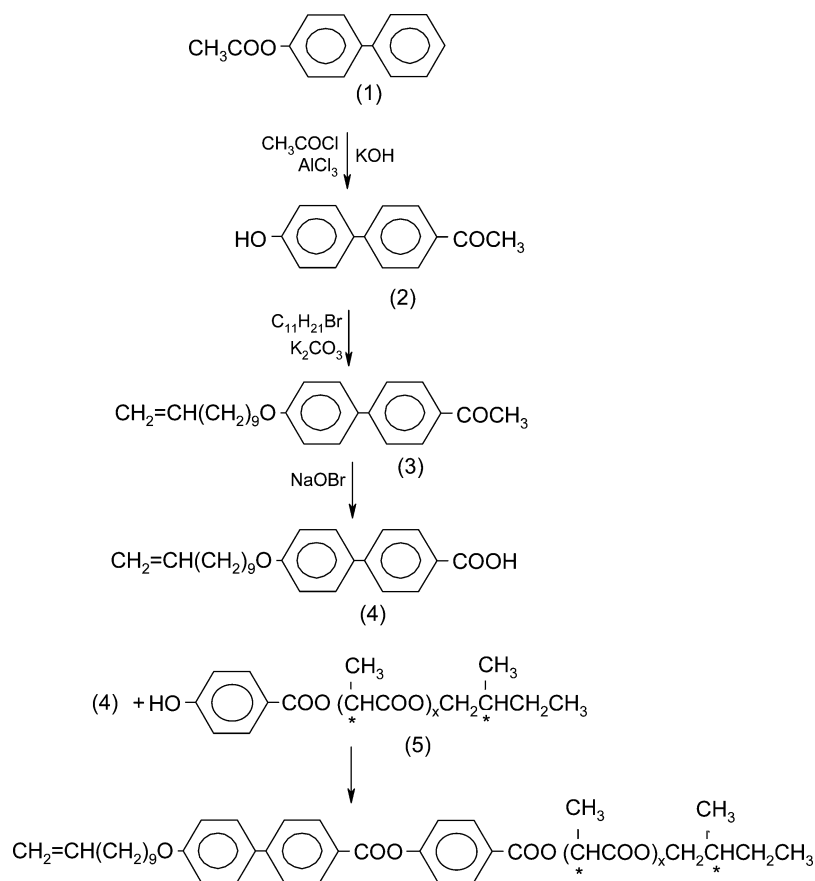
In this work, two new chiral liquid crystalline monomers having bilactate (**2L**) or trilactate units (**3L**) were synthesized and studied. These monomers have three and four chiral centres in the molecule in total because, besides the lactate centres, the optically active 2-methylbutyl moiety is also present in the chiral terminal chain. The synthesized monomers, with a double bond at the end of the achiral terminal chain, were used for grafting onto a polysiloxane, leading to liquid crystalline side chain polysiloxanes denoted as **PS-2L** and **PS-3L**.

The aim of this work was to establish the influence of the type of chiral chain of the molecule and its total length on the formation of the monomer mesophases, and on their polar properties including the response to an electric field in the smectic mesophases. The synthesis and properties of the respective polysiloxanes are also presented.

2. Synthesis

The general procedure for preparation of the monomers with three or four chiral centres is presented in scheme 1. The structures of intermediates and final products were characterized by ¹H NMR spectroscopy using a 200 MHz Varian NMR spectrometer and solutions in CDCl₃ or perdeuterated dimethylsulfoxide (DMSO) with tetramethylsilane as an internal standard.

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Scheme 1. General procedure for synthesis of the monomers **2L** ($x=2$) and **3L** ($x=3$).

2.1. 4,4'-hydroxybiphenylmethylketone (2)

4-Acetyloxybiphenyl (**1**) was acylated with acetylchloride in 1,2-dichloroethane. The reaction mixture was stirred for two days at room temperature and the mixture of two isomers was isolated by usual methods. The separation of the isomers is easily accomplished with diethyl ether which readily dissolves the low melting ketone isomer (*ortho*) and leaves the other isomer (*para*) as a residue. The product was hydrolyzed by potassium hydroxide in ethanol, acidified with HCl and separated by suction. ^1H NMR spectrum of **2** (200 MHz, DMSO): 7.95d (2H, *ortho* to $-\text{CO}$); 7.70 and 7.60dd (4H, *ortho* to $-\text{Ar}$); 6.90d (2H, *ortho* to $-\text{OH}$); 2.60s (3H, CH_3).

2.2. 4,4'-(10-undecenyl)biphenylmethylketone (3)

Compound **3** was prepared by etherification of **2** with 11-bromo-1-undecene according to the Williamson synthesis, using dry potassium carbonate in acetone. White crystals were obtained after repeated crystallization from acetone. ^1H NMR spectrum of **3** (200 MHz, CDCl_3): 8.00d (2H, *ortho* to $-\text{CO}$); 7.60dd

(4H, *ortho* to $-\text{Ar}$); 6.98d (2H, *ortho* to $\text{RO}-$); 5.80m (1H, $=\text{CH}-$); 4.90–5.00dd (2H, $\text{CH}_2=$); 4.00t (2H, CH_2-OAr); 2.60s (3H, CH_3); 2.00q (2H, $=\text{CH}-\text{CH}_2$); 1.20–1.80 m (14H, CH_2).

2.3. 4-(10-Undecenyl)-4'-biphenylcarboxylic acid (4) and the final products

To obtain the final products **2L** and **3L** according to [12], the acid **4** was obtained and reacted with compounds **5**. The product purity was determined by high performance liquid chromatography (HPLC) using a HPLC chromatograph (Ecom) and a silica gel column (Separon 7 μm , 3×150 , Tessek) with a mixture of 99.9% toluene and 0.1% methanol as eluant. The eluting products were detected by a UV-Vis detector ($\lambda=290$ nm). ^1H NMR spectrum of **4** (200 MHz, DMSO): 8.00d (2H, *ortho* to $-\text{COOH}$); 7.60–7.80dd (4H, *ortho* to $-\text{Ar}$); 7.00d (2H, *ortho* to $\text{RO}-$); 5.80m (1H, $=\text{CH}-$); 4.90–5.05dd (2H, $\text{CH}_2=$); 4.00t (2H, CH_2-OAr); 2.00m (2H, $=\text{CH}-\text{CH}_2$); 1.20–1.70m (14H, CH_2). ^1H NMR spectrum of **2L** (200 MHz, CDCl_3): 8.20dd (4H, *ortho* to $-\text{COO}$); 7.60–7.70m

(4H, *ortho* to -Ar); 7.33d (2H, *ortho* to OCO-); 7.00d (2H, *ortho* to RO-); 5.80m (1H, =CH-); 5.40q(1H, ArCOOC*H); 5.22q (1H, C*COOC*H); 4.90–5.05dd (2H, CH₂=); 4.02m (4H, CH₂O); 2.00m (2H, =CH-CH₂); 1.75 and 1.58 d+d (3H+3H, CH₃C*); 1.20–1.70m (17H, CH₂CH); 0.90–0.95m (6H, CH₃). ¹H NMR spectrum of **3L** (200 MHz, CDCl₃): 8.20dd (4H, *ortho* to -COO); 7.60–7.70m (4H, *ortho* to -Ar); 7.33d (2H, *ortho* to OCO-); 7.00d (2H, *ortho* to RO-); 5.80m (1H, =CH-); 5.40q(1H, ArCOOC*H); 5.22q (2H, C*COOC*H); 4.90–5.05dd (2H, CH₂=); 4.02m (4H, CH₂O); 2.00m (2H, =CH-CH₂); 1.75 and 1.62 and 1.58, d+d+d (9H, CH₃C*H); 1.20–1.70m (17H, CH₂CH); 0.90–0.95m (9H, CH₃).

2.4. Polysiloxanes

Polysiloxanes **PS-2L** and **PS-3L** with two or three lactate groups were prepared by grafting the respective monomers **2L** and **3L** onto a preformed poly[hydrosiloxane] (average degree of polymerization $n=35$) by a platinum(II)-catalysed hydrosilylation reactions, see scheme 2. The progress of the reaction was checked by FTIR, detecting the progressive decrease of the absorption bands at 2160 cm⁻¹ (Si-H) and 950 cm⁻¹ (vinyl C=C). Quantitative conversion was achieved in 15–24 h reaction time.

In a typical reaction, 0.16 g (0.23 mmol) of monomer **PS-2L**, 12 mg (0.21 mmol Si-H group) of polysiloxane and 10 μl (4.2×10^{-7} mol) of Pt(*endo*-dicyclopentadienyl)dichloride were dissolved in 20 ml of dry toluene under nitrogen. The reaction was conducted at room temperature for 24 h. The polymer was then precipitated in cold methanol, centrifuged and dried. The polymer was further purified by repeated precipitations from chloroform into methanol and finally eluted on a

neutral alumina column (70–230 mesh) with chloroform. Polymer yield 65%, $[\alpha]_D^{25} = -1.2$ (chloroform), $M_n=18\,000$, $M_w/M_n=2.7$. ¹H NMR spectrum for **PS-2L** (200 MHz, CDCl₃): 8.10 (4H, *ortho* to -COO); 7.60 (4H, *ortho* to -Ar); 7.10 (2H, *ortho* to OCO-); 6.90 (2H, *ortho* to RO-); 5.40–4.90 (2H, COO*CH); 3.90 (4H, CH₂O); 1.80–1.30 (21H, CH₂CH); 1.20 (6H, CH₃C*); 0.90 (6H, CH₃); 0.50 (2H, CH₂Si); 0.20 (3.5H, CH₃Si). In all cases the signals are broad.

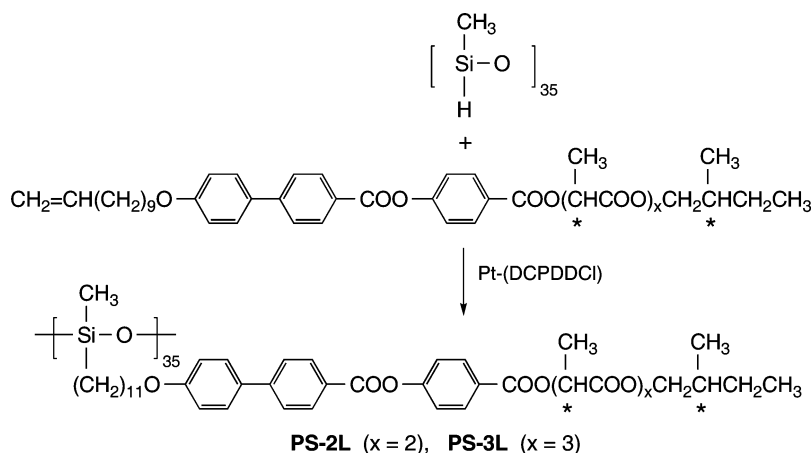
3. Experimental results

In preparing monomer samples for examination, the LC materials were filled into glass cells with indium tin oxide (ITO) transparent electrodes and polyimide layers unidirectionally rubbed, which ensured planar (book-shelf) geometry. The sample thickness was defined by mylar sheets as 25 μm. The alignment was improved by an electric field (10–20 Hz, 40 kV cm⁻¹) applied for 5–20 min. For DSC studies, samples of 3–5 mg were placed in a nitrogen atmosphere and hermetically sealed in aluminium pans.

Polysiloxane samples were again prepared between two ITO-coated glass plates. The distance between the glass plates was maintained by evaporated silicon monoxide spacers of 3 μm thickness. The orientation of the smectic layers was such that they were mutually parallel with the layer normal parallel to the glass plates. This orientation was achieved by shearing the plates relative to each other in a specially constructed shear cell-holder [15].

3.1. Mesomorphic properties of the monomers

For the monomers, the sequence of phases and phase transition temperatures were determined on cooling from characteristic textures and their changes observed



Scheme 2. General procedure for preparation of the side chain polysiloxanes. Number average degree of polymerization is $n=35$; number of lactate groups is $x=2, 3$.

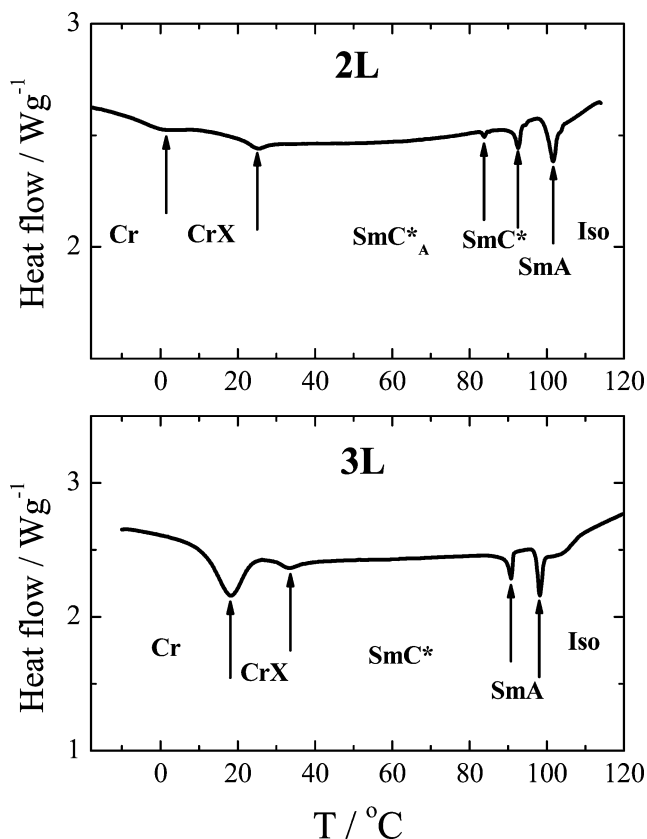


Figure 1. DSC traces on cooling runs for monomers **2L** and **3L**.

in a polarizing microscope. A Linkam LTS E350 heating stage with TMS-93 temperature programmer was used for temperature control, giving temperature stability within ± 0.1 K. The phase transition temperatures were checked by differential scanning calorimetry (DSC-Pyris Diamond Perkin-Elmer 7) on cooling/heating runs at a rate of 5 K min^{-1} .

In figure 1, DSC traces for cooling runs of **2L** and **3L** are shown. The arrows indicate the phase transition temperatures between indicated phases. For the monomers, the sequence of phases, melting points and phase transition temperatures, determined on cooling by DSC and microscopic observations of the characteristic

textures, are summarized in table 1. The monomers show the paraelectric SmA and ferroelectric SmC* phases. The antiferroelectric SmC*_A phase was detected only for the monomer possessing two lactate groups. For both monomers, a low temperature monotropic phase, denoted as CrX, was seen. This non-polar phase could be a low temperature orthogonal smectic phase or a crystal modification.

3.2. Spontaneous parameters of the monomers

Values of the spontaneous polarization (P_s) have been evaluated from the $P(E)$ hysteresis loop detected during P_s switching in an a.c. electric field E of frequency 60 Hz. Well aligned samples were used for the spontaneous tilt angle (θ_s) measurements. Values of θ_s were determined optically from the difference between extinction positions at crossed polarizers under opposite d.c. electric fields ($\pm 40\text{ kV cm}^{-1}$). The temperature dependence of spontaneous polarization and spontaneous tilt angle for the monomers **2L** and **3L** are depicted in figure 2.

The spontaneous polarization and the spontaneous tilt angle increase continuously from zero as the temperature decreases from the SmA–SmC* phase transition temperature. The spontaneous polarization is higher for **2L** than for **3L** (at saturation, 95 and 70 nC cm^{-2} , respectively); while the tilt angle (about 20° at saturation) remain nearly the same. For **2L** no anomalies in the temperature dependence of these parameters were detected at the SmC*–SmC*_A phase transition.

3.3. Dielectric properties of the monomers

For both monomers, the complex permittivity $\epsilon^*(f) = \epsilon' - i\epsilon''$ was measured on cooling as a function of frequency using a Schlumberger 1260 impedance analyser in the frequency range $1\text{ Hz} - 1\text{ MHz}$. Planar-aligned samples were used for these studies. Temperature dependences of the real part of the permittivity are shown in figures 3(a, b) at indicated frequencies.

The dielectric dispersion data taken at temperatures stabilized within ± 0.1 K were analysed over the whole

Table 1. Sequence of phases, melting points (m.p., $^\circ\text{C}$) and phase transition temperatures ($^\circ\text{C}$), measured on cooling (5 K min^{-1}) by DSC for the monomers studied. The associated enthalpy changes (J/g) are given in square brackets.

Monomer	m.p.	Cr	CrX	SmC* _A	SmC*	SmA	I
2L	64 [23.1]	•	1 [−1.4]	•	25 [−0.6]	•	85 [−0.02]
						•	92 [−0.4]
						•	103 [−1.8]
3L	74 [26.6]	•	18 [−6.9]	•	34 [−0.8]	—	•
						•	91 [−0.8]
						•	99 [−1.1]

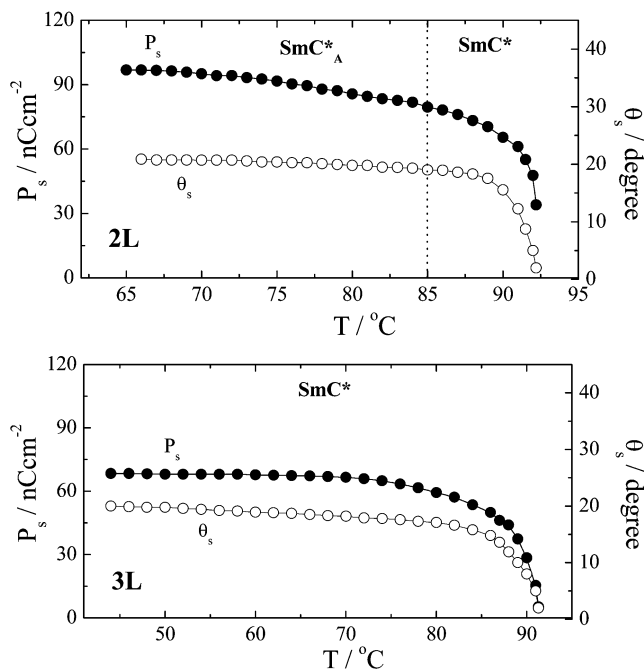


Figure 2. Temperature dependence of the spontaneous polarization and spontaneous tilt angle for monomers **2L** and **3L**. The dotted line indicate the $\text{SmC}^* \rightarrow \text{SmC}_A^*$ phase transition temperature.

temperature range of the SmA , SmC^* and SmC_A^* phases using the Cole–Cole formula for the frequency-dependent complex permittivity:

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + (if/f_r)^{(1-\alpha)}} - i \frac{\sigma}{2\pi\varepsilon_0 f^n} + Af^m$$

where f_r is the relaxation frequency, $\Delta\varepsilon$ is the dielectric strength, α is the distribution parameter of the mode, ε_0 is the permittivity of the vacuum, ε_∞ is the high frequency permittivity and n , m , A are parameters of fitting. The second and third terms on the right-hand side of the equation are used to eliminate a low frequency contribution to ε'' from d.c. conductivity σ and a high frequency contribution from the ITO electrodes, respectively. Frequency dispersion data show the soft mode in the paraelectric SmA phase, the Goldstone mode in the ferroelectric SmC^* phase and a high frequency mode in the antiferroelectric SmC_A^* phase. The fitting of the data yields the relaxation frequency and the dielectric strength of the modes, see figures 4(a, b) for monomer **2L**.

In the paraelectric SmA phase, the frequency of the soft mode decreases, see figure 4(a), and the dielectric strength steeply increases, see figure 4(b), when approaching the transition to the ferroelectric SmC^* phase. In the SmC^* phase, the relaxation frequency is low, about 1 kHz see figure 4(a), and the dielectric

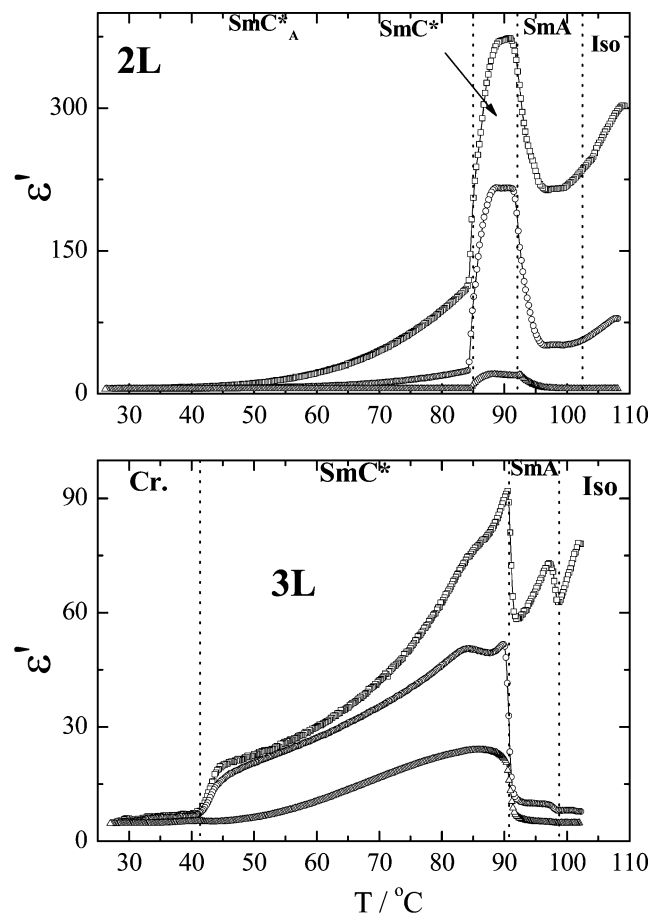


Figure 3. Temperature dependence of the real part of the complex permittivity at frequencies of 35 Hz (\square), 100 Hz (\circ) and 1 kHz (Δ) for monomers **2L** and **3L**. The dotted lines indicate the phase transition temperatures.

strength is high with respect to both paraelectric and antiferroelectric phases. Such behaviour is a typical feature of the Goldstone mode. In the antiferroelectric SmC_A^* phase, a high frequency mode was detected, see figures 4(a, b). This so called ‘anti-phase’ mode could be attributed to azimuthal director fluctuations, which deform the anticlinic ordering [16, 17]. The dielectric strength of this mode remains very low while the relaxation frequency decreases on cooling from about some MHz to several tens of kHz. Such a decrease can be explained by a gradual increase in the viscosity on cooling. For monomer **3L** the same qualitative behaviour as for **2L** was found for the soft and Goldstone modes in the SmA and SmC^* phases.

3.4. Properties of the polysiloxanes

Polymers **PS-2L** and **PS-3L** clearly exhibited thermotropic liquid crystalline behaviour, as revealed by polarizing optical microscopy. However, using commercial planar cells, it was impossible to obtain

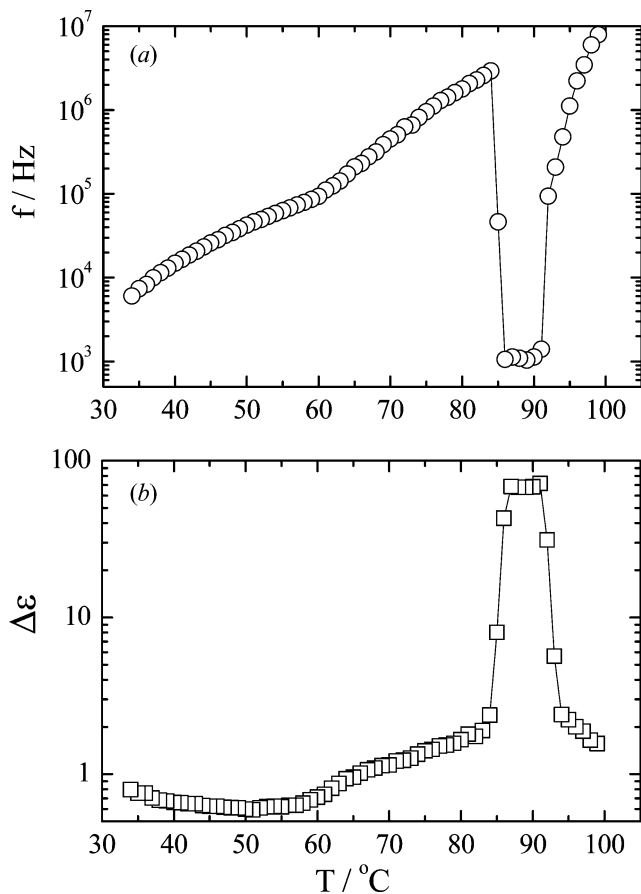


Figure 4. Results of fitting (a) relaxation frequency and (b) dielectric strength of the detected relaxation modes for monomer **2L**.

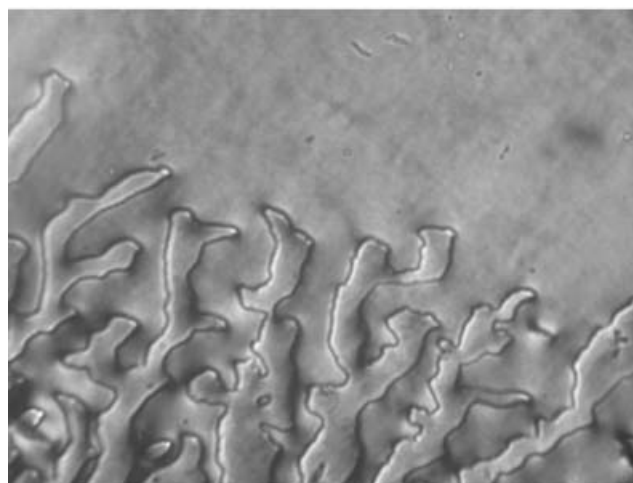
homogeneous specific planar textures, as the homeotropic texture was formed spontaneously. By applying a unidirectional shear, a good planar alignment was obtained, see figure 5(a), but there was a slow deterioration with time, see figures 5(b, c).

The phase transition temperatures determined on cooling are: **PS-2L** glass $\sim 20^\circ\text{C}$ smectic 155°C I; **PS-3L** glass $\sim 15^\circ\text{C}$ smectic 95°C I. The polysiloxanes were studied by DSC; however, no phase transition enthalpy was detectable by calorimetric analysis, probably because the transition extended over a relatively broad temperature range. The glass transition is also spread over a large temperature range. On cooling, no changes of texture were observed down to about room temperature.

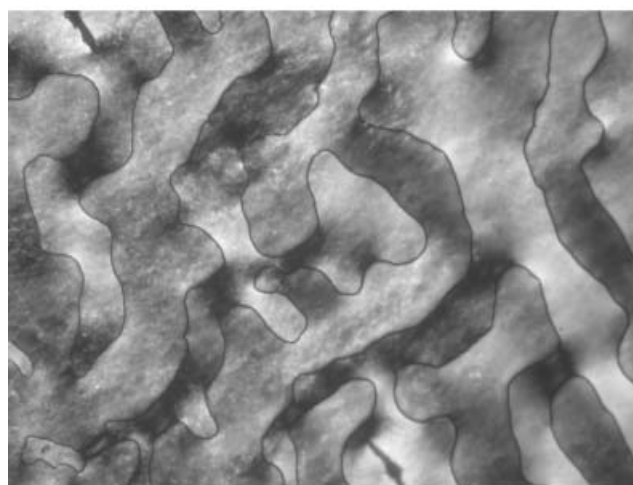
X-ray diffraction studies indicated a layered structure, which confirmed the smectic phase. However, the small angle diffraction signal associated with the smectic layer spacing d was generally not sharp. This indicates that there is very short range interlayer correlation owing to a weak microphase segregation



(a)



(b)



(c)

Figure 5. Photomicrographs of the optical texture for **PS-2L** polysiloxane obtained (a) at 100°C after shearing, (b) after about 2.5 h, (c) after 24 h. The width of the pictures is about $400\ \mu\text{m}$.

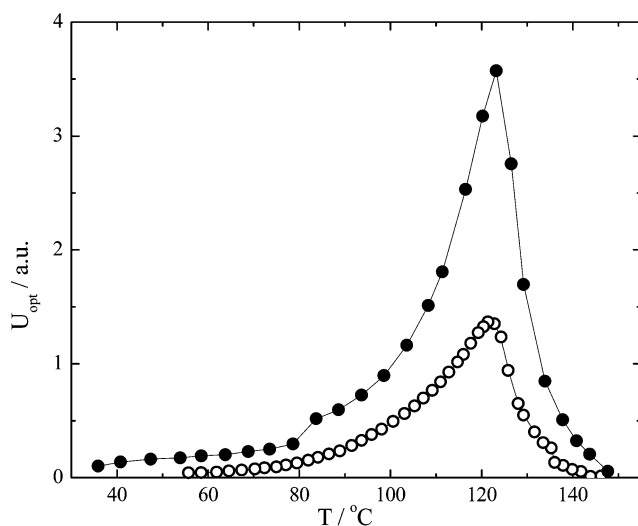


Figure 6. Temperature dependence of the electro-optical response of **PS-2L** polysiloxane after alignment by shearing measured at a sinusoidal voltage of $210 V_{pp}$ (19 Hz) on heating (o) and cooling (•) (cell thickness is about $3 \mu\text{m}$).

of the polysiloxane backbone from the mesogenic side groups. Besides, d was unaffected by temperature changes and remained constant up to the transition to the isotropic liquid. For example, d is $39.5 \pm 0.4 \text{ \AA}$ for **PS-2L**, corresponding to a maximum tilt angle of 33° (intermolecular distance $D \approx 5.4 \pm 0.2 \text{ \AA}$).

The electro-optic response of the polysiloxanes was detected at very high voltages of $V_{pp} = 210 \text{ V}$ (19 Hz). No current bumps were detected under this field. The temperature dependence of the electro-optical response (U_{opt}) detected by a lock-in amplifier is shown in figure 6. Slow deterioration of alignment affected the measured temperature dependences. Different amplitudes in the electro-optical response were detected on cooling and subsequent heating, lower values being observed on heating due to deterioration. The frequency dependence of the electro-optical response was measured on a **PS-2L** sample after alignment by shearing at selected temperatures under an applied sinusoidal voltage. The results show a strong relaxation process.

4. Discussion and conclusions

4.1. Monomers

Both chiral liquid crystalline monomers synthesized show the paraelectric SmA phase and the ferroelectric SmC* phase. The antiferroelectric SmC_A* phase was detected in a rather broad temperature range only for monomer **2L** with two lactate groups. Recently, the

same behaviour has been found in structurally related materials without the double bond in the non-chiral alkyl chain [12], and for materials with a keto group attached to the molecular core [13, 14]. It may be concluded that in these classes of compound two lactate groups at the chiral centre are crucial for the occurrence of the antiferroelectric phase.

In polar phases of monomers **2L** and **3L** the spontaneous polarization decreases with increasing number of lactate groups, while the tilt angles remain almost constant. Such behaviour seems to be typical even for other materials differing in numbers of lactate groups [13, 14]. In addition, the presence of the double bond decreases the spontaneous polarization, as follows from a comparison with closely similar materials without a double bond [12]. This chemical modification of the periphery of the liquid crystalline molecule does not affect its polar properties to any significant extent, but does provide a functional group for easy incorporation into a polymer structure.

4.2. Polysiloxanes

The first polysiloxanes from monomers with two (**2L**) or three (**3L**) lactate groups have been prepared. They possess a smectic liquid crystalline phase responding to an electric field over a relatively broad temperature range. On shearing, a well aligned planar texture can be achieved, which relaxes slowly to a homeotropic texture. The polysiloxanes studied exhibit high viscosity. The glass transition temperature, T_g , was found to be around room temperature, which is a much higher temperature than in conventional polysiloxanes. For example, poly(dimethylsiloxane) has one of the lowest known glass transition temperatures ($T_g = -120^\circ\text{C}$). This finding is attributed to the attachment of the rigid, high aspect ratio side groups consisting of three phenyl rings that stiffen significantly the main polymer chain. However, this results in the onset of the smectic phase at room temperature. The preliminary results of electro-optic studies suggest the polar character of the detected liquid crystalline phase. More detailed studies including the dielectric spectroscopy are under way.

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