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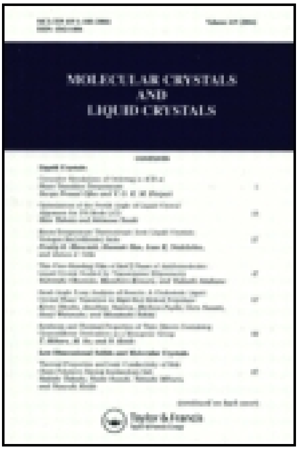

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The Mesophase Structure of Chiral Liquid Crystalline Polysiloxanes for Electro-Optical Applications

G. Galli [a], C. Cesarino [a], B. Gallot [b], L. Komitov [c] & E. Chiellini [a]

[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56126, Pisa, Italy

[b] Laboratoire des Matériaux Organiques à Propriétes Spécifiques, CNRS, 69390, Vernaison, France

[c] Department of Microelectronics and Nanoscience, Chalmers University of Technology, 41296, Göteborg, Sweden

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The Mesophase Structure of Chiral Liquid Crystalline Polysiloxanes for Electro-Optical Applications

G. GALLI[a], C. CESARINO[a], B. GALLOT[b], L. KOMITOV[c] and E. CHIELLINI[a]

[a]*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56126 Pisa, Italy,* [b]*Laboratoire des Matériaux Organiques à Propriétes Spécifiques, CNRS, 69390 Vernaison, France and* [c]*Department of Microelectronics and Nanoscience, Chalmers University of Technology, 41296 Göteborg, Sweden*

Homopolysiloxanes poly(**1**) and poly(**2**) and copolysiloxanes poly(**1**-*co*-**3**) were synthesized. Their mesophase structures were investigated by X-ray diffraction, and the electron density profiles along the layer normal were derived. A linear response with the applied electric field was detected in the chiral smectic (C^* or A^*) phases of poly(**1**) and poly(**2**).

Keywords: chiral polysiloxane; electro-optics; liquid crystalline polymer; mesophase structure; X-ray diffraction

INTRODUCTION

Ferroelectric displays offer some advantages over traditional nematic

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displays, such as shorter response time, wider viewing angle, and better levels of grey scale and multiplexability [1]. In addition to the bistable switching of SmC* liquid crystals, the electroclinic effect in the SmA* and unwound N* phases and the flexoelectric effect in the short-pitch N* phase are very attractive for different kinds of liquid crystal applications [2-4].

The potential of chiral liquid crystalline polymers as materials for application in electro-optics is well documented [5]. Recently, a new method for fast in-plane switching of achiral (smectic or nematic) liquid crystals has been reported, so-called electrically commanded surfaces (ECS) [6]. According to this method, a thin layer of a ferroelectric liquid crystal polymer (FLCP) acts as alignment layer for the achiral liquid crystal occupying the cell gap. The applied electric field switches the molecules of the FLCP and, due to elastic forces, the molecules of the achiral liquid crystal will follow them. The method of ECS may open a new field for application of ferroelectric liquid crystal polymers.

In a previous paper we presented the electro-optical response of chiral liquid crystalline polysiloxanes that exhibited a fast switching in their SmC* or SmA* phases [7]. In this work we synthesized closely related chiral polysiloxanes poly(**1**) and poly(**2**) and copolysiloxanes poly(**1**-*co*-**3**) in which the mesophase structure could be varied by changing the nature of the chiral substituent and by adjusting the chemical composition. We also investigated the mesophase structures by X-ray diffraction and carried out initial electro-optical measurements in view of assessing the polymers as alignment layers for ECS.

EXPERIMENTAL PART

Synthesis

Monomers **1** and **2** were synthesized according to a similar reaction

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procedure (Fig. 1), which is described here in detail for **2**. Monomer **3** was synthesized according to a literature procedure [8]. Polysiloxanes and copolysiloxanes were prepared according to a similar procedure (Figs. 1 and 2), which is described here in detail for poly(**2**) and poly(**1**-*co*-**3**)a.

(+)-(S) Ethyl 3-nitro-4-(2-methylbutyloxy)benzoate (12): 2.4 g (26 mmol) of (-)-(*S*)-2-methyl-1-butanol (**11**), 7.2 g (26 mmol) of triphenylphosphine and 5.5 g (26 mmol) of ethyl 4-hydroxy-3-nitrobenzoate (**10**) [7] were dissolved in 200 ml of dry diethyl ether. 4.6 g (26 mmol) of diethyl azodicarboxylate (DEAD) were then added slowly under vigorous stirring, and the rection was carried out at room temperature for an additional 48 h. The precipitate was filtered and the residual solution was evaporated to dryness. The residue was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate 2:1 by volume giving 3.4 g (47% yield) of **12** ($R_f = 0.6$): mp. 68-69 °C; $[\alpha]^{25}_D$ = + 3.8 (CH_2Cl_2).

(+)-(S) 3-Nitro-4-(2-methylbutyloxy)benzoic acid (13): A solution of 2.9 g (10 mmol) of **12**, 0.9 g (16 mmol) of KOH, 30 ml of water and 50 ml of ethanol was refluxed for 6 h. It was then cooled and acidified with 36% HCl. The precipitate was filtered, washed with water and dried giving 2.0 g (82% yield) of **13**: mp. 177-178 °C; $[\alpha]^{25}_D$ = +4.0 (CH_2Cl_2).

(+)-(S) 4-(7-Octenyloxy)phenyl 3-nitro-4-(2-methylbutyloxy)-benzoate (2): 0.6 g (2.4 mmol) of **13**, 0.5 g (2.4 mmol) of 4-(7-octenyloxy)phenol (**8**) [7] and 0.1 g (0.7 mmol) of pyrrolidinopyridine (PPy) were dissolved in 30 ml of dry CH_2Cl_2 under nitrogen atmosphere. A solution of 0.6 g (2.8 mmol) of dicyclohexylcarbodiimide (DCCI) in 10 ml of dry CH_2Cl_2 was slowly added. The reaction mixture was stirred at room temperature for 24 h. The precipitate was then filtered and the solution was washed with 5% HCl, 5% $NaHCO_3$, water, dried over Na_2SO_4, and evaporated to dryness. The crude residue was purified by column chromatography on silica gel with $CHCl_3$ giving 0.7 g (67%

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yield) of **2** ($R_f = 0.7$): mp. 61-62 °C; $[\alpha]^{25}_D = +5.8$ ($CHCl_3$).

^{1}H-NMR ($CDCl_3$) δ (ppm): 8.6 (s, 1H, 2-aromatic), 8.3 (d, 1H, 6-aromatic), 7.1 (m, 3H, 5-, 2'-, and 6'-aromatic), 6.8 (d, 2H, 3'- and 5'-aromatic), 5.7 (m, 1H, $C\underline{H}{=}CH_2$), 5.0 (m, 2H, $CH{=}C\underline{H}_2$), 4.1 and 3.9 (2m, 4H $ArOC\underline{H}_2$ and $ArOC\underline{H}_2CH$), 2.1 (m, 2H, $C\underline{H}_2CH{=}CH_2$), 1.8 (m, 2H, $ArOCH_2C\underline{H}_2$), 1.4 (m, 8H, aliphatic), 1.1 (d, 3H, $CHC\underline{H}_3$), 0.9 (t, 3H, $CH_2C\underline{H}_3$).

Poly(2): 0.6 g (1.4 mmol) of **2** and 0.08 g (1.4 mmol r.u.) of poly(hydrogenmethyl siloxane) **14** ($DP_n = 35$) were dissolved in 40 ml of dry toluene under nitrogen atmosphere. 70 μl of a 2% xylene solution of platinum divinyltetramethyl disiloxane (PtDVDS) were added and the solution was stirred at 50 °C for 9 h and at room temperature for 15 h. Finally, 1 ml of 1-octene was added and the mixture was let to react for an additional 2 h. The solution was poured into a large excess of methanol and purified by repeated precipitations from chloroform solution into methanol, and from diethyl ether into *n*-hexane, giving 0.5 g (68% yield) of poly(**2**).

^{1}H-NMR ($CDCl_3$) δ (ppm): 8.5 (m, 1H, 2-aromatic), 8.3 (m, 1H, 6-aromatic), 7.1 (m, 3H, 5-, 2'-, and 6'-aromatic), 6.9 (m, 2H, 3'- and 5'-aromatic), 3.9 (m, 4H, $ArOC\underline{H}_2$ and $ArOC\underline{H}_2CH$), 1.8-1.4 (2m, 15H, aliphatic), 0.9-1.0 (2m, 6H, $CHC\underline{H}_3$ and $CH_2C\underline{H}_3$), 0.5 (m, 2H, $SiCH_2$), 0.1 (m, 3.5H, $SiCH_3$).

Poly(1-co-3)a: 1.0 g (2.1 mmol) of **1**, 0.3 g (0.9 mmol) of **3** and 0.18 g (2.7 mmol r.u.) of poly(hydrogenmethyl siloxane) **14** were dissolved in 40 ml of dry toluene under nitrogen atmosphere. 84 μl of a 2% xylene solution of PtDVDS were added and the solution was stirred at 50 °C for 9 h and at room temperature for 15 h. Finally, 1 ml of 1-octene was added and the mixture was let to react for an additional 2 h. The solution was poured into a large excess of methanol and purified by repeated precipitations from chloroform solution into methanol, and from diethyl ether solution into *n*-hexane, giving 1.1 g (77% yield) of poly(**1**-*co*-**3**)a.

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^{1}H-NMR ($CDCl_3$) δ (ppm): 8.6 (m, 0.78H, 2-aromatic (**1**)), 8.2-8.1 (2m, 1.22H, 6-aromatic (**1**), 2-, and 6-aromatic (**3**)), 7.1-6.8 (2m, 5.22H, 5-, 2'-, 3'-, 5'-, and 6'-aromatic (**1**), 3-, 5-, 2'-, 3'-, 5'-, and 6'-aromatic (**3**)), 4.6 (m, 0.80H, ArOC$\underline{H}$), 3.9-3.7 (2m, 3.40H, ArOC$\underline{H}_2$ and OCH_3), 1.9 and 1.3 and 0.8 (3m, 22.2H, aliphatic), 0.6 (m, 2.00H, $SiCH_2$), 0.1 (m, 3.50H, $SiCH_3$).

Characterization

The transition temperatures were taken by DSC at a 10 °C/min rate as corresponding to the maximum in the enthalpic peaks of samples that had previously been annealed by cooling from the isotropic melt.

X-ray diffraction experiments were performed on unaligned samples with a pinhole camera with Ni-filtered CuKα beam (λ = 1.54 Å). Intensities I_n of the reflections were measured with a home-made microdensitometer. Experimental amplitudes a_n of diffraction of the different n orders of reflections on the smectic layers were corrected for the Lorentz-polarization factor and normalized to that of the strongest one.

For the electro-optical measurements, the polymer was introduced into a conventional sandwich cell (2 μm gap) consisting of two glass plates with inner surfaces with ITO electrodes coated by SiO_x alignment layer. Unidirectional shearing of the polymer gave a uniform alignment of the polymer in the bookshelf geometry. The electric field was applied parallel to the smectic planes and perpendicular to the side-chain molecules in an experimental set-up as described in [2,9].

RESULTS AND DISCUSSION

The side-chain monomers **1** and **2** containing an (*R*)-2-octyloxy and an

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(*S*)-2-methylbutoxy chiral group, respectively, were synthesized according to the reaction scheme which is outlined in Figure 1. The respective polysiloxanes poly(**1**) and poly(**2**) were prepared by a Pt-catalyzed hydrosilylation reaction of the side-chain monomers onto a preformed poly(hydrogenmethyl siloxane) **14** (DP_n = 35) (Fig. 1). Copolysiloxanes poly(**1**-*co*-**3**) were prepared by the same reaction procedure by starting from appropriate mixtures of monomers **1** and **3** with different molar compositions (Fig. 2).

It was found that a mesophase occurred above the glass transition temperature, T_g, the nature and stability of which depended upon the structure of the chiral group in the homopolysiloxanes (Tab. I) and the chemical composition, *y*, in the copolysiloxanes (Tab. II). The mesophase was identified by X-ray diffraction by comparing the smectic layer periodicity, *d*, with the calculated length, *L*, of the polymer side chains. While poly(**1**) formed a monolayer SmC* phase with apparent tilt angle, *θ*, of 19° (*d*= 34.0 Å, *L* = 36.0 Å), poly(**2**) formed a monolayer SmA* phase (*d*= 31.2 Å, *L* = 31.0 Å). Copolysiloxane poly(**1**-*co*-**3**)a with a low content of units from **3** (*y* = 2 mol%) also presented a SmC* phase, that turned into a N* phase in samples with more substantial incorporation of nematic units from **3**, e.g. *y* = 44 mol% for poly(**1**-*co*-**3**)b, (Fig. 3).

TABLE I. Transition temperatures of homopolysiloxanes poly(**1**) and poly(**2**).

sample	$x^{a)}$ (%)	$[\alpha]^{25}_{D}{}^{b)}$ (deg)	$M_n{}^{c)}$ (g/mol)	T_g (°C)		T_i (°C)
poly(**1**)	100	-2.8	21000	-7	SmC*	35
poly(**2**)	100	+2.4	28000	11	SmA*	119

a)Molar content of units from **1** (or **2**). b)Optical rotatory power, in $CHCl_3$. c)Number average molar mass, by SEC; M_w/M_n = 2.2.

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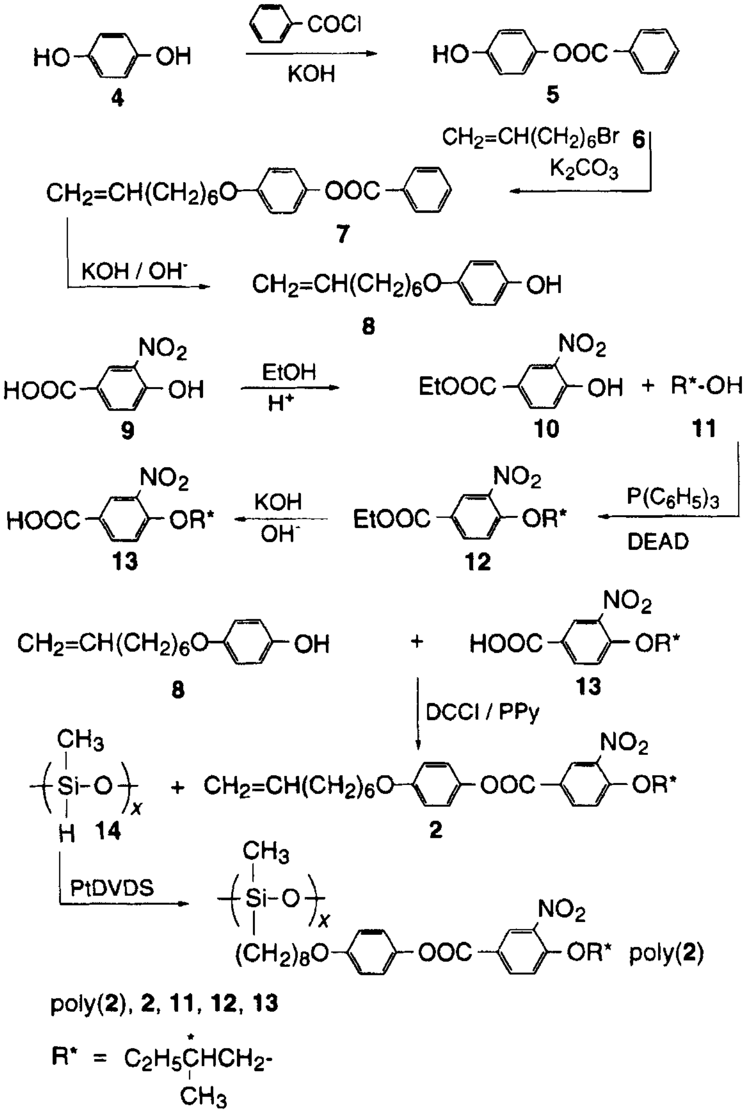

FIGURE 1. Reaction scheme for the synthesis of monomer **2** and polysiloxane poly(**2**) (for monomer **1** and polysiloxane poly(**1**). R* = (*R*)-2-octlyoxy).

TABLE II. Transition temperatures of copolysiloxanes poly(**1**-*co*-**3**).

sample	$y^{a)}$	$[\alpha]^{25}{}_{D}{}^{b)}$	$M_n{}^{c)}$	T_g		T_i
	(%)	(deg)	(g/mol)	(°C)		(°C)
poly(**1**-*co*-**3**)a	22	-2.0	15000	-2	SmC*	23
poly(**1**-*co*-**3**)b	44	-1.2	14500	1	N*	20
poly(**1**-*co*-**3**)c	78	-0.8	12500	11	N*	36

[a]Molar content of units from **3**. [b]Optical rotatory power, in $CHCl_3$. [c]Number average molar mass, by SEC; M_w/M_n = 2.5-3.5.

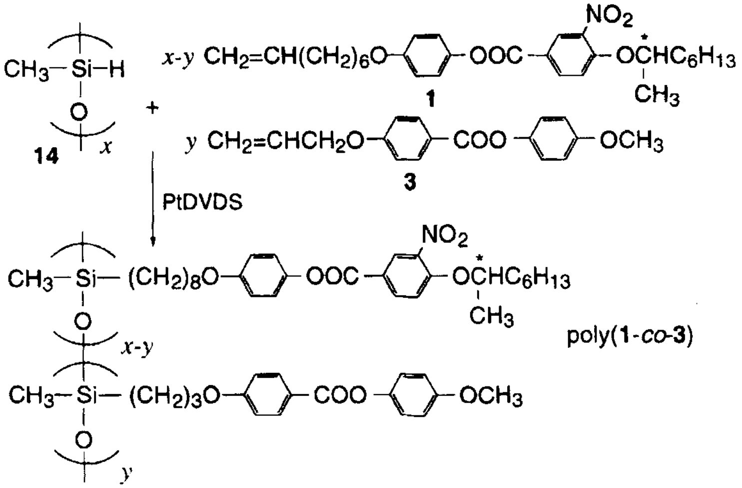

FIGURE 2. Reaction scheme for the synthesis of copolysiloxanes poly(**1**-*co*-**3**).

In the former copolymer the apparent θ was 32° (d= 30.4 Å, L = 36.0 Å), probably because the dilution of the units from **1** by units from **3** permitted a greater tilting of the side chains within the smectic layers with respect to the homopolymer. In any case θ was independent of temperature and vanished at the clearing temperature, T_i.

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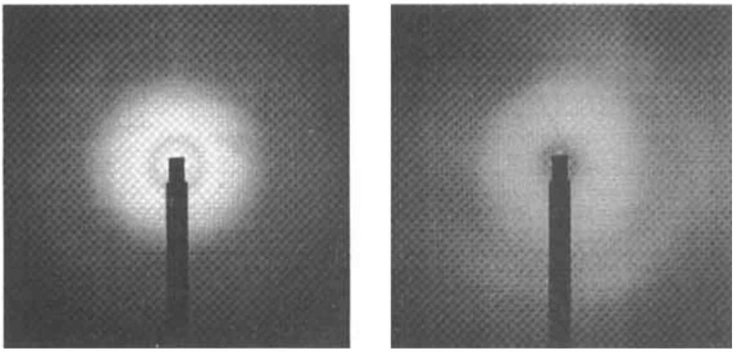

FIGURE 3. X-ray diffraction patterns of poly(**1**-*co*-**3**)a in the monolayer smectic C phase at 23 °C (left) and poly(**1**-*co*-**3**)c in the N* phase at 24 °C (right).

Both poly(**1**) and poly(**2**) gave rise to several low-angle orders of reflections on the smectic layers (Fig. 4), and accordingly we could derive the corresponding electron density profiles $\rho(z)$ along the layer normal.

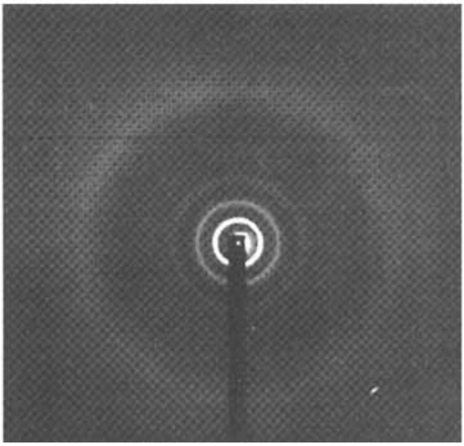

FIGURE 4. X-ray diffraction pattern of poly(**2**) in the monolayer smectic A phase at 25 °C.

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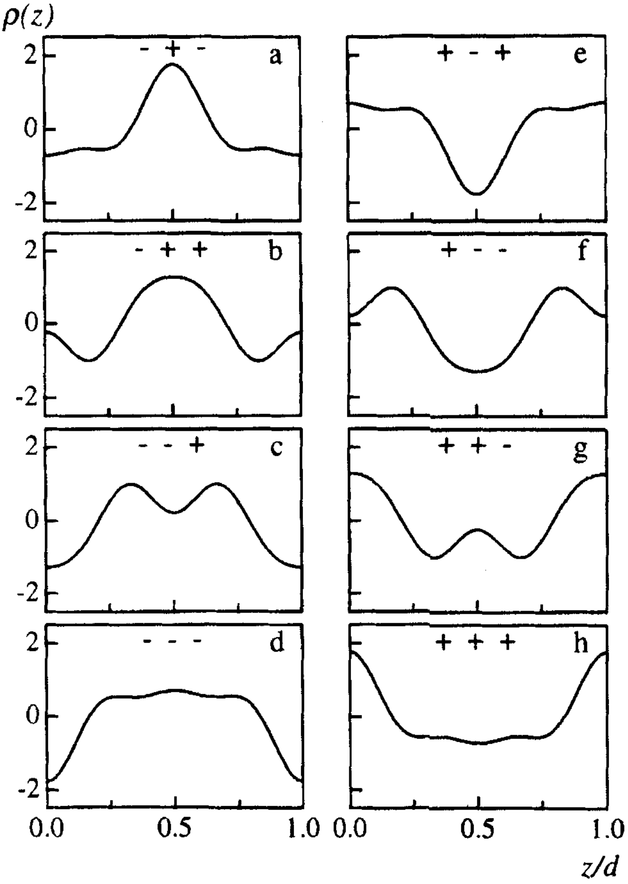

FIGURE 5. Electron density profiles $\rho(z)$ for the eight combinations of a_n signs of the monolayer smectic A phase of poly(**2**) (corrected and normalized amplitudes $a_1 = 1.0$, $a_2 = 0.53$, $a_3 = 0.24$).

This procedure is illustrated here for poly(**2**). By taking into account the symmetry of the smectic A phase and the fact that we measured only the fluctuations around the average electron density ρ_0, $\rho(z)$ was given [10]

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by:

$$\rho(z) = \Sigma\, a_n \cos(n2\pi z/d)$$

As experimentally we measured the intensity I_n of the reflections, we lost the sign of the structure factors a_n, and for $n = 3$ reflections we obtained $2^n = 8$ electron density profiles $\rho(z)$ [11] (Fig. 5).

In order to choose the most acceptable $\rho(z)$, we calculated the electron densities ρ_0 of the different parts of the repeating unit of the polymers by dividing the number of electrons comprised in each part by the relevant length measured on the CPK models.

We found 12.1 e/Å for the mesogenic core, 6.4 e/Å for the spacer, 7.2 e/Å for the methylbutoxy tail, and 7.8 e/Å for the backbone considering it as segregated between the smectic planes. Profile of Figure 5b, corresponding to the ρ_{-++} combination of a_n signs, was chosen as the most physically acceptable one in that it presented a central prominent maximum for the fully overlapping mesogenic cores, flanked by minima for the spacers and slightly pronounced secondary maxima for the main chains. This confirmed that the siloxane backbone was incompatible with the remainder of the side chain unit and was confined in a microseparated sub-phase. Segregation of the siloxane backbone was more evident in the copolymers as manifested by a rather intense, diffuse signal in the intermediate-angle region at 7-10 Å [12] (Fig. 3).

We studied the electro-optical response in the chiral smectic phases of poly(**1**) and poly(**2**). The detected response of poly(**1**) was characterized by a partial switching of the molecules around the cone in the SmC* that resulted in a linear electro-optical response (Fig. 6). Even at very high electric fields it was impossible to obtain a complete ferroelectric switching. On the other hand, the incomplete switching resulted in a linear-like electro-optical effect with a response time, τ, in the ms range (Fig. 7). The electro-optical response in the SmA* phase of poly(**2**) was typical of an electroclinic effect with a rather small induced tilt angle ($\theta_{ind} \approx 1°$) and a very short response time in the μs region (Fig.

8). A detailed account of the electro-optical properties of the polymers was given elsewhere [7].

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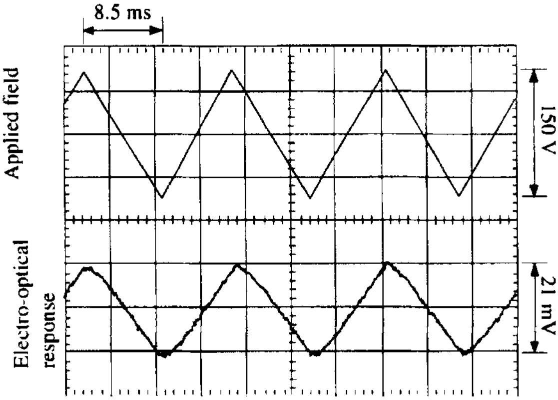

FIGURE 6. Linear electro-optical response for poly(**1**) in the SmC* phase at 22 °C (U_{pp} = 150 V, f = 100 Hz).

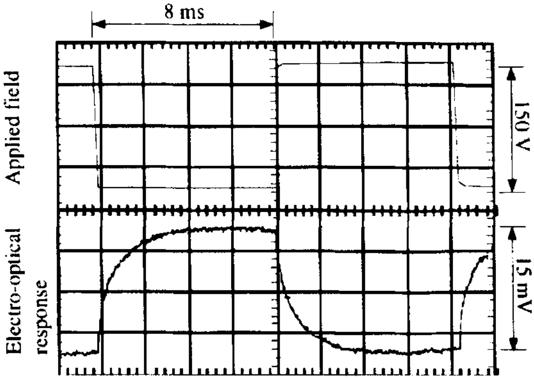

FIGURE 7. Electro-optical response for poly(**1**) in the SmC* phase at 22 °C (U_{pp} = 150 V, f = 100 Hz, τ = 2 ms).

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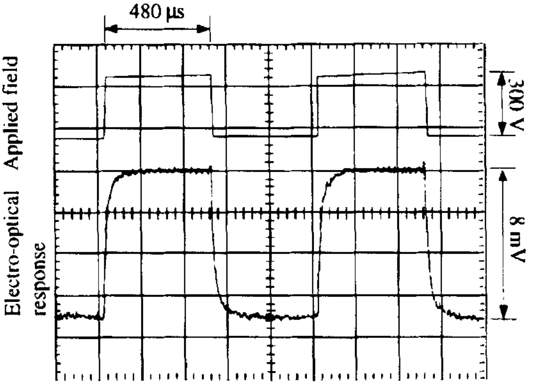

FIGURE 8. Electro-optical response for poly(**2**) in the SmA* phase at 80 °C (U_{pp} = 300 V, f = 100 Hz, τ = 50 µs).

CONCLUSION

The mesophase structures of chiral polysiloxanes and copolysiloxanes were investigated by X-ray diffraction, and a simple structural model was proposed. The polymers presented a linear electro-optical response at room temperature and might be interesting materials for applications in which grey scale and speed are important materials requirements. We also plan to use these materials for preparation of electrically commanded surfaces and to study the switching process in liquid crystal cells with such surfaces.

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