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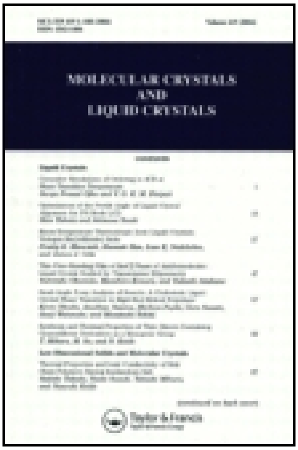

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Synthesis and Electrooptical Properties of Polysiloxanes Containing Chiral Phenyl Nitrobenzoate Side Chains

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Synthesis and Electrooptical Properties of Polysiloxanes Containing Chiral Phenyl Nitrobenzoate Side Chains

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Two new classes **1-n** and **2-n** of chiral liquid crystalline polysiloxanes were prepared which contained a phenyl nitrobenzoate mesogenic unit and the (*S*)-2-octyl group and (*S*)-2-methylbutyl group, respectively. The former polymers exhibited an S_C^* phase, and the latter an S_A^* phase. Their electro-optical characteristics were studied. The response time of the electroclinic switching in some of the materials was found to be in the microsecond range although they were highly viscous.

Keywords: liquid crystalline polymers; chiral smectic; electroclinic effect

INTRODUCTION

Since the discovery of surface stabilized ferroelctric liquid crystals (SSFLC),

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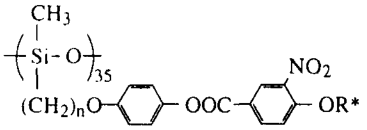
ferroelectric liquid crystals have attracted the interest of scientists and engineers, due to their great potential for device applications. In the past decade, considerable interest has been focused on synthesis of liquid crystalline materials exhibiting ferroelectric properties. In order to overcome some disadvantages of the low molar mass ferroelectric liquid crystalline materials, as low shock resistance, difficult to obtain a good uniform alignment and to sustain it, new ferroelectric systems, namely oligomeric and polymeric liquid crystalline materials, has been developed.

In this work we have prepared two new classes of chiral smectic polysiloxanes **1-n** and **2-n** and investigated their electrooptical behavior in either the S_C* or the S_A* phase.



1-n (n = 4,5,8; R* = $CH^*(CH_3)C_6H_{13}$)

2-n (n = 5,8; R* = $CH_2CH^*(CH_3)C_2H_5$)

EXPERIMENTAL

Synthesis

*4-Hydroxyphenyl benzoate (**4**)*: 20.0 g (182 mmol) of hydroquinone (**3**) and 7.6 g (136 mmol) of KOH were dissolved in 300 ml of water under nitrogen atmosphere and the solution was cooled to 0°C. 19.0 g (133 mmol) of benzoyl chloride were then added portion-wise over 1 h. The reaction mixture was stirred at 0°C for an additional 1 h and then poured into $NaHCO_3$ saturated water. The solid precipitate was filtered, washed with water, dried and crystallized from 70% ethanol, giving 18.3 g (47% yield) of **4**: mp. 163-165°C.

*4-(7-Octenyloxy)phenyl benzoate (**6-8**)*: 5.1 g (24 mmol) of **4** were dissolved in 100 ml of dry 2-butanone in the presence of 5.2 g (36 mmol) of anhydrous K_2CO_3. 5.0 g (26 mmol) of 8-bromo-1-octene (**5-8**) in 5 ml of dry 2-butanone

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were then added over 30 min and the reaction mixture was refluxed for 48 h. The solid was then filtered and the solution was evaporated to dryness. The residue was crystallized from methanol giving 4.3 g (55% yield) of **6-8**: mp. 158-160°C.

4-(7-Octenyloxy)phenol (7-8): A solution of 3.7 g (11 mmol) of 6-8, 40 ml of ethanol, 30 ml of water and 1.6 g (27 mmol) of KOH was refluxed for 5 h. After cooling, the mixture was acidified with 3M HCl, and the water phase was washed with CH_2Cl_2. The organic phases were collected, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography on silica gel with n-hexane/ethyl acetate 3:1 by volume giving 2.2 g (90% yield) of **7-8**: mp. 36-38°C; ($R_f = 0.5$).

Ethyl 4-hydroxy-3-nitrobenzoate (9): A mixture of 14.5 g (79 mmol) of 4-hydroxy-3-nitrobenzoic acid (**8**), 150 ml (2.6 mol) of absolute ethanol and 2 ml of 98% H_2SO_4 was refluxed for 7 h. After cooling, it was poured into 2% $NaHCO_3$ and the precipitate formed was filtered, dried and crystallized from 50% ethanol giving 11.2 g (67% yield) of **9**: mp. 68-69°C.

(+)-(S) Ethyl 3-nitro-4-(2-octyloxy)benzoate (12): 5.0 g (38 mmol) of (-)-(*R*)-2-octanol (**10**), 10.4 g (38 mmol) triphenylphosphine and 8.0 g (38 mmol) of **9** were dissolved in 200 ml of dry diethyl ether. 7.5 g (43 mmol) of diethyl azodicarboxylate were then added slowly under vigorous stirring, and the rection was carried out at room temperature for an additional 72 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 7.4 g (60% yield) of **12** as a viscous oil ($R_f = 0.7$). $[\alpha]^{25}_D = +13.9$ (CH_2Cl_2).

(+)-(S) 3-Nitro-4-(2-octyloxy)benzoic acid (14): A solution of 6.5 g (20 mmol) of **14**, 1.7 g (30 mmol) of KOH, 50 ml of water and 70 ml of ethanol was refluxed for 6 h. It was then cooled, acidified with 37% HCl and washed with CH_2Cl_2. The organic phases were collected, dried over Na_2SO_4 and evaporated to dryness giving 6.4 g (100% yield) of **14**: $[\alpha]^{25}_D = +14.8$ (CH_2Cl_2).

(+)-(S) 4-(7-Octenyloxy)phenyl 3-nitro-4-(2-octyloxy)benzoate (16-8): 1.4 g (4.7 mmol) of **14**, 1.0 g (4.5 mmol) of 7-8 and 0.2 g (0.9 mmol) of pyrrolidinopyridine were dissolved in 30 ml of dry CH_2Cl_2 under nitrogen

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atmosphere. A solution of 1.1 g (4.5 mmol) of dicyclohexylcarbodiimide in 15 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 1.7 g (76% yield) of **16-8** as a yellow viscous oil: $[\alpha]^{25}_D = +8.6$ ($CHCl_3$); $R_f = 0.7$.

^{1}H-NMR ($CDCl_3$) δ (ppm): 8.5 (s, 1H, 2-aromatic), 8.3 (d, 1H, 6-aromatic), 7.1 (m, 3H, 5-, 2'-, and 6'-aromatic), 6.9 (d, 2H, 3'- and 5'-aromatic), 5.8 (m, 1H, $C\underline{H}=CH_2$), 5.0 (m, 2H, $CH=C\underline{H}_2$), 4.6 (q, 1H ArOCH), 3.9 (t, 2H, $ArOCH_2$), 2.1 (m, 2H, $C\underline{H}_2CH=CH_2$), 1.7-1.3 (m, 17H, aliphatic), 0.8 (s, 3H, CH_3).

Polysiloxane **1-8**: 0.9 g (1.7 mmol) of **16-8** and 0.10 g (1.7 mmol r.u.) of poly(hydrogenmethyl siloxane) **18** ($DP_n = 35$) were dissolved in 40 ml of dry toluene under nitrogen atmosphere. 75 μl of a 2% xylene solution of platinum divinyltetramethyl disiloxane 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 0.4 g (42% yield) of **1-8**: $[\alpha]^{25}_D = +8.6$ (CH_2Cl_2).

^{1}H-NMR ($CDCl_3$) δ (ppm): 8.3 (m, 1H, 2-aromatic), 8.1 (m, 1H, 6-aromatic), 7.1 (m, 3H, 5-, 2'-, and 6'-aromatic), 6.9 (m, 2H, 3'- and 5'-aromatic), 4.6 (m, 1H ArOCH), 3.9 (m, 2H, $ArOCH_2$), 1.8-1.4 (2m, 25H, aliphatic), 0.8 (m, 3H, CH_3), 0.5 (m, 2H, $SiCH_2$), 0.1 (m, 3.5H, $SiCH_3$).

Characterization

Differential scanning calorimetry analysis was carried out with a Mettler TA4000 system using 10 K/min scanning rate. The isotropization or clearing (T_i) temperature was taken as corresponding to the maximum in the enthalpic peak of samples that had been annealed by cooling from the isotropic melt. The glass transition temperature (T_g) was taken at the temperature of half-devitrification.

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X-ray diffraction experiments were performed on unaligned samples with a pinhole camera with Ni-filtered CuKα beam (λ = 1.54 Å) at various temperatures between 20°C and T_i.

The polymer liquid crystal material was sucked into the 2 μm gap of conventional sandwich cell by the capillary forces. The cell consisted of two glass plates with inner surfaces with ITO electrodes coated by SiO_x alignment layer. The plates were assambled as a sandwich cell in a holder which allowed to apply a unidirectional shear to the cell just by moving one of the plates with respect to the other. Such a shear gives a uniform alignment of the liquid crystal polymer material. The electro-optic studies were performed in a set-up described in details elsewhere[11].

RESULTS AND DISCUSSION

The side-chain monomers **16-n** and **17-n** were synthesized according to the reaction scheme which is outlined in Fig.1. They consisted of a 4,4'-disubstituted phenyl nitrobenzoate mesogenic core bearing an ϖ-alkenyl segment of variable length (n = 4, 5, or 8) and a chiral group, either an (*S*)-2-octyloxy or an (*S*)-2-methylbutoxy group. It should be noted that none of the monomers formed any mesophases.

The respective polysiloxanes **1-n** and **2-n** were prepared by a conventional Pt-catalyzed hydrosilylation reaction of the side-chain monomers onto a preformed poly(hydrogenmethyl siloxane) (DP_n = 35)[2] (Fig.1).

It was found that the nature and stability of the mesophase of the polysiloxanes greatly depended upon the structure of the chiral substituent and the length of the spacer segment (Table I). In fact, while polysiloxane **1-4** (n = 4) containing the shortest spacer did not show mesomorphic behavior, the other **1-n** samples containing longer spacers (n = 5 or 8) exhibited an S_C* phase. Polysiloxanes **2-n** formed an S_A* phase. In any case, the polymers were amorphous and their mesophase formed above the glass transition temperature ($T_g \leq$ 290 K) at room temperature and transformed directly to the isotropic. The range of existence (T_i - T_g) was narrow ($\leq$ 42 K) for the S_C* of **1-5** and **1-8**, but it was rather broad for the S_A* of **2-5** (86 K) and **2-8** (108 K). Thus, lengthening of the spacer favored the onset of a more stable and persistent mesophase, in agreement with a general trend for side-chain liquid crystalline polymers.

X-ray diffraction experiments on unaligned samples confirmed these results, and enabled us to measure an apparent tilt angle θ of 30° and 20° for **1-5** and **1-8**, respectively. For each polymer, θ was independent of temperature and vanished at T_i. A detailed structural investigation of the mesophases will be reported elsewhere.

TABLE I Transition temperatures of liquid crystalline polysiloxanes **1-n** and **2-n**.

sample	n	$[\alpha]^{25}_D$ (deg)	M_n (g/mol)	M_w/M_n	T_g (K)	T_i (K)	ΔH_i (kJ/mol)
1-4	4	6.5	19,500	4.4	279	--	--
1-5	5	11.0	18,500	1.8	284	303	0.2
1-8	8	8.9	21,000	3.5	266	308	0.4
2-5	5	2.4	21,500	2.9	290	376	1.5
2-8	8	2.2	28,000	1.9	284	392	1.1

We measured the electro-optic response in the chiral smectic polysiloxanes **1-5**, **1-8**, **2-5** and **2-8**. The detected response in the polysiloxanes **1-n**, possessing S_C* phase, is characterized by partial switching of the molecules around the cone. Even at very high electric fields it was impossible to obtain a complete ferroelectric switching. On the other hand, the incomplete switching results in a linear-like electro-optic response depicted in Fig.2 for the case of polysiloxane **1-8** (**1-5** exhibited almost the same behavior). As seen, the field-induced deviation of the sample optic axis θ_{pp} is very linear with the applied electric field and depends strongly on the uniformity of the alignment achieved by means of SiO_x layer and mechanical shear. The induced deviation of the optic axis is found to depend also on temperature (Fig.3). The detected response time in **1-n** polysiloxanes is a few milliseconds, quite reasonable

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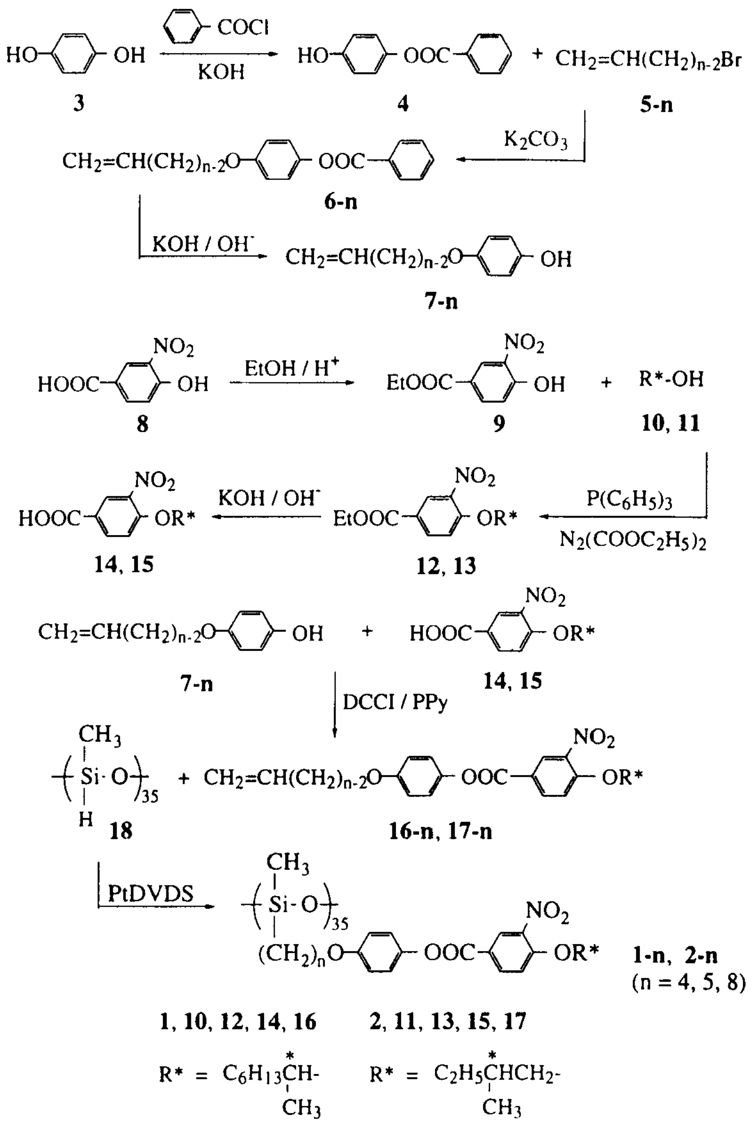

FIGURE 1 Reaction scheme for the synthesis of side-chain monomers **16n** and **17-n** and polysiloxanes **1-n** and **2-n**.

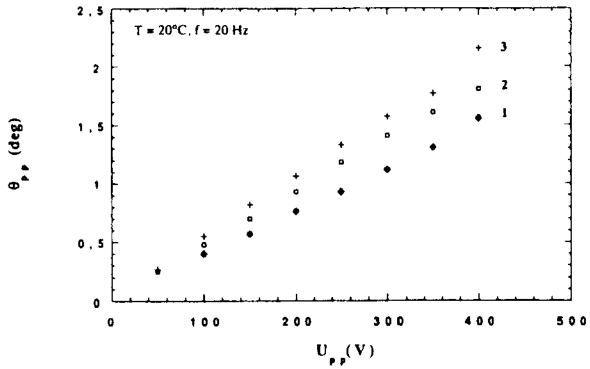

FIGURE 2 The field-induced deviation of the optic axis in the S_C* phase of polysiloxane **1-8**. In order to achieve a uniform alignment, a mechanical shear is applied. The strength of the shear increases from 1 to 3.

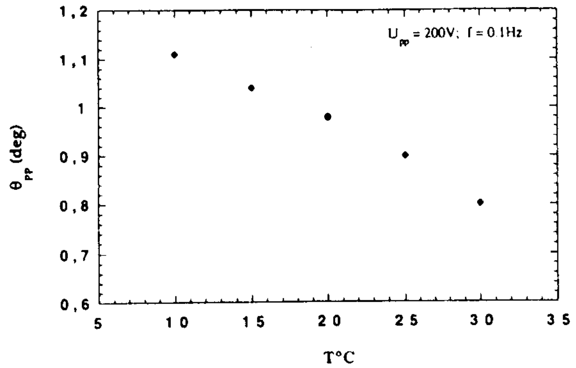

FIGURE 3 The temperature dependence of the field-induced deviation of the optic axis in the S_C* phase of polysiloxane **1-8**.

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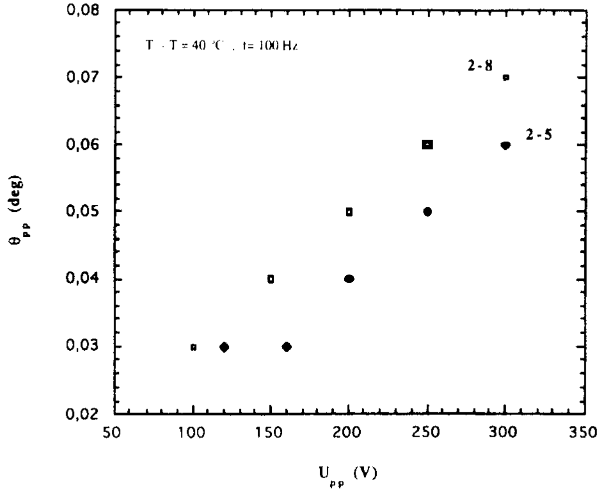

FIGURE 4 The field-induced deviation of the optic axis in the S_A* phase of polysiloxane **2-5** and **2-8** measured at temperature 40°C below the clearing point T_i.

value for ferroelectric liquid crystal materials with such a high viscosity, as these materials are. The polysiloxanes **2-5** and **2-8** exhibit a typical electroclinic switching with response time in the microsecond region (of about 100μs). The measured field-induced tilt of the optic axis θ_{pp} is rather small, about 0.1 degree (see Fig.4) and seems to follow a linear dependence on the applied electric field, typical for the electroclinic response in the chiral orthogonal smectic phases as S_A* phase, for instance. It might also be seen that the value of θ_{pp} in the compound **2-8** is larger than the one measured in **2-5**. This can be expected since in the compound **2-8** the decoupling of the mesogenic units from the backbone is more efficient.

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CONCLUSION

Two new classes of chiral smectic polysiloxanes were prepared from non-mesogenic side-chain monomers. Therefore, incorporation of the monomers into the polymers greatly stabilized the mesophase, which was either S_C* or S_A* depending on the chiral substituent on the phenyl nitrobenzoate unit. Their electro-optical characteristics were studied with respect to the response time and the field-induced deviation of the optic axis in uniformly aligned samples. Linear-like electro-optic response was found in all these materials.

Acknowledgments

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