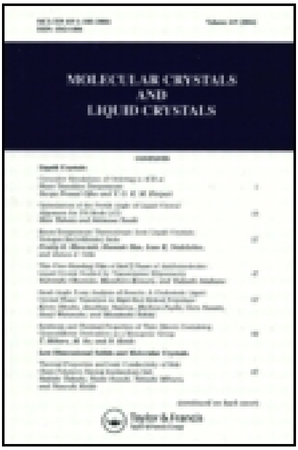

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis and Mesophase Structure of Chiral Liquid Crystalline Polysiloxanes Containing a New Phenyl Benzoate Mesogen

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Synthesis and Mesophase Structure of Chiral Liquid Crystalline Polysiloxanes Containing a New Phenyl Benzoate Mesogen

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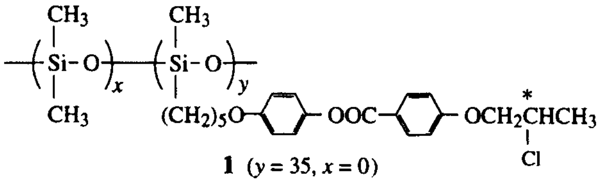
Polysiloxane **1** and copolysiloxane **2** consisting of a new spaced phenyl (*R*)-(2-chloropropoxy)benzoate mesogen were synthesized. The SmA1 structure of **1** and **2** was investigated by X-ray diffraction. This permitted to draw electron density profiles along the smectic layer normal, among which the most physically acceptable one was chosen.

Keywords: smectic polysiloxanes; mesophase structure; X-ray diffraction

INTRODUCTION

The direct coupling between the chiral center and dipole moment, e.g. along a C-Cl bond, of ferroelectric liquid crystals is expected to result in large values of spontaneous polarization and short response times. Accordingly, diverse chiral groups with chloro substituents have been used to induce chirality in liquid crystals, including chiral groups derived from lactic acid or valine[1-3]. To the best of our knowledge, the chiral 2-chloropropoxy group has never been incorporated into liquid crystalline polymers.

We have recently undertaken a systematic investigation into the synthesis and mesophase structure of polymers consisting of a phenyl benzoate mesogenic core variously spaced from the polymer backbone and of different chiral groups. In this work we describe the synthesis of new polysiloxanes **1** and **2** containing the phenyl (*R*)-(2-chloropropoxy)benzoate mesogen, and a characterization of their mesophase structure by X-ray diffraction.



1 ($y = 35, x = 0$)
2 ($y = 7, x = 7$)

EXPERIMENTAL PART

Poly(hydrogenmethyl siloxane) ($y = 35$, $x = 0$)) (**15**) and poly(hydrogenmethyl siloxane-co-dimethyl siloxane) ($y = x = 7$) (**16**) were used as received from Petrarch.

Synthesis

4-Hydroxyphenyl benzoate (4): 19.0 g (133 mmol) of benzoyl chloride were added portion-wise over 1 h to a solution of 20.0 g (182 mmol) of hydroquinone (**3**) and 7.6 g (136 mmol) of KOH in 300 ml of water at 0°C under nitrogen atmosphere. The reaction mixture was stirred at 0°C for an additional 1 h and then poured into $NaHCO_3$ saturated water. The 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-(4-Pentenyloxy)phenyl benzoate (6): 5.0 g (23 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. 3.7 g (25 mmol) of 5-bromo-1-pentene (**5**) in 5 ml of dry 2-butanone 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 2.5 g (38% yield) of **6**: mp. 148-150°C.

4-(4-Pentenyloxy)phenol (7): A solution of 2.2 g (8 mmol) of **6**, 25 ml of ethanol, 20 ml of water and 1.1 g (19 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 1.9 g (87% yield) of **7**: mp. 49-51°C; ($R_f = 0.4$).

(-)-(R)-2-Chloropropanol (10) ($[\alpha]^{25}_D = -20.6$ (neat)) was synthesized from (-)-(*S*)-ethyl lactate (**8**) according to a previous procedure[2].

(-)-(R)-Ethyl 4-(2-chloropropoxy)benzoate (12): 2.9 g (30 mmol) of **10**, 8.1 g (30 mmol) triphenylphosphine and 5.4 g (32 mmol) of ethyl 4-hydroxybenzoate (**11**) were dissolved in 200 ml of dry diethyl ether. 5.8 g (33 mmol) of diethyl azodicarboxylate in 20 ml of dry diethyl ether 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 solution was evaporated to dryness. The residue was purified by column chromatography on silica gel with chloroform giving 5.5 g (76% yield) of **12**: mp. 42-43°C; ($R_f = 0.7$); $[\alpha]^{25}_D = -9.1$ (CH_2Cl_2).

(-)-(R)-4-(2-Chloropropoxy)benzoic acid (13): A solution of 4.9 g (19 mmol) of **12**, 1.9 g (33 mmol) of KOH, 40 ml of water and 70 ml of ethanol was refluxed for 6 h. It was then cooled and acidified with 37% HCl. The precipitate formed was filtered and dried under vacuum giving 3.7 g (85% yield) of **13**: mp. 157-158°C; $[\alpha]^{25}_D = -7.1$ (CH_2Cl_2).

(+)-(R)-4-(4-Pentenyloxy)phenyl 4-(2-chloropropoxy)benzoate (14): 1.3 g (6.2 mmol) of **13** were dissolved in 5 ml of dry tetrahydrofuran and added to a solution of 1.0 g (5.6 mmol) of **7** and 0.3 g (1.7 mmol) of pyrrolidinyl pyridine in 20 ml of dry CH_2Cl_2 under nitrogen atmosphere. A solution of 1.3 g (6.2 mmol) of dicyclohexyl carbodiimide in 20 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 crystallizations from methanol giving 1.1 g (52% yield) of **14**: mp. 75-76°C; $[\alpha]^{25}_D = +2.1$ ($CHCl_3$).

^{1}H-NMR ($CDCl_3$) δ (ppm): 8.1 (2d, 2H, 2-, and 6-aromatic), 7.1 and 6.9 (2m, 6H, 2'-, 3-, 3'-, 5-, 5'- and 6'-aromatic), 5.8 (m, 1H, $C\underline{H}=CH_2$), 4.9 (m, 2H, $CH=C\underline{H}_2$), 4.3 and 4.0 (2m, 3H, $ArOC\underline{H}_2CHCl$, $ArOCH_2C\underline{H}Cl$), 3.9 (t, 2H, $ArOCH_2$), 2.2 (m, 2H, $C\underline{H}_2CH=CH_2$), 1.9 (m, 2H, $ArOCH_2C\underline{H}_2$), 1.6 (d, 3H, CH_3).

Polysiloxane ***1***: 0.4 g (1.0 mmol) of **14** and 0.06 g (1.0 mmol r.u.) of poly(hydrogenmethyl siloxane) (**15**) were dissolved in 30 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 the coagulated polymer was purified by repeated precipitations from dichloromethane solution into n-hexane, giving 0.31 g (70% yield) of **1**.

^{1}H-NMR ($CDCl_3$) δ (ppm): 8.1 (m, 2H, 2- and 6- aromatic), 7.1 and 6.9 (2m, 6H, 2'-, 3-, 3'-, 5-, 5'- and 6'-aromatic), 4.3 and 4.1 (2m, 3H, $ArOC\underline{H}_2CHCl$, $ArOCH_2C\underline{H}Cl$), 3.8 (m, 2H, $ArOCH_2$), 1.8-1.2 (m, 9H, aliphatic), 0.5 (m, 2H, $SiCH_2$), 0.1 (m, 3.5H, $SiCH_3$).

Characterization

The transition temperatures were taken (10 K/min scanning rate) as corresponding to the maximum in the enthalpic peaks of samples that had 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 ($\lambda = 1.54$ Å). Several exposures were taken so as to detect the strongest and the weakest reflections. Intensities I_n of the reflections were measured with a home-made microdensitometer. Experimental amplitudes a_n of diffraction of the different orders of reflections on the smectic layers were corrected for the Lorentz-polarization factor[4] and normalized to that of the strongest one.

RESULTS AND DISCUSSION

Monomer **14** and the corresponding polysiloxane **1** were synthesized following the reaction scheme outlined in Fig.1. Homopolysiloxane **1** and copolysiloxane **2** were prepared by a conventional Pt-catalyzed hydrosilylation reaction of monomer **14** onto a preformed poly(hydrogenmethyl siloxane) ($y = 35$, $x = 0$) (**15**) (Fig.1) and a poly(hydrogenmethyl siloxane-co-dimethyl siloxane) (**16**) ($y = x = 7$), respectively[5], by following the procedure reported in the last step in Fig.1.

Some physicochemical properties and phase transitions of the polymers are summarized in Table I. **1** and **2** formed a smectic mesophase between the melting (T_m) and the isotropization (T_i) temperatures. Below T_m, the X-ray diffraction spectra of both **1** and **2** exhibited in the low-angle region two or three sharp ($00l$) reflections of a layered structure of periodicity $d = 27.9$ Å and 34.2 Å, respectively (Fig.2). Comparison of d with the length L of the polymer repeat unit in its fully extended conformation ($L = 26 \pm 1$ Å) shows that the side chains are perpendicular to the layers (tilt angle $\theta = 0$ °).

At low angles three reflections were detected which could be indexed as the (100), (010) and (110) reflections of a rectangular lattice, the parameters of which were $a = 4.5$ Å and $b = 4.0$ Å for **1** (Table II). Accordingly, the surface S available per side chain was rather small, eg. 18 Å^2 for **1**.

TABLE I Transition temperatures of polysiloxanes **1** and **2**.

sample	y	$[\alpha]^{25}_D$	M_n (g/mol)	M_w/M_n	T_m (K)	T_i (K)	ΔH_i (kJ/mol)
1	35	-3.5	17,000	2.4	348	417	2.3
2	7	-2.5	8,500	1.4	346	383	3.8

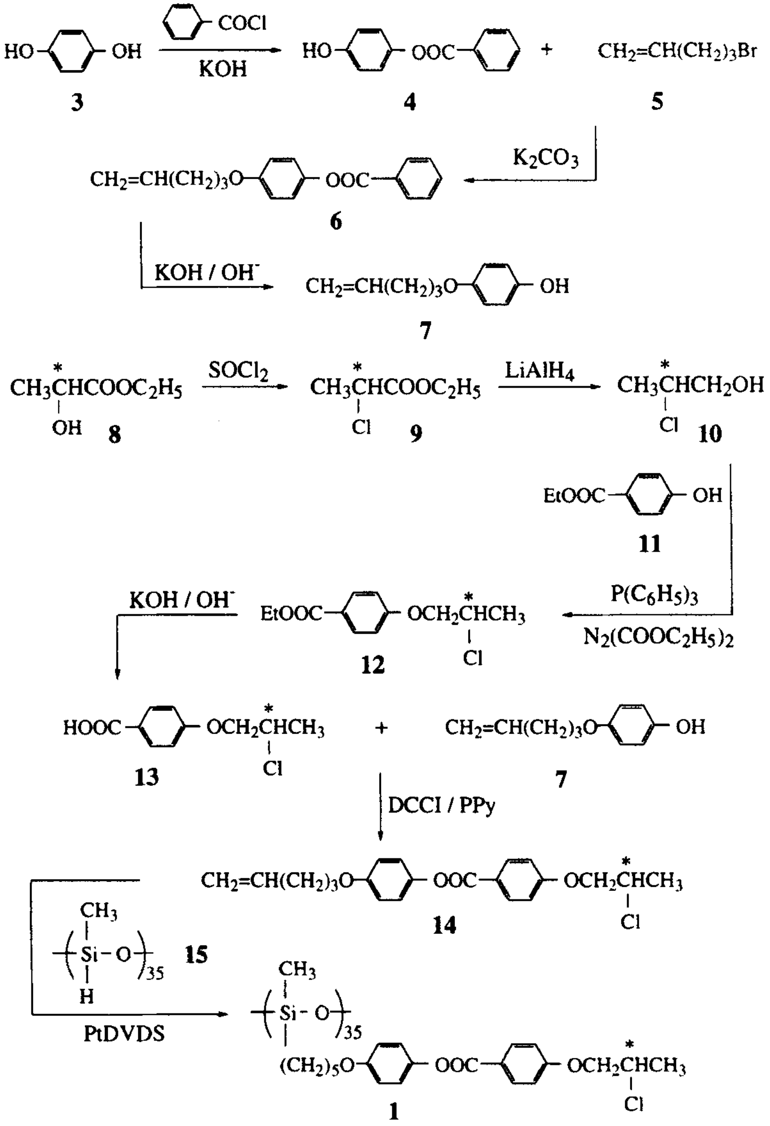


FIGURE 1. Reaction scheme for the synthesis of monomer **14** and polymer **1**.

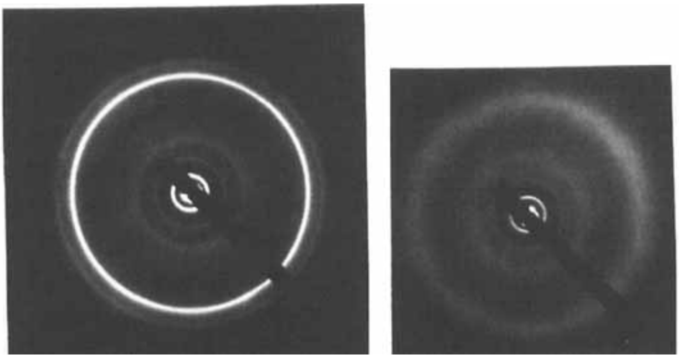


FIGURE 2. X-ray diffraction spectra of **1** in the crystalline phase at 27 °C (left) and SmA1 phase at 100 °C (right).

TABLE II Lattice parameters of the different phases of the polysiloxanes.

	polysiloxane **1**	copolysiloxane **2**
Structure	crystal	crystal
$d \pm 0.2$ Å	27.9	34.2
$a \pm 0.1$ Å	4.5	4.7
$b \pm 0.1$ Å	4.0	4.2
θ / deg	0	0
Structure	SmA1	SmA1
$d \pm 0.2$ Å	28.8	33.2
$D \pm 0.1$ Å	4.6	4.6
θ / deg	0	0

This suggests the occurrence of a truly crystalline phase, rather than a smectic crystal E phase for which much greater surfaces of the rectangular lattice are usually observed in side-chain polysiloxanes[6]. A slightly larger area ($S = 20$ Å^2) was evaluated for **2**, and therefore dilution of the mesogenic side chains in the copolymer resulted in a looser packing but did not prevent crystallization.

In the mesophase up to T_i, the wide-angle Bragg reflections were replaced by a diffuse band characteristic of a disordered smectic structure (intermolecular distance $D = 4.6$ Å), such as the SmA1 ($d = 28.8$ Å for **1**) (Fig.2). In addition, copolysiloxane **2** exhibited a broad band at 7.9 Å (Fig.3) originating from microphase separated dimethylsiloxane polymer chains[7]. In the copolymer the unsubstituted siloxane units were rejected into a separate sub-layer, resulting in a much increased smectic periodicity ($d/L = 1.3$).

Both **1** and **2** gave rise to two low-angle orders of reflections on the smectic layers (Fig.2), and we derived the corresponding electron density profiles $\rho(z)$ along the layer normal. This procedure is illustrated here for **1**. By taking into account the symmetry of the SmA1 phase and the fact that we measured only the fluctuations around the average electron density ρ_0, $\rho(z)$ was given by[8]:

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

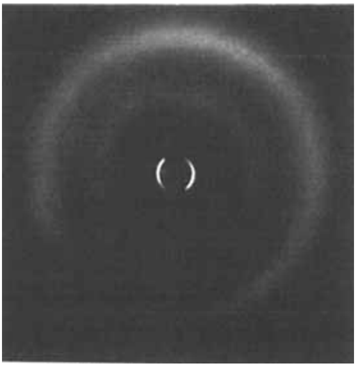


FIGURE 3. X-ray diffraction spectrum of **2** in the SmA1 phase at 90 °C.

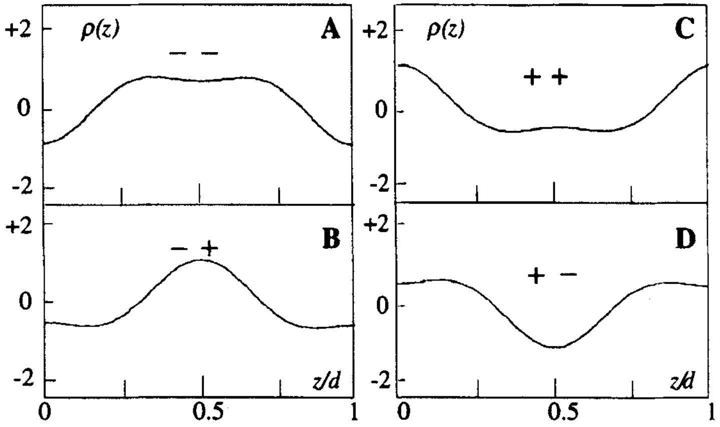


FIGURE 4. Electron density profiles $\rho(z)$ for the four combinations of a_n signs of the SmA1 phase of **1** (corrected and normalized amplitudes $a_1 = 1, a_2 = 0.41$).

As experimentally we measured the intensity I_n of the reflections, we lost the sign of the structure factors a_n, and for n reflections we obtained $2^n = 4$ electron density profiles $\rho(z)$[9] (Fig.4). 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 9.8 e/Å for the mesogenic core, 6.4 e/Å for the spacer, 9.4 e/Å for the chloroalkyl tail, and 7.8 e/Å for the backbone considering it as confined in the smectic planes. Therefore, profile of Fig.4B, corresponding to the ρ_{-+} combination of a_n signs, was chosen as the most physically acceptable one because it presented a central prominent maximum for the overlapping mesogenic cores, flanked by minima for the spacers and slightly pronounced maxima for the main chains as one should expect for monolayer smectic phases.

CONCLUSION

New chiral polysiloxanes were synthesized which incorporated a spaced phenyl benzoate mesogen bearing a (*R*)-2-chloropropoxy substituent. The mesogenic side chains were organized in a fully interdigitated SmA1 structure, in which the siloxane polymer chains were confined into a separate sub-layer.

Acknowledgments
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