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# The first high polarization ferroelectric main chain liquid crystalline polymers

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The first high polarization ferroelectric main chain liquid crystalline polymers have been synthesized via hydrosilation polyaddition using $\alpha,\omega$-dihydro(tetramethyldisiloxane) and chiral, low molar mass mesogenic compounds bearing at each end an olefinic group. They exhibit broad, chiral smectic C and smectic A mesophases. Aligned samples have been obtained using a combination of surface and mechanical effects, giving opportunities for fully characterizing the electro-optical properties of the polymers. Very high polarizations have been measured: 600 nC cm$^{-2}$ at room temperature.

Since the discovery of ferroelectric liquid crystals [1] (FLCs), and the subsequent realization of surface stabilized FLC devices [2], much effort has been given to synthesizing new materials with high spontaneous polarizations and other "optimized" chemical and physical properties (chemical stability; suitable range of temperature; low viscosity; suitable tilt angle...). All this systematic work has led to a better understanding of the relationship between physical properties and chemical structure in FLCs [3].

Recently, the search for new ferroelectric liquid crystalline materials has expanded to the field of liquid crystalline polymers (LCPs). Using chiral mesogenic groups already used in low molar mass FLCs, numerous ferroelectric liquid crystalline polymers (FLCPs) have been synthesized and their physical properties investigated [4, 5].

Surprisingly, most of the FLCPs described so far belong to two families of LCPs, side chain and combined liquid crystalline polymers, and almost no main chain FLCP have been described [6–8].

In this communication, we present initial results of a study aimed at the synthesis and characterization of new main chain FLCPs with high spontaneous polarization and useful second order non-linear optical properties.

*Synthesis.* Main chain LCPs are usually obtained by polycondensation reactions of diacids (or diacid chlorides) with diols, or by polycondensation of diphenols with $\alpha,\omega$-dihalogenoalkanes. Main chain LCPs with lower phase transition temperatures have been obtained by incorporating in the spacers dimethylsiloxane segments via hydrosilation polyaddition using $\alpha,\omega$-dihydro-oligo(dimethylsiloxane) and diallyl (or vinyl) monomers [9–11].

Following that last approach, we have prepared the main chain FLCPs **3** via hydrosilation polyaddition using $\alpha,\omega$-dihydro(tetramethyldisiloxane) **2**, chiral low molar mass mesogenic compounds **1a, b, c** bearing at each end a reactive group (i.e. a carbon–carbon double bond) and dicyclopentadienyl platinum dichloride as catalyst [12] (see scheme 1).

Chiral mesogenic compounds **1a, b, c** have been designed in order to incorporate in their chemical structures various groups, the association of which has been shown to give FLCs with high spontaneous polarizations and promising non-linear optical properties [13, 14].

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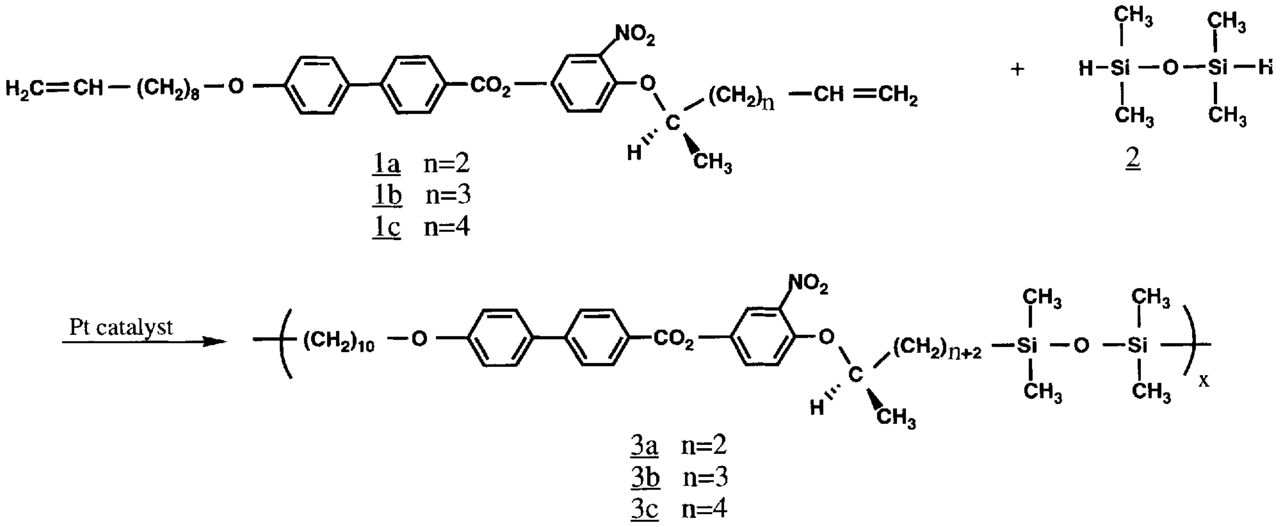
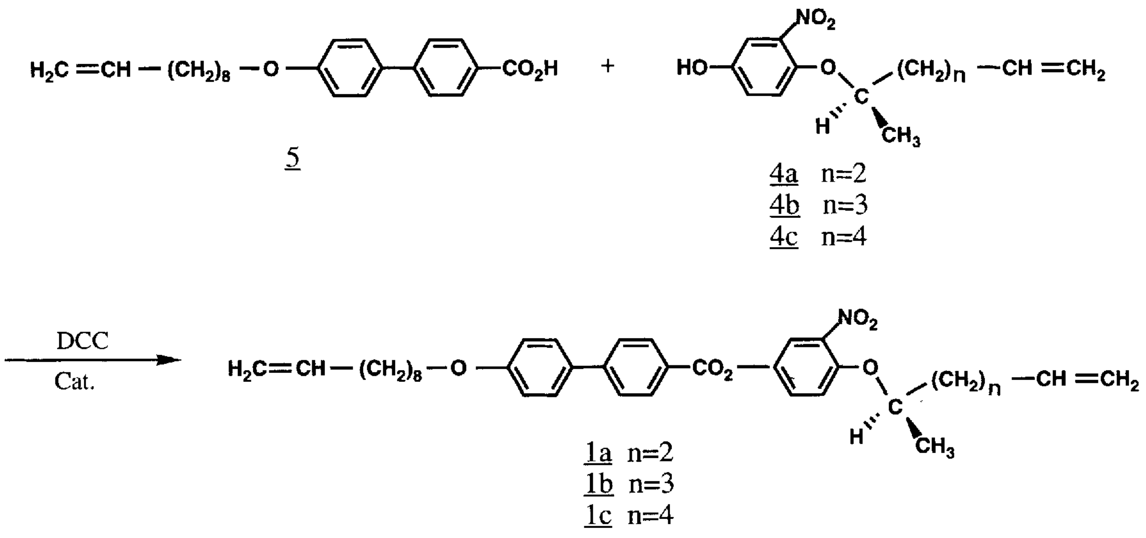
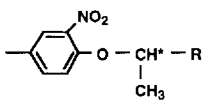


Scheme 1.



Scheme 2.

The "active" part consists of the 4-((*R* or *S*)-1-methylalkyloxy)-3-nitrophenyl moiety:



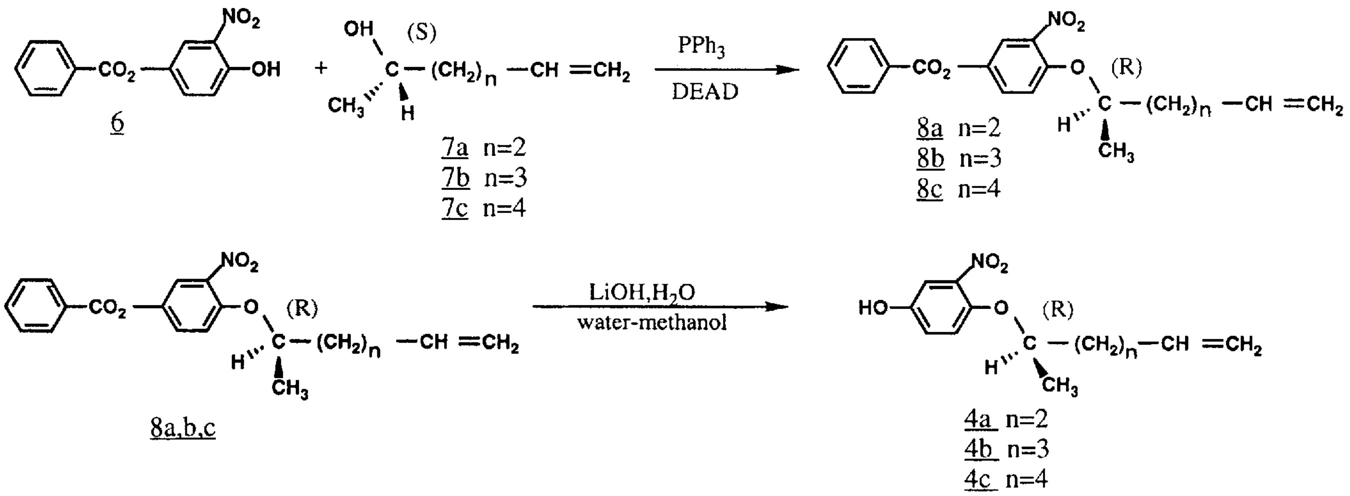
$$-C_6H_3(NO_2)-O-\underset{\displaystyle CH_3}{\underset{|}{CH^*}}-R$$

Thus, chiral mesogenic compounds **1a, b, c** were obtained by esterification of 4-(4′-(dec-9-enyloxy)phenyl)benzoic acid **5** with various substituted phenols **4a b, c** using dicyclohexylcarbodiimide (DCC) as dehydrating agent and pyrrolidinopyridine (PP) as catalyst [15] (see scheme 2).

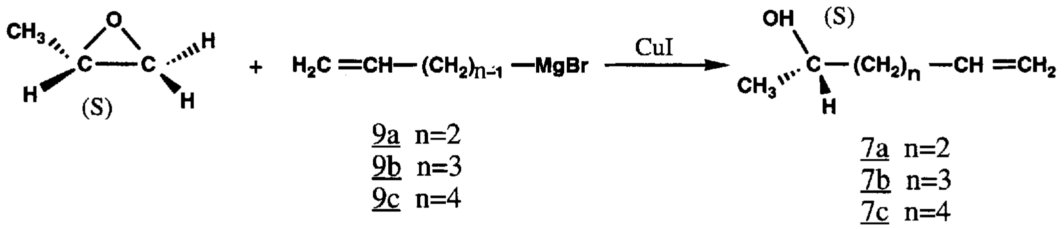
Phenols **4a, b, c** have been synthesized by a two-step procedure from 3-nitro-4-hydroxyphenyl benzoate **6** [16]. Phenol **6** was first etherified by the (*S*)-alken-2-ol **7a, b, c** using the Mitsunobu reaction [17] to give the intermediates **8a, b, c** which were then saponified using lithium hydroxide in a water–methanol mixture to give the phenols **4a, b, c** (see scheme 3).

The (*S*)-alken-2-ols **7a, b, c** were prepared by stereospecific opening of the commercially available (*S*)( − )-methyloxirane by the Grignard reagents **9a, b, c** (from the corresponding 1-bromo-ω-alkenes) catalyzed by copper (I) iodide [18, 19] (see scheme 4).

Quantitative $^1$H NMR end-group analysis (integration of the terminal olefinic proton signals versus the signal of the single proton on the asymmetric carbon) have been



Scheme 3.



Scheme 4.

used to estimate the degree of polymerization (DP) of the polymers. DPs are low and around 10 for the three polymers (see table 1).

*Mesomorphic properties.* The mesomorphic properties of the synthesized chiral main chain LCPs **3a, b, c** have been studied by optical microscopy and differential scanning calorimetry. They are summarized in the table 1.

Typical textures were established for the chiral smectic C phases (broken fan-shaped texture with superimposed dechiralization lines) and smectic A phases (focal conics) after annealing the polymers for some hours within the temperature ranges of the mesophases.

The mesomorphic behaviour of the three polymers is the same. All show a narrow ( ~ 20°) smectic A phase above a broad ( ~ 120°) chiral smectic C phase. The polymers are in the $S_C^*$ phase at room temperature and exhibit a transition to a glassy state around 6°C.

*Physical properties.* The electro-optical characterization of the polymers has been successfully achieved because well-aligned samples were obtained using a combination of surface effects (brushed nylon alignment

Table 1. Degrees of polymerization (DP) and transition temperatures for the main chain liquid crystalline polymers 3.

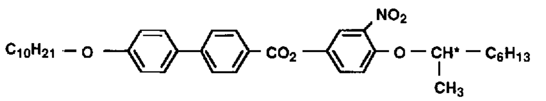
| | | Transition temperatures/°C | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Polymer | DP | g | | $S_C^*$ | | $S_A$ | | I |
| **3 a** | 12 | ● | 6 | ● | 127 | ● | 151 | ● |
| **3 b** | 9 | ● | 6 | ● | 124 | ● | 143 | ● |
| **3 c** | 10 | ● | 4 | ● | 120 | ● | 144 | ● |

Table 2. Physical properties of polymer 3c (Electric field: 14·5 V $\mu$m$^{-1}$; thickness of the cell: 10 $\mu$m).

| T/°C | $P_s$/nC cm$^{-2}$ | $\tau$/$\mu$s | $\theta$/degree |
|---|---|---|---|
| 115 | 204 | 259 | 23·5 |
| 100 | 313 | 382 | 30 |
| 90 | 366 | 473 | 32 |
| 70 | 445 | 953 | 33·5 |
| 50 | 523·5 | 2694 | 34 |
| 40 | 565 | | 34 |
| 30 | 591 | 59600 | 34 |
| 25 | 621 | 89800 | 34 |

layer composed of Du Pont Elvamide) and shear, as described previously for side chain FLCPs [20]. Thus, we have been able to evaluate, as a function of temperature, the spontaneous polarization, the tilt angle and the response time as well, over the whole temperature range of the $S_C^*$ phase for polymer **3c**. Results are gathered in the table 2.

A high polarization (over 600 nC cm$^{-2}$) is obtained at room temperature. This value is similar to that reported for the structurally related low molar mass compound W314 [13(*a*)]: $-560$ nC cm$^{-2}$ at room temperature.



W314

On the other hand, very long response times have been measured for the polymer (from 259 microseconds close to the $S_C^*$ to $S_A$ transition to 90 milliseconds at room temperature), reflecting the expected high orientational viscosity of the FLCP.

In conclusion, chiral main chain FLCPs exhibiting $S_C^*$ and $S_A$ phases have been synthesized via hydrosilation polyaddition using $\alpha,\omega$-dihydro(tetramethyldisiloxane) and chiral difunctionnal mesogenic monomers.

Aligned samples have been obtained using a combination of surface and mechanical effects, giving us opportunities for fully characterizing the electro-optical properties of the ferroelectric main chain LCPs. Very high polarizations have been measured: over 600 *n*C cm$^{-2}$ at room temperature.

Non-linear optical properties of these polymers have now to be evaluated. Work is in progress toward this goal.

Further synthetic work is also in progress in order to prepare high polarization ferroelectric main chain LCPs with higher glass transition temperatures (above room temperature) in order to be able to stabilize a polar order in the glassy state at room temperature.

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## References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. Phys. Lett.*, Paris, **36,** L69.

[2] Clark, N. A., and Lagerwall, S. T., 1980. *Appl. Phys. Lett.*, **36,** 899.

[3] Walba, D. M., 1991, *Ferroelectric Liquid Crystals: A Unique State of Matter*. In *Advances in the Synthesis and Reactivity of Solids*, edited by T. T. Mallouk (Jai Press Ltd, Greenwich, CT), Vol. 1, p. 173, and references therein.

[4] LeBarny, P., and Dubois, J. C., 1989, *Side Chain Liquid Crystalline Polymers*, edited by C. B. McArdle (Blackie, Glasgow), p. 130, and references therein.

[5] Kozlovsky, M. V., and Beresnev, L. A., 1992, *Phase Transition*, **40,** 129, and references therein.

[6] Fayolle, B., Noel, C., and Billard, J., 1979, *J. Phys., France Coll. C3*, **40,** 485.

[7] Chiellini, E., Galli, G., Cioni, F., and Dossi, E., 1993, *Makromolek. Chem., Macromolek. Symp.*, **69,** 51, and references therein.

[8] Watanabe, J., and Kinoshita, S., 1992, *J. Phys. II, France*, **2,** 1237.

[9] Ringsdorf, H., and Schneller, A., 1981, *Br. Polym. J.*, **13,** 43.

[10] Aguilera, C., Bartulin, J., Hisgen, B., and Ringsdorf, H., 1983, *Makromolek. Chem.*, **184,** 253.

[11] Diaz, F., Tagle, L. H., Valdebenito, N., and Aguilera, C., 1993, *Polymer*, **34,** 418.

[12] Apfel, M. A., Finkelmann, H., Janini, G. M., Laub, R. J., Luhmann, B. H., Price, A., Roberts, W. L., Shaw, T. J., and Smith, C. A., 1985, *Anal. Chem.*, **57,** 651.

[13] (*a*) Walba, D. M., Ros, M. B., Clark, N. A., Shao, R., Robinson, M. G., Liu, J. Y., Johnson, K. M., and Doroski, D., 1991, *J. Am. chem. Soc.*, **113,** 5471; (*b*) Walba, D. M., Ros, M. B., Sierra, T., Rego, J. A., Clark, N. A., Shao, R., Wand, M. D., Vohra, R. T., Arnett, K. E., and Velsco, S. P., 1991, *Ferroelectrics*, **121,** 247; (*c*) Walba, D. M., Ros, M. B., Clark, N. A., Shao, R., Johnson, K. M., Robinson, M. G., Liu, J. Y., and Doroski, D., 1991, *Molec. Crystals liq. Crystals*, **198,** 51; (*d*) Liu, J. Y., Robinson, M. G., Johnson, K. M., Walba, D. M., Ros, M. B., Clark, N. A., Shao, R., and Doroski, D., 1991, *J. appl. Phys.*, **70,** 3426.

[14] (*a*) Kapitza, H., Zentel, R., Twieg, R. J., Nguyen, C., Vallerien, S. U., Kremer, F., and Willson, C. G., 1990, *Adv. Mater.*, **2,** 539; (*b*) Poths, H., Andersson, G., Sharp, K., and Zentel, R., 1992, *Adv. Mater.*, **4,** 792.

[15] Hassner, A., and Alexanian, V., 1978, *Tetrahedron Lett.*, 4475.

[16] Keller, P., 1994, *Bull. Soc. Chim. France*, **131,** 27.

[17] Mitsunobu, O., 1981, *Synthesis*, 1.

[18] Huynh, C., Derguini-Boumechal, F., and Linstrumelle, G., 1979, *Tetrahedron Lett.*, 1503.

[19] (*a*) Johnston, B. D., and Slessor, K. N., 1979, *Can. J. Chem.*, **57,** 233; (*b*) Kandil, A. A., and Slessor, K. N., 1983, *Can. J. Chem.*, **61,** 1166.

[20] Parmar, D. S., Clark, N. A., Keller, P., Walba, D. M., and Wand, M. D., 1990, *J. Phys., France*, **51,** 355.