

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Synthesis and characterization of twin mesogens containing siloxane units as central spacers

F. Dia<sup>a</sup>; N. Valdebenito<sup>a</sup>; L. H. Tagle<sup>a</sup>; C. Aguilera<sup>b</sup>

<sup>a</sup> Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile <sup>b</sup> Departamento de Química, Facultad de Ciencias Universidad de Concepción, Concepción, Chile

**To cite this Article** Dia, F. , Valdebenito, N. , Tagle, L. H. and Aguilera, C.(1994) 'Synthesis and characterization of twin mesogens containing siloxane units as central spacers', *Liquid Crystals*, 16: 1, 105 – 113

**To link to this Article:** DOI: 10.1080/02678299408036523

**URL:** <http://dx.doi.org/10.1080/02678299408036523>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Synthesis and characterization of twin mesogens containing siloxane units as central spacers

by F. DÍAZ\* A., N. VALDEBENITO M., and L. H. TAGLE

Facultad de Química, Pontificia Universidad Católica de Chile,  
Casilla 306, Correo 22, Santiago, Chile

and C. AGUILERA

Departamento de Química, Facultad de Ciencias Universidad de Concepción,  
Casilla 3-C, Concepción, Chile

(Received 28 January 1993; accepted 6 June 1993)

A mesogenic ester, 4-hexyloxyphenyl 4-vinyl benzoate was synthesized and studied. The synthesis and characterization of bimesogenic molecules employing this ester with oligosiloxane spacers of different lengths are described. The compounds were characterized by IR  $^1\text{H}$  NMR, elemental and thermal analysis, and polarized light microscopy.

### 1. Introduction

A strategy employed for lowering the transition temperatures of liquid crystal compounds has been the introduction of flexible spacers between the mesogenic units to produce bimesogenic compounds and main-chain liquid crystal polymers. The flexible spacer are often polymethylene, poly(methylene oxide) or polysiloxane units; a decrease in the transition temperatures is observed with an increase in the spacer length [1–6]. Polysiloxane spacers have been shown to remarkably reduce the  $T_g$ ,  $T_m$  and  $T_c$  of compounds with a wide mesophase range, because of the bulky structure of the methyl groups and the irregular conformations of the siloxane units. Bimesogenic compounds (i.e. twins/dimers) with siloxane spacers have been successfully prepared [7–8] but have been studied to a lesser degree as compared to alkyl spacers.

Our interest in these dimers was to develop liquid crystals with wide mesophase ranges. Furthermore, they can be used as models of thermotropic main-chain polymers.

### 2. Experimental

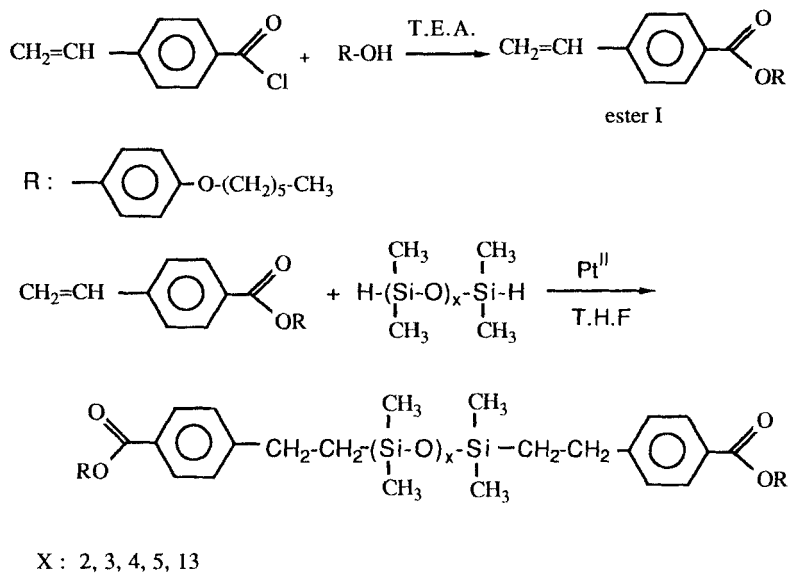
All chemicals and solvents were obtained from Aldrich and Merck Ltd. IR spectra were determined in KBr pellets using a Perkin–Elmer model 567 spectrophotometer.  $^1\text{H}$  NMR spectra were obtained on a Varian XL-100 NMR spectrometer. Elemental analyses were performed on a CH Heraeus Mikrostandart analyser. Thermal analysis of the ester was performed with a Perkin–Elmer DSC-1B differential scanning calorimeter, with a heating rate of  $4^\circ\text{C min}^{-1}$  under a nitrogen atmosphere. Thermal analyses of the dimers were performed with a Perkin–Elmer DSC 7 differential scanning calorimeter with a heating rate of  $10^\circ\text{C min}^{-1}$ . The transition temperatures and phase textures were determined with a Leitz Ortholux Pol BKII polarizing light

\* Author for correspondence

microscope equipped with Linkam THMS-600 hot stage, at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . Thermogravimetric analyses were carried out with a Perkin-Elmer TGS-1 thermobalance equipped with a Perkin-Elmer UU-1 programmer at a heating rate of  $20^{\circ}\text{C min}^{-1}$  under a nitrogen atmosphere. The overall synthetic route is given in the scheme and detailed in the following sections.

### 2.1. Synthesis of 4-hexyloxyphenyl 4-vinylbenzoate (ester I)

10 mmol of 4-hexyloxyphenol were dissolved in 3.0 ml of dry THF and equimolar at quantities of *p*-vinylbenzoyl chloride [9] and triethylamine (TEA) were added to the solution stirred at  $5^{\circ}\text{C}$ . After stirring for 4 h, the reaction was left to stand for 16 h at room temperature. The product was dissolved in  $\text{CH}_2\text{Cl}_2$ , washed successively with HCl 5 per cent, cold water, NaOH 5 per cent, water and dried over  $\text{Na}_2\text{SO}_4$ . The  $\text{CH}_2\text{Cl}_2$  was evaporated and the ester was purified by recrystallization from methanol. Further purification was achieved by chromatography (eluent:  $\text{CH}_2\text{Cl}_2$ -hexane, 1:1), over silica gel 70-230 mesh. Yield 70 per cent. The analytical results are summarized in table 1 and are in agreement with the ester structure.



Scheme.

Table 1. IR,  $^1\text{H}$  NMR and elemental analyses of 4-hexyloxyphenyl 4-vinylbenzoate.

C/per cent	H/per cent	IR $\text{cm}^{-1}$	$^1\text{H}$ NMR d ( $\text{CDCl}_3$ )
Calculated 77.78	7.45	1 730 (C=O)	7.8 (dd arom. vinyl)
Found 77.47	8.58	1 280 (C-O)	7.0 (dd arom. phenol)
		1 080 (C-O)	6.7 (dd, -CH=)
			5.7 (dd, $\text{CH}_2=$ )
			4.0 (t, O- $\text{CH}_2$ -)
			1.5 (m, - $\text{CH}_2$ -)
			0.9 (t, - $\text{CH}_3$ -)

### 2.2. Synthesis of twin mesogens containing polysiloxane spacers

10.5 mm of the  $\alpha$ -dimethylsilanyl- $\omega$ -hydrogenoligomethyl-siloxane [10] in dry THF was added dropwise over 1 mmol of 4-hexyloxyphenyl 4-vinylbenzoate dissolved in 1 ml of THF with a Wacker-oil catalyst, based on  $H_2PtCl_6$  (Wacker Oil, Wacker Chemie, Burghausen, Germany). The reaction mixture was stirred for 24 h at 60°C under a nitrogen atmosphere, poured into methanol. The reaction was stopped when the IR absorption band at 2140  $cm^{-1}$  of the Si-H group had disappeared. Yield 55–70 per cent. Each dimer was purified by column chromatography over silica gel 70–230 mesh.

Compound	Eluent
<b>I<sub>2</sub></b>	Benzene : $CHCl_3$ , 2 : 3.
<b>I<sub>3</sub></b>	Benzene : $CHCl_3$ , 2 : 3.
<b>I<sub>4</sub></b>	(1) benzene, (2) $CHCl_3$ .
<b>I<sub>5</sub></b>	(1) benzene, (2) $CHCl_3$ .
<b>I<sub>3</sub></b>	<i>n</i> -hexane : $CHCl_3$ , 5 : 2.

The elemental analyses of all molecules are summarized in table 2. A typical IR spectra of the twin mesogens is shown in figure 1 for **I<sub>3</sub>**. Some of the absorption frequencies ( $cm^{-1}$ ) are 2960 ( $-CH_3$ ), 1720 (C=O), 1260 (C-O), 1020 (Si-O), 1045 (Si- $CH_2$ ) and 800 ( $-Si(CH_3)_2$ ). All twin molecules present similar  $^1H$  NMR spectra, as shown for **I<sub>3</sub>** in figure 2.

Table 2. Elemental analyses of the twin molecules.

Molecule	C calculated/per cent	C found/per cent	H calculated/per cent	H found/per cent
<b>I<sub>2</sub></b>	67.25	67.27	7.99	7.37
<b>I<sub>3</sub></b>	64.47	64.95	8.00	7.89
<b>I<sub>4</sub></b>	62.11	62.11	8.02	7.64
<b>I<sub>5</sub></b>	60.07	60.54	8.03	8.28
<b>I<sub>13</sub></b>	50.26	49.30	8.07	8.30

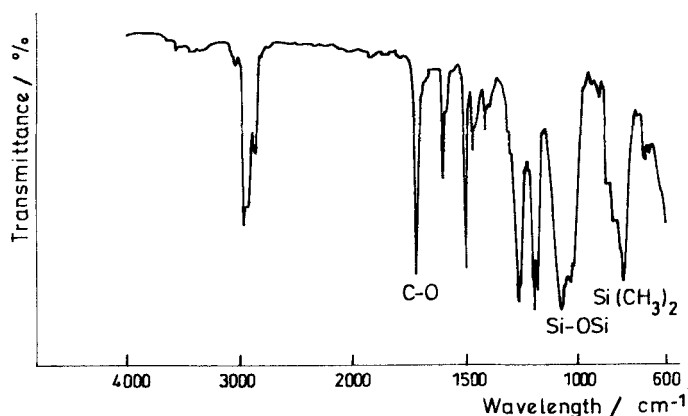


Figure 1. IR spectra of the dimer **I<sub>3</sub>**.

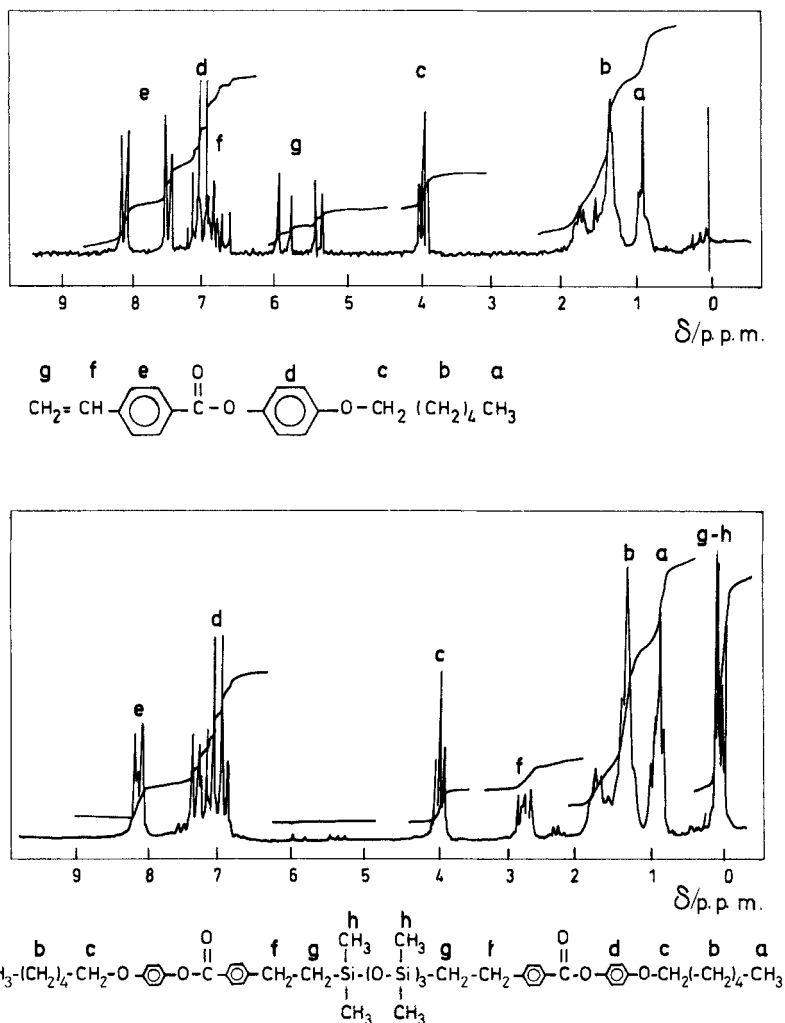


Figure 2. <sup>1</sup>H NMR spectra of the dimer I<sub>3</sub> and of the ester I.

### 3. Results and discussion

#### 3.1. 4-Hexyloxyphenyl 4-vinylbenzoate (ester I)

The DSC of I is shown in figure 3. A splitting of the supercooled crystallization peak at 47 and 46°C can be observed. On subsequent heating, a splitting of the crystal-liquid crystal transition can also be seen, and has been assigned to the successive melting of two different crystal phases formed after the first heating [11]. This polymorphism must be confirmed by X-ray diffraction analysis.

Polarized light microscopy of the ester showed a schlieren texture characteristic of the nematic mesophase (see figure 4). The clearing point was at 87°C by DSC and over 90°C by microscopy. An analogous vinyloxyester has been reported by Finkelmann and Rehage having a nematic mesophase with similar transition temperatures [12].

The thermogravimetric analysis of the ester I showed a 1.4 per cent weight loss at 170°C (see figure 5).

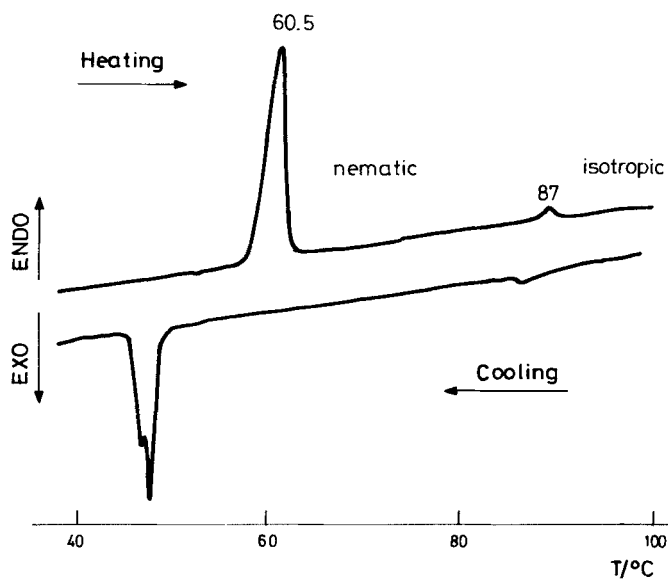


Figure 3. Differential scanning calorimetry trace of 4-hexyloxyphenyl 4-vinyl benzoate.



Figure 4. Polarizing light microscopic texture of the 4-hexyloxyphenyl 4-vinyl benzoate at 85°C.

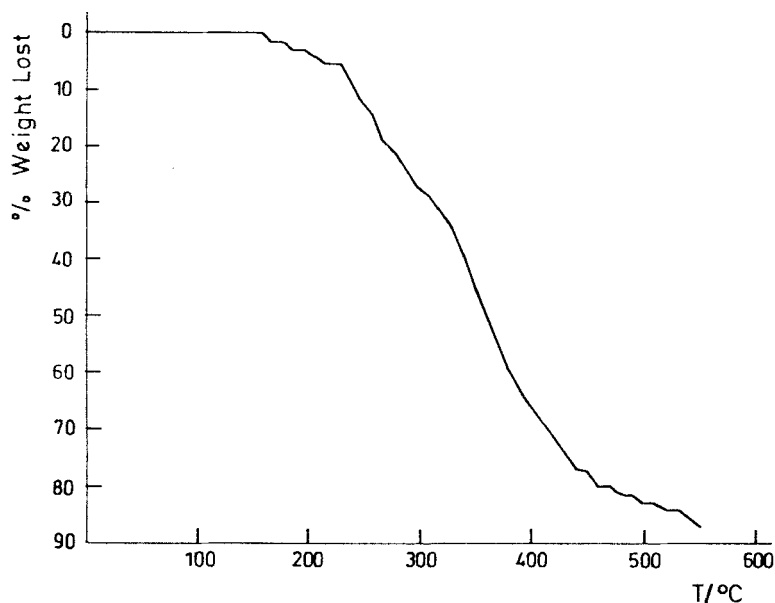


Figure 5. Thermogravimetric trace of the ester I.

### 3.2. *Twin mesogens*

Transition temperatures,  $\Delta H$ ,  $\Delta S$  and  $\Delta C_p$  values are given in table 3. The dimers  $I_{2-4}$  exhibit two endothermic peaks on heating and two exothermic peaks on cooling in the thermograms, as shown in figure 6 for  $I_4$ , i.e. they are enantiotropic liquid crystal materials. Smectic mesophases below room temperature, were observed for all the twin mesogens (for example, see figure 7 showing the smectic phase texture of  $I_5$  at  $-20^\circ\text{C}$ ), and all exhibited glass transitions.

The  $T_g$  values decrease dramatically with an increase in the siloxane spacer length: temperatures as low as  $-73.26^\circ\text{C}$  were achieved in  $I_{13}$ .

The clearing temperatures of  $I_{2-5}$  show a gradual downward trend, and an odd–even effect, the dimers with an odd number of siloxane units in the spacer having the higher clearing transition temperatures. For  $I_{13}$ , a large decrease is observed in the  $T_c$ . The molecules have greater flexibility and the stronger core–core interactions have been diluted by the longer spacers. A greater birefringence was observed for the longer spacers.

The compound  $I_{13}$  revealed only one endothermic peak on heating and one exothermic peak on cooling corresponding to the glassy–isotropic and isotropic–glassy transitions, respectively. Polarized light microscopy of  $I_{13}$  showed a smectic mesophase below  $-30^\circ\text{C}$ . The behaviour of this compound was remarkable because the low temperature mesophase was frozen at the glass transition, the molecular order introduced by the mesophase being retained, and a glassy compound having liquid crystal structure was formed. Although this state has been observed in side-chain liquid crystal polymers [13, 14] this behaviour is also present in  $I_{13}$  having a molecular weight of  $1673\text{ g mol}^{-1}$ .

The enthalpies of the clearing transitions varied between the limits normally formed for smectic phases [15].

Table 3. Thermal data for twin mesogens.

Compound	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$	$\Delta H_m/\text{J g}^{-1}$	$\Delta S_m \cdot 10^3/\text{J g}^{-1} \text{K}^{-1}$	$T_c/^\circ\text{C}$	$\Delta H_c/\text{J g}^{-1}$	$\Delta S_c \cdot 10^3/\text{J g}^{-1} \text{K}^{-1}$	$\Delta C_p T_g/\text{J g}^{-1} \text{K}^{-1}$
<b>I<sub>2</sub></b>	-40.13	-11.60	1.10§	4.2	2.59	1.95	7.10	†
<b>I<sub>3</sub></b>	-40.08	-0.33	†	†	3.95	†	†	0.293
<b>I<sub>4</sub></b>	-57.95	-5.52	4.02§	15.18	2.13	8.80 <sup>c</sup>	31.98	0.654
<b>I<sub>5</sub></b>	-65.57	-6.37	5.26§	27.30	3.16	6.61	23.76	0.531
<b>I<sub>13</sub></b>	-73.26	—	—	—	-34.56	1.83	7.67	†

† Values unavailable due to overlapping.

‡  $T_g$  too small for measure  $C_p$ .

§ Values taken from cooling.



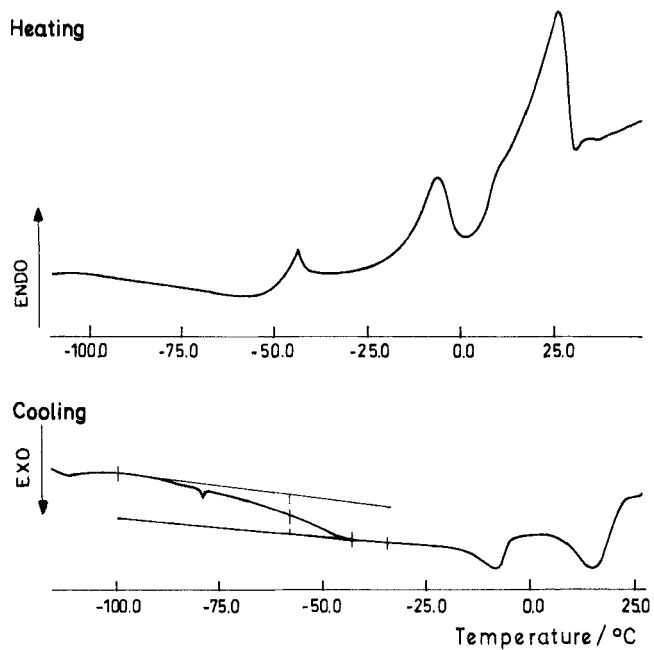


Figure 6. DSC curves of the dimer  $I_4$ . Sample weight 9.720 mg, at  $10^\circ\text{C min}^{-1}$ .

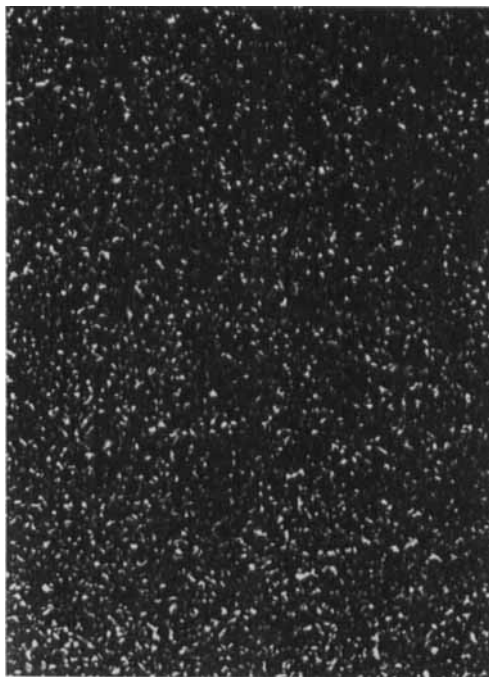


Figure 7. Polarizing light microscopic texture of  $I_5$  measured at  $-20^\circ\text{C}$ .

#### 4. Conclusions

All the dimeric compounds exhibited liquid crystalline behaviour, forming low temperature smectic phases. The twin mesogen  $I_{13}$  showed a glassy state which retained the smectic order introduced by the mesophase. Longer spacers produced  $T_g$  temperatures as low as  $-73.26^\circ\text{C}$ , with increased mesophase ranges.

The authors thank Professor Finkelmann, in whose laboratory some of the thermal parameters were determined. The authors are grateful to Fondo Nacional de Investigaciones Científicas (FONDECYT) for financial support of this work.

#### References

- [1] KROSCWITZ, J. J., 1987, *Polymers*, first edition (J. Wiley & Sons), p. 540.
- [2] STRZELECKI, L., and VAN LUYEN, D., 1980, *Eur. Polym. J.*, **16**, 299.
- [3] VAN LUYEN, D., and STRZELECKI, L., 1980, *Eur. Polym. J.*, **16**, 303.
- [4] GORDON, M., and PLATÉ, N. A., 1984, *Liquid Crystals Polymers*, Vol. I (Springer-Verlag), p. 120.
- [5] JIN, J. I., and PARK, J. H., 1984, *Molec. Crystals liq. Crystals*, **110**, 193.
- [6] AGUILERA, C., AHMAD, S., and BARTULÍN, J., 1988, *Molec. Crystals liq. Crystals*, **162 B**, 277.
- [7] AGUILERA, C., and BERNAL, L., 1984, *Polym. Bull.*, **12**, 383.
- [8] RIVAS, B. L., HISGEN, B., SCHMIDT, H. W., and RINGSDORF, H., 1987, *Boln Soc. chil. Quim.*, **32**, 143.
- [9] JAGER, P., and WRIGHT, E. S., 1963, *J. chem. Soc.*, p. 1339.
- [10] GREBER, G., and METZINGER, L., 1960, *Makromolek. Chem.*, **39**, 167.
- [11] MATHOT, V. B. F., and PIJPER, M. F. J., 1989, *Thermochim. Acta*, **151**, 241.
- [12] FINKELMANN, H., and REHAGE, G., 1980, *Makromolek. Chem. rap. Commun.*, **1**, 31.
- [13] MCARDLE, C. B., 1989, *Side-Chain Crystal Polymers* (Chapman & Hall), p. 224.
- [14] GORDON, M., 1984, *Liquid Crystals Polymers*, Vol. II (Springer-Verlag), p. 180.
- [15] GRAY, G. W., and GOODBY, J. W., 1984, *Liquid Crystals* (Leonard Hill), p. 19.