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Liquid Crystals

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Studies of first- and second-order phase transitions in LC methacrylic monomers based on the ω-hexyloxysalicylaldimine group

E. A. Soto-Bustamante[a]; C. M. González-Henríquez[a]; G. A. Rodríguez-Lehyt[a]; R. O. Vergara-Toloza[a]
[a] Universidad de Chile-Facultad de Ciencias Químicas y Farmacéuticas, Santiago 1, Chile

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Studies of first- and second-order phase transitions in LC methacrylic monomers based on the ω-hexyloxysalicylaldimine group

E.A. SOTO-BUSTAMANTE*, C.M. GONZÁLEZ-HENRÍQUEZ, G.A. RODRÍGUEZ-LEHYT and R.O. VERGARA-TOLOZA

Universidad de Chile-Facultad de Ciencias Químicas y Farmacéuticas, Olivos 1007, casilla 233, Santiago 1, Chile

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The synthesis and phase characterization of two liquid crystalline methacrylic monomers based on the ω-hexyloxysalicylaldimine group with octyl and decyloxy chain substitutions is presented. The liquid crystalline materials were characterized by polarizing optical microscopy, differential thermal analysis and X-ray diffractometry. Nematic and tilted smectic C phases were observed in the compounds. Their liquid crystalline properties where compared with previously studied samples of homologous compounds. In contrast to previous results, this structural modification induces pronounced enantiotropic first-order phase transitions between nematic and smectic C mesophases. A correlation between the phase transition behaviour and structural features of the sample is included.

1. Introduction

Structural modifications in liquid crystal molecules have been subjected to intensive studies. In our studies, the lateral distribution of hydroxy groups and their ability to form an interpenetrating network through the mesophase require further investigation. Our polymer/monomer systems [1] show a rather strong collective polar phenomenon, which we believe is related to the ability of the hydroxyl group in both polymer and monomer to form a network perpendicular to the smectic layer, in a three-dimensional space. This can be understood as an interpenetrating network, which may ultimately be responsible for the observed ferro- or antiferroelectricity. It is therefore important to change our monomer structures and then investigate their influence on the electrical response.

One of our strategies was to synthesize a structural modification with the aromatic rigid core in opposite direction with respect to previously studied samples. This modification would allow us to understand whether the lateral orientation of the hydroxy group can influence the physical characteristics of our materials.

Our original compounds possess a salicylaldimine rigid core, linked to a methacrylic moiety via an aliphatic spacer of usually six methylenic groups [2]. In this study we have modified this ensemble by now forming the linkage of the salicylaldimine group with the aliphatic spacer. Thus, compared with the reference materials, the aromatic core is now positioned in the opposite direction (see figure 1).

The reference samples are denoted as in our previous studies as M*n*R*m* [3–6], where M*n* is as above but bonded to the aromatic phenylimine rigid core (R). This group has, in its *para* position, an alkoxy chain with m=6 and 10 methylene units. All these compounds posses a similar liquid crystalline mesomorphism already presented [3, 4], and will be used in the following discussion.

It is well known that pure substances, such as helium, glass, polymers and liquid crystals, show behaviour other than a first-order transition in their phase changes at constant pressure [7]. In the case of liquid crystals this situation usually occurs at the SmA–SmC phase transition, where second order-like is the most observed case, a situation well described by several authors [8, 9]. The phase transition from SmA to SmC is related to the tilt angle of the mesophase and to how this order parameter is slightly (second order-like) or abruptly (first order) modified as the temperature decreases. In the case of a first-order phase transition, its behaviour is directly dependent on the C_p variation and therefore easily observed by differential thermal analysis. For a second-order phase transition the situation is different, since no changes in C_p can be easily detected. Here the

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*Corresponding author. Email: esoto@ciq.uchile.cl

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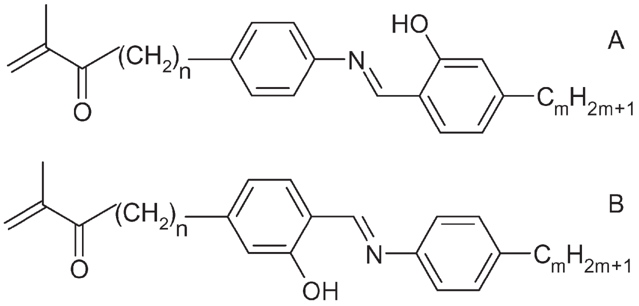


Figure 1. Structures of the investigated compounds: A, *n*=6, *m*=8, M68R; *n*=6, *m*=10, M610R; references B, *n*=6, *m*=8, M6R8; *n*=6, *m*=10, M6R10.

new mesophase can be recognized by polarizing light microscopy (POM) due to changes of birefringence in free standing films, as has already been reported [10]; we now discuss this behaviour in relation to the newly prepared compounds.

2. Experimental

2.1. *General considerations*

The compounds investigated were characterized by ^{1}H NMR spectroscopy using a 300 MHz spectrometer (Bruker, WM 300), infrared spectroscopy (FTIR Perkin-Elmer) and elemental analysis (Perkin-Elmer, 240 B).

The phase transition temperatures were determined using a differential temperature analyser (Mettler, FP90 DTA), with an accuracy of ±0.1 K. A polarizing microscope (Leica, DLMP), equipped with a heating stage (Linkam THMSE 600) was used for temperature-dependent investigations of liquid crystal textures. A video camera (Panasonic WVCP414P), installed on the polarizing microscope, was coupled to a video capture card (Miro DC-30), allowing real-time video capture and image saving. The samples were suspended in a copper plate with a 4 mm diameter hole and studied as free-standing films.

X-ray measurements were performed using CuK_α radiation; the samples were contained in 1.0 mm glass capillaries (Lindemann) and held in a copper block. Precise data for aligned samples in the small-angle region were obtained with a focusing horizontal two-circle X-ray diffractometer (STOE STADI 2) with a linear position-sensitive detector for data collection [11, 12]. By means of one differential temperature stabilizer near the location of the sample it was possible to improve the control to better than ±0.1 K in the range 30–100°C during the measurements. The samples were oriented using permanent magnets with field strength of 0.3 T.

2.2. *Synthesis*

The syntheses of compounds M68R and M610R were carried out using the convergent synthetic pathway described in figure 2 for M68R; in a first step, the aromatic rigid core (A8R), prepared via condensation of the corresponding aniline and the 4-octyloxy-2-hydroxybenzaldehyde, is finally reacted with M6I. The preparation of M6I was described previously [13]. A brief description of M68R synthesis follows.

2.2.1. 2-hydroxy–4–octyloxybenzaldehyde (8R). To a mixture of 24.07 mmol of 2,4-dihxydroxybenzaldehyde

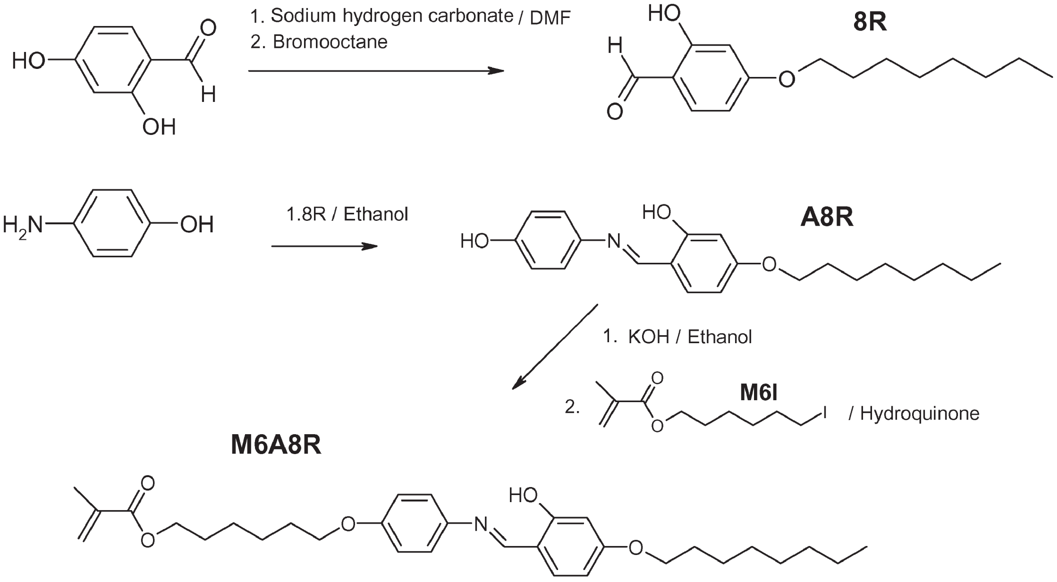


Figure 2. Synthetic pathway for the preparation of M68R.

in 35 ml of *N*,*N*-dimethylformamyde, 24.07 mmol of sodium hydrogen carbonate was added and the mixture allowed to react for 1 h at 100°C. Then 27.68 mmol of bromoctane was added and the mixture heated at 100°C. The reaction progress was followed by thin-layer chromatography, and was complete in 12 to 24 h. The reaction was then cooled and water added. The product was extracted three times with diethyl ether, and the organic extracts washed extensively with water, separated, dried with anhydrous Na_2SO_4 and the solvent distilled off at reduced pressure. Column chromatography in silica using toluene:ethyl acetate (10:1) as eluent gave 8R with a total yield of 80%. ^1H NMR, δ ppm, $CDCl_3$: 10.26 (s, 1H, Ar–CHO); 7.74 (d, 1H, H–Ar); 6.35 (d, 1H, H–Ar); 6.35 (s, 1H, H–Ar); 3.96 (t, 2H, αCH_2–O); 1.74 (m, 2H, βCH_2–O); 1.20 (m, 10H, –CH_2-); 0.83 (t, 3H, CH_3-).

2.2.2. 2-(4-Hydroxyphenyliminomethyl)-5-octyloxyphenol (A8R). Compound A8R was prepared by refluxing an ethanolic solution (15 ml) of an equimolar amount of 3.6 mmol of 8R with 4-aminophenol for 2 h. After recrystallization twice from cold ethanol (below 15°C), pale yellow plates of A8R were obtained in 60% yield. ^1H NMR, δ ppm, $CDCl_3$: 8.49 (s, 1H, Ar–N=CH–Ar); 7.19 (m, 1H, Ar–H); 7.16 (m, 2H, Ar–H), 6.88 (m, 2H, Ar–H); 6.48 (d; 2H, Ar–H); 3.98 (t, 2H. αCH_2–O); 1.79 (m, 2H, βCH_2–O), 1.26 (m, 10H, –CH_2-); 0.88 (t, 3H, CH_3-) (see table 1).

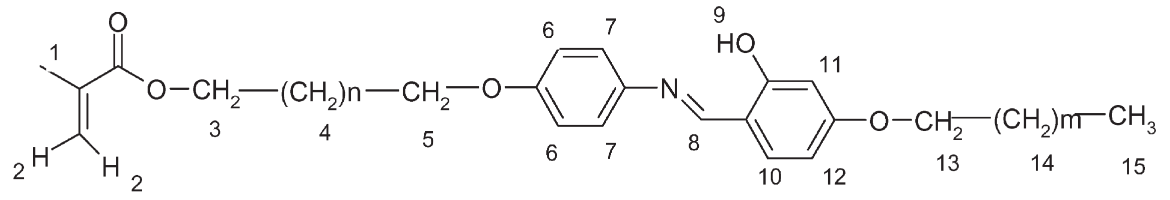
2.2.3. 6-[4-(2-hydroxy-4-octyloxyphenylmethylenimino)-phenoxy]hexyl 2- methylacrylate (M68R). To a mixture of 2.17 mmol of A8R in 25 ml of ethanol and an equimolar amount of KOH, a 10% excess of M6I (2.38 mmol) was added with a catalytic amount of hydroquinone as stabilizer. The mixture was heated under reflux and the reaction monitored by thin-layer chromatography. After 12 h the mixture was cooled, concentrated and submitted to flash chromatography in silica using toluene:ethyl acetate (10:1) as eluent. The methacrylate M68R was obtained in a total yield of 60%. IR (cm^{-1}) (film): 2924.52 C–H arom.; 2851.41 C–H aliph.; 1738.51 C=O; 1620.96 C=N; 1571.7 y 1470 C=C erom.; 1286.29 C–O; 814.78 C=C arom.

3. Results

3.1. *Texture identification*

In POM examination of M68R and M610R, the nematic phase can be seen as droplets forming on cooling from the isotropic state in a 20–10°C temperature range. For M68R a texture with a topological defect of $s=\pm 1$ and $s=\pm \frac{1}{2}$ is observed in this phase, which is also observed in M610R (see figure 3a). These singularities can occur in nematic liquid crystals, corresponding to strong distortion of the director field and therefore with relatively high distortion energy. On further cooling, the smectic C mesophase is formed before crystallization is reached. In this SmC phase, schlieren textures with singularities of $s=\pm 1$ were observed (see figure 3b), in the case of M610R, a focal conic texture was observed in this mesophase. In compound M68R some disclination points with $s=\pm 3/2$ can also be recognized; this is only observed in smectic C phases [14].

Table 1. ^1H NMR spectroscopy characterization (δ ppm, $CDCl_3$) and elemental analysis for M68R and M610R.



Compound	H_1 **s**	H_2 **d** *cis*	H_2 **d** *trans*	H_3 **t**	H_5, H_{13} **m**	H_8 **s**
M68R	2.00	5.70	6.29	3.95	3.66	8.44
M610R	2.00	5.70	6.29	3.93	3.66	8.44
	H_9 **s**	H_{10}, H_7 **m**	H_6 **d**	H_{11}, H_{12} **d**	H_4, H_{14} **m**	H_{15} **t**
M68R	13.53	7.22	7.11	6.43 6.41	1.75–1.22	0.82
M610R	13.53	7.22	7.07	6.43 6.41	1.73–1.20	0.81

	C/% (calc.)	H/% (calc.)	N/% (calc.)
M68R	72.95 (73.05)	8.37 (8.50)	3.02 (2.75)
M610R	72.95 (73.71)	8.37 (8.81)	3.02 (2.60)

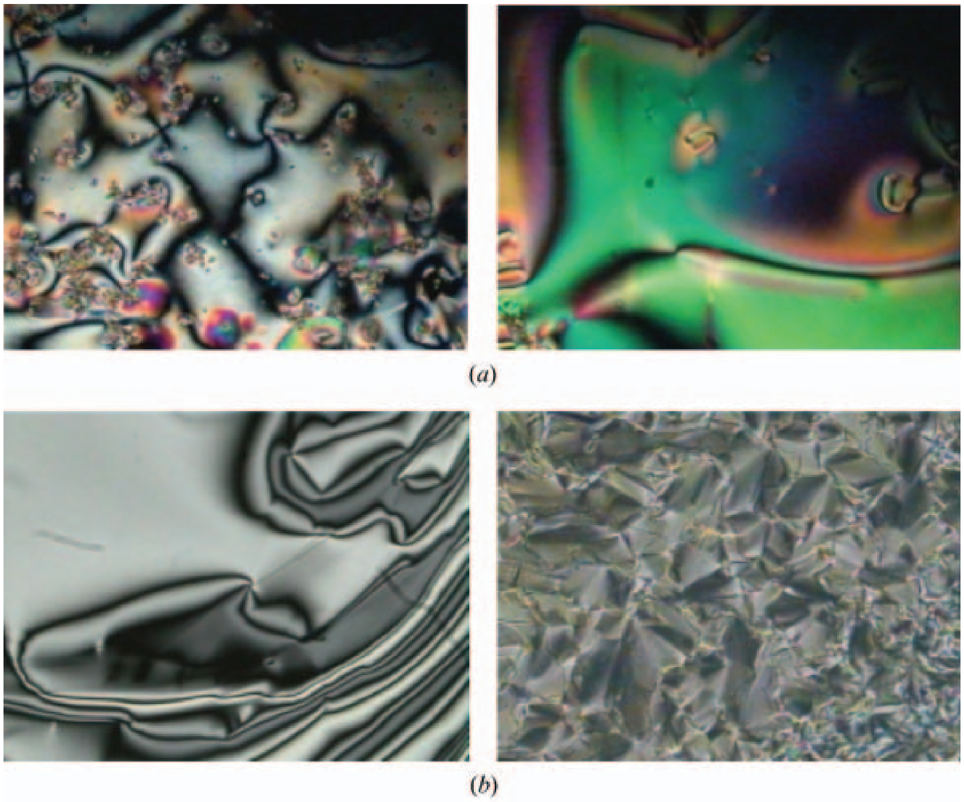
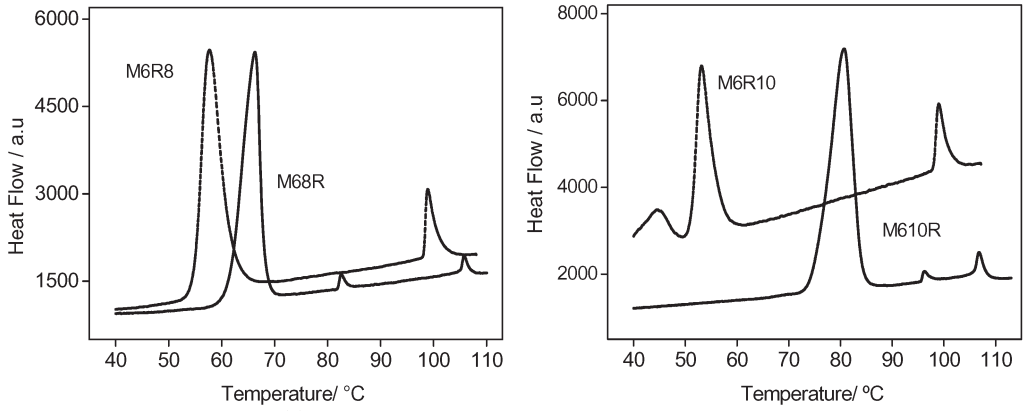


Figure 3. Observed textures on cooling: (a) schlieren texture of the nematic phase for M68R (T=100°C) and M610R (T=90°C); (b) schlieren texture of the smectic C phase for M68R (T=79°C) and focal conic texture of the SmC for M610R (T=86°C).



(*a*) (*b*)

Figure 4. DTA traces at a heating rate of 5°C min^{-1} for (a) M68R and (b) M610R compared with their reference compounds (dashed lines).

3.2. *Thermodynamic results*

The reported thermograms were taken on heating and the transition temperatures were confirmed by polarizing microscopy. In both cases, the SmC–N transition enthalpy was well defined, and indicated the first-order character for this transition. The opposite was observed in the homologous compounds M6R8 and M6R10, the SmA–SmC phase transition temperatures of which were observed only by POM [3, 4]. Figure 4 shows the corresponding thermograms on heating, comparing the new compounds M68R and M610R with their corresponding reference compounds. In the case of M68R compared with M6R8, the phase transition temperatures to the isotropic and clearing points are shifted to

Table 2. Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}) for the investigated compounds and reference compounds.

Sample	Mesophases	Enthalpies
M6R8[a]	Cr–54.7–SmC–80.0–SmA–97.9–I	39.38–n.d.–5.80
M6R10[a]	Cr–48.3–SmC–83.3–SmA–96.6–I	30.02–n.d.–6.82
M68R	Cr–39.4–SmC–80.2–N–104.7–I	18.80–0.73–1.25
M610R	Cr–64.6–SmC–97.3–N–107.6–I	54.31–0.64–2.34

[a]Literature data [3, 4]

higher temperatures by some degrees. The comparison of M610R and M6R10 is similar, the melting point being enhanced, indicating a more stabilized solid structure. These results are summarized in table 2.

3.3. *X-ray studies*

X-ray diffractometry (XRD) was carried out on both new compounds. Diffractograms for M68R are displayed in figure 5. At high temperature, below the isotropic transition point, the diffraction shows wide small-angle peaks associated with the nematic character of the mesophase (figure 5a). At lower temperature, within the SmC phase range, a sharp diffraction peak in the small-angle areas can be observed, typical for a smectogenic mesophase (figure 5b). The diffuse wide-angle peaks in both cases, at around 20° in 2θ, are related to the degree of disorder of the nematic and smectic phases.

The experimental interlayer distance, taken from X-ray measurements, is shown in figure 6 for the M68R molecules. The temperature dependence of the first-order reflection shows the existence of just one region

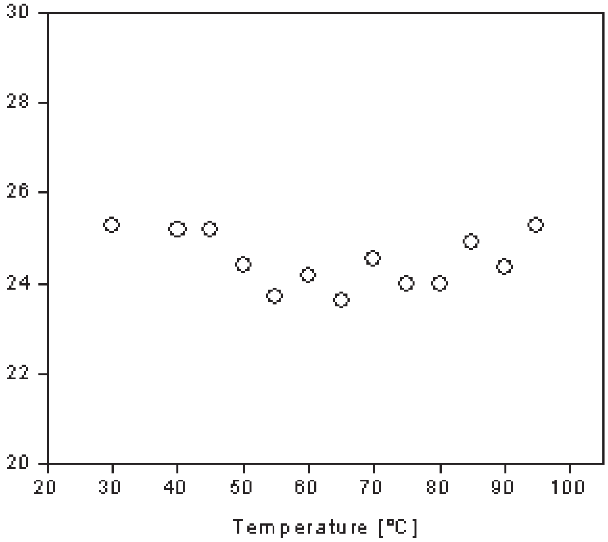
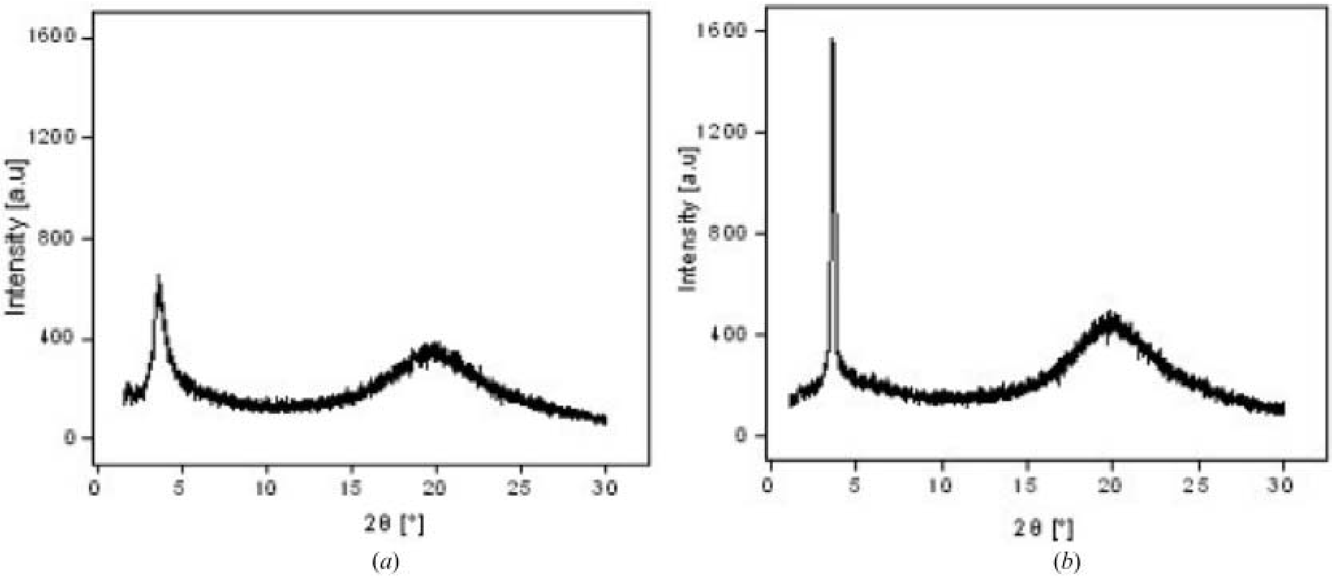


Figure 6. Temperature dependence of the interlayer spacing, *d*, corresponding to the first reflection for M6AR8.



(*a*)

(*b*)

Figure 5. X-ray diffraction for M68R compound at different temperatures: (a) nematic phase at 85°C; (b) smectic C phase at 60°C.

that can be split into two zones, with a nematic mesophase at high temperature followed by a decrease in the interlayer distance associated with the smectic C phase.

The molecular length, *L*, of the monomers, calculated using MOPAC 7 molecular approximation software, is given in table 3; data for the reference compound M6R8 were those obtained previously [4]. *L* is the distance, in the stretched molecular conformation, between the terminal carbon atom in the aliphatic chain and the first methylenic carbon atom of the methacrylic group. Taking the experimental interlayer distance, *d*, and molecular full length, *L*, we can calculate the tilt angle θ as $\arccos d/L$ in the smectic C phase.

4. Discussion

From these results, it can be seen that a smooth structure modification dramatically influences the mesomorphic behaviour of these liquid crystals, in comparison with their reference compounds M6R8 and M6R10. This destabilization of the layering structure present in the lamellar SmA phase, provokes the spontaneous formation of the more disordered nematic phase, as indicated by POM and XRD. The change in textures is obvious, as can be seen in figure 3. The transition from the SmA to the SmC phase in the reference compounds was easily seen in suspended films [4] when homeotropic and oriented samples developed birefringence textures.

As expected, the thermograms indicated that the nematic to SmC changes were truly first-order phase transitions, with well defined latent heats (see figure 4), when compared with the corresponding reference compounds. The XRD results support these observations with the typical diffraction patterns for nematic and disordered smectic phases. The first reflection at higher temperature is broader than the 001 reflection at lower temperature. For both mesophases, the typical wide-angle reflection for disordered phases is observed.

A quite unusual situation was observed in the new compounds. In the case of M610R, the X-ray diffractograms showed a pattern characteristic for side-chain polymers. The presence of 001 and 002 reflections were indicated by 2θ values corresponding to almost twice the molecular length of this molecule. The diffractogram for PM6R8 polymer from previous results [3] is also included for comparison with M68R. Some M68R diffractograms show the coexistence of nematic and bilayered smectic phases. Figure 7 summarizes these results, which indicate thermal degradation of the monomers.

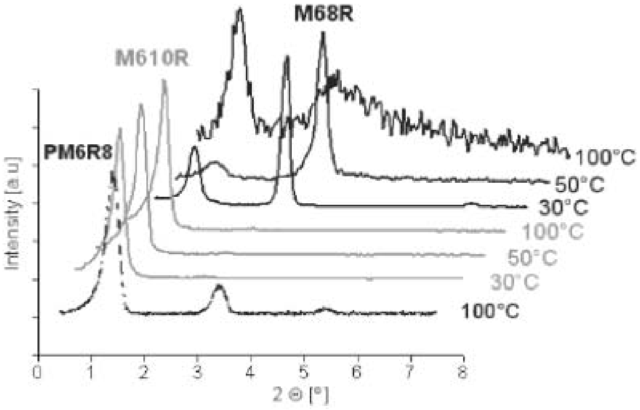


Figure 7. M68R and M610R XRD results in the small-angle zone, compared with PM6R8 polymer.

We suggest that the occurrence of the nematic phase can promote polymerization. However, subsequent attempts to reproduce the polymerization, by annealing the sample within the nematic phase range or slightly above the clearing point, were unsuccessful.

Finally, we suspect that the OH disposition at the aromatic core is responsible for the disruption of the smectic A phase to form the nematic mesophase in M68R. It appears that the OH group, in the opposite direction with respect to M6R8, reduces interaction between the methacrylic groups of adjacent molecules, thus promoting a nematogenic fluid formation.

5. Conclusion

The synthesis and phase characterization of two new liquid crystalline monomers were carried out. They exhibit thermotropic liquid crystalline behaviour with the formation of nematic and tilted SmC phases. The existence of a disordered lamellar tilted SmC phase was determined by POM and XRD. The nematic phase, before reaching the isotropic transition, was also detected using both methods. The liquid crystalline properties of the new compounds were compared with previously studied samples of homologous compounds.

Table 3. Calculated length *L*, average molecular distance *D*, experimental interlayer distance *d* and tilt angle θ in the smectic C phase at the indicated temperature for M68R and M6R8 [4].

Monomer	*L*/Å	*D*/Å	*d*/Å	θ/°	Temp./°C
M6R8	34.89	4.35	34.06	12.53	55.5
M68R	34.89	4.46	24.51	45.37	70.0

In contrast to our previous results, this structural modification induces pronounced enantiotropic first-order phase transitions between the nematic and smectic C mesophases.

Acknowledgements

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References

[1] E.A. Soto-Bustamante, S.V. Yablonsky, L.A. Beresnev, L.M. Blinov, W. Haase, W. Dultz, Y.G. Galyametdinov, (22.12.95), DE 195 47 934, 26 Jun 1997; EP 780 914, 25 Jun 1997; JP 237921/907 9 Sep 1997; US 5 833 833, 10 Nov 1998.

[2] E.A. Soto-Bustamante, S.V. Yablonsky, B.I. Ostrovskii, L.A. Beresnev, L.M. Blinov, W. Haase. *Chem. Phys. Lett*, **260**, 447 (1996).

[3] B.I. Ostrovskii, E.A. Soto-Bustamante, S.N. Sulianov, Y. Galyamedtinov, W. Haase. *Mol. Mater*, **6**, 171 (1996).

[4] E.A. Soto-Bustamante, D. Saldaño-Hurtado, R.O. Vergara-Toloza, P.A. Navarrete-Encina, M.A. Athanassopoulou. *Liq. Cryst*, **30**, 17 (2003).

[5] R. Werner, E.A. Soto-Bustamante, P.A. Navarrete-Encina, W. Haase. *Liq. Cryst*, **29**, 713 (2002).

[6] E.A. Soto-Bustamante, R. Werner, T. Weyrauch, P. Navarrete-Encina, W. Haase. *Chem. Phys. Lett*, **322**, 45 (2000).

[7] E. Abuin, S.E. Lissi, G.M. Paez, C.M.S. Ureta. *Fisicoquímica Tomo I*, pp. 253–272, Universidad de Santiago, Santiago (2003).

[8] Y.H. Jeong, K.J. Stine, C.W. Garland. *Phys. Rev. A*, **37**, 3465 (1988).

[9] X. Wen, C.W. Garland. *Phys. Rev. A*, **42**, 6087 (1990).

[10] E.A. Soto-Bustamante, C.M. González-Henríquez, G.A. Rodriguez-Lehyt, R.O. Vergara-Toloza. *Liq. Cryst.*, **31**, 1115 (2004).

[11] Z.X. Fan, W. Haase. *J. chem. Phys.*, **95**, 6066 (1991).

[12] W. Klämke, Z.X. Fan, W. Haase, H.J. Müller, V. Gallardo. *Ber. Bunsenges. Phys. Chem*, **93**, 478 (1989).

[13] E.A. Soto-Bustamante, W. Haase. *Liq. Cryst.*, **23**, 603 (1997).

[14] S. Elston, R. Sambles. *The Optics of Thermotropic Liquid Crystals*, p. 348, Taylor & Francis, London (1998).