Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 7–15

COMPARATIVE THERMOPHYSICAL STUDY OF SOME METALLOMESOGENS
Thallium(I), lead(II) and copper(II) carboxylates series

J. A. R. Cheda[1*], *M. V. García Pérez*[1], *M. I. Redondo Yélamos*[1] *and A. Sánchez Arenas*[2]

[1]Departamento Química Física I, Facultad de Ciencias Químicas
[2]Sección Departamental de Física Aplicada I, Facultad de Veterinaria, Universidad Complutense, Madrid 28040, Spain

Abstract

Similarities and differences in the physical chemistry behaviour among several metal alkanoate series (thallium(I), lead(II) and copper(II)) previously studied are shown here. The presence of a 'condis' phase in the first two series is studied. The thallium and lead series present a smectic A mesogenic behaviour, while the copper(II) one forms molecular aggregates which develop columnar discotic liquid crystal phases. Finally, the monovalent cation salts form acid soaps with the acid; instead, when the cation is bivalent, the acid behaves as a polar solvent similarly to the water-surfactants systems.

Keywords: acid soaps, discotic columnar phase, ionic liquid crystals, lyotropic, metal alkanoates, metallomesogens, smectic A, thermotropic

Introduction

Metallomesogens are considered compounds containing metals that may behave as plastic crystals, liquid crystals (thermotropic and lyotropic) or 'condis' phase (conformational disordered crystal phase). An interesting review has been published recently on this subject [1]. Metal alkanoates, considered for long time as ionic liquid crystals, belong to this family of compounds. Among others, their main interest is 'due to the fact of the easy of organic anion or cation can be varied (charge and shape) for a particular behaviour to be moved into other desired experimental conditions' (Duruz, Michels and Ubbelohde) [2]. An increasing interest for these pure or dye-doped materials exists as lyotropic smectic mesogens due to their electro-optic properties [3]. As bilayered compounds they may be used as models for the biomembrane studies. They may also be used as catalysts in organic synthesis.

Experience has been accumulated for us during last years by studying several alkanoate series (thallium(I) [4], lead(II) [5], copper(II) [6, 7], sodium [8], potassium [9],

---

[*] Author for correspondence: E-mail: cheda@quim.ucm.es

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

the 14–18 shortest chain members of each series), as pure compounds or in solution. Different experimental techniques (DSC and adiabatic calorimetry, vibrational spectroscopy, polarizing light microscopy, NMR, X-ray diffraction, conductimetry and vapor pressure osmometry) have been used for this study.

A discussion about the formation of a 'condis phase' previous to the mesophases, the study of the nature of the 'neat' phase, the molecular aggregates forming columnar mesophases, and the differences in behaviour of the binary acid–salt systems [10, 11] depending on the charge of metallic cation are presented here.

The 'condis' phase

A third mesomorphic state of the matter has been proposed by Wunderlich [12], which can be understood in terms of crystal order. For a substance be able to form a 'condis' phase it needs to have, besides the orientational and positional order, a new one: internal conformational order. Alkyl chains in 'all-trans position' are completely ordered, but C–C bonds can start to rotate on heating to a g^+ or g^- position. In the solid-state this rotation is only possible if two $g^+ \, t \, g^-$ defects are formed ('kink' defect), without loosing the chain long-range orientational order.

This 'melting' of the chain may happen:

- cooperatively at one particular temperature, as a first order transition to a solid phase ('condis' phase), which can be easily seen by calorimetry and FTIR. Lead(II) alkanoate series [5] is a good example of this behaviour.
- non-cooperatively at a broad interval of temperature, without showing a pick but only an enhancement in the lattice heat capacity curve. Thallium(I) alkanoates behave like this.

The case of lead(II) alkanoate series

The thermal behaviour of this series has shown three first order transitions (Fig. 1) in the 'melting process' from the completely ordered crystal at low temperature to the isotropic liquid. Several authors had considered the presence of poly-mesomorfism for these compounds, with the formation of two liquid crystal phases above the solid crystalline phase [13–15]. Infrared spectra of lead(II) alkanoates [5], taken at different temperatures, showed that the intensity of CH_2 wagging progression bands, characteristic of chains with all-*trans* conformation, decreases on increasing temperature and that the regular pattern is lost at a temperature close to that of the solid II–solid I transition as measured by DSC (Fig. 2). At the same temperature a band around 1306 cm^{-1}, characteristic of 'kink' structures ($g^+ \, t \, g^-$) appears. The intensity of this band increases slowly from this point up to the isotropic liquid. These spectral features prove that the ordered conformation of the alkyl chains is lost in the transition solid II–solid I where the alkyl chains present 'kink' defects. This shows that solid I is actually a phase with internal conformational disorder ('condis' phase).

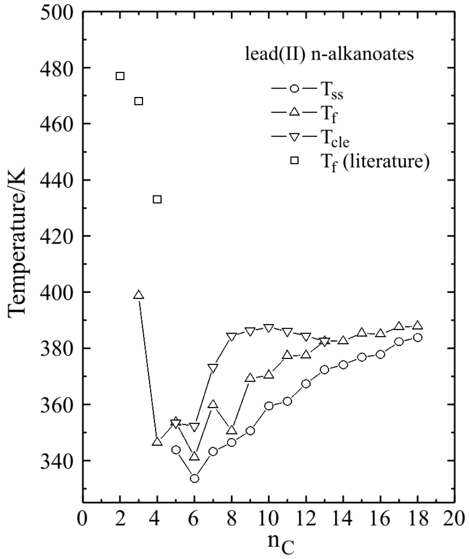

Fig. 1 Transition temperatures *vs.* n_C for $(Cn)_2Pb$ series. T_{SS}=solid–solid transition temperatures, T_f=fusion, T_{cle}=‘clearing’

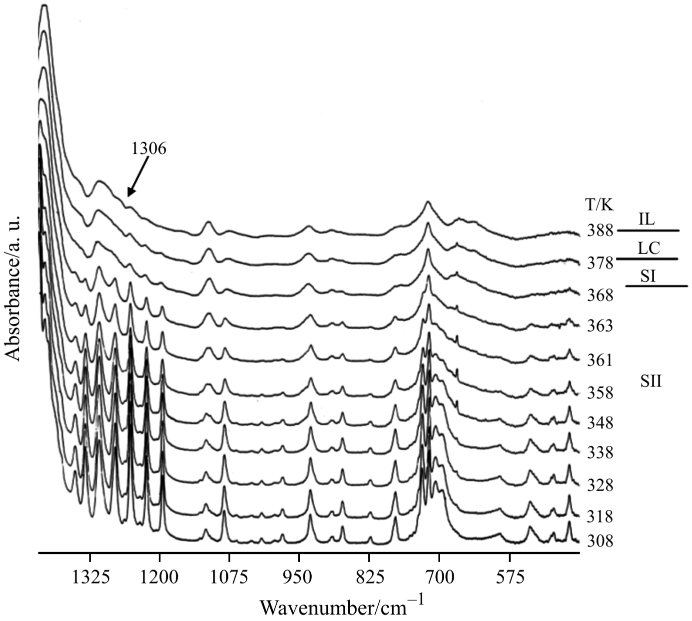

Fig. 2 FTIR CH_2 ‘wagging’ progression bands for $(C12)_2Pb$

On the other hand, experiments described later (paragraph 3) with polarizing light microscopy have shown that the solid-state is maintained (no spherical droplets were formed) in the whole temperature range of this phase. This may be considered as a proof that the poly-mesomorphism of the lead(II) alkanoate series consists not in the formation on heating of two liquid crystal phases but in the formation of a ‘condis’ phase, followed by a liquid crystal one before going into the isotropic liquid.

The case of thallium(I) alkanoate series

The thallium(I) alkanoates series [4] presents many first order solid-to-solid transitions previous to the fusion and ‘clearing’ points of the smectic phase (Fig. 3a). Alternatively to the lead(II) alkanoate series, in the thallium one, the loss of the conformational order takes place non-cooperatively in a broad interval of temperature. In this case, a shoulder in the lattice heat capacity curve [4 b] of the compounds is observed instead of the typical first order transition (Fig. 3b). Depending on the member of the series, the first order transitions of other nature (polymorphic, tilt of the chain, etc.) appear at different temperatures independently to the shoulder in the lattice heat capacity curve.

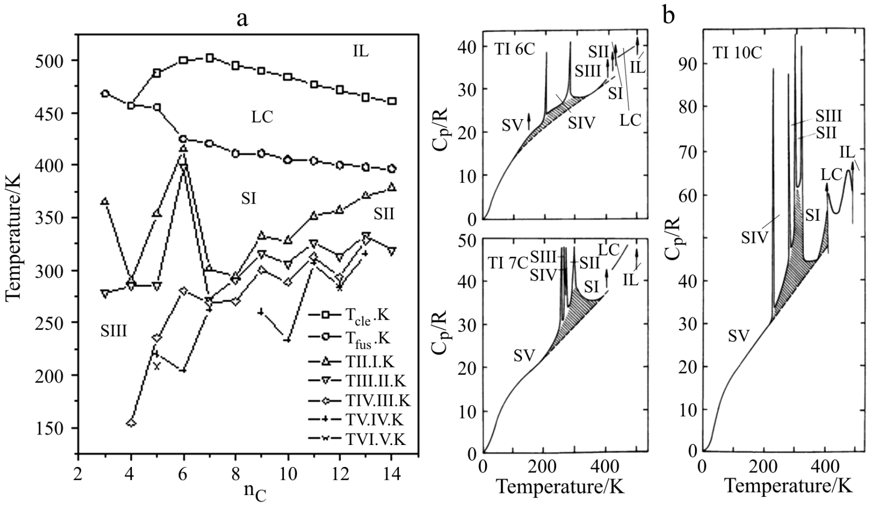

Fig. 3 a – Transition temperatures of the thallium(I) *n*-alkanoates *vs.* number of carbon atoms (*n*) in the chains. SI, SII, etc. designate solid phases; CL, liquid crystal; and IL, isotropic liquid. ‘Clearing’; ○, fusion; △, ▽, ◇, +, x solid-to-solid transitions. b – shaded area, enhancement of the lattice heat capacity for some thallium(I) alkanoates

A careful FTIR study shows that temperature rising makes the intensity of CH_2 ‘wagging’ progression bands (Fig. 4) to decrease in a continuous way and simultaneously the intensity of new bands ascribable to gauche and kink structures increases, leading to the loss of regular band pattern characteristic of all-*trans* conformation. This ‘chain melting’ temperature is always lower than that of the last solid–solid transition and

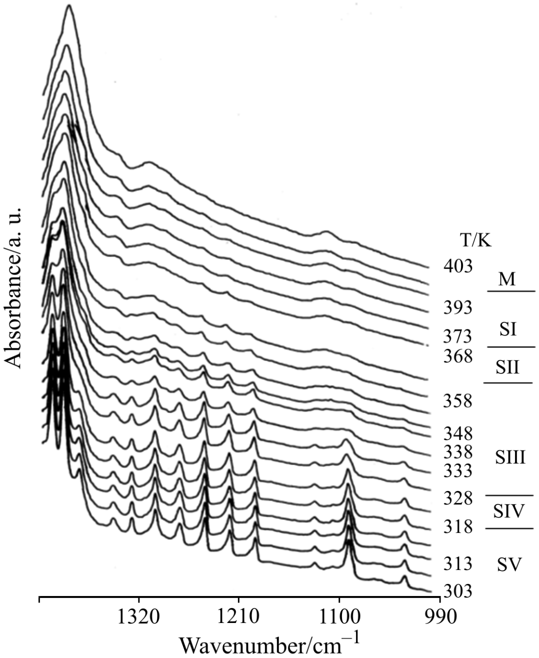

Fig. 4 FTIR 'wagging' progression bands for C13T1 sample

coincides with the maximum of the broad enhancement (shoulder) observed mainly by adiabatic calorimetry (and DSC) in the heat capacity curve.

The different behaviour of both series can easily be understood in terms of the different size and charge of the metallic cation. The internal rotation of the chains has to be more hindered in the lead(II) series than in the thallium(I) one due to the double amount of chains and smaller cation in the former.

The 'condis' phase is compatible in the same compound with the formation on heating of either a plastic crystal (loosing the orientational order first) or a liquid crystal (loosing partially or totally the positional order). In both cases (lead(II) and thallium(I) series), the condis phase goes into a thermotropic smectic phase.

The nature of the thermotropic neat phase

The ionic liquid crystal phase has been for long time called 'neat' phase or 'smectic A like'. It was considered by some authors the possibility of this neat phase being 'smectic C like' (tilted chains to the layers), due to the fact that a too short distance between layers was found by X-ray diffraction. There are three possibilities to explain this: the chains are perpendicular to the layers but 'melted' ('condis' phase), the chains are 'all trans' and 'tilted', or both cases. We used polarizing light microscopy to investigate this point. Two proofs were developed:

- one consisted in the careful observation of the focal-conic domains obtained on cooling the samples from the isotropic liquid, and the movement of the maximum intensity of light with respect to the cross polars (Fig. 5a). The maximum intensity of light coinciding with any of the polars orientation confirms the S_A structure of the smectic phase (concentric layers and perpendicular chains to layers).
- the other one consisted in the microscopic observation of the 'droplets' when powdered crystals suspended in oil are heated up to the liquid crystal phase. Only a fluid phase is able to form spherical 'droplets'. No droplets are formed until the transition temperature to the liquid crystal phase, confirming the solid-state nature of the 'condis' phase (Fig. 5b). The lack of any disclination line in the droplets all the way around confirms that the mesophases for all the series studied are smectic A [6]. Moreover, the series studied have only a liquid crystal phase.

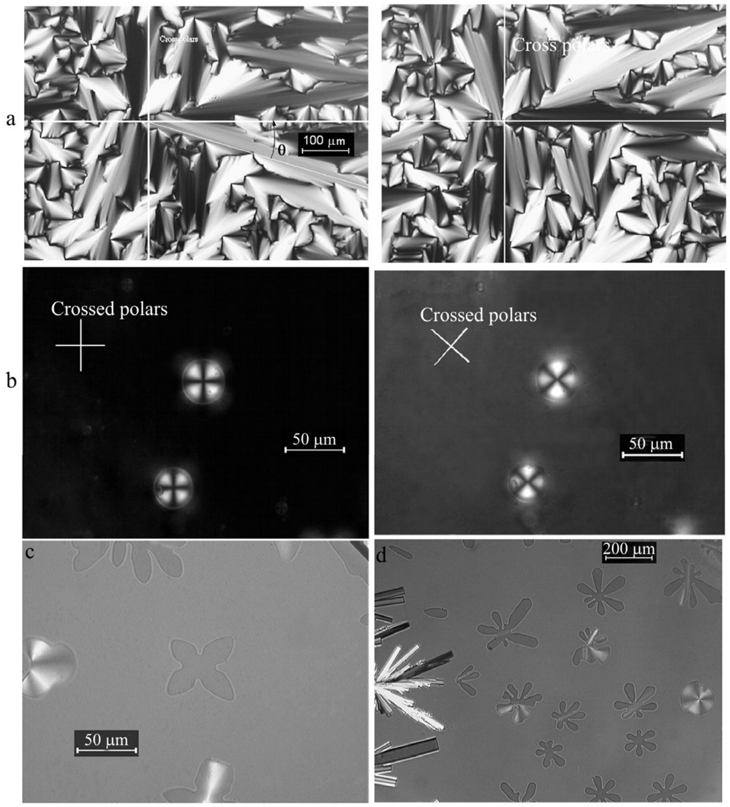

Fig. 5 Pictures taken on a polarizing light microscope. a – Focal conic (fans) domains for Pb(C10)$_2$ at 120.6 C, rotation angle of the cell. b – 'Droplets', at 95 C, indicating the solid-state nature of the 'condis' phase and the S_A structure. Rotation of both crossed polars of 45 . Oil: Brookfield, 30000, viscosity 29920. c –Homeotropic domains: tetragonal domains of copper(II) di-butanoate at 178 C, decrossed polars 10°. d – hexagonal domains of copper dipentanoate at 98.7 C, decrossed polars 20°

The case of the copper(II) series

The copper(II) alkanoates have an especial and very different behaviour (as well as other cations of some transition metals, as Rh, Ru, Mo, Cr, and W) [1]. High member of the series with *n*=14, 16, 18, and its pyridine adducts have been studied recently [16, 17]. These metals form di-metal tetra-alkanoates molecular associations presenting a bilayered crystal structure in the solid-state and melting to a columnar discotic mesophase, and irreversibly decomposing on heating before reaching the isotropic liquid. The structure of these columnar phases has been studied by X-ray diffraction on swelled samples (with paraffines) [18]. We were able to prove these structures obtaining textures on mixtures of the samples with their corresponding acid by only polarizing light microscopy [7]. We have proved the columnar discotic phase to have a tetragonal arrangement for the copper di-butanoate and hexagonal for all the other higher members of the series (Figs 5c and d).

Binary systems with acid

Salts with monovalent cation can easily aggregate with the corresponding acid to form an acid soap with a very strong hydrogen bond, which may melt congruent or incongruently (peritectic). In Fig. 6a, the incongruent melting of the molecular complex is shown for the system thallium(I) undecanoate+undecanoic acid (TlC11+HC11) [19]. On the other hand, salts with bivalent cation behave completely different: the phase diagram reminds

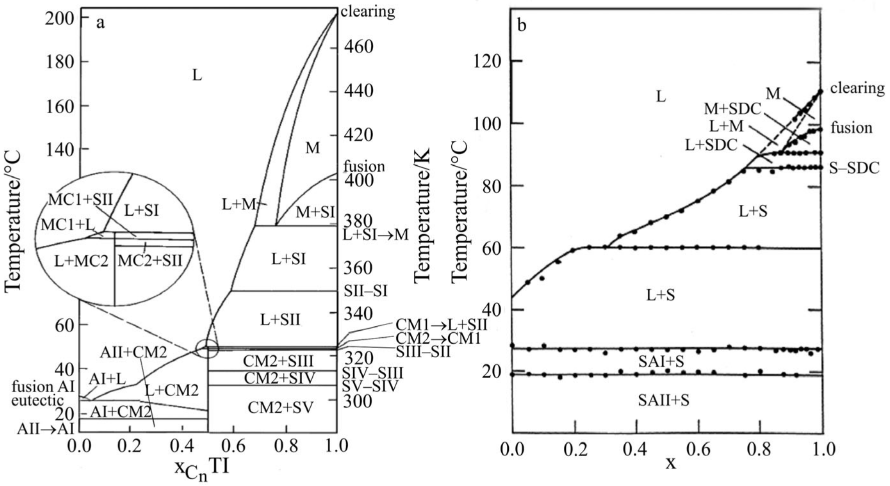

Fig. 6 Salt–acid binary phase diagrams: a – for T1C11+HC11; AI, II=acid, solids I and II; L=homogeneous liquid phase; CM1,2=molecular complex, solids 1 and 2; SI, II, III, IV and V= solid phases of salt; M=homogeneous lyotropic liquid crystal phase; b – for ($Pb(C11)_2$+HC11); L=homogeneous liquid phase; AI, II=acid, solids I and II; S=crystalline solid phase of the salt; SDC=solid 'condis' phase; M=homogeneous lyotropic liquid crystal phase

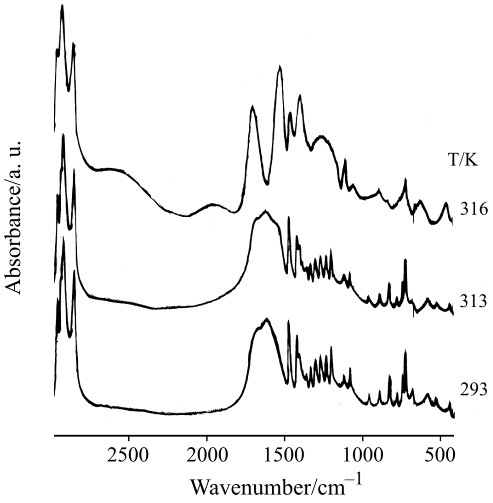

Fig. 7 FTIR spectra of the molecular binary system thallium(I) decanoate+decanoic acid

that of the surfactants with polar solvents, showing the typical Krafft point. In Fig. 6b [11] the phase diagram for the system lead(II) undecanoate+undecanoic acid ($Pb(C11)_2$+HC11) is shown. In all cases, when the pure salt behaves as a thermotropic mesogen, the acid gives always thermal stability to this phase by the formation of a lyotropic homogeneous region in the binary phase diagram (M in Figs 6a and b). The structure of these mesophases is always the same as that of the pure salt.

The nature of molecular association in the acid soaps has been studied for the CnTl(I) series [10 b] by FTIR. The FTIR spectra of crystalline equimolecular compounds change at a temperature near the melting point. New broad bands, (A, B, C), at around 2900, 2450 and 1900 cm^{-1} typical of systems with moderated to strong hydrogen bond appear and the bands assigned to ν (C=O) stretching mode of the acid and those of carboxylate group substitute for the broad carbonyl band observed in the spectrum of associated compound. As an example, FTIR spectra of the molecular binary system thallium(I) decanoate+decanoic acid is shown in Fig. 7.

Conclusions

The organic salts studied by us behave as thermo- and lyotropic mesogens. Most of them form real smectic A liquid crystals. Some alkanoate salts of some transition metals form molecular aggregates that develop columnar discotic phases. The monovalent metal cation alkanoates can associate with their corresponding acids by a very strong hydrogen bond to give acid soaps. The bivalent cation ones, instead, behave with their corresponding acids similarly to surfactants in water.

* * *

Partial support of this research by the DGICYT of the Spanish Ministerio de Educación, Cultura y Deportes (Project BQU2001-2021) is gratefully acknowledged. Authors want also to thank for the experimental facilities supplied Prof. O. D. Lavrentovich (Liquid Crystal Institute, Kent State University, Kent. OH, US), during the stay of one of us (J.A.R. Cheda), grant in add by the Spanish 'Ministerio de Educación, Cultura y Deportes'.

References

1 B. Donnio, Current Opinion in Colloid and Interface Science, 7 (2002) 371.

2 J. J. Duruz, H. J. Michels and A. R. Ubbelohde, Proc. Roy. Soc., A322 (1971) 281.

3 G. Klimusheva, A. Kovalchuk, N. Volynets and A. Vakhnin, Opto-electronics Review, 10 (2002) 39.

4 a M. V. García, M. I. Redondo, J. A. R. Cheda, E. F. Westrum Jr. and F. Fernández-Martín, Applied Spectroscopy 48 (1994) 338.
b J. A. R. Cheda, M. I. Redondo, M. V. García, F. L. López de la Fuente, F. Fernández -Martín and E. F. Westrum Jr., J. Chem. Phys., 111 (1999) 3590 (and references therein).

5 A. Sánchez Arenas, M. V. García, M. I. Redondo, J. A. R. Cheda, M. V. Roux and C. Turrión, Liq. Cryst., 3 (1995) 431.

6 M. V. García, M. I. Redondo, M. J. González Tejera and J. A. R. Cheda, Spectrochim. Acta, 51A (1995) 341.

7 J. A. R Cheda, M. V. García, M. I. Redondo, S. Gargani and P. Ferloni, Liq. Cryst., 31 (2004) 1.

8 J. A. R. Cheda, M. Sáez Díaz, G. González Gaitano and G. Tardajos Rodríguez, 'Control of an Acid-Soap Impurity in Sodium Laurate and Myristate Salts by a DSC Study', Book of Abstracts, 15th IUPAC Conference on Chemical Thermodynamics, Porto (Portugal) 1998.

9 M. V. García, M. I. Redondo and J. A. R. Cheda, Vibr. Spectr., 6 (1994) 301.

10 a M. Fernández-García, J. A. R. Cheda and F. Fernández-Martín, Coll. Int. Sci., 185 (1997) 381.
b M. Fernández García, M. V. García, M. I. Redondo, J. A. R. Cheda, M. Fernández García, E. F. Westrum Jr. and F. Fernández-Martín, J. Lipid Research, 38 (1997) 361.

11 A. Sánchez Arenas, J. A. R. Cheda, M. V. Roux and C. Turrión, Langmuir, 12 (1996) 2367.

12 B. Wunderlich, M. Moller, J. Grevowicz and H. Baur, 'Conformational Motion and Disorder in Low and High Molecular Mass Crystals', Springer, London 1988.

13 S. A. Adeosun and S. J. Sime, Thermochim. Acta, 27 (1978) 319.

14 A. M. Amorin da Costa, H. D. Burrows, C. F. C. G. Geraldes, J. J. C. Teixeira-Dias, C. C. Bazuin, D. Guillon, A. Skoulios, E. Blackmore, G. J. T. Tiddy and D. L. Turner, Liq. Cryst., 1 (1986) 215.

15 G. Feio, H. D. Burrows, C. F. C. G. Geraldes and T. J. T. Pinheiro, Liq. Cryst., 9 (1991) 417.

16 M. Pajtasova, E. Jona and P. Simon, J. Therm. Anal. Cal., 67 (2002) 129.

17 K. Mészáros Szécsényi, T. Wadsten, B. Carson, É. Bencze and G. Liptay, J. Therm. Anal. Cal., 68 (2002) 81.

18 M. Ibn-Elhaj, D. Guillon, A. Skoulios, Giroud-Godquin and J. C. Marchon, J. Phys. II France, 2 (1992) 2197.

19 A. Vetter, Master Degree Dissertation, Faculty of Chemistry, University Complutense, Madrid 1992.