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The role of calorimetry in the structural study of mesophases and their glass states

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Abstract Four mesomorphic states of matter are known: liquid crystal, plastic crystal, condis phase, and rotator phase, all of them are solid phases, except liquid crystal, which is fluid. Plastic crystal (also called ODIC, *o*rientational *di*sordered *c*rystal), rotator phase, and even condis phase have been considered the same phase by many authors. Differences between them will be established to define their own characteristics. Two organic salts series have been used for discussion in this presentation: (1) thallium(I) alkanoate series, that presents a condis mesophase, and (2) lead(II) alkanoate series, that present a rotator one, both forming a smectic A-like liquid crystal phase. Based in the literature data of the alkyl ammonium bromide series it can be established that the short chain length members would present a rotator phase, and, the large chain ones, a condis phase. Five different glass states are known (four with partial crystalline order), corresponding with the above mentioned mesophases, and the ordinary (amorphous) glass state.

Keywords Organic salts · Thallium(II) alkanoates · Lead(II) alkanoates · DSC · TG · Adiabatic calorimetry · FTIR · Powder XRD · Single crystal XRD · NMR · Mesophases · Liquid crystal · ODIC · Plastic crystal · Rotator phase · Condis phase · Amorphous glass · Plastic crystal glass · Liquid crystal glass · Rotator glass · Condis glass · Step-wise melting process

Introduction

Mesophases

Meso in Greek means *between*. Thus, *mesophase* is the generic name used since more than 100 years ago to describe those new phases *between* the *solid* and *liquid* ones, whose behavior did not fit with any of these traditional states.

The first mesophase discovered was the *liquid crystal*, followed by the *plastic crystal*. More recently, *condis* (*con*formational *dis*ordered) and *rotator* have appeared *with their own entity* clearly differentiated from any other known state of matter.

Liquid crystal and plastic crystal are rather well known, at least better than the other two, worse understood. As a matter of fact, there is still some controversy about them. This lecture will deal with these last two mesophases. The large family of organic salts will be used as a support for this presentation.

Organic salts

Examples: metal alkanoates (e.g., Na, K, Li, thallium(I), lead(II), copper(II), etc.), or alkyl ammonium halides (e.g., three-ethyl hexadecyl ammonium bromides). It is important to study systematically all of the members because it helps to understand the whole series, and, at the same time, it allows to establish correlation rules.

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Their main features are:

- Organic cation and/or anion
- Easy to move a particular physical property to other conditions of interest by changing the size and/or the charge of the cation and/or the anion [1]
- Polymorphism and/or polymesomorphism, and monotropic polymorphism [2]
- *Surfactants* in solution
- Some of them behave as *Ionic Liquids* (ionic liquid below 100 °C, according to IUPAC definition of "Ionic Liquid") [3]
- They present different dimensionalities: they are 1D, 2D, or 3D coordination polymers or metal–organic frameworks (MOFs) [4]
- Able to quench into different types of *glass* states
- Binary mixtures may form intermediate compounds (*co-crystals*) [5]
- Electro-optical properties of metal organic ionic liquid crystals (ILC) [6]
- They show a *step-wise melting process*: from the totally ordered crystal at temperatures near 0 K up to the isotropic liquid.

The step-wise melting process

This process can be *very simple*; for instance: (1) the *n*-alkanes, that have their *all-trans* conformation in their chains until the melting point, preceded by a small transition (to rotator phase), (2) the lead(II) *n*-alkanoate series, [7, 8] (Pb(C*n*)$_2$, hereafter, where C*n* means carboxylate with *n* carbon atoms, included that of the carboxylate), with only three transitions at high temperatures (see Fig. 1).

Or rather complicated, for example, the thallium(I) alkanoate series [9–11] (TlC*n*, hereafter, where C*n* means carboxylate with *n* carbon atoms, included that of the carboxylate) where, in addition to several polymorphic transitions starting below room temperature, other mesomorphic ones appear at higher temperatures (see Fig. 2).

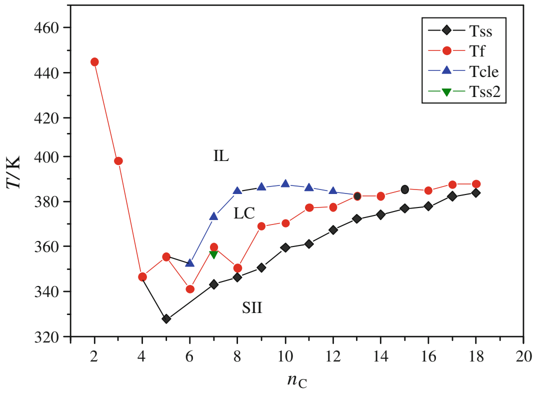


Fig. 1 Lead (II) alkanoates: temperatures of transitions versus n_C. Symbols: *filled diamond*, SII-SI, or solid-to-solid transitions; *filled circle*, fusion; *filled triangle* clearing (with permission)

The energy involved in this process can be thermally evaluated *by measuring the enthalpy* of all the phase transitions appearing from 0 K to the isotropic liquid.

Crystalline structures

The structures of the pure salts are bilayered: (1) an *ionic* layer, formed by carboxylate anions and metal cations (with strong ionic interactions), and (2) a *lipidic* layer, formed by the –CH$_3$ groups at the chain-end (with weak Van der Waals interactions) (See Fig. 3).

Experimental techniques

The more techniques used, the more valuable is the information obtained. Also, simple and short experiments are sometimes decisive in understanding the phase behavior of the series (e.g., the *drops experiment* to detect the solid nature of SI en Pb(C*n*)$_2$, or TMA in Pb(C5)$_2$, to prove a decrease of the density in this phase (see Fig. 15, and text). The following are the most common techniques used in the structural characterization and in the physico-chemical studies of organic salts:

- DSC and adiabatic calorimetries (AC)
- TG and TMA

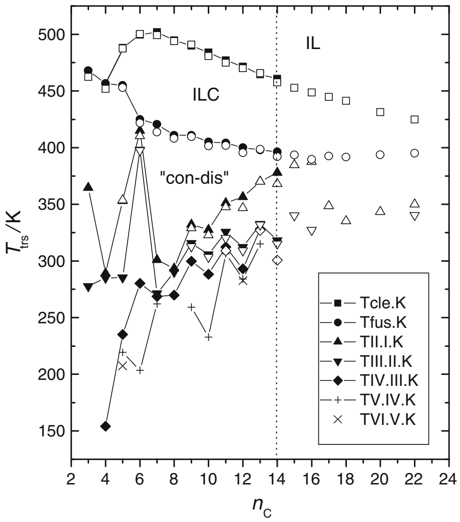


Fig. 2 Thallium (I) alkanoates: temperatures of transitions versus n_C. Symbols drawn in the plot: *cle* clearing point; *fus* fusion; Roman digits from I to VII; solid-to-solid transitions. Symbols: *filled diamond*, *filled inverted triangle*, *filled triangle*, *filled circle*, *filled square* Ref. [9]; *plus sign*, *times symbol*, *unfilled diamond*, *unfilled inverted triangle*, *unfilled triangle*, *unfilled circle*, *unfilled square*, Refs. [10] and [11] (with permission)

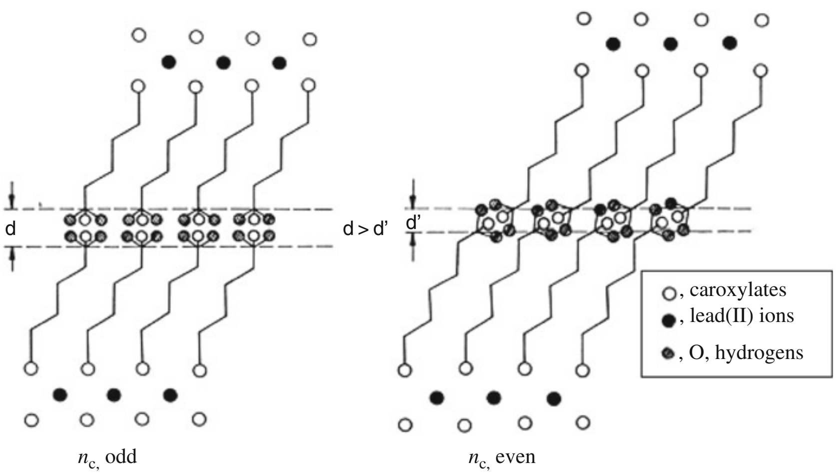


Fig. 3 Schematic representation of the bilayered structure for many metal alkanoates, with tilted arrangement of the alkyl chains. *Filled circle* bivalent metal cation; *unfilled circle* carboxylate group

- FTIR and Raman spectroscopies
- SC-XRD and P-XRD
- NMR in solid state
- Polarizing light microscopy

Sometimes, there is a difficulty in finding some of these equipments prepared to measure *as a function of temperature*.

Crystalline orders and disorders: mesophases

We can state that there exist up to four types of orders in a crystal:

- Positional (or translational)
- Orientational (external)
- Conformational (internal)
- Orientational (internal)

These types of orders (and dynamic disorders) will be the basis to define operatively the mesophases which are partially crystalline (with some of those orders). Subsequently, the corresponding static disorders will be the basis to define the different vitreous phases.

Positional (or translational)

Positional order is inherent to all of the crystals. The positional order leads to a solid with well-defined, regular shape. Its regularity is due to the arrangement of structural units into an orderly array *or crystal lattice*. We can imagine this crystal lattice to be formed by stacking together identical small portions of the crystal or unit cells. A big crystal is the result of repeating this unit cell in three dimensions. There are seven basic possible shapes, which give rise to the seven crystal systems used to classify crystals, corresponding to different possible angles and lengths of the edges.

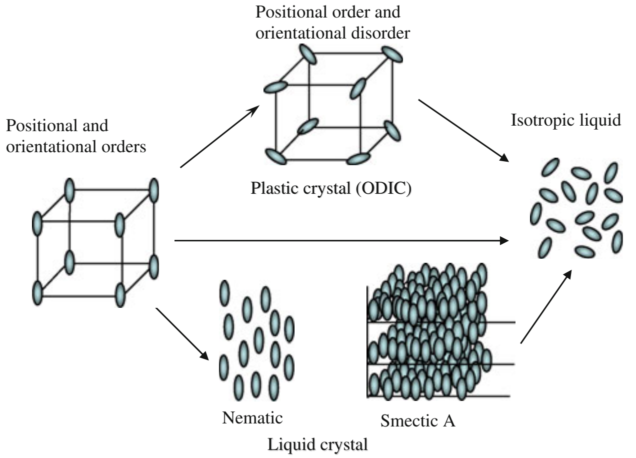
Orientational (external)

If the crystal is constituted by orientable molecules (or ions), a second order is possible: orientational order. A crystal that has both orders may behave on heating according the three possibilities shown in Scheme 1. Two mesophases are possible, liquid crystal (LC) and plastic crystal (PC). PC mesophase is also known by orientational disordered crystal (ODIC), [12] name recommended to be used preferably, and largely used in the literature.

For a crystal to be able to form mesomorphs, it is absolutely necessary (but not sufficient) to have other crystalline orders in addition to the positional one. Obviously, LC and PC are excluding each other. Thus, they can not exist in the same compound.

Plastic crystals: as simple as nitrogen

The fusion enthalpy of solid N_2 measured by calorimetry is smaller than that of solid O_2. To explain this, a thorough study was developed finding a transition (ordered crystal to



Scheme 1 Total or partial positional disorder and orientational order

plastic crystal) at 14 K, below the melting point. The enthalpy of this transition was the remaining energy needed to equal the fusion enthalpy of oxygen.

In the 1990′s decade [13], the solution of the solid N_2 phase diagram was done finding two phases (α y β) at atmospheric pressure. Phase α is a positional and orientational ordered crystal, while phase β is a plastic crystal (with positional order and orientational dynamic disorder). The formation of a Plastic crystal mesophase is possible because the diatomic N_2 molecules have a geometric factor that makes them orientable. That is, the fusion of the solid N_2 at atmospheric pressure comes from a plastic crystal. Calorimetry was the hint to this discover.

Liquid crystals

There is a huge amount of organic compounds that behave as liquid crystals, but their importance is due mainly to their technological applications. They can be classified according to different points of view:

molecular geometry	calamitic (linear rigid core) discotic
according their formation	thermotropic lyotropic
according their type of bond	molecular ionic (*electrical charge anisotropy*)

Most of the organic salts behave as ILC, thermotropic, and lyotropic. ILC have been broadly studied [14]. One aspect of them may be emphasized here: the geometrical orientational factor necessary (but not sufficient) for these compounds to be mesogens lies in the anisotropic distribution of the COO^- electrical resonant charge.

Another two types of mesomorphism: condis and rotator phases

Condis phase

Besides the positional and orientational orders, a 3rd order still exists: an internal conformational order due to the *all-trans* configuration of the CH_2 groups (See Fig. 4). If this internal conformational order is lost on heating at one particular temperature without losing the other two orders (positional and orientational), a *con*formational *dis*order phase is formed (*condis* phase). In our knowledge, this name was proposed by Wunderlich et al. [15] as the *third mesomorphic state of the mater*. More recently, in an interesting thermodynamical description of all of the condensed phases [16], this author insisted on this classification, for *macrophases*, in which surface effects are negligible.

Condis phase can be understood on the basis of the third crystalline order described above. For a substance to be able to form a *condis* mesophase, it is necessary to have, besides the *orientational and positional* orders, a third one, an *internal conformational order*. In the organic salts we are referring to (e.g., $Pb(C7)_2$) [17], the *all-trans* conformation of the alkyl chains.

A compound presenting a condis phase has the possibility to transform on heating either into a plastic crystal (losing the orientational order) or into a liquid crystal (losing partially or totally the positional order) (See Scheme 2).

One more mesomorphic state: rotator phase

Besides the positional, orientational, and internal conformational orders, a fourth order still exists: internal

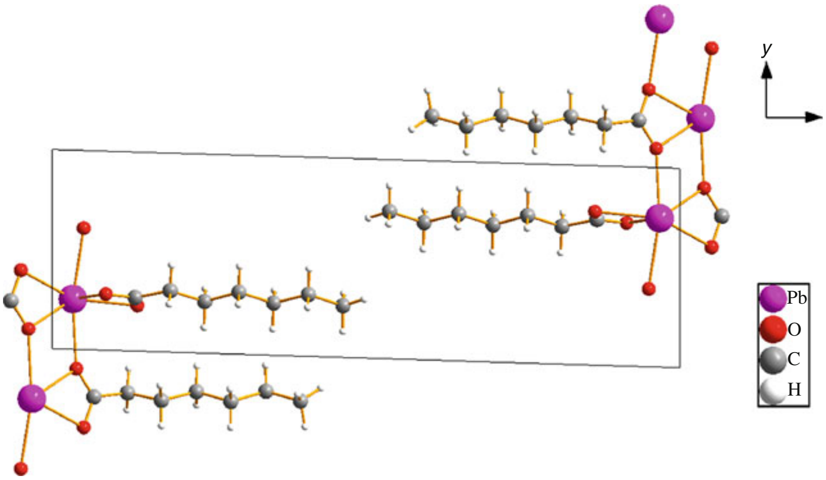
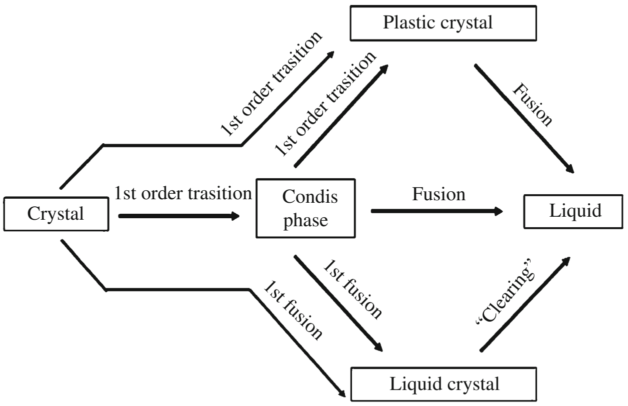


Fig. 4 Unit cell of the lead(II) heptanoate ($Pb(C7)_2$) [17] showing the: (1) positional (triclinic), (2) external orientational (main axis of the alkyl chains), and (3) internal conformational (CH_2 groups *all-trans*) orders. Note that there are two types of COO^- groups: *only chelating* (drawn inside the cell) and *bridging-chelating* (drawn outside the cell), at a 50% each



Scheme 2

orientational order (in this case, equivalent to a *herring-bone* or *chevron* order) (see Fig. 5).

At a particular temperature on heating the sample, the chains can start to rotate around their axis (it is easier than to form *gauche* defects), if the chains are maintained in an *all-trans* conformation, due to a strong steric hindrance in the completely crystalline solid. It is easily understandable that this rotation compels the chains to pack in a hexagonal array, with an increase in the volume. Actually, the rotator phases known are hexagonal or pseudohexagonal [18, 19].

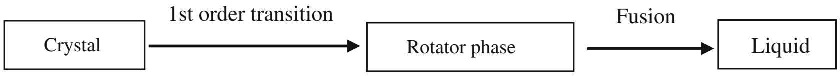
Rotator phase

In the Compendium of Chemical Terminology (1994, *66*, 589, IUPAC 2nd Edition, 1997) it is written (sic):

"*Rotator phase transition*: A transition from a fully ordered crystal of *globular* or *quasi-spherical* molecules to a crystal that retains translational order but exhibits dynamic orientational disorder and is usually mechanically soft (plastic phase). Example: the transition of CBr_4 to a plastic phase which exists from 319 to 365 K".

This definition should be reviewed, because it is very well known and generally accepted that *n-alkanes form rotator phase* [19–21]. Their crystals really have the four orders described before, maintaining all of them almost up to the melting point. A few degrees below melting, a small crystal-to-rotator transition appears, loosing the herring-bone or *chevron* structure, and forming a hexagonal arrangement of the chains. They present a mesomorphic behavior of rotator phase, and they are not *globular* molecules. Schematically, the *step-wise melting process* for *n*-alkanes is shown in Scheme 3.

Scheme 3



A rotator phase can be understood in terms of the 4th order (*external orientational order*): the *herring-bone* structure of the *all-trans* planes in the hydrocarbon chains (see Fig. 5). The other three orders (positional, orientational, and internal conformational) are maintained in this phase.

Some authors have considered this phase as a *disordered plastic crystal*. However, contrary to what happen with *the plastic crystal phase* (in the sense that it *can not be transformed into a liquid crystal*, see Scheme 4), the *rotator phase can* be transformed into a liquid crystal (see the lead(II) alkanoate series study below). This point reinforces the proposal of the *rotator* phase to be considered a mesomorphic state different to the *plastic crystal*. Moreover, *rotator* phase should be considered a solid phase, as it will be shown later (see lead(II) alkanoate series again).

However, globular functional groups (as the sulfate ion, or the methyl group) can start to rotate (also forming a rotator phase), but this is not exclusively for globular molecules, as the IUPAC definition states.

Rotator phase was not included in the Wunderlich′s classification [16] of *macrophases*, but similar phases to the

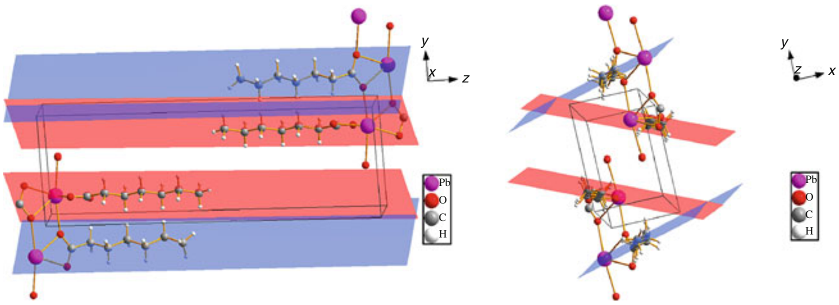
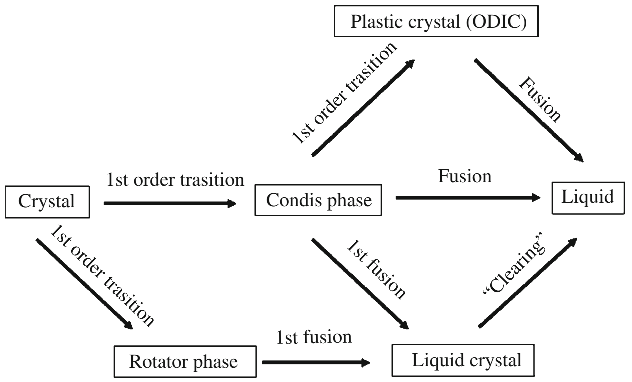


Fig. 5 Unit cell of the lead(II) heptanoate ($Pb(C7)_2$) [17] showing the 4th order: internal orientational order (the *all-trans* CH_2 group planes shown in this unit cell have two internal orientations (planes *blue* and *pink*, at the left), forming their projections on the *x*–*y* plane (at the *right*) a *chevron* or *herring-bone* structure



Scheme 4

rotator described here (and *glasses*) appear classified there as *micro* or *nanophases* [22], typical of macromolecules, where surface or no bulk properties effects are not negligible at all, respectively, when studying samples of these compounds.

On the other hand, Corkery [23] have described as CrB (*cristalline smectic rotor phase*), a phase that he finds in some metal alkanoates (alkaline earth, transition metals, and lanthanides). This phase is the same as the one we are calling here *rotator* phase, so far. In our opinion, the word *smectic* included in the CrB description is confusing, because this phase is not fluid, but solid. There is no doubt that this author refers to *crystalline* with the meaning of *solid crystal*. It is interesting to observe that some lanthanide alkanoates studied by Corkery behave very similarly to lead alkanoates in their melting process, according to this sequence:

$$\begin{aligned}&\text{Crystal} - \text{CrB(rotator)} - \text{Sm A1(liquid crystal)}\\&\quad - \text{Sm A2(liquid crystal)} - \text{isotropic liquid}\end{aligned}$$

that is, showing polymesomorphism (rotator followed by two liquid crystal phases instead of one, smectic A1 and smectic A2, in this case).

Possible conformational defects of alkyl chains in a rotator phase

An alkyl chain may present several conformational defects [19] shown in Fig. 6. All of them are possible in the *rotator phase*, except the last two to the right, the case of the chain with only a *gauche* defect in the middle, and the one with a random conformation (*melted*), because of the steric hindrance that exists in solid state. All of the other ones are possible without loosing the positional, and external orientational orders, keeping almost all the internal conformational order.

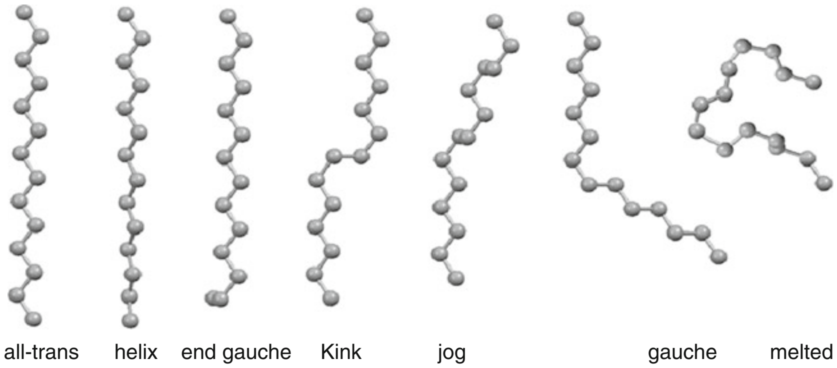


Fig. 6 Possible conformational defects of alkyl chains in a *rotator* phase: all but the last two to the right (Ref. [19], with permission)

Types of mesophases

According to the orders (and dynamic disorders) described above, a classification of the different types of mesomorphs is shown in Table 1.

Metallic alkanoate series

To better understand these last two mesophases, results from two organic salt series studied by us with different *step-wise melting processes* will be used: (i) the thalium(I) alkanoates [9], which presents polymorphism and polymesomorphism (condis and liquid crystal), and (ii) lead(II) alkanoates [7, 8, 24, 25], which besides the room temperature ordered crystal, only has poly-mesomorphism (rotator and liquid crystal).

Thalium(I) alkanoate seriescalorimetry

Calorimetry

The phase behavior (temperatures of transitions vs. n_C) for the thallium(I) alkanoate series ([9], and references therein) is represented in Fig. 2. In Fig. 7, all the calorimetric results carried out by both AC and DSC are shown: (a) evaluation of the contribution to the total ΔH and ΔS of the *step-wise melting process*, due to internal rotation with formation of *gauche* defects in the alkyl chains as a non-cooperative effect (see Ref. [9], for details).

Its *step-wise melting process*, which is summarized in Scheme 5, is rather complicated, but of great interest. The ΔH and ΔS of all of the transitions were measured by AC and DSC, covering the whole temperature range from the normal boiling point of helium (4.2 K) up to temperatures of the isotropic liquids of the salts ([9], and references therein).

Table 1 Different types of mesophases classified according to their possible orders-disorders

Phase/mesophase	Order	Dynamic disorder
Isotropic liquid	None	All
Liquid crystal	Positional (none or partial) external orientational	Positional (total or partial)
Plastic crystal	Positional	External orientational
Condis	Positional external orientational	Internal conformational
Rotator	Positional (hexagonal or pseudohexagonal) external orientational internal conformational	Internal orientational (rotational)
Crystal	All	None

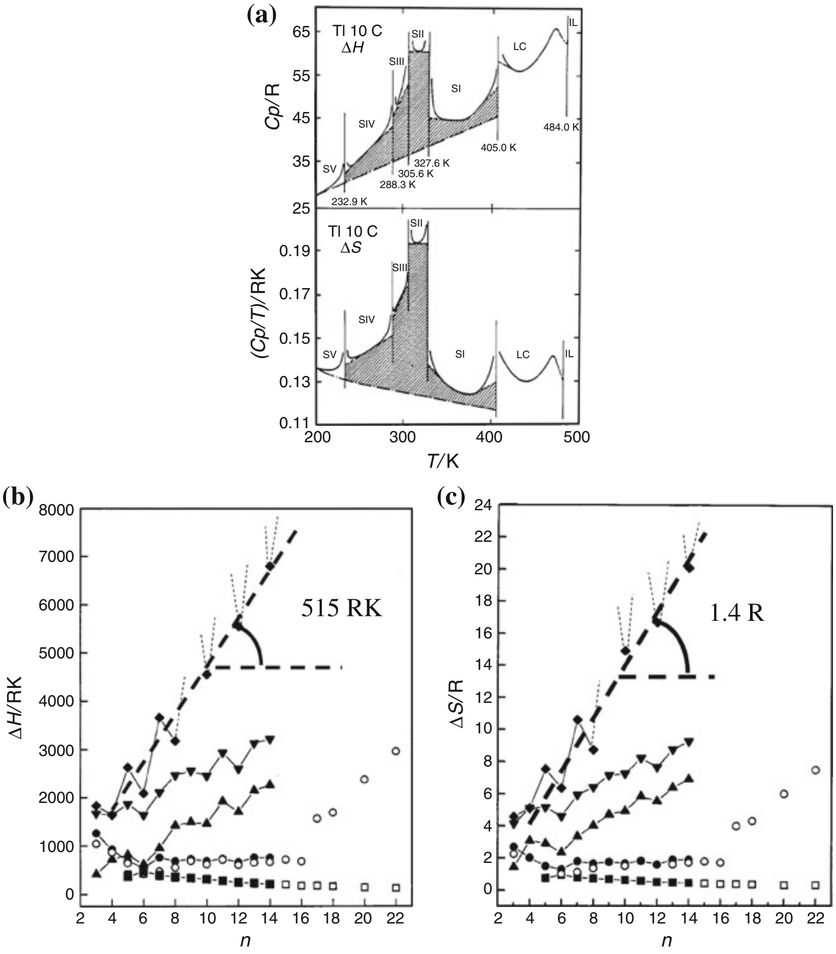


Fig. 7 Thallium I alkanoates ([9] and): **a** Evaluation of the contribution to the total ΔH and ΔS of the *step-wise melting process* due to the formation of gauche defects in a broad range of temperature. Symbols: *filled inverted triangle*, total ΔH or ΔS, except the non-cooperative effect; *filled triangle*, total ΔH or ΔS of solid-to-solid transitions; *unfilled circle*, fusion (Refs. [10, 11]; *filled circle*, fusion (Ref. [9]); *unfilled square*, clearing [10, 11]; *filled square*, clearing; *filled diamond*, total ΔH or ΔS of the melting process. (Ref. [9], with permission)

Scheme 5

The ΔH, and ΔS versus n_C of transitions measured by DSC and AC are represented in Fig. 7b, c, together with an example of the energy evaluation associated with the *gauche* defects formation (Fig. 7a). Shaded area in Fig. 7a had to be evaluated to be added to the total enthalpy and entropy of the melting process, thus approaching the values

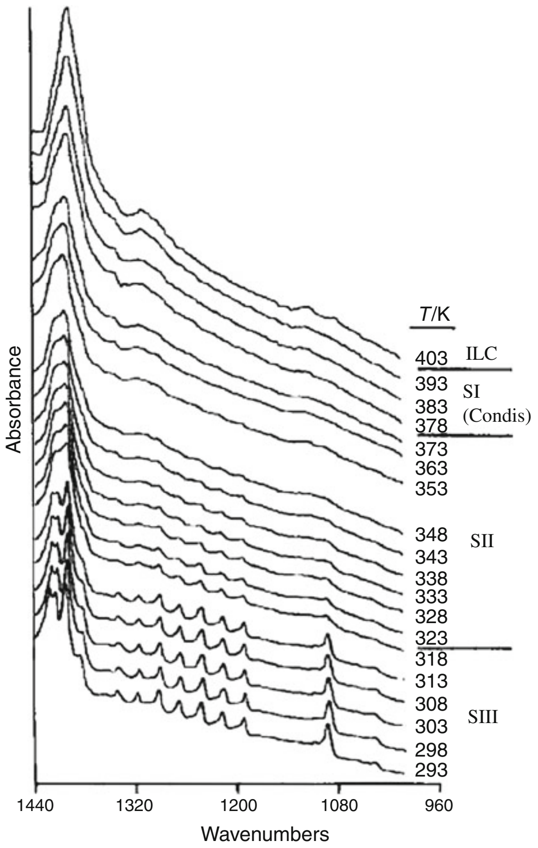


Fig. 8 FTIR spectra of CH_2 *wagging* progression vibrational modes of TlC14, recorded at the indicated temperatures. (Ref. [30], with permission)

of 515RK (4.282 kJ·mol^{-1}) (estimated value) [26–29], and 1.4 R (11.6 J·K^{-1}·mol^{-1}), for the enthalpy and the entropy contribution ($R \ln \Omega$, where $\Omega = 3$, is the number of microstates, t, g^+ and g^-) of the CH_2 group, respectively.

It is important to note in Fig. 7b, c, that the $\Delta_{\mathrm{fus}}H$ and $\Delta_{\mathrm{fus}}S$ are practically constant from $n_C = 5$ until $n_C = 14$ (all the members presenting ILC phase) (see also Fig. 16). This clearly shows that these functions are independent of the chain length, that is, chains can be considered already *melted* in the solid phase just before the ILC, and consequently, this solid is a *condis* phase. The external orientational factor needed in a LC (ILC in this case) is the anisotropic distribution of the COO^- electrical resonant charge [14].

FTIR

Apart from localized vibrations such as carboxylate or CH stretching modes, the alkyl chain vibrations present non-localized movements that involve the entire chain. These non-localized vibrations give rise to band progressions in which intensity is increased in the organic salts due to the high polar carboxylate group. These progression bands appear in the wagging (1170 and 1380 cm^{-1}) (Fig. 8) and rocking regions (1100–700 cm^{-1}) and are characteristic of all-trans chains.

In the thallium series [30], the conformational order is lost in a progressive way during an interval of temperatures. In the lowest solid-to-solid phase transitions, the alkyl chains remain, mainly, in a totally trans-planar conformation, but the concentration of non-planar conformers increases continuously as the temperature rises, and at a particular value (different for each compound), the CH_2 wagging progression bands disappear. The temperature range at which this chain *melting* takes place coincides with the final steps of the calorimetric enhancement of the heat capacity. As can be observed, features at around 1440 and 1306 cm^{-1} characteristic of gauche and *kink* structures are evident at this temperature. These features increase their intensity with temperature, becoming the band at 1306 cm^{-1} a relatively strong band in the mesophase. This fact agrees with the assignment of the last solid phases previous to ILC as conformational disordered mesophases.

Polarizing light microscopy: identification of mesophases

Experiment of droplets

This experiment [31] consists in the observation through a polarizing light microscope, of a powdered sample of microcrystals suspended in a mineral oil (30000 of Brookfield, viscosity 29920, lot number 030299), where it is insoluble. The suspension is placed into a glass container without cover into a hot stage. The microcrystals transform into *drops* on heating, only when the transition is to a fluid phase (e.g., liquid crystal or isotropic liquid), because of the minimum surface principle. In the case of TlCn, this experiment confirmed that all of its phases were solid except the ILC and the isotropic liquid. All of the phases from SI to SVII are solid. SI is a solid, but a condis mesophases (FTIR have proved the internal conformational disorder of the chains).

Doing regular observations of the samples in the microscope, the *batonnetes* formation on cooling from the isotropic liquid to ILC phase (Fig. 9a) and the *con-focal*

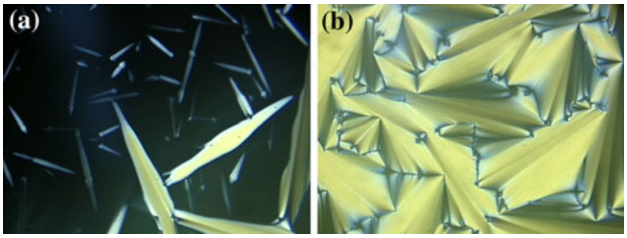


Fig. 9 Polarizing light microscope observation on Tl(C8) on cooling from the isotropic liquid

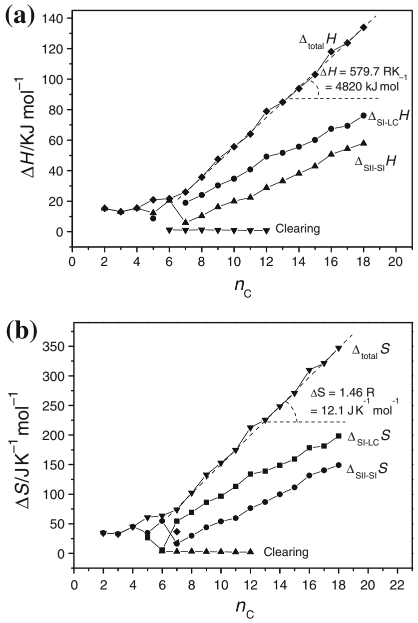


Fig. 10 Lead (II) Alkanoates, Pb(C*n*)$_2$: **a** Enthalpies and **b** Entropy of transition (*filled circle*: crystal-to-rotator phase; *filled square*: fusion; and *filled triangle*: clearing) versus n_C of the alkyl chain (Ref. [7, 8], with permission)

texture or *fan-shape* observed (Fig. 9b) show that the ILC phase is a *smectic A-like* or *neat* phase.

Lead(II) alkanoate series

Calorimetry

The phase behavior (temperatures of transitions vs. n_C) for the lead(II) alkanoate series is represented in Fig. 1. In Fig. 10, all the calorimetric results carried out by DSC are shown. The *step-wise melting process* of this series, summarized in Scheme 6, is more simple than the one of the thallium(I) series. We proved experimentally that these compounds do not present any transition below room temperature at least until 90 K.

The ΔH, and ΔS of all the transitions versus n_C, measured by DSC [7, 8] are represented in Fig. 10a and b. On the contrary to what happen with the thallium(I) series, the estimated values for the CH$_2$ contributions of 579.7*RK* (4.820 kJ·mol^{-1}) and 1.46*R* (12.1 J·K^{-1}·mol^{-1}) coincide within the experimental error, with the enthalpy and the entropy, respectively, calculated from the slope of the total ΔH and ΔS versus n_C, proving that no transition would appear under room temperature.

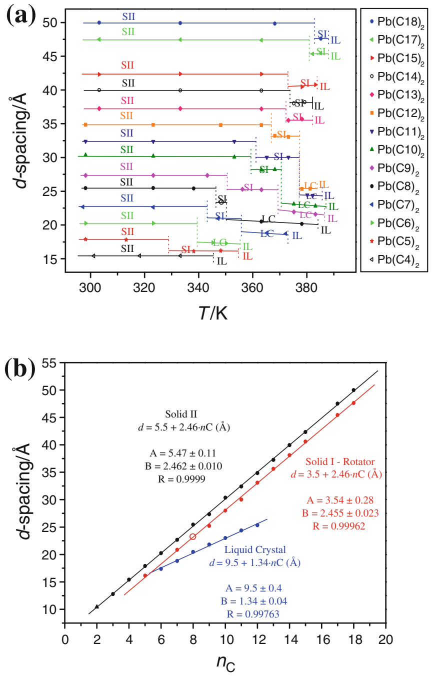


Fig. 11 Powder XRD *d*-spacings for the members from $n_C = 6$ up to $n_C = 12$ of lead(II) alkanoates (bottom to top): **a** for the different phases versus temperature; **b** versus n_C, at one specific temperature. Symbols of **b** *right angle filled triangle*, crystal at room temperature; *unfilled square*, SI (rotator phase); *filled circle*, liquid crystal (XRD data of $n_C > 12$, unpublished results; others, Ref. [8], with permission)

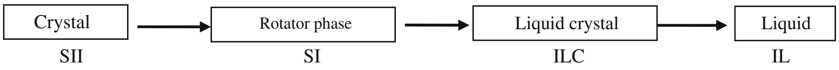
It is important to note in Fig. 10a and b, that contrary to what happens in the thallium(I) series, the $\Delta_{fus}H$ and $\Delta_{fus}S$ depend on the n_C, thus indicating that the chains, that were all of them in *all-trans* conformation at the rotator phase, melt at the transition from rotator (SI) to ILC (see also Fig. 16). This is another evidence more of the *rotator* nature of SI.

Evidences that phase SI is a rotator mesophase

Powder X-ray diffraction (PXRD) The *d*-spacings, measured by powder XRD, are represented for members from $n_C = 6$ until $n_C = 12$ in Fig. 11. The slopes of the *d*-spacing's versus n_C of the SII (crystal) and the SI (rotator phase) versus n_C are roughly the same (2.43 and 2.42 Å per 2 CH$_2$ groups) which is practically the contribution of two CH$_2$ groups in a *trans* position slightly tilted. In this phase, the chains are rotating around their axis with the possibility of certain % of them having the allowed defect described in Fig. 6, thus confirming again the rotator nature of SI phase.

Infrared spectroscopy (FTIR) As an example, the infrared spectra of Pb(C12)$_2$ at temperatures, corresponding to the phases detected by DSC, are displayed in Fig. 12. The presence of progression bands in the solid SI is an

Scheme 6



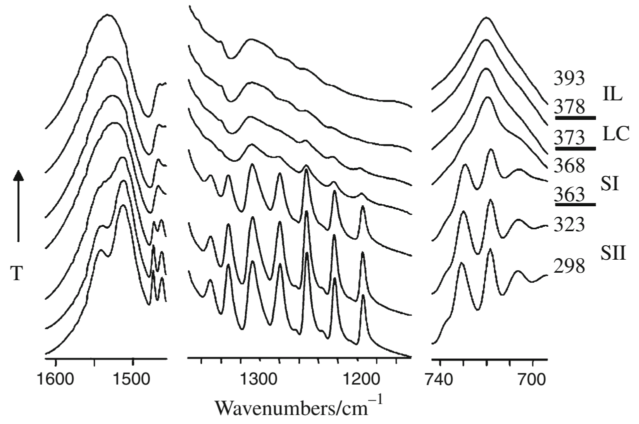


Fig. 12 FTIR spectra of CH_2 *wagging* progression vibrational modes of $Pb(C12)_2$, recorded at the indicated temperatures (Ref. [8], with permission)

indication of *all-trans* chains confirming once more the rotator phase nature of this solid.

Nuclear magnetic resonance (NMR) Experiments of ^{13}C-NMR in solid state, in function of temperature, were carried out on $Pb(C5)_2$, a member that easily quench into glass states. This technique was decisive to prove the rotator nature of SI phase. The corresponding spectra are shown in Fig. 13. In Fig. 13a, twin peaks correspond to the chemical shifts due to two well differentiated carboxylic chains: 50% with the COO^- "*only chelating*", and the other 50% *bridging-chelating* coordinations to the Pb^{2+} ions. These two types of coordinations can easily be seen in the unit cell of Fig. 4.

Figure 13b shows the rotator phase in its dynamic rotational motion at 343 K. The tails (CH_3) have more mobility than the carboxylates that are more attracted by ionic layer. In Fig. 13c, the spectra correspond to the rotator glass, where the rotational motion is frozen: It looks like a shot of the rotator phase. The six maxima in the carboxylic groups points clearly to the hexagonal arrangement of the rotating chains.

Polarizing light microscopy A similar experiment to that described for the thallium(I) series was carried out on several members of the lead(II) alkanoate series. Spherical particles were only seen for the isotropic liquid and ILC. When the temperature of SI was reached on cooling, the spherical droplets lost their spherical shape, confirming the solid nature of this phase.

A regular experiment was developed on some members of the lead(II) alkanoate series, observing the changes on cooling the sample inside a hot stage. In Fig. 14, the sequence of different pictures taken on cooling a sample of $Pb(C10)_2$, starting at a temperature of about 380 K (ILC phase), passing the fusion (379.4 K), until a temperature about 365 K (SI, rotator), showing an hexagonal growth, pointing to a rotator nature of this phase. These hexagons should correspond to a homeotropic growth (rotation axis perpendicular to the surfaces) texture of the rotator phase from the ILC phase (neat phase).

Moreover, it was proved that the rotator phase does not exhibit shear nor flow properties under stress. This proof was done by pushing the coverlid on the microscopic preparations of the samples inside the hot stage used in the polarizing light observations. Other experiments facts,

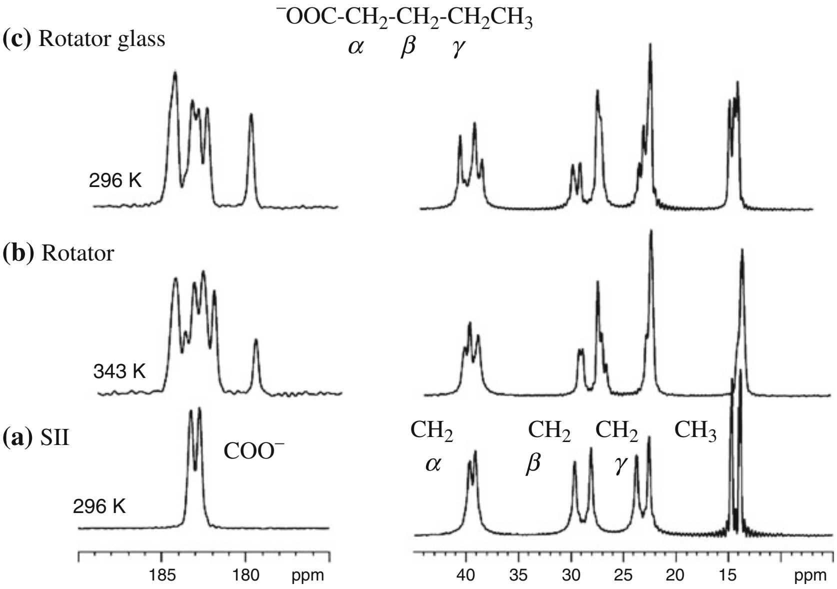


Fig. 13 ^{13}C-NMR spectra of $Pb(C5)_2$ at the specified temperatures: **a** Crystal at 296 K (room temperature, SII); **b** at 343 K (SI, rotator phase); **c** Glass corresponding to the frozen rotator phase, that is, rotator glass (Ref. [25], with permission)

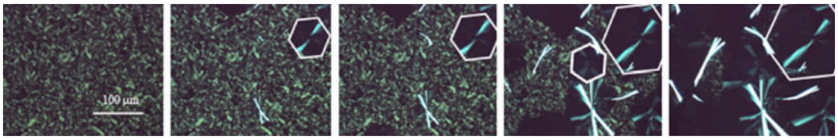


Fig. 14 Sequence of different pictures taken at intermediate temperatures starting at the ILC phase (at the *left*), and ending at the SI (rotator phase), showing the hexagonal growth of this phase

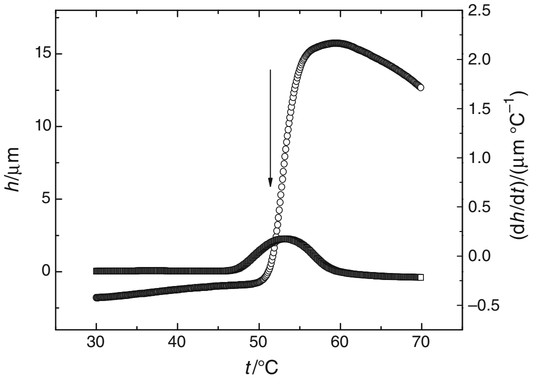


Fig. 15 A TMA thermogram obtained on a $Pb(C5)_2$ sample showing a volume expansion at the SII to SI transition (marked with an *arrow* at the first derivative inflexion point). Ref. [25]

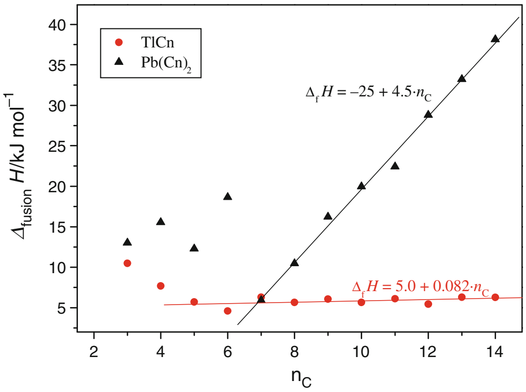


Fig. 16 Comparison between the fusion enthalpies, $\Delta_{fus}H$, for the TlC*n* and Pb(C*n*)2 series, showing that is practically constant in the thallium(I) series and linearly dependent with n_C, in the lead(II) one

recommended by Gray and Goodby [32] to differentiate a smectic B from a hexagonal solid phase, also point to the solid nature of this phase. For instance, the two transitions limiting the rotator phase in lead(II) alkanoates undergo clearly supercooling (between, 3° and 10°). Unfortunately, Mossbauer spectra, that could inform us about a possible Sm B fluid phase, could not be carried out on these samples because the presence of lead(II) cations.

TMA Powder XRD experiments show that the *d*-spacings decrease from the crystal to the rotator phase (see Fig. 11b). Consequently, a volume decrease should take place in this transition. However, for the chains to start to rotate a big increase of the volume would be absolutely necessary. In Fig. 15, the thermogram obtained in a TMA (Thermo Mechanical Analyzer) on a $Pb(C5)_2$ sample is shown, in which the variation of the distance between a sensor, located on the top of the solid sample, and a platform that support it is represented in function of temperature (and the first derivative, as well). As can be seen, at the SII to SI transition temperature a big expansion of the sample takes place, allowing the chains start to rotate. This is an example of how simple experiments sometimes can be useful to confirm some hypothesis.

Comparative study of the thallium(I) and lead(II) alkanoate series: a summary

Either the Tl^+ or the Pb^{2+} ions are both rather big (the second one, smaller). In the case of Pb^{2+} (due to its double charge), the number of chains is twice that of Tl^+. At the same time, the ionic bond is obviously stronger in this series. Consequently, the chains are more packed, and a much more hindered internal rotation is expected in the lead(II) alkanoate series. The chains have more space to move in the thallium(I) alkanoate series, forming defects (*gauche*, *kink jog*, etc.) easily, even starting at low temperatures. Actually, this is what happen (proved by FTIR vs. temperature, see Fig. 8) as a non-cooperative effect, showing a *shoulder* in the heat capacity morphology of almost all the members of this series (see Fig. 7a). As a matter of fact, the last solid phase (SI) has the chains already *melted* (that is, it is really a condis phase). Moreover, the constant value of the fusion enthalpy to liquid crystal proves this point, since it is not dependent of the chain length (see Figs. 7b and 16). The liquid crystal structure is “*smectic A-like*” or “*neat*” phase.

On the contrary, in the lead(II) alkanoate series the chains are maintained *all-trans* even when they start to rotate cooperatively at the SII–SI transition above room temperature (see Fig. 12) thus forming a *rotator* phase. The packing must be *hexagonal* (or *pseudo-hexagonal*) in this phase due to symmetry reasons. The internal rotation (formation of *gauche*, *kink*, *jog*, etc.) in this series coincides with the fusion to ILC (*smectic A-like* or *neat* phase, identical to the thallium(I) alkanoates one), as it can be deduced because $\Delta_{fus}H$ increases with increasing n_C (see Fig. 16). Lead(II) alkanoates do not show a condis, but a *rotator phase*.

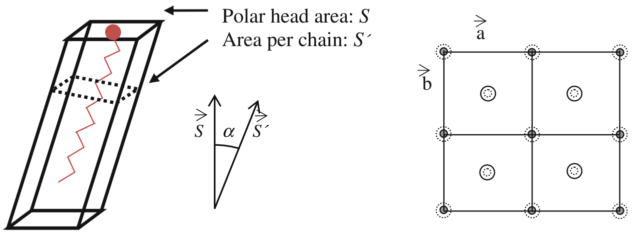


Fig. 17 Relation between S and S'

The area per polar head (S)

It is important to note that the study of the crystal structure of regular organic salts becomes fundamental not only to describe not only the solid crystals, but also to explain their thermal behavior and formation of mesophases.

The previous section was a qualitative analysis to explain that thallium(I) and lead(II) alkanoates form a condis, and a rotator mesogenic phases, respectively. However, there is another way to do it more rigorous and quantitative through the *area per polar head* (S) and *the cross-section area* of the alkyl chains (S'), defined in Figs. 17 [33–36], that can be calculated from the crystal structures. S' is the space that alkyl chains have to form *gauche* defects. These parameters will permit to distinguish between both mesophases. Actually, S' is associated to the space that alkyl chains have to form *gauche* defects. The relation between S and S' is: $S' = S \cdot \cos\alpha$. If the chain is melted: $S = S'$, $\alpha = 0°$.

There is a direct dependence between the *cross-section area* of the alkyl chains and their ability to show chain defects in the different polymorphic or mesomorphic states, which are involved in the *step-wise melting process*. It is important to remember that rotator phases allow certain conformational defects in the alkyl chains [19, 20], such as *kink* or *end-gauche* defects (see Fig. 6). The formation of these defects is controlled by the *thermal* and the *steric* factors. The first one can be quantified approximately by the Maxwell–Boltzmann distribution law, that is, the number of *trans* and *gauche* defects must be 33.3 and 66.7%, respectively, at the classic limit. At a particular temperature, the second factor changes these values: the higher the steric hindrance is, the lower the gauche defects percentage is. The cross-section area is then a fundamental parameter to study in depth mesomorphic phases, such as rotator or condis, which are not currently well characterized.

Accordingly, the value of S' in SI of the lead(II) alkanoates (21.5 Å^2) is comparable to the values obtained for the rotator phases of n-alkanes (20 Å^2) [37], lithium n-hexadecanoate (20.7 Å^2) [38], lithium 16-hydroxy-hexadecanoate (21.5 Å^2) [39], or those calculated through Langmuir monolayers of alkyl chain surfactants in water (19.7–20.2 Å^2) [40, 41]. This value of S (and S') for thallium(I) alkanoates at the highest temperature solid phase (SI) is (29 Å^2), which is much bigger, explaining the presence of disorder in the chains (condis phase). In Table 2, a summary of the steric and thermal factors (at the specified phases) is given for comparison between thallium(I) and lead(II) alkanoate series.

Other series: alkyl ammonium chlorides

Alkyl ammonium halides are cationic organic salts at the contrary to metal alkanoates which are anionic. However, their behavior is quite similar. The n-alkyl ammonium chlorides series have been studied by Busico et al. [45], and by Iwai et al. [46], existing a controversy about the identification of the phases found by them. The former group establishes this sequence:

Ordered crystal – conformational melting (or plastic phase)
– liquid crystal – isotropic liquid

meanwhile the later one proposes this one:

Ordered crystal – plastic crystal – rotator phase
– smectic – isotropic liquid

Table 2 A comparison between thallium(I) and lead(II) alkanoate series of the steric and thermal factors at different phases

Series	TlCn	Pb(Cn)$_2$
Solid phase at room temperature	SIII	SII
S/Å^2	25.6 (calculated) [33]	17.7 (calculated) [17]
S'/Å^2	22.2 (calculated) [33]	17.7 (calculated) [17]
Chains	*All-trans* (only a few possible defects)	*All-trans*
Solid phase previous to fusion	SI	SI
S and S' ($\alpha \sim 0$)/Å^2 (steric factor)	29 (calculated) [42] [43]	21.5 (calculated) [44]
T_{fus}/K (thermal factor)	420	350
Chain	Melted (50% of defects)	*All-trans* (only a few possible defects)
Phase	Condis	Rotator
SI to ILC	Only fusion of the ionic layer	Fusion of chains and ionic layer

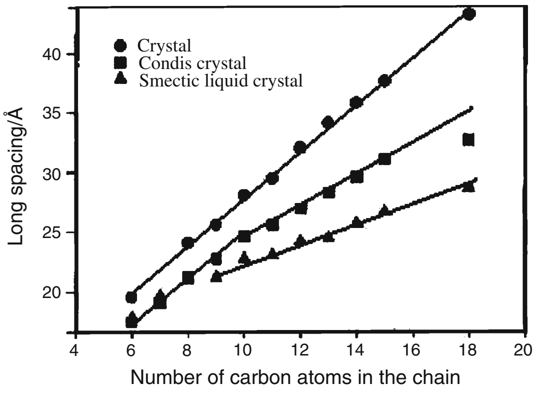


Fig. 18 Long spacing of XRD as a function of carbon atoms in *n*-alkylammonium chlorides. *Straight lines* added to the plot (Ref. [45], with permission)

Using the XRD data from [19] and [20], a representation of the *d*-spacings versus n_C is shown in Fig. 18. According to what happen in lead(II) alkanoate series, it could be established that low members may behave as rotator phase, and the higher ones as condis phase mesogens.

Glass states of lead(II) alkanoates

Regular glass (amorphous)

Lead(II) alkanoate series easily quench into different glass states. Short member of the series (from acetate to pentanoate) [24], which are not mesogens, quench into a regular glass or amorphous when cooled at moderated cooling rates. In Fig. 19a, b, the DSC thermograms show the glass transition measured at 5 °C min^{-1}.

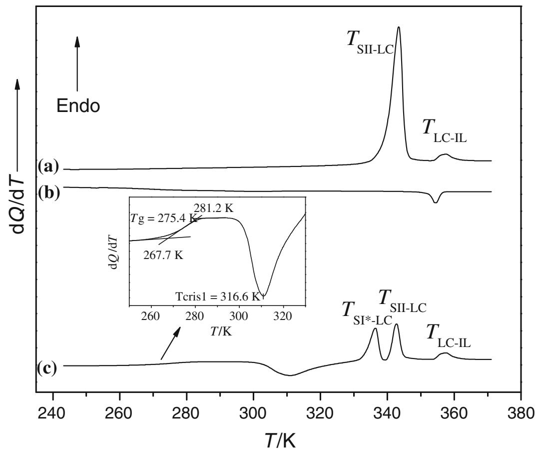


Fig. 21 Pb(C6)$_2$: DSC thermograms: *A*) first heating, *B*) cooling, and *C*) second heating measured immediately after being cooled, all of them registered at a rate of 5 K min^{-1} (Not published results)

Rotator glass

The Pb(C5)$_2$ member has an atypical behavior [25] on its quenching into the glass state: at moderate cooling rate of 5 °C min^{-1}, a rotator glass is formed; at higher cooling rates of 20–30 °C min^{-1}, a rotator and amorphous glass mixture is obtained, instead. This last behavior is shown in Fig. 20.

Fig. 19 Thermograms for the *a* first and *b* second and next heatings: **A** Pb(C2)$_2$: DSC; **B** Pb(C3)$_2$ DSC (Ref. [24], with permission)

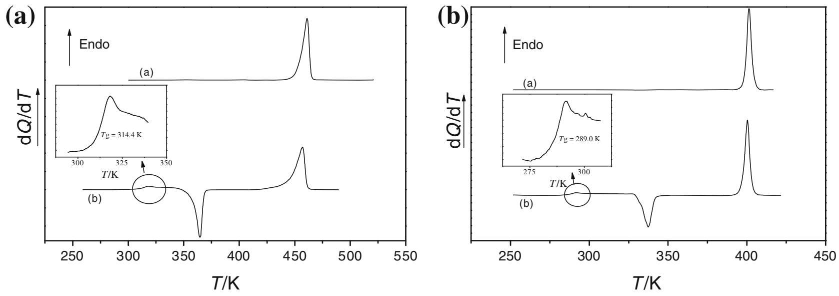


Fig. 20 Pb(C5)$_2$: **a** DSC thermograms obtained after a slow quenching from the isotropic liquid, registered on heating, at the specified rates, to measure its evolution. **b** Enlargement of the thermogram at 20 K min^{-1}, showing the glass transition (Ref. [25], with permission)

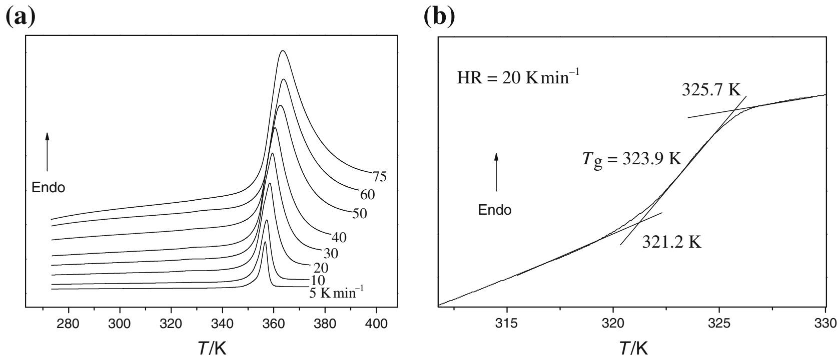


Table 3 Different types of glasses classified according to their possible orders-disorders

Vitreous phase	Order	Static disorder
Glass (amorphous)	None	All (amorphous)
Liquid crystal Glass	Positional (total or partial) orientational	Positional (total or partial)
Plastic crystal Glass	Positional	External orientational
Condis glass	Positional external orientational	Internal conformational
Rotator glass	Hexagonal or pseudohexagonal internal orientational	Internal orientational (rotational)
Crystal	All	None

Liquid crystal glass

Finally, a liquid crystal glass was observed by quenching $Pb(C6)_2$, from the isotropic liquid (Fig. 21). The typical fan-shape of this *neat* phase was still observed by polarizing microscopy at temperatures below the glass transition, proving that this glass still has order. Liquid crystal and rotator glasses keep their orders as well, and only their motions are frozen.

In Table 3, a classification of the different glass states is given.

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References

1. Duruz J, Michels HJ, Ubbelohde AR. Molten fatty acid salts as model ionic liquids I. Thermodynamic and transport parameters of some organic sodium salts. Proc R Soc Lond Ser A. 1971;322:281–99.
2. Ramos Riesco M, Martínez Casado FJ, López-Andrés S, García Pérez MV, Redondo Yélamos MI, Torres MR, Garrido L, Rodríguez Cheda JA. Monotropic polymorphism in copper(II) decanoate. Cryst Growth Des. 2008;8:2547–54.
3. Earle MJ, Seddon KR. Ionic liquids Green solvents for the future. Pure Appl Chem. 2000;72:1391–8.
4. Rao CNR, Natarajan S, Vaidhyanathan R. Metal carboxylates with open architectures. Angew Chem Int Ed. 2004;43:1466–96.
5. Patrick Stahly G. A survey of cocrystals reported prior to 2000. Cryst Growth Des. 2009;9:4212–29.
6. Klimusheva G, Koval'Chuk A, Volynets N, Vakhnin A. Electrooptical properties of metal organic ionic liquid crystals. Opto-Electron Rev. 2002;10(1):39–42.
7. Sánchez Arenas A, García Pérez MV, Redondo MI, Cheda JAR, Roux MV, Turrión C. Thermophysical study of lead(II) n-alkanoates by DCS, optical microscopy, FTIR, and Raman spectroscopy. Liq Cryst. 1995;18(3):431–41.
8. Martínez Casado FJ, García Pérez MV, Redondo Yélamos MI, Cheda JAR, Sánchez Arenas A. Intermediate rotator phase in lead(II) alkanoates. J Phys Chem C. 2007;111(18):6826–31.
9. Cheda JAR, Redondo MI, García MV, López de la Fuente FL, Fernández-Martín F, Westrum EF Jr. A thermophysical study of the melting process in alkyl chain metal *n*-alkanoates: the thallium(I) series. J Chem Phys. 1999;111:3590–8. And all of our references therein.
10. Lindau J, Diele S, Kruger H, Dorfler HD. Thermal phase-behavior of thallium (I) salts of aliphatic carbonic-acids. Z Phys Chem Leipzig. 1981;262:775–84.
11. Lindau J, Konig HJ, Dorfler HD. Systemization of the low-temperature modifications of homologous thallium(I) salts of aliphatic carbonic-acids through their mixability relationships. Colloid Polym Sci. 1983;261:236–40.
12. Orientational disorders in crystals. In: Rudman R, Smith GW, editors. ODIC Newsletter. 1976;1:1–4.
13. Gregoryanz E, Goncharov AF, Hemley RJ, Mao H, Somayazulu M, Shen G. Raman, infrared, and x-ray evidence for new phases of nitrogen at high pressures and temperatures. Phys Rev B. 2002; 66:224108.
14. Binnemans K. Ionic liquid crystals. Chem Rev. 2005;105: 4148–204.
15. Wunderlich B, Moller M, Grebowicz J, Baur H. Conformational motion and disorder in low and high molecular mass crystals. London: Springer–Verlag; 1988. (Advances in Polymer Science, vol no. 87).
16. Wunderlich B. Thermodynamic description of condensed phases. J Therm Anal Calorim. 2010;102:413–24.
17. Lacouture F, Francois M, Didierjean C, Rivera JP, Rocca E, Steinmetza J. Anhydrous lead(II) heptanoate. Acta Crystallogr. 2001;C57:530–1.
18. Ryckaert JP, Klein ML, McDonald IR. Disorder at the bilayer interface in the pseudohexagonal rotator phase of solid *n*-alkanes. Phys Rev Lett. 1987;58:698–701.
19. Marbeuf A, Brown R. Molecular dynamics in *n*-alkanes: premelting phenomena and rotator phases. J Chem Phys. 2006;124:054901.
20. Shinohara Y, Kawasaki N, Ueno S, Kobayashi I, Nakajima M, Amemiya Y. Observation of the transient rotator phase of n-hexadecane in emulsified droplets with time-resolved two-dimensional small- and wide-angle X-ray scattering. Phys Rev Lett. 2005; 94:097801(1-4).
21. Spitalsky Z, Bleha T. Energetics of stretching of conformational defects in extended poly(methylene) chains. Macromol Theory Simul. 2001;10(9):833–41.
22. Wunderlich BJ. Thermal properties of aliphatic nylons and their link to crystal structure and molecular motion. J Therm Anal Calorim. 2008;93:1–17.
23. Corkery RW. Metal organic framework (MOF) liquid crystals. 1D, 2D and 3D ionic coordination polymer structures in the thermotropic mesophases of metal soaps, including alkaline earth, transition metal and lanthanide soaps. Curr Opin Colloid Interface Sci. 2008;13:288–302.
24. Martínez-Casado FJ, Sánchez Arenas A, García Pérez MV, Redondo Yélamos MI, López de Andrés S, Cheda JAR. Short chain lead (II) alkanoates as ionic liquids and glass formers: a DSC, X-ray diffraction and FTIR spectroscopy study. J Chem Thermdyn. 2007;39(3):455–61.
25. Martínez Casado FJ, Ramos Riesco M, Sánchez Arenas A, García Pérez MV, Redondo MI, López-Andrés S, Garrido L, Cheda JAR. A novel rotator glass in lead(II) pentanoate: calorimetric and spectroscopic study. J Phys Chem B. 2008;112(51):16601–9.

26. Nagle JF. Theory of biomembrane phase transitions. J Chem Phys. 1973;58:252–3.
27. Nagle JF. Theory of the main lipid bilayer phase transition. Annu Rev Phys Chem. 1980;31:157–96.
28. Nagle JF, Goldstein M. Decomposition of entropy and enthalpy for the melting transition of polyethylene. Macromolecules. 1985; 18:2643–52.
29. Flory PJ. Statistical mechanics of chain molecules. New York: Wiley; 1969.
30. García Pérez MV, Redondo Yélamos MI, López de la Fuente FL, Cheda JAR, Westrum EF Jr, Fernández-Martín F. Temperature dependence of the vibrational spectra of thallium(I) alkanoates. Appl Spectrosc. 1994;48:338–44.
31. Kurik MV, Lavrentovich OD. Defects in liquid crystals: homotopy theory and experimental studies. Sov Phys Uspekhi. 1988;31: 196–224.
32. Gray GW, Goodby JWG. Smectic liquid crystals textures and structures. Glasgow & London: Leonard Hill; 1984. p. 23–44.
33. Martínez Casado FJ, Ramos Riesco M, García Pérez MV, Redondo Yélamos MI, López-Andrés S, Cheda JAR. Structural and thermodynamic study on short metal alkanoates: lithium propanoate and pentanoate. J Phys Chem B. 2009;113(39): 12896–902.
34. Martínez Casado FJ, Ramos Riesco M, Da Silva I, Labrador A, Redondo MI, García Pérez MV, López-Andrés S, Cheda JAR. Thermal and structural study of the crystal phases and mesophases in the lithium and thallium(I) propanoates and pentanoates binary systems: formation of mixed salts and stabilization of the ionic liquid crystal phase. J Phys Chem B. 2010;114(31): 10075–85.
35. Martínez Casado FJ, Ramos Riesco M, Da Silva I, Redondo MI, Labrador A, Cheda JAR. Lithium and lead(II) butyrates binary system. Pure compounds and an intermediate salt: from 2D to 3D coordination polymers. Cryst Growth Des. 2011;11(3):759–67.
36. Martínez Casado FJ, Ramos Riesco M, Da Silva I, Redondo MI, Cheda JAR. Lithium-thallium (I) butyrates binary system: an intermediate salt and liquid crystal from non-mesogenic compounds. RSC Adv. 2011;1:147–55.
37. Strobl G, Ewen B, Fischer EW, Piesczek W. Defect structure and molecular motion in the four modifications of n -tritriacontane. I. Study of defect structure in the lamellar interfaces using small angle x-ray scattering. J Chem Phys. 1974;61(12):5257–64.
38. Busico V, Ferraro A, Vacatello M. Polymorphism and liquid-crystalline behavior of lithium n-hexadecanoate. J Phys Chem-US. 1984;88(18):4055–8.
39. Busico V, Ferraro A, Vacatello M. A study of the "rotator" phase of 16-hydroxy-lithlum-hexadecanoate. J Chem Phys. 1986;84(1): 471–5.
40. Sirota EB. Remarks concerning the relation between rotator phases of bulk n-alkanes and those of Langmuir monolayers of alkyl-chain surfactants on water. Langmuir. 1997;13(14):3849–59.
41. Vollhardt D. Effect of unsaturation in fatty acids on the main characteristics of Langmuir monolayers. J Phys Chem C. 2007; 111(8):6805–12.
42. Dorfler HD, Brandt A. X-ray diffraction studies on homologous thallium soaps below the temperature range of the neat phase 1. Calculation and comparison of the structure parameters of unit cells. Colloid Polym Sci. 1992;270(3):267–81.
43. Dorfler HD, Brandt A, Kolbe A. X-ray diffraction studies on homologous thallium soaps below the temperature range of the neat phase 2. Structure models of crystalline modifications in the temperature range below the neat phase. Colloid Polym Sci. 1992; 270(3):282–97.
44. Bazuin CG, Guillon D, Skoulios A, Amorim da Costa AM, Burrows HD, Geraldes CFGC, Teixeira-Dias JJC, Blackmore E, Tiddy GJT. Thermotropic polymorphism in liquid-crystalline lead(II) alkanoates. Liq Cryst. 1988;3(12):1655–7.
45. Busico V, Cernicchiaro P, Corradini P, Vacatello M. Polymorphism in anhydrous amphiphilic systems long-chain primary *n*-alkylammonium chlorides. J Phys Chem-US. 1983;87:1631–5.
46. Iwai S, Hattori M, Nakamura ID, Ikeda R. Ionic dynamics in the rotator phase of n-alkylammonium chlorides (C-6-C-10), studied by H-1 nuclear-magnetic-resonance, electrical-conductivity and thermal measurements. J Chem Soc Faraday Trans. 1993;89(5): 827–931.