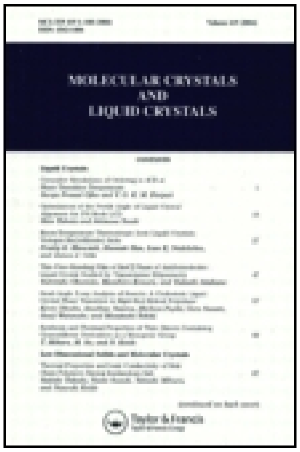

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Thermotropic Phase Transitions in Some Lead(II) Carboxylates

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Thermotropic Phase Transitions in Some Lead(II) Carboxylates

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Differential scanning calorimetry (DSC) is used to determine the phase transition temperatures and heats of phase changes for the even-chain-length lead(II) carboxylates from hexanoate to octadecanoate inclusive. Phase texture studies by polarising light microscopy and x-ray diffraction suggest the phase sequence:

$$\text{Crystal}\ \underset{\longleftarrow}{\xrightarrow{337\text{-}382\text{K}}}\ \text{Crystal}\ \underset{\longleftarrow}{\xrightarrow{343\text{-}379\text{K}}}\ \text{Smectic C}\ \underset{\longleftarrow}{\xrightarrow{352\text{-}378\text{K}}}\ \text{Isotropic Liquid}$$

for the dodecanoate and shorter chain length compounds. For tetradecanoate and above, the smectic phase is absent and the high temperature crystal phase melts directly to isotropic liquid. The results are consistent with a stepwise disordering of the hydrocarbon chains in the lattice in forming the various phases.

Keywords: Lead(II) Carboxylates, Smectic C, Crystal Polymorphism, Mesophases, X-ray diffraction

INTRODUCTION

The existence of one or more thermally induced mesophases between the solid and isotropic liquid, for certain divalent metal carboxylates, has been suggested by Spegt,[1,2] Luzzati and co-workers.[3,4] They proposed various structures, for these mesophases, consistent with their

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x-ray data. Nevertheless, there is still some controversy in the literature concerning the correct classification of these structures based solely on x-ray data. For example, Winsor[5] has questioned the reliance of the data on the assumption that the mesophases were quasicrystalline. More recently, Sime and Adeosun[6] reported a phase sequence, based on differential thermal analysis (DTA) and hot-stage polarising microscopy data, for the even-chain-length lead(II) carboxylates from hexanoate to octadecanoate. A tentative phase sequence:

$$\text{Crystal} \xrightarrow{335\text{-}336\text{K}} \underset{(\text{smectic})}{\text{G}} \xrightarrow{338\text{-}378\text{K}} \underset{(\text{cubic Isomorphous})}{V_2} \xrightarrow{350\text{-}368\text{K}} \underset{\text{Liquid}}{\text{Isotropic}}$$

was proposed for the dodecanoate and shorter chain length compounds. In the tetradecanoate and above the smectic phase was reported to melt directly to isotropic liquid.

However, a careful examination of those authors thermodynamic data suggests that their phase sequence might be in error. It seems unreasonable to interpret the relatively large enthalpy values measured for phase transitions on the low temperature side as being due to mesophase transitions. Rather, the values are indicative of crystal to crystal transitions; and, the high temperature transition to isotropic liquid, being of the order of 1 kJ mol^{-1}, consistent with a transition from a mesophase. Because of these possible contradictions, the thermal properties of these compounds have been reinvestigated here.

Accordingly, differential scanning calorimetry and hot-stage polarising light microscopy in conjunction with x-ray diffractometry were used to determine phase transition temperatures and phase structures, respectively, for the even-chain-length lead(II) hexanoate to octadecanoate inclusive (hereafter abbreviated to PbC_n; $n = 6 \ldots . 18$).

EXPERIMENTAL

Materials

The preparation and purification of lead(II) carboxylates have been described previously.[7,8]

Physical Measurements

DSC measurements were performed on a Perkin-Elmer DSC-4-TADS system. For the determination of heats of phase changes, samples of between 2-10 mg were sealed into aluminum crucibles and scanned at 1.0K min^{-1}. Measurements were made at least in triplicate on fresh samples in both a heating and cooling cycle.

Phase structures, and in addition, transition temperatures were determined with a Leitz polarising light microscope fitted with a Mettler FP-2 heating stage (scan rate 2K min^{-1}). Studies were performed with the crystalline sample sandwiched between a clean microscope slide and coverslip. For conoscopic studies, microscope slides were coated with a 0.1% solution of Dowex X2-2-2300 prepared in an isopropyl alcohol (25 cm^3): water (75 cm^3) mixture. The slides were first dipped into this solution, rinsed with water, air dried and then heated in an oven at 273K. They were removed from the oven after 1 hr. and cooled to room temperature prior to their use. Coverslips were treated in a similar manner.

X-ray experiments were carried out on a conventional powder diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5418 Å). Samples were introduced and sealed in thin walled capillary tubes of 0.7mm diameter by a vacuum melt technique. In a typical experiment, a capillary tube containing the sample was fitted into a temperature controlled copper block, which also served as a collimator for the x-ray beam, and irradiated for 1 hr. The diffraction patterns were recorded on flat polaroid films (type 57) perpendicular to the incident beam at a sample to film distance of 80.03 mm.

RESULTS

DSC curves for all the compounds in the heating cycle are shown in Figure 1. At least one or more phase transitions are observed between the crystalline solid and melt in all the compounds. Transition temperatures, heats (ΔH) and entropy (ΔS) of transition are given in Table I. Since transition temperatures determined by microscopy were almost identical to those determined by DSC, the values quoted here are DSC values only and were recorded upon heating. Where there has been an overlap in curves, the ΔH values quoted were obtained on cooling from the isotropic liquid when separation occurred. Most of the transition temperatures and enthalpies are in good accordance with literature values.[6]

An examination of Figure 2 shows that all the compounds, with the exception of PbC_6, exhibit enantiotropic phase behaviour. Considerable supercooling (Ca. 7-11K) was observed in all low temperature transitions and, in addition, in the transitions from the melt for

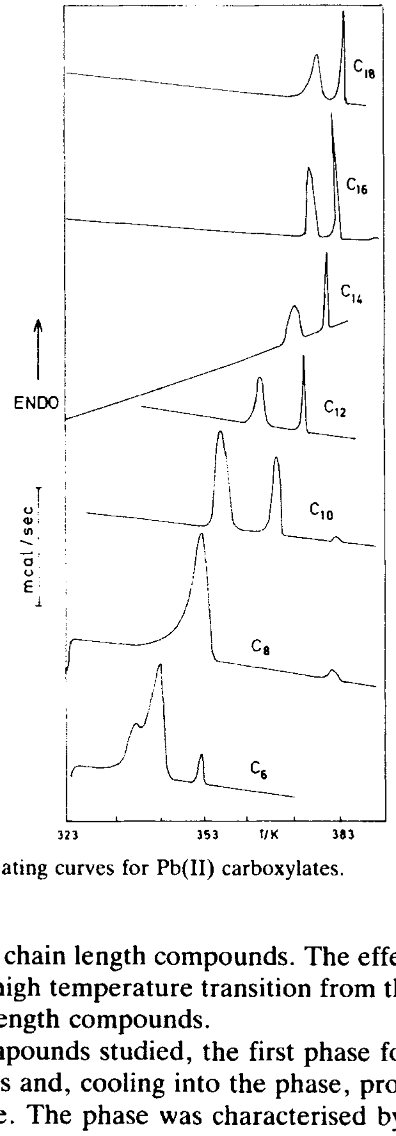

FIGURE 1 DSC heating curves for Pb(II) carboxylates.

PbC_{14} and longer chain length compounds. The effect, however, was negligible in the high temperature transition from the melt for PbC_{12} and short chain length compounds.

For all the compounds studied, the first phase formed on heating was highly viscous and, cooling into the phase, produced a typically crystalline texture. The phase was characterised by its resistance to a shear stress applied to the coverslip. Further, the crystalline integrity of the phase was maintained upon reheating to the melting point, typical of such phases. Crystalline textures were similarly identified for the second low temperature phase in PbC_8, PbC_{10} (Figure 3) and PbC_{12} and were the only textures observed on cooling PbC_{14} and longer chain length compounds from the isotropic liquid to the room temperature solid. In the case of PbC_6, the change to the crystalline

TABLE I

Thermodynamic Data for Phase Changes

Carbon Chain Length	T/K	ΔH/kJmol^{-1}	ΔS/JK^{-1}mol^{-1}
Crystal	⟶ Phase I		
6	337.6	1.02	3.03
8	353.8	24.21*	68.41
10	359.0	38.53	107.33
12	369.2	47.55	128.81
14	376.9	52.12	138.28
16	380.8	52.69	138.37
18	381.9	55.80	146.13
Phase I	⟶ Phase II		
6	343.3	23.25	67.72
8	353.8	8.54*	24.15
10	371.4	18.11	48.76
12	378.4	28.64	75.68
Phase II	⟶ Isotropic		
6	352.6	1.24	3.53
8	382.8	1.03	2.70
10	384.2	0.80	2.09
12	378.4	0.10*	0.27
Phase I	⟶ Isotropic		
14	384.1	38.79	100.98
16	386.8	45.40	117.38
18	388.1	53.90	138.88

*Values obtained on cooling. Errors in value are quoted within ±2%.

phase occurred slowly (overnight). However, when PbC$_{12}$ and shorter chain length compounds were cooled from the isotropic liquid into the high temperature phase, fan textures appeared (Figure 4) identical to those described for a smectic phase and, in particular, a mesophase of type C(S$_c$).[9] These phases were formed without supercooling and were observed to be fluid and weakly biaxial.

Because the x-ray pattern from the mesophase consisted of a relatively sharp inner ring and a diffuse liquid like outer ring, a smectic phase of type C was confirmed. In the light of this evidence, it is reasonable to suppose that the fan texture was formed from a lamellar structure. For PbC$_{10}$, the lamellar spacing (d spacing) was calculated from the diameter of the inner diffraction ring using the formulae:

$$n\lambda = 2d \sin \theta$$

where n is the order of diffraction, λ is the wavelength of radiation used (1.5418 Å) and θ is the diffraction angle. A d spacing of $\approx$32 Å was

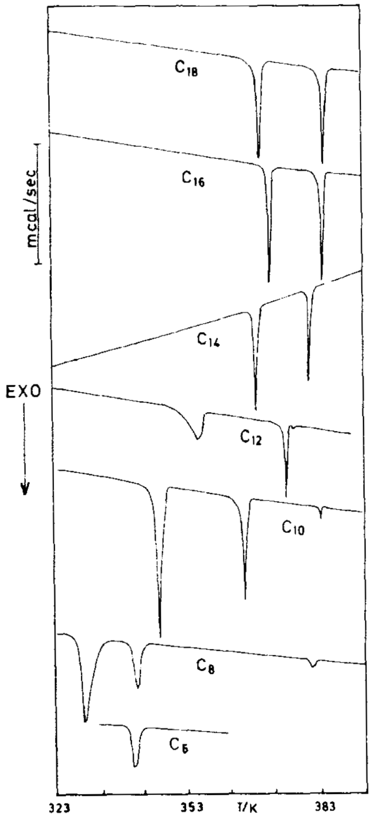

FIGURE 2 DSC cooling curves for Pb(II) carboxylates.

measured at ambient temperatures. This value decreased to ≈29.8 Å in the first crystalline phase (365K) and to 22.9 Å in the smectic C phase (377.2k).

DISCUSSION

Polymorphic modifications in certain divalent metal carboxylates have been reported[1,6,7,10,11] and several interesting structures, based on x-ray and other studies, have been proposed for these polymorphs. The correct assignment of some of these structures has been questioned by other workers[5] and has led, in a few cases, to a revision and re-interpretation of the data.[2-4] It seems clear then that the phase structures formed on heating these compounds to the isotropic liquid or

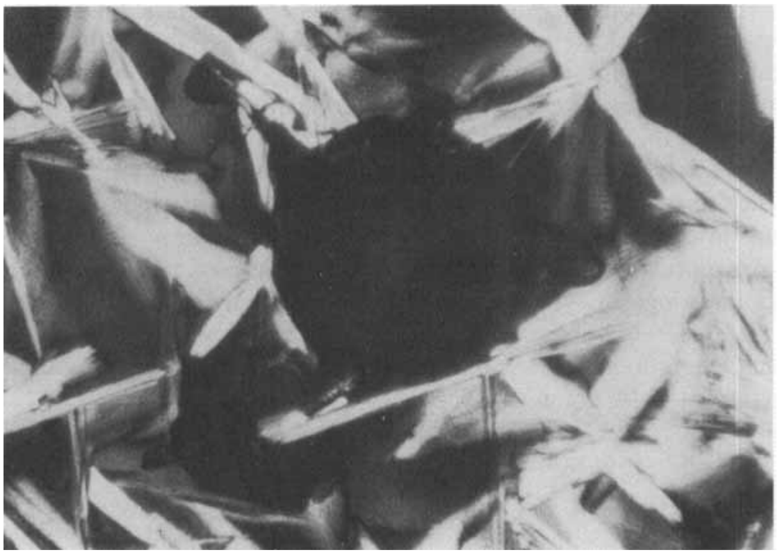

FIGURE 3 Texture of PbC_{10} crystalline phase adjacent to smectic phase at 366.8K; mag. × 40

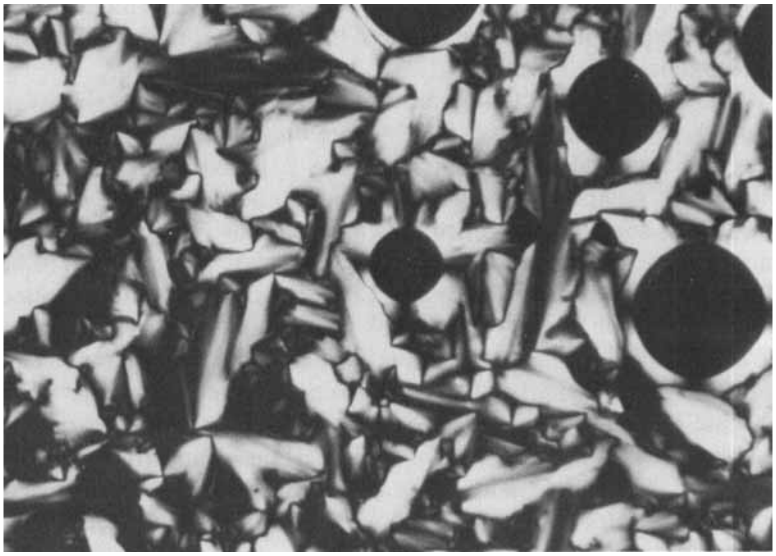

FIGURE 4 Texture of PbC_{10} smectic phase at 382.5K; mag. × 40

cooling the isotropic liquid to the room temperature solid are not well understood. Nevertheless, it is generally agreed that in the room temperature solid, the molecules are arranged in a bilayer structure with the carboxylate ends forming an electrically balanced double layer with the hydrocarbon chains sticking out parallel to each other from both sides of this layer.[10,12] Such an interpretation for the present structure is supported by U.V. evidence for copper-copper interactions in copper(II) decanoate[13] and by our x-ray data.

An approximate molecular length for PbC_{10} can be calculated given the following: a C—C bond length, in a zigzag arrangement, of 1.57 Å; a C—C—C bond angle of 110.2°.[14] Further, we take the H—C bond length to be 1.17 Å, the C—O bond length equal to 1.36 Å and the radius of Pb equal to 1.2 Å.[15] A molecular length is then:

$$1.17(\mathrm{H{-}C}) + 9 \times 1.57 \sin 55^\circ\,(\mathrm{C{-}C}) + 1.36\,(\mathrm{C{-}O}) + 1.2\,(\mathrm{Pb}) = 15.30\ \text{Å}.$$

This value, when compared with a d spacing of $\simeq 32$ Å, is consistent with an orthogonal arrangement of molecules within the planes as the unheated crystal structure. The molecules must then tilt with respect to the normal of the layer planes on forming the crystalline and smectic phases. The first crystalline phase was formed at a molecular tilt angle of $\simeq 77°$ and the S_c phase at $\simeq 48°$. A similar value for molecular tilt angle in the S_c phase has been reported for thallium octadecanoate.[16]

A plot of transition temperature versus chain length is shown in Figure 5. Connecting curves were drawn on the basis of optical textures and x-ray diffraction patterns. The S_c phase is present in the PbC_6 to C_{12} compounds only and appears to be most stable in those compounds containing eight to ten carbon atoms. The phase is least stable in PbC_{12}. The various crystalline forms are not expected to be of similar structure. For example, Lomer and Perera[17] have found that hydrocarbon chains do not pack into the crystal structure in the same way even in going from copper(II) octanoate to decanoate. This could account, in part, for the differences observed in the polymorphic behaviour between the short and long-chain compounds. Clearly, thermal agitation of the hydrocarbon chain brings about a change in the arrangement of the molecules in the lattice resulting in a mesomorphic change of state. With increasing chain length the effect is reduced, as demonstrated by PbC_{14} and longer chain-length compounds, where crystal polymorphism is observed only.

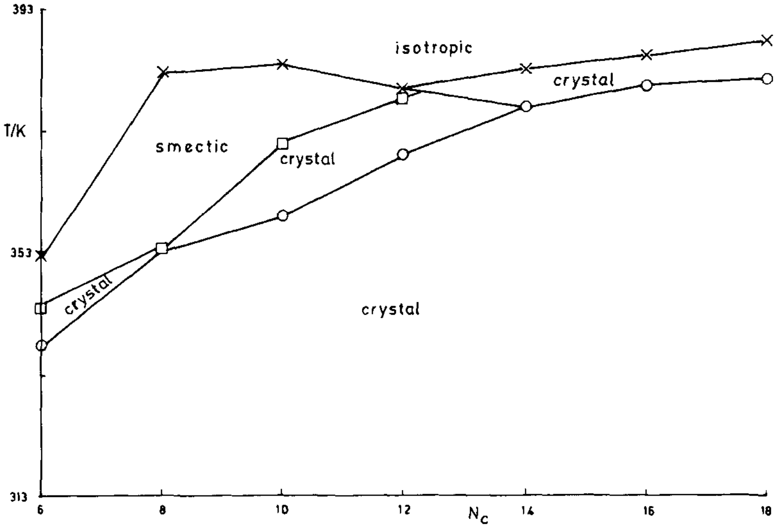

FIGURE 5 Transition temperature versus chain length.

A plot of entropy change versus chain length is shown in Figure 6. A marked increase in entropy with increasing chain length, for crystal to crystal transitions, is observed with the trend becoming less prominent above PbC_{12}. This is consistent with the idea that the major process occurring during formation of this phase is the disordering

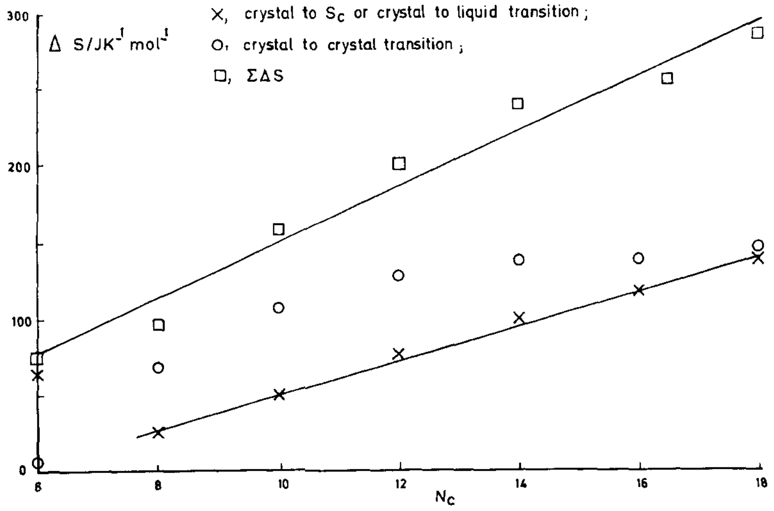

FIGURE 6 Entropy of phase transitions versus chain length. ×, crystal to S_c or crystal to liquid transitions; O, crystal to crystal transitions; □, $\Sigma\Delta S$.

of hydrocarbon chains in the lattice. In addition, the results are interesting in that the near linearity of the plot for the low temperature crystal to S_c or isotropic transition, suggests that the S_c phase is probably similar in structure to this crystalline phase. It is unclear why PbC_6 is an exception. Nevertheless, when total entropy change, $\Sigma\Delta S$, versus carbon chain length is plotted (Figure 6) an excellent linear relationship is obtained with a correlation coefficient of 0.99. The resulting equation of the line, given that N_c is the chain length and R, the gas constant, is:

$$\sum \Delta S/R = -4.10 \pm 2 + 2.22 \pm 0.2\, N_c\,.$$

It is interesting to note that the increment in $\Sigma\Delta S$ for CH_2 group corresponds closely to 2 R ln 3, the expected entropy increase for rotations about two carbon-carbon bonds.

Acknowledgments

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