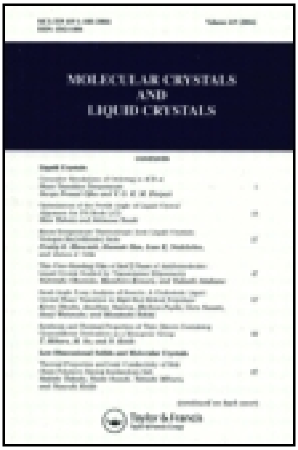

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Thermal Phase Behaviour of Thallium (I) Branched Alkanoates—Influence of Chain Length and Position of Branching on the Occurrence of the (Anhydrous) Neat Phase

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Thermal Phase Behaviour of Thallium (I) Branched Alkanoates— Influence of Chain Length and Position of Branching on the Occurrence of the (Anhydrous) Neat Phase

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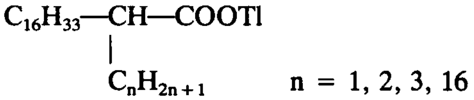
The thermotropic phase behaviour of anhydrous thallium (I) salts of branched chain aliphatic carboxylic acids was investigated by means of DSC and optical polarisation microscopy. The influence of the alkyl chain length and position of branching on the thermotropic phase behaviour was studied. The salts of α-branched acids did not show a stable neat phase. Salts which are alkyl substituted in the β and higher positions do however show stable neat phases. These results are compared with those found for alkali metal alkanoates.

Keywords: neat phase, thallium alkanoates, branched chains

INTRODUCTION

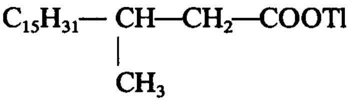
We have recently described the thermal behaviour of water-free thallium (I) salts of homologous aliphatic, alicyclic, and aromatic carboxylic acids with unbranched alkyl chains.[1,2] Most of the salts investigated form the liquid-crystalline neat (lamellar) phase.

In this study the influence of the alkyl chain length and position of branching on the thermotropic phase behaviour of the anhydrous thallium (I) salts of aliphatic carboxylic compounds was investigated by means of differential scanning calorimetry (DSC) and optical polarisation microsocopy:



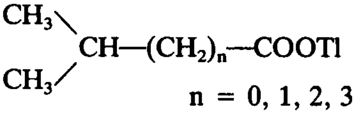
$$C_{16}H_{33}-\underset{\underset{\displaystyle C_nH_{2n+1}}{|}}{CH}-COOTl \qquad n = 1, 2, 3, 16$$

tallium (I)-α-*n*-alkyloctadecanoates



$$C_{15}H_{31}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-COOTl$$

tallium (I)-β-methyloctadecanoate



$$\begin{matrix} CH_3\diagdown \\ CH-(CH_2)_n-COOTl \\ CH_3\diagup \end{matrix} \qquad n = 0, 1, 2, 3$$

thallium (I)-iso-alkanoates

The temperature range investigated was from 300 K to the transition of the salts into the isotropic liquid.

EXPERIMENTAL

Methods

Optical studies of the phases were carried out on a polarising microscope equipped with a hot stage. DSC measurements were made on a Perkin-Elmer DSC-1B apparatus, using sealed aluminium pans. The temperature scale was calibrated by use of the known phase-transition temperatures of azobenzene, benzil, acetanilide, indium and tin. Indium was chosen for the calibration of the transition enthalpies. The error of the measured transition enthalpies amounts to about ±5%. The errors in the temperature measurement are within the limits of 1°K.

Preparation

The α-ethyloctadecanoic acid, α-*n*-propyloctadecanoic acid, and isobutylacetic acid were prepared by the reaction of diethyl malonate with the corresponding alkyl halides, saponification of the alkyl malonic esters and decarboxylation of the alkyl malonic acids.[3] The transition temperatures of the synthesised acids and of the α-methyloctadecanoic acid used, β-methyloctadecanoic acid, and α-n-hexadecyloctadecanoic acid were consistent with the previously published data.[4,5,6,7]

The commercial isobutylic, isovaleric, and isoamylacetic acids were used without further purification.

The salts were produced by neutralisation of the carboxylic acids in alcohol wth aqueous thallium hydroxide solution. They were recrystallised and dried in vacuum. The thallium content of the thallium-α-*n*-alkyloctadeanoates was checked by chemical analysis. The deviations from the stoichiometric composition of the thallium-α-methyloctadecanoate, α-ethyloctadecanoate, and α-n-propyloctadecanoate samples were lower than 0.5%, the deviation for thallium-α-n-hexadecyloctadecanoate was 2%.

RESULTS

The temperatures and enthalpies of the phase transitions are listed in Table I. The different solid phases following the neat phase or the isotropic liquids at lower temperatures were numbered phase 1 and phase 2. This should not be taken to indicate the identity of the type of structures.

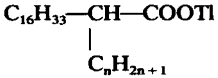
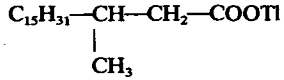
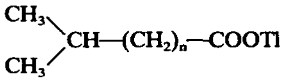
In contrast to the unbranched thallium-octadecanoate,[1] α-branched alkanoates do not exhibit a neat phase. In addition to the solid-isotropic transition in the short-chain compounds (2,3,4) in the substance 5, there was a solid-solid transition also.

All these α-branched thallium-octadecanoates showed supercooling effects and a tendency to form metastable modifications (unlike the fatty acid thallium salts[1]). Therefore, to obtain reproducible transition data a different procedure was necessary in each case. For substance 2 the heating rate was 2 K/min. and for reproducible data a 30 minutes tempering of the samples at 335K was necessary. Investigations of compound 3 were carried out with 8 K/min heating and cooling rates. On cooling of the isotropic melt a transition to an unstable modification was observed. Within a few minutes the unstable modification changed to the stable form. Heating and cooling rates of 2 K/min were used for substance 4. The isotropic–solid transition showed a supercooling of 15°K. The enthalpies observed during cooling agreed well with those obtained by heating. DSC traces of subsequent heating runs were in agreement with those from samples kept at room temperature for five days. The substance 5 was investigated with heating rates of 8 K/min. Only the first heating runs could be employed for data evaluation.

The neat phase of the β-branched compound 6 was identified by its fan texture. The temperature range of the neat phase is small.

TABLE I

Phase transitions of thallium branched alkanoates

		Phase 2–Phase 1		Phase 1–neat		neat–isotropic		Phase 1–isotropic	
		T	ΔH	T	ΔH	T	ΔH	T	ΔH
	 $C_{16}H_{33}{-}\underset{C_nH_{2n+1}}{\underset{\vert}{CH}}{-}COOTl$								
1	n = 0	335.3	14.1	391.6	14.0	441.3	1.3		
2	n = 1							346.4	27.2
3	n = 2							332.7	47.8
4	n = 3							317.0	25.6
5	n = 16	326.0	6.2					339.0	11.4
6	 $C_{15}H_{31}{-}\underset{CH_3}{\underset{\vert}{CH}}{-}CH_2{-}COOTl$	332.1	31.8	350.9	20.4	356.8	1.1		
	 $\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH{-}(CH_2)_n{-}COOTl$								
7	n = 0	349.0	2.6					396.0	6.4
8	n = 1			430.5	5.6	447.6	2.2		
9	n = 2			391.0	4.5	503.4	3.7		
10	n = 3			396.1	7.0	494.9	3.8		

T—transition temperature in K, ΔH—transition enthalpy in kJ/mol.

The thermotropic phase behaviour was complicated by the occurrence of metastable modifications. The first heating run showed the three transitions: phase 2–phase 1 (solid-solid), phase 1–neat, and neat–isotropic. In subsequent heating and cooling runs the solid-solid transition vanished and only the phase 1–neat and neat–isotropic transitions were observed. After cooling a sample (8°K/min) from the isotropic melt to room temperature and keeping the sample at this temperature for 12 hours a subsequent heating run did not show the neat phase and a transition from metastable solid to metastable isotropic took place at 347°K. After keeping this sample at 352°K for three hours subsequent heating and cooling runs showed the phase 1–neat and neat–isotropic transitions.

The phase behaviour of the thallium-isoalkanoates is shown in Figure 1. Some of these salts had previously been studied by Walter[8] using polarisation microscopy and the observed transition temperatures were in good agreement.

By cooling the isotropic melt of substance 7 an unstable neat modification with a short lifetime could be observed. Substance 8 with a branching in the β-position showed a stable neat modification over a small temperature range. In the cases of the next members (n =

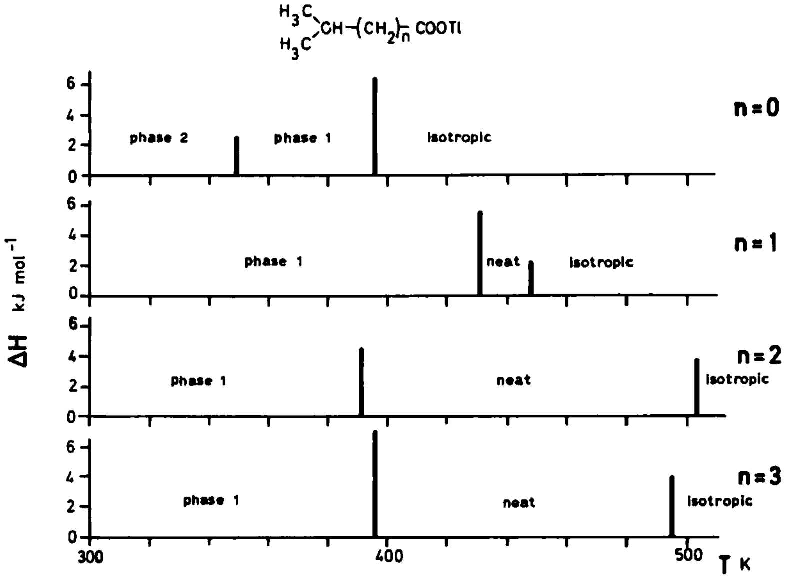


FIGURE 1 Transition temperatures and transition enthalpies of thallium-isoalkanoates.

2,3), extended regions of the neat phase were observed. Because of thermal decomposition only first heating runs were employed for data evaluation of the neat–isotropic values. The neat modifications were again identified by their characteristic fan textures. The textures and the mechanical behaviour of the phases 1 and 2 indicated that they were both crystalline solids.

DISCUSSION

Three general points emerge from the results listed in Table I.

a) None of the thallium-alkanoates which are alkyl-substituted in the position of the second C-atom (α-branched) have a stable neat phase. This was found for compounds with a combination of two short hydrocarbon chains in the 2-position (7), for short/long chain combinations (2,3,4) and a long/long chain combination (5).

b) Those thallium-alkanoates which are alkyl-substituted at the third and higher C-atoms exhibit a stable neat phase. This is true for compounds with two CH_3-groups at the terminal branching position (8,9,10), and for the long/short chain combination (6).

c) When compared with *n*-alkanoates of the same number of C-atoms (see Ref. 1) the β-branched compounds (6 and 8) have distinctly lower clearing temperatures and the temperature range of the neat phase is reduced (see Figure 1).

Note the appearance of a short-lived monotropic neat phase for the α ($n = 0$). Therefore in principle such compounds can form a neat phase but it lies below the crystal-isotropic transition and can only be reached by supercooling.

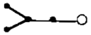
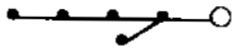
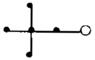
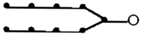
We cannot meaningfully compare solid-neat transition temperatures because the structures of the solid phases of the branched alkanoates and the *n*-alkanoates are unknown.

The ΔH values for the neat–isotropic transition are comparable with those for the n-alkanoates (about 3.5kJ/mol in the *n* C_5 and *n* C_6 compounds and lower values eg. 1.1 kJ/mol in the *n* C_{18} compound).

The neat phases have a layer structure. The layer thickness is less than twice the length of the fully extended molecule but greater than the length of one molecule. There is a head to head alignment of the molecules in the layers. Both the headgroup region and hydrocarbon regions are flexible in a "melting-state."[9] This was also found in the neat phases of the thallium-*n*-alkanoates.[1] It appears that α-branch-

TABLE II

The occurrence of neat phases of thallium- and alkali metal-alkanoates

			Tl	Li	Na	K	Rb	Cs
C_4	unbranched		$-^{1}$	$-^{11}$	$+^{10}$	$+^{10}$	$-^{11}$	$-^{11}$
	α		$+^{8}$ monotr.	$-^{12}$	$-^{12}$	$+^{12}$	$+^{13}$	
C_5	unbranched		$+^{1}$	$-^{14}$	$+^{10}$	$+^{10}$	$+^{14}$	$-^{15}$
	α				$-^{13}$	$+^{13}$		
				$-^{16}$	$-^{16}$	$+^{16}$		
	β			$-^{12}$	$+^{12}$	$+^{12}$		
C_6	unbranched		$+^{1}$	$-^{14}$	$+^{10}$	$+^{10}$	$+^{14}$	$+^{15}$
	α				$-^{13}$	$+^{13}$	$+^{13}$	
			$-^{8}$	$-^{16}$	$-^{16}$	$+^{16}$	$+^{13}$	
	β			$-^{16}$	$-^{16}$	$+^{16}$		
	γ			$-^{12}$	$+^{12}$	$+^{12}$		
C_7	unbranched		$+^{1}$	$-^{14}$	$+^{10}$	$+^{10}$	$+^{14}$	$+^{15}$
	α				$+^{13}$	$+^{13}$		
	δ		$+^{8}$		$+^{13}$	$+^{13}$		
C_8	unbranched		$+^{1}$	$-^{14}$	$+^{10}$	$+^{10}$	$+^{14}$	$+^{15}$
	α		$-^{8}$		$-^{13}$	$+^{13}$		
C_{10}	unbranched		$+^{1}$	$-^{14}$	$+^{10}$	$+^{10}$	$+^{14}$	$+^{15}$
	α		$-^{17}$					

ing, strongly affects the interaction between headgroups and β-branching has a smaller effect. Branching at higher positions has a diminishing influence on the headgroup region and also the interactions within the hydrocarbon region seem to be scarcely affected.

In Table II the effect of chain branching on the whole range of neat phases known for thallium and alkali metal alkanoates is summarised. The presence or absence of a neat phase is indicated by + or −, respectively. None of the lithium soaps studied exhibit a neat phase. However all of the potassium soaps form a stable neat phase (including those with α-branching). For thallium and sodium soaps, the patterns of occurrence of the neat phases were virtually identical (the only exception being the C_4 compounds)—despite the marked differences in the melting and clearing point temperatures. Only a few observations of rubidium and caesium alkanoates have been reported.

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