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Mesomorphic behaviour of praseodymium(III) alkanoates

LIESBET JONGEN, KOEN BINNEMANS*
Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200F,
B-3001 Leuven, Belgium

DIRK HINZ and GERD MEYER
Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6,
D-50939 Köln, Germany

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In this paper, we describe the synthesis, characterization and thermal behaviour of praseodymium(III) alkanoates. The compounds have the stoichiometry $[Pr(C_xH_{2x+1}COO)_3]$, where $x = 5–19$, and were characterized by elemental analysis and infrared spectroscopy. The thermal behaviour was investigated by hot-stage polarizing optical microscopy, DSC and high temperature X-ray diffraction. A highly viscous mesophase M and a smectic A phase were observed for the shorter chain compounds ($x = 5–8$), whereas only a smectic A phase was observed for the longer chain compounds of this type of metallomesogens. The chain length has a pronounced effect on the transition temperatures.

1. Introduction

Metal soaps with elements from the lanthanide series (La, Ce–Lu) were synthesized for the first time by Misra *et al.* in the early 60s [1–2]. These compounds are interesting for their uses as polymer stabilizers, catalysts or optical polymer fibres [3–7]. Surprisingly less information has been reported on the physicochemical properties of lanthanide-containing metal soaps. Most of the reported studies relate almost exclusively to results for complexes in solution, infrared studies or XRD studies at room temperature [8–13]. However, in spite of these results, few data are available on the thermal properties of these compounds. Mehrotra *et al.* [14] and Upadhyaya *et al.* [15] reported the thermal decomposition of lanthanum(III), cerium(III) and terbium(III) soaps, and it was not until very recently that the mesomorphic behaviour of rare-earth soaps was discovered. Marques *et al.* [16] found liquid crystallinity in cerium(III) soaps with long alkyl chains, and observed a pronounced effect of the chain length on the melting point. Binnemans *et al.* [17] identified the mesophase behaviour of lanthanum(III) tetradecanoate and higher homologues as a smectic A phase. Unexpectedly, no liquid crystallinity was observed for the dodecanoates $[Ln(C_{11}H_{23}COO)_3]$, where Ln = Sm–Lu, whereas a mesophase was found for the lanthanum(III), cerium(III), praseodymium(III) and neodymium(III) dodecanoates [18].

In this paper we report on the effect of the chain length on the thermal behaviour of praseodymium(III) alkanoates.

2. Experimental

CH elemental analyses were performed on a CE Instruments EA-1110 elemental analyser. Differential scanning calorimetry (DSC) measurements were made on a Mettler-Toledo DSC 821e-module. Optical textures of the mesophases were observed with an Olympus BX60 polarizing optical microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS 93 programmable temperature controller. High temperature X-ray diffractograms were measured on a STOE Transmission Powder Diffractometer System STADI P, with a high temperature attachment and using monochromatic Cu-K_α ($\lambda = 1.54$ Å) radiation. FTIR spectra were recorded on a Bruker IFS-66 spectrometer, using KBr pellets. Reagents and solvents were used as received without further purification. Analytical grade solvents were used for the recrystallization and washing of the soaps (water contents: ethanol $<0.2\%$; 1-pentanol $<0.2\%$; acetone $<0.3\%$). Praseodymium(III) nitrate hexahydrate was purchased from Aldrich.

3. Results and discussion

3.1. *Synthesis and characterization*

The series of homologous praseodymium(III) alkanoates from praseodymium(III) hexanoate, $[Pr(C_5H_{11}COO)_3]$, to praseodymium(III) eicosanoate, $[Pr(C_{19}H_{39}COO)_3]$,

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*Author for correspondence;
e-mail: Koen.Binnemans@chem.kuleuven.ac.be

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was synthesized by a metathesis reaction between the sodium salt of the corresponding fatty acid and praseodymium(III) nitrate hexahydrate. An aqueous ethanol solution (ethanol : water = 1 : 1) was used for the series [Pr(C_8H_{17}COO)$_3$]–[Pr($C_{12}H_{25}$COO)$_3$]. For the praseodymium(III) alkanoates with short chain lengths (praseodymium(III) octanoate and shorter homologues), water was the reaction medium, because the praseodymium(III) soaps are too soluble in an ethanol : water mixture. For the compounds with the longest chain lengths (praseodymium(III) tetradecanoate and the higher homologues), it was necessary to carry out the reactions in absolute ethanol due to solubility problems with the corresponding sodium salts.

The crude soaps (praseodymium(III) nonanoate and the higher homologues) were recrystallized from a 1-pentanol : ethanol mixture (5 : 1). It was found experimentally that this mixture gave the best crystalline precipitate. The lower homologues were not recrystallized because their purity was sufficiently high after synthesis and careful washing with ethanol and acetone. All the soaps were dried for 24 h *in vacuo* at 40°C.

The carbon and hydrogen contents of the praseodymium(III) soaps were determined by CH elemental analysis. The analysis results are consistent with an alkanoic acid to praseodymium(III) ratio of 3 : 1, but also indicate that under the given reaction conditions only the longer homologues (praseodymium(III) heptadecanoate and longer homologues) can be obtained in a totally anhydrous form. In all the shorter praseodymium(III) alkanoates, water molecules were present. These shorter compounds were hemihydrates [(Pr(C_xH_{2x+1}COO)$_3$] 1/2H_2O, or monohydrates, [(Pr(C_xH_{2x+1}COO)$_3$] H_2O. The degree of hydration does not depend on the drying conditions. When the alkyl chain is longer the complexes are more hydrophobic, so it can be expected that the degree of hydration decreases with increasing chain length. The analysis results for the praseodymium(III) soaps are summarized in table 1. However, thermogravimetric study showed that the water molecules are lost before or at the melting point. In general, the complexes with short chain lengths lose water before the melting point, whereas the hydrated longer homologues lose water at the melting point. For instance, praseodymium(III) octanoate loses its water of hydration at 80–85°C, whereas the compound melts at 90°C (figure 1).

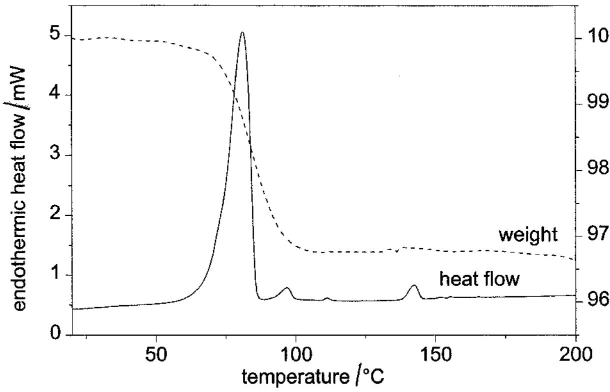

Figure 1. DSC curve (first heating run) and TG curve (dotted line) for praseodymium(III) octanoate. Heating rate is 5°C min^{-1}. The intense endothermic peak is due to the loss of water; the other endothermic peaks correspond to the Cr → M, M → SmA and the SmA → I transitions, respectively.

Table 1. Elemental analysis results for the praseodymium(III)alkanoates. Calculated values are given in brackets and take into account the number of water molecules listed in the right hand column.

Compound	%C	%H	Moles H_2O
[Pr(C_5H_{11}COO)$_3$]	42.71 (42.86)	6.82 (6.99)	1
[Pr(C_6H_{13}COO)$_3$]	46.54 (46.16)	7.58 (7.56)	1
[Pr(C_7H_{15}COO)$_3$]	49.14 (48.98)	8.12 (8.05)	1
[Pr(C_8H_{17}COO)$_3$]	51.06 (51.42)	8.35 (8.47)	1
[Pr(C_9H_{19}COO)$_3$]	53.41 (53.36)	9.13 (8.84)	1
[Pr($C_{10}H_{21}$COO)$_3$]	55.45 (55.45)	9.06 (9.17)	1
[Pr($C_{11}H_{23}$COO)$_3$]	57.03 (57.13)	9.40 (9.46)	1
[Pr($C_{12}H_{25}$COO)$_3$]	58.40 (58.63)	9.71 (9.71)	1
[Pr($C_{13}H_{27}$COO)$_3$]	60.17 (59.98)	9.84 (9.95)	1
[Pr($C_{14}H_{29}$COO)$_3$]	61.93 (61.83)	10.04 (10.18)	0.5
[Pr($C_{15}H_{31}$COO)$_3$]	62.86 (62.93)	10.20 (10.37)	0.5
[Pr($C_{16}H_{33}$COO)$_3$]	64.54 (64.53)	10.47 (10.51)	0
[Pr($C_{17}H_{35}$COO)$_3$]	64.77 (65.43)	10.54 (10.68)	0
[Pr($C_{18}H_{37}$COO)$_3$]	65.91 (66.25)	10.88 (10.83)	0
[Pr($C_{19}H_{39}$COO)$_3$]	66.64 (66.74)	11.02 (10.96)	0

3.2. *Infrared spectroscopy*

Vibrational spectroscopy of long chain carboxylates provides information on the metal-ion/carboxylate coordination, on the chain conformation and on the packing of the alkyl chain. Infrared spectra in the region 400–4000 cm^{-1} were recorded for all praseodymium(III) carboxylates. In figure 2 the IR spectrum of praseodymium(III) tridecanoate is given.

The symmetric and asymmetric stretching modes for the methyl and methylene groups occur in the 3000–2800 cm^{-1} region. The C=O stretching vibration observed in the alkanoic acid around 1700 cm^{-1} disappears in the praseodymium(III) alkanoates and is replaced by two new absorption bands. These bands correspond to the symmetric (1410–1420 cm^{-1}) and asymmetric (1520–1550 cm^{-1}) stretching vibrations of the carboxylate ion. According to several authors [16, 19, 20], the interaction between the praseodymium ion and the carboxylate group can be evaluated by considering the splitting of the two carboxylate bands, $\Delta\nu = \nu_{\text{asymm}} - \nu_{\text{symm}}$; this is 120–130 cm^{-1} in our complexes. This splitting is lower than the carboxylate stretching vibrations in alkali soaps ($\Delta\nu = 138$ cm^{-1}) [21], but indicates that the praseodymium(III)–carboxylate bond is largely ionic. From the observed splitting we could conclude that the praseodymium(III)–carboxylate interaction must be bidentate chelating. However, we do not think this approach is very suitable for lanthanide(III) alkanoates. The splitting of the asymmetric and symmetric stretching vibration of the carboxylate anion does not depend on the chain length, or on the lanthanide ion [18, 22]. We were able to determine the single crystal structure of neodymium(III) butyrate monohydrate [22]. It was found that there are several types of neodymium(III)–carboxylate coordination (i.e. bridging bidentate and bridging tridentate), although the splitting of these bands is the same (125 cm^{-1}) as for the longer lanthanide(III) soaps. This indicates that more than one type of carboxylate coordination is present in these compounds.

Further structural information is obtained from the number of CH$_2$ wagging progression bands in the 1350–1150 cm^{-1} region. There is an experimental relation between the number of wagging bands and the alkyl chain length, if the alkyl chain is in an all-*trans* conformation [23]. For an even number of carbon atoms in the alkyl chain, the number of IR bands is $n/2$ (n being the total number of C atoms in the chain). For an odd number of C atoms, the number of IR bands is equal to $(n+1)/2$. This relation can easily be seen in all the IR spectra of the praseodymium(III) alkanoates.

Information about the chain packing can be obtained from a band of medium intensity at 720 cm^{-1} [23]. This band is assigned to the in-phase rocking mode of CH$_2$ groups. The shape of this peak is highly dependent on the alkyl chain packing geometry for aliphatic compounds. For triclinic or hexagonal chain packing a single band is expected. This is the case for the praseodymium(III) alkanoates.

3.3. *Thermal behaviour*

The thermal behaviour of the praseodymium(III) alkanoates was investigated by DSC, hot-stage polarizing optical microscopy (POM) and by XRD at high temperatures. The compounds of the series [Pr(C$_5$H$_9$COO)$_3$]–[Pr(C$_{19}$H$_{37}$COO)$_3$] show in the DSC curves multiple melting phenomena, indicating the presence of a mesophase. This was confirmed by microscopic observations. In figure 3 the DSC trace of [Pr(C$_{13}$H$_{27}$COO)$_3$] is shown (first heating and cooling cycle). Both melting and clearing peaks are quite distinct. In the cooling run, a supercooling is observed for the clearing peak. This is due to the ionic nature of the compounds.

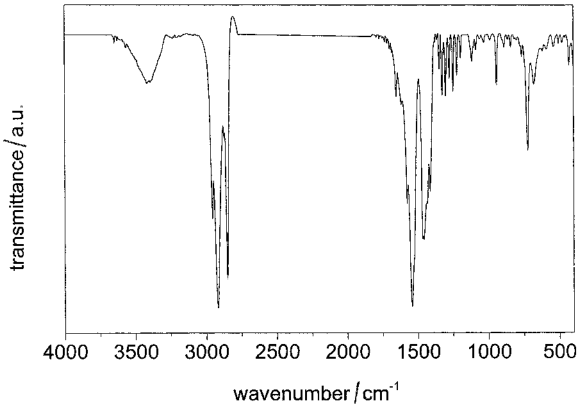

Figure 2. Infrared spectrum of praseodymium(III) tridecanoate.

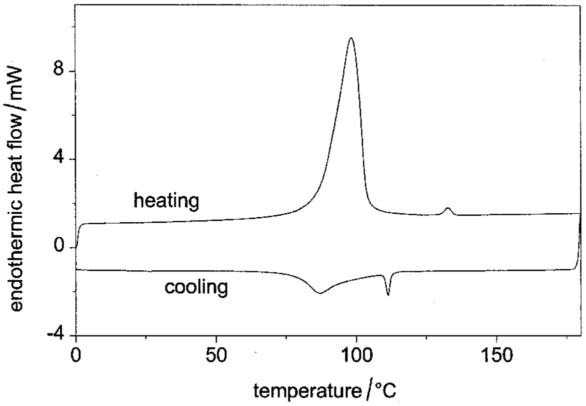

Figure 3. DSC thermogram of praseodymium(III) dodecanoate (first heating–cooling cycle). Endothermic peaks point upwards.

The mesophase was investigated by hot-stage POM, although it is not easy to obtain a good optical texture. Most often, the texture had a grainy appearance with white–yellow zones on a dark background. The textures looked very similar to those reported by Marques *et al.* for cerium(III) soaps [16]. The mesophase type could be determined unambiguously only by high temperature XRD.

The X-ray diffractogram of [$Pr(C_{11}H_{23}COO)_3$] at room temperature is given in figure 4. Up to six peaks were observed in the low angle region of the X-ray powder diffractogram of the solid praseodymium(III) alkanoates, with the peak at the lowest angle having by far the highest intensity. The *d*-spacing values are in the ratio 1 : 1/2 : 1/3 ... 1/*n*. These diffraction peaks correspond to the successive (0 0 *l*) reflections, and indicate the presence of a lamellar structure. The polar groups of the praseodymium(III) alkanoates are localized in infinite, parallel and equidistant planes. These planes are separated from each other by a bilayer of alkyl chains in the all-*trans* conformation. The interplanar layer spacing *d* corresponds to the distance between two successive layers of praseodymium(III) ions. In figure 5 a schematic representation of the bilayered structure at room temperature is given.

It should be noted that although these compounds are not anhydrous, the presence of water influences neither the lamellar structure nor therefore the mesophase behaviour. This is because the water molecules are situated in the ionic layer of these compounds. In figure 6 the X-ray diffractogram of [$Pr(C_{11}H_{23}COO)_3$] in the mesophase is given. In the mesophase, the lamellar bilayer structure is retained, but a distinct decrease in *d*-spacing is observed at the solid–mesophase transition. This indicates that the alkyl chains lose their all-*trans* conformation and that some kind of folding occurs. At the clearing point, all structure is lost, and an ionic melt is formed. The temperature dependence of the *d*-spacing in the mesophase (decrease of *d*-spacing with increasing temperatures) corresponds to the behaviour expected for

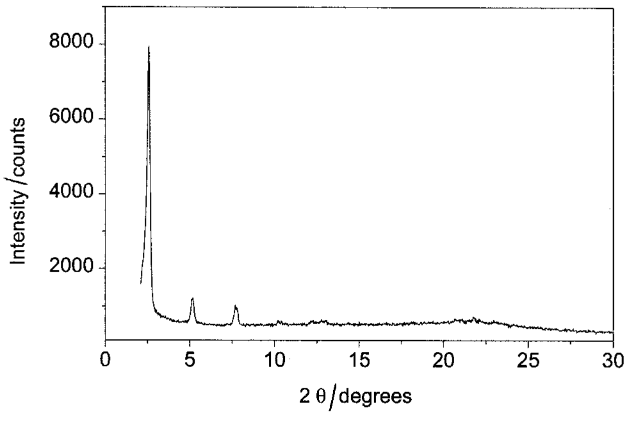

Figure 4. Room temperature X-ray diffractogram of praseodymium(III) dodecanoate.

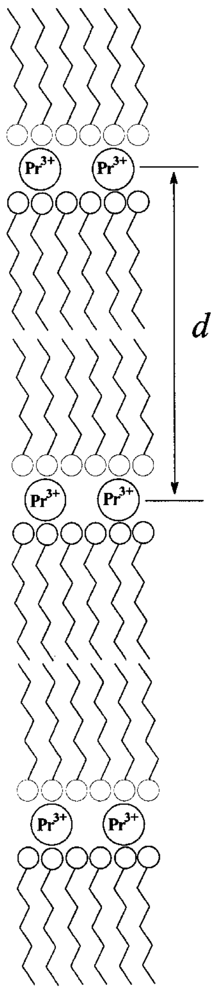

Figure 5. Schematic structural representation of praseodymium(III) heptanoate at room temperature.

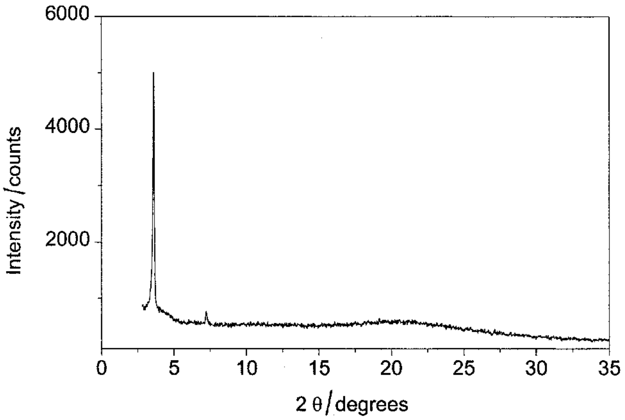

Figure 6. High temperature X-ray diffractogram of praseodymium(III) dodecanoate in the mesophase at 120°C.

a smectic A phase (figure 7) [24]. On the other hand, the *d*-spacing of the solid compound is virtually independent of temperature.

The whole series of compounds synthesized exhibits mesomorphism, although there is a marked influence of the chain length on the transition temperatures. Whereas the melting point increases when the chain length increases, the clearing point decreases. This destabilization of the mesophase with increasing chain length is due to less favourable interactions of the alkyl chains with increasing length, and is also known for neodymium(III) alkanoates [22]. Although there is a similar influence of the chain length on the thermal behaviour to that for the neodymium(III) alkanoates, there is still a difference, i.e. no mesomorphism is shown by neodymium(III) alkanoates when the total number of carbon atoms in the ligand is larger than 15—neodymium(III) pentadecanoate is mesomorphic, neodymium(III) hexadecanoate is not.

Another influence of the chain length on the thermal behaviour (table 2) is the occurrence of a second mesophase for shorter chain lengths, praseodymium(III) hexanoate to nonanoate. This mesophase was detected

Table 2. Thermal behaviour of the praseodymium(III) alkanoates. Cr = crystalline phase; M = mesophase; SmA = smectic A phase; I = isotropic liquid. The temperatures listed are those observed by hot-stage POM.

Compound	Transition	Temperature/°C	ΔH/kJ mol^{-1} [a]
$[Pr(C_5H_{11}COO)_3]$	Cr → M	86	n.d.[b]
	M → SmA	109	n.d.
	SmA → I	142	4.08
$[Pr(C_6H_{13}COO)_3]$	Cr → M	90	n.d.
	M → SmA	111	n.d.
	SmA → I	144	2.11
$[Pr(C_7H_{15}COO)_3]$	Cr → M	90	6.78
	M → SmA	112	0.14
	SmA → I	144	1.89
$[Pr(C_8H_{17}COO)_3]$	Cr → M	86	65.8
	M → SmA	95	n.d.
	SmA → I	135	0.72
$[Pr(C_9H_{19}COO)_3]$	Cr → SmA	90	86.6
	SmA → I	136	1.03
$[Pr(C_{10}H_{21}COO)_3]$	Cr → SmA	99	116.8
	SmA → I	133	1.17
$[Pr(C_{11}H_{23}COO)_3]$	Cr → SmA	102	123
	SmA → I	129	0.96
$[Pr(C_{12}H_{25}COO)_3]$	Cr → SmA	105	134
	SmA → I	124	1.02
$[Pr(C_{13}H_{27}COO)_3]$	Cr → SmA	106	88.3
	SmA → I	122	0.96
$[Pr(C_{14}H_{29}COO)_3]$	Cr → SmA	110	62.0
	SmA → I	120	1.51
$[Pr(C_{15}H_{31}COO)_3]$	Cr → SmA	112	61.5
	SmA → I	120	0.94
$[Pr(C_{16}H_{33}COO)_3]$	Cr → SmA	113	n.d.
	SmA → I	118	n.d.
$[Pr(C_{17}H_{35}COO)_3]$	Cr → SmA	115	n.d.
	SmA → I	119	n.d.
$[Pr(C_{18}H_{37}COO)_3]$	Cr → SmA	116	n.d.
	SmA → I	120	n.d.
$[Pr(C_{19}H_{39}COO)_3]$	Cr → SmA	117	n.d.
	SmA → I	122	n.d.

[a] First heating run.
[b] n.d. = not determined.

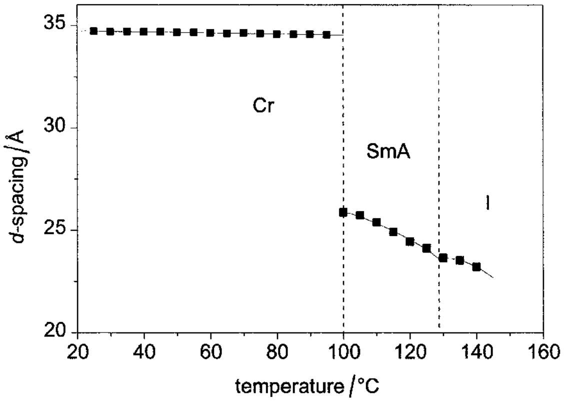

Figure 7. Change in the *d*-spacing of praseodymium(III) dodecanoate as a function of temperature.

by DSC and by hot-stage POM. However, there is no change in *d*-spacing in the X-ray diffractograms at the transition temperature, although we observed a marked decrease in viscosity when going from mesophase M to the SmA phase (figure 8). Therefore we propose for this mesophase M a bilayer structure with molten alkyl chains, but with restricted rotation due to the two-dimensional network structure of the ionic layer. This is in contrast to the SmA phase where the lanthanide ions can rotate in the ionic layers. DSC traces show that the M↔SmA transition is reversible.

The occurrence of this kind of lamellar mesophase was also observed for the shorter homologues of the neodymium(III) alkanoates [22]. In figure 9 the phase diagram of the praseodymium(III) alkanoates is shown. The transition temperatures were determined by DSC and confirmed by hot-stage POM.

Although it could be expected for these compounds, an odd–even effect is not observed. This can easily be understood by considering the bilayered structure of these compounds. Thus, when one methylene group is added to an alkanoic acid, the bilayered praseodymium(III) alkanoate is enlarged by two additional methylene groups and the total number of carbon atoms in the lamellar structure is always even.

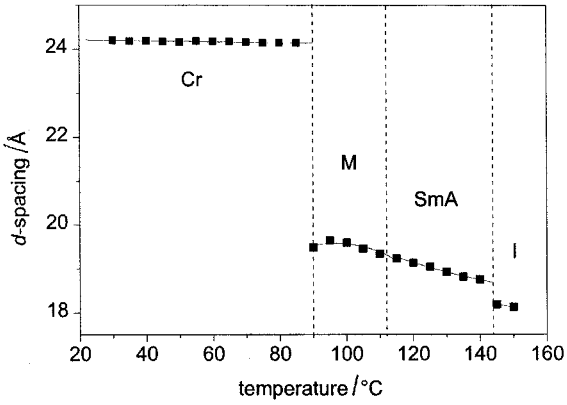

Figure 8. Change in the *d*-spacing of praseodymium(III) octanoate as a function of temperature.

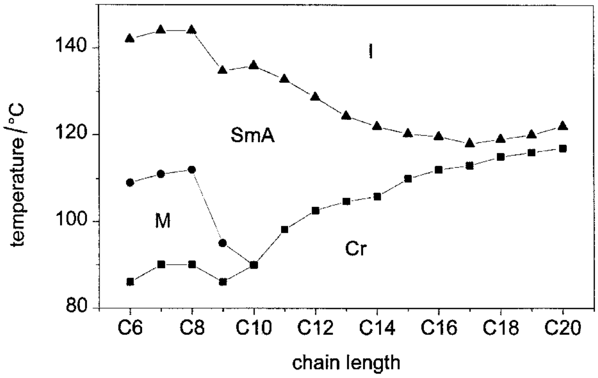

Figure 9. Phase diagram of the praseodymium(III) alkanoates. The compounds are labelled with the number of carbon atoms in the alkanoate groups, e.g. C10 stands for praseodymium(III) decanoate.

The loss of water of hydration does not affect the transition temperatures. The temperatures are the same in the first and second heating runs. Differences in melting enthalpy were however observed between the first and the second heating runs; especially for the hydrated longer homologues, the differences in enthalpy were large. This is because these compounds lose their water of hydration at the melting point, contributing to the enthalpy of the endothermic peak.

4. Conclusion

We have reported the synthesis, characterization and thermal behaviour of praseodymium(III) alkanoates. The compounds have the stoichiometry [$\mathrm{Pr(C_xH_{2x+1}COO)_3}$]. From infrared spectroscopy and from comparisons with single crystal data for analogous compounds, it was found that several forms of praseodymium–carboxylate ion coordination are present in the compounds and that the alkyl chain is in the all-*trans* conformation. A lamellar mesophase was identified as a smectic A phase by hot-stage POM and XRD at high temperatures, although a mesophase M is also present for the shorter homologues at lower temperatures.

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