Structure and Mesomorphism of Silver Alkanoates

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Silver salts of the higher straight-chain alkanoic acids (silver soaps) and especially silver(I) behenate and silver(I) stearate are being used as the silver source in thermographic and photothermographic materials. The silver(I) alkanoates exhibit a complicated thermal behavior, and different phase transitions can be detected between the solid, crystalline state and the onset point of thermal decomposition. The phase transitions are due to a gradual breakdown of the layerlike structure of these compounds, and some of the phases are viscous mesophases. The silver alkanoates of the homologous series between silver propionate ($C_3H_5O_2Ag$) and silver tetracosanoate ($C_{24}H_{47}O_2Ag$) have been prepared, as well as silver hexacosanoate ($C_{26}H_{51}O_2Ag$) and silver octacosanoate ($C_{28}H_{55}O_2Ag$). The light stability of the compounds increases with increasing chain length. The room-temperature X-ray diffractograms indicate that the silver alkanoates consist of a bilayer structure. The thermal properties of these silver-containing metallomesogens were investigated by high-temperature X-ray diffraction, differential scanning calorimetry, and polarizing optical microscopy. The number and the nature of the phase transitions depends on the alkyl chain length. The thermal decomposition of the silver alkanoates with long alkyl chains proceeds in a liquid-crystalline state (mesophase), and leads to the formation of silver. The thermal behavior of silver behenate is discussed in detail.

Introduction

Silver salts of the long-chain alkanoic acids (fatty acids) are being used as the silver source in thermographic and photothermographic materials.[1−4] A visible image is created by reduction of the silver(I) ions to silver(0) nanoparticles during the development process. In contrast to the silver halides, the silver alkanoates in dry imaging materials are quite light insensitive and this insensitivity toward light increases with increasing alkyl chain length. The most often used silver alkanoates in thermographic materials are silver behenate, silver stearate, or a mixture thereof.[1] Because of its well-defined layer periodicity with large interlayer spacings, silver behenate also finds application as a low-angle calibration standard for X-ray diffractometers[2] and for small-angle neutron scattering (SANS) instruments.[3]

Although the layerlike structure of silver behenate and the other long-chain silver alkanoates was observed for the first time more than half a century ago,[4,5] until recently hardly anything was known about the position of the silver ions in the unit cell and about their coordination. This lack of data was mainly due to the difficulties in obtaining single crystals of a quality sufficient for single-crystal X-ray diffraction. Tolochko et al. refined the structure of silver stearate by using EXAFS data and unit cell parameters obtained from XRD powder data.[6] They found that in the solid state, silver stearate is a dimer, consisting of two silver ions bridged by two bidentate carboxylate groups of the stearate molecules. The silver−silver distance (2.90 ± 0.03 Å) in the eight-membered chelate rings is very similar to the silver−silver distance in metallic silver. The dimers are stacked one next to another and there

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are weak silver−oxygen−silver interactions between neighboring molecules, so that a layerlike structure is formed. The layers containing the silver atoms can be considered as sheetlike coordination polymers.

The knowledge of the thermal behavior of the silver alkanoates is of importance for an understanding of the thermographic process. Silver behenate and the other silver alkanoates do not simply melt in one step upon heating, but they undergo a series of phase transitions before they melt with thermal decomposition.[7−12] Although some of these transitions are crystal-to-crystal transitions, most of them are mesophase transitions. The thermal behavior of the silver alkanoates is much more complex than the thermal behavior of the other transition-metal alkanoates or of the lanthanide(III) alkanoates[13,14] and is more reminiscent to that of the alkanoates of the alkali and earth-alkaline metals[15,16] or of thallium(I).[17−20] Whereas the thermal behavior of the alkali and earth-alkaline metals has been studied in depth, much less is known about the nature of the phase transitions in the silver alkanoates.[7−12] The most detailed study of the thermal properties so far, is the work of Bokhonov et al.[12] These authors have studied the thermal behavior of silver laurate, myristate, palmitate, and stearate by DSC, polarizing optical microscopy, and in-situ high-temperature small-angle X-ray scattering. They found that the silver soaps undergo an irreversible phase transition in the 110−120 °C temperature range. The high-temperature phase has a higher symmetry than the crystalline phase at ambient temperatures. It was also shown that mechanical activation of the compounds by ball-milling induces phase transitions. Of interest is also the formation of silver nanoparticles by thermal decomposition of silver alkanoates of perfluoroalkanoates.[21,22]

In this paper, the lamellar structure and mesomorphism of the members of the homologous series of silver alkanoates (silver soaps) is discussed. The thermal behavior of the compounds has been investigated by high-temperature X-ray diffraction, differential scanning calorimetry (DSC), and polarizing optical microscopy (POM). Throughout the paper, the silver alkanoates are labeled by a short notation, AgC_x, which indicates the total number of carbon atoms in the alkanoate group. For instance, AgC_{18} stands for silver stearate.

Experimental Section

Materials and Methods. Elemental analyses (C, H) were carried out on a CE Instruments EA-1110 elemental analyzer. Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC 821e module. Samples of 2−5 mg were put in aluminum crucibles with a pierced lid and were heated or cooled at a scan rate of 10 °C min^{-1} under a helium flow. Indium metal was used as standard for the calibration of the instrument ($T_m = 156.6 \pm 0.3$ °C, $\Delta H_m = 28.45 \pm 0.6$ J g^{-1}). Optical textures of the mesophases were observed with an Olympus BX60 polarizing optical microscope equipped with a LINKAM THMS600 hot stage and a LINKAM TMS93 programmable temperature-controller. XRD measurements were carried out with a Philips X′Pert X-ray diffractometer (Cu Kα_1 radiation, 1.54 Å), equipped with a high-temperature chamber (Anton Paar HTK16, with a platinum filament and an Anton Paar TCU2000 heat controller). To obtain an overview of the temperature phenomena, in-situ temperature profiling occurred in the range from 25 to 200 °C with temperature intervals of 10 °C, and the XRD area was scanned from 5°−55° 2θ. The error on the experimentally determined *d*-spacings is estimated to be ±0.05Å.

General Procedure for the Synthesis of the Silver Alkanoates. The organic silver salts $C_xH_{2x-1}O_2Ag$ (AgC_x), $x = 3-24$, 26, 28, were prepared by a metathesis reaction between an ethanolic solution of the sodium salt of the corresponding fatty acid (alkanoic acid) and an aqueous solution of silver nitrate. To avoid photochemical decomposition, the glassware was wrapped in aluminum foil. The alkanoic acid (2.94×10^{-3} mol) was dissolved in 150 mL of ethanol and transformed into the corresponding sodium carboxylate by adding an equivalent amount of a 0.5 M NaOH standard solution (addition via a buret). Subsequently an aqueous solution of silver nitrate (2.94×10^{-3} mol) was added dropwise to the sodium alkanoate solution. A white precipitate immediately formed. After addition was complete, the solution was stirred for 1 h at ambient temperature. Subsequently the precipitate was filtered off on a Büchner funnel and thoroughly washed with water. Finally, the silver alkanoate was dried for 24 h in vacuo at room temperature. The purity of the organic silver salts was checked by C, H elemental analysis (combustion analysis). The C, H data are available as Supporting Information. After neutralization of the alkanoic acid by the sodium hydroxide solution, one has to check that the solution is neutral and not alkaline. If necessary, the pH has to be adjusted to pH 7 by addition of some drops of a diluted HNO_3 solution. When the solution of the sodium alkanoate is too alkaline, a precipitation of silver(I) hydroxide (AgOH, gray) or silver(I) oxide (Ag_2O, brown) is formed.

Results and Discussion

Synthesis. The silver alkanoates of the homologous series between silver propionate (AgC_3) and silver tetracosanoate (AgC_{24}) and in addition silver hexacosanoate (AgC_{26}) and silver octacosanoate (AgC_{28}) were prepared by a metathesis reaction between the sodium salt of the corresponding alkanoic acid and silver nitrate. The complexes were prepared in glassware that was wrapped in aluminum foil to shield the silver salts from light. The compounds were obtained as white powders. The light stability decreases with decreasing alkyl chain length: the color of the compounds with a

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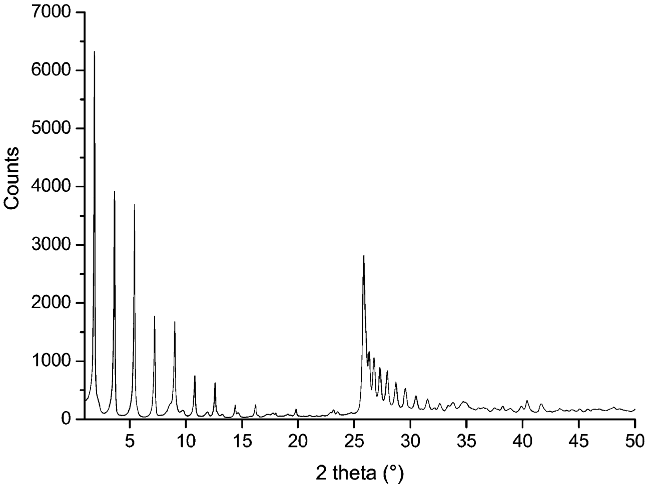

Figure 1. Room-temperature X-ray powder diffractogram of silver behenate (AgC_{22}).

short chain turns from white to whitish purple upon exposure to day light, indicating the formation of small silver metal clusters. This behavior was not observed for the silver alkanoates with long alkyl chains.

Room-Temperature XRD. Room-temperature X-ray powder diffractograms were recorded for the series of silver compounds ranging from AgC_6 to AgC_{24}. The X-ray diffractogram of silver behenate at room temperature is shown in Figure 1. In the small angle region a set of well-defined diffraction peaks is observed. The d-spacing values of these diffraction peaks are in the ratio $1:{}^1/_2:{}^1/_3:...:{}^1/_n$. These diffraction peaks belong to the ($00l$) reflections. Such a diffraction pattern is consistent with a layer structure. The fact that more than six higher order diffraction peaks can be observed indicates the presence of well-defined layers. Because the d-spacing (interlayer distance) is about twice the calculated length of the silver behenate molecule, the compound has a bilayer structure. In the room-temperature X-ray powder diffractogram of silver behenate, we observe around $2\theta = 26$ ° an intense peak that disappears when the compound is heated above 120 °C. Presently, we do not know whether this feature is an artifact or whether it is for instance caused by preferential orientation of the crystal particles.

The X-ray diffractograms of the other compounds have a similar appearance as the diffraction pattern of silver behenate. Of course, the absolute position of the diffraction peaks depends on the alkyl chain length. The maximum average d-spacing of the bilayer structure ($d_{\max}$) was calculated for an all-trans conformation of the alkyl chain perpendicular to the metal ion base plane by the use of eq 1[24]

$$d_{\max} = 2d_{C-H} + 2(n-1)d_{C-C}\sin 55° + 2d_{C-O} + r_{Ag+} \quad (1)$$

where n is the total number of carbon atoms in the chain and taking $d_{C-H} = 1.09$ Å, $d_{C-C} = 1.54$ Å, $d_{C-O} = 1.36$ Å, and $r_{Ag+} = 1.15$ Å. In Table 1, the experimental and calculated d-spacings of the silver alkanoates as a function of the number of carbon atoms in the alkanoate group are given. The experimental d-spacings (d_{exp}) were obtained by measuring the position of the (001) reflections of the silver alkanoates with short alkyl chains and the position of the (002) reflections of the silver alkanoates with long alkyl chains [because for the latter compounds the (001) reflection was outside the detector range]. The interlayer distances of the silver soaps increase linearly with the number of carbon atoms in the alkanoate group, or equivalently, the interlayer distances increase linearly with the number of methylene groups of the alkyl chain. It may be noted that the long spacings of these metal soaps increase linearly with the number of carbon atoms in the fatty acids. Linear regression analysis of the experimental interlayer spacing as a function of the number of methylene groups gave a slope of 1.21 Å per CH_2 group and an intercept of 10.08 Å. The intercept takes into account the size of the methyl group and the coordinating unit (carboxylate group and silver atom). These results can be rewritten as $x = 10.08 + 2.42(y - 2)$, where y is the number of carbon atoms in the alkanoate group. This equation allows the estimation of the d-spacing of silver alkanoates other than those studied here. Matthews et al.[5] gave for the silver alkanoates the equation $x = 9.85 + 2.44(y - 2)$, which is comparable with our results. The increment of 1.21 Å per CH_2 group is close to the increment calculated by applying eq 1 for the idealized double layer structure with the chains in the all-trans conformation, 1.26 Å. For the homologues series of silver thiolates, 1.25 Å per CH_2 group and an intercept of 7.85 Å have been found.[25] The differences in the intercept between the silver thiolates and the silver alkanoates can be related to the differences in size of the thiolate group in comparison with the carboxylate group. The all-trans conformation of the alkyl chains in silver alkanoates was also discussed by Lee et al.[21]

Table 1. Experimental and Calculated d-Spacings of the Silver Alkanoates[a]

compd	d_{exp} (Å)	d_{calc} (Å)	compd	d_{exp} (Å)	d_{calc} (Å)
AgC_6	19.59	18.66	AgC_{16}	43.91	43.89
AgC_7	22.37	21.19	AgC_{17}	46.87	46.42
AgC_8	24.61	23.71	AgC_{18}	48.54	48.94
AgC_9	27.29	26.23	AgC_{19}	51.72	51.46
AgC_{10}	29.22	28.76	AgC_{20}	53.48	53.99
AgC_{11}	32.24	31.28	AgC_{21}	56.63	56.51
AgC_{12}	34.11	33.80	AgC_{22}	58.43	59.03
AgC_{13}	37.06	36.33	AgC_{23}	61.56	61.56
AgC_{14}	38.92	38.85	AgC_{24}	63.10	64.08
AgC_{15}	42.07	41.37			

[a] The d_{exp} values were determined by X-ray powder diffraction, and the d_{calc} values were calculated using eq 1.

Because the average $d_{\max}$ values obtained experimentally by X-ray diffraction, which correspond to the distance between two consecutive silver-containing basal planes, are in good agreement with the values calculated for a lamellar bilayer arrangement, there is little interdigitation of the ends of the alkyl chains into the next layer, and the alkyl chains are only slightly titled to the metal ion layers. In the case of interdigitation or tilting, the experimental d-spacing would be smaller than the calculated value. We found that consistently the experimental d-value of the silver

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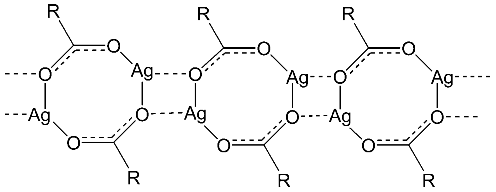

Figure 2. Schematic representation of a silver behenate dimer.

alkanoates with short alkyl chains is larger than the calculated values. It is difficult to explain these findings with a structural model. The most likely explanation is that the compounds with a short alkyl chain contain a small amount of crystal water (which remained undetected by C, H analysis). Incorporation of water molecules in the crystal lattice can cause expansion of the crystal lattice. Our experimental results are consistent with the structural model of Tolocho et al. for silver stearate.[6] This model is based on EXAFS measurements and the single-crystal structure of silver alkanoates with short alkyl chains. According to Tolocho's model, the silver ions are bridged by the carboxylate group of the alkanoate molecules, forming eight-membered chelate rings (two silver atoms, four oxygen atoms, two carbon atoms). Therefore, the structure of the silver alkanoates consists of $[Ag(C_nH_{2n+1}COO)]_2$ dimers (Figure 2). The bilayer structure of silver behenate is presented in Figure 3. The layers are parallel to one another and have in principle an infinite extension (in practice, the layers are extended up to the domain borders). Because of the structure of inorganic layers (the carboxylate groups and the silver ions) alternating with an organic layer (the double layers of alkyl chains), the silver alkanoates can be considered as *inorganic–organic hybrid materials*.

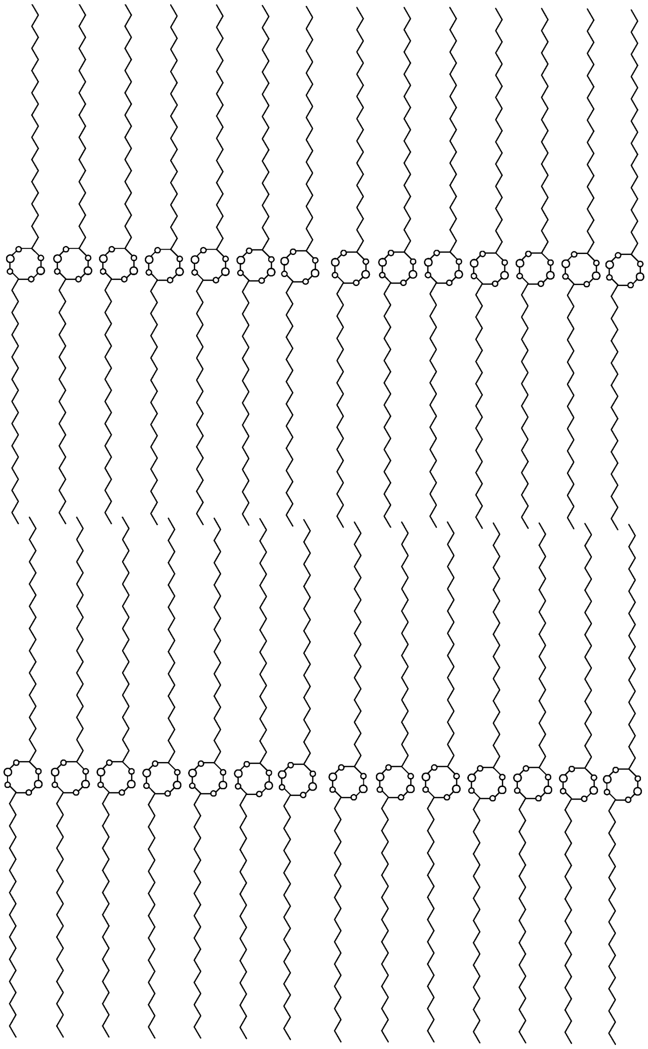

Figure 3. Schematic representation of the bilayer structure of silver behenate at room temperature.

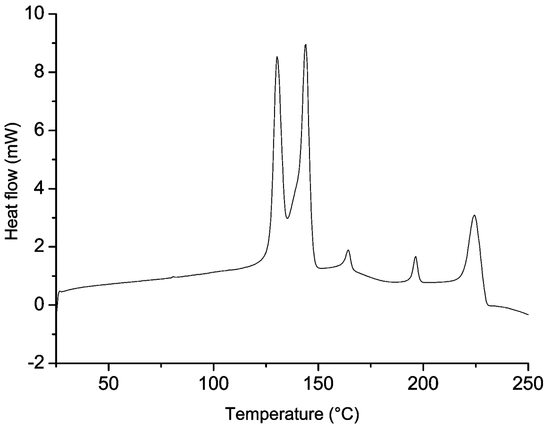

Figure 4. DSC curve of silver behenate. Endothermic peaks are pointing upward. Transitions are observed at 131, 145, 166, 194, and 219 °C. The second transition (145 °C) corresponds to the melting point of the compound.

Thermal Behavior. The thermal behavior of silver behenate (silver docosanoate, AgC_{22}) and the other silver alkanoates was investigated by differential scanning calorimetry (DSC) and by polarizing optical microscopy. For silver behenate, X-ray powder diffractograms were recorded at different temperatures. The DSC thermogram of silver behenate is shown in Figure 4. When silver behenate is heated on a hot-state and observed between crossed polarizers by POM (also use of a $\lambda/4$ plate was made), no changes are observed until 145 °C, although an intense endothermic peak is observed in the DSC at 131 °C ($\Delta H = 70$ J/g). In the XRD diffractograms a drastic decrease of the crystallinity of silver behenate crystals is observed. At 145 °C, also in the DSC an endothermic peak is observed ($\Delta H = 74$ J/g), but when we press on the cover glass with a needle, the compound is found to flow under the applied pressure and a birefringent liquid is obtained. The texture did not show typical features, except that it had a grainy appearance (alike the texture of a poorly aligned smectic phase). No texture changes were observed by POM for the endothermic peak in the DSC-trace at 166 °C ($\Delta H = 6$ J/g), but it can be noticed that the product that was colorless so far starts to show some brown spots and that the viscosity decreases slightly. This transition is a mesophase-to-mesophase transition. Above 194 °C, the product turns brown rapidly due to thermal decomposition, and a sharp decrease in viscosity is observed. In the DSC trace an endothermic peak with $\Delta H = 5$ J/g was observed. The liquid is still birefringent, but the mesophase has a stronger tendency to align homeotropically. At 219 °C a sharp decrease in viscosity is observed; this is most probably the clearing point, although this was difficult to assess because of the strong thermal decomposition. The DSC thermogram shows an endothermic peak ($\Delta H = 30$ J/g).

At room temperature, the structure of silver behenate is as discussed above and as shown in Figure 3. The alkyl chains are in the all-trans conformation with the alkyl chain perpendicular to the layers formed by the carboxylate groups and the silver atoms. The transition at 131 °C is a transition in the solid state, a so-called crystal-to-crystal transition. What happens is that the alkyl chains are packed in a different manner. We do not have evidence that this transition is one from a less to a more symmetric phase (as was observed by Bokhonov et al.[12] for the silver alkanoates with shorter chain lengths), because of the decrease of the intensities of the diffraction peaks in the X-ray diffractogram. At 145 °C, the alkyl chains are transformed from an ordered crystalline state to a disordered liquid state, while the layer structure remains intact. The alkyl chains are now in a molten state. One can say that 145 °C is the melting point of silver behenate and the compound is transformed into a mesophase. It is difficult to observe the melting point visually by just having a look at the compound, because the mesophase has a high viscosity. However, the fact that the compound flows when one presses with the tip of a needle on the cover glass shows that this phase is no longer a crystalline phase. It is not a waxy phase either, because a wax deforms irreversible when one presses with a needle on the cover glass. The mesophase has some "elasticity". The identification of the mesophases of silver behenate (and of the other silver alkanoates) by making use of the textures observed between crossed polarizers in a polarizing optical microscope is very difficult, because well-formed textures could not be obtained. In principle, the best textures are observed when the mesophase is obtained by cooling the isotropic liquid, rather than by heating the solid compound. Because of the thermal decomposition of the compounds in the high-temperature mesophases and in the isotropic liquid, this could not be done. The mesophase formed at 145 °C is a highly ordered smectic mesophase, but exact identification is impossible. The gradual decrease of the viscosity upon further heating indicates that the mesophase becomes more and more alike a smectic A phase (i.e. the least ordered among the different smectic phases). Because the silver nanoparticles start to form above the temperature of the 166 °C transition, it is likely that a higher silver(I) ion mobility is associated with this transition. The same can be said for the transition at 194 °C, where not only a faster thermal decomposition of silver behenate is observed but also a decrease of the viscosity. This is an indication that the structure breaks up into smaller smectic domains. As mentioned above, it is impossible to observe the clearing point, because of the strong thermal decomposition of silver behenate at higher temperatures. Another explanation for the different mesophases is that at the melting point (145 °C) only the end part of the alkyl chain is transformed into a disordered state, while the other parts keep the all-trans conformation. At each phase transition, another part of the long alkyl chain becomes disordered. Such a sequence is reasonable, because of the length of the alkyl chains. In any case, the phase transitions do not correspond to smectic mesomorphism of the same type as what we have for the molecular liquid crystal (for instance SmC → SmA). The whole process of the different phase transitions is one of a stepwise melting process of a highly ordered solid to the disordered liquid state.

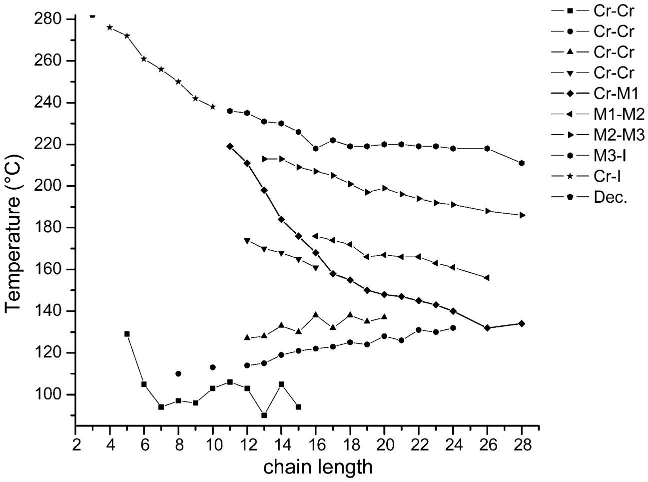

Figure 5. Dependence of the phase behavior of the silver alkanoates on the alkyl chain length. On the *X*-axis the total number of carbon atoms is given, i.e., 22 represents silver behenate.

The other silver alkanoates exhibit a complex thermal behavior as well. This is evident from the presence of several endothermic peaks in the DSC thermograms when these compounds are heated. The silver alkanoates in the homologous series AgC_3–AgC_{28} can be subdivided into several classes. Silver propionate (AgC_3) decomposes without melting. The compounds with a short chain length (from AgC_4 to AgC_7) melt with decomposition. Except for AgC_4, crystal-to-crystal transitions are observed for these compounds. For AgC_8, AgC_9, and AgC_{10}, two crystal-to-crystal transitions are observed, but no mesophase. For the series of alkanoates from AgC_{11} to AgC_{19}, a complex thermal behavior is observed with crystal-to-crystal phases and mesophases. A similar behavior is displayed by the long-chain homologues AgC_{20} to AgC_{28}, although fewer transitions are observed than for the homologues with an intermediate length of the alkyl chains. When the chain length of the silver alkanoates increases, the transition temperatures of most of the phase transitions decrease. At room temperature, the alkyl chains of the silver salts are arranged in the all-trans conformation. During heating the all-trans conformation disappears and the silver salts are turned into a state in which the conformation of the alkyl chains is slightly disordered in comparison with the all-trans conformation in the room temperature crystal structure (crystal-to-crystal transition). In the mesophase, the alkyl chain has considerable conformational disorder but not enough to be considered as totally molten. An overview of the crystal and mesophases of the silver alkanoates is given in Figure 5, and the corresponding numerical data is given in Table 2. Accurate determination of the transition temperatures for the transitions at a temperature higher than 175 °C was difficult, because of the thermal decomposition of the silver alkanoates at these temperatures.

The detailed study of the phase transitions by high-temperature X-ray diffraction was hampered by the thermal instability of the silver alkanoates. In addition, our high-temperature setup did not allow us to measure

Table 2. Phase Behavior of the Silver Alkanoates[a,b]

compd	Cr−Cr	Cr−Cr	Cr−Cr	Cr−Cr	Cr−M1	M1−M2	M2−M3	M3−I	Cr−I (dec)
AgC_3									c
AgC_4									276
AgC_5			129						272
AgC_6	105								261
AgC_7	94								256
AgC_8	97	113							250
AgC_9	96								242
AgC_{10}	103	113							238
AgC_{11}	106				219			236	
AgC_{12}	103	114	127	174	211			235	
AgC_{13}	90	115	128	174	198		213	231	
AgC_{14}	105	119	128	170	181		214	233	
AgC_{15}	94	121	133	165	176		209	226	
AgC_{16}		122	138	161	168	177	207	218	
AgC_{17}		123	132		158	174	205	222	
AgC_{18}		125	132		155	172	201	219	
AgC_{19}		124	135		150	166	197	219	
AgC_{20}		128	137		148	167	199	220	
AgC_{21}		126			147	166	196	220	
AgC_{22}		131			145	166	194	219	
AgC_{23}		130			143	163	192	219	
AgC_{24}		131			140	161	191	218	
AgC_{26}					133	156	188	217	
AgC_{28}					135	149	177	211	

[a] The phase transitions are expressed in degrees centigrade (°C). [b] Abbreviations: Cr = crystalline solid state; M = mesophase; I = isotropic liquid; dec = decomposition. [c] Silver propionate, AgC_3, decomposes without melting around 280 °C.

diffraction angles smaller than $2\theta = 5°$. X-ray diffractograms of silver behenate at different temperatures are given as Supplementary Information. One could argue that a variable-temperature X-ray diffraction study with X-ray radiation from a synchrotron source could solve the problem, because by this technique very fast data collection is possible. However, in these cases one should not overlook the kinetics of the phase transitions.

The thermal decomposition of the silver alkanoates is complex and has not been studied in detail yet. Moreover, it should be realized that the thermal decomposition of these compounds is different when pure samples are heated than when the compounds are heated in the presence of a reductant. In the thermographic process, the silver ions are reduced by the reductant to silver atoms (silver nanoparticles) and the reductant transfers hydrogen atoms to the carboxylate groups, resulting in the formation of the free alkanoic acid. Typical reducing agents used in the thermographic process are hydroquinone or catechol (or structurally related compounds). Thus, during the thermal development of a film containing silver behenate, metallic silver and behenic acid are formed. When the thermal decomposition of the pure silver alkanoates is studied by polarizing optical microscopy, also the formation of gas bubbles is observed. Taking the chemical structure of the silver alkanoates into account, the evolved gas is most likely carbon dioxide. In addition, a strong odor typically of the corresponding fatty acid can be smelled. When no reductant is present, the originally white product turns first yellow-brown and subsequently dark brown. This indicates that the formed silver particles are small. From the peak width of the X-ray diffractograms it can be concluded that the silver particles have a size ranging between 4 and 10 nm. These data are consistent with those obtained by TEM measurements. The brown spots observed during the heat treatment of silver alkanoates are due to the formation of silver(0) nanoparticles and not to silver(I) oxide nanoparticles. Silver(I) oxide is thermally and photochemically unstable. Moreover, XRD of bulk samples that were thermally treated show clearly in the diffractograms the presence of diffraction peaks of metallic silver. In the thermographic process, a tone modifier (e.g. glutaric acid) is added in order to obtain relatively large aggregates of silver nanoparticles with a uniform black color. Another contribution to the yellow brown color could come from small carbon particles (caramel color). The complex thermal behavior of the silver alkanoates is reflected by the contradicting results found in the literature. As early as 1886, Iweg and Hecht reported that silver butanoate is thermally decomposed into butanoic acid, carbon dioxide, carbon, and silver: $8C_3H_7COOAg \rightarrow 7C_3H_7COOH + CO_2 + 3C + 8Ag$.[26] These authors mentioned that side reactions should occur, because too much carbon dioxide is formed and because the formed butanoic acid is not pure. Judd et al. investigated the thermal decomposition of silver acetate.[27] They found that acetic acid and carbon dioxide were the main decomposition products. The decomposition reaction they propose is $2CH_3COOAg \rightarrow 2Ag + CH_3COOH + CO_2 + H_2 + C$, although they were not able to detect hydrogen gas. Andreev et al. reported that the long-chain silver alkanoates decompose into metallic silver, carbon dioxide, and into alkyl radical: $C_nH_{2n+1}COOAg \rightarrow Ag + CO_2 + C_nH_{2n+1}^{\bullet}$.[8] This radical can combine with another radical to form a linear alkane, $C_{2n}H_{4n+2}$. Taking into account the results of Akenni et al.,[28] who found that mercury(II) alkanoates decompose into mercury metal, carbon dioxide, the corresponding alkanoic acid, and a straight-chain terminal alkene with one carbon less than the alkanoic acid, the thermal decomposition of the silver alkanoates could be presented as $2C_nH_{2n+1}COOAg \rightarrow 2Ag + CO_2 + C_nH_{2n+1}COOH + C_nH_{2n}$. In this model,

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(26) Iwig, F.; Hecht, O. *Ber.* **1886**, *19*, 238.

(27) Judd, M. D.; Plunkett, B. A.; Pope, M. I. *J. Thermal Anal.* **1974**, *6*, 555.

(28) Akanni, S. M.; Burrows, H. D.; Begun, P. B. *Thermochim. Acta* **1984**, *81*, 45.

the decomposition of silver behenate (AgC_{22}) is $2CH_3(CH_2)_{20}COOAg \rightarrow 2Ag + CO_2 + CH_3(CH_2)_{20}COOH + CH_3(CH_2)_{18}CH{=}CH_2$. As long as no detailed study of the mechanism of the thermal decomposition of the silver soaps is available, the reaction pattern we propose is not more than a working hypothesis. However, this working hypothesis can explain the formation of silver nanoparticles, the evolution of carbon dioxide gas, and the formation of the alkanoic acid (fatty acids). The formation of a terminal alkene is more likely than the formation of a long alkane (by coupling of two alkyl radicals), because of the restricted mobility of the alkyl chains in the mesophase.

Conclusion

The silver alkanoates of the homologous series between silver propionate (AgC_3) and silver tetracosanoate (AgC_{24}) have been prepared, as well as silver hexacosanoate (AgC_{26}) and silver octacosanoate (AgC_{28}). The compounds all form a bilayer structure. Investigation of the thermal behavior of these silver alkanoates by high-temperature X-ray diffraction, differential scanning calorimetry (DSC), and polarizing optical microscopy (POM) revealed the presence of several phase transitions. The number and nature of the phase transitions depends on the alkyl chain length. The ordered crystalline structure is in a stepwise manner transformed into a disordered liquid. The mesophases are similar to smectic phases in classical liquid crystals. The thermal decomposition of the silver alkanoates proceeds in the mesomorphic state. A detailed study of the phase transitions is hampered by the thermal instability of these compounds. However, the rich polymorphism of the silver alkanoates revealed by this study can be the starting point for the in-depth investigation of the thermodynamical and structural properties of the high-temperature phases. Additionally, the reaction mechanism of the thermal decompositions is waiting for further exploration.

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Supporting Information Available: C, H microanalysis values and yields of the silver alkanoates, and X-ray diffractograms of silver behenate at different temperatures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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