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In Situ X-ray Investigation of the Formation of Metallic Silver Phases During the Thermal Decomposition of Silver Behenate and Thermal Development of Photothermographic Films

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Abstract. *Metallic silver formation, resulting from the thermal decomposition of silver behenate, AgBe, and from the thermally induced reduction of AgBe incorporated into a photothermographic imaging construction, has been compared by in situ x-ray investigation. In the case of the thermal decomposition of individual AgBe crystals, the main factor that determines the growth of the silver particles is the change in the AgBe crystal structure, leading to the formation of intermediate mesomorphic phases that still retain characteristic layer structure. By contrast, development of AgBe-containing photothermographic films generates silver particles by the reduction of intermediate silver complexes, which are in a liquid state during the development process. The silver nanoparticles resulting from these processes exhibit different sizes and morphologies that are important for optimizing the optical properties of photothermographic films. © 2007 Society for Imaging Science and Technology.*
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INTRODUCTION

Silver behenate, $[\mathrm{Ag(O_2C_{22}H_{43})}]_2$, is one of the fundamental components of photothermographic materials because it provides the silver ions for reduction in the thermal development process that leads to the formation of a visible image.[1–4] In the literature, there are a large number of reports devoted to the investigation of the phase changes of long, saturated-chain silver carboxylates, including silver behenate, in thermal systems as well as the effect of individual components added to “dry silver” photothermographic formulations.[5–11] The x-ray investigation of silver carboxylates with carbon atoms from 2 to 22[12] showed that all of these crystal structures fall into the triclinic class and contain two molecules in the unit cell. Among the dominant characteristics of the silver carboxylate crystal structures, which are defined by their significant anisotropic physical and chemical properties,[1,13] is the presence of a layered structure in which a double layer of silver ions separates a double layer of long methylene chains. For example, the solid-state crystal structure of silver stearate (AgSt, $[\mathrm{Ag(O_2C_{22}H_{43})}]_2$) shows that the molecules are actually dimers connected together forming a polymer.[3]

Thermally induced phase changes in the silver carboxylate crystals have been investigated by various analytical methods, such as NMR, IR, conductivity, DSC, and XRD. The temperatures of the multiple-phase transitions for silver carboxylates having various chain lengths have been characterized.[5,14–17] Upon transition from the crystalline state to the isotropic liquid, the silver carboxylates undergo up to six to seven phase changes of the following sequence: crystal state → curd → super curd (SUC) → sub-waxy (SW) → waxy (W) → super waxy (SUW) → sub-neat (SN) → neat (N) → isotropic liquid.[5,18] It may be relevant that the phase changes in the silver carboxylate from the crystalline state into the super curd (SUC) or sub-waxy (SW) phase occur in the 120–125°C range, the temperature at which the thermal development in photothermography is normally carried out.

X-ray diffraction, calorimetric, and IR methods were used in the investigation of the structural changes in the silver stearate crystal lattice.[5] It was shown that, upon heating, the silver stearate structure proceeded through a series of mesomorphic states. That is, the first phase transition occurred at 122°C, which was associated with a packing disorder of the aliphatic chains, manifested by a significant decrease in the separation between silver ion layers. It was proposed that increasing the temperature above 130°C leads to further disorder and the breakup of the silver ion layers, and it is responsible for the onset of the thermal decomposition reaction of the silver stearate, resulting in the formation of metallic silver and paraffin byproducts.

The structure transformation of polycrystalline silver behenate was also studied by x-ray diffraction during *in situ* heating.[15] In contrast to the results reported in Ref. 5, these authors[15] observed an increase in the interlayer spacing dur-

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ing the heating of silver behenate crystals. The authors also indicated that heating silver behenate over 120°C irreversibly transforms it from a crystalline to an amorphous state. Further, at 138–142°C, the first phase changes are observed, established by the appearance of diffraction peaks at the smaller 2θ Bragg angles, which correspond to an increase in interlayer distance in the silver behenate structure. In agreement with these results, upon heating above 145°C, the silver behenate crystals transform into a liquid-crystalline state and generate metallic silver phases at 180°C. The authors of this report consider that the initial stage of heating is the disordering of the silver behenate aliphatic chains. However, despite the agreement in the explanation of the structure transformations occurring in the silver behenate[15] and silver stearate,[5] there is a significant difference in the explanation of the subsequent structure changes in the phase transformations of these silver carboxylates. While heating silver stearate decreases its interlayer spacing,[5] heating silver behenate crystals initially proceeds through an amorphous phase followed by an increased distance between the layers.[15] Such a contradictory heating behavior between the silver stearate and behenate seems to be quite surprising because of the close similarities between the silver stearate and behenate structures (C_{18} and C_{22} chain length, respectively) and their phase-transformation temperatures. In addition, we have recently reported the thermal decomposition of silver myristate, AgMy, $[Ag(O_2C_{14}H_{27})]_2$ under conditions similar to the AgSt and noted similar behavior.[5] Considering the importance of AgBe as a material for photothermographic imaging products and the contradiction between the trend observed for thermal decomposition of AgMy and AgSt (in solids and in photothermographic films) relative to the interlayer spacing differences reported for the AgBe, we have continued the systematic investigation of the effect of increasing the chain length on the thermal properties of the AgBe component in this series. Once the reasons for the formation of the solid products from these chemical reactions are better understood, novel routes to achieve control of these processes should be possible, and photothermographic properties can be further improved. In this work, we show the results of our *in situ* x-ray diffraction investigation related to the formation of metallic silver from the thermal decomposition of pure silver behenate, as well as from the thermal development of photothermographic materials based on silver behenate.

EXPERIMENTAL

The synthesis of silver behenate was carried out by the exchange reaction between sodium behenate and silver nitrate, as typically practiced.[5] Photothermographic films were prepared from pure AgBe (not a mixture of chain lengths as is common in photothermography) and preformed AgBr, along with the normal additional imaging components, as described elsewhere.[19]

X-ray experiments were carried out at the time-resolved diffractometry station—channel 5b of VEPP-3, BINP ($\lambda = 1.506$ Å). Transmission mode was used for small-angle scattering (SAXS). X-ray patterns were obtained on the one-coordinate detector OD-3 with a 0.01° angular resolution and a 30 s recording time per frame. Samples were heated at 1°C/min in a special tube furnace, and sample temperatures were controlled by a thermocouple.

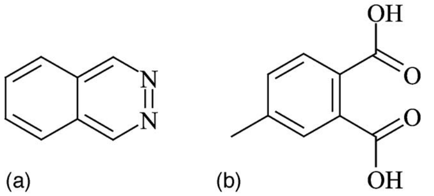

Figure 1. Phthalazine and 4-methylphthalic acid.

RESULTS AND DISCUSSION

Despite the fact that the thermal decomposition of silver carboxylates and the development of photothermographic films both produce solid products of metallic silver, the chemical transformations occurring within these processes are completely different. If the thermal decomposition of silver carboxylate proceeds according to the following scheme:[7]

$$[Ag(O_2C_nH_{2n-1})]_2 \rightarrow 2Ag + 2CO_2 + C_{2(n-1)}H_{2(2n-1)} \qquad (1)$$

with the formation of metallic silver and paraffin, then the development stages of photothermographic films are more complicated. Thermally induced reduction of the silver ions during film development can be summarized in a more simplified form as follows:

$$[Ag(O_2C_nH_{2n-1})]_2 \rightarrow [\text{silver ion intermediates}] \rightarrow 2Ag + 2HO_2C_nH_{2n-1}. \qquad (2)$$

This reduction reaction is the result of preliminary exposure of the silver halide in the film, which forms active latent image centers that catalyze the thermal development step at 110–130°C. The silver ion intermediates are reduced at the latent image centers, resulting in crystalline silver particles, which comprise the visible image. It is generally accepted that the silver ion source for silver particle formation at the latent image center is the silver carboxylate,[1–4] which is not light sensitive in the visible region of the spectrum, and that the transport of silver ions from the silver carboxylate to the latent image center is from the thermally initiated formation of the various silver complexes obtained with the components added into the formulation (developers, toners, and antifoggants).[1–6]

A recent investigation into the composition of phase changes occurring during the development process raised doubts about the source of the silver ions forming the visible image coming only from the silver carboxylate phase.[20] Contrary to all other literature,[1–4] the reduction of a model system composition (AgBe/AgBr with phthalazine (PHZ, Figure 1) 4-methyl-phthalic acid (4MPA, Fig. 1), and developer) resulted in a significant decrease (~45%) in the x-ray peak intensity for the AgBr phase. This change was proposed to be related to the contribution of silver ions from the AgBr in the formation of the metallic silver particles of the image. As discussed below, in the full photothermographic imaging formulation, we see no change in the AgBr signal.

The *in situ* investigation of the structural and phase changes in the thermal decomposition of silver behenate and the development of the photothermographic films prepared from it showed that the processes accompanying the thermal formation of the silver particles are significantly different.

In Situ Investigation of the Phase Formed in the Process of Thermal Decomposition of AgBe

The change in the diffraction characteristics of AgBe in the small angle region ($2\theta = 0.4-10°$) during *in situ* heating from 20–220°C is shown in Figure 2(a).

Increasing the temperature through this range is accompanied by a change in the AgBe x-ray diffraction pattern that is due to phase transformations occurring within the heated powder. As the temperature is increased, the reflections of the high temperature phases shift to the high diffraction angle regions, which confirm the decrease in the interlayer spacing in the silver carboxylate structure. Analysis of the diffraction data of these phases in this temperature interval allows us to separate out at least six phases that have different structural characteristics, Fig. 2(b).

It should be noted that the similar structural changes in AgBe and AgMy, with the formation of intermediate phases, were established previously.[5,6,21] According to the authors,[5] the first three phases correspond to the transitions within the AgBe crystalline state, but then at 155°C, silver behenate transforms into a liquid-crystalline material.

The x-ray diffraction patterns of the intermediate phases formed during heating, Fig. 2(b), include at least two series of layer reflections, which are evidence for the formation of a two-dimensional structure. Increasing the temperature above 230°C leads to the disappearance of the diffraction image of a layered structure. At the same time in the small 2θ angle region, an increase in SAXS intensity is observed, the maximum of which is at ~1.17°, Fig. 2(c).

Subsequent heating to 250°C corresponds to a change in the shape of the small angle scattering peak, which appears as a decrease in the intensity of the SAXS maximum. Simultaneously, peaks appear in the small angle scattering angles at $2\theta < 0.8°$.

The *in situ* x-ray diffraction of the thermal decomposition of AgBe in the wide-angle region is (WAXS, $2\theta = 25-55°$). Figure 3 showed that heating the powder to 140°C does not appear to significantly change the diffraction pattern. Upon heating to higher than 145°C, the crystal-phase reflections of AgBe disappear, and beginning at 230°C broad reflections are observed because of the (111) and (200) planes of metallic silver, Fig. 3, the intensity of which increases as the temperature is increased. Given that the first phase transition in silver behenate occurs at 128°C, the presence in the x-ray diffraction of the crystalline phase of AgBe is evidence that the first phase transition occurs from one crystalline state to another.

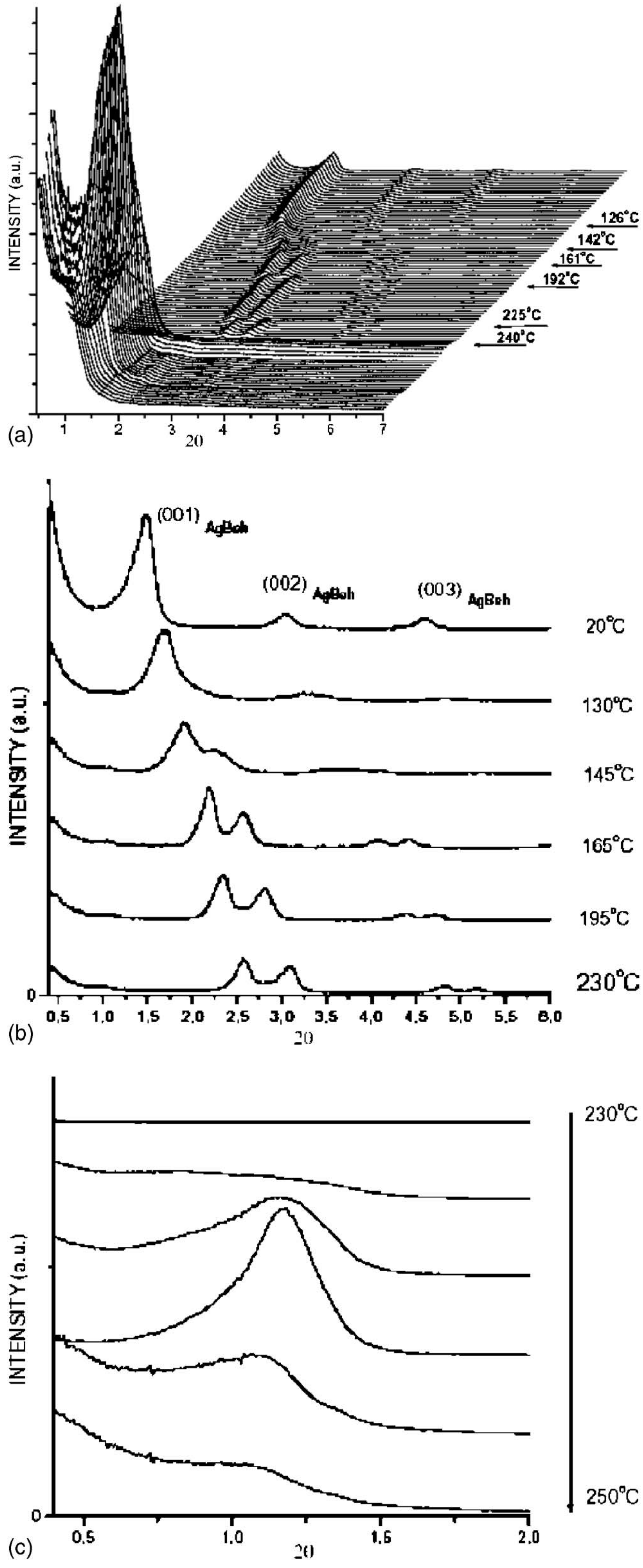

Figure 2. (a) Change in the x-ray diffraction pattern of silver behenate during *in situ* heating. (b) X-ray diffraction pattern for the initial (20°C) and intermediate phases formed in the heating of AgBe. (c) SAXS of AgBe.

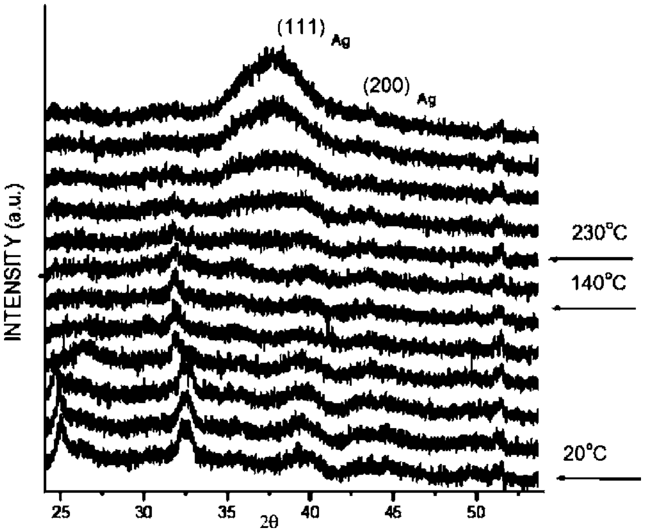

Figure 3. WAXS of AgBe during *in situ* thermal decomposition.

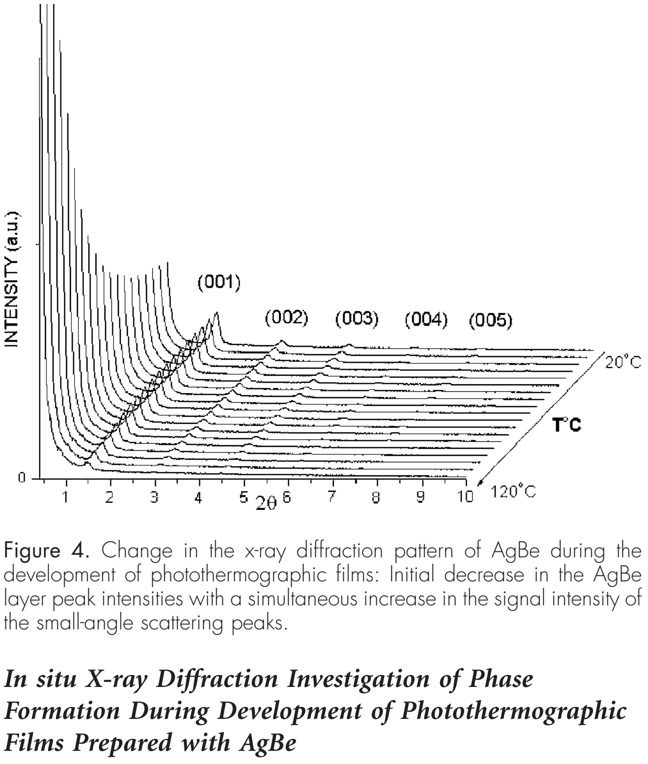

Figure 4. Change in the x-ray diffraction pattern of AgBe during the development of photothermographic films: Initial decrease in the AgBe layer peak intensities with a simultaneous increase in the signal intensity of the small-angle scattering peaks.

In situ X-ray Diffraction Investigation of Phase Formation During Development of Photothermographic Films Prepared with AgBe

The *in situ* x-ray investigation of the formation of phases during the development of photothermographic films prepared with AgBe showed that the formation of the silver phases occurs at temperatures significantly lower than the temperature of the first phase transformation (126°C). There are no shifts in the AgBe reflections observed during heating the photothermographic films from 20–80°C. After 80°C, however, the intensity of the x-ray diffraction peaks related to the layered structure of AgBe (001) decrease, which corresponds to the simultaneous increase in the intensity in the small-angle scattering region of SAXS $2\theta = 0.4 - 1.2°$, Figure 4.

The *in situ* x-ray diffraction pattern over 24–54° 2θ showed that the reflections that were due to the metallic silver appear as low as 80°C, Figure 5. Upon increasing the temperature (or the development time), the peak intensity of the silver reflections increases.

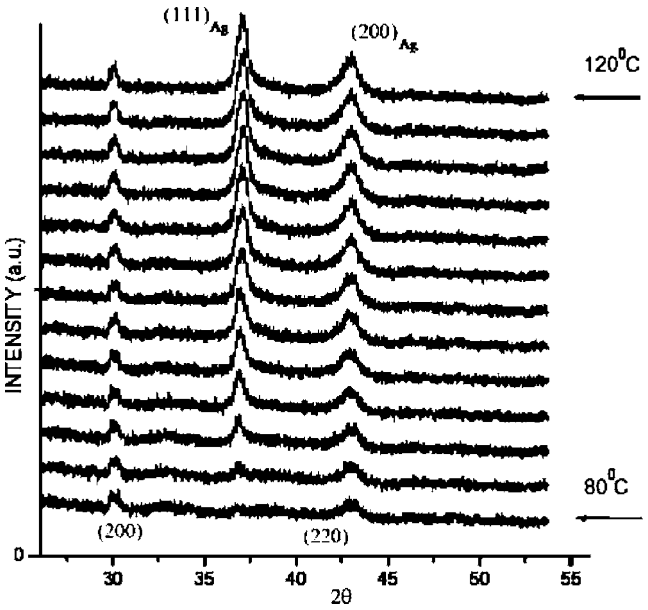

Figure 5. Change in the x-ray diffraction pattern of photothermographic films during thermal development.

It is important to note that the *in situ* investigation of the thermal development of films did not reveal any kind of additional reflections from intermediate solid phases. More significantly, the reflection intensity for silver bromide (200) up to and after processing remained completely unchanged, Fig. 5.

Comparing the half-widths of the silver reflections (111) and (200) recorded during the decomposition of AgBe, Fig. 3, and the developed photothermographic films, Fig. 5, provide clear evidence that the size of the silver crystals in the developed films are significantly larger than that formed in the process of the thermal decomposition of pure AgBe, similar to that observed in AgMy.[6]

All of these results on the thermal decomposition of AgBe and thermal development of photothermographic films can be summarized as follows.

The formation of metallic silver phases from the thermal decomposition of pure AgBe occurs through the formation of a series of intermediate mesomorphic phases. The formation of silver particles, established by the appearance in the x-ray diffraction pattern of *in situ* heated signal in the small-angle scattering, proceeds after the destruction of the AgBe layer structure.

The development of the photothermographic films shows the formation of silver phases at 80°C that correspond to the decreasing intensity of the silver behenate layer structure reflections with a simultaneous increase in the intensity of the SAXS. In particular, it must be emphasized that the formation of the silver phase does not proceed through any change in the intensity of the silver halide peaks, and it is clear that the silver particles form from the reduction of silver ions originating only from the AgBe crystals.

Overall, all of these results are in good agreement with previous reports.[22,23] That is, the initial stages of thermal decomposition of individual silver carboxylate form nanosized (2–5 nm) particles of silver, which subsequently agglomerate up to 10–15 nm, crystallizing on the lateral planes of the silver carboxylate crystals. In our opinion, this stage of silver particle growth is the cause of the curve shape changes in the small-angle scattering in which a decrease in intensity and a shift to the small-angle region of the SAXS maxima was observed. Finally, it should be noted that the difference between the thermal behavior of pure AgBe described in here and Ref. 16 could be attributed to the differences in the preparation procedures. The same effect may influence the x-ray results during the study of the role of AgBr in the photothermographic process.[15]

CONCLUSIONS

The differences in the diffraction data during the development of photographic films and the thermal decomposition of pure AgBe are related to the differences in the chemical transformations in these processes: in contrast to the thermal decomposition of pure AgBe, development of the photothermographic films generates silver particles by the reduction of intermediate silver complexes, which are in the liquid state (not observable by x-ray diffraction). In the case of the thermal decomposition of individual AgBe crystals, the main factor that determines the growth of the silver particles is the change in the structure, leading to the formation of intermediate mesomorphic phases, which still retain the characteristic layer structure.

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