

Thermal Behavior of a Self-Assembled Silver *n*-Dodecanethiolate Layered Material Monitored by DSC, FTIR, and ¹³C NMR Spectroscopy[†]

R. Voicu,[‡] A. Badia,[‡] F. Morin,[§] R. B. Lennox,[§] and T. H. Ellis^{*,‡}

Département de chimie, Université de Montréal, C.P. 6128, Succursale Centre-ville, Montréal, Québec H3C 3J7, Canada, and Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montréal, Québec H3A 2K6, Canada

Received February 29, 2000. Revised Manuscript Received July 8, 2000

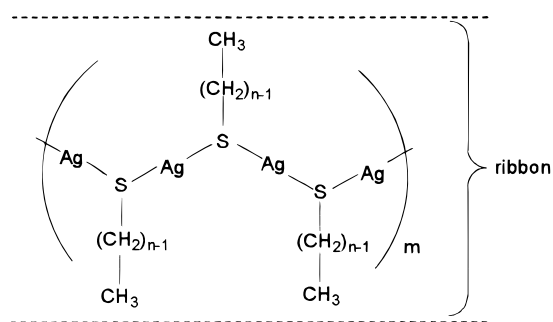
The thermal behavior of a self-assembled silver alkanethiolate layered material (AgSC_{*n*}, *n* = 12) has been explored using two spectroscopic techniques: ¹³C CPMAS NMR (¹³C cross-polarization magic angle spinning NMR) and FTIR (Fourier transform infrared) spectroscopy. The goal was to correlate structural changes monitored by spectroscopy with the phase transition detected by DSC (differential scanning calorimetry). Variable-temperature ¹³C CPMAS NMR was used for the first time to study silver alkanethiolates in order to obtain conformational and structural information about each of the C positions in the alkyl chain as a function of the temperature. In the low-temperature domain, a subtle change in the chain packing is observed, as evidenced by the chemical shift of the internal methylenes in the ¹³C CPMAS NMR spectra. A remarkable degree of conformational order is observed, which is retained up to 120 °C. A sharp phase transition between 125 and 130 °C is associated with conformational changes, from all-trans to gauche containing bonds, as detected by IR and ¹³C CPMAS NMR. The complete reversibility of these structural changes indicates that the alkyl chains remain anchored to the Ag–S backbone above the transition. The key determinants of the thermal behavior of the layered system are the strong Ag–S bonding and the high conformational degree of order conferred by the polymeric character of the compound.

Introduction

The interest in metal–thiolate layered materials is motivated by the consideration of these compounds as model systems for self-assembled monolayers (SAMs). Metal alkanethiolate bilayers are a highly ordered system at room-temperature whose high surface/volume ratio allows them to be studied by a wide range of characterization techniques, such as transmission FTIR, NMR, DSC and powder X-ray diffraction. This system can be seen, perhaps, as being midway between SAMs on planar substrates (2D SAMs)¹ and thiol-capped nanoparticles (3D SAMs).²

Our previous characterization of the layered silver alkanethiolates^{3,4} showed that the hydrocarbon chains have a remarkably high degree of conformational order (all-trans conformation) even at room temperature. A

diagonal coordination between the silver and sulfur atoms is indicated by the UV–vis spectra.⁴ It is known in the literature that the silver *n*-alkanethiolates are insoluble, suggesting that high molecular weight polymer chains predominate.^{5,6} Our proposed structure^{3,4} for the silver alkanethiolates starts with a ribbon whose backbone is made up of a polymeric Ag–S “zigzag”.



In the present model, strong coordinative bonds exist between the silver and the sulfur. The “ribbon” in this model has a height equal to 2 times an extended chain plus the height of the Ag–S chain and has been measured by X-ray diffraction.⁴ These silver alkanethi-

[†] Presented in part at the 82nd Canadian Society for Chemistry Conference and Exhibition, May 30–June 2, 1999, Toronto, Canada and at the 73rd ACS Colloid and Surface Science Symposium, June 13–16, 1999, Boston, USA.

* To whom correspondence should be addressed. Phone: (514) 343-6911. Fax: (514) 343-7586. E-mail: ellis@chimie.umontreal.ca.

[‡] Université de Montréal.

[§] McGill University.

(1) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.

(2) Templeton, A. C.; Wuelfing, M. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.

(3) Bensebaa, F.; Ellis, T. H.; Kruus, E.; Voicu, R.; Zhou, Y. *Can. J. Chem.* **1998**, *76*, 1654.

(4) Bensebaa, F.; Ellis, T. H.; Kruus, E.; Voicu, R.; Zhou, Y. *Langmuir* **1998**, *14*, 6579.

(5) Dance, I. G.; Fisher, K. J.; Banda, R. M. H.; Scudder, M. L. *Inorg. Chem.* **1991**, *30*, 183.

(6) Dance, I. G.; Fitzpatrick, L. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 3785.

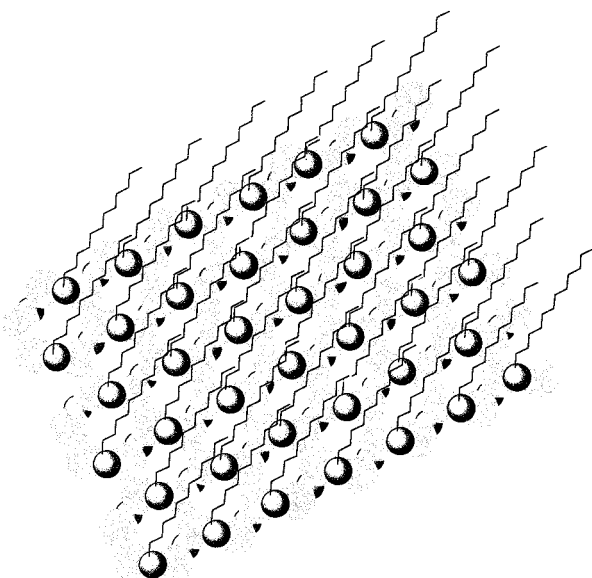


Figure 1. Top view of one plane of the silver alkanethiolate multilayered structure, showing the stacking of the ribbons. The alkyl chains extending to the bottom are not shown (not a perspective view). The gray circles are the Ag atoms, the shaded circles are the S atoms, and the tilted alkyl chains are represented by solid lines.

olate ribbons assemble side-by-side via the extensive van der Waals interaction to form a single layer, and these layers stack to yield the final lamellar structure (Figure 1). The spacing between ribbons reflects the balance of repulsive interactions between nonbonded silver atoms and attractive interactions between the alkyl chains. It appears that an almost perfect match of distances (Ag–S and Ag–Ag) arises in order that a close packing state between the alkanethiolate chains is obtained.

The temperature-dependent behavior of these compounds provides additional insight into the nature of these structural interactions. Previous studies (DSC,⁷ powder X-ray diffraction,⁷ FTIR)⁸ suggest that the long-chain silver *n*-alkanethiolates undergo a dominant and reversible transition at ca. 130 °C which has been associated with changes in the chain conformational and packing properties. To elucidate the molecular origin of these thermally induced structural changes, we undertook a detailed spectroscopic study by means of variable temperature ¹³C CPMAS NMR and IR. The ¹³C CPMAS NMR spectroscopy used here offers an important advantage over the spectroscopic techniques previously used to study the thermal properties of layered alkanethiolates. The distinctly different chemical shifts of the carbons⁴ along the alkyl chain allow the behavior of individual carbons to be followed independently from other parts of the chain, so that the site of the thermally induced chain conformational changes can be revealed.

We have synthesized a large number of silver alkanethiolate (AgSC_{*m*}, *n* = 7, 8, 12, 16, 18) bilayers and analogous copper bilayers (CuSC_{*m*}, *n* = 8, 12, 18).³ AgSC₁₂ was chosen as representative of the behavior of the long chain metal alkanethiolates for the variable

temperature ¹³C CPMAS NMR measurements. In a future publication, we will show that the short chains (AgSC₈) behave somewhat differently.

Experimental Section

Materials and Reagents. 1-¹³C-dodecanoic acid (99%) was purchased from Cambridge Isotope Laboratories, Inc. The 1-¹³C-dodecanethiol, CH₃(CH₂)₁₀*CH₂SH, was synthesized using 1-¹³C-dodecanoic acid, CH₃(CH₂)₁₀*COOH, as the starting material, following a published literature procedure.⁹ After purification with a chromatographic column (silica gel, *n*-hexane), the 1-¹³C-dodecanethiol purity was confirmed by TLC and ¹³C NMR spectroscopy. The silver alkanethiolate material was synthesized as previously reported.^{3,4} The *n*-alkanethiols (Aldrich) were used without further purification. All other reagents were acquired from general sources and used as received.

Differential Scanning Calorimetry. DSC experiments were performed on a Thermal Analyst 2900 instrument calibrated by means of an indium standard. Thermograms were run on samples of ~7 mg of AgSC_{*n*} (*n* = 8, 12, 16, 18) powder in sealed aluminum pans under a purging atmosphere of helium gas at heat-cool rates of 10 °C/min. The temperature was cycled from room temperature up to 150 °C and back to room temperature. Several measurements for AgSC₁₂, for example, resulted in a standard deviation of ±0.5 °C and ±0.6 kJ mol⁻¹ for the maximum temperature and the enthalpy, respectively. Heat-cool rates lower than 10 °C/min, such as 3 °C/min and 5 °C/min, did not result in significant different results (in terms of other possible phase transitions). When scanned at 3 °C/min, the separation between the exo- and endotherm is diminished by 2.7 °C with respect to a scan rate of 10 °C/min. The full width at half-maximum of the endotherm peak was reduced from 2.7 °C at 10 °C/min to 1.4 °C at 3 °C/min.

Infrared Spectroscopy. The AgSC₁₂ particles were deposited onto a KBr disk from a concentrated toluene suspension. Infrared spectra were acquired using a Perkin-Elmer FTIR microscope Model 16PC (MCT detector) equipped with a Mettler FP 52 hot stage for variable temperature experiments (25–160 °C). Spectra were collected in the transmission mode at a resolution of 2 cm⁻¹ with 128 scans. The IR sample was purged with nitrogen and maintained at each temperature for 10 min before a spectrum was acquired. Background spectra of the clean KBr disk were collected at the same temperatures and subtracted from the sample spectra.

NMR Spectroscopy. Two series of ¹³C CPMAS NMR measurements were performed. First, at Université de Montréal, solid-state 75.47 MHz ¹³C CPMAS NMR spectra (Figures 2 and 3) were obtained using a Bruker DSX-300 NMR spectrometer with a 4 mm ZrO₂ rotor. The delay time between pulses was 4 s and contact times of 5 ms were used. The samples were typically spun at 5 kHz and an average of ~300 scans were taken. Second, the ¹³C enriched samples were studied at McGill University (Figures 4 and 5) on a Chemagnetics CMX-300 NMR spectrometer with a 7.5 mm Chemagnetics PENCIL probe (the delay time between pulses was 5 s and contact times of 3 ms were used; the samples were spun at 3.5–5.5 kHz and 16 scans were taken). For the variable temperature CPMAS experiments at Université de Montréal, the temperature was calibrated by means of the known thermal variation of the chemical shift of lead nitrate.¹⁰ At McGill University, the sample temperature was controlled to within ±1 °C by a Chemagnetics temperature controller. For each silver alkanethiolate sample, an initial spectrum (referenced to glycine at 176.03 ppm) was acquired at 25 °C and then spectra were collected at progressively lower temperatures. The cooled sample was then gradually reheated past 25 °C and spectra were collected at higher temperatures. After

(7) Baena, M. J.; Espinet, P.; Lequerica, M. C.; Levelut, AM. *J. Am. Chem. Soc.* **1992**, *114*, 4182.

(8) Bardeau, J.-F.; Parikh, A. N.; Beers, J. D.; Swanson, B. I. *J. Phys. Chem. B* **2000**, *104*, 627.

(9) Badia, A.; Cuccia, L.; Demers, L.; Morin, F.; Lennox, R. B. *J. Am. Chem. Soc.* **1997**, *119*, 2682.

(10) Bielecki, A.; Burum, D. P. *J. Magn. Reson.* **1995**, *116*, 215.

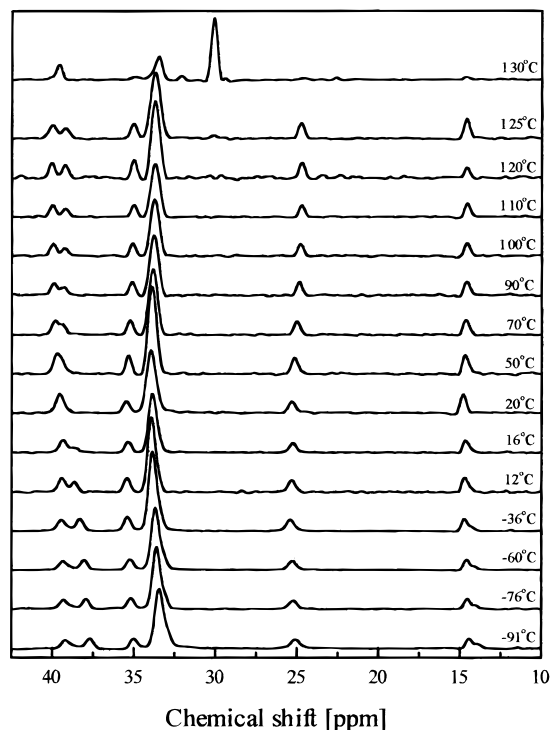


Figure 2. Variable-temperature ^{13}C CPMAS NMR (75.47 MHz) spectra of silver dodecanethiolate. A contact time of 5 ms, a delay time of 4 s, and ~ 300 scans were used to acquire each spectrum.

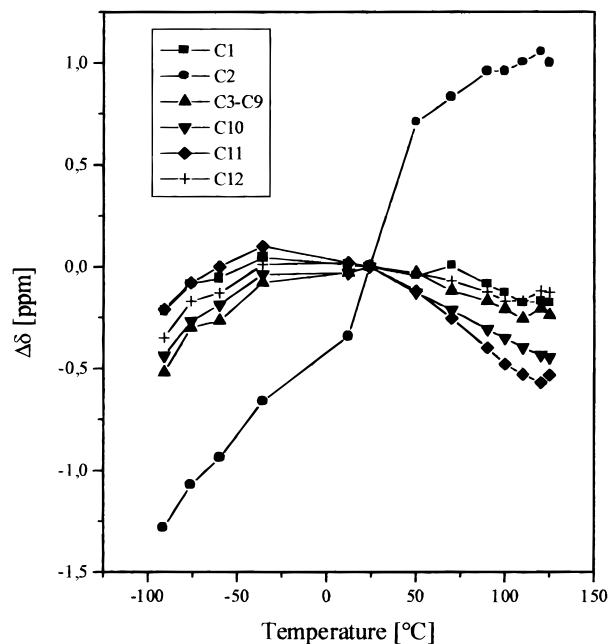


Figure 3. Variation of the chemical shift (relative to the value at 25 °C) of each alkyl carbon in AgSC_{12} as a function of the temperature, up to 125 °C ($\Delta\delta = \delta_T - \delta_{25}$ °C).

heating past the melting transition, the sample was returned to room temperature and a final spectrum was acquired to establish the degree of reversibility of the thermally induced changes.

“Solution” ^{13}C NMR experiments (i.e., measurements in a liquid spectrometer) were obtained on a Varian NMR spectrometer (75.47 MHz). Variable temperature ^{13}C NMR of the AgSC_{12} powder was carried out using a deuterated benzonitrile coaxial insert as a field/frequency lock. For the variable temperature experiments in the domain of 25–140 °C, the

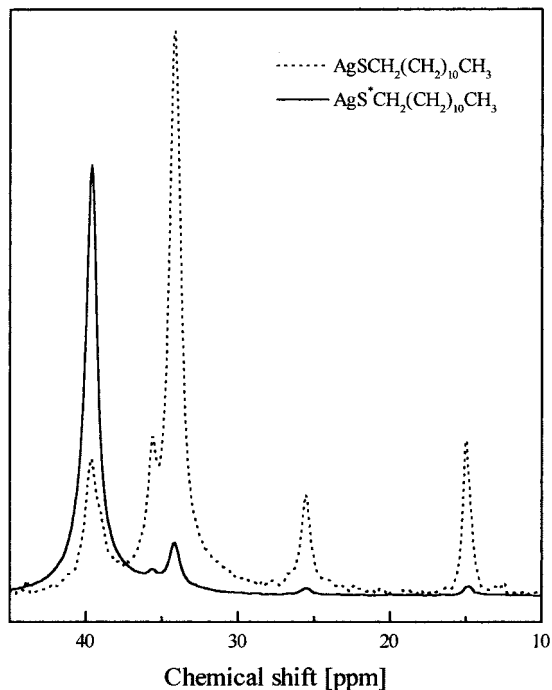


Figure 4. The ^{13}C CPMAS NMR (75.34 MHz) spectra of AgSC_{12} C1- ^{13}C -enriched (solid line) and unenriched (dotted line) at the room temperature. A contact time of 3 ms, a delay time of 5 s, and 16 scans were used to acquire each spectrum.

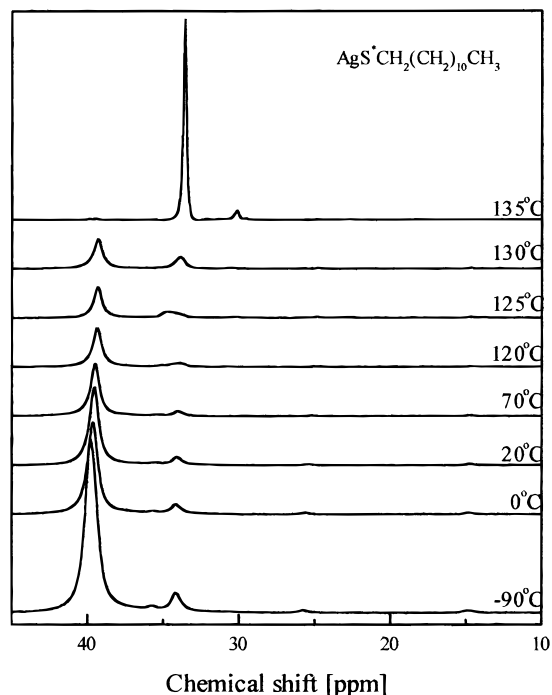


Figure 5. Variable-temperature ^{13}C CPMAS NMR (75.34 MHz) spectra of C1- ^{13}C AgSC_{12} . A contact time of 3 ms, a delay time of 5 s, and 16 scans were used to acquire each spectrum.

sample temperature was controlled to within ± 2 °C by a Varian temperature controller.

Results

DSC. In a previous study, the thermal properties of AgSC_{12} were characterized by DSC.⁴ The results for layered compounds of different chain lengths (AgSC_n , where $n = 8, 12, 16, 18$) are tabulated in Table 1. The

Table 1. A Comparison of the DSC-derived Thermal Properties of Layered Silver Alkanethiolates, *n*-Alkanes, and Lamellar Sodium Alkylphosphonates

<i>C_n</i>	AgSC _{<i>n</i>}			<i>n</i> -alkanes ^a			Na(HO ₃ PC _{<i>n</i>} H _{2<i>n</i>+1}) ^b		
	<i>T</i> ^o C	Δ <i>H</i> /kJ mol ⁻¹	Δ <i>S</i> /J K ⁻¹ mol ⁻¹	<i>T</i> ^o C	Δ <i>H</i> /kJ mol ⁻¹	Δ <i>S</i> /J K ⁻¹ mol ⁻¹	<i>T</i> ^o C	Δ <i>H</i> /kJ mol ⁻¹	Δ <i>S</i> /J K ⁻¹ mol ⁻¹
8	129	19.6	48.7	-56.8	20.6	95.5	139	9.3	22.6
12	131.8	33	81.6	-9.6	36.6	139	141	25.3	61
16	133.5	49.4	121.5	18.2	50	172	133	39	96
18	134.1	56.6	139	28.2	61.4	203.8	131	59.5	147.4
188				124.5					

^a CRC Handbook of Chemistry and Physics, 70th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1989–1990. ^b From ref 11.

Table 2. Chemical Shifts of HSC₁₂ and AgSC₁₂ at 25 °C

carbon <i>i</i>	HSC ₁₂ ^a	AgSC ₁₂ ^b
1 ^c	24.6	39.6 ^d
2	34.3	39.2 ^e
3	28.6	added to the C5–C9 signal
4	29.4	
5–9	29.8	34.0
10	32.1	35.4
11	22.8	25.3
12	14.2	14.7

^a NMR spectrum (75.47 MHz) was obtained in CDCl₃ and was referenced to TMS. ^b The ¹³C CPMAS NMR spectrum was referenced to glycine at 176.03 ppm relative to TMS. ^c C1 is the carbon attached to the sulfur and C12 is the terminal CH₃. ^d From ¹³C CPMAS NMR spectra using a C1-¹³C-enriched sample. ^e As a weak shoulder of the 39.6 ppm peak.

peak maximum temperature of the endothermic transition detected by DSC ranged from 129 °C for AgSC₈ to 134 °C for AgSC₁₈ and are similar to the values already published.⁷

On cooling, an exothermic transition is observed at approximately 10 °C below the endotherm maximum. Moreover, the thermal processes were found to be reversible given that Δ*H*_{endo} = Δ*H*_{exo}. This behavior was observed with all the layered silver alkanethiolates studied here. Our variable temperature ¹³C CPMAS NMR and FTIR studies establish that the transitions observed in DSC are due to chain melting and recrystallization (vide infra).

¹³C CPMAS NMR. The solid-state ¹³C NMR spectra of AgSC₁₂ between -91 and 135 °C are shown in Figure 2. The peak assignments (Table 2) were previously reported.⁴ In the present study, ¹³C enriched samples were used to assign the spectral positions of C1 and C2 in AgSC₁₂. The assignment of these two peaks is reversed when compared with ref 4 (vide infra). An important characteristic of this system is the remarkably high degree of conformational order of the alkyl chains of AgSC₁₂ even at room temperature; the internal methylenes exhibit a resonance at 34.0 ppm, confirming their all-trans conformation. The relative populations of trans and gauche conformations are given by the chemical shift value of the interior methylene carbons. For the *n*-alkanes, these carbons appear at 30 ppm in solution, where there are equilibrium populations of trans and gauche conformations. On the other hand, the methylenes in an all-trans conformation observed in the crystalline state have a chemical shift of 33–34 ppm.^{12,13}

Carbons C3 through C12 in AgSC₁₂ exhibit a similar thermal behavior, as shown in Figure 3. A *downfield* shift (Δδ increases) is observed in the low-temperature range, followed by an *upfield* shift (Δδ diminishes) in the high-temperature domain. One can divide the thermal behavior into two regimes. First, in the low-temperature range we observe a chemical shift that is

reminiscent of packing changes previously observed in solid alkanes.^{14,15} This is apparent from the chemical shift of the internal methylenes, which varies continuously from 33.4 ppm (Δδ ~ -0.6 ppm) at -91 °C to 34 ppm (Δδ = 0 ppm) at room temperature. Second, from 25 °C up to 125 °C (below the DSC-detected temperature), the tendency is toward chain disordering;^{11,16} the *upfield* shift in the methylene peak is consistent with this.

At 125 °C (ca. 5 °C below the phase transition temperature) the ¹³C NMR spectrum retains a strong peak at 33.6 ppm, corresponding to the all-trans conformation of the alkyl chains. However, a very small resonance at 30 ppm marks the occurrence of some gauche defects. At 130 °C, we clearly see the appearance of an intense peak at 30.1 ppm, corresponding to a large gauche population in the interior of the hydrocarbon chain.^{11,14,15} Also, the C12, C11, and C10 signals are absent in this spectrum, probably due to the high mobility now existing at the chain end. Under these conditions, the cross-polarization process is no longer efficient for these terminal positions.¹¹ The sharp phase transition is clearly associated with the appearance of gauche conformers in the chain and, by inference, chain "melting". However, a sharp signal in the C1/C2 region is still observed in the 130 °C spectrum, suggesting that the alkyl chains remain anchored to the intact Ag-S backbone. All of the chemical shift values return to their original values upon cooling to room temperature.

The resonance characteristics of the two first carbon atoms (around 40 ppm) show some interesting features. The C1 peak follows a behavior similar to C3–C12 over the whole temperature range investigated. On the other hand, the C2 peak exhibits a continuous and relatively large *downfield* shift (Δδ increases) with increasing temperature. At 130 °C, only one peak appears near the 40 ppm region. The variable temperature behavior of the C1-¹³C AgSC₁₂ suggests that this signal is due to C2 (vide infra).

¹³C CPMAS NMR of Enriched Samples. The spectrum of AgSC₁₂ enriched in ¹³C at C1 is shown in Figure 4. The signal obtained from the enriched carbon is sharp and very well defined, suggesting that all the Ag-S bonding sites are homogeneous. This is in contrast to similar experiments, performed on thiolate-capped gold nanoparticles,¹⁷ that showed a very broad

(11) Gao, W.; Dickinson, L.; Morin, F. G.; Reven, L. *Chem. Mater.* **1997**, *9*, 3113.

(12) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12*, 762.

(13) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.

(14) Möller, M.; Cantow, H.-J.; Drotloff, H.; Emeis, D.; Lee, K.-S.; Wegner, G. *Makromol. Chem.* **1986**, *187*, 1237 and refs therein.

(15) VanderHart, D. L. *J. Magn. Reson.* **1981**, *44*, 117.

(16) Badia, A.; Gao, W.; Singh, L.; Demers, L.; Cuccia, L.; Reven, L. *Langmuir* **1996**, *12*, 1262.

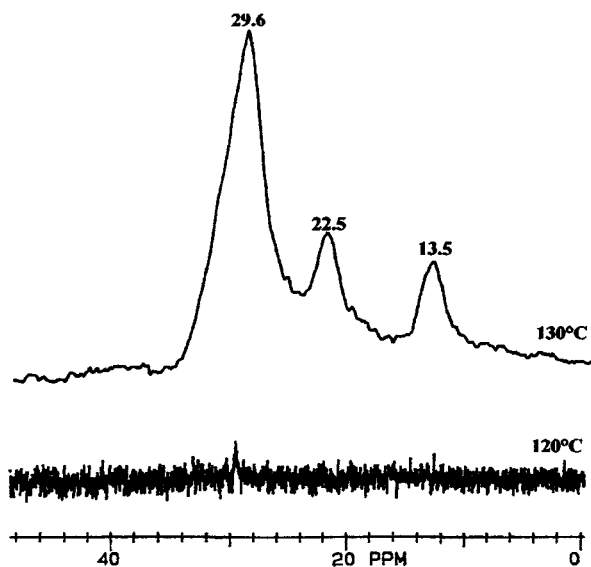


Figure 6. Variable-temperature ^{13}C NMR (75.47 MHz) spectra of AgSC_{12} acquired using a liquid spectrometer.

signal from the C1 carbon attributable to the polydispersity in the nanoparticle size and the presence of different bonding sites.

The spectra recorded for the C1- ^{13}C -enriched sample at several temperatures are given in Figure 5. These show that the C1 peak shifts only slightly with temperature between -90 and 130 °C. Therefore, the peak exhibiting the largest temperature variation in the natural abundance AgSC_{12} sample is assigned to the C2 carbon.

A transition is detected between 130 and 135 °C in the C1- ^{13}C -enriched sample. (This is about 5 °C higher than that observed in Figure 2, most probably because the data were recorded on different spectrometers, with different temperature calibrations.) Above the transition temperature, an intense peak appears at 33.6 ppm. If this signal arises from the C1 carbon, then its chemical environment has changed significantly. This could result from a change in the Ag-S backbone, which is also suggested by a color change (from white to yellow) observed at the phase transition. However, since this peak is very close to the position of the internal methylenes, we cannot completely rule out chain conformation or magnetization transfer effects that may have enhanced the intensity of the nonenriched (internal methylene) peak.

“Solution” ^{13}C NMR. Variable temperature ^{13}C NMR spectra of AgSC_{12} were also recorded in a liquid-state NMR spectrometer. The principal of these experiments is that a signal would be observable only if there is significant chain mobility. The most important spectra in the temperature regime studied (room temperature up to 140 °C) are shown in Figure 6. No signal is detected up to 120 °C, as expected for a solid. At 130 °C, relatively sharp peaks arise at 13.5 , 22.5 , and 29.6 ppm, corresponding to C12, C11, and the internal gauche methylene conformers, respectively. This clearly indicates that there is higher mobility at these positions above the DSC phase transition temperature. No signal is observed in the C1/C2 region. Again, it is important

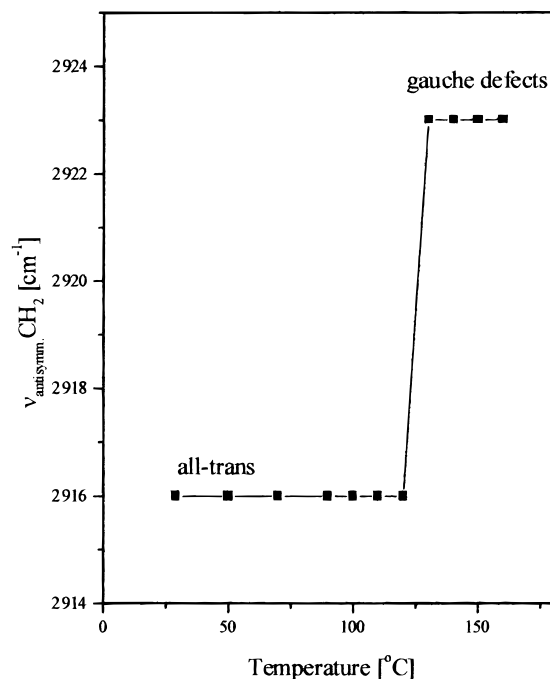


Figure 7. Peak position of the antisymmetric CH_2 stretching mode as a function of the temperature.

to note that the temperature range over which these changes occur is narrow.

IR Spectroscopy. Infrared spectroscopy is very sensitive to bond conformations. A variable temperature study conducted from 25 to 160 °C yields a sharp transition at ~ 125 °C, as indicated by the sudden 7 cm^{-1} upward shift in the CH_2 antisymmetric stretching vibration (Figure 7). Spectra of the CH_2 stretching region recorded at different temperatures are given in Figure 8a. In the temperature range below 125 °C, all of the sharp peaks in the low wavenumber region (which are characteristic of a highly ordered structure)⁴ remain unchanged. However, these disappear at the phase transition (Figure 8b). Further heating of the material up to 160 °C does not induce any additional change in the infrared spectra. The alkyl chains remain disordered. Cooling the sample to room temperature establishes that the observed structural changes are completely reversible.

A recently published variable-temperature FTIR study of silver dodecanethiolate reports a fully reversible conformational transition at ~ 130 °C,⁸ which is in complete agreement with the results presented here. Also reported was the existence of a “premelting” transition starting at 100 °C. Our own FTIR results reveal a much sharper transition, although a few of our samples also showed increased disorder just below the phase transition. We believe that this may be due to impurity sites.

Discussion

DSC. The nearly constant transition temperatures (Table 1) are reminiscent of other layered systems, such as clays with electrostatically attached surfactant molecules^{18,19} and long-chain metal alkylphosphonates.¹¹

(17) Badia, A.; Demers, L.; Dickinson, L.; Morin, F. G.; Lennox, R. B.; Reven, L. *J. Am. Chem. Soc.* **1997**, *119*, 11104.

(18) Wang, L.-Q.; Liu, J.; Exarhos, G. J.; Flanigan, K. Y.; Bordia, R. *J. Phys. Chem. B* **2000**, *104*, 2810.

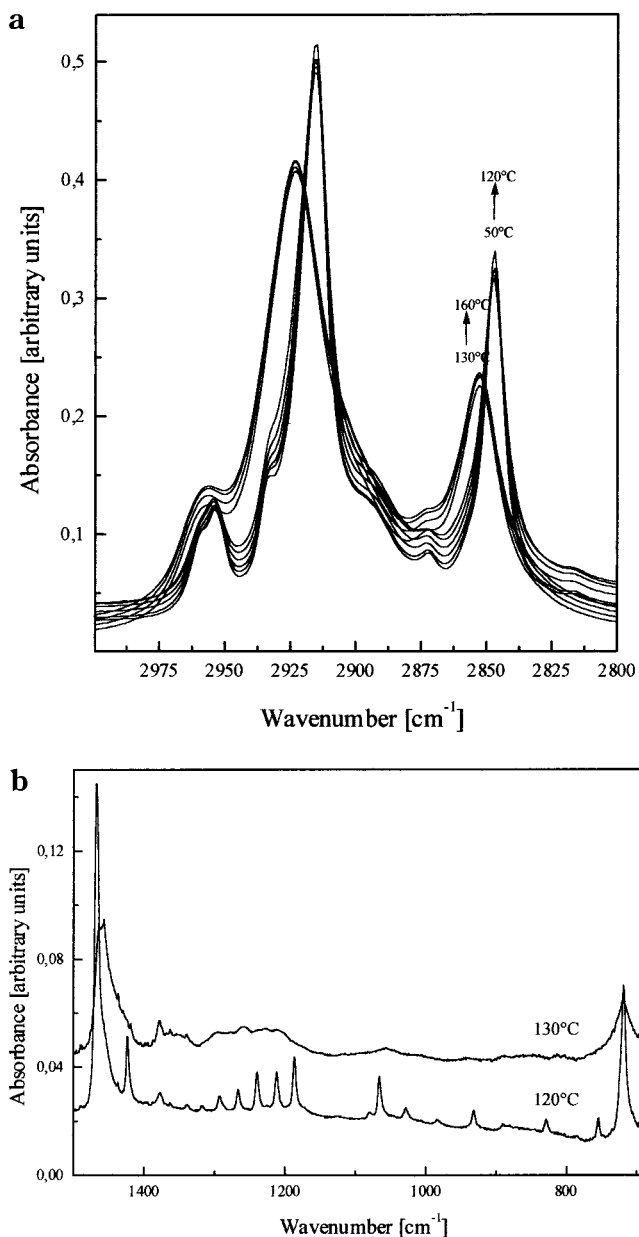


Figure 8. Variable-temperature IR spectra of AgSC₁₂ in the (a) high-wavenumber and (b) low-wavenumber region.

For the layered clays,¹⁸ it was proposed that the ordered all-trans conformation observed for the surfactant molecules is largely attributed to the constraining effects of the inorganic layers which force the chains to adopt the ordered conformation. For the metal alkylphosphonates, the independence of the transition temperature on the chain length was proposed to originate from the dominance of the electrostatic metal–phosphonate forces over the chain–chain van der Waals forces.¹¹ Similarly, the Ag–S backbone in silver dodecanethiolate would force the chains to reside in almost the same space up to the chain melting transition. The phase transition parameters (Table 1) indicate that the enthalpy of the transition (per mole of AgSC_{*n*} units) is very similar to that of analogous *n*-alkanes, whereas the transition temperatures are much higher. To predict the thermal behavior of the silver alkanethiolates, which we propose

are composed of close-packed polymeric ribbons, a starting point of comparison is the case of extremely long linear alkyl chains. As a general rule, the chain melting transition temperature of alkanes increases nonlinearly with the molecular mass, reaching an asymptote at ca. 140 °C. It is notable that these high transition temperatures occur only in highly ordered systems, as unannealed *n*-alkanes and low molecular weight polyethylene melt at lower temperatures.¹⁴ On the other hand, when chain folded lamellar crystals of C₁₈₈H₃₃₈ with extended all-trans chains are obtained by annealing, the resulting highly crystalline material has a melting point at 124.5 °C.¹⁴ Moreover, ultrahigh molecular weight polyethylene in the all-trans conformation (packed in an orthorhombic unit cell) has a melting point at 141 °C.²⁰ We therefore conclude that the high, relatively constant transition temperature of the silver alkanethiolates is a direct consequence of the presence of high molecular weight units.

The enthalpy values (Table 1) are given per mole of AgSC_{*n*}, rather than per mole of polymeric unit, since we have no measure of the average length of the ribbons. The comparison of the silver alkanethiolate enthalpies and the *n*-alkanes highlights the fact that the transition is characteristic of the melting of weakly interacting alkyl chains. This further suggests that the phase transition does not need to involve the breaking of covalent bonds, despite the high temperature.

Spectroscopy. ¹³C NMR and FTIR spectroscopies together provide a detailed description of the behavior of the silver alkanethiolate layered compound at different temperatures.

First, at *low temperatures*, the ¹³C CPMAS NMR spectra show a slight *upfield* shift after cooling below room temperature. Although shifts in this direction are often associated^{11,16} with disordering, another explanation is possible. The different molecular packing of methylene groups in a *n*-alkane crystalline form having two chains per unit cell results in a slight *upfield* shift compared to the triclinic subcell (where there is one chain per unit cell).^{14,15} We have not yet detected a low-temperature phase transition by DSC, but the ¹³C NMR data suggests that subtle changes in the chain packing might indeed be occurring. Preliminary FTIR experiments at low temperatures clearly establish that the alkyl chains are even more ordered than at room temperature. This fact is evidenced by the shift of 0.5 and 2.6 cm⁻¹ toward lower wavenumbers of the anti-symmetric and symmetric methylene stretching, respectively. The peaks are narrower at low temperature, further supporting the idea of chain ordering. The peak most sensitive to chain packing (CH₂ deformation) does not split at low temperatures, eliminating the idea of an abrupt transition to an orthorhombic packing. However, an upward shift of this peak (0.7 cm⁻¹) and important changes to the shape of the P1 (CH₂ rocking-twisting) peak suggest subtle changes in the chain packing, in agreement with the ¹³C CPMAS NMR measurements. The pinning of the alkyl chains to the Ag–S backbone probably hinders the complete transformation to an orthorhombic phase at low temperatures.

(19) Ginzburg, V. V.; Singh, C.; Balazs, A. C. *Macromolecules* **2000**, *33*, 1089.

(20) de Langen, M.; Prins, K. O. *Chem. Phys. Lett.* **1999**, *299*, 195.

Second, a *continuous pretransition* in the 25–120 °C domain is observed. The ^{13}C CPMAS NMR spectra show a *continuous upfield* change in the C3 to C12 chemical shift in this pretransition domain. The IR spectra however show that the system is conformationally ordered up to 120 °C. Furthermore, during the ^{13}C NMR experiment in a liquid spectrometer, no signal is detected up to 120 °C, suggesting that there is no significant mobility and/or disordering of the all-trans alkyl chains below this temperature. The continuous ~ 0.6 ppm shift of the C3–C9, C10, C11, and C12 peaks could thus be the result of some disorder experienced by chains at or near the edges of AgSC_{12} crystallites. These chains would be more likely to disorder below the phase transition temperature than chains within domains. In these locations, more free volume is available for the upper part of the chain (toward the methyl group). It is worth noting that the IR measurements are insensitive to this subtle disordering.

Third, the ca. 130 °C *phase transition* is very sharp as evidenced by all of the spectroscopic techniques used in this study. By comparison, the gold thiolate-capped nanoparticles with similar alkyl chain length show a much broader phase transition.²¹ At the phase transition, the backbone of the ribbons apparently remains intact and the alkyl chains remain bonded to a Ag–S backbone, but the population of the gauche defects abruptly increases. Several possibilities could be described; none, however, is experimentally supported yet. It has been proposed that the post-130 °C phase is composed of disks (ring-shaped Ag–S backbone with outward-pointing alkyl chains) which stack into a columnar mesophase.^{7,22} The formation of these rings would require a reversible modification of the covalently bonded Ag–S backbone.^{7,22} Such a ring system would have significant axial motion. A second possibility would be that the entire Ag–S backbone undergoes rotation about its axis. A third possibility would consist of a transformation of the backbone from a linear zigzag form to another form, such as a helix.²³ This would require a change in the silver–sulfur coordination; changes in coordination (perhaps di to tri-coordinate) do in fact occur at the transition (supported by the color change observed at the phase transition). Due to the curvature of the backbone, the chains will have the

volume required for the observed gauche conformations and increased mobility. It is not possible at the present time to be definitive about the structure of the post-130 °C phase. We are currently undertaking ^2H NMR experiments to probe the dynamics of this phase.²⁴

As a final point, we note that most of our experiments have probed the properties of the alkyl chains, and no information has been directly obtained about the Ag–S backbone. Our ^{13}C NMR results concerning the C2 carbon may indirectly provide some information. As can be seen in Figure 1, the hydrogens of the C2 carbon are in a position to interact with the charge distribution in the Ag–S backbone (a β -hydrogen effect). Such an interaction would explain the unique thermal behavior observed for the C2 carbon. It shows that continuous, subtle structural changes are occurring over the entire temperature range (–90–120 °C), while the alkyl chains remain in the same all-trans conformation. The C2 chemical shift may simply be responding to a thermal expansion, but it is clearly one of the parameters that is most sensitive to small structural perturbations.

Conclusions

^{13}C solid-state NMR spectroscopy, in combination with IR spectroscopy and DSC, has been used to probe the thermal behavior of layered silver *n*-dodecanethiolate. The alkyl chains are found to be in an all-trans conformation up to 130 °C. At higher temperatures, we observed the appearance of mobile gauche conformers. The thermally induced structural changes are reversible. The high degree of order and thermal stability of this system arises from the polymeric structure of the Ag–S backbone, which allows for extensive van der Waals interactions between the alkyl chains.

Acknowledgment. We thank Prof. Michel Lafleur and Chantal Paré for helpful discussions and Dr. Minh Tan Phan Viet and Robert Mayer (Université de Montréal) for their expertise in ^{13}C solid-state NMR measurements. The financial support of the Natural Sciences and Engineering Research Council of Canada and the Groupe de Recherche en Physique et Technologie des Couches Minces is gratefully acknowledged. We also thank Prof. G. R. Brown (McGill University) for the use of the variable temperature IR spectrometer.

CM000187T

(21) Badia, A.; Singh, S.; Demers, L.; Cuccia, L.; Brown, G. R.; Lennox, R. B. *Chem. Eur. J.* **1996**, *2*, 359.

(22) Espinet, P.; Lequerica, M. C.; Martín-Alvarez, J. M. *Chem. Eur. J.* **1999**, *5*, 1982.

(23) Wegner, G. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1326.

(24) Voicu, R.; Badia, A.; Morin, F.; Lennox, R. B.; Ellis, T. H. Manuscript to be submitted.