Structure and Dynamics of Selectively Deuterated Self-Assembled Silver *n*-Octadecanethiolate Layered Materials[†]

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The dynamics of the alkyl chains below and above the chain-melting transition temperature of long-chain silver *n*-alkanethiolate layered compounds were studied using variable-temperature ^{2}H NMR and IR spectroscopies. Two specifically deuterated compounds, silver-d_{35}-octadecanethiolate [$AgSCH_2(CD_2)_{16}CD_3$] and silver-1,1-d_2-octadecanethiolate [$AgSCD_2(CH_2)_{16}CH_3$], were used to identify the behavior of different regions of the chains. The ^{2}H NMR studies provide details about the alkyl chain motion, whereas IR spectroscopy provides details of the alkyl chain conformation. A key structural component of these materials is a polymeric −Ag−S− backbone from which the alkyl chains extend outward from both sides. The result is a two-dimensional, ribbonlike structure. The alkyl chains are highly ordered and adopt an extended all-trans conformation, which is maintained up to a few degrees below the phase transition temperature. The occurrence of a significant gauche population is observed above the phase transition temperature. The thermally induced structural changes are reversible. Above the phase transition temperature, the alkanethiolate chains experience complex motions. The structure of the post-transition phase is discussed in the context of related systems.

Introduction

Silver *n*-alkanethiolate ($AgSC_nH_{2n+1}$) compounds form a particularly interesting metal alkanethiolate self-assembled system given that the alkyl chains adopt a highly ordered, layered structure at room temperature.[1−10] We and others have proposed that these materials have a polymeric component to their structure.[3−6] The organization of the materials proceeds in two steps. First, a zigzag motif is created by diagonal Ag−S coordination (S−Ag−S angle ≈ 180° and Ag−S−Ag angle ≈ 100°).[5] The result is that the S-bonded alkyl chains extend from either side of this Ag−S backbone. Because the alkyl chains lie in the same plane as the Ag−S backbone, the total $(AgSR)_m$ assembly resembles a ribbon. van der Waals interactions then cause the ribbons to self-organize, yielding the final lamellar structure (Figure 1). These materials exhibit interesting thermal properties, including a pronounced phase transition at ca. 130 °C.[1,3,5,6,10] The strong Ag−S bonds combined with the extensive van der Waals interactions between the alkyl chains in this polymeric complex apparently lead to the thermal stabilization. DSC (differential scanning calorimetry) and ^{13}C solid-state NMR studies have demonstrated that the 130 °C transition is largely independent of the alkyl chain length.[3] These techniques, however, provide motional information about neither individual chains nor the ribbons themselves. Because dynamical information is central to understanding the structural details of these materials, we have used FTIR and ^{2}H NMR spectroscopies to provide a convergent description of the dynamics of this system. Metal−thiolate layered materials are considered as model systems for the metal−alkanethiolate self-assembled systems (either as monolayers or as thiolate-capped nanoparticles).

FTIR and ^{2}H NMR spectroscopies have been very useful in determining the structure and dynamics of lipid membranes,[11−13] polyethylene,[14] rigid-rod polymers

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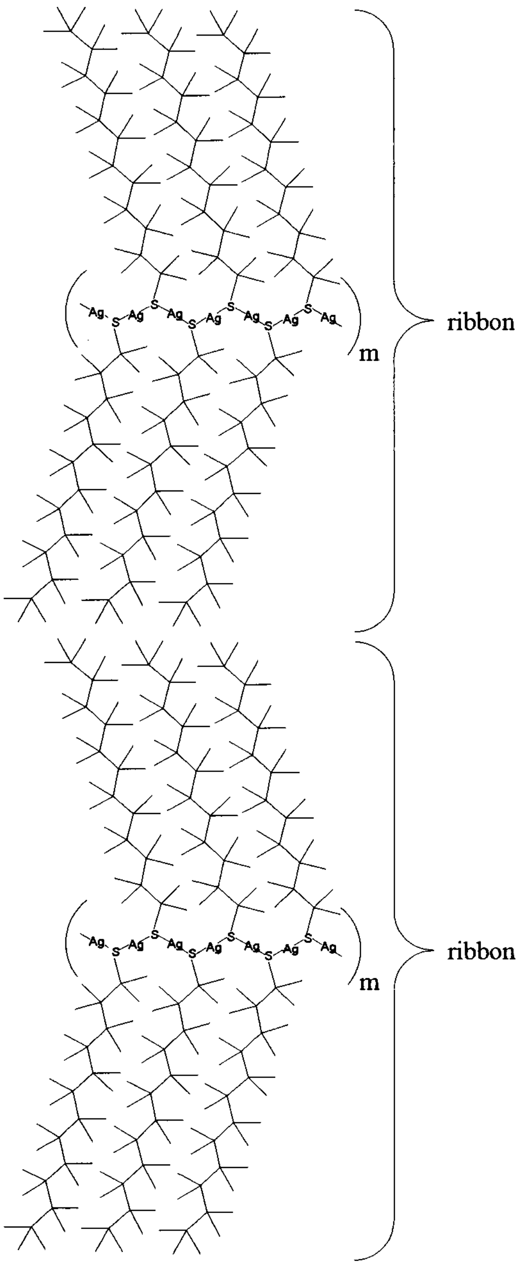

Figure 1. Schematic representation of the silver alkanethiolate structure.

with alkyl side groups,[15,16] and layered alkylammonium compounds.[17] Because FTIR spectroscopy probes a time scale that is less than 10^{-10} s,[18] it is ideally suited to probe the population of different conformers in a given phase. ^{2}H NMR spectroscopy allows one to probe a much longer time scale than most other spectroscopic techniques, as molecular motions with correlation times of ca. $10^{-7}-10^{-4}$ s can be studied.[19] The dynamics of individual bond segments can thus be investigated when specifically deuterated compounds are used. Specific deuteration is also very useful in FTIR studies, as the labeled methylene groups have characteristic CD_2 vibrational bands in a region of the spectrum that is usually free of other vibrational bands. The conformations of individual chain segments are thus accessible in both FTIR and ^{2}H NMR experiments in two very different time windows.[20]

We report here an FTIR and ^{2}H NMR study of layered silver octadecanethiolates synthesized using two specifically deuterated HSC_{18} chains. One octadecanethiol is deuterated only at the C1 position [$HS\mathbf{CD_2}(CH_2)_{16}CH_3$] and the other octadecanethiol is deuterated at positions 2−18 [$HSCH_2\mathbf{(CD_2)_{16}CD_3}$]. The resulting analyses provide a detailed and highly complementary description of the temperature-induced transitions in dynamical terms.

Experimental Section

Materials. $HSCH_2(CD_2)_{16}CD_3$ and $HSCD_2(CH_2)_{16}CH_3$ were available from a previous study.[21] *n*-Octadecanethiol (98% Aldrich) was used without further purification. All other reagents were acquired from general sources and used as received. The silver octadecanethiolates were synthesized as previously described.[1,2] In brief, a toluene solution of the corresponding alkanethiol is added under stirring to an aqueous solution of silver nitrate. The $AgNO_3$/RSH stoichiometric ratio is 1/1.42. After 2 h, the two phases are separated and the organic phase is washed three times with water. The organic phase containing the solid is then centrifuged three times and rinsed with toluene, and the resulting white to pale yellow solid is dried under vacuum. The purity of the silver octadecanethiolate is assessed using FTIR and DSC (vide infra).

Differential Scanning Calorimetry. DSC experiments were performed on a Thermal Analyst 2900 instrument calibrated for temperature and enthalpy by means of an indium standard. A typical thermogram was acquired on ~5 mg of $AgSC_{18}$ powder in sealed aluminum pans under an atmosphere of helium gas using heat−cool rates of 10 °C/min. The samples were submitted to two cycles: a heating cycle from 0 to 110 °C followed by cooling to 0 °C, and a second cycle involving heating from 0 to 150 °C, followed by cooling to 0 °C. For the completely hydrogenated samples, e.g., $AgSC_{18}$, several DSC measurements resulted in an average value for the maximum temperature of 132.1 ± 1.4 °C. For the present study, DSC has been primarily used as a quality control measure of the compounds studied by spectroscopic techniques.

Infrared Spectroscopy. The $AgSC_{18}$ powder was deposited onto a KBr disk from a concentrated toluene suspension. A uniform film was obtained after toluene evaporation. 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 (25−150 °C). Spectra were collected in the transmission mode at a resolution of 2 cm^{-1} with 136 scans and a spectral window of 4000−400 cm^{-1}. The IR sample was purged with nitrogen and maintained at each temperature for 15 min before a spectrum was acquired. Background spectra of a clean KBr disk were collected at the same temperatures and subtracted from the sample spectra. The purity of the completely hydrogenated samples, e.g., $AgSC_{18}$, was confirmed by the FTIR spectra at room temperature.

Solid-State ^{2}H NMR Spectroscopy. Samples for ^{2}H NMR experiments were prepared by packing a shortened 5-mm NMR tube with ~100 mg of ^{2}H-labeled $AgSC_{18}$ powder and

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sealing the tube with Teflon tape. ^{2}H NMR spectra were recorded on a Chemagnetics 300-MHz spectrometer operating at a frequency of 46.045 MHz. A quadrupole echo sequence $(90°_{\pm x}-\tau_1-90°_y-\tau_2)$[22] with transmitter blanking was used, and a 500-kHz spectral window was scanned. τ_1 and τ_2 were 40 and 20 μs, respectively, and the 90° pulse width was 2 μs. Spectra were collected with pulse delays of 60 s before and after the phase transition; a delay of 2 s or 250 ms was used for $AgSCH_2(CD_2)_{16}CD_3$ or $AgSCD_2(CH_2)_{16}CH_3$, respectively. Forty-eight transients were acquired for $AgSCH_2(CD_2)_{16}CD_3$ and 128 for $AgSCD_2(CH_2)_{16}CH_3$. The FID was left-shifted by the correct number of points so that, for each spectrum, the FID was Fourier transformed starting at the echo maximum. Heating and cooling of the NMR sample was performed using compressed air and a calibrated temperature-control unit (Chemagnetics). At each temperature, a 15-min sample equilibration time was allowed before spectral acquisition. For each ^{2}H-labeled $AgSC_{18}$ sample, an initial spectrum was recorded at 25 °C, and spectra were then acquired at higher temperatures. After being heated past the 130 °C transition, the sample was cooled back to 25 °C, and a final spectrum was collected to check the reversibility of the process.

Results

Differential Scanning Calorimetry. The thermal properties of the silver alkanethiolate layered materials were characterized in macroscopic terms by calorimetry.[1,3] Only one endotherm was detected in the 0−150 °C heating cycle. The temperature of the transition maxima are as follows: $AgSCH_2(CH_2)_{16}CH_3$, $T_m = 131.4$ °C, fwhm = 6.6 °C; $AgSCD_2(CH_2)_{16}CH_3$, $T_m = 123.1$ °C, fwhm = 6.8 °C; and $AgSCH_2(CD_2)_{16}CD_3$, $T_m = 127.8$ °C, fwhm = 4.5 °C. Thermal annealing (to 150 °C) has no effect on the width of the endotherms. The enthalpies associated with the $AgSC_{18}$ endotherms are ca. 42 kJ/mol. The exotherm transition maxima observed on cooling are 7−10 °C below those of the corresponding endotherms. The exothermic enthalpies are the same as the endothermic enthalpies. When reheated, each silver alkanethiolate measured exhibits a transition whose enthalpy and peak-maximum temperature is the same as in the first cycle. The fact that this phase transition is reversible also suggests that the material is stable to decomposition (under helium atmosphere) up to at least 150 °C.

^{2}H NMR Spectroscopy. ^{2}H NMR spectra of $AgSCH_2(CD_2)_{16}CD_3$ and $AgSCD_2(CH_2)_{16}CH_3$ obtained at different temperatures are shown in Figures 2 and 3, respectively. At room temperature, both compounds exhibit static Pake patterns,[12] with a quadrupolar splitting ($\Delta\nu_Q$) of 121 kHz for the CD_2 groups. A second set of peaks corresponding to the methyl group ($\Delta\nu_Q = 40$ kHz) is also observed in the spectrum of $AgSCH_2(CD_2)_{16}CD_3$.

With increasing temperature, the peaks observed for $AgSCH_2(CD_2)_{16}CD_3$ gradually broaden (Figure 2). The quadrupolar splitting of the CD_2 peaks decreases from 121 kHz at 23 °C to 106 kHz at 120 °C. Above 75 °C, a peak appears at the center of the spectrum (0 kHz). At 130 °C (i.e., at the DSC-determined phase transition temperature of this material, $T_m = 127.8$ °C, vide supra), the spectrum has been completely transformed. A single narrow peak at 0 kHz is observed, which has a broader contribution at its base.

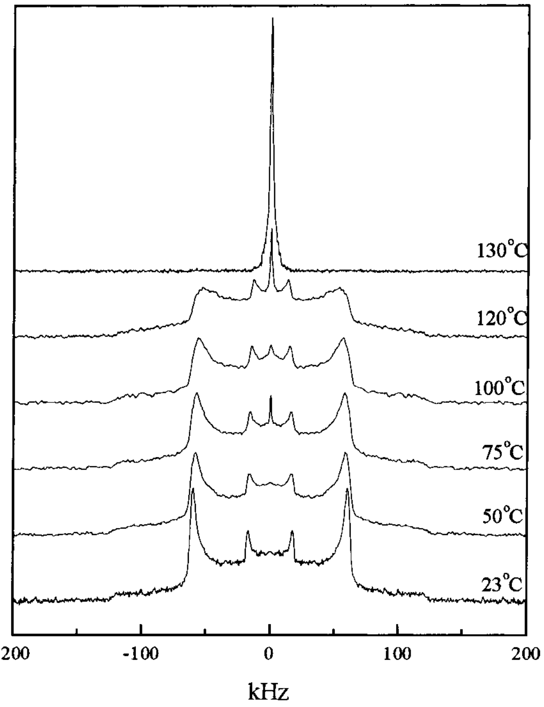

Figure 2. ^{2}H NMR (46.045 MHz) spectra of $AgSCH_2(CD_2)_{16}CD_3$ acquired at different temperatures.

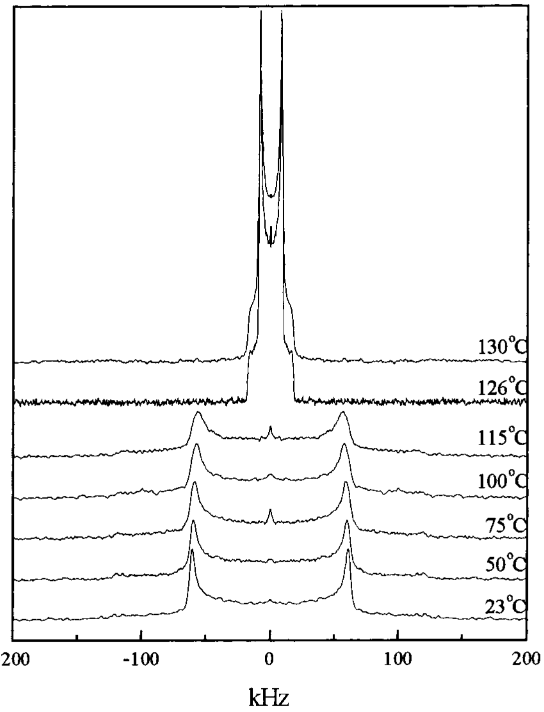

Figure 3. ^{2}H NMR (46.045 MHz) spectra of $AgSCD_2(CH_2)_{16}CH_3$ acquired at different temperatures.

The temperature dependence of the ^{2}H NMR spectra of $AgSCD_2(CH_2)_{16}CH_3$ (Figure 3) provides an important comparison. Neither the changes in $\Delta\nu_Q$ (from 121 kHz at 23 °C to 114 kHz at 115 °C) nor the extents of the CD_2 peak broadening with the temperature are significantly different in the two materials up to ~120 °C. However, a marked difference occurs above 120 °C. Whereas d_{35}-$AgSC_{18}$ shows an isotropic-like peak, d_2-C1−$AgSC_{18}$ retains its Pake line shape above 120 °C, but with $\Delta\nu_Q$ reduced to 16 kHz. Cooling back to room-temperature yields the initial spectrum for both compounds, establishing that the thermally induced changes are reversible.

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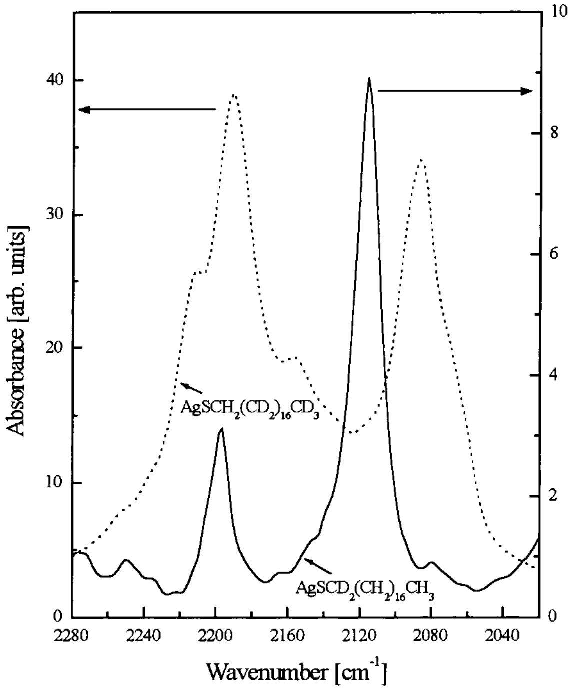

Figure 4. Transmission IR spectra of $AgSCD_2(CH_2)_{16}CH_3$ (solid line) and $AgSCH_2(CD_2)_{16}CD_3$ (dotted line) at 25 °C. The peaks were normalized in order to have full scale intensity.

FTIR Spectroscopy. The CD_2 stretching region of deuterated chains exhibits a higher energy peak ($\sim$2200 cm^{-1}) assigned to the CD_2 antisymmetric stretch ($\nu_{asym}CD_2$) and a lower-energy peak ($\sim$2100 cm^{-1}) assigned to the CD_2 symmetric stretch ($\nu_{sym}CD_2$).[23] Figure 4 presents a comparison of this spectral region for the two silver layered compounds at 25 °C. The spectrum of $AgSCH_2(CD_2)_{16}CD_3$ is more complex than that of $AgSCD_2(CH_2)_{16}CH_3$, as in addition to the two CD_2 stretching modes, one also observes the stretching modes of the CD_3 group (symmetric CD_3 stretch at 2156 cm^{-1} and antisymmetric CD_3 stretch at 2210 cm^{-1}). The position of the symmetric CD_2 stretch shows that the first methylene is shifted when compared to the rest of the chain. This mode occurs at 2115 cm^{-1} in $AgSCD_2(CH_2)_{16}CH_3$ and at 2086 cm^{-1} in $AgSCH_2(CD_2)_{16}CD_3$. Figure 5 tracks the thermal behavior of the symmetric CD_2 stretching vibrations of $AgSCH_2(CD_2)_{16}CD_3$ and $AgSCD_2(CH_2)_{16}CH_3$. For $AgSCH_2(CD_2)_{16}CD_3$ (Figure 5a), an abrupt shift of 12 cm^{-1} in the peak position of the symmetric CD_2 stretch is observed upon heating from $\sim$115 to 130 °C, and the inflection point corresponds to $\sim$126 °C (DSC-detected maximum temperature = 127.8 °C). Although there is no change in the position of the symmetric stretch of $AgSCD_2(CH_2)_{16}CH_3$ up to 120 °C, there is a shift of 9 cm^{-1} between 120 and 130 °C (Figure 5b). The IR-detected transition temperature for this compound is $\sim$125 °C, in excellent agreement with the DSC-measured maximum temperature of 123 °C. These thermally induced changes in the alkyl chain conformation are reversible, given that on cooling, the initial room-temperature spectra are obtained for the two compounds.

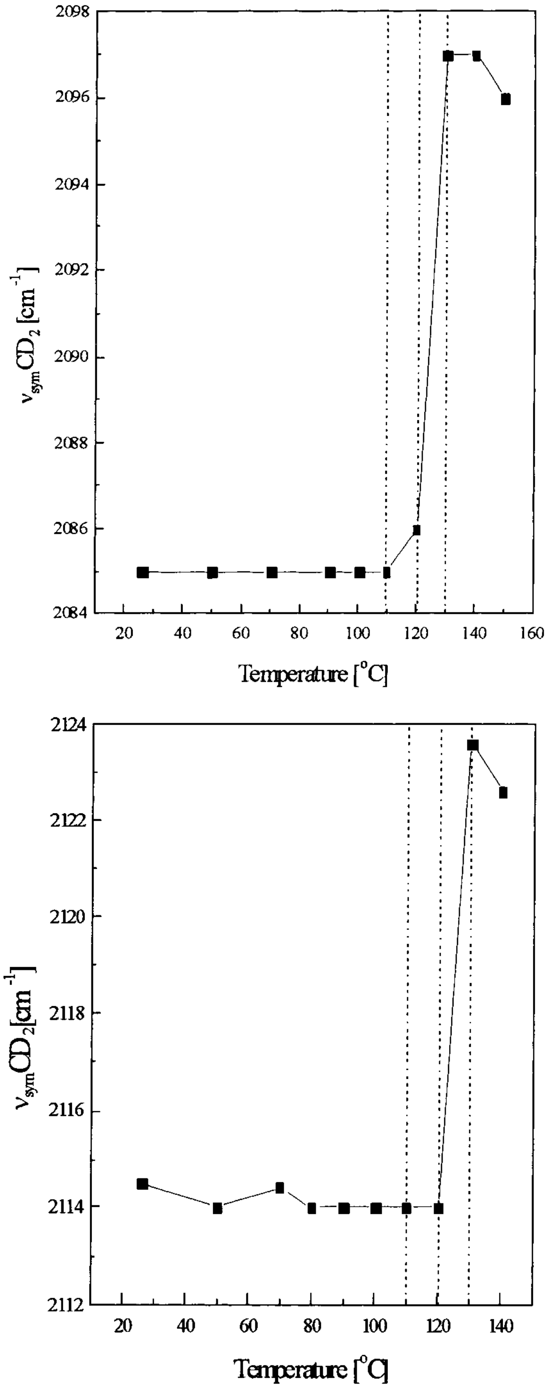

Figure 5. Peak position of $\nu_{sym}CD_2$ as a function of temperature for (a) $AgSCH_2(CD_2)_{16}CD_3$ and (b) $AgSCD_2(CH_2)_{16}CH_3$. The uncertainties in the given peak position values are (a) 0.3 cm^{-1} and (b) 0.1 cm^{-1}. The dotted lines are used as a guide for the eyes.

Discussion

FTIR spectroscopy provides a “snapshot” (on a time scale of less than 10^{-10} s)[18] of the relative trans and gauche equilibrium bond populations as a function of the temperature. The room-temperature spectra of the two deuterated materials show that the first methylene behaves differently than the other methylene groups in the chain. In our previous IR study,[1] a plot of the normalized intensity of the CH_2 stretching modes with respect to the number of methylene groups in the alkyl chain suggested that there is a frequency shift for the

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first three methylenes in the silver alkanethiolates. The present study is consistent with this observation. Labeling of the first methylene yields a shift of 29 cm^{-1} (toward higher wavenumber) for the CD_2 symmetric stretch in comparison with the rest of the chain. A similar tendency is also observed when the two deuterated bulk thiols are compared. The presence of the electronegative S atom seems to induce changes in the vibrational constant of the first methylene stretching mode.

Moreover, the two deuterated silver alkanethiolate materials are in all-trans conformations below the phase transition, as evidenced by the position of the CD_2 stretching modes. The positions of the methylene symmetric and antisymmetric stretches modes are known to be very sensitive to the populations of trans and gauche conformers.[23-29] At room temperature, the $\nu_{sym}CD_2$ positions at 2086 cm^{-1} for $AgSCH_2(CD_2)_{16}CD_3$ and at 2114 cm^{-1} for $AgSCD_2(CH_2)_{16}CH_3$ are lower than those of the same vibrational mode in the gel phase of the deuterated phospholipid bilayer membranes,[30] indicating an improved conformational order in the silver alkanethiolate materials. The supposition of an all-trans conformation in these materials is also supported by previous measurements at room temperature.[3] Specifically, no defect modes were observed in the full IR spectrum, and the positions of each of the ^{13}C peaks are as expected for an all-trans conformation.[3]

Naumann et al.[23] have reported that the symmetric CD_2 stretching peak position of deuterated phospholipid bilayers supported on spherical microbeads exhibits a shift to higher wavenumbers (as the temperature is increased) that is a direct function of the average number of gauche conformers per acyl chain. Our measurements (Figure 5) clearly show that there is a sharp increase in the gauche bond population at the DSC-detected phase transition. Furthermore, the smaller change in the CD_2 stretching vibration noted for the transition of $AgSCD_2(CH_2)_{16}CH_3$ (i.e., 9 cm^{-1}) than for the transition of $AgSCH_2(CD_2)_{16}CD_3$ (i.e., 12 cm^{-1}) suggests that there are fewer gauche conformations in the alkyl chain near the sulfur atom. This is consistent with the chain being tethered to the Ag$-$S backbone.

Unlike IR spectroscopy, the time scale[18] of ^2H NMR is long enough to give rise to an appreciable averaging of the molecular motions.[13] The time scale probed by ^2H NMR spectroscopy provides insight into the motional processes involved in the phase transition process. Qualitative information about the mechanisms and time scales of molecular motion at a particular chain segment can be determined from an analysis of the line shape and line width of the ^2H NMR spectra. The signature of rigid $C-^2H$ bonds is a quadrupolar splitting ($\Delta\nu_Q$) value of ca. 130 kHz between the peak maxima ($\theta = 90°$) and twice this value between the steps at the wings ($\theta = 0°$) of a powder (Pake) pattern.[31] A decreased $\Delta\nu_Q$ value results from molecular motions on the $10^{-7}-10^{-4}$ s time scale.[31,32]

We begin by discussing the spectra of $AgSCH_2(CD_2)_{16}$-CD_3 (Figure 2). First, the powder pattern indicates that, at room temperature, the silver octadecanethiolate is essentially rigid on the NMR time scale. This direct measurement of the restricted alkyl chain mobility complements the structural information obtained from our previous ^{13}C NMR[3] and IR spectroscopic experiments,[1] as well as the IR spectra presented in this work, which show that the alkyl chains are entirely in an all-trans conformation at room temperature. As expected, the quadrupolar splitting of the CD_3 group ($\Delta\nu_Q = 40$ kHz) is three times less than that of the CD_2 groups because of the rapid internal motion about the C_3 axis.[17,18,32] This value is consistent, however, with the orientation of the $C-CD_3$ bond being static on the time scale of this experiment, which is on the order of the inverse of the full spectral line width of 250 kHz.[17,18,32] It is important to note that the Pake doublets characteristic of the CD_2 and CD_3 groups are well-defined. The fact that only one CD_2 doublet is observed in d_{35}-$AgSC_{18}$ suggests that there is not a mobility gradient along the alkyl chain and that the mobility that does exist is limited.[11,33]

When the sample is heated to 120 °C, a gradual broadening of the Pake pattern is observed with an associated change in $\Delta\nu_Q$ to 106 kHz (at 120 °C). Broadening of the peaks can lead to a shift of the maxima, as modeled by de Langen and Prins, which is the result of small-angle reorientations of methylene groups about a rigid alkyl chain axis.[14] Furthermore, when the temperature exceeds 75 °C, a narrow peak at 0 kHz becomes evident in the presence of the persistent rigid Pake pattern. This feature could be due to the melting of the chains localized at domain boundaries or the contribution from a low level of impurities. The key point, however, is that the motion of the alkyl chains is highly limited right up to the transition temperature. When the temperature is further increased to 130 °C (exceeding the DSC transition temperature of 127.8 °C), the spectrum undergoes dramatic changes and a Pake pattern is no longer observed. The sharp peak observed at 0 kHz (Figure 2) can arise if there is a rapid exchange between gauche and trans populations, yielding equal populations of these two conformers.[20] However, the broader component observed at the base of this sharp peak establishes that the alkanethiolate chains are undergoing complex, but not pure, isotropic motions at 130 °C.

In a complementary experiment, we explored the temperature dependence of the C1 position using $AgSCD_2(CH_2)_{16}CH_3$ (Figure 3). As expected from the $AgSCH_2(CD_2)_{16}CD_3$ results, the $AgSCD_2(CH_2)_{16}CH_3$ spectra exhibit a Pake pattern from room temperature to 115 °C. Unlike $AgSCH_2(CD_2)_{16}CD_3$ however, $AgSCD_2$-$(CH_2)_{16}CH_3$ retains a Pake pattern above its phase

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transition temperature as shown in the 126 °C spectrum. The $\Delta\nu_Q$ of this spectrum is however reduced by a factor of 7.6, compared to that of the room-temperature spectrum. The fact that the Pake doublet is retained at these high temperatures establishes that, although the C1 position experiences motion, it has significantly less motional freedom than does the rest of the alkyl chain.

Motions of the ribbon itself, changes in the ribbon geometry or breakdown of the ribbon into mobile small-molecular-weight entities, could be the source of the large change in $\Delta\nu_Q$. These different possibilities can be discussed in the context of structurally related systems.

For example, ultrahigh-molecular-weight polyethylene (UHMWPE) exhibits T_m values similar to those of the compounds studied here.[14] A double reorientation model has been proposed for the hexagonal phase of UHMWPE studied under high-pressure and high-temperature conditions (4900 bar, 503 K).[14] Under these conditions, the polyethylene chains undergo rapid reorientation about the chain axis, whereas the chain axis reorients locally, leading to a reduction in $\Delta\nu_Q$ by a factor of 2.5.[14]

Discotic liquid-crystalline polymers in the columnar mesophase[15] have similarities[34] to a proposed columnar phase (studied at 170 °C by X-ray diffraction) of $AgSC_{18}$[6] and $Cu(I)SC_{10}$.[7] The columns in this description consist of stacks of disks that are separated by 0.5 nm.[6] Because each "disk" is a $(AgSR)_n$ ring,[6] such a structure must result from bond reorganization, going from a semi-infinite ribbon to a collection of individual molecules. The most prominent motion in the monomeric discotics, composed of heptyloxy-substituted triphenylenes,[15,35] is rotation of the disks about the column axis (axial motion). The ^2H NMR spectrum of the mesophase of heptyloxy-substituted triphenylenes deuterated in the 1 position of the heptyloxy side groups exhibits a motionally narrowed Pake pattern. This narrowing reflects the combined axial motion[35] and librational motion (involving torsional motion about a tetrahedral axis)[36] of the methylene chains. The $\Delta\nu_Q$ value is reduced by about a factor of 2 in this case.

Another relevant system is the lamellar model membrane formed when a methacrylate is attached to a lipid headgroup via a spacer.[32] The ^2H NMR spectra of the liquid-crystalline phase resembles a motionally averaged Pake pattern, exhibiting a 10-fold reduction in $\Delta\nu_Q$ compared to the value for the gel phase at room temperature.[32] In this system, the complex molecular mobility was modeled using a simple six-site jump model involving chain conformational changes and axial rotation of the lipid molecules.[32]

Given these comparisons, it is interesting to then ask: What is the post-130 °C structure that can explain the observed $\Delta\nu_Q$ reduction by a factor of 7.6? Two limiting possibilities can be considered, but it is difficult to be definitive at this stage. One possibility is that the semi-infinite Ag−S backbone remains intact (i.e., there is no Ag−S cleavage) but the ribbon−ribbon interactions become disrupted above T_m. This would introduce new, but limited, degrees of freedom to the ribbon where perhaps some twisting and undulations of the ribbon occur in combination with the alkyl chain motion. Alternatively, the Ag−S backbone might undergo a structural reorganization to form rings.[5] (In fact, 12-membered rings are known for silver thiolate compounds for which the alkyl chains have been replaced by more bulky ligands.[5]) The stacking of these or related rings could form the discotic columnar phase suggested by Baena et al.,[6] but the dynamics would have to be more complex than that observed in analogous discotic systems.[35] The distinction between these two models cannot presently be resolved with the ^2H NMR and FTIR data. The reversibility of the phase transition suggests, but does not prove, that the intact ribbon model is viable. Future work involving temperature-dependent X-ray diffraction might help to distinguish between these models.

Conclusions

The combined study of two specifically deuterated silver octadecanethiolate layered compounds using variable-temperature ^2H NMR and IR spectroscopies provides a clearer picture of the chain motions occurring in these materials at the DSC-detected phase transition of ca. 130 °C. The static Pake pattern observed in the room-temperature spectra demonstrates that the layered silver alkanethiolate structure places the alkyl chains in rigid, extended all-trans conformation. At the phase transition temperature, there is a significant frequency shift in the IR spectrum, corresponding to a significant increase in the gauche bond population. Whereas the rest of the alkyl chains exhibits isotropic-like motion at T_m, the C1 atom experiences a more restricted motion.

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