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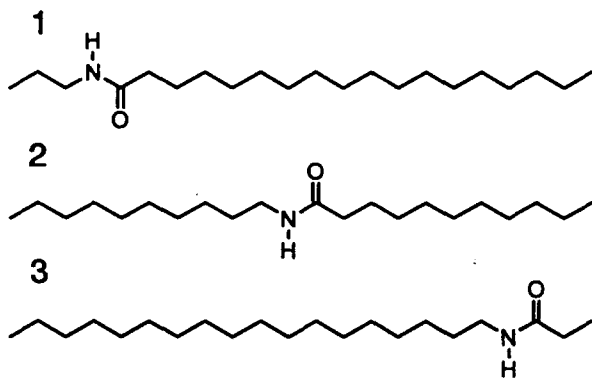
Molecular Motions in Low Molar-Mass Alkyl Amides: Models For Molecular Motions in Polyamides

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Introduction

Sub-melting transitions are well known for normal alkanes,¹ fatty acids,² biological lipid membranes,³ and normal alkyl ammonium salts.⁴ The transitions are thought to involve crystallographic changes, formation of rotator phases, the onset of conformational disorder, or partial melting of portions of the alkyl residues before collapse of the crystal occurs. Understanding these transitions is fundamental to knowing what gives rise to lipid membrane fluidity or crystal-crystal transitions in commercial thermoplastics. Several techniques used in the analysis of these transitions are variable temperature FT-IR, Raman, DSC, X-ray, and solid-state NMR. Each technique gives a particular piece of evidence leading to a better understanding of molecular-level events.

It seems reasonable that derivatives of fatty acids other than those mentioned above should show similar thermal behavior. For example, we have shown that oligomeric thioethylene compounds⁵ possess sub-melting transitions that involve both pre-melting of the alkyl portions of the molecule. This could lead to polythioethylenes analogues which have combined properties of polythioethylene and a second component. We report here thermal transitions observed for fatty acid-derived normal alkyl amides containing a total of 21-carbon atoms. N-Propylstearamide (1), N-decylundecanamide (2), and N-stearylpropanamide (3) show pre-melt behavior involving the alkyl segments and the amide unit. Variable temperature methods (FT-IR, DSC, and solid-state NMR) are used to characterize the behavior, particularly focusing on the solid-state NMR data.



Experimental

Normal alkyl amides were typically prepared by reaction of equal molar amounts of commercially available amines and acid chlorides in dry methylene chloride at 0 °C using triethylamine as acid scavenger. The solid amides were recrystallized from ethanol-water at least 5-times before use. Yields ranged from 70 to 80 % before recrystallization. Differential scanning calorimetry was performed using a PE DSC-7 equipped with a microcomputer. DSC calibration was performed before data collection using indium and tin as standards. Scans were taken at 1 °C/minute in order to establish near equilibrium conditions.⁶ Transition temperatures in the other experiments were approached in a similar manner. FT-IR spectra were collected using a PE-1600 on films precipitated onto KBr plates from methylene chloride. An Omega thermal controller was used to control the IR cell temperature. Solid-state NMR data⁷ were

collected on a Bruker MSL-200 (20.287 MHz for ¹⁵N and 50.32 MHz for ¹³C) with a standard 7-mm MAS probe.

Results and Discussion

The synthetic procedure used gave amides of high purity and in good yields which allowed facile thermal analysis without the problem of impurities. The thermal data is shown below in Table 1.

Table 1. Thermal Transition Data For Normal Alkyl Amides

	1	2	3
T _{cr} , °C	74.9	63.3	63.7
(ΔH, J/g)	(49.2)	(2.0)	(5.6)
T _m , °C	80.7	71.3	76.2
(ΔH, J/g)	(153.7)	(130.4)	(172.1)

The sub-melting transitions are reversible in that the transitions may be traversed several times (without crossing the melt) without loss of position or heat contribution. The first, second, and third heating thermograms for 1, 2, and 3 contain two transitions separated by at least 8 degrees. However, on the second run, the lower temperature transition heat of fusion (ΔH) for 1 is reduced (and in subsequent runs) by an order of magnitude (49.2 J/g to 6.7 J/g). Amide 1 is the only compound showing different thermal behavior on melt recrystallization. This may suggest that the melt crystallized 1 possesses some disorder that is not present in the solution crystallized amide.

A typical set of variable-temperature FT-IR spectra below and above the transition temperatures for 1 is shown in Figure 1. There are several prominent features of the region for methylene rocking between 1100 and 700 cm⁻¹ showing a clear change on crossing the 75 °C-transition. These bands decrease in intensity with increasing temperature then disappear above the transition. Similar behavior has been seen for other linear alkanes^{8,9} below and above their respective transition temperatures, in which the differences between the spectra are rationalized in terms of the onset of conformational disorder which disrupts the short-range order above the transition. The conformational disorder probably involves the formation of a rotator phase in which the methylene units acting as a whole rotate about their long axis. Here, the conformational disorder is probably the onset of 180 °-jumps of the stearyl segment. The anchoring amide unit restricts the motion near its end of the chain however.

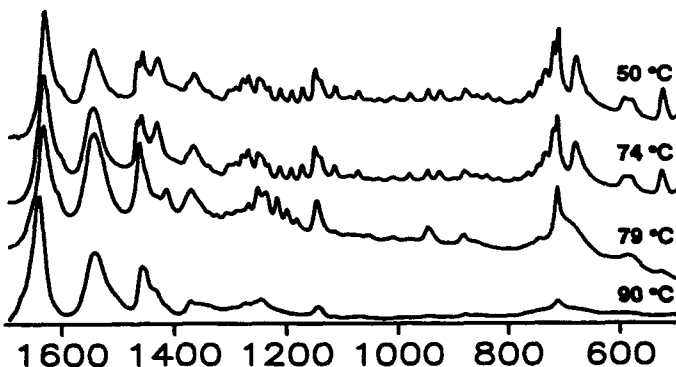


Figure 1. FT-IR spectra (1700 to 500 cm⁻¹) of 1 at temperatures below and above the transitions and in the melt at 90 °C.

Other features of the FT-IR spectra are the amide V and IV modes near 680 cm⁻¹ and 600 cm⁻¹, respectively. Nylons have similar bands with their position and number indicating what type of crystal form is present.¹⁰ For 1, the intensity of the 680 and 600 cm⁻¹ bands decrease with increasing temperature. After crossing the transition, it is clear that the bands are still present, but much peak

definition has been lost and the bands are clearly absent in the melt.

Changes are seen in the solid-state ^{13}C and ^{15}N NMR spectra (not shown) for 1 as well. For example, the all-trans carbons appear at 32.9 ppm at ambient temperature and move to 33.6 ppm on crossing the transition. This is consistent with the onset of conformational disorder as seen by other workers¹¹ for normal alkanes. The chemical shift of the nitrogen atom shifts from 92.3 ppm at 30 °C to 85.5 ppm at 76 °C and then back to 92.3 ppm on cooling. The propyl segment is probably static at ambient temperature but is melted at elevated temperatures. The stearyl portion on the other hand remains unmelted up to T_m but undergoes rapid 180 °-jumps above 74 °C.

A typical set of solid-state ^{13}C CP/MAS NMR spectra is shown in Figure 2 for 2. Below the DSC transition at 63 °C, the carbon directly attached to the nitrogen side of the amide unit is seen at 39.2 ppm and shifts to 40.3 ppm above the transition. Similarly, the carbon on the carbonyl side of the amide unit moves down field from 36.8 ppm to 37.6 ppm, consistent again with a change in the average conformation about the amide unit. The sharpening of all of the peaks (except for the carbon attached to nitrogen) suggests that the alkane segments are undergoing rapid molecular reorientation but are not melted as supported by the fact that all carbons remain observable under CP/MAS conditions below T_m . In the melt and rotator phases, cross-polarization (CP) is ineffective.

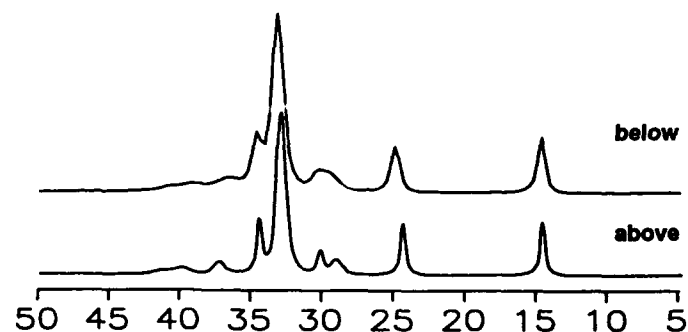


Figure 2. Solid-state ^{13}C CP/MAS NMR spectra (between 5 and 50 PPM) of 2 below and above the sub-melting transition.

The FT-IR spectra of 2 taken at temperatures below and above the thermal transitions show similar behavior as with 1. Several methylene rocking bands and amide modes decrease in intensity with increasing temperature and nearly disappear prior to melting. The onset of rapid jumps or screw-like motion (conformational disorder) probably occurs above the transition temperature.

Solid-state ^{15}N CP/MAS NMR spectra for 3 are seen in Figure 3. The chemical shift of the nitrogen atom below the sub-melting transition is 84.0 ppm which is consistent with the amide unit being coplanar with the methylene units. Above the first transition (above 64 °C but below 76 °C) the peak for the amide nitrogen moves to 87.1 ppm. This chemical shift is similar to that for the amide nitrogen of amorphous domains in nylons.¹² The chemical shift of the carbons immediately surrounding the amide unit also change upon crossing the transition; the carbon next to the nitrogen moves upfield from 42.0 to 39.8 ppm and the carbon on the other side of the amide moves upfield from 35.6 to 35.0 ppm. The peak position of the all-trans methylenes shifts from 34.0 ppm to 33.6 ppm which is consistent with the onset of rapid molecular motion, probably 180 °-jumps that maintain the all-trans conformation of the stearyl chain. No conformational disorder similar to melting is seen above the sub-melting transition to about 5 °C below the melt for 3.

The variable-temperature FT-IR spectra of 3 show changes similar to those seen for 1. Methylene rocking bands decrease in intensity with increasing temperature then disappear above the first transition. The amide V and VI modes undergo intensity changes and the methylene rocking and amide modes are absent in the melt.

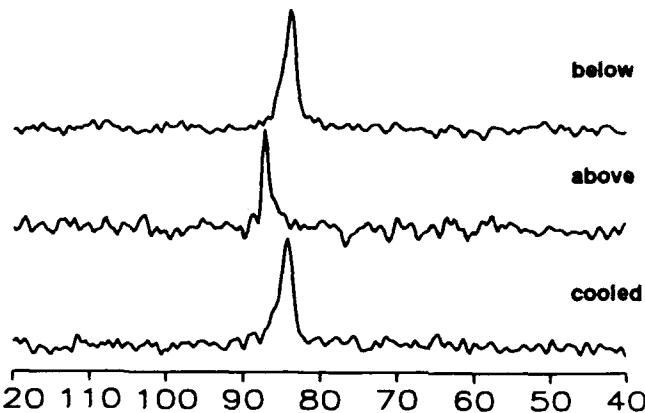


Figure 3. Solid-state ^{15}N CP/MAS NMR spectra (between 40 and 120 PPM) of 3 below and above the sub-melting transition and cooled back to ambient temperature.

Conclusions

Alkyl amides 1, 2, and 3 undergo DSC transitions. The fact that differences are seen in the FT-IR and solid-state NMR spectra confirm that the transitions are real. They probably involve rapid jump-like motions of the all-trans alkyl portions of the chains. However, the chains are not melted since cross-polarization NMR experiments show the carbons to be rigid above the sub-melting transitions. Crystallographic changes may also occur at the transitions for the amide unit and the alkyl portion of the molecules.

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