Small-Angle X-ray Scattering of *n*-Hexacontane as a Function of Temperature

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Introduction

Although the *n*-alkanes have a rather simple chemical repeat, they exhibit a variety of different crystalline structures and phase transitions between them. This is true not only for the different alkanes but within a given alkane, depending on the crystallization mode. Premelting, even for very pure alkanes, further complicates structural analyses. The premelting of interest here involves the conformational disordering of the end sequences and has been demonstrated to occur in a large number of *n*-alkanes by a variety of experimental methods.[1]

Hexacontane, $C_{60}H_{122}$, is a key alkane in studying the crystalline structures and the premelting phenomenon. It is a sufficiently long chain that does not display the hexagonal structure, or rotator phase. Thus, this complicating feature is removed from consideration. A variety of studies such as vibrational spectroscopy,[2] small-angle X-ray scattering (SAXS),[3,4] solid-state ^{13}C NMR,[5] and thermal expansion[6] of this alkane can be interpreted in terms of premelting.[1] However, different ordered structures can develop in *n*-hexacontane at ambient temperature, depending on the method of crystallization. Of additional interest is the origin of the small endothermic peak that is observed subsequent to crystallization from the pure melt.[4,5] To correlate the results of different measurements and to examine the nature of this endothermic transition, we have studied the SAXS temperature dependence of *n*-hexacontane. The two samples investigated were crystallized under the exact same conditions as those previously studied by solid-state ^{13}C NMR,[5] differential scanning calorimetry (DSC),[5] and thermal expansion.[6]

Experimental Section

The *n*-hexacontane sample was purchased from Fluka and crystallized in the manner described previously.[5] Two crystallization procedures were used. In one of these the sample was rapidly crystallized from the melt, sample A. In the other it was rapidly crystallized from a butyl acetate solution, sample B. The procedure used to obtain the thermograms have also been described.[5]

The SAXS experiments were performed at the SAXS facility at Stony Brook. An Enraf-Nonius rotating-anode X-ray generator was used at 40 kV and 80 mA with a fine focus (0.3 × 3 mm^2). A Ni filter was used to eliminate the Cu Kβ portion. A Kratky collimation system was used in combination with a pulse height discriminator and proportional counter. The samples with defined thermal history were inserted into Mark capillary tubes that were then put in a temperature-controlled (±0.5 °C) sample holder. The sample temperature was calibrated by replacing the sample tube with a sensor of comparable geometry in the sample holder. The SAXS measuements were started at least 15 min after the sample reached the desired temperature. The measurement time for the complete angular scan was on the order of 3-10 h and could be reproduced. Therefore, we believe that the measurements were performed under equilibrium conditions. The sample temperature was increased monotonically during each incremental temperature increase for the SAXS experiment. Temperature loop (over heating) during the heating-up process was negligible.

The SAXS curves were standardized to the same measurement time period and corrected for the absorption effect and the background (empty capillary tube). The smeared relative intensity data were desmeared by using the algorithm developed by Lake.[7] The maxima in the desmeared, Lorentz-corrected scattering patterns were converted to spacings (L) according to Bragg's law.

Results and Discussion

The thermograms for the samples generated by the two different crystallization procedures have already been given,[5] so they need not be repeated here. The thermogram for sample B (solution crystallized) showed only one sharp endothermic peak at 99 °C, which represents the complete melting of the sample. The thermogram for sample A (bulk crystallized) displays a consistent and reproducible small endothermic peak at 71 °C in addition to the sharp melting peak at 99 °C.

The product of Iq^2 for samples B and A are plotted against q at a series of temperatures in Figures 1a and 2a, respectively. Here, Iq^2 is the desmeared, Lorentz-corrected scattering intensity at the scattering vector $\mathbf{q}$, whose magnitude is $(4\pi/\lambda)\sin\theta$, with 2θ and λ being the scattering angle and the X-ray wavelength, respectively. The scattering patterns in the two figures are qualitatively similar to one another. Two orders of diffractions were observed, with the apparent maxima at $q \sim 0.1$ nm^{-1} being susceptible to artifacts. The intensities and positions of the maxima vary with temperature in a manner that is similar to what has been reported for other *n*-alkanes.[8] Of particular interest in the present work is the change in the angular position of the maxima at $q \sim 0.8$ nm^{-1} with temperature, as shown in a more expanded version of the scattering patterns in Figures 1b and 2b. We examine this point in more detail by converting the maxima to long spacings, L, by means of Bragg's law with $L = 2\pi/q_{max}$ and $n = 1$. The results of this conversion are plotted in Figures 3 and 4 for samples B and A, respectively.

It is most convenient to examine the results for the solution-crystallized sample (sample B) first. As is shown in Figure 3 for this sample, there is a continuous decrease in L with temperature. There is no indication of any discontinuity or transition. A temperature dependence of this kind has been generally found in many *n*-alkanes[3,4,8,9] and in particular for *n*-hexacontane crystallized in this manner.[3,4] The long spacing at room temperature, 82 Å ± 2%, is similar to other reported values.[3,4] It is consistent with a lamellar crystallite of untilted chains that form an orthorhombic unit cell. The unit cell structure cannot be determined solely from the wide-angle X-ray pattern since untilted as well as tilted chains having a monoclinic structure yield the same orthorhombic subcell.[10] There is a very modest decrease in the long spacing with temperature until the range of 70-75 °C is reached. At this point, there is a continuous, but rapid decrease in L with increasing temperature which persists up to melting. These results are qualitatively similar to those observed by Takamizawa et al.[4] and by Strobl.[3] In the former case the temperature at which the main decrease in L started was 82 °C, somewhat higher than ours. However, their orthorhombic form also showed a small endothermic peak at this temperature, indicating that there are some differences between our samples.

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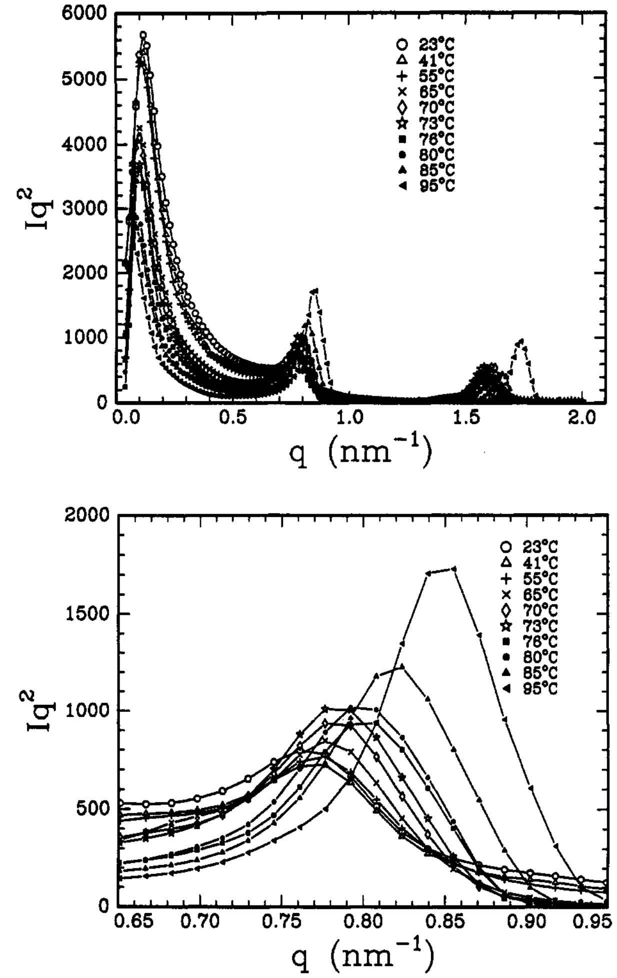

Figure 1. SAXS profiles of solution-crystallized $C_{60}H_{122}$ (sample B) as a function of temperature.

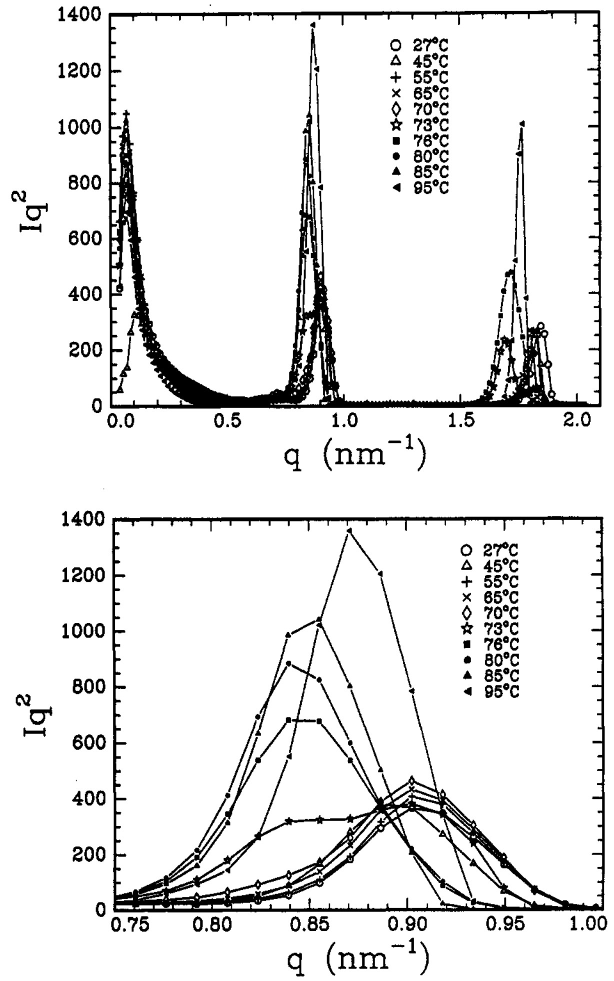

Figure 2. SAXS profiles of melt-crystallized $C_{60}H_{122}$ (sample A) as a function of temperature.

Strobl's results, which are based only on three data points at elevated temperatures, are qualitatively similar to ours.[3] The decrease in the long spacing appears to begin at ~ 75 °C.

In addition to SAXS measurements, a variety of other measurements such as ^{13}C NMR,[5] vibrational spectroscopy,[2] and thermal expansion[6] have demonstrated that premelting in *n*-hexacontane begins in the temperature region 70–75 °C.[1] Raman, infrared,[2] and ^{13}C NMR[5] studies have explicitly shown that the type of premelting that is observed involves the conformational disordering of sequences at the chain ends. This behavior is typical of all *n*-alkanes[1] and is expected theoretically.[11] The continuous decrease in L with temperature, once premelting is initiated, can be the result of further disordering of chain units, chain tilting, or a combination of both. Chain tilting and lattice expansion are two structural changes that satisfy the requirement to reduce the chain flux density at the basal plane of the lamellar crystallite.[12–16] Since L decreases continuously with temperature, at the elevated temperatures, a specific monoclinic form with indexable end groups cannot be assigned to the structure in this region.[4,9]

The long spacings for the bulk-crystallized sample, which gives the small endotherm peak, are given in Figure 4 and are seen to be quite different from the previous results. At the lower temperatures there is very little change in the long spacing. However, in contrast to the results in Figure 3, a discontinuous increase of ~5 Å is observed at ~72 °C. This temperature coincides almost exactly with the small low-temperature endothermic peak.[5] It is evident from both the DSC and SAXS results that a cooperative transition takes place at this temperature. As the temperature is increased beyond the transition point, the long spacing gradually decreases.

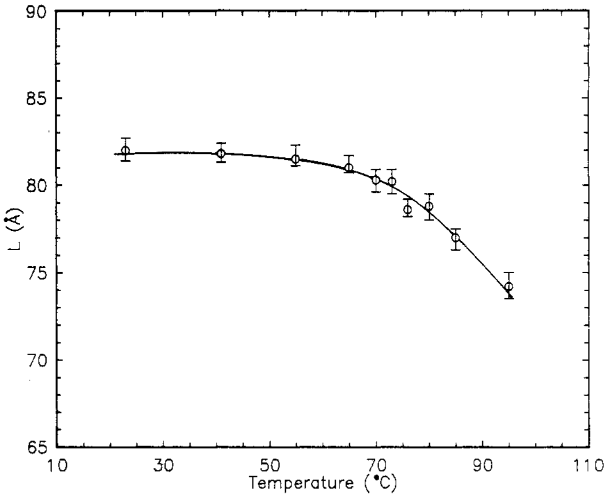

Figure 3. Dependence of the long spacing L upon temperature for the solution-crystallized $C_{60}H_{122}$ (sample B).

There are no other reports of SAXS studies for a $C_{60}H_{122}$ specimen crystallized in this manner. However, Strobl has performed similar studies with $C_{62}H_{126}$ crystallized from the pure melt.[3] Unfortunately, a sufficient number of data points were not obtained to allow for a definitive comparison with the results for $C_{60}H_{122}$. From this report,[4] L increased by at least 3–4 Å in the vicinity of 75 °C and decreased subsequently as the temperature was increased further. These results are thus consistent with those

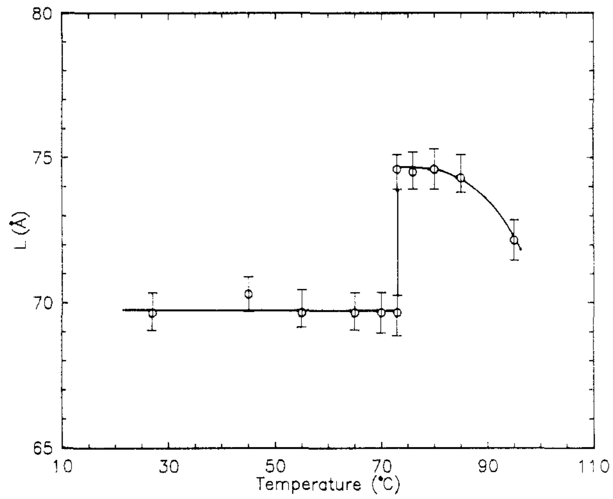

Figure 4. Dependence of the long spacing L upon temperature for the melt-crystallized $C_{60}H_{122}$ (sample A).

obtained here for $C_{60}H_{122}$. Takamizawa et al.'s[4] study of $C_{48}H_{98}$ gives results that are very similar to those reported here for $C_{60}H_{122}$. A sharp increase in L of ~2.5–3 Å was observed at 75 °C. This temperature also corresponds to the small endothermic peak observed before melting.[17] As has been described for the other alkanes, a decrease in L is also observed in $C_{48}H_{98}$ as the temperature is increased further. Thus, these bulk-crystallized n-alkanes initially develop a monoclinic structure (cf. seq.) and then undergo a highly cooperative solid-solid transition at an elevated temperature.

Since the orthorhombic and monoclinic structures have the same orthorhombic unit subcell, structural assignments have to made on the basis of the long period. This involves the inherent assumption that one has flat end planes; i.e., the end groups can be indexed. Although there should be no problem with this assumption at ambient temperatures, premelting and the disordering of the end-group sequences introduce complications at elevated temperatures. At room temperature, L = 69–70 Å for the bulk-crystallized sample. We use the scheme that has been proposed to index the monoclinic structures that can form.[4,9] The M_{011} form corresponds to L = 70.2 Å.[4,18] The long spacing for the M_{201} form is also in the range 69–70 Å, based on interpolation of Takamizawa's data.[4] Thus, the observed long spacing is compatible with either of these two monoclinic structures. However, electron diffraction studies indicate that melt-crystallized paraffins exhibit an M_{201} structure at room temperature.[6]

If one assumes that the chain ends can be indexed, then, based on the interpolation of data given by Takamizawa, the 75-Å spacing, which results from the solid–solid transition, can be classified as an M_{101} monoclinic structure. However, the temperature of this transition is in the premelting range. Solid-state ^{13}C NMR has shown that $C_{60}H_{122}$ crystallized in the described manner undergoes a rapid conformational disordering, indicative of premelting, starting at 74 °C. Thus, within the limitations of temperature discrimination, one cannot definitively index the end groups nor assign a specific monoclinic structure. However, it is clear that a cooperative transition from one type of tilted chain packing to another has taken place. One cannot decide as to whether premelting takes place simultaneously with, prior to, or subsequent to the transition. A much finer temperature discrimination is needed for each of the experiments to decide this issue.

In summary, the SAXS–temperature results for the solution-crystallized orthorhombic form of n-hexacontane agree with other physical–chemical measurements. The fusion process is a continuous one, with premelting beginning in the range 70–75 °C. Above this temperature a definitive monoclinic structure cannot be assigned, since the terminal groups can no longer be indexed. In contrast, the bulk-crystallized sample undergoes a sharp transition at ~72 °C, in accord with DSC studies. The original monoclinic form is cooperatively transformed to another structure that also is composed of tilted chains. Since this transition takes place in the premelting range, it is very treacherous to assign a definite crystalline structure.

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