A CRAMPS and $^{13}$C CP/MAS NMR Examination of Solid-State Transitions in n-Hexatriacontane

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The normal paraffins can undergo several transitions before melting and may thus serve as interesting model compounds for polyethylene, which also undergoes solid-solid transitions, the strongest and best-known being the so-called α transition. Our examination of n-hexadecane (C₁₆) has been greatly furthered by the use of the solid-state ¹H NMR technique known as CRAMPS (Combined Rotation And Multiple Pulse Spectroscopy).² This technique, combined with DSC and ¹³C CP/MAS NMR, has allowed us to make tentative assignments for the molecular motions occurring at different temperatures below the melting point.

DSC of C₁₆ crystallized by various methods at several cooling rates displays several different patterns of endothermic transitions in the solid phase; depending on the sample treatment, as many as three solid-solid or "premelt" transformations can be seen to occur. DSC measurements were conducted on these samples using a TA Instruments Model 2920 DSC in standard mode with a heating rate of 0.5 °C/minute in a nitrogen atmosphere. NMR measurements were conducted on a Bruker MSL-400 spectrometer (400.13 MHz ¹H, 100.43 MHz ¹³C) using standard and high-temperature Bruker double-air-bearing magic-angle-spinning (MAS) probes. ¹³C spectra were collected at approximate 1 K thermal intervals using cross-polarization (CF) and MAS. ¹³C experimental times were shortened by the use of a flipback pulse (negative 90° ¹H pulse). CRAMPS spectra were acquired using the BR24 pulse sequence.⁵

A representative DSC trace of a melt-crystallized C₁₆ sample is shown in Figure 1. This sample was heated above the melt in the DSC, then the sample pan was removed and placed on a room-temperature aluminum sheet. Two large transitions, corresponding to the transition to the pseudo-hexagonal or "rotator" phase (72.73 °C) and to the melting transition (74.94 °C), are readily apparent. Also visible are two smaller premelt transitions (70.72 and 69.93 °C) that become more defined upon enlargement of the thermogram.

The DSC thermogram of the other applied sample treatment is shown in Figure 2. This sample was melted in a small beaker in a water bath, then poured into liquid nitrogen, collected, dried, and placed in a DSC sample pan. Note that the melting (75.0 °C), pseudo-hexagonal (72.73 °C), and smaller premelt (70.24 °C) transition are very similar to those seen in Figure 1. In fact, the premelt transition seen here appears to be a combination of the two premelt transitions seen in Figure 1. By correlating the thermal transition seen in these DSC spectra with the solid-state NMR spectra for the same sample treatments, it is possible to assign types of molecular motions to each of the transitions.

Figure 3 shows a stack plot of significant spectra in the variable-temperature ¹³C CP/MAS series for a sample treatment similar to that of the sample whose DSC thermogram is shown in Figure 1. The 25.8 °C spectrum displays two broad methyl peaks, at 14.6 and 15.2 ppm. Both of these are also present in the 66.8 °C spectrum, but only a sharp 14.8 ppm methyl peak remains at 70.8 °C. This peak gradually drifts upfield and sharpens a bit more, reaching 14.4 ppm in the pseudo-hexagonal phase at 73.0 °C. The α-CH₃ peak behaves similarly, a broad, low 24.9 ppm peak at 25.8 °C which sharpens and moves upfield to 24.6 ppm at 70.8 °C, where one can see evidence of a shoulder peak growing in on the upfield side of the peak. By 71.6 °C, all of the α-CH₃ resonance has moved to this upfield chemical shift (24.0 ppm).

The changes in both the methyl and α-CH₃ resonances are non-cooperative transitions; i.e., a gradual transition occurs between discrete states, without a significant chemical shift change in either of the peaks. The examples of this phenomenon are the two methyl peaks changing intensity from 25.8-70.8 °C and the intensity change in the α-CH₃ peaks over the 66.8-71.6 °C range.

The all-trans -CH₂ peak at 32.9 ppm also narrows with increasing temperature, and shoulder peaks begin to be seen at 70.8 °C, just before the pseudo-hexagonal transition. Upon entry into the pseudo-hexagonal phase, the internal methylene peak narrows sharply and moves downfield to 33.5 ppm, showing two peaks that were hidden beneath it in the γ-CH₂ (31.9 ppm) and δ-CH₂ (32.4 ppm) peaks.

Significant spectra from the CRAMPS variable-temperature series are shown in Figure 4, along with text showing the correlations between the changes seen in the CRAMPS spectra and transitions observed in the DSC thermograms and ¹³C spectra. These spectra clearly show the peak resolution of the CRAMPS technique, and the advantage of this technique over standard MAS ¹H NMR is easily seen. Close correlation with ¹³C and DSC transitions is observed. The disappearance of the methyl peak at 0 ppm (NOTE: chemical shifts are unrefined, and the largest peak, which we assign to the main-chain -CH₂- protons and appears to be consistent in all spectra, was arbitrarily set at 1.2 ppm) between 55.5 and 66.0 °C correlates with the baseline shift seen in DSC (see below) and small chemical shift changes in the upfield methyl and α-CH₃ peaks. A narrowing of the internal -CH₂ peak between 69.2 and 70.0 °C is assigned to greater chain freedom associated with the onset of the DSC premelt transitions.

Between 71.7 and 73.5 °C, the CRAMPS spectra show entry into the pseudo-hexagonal phase, as seen by the appearance of two downfield shoulder (1.4 and 1.8 ppm) on the internal -CH₂- peak and baseline resolution of the internal -CH₂- and methyl (0.5 ppm) peaks. These shoulder peaks continue to become more defined until the melting transition between 76.5 and 79.7 °C, at which point the 1.4 ppm shoulder peak on the internal -CH₂- peak diminishes greatly and the 1.8 ppm peak increases in intensity. A third shoulder peak at 1.3 ppm may be discerned in the 76.5 °C spectrum.

We have not as yet been able to assign these peaks to specific molecular motions, but the correlation with the ¹³C and DSC data encourages the conclusion that the changes in the CRAMPS spectra reflect the same transitions.

It is perhaps easier to see the correlation between the chemical shift changes in the ¹³C CP/MAS spectra and thermal transitions by looking at Figure 5, which overlays the chemical shift peak values from collected CP/MAS spectra onto a greatly enlarged rendition of the thermogram from Figure 1. At this level of enlargement, another previously unseen DSC transition is observed at approximately 58 °C, which may correlate with an approximately ±0.1 ppm oscillation in the α-CH₃ peak chemical shift seen from 50 to 60 °C.

Another item of note observed from Figure 5 is that changes in chemical shift occur at the onset of thermal transitions in the DSC. Perhaps the most obvious point at which this occurs is at the pseudo-hexagonal transition. NMR onset (discontinuities in the all-trans region near 30 ppm and in the α-CH₃ region near 25 ppm) for this transition is 72.2 °C, which correlates well with the DSC onset of 72.1 °C. Following this argument, the disappearance of the downfield methyl peak and a slight upfield shift (0.1 ppm) of the upfield methyl peak may be correlated with the onset of the DSC transition that peaks at 69.9 °C.
It can be seen that CRAMPS NMR represents a valuable addition to available characterization techniques. Work is currently in progress in our group to apply CRAMPS to other sample segments of C6 to gain a better, more comprehensive understanding of the peremt transitions in this material.

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REFERENCES


Figure 1 DSC thermogram of hexadecane melt-quenched onto room-temperature aluminum sheet.

Figure 2 DSC thermogram of hexadecane melt-quenched into liquid nitrogen.

Figure 3 Significant spectra from the variable-temperature CP/MAS experiment series.

Figure 4 Spectra from the variable-temperature CRAMPS experiment series.

Figure 5 Correlation of peak chemical shift values from variable-temperature CP/MAS with DSC thermal transitions of the same sample treatment.