

Supplemental Material
for
**Raman analysis of bond conformations in the rotator state and premelting of
normal alkanes**

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NCCT mass fraction

Figure A1 shows the NCCT mass fraction versus temperature for the alkanes ranging from C_{21} to C_{60} . The NCCT mass fraction in the higher alkanes (C_{40} to C_{60}) are plotted individually in a truncated temperature window to highlight changes in the NCCT mass fraction near the melt temperature. The C_{21} to C_{37} alkanes exhibit a transition over a temperature range of approximately (1 to 2) °C from a small amount of chains in the NCCT conformation to a maximum value well above 70 % by mass. The Raman spectra corresponding to this large increase in the NCCT mass fraction resembles the rotator phase spectra in Figure 1a of the main text. In the case of the C_{37} alkane, the sharp increase in NCCT is preceded by small amount of NCCT conformers that initially reach mass fractions of approximately 0.06 at 66 °C and increase to 0.10 at a temperature of 77 °C. After reaching a maximum, the NCCT mass fraction in the C_{21} to C_{37} alkanes decreases with increasing temperature until an abrupt transition occurs at a higher temperature. The width of the temperature window where the NCCT mass fraction exceeds 0.5 gets narrower as the alkane chain length increases, ranging from approximately 9 °C for the C_{21} alkane to 2 °C for the C_{37} alkane. Immediately prior to the sharp loss of NCCT mass fraction, the C_{21} to C_{27} alkanes approach values in the range of $0.67 < \alpha_{\text{ncct}} < 0.70$, whereas the C_{37} alkane reaches a smaller mass fraction of 0.57 ± 0.03 just prior to an abrupt decrease.

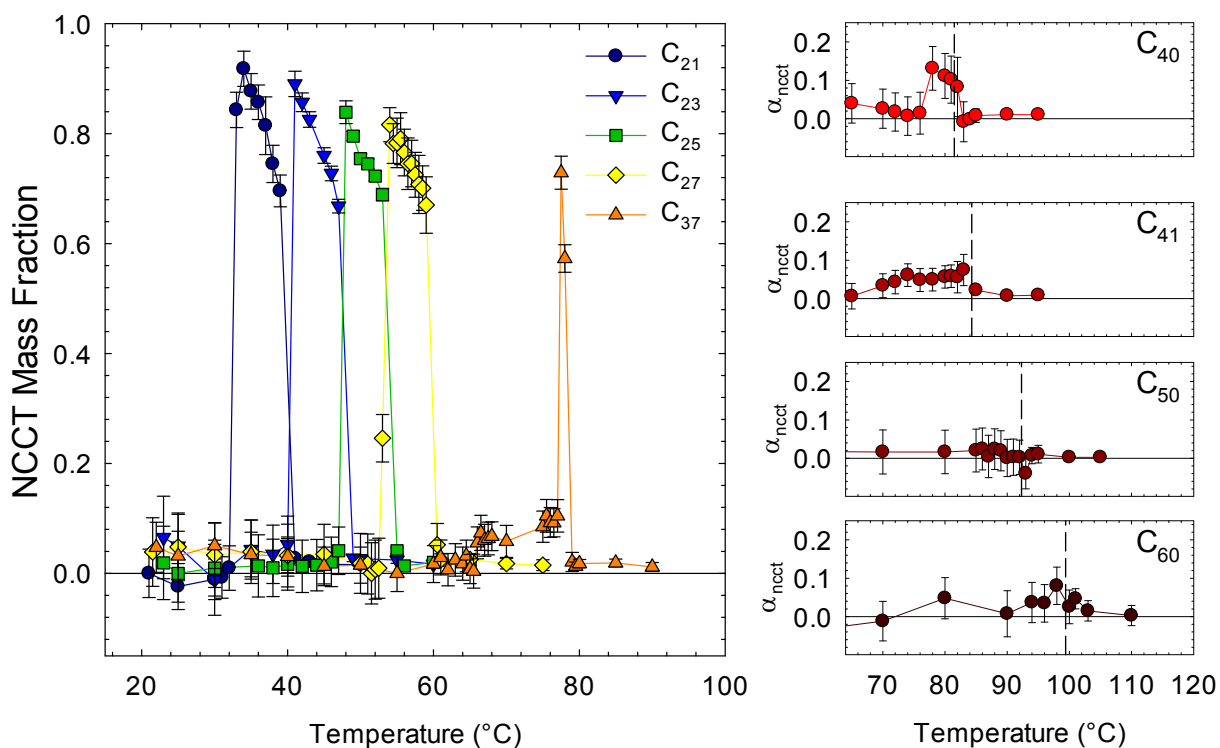


Figure A1. Mass fraction of NCCT conformers versus temperature for different alkanes. The left plot shows the alkanes C₂₁ through C₃₇. Plots for the alkanes C₄₀ through C₆₀ near the melting transition temperature are shown on the right, with the alkane denoted in the upper right corner of each plot. The vertical dashed lines indicate the melting temperature for the alkanes C₄₀ to C₆₀.¹

Unlike the alkanes exhibiting a large NCCT mass fraction during heating, the C₄₀ to C₆₀ alkanes display much smaller NCCT mass fractions with less pronounced transitions. Of the four alkanes in this chain length range, the C₄₀ alkane has the largest transition near 78 °C, going from negligible NCCT mass fractions to a maximum value of 0.13 ± 0.06 . This mass fraction decreases with increasing temperature up to 82 °C, above which the mass fraction sharply decreases to negligible amounts. The increase in the NCCT mass fraction with temperature is more gradual for the C₄₁ alkane, as noted in the results describing Figure 2b. Increasing the chain length even further to the C₅₀ alkane leads to values within measurement uncertainty over the entire temperature range. The C₆₀ alkane exhibits a slight increase in the NCCT mass fraction with increasing temperature

to a maximum value of 0.08 ± 0.05 at $98\text{ }^{\circ}\text{C}$ before decreasing to negligible values within measurement uncertainty.

The temperature at which the NCCT mass fraction dominates the mass fraction distribution coincides with the crystal-rotator transition temperature for the alkanes C_{21} through C_{37} measured using calorimetry techniques.^{2,3} Likewise, the temperature where there is a sharp decrease in the NCCT mass fraction to negligible values corresponds to the previously measured rotator-melt transition temperature.^{2,3} Chains longer than the C_{39} alkane exhibit a crystal-melt phase transition without passing through a rotator phase, which has been shown in prior DSC measurements.⁴ The C_{40} , C_{41} , and C_{60} alkanes generate a non-negligible amount of chains in an NCCT conformation that decreases at the crystal-melt transition temperatures tabulated in ¹. The C_{50} alkane does not.

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