DETERMINATION OF PHASE TRANSITIONS IN Y-SHAPED, BRANCHED ALKANE, $C_{120}H_{241}CH(C_{195}H_{391})C_{119}H_{23}$ USING RAMAN SPECTROSCOPY

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ABSTRACT

Raman spectroscopy has been used to identify solid – solid phase transitions in the symmetrically branched alkane, $C_{120}H_{241}CH(C_{195}H_{391})C_{119}H_{239}$ during real-time heating. The vibrational modes in the region from 1700 to 200 cm^{-1} were studied. A single phase transition was identified at 87°C $\pm$ 5°C in this alkane based on the changes in the band intensities. It was revealed that the crystalline bands show subtle changes whereas the disorder bands show the most significant changes at this transition.
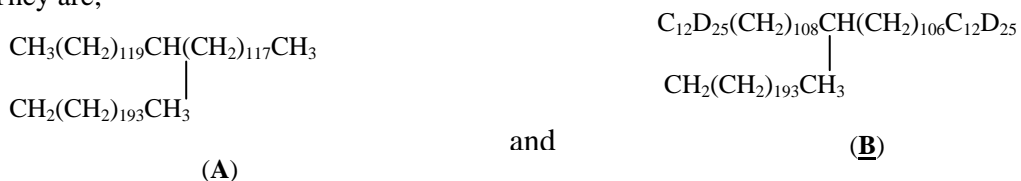
Key words: Monodisperse alkanes, vibrational spectroscopy, crystal structures

INTRODUCTION

Monodisperse linear long chain alkanes (partially deuterated and undeuterated) and their binary mixtures have been successfully studied during the past two decades with a view to relate their crystallisation processes and crystal morphologies to those of linear polyethylene. For an extensive review on the past work on long chain alkanes see Ungar & Zeng (2001). Similarly, monodisperse branched alkanes are becoming popular as model compounds for branched polyethylene. With this aim several single-branched alkanes having short (C_1 and C_4) (Brooke *et al*., 1996) and long (C_{61} and C_{195}: Y-shaped molecules) (Brooke *et al*., 2001) branches have been chemically synthesised.

The crystalline structures of short-branched alkanes and the Y-shaped alkane with a C_{61} branch have been studied and well established (Ungar & Zeng, 2001). Short branched, symmetrical $C_{96}H_{193}CH(CH_3)C_{94}H_{189}$ and $C_{96}H_{193}CH(C_4H_9)C_{94}H_{189}$ always produced the once-folded (F2) conformation. This is formed via a short-lived 'NIF' stage. However, short branched, asymmetrical $C_{191}H_{383}CH(CH_3)C_{99}H_{199}$ shows two semicrystalline forms depending on the crystallisation temperature, T_c. Electron density reconstruction has shown that each structure contains alternating amorphous and crystalline layers. They are similar to the 'NIF' structure in linear and symmetrically branched alkanes. Upon cooling these semicrystalline forms transform into a double and triple layer superlattice structures in each case. Y-shaped symmetrical alkane with a long branch, $C_{120}H_{241}CH(C_{61}H_{123})C_{119}H_{239}$, also shows a semicrystalline form at higher temperature (Ungar & Zeng, 2001). A double layer superlattice form has been achieved for the low temperature form. In this superlattice, one layer consists only of the long arm of the molecule while the other layer consists of both the extended short arm and folded long arms. At present, two C_{195}-branched symmetrical alkanes are available, one being the deuterated analogue of the other. They are;

$CH_3(CH_2)_{119}CH(CH_2)_{117}CH_3$

$CH_2(CH_2)_{193}CH_3$

(**A**)

and

$C_{12}D_{25}(CH_2)_{108}CH(CH_2)_{106}C_{12}D_{25}$

$CH_2(CH_2)_{193}CH_3$

(**B**)

Different crystal structures of C195 – Y shaped alkanes are still being investigated by vibration spectroscopy, small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS). We suspect **A** and **B** also show a high temperature semicrystalline form and a low temperature superlattice structure as in C_{61}- Y shaped branched alkane. The aim of this work is to identify this semicrystalline to superlattice transition in **A** during real-time heating, using Raman spectroscopy. Parallel SAXS work is also being carried out in this regard (Ungar *et al*., unpublished data). Prior to this analysis, short chain alkane, $C_{34}H_{70}$ which shows a well established monoclinic to rotator transition, was investigated by Raman spectroscopy in order to establish a suitable methodology for this work (Wickramarachchi & Spells, 2007).

The above transitions are associated with increased conformational disorder in the crystal structure. Raman spectrum is sensitive to these conformational changes. A detailed description of the vibrational modes which are sensitive to conformational

changes in the region of 1700 – 200 cm^{-1} of the Raman spectrum is given in elsewhere (Wickramarachchi *et al*., 2007). Only a brief account of these modes is given here. CH$_3$ rocking region from 900 – 830 cm^{-1} shows various conformational bands. Separate Raman bands have been observed for *tt-, gt-, gg-* and *tg-* chain ends of an otherwise all-*trans* chain in this region (Kim *et al*., 1989). The CH$_2$ twisting band is a combination of two vibrational modes: 1295 cm^{-1} crystalline and 1305 cm^{-1} gauche counterpart (Naylor *et al*., 1995). The C-C stretching region from 1000 to 1200 cm^{-1} comprises of two strong bands at 1060 and 1130 cm^{-1} arising from *trans* C-C bonds and a broad band centred around 1080 cm^{-1} due to gauche conformers (Naylor *et al*., 1995; Tarazona *et al*., 1997). This study intends to determine the semicrystalline to superlattice transition in **A** using the above mentioned conformational bands.

EXPERIMENTAL

A sample (about 3 mg) of **A** was placed on the lid of a DSC pan (Mettler design). This formed the sample holder which was used here. Sample **A** was melt crystallised (0.2^0 C min^{-1}) in the sample holder to obtain a thin film. Then the sample holder with the sample was covered by a circular aluminium foil to obtain a better temperature control. The diameters of the sample holder and the aluminium foil were roughly equal. A small hole with a 2 mm diameter was made on the aluminium foil to allow the light to pass through. The spectra were collected as a function of temperature between 60° and 130° C using a Renishaw Raman Spectrometer. A Linkam hot stage was used for these heating runs. The hot stage was fixed on to an Olympus microscope stage. A diode laser at 785 nm was used as the excitation source. Laser light was focussed on the sample using a 20× microscope objective. The spectra were measured between 1700 and 150 cm^{-1} with a resolution of 2 cm^{-1}.

The analysis of the Raman spectra involved the baseline correction and curve fitting procedures. The curve fitting was performed using GRAMS 32 software.

RESULTS AND DISCUSSION

The Raman spectrum of C$_{34}$H$_{70}$ (Wickramarachchi & Spells, 2007) demonstrated very clear changes in crystalline and amorphous bands in region 1: CH$_2$ bending (1600 – 1400 cm^{-1}), region 2: CH$_2$ twisting (~ 1300 cm^{-1}), region 3: C-C stretching (1200 – 1000 cm^{-1}) and region 4: CH$_3$ rocking conformations (~ 900 cm^{-1}) at the phase transitions of C$_{34}$H$_{70}$ (Wickramarachchi & Spells, 2007). These regions are illustrated in figures 1 and 2.
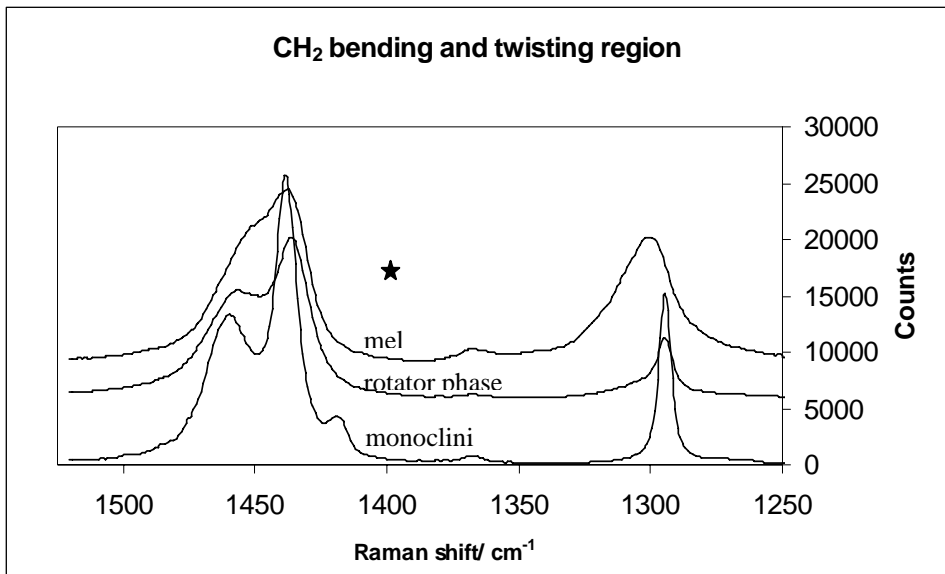
Figure 1 : **CH$_2$ bending (region 1) and twisting (region 2) modes of the Raman spectrum of C$_{34}$H$_{70}$ in monoclinic, rotator, and melt phases at 62, 71, and 76 °C respectively.**
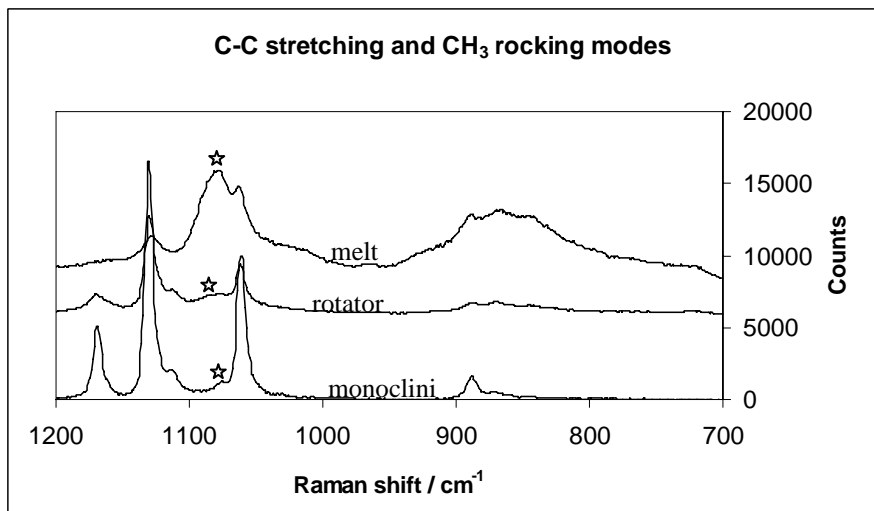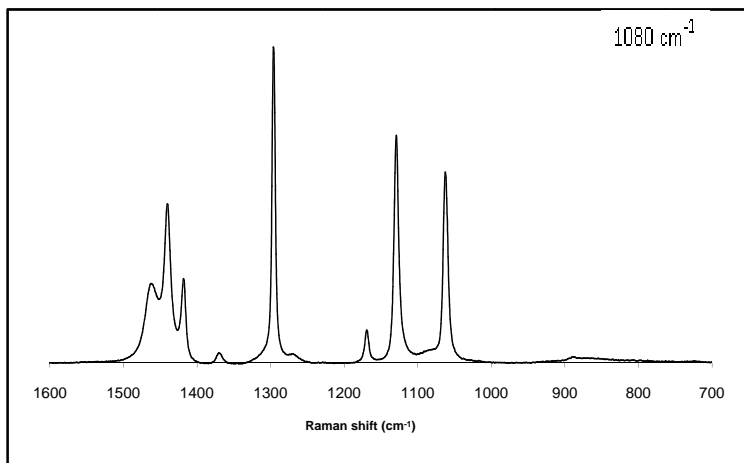

Figure 2 : **C-C stretching (region 3) and CH$_3$ rocking (region 4) modes of C$_{34}$H$_{70}$ for different phases at 62, 71, and 76 °C respectively.**

Figure 3 :   Raman spectrum of <u>A</u> at 70° C in the region from 1600 to 700 cm^{-1}.

Figure 3 shows the Raman spectrum of <u>**A**</u> at 70° C. We can identify a gauche band at 1080 cm^{-1} (*) and CH_3 rocking conformational bands around 900 cm^{-1} in the spectrum of <u>**A**</u> even at this relatively low temperature. Although the 1305 cm^{-1} twisting mode due to gauche conformers is hardly visible in this spectrum, it is identifiable by curve fitting. These observations suggest that branching incorporates some disorder to the crystal lattice. CH_2 bending mode which is sensitive to the lattice geometry was unaffected until melting of the sample. The 1418 cm^{-1} band which indicates an orthorhombic lattice (Boerio *et al.*, 1970) was observable until melting. This suggests that they keep the original geometry even at higher temperature phase.

The CH_2 twisting and the C-C stretching regions of the Raman spectra collected from 60° C up to melting, during a stepwise, real-time heating run of sample <u>**A**</u> are shown in figures 4 and 5 respectively. Figure 6 shows an expanded view of the 1080 cm^{-1} band. This band was somewhat noisy so the spectra have been smoothed by 30% using the GRAMS 32AI Fourier smoothing function. From 60° to 82° C we can observe a gradual increase of the intensity of 1080 cm^{-1} gauche band with increasing temperature. Then from 82° C to 96° C this increase become very rapid and slows down again from 96° C and above until just below melting (118° C) of the sample. When the sample starts melting it increases very rapidly and in the melt spectrum both 1060 and 1130 cm^{-1} bands disappear and the 1080 cm^{-1} band dominates (Figure 5). In figure 6 only a part of the melt spectrum is shown. The rapid increase of the 1080 cm^{-1} band from 82° C to 96° C could be due to the phase transition occurring in this

temperature range. The NIF state is more disordered and therefore the gauche content of chains would be expected to be large.
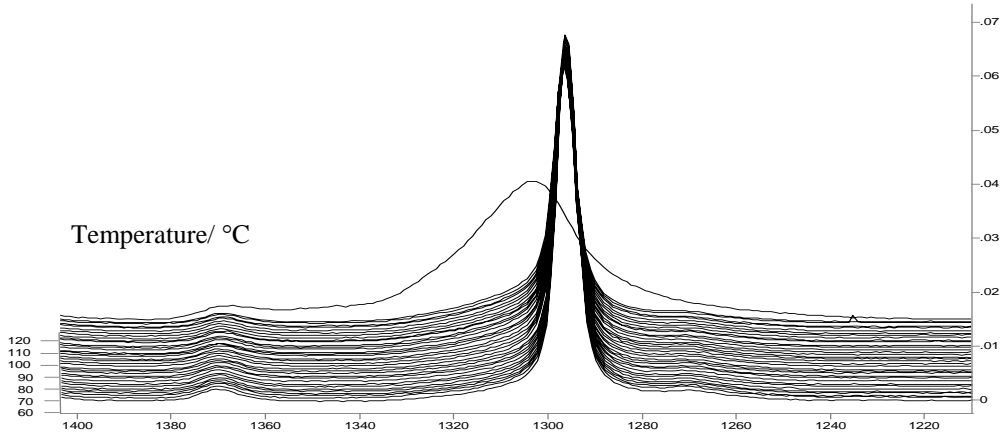
Figure 4: **The waterfall arrangement of the CH$_2$ twisting mode of the Raman spectra of <u>A</u> during stepwise heating. The spectra are arranged from 60° to 128° C at 2° intervals in an upward direction.**
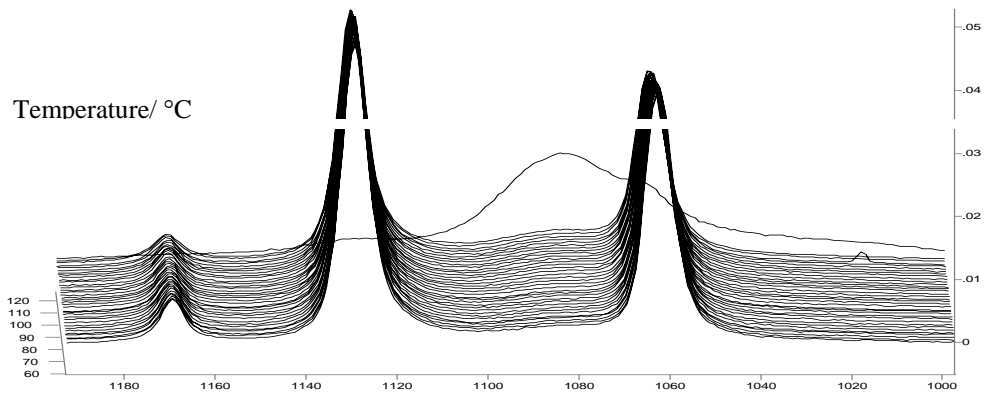
Figure 5: **The waterfall arrangement of C-C stretching mode in the Raman spectra of <u>A</u> during stepwise heating. The spectra are arranged from 60° to 128° C at 2° intervals in an upward direction.**
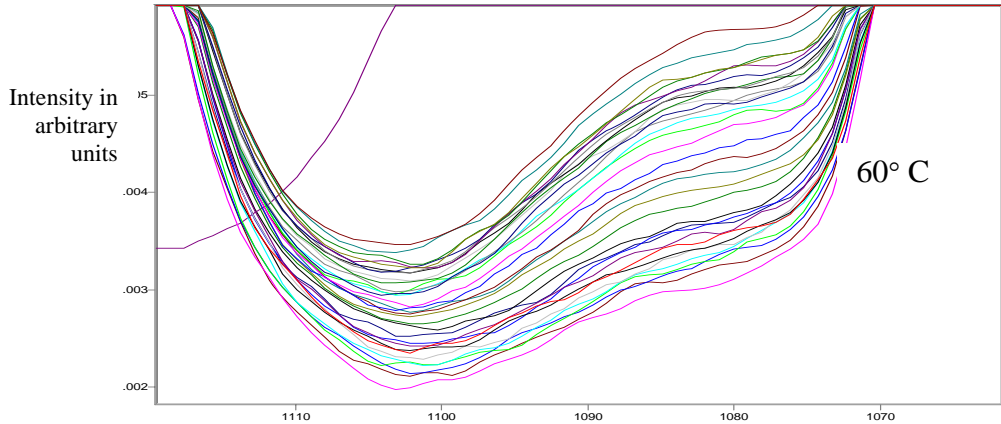
Figure 6 : An expanded, overlaid view of the 1080 cm⁻¹ band   from 60° C to melting at 2° interval during a stepwise heating run of sample A.

The areas of crystalline and disorder bands in regions 2, 3 and 4 were determined by curve fitting. The changes of each of the bands in regions 2, 3 and 4 in some runs of sample **A** are illustrated in figures 7 and 8. The most significant changes could be observed only in the disorder bands. No significant changes at the phase transition were observed in the strong crystalline bands (1295, 1130 and 1060 cm^{-1}). The time associated with the chart title is the total scan time of each spectrum. The grating of the Raman spectrometer slipped sometimes while the experiments were in progress. This caused significant intensity differences between spectra as well as frequency. The frequency shift was corrected by calibrating the spectrometer against a silicon band at 520 cm^{-1}. In order to correct the intensity difference the spectra were normalised to the integrated area of the C-C stretching region. Raw data are represented for runs where the grating slippage did not occur. The figures at melting are omitted to expand the scale.
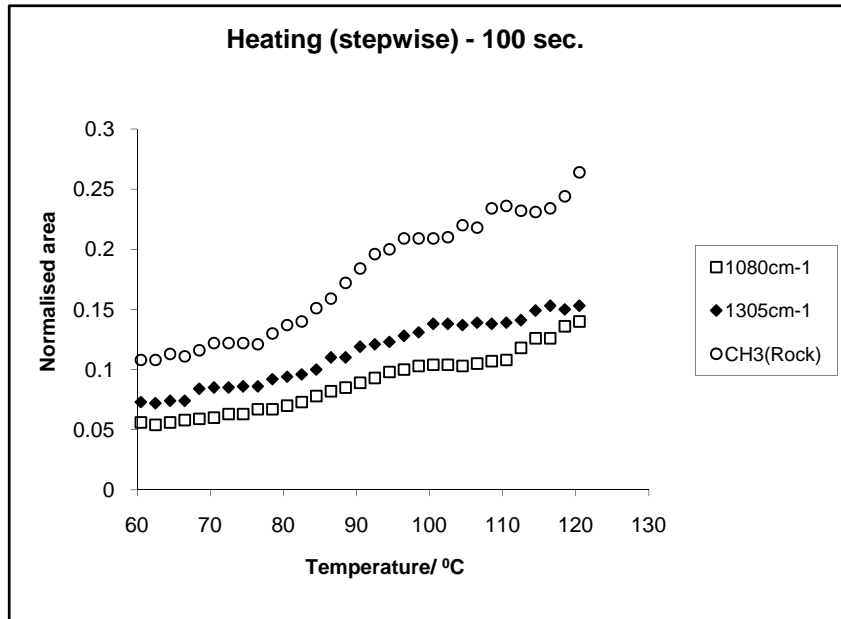
Figure 7 : **The variation of area of the disorder bands in regions 2, 3 and 4 with temperature during a stepwise heating run at 1° C min^{-1}.**

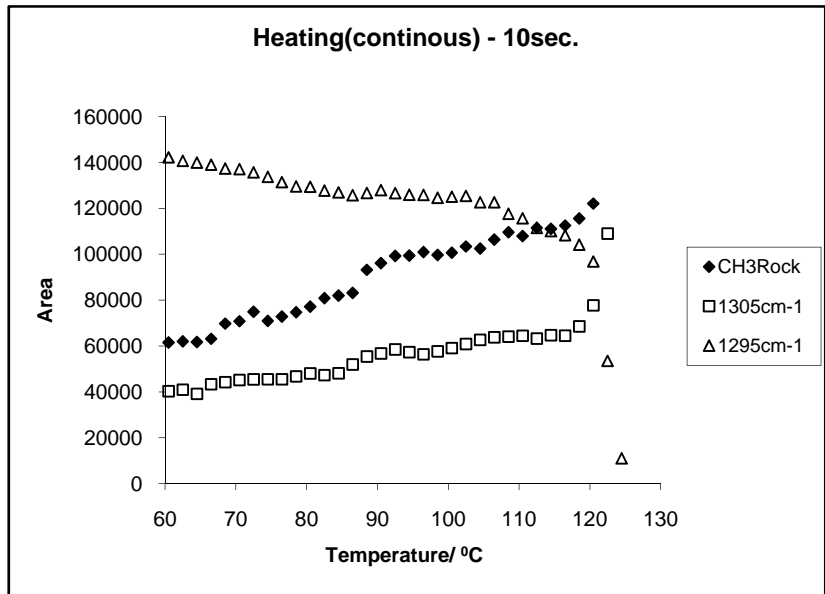**Figure 8 :** **The variation of area of the bands in regions 2, 3 and 4 with during a continuous heating run at 1° C min^{-1}.**

In figure 7 we could observe an increase in the relative intensities of the disorder bands between about 82°C and 96°C (also see figure 6) and in figure 8 this was observed from 84° to 94°C. In addition, in figure 8 we could see a change of the gradient of the 1295 cm^{-1} crystalline band around 84° C. These changes were identified as the superlattice to semicrystalline phase transition as we know that this transition is associated with the disordering of the crystal structure (Ungar & Zeng, 2001). SAXS studies too has shown a similar temperature change for this transition (Ungar & Zeng, unpublished data).

CONCLUSIONS

Vibrational spectroscopy is sensitive to both the crystalline structure as well as to the conformational changes. Here use is made of Raman spectroscopy to identify the superlattice to semicrytalline transition which is associated with an increase in the conformational disorder, in branched chain alkane sample **A**. Regions 1, 2, 3, and 4 of the Raman spectrum of sample **A** were monitored. No changes could be observed in region 1 whereas the rest of the regions were found to be sensitive to the transition. We identified a single solid phase transition from Raman data. The changes in the crystalline bands were subtle whereas the disorder bands showed the most significant changes at this transition. Raman results suggest that this   phase transition occurs around $\sim 87° \pm 5°$ C during heating. This figure is very close to the figure obtained from SAXS data.

ACKNOWLEDGMENT

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