FTIR Studies of Molecular Disorder in Long Chain n-Alkanes: Chain Tilt and Chain End Disorder

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Summary: Successive heat annealing and cooling of the extended chain form of $C_{198}H_{398}$ leads to a "perfecting" of the chains, on the evidence of FTIR data. A similar sample of $CD_3(CD_2)_{11}(CH_2)_{192}(CD_2)_{11}CD_3$ allows the deuterated end segments to be analysed separately. It is shown that the end segments develop better register, while the chain interior is scarcely affected by annealing. The alignment of chain ends coincides with the development of chain tilt (from SAXS data), the tilt angle increasing as the chain ends become more "defect-free" to a figure close to the maximum values obtained for polyethylene.

Introduction

Chain tilt is a familiar phenomenon in polymer crystals and has recently been observed in long chain n-alkanes. Indeed, polymorphism in short chain n-alkanes can also result in two monoclinic forms, corresponding to different tilt angles (e.g. $C_{44}H_{90}$ - see reference (1)). The extent of chain disorder in the long chain n-alkanes may be varied by changing the crystallisation conditions or by heat annealing. In this contribution, we address the question of how chain tilt is related to crystal disorder, using monodisperse long chain n-alkanes in extended chain conformations as "model" systems. These materials were synthesized at the University of Durham[2] and are the subject of wider studies of crystallisation and crystal structure.

Experimental Part

Two materials were used, $C_{198}H_{198}$ and an alkane with perdeuterated end caps, $CD_3(CD_2)_{11}(CH_2)_{192}(CD_2)_{11}CD_3$. Both materials were crystallised from approximately 1% solution in toluene for 6 hours at 82^0C to obtain lamellar crystals with purely

extended chains (on the evidence of small angle X-ray scattering (SAXS) data). The samples were filtered, dried and lightly pressed before FTIR measurements.

Transmission FTIR measurements were made using a Mattson Galaxy 6020 spectrometer. Samples were held between KBr microscope slides in a Graseby-Specac 21500 cryostat, with temperature controlled by a 10120 temperature controller. The sample space was evacuated and the spectrometer was purged with dry air. Spectra were obtained at 1 or 2 cm^{-1} resolution, using typically 200 scans.

A range of IR bands was used. The CH_2 wagging region includes bands characteristic of *gtg* and *gtg'* conformers (1368 and 1308 cm^{-1}), *gg* conformers (1352 cm^{-1}) and the end-*gauche* bond (1344 cm^{-1})[3]. These have been widely used in characterising chain disorder and some of these conformations are illustrated schematically in Figure 1.

Unfortunately, mode mixing in deuterated polymethylene chains does not allow the similar use of CD_2 wagging modes: recent normal mode calculations highlight isotopic variations in the relevant dispersion relations[4]. In-phase C-C stretching and methylene twisting vibrations at 1133 and 1050 cm^{-1} bracket a band progression in the case of purely hydrogenous alkanes[3]. These bands are sensitive to the all-*trans* chain length present, while additional peaks can arise from chain disorder.

The CD_2 bending vibration (1060 - 1120 cm^{-1}) shows a crystal field splitting in the case of fully deuterated polymethylenes. For blends of deuterated and hydrogenous species, the magnitude is related to both the size of groups of {110} adjacent deuterated chain segments and the spatial arrangement of these segments. The technique of mixed crystal IR spectroscopy has been developed to determine the detailed chain conformation in polyethylene crystals[5]. The principle of the technique in relation to the end-deuterated alkane is shown schematically in Figure 2.
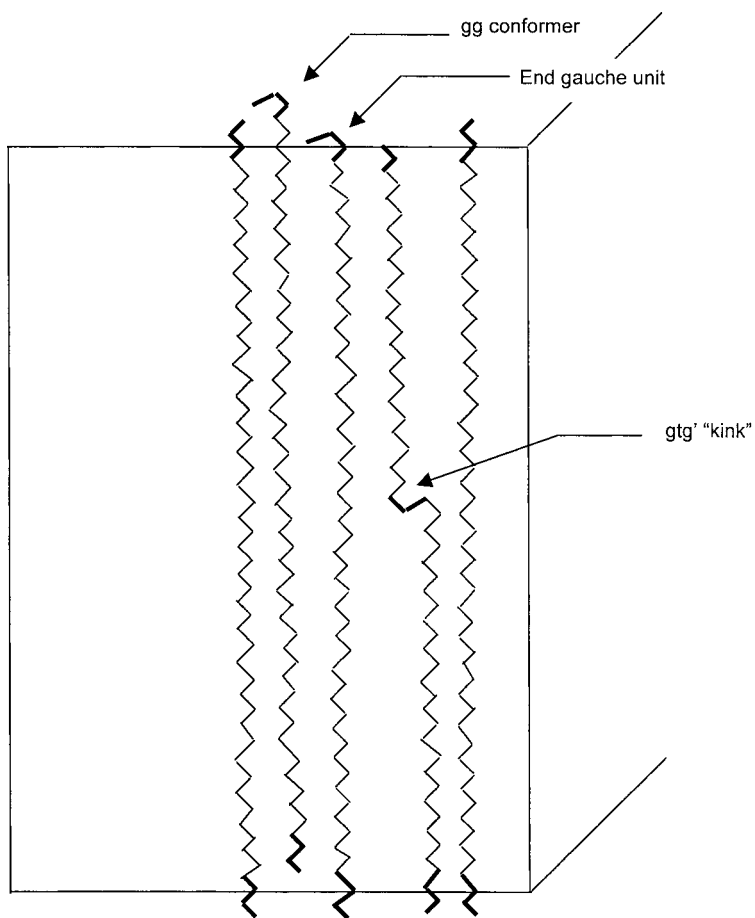
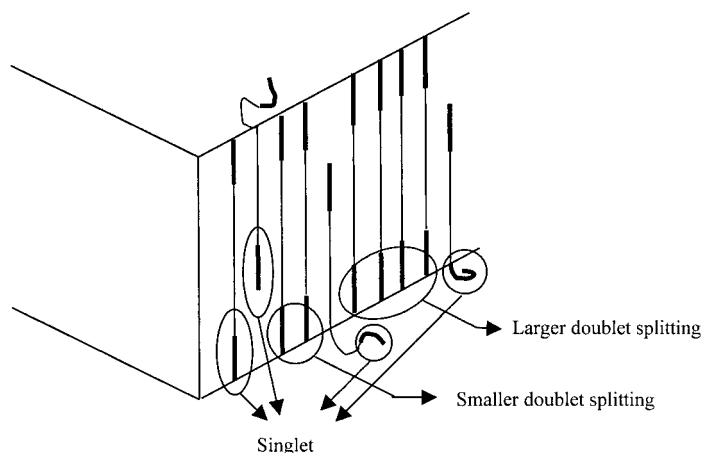Figure 1. Schematic diagram of some non-planar conformers in polyethylene.

Larger doublet splitting

Smaller doublet splitting

Singlet

Figure 2. Schematic arrangement of alkane chains, showing some crystal surface disorder. Deuterated chain ends are denoted by thicker lines.

Results

1)   Effects of Annealing / Cooling on $C_{198}H_{398}$

Both the CH_2 wagging and CC stretching / CH_2 twisting regions of the IR spectrum (Figures 3 and 4) show the effects of crystal "perfecting" with successive annealing, followed by cooling to liquid nitrogen temperatures (all spectra are recorded at -173^0C). CH_2 wagging vibrations related to non-*trans* conformers, after spectral normalisation using the 2558 - 2690 cm^{-1} combination bands, show a successive reduction in absorbance, while the progression bands (Figure 4) become sharper and better resolved. This last point indicates a narrowing of the distribution of all-*trans* chain lengths, particularly after annealing at 110 ^{0}C. In order to index these progression bands, we used the frequency - phase curve derived by Snyder and Schachtschneider for short chain n-alkanes[6] to determine the phase difference for each band. The best estimate for the number of carbon atoms (n_c) in the extended part of the molecule was obtained by an iterative process, using different values of n_c to calculate the corresponding k index for each band. In this case, the best fit was obtained for $n_c = 192$, indicating a very small region of surface disorder. The disappearance of the 1056 cm^{-1} band, previously attributed to *gauche* bonds, gives further evidence of "perfecting".
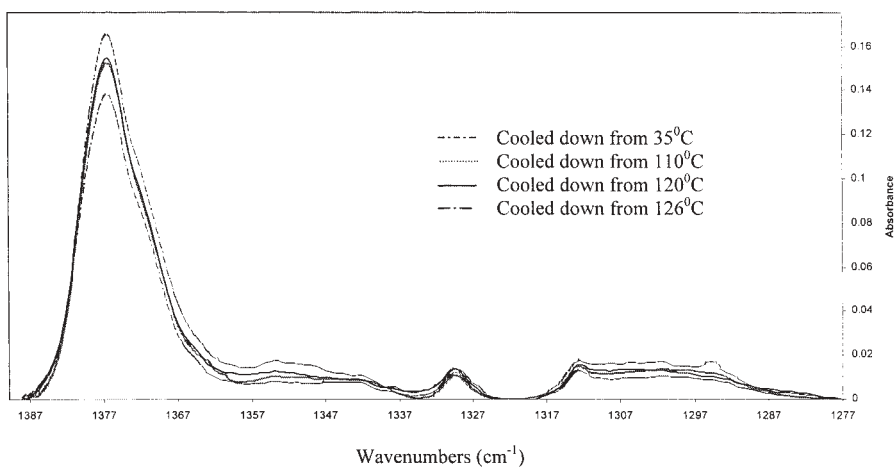
Figure 3. Low temperature FTIR spectra of $C_{198}H_{398}$ in the extended form after annealing at successively higher temperatures: CH_2 wagging region.
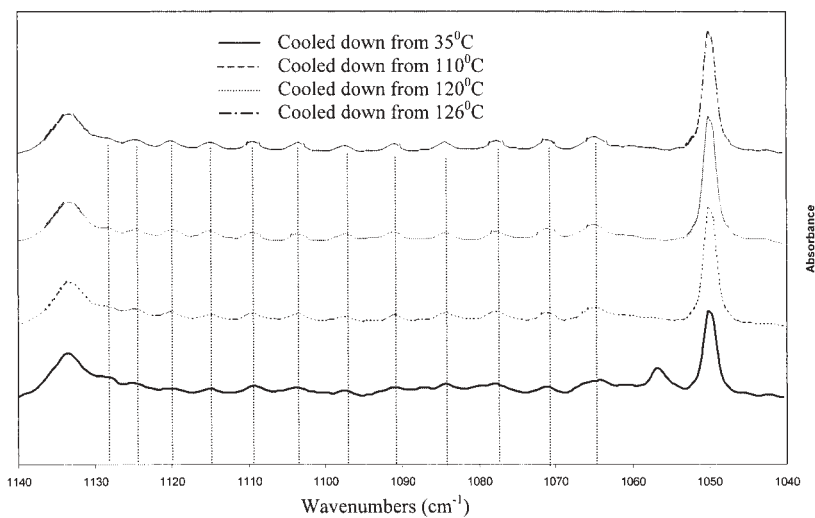
Figure 4. Low temperature FTIR spectra showing development of CC stretching CH_2 twisting band progression with successive annealing. Vertical dotted lines denote final band positions.

2)   A Comparison of Extended Chain $C_{198}H_{398}$ and $CD_3(CD_2)_{11}(CH_2)_{192}(CD_2)_{11}CD_3$

Low temperature IR spectra of these two samples are compared in Figure 5, after normalisation. The absence of CH_3 groups in the end-deuterated alkane means that the *gtg* / *gtg'* band at 1370 cm^{-1} appears, for the first time, without overlap from the 1378 cm^{-1} methyl group deformation: it can now be seen as a symmetrical peak, close in frequency to results from curve fitting on hydrogenous n-alkanes[1]. The region from 1270 to 1320 cm^{-1} contains additional bands arising from the deuterated segments, but otherwise the CH_2 wagging mode absorbances are similar, as would be expected for $(CH_2)_n$ sequences of similar length.
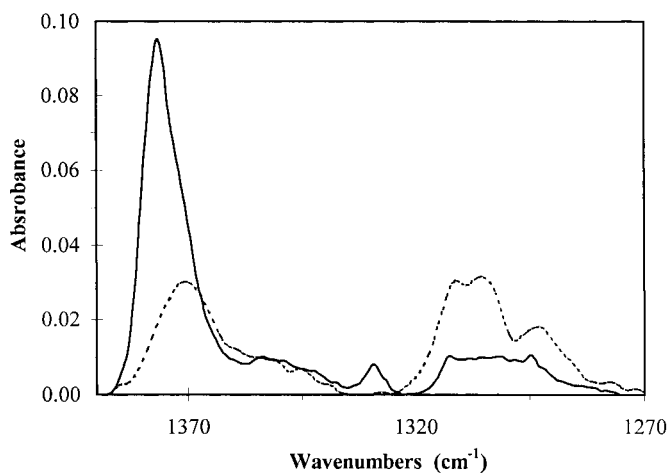

Figure 5. Comparison between low temperature FTIR spectra of extended chain molecules with (dotted line) and without (solid) deuterated chain ends.

3) Effects of Annealing / Cooling on the CD_2 Bending Vibration in $CD_3(CD_2)_{11}(CH_2)_{192}(CD_2)_{11}CD_3$

Low temperature spectra after annealing at successively higher temperatures show a progressive development of the CD_2 bending doublet (Figure 6), while the proportion of the central singlet (arrowed in Figure 6) is reduced (Figure 8), on the basis of curve fitting.

The doublet splitting increases from 6.75 to 7.9 cm^{-1} (Figure 7), whereas the CH_2 bending vibration shows little change. The qualitative interpretation is that increasing regularity of chain end packing causes an increase in the size of domains over which the deuterated chain segments are in register. In the terminology of mixed crystal IR spectroscopy[5], the increased doublet splitting corresonds to an increase in the size of groups of deuterated segments, while the increasing proportion of the doublet means that fewer deuterated segments are either outside the crystals or inside and surrounded by hydrogenous chain segments. For a quantitative interpretation, we make the assumption that the $C_{12}D_{25}$ end cap is sufficiently long to allow the full 10.2 cm^{-1} splitting (characteristic of perdeuterated polyethylene[5]) to develop, provided that the chain ends are in perfect register. The observed increase in splitting then corresponds to a change in the size of groups of labelled chain ends from 6 - 8 to 9 - 12[5]. It should be noted that any reduction in the maximum achievable splitting for the $C_{12}D_{25}$ end cap would result in a significantly larger increase in group size. Nevertheless, the result shows a marked improvement in the ordering of chain ends.
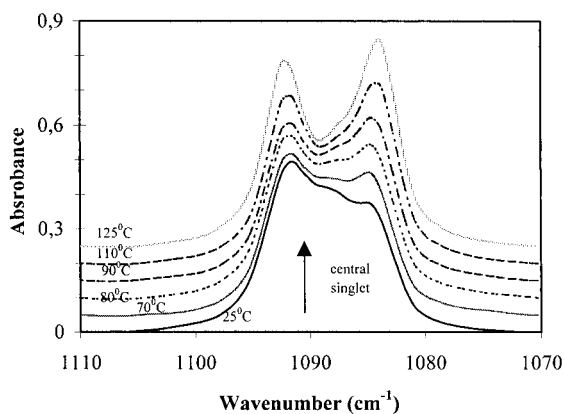

Figure 6. Development of CD_2 bending doublet in FTIR spectrum with annealing.
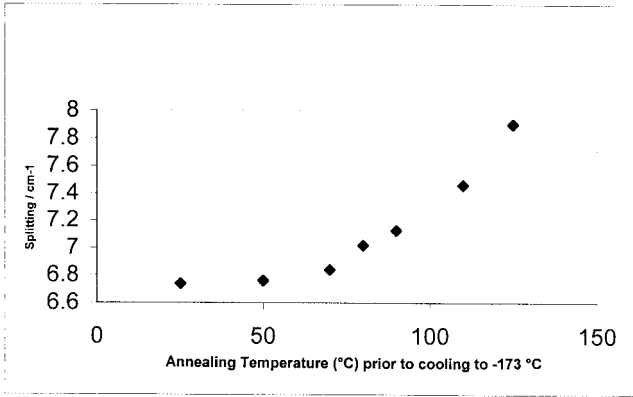
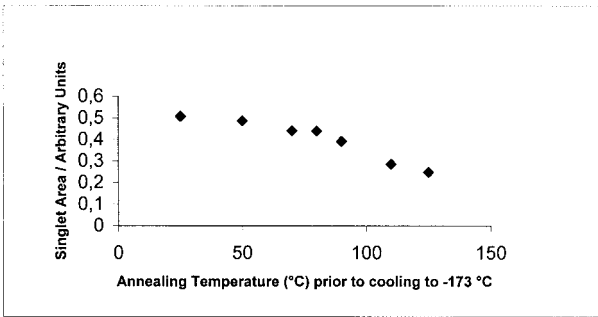Figure 7. Development of CD_2 bending splitting with annealing.

Figure 8. Development of CD_2 bending singlet area with annealing.

With the aid of SAXS measurements (courtesy of Drs. G. Ungar and X.B. Zeng, University of Sheffield), the relationship with chain tilt can be explored. Measurements were made at room temperature after stepwise heating. Figure 9 shows the development of chain tilt, with maximum values similar to those achievable for polyethylene.
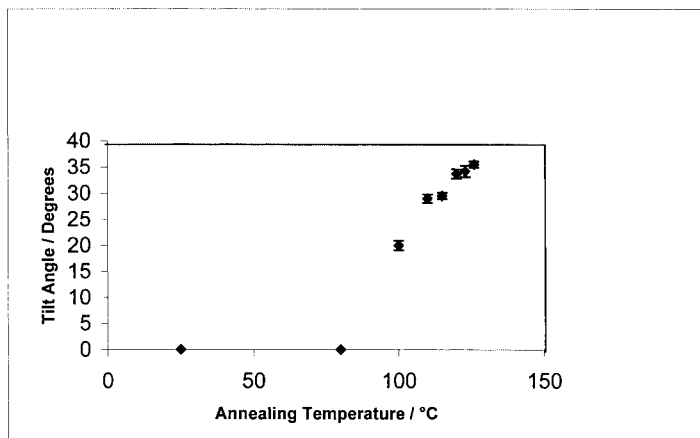
Figure 9. Development of chain tilt in alkane with deuterated end caps with annealing.

Comparing Figures 7 and 9, the tilt angle develops above 80 ^{0}C, while the most significant change in CD_2 bending splitting also occurs above 80 ^{0}C. The two phenomena - the development of chain tilt and an ordering of the chain ends - are thus seen to be related. The behaviour of the CH_2 wagging region of the IR spectrum is shown in Figure 10.
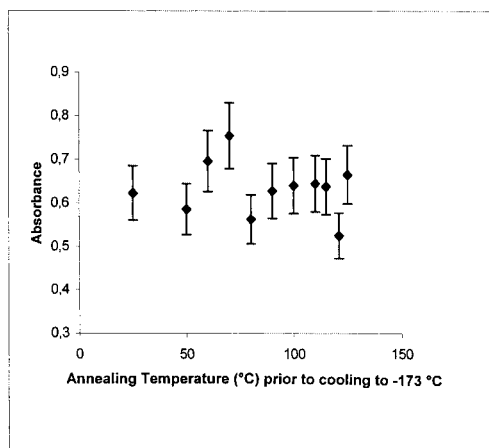

Figure 10. Development of the integrated CH_2 wagging absorbance of alkane with annealing.

4) The Effect of Heating on the CD_2 Bending Vibration of $CD_3(CD_2)_{11}(CH_2)_{192}(CD_2)_{11}CD_3$

Starting at -173 ^{0}C, this sample was warmed up. Figure 11 shows the reduction in CD_2 bending splitting, reflecting the increased disorder near the chain ends.

Groups of labelled chain ends become smaller as some chain ends move outside the crystals and a rough crystal surface develops. Note that subsequent cooling is necessary to achieve "perfecting" of the crystal surface.
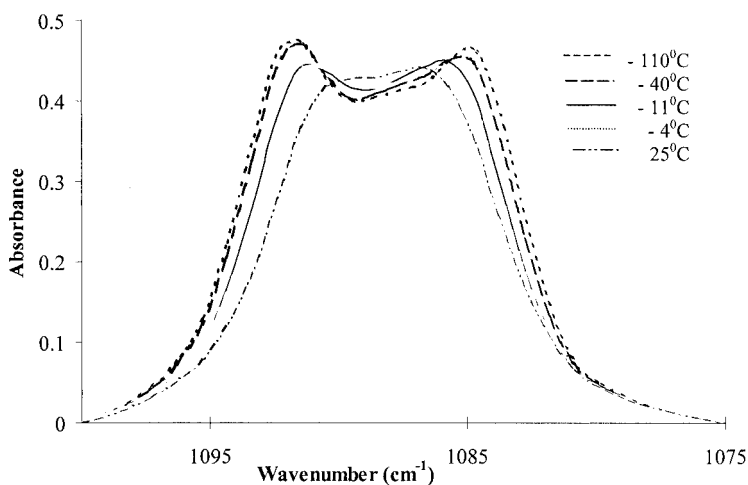

Figure 11. Reduction in CD_2 bending splitting in alkane with deuterated end groups with annealing.

Conclusions

On successively heat annealing and cooling an extended chain sample of $C_{198}H_{398}$, crystallised from solution, a "perfecting" of the chains occurs. This is evident from both the CH_2 wagging region of the IR spectrum and the CC stretching/ CH_2 twisting progression bands. Experiments using $CD_3(CD_2)_{11}(CH_2)_{192}(CD_2)_{11}CD_3$ show an increased doublet component and doublet splitting, attributed to the deuterated segments coming into register. Conversely, the CH_2 wagging data, which serve as a probe for the central section of the molecule, show no significant change. The ordering of the chain ends causes a smoothing of the crystal surface, which appears to instigate

the development of chain tilt. The tilt angle progressively increases as the chain becomes more "defect-free". This change is shown schematically in Figure 12.
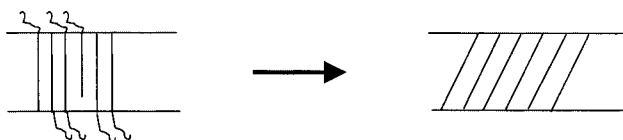

Figure 12. Schematic view of ordering of the alkane chain ends resulting in chain tilt.

Measurements made on heating the $CD_3(CD_2)_{11}(CH_2)_{192}(CD_2)_{11}CD_3$ sample show a progressive reduction in the CD_2 bending doublet splitting, indicating that both annealing and cooling are necessary for the "perfecting" process.

Having identified a mechanism for chain tilt in extended chain, long n-alkanes, it is important to consider the relevance of these results to polymers, and in particular to polyethylene. In semi-crystalline polymers, the presence of an interface separating crystalline and amorphous regions of differing density requires a proportion of chain folding in order to avoid the overcrowding problem at the crystal surface. The only alternative, as pointed out by Frank[7], is to have an interface oblique to the chain axes. The obliquity required was shown to be well in excess of observed tilt angles. However, the close correspondence of maximum tilt angles observed here and for polyethylene elsewhere suggests some common elements in their origins.

References

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