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FTIR studies of conformational disorder: crystal perfecting in long chain *n*-alkanes

Jean-Philippe Gorce[1], Stephen J. Spells*

School of Science and Maths, Materials Research Institute, Sheffield Hallam University, City Campus, Pond Street, Sheffield S1 1WB, UK

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Abstract

The low temperature FTIR spectra of long chain *n*-alkanes $C_{198}H_{398}$ and $C_{246}H_{494}$, crystallised from solution in both extended and once-folded forms, have been investigated in the CH_2 wagging region. Successive annealing and cooling stages result in a significant reduction in the number of non-planar C–C bond conformers in all cases. This is evidence of a 'perfecting' process within the crystals. The time dependence of this behaviour shows that, on raising the annealing temperature, the level of disorder reaches a maximum before declining. In addition, in a continuous heating run on once-folded $C_{198}H_{398}$, all types of conformational disorder except end-*gauche* bonds are shown to pass through a maximum near 118 °C, in the region of the transformation to extended chain crystals.

Keywords: Long chain alkanes; FTIR; Crystal perfecting

1. Introduction

Vibrational spectroscopy of long chain *n*-alkanes has recently proved to be a key technique in investigating structural features of these model molecules. The synthesis of these monodisperse materials is detailed elsewhere [1]. The ability of *n*-$C_{198}H_{398}$ to crystallise from solution in either a once-folded or extended chain conformation, depending on crystallisation temperature, has allowed an infra-red spectrum of the fold to be obtained [2], together with the concentrations of non-planar conformers which give rise to CH_2 wagging vibrations. The spectrum closely follows the calculated behaviour [3] for a tight (110) fold. The spectral region between the C–C stretching and CH_2 twisting fundamentals (1050–1133 cm^{-1}) has also proved useful: the progression bands in this region are sensitive to the chain regularity within the crystals, depending on the all-*trans* sequence length in them. Successive annealing and cooling stages applied to a sample of *n*-$C_{198}H_{398}$ showed an increase in regularity of these progression bands [4], which was interpreted in terms of a crystal 'perfecting' process. Assignment of the individual bands allowed the sequence length to be determined for various long chain *n*-alkanes, including centre-branched molecules. In the present work, the crystal perfecting is further studied, using the CH_2 wagging vibrations.

Recent detailed studies of *n*-$C_{198}H_{398}$ and the partially deuterated alkane $C_{12}D_{25}C_{192}H_{384}C_{12}HD_{24}$ [5,6] involved a combination of small angle X-ray scattering (SAXS) and IR spectroscopy. The relationship between chain tilt and disorder was investigated for solution grown materials. The CH_2 and CD_2 wagging vibrations allowed the state of disorder of the crystal interior and the chain ends to be independently assessed, while the CD_2 bending vibration allowed the degree of register of the chain ends to be determined. Thus, it was shown that the as-grown crystals, with chains perpendicular to the lamellar surfaces, have significant surface disorder. On annealing above about 90 °C, the chains start to tilt with respect to the layer normal, the tilt angle increasing to 35° prior to melting. At the same time, the translational surface order was shown to improve with annealing at successively higher temperatures. Conformational disorder, as indicated by the CH_2 and CD_2 wagging modes, was shown to increase reversibly with increasing temperature. The changes were found to occur predominantly in the deuterated end caps, rather than in the

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* Corresponding author. Tel.: +44-114-225-3428; fax: +44-114-225-3066.

E-mail address: s.j.spells@shu.ac.uk (S.J. Spells).

[1] Present address: Department of Engineering Materials, University of Sheffield, Sheffield S1 3JD, UK.

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(hydrogenous) crystal interior. This led to the important conclusion that the absence of tilt in the as-grown crystals was due to surface disorder and that tilt becomes necessary as the crystal surface becomes more ordered during annealing. This situation should be compared with that of shorter odd *n*-alkanes, where the absence of initial tilt is due to a high degree of surface *order*.

In this work, we make use of the CH_2 wagging vibrations in the alkanes $C_{198}H_{398}$ and $C_{246}H_{494}$ to investigate their annealing behaviour in both once-folded and extended chain conformations. This region of the spectrum has proved to be invaluable in characterising the type and extent of disorder in a diverse range of systems including polyethylene [7,8], carboxylic acids [9], phospholipids [10] and surfactants [11].

2. Experimental

The synthesis of *n*-$C_{198}H_{398}$ and *n*-$C_{246}H_{494}$ is described in Ref. [1].

Sample F198: A 1.4% w/v solution of *n*-$C_{198}H_{398}$ in toluene was crystallised at 73.2 ± 0.4 °C for 90 min. Crystals were filtered and the mat was allowed to dry before pressing at less than 40 MPa.

Sample E198: A 0.8% w/v solution of *n*-$C_{198}H_{398}$ in toluene was crystallised at 81.5 ± 0.4 °C for 6 h. These crystals were filtered and dried before pressing at less than 40 MPa.

Sample F246: A 1.35% w/v solution of *n*-$C_{246}H_{494}$ in toluene was crystallised at 81.6 ± 0.4 °C for 90 min. Crystals were filtered and dried before pressing at less than 40 MPa.

The verification of once-folded and extended chain conformations of F198 and E198, respectively, has been described earlier [2], together with Raman LAM (Longitudinal Acoustic Mode) characterisation.

SAXS measurements were made on sample F246 using a Regaku-Denki camera, filtered Cu K_α radiation and 300 μm pinholes (courtesy of Prof. Goran Ungar, University of Sheffield). Photographic film was used for detection, with the aid of microdensitometry. It should be noted that this method is somewhat insensitive to changes in shape of diffraction peaks: the use of radially averaged intensities from an area detector, together with curve fitting, provides a more accurate indication of chain tilt in such systems. This latter approach has been used in previous work (e.g. Refs [5, 6]). The layer periodicity obtained was 158.6 Å, compared with a calculated value of 158 Å for once-folded chains. Further SAXS measurements following annealing are discussed later.

Low frequency Raman measurements were made using a Dilor XY triple grating spectrometer, with the 514.5 nm argon ion line for excitation and 100 μm slits (courtesy of Dr W. Gembicki, Technical University of Warsaw). Sample F246 showed a first order longitudinal LAM at 19.2 cm^{-1}. Using the method previously employed [2], this was found to correspond to 127 carbon atoms, showing that close to half the number of carbon atoms in F246 are involved in the LAM.

Transmission IR spectra were recorded using a Mattson Galaxy 6020 FTIR spectrometer with an MCT detector and a dry air purge. A resolution of 1 cm^{-1} and typically 200 scans were used.

Samples were sandwiched between two potassium bromide microscope slides in a Graseby/Specac 21500 cryostat, using a 20120 temperature controller. The cryostat was evacuated and samples were successively annealed and cooled to − 173 °C at around 10 °C min^{-1}.

3. Results

3.1. (1) F198

This sample was annealed successively at 51, 95 and 110 °C. The respective tilt angles, as measured by SAXS, were 0 °C, 14 ± 3° and 15 ± 3°. The first order LAM was shown to have an unchanged frequency after annealing at 110 °C, confirming that the once-folded form was unaffected by annealing. Recent FTIR measurements on the short chain alkane, $C_{44}H_{90}$ [12] indicate that the symmetric methyl bending vibration is sensitive to changes in crystal structure, due to differences in the methyl group environment. There is also evidence in the subtraction spectrum obtained by comparing IR spectra of F198 and E198 of a shift in frequency for this band [2]. The use of the 1377 cm^{-1} band for spectral normalisation is, therefore, dubious. This was investigated in the low temperature. FTIR spectrum of sample F198. Fig. 1 shows the dependence on annealing temperature of integrated band areas for various methyl and one methylene (1174 cm^{-1}) group bands. Of the bands illustrated, the 1377 cm^{-1} one shows the largest variation in area with annealing temperature, after carrying out a baseline subtraction using baselines from 1280 to 1325 cm^{-1} and from 1325 to 1391 cm^{-1}. We have, therefore, chosen to use the integrated absorbance of 2558–2690 cm^{-1} combination band region of the spectrum, which varies by less than 5% from its maximum value, for spectral normalisation.

Fig. 2 shows low temperature FTIR spectra for F198 after each annealing stage. The most intense band at 1377 cm^{-1} corresponds to the symmetric methyl bending mode, while most of the other bands can be ascribed to localised methylene wagging vibrations. In particular, a band at 1368 cm^{-1} has been assigned to *gtg* sequences [13], one at 1308 cm^{-1} to both *gtg* and *gtg'* sequences, a band at 1352 cm^{-1} to *gg* conformations and one at 1344 cm^{-1} to the end-*gauche* conformation [14]. In order to identify peak positions and areas with accuracy, second derivatives and self-deconvolution methods were used, followed by curve fitting. Bands at 1354 and 1341 cm^{-1} were thus identified as

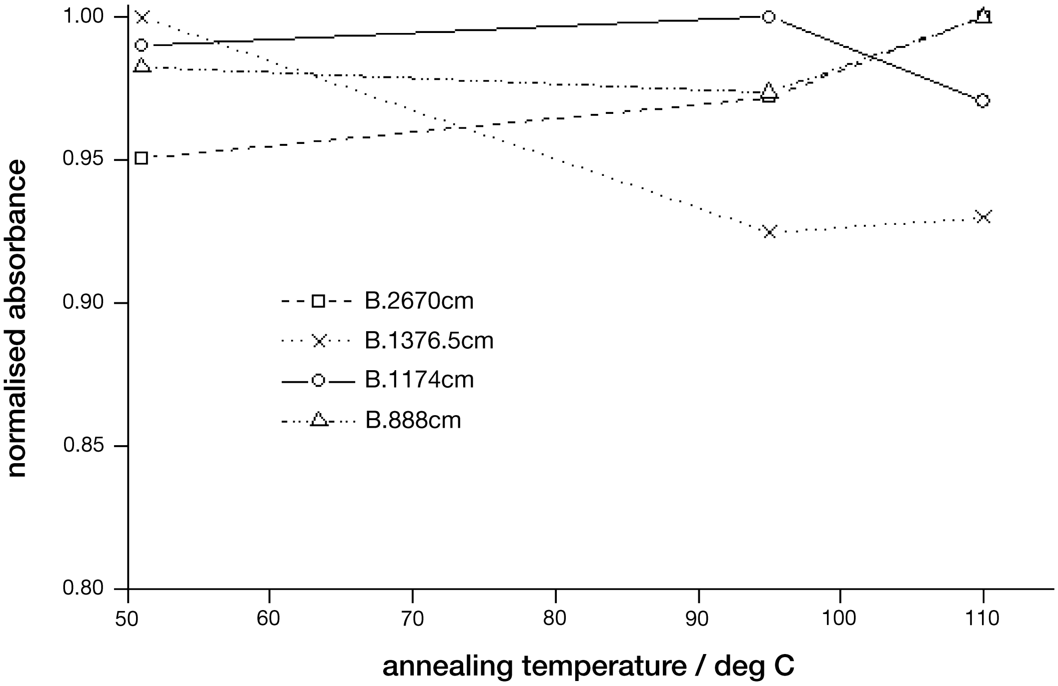

Fig. 1. Areas of several FTIR bands in the low temperature spectrum of F198, as a function of annealing temperature. The normalisation is applied to bring the maximum absorbance for each band to 1.0. The lines are intended simply to guide the eye. The 1376.5, 888 and 1174 cm^{-1} bands are attributed, respectively, to symmetric methyl bending, methyl rocking and methylene wagging modes, while the 2558–2690 cm^{-1} combination band region was chosen for future spectral normalisation.

relating to *gg* and end-*gauche* conformers, respectively. Bands at 1369 and 1307 cm^{-1} were assigned to *gtg* and both *gtg* and *gtg′* conformers, respectively. Two additional bands were obtained in this process: there is a shoulder at 1364 cm^{-1}, which corresponds in frequency to a band previously attributed to the CH_2 wagging mode of a distorted *gtg* sequence [2,11]. Secondly, a peak at 1329 cm^{-1} has again been tentatively assigned to a methyl group vibration [2].

Fig. 2 clearly shows a general decrease in absorbance of

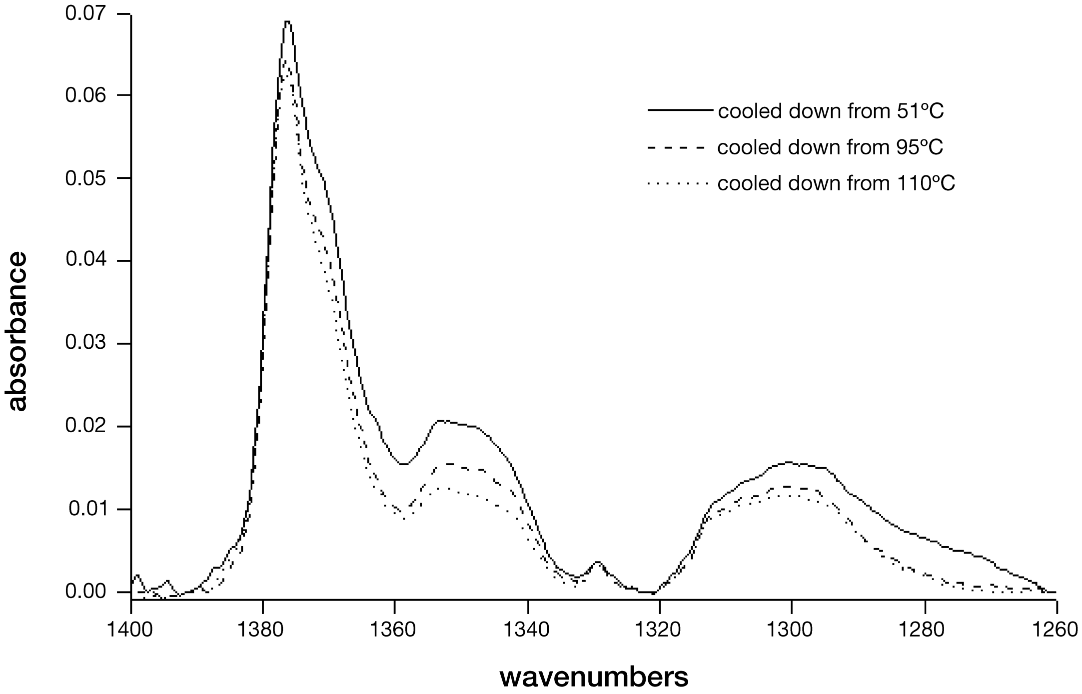

Fig. 2. Low temperature FTIR spectra for F198 after annealing at various temperatures. The progressive reduction in absorbance of methylene wagging modes with increasing annealing temperature indicates a decrease in chain disorder.

wagging modes with successive annealing, indicating a ‘perfecting’ of the crystals in terms of conformational disorder. Since the absorbance also decreases in the region of the 1346 cm^{-1} ‘fold band’, the perfecting may extend to the fold itself.

3.1.1. Time dependence of spectra

In order to investigate the relationship between tilt angle and chain conformational disorder, a sample of F198 was first heated to 85 °C for 20 h before cooling down to − 173 °C and recording a spectrum. This long annealing time should allow the removal of the maximum number of non-planar conformers possible at that temperature, while the temperature is too low to enable any chain tilt to occur. Spectra were then recorded after heating to 95 °C for 2 min, 10 min and 64 h, in each case with the sample cooled to − 173 °C. At these three time intervals, SAXS data showed the respective tilt angles to be 0°, 15 ± 5° and 15 ± 3°. The corresponding FTIR spectra are shown in Fig. 3, after the normalisation procedure described above. Compared with the spectrum for an annealing temperature (T_a) of 85 °C, the 95 °C (2 min) spectrum shows an increase in all the CH_2 wagging mode absorbances. There is a further increase after heating for 10 min, but the spectrum after 64 h at 95 °C shows a substantial decrease. In the case of the 1340–1360 cm^{-1} region, the absorbance reached is lower than for a T_a value of 85 °C.

The initial effect of raising the annealing temperature is, therefore, that of introducing additional conformational disorder. It has been shown previously [5] that the development of chain tilt coincides with the formation of a progressively smoother lamellar surface. After 10 min at 95 °C, sample F198 shows a significant chain tilt—and thus, presumably, a smoother lamellar surface—while having enhanced conformational disorder. Indeed, this disorder, predominantly near to the chain ends [5], is likely to be associated with the development of the smoother lamellar surface. After 64 h at 95 °C, an equilibrium surface roughness and translational ordering has been achieved with the appropriate tilt angle, and non-planar conformers near to the chain ends have been ‘annealed out’. It is also conceivable that the development of chain tilt leads to a change in the conformation of the (110) fold, explaining the observed decrease in the absorbance of the 1346 cm^{-1} band ascribed to (110) folds.

3.1.2. The transformation from once-folded to extended chains

From DSC measurements, the transformation from folded to extended chain crystals of n-$C_{198}H_{398}$ occurs at 119 °C. The melting point of extended chain crystals is 126.7 °C [15]. Sample F198 was annealed at 110 °C for one hour and then heated up to 121.6 °C at a rate of 0.4 °C min^{-1}. A spectrum was recorded every four minutes.

Fig. 4 shows the corresponding data. There is a clear indication of increasing absorbance in various CH_2 wagging vibrations around 119 °C. This can be associated with the transformation to extended chains. It is, however, noticeable that the absorbances are reduced at slightly higher temperatures. After the usual procedure of spectral normalisation, deconvolution and curve fitting, the peak absorbances of various components are plotted in Fig. 5. The

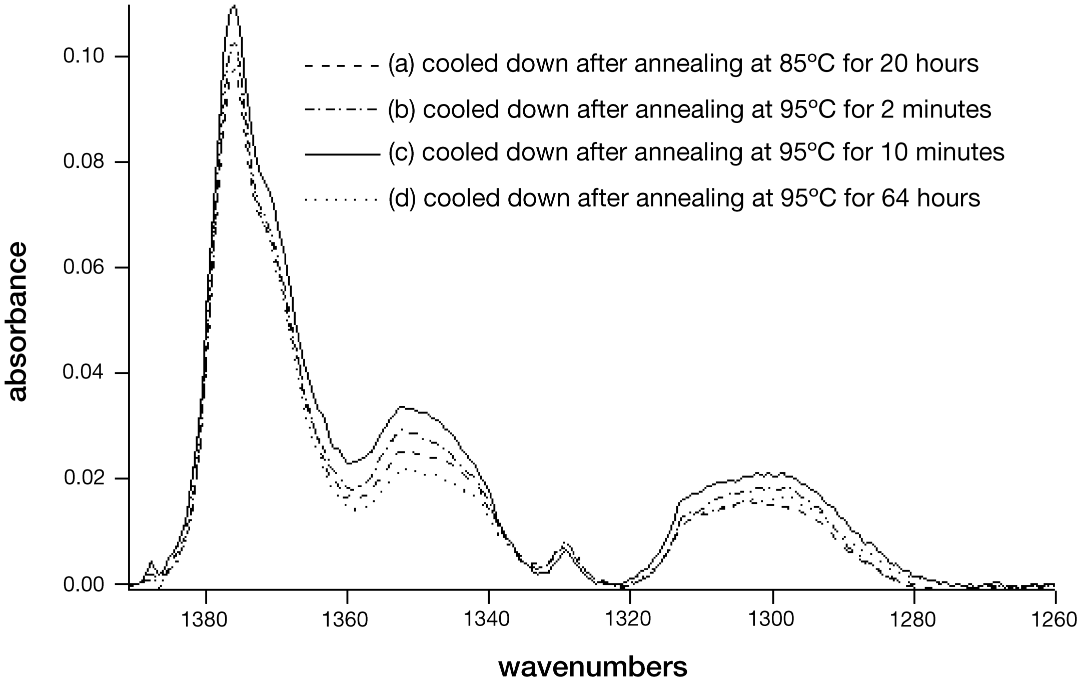

Fig. 3. Low temperature FTIR spectra for F198 after different annealing treatments, showing the time dependence of methylene wagging mode absobances at 95 °C.

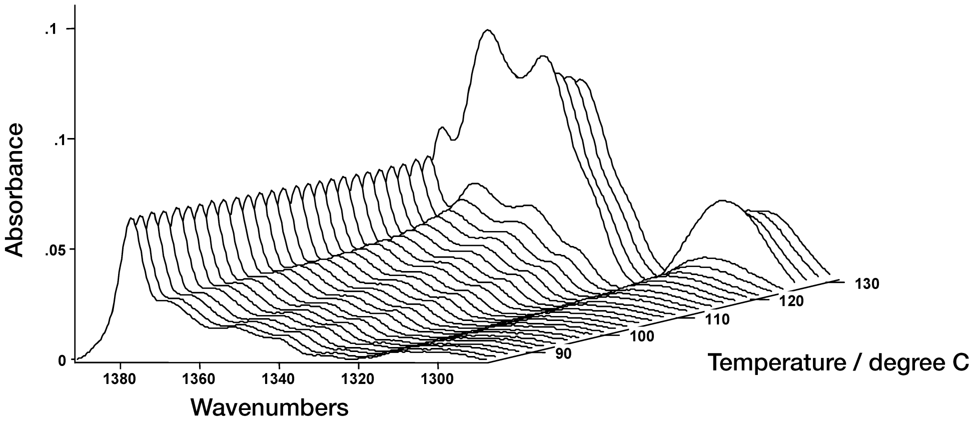

Fig. 4. FTIR spectra recorded for F198 during heating from 110.0 to 121.6 °C at a rate of 0.4 °C min^{-1}. The increase in methylene wagging absorbances around 119 °C, close to the transition to the extended chain form, is apparent.

variation in absorbance of the 1377 cm^{-1} peak is within 5% over this temperature range. The 1351 and 1365 cm^{-1} peaks, corresponding to *gg* and *gtg* conformers, respectively, show similar behaviour, with the maximum absorbance at 118.4 °C. The 1307 cm^{-1} band (not shown here) behaved similarly. However, the 1341 cm^{-1} band, attributed to end-*gauche* conformers, shows no maximum as a function of temperature, but rather a continuous decrease, apart from the final data point at 121.6 °C. These results indicate that the crystals become most disordered at the transition to the extended chain form and that the conformation of the chain ends is not significantly affected by the transition. It seems likely that a similar disordering occurs at other transitions between integrally folded forms (e.g. twice folded to once folded) of the long *n*-alkanes.

3.2. (2) E198

This sample was annealed at various temperatures, to evaluate the extent of crystal ‘perfecting’ which occurs. The number of orders of the crystal long spacing obtained in a 24–25 h SAXS exposure increased from three for the unannealed sample to nine for a sample annealed at 115 °C. This observation indicates a significant improvement in crystal stacking, as would be expected from the evidence of chain end ordering in partially deuterated molecules [5]. Low temperature FTIR spectra of sample E198, following various annealing procedures, are shown in Fig. 6 in the CH_2 wagging region. Data are shown after background subtraction and normalisation, as described earlier. There is clearly a general decrease in absorbance with successively

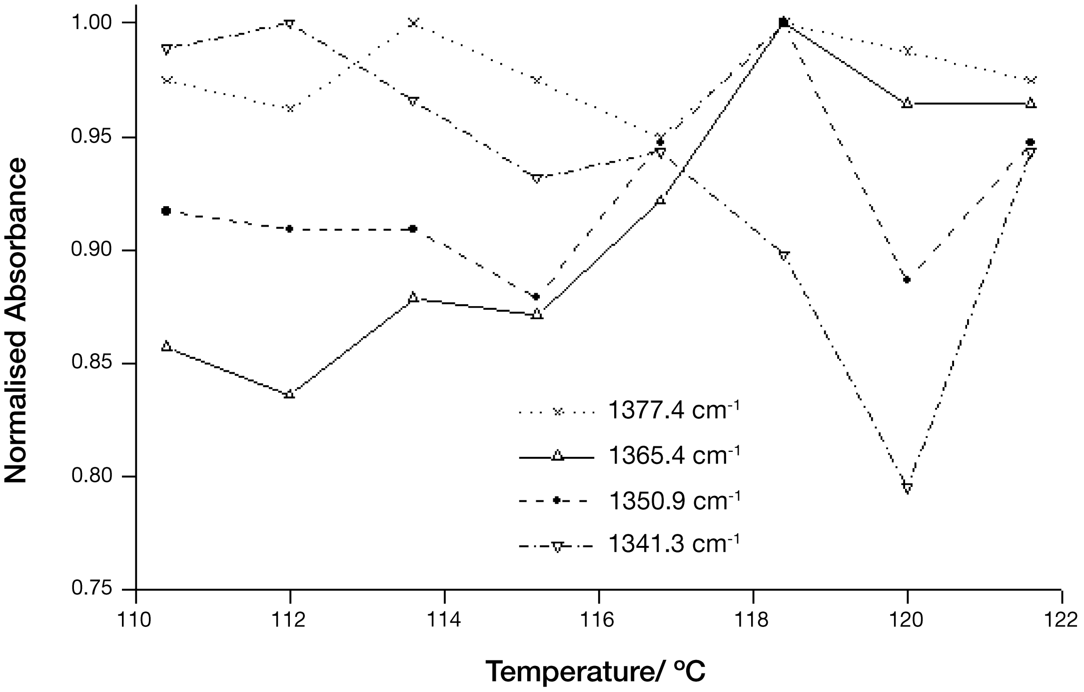

Fig. 5. Normalised peak absorbances for the major bands shown in Fig. 4 as a function of temperature. The lines are intended for guidance only.

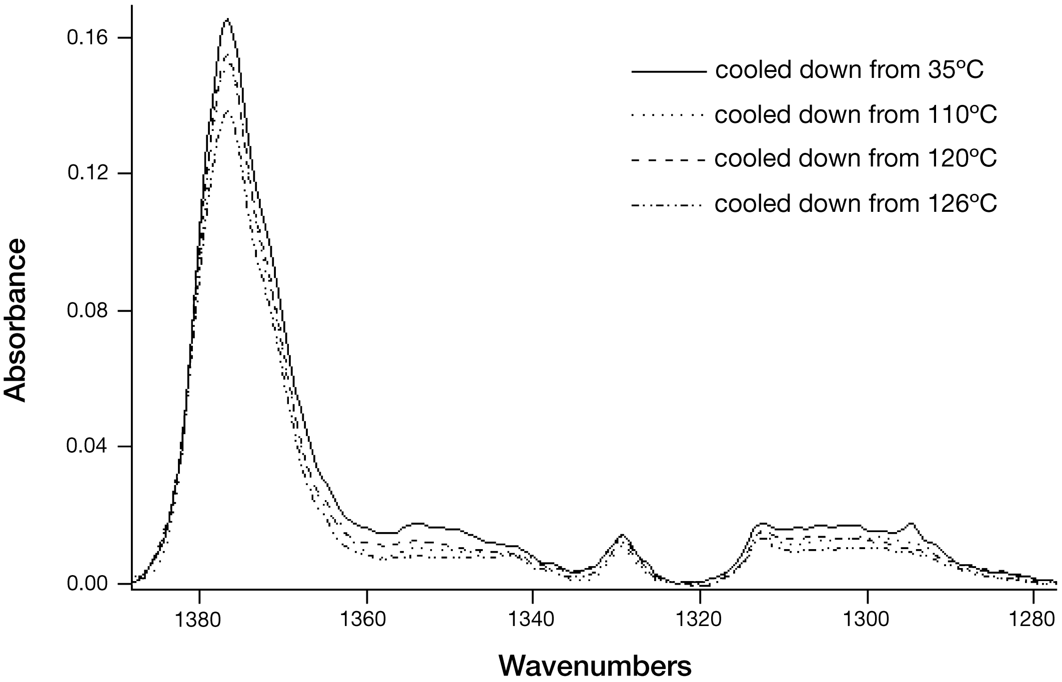

Fig. 6. Low temperature FTIR spectra for sample E198 after annealing at various temperatures, again showing evidence of crystal perfecting.

higher annealing temperatures, indicating a progressive ‘perfecting’ of the crystals, through a reduction in conformational disorder. This result is in contrast to measurements on the partially deuterated *n*-alkane, $C_{12}D_{25}C_{192}H_{384}C_{12}HD_{24}$, which showed that disorder in the central $-(CH_2)_n-$ portion of the chain is little affected by annealing [5]. This reinforces the previous conclusion, namely that the improvement in conformational order occurs predominantly near the chain ends. A combination of Fourier self-deconvolution and curve fitting was used to estimate the component bands in the spectra. A band centred at 1346 cm^{-1} could be assigned to a (110) fold band [2], arising from a small proportion of folded chains in the initial sample. This assignment is supported by evidence that the absorbance decreased significantly after cooling from 120 °C, since the transformation of folded to extended chains occurs at 119 °C.

3.3. (3) F246

Having demonstrated the reduction in conformational disorder in both extended and folded chain crystals of $C_{198}H_{398}$ with increased annealing temperature, this alkane was used to investigate the generality of this behaviour. The initial layer periodicity of sample F246 was found, using SAXS, to be 158.6 Å. After annealing at 105, 115 and 122 °C, values of 157.8, 157.8 and 315.5 Å were determined, respectively. The absence of significant chain tilt here is surprising, but comments made in the Section 2 on the shortcomings of the photographic film method used are relevant here: the peak position was measured, without taking into account any line broadening. The results indicate that a transformation to the extended chain form has occurred on annealing at 122 °C. Low temperature FTIR spectra of F246 are shown in Fig. 7 after baseline subtraction. These clearly show a general reduction in conformational disorder for the once-folded crystals with increasing annealing temperature. There is a further major reduction in disorder on transformation to extended chains (sample cooled from 122 °C). The invariance with annealing temperature of the 1329 cm^{-1} band, previously tentatively assigned to a methyl group vibration, is notable.

The differences between spectra obtained after cooling from 115 °C and from 122 °C are largely due to the previously documented contributions from the fold itself [2].

4. Discussion and conclusions

The general feature to emerge from this work is a decrease in conformational disorder observed in both extended and folded chain crystals of long chain *n*-alkanes, through annealing at successively higher temperatures. The information obtained complements studies of the C–C stretching/CH_2 twisting progression bands already published [4]. We have recently shown [5] that this decrease in disorder is largely confined to regions near to the chain ends. The use of time-dependent measurements on once-folded crystals of $C_{198}H_{398}$ has revealed that, on raising the annealing temperature to 95 °C, conformational disorder initially increases, before decreasing. Furthermore, it appears that translational ordering leads to the development of chain tilt, before a reduction in conformational disorder.

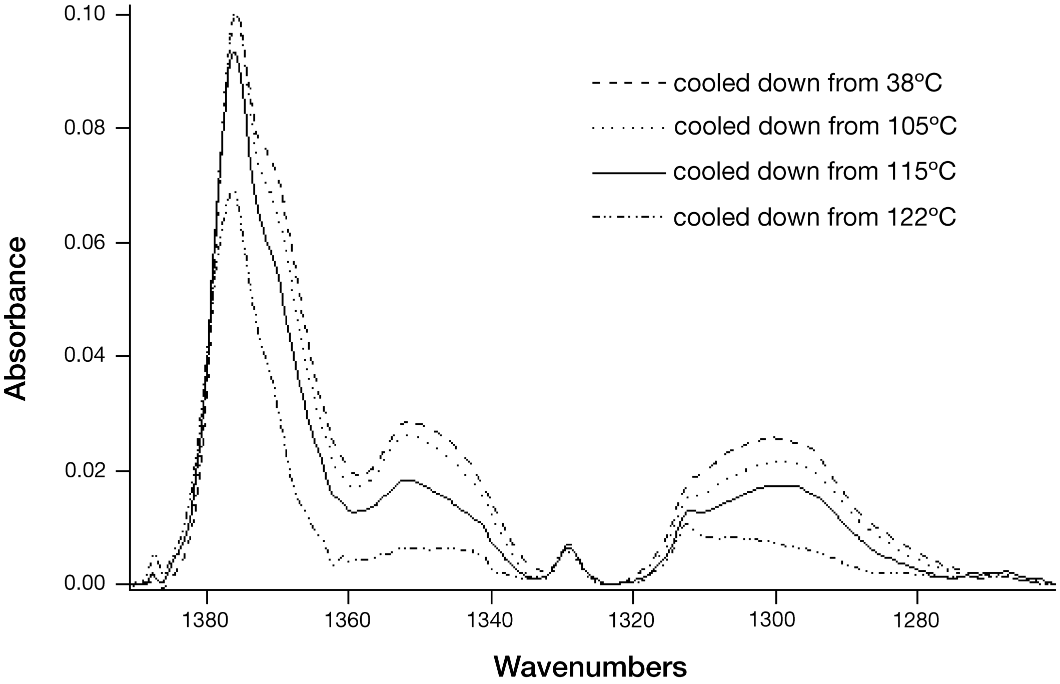

Fig. 7. Low temperature FTIR spectra for sample F246 after annealing at various temperatures. A reduction in methylene wagging absorbances indicates crystal perfecting, while the final spectrum after heating to 122 °C is characteristic of the extended chain form.

On heating further, the proportions of all the non-planar conformers except the end-*gauche* one are found to pass through a maximum at a temperature of 118.4 °C. This is attributed to the transformation to extended chain crystals, which involves movement and combination of defects in the crystal interior, without affecting the terminal C − C bonds significantly.

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