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Infra-red spectrum of the tight (110) fold in *n*-$C_{198}H_{398}$

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Abstract

The alkane *n*-$C_{198}H_{398}$ has been crystallised in both extended chain and once-folded forms and annealed to produce materials with low concentrations of *gauche* bonds. The concentrations of the specific conformers detected by FTIR spectroscopy at −173 °C are calculated, using measurements on liquid *n*-hexadecane for calibration: values are all generally less than 2.0 per 100 carbon atoms, with extended chain samples showing values less than 1.0 per 100 carbon atoms. A subtraction spectrum (Once-folded chain sample minus Extended chain sample) shows positive bands at 1298, 1340, 1347 and 1369 cm^{-1}, which are predicted in earlier calculations for a (110) fold, while additional positive bands at 1353 and 1363 cm^{-1} are assigned, respectively, to *gg* conformers and (tentatively) to strained *gtg* or *gtg'* conformations. © 2002 Published by Elsevier Science Ltd.

Keywords: Fold; *n*-Alkane; Molecular conformations

1. Introduction

Determination of the conformation of chain folds in polymer crystals has proved to be a difficult problem. Solution-crystallised polyethylene (PE) has a high degree of regularity in the arrangement of crystal ‘stems’ (the individual molecular traverses of the crystals). Nevertheless, direct imaging of the fold by atomic force microscopy has been frustrated by problems such as molecular mobility at the fold surface. Indirect methods, such as those based on isotopic labelling (i.e. neutron scattering and mixed crystal infra-red spectroscopy; e.g. Refs. [1,2]) can only provide evidence of labelled stem adjacency and direction: the extent of adjacent *folding* remains ambiguous and the fold conformation cannot be addressed.

It has long been known that the methylene wagging region of the IR spectrum can provide detailed information on the disorder present in polymethylene chains (e.g. Ref. [3]). Painter et al. studied a similar region of the spectrum of single crystal PE samples after annealing [4]. On subtracting spectra after annealing from the original unannealed spectrum, a positive difference band was observed at 1346 cm^{-1}. This was assigned to a ‘regular’ fold conformation characteristic of single crystals. Later IR studies, involving a systematic variation in crystal habit, and hence in the proportions of 100 and 110 fold sectors, revealed a band at 1346 cm^{-1}, characteristic of a regular and possibly adjacent fold [5]. This did not appear to be associated uniquely with one particular type of fold.

The recent synthesis of uniform, monodisperse long chain *n*-alkanes [6] raises the possibility of preparing crystals in either the extended chain or once-folded forms, using a suitable choice of crystallisation conditions. Since the latter form is known to crystallise from solution with sharp, adjacent folds [7], a subtraction spectrum should provide a fingerprint for a (110) adjacent fold. This procedure was adopted for an earlier preparation of *n*-$C_{198}H_{398}$ [8]. Extended chain and once-folded forms were crystallised from solutions in toluene. IR spectra were recorded at 110 K and the subtraction spectrum led to the assignment of bands at 1345 and 1298 cm^{-1} to a regular, adjacent (110) fold conformation. In addition, the 1369 cm^{-1} band previously attributed to *gtg*/*gtg'* conformations was also found. The value of low temperature measurements, in reducing the number of non-planar conformations from the crystal interior, was clearly demonstrated.

More recently, the experimental work described earlier has been supported by calculation of the defect density of states for the tight (110) fold. Wolf et al. applied the Green’s function method to the approximately *g'g'ggtg* conformation of the (110) fold [9], with the valence force field of Snyder [10]. Resonance modes at 1374, 1348, 1342 and

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1288 cm^{-1} were reported to correspond to bands observed at 1369, 1346, 1342 and 1298 cm^{-1}, respectively, by Ungar and Organ for n-C$_{198}$H$_{398}$. It is worth noting that a more recent conformational energy calculation supported previous calculations in the conclusion that the lowest energy fold structure ('fold A') approximates to $g'g'ggtg$, although significant differences were found in the torsional angles [11]. Furthermore, another fold conformation ('fold B') was found to have a higher energy by only 0.21 kcal mol^{-1}. In the present context, the conformation of this second possible fold—approximately *ggtggtg*—is interesting in that it involves *gg* sequences isolated by *t* bonds.

Since the previous IR studies of n-C$_{198}$H$_{398}$ [8], larger quantities of these alkanes have become available. In the course of detailed IR and X-ray work on the annealing behaviour of these systems [12], it has become clear that a heating/cooling cycle leads to a 'perfecting' of the alkane chains, which in turn is related to the development of chain tilt. It is therefore important to make IR measurements on samples where the number of non-planar conformations is minimised, in order to minimise the contribution of such conformers in the crystal interior. It also appears sensible to use conditions where chain tilt has not yet started. In this paper, we select appropriate annealing regimes for both extended chain and once-folded crystal forms. In addition, we give estimates for the concentrations of various non-planar conformations in the samples used.

2. Experimental

The synthesis of n-C$_{198}$H$_{398}$ is described elsewhere [6].

Sample F was prepared by crystallisation of a 1.4% w/v solution in toluene at 73.2 ± 0.4 °C for 90 min. The crystals were filtered and the mat was allowed to dry before pressing (<0.4 t cm^{-2}). Sample E was prepared by crystallisation of a 0.8% w/v solution in toluene at 81.5 ± 0.4 °C for 6 h. These crystals were also filtered and the mat was allowed to dry before pressing (<0.4 t cm^{-2}).

Small angle X-ray scattering (SAXS) measurements were made using a Rigaku–Denki camera, filtered Cu Kα radiation and 300 μm pinholes (courtesy of Dr Goran Ungar, University of Sheffield). SAXS layer periodicities of samples F and E were found to be 124.7 and 253.3 Å, respectively, compared with a calculated value of 254 Å for extended chains, confirming that the samples involve once-folded and extended chain crystals, respectively.

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 F showed an intense longitudinal acoustic mode (LAM) at 25 cm^{-1} and a weaker peak (third order) at 70.9 cm^{-1}. The number (n_c) of carbon atoms in the crystal stem was calculated using the relationship derived from Ref. [13]:

$$n_c = \frac{1}{1.27}\left(\frac{3169}{\Delta\bar{\nu}} - 2\right) \qquad (1)$$

where $\Delta\bar{\nu}$ is the frequency (cm^{-1}) of the first order LAM. This gave a figure of 98 carbon atoms for sample F, almost exactly half the chain length.

Sample E showed Raman bands at 13.2 and 35.9 cm^{-1} (first and third order LAMs of the extended chain conformation), but also a weak feature at 23.6 cm^{-1}. This last band was attributed to a small proportion of once-folded crystals which had not been detected by SAXS.

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 and discussion

For annealing temperatures above 90 °C, the once-folded alkane chains are expected to show tilt with respect to the crystal surfaces [14]. The tilt angle increases with increasing temperature. Sample F was annealed at 51 °C, a temperature chosen to give significant crystal 'perfecting', as indicated by methylene wagging intensities after cooling to −173 °C, but without the appearance of chain tilt. This perfecting process and its relationship with chain tilt is investigated in further detail in a forthcoming paper [12]. The FTIR spectrum is shown in Fig. 1, after baseline subtraction using reference points at 1391.0, 1324.9 and 1280.1 cm^{-1}.

Sample E was annealed at successively higher temperatures, up to 126 °C, in each case showing

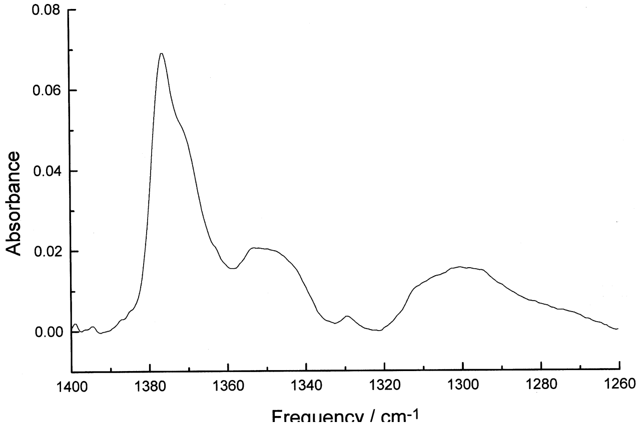

Fig. 1. Low temperature FTIR spectrum of sample F after annealing at 51 °C.

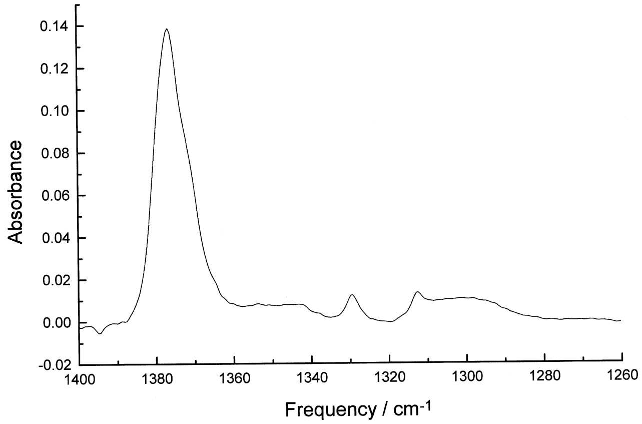

Fig. 2. Low temperature FTIR spectrum of sample E after annealing at 126 °C.

enhanced ‘perfecting’ of the crystals. In no case was any chain tilt observed, on the evidence of SAXS data. An annealing temperature of 126 °C was therefore used for comparison with sample F. The FTIR spectrum is shown in Fig. 2 after baseline subtraction. Using the methyl umbrella deformation at 1378 cm^{-1} as a reference, the methylene wagging vibrations of non-planar conformers in the range 1280–1370 cm^{-1} can be seen to be considerably reduced in absorbance by comparison with sample F (Fig. 1). This adds support to the assumption that the low temperature spectrum of sample F is dominated, in this region, by the ‘fold spectrum’. Indeed, the shape of the bands in the region 1335–1365 cm^{-1} (primarily the *gtg*/*gtg*$'$ band at 1365 cm^{-1} and the *gg* band at 1350 cm^{-1}) can be taken as characteristic of chain folds. Other features of the IR spectrum dominated by contributions from the folds will be demonstrated in a future paper [15].

In order to estimate the numbers of different conformers present and contributing to the spectra in Figs. 1 and 2, a calibration was performed using the FTIR spectrum of liquid *n*-hexadecane. The ratio of absorbances of any CH_2 wagging vibration of hexadecane to that of the CH_3 deformation at 1378 cm^{-1} (using curve fitting) can be compared with the predicted value, using Rotational Isomeric State statistics. Comparisons can then be made with the *n*-$C_{198}H_{398}$ spectra, after similar curve fitting and normalisation with the 1378 cm^{-1} band. This procedure is described in more detail elsewhere [16]. In this case, neighbouring bands (e.g. 1364 and 1353 cm^{-1}) were assumed to have the same absorptivity. The bands used for curve fitting, their assignments and the numbers of such conformations observed per molecule are listed in Table 1. It was found necessary to include a component in the curve fitting at 1364 cm^{-1}. This is at a rather lower frequency than the main *gtg*/*gtg*$'$ peak, identified at 1370 cm^{-1} here. A similar peak was determined previously for the surfactant lithium phenyl stearate, and tentatively attributed to a distorted *gtg* or *gtg*$'$ conformer [16]. We make a similar, tentative assignment in this case. It is notable that no component at this frequency is predicted by Wolf et al. [9]. The 1374 cm^{-1} component predicted by Wolf has probably been included here with the CH_3 deformation band, while the 1346 and 1341 cm^{-1} components in the curve fitting both correspond to bands associated with the (110) fold [9]. In every case, the estimated number of such conformations per molecule is less than two. All components are substantially reduced in number for the extended chain form, although the ‘fold bands’ at 1341 and 1346 cm^{-1} still appear: this may be related to residual folded chain crystals in sample E, although annealing above 124 °C is expected to transform the material to the extended chain form.

Table 1
Estimates of the numbers of specific conformers in once-folded (F) and extended (E) *n*-$C_{198}H_{398}$ crystal forms at −173°C

Band position (cm^{-1})		Assignment	Number of conformations per molecule	
F	E		F	E
1370.1	1370.7	*gtg*/*gtg*$'$ conformers	1.4	0.8
1363.8	1364.2	Strained *gg* ?	1.3	0.4
1353.4	1353.7	*gg* conformers	1.8	0.3
1346.4	1346	(110) fold	0.8	0.2
1341	1341	(110) fold	0.7	0.2

As the normalising band for spectral subtraction, the broad combination band between 2558 and 2690 cm^{-1} was used. This appears to be the least conformationally sensitive [12]. The result of subtracting the spectrum of sample E after annealing at 126 °C (Fig. 2) from that of sample F after annealing at 51 °C (Fig. 1) is shown in Fig. 3. The results are broadly similar to previous ones [8], but now a direct comparison with calculations for the approximately *g*$'$*g*$'$*ggtg* (110) fold [9] can be made. Positive features in the subtraction spectrum at 1369, 1347, 1340 and

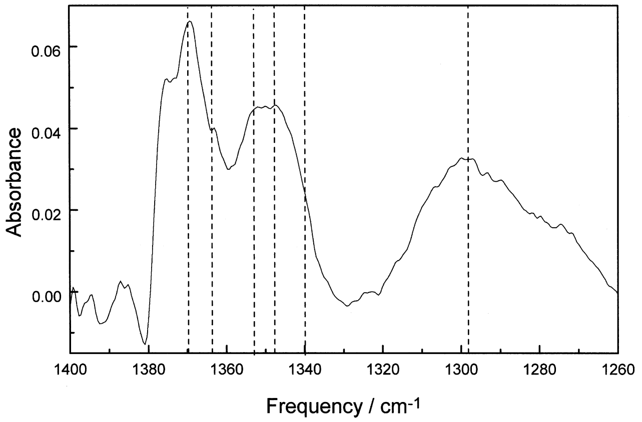

Fig. 3. Result of subtracting the low temperature spectrum of annealed sample E from the low temperature spectrum of annealed sample F. Dotted vertical lines represent frequencies of 1369, 1363, 1353, 1347, 1340 and 1300 cm^{-1}.

1298 cm^{-1} can be related to predicted peaks at 1374, 1348, 1342 and 1288 cm^{-1}, respectively. As noted earlier, the 1363 cm^{-1} peak is tentatively assigned to a strained *gtg* or *gtg'* conformation, while the 1353 cm^{-1} component is attributed to the *gg* conformer. Such a band might be anticipated if the fold conformation approximates to the 'fold B' conformation of Chum et al. [11]: since this approximates to *ggtggtg*, there would be two isolated *gg* conformers per molecule. This provides some indication that a second type of tight (110) fold may be present. Otherwise, it is difficult to envisage how a *gg* conformer might be accommodated within the crystal lattice. In the region 1372–1385 cm^{-1}, the subtraction spectrum has a characteristic shape indicating a frequency shift. The positive component at 1375.5 cm^{-1} and the negative component at 1381 cm^{-1} symmetrically span the usual CH_3 umbrella deformation frequency of 1378 cm^{-1}. We suggest that this band is sensitive to crystal form, shifting to lower frequency for the folded form (sample F). Indeed, work on the short chain alkanes, without the complication of chain folding, has shown that this band is sensitive to crystal structure, presumably through different local arrangements of the methyl groups (e.g. Ref. [17]). Finally, two negative peaks appear in the subtraction spectrum at 1321 and 1329 cm^{-1}, with a (negative) shoulder at 1312 cm^{-1}. Positive peaks corresponding to the 1312 and 1329 cm^{-1} features are revealed in the extended chain spectrum at low temperatures and they are tentatively assigned to methyl group vibrations. At this stage, the origin of the 1321 cm^{-1} subtraction band is unknown.

4. Conclusions

By careful choice of sample annealing conditions, we have prepared once-folded and extended chain samples of n-$C_{198}H_{398}$ which show remarkably low concentrations of non-planar conformations at low temperatures—less than 1 per 100 carbon atoms for the folded chain form and less than 0.5 per 100 carbon atoms for the extended chain form. In the former case, the majority of the absorbance clearly arises from the fold itself. A subtraction spectrum (F − E) showed bands at 1298, 1340, 1347 and 1369 cm^{-1} which are expected from calculations for a (110) fold approximating to *g'g'ggtg*. Additional features were attributed to *gg* (1353 cm^{-1}) and tentatively to strained *gtg* or *gtg'* (1363 cm^{-1}) conformations. The *gg* conformers may arise from a fold approximating to a *ggtggtg* conformation, with a marginally higher conformational energy than the minimum energy conformation, which approximates to *g'g'ggtg*. The CH_3 umbrella deformation shifts to lower frequency in the once-folded form.

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