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Polymer 43 (2002) 4043–4046

polymer

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Structural information from progression bands in the FTIR spectra of long chain *n*-alkanes

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Received 3 January 2002; received in revised form 25 February 2002; accepted 27 February 2002

Abstract

The low temperature FTIR spectrum of long chain *n*-alkanes has been investigated in the region between the C–C stretching and CH_2 twisting fundamentals (1050–1133 cm^{-1}). With successive annealing and cooling stages, extended chain crystals of *n*-$C_{198}H_{398}$ show an improvement in the regularity of the progression bands observed. This is related to a 'perfecting' of the crystals. A once-folded sample of the same alkane shows additional features between 1050 and 1100 cm^{-1}, attributed to resonance modes from a tight (110) fold. These disappear on transformation to the extended form, to be replaced by progression bands. Assignment of the individual bands enables the length of the all-*trans* chain to be estimated and this method is used to show that centre-branched long chain *n*-alkanes have a folded conformation. It is also shown that the chain length derived from such FTIR data for a 1:1 molar mixture of *n*-$C_{162}H_{326}$ and *n*-$C_{246}H_{494}$ is consistent with a triple layer superlattice structure.

Keywords: FTIR; Progression bands; *n*-alkanes

1. Introduction

Vibrational spectroscopy has been widely used to characterise both the type and the extent of disorder in semicrystalline polymers and oligomers. Disorder in long chain *n*-alkanes (at least in the pure materials) is usually limited. Nevertheless, FTIR spectroscopy has proved useful in characterising the disorder both at the crystal surfaces and in the interior [1,2]. The CH_2 wagging modes which have provided much of this information are separable into bands arising from several non-planar bond conformations [3]. We have recently demonstrated that several features in this 1250–1400 cm^{-1} region of the spectrum of *n*-$C_{198}H_{398}$ [2] correspond in frequency to modes calculated by Wolf et al. for a tight (110) fold in polyethylene [4]. These calculations assumed an approximately $g'g'ggtg$ conformation for the fold. For comparison, low temperature spectra of extended chain and once-folded crystals of *n*-$C_{198}H_{398}$ were collected and a subtraction spectrum (folded minus extended) was obtained. Apart from bands predicted by Wolf et al. additional positive bands were observed at 1353 and 1363 cm^{-1}, assigned, respectively, to *gg* conformers and (tentatively) strained *gtg* or gtg' conformers.

It has recently been shown that the development of chain tilt in extended chain crystals of *n*-$C_{198}H_{398}$ accompanies the ordering of the chain extremities, suggesting that the phenomenon of chain tilt results from an ordering of the crystal surface [1]. It has also been shown that the development of a tilt angle in row-nucleated polyethylene can be related not only to an improvement in chain order, but also to a change in crystal morphology [5]. The characterisation of chain disorder and the nature of the fold surface are thus seen as important factors in understanding polymer morphology.

As part of a broader study of crystal structures formed by long chain *n*-alkanes, we demonstrate here the use of progression bands in characterising both order and disorder in these systems. The spectral region used is bounded by bands at 1050 and 1133 cm^{-1}, assigned to a CH_2 twisting vibration and an in-phase C–C stretching mode. Within this region, a band at 1078 cm^{-1} has been ascribed to amorphous regions [6], and more specifically to a localised end-*gauche* vibration involving CH_2 wagging and C–C stretching [3].

2. Experimental

The synthesis of *n*-$C_{198}H_{398}$ is described in Ref. [7].

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0032-3861/02/$ - see front matter
PII: S0032-3861(02)00169-6

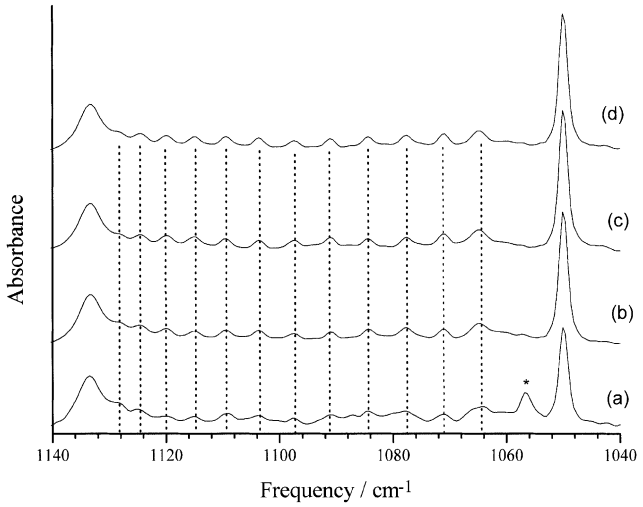

Fig. 1. Development of the C–C stretching/CH_2 twisting progression bands in the FTIR spectrum of sample E with successive annealing and cooling to −173 °C. Spectra were recorded at −173 °C after cooling from (a) 35 °C; (b) 110 °C; (c) 120 °C, and (d) 126 °C.

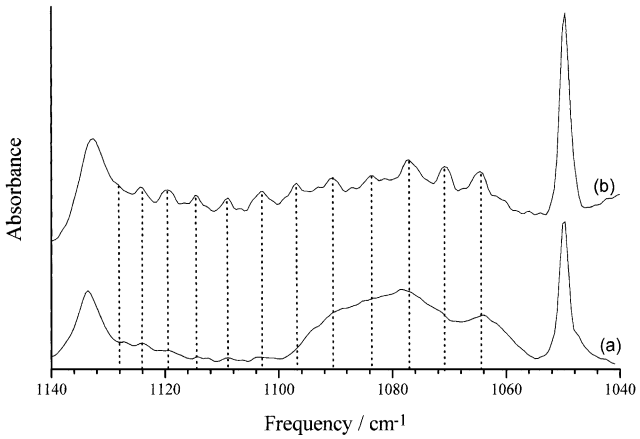

Fig. 2. Changes in the C–C stretching/CH_2 twisting region of the FTIR spectrum of sample F with annealing. Spectra were recorded at −173 °C after cooling from (a) 110 °C and (b) 124 °C. The latter temperature is above the transition temperature from once-folded to extended chain crystals.

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 (<40 MPa). 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 (<40 MPa).

The verification of once-folded and extended chain crystal structures by small angle X-ray scattering (SAXS) has been described earlier [2], together with Raman LA mode characterisation. This indicated a small proportion of once-folded crystals in sample E.

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

3.1. Crystal perfecting by annealing/cooling

As previously noted [2], successive annealing and cooling of long chain *n*-alkane crystals leads to a 'perfecting' of the crystals, on the evidence of changes to the localised CH_2 wagging mode spectrum. The effect of this thermal treatment on the IR progression bands of sample E, as recorded at liquid nitrogen temperature, is shown in Fig. 1. The unannealed sample (Fig. 1(a)) clearly shows the presence of progression bands, with some indication of more than one series. Among these, the peak with the largest absorbance is at 1056 cm^{-1}. It is clear that annealing at higher temperatures significantly improves the regularity of the bands: the dotted lines indicate their ultimate positions. At the same time, the 1056 cm^{-1} peak disappears. The data are interpreted on the basis that the distribution of all-*trans* extended chains becomes narrower as a result of the thermal treatment. The calculation of the all-*trans* chain length from the band frequencies is described later: we simply note here that the data after heat treatment can be understood in terms of a single all-*trans* chain length. The disappearance of the band at 1056 cm^{-1} with heat treatment suggests that this band is related to chain disorder.

3.2. Transformation from once-folded to extended chain crystals

Solution grown once-folded crystals of *n*-$C_{198}H_{398}$ have previously been shown to transform to the extended chain form at around 119 °C [8]. Representative spectra for sample F annealed both above and below this temperature are shown in Fig. 2. In both cases, bands at 1050 and 1133 cm^{-1} are observed. After annealing at 124 °C, progression bands characteristic of the extended chain form are evident, although there is less regularity than for the as-grown extended chain crystals shown in Fig. 1. Nevertheless, the main component frequencies (dotted in Fig. 2) correspond closely to those observed in Fig. 1. The implication is of less highly ordered chains, with some variations in the all-*trans* chain length.

The spectrum after annealing at 110 °C shows marked differences. A broad band at 1078 cm^{-1}, with a shoulder around 1090 cm^{-1}, together with a peak at 1064 cm^{-1} obscure any progression bands in this region. The association of the 1078 and 1090 cm^{-1} bands with the (110) fold is supported by the calculation of resonant mode frequencies of 1082.5 and 1101 cm^{-1} for the tight (110) fold [4]. It

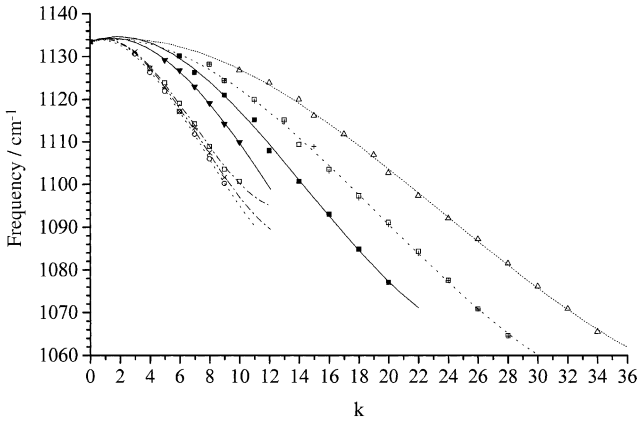

Fig. 3. Frequencies of progression bands observed for a range of long chain *n*-alkane samples as a function of the integer *k* are used to characterise the modes. Samples involved are, from left to right: ○ plus spaced dotted line: $C_{96}H_{193}CH(CH_2)_3CH_3C_{94}H_{189}$ crystallised from toluene solution to obtain once-folded crystals; × plus dot-dash line: $C_{96}H_{193}CHCH_3C_{94}H_{189}$ crystallised from toluene solution to obtain once-folded crystals; □ plus dot-dash line: sample F; ▼ plus solid line: $C_{246}H_{494}$ crystallised from toluene solution to obtain once-folded crystals; ■ plus solid line: binary 1:1 molar mixture of *n*-$C_{162}H_{326}$ and *n*-$C_{246}H_{494}$ prepared by cooling from the melt at 2 °C min^{-1} from 130 to 80 °C and left at 80 °C for 120 min before further cooling to room temperature (triple layer structure): □ plus spaced dotted line: sample E; + plus spaced dotted line: extended chain sample obtained by heating sample F above the transition temperature; △ plus close dotted line: extended chain sample obtained by heating a once-folded sample of $C_{246}H_{494}$ above the transition temperature.

appears, then, that the 1055–1100 cm^{-1} region of the low temperature IR spectrum provides a useful 'fingerprint' for the tight (110) fold. Above 1100 cm^{-1}, the spectrum shows some evidence of weak progression bands. The frequencies of the main components again appear to match those found in the extended chain crystals, as indicated by the dotted lines in Fig. 2. This might appear to indicate a small proportion of extended chains in the original sample F, with the majority of highly disordered folded chains making little contribution to the progression bands. However, measurements on the perfecting of once-folded crystals on annealing below the temperature of transformation to the extended form show the same progression band frequencies, with improved clarity. A possible explanation of this behaviour involves a change in symmetry in switching from once-folded to extended chains. If both the odd and even order progression bands are observed in the case of once-folded chains (as opposed to only odd orders in extended chains), then indexation of the orders leads to a realistic estimate of the all-*trans* chain length, as discussed in Section 3.3. The absence of a flat baseline in the spectrum obtained after heating to 124 °C suggest a small contribution from the 1064, 1078 and 1090 cm^{-1} bands, due to residual folded chain crystals.

3.3. Calculation of the all-trans chain length

In order to identify individual progression bands, the frequency–phase relationship for the C–C stretching/CH_2 twisting progression can be used. This was determined by Snyder and Schachtschneider for the short chain *n*-alkanes *n*-$C_{20}H_{42}$ to *n*-$C_{30}H_{62}$ [9]. The phase difference, ϕ_k, is related to the number of carbon atoms, n_c, involved in the vibration through the integer *k*

$$\phi_k = \frac{k\pi}{n_c - 1} \quad (1)$$

where the value of n_c represents the all-*trans* chain length. To achieve the best estimate for n_c, an initial estimate was made (normally the highest possible number of carbon atoms: 198 in the case of extended chain *n*-$C_{198}H_{398}$). A series of *k* values was then calculated, using the experimental band frequencies, the frequency–phase curve and Eq. (1). This process was then repeated, using a new estimate for n_c (usually one less than the previous estimate). Typically, around 15 iterations were used, and the iteration providing the closest correspondence of the *k* values with integers was chosen as the best fit. The corresponding value of n_c was then selected as the best estimate for the all-*trans* chain length. Rounding the *k* values for this iteration resulted in the plots shown in Fig. 3 for a range of long chain *n*-alkane systems.

The value of these progression bands in terms of structural information becomes clear when we consider the branched alkanes $C_{96}H_{193}CHCH_3C_{94}H_{189}$ (×) and $C_{96}H_{193}CH(CH_2)_3CH_3C_{94}H_{189}$ (○) and the binary 1:1 molar mixture *n*-$C_{162}H_{326}$ and *n*-$C_{246}H_{494}$ (■). The curves in Fig. 3 relating to the branched alkanes closely follow that for the once-folded form of *n*-$C_{198}H_{398}$ (□ plus dot-dash). Since the all-*trans* chain length in the latter case must be around 99 carbon atoms, the same must be true for the branched molecules, indicating a once-folded conformation. The curve for the *n*-$C_{162}H_{326}$/*n*-$C_{246}H_{494}$ mixture (■) falls between those for the extended chain *n*-$C_{198}H_{398}$ (□ plus spaced dotted line) and once-folded *n*-$C_{246}H_{494}$ (▼). We conclude that the all-*trans* chain length for the binary mixture lies between approximately 198 and 123. This clearly excludes extended chains of *n*-$C_{246}H_{494}$ in the mixture and implies that the *n*-$C_{162}H_{326}$ chains are extended.

Table 1 lists the best estimates for the number of carbon atoms in the all-*trans* chains for the same systems. For comparison, the number of carbon atoms corresponding to the SAXS long period and the Raman LA mode are also reported, where available. The values obtained from IR measurements show significantly larger errors than those from the other methods, because of the iteration techniques used. Nevertheless, it is clear that chain lengths determined by the IR method are generally shorter than those obtained from SAXS. This reflects the fact that SAXS data are related to the periodicity within crystal stacks, while progression bands are related only to the ordered segments of the molecules.

Considering the values of n_c determined from IR measurements, the figure of 90 for once-folded $C_{198}H_{398}$ is

Table 1
Estimates for the numbers of carbon atoms in the straight chain portions of various samples. See Fig. 3 caption for key to samples

Sample	Result from SAXS periodicity	Result from Raman LAM frequency	Result from FTIR progression band fitting
○	99 ± 2	–	98 ± 2
×	94 ± 1	94 ± 2	101 ± 2
F	97 ± 1	98 ± 2	90 ± 16
▼	123 ± 1	128 ± 2	–
■	–	–	158 ± 15
E	198 ± 1	187 ± 2	192 ± 12
+	194 ± 1	–	191 ± 8
△	247 ± 2	–	244 ± 13

significantly smaller than half the chain length, while values of 191 and 192 for extended chain $C_{198}H_{398}$ are closer to the chain length. This indicates a larger disordered region in the once-folded crystals. While it was not possible to obtain a value of n_c for once-folded *n*-$C_{246}H_{494}$ because of the low absorbance of the bands, the value of 244 for extended chain *n*-$C_{246}H_{494}$ is also very close to the chain length. Values of n_c for the branched alkanes (101 and 98) closely correspond to half the molecular length (95.5 carbon atoms), indicating once-folded chains.

The figure of 158 carbon atoms for the *n*-$C_{162}H_{326}$/*n*-$C_{246}H_{494}$ mixture confirms that the structure involves the shorter alkane in extended chain form. This is entirely consistent with the triple layer superlattice structure proposed by Zeng and Ungar, on the basis of SAXS studies [10]. In this structure, the outer layers contain the extended shorter alkane, while the middle layer contains only the surplus length of the longer alkane and is separated by disordered regions. The regularity of the longer alkane is thus disrupted at the layer boundaries. For this reason, we would not expect to see IR progression bands corresponding to extended *n*-$C_{246}H_{494}$ molecules.

4. Conclusions

We have demonstrated the value of the C–C stretching/CH_2 twisting progression bands in the low temperature FTIR spectrum of *n*-alkanes: they have been used to compare the regularity of chains within crystals, as a fingerprint for chain folds and to determine the all-*trans* chain length in crystals.

The perfecting of extended chain *n*-$C_{198}H_{398}$ crystals with successive annealing and cooling cycles is evident from the improved regularity of the progression bands with increasing annealing temperature. The bands become better resolved, while the disappearance of the 1056 cm^{-1} band indicates that this feature is related to chain disorder. By contrast, once-folded crystals of *n*-$C_{198}H_{398}$ show broad features at 1064 and 1078 cm^{-1}, with a shoulder at 1090 cm^{-1}. In the light of resonance mode calculations for a tight (110) fold [4], it appears that most, if not all, of these bands are related to the fold conformation. Weak progression bands at frequencies above 1100 cm^{-1} appear to originate from odd and even orders for the once-folded structure, due to the different molecular symmetry as compared to extended chains. Transformation of the crystals to the extended form restores the sequence of progression bands observed for as-grown extended chain crystals, although the degree of chain disorder is greater.

By assigning the individual progression bands, an estimate can be made of the all-*trans* chain length in the crystals. Since this measurement relates to the ordered chain length, the information differs from the SAXS periodicity. Indeed, the value obtained is generally smaller. This method has been used to verify that two branched long chain *n*-alkanes are in a folded conformation. Additionally, the all-*trans* chain length (158 carbon atoms) for a 1:1 molar mixture of *n*-$C_{162}H_{326}$ and *n*-$C_{246}H_{494}$ has been shown to be consistent with a triple layer superlattice structure with the *n*-$C_{162}H_{326}$ (but not *n*-$C_{246}H_{494}$) molecules in extended form.

Acknowledgements

We are indebted to Drs G.N. Brooke and S. Mohammed of the University of Durham for supplying the long chain *n*-alkanes. We would like to thank Dr Goran Ungar (University of Sheffield) for assistance with SAXS measurements and Dr X.B. Zeng (University of Sheffield) for preparing the binary mixture.

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