Infra-red 'defect modes' in polyethylene single crystals with relevance to chain folds

S. J. Spells, S. J. Organ and A. Keller
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

and G. Zerbi
Istituto de Chimica Industriale del Politecnico, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

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The CH_2 wagging region in the infra-red spectrum has been investigated for polyethylene single crystals grown from a range of solvents and with a range of characterized crystal habits, for the purpose of identifying 'fold band(s)' and studying their variation with crystal habit. Peaks in the region previously identified using subtraction techniques with regular folding at the crystal surface are now revealed directly, using Fourier self-deconvolution. One such peak, at 1342 cm^{-1}, corresponds in frequency to a band assigned to a *ggtgg* defect in model systems, suggesting a contribution from this defect to the polyethylene spectra. The wagging mode region shows variations with crystal habit. Furthermore, the decrease in intensity around 1346 cm^{-1} on either annealing or quenching from the melt supports the assignment to a regular and possibly adjacent fold arrangement. Nevertheless, there appears to be no unique assignment of the wagging modes to one particular type of fold.

(Keywords: polyethylene; single crystals; *FT*i.r. spectroscopy; chain folding; defect modes)

INTRODUCTION

Since the demonstration of chain-folding in polyethylene crystals[1], the fold structure has been a subject of interest and controversy. Of the various experimental techniques which have been utilized to study the fold structure, infra-red spectroscopy has been shown to be particularly sensitive to departures from the all-*trans* chain conformation, as must occur within the fold region[2-4]. In this communication, we apply some of the more recent methods of Fourier Transform infra-red (*FT*i.r.) spectroscopy to polyethylene single crystals, whose habits are varied by changing the crystallization temperatures and solvents used to grow them. The habits are characterized by electron microscopy. The preliminary results presented here form the first such study of polyethylene, using crystals with well-characterized morphologies and introducing a deliberate and systematic variation in crystal morphology. The technique of Fourier self-deconvolution is used to identify separate components within overlapping infra-red band profiles.

BACKGROUND

Bands in the infra-red spectra of several polymers were associated at an early stage with types of fold present in the crystal structure[2,5]. More recently, lattice dynamical calculations for both n-alkanes[6] and polymethylene chains[3,4] have confirmed the origin of various localized CH_2 wagging vibrations. Leaving aside the 'end-*gauche*' modes, which only have significant intensity in shorter chain alkanes, the conformational assignments of these 'defect modes' are:

$$\left.\begin{array}{l}1365\,\mathrm{cm}^{-1}\\ 1306\,\mathrm{cm}^{-1}\end{array}\right\} gtg' \text{ and } gtg$$

$$1350\,\mathrm{cm}^{-1} \quad gg$$

where g and g' represent the two *gauche* conformations and t the *trans* one.

For further assignment cyclic alkanes have proved to be informative. It has long been known that for sufficiently large rings, the molecule within the crystal consists of two parallel segments[7], with the bridging portion providing a possible model for folding in polyethylene[8]. The detailed X-ray structure of the cyclic alkane $C_{34}H_{68}$ was determined by Kay and Newman[9] (based on the unit cell containing a triclinic subcell and preliminary structure determined by Burbank and Keller[10]), who showed that the fold portion is closest to a *ggtgg* sequence, yet somewhat distorted. Subsequent infra-red spectroscopic work has aimed at identifying vibrations associated with such configurations. Schonhorn and Luongo reported a strong band at 1340 cm^{-1} in the infra-red spectrum of $C_{34}H_{68}$,[11] but no equivalent band was observed for solid n-alkanes. The band was later reported at 1342 cm^{-1} and attributed to a CH_2 wagging mode in the fold region[12]. In this case, the band was considered to have the same origin as the *gg* mode observed at 1355 cm^{-1}, and the frequency shift was taken to arise from the distortion out of a *gg* conformation in the fold.

Later measurements for a series of cyclic alkanes indicate that the position of the predominant band at

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1342 cm^{-1} is insensitive to molecular weight, at least for a few molecules of the series C_nH_{2n} ($n = 36, 48, 60$ and 72)[13]. Furthermore, the band intensities are reported to decrease with increasing *n*, a trend expected if the vibration is localized within the fold. Later work on the infra-red spectrum of $C_{32}H_{68}$[14] shows again the band at 1342 cm^{-1}, accompanied on either side by weaker satellites, as observed later for larger molecules. These results are consistent with the invariance in the fold conformation as a function of molecular weight and strongly suggests that the observed i.r. band originates from the *ggtgg* defect.

More recent calculations for n-alkanes have included the prediction of normal modes possibly localized in energy and topologically localized on the conformational defects of n-alkanes. Calculations included both classical normal mode analysis of disordered chains[4] and the prediction of absorption intensities through the so-called electro-optical parameters[15,16]. Calculations were also made on the cyclic molecule $C_{34}H_{68}$,[14] whose geometry was approximated to two planar stems linked by *ggtgg* folds similar to the structure proposed by Kay and Newman[9]. A critical analysis was made on the effect of the force fields in giving the calculated normal frequencies and the corresponding eigenvectors which describe the normal modes of the 'in band, pseudo-localized' defect modes[14,16]. The combination of frequencies and intensities calculated with the use of the valence force field by Shimanouchi *et al.*[17] shows good agreement with experimental data[14]. In particular, two modes are calculated to be at 1349 and 1353 cm^{-1}, both highly localized in the *gg* sections of the folds. Calculations also predict an out-of-band defect mode below the cut-off frequency of the CH_2 rocking progression with $k = 0$ band edge mode near 715 cm^{-1}.[14] The lower frequency band, together with those calculated for the CH_2 wagging modes, are observed in the i.r. spectrum of the cyclic molecules as medium-weak absorptions whose intensities decrease with increasing ring size. The observed sharp, medium intensity band at 1342 cm^{-1} in the cyclic molecule is associated with the mode calculated at 1359 cm^{-1} [14] or 1353 cm^{-1} [16] and originates from the CH_2 wagging vibration within the *ggtgg* defect.

Turning now to polyethylene itself, Painter *et al.*[18] report measurements on single crystal samples which were given annealing treatments. Spectra after annealing were subtracted from the original single crystal spectra and a positive difference band was observed at 1346 cm^{-1}. On the basis of spectral variations with annealing time and with melt quenching, it was concluded that a 1346 cm^{-1} component in the polyethylene infra-red spectrum corresponded to a 'regular' fold conformation characteristic of single crystals.

Various experimental techniques have been established to study the chain conformation in polymer crystals. Principal amongst these are two which rely on isotopic labelling of a small fraction of the molecules. Neutron scattering and infra-red spectroscopy of mixed normal and deuterated polyethylene have provided a detailed model of the crystal stem arrangement in samples grown at high supercoolings from xylene solution[19–22]. Both techniques provide information on the arrangement of stems belonging to one molecule within the lattice. They are both insensitive to the arrangement of the polymer chain in the fold region, although some features of the fold surface can be *implied* from the stem positions. The placement of labelled stems preferentially along sheets in the {110} direction, for example, implies that the connecting folds lie in the same plane. Similarly, the existence of a high proportion (75%) of adjacent re-entry implies a large number of short folds. However, these techniques provide no *direct* evidence for either of these conclusions, and a different system of folding may still be compatible with the established stem arrangement.

The apparent sensitivity of 'defect' CH_2 wagging vibrations to the chain conformation provides the possibility of studying the fold structure directly. Furthermore, crystals exhibiting any of the wide range of morphologies recently demonstrated for polyethylene grown isothermally from various solvents[23] are amenable to the technique. At highest supercoolings lozenge-shaped crystals, bounded by four {110} faces are obtained. These become truncated with {100} faces with increasing crystallization temperature (T_c). The extent and the curvature of these {100} faces increases with T_c, the crystals approaching a leaf shape for the higher values of T_c. With appropriate crystallization conditions, crystals can be obtained with any well-defined morphology within this range. Use of the self-seeding technique[24] ensures the uniformity of crystals, so that a small sample is representative of the whole. Thus, the area ratio of {110} to {100} sectors is experimentally variable (by changing T_c), so that any variation in fold type within sectors bounded by {110} and {100} faces can, in principle, be investigated.

Infra-red techniques

Spectra were obtained using a Nicolet 7000 series interferometer, with a resolution of 1 cm^{-1}. 300 scans were generally made. Two methods have then been used to analyse the data. Spectral subtraction is a well-established method for measuring differences in band profiles between samples, although an intrinsic limitation is the suitability of the reference band whose intensity is used as the criterion for determining the correct scaling factor. Fourier self-deconvolution is a method being increasingly applied to general spectroscopic problems[25]. With regard to infra-red spectroscopy of polyethylene, the technique has been described elsewhere[21,22] and only an outline will be given here.

Generally, Fourier self-deconvolution provides a separation of overlapping components in a complex spectrum. In polymer spectroscopy, its use has mainly been restricted to qualitative or semi-qualitative applications, although in principle quantitative analysis is possible through the invariance of the integrated peak intensity on deconvolution[26]. In the present context, self-deconvolution is used to provide an indication of the number of bands present within an overlapping band profile.

Differences between individual samples are more readily seen using spectral subtraction, so the two techniques have been used here in conjunction.

For the self-deconvolution, the intrinsic lineshape function was assumed, as in previous cases, to be Lorentzian. This was deconvoluted from the experimental spectrum. As was explained previously[21], the optimization procedure involves two parameters, the half-width (2σ) of the Lorentzian and a resolution parameter, K. The value of 2σ is initially estimated from the experimental linewidths. Too large a value results in side-lobes to the deconvoluted components. The optimum value corresponds to the largest figure for which such side-lobes are not introduced. The parameter K determines the final signal:noise ratio and was increased to a value where the noise amplitude was comparable to the size of the smallest resolved peak components. Parameters generally used were 6.0 cm^{-1} for 2σ and 2.0 for K. (In the case of sample D the lower original signal:noise ratio limited K to 1.7.) The value of 2σ was limited by the narrowest line in the region studied, namely the 1377 cm^{-1} methyl group band. A larger number of sample scans would have allowed the use of a higher value for K, but this was found unnecessary for revealing the components discussed here. (A full analysis of the 1307 cm^{-1} peak would nevertheless require a considerably larger number of scans.)

Spectral subtractions were made using the criterion for the subtracted spectrum scaling factor that the 1475/1465 cm^{-1} CH_2 bending doublet should be reduced to zero intensity. (The CH_2 rocking doublet could equally well have been used for this purpose.) Since the doublet arises from the solid state splitting, this procedure amounts to subtraction of the crystalline component of the spectrum. The concentration of crystal defects may, however, still differ in two samples crystallized at different temperatures. We have not, therefore, necessarily achieved a separation of the contributions to defect mode intensities from the crystal interior and from the fold surface. Determination of the scaling factor is not a precise operation; in order to obtain adequate intensities in the defect modes, the samples generally yield absorbances well in excess of 1.0 for the CH_2 bending doublet. For this reason, the wings of this band were used to obtain the scaling factor.

EXPERIMENTAL

Nascent Rigidex 50 was used as the starting material. For crystallization from xylene solution, initial removal of higher molecular weight material was necessary to obtain well-defined crystal habits. This was achieved by making a 1% solution of polymer in xylene and crystallizing at 94°C. The suspension was filtered at 94°C and the filtrate recrystallized at the required temperature. The established technique of self-seeding[24] was used with all solvents. After crystallization, the suspensions were filtered at the crystallization temperature and re-suspended in fresh solvent. The less volatile solvents ethyl undecanoate and tetradecanol were exchanged for xylene to facilitate sample preparation. A small portion of each suspension was retained for electron microscopy studies and the remainder allowed to sediment slowly during filtration to form a mat. Mats were dried and then pressed at about 60°C to remove voids, which contribute to a large frequency-dependent background in the infra-red spectra.

The samples used were:

A Crystallized from xylene at 70°C after pre-crystallization (1% concentration in xylene) at 94°C.
B Crystallized from xylene at 75°C after pre-crystallization (1% concentration in xylene) at 94°C.
C Crystallized from xylene at 80°C after pre-crystallization (1% concentration in xylene) at 94°C.
D Crystallized from 0.05% solution in octane at 90°C.
E1 Crystallized from 0.05% solution in ethyl undecanoate at 105.2°C, no pressing.
E2 Crystallized from 0.05% solution in ethyl undecanoate at 105.2°C, mat pressed.
F Crystallized from 0.05% solution in tetradecanol at 110.8°C.
G Crystallized from 0.1% solution in xylene at 70°C without prior crystallization.

Crystals from each of the preparations were deposited onto carbon-coated grids and shadowed with platinum/palladium, then examined in a Philips 301 transmission electron microscope. Their morphologies were characterized in terms of the axial ratio, A/B, and the curvature of the {100} faces, x/y, as defined in *Figure 1*.

Single crystal results

Raw data and deconvoluted spectra for samples crystallized at various temperatures are shown in *Figures 2* and *3*. The corresponding crystal habits are illustrated in the electron micrographs, *Figure 4*. *Table 1* shows the variation in A/B and x/y for the different crystal types and also lists the approximate proportion of {100} sector in each case, assuming sharp sector boundaries as in *Figure 1* and making no allowance for collapsed material.

The most significant difference amongst the spectra is that the 1377 cm^{-1} methyl group band has higher intensity in samples crystallized from xylene than in crystals formed in other solvents. This is a result of the method of preparation for samples crystallized from xylene, described in the previous section. The removal of the higher molecular weight material in the preliminary crystallization significantly reduces the molecular weight for the final crystals. Molecular weights determined by g.p.c. are listed in *Table 2*. The large intensity of the methyl group vibration in sample F, relative to that in samples D and E which were prepared from the same starting material, is probably associated with a small amount of residual tetradecanol in the mat.

In all cases, deconvolution of sample spectra reveals shoulders to the 1351 cm^{-1} *gg* defect mode. One at about 1347 cm^{-1} is present in all deconvoluted spectra and another is usually less well resolved at 1343 cm^{-1}. Although there is usually a clear asymmetry in the 1351 cm^{-1} bandshape, this is the first time that the components have been resolved without spectral subtraction. Furthermore, both components are observed for the range of crystal habits shown in *Figure 4*, from lozenge-shaped forms to those with appreciable curved faces and a large proportion of {100} sector. This

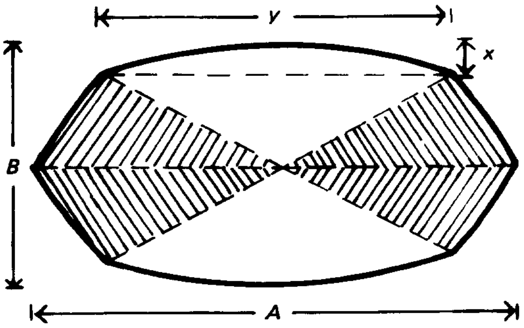

Figure 1 Parameters used to characterize the crystal morphology. The {110} sectors are shaded

indicates that the shoulders are not uniquely associated with, for example, a {110} crystal sector, since these become much smaller at the higher crystallization temperatures.

The effect of pressing a sample is shown in *Figure 5*. The spectrum before pressing is superimposed on a large sloping background. This is removed by pressing with an improvement in signal:noise ratio. There are some changes in the defect mode intensities, as indicated by the undulations in the subtraction spectrum. However, these

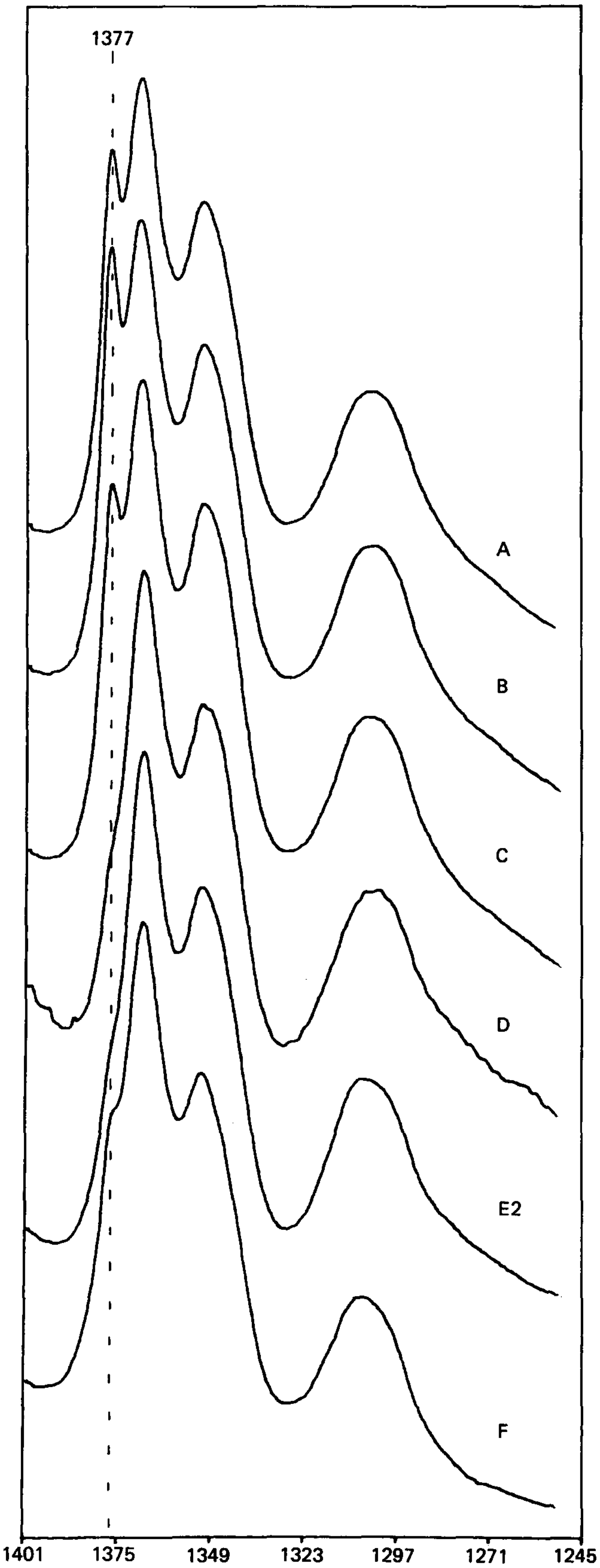

Figure 2 Raw infra-red data for samples crystallized from various solvents. See experimental section for key

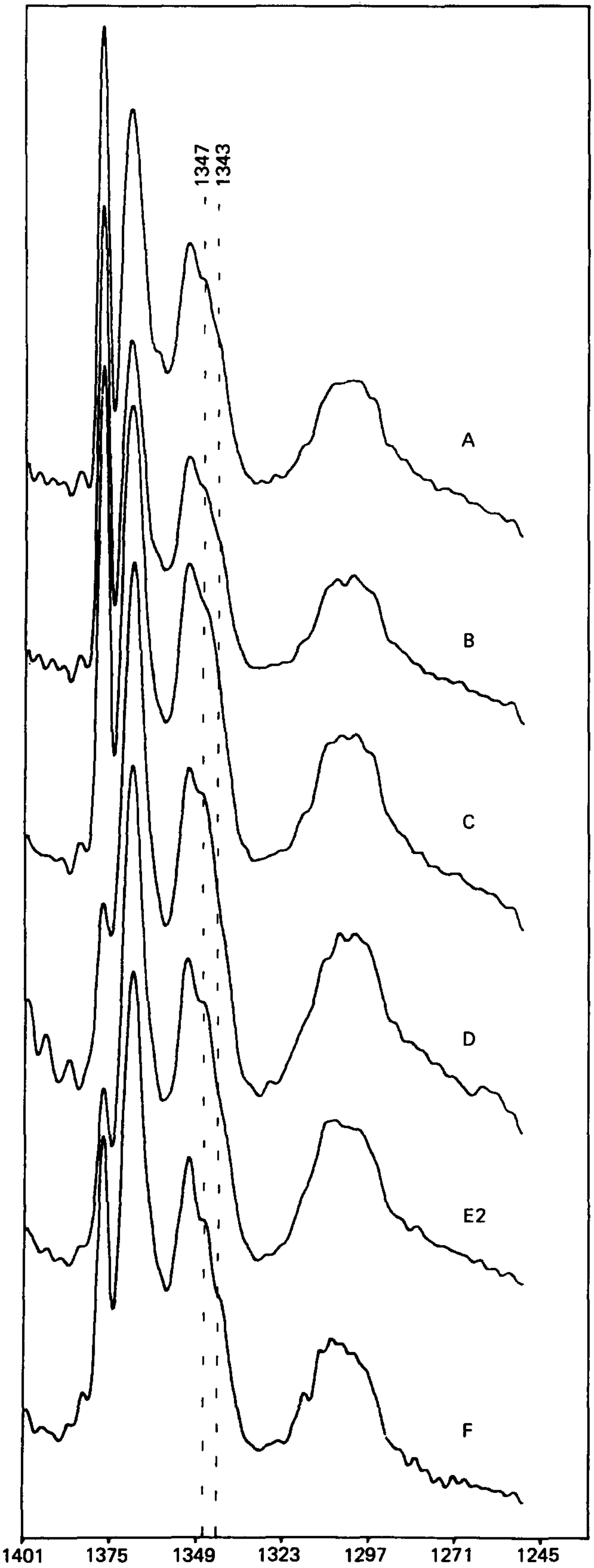

Figure 3 Spectra from *Figure 2* after Fourier self-deconvolution. See text for parameters

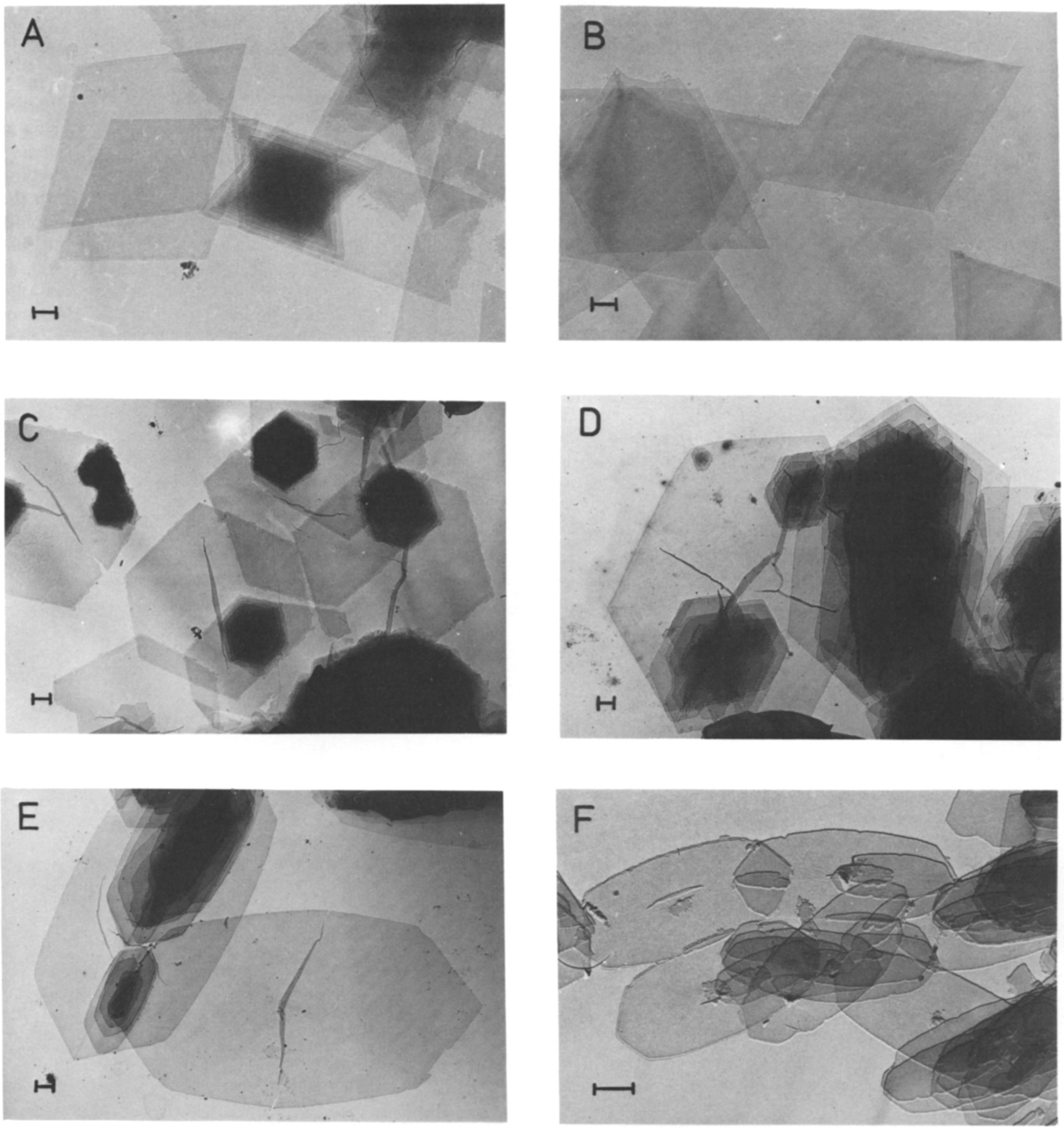

Figure 4 Electron micrographs of samples A, B, C, D, E (the suspension used for E1 and E2) and F. The markers represent 1 micron

Table 1 Characterization of solution-grown crystals

Sample	Long spacing (nm)[a]	A/B[b]	$\frac{x}{y}10^{2}$[b]	% in {100} faces
A	11.9	0.7	–	0
B	12.2	0.7	–	0
C	13.0	1.2	1.6	31
D	12.8	1.5	–	35
E	15.8	2.0	6.9	45
F	17.7	2.3	7.2	55

[a] Measured using Raman LA mode
[b] Measured from electron micrographs

Table 2 G.p.c. values for molecular weights of samples

Sample	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting material: Rigidex 50 Nascent	48 900	6.7
Crystals obtained directly from xylene at 70°C	36 000	4.8
Crystals obtained from xylene at 75°C (B) after precrystallization	5 200	1.5
Crystals from xylene at 80°C (C) after precrystallization	7 000	2.0

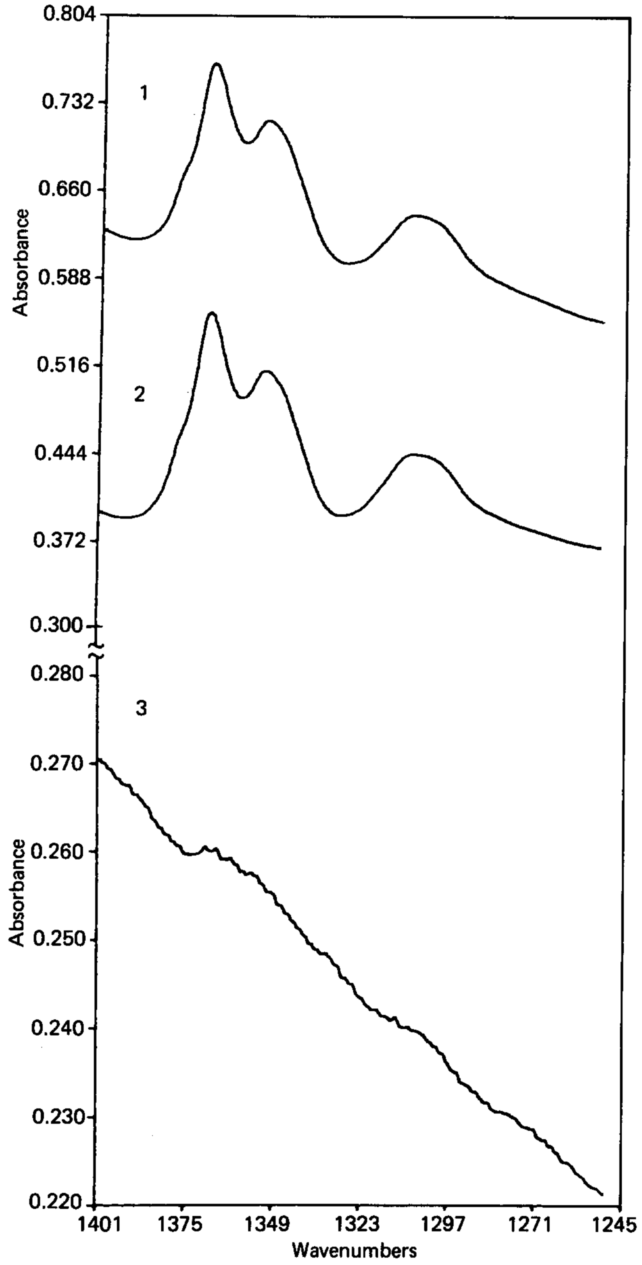

Figure 5 (1) Infra-red data for sample E1. (2) Infra-red for E2. (3) E2–E1. Note that 1 and 2 are plotted on the same scale of absorbance

amount to less than 2% of the original band intensities, and are considered to be insignificant in relation to the improvement in quality of spectra obtained after pressing.

Subtraction of sample A from a sample crystallized from xylene at the same temperature (70°C) but without prior extraction by crystallization (G) gives the difference spectrum in *Figure 6*. The latter method of crystallization results in irregular 'fir-tree' crystals (*Figure 7*) and the infra-red result shows that all forms of defects are more numerous here. The negative band from the methyl group vibration at 1377 cm^{-1} is due to the differences in molecular weight described earlier. It is evident, then, that a more disorganized crystal morphology is associated with a higher concentration of defects, either within the crystals themselves or in the fold region.

The results of subtractions of spectra from samples with different crystallization temperatures are shown in *Figure 8*. The spectrum subtracted in each case is that for crystallization from xylene at 70°C after pre-crystallization (sample A). In each of the difference spectra there is an intense negative peak at about 1377 cm^{-1}, arising from the lower molecular weight of the sample crystallized at 70°C. The other general feature is a broad negative band centred around 1295 cm^{-1}. When there is a large difference in crystallization temperatures there is also a negative peak, appearing at 1350 and 1346 cm^{-1} in two of the spectra. The 1295 cm^{-1} band can be assigned to the *gtg* and *gtg'* CH_2 wagging mode, despite the frequency shift as compared with the original spectra (1307 cm^{-1}); it is clear from studies of its temperature dependence that this band includes at least two different components. The negative peak at 1346 cm^{-1} in spectrum 3 is probably not wholly associated with the main *gg* band, but partly with one of the shoulders revealed in the original spectra after deconvolution (*Figure 3*). The width is comparable with that of the original 1351 cm^{-1} peak, so it is likely that more than one component is present. Spectrum 2 indeed shows signs of at least two components, although this and spectrum 1 are both complicated by other features.

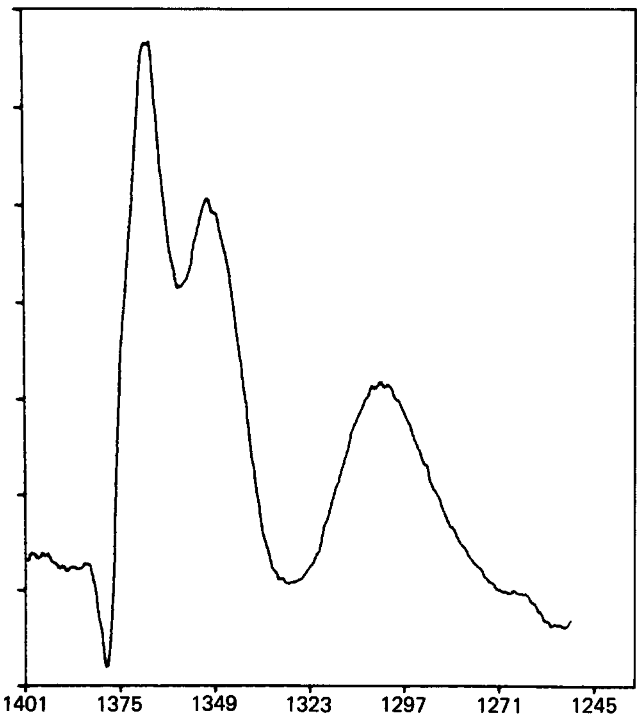

Figure 6 Infra-red difference spectrum G–A

Figure 7 Electron micrograph of sample G

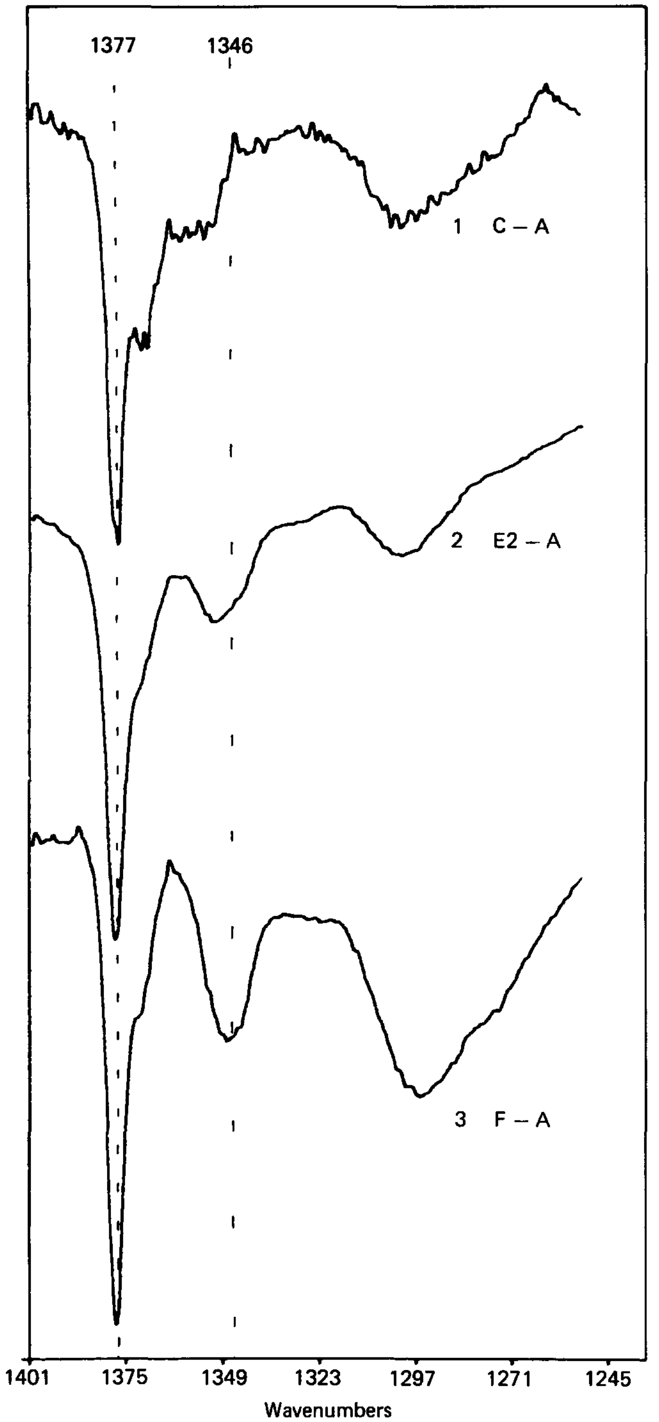

Figure 8 Infra-red difference spectra: (1) C–A, (2) E2–A, (3) F–A

The difference spectra described above indicate that the defect mode region of the infra-red spectrum is sensitive to variation in crystal habit achieved by changing the crystallization temperature. The differences still await a detailed analysis. As a future prospect the model system of a long-chain alkane, obtainable in either the fully extended or once-folded conformation[27] should provide useful information on the specific type of fold. Preliminary results indicate a reduction in the peak intensities of all 'defect modes' in the extended, as compared with the once folded form. The intensities here are normalized with respect to the CH_3 wagging vibration at 1368 cm^{-1}. The limited analysis made so far indicates that, unlike the cyclic alkanes, the fold in this case is not uniquely related to a single i.r. band.

Annealing single crystals

The effect of heat annealing on the defect mode infra-red spectrum of polyethylene single crystals has already been reported[18]. However, the original crystals in reference 18 were obtained simply by cooling solutions of unfractionated polymer. It is therefore important to confirm the observed behaviour of the difference band at 1346 cm^{-1}—namely a decrease in the absorption of this band on annealing and subsequent cooling—for crystals with a well-defined morphology. This is especially important in view of the differences noted in the previous section between samples A and G, both of which were crystallized from xylene at 70°C.

A mat crystallized from dilute xylene solution at 70°C (sample A) was held in a heating cell between KBr plates. The spectrum was obtained at room temperature before heating to 122°C for 1 h and again running the spectrum. The cell was allowed to cool to 28°C and the spectrum recorded. The results are shown in *Figure 9*. On heating to 122°C, there is a general increase in band intensities, as is expected for thermal population of defects. On cooling to room temperature, it is clear that most of the changes are reversible, although the bottom curve in *Figure 9* shows that on subtracting the original spectrum from the final one, we obtain both positive and negative difference bands. The negative peak at 1345 cm^{-1} represents a decrease in the intensity of the shoulder observed in *Figure 1* on annealing. This feature is in agreement with

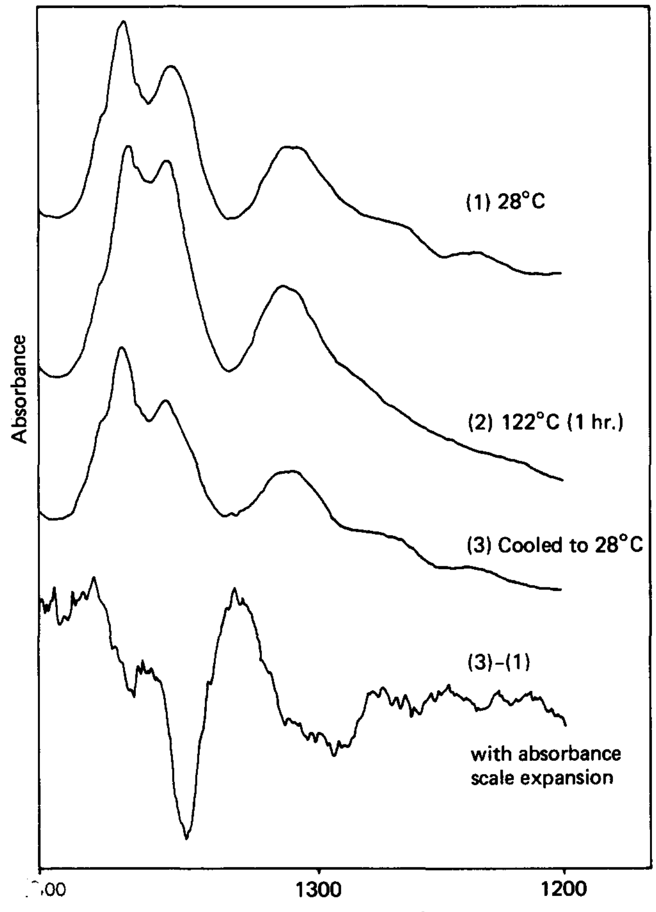

Figure 9 Infra-red spectra: (1) before, (2) during and (3) after annealing treatment of a single crystal mat of type A. (1), (2) and (3) have the same absorbance scale, but the subtraction (bottom) has an expanded absorbance scale

the earlier observations of Painter *et al.*[18] Other changes in the region 1270–1330 cm^{-1} are probably associated with the 1307 cm^{-1} band in the original crystals.

On melting and quenching a similar single crystal, sample (A), a difference spectrum of the original spectrum subtracted from the final spectrum also showed a strong negative band at 1345 cm^{-1}, again in agreement with earlier results[18].

These results are consistent with the conclusions of Painter *et al.*[18], that a peak at 1346 cm^{-1} is associated with regular tight folding in polyethylene. Our chain conformation model for single crystals grown from xylene solution at 70°C incorporates a large proportion (75%) of neighbouring lattice sites occupied by stems from the same molecule[19,20]. We infer that there is a correspondingly high proportion of adjacent re-entry. Current proposals for the molecular mechanisms involved in annealing[28] envisage a decrease in the number of folds with adjacent re-entry accompanying the increase in long period. Furthermore, the chain conformation proposed for melt quenched polyethylene on the basis of neutron scattering results[29] involves very small groups of neighbouring stems connected to other groups at considerably larger separations. The proportion of adjacent re-entry is therefore expected to be small in this case. The behaviour of the 1346 cm^{-1} infra-red band shown in this section is thus fully consistent with its association with regular adjacent folding.

CONCLUSIONS

Polyethylene single crystal mats with well defined and systematically varied morphologies have been studied in the CH_2 wagging ('defect mode') region of the infra-red spectrum. After Fourier self-convolution, peaks in a region (1342–1348 cm^{-1}) previously associated with regular chain folding were observed directly for the first time in crystals obtained at various crystallization temperatures. Also, the behaviour of the 1346 cm^{-1} band on both annealing and quenching from the melt is consistent with its origin in regular and probably adjacent folding. Differences in the infra-red spectrum with crystallization temperatures are demonstrated. Nevertheless, there was no unique correlation between the bands and the crystal habit and associated sector ratios (encompassing a wide range in our preparation with axial ratios between 0.7 and 2.3 and with up to 55% of polymer chains in {110} sectors). The *ggtgg* defect has been associated with a band at 1342 cm^{-1} in $C_{34}H_{68}$[14,16], and similar conformations are possible as {200} folds in polyethylene crystals. However, it should be noted that some of the crystals considered here have only {110} sectors, with compelling evidence for primarily {110} folds. From this it appears that: (a) at least at the present stage, peaks in the 1342–1348 cm^{-1} region cannot be uniquely associated with one particular type of fold and (b) alternatively, geometries distorted from the ideal *ggtgg* defect may exist. A full analysis is awaited on the basis of model long chain alkanes.

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