A new far infra-red absorption band at 39 cm^{-1} in the spectrum of high-pressure crystallized polyethylene

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High-pressure annealed samples of polyethylene (PE), currently thought to contain the extended chain form, show a new band at 39 cm^{-1} in the absorption spectrum when the sample temperature falls below 170K. This band shows a strong temperature dependence of intensity but no shift in frequency as the temperature varies. Possible assignments of the band are discussed. The preferred interpretation, with some reservations, is that it arises from a mode analogous to the forbidden A_u mode of orthorhombic PE but which is now active in the monoclinic form produced by the annealing.

INTRODUCTION

When polyethylene (PE) is annealed for a long time at a high temperature under high hydrostatic pressure, and then allowed to cool slowly with the pressure maintained, material is produced which has enhanced density (0.99 g/cm^3) and enhanced crystallinity. The structure of this material is not known for certain, but it has been shown that in it the long period has increased from about 200 Å up to about 1000 Å. Low-frequency vibrational studies[1-13] have yielded much information about conventional forms of PE in the past and in particular have established that the two allowed lattice modes of the orthorhombic unit cell, the B_{1u}, 73 cm^{-1} at 300 K, and the B_{2u} mode, 108 cm^{-1} at 120 K, shift to higher frequencies and intensify as the temperature falls. Calculations of the frequencies of the lattice modes of PE[2,3] have given good agreement with these values and with this behaviour and they also indicate that the forbidden A_u mode should lie below the other two near 57 cm^{-1}. It is therefore interesting to extend the far infra-red study of PE to this new form especially since the calculations are more appropriate to an extended chain than to a folded chain crystal.

EXPERIMENTAL

The samples of high density PE used were Lupolen 6011 L and Rigidex 50. These were subjected to high temperature (498–503 K) annealing under a pressure of about 5 kbar for times between 5 and 45 hours. At this pressure the melting point is 515 K. Two different experimental rigs were used, one at Ulm and the other at NPL, so one might hope to detect any dependence of the spectrum on details of the preparative procedure. However, in the event, all the spectra of all the specimens were virtually identical. The samples after annealing and slow cooling were studied using Beckmann–RICC and NPL–Grubb–Parsons far infra-red interferometers. The spectral resolution used, of between 2 and 2.5 cm^{-1}, was adequate to delineate fully all the discrete features since these had half-widths of at least this order even at liquid nitrogen temperature. The temperature range investigated was from room temperature down to 12 K. The instrumentation would be capable of determining the centre frequency of a sharp resonance to ±0.2 cm^{-1} under the chosen conditions but the polymeric bands are not very sharp and, moreover, there is the noise to be considered. We found it difficult therefore to determine the centre frequency of the 39 cm^{-1} feature in the spectra of these particular specimens to much better than about ±0.5 cm^{-1}.

RESULTS

The room temperature spectra of the annealed material were similar to those of the feed stock except that the 73 cm^{-1} band appeared to be slightly more intense — this accords well with the enhanced crystallinity. On cooling down, the 108 cm^{-1} band appeared as expected but below 170 K a new very weak band at 39 cm^{-1} could be discerned. This band intensified and sharpened as the temperature fell further but no shift with temperature could be detected within the limits mentioned above. Spectra of the 40 cm^{-1} region for melt crystallized and high-pressure annealed PE at 100 K are shown in *Figure* 1 and the variation of the intensity of the 39 cm^{-1} band as a function of temperature is shown in *Figure* 2. At the lowest temperature reached (12.5 K), the 39 cm^{-1} band had a

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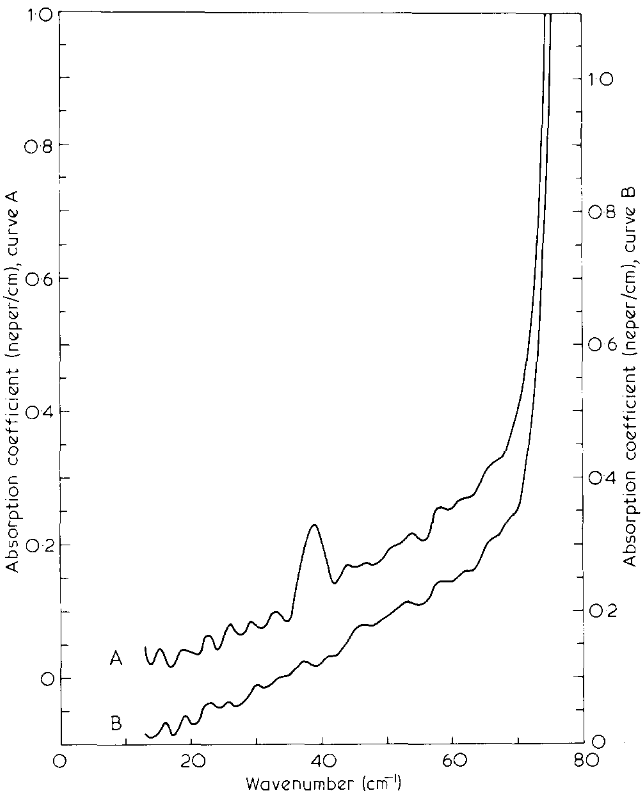

Figure 1 Far infra-red absorption spectra of high pressure crystallized material (A) and original HDPE (Rigidex) (B). The sample temperature was 120 K and the spectral resolution 2 cm^{-1}

peak height of 0.23 neper/cm, that is it is more than ten times weaker than the 73 cm^{-1} band whose peak height is in excess of 3 neper/cm.

DISCUSSION

There are several possible explanations of the appearance of this new band but we can at once discount interpretations in terms of an impurity introduced by the annealing process. This operation was carried out carefully in oxygen free conditions in the two laboratories so there should not be any impurities in the first place and in the second a sharp band such as we have observed demands the existence of long range order; in other words the presence of a crystalline form.

We can discount a phase transition, firstly because of the low temperature, and secondly because other means of measurement show no evidence for it. The 39 cm^{-1} band, at first sight, looks different from the crystal bands at 73 cm^{-1} and 108 cm^{-1} because of its lack of temperature shift, but it might not show a large shift if its transition moment lay along the c-axis since the coefficient of expansion of PE is small in this direction. In fact the coefficient of expansion in the c-direction is negative at room temperature (-13×10^{-6}), this arising from the thermal motion causing a disordering of the perfect planar zig-zag symmetry and hence a contraction along c. With cooling down to cryogenic temperatures this thermal disordering is progressively removed and the symmetry becomes more perfect. It is reasonable therefore to assume that the band is due to a crystalline form of polyethylene.

There are then three possible explanations. First, there is the possibility that the normally forbidden A_u mode in polyethylene is, in fact, observable for particular conditions of crystallinity/disorder and that these conditions are produced by the high pressure annealing process. One would not normally expect a forbidden mode of a crystal to be activated by a process that increases the crystal order, but it could be the case that the line-width of the A_u mode in polyethylene is so sensitive to disorder that, although one could not see it in a perfect crystal, the small amount of disorder present in the chain-extended material is sufficient to activate it but not sufficient to broaden it beyond observability. One would then go on to assume that the much increased disorder present in normal HDPE has so increased its line width that the band is no longer distinguishable. The sudden appearance of the band for temperatures below 170K might, within the framework of this interpretation, may be a consequence of the freezing out of the disordering γ process (sometimes thought to

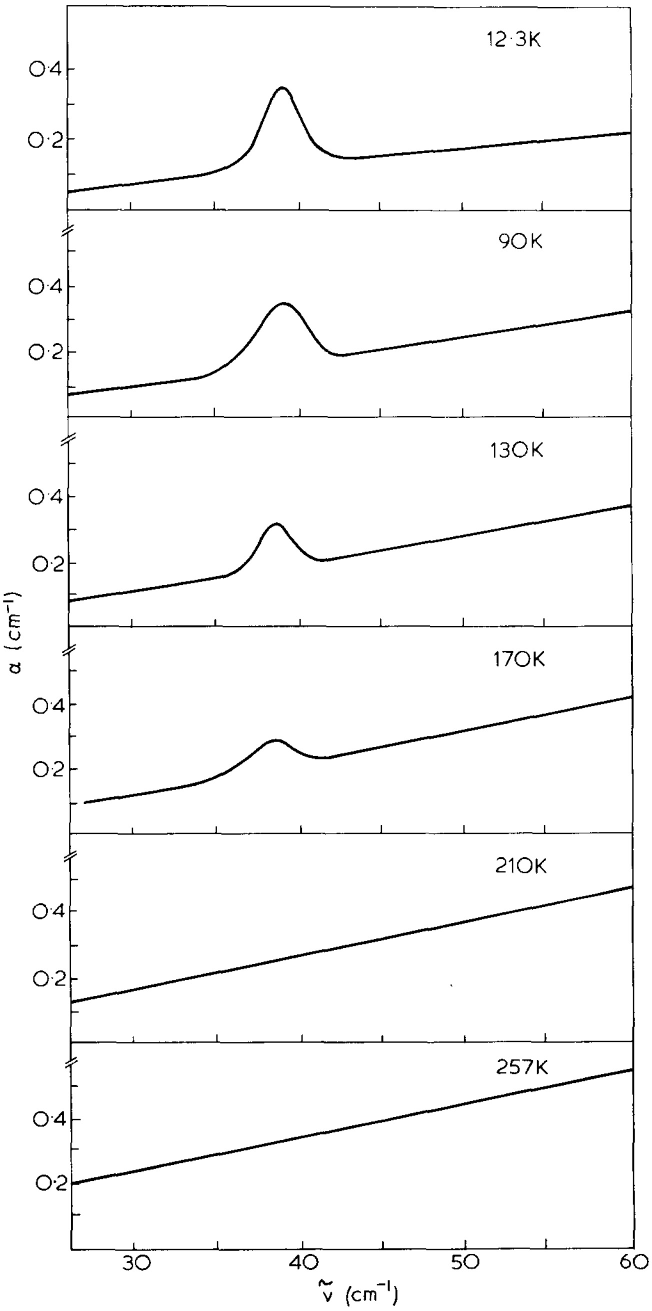

Figure 2 The low frequency band at 39 cm^{-1} for high pressure crystallized HDPE (6011 L) shown at various temperatures

involve a 'crankshaft' type of motion) which occurs at about 160K.

The other two possible explanations involve the appearance of a second crystalline structure. Evidence for this is found in the wide-angle X-ray scattering (WAXS) results which show additional lines that could be interpreted as arising from a monoclinic modification present in low concentration. Details of this will be published elsewhere by some of us. The band could then be either the equivalent of the B_{1u} mode shifted in frequency by the change of the setting angle, or the equivalent of the A_u mode made active by the lowering of symmetry of the crystal from the orthorhombic to monoclinic form. Frank *et al.*[14] have shown that the frequency of the B_{1u} mode is very sensitive to setting angle (i.e. the angle of rotation of one chain with respect to its neighbour) and have furthermore shown that the range of frequency corresponding to physically possible angles could go as low as 39 cm^{-1}. But because a B_{1u} mode arises from a transverse motion, it follows that there should be a dependence of the band frequency on the temperature, so it is difficult to reconcile this explanation with the fact that we find no temperature dependence.

The final explanation involves the analogue of the A_u mode for this new crystalline form. A monoclinic modification has a reduced symmetry of the unit cell, and in this new symmetry the equivalent mode may no longer be infra-red inactive. As this mode is longitudinal, one has a ready explanation of the lack of temperature dependence and its arising in a different crystalline modification would explain why the band is only found when the additional WAXS lines are also observed in the high pressure crystalline material. This last explanation seems to us to be the most probable in that it covers most of our current experimental facts, but there can be only a small amount of the monoclinic form present and it follows that the new band would have to have an uncomfortably high absolute intensity if this explanation is to be correct.

All the explanations have some obvious drawbacks and we therefore feel that more experimental work and a fuller characterization of these materials is needed before a final conclusion can be reached.

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