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random dilution. The general conclusions that lateral displacements of stems are minimized tend to support the view that for the type of annealing studied here the rearrangement is a solid-state one, involving no melting even on a local scale. In the following paper it is shown that the infrared data, at least for higher guest molecular weights, favor the shrinkage of groups from their ends, and the models are discussed further.[13]

Acknowledgment. We are very grateful to Professor Andrew Keller for his sustained interest and encouragement throughout this work and to the staff of the Institut Laue Langevin (Grenoble) and AERE (Harwell, in particular Vic Rainey) for assistance with neutron scattering measurements. We also thank the staff of the SRS (Daresbury) for assistance with X-ray diffraction measurements and SERC for financial support for S.J.S.

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Mixed-Crystal Infrared Spectroscopy of Annealed Solution-Grown Crystals of Polyethylene[†]

Stephen J. Spells*

Department of Applied Physics, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, England

David M. Sadler

H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, England. *Received November 15, 1988; Revised Manuscript Received March 21, 1989*

ABSTRACT: The CD_2 bending vibration is analyzed in annealed solution-grown polyethylene crystals in terms of conformational changes. The results are compared with calculations from a range of models which involve "annealing zones" of various dimensions. The same model as was favored by neutron scattering measurements was found to give an adequate fit to IR data for moderate molecular weights ($\leq$100 000). However, for higher molecular weights the IR band shapes show a better agreement with a model where the stems are preferentially removed from the ends of groups of adjacent stems. This discrepancy is discussed in light of possible refinements to the models. Analogous IR measurements on deuterated matrix samples show smaller reductions in CH_2 bending splittings on annealing, consistent with the suggested heterogeneity.[1]

Introduction

Wide-angle neutron scattering (WANS) measurements and Fourier transform infrared spectroscopy (FTIR) have recently been used in conjunction to obtain a detailed model of the chain conformation in solution-grown polyethylene (PE) crystals.[2-4] In combination with independent evidence, the possible ambiguity in describing the conformation was minimized. The same experimental techniques can now be applied to annealed single crystals, using our previous model for unannealed crystals as the starting point. Recent improvements in the method of calculating FTIR spectra on the basis of molecular models[5] can also be applied in this study of annealing.

Studies of the annealing behavior of PE single crystals are reviewed in more detail in the preceding paper.[1] The annealing falls into at least three distinct regimes. At the lowest temperatures (T_a), the number of crystal dislocations increases without any simultaneous increase in la-

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[†] The work described in this paper represents a combined study undertaken over several years. David Sadler pursued the analysis of the neutron scattering results in 1987 and early 1988 and prepared an initial manuscript on which the present neutron scattering paper is largely based. I subsequently continued to analyze the infrared data and to make comparisons with molecular model calculations. Sadly, David's tragic death in 1988 prevented him from seeing how these fit his own conclusions. Consequently, the comparison of results from the two techniques and the conclusions drawn are the work of Stephen Spells.

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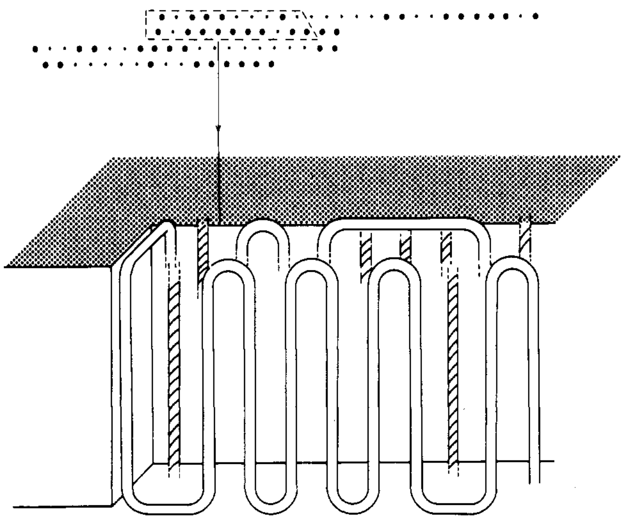

Figure 1. Schematic three-dimensional sketch of the conformation in solution-grown crystals prior to annealing.[2] At the top is shown the structure as projected on to the {001} plane, with the larger dots representing stems from one molecule.

mellar thickness.[6] At higher values of T_a, the lamellar thickness increases, in general irreversibly, but without large-scale molecular motion. This is the regime of principal interest here. A third region, for annealing at higher T_a, shows partial melting from the evidence of X-ray diffraction.[7] The changes in lamellar thickness may typically be from about 105 Å for crystals as grown from xylene at 70 °C to 300 Å for crystals after annealing at 124 °C. The main questions addressed here and in ref 1 (using neutron scattering) is the degree to which annealing in the second regime corresponds to a solid-state transformation and to what extent partial melting can be excluded. Clearly, the investigation of conformation by the use of "labeling" techniques (neutron scattering and IR) can play a crucial part.

It should be emphasized that this work is concerned with annealing conditions of $T_a \leqslant 123$ °C and a heating rate of 10 deg min^{-1} and that conformational changes occurring under other annealing conditions may differ significantly.

Initial Conformation. The starting point for any molecular rearrangement is taken as our model for the chain conformation in crystals grown from xylene solution at 70 °C. The full details of this model appear in the preceding paper,[1] and only the major points will be restated here. The model incorporates sheets of crystal stems, with the fold plane diluted with 50% of stems arising from other molecule(s). The probability of chain reentry at the adjacent lattice site is $p = 0.75$. This defines the probability distribution for finding a sequence of n adjacent stems. The molecule superfolds into a neighboring fold plane. The resulting multiple-sheet arrangement has an average molecular weight (M_w) per sheet of 21 000. The only modification necessary to the model on changing the labeled molecular weight is to change the number of sheets. The most important feature of this model with regard to the stem rearrangement on annealing is the size of groups of neighboring labeled stems. If, in contrast to this model, we had chosen a model with uninterrupted adjacent reentry, then there would be few topological constrants on the conformations accessible to a labeled chain. (This leaves aside any consideration of energetic constraints.) However, Figure 1 shows that the groups of adjacent stems in our model are generally small (the average number would be four stems for an infinite sheet). It is convenient to define for any annealing model a distance scale L_a over which chain rearrangement occurs (see also ref 1). At one extreme, melting the polymer corresponds to a rearrangement scale equal to the molecular length. Conversely, at low annealing temperature L_a may only be of the order of the stem diameter. In the latter case, the process is effectively a solid-state transformation.

It should be noted here that both neutron scattering and infrared techniques, as previously applied to solution-grown crystals,[2-5] are primarily sensitive to the arrangement of labeled crystal stems within the lattice and provide no simple direct information on the nature of the folds. However, the sheetlike conformation obtained for single crystals suggests that the labeled stems are connected by folds in the plane of the sheet (i.e., {110} folds), and the simplest arrangement would incorporate the maximum number of adjacent folds, consistent with this stem arrangement. On the other hand, this does not preclude an arrangement involving "leap-frogging" of folds connecting nonadjacent sites.[6] Clearly, the topological constraints to refolding involved in the two cases would be quite different, and this is an argument against the formulation of a very detailed molecular model of annealing without direct information on the distribution of folds present.

As in ref 1, the problem will be approached by first considering the simplest way of reducing the number of stems, namely, by removing stems from each molecule in a random manner. It has already been noted[1] that this scheme, though computationally simple, may not necessarily involve a simple molecular rearrangement, in view of the chain topology. However, at this stage it is considered to be more important to establish the general level of mobility involved during annealing rather than to define the precise path taken by the rearranging molecule.

Mixed-Crystal Spectroscopy. The combined use of neutron scattering and infrared spectroscopy on mixed polyethylene crystals provides a very sensitve means of determining the chain conformation, as has previously been noted.[2,3] There is very little ambiguity in the possible chain conformations if data from both techniques fit model calculations. To a large extent the two methods are complementary: neutron scattering is dependent on chain correlations over a wide range of distances, whereas the infrared technique is predominantly dependent on nearest-neighbor interactions.[9] (Nevertheless, these interactions may extend over a much larger distance, depending on the statistical arrangement of labeled stems.)

The details of the technique have been described elsewhere[3-5] and only a brief outline will be given here. Various arrangements of labeled crystal stems within a predominantly unlabeled crystal lattice can give rise to splittings in infrared vibrations of the labeled species. These splittings result from labeled stems that are adjacent to one another in a {110} directon. In general, the splittings increase with the size of a group of such adjacent labeled stems, but they also depend on the detailed arrangement of stems. On an orthorhombic lattice, there are four possible sites for nearest neighbors in {110} directions. If all these sites around a labeled stem are also occupied by labeled stems, the doublet splitting will be maximized.

The methods used here are equally applicable to a deuterated polyethylene (PED) matrix or a normal polyethylene (PEH) matrix.[5] The CX_2 bending vibration (PEX = guest species) has been found to be the most suitable for this work. The first calculations of doublet splittings for finite groups of labeled stems involved the coupled oscillator model, with the repeating unit as the two nonequivalent stems in the unit cell (i.e., a pair of oscillators).[10] Multiple-sheet structures were considered in this way, but the analysis was restricted to what we have termed "closed groups"[3]—i.e., groups with equal numbers of labeled stems in each sheet, all sheets starting in a single crystallographic plane and with no dilution of these planes by other molecule(s). It became apparent from our experiments that this picture of regular blocks of labeled stems was inadequate in dealing with real physical situations. Realistic models, incorporating statistical arrangements of labeled crystal stems, would result in less regular groups, with unequal numbers of stems within sheets and dilution of labeled stems with host molecule(s).

We have previously extended the use of the coupled oscillator model to handle any statistical arrangement of stems.[3,5] In the case of annealed polyethylene single crystals, the calculation of the CX_2 (PEX = guest species) bending vibration line shape follows along similar lines to our earlier work.[3,5] First, the statistical model for the chain conformation in as-grown polyethylene single crystals is used to generate a set of molecular conformations (such as that shown in Figure 1). These arrangements of labeled stems are then divided into groups of stems in which there are {110} nearest-neighbor interactions between all the labeled stems. A group transformation is then performed to obtain a simpler arrangement of stems for each group, but retaining the number of stems and distribution of nearest-neighbor interactions. The transformed group has been termed an "equivalent group".[3] The splitting of equivalent groups is then calculated by using an interpolation based on calculated splittings for closed groups. The whole set of computer-generated molecular conformations is analyzed in this way and the doublet components are summed, using empirical relationships established between the frequencies of both doublet components and the doublet splittings.[5] The doublet absorbances are weighted by the number of stems contributing to them. This approximation has previously been justified.[5]

As in previous work, a singlet component is included in the calculation. This includes contributions from labeled crystal stems that are isolated with regard to nearest-neighbor labeled stems in the {110} directions and from noncrystalline chain segments. Representative crystallinities for PEH and PED matrix samples were taken as 0.8 and 0.75, respectively, on the basis of DSC measurements. These values were used to calculate the singlet contribution from amorphous material. Finally, the calculated spectra were broadened by using a Lorentzian of half-width 0.5 cm^{-1}.

Models for Annealing

In ref 1, particular attention was paid to annealing conditions resulting in a lamellar thickness (l) with twice its original value (l_0). This is convenient for model calculations and, as outlined in ref 1 and discussed here, there is some experimental evidence for a preferred doubling of thickness. All calculations in the present work therefore refer to the situation where $l_0/l = 0.5$.

1. **Random Stem Removal.** Removal of half the crystal stems at random from each molecule in the original conformation has the effect of reducing the size of the groups of labeled stems that are responsible for IR doublet splittings. The singlet and smaller doublet components of the CX_2 bending vibration are therefore expected to increase in intensity relative to the larger doublet components. It should be noted that, unlike models discussed later, this scheme preserves the feature of superfolded sheets. Figure 2 shows the results of this calculation. The largest splittings present in the spectra are considerably reduced by the stem removal, and the variation in spectra with number of sheets (proportional to molecular weight) has become negligible for greater than seven sheets. It will be recalled that the groups of labeled stems responsible for the IR splittings may extend over several of these superfolded sheets. The asymptotic behavior of the calculated spectra in Figure 2 for $l_0/l = 0.5$ therefore indicates that the smaller groups present after random stem removal do not, in general, extend over anything approaching seven sheets.

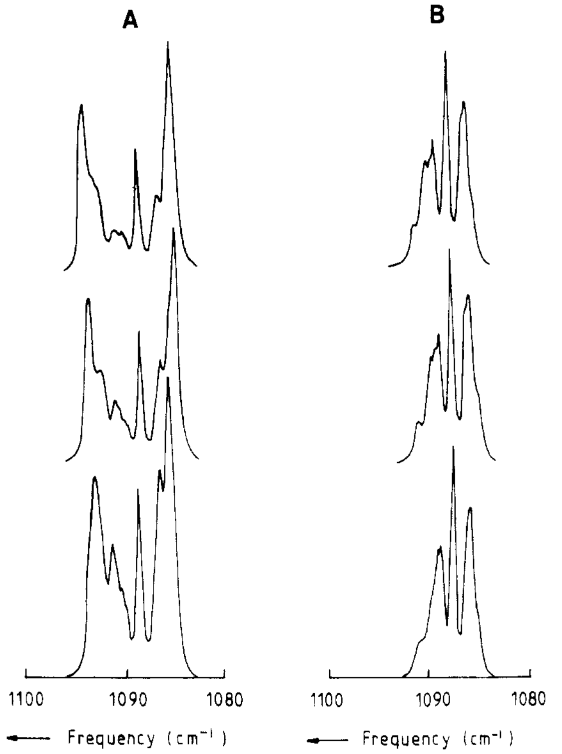

Figure 2. (A) Calculated infrared CD_2 bending band shapes for as-crystallized single crystals. The model as represented by Figure 1 was used to calculate the variation with molecular weight: 3 sheets (bottom), 7 sheets (middle), and 11 sheets (top) (one sheet corresponds to a molecular weight of 21 000). (B) Calculated band shapes after using the random dilution model (1 in text) to show the effect of annealing to the extent of doubling the crystal thickness ($l/l_0 = 2$): 3 sheets (bottom), 7 sheets (middle), and 11 sheets (top). The comparative intensities of different curves have no relevance in this or any other figure. All experimental and calculated data here are represented in terms of absorbance.

2. **Stem Removal from Group Ends.** A more site-specific rearrangement of stems occurs here. We now make the distinction between groups of stems as discussed in the previous section and single-sheet groups. The former are the objects that determine the observed IR doublet splittings. If one particular labeled molecule occupies n sheets, then a group of stems, sharing {110} nearest-neighbor interactions may extend over a maximum of n sheets. By contrast, a single-sheet group (SSG) represents a sequence of labeled stems within a single sheet which is not interrupted by another molecule.

This model for annealing preserves the number of sheets in the as-crystallised conformation, but the rearrangement of stems within these sheets ensures that the SSGs remaining are as large as possible. (Note that the effect of this model on neutron scattering intensities was to destroy the sheetlike scattering of the original conformation. This followed from the large gaps between SSGs, even though the number of sheets was preserved.)[1] Stems are removed from each SSG until the original group is halved in size. For groups with an odd number of stems (M_0), the final SSG size is $M_0/2 \pm 0.5$, the two values having equal probabilities. An SSG of a single stem has a removal probability of 0.5.

This approach differs from that used in ref 1, where the

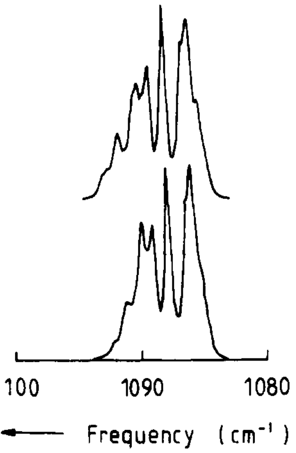

Figure 3. Calculated CD_2 bending band shapes after using model 2 (removal of stems from the ends of groups); $l/l_0 = 2$: 3 sheets (bottom), 11 sheets (top).

annealed conformation was obtained by using the same statistical model as for the original conformation but with a probability of adjacency among the remaining labeled stems of P_0^2, where P_0 is the probability of adjacency in the unannealed crystals. It does, however, lead to the same distribution of labeled stems.

Figure 3 shows the results of these calculations for two molecular weights. In comparison of the three-sheet result with the random dilution model (Figure 2), there are seen to be small differences, notably in that an additional component has appeared on the high-frequency side. Changes for the 11-sheet model are much more apparent, with the outermost splittings increasing significantly for the present model (Figure 3). Qualitatively, these differences between the two sets of calculations are expected since the group end removal model retains the maximum possible size of SSG after reorganization. This also favors large groups of interacting stems and hence large doublet splittings.

Models 1 and 2 above refer to situations where L_a is either smaller than or of similar magnitude to typical SSG sizes. We now consider models where L_a is larger.

3. Randomization within Sheets. Here L_a is taken to be greater than the average SSG size but considerably less than the overall molecular length. The molecule can be regarded as "pinned" on every sheet on either side of the rearrangement zone. Within the zone, a randomization of the labeled stem positions occurs, but stems are constrained to sites on the original sheets. The original number of sheets is therefore preserved on annealing, but the distributions along the sheets are randomized. Hence the labeled stems are not confined to some of the sites they previously occupied in the original conformation, unlike models 1 and 2. The model clearly implies a smaller proportion of adjacent reentry than those models.

The result of this calculation is shown in Figure 4 (bottom) for a three-sheet model. The singlet:doublet absorbance ratio is evidently greater than for models 1 and 2, and splittings are generally reduced.

4. Partial Melting. If the entire molecule is capable of rearrangement, then L_a exceeds the molecular end-to-end distance. A simple randomization of the conformation over the crystal lattice is, however, incompatible with the observed invariance of the radius of gyration within the lamellar plane, as observed in this range of annealing temperature.[11] The closest approach to randomization obtains if the molecule occupies a "puddle" of dimensions determined by the in-plane radius of gyration. With the stem placements at random within the puddle, probabilities for various groups of adjacent labeled stems may be calculated. For $l_0/l = 0.5$, the proportion of stems within groups of three stems or less is 0.98. The pattern of folds is quite similar to that proposed for melt crystallization of polyethylene.[12] Whatever the annealing process, it seems unlikely that the final stem arrangements would have less adjacency than this. The proportion of large groups is drastically reduced by comparison with the starting conformation.

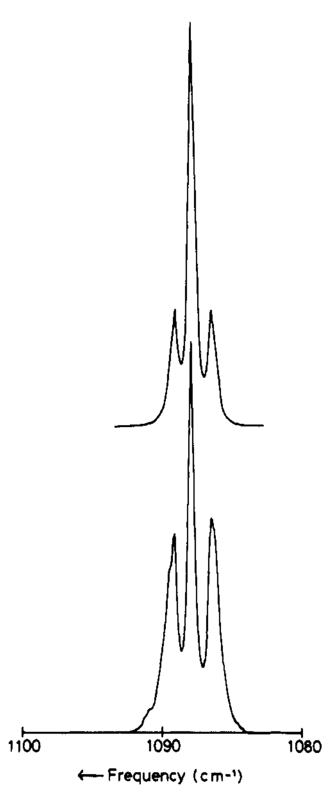

Figure 4. Calculated CD_2 bending band shapes after using models 3 (bottom, randomization within sheets) and 4 (top, partial melting). In each case $l/l_0 = 2$ and three-sheet models were used.

Taking the particular case of a three-sheet starting model, with 20 labeled stems in each sheet, the proportion of labeled stems in the final cylindrical volume is 0.072. The statistical proportions of various groups of adjacent stems can then be calculated. Truncating the calculation at a maximum of four stems in a group leaves about 0.6% of stems unaccounted, an error that was taken to be acceptable. The resulting spectrum is shown in Figure 4 (top). As must be expected with such a low concentration of labeled stems, most stems are either isolated (giving rise to a singlet) or in adjacent pairs (producing the predominant doublet, with its very small splitting). The band shape is clearly characteristic of a highly disordered conformation.

This model corresponds to partial melting, as it is generally understood. On the other hand, models similar to 1 and 2 are effectively solid-state reorganizations. These are discussed later, but first the significance of the concept of an annealing zone will be considered.

Annealing Zones. Annealing is clearly a cooperative process, involving stacks of complete crystals. To visualize conformational changes, it is necessary to visualize changes within the crystals. Although completely molten zones probably do not occur in the second regime, it nevertheless seems necessary to postulate "annealing zones" that are more mobile than the crystals either before or after annealing and that sweep through two or more lamellae. From this point of view, Peterlin[13] has considered the processes of initiating (nucleating) the thickened crystal and transporting the material once a thickened portion is formed and starts to grow through the sample. From the dependence of thickening rate on time and temperature, he concluded that motion was due to complete stems rather than a series of consecutive movements of defects along the stems.

This is consistent with the movement of annealing zones, where drastic changes occur, rather than a uniform thickening of the whole crystal. Such annealing zones are also more plausible in the light of the topological constraints on molecules during thickening. Sooner or later, a lengthening stem must displace material at its end, and it is very difficult to envisage a mechanism without making substantial changes to a large number of stems near the lengthening one.

The question now arises of whether, as one extreme, the thickness changes to its final value as a result of just one passage of the annealing zone through each crystal or whether successive passes of the zone occur. The general case of annealing almost certainly includes multiple passes of the annealing zone. This is likely to be the case when samples are heated relatively slowly to T_a: annealing may initially occur at below T_a to l values that are in turn too small for stability when T_a is finally reached. However, for simplicity we will consider only the case of changing from l_0 to λl_0 as the result of one pass of the annealing zone, with the case $\lambda = 2$ particularly in mind.

Thickening by Integer Factors. On annealing nylon 66, there is a strong tendency for l/l_0 to be an integer[14] although $l_0 < l < 2l_0$ can be observed.[15] A model for the pulling out of folds was suggested on this basis.[15] The change from four stems (with three connecting folds) to two longer stems (with one fold) clearly minimizes the conformational changes that have to occur when a folded ribbon undergoes thickening. This factor must be sufficiently important in the case of nylon 66 for integer ratios l/l_0 to be preferred.

There are some indications that this may also, at least to some degree, be true for polyethylene. The small-angle X-ray diffraction maxima are very broad after annealing, and a wide distribution of stem lengths is also suggested by Raman spectroscopy.[17] Analysis of crystal diffraction peak profiles suggests that the distribution of crystal thicknesses includes integer multiples of the original value.[18] The ratio R_z/l, where R_z is the radius of gyration of labeled molecules in the direction of the lamellar normals, is consistent with molecules being confined to individual lamellae only when $l = l_0$ and $l \simeq 2l_0$.[11] For intermediate values, the ratio R_z/l is significantly larger, suggesting a mixed population. This may, for example, comprise thicknesses, l_0 and $2l_0$. (R_z and l measured by diffraction result in different averages.[11]) Finally, the limit of the second range of annealing happens to coincide with $l \gtrsim 2l_0$: perhaps partial melting is required for $l > 2l_0$, since pulling out of folds would not give a sufficiently large l for stability.

More Detailed Solid-State Rearrangements. As indicated above, the pulling out of folds is clearly a possible process for rows of adjacent stems with an integral multiple of four stems. To specify a conformation following annealing, we require an algorithm that accounts for the fate of other groups of stems. This could involve the interchange of stems between nearby groups along the fold plane. A model based on pushing folds into the crystal is also conceivable. At the present stage, we consider that such a detailed model presents too many alternatives for a reasoned choice to be made on the basis of the two experimental techniques that have been used here and in the preceding paper. For this reason, we limit our considerations to models 1–4, described above.

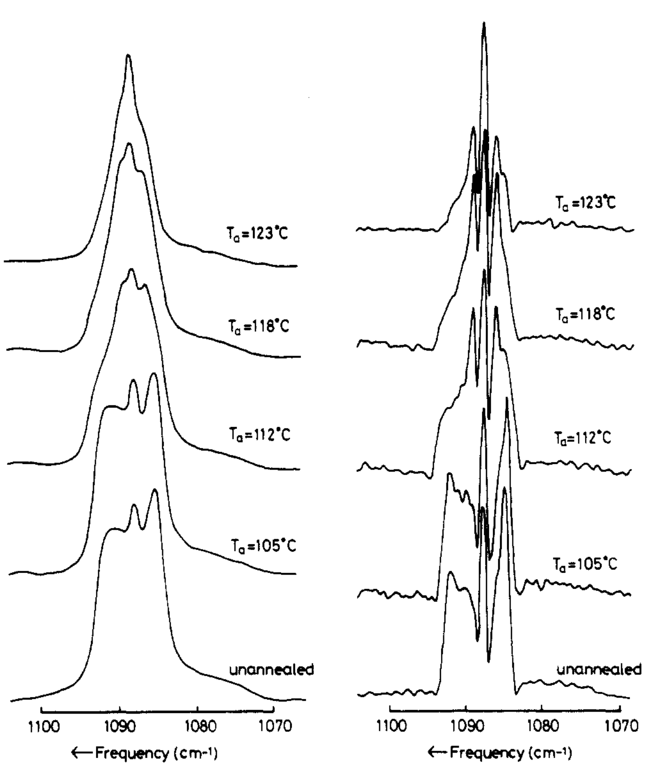

Figure 5. Infrared data for a hydrogenated matrix (HM) sample with molecular weight 54 000. Raw data (left) and Fourier self-deconvoluted data (right) are shown for various annealing temperatures. PED concentration = 3%.

Experimental Section

The preparation of mixed-crystal mats of PE from xylene solution has previously been described.[19] In all cases a crystallization temperature of 70 °C was used. Dried oriented mats were pressed below the crystallization temperature to minimize void scattering. Samples cut to the necessary dimensions were annealed on a Mettler hot stage with a heating rate of 10 °C/min. They were then cooled in air.

The molecular weights of PE starting materials, prepared by liquid–liquid fractionation, were determined by GPC. Long spacings were measured by Raman spectroscopy (LA mode) and small-angle X-ray diffraction. The lamellar orientation was monitored by using the small-angle X-ray facility at the Synchrotron Radiation Source (Daresbury), and the results are shown in ref 1 (Figure 2).

A Nicolet 7199 Fourier transform interferometer was used, together with a cooling cell using liquid nitrogen. A resolution of 1 cm^{-1} was used, with approximately 500 scans for each spectrum. The method of Fourier self-deconvolution, previously described,[4] was used to improve the spectral resolution of bending vibrations. Representative values of the deconvolution parameters 2σ and K[4] were 1.6 cm^{-1} and 2.5, respectively.

IR Spectra. Figure 5 (left) shows experimental data for a sample with PEH matrix for a variety of annealing temperatures. Deconvoluted spectra are shown in Figure 5 (right). The doublet with maximum absorbance changes from the outermost doublet (splitting 6.9 cm^{-1}) for the unannealed crystals to the innermost doublet (splitting 3.1 cm^{-1}) for an annealing temperature of T_a = 112 °C. The splitting of this innermost doublet remains insensitive to T_a for $T_a \geq 112$ °C. The absorbance of outer doublets clearly decreases with increasing T_a, and the singlet and innermost doublet components become predominant.

Figure 5 involves a maximum annealing temperature of 123 °C. An extension of the temperature range to 128 °C (Figure 6) produces a small increase in the largest doublet splittings. This result is consistent with the conclusion, from small-angle neutron scattering, that large-scale molecular motion leads to isotopic fractionation for $T_a \geq 125$ °C. This would give rise to larger groups

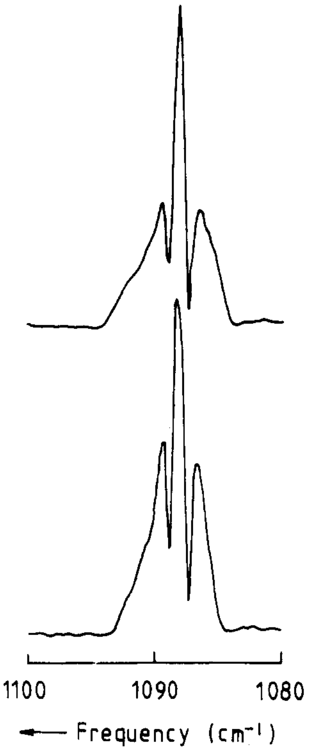

Figure 6. Deconvoluted IR data for an HM sample of molecular weight $\bar{M}_w$ = 90 300 after annealing at 125 °C (bottom) and 128 °C (top). PED concentration = 3%.

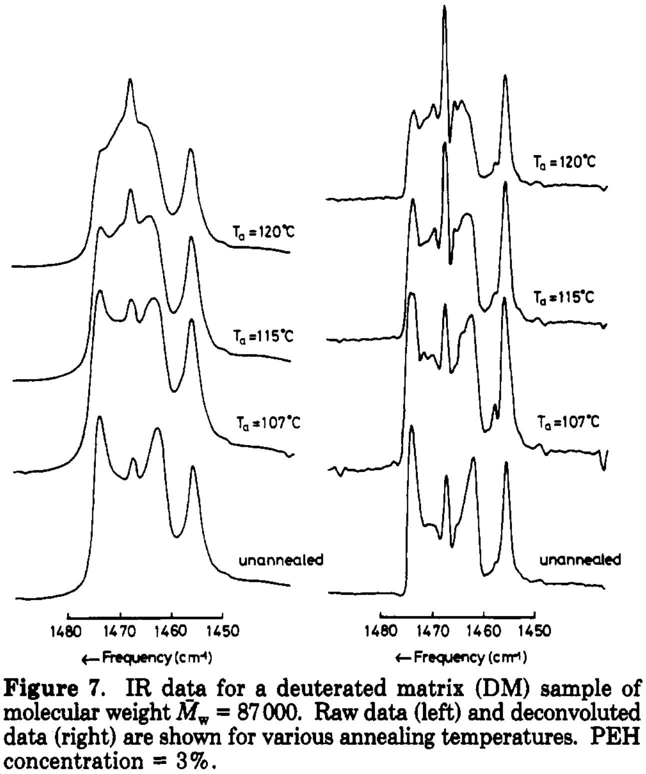

Figure 7. IR data for a deuterated matrix (DM) sample of molecular weight $\bar{M}_w$ = 87 000. Raw data (left) and deconvoluted data (right) are shown for various annealing temperatures. PEH concentration = 3%.

of adjacent labeled crystal stems and hence to larger doublet splittings. The increase in doublet splitting is, however, not expected to be large, as the large-scale mobility is unlikely to result in reformation of sheets of stems along the {110} direction. It is more likely that a puddle of labeled stems will be formed with, as was shown earlier, smaller splittings than for regular adjacent reentry within the {110} plane.

The general behavior seen in Figure 5 for PEH matrix samples is also shown by PED matrix samples (Figure 7). In the latter case, the decrease in absorbance of the outermost doublet appears to be slower, with the outermost and innermost doublets having similar absorbances at the highest annealing temperature used, 120 °C. This behavior is consistent with the conclusion from ref 1 that isotopic fractionation occurs in the PED matrix samples during annealing. For this reason, only the PEH matrix data are used for comparison with model calculations.

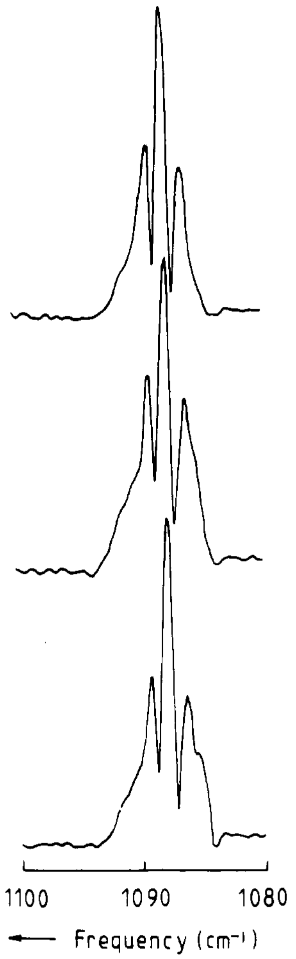

Figure 8. Deconvoluted IR data for HM samples of molecular weights $\bar{M}_w$ 64 000 (bottom), 54 000 (middle), and 54 000 (with different matrix) (top). PED concentration = 3%. All samples were annealed at 123 °C.

In Figure 8 are collected spectra for samples with molecular weights corresponding to approximately three sheets of stems (on the basis of a molecular weight of 21 000 per sheet). By comparison with Figure 4, the experimental splittings extend to larger values than those calculated. The model calculations of Figures 2 and 3 show, on the other hand, better agreement in terms of the larger splittings. In both three-sheet calculations in Figures 2 and 3 the singlet:doublet absorbance ratio is smaller than for experimental data, although this discrepancy was anticipated.[5] Overall, there is little to choose between models 1 and 2 in reproducing the experimental data of Figure 8.

Spectra for samples with molecular weights corresponding to 11 or more sheets are shown in Figure 9. It should be noted that for all models considered, both the IR CD_2 bending band shape and the neutron scattering data at intermediate angles are very close to their asymptotic limits, as functions of increasing molecular weight. The agreement between IR data (Figure 9) and calculations from models 3 and 4 (not shown) was again poor, indicating the necessity of retaining larger groups of stems. Calculations for models 1 and 2 (Figures 2 and 3) show better agreement, with model 2 reproducing the larger splittings to a greater degree.

It is clear from these comparisons that models 3 and 4 are generally inadequate in reproducing most features of the experimental spectra. A more localized rearrangement of crystal stems is clearly involved, and the results for the higher molecular weight samples (Figure 9) favor model 2, which retains the largest possible groups of adjacent stems, consistent with the change that occurs in l.

Figure 9. Deconvoluted IR data for HM samples of molecular weights $\bar{M}_w$ 386 000 (top), 200 000 (middle), and 234 000 (bottom). PED concentrations 3, 3, and 5%, respectively. All samples were annealed at 123 °C.

Correlation between Infrared Spectroscopy and Neutron Scattering. Both techniques have clearly shown that any process involving mobility of either the whole molecule or a substantial part of it, during annealing in what we have called the second annealing regime, can be dismissed. Over this temperature range, the molecular rearrangement is much more localized, with the dimension L_a of the "annealing zone" confined to no more than the size of a single-sheet group (namely, a few lattice spacings). There is, however, a difference in the molecular models that give the closest fits to data from the two experimental techniques: the neutron scattering data favors a model with stems removed at random from groups of adjacent stems whereas the infrared method, although giving data consistent with this model for moderate molecular weights ($\leqslant$100 000), points to a model involving the removal of stems from the ends of groups for higher molecular weights.

This apparent contradiction requires further comment: possible inadequacies in the models considered here will now be discussed. It should first, however, be noted that differences between the two favored models are relatively minor. Both involve a localized solid-state transformation rather than any melting in the true sense. The dimension L_a, as noted above, is of similar magnitude in the two cases. Indeed, this fact raises the possibility that both processes may occur together. The effective "averaging" of molecular conformations by the two techniques does not occur in the same way. This is evident from the IR spectra, where there is a clear separation between groups of differing size. Hence, we may expect the two techniques to stress different aspects of the molecular conformations.

The basic limitations of our models include neglecting the polydispersity of the guest molecules. To avoid an unnecessarily large number of variables, a single number of sheets has been used, rather than a distribution. Stems from a single molecule have also been strictly confined to these sheets, without any possibility of the occasional sequence (other than a superfolded ribbon) in another sheet. Effects such as these may become more significant when the groups are reduced in size during annealing, through the topological constraints involved. We have so far considered the dimension L_a of the rearrangement zone only in relation to distances along the {110} direction (e.g., sizes of SSGs). If we consider L_a with respect to other directions, there arises the possibility of stems being removed into neighboring sheets. The loss of sheetlike intermediate angular dependence of neutron scattering data may be accountable in this way, while the extent of SSGs along the fold plane after annealing may be maximized by something approaching the model of stem removal from the ends of groups. Such a scheme may provide consistency with the IR data presented here.

Combined neutron scattering and infrared spectroscopy of solution-grown polyethylene crystals have previously been shown to be consistent with a simple molecular model with a single variable.[1,2] Here we have attempted to obtain a simple molecular rearrangement consistent with both techniques, as applied to annealed crystals. The results from both methods indicate a very localized rearrangement. Possible refinements to the models have been indicated above. At this stage, in the absence of independent evidence (for example, of the distribution of fold types within the crystals), we consider it impracticable to extract further information from the data.

Acknowledgment. We are grateful to both Professor Andrew Keller for his enthusiastic encouragement throughout this work and to SERC for financial support for S.J.S.

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