

## Infrared Study of Lamellar Linking by Cilia in Polyethylene Single-Crystal Mats

M. I. BANK\* AND S. KRIMM

*Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48104*

The infrared spectra of single-crystal mats of physical mixtures of polyethylene and perdeuteropolyethylene show splittings of  $\text{CH}_2$  and  $\text{CD}_2$  bending and rocking modes which are smaller than those for the pure species. This is believed to be a result of the penetration of cilia from the surface of one crystal into the lattice of an adjacent crystal. Calculations of the concentration of cilia are in good agreement with percentages derived from the study of a mixed-crystal paraffin system, and these concentrations change with crystal thickness as is predicted. Such cilia can account for most of the amorphous component of polyethylene single crystals.

### INTRODUCTION

A large portion of the experimental evidence on solution-grown single crystals of polyethylene supports the view that in these thin lamellar crystals the molecular chains are folded with the chain axes essentially perpendicular to the surface of the crystal.<sup>1-4</sup> Infrared studies on mixed crystals of linear polyethylene and linear perdeuteropolyethylene<sup>5,6</sup> provide direct evidence at the molecular level for such folding and indicate that the folding is predominantly regular with adjacent reentry of the chain in the (110) crystallographic plane. This structure had been deduced previously but primarily from indirect methods such as electron microscopy.<sup>2</sup> In a solution-grown crystal, therefore, a molecule traverses the body of the crystal a number of times, depending on the length of the molecule, the (assumed relatively constant) thickness of the crystal, and the number of  $\text{CH}_2$  groups comprising the fold.

This picture of a polyethylene single crystal would appear to imply a density close to the crystallographic density of 1.00 g/cc.<sup>7</sup> However, observed densities<sup>8-11</sup> are usually found to be lower, in the range of 0.96-0.98 g/cc, and this has led to the suggestion that single crystals have an amorphous content of 15%-20%. Although the crystallographic density of 1.00 g/cc has been shown not to be unique,<sup>5,12</sup> the variations observed in unit cell dimensions can only account for a maximum

decrease in the above amorphous content of 2%-5%. The amorphous component has been attributed to an overlayer in the surface region of the crystal arising from nonadjacent reentry and "loose loop" folds.<sup>13,14</sup> However, such a large degree of irregular folding is discounted by our previous infrared studies.<sup>5,6</sup> Observed densities close to 1.00 g/cc have been reported,<sup>15</sup> but further investigations<sup>16,17</sup> indicate that the density is sensitive to many factors, such as sample preparation, crystallization temperature, molecular weight, and crystal conditions (suspended crystals or dried mats), and density therefore may not be a quantitatively reliable measure of amorphous content. Nevertheless, the existence of a density defect, as well as evidence from low-angle x-ray measurements,<sup>18</sup> would appear to substantiate the idea that there is some kind of a disordered component associated with the surface layer of single crystals.

One possible source of this disordered component which has been proposed is that it may arise in part from chain end segments which have been excluded from the body of the crystal.<sup>19</sup> By reacting single crystals with ozone it has been inferred that about 90% of the chain ends are excluded from the crystal.<sup>20</sup> These segments, of varying lengths, would form "cilia" on the surface of the crystal, presumably because they were not long enough (whatever that length may be) to fold over and be incorporated into the body of the crystal.

In the course of studying the infrared spectra of mixed mats composed of a physical mixture of single crystals of polyethylene and perdeuteropolyethylene, we have encountered direct evidence at the molecular level for such cilia. These spectral studies furthermore indicate that cilia from the surface of one crystal can

\* Present address: Polymer Research Section, NCR, Dayton, Ohio.

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TABLE I. Splittings of bending and rocking modes in single-crystal mixed mats.

Sample	$\Delta\nu_b(\text{CH}_2)$	$\Delta\nu_b(\text{CD}_2)$	$\Delta\nu_r(\text{CH}_2)$	$\Delta\nu_r(\text{CD}_2)$	%H in D	%D in H	(%H in D)
							(%D in H)
Pure species							
$(\text{CH}_2)_n$	10.3	...	10.8	...			
$(\text{CD}_2)_n$	...	7.7	...	6.9 <sub>6</sub>			
1:1 Mixed mats							
89°, 18.5 h <sup>a</sup>	~9.9	7.2 <sub>6</sub>	10.3	6.4 <sub>6</sub>	7.0	4.9	1.4 <sub>6</sub>
82°, 36 h		7.1 <sub>6</sub>	10.2 <sub>6</sub>	6.3 <sub>6</sub>	8.2 <sub>6</sub>	5.2 <sub>6</sub>	1.5 <sub>7</sub>
78°, 90 h	9.9	7.2 <sub>6</sub>	10.3	6.5 <sub>6</sub>	7.0	4.9	1.4 <sub>6</sub>
71°, 19 h	~10.1	7.4 <sub>6</sub>	10.4 <sub>2</sub>	6.6	4.5	3.7	1.3 <sub>9</sub>

<sup>a</sup> Temperature and time of crystallization.

penetrate into the crystal lattice of a superimposed crystal. The extent of ciliation can be estimated quantitatively, and it appears that such cilia constitute a sizable portion of the amorphous component of single crystals.

## EXPERIMENTAL

### A. Sample Preparation

Single-crystal mats were prepared which consisted of a physical mixture of polyethylene and perdeuteropolyethylene. The polyethylene was Marlex 6009, a linear high-density polymer with  $\bar{M}_w = 155\,000$  and  $\bar{M}_n = 14\,300$ . The perdeuteropolyethylene was also a linear high-density polymer (obtained from Volk Radiochemical Co.), with  $\bar{M}_w = 245\,000$ . The two kinds of crystals were present in the mats in a 1:1 molar ratio.

Crystals were grown from dilute solution (0.75–1 mg/10 ml) in p-xylene. The polymers were dissolved separately by boiling in p-xylene for at least  $\frac{1}{2}$  h, and then crystallized at a pre-set temperature  $T_{xt}$ . Crystals grown at  $T_{xt} > 87^\circ\text{C}$  were prepared by the self-nucleation technique.<sup>21</sup> When crystallization was complete (times of crystallization are listed in Table I), the suspensions were cooled to room temperature, then combined in a single flask, stirred, and immediately filtered. The mats were removed from the filters by soaking in  $\text{CS}_2$  where necessary. They were then dried by heating overnight in an oven at  $55^\circ\text{C}$ . The presence of solvent in a mat before drying was obvious from its infrared spectrum, but neither the presence of solvent nor its subsequent removal affected the results. Films of the pure species were prepared, as previously,<sup>6</sup> by casting from p-

xylene solution ( $\sim 1$  mg/ml) and evaporating the solvent at  $\sim 60^\circ\text{C}$ .

The mixed mats were filtered in two ways, rapidly and slowly. In the former case the combined crystal suspension was filtered under suction through filter paper, the process taking about 5 min for 300 ml of solution. In the latter case the suspension was allowed to sediment slowly under suction onto a fritted disk filter (ultrafine), the process taking about 3 h for 300 ml of solution.

The time interval between cooling the suspension to room temperature and the initiation of mixing and filtering varied from a few hours to 4–5 days, but this did not appear to affect the results. The possibility that dissolved polymer might be influencing the results was tested by decanting  $\sim 60\%$  of the supernatant before mixing and replacing it by fresh p-xylene, but this had no effect. The amount of dissolved polymer must be minimal, since no precipitate could be detected by adding a nonsolvent to the decanted supernatant.

### B. Spectroscopy

Infrared spectra were obtained on a Perkin-Elmer 421 spectrophotometer. The splittings of the bending,  $\Delta\nu_b(\text{CX}_2)$ , and rocking,  $\Delta\nu_r(\text{CX}_2)$ , modes were determined from spectra obtained with a 10X expanded frequency scale and a very slow scanning speed ( $\sim 1.5$   $\text{cm}^{-1}/\text{min}$ ). The estimated accuracy in the measurement of the splittings is  $\pm 0.1_6$   $\text{cm}^{-1}$ .

## RESULTS

The values of  $\Delta\nu_b(\text{CX}_2)$  and  $\Delta\nu_r(\text{CX}_2)$  for the mixed mats were a function of the filtering conditions. For the rapidly filtered mats the splittings were *identical* to those of the pure species, which are shown in Table I. In this case, therefore, the infrared spectrum is that of

<sup>21</sup> D. J. Blundell, A. Keller, and A. J. Kovacs, J. Polymer Sci. B4, 481 (1966).

TABLE II. Splittings in mixed mats with component crystals of different thickness.

Sample	$\Delta\nu_b(\text{CD}_2)$	$\Delta\nu_r(\text{CH}_2)$	%H in D	%D in H	%H in D
					%D in H
$T_{xl}(\text{H}) = 85^\circ\text{C}$	7.3	10.5	6.2	2.5	2.5
$T_{xl}(\text{D}) = 74^\circ\text{C}$					
$T_{xl}(\text{H}) = 91^\circ\text{C}$	7.5 <sub>6</sub>	10.7 <sub>6</sub>	3.3	~0	...
$T_{xl}(\text{D}) = 75^\circ\text{C}$					

a simple physical mixture in which there is no interaction between the components: The spectrum is then just a sum of the contributions from the individual pure components.

For the slowly filtered mats, however, the splittings were *different* from those of the pure species: Both  $\Delta\nu(\text{CH}_2)$  and  $\Delta\nu(\text{CD}_2)$  are smaller for the mixed mats than for the pure species, as shown in Table I. Furthermore, the splittings tend to vary with  $T_{xl}$ , being generally smaller for the higher  $T_{xl}$ . It is clear that interaction between the component crystals in the mixed mat is occurring in this case.

In order for the slight decrease to occur in  $\Delta\nu(\text{CH}_2)$  and  $\Delta\nu(\text{CD}_2)$  as compared to the pure species, it is necessary for the domain of similar interacting oscillators in a host crystal to be reduced in size by the presence of dissimilar oscillators.<sup>6,22,23</sup> In the present case these dissimilar oscillators would correspond to H chains in the D crystal lattice and D chains in the H crystal lattice, the foreign chains arising from cilia emanating from adjoining crystals. Since the proportion of cilia is relatively small, and their distribution on the surface of a crystal is presumably random, the insertion of cilia into an adjoining crystal of opposite species should result in a random mixing of the two kinds of chains within the lattice. This corresponds to the kind of random mixing achieved in co-crystals of  $n\text{-C}_{36}\text{H}_{74}$  and  $n\text{-C}_{36}\text{D}_{74}$ ,<sup>6</sup> and therefore the change in splittings with changing composition for the paraffin system<sup>6</sup> should provide a means for determining the percentage of foreign chains in a host lattice for the present mixed mat system. The data for the paraffin system<sup>6</sup> are shown in graphical form in Fig. 1. From these plots the percentages of foreign chains in the host crystal were determined, and are listed in Table I. (It should be noted that these represent lower limits because, as a result of the slightly different lattice parameters for the  $n$ -paraffin as compared to polyethylene, the splittings

for the pure species are slightly higher for the latter than for the former.<sup>6</sup>)

Since the surface concentration of cilia is dependent on crystal thickness, which in turn depends on  $T_{xl}$ , the variations in splitting with  $T_{xl}$  shown in Table I are to be expected. In order to enhance this effect, mixed mats were made from crystals of different  $T_{xl}$ . Two of these cases, corresponding to H crystals grown at higher temperatures than the D crystals, are shown in Table II. The ratios (%H in D)/(%D in H) are quite different from these ratios for crystals grown at the same temperature (see Table I), and the significance of this will be considered below.

## DISCUSSION

A number of arguments based on the above results support the conclusion that cilia emanating from the fold surfaces of single crystals can, under appropriate conditions, interpenetrate into the lattice of adjoining crystals. The considerations leading to this conclusion will be discussed now.

If ciliary interpenetration of the kind proposed above

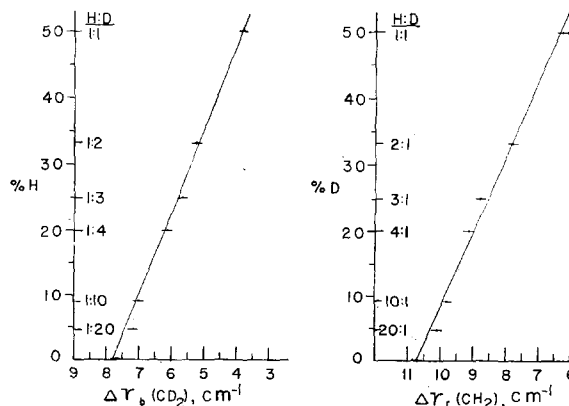


FIG. 1. Splittings of  $\text{CD}_2$  bending and  $\text{CH}_2$  rocking modes in  $\text{C}_{36}\text{H}_{74}\text{-C}_{36}\text{D}_{74}$  mixed crystals as a function of the % of H chains and the % of D chains, respectively.

<sup>22</sup> M. Tasumi and S. Krimm, *J. Chem. Phys.* **46**, 755 (1967).

<sup>23</sup> M. Tasumi and S. Krimm, *J. Polymer Sci. Part A-2*, **6**, 995 (1968).

TABLE III. Calculation of ciliary interpenetration in polyethylene mixed mats.

$T_{zi}$ , °C	$l$ , Å	$N_H$	$N_D$	$C_H \times 10^{-5}$	$C_D \times 10^{-5}$	$(C/L)_H$	$(C/L)_D$	%H in D	%D in H	%H in D
										%D in H
90	150	3.67	5.75	7.37	4.70	13.6	8.70	12.5	7.65	1.64
87	138	4.00	6.25	6.76	4.33	12.5	8.00	11.6	7.11	1.63
82	125	4.45	6.92	6.08	3.91	11.2	7.22	10.5	6.50	1.62
78	118	4.73	7.34	5.72	3.69	10.6	6.81	9.9	6.16	1.61
75	112	5.01	7.76	5.40	3.48	9.98	6.44	9.3	5.85	1.59
90(H) } 75(D) }								12.8	5.66	2.26

does indeed occur, then it should be possible to predict the percentage of foreign chains within a host lattice and how this percentage depends upon crystal thickness. We have made a calculation based on fairly reasonable assumptions (details are given in an Appendix), and the results are shown in Table III. These are to be compared with the observed percentages given in Table I. The calculated percentage values are consistently higher than the observed values. This is not surprising in view of the fact that (a) total interpenetration was assumed (whereas in the real mats some cilia may be "lost" by penetration back into the parent crystal as well as penetration into a like adjacent crystal), and (b) the observed values (as noted above) are expected to be somewhat low as a result of using a paraffin system as a standard for polyethylene. Despite the approximations involved, the agreement is satisfactory, and at least indicates that the proposed penetration mechanism is not unreasonable.

Further support for ciliary penetration is provided by the variation in percentage of chain ends with crystal thickness. The calculations (see Table III) show that this percentage increases with increasing  $T_{zi}$ , and therefore increasing crystal thickness,<sup>2</sup> and this is qualitatively supported by the data (see Table I). The decrease in percentage observed for the highest  $T_{zi}$  specimen seems to be real, and is unaccounted for at present. It should be noted that the situation may be more complicated than is implied by our simple model. For example, the longer cilia associated with the higher  $T_{zi}$  crystals may tend to interact more with one another in the interlamellar region thus reducing the tendency toward interpenetration into neighboring crystals. Also, interaction may be sensitive to sample preparation and resulting sample morphology.<sup>2</sup> (For instance, three samples for which  $T_{zi} > 85^\circ\text{C}$  showed little or no interpenetration.) It might be expected, however, that such factors would influence both kinds of crystals about equally, and therefore the ratio (%H in D)/(%D in

H) should be more representative of the extent of agreement. This seems to be the case (cf. observed ratios in Table I with calculated ratios in Table III).

The above effect of crystal thickness should be enhanced if mixed mats are made with crystals of different thickness. The results of such an experiment are shown in Table II, where thick crystals of polyethylene have been mixed with thinner crystals of perdeuteropolyethylene. A calculation for a model of this kind (cf. Table III) indicates that the ratio (%H in D)/(%D in H) should increase as compared to the case of crystals of the same thickness, and the results in Table II show that this is indeed found. In view of the possible complexity in forming mats from crystals which may exhibit morphological differences,<sup>2</sup> the absence of close quantitative agreement is not critical. There may also be a problem associated with the shorter cilia of thin crystals not completely penetrating into the thick crystals. This would have the effect of giving a larger ratio than that predicted from the calculation (which implicitly assumed comparable penetration), and this is in fact the trend of the observed results (cf. Table II). The qualitative and semi-quantitative features of these studies thus strongly support the proposal of ciliary penetration in polyethylene single-crystal mats.

The behavior of such mats upon annealing provides additional evidence for such tie molecules. The  $T_{zi} = 82^\circ\text{C}$  mat was annealed for 10 min at  $110^\circ$ ,  $115^\circ$ ,  $120^\circ$ ,  $125^\circ$ , and  $130^\circ\text{C}$ , and finally melted completely above  $140^\circ\text{C}$ . At  $110^\circ\text{C}$  an initial increase in splittings was observed, approaching the values for the pure species. At  $115^\circ$ – $120^\circ\text{C}$  the splittings decreased to about their values before annealing. At annealing temperatures above  $120^\circ$ – $125^\circ\text{C}$  the splittings decreased further and approached those observed in 1:1 co-crystals of polyethylene and perdeuteropolyethylene.<sup>6</sup> Upon melting, the splittings became the same as for 1:1 co-crystals. These results indicate that chains from adjacent super-

imposed lamellae can intermingle upon annealing. The initial increase in splitting may be due to the effect of crystal thickening with annealing above  $T_{zi}$ .<sup>2</sup> Such thickening would result in a partial "sucking in" of cilia into a parent crystal, thus reducing the extent of their interpenetration into adjacent crystals. With increasing annealing temperature, and therefore increasing chain mobility, interpenetration increases again. It should be noted that the annealing and melting of mixed mats appears to result in an intimate mixing of chains, the distribution of foreign chains in a crystal being initially random and leading finally to a system indistinguishable from a co-crystal. If foreign chains were only to occupy the large holes which are thought to develop in a crystal upon annealing,<sup>24</sup> the observed decreases in splittings would not occur. The intermixing must be on the level of individual chains and not large aggregates of chains.

The nature of the interpenetration mechanism is not provided by these studies, but the dependence on filtering conditions suggests some of the factors involved. It should be noted first, of course, that the presence of cilia on a growing single crystal is not inconsistent with a subsequent penetration of cilia into adjacent crystals. Two different processes are involved, one that of crystal growth and the other that of crystal interaction. It may well be that the total interaction energy between adjacent crystals is lowered more by allowing ciliary penetration so that the crystals can get closer together than would otherwise be possible without such penetration. In any case, the mobility of the cilia seems to be an important factor in bringing this about, as appears to be indicated by the effect of filtering. It is probable that in rapid filtering the solvent between crystals is removed quickly enough so that cilia lose their mobility and therefore access to the surface of an adjacent crystal. In the case of slow filtering, however, the cilia would be more extended from the surface of their parent crystal, and would remain mobile for longer periods while in the vicinity of adjacent crystals. This mobility, plus the dynamic internal motion of the adjoining crystal lattice, probably makes penetration feasible. After penetration a cilium would occupy a regular lattice site in the crystal, any distortions of the lattice being localized in the interior of the crystal near the chain end.

### CONCLUSION

The infrared spectra of slowly filtered mixed mats of single crystals of polyethylene and single crystals of perdeuteropolyethylene show splittings of  $CX_2$  bending and rocking modes which are smaller than those for the pure species. The source of these diminished splittings is the presence of small amounts of foreign species

chains in a host lattice, the foreign chains corresponding to loose chain ends, or cilia, emanating from the surface of an adjoining crystal. This model is supported by calculations which satisfactorily predict the percentage of foreign chains in a lattice from knowledge of the molecular weights of the two kinds of polymers, as well as how this percentage changes with crystal thickness. The annealing behavior of such mixed mats is also indicative of interpenetrant cilia. It would appear that dilute solution crystallization of polyethylene gives rise to a "hairy crystal."

The presence of cilia on the surfaces of dilute-solution single crystals will naturally influence the amorphous content of these crystals. For example, depending on their lengths, there might easily be 10%–20% of the material located in the cilia. Their presence must contribute to the measured amorphous component of single crystals found by various techniques. Thus, the observed density defect need not be attributed to an absence of regular folding but may be largely a result of surface cilia. Incidentally, variations in measured densities of single crystals may be a result of preparative methods which alter the surface ciliary structure.

The penetration of cilia from one crystal into an adjacent crystal must have an important bearing on the determination of the physical properties of such a system. Since such tie molecules can also occur in melt-crystallized polymer, this must provide a general mechanism for connecting crystalline regions. Other factors than those discussed here may be relevant to the characteristics of such systems. For example, a mixed mat which exhibited interpenetration after being prepared did not show any a year later (after storage on a shelf at room temperature). Thus time may influence physical properties by affecting the extent of ciliary connection between crystalline regions. The method of mixed-crystal mats should provide a useful technique for studying such problems.

### ACKNOWLEDGMENTS

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### APPENDIX

The calculation of the percentage of H chains in the D lattice and the percentage of D chains in the H lattice is based on a number of assumptions. These are discussed first:

(1) The number of chain ends will be determined by the length of a molecule, and therefore by the number average molecular weight. For the polyethylene used in this study  $\bar{M}_n = 14\,300$ . For the deuteropolyethylene this quantity was not known, but was assumed to be  $0.1\bar{M}_w$ , i.e. 24 500.

\* W. O. Statton, J. Appl. Phys. 38, 4149 (1967).

(2) Each molecule was assumed to contribute two cilia, one per crystal surface.

(3) The length of each cilium was taken as constant, and equal to half the thickness of the crystal.

(4) The folds were assumed to be regular, and to contain 5 CH<sub>2</sub> (or CD<sub>2</sub>) groups.

(5) All cilia were assumed to interpenetrate into the lattice of adjacent crystals, and to occupy normal lattice sites. This of course implies that there must be some lateral expansion of a crystal if cilia are to be incorporated into it.

The percentage of, say, H chains in a D crystal will be known once we know the percentage of H cilia on the surface of its own crystal. This is true because we assume lattice sites on both crystals to be juxtaposed. Therefore, if, for example, 10% of the lattice sites in a square micron on the surface of the H crystal have cilia emerging from them, and if all of these occupy lattice sites in the adjacent D crystal, then 10% of the lattice sites in the D crystal are occupied by H chains. Thus, to get the %H in D we only need to know the %H cilia on the surface of the H crystal.

The percentage of H cilia on the surface of an H crystal which is interacting with an adjacent D crystal is determined by two factors: (1) the number of H cilia per μ<sup>2</sup> which were originally on the surface of the isolated H crystal, and (2) the number of D cilia per μ<sup>2</sup> which penetrate into the H crystal. The latter must be taken into account since their effect is to dilute the surface concentration of H cilia. This factor will only be included in first approximation, i.e., as equal to the number of D cilia per μ<sup>2</sup> on the isolated D crystal.

If we let  $N$  = number of folds on one surface of a crystal per polymer chain,  $a$  = area of a unit cell ( $36.95 \times 10^{-8} \mu^2$ ),  $C$  = number of cilia per μ<sup>2</sup>, and  $L$  = number of lattice sites per μ<sup>2</sup>, then

$$C = 1/Na \quad (1)$$

and

$$L = 2/a = 5.41 \times 10^6, \quad (2)$$

where

$$N = \frac{1}{2} \left[ \left( \frac{\bar{M}_n}{M_{CX_2}} - \frac{l}{1.27} \right) / \left( \frac{l}{1.27} + 5 \right) \right], \quad (3)$$

$M_{CX_2}$ , being the molecular weight of a CH<sub>2</sub> or CD<sub>2</sub> group,  $l$  being the thickness of the crystal, and 1.27 Å being the axial length per CX<sub>2</sub> group. The percentage of cilia on the surface of the isolated crystal is therefore

$$C/L = 1/2N. \quad (4)$$

To get the %H in D we must include, as we noted above, the effect of D cilia in altering the initial surface concentration given by (4). For this particular case

$$\%H \text{ in D} = C_H / (L + C_D). \quad (5)$$

A similar equation holds for %D in H.

The results of such a calculation for crystals of various  $T_{xl}$  are given in Table III. Crystal thicknesses corresponding to these  $T_{xl}$  are known.<sup>2</sup> The calculation is only slightly sensitive to the choice of 5 methylene groups/fold. For example, if 10 is assumed, then for the 90°C crystals the %H in D becomes 13.0, the %D in H becomes 7.94, and the ratio (%H in D)/(%D in H) is unaltered.