

# Some Orientation Studies on Blown Polyethylene Films by Infrared Spectroscopy

M. A. McRAE AND W. F. MADDAMS,

*Group Research and Development Department, The British Petroleum Company Limited, Sunbury-on-Thames, Middlesex TW16 7LN, England*

## Synopsis

Infrared dichroic measurements have been made on a number of blown polyethylene films for which x-ray diffraction pole figure studies are reported in the three preceding papers; they complement them in some respects, and lead to several conclusions. *Gauche* chain conformations in loose chain folds in amorphous regions, characterized by bands at 1303, 1352, and 1368  $\text{cm}^{-1}$ , show appreciable orientation in films with high-stress orientation but very little with low-stress orientation. Conversely, extended tie chains in amorphous regions, assessed by the band at 1080  $\text{cm}^{-1}$ , are appreciably orientated with the more normal type of low-stress film but not with high-stress films. It is therefore possible, rapidly and inexpensively, to distinguish between the two types of orientation. The method for studying the orientation of extended tie chains is capable of further development. There is probably an empirical correlation between the dichroic ratios at 720 and 730  $\text{cm}^{-1}$  and the tear strengths and balances of the films with low-stress orientation.

## INTRODUCTION

X-Ray diffraction pole figure measurements provide a valuable method for characterizing the orientation in blown polyethylene films. This is evident from the work of Lindenmeyer and Lustig<sup>1</sup> and of Desper,<sup>2</sup> confirmed and extended by the results presented in the three preceding papers.<sup>3-5</sup> It has proved possible to approximately predict relative tear strengths in the machine and transverse directions from the measurement of the *c*-axis concentrations along the machine direction, and to account for the variation in tear strengths, because of the change in the *c*-axis orientation, with different blowing conditions. The pole figures have also shown that there are two types of orientation, resulting from low- and high-stress crystallization; these may be present simultaneously, or one type may predominate. The high-stress crystallization process is the less typical. It is obtained over a fairly wide range of blowing conditions in the case of Hostalen GM 9955F but is formed much less readily with an experimental Rigidex polymer and Shell LPPE 040.

As an adjunct to this work<sup>3-5</sup> a limited number of infrared dichroic measurements were made and are presented here for two reasons. The results indicate that the technique can serve as a simple, cheap, and rapid screening process, prior to x-ray diffraction work, if a substantial number of films are to be examined. Secondly, they suggest that a more detailed study is warranted as there are indications that information complementary to that from pole figure measurements will be forthcoming. This is particularly so for the alignment of tie chains and loose chain folds in amorphous regions, as had been anticipated from previous work on cold drawn polyethylene specimens.<sup>6,7</sup>

These results must be considered in the light of the known limitations of the

technique. Holmes, Miller, Palmer, and Bunn<sup>8</sup> measured polarized infrared spectra of films blown from low-density polyethylene. They obtained dichroic ratios for the  $720\text{ cm}^{-1}$  band and, ignoring the contribution to the total intensity from chains in crystalline regions, they deduced that the amorphous chains have their axes parallel to the machine direction (MD). In contrast, the crystalline chains have their  $c$  axes perpendicular to MD from dichroic results on the  $730\text{ cm}^{-1}$  band. Keller and Sandeman<sup>9</sup> subsequently pointed out the limitations of this approach and hence that the deductions of Holmes and co-workers do not follow as a necessary consequence of the opposite dichroism of the two bands.

This difficulty led Aggarwal, Tilley, and Sweeting<sup>10</sup> to examine the usefulness of other bands and they measured dichroic ratios for the amorphous ones at  $1340$  and  $1355\text{ cm}^{-1}$ . They concluded that the orientation in amorphous regions was not marked and that when it occurs the chains are perpendicular to MD, that is, the behavior is similar to that occurring in crystalline regions.

More recently, Desper<sup>2</sup> has made dichroic measurements on bands at  $720$ ,  $730$ ,  $1300$ ,  $1380$ ,  $1468$ ,  $1480$ ,  $1903$ , and  $2030\text{ cm}^{-1}$ , some of which are crystalline bands, some amorphous and the remainder a combination of both. The examination of films blown from low-density polyethylene showed that in crystalline regions the degree of  $a$ -axis orientation increased considerably as the cooling rate was increased and the  $c$ -axis orientation changed from the mildly parallel to the mildly perpendicular type. Furthermore, the degree of orientation in amorphous regions is low.

## EXPERIMENTAL

Two groups of films, all blown from high-density polyethylenes, were examined. The first comprised five prepared on an experimental Brabender unit and only limited details of the machine conditions are available for these. The films are generally similar to but not identical with those used for the preliminary x-ray diffraction orientation studies already reported.<sup>3</sup> The tear strengths were measured by the method described previously.<sup>3</sup> The remaining 13 were blown on a Demag unit, 12 of them from Hostalen 9955F. The majority consist of films previously studied by x-ray diffraction.<sup>4,5</sup> The blowing conditions are given in Table I.

The infrared dichroic measurements were made on Perkin-Elmer PE457 and Grubb Parsons "Spectromaster" spectrometers, using a wire grid polarizer. The draw down direction, which was apparent from a visual inspection of the films, was set at an angle of  $45^\circ$  to the spectrometer entrance slit to minimize any effects resulting from partial polarization of the radiation by the spectrometer optics.<sup>11,12</sup> In view of the known variation of orientation with film thickness<sup>6</sup> specimens of approximately equal thickness were selected, as far as possible. Values of about  $30\text{ }\mu\text{m}$  were used and these proved ideal for the measurements on the bands at  $720$  and  $730\text{ cm}^{-1}$ . In the case of weaker bands, such as the one at  $1080\text{ cm}^{-1}$  specific for tie chains in amorphous regions, the absorption obtained from  $30\text{ }\mu\text{m}$  films was considerably lower than optimum; nevertheless, it was possible to make useful semiquantitative measurements of the dichroic ratios. Some variation of the measured ratios was found at different points on particular films and mean values were obtained. The spread of values for an individual film was not large and the precision of the measurements is significantly better than the

TABLE I  
Preparational Details for the 18 Blown Polyethylene Films Examined

Film No.	Polymer	Blowup ratio	Draw ratio
1	Shell LPPE 040	4.0	?
2	Shell LPPE 040	5.5	7.4
3	Shell LPPE 040	5.3	?
4	Manolene 47100	4.7	7.8
5	Experimental Rigidex polymer	4.5	7.8
6	Hostalen 9955F	2.5	5.5
7	Hostalen 9955F	3.3	3.4
8	Hostalen 9955F	2.9	9.2
9	Hostalen 9955F	4.0	6.8
10	Hostalen 9955F	4.8	5.1
11	Hostalen 9955F	2.8	13.7
12	Hostalen 9955F	5.0	5.3
13	Shell LPPE 040	2.0	8.9
14	Hostalen 9955F	6.2	5.8
15	Hostalen 9955F	3.2	12.1
16	Hostalen 9955F	6.3	5.9
17	Hostalen 9955F	3.1	13.3
18	Hostalen 9955F	2.0	11.6

differences between the more closely related films, except in the case of the 1080  $\text{cm}^{-1}$  band.

## RESULTS

Dichroic ratios for the 720 and 730  $\text{cm}^{-1}$  bands only were measured for the five Brabender films. The results, together with the tear strengths along the machine and transverse directions, are given in Table II. Films 1, 2, and 3, with the greater degree of perpendicular dichroism, are the three with the high tear strengths; furthermore, when the ratio of the tear strengths in the machine-transverse direction is greater than or equal to unity, as is the case with films 1 and 2, the dichroic ratios at 730  $\text{cm}^{-1}$  are significantly in excess of unity. Hence, it is possible to discern a relation between the two dichroic ratios, the tear strength and the balance. If, as expected, this can be substantiated by measurements on a larger number of films a rapid empirical method is available for obtaining semiquantitative information on tear strengths. This would be useful for a first assessment of films obtained from work in which the various blowing parameters are varied appreciably.

TABLE II  
Infrared Dichroic Ratios at 720 and 730  $\text{cm}^{-1}$  and Measured Tear Strengths for Five Films Blown on Experimental Brabender Unit

Film No.	Dichroic ratio		Tear strength (mN)	
	720 $\text{cm}^{-1}$	730 $\text{cm}^{-1}$	MD	TD
1	0.66	1.33	354	203
2	0.68	1.24	345	347
3	0.77	1.05	158	375
4	0.89	1.11	41	50
5	0.93	1.08	123	98

The dichroism of the  $730\text{ cm}^{-1}$  band is a measure of the degree of  $a$ -axis orientation along MD in the plane of the film, because the radiation is incident along the sheet normal direction. Film 1 therefore has the greatest degree of  $a$ -axis orientation, followed by films 2, 4, 5, and 3, with very little difference between the last three. This has been confirmed by pole figure measurements of the type described previously.<sup>3</sup> Film 1 has substantial  $a$ -axis orientation, films 2 and 3 have their (200) pole maxima at angles of  $30^\circ$  to  $30^\circ$  from sheet normal (SN) and films 4 and 5 are similar except there is less overall preferred orientation. This approach, which has the merit of simplicity, should be useful in the case of films blown from low-density polyethylene as these have appreciable  $a$ -axis orientation along MD, unlike the majority of those blown from the high-density polymer.<sup>5</sup>

The results for the 13 Demag films have been divided into two groups on the basis of the previous x-ray diffraction pole figure measurements,<sup>4,5</sup> namely, those with low-stress orientation only and those with a significant degree of high-stress orientation. The results, respectively, are given in Tables III and IV and all the dichroic ratios were measured in pairs, along the draw direction and at  $45^\circ$  to it.

In the case of the low-stress orientation films (Table III) the dichroic ratios at  $730\text{ cm}^{-1}$  are close to unity, indicating that there is very little  $a$ -axis orientation in the plane of the films, in agreement with the x-ray diffraction results. The measurements on the  $720\text{ cm}^{-1}$  band show that there is, in general, a reasonable degree of perpendicular dichroism along the draw direction and much less along the  $45^\circ$  position. Hence, the  $b$ -axis tends to lie along the blow direction. One interesting empirical correlation emerges from a comparison of the dichroic ratios at  $720\text{ cm}^{-1}$  along the draw direction (DD) with the ratio of the draw to blowup ratios; the smaller the ratio of the two machine parameters the smaller is the perpendicular dichroism. For example, the values are 0.90 and 1.02 at one extreme with film 7 and 0.38 and 4.4 at the other with film 11.

The three bands at  $1368$ ,  $1352$ , and  $1303\text{ cm}^{-1}$ , all associated with gauche chain conformations probably in loose chain folds, give dichroic ratios which do not differ greatly from unity. Hence, these types of chain units show little or no preferred orientation. In the case of the weak  $1080\text{ cm}^{-1}$  band, which is associated with extended tie chains having the trans conformation, the dichroic ratios are appreciably greater than unity, showing that there is a significant degree of orientation of such units. No great significance attaches to the differences between the DD and  $45^\circ$  values as these are often comparable to the measuring errors. The other interesting feature to emerge from the measurements on the four bands considered collectively is that, by comparison with the previous work on cold drawn polyethylene,<sup>7</sup> the dichroism of the extended tie chains is relatively much greater than that of loose chain folds.

In the case of the five films with high-stress crystallization orientation (Table IV), the dichroism of the  $720$  and  $730\text{ cm}^{-1}$  bands is not markedly different from that of the eight films with low-stress orientation. There is very little  $a$ -axis orientation in the plane of the films but there is a clear tendency for the  $b$  axis to lie along the blow direction. However, there is a definite difference in the case of the three Gauche bands, particularly the one at  $1352\text{ cm}^{-1}$ , and it is clear that the orientation of the loose chain folds is greater in the case of the high-stress orientation than with the low-stress form. This indicates that the crystalline

TABLE III  
Infrared Dichroic Ratios for Six Bands of Blown Polyethylene Films with Low-Stress Crystallization Orientation

Film no.	730 cm <sup>-1</sup>		720 cm <sup>-1</sup>		1368 cm <sup>-1</sup>		1352 cm <sup>-1</sup>		1303 cm <sup>-1</sup>		1080 cm <sup>-1</sup>	
	DD <sup>f</sup>	C <sup>a</sup> 45°g	DD	C + A <sup>b,c</sup> 45°	DD	A(G) <sup>d</sup> 45°	DD	A(G) 45°	DD	A(G) 45°	DD	A(T) <sup>e</sup> 45°
6	1.10	1.00	0.70	0.99	1.07	0.98	1.03	0.97	1.13	1.14	1.3	1.5
7	1.07	1.00	0.90	1.01	1.03	0.97	0.94	0.99	1.07	0.98	1.2	1.4
8	1.16	0.93	0.54	1.03	1.04	0.90	0.96	0.96	1.06	1.06	1.2	1.4
9	1.08	0.89	0.74	1.20	0.88	1.07	1.06	0.98	1.07	0.86	1.4	1.3
10	1.10	1.04	0.81	0.90	0.94	1.02	1.10	1.02	0.86	1.17	1.2	1.3
11	0.97	0.96	0.38	1.20	1.10	0.90	1.07	0.91	0.86	0.86	1.6	1.2
12	0.95	1.02	0.45	1.02	1.00	1.08	0.89	1.00	1.00	1.30	1.0	1.0
13	1.30	0.95	0.54	1.15	1.08	1.06	1.02	1.04	0.95	0.90	1.4	1.5

<sup>a</sup> C denotes crystalline.

<sup>b</sup> A denotes amorphous.

<sup>c</sup> C + A represents the crystalline and amorphous components.

<sup>d</sup> G are the Gauche sequences.

<sup>e</sup> T are extended trans-sequences.

<sup>f</sup> DD are measurements made along the draw direction.

<sup>g</sup> 45° is the measurement made at 45 deg to the draw direction.

TABLE IV  
Infrared Dichroic Ratios for Six Bands of Blown Polyethylene Films having some High-Stress Crystallization Orientation

Film no.	730 cm <sup>-1</sup> C <sup>a</sup>		720 cm <sup>-1</sup> C + A <sup>b,c</sup>		Dichroic ratio				1303 cm <sup>-1</sup> A(G)		1080 cm <sup>-1</sup> A(T) <sup>e</sup>	
	DD <sup>f</sup>	45° <sup>g</sup>	DD	45°	1368 cm <sup>-1</sup> A(G) <sup>d</sup>	45°	DD	45°	DD	45°	DD	45°
14	0.97	1.04	0.69	1.16	1.14	1.00	0.88	1.11	1.29	1.16	1.0	1.0
15	0.94	1.03	0.72	1.06	1.17	1.05	0.74	1.16	1.31	1.20	1.1	1.0
16	0.90	0.99	0.61	1.11	1.09	0.92	0.91	1.06	1.26	1.06	1.1	1.0
17	1.03	0.81	0.53	1.50	1.10	0.98	1.09	1.06	1.10	0.96	1.3	1.4
18	0.83	1.00	0.56	1.02	1.10	1.13	1.05	1.06	1.09	1.22	1.0	1.1

<sup>a</sup> C denotes crystalline.

<sup>b</sup> A denotes amorphous.

<sup>c</sup> C + A represents crystalline and amorphous components.

<sup>d</sup> G are the Gauche sequences.

<sup>e</sup> T are extended trans-sequences.

<sup>f</sup> DD are measurements made along the draw direction.

<sup>g</sup> 45° is the measurement made at 45° to the draw direction.

lamellae in the high-stress films are aligned in a more regular fashion, in agreement with the results of preliminary small-angle x-ray diffraction measurements.<sup>13</sup>

The normally weak  $1080\text{ cm}^{-1}$  band is even less intense in the case of the five high-stress orientation films, indicating that the concentrations of the extended tie chains are low. There is no significant orientation and this is the result of two opposing effects. All the films contain a significant amount of the low-stress type or orientation, as shown by their pole figures, and this has a dichroic ratio in excess of unity. Dichroic ratios as low as 0.4 were obtained from heavily cold-drawn linear polyethylene<sup>7</sup> showing that the value is less than unity in high-stress conditions.

## DISCUSSION

The present results confirm what is evident from the earlier work,<sup>8,9</sup> that the dichroic ratios at  $720$  and  $730\text{ cm}^{-1}$  are of limited value for orientation studies. Hence, it is unnecessary to consider in detail the various problems,<sup>14</sup> including overlap of the two peaks one of which is asymmetrical<sup>15,16</sup> and the occurrence of transcrystalline surface layers,<sup>17</sup> which would have to be taken into account if a quantitative interpretation were attempted. Nevertheless, the practical value of the empirical correlation between the two dichroic ratios, the tear strength and the balance should not be overlooked.

The infrared technique is of greater value for the assessment of orientation in amorphous regions and there are clear indications of its merit as a simple diagnostic method and as a complement to x-ray pole figure studies. It is possible to distinguish unambiguously between high- and low-stress orientation, from the orientational behavior of both the extended tie chains and the loose chain folds. This represents a significant step forward from the results of Desper<sup>2</sup> who, because he was working with films from low-density polyethylene which had very low-stress orientation and also because he examined bands characteristic for Gauche conformations in amorphous regions, observed no significant orientation. The present results show that these bands, particularly the one at  $1303\text{ cm}^{-1}$ , are more useful in the case of films with high-stress orientation.

On the other hand the  $1080\text{ cm}^{-1}$  band, characteristic for the trans sequence in extended tie chains, is useful for the study of amorphous orientation in the more normal type of low-stress orientation. This conclusion is in line with the findings of Read and Stein,<sup>14</sup> who studied uniaxially cold drawn low-density polyethylene specimens. Although the present results for the  $1080\text{ cm}^{-1}$  band are no more than semiquantitative, because of its weakness, there is considerable scope for improving the precision of the measurements. Scale expansion facilities are now often available with medium performance infrared spectrometers and, at a rather more sophisticated level, the data smoothing and signal accumulation methods already applied to the estimation of low levels of chain branching in polyethylene<sup>18</sup> should be valuable. An improvement in the precision of the dichroic ratio measurements at  $1080\text{ cm}^{-1}$  by an order of magnitude is feasible and this should lead to a fuller interpretation of the orientation of tie chains as a function of the blowing parameters used in film production.

To summarize, the present measurements, the most detailed yet reported on films blown from high-density polyethylene, lead to several conclusions. (1)

Gauche chain conformations, in loose chain folds in amorphous regions, show appreciable orientation in the case of films with high-stress orientation but very little with low-stress orientation. (2) Extended tie chains in amorphous regions are appreciably orientated with the more normal low-stress type of orientation but not with the high-stress films. (3) Hence, it is possible, rapidly and inexpensively, to distinguish between the two types of orientation. (4) The method for studying the orientation of extended tie chains is capable of further development and exploitation. (5) There is probably an empirical correlation between the dichroic ratios at 720 and 730  $\text{cm}^{-1}$  and the tear strengths and balances of the films with low-stress orientation.

The authors are indebted to Dr. J. E. Preedy for helpful discussions and to Dr. G. W. Downs, D. K. Howell, and P. Jones, BP Chemicals Ltd., for supplying the various films examined. Permission to publish this paper has been given by The British Petroleum Company Ltd.

### References

1. P. H. Lindenmeyer and S. Lustig, *J. Appl. Polym. Sci.*, **9**, 227 (1965).
2. C. R. Desper, *J. Appl. Polym. Sci.*, **13**, 169 (1969).
3. W. F. Maddams and J. E. Preedy, *J. Appl. Polym. Sci.*, **22**, 2721 (1978).
4. W. F. Maddams and J. E. Preedy, *J. Appl. Polym. Sci.*, **22**, 2739 (1978).
5. W. F. Maddams and J. E. Preedy, *J. Appl. Polym. Sci.*, **22**, 2751 (1978).
6. M. A. McRae and W. F. Maddams, *Makromol. Chem.*, **177**, 473 (1976).
7. M. A. McRae, W. F. Maddams, and J. E. Preedy, *J. Mater. Sci.*, **11**, 2036 (1976).
8. D. R. Holmes, R. G. Miller, R. P. Palmer, and C. W. Bunn, *Nature*, **171**, 1104 (1953).
9. A. Keller and I. Sandeman, *J. Polym. Sci.*, **15**, 133 (1955).
10. S. L. Aggarwal, G. P. Tilley, and O. J. Sweeting, *J. Appl. Polym. Sci.*, **1**, 91 (1959).
11. J. E. Stewart, *Infrared Spectroscopy: Experimental Methods and Techniques*, Marcel Dekker, New York, 1970, p. 146.
12. R. S. George, *Appl. Spectrosc.*, **20**, 101 (1966).
13. W. F. Maddams and J. E. Preedy, *J. Appl. Polym. Sci.*, **22**, 3027 (1978).
14. B. E. Read and R. S. Stein, *Macromolecules*, **1**, 116 (1968).
15. R. G. Snyder, *J. Chem. Phys.*, **47**, 1316 (1967).
16. C. G. Opaskar and S. Krimm, *Am. Chem. Soc., Polym. Prepr.*, **8**, No. 2, 1124 (1967).
17. R. K. Eby, *J. Appl. Phys.*, **35**, 2720 (1964).
18. C. Baker and W. F. Maddams, *Makromol. Chem.*, **177**, 437 (1976).

Received April 7, 1977

Revised September 15, 1977