The setting angle of extended chain linear polyethylene

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The unit cell parameters and the setting angle have been estimated for a series of linear polyethylene specimens crystallized at pressures from atmospheric to 6 kbar. Slight variations in unit cell parameters occur, however, significant differences can be discerned in the setting angles as a function of crystallization pressure. It is suggested that the setting angle of extended chain crystals is the equilibrium value for the crystal and that the setting angle is influenced by the presence of folded chains and the structure of the fold surface. Such a hypothesis would account for the spread in published values of setting angles for specimens crystallized both at atmospheric pressure and under strain.

(Keywords: polyethylene; extended chain; unit cell; setting angle; pressure; crystallinity)

INTRODUCTION

Although the unit cell parameters of the polyethylene crystal have been well established for a long time the same cannot be said for the setting angle[1]. It is clear that variables such as crystallization conditions, annealing and deformation influence the unit cell dimensions in a manner which has been well characterized[2]. It is also known that the lamellar thickness is a major factor in these changes[3] presumably indicating an influence of fold structure. Studies of the setting angle dependence have been less systematic but it is clear that not only such molecular variables as degree of branching are important but also the method of preparation of the specimens. Published values range from 40° to 50° with good reliability factors[4]. The temperature coefficient of the angle is well established for a given specimen[4] being related to the overall change in unit cell shape that occurs as temperature is raised[3]. Since the measured values vary with crystallization temperature and prestrain it might be inferred that stresses present in the crystal surfaces due to folds and tie-chains could be affecting the setting angle. In order to test this hypothesis it is necessary to measure the setting angle of extended chain crystals where presumably the minimization of fold and tie-chain content would result in the least perturbed crystal. The results of such experimentation will be reported in this contribution.

EXPERIMENTAL

Specimen preparation

The material used in this experimentation was Sclair 2907, supplied by Dupont of Canada, which is a linear polyethylene with $\bar{M}_N$, $\bar{M}_W$, $\bar{M}_Z$ and $\bar{M}_{Z+1}$ of 17 457, 61 000, 206 770 and 465 530 respectively.

Cut sections of moulded sheet were placed in the bomb and melted under pressure. After maintaining melt temperature for 20 min the cell was cooled at a rate of 1°C per

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min until the chosen crystallization temperature was reached. That temperature was held for 6 h before cooling to room temperature and subsequent release of pressure. The melt temperature was chosen as 10°C above the highest melting points on the phase diagram of Bassett and Turner[6]. Below 3 kbar this was the melting point of the orthorhombic phase and above 3 kbar the melting point of the hexagonal phase. Crystallization temperatures were 20°C below those same equilibrium melting temperatures. Bassett's melting temperatures are generally 10°C above those of other workers[7,8].

Specimen characterization

Melting curves were obtained at atmospheric pressure using a Perkin Elmer DSC II differential scanning calorimeter at heating rates of 10°C min^{-1}. Melting points and heats of fusion were extracted from such data following conventional procedures.

Scanning electron microscopy of etched[9] microtomed sections was used to confirm the presence of extended chain crystals.

X-ray diffraction studies

All measurements were carried out at atmospheric pressure. Unit cell dimensions were obtained using a least squares procedure from observed wide angle peak positions obtained using a Debye–Scherrer camera. Setting angles were obtained from X-ray diffractometry traces obtained using a fixed time mode step scanning technique on a Diano SPG 10 A instrument with xenon-filled counter.

RESULTS

Specimen characterization

Differential scanning calorimetric traces for the specimens are shown in *Figure 1* where it can be seen that for specimens crystallized below 4 kbar a conventional folded chain crystal melting point occurs. Specimens crystallized

at 5 and 6 kbar show a high melting point close to that of extended chain material, the specimen crystallized at 4 kbar being intermediate. A small high temperature peak was observed at 3 kbar; small low temperature peaks being observed at 4 and 5 kbar.

Scanning electron microscopy confirmed the presence of extended chain crystals for the specimens crystallized at
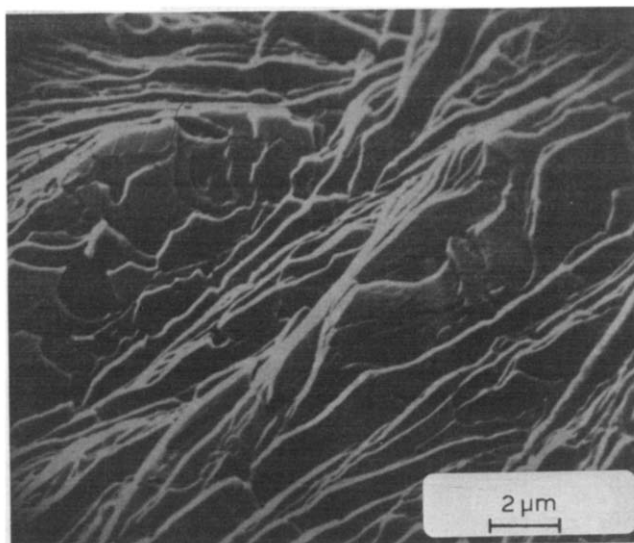

Figure 2 Scanning electron micrograph of an etched surface of a specimen crystallized at 5 kbar

5 and 6 kbar (*Figure 2*) thicknesses generally ranging from 1000 to 5000 Å. Extended chain lengths for molecules characteristic of the $\bar{M}_N$ and $\bar{M}_W$ values are 1583 and 5542 Å respectively. Samples crystallized at pressures up to 3 kbar showed banded spherulites whereas at 4 kbar non-banded spherulites were observed.

X-ray diffractometry

Unit cell parameters: Values obtained for the three lattice parameters are presented as a function of crystallization pressure in *Table 1*. The values of all three parameters for the pressure crystallized samples are closely similar, there being a slight tendency for the *a* and *b* parameters to decrease with increasing pressure of crystallization. Values for the atmospheric pressure crystallized sample, which are included for completeness, are somewhat different since it was quenched and, hence, not crystallized under identical conditions to the other specimens. This effect has already been noted by other researchers[4,8] and is presumably due to an uneven fold surface in which an appreciable amount of nonadjacent reentry occurs. Our results are within 0.1% of the literature data[5] for similar preparation.

Setting angles: Examples of the diffraction data used in the calculations are shown in *Figure 3*, the intensities of the 110 and 200 peaks being reduced in order to show the details of the higher angle peaks. It can be seen that the high pressure samples show narrower 110 and 200 peaks than the folded chain material. The 210 peaks are both narrower and more intense. Major variations in both
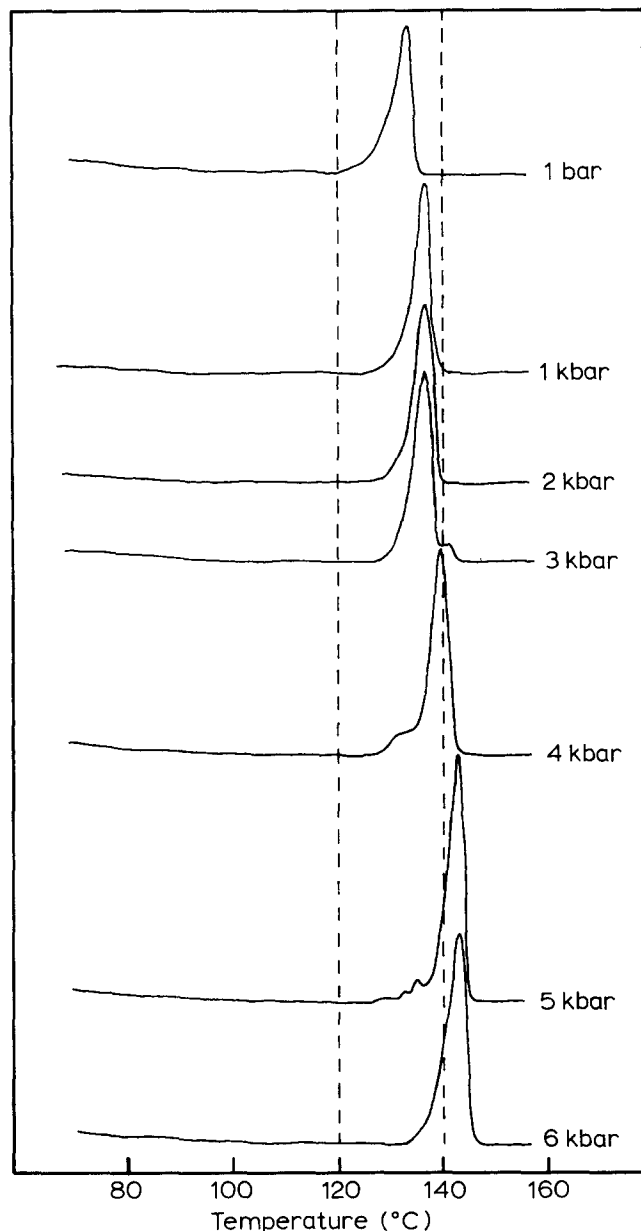

Figure 1 Differential scanning calorimetric traces for specimens crystallized at the pressure indicated

Table 1 Results of X-ray diffraction analyses

Crystallization conditions		Unit cell data				Reliability factor
Pressure	Temperature	*a*(Å)	*b*(Å)	*c*(Å)	θ	*R*(%)
1 bar	quench	7.38	4.90	2.55	48	9.86
1 kbar	150°C	7.41	4.92	2.55	47	8.46
2 kbar	170°C	7.44	4.92	2.55	48	9.0
3 kbar	190°C	7.40	4.93	2.55	47	8.89
4 kbar	210°C	7.41	4.92	2.55	45	7.64
5 kbar	227°C	7.41	4.93	2.55	44	5.58
6 kbar	243°C	7.40	4.92	2.54	43	6.71

absolute and relative intensities of the peaks between 37° and 45° can easily be discerned. A minor peak appears at ~19° with residual hexagonal phase[10].

Setting angles have been determined using the method of Kavesh and Schultz[5] together with the temperature coefficient corrections of Kobayashi[4]. The definition of setting angle used was the original one of Bunn[1], namely the angle subtended by the chain to the *b*-axis of the crystal. Values are presented graphically in *Figure 4* and exactly in *Table 1* together with the reliability (*R*) factors. Values of calculated and measured structure factors are shown in *Table 2* for all materials. Setting angles have been estimated using the lattice parameters determined here and also using literature values[5] however, variations so produced in the setting angle are an order of magnitude lower than the intrinsic error. It is clear that the folded chain crystals show a setting angle of 47° to 48° and that the extended chain crystals manifest values which decrease with increasing crystallization pressure. The lowest value observed was that for the material crystallized at 6 kbar which is over 4° lower than that characteristic of folded chain material.

DISCUSSION

A very clear difference in setting angle is observed between folded chain and extended chain crystals, all of which were produced by slow cooling followed by a long period at the chosen crystallization temperature. Despite these slow crystallization conditions the setting angle continued to decrease with increasing crystallization pressure. Although it is well known[11,12] that molecular weight fractionation occurs under the conditions used, it is also clear that the higher molecular weight fractions cannot be fully extended since crystals are not observed of appropriate thickness. Some folded chain material is therefore likely to be present in an amount dependent on the molecular weight distribution. A possible explanation for the continued decrease in setting angle with increasing pressure could therefore be that the higher melt temperatures permit better organization of the longer more sluggish molecules. The lowest measured value of 43°–44° may therefore not be the true unperturbed value but an average dependent on the folded chain content. The
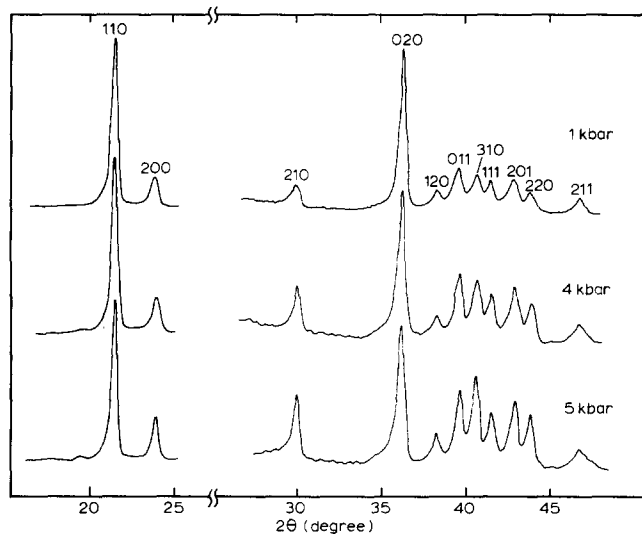

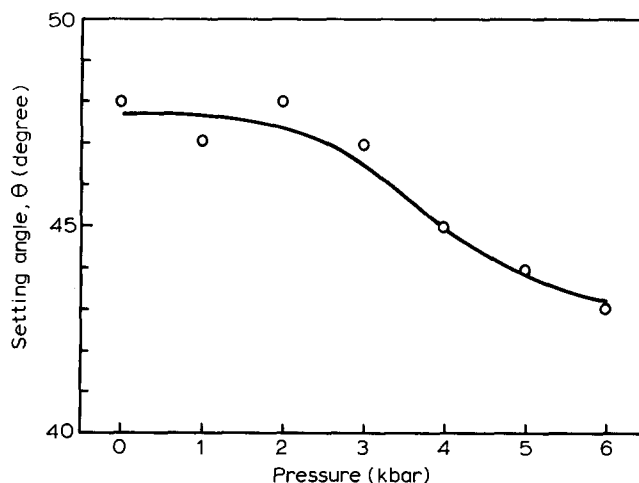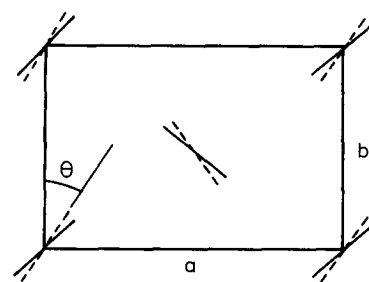**Figure 3** Diffraction traces of specimens crystallized at 1, 4 and 5 kbar

Figure 4 Variation of setting angle with crystallization pressure

Table 2 Observed and calculated structure factors of LPE at various pressures

	1 bar		1 kbar		2 kbar		3 kbar		4 kbar		5·kbar		6 kbar	
	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c
110	20.10	19.80	19.20	19.77	19.05	19.76	18.90	19.77	18.60	19.65	18.10	19.60	18.22	19.55
200	15.80	17.26	16.30	17.35	16.40	17.31	16.40	17.35	16.90	17.50	17.62	17.56	18.10	17.65
210	2.90	3.07	3.16	3.06	3.15	3.06	3.12	3.06	3.53	3.02	3.28	2.99	3.14	2.97
020	13.01	11.75	12.74	11.61	13.10	11.76	12.71	11.61	11.25	11.29	10.95	11.13	10.40	10.98
120	3.57	2.82	3.70	2.83	3.60	2.83	3.32	2.83	3.01	2.82	2.96	2.81	2.62	2.80
011	6.07	7.08	6.60	7.28	6.70	7.04	7.10	7.18	7.84	7.34	7.92	7.42	8.10	7.51
310	6.03	7.71	6.45	7.79	6.38	7.74	6.32	7.79	7.20	7.93	8.60	8.01	8.40	8.09
111	4.84	4.77	5.25	4.70	5.29	4.78	5.60	4.70	5.07	4.51	4.62	4.46	4.50	4.38
201	9.72	8.18	9.02	8.08	8.90	8.16	9.10	8.08	8.94	7.84	8.60	7.75	9.10	7.60
220	5.16	6.07	5.35	6.05	5.47	6.09	5.46	6.05	5.37	5.96	6.11	5.92	6.40	5.89
211	5.83	4.82	6.47	4.90	5.86	4.81	5.97	4.90	5.99	5.03	4.79	5.10	4.65	5.17
400	6.34	6.67	6.30	6.67	6.10	6.66	6.00	6.67	6.30	7.11	6.45	7.25	6.37	7.41

differential scanning calorimetric traces cannot assist here since the folds with which we are concerned are present in extended chain crystals. Further detailed analyses of the lamellar thicknesses may be of assistance. However since crystals are observed of thicknesses comparable to the extended lengths of molecules of both number and weight average degrees of polymerization the fraction of folded chain material should be relatively small and the value of 43°–44° cannot be much above the unperturbed value.

It has been known for some decades that the growth of polyethylene lamellae in the bulk follows the b-axis. The exact nature of the growth face and hence the fold plane, if such an organized entity exists, is still unknown. (110) and (200) growth faces are well known in polyethylene single crystals[13] even from poor solvents[14]. Supercooling effects are known to produce skeletalization and the conversion of lozenge shaped crystals to laths[15] reminiscent of growth in the bulk. Recent studies of lamellar profiles in linear polyethylene[16] have shown that S-shapes are common in banded spherulites. Regardless of the molecular origin of the S-shape it seems likely that the cause is some type of surface stress[17]. Non-twisted lamellae such as are commonly encountered in, for example, cis-polyisoprene[18] have rectanguloid cross sections. Single crystals of polyethylene as well as axialitic bulk polyethylene have profiles different from both. In single crystals hollow pyramids generally occur whereas axialites have a corrugated growth front, both of which arise from a fold surface which is oblique to the unit cell.

It has been shown that the setting angle of single crystals of polyethylene is 48°–50°[4], which is slightly larger than the 47°–48° observed here for folded chain polyethylene but further from the presumably unperturbed value of 43°–44° which we have obtained for extended chain material. Should the presence of adjacent reentry chains influence the setting angle then single crystals would be expected to show the greatest divergence from the extended chain value. Setting angle measurements are averages, like all other parameters from X-ray diffraction studies. The values obtained for specimens other than extended chain material must of necessity be an average of unperturbed chains in the central portions of the lamellae and those near the surfaces which have been perturbed by the folds. It might therefore be expected that as lamellar thicknesses increase, the setting angle should decrease and approach that of extended chain material. Quenched samples have been reported[4] as having a setting angle of 46°–48° whereas slowly crystallized non-banded crystals have a value of 44°–46°.

It is interesting to note that the range of permissible theoretical values is from 44° to 49°[18]. Folded chain single crystals show the upper limit and extended chain materials the lower limit. Errors of ±1° are reasonable even for the most elaborate of data analyses. Reliability factors for our extended chain material are better than for our banded spherulitic material (see *Table 1*) largely due to the much narrower peaks observed for the former. Since the setting angle of the folded chain single crystal is at the maximum permissible value, this value of 49° may be taken as that of a maximally perturbed crystal and presumably is characteristic of all the chains in the crystal. Half the single crystal thickness (50–60 Å) would therefore correspond to the minimum depth of crystal perturbed by regular adjacent reentry folding. Annealing of the same

crystal[2] to a lamellar thickness of 270 Å permitted a setting angle of 46°–48° consistent with measurements for bulk crystallized quenched material.

In practice there must be a transition zone, perhaps only a few bonds long, in which the setting angle changes from 49° in the surface region to the 44° in the central core. However, if we assume that it is small compared to both the surface and core regions then a very simple model can be used to predict the effect of lamellar thickness on setting angle. If the volume fractions of surface and core material are V_s and V_c respectively then the observed setting angle, θ, can be written in terms of the setting angles of the surface and core materials, θ_s and θ_c respectively as:

$$\theta = V_c\theta_c + V_s\theta_s$$

Defining the surface thickness as Δl permits the volume fractions, V_s and V_c, to be written as $2\Delta l/l$ and $(l - 2\Delta l)/l$ where l is the lamellar thickness. Hence:

$$\theta = \theta_c + \frac{2\Delta l}{l}(\theta_s - \theta_c)$$

Assuming a Δl of 60 Å from single crystal data and that θ_c and θ_s are at the theoretical limiting values leads to:

$$\theta = 44° + \frac{120}{l}(5°)$$

This leads to calculated values of 46.2° and 45.6° for crystals of thicknesses 270 and 388 Å respectively whereas measured values are 46°–48° and 44°–46° respectively[4]. A better comparison is not possible because of the ±1° uncertainty in setting angle values. The value of 60 Å for a perturbed layer is the minimum possible if indeed the value of 49° is the highest possible setting angle. It is also highly likely that the perturbed layer will vary in depth with crystallization conditions. Slow crystallization whilst producing thicker crystals would also increase the adjacent reentry fraction and be partially self compensating, whereas quenching whilst reducing the adjacent reentry fraction would produce other types of surface structure and hence perturbing forces. So it is believed that although a simple model can predict observed values, further elaboration would be futile due to the intrinsic errors of setting angle determinations.

It is however clear that theoretical calculations of (a) the crystal structure of polyethylene should consider 44° to be the setting angle of the unperturbed crystal and (b) the conformation of tight folds should consider 49° to be the setting angle near the surface.

REFERENCES

1   Bunn, C. W. *Trans Faraday Soc.* 1939, **35**, 482
2   Davis, G. T., Eby, R. K. and Martin, G. M. *J. Appl. Phys.* 1968, **39**, 4973
3   Davis, G. T., Eby, R. K. and Colson, J. P. *J. Appl. Phys.* 1970, **41**, 4216

4   Kawaguchi, A., Ohara, M. and Kobayashi, K. *J. Macromol. Sci.* 1979, **B16**, 193
5   Kavesh, S. and Schultz, J. M. *J. Polym. Sci. A-2*, 1970, **8**, 243
6   Bassett, D. C. and Turner, B. *Phil. Mag.* 1974, **29**, 925
7   Davidson, T. and Wunderlich, B. *J. Polym. Sci., A-2*, 1969, **7**, 377
8   Yasuniwa, M., Nakafuka, C. and Takemura, T. *Rep. Prog. Polym. Phys. Jpn.* 1972, **15**, 133
9   Naylor, K. L. and Phillips, P. J. *J. Polym. Sci., Polym. Phys. Edn.* in press
10   Bassett, D. C., Block, S. and Piermarini, G. J. *J. Appl. Phys.* 1974, **45**, 4146
11   Prime, R. B. and Wunderlich, B. *J. Polym. Sci., A-2*, 1969, **7**, 2061
12   Rees, D. V. and Bassett, D. C. *J. Polym. Sci., A-2*, 1971, **9**, 385
13   Keller, A. *Polymer* 1962, **3**, 393
14   Khoury, F. *Discuss. Faraday Soc.* 1979, **68**, 404
15   Wunderlich, B., James, E. A. and Shu, S.-W. *J. Polym. Sci.* 1964, **A-2**, 2759
16   Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc.* 1981, **A377**, 25, 39, 61
17   Keith, H. D. and Padden, F. J., to be published
18   Edwards, B. C. and Phillips, P. J. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 2117
19   McCullough, R. L. and Lindenmeyer, P. H. *Kolloid Z-u-Z Polymere* 1972, **250**, 440