The location of comonomer units in crystallizable copolymers: Brominated polyethylene

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Single crystals of polyethylene brominated in suspension contained 0% to 19.1% bromine (Br) on their fold surfaces. 'As brominated' crystals, crystals annealed at 388 K and 'melt-crystallized' samples were all characterized using d.s.c. and WAXS. Melting points decreased with increasing levels of bromine for each set of samples. Heats of fusion for the 'as brominated' crystals were approximately constant up to 19.1% Br content. The annealed and 'melt recrystallized' brominated samples all possessed lower ΔH_f values than the 'as brominated' crystals. Polyethylene unit cell dimensions for the 'as brominated' were constant to approximately 7% Br. At a concentration of 19.1% Br both the '*a*' and '*b*' dimensions of the unit cell increased, presumably because of distortions at the crystal/fold surface interface. The '*a*' and '*b*' dimensions of the annealed crystals increased at low levels of Br (<1 Br atom/fold) then decreased at higher Br concentrations (>1 Br atom/fold). These dimensions increased continuously with Br concentration in the 'melt crystallized' samples. Both the observed WAXS and d.s.c. data on these materials are consistent with the inclusion of comonomer units in the polyethylene crystals.

(Keywords: comonomer units; crystallizable copolymer; brominated polyethylene)

INTRODUCTION

A large number and diversity of experiments have been conducted on crystallizable copolymers in an attempt to determine the role of comonomer units in crystallization, annealing and melting. Interpretation of results obtained from these studies is often very difficult because the distribution of comonomer units throughout the copolymer chain is not well defined. In addition, these units may be partitioned between crystalline and amorphous phases of the copolymer. The concentration and distribution of comonomer units may be very different within each phase.

Frequently, wide-angle X-ray scattering (WAXS) is used to study the structure of semi-crystalline copolymers. The effects of copolymer composition on unit cell parameters have been investigated by several workers[1-11]. Baker and Mandelkern analysed two sets of branched polyethylene (PE) samples using WAXS[6]. An increase in the '*a*' dimension of the PE unit cell was observed as the number of methyl or n-propyl branches along the PE chain was increased. This effect was attributed to incorporation of branches into the crystalline phase of PE. However, for any specified level of chain branching the observed change in '*a*' was smaller for the n-propyl branched system. This was attributed to a lower concentration of n-propyl branches in the crystalline phase of the sample. Presumably the smaller methyl branch is more easily incorporated into the crystal structure of PE.

Roe and Greniewski studied the effects of chlorination on the crystallization of PE[5]. As the concentration of chlorine (Cl) atoms along the backbone become larger the '*a*' dimension of the unit cell for PE increased. This behaviour was attributed to greater levels of Cl incorporation into the crystalline phase of PE. This trend is consistent with their experimentally determined heat of fusion (ΔH_f) values. ΔH_f was observed to decrease as the degree of chlorination increased. Small-angle X-ray scattering (SAXS) studies performed on these materials by Roe and Greniewski showed that the chlorinated units were partitioned between the crystalline and amorphous phases of PE.

WAXS was used to study the crystal structure of a series of vinylidene chloride–methyl acrylate (VDC–MA) copolymers[9]. The '*a*' dimension of the unit cell for the 'as polymerized' samples was observed to increase as the fraction of MA was increased from 4% to 8.5%. These results combined with information obtained from SAXS and theoretical sequence distribution calculations indicated that MA units were being incorporated into the crystal structure of poly(vinylidene chloride) (PVDC).

A detailed structural analysis of ethene/propene and ethene/1-butene copolymers was conducted by Holdsworth and Keller using nitric acid etching techniques[11]. For increasing etching times the '*a*' dimension of the unit cell was observed to decrease and approach that of pure PE. Since etching presumably primarily attacks amorphous regions (fold surfaces) it was postulated that many of the comonomer units were in this region.

In each of the previously described studies changes in unit cell dimensions were observed with changing

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copolymer composition. Generally, this effect is attributed to the incorporation of comonomer units into the crystalline phase of the material. This interpretation assumes that only comonomer units which are incorporated into the crystal will effect observed cell dimensions. However, if comonomer units are grouped at sites adjacent to the crystalline part (fold surfaces) then distortions may exist in nearby crystalline regions. These distortions may cause observable changes in the cell dimensions of the crystalline component.

Several workers have studied 'model' copolymer systems to determine the effects of primarily excluded comonomer units on observed structural data. These materials were produced by chemically modifying the fold surface of single crystals held in suspension. Harrison and Baer analysed single crystals of PE which were halogenated (chlorinated or brominated) in suspension (ref. 12, 13). Results obtained from kinetic, thermal and infrared studies indicated that the halogenation reaction was selective to the fold surface of the crystals. No changes were observed in the ΔH_f values for each of the halogenated (as prepared) crystals. However, after these crystals were melted, then recrystallized, a significant drop in ΔH_f was observed. SAXS measurements showed no significant increase in fold period with increasing levels of bromination on the as prepared materials. However, after annealing the crystals containing lower levels of Br showed a significant increase in fold period. At higher Br concentrations very little change in fold period was observed. Apparently as the Br content on the fold surface increases, movement of fold material into the crystal becomes increasingly more difficult.

Similar behaviour was observed by Marchetti and Martuscelli for single crystale of polybutadiene (PBD) brominated in suspension[14]. From SAXS measurements it was found that the ability of the crystals to anneal was inhibited by the presence of the Br atoms on the fold surface. The fold period of these materials did not change significantly after annealing.

It is apparent from the literature on copolymer crystallization that the location and distribution of comonomer units in a semi-crystalline copolymer can vary considerably. Without prior knowledge of comonomer distribution and location, experimental results can be correlated only to existing copolymer theory. Unfortunately assumptions and requirements underlying present copolymer crystallization theory are not met under practical crystallization conditions.

In this study an attempt is made to correlate a known copolymer structure to experimentally observed structural and thermal behaviour. PE single crystals brominated in suspension to various degrees are employed because the location, concentration and to some degree the distribution of comonomer units (CHBr) within the system are known. (The Br units are presumably located almost exclusively on the surface of the crystals.) The techniques of WAXS and differential scanning calorimetry (d.s.c.) will be used to study the role of comonomer units during crystallization in these materials. The type of information gathered here is used to assist in the analysis of the effects of comonomer exclusion on unit cell parameters, heat of fusion and melting point of PE. Once these effects are determined, the crystals will be annealed and melt crystallized in separate experiments. Structural and thermal data obtained from these sets of samples will be compared with that obtained from the 'excluded comonomer' system studied previously. It is hoped that this work will provide a basis for deciding whether or not (CHBr) units are incorporated into the crystalline lattice of PE after thermal treatment. If the comonomer units are incorporated, then one can examine in detail its effects on the thermal properties and structural parameters of PE.

EXPERIMENTAL

Single crystals of Marlex 6001 were previously grown from a 0.1% xylene solution at 370 K (T_c) using a self-nucleation technique. The crystals were washed several times with fresh xylene heated to T_c. The suspension was cooled and transferred to distilled CCl_4 and placed in a reaction vessel heated to 303 K under a nitrogen atmosphere. Elemental bromine was added in the ratio: 1 g crystals/240 ml CCl_4/6 ml Br_2. After illuminating the mixture with ultraviolet (u.v.) light for an appropriate time, samples were withdrawn and washed with CCl_4 in order to remove excess bromine. The crystals were then exchanged to acetone to remove CCl_4 and residual bromine. The samples were tested for bromine and chlorine content by neutron activation analysis. Little or no chlorine was detected in any sample. The weight per cent bromine present on the fold surface of each sample is listed in *Table 1*. Also listed are the approximate number of Br atoms per fold in the crystal. These numbers were calculated by assuming a fold period of 150 Å for the single crystals.

Crystalline melting points (T_m) of pure PE single crystals and the brominated crystals were measured using d.s.c. Melting points were obtained by heating 0.3 mg samples at 20 K/min. The temperature of the extrapolated onset of the melting endotherm was recorded as T_m.

Heats of fusion (ΔH_f) were obtained for each sample by heating approximately 2 mg of the crystals at a rate of 20 K/min. ΔH_f values were determined by constructing a baseline from similar starting and ending temperatures for each sample and measuring the enclosed area per known weight of sample. An average of at least two samples of each composition was used to determine ΔH_f. To ensure consistent measurement of peak areas (ΔH_f) and T_m, daily temperature calibration and area normalization were performed by heating a known weight of an indium standard.

Samples of pure PE crystals and brominated crystals were annealed in the differential scanning calorimeter (d.s.c.) cell at 388 K for 1 h. The thermal correction for the isothermal annealing temperature was determined by heating an indium standard at rates of 80, 40, 20, 5 and 2.5 K/min. The necessary temperature correction

Table 1 Composition of brominated polyethylene single crystals

Wt% Br on fold surface	Approximate Br atoms/fold
0	0
0.9	0.2
1.1	0.25
1.8	0.4
3.6	0.8
6.7	1.5
19.1	4.1

was obtained by constructing a plot of the error in the indium melting temperature versus heating rate and extrapolating back to zero heating rate. Melting points and heats of fusion for these materials were recorded as described previously.

Samples of pure PE crystals and brominated crystals were also cooled (20 K/min) and quenched (~60 K/min) from the melt. Each sample was heated to 426 K then cooled in the d.s.c. at the desired rate. Again T_m and ΔH_f were determined for these samples as described previously.

Wide-angle X-ray scattering studies were conducted on the pure PE crystals and brominated crystals using the Debye–Scherrer powder method. The asymmetrical method of film loading was used. CuKα ($\lambda = 1.541838$ Å) radiation was used to obtain the X-ray patterns. CuKβ was removed from the X-ray beam using a nickel filter. The X-ray tube was operated at 40 kV and 20 mA. Diffraction arcs were recorded on narrow strips of film placed inside the Debye–Scherrer camera. An NBS (National Bureau of Standards) silicon standard was used to correct for any film shrinkage or stretching which may have occurred during film processing. Correct silicon to sample ratios were developed through trial and error.

Powder diffraction studies were also performed on samples of each composition annealed at 388 K for 1 h. These samples were prepared by placing the crystals in an annealing chamber held over a beaker of refluxing pyridine (boiling point = 388.1 K). The samples were then removed from the chamber and allowed to cool in air at room temperature.

Both the brominated and pure PE samples were melt-recrystallized by the following scheme. The samples were placed in an annealing chamber held at 426 K over refluxing *N*,*N*-dimethylformamide (boiling point = 426 K) for 90 s. The samples were then removed from the chamber and allowed to cool in air at room temperature. Apparently no significant level of dehydrohalogenation occurred at 426 K as the samples remained white after this treatment.

X-ray exposure times for each sample are listed in *Table 2*. For longer exposure times less standard was required to obtain silicon lines of good intensity.

A computer program written by Appleman and Evans was used to calculate unit cell dimensions from the observed WAXS reflections[15]. The program accepts as input any combination of indexed and/or unindexed 2-theta or '*d*' values, along with the crystal system, extinction criteria and approximate lattice parameters. Peak positions calculated by the program from the input crystal system and cell parameters are compared with the experimentally observed peak position. A match between calculated and observed peak positions is made when the difference ($2\theta_{calc} - 2\theta_{obs}$) or ($d_{calc} - d_{obs}$) lies within statistical criteria defined by the user. Satisfactorily indexed observed peaks were used to compute new lattice parameters by least-squares refinements. Errors in the cell parameters were determined by calculating the standard deviation of the least-squares plot.

Table 2 X-ray exposure times (hours) for the brominated PE samples after various thermal histories

% Br	As brominated	Annealed	Melt-recrystallized
0	39.8	43.1	128
0.9	40.2	44.6	130
1.1		50.2	163
3.6		48.9	179
6.7		73.1	289
19.1	42.4	75.1	426

RESULTS AND DISCUSSION

The observed melting points obtained from d.s.c. of pure PE crystals and as brominated crystals are listed in *Table 3*. It is apparent from the data that the melting point of these materials continuously decreases in temperature up to approximately 4–5 % bromine (Br). This concentration range corresponds to approximately 1 Br atom per fold. However, the T_m of the brominated crystals containing 19.1 % Br (~4 Br atoms/fold) is not significantly different from that of a crystal containing 3.6% Br (~1 Br atom/fold). A similar trend in melting behaviour was observed for brominated single crystals of PE studied by Harrison and Baer[12]. The observed trend was attributed to several factors. A decrease in fold surface entropy, an increase in fold surface energy and a loss in the ability of the polymer to anneal during heating were considered possible causes.

Melting points for annealed crystals and melt recrystallized materials are also listed in *Table 3*. Annealed crystals containing low Br concentrations melt at higher temperatures than the original crystals of similar composition. However, at 19.1 % Br composition, the annealed and unannealed brominated crystals melt at approximately the same temperature. The initial increase in melting temperature for annealed samples may be caused by an increase in fold period and crystal perfection in these materials. It is also possible that during annealing some isolated bromine atoms may be pulled into the crystal. This can produce a decrease in the surface energy and an increase in surface entropy of the fold. This in turn would cause the melting point of the crystal to increase. At higher concentrations of Br (19.1 %) the large quantity of these units in the folds apparently prevents any significant amount of annealing from occurring. Hence no difference is observed in the melting behaviour of this sample after annealing.

Table 3 Observed d.s.c. melting temperatures (extrapolated onsets) for brominated PE samples after various thermal histories. Heating rate, 20 K/min

Sample	Wt % Br	Onset T_m (K)
As Brominated	0	396.5
	0.9	395.5
	1.1	395.2
	1.8	395.0
	3.6	394.3
	19.1	393.9
Annealed	0	397.0
	0.9	396.5
	1.1	396.2
	1.8	396.2
	3.6	395.2
	19.1	394.3
Melt-recrystallized	0	399.2
	0.9	397.9
	1.1	396.4
	1.8	395.6
	3.6	391.4
	19.1	381.4

It must be realized that at a concentration of approximately 4.7 wt% Br (1 Br atom/fold) a transition from increasing numbers of 'defects' (isolated Br units) to increasing size of 'defects' (groups of Br units) is occurring in these samples. This trend is pictorially represented in *Figure 1*. One might expect that materials with Br concentration less than 1 Br atom/fold (small defects) will be able to anneal and those with greater than 1 Br atom/fold will anneal with increasing difficulty. This assumption is supported by small-angle X-ray scattering studies performed by Harrison and Baer on these materials[12]. After annealing an increase in '*l*' was observed at low Br contents, but decreased as the level of Br was raised. At approximately 10% Br the long periods of the original and annealed crystals were nearly equal. Clearly the ability of these systems to anneal decreases as the amount of Br on the fold surface is raised.

Melting points of melt-crystallized materials show a different trend compared with those of annealed or original crystals. At low levels of Br the melting point of the melt recrystallized materials is higher than the original or annealed crystals. However, at higher concentrations of Br the melting temperatures drop to well below those of the original crystals. Perhaps, as the initial concentration of Br is increased (to a level of 1 Br atom/fold) isolated comonomer units are added to the polymer at a decreasing distance apart along the chain. Presumably these isolated comonomer units can be incorporated as defects into the crystalline structure of PE. As the number of defects increases, the level of perfection in the crystal decreases and the melting temperature drops. At one Br unit per fold a maximum number of isolated co-units are present in the material each separated by a minimum distance along the polymer chain (one fold length). Additional quantities of bromine serve only to increase the size of the defect (grouped Br units). As the size of the defect increases a greater distortion occurs when these units are incorporated into the crystalline structure. This may greatly depress the melting point of the material.

However, if one assumes that a complete rejection of comonomer units (Br) occurs in these systems then a decrease in melting point would also be expected over this composition range. This would result from a diminished crystallizable sequence length, as well as an increased entropy of melting, as we increase the Br concentration. After the addition of 1 Br atom per fold, an increased depression in T_m may occur because of reasons described for the as brominated materials, namely the size of the defect increases. A theoretical description of the functional equivalence of the influence of comonomer inclusion and rejection on melting has been discussed elsewhere[16].

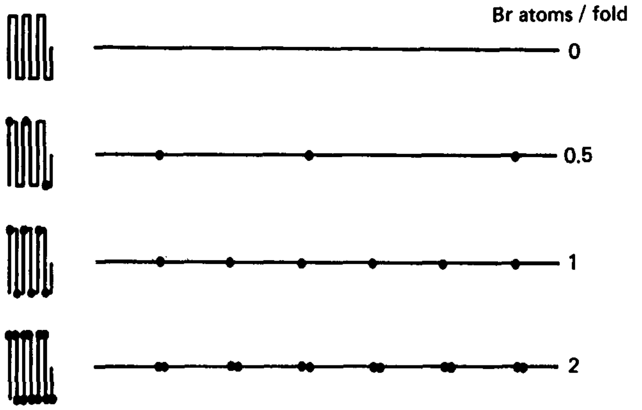

Figure 1 Folded chain crystal brominated to varying degrees (left). The extended chain on the right. The numbers refer to the number of Br units per fold. Proceeding from 0 to 1 Br atom/fold one increases the number of isolated Br units (defects) and decreases the distance between them. On going from 1 to 2 Br atoms/fold the number of defects and the distance between them stay approximately constant, only defect size changes

Table 4 Comparison of the observed melting temperatures (endothermic peaks) with those calculated from equation (1)

Sample	Wt% Br	$T_m(K)_{obs}$	$T_m(K)_{calc}$	$\Delta T_m(K)$
Melt-recrystallized	0	–	–	–
	0.9	404.7	396.2	8.5
	1.1	403.6	392.6	11.0
	1.8	402.6	377.5	25.1
	3.6	400.0	354.8	45.2
	19.1	387.4	218.0	169.4

Table 5 Experimentally determined heats of fusion for brominated PE samples after various thermal histories

Wt% Br	As brominated	Annealed	Melt-recrystallized
0	54.7	55.3	45.7
0.9	54.9	54.1	43.1
1.1	54.6	53.2	42.0
1.8	54.4	51.1	39.3
3.6	54.4	49.8	35.5
19.1	52.5	48.9	19.1

A comparison was made between the endothermic peak temperatures of melt-recrystallized materials and the theoretical melting temperatures calculated from the Flory equation. These results appear in *Table 4*. The melt-recrystallized materials containing low concentration of Br exhibit a melting point depression similar to that predicted by the Flory copolymer melting equation:

$$1/T_m - 1/T_m^0 = R/\Delta H_f^0 \ln X_A \qquad (1)$$

This suggests that these materials are behaving similarly to random copolymers during melting. However, at higher concentrations of Br the difference between observed and predicted melting temperatures becomes very large. The experimental values for 'melting point' are always much higher than predicted. This is the type of behaviour which would be expected from a copolymer having a more blocky distribution of comonomer units. Increasing the Br concentration above that of 1 Br atom/fold will produce clusters of Br units (blocks) on the fold surface of the crystal.

Heats of fusion (ΔH_f) for the original crystals, annealed crystals and melt recrystallized materials are listed in *Table 5*. The ΔH_f values are normalized per weight per cent of polyethylene in the sample. For the original crystals ΔH_f remains relatively constant over the entire composition range. A slight decrease in ΔH_f is noted for the 19.1% Br sample. Possibly the large concentration (>4 Br atoms/fold) of Br in this sample places strain on the crystalline region adjacent to the fold surface and this could decrease ΔH_f. At all other compositions it appears that the crystalline portion of the single crystals is unchanged upon bromination.

The ΔH_f values for annealed crystals are initially higher (0% Br) than the original crystals, but fall below them as

Br is added to the system. At low concentrations of Br (<1 Br atom/fold) some of these co-units may be incorporated into the crystal as defects during annealing. This depresses the ΔH_f (crystallinity) of the material. At Br concentrations greater than 1 Br atom/fold, incorporation of 'defects' becomes more difficult due to their increased size. However, when one of these larger defects is 'pulled' partially into the crystal during annealing, severe disordering of the structure in this region may occur. This would result in a larger decrease in the ΔH_f of the material. Based on the ΔH_f results obtained here and the SAXS results discussed previously it appears as though isolated Br units can be 'pulled' into the structure during annealing. The long periods of these types of samples increased while their ΔH_f values decrease.

A very large decrease in ΔH_f is observed for melt recrystallized materials with increasing levels of Br. This is consistent with the inclusion of comonomer units (defects) within a crystal structure. At small comonomer concentrations isolated Br units can become incorporated into the crystal. At higher levels of Br, groups of co-units may be 'trapped' in the crystal during cooling from the melt. As the concentration or size of defects in a crystal increases the ΔH_f associated with that material will decrease.

To define more accurately the location of comonomer units in the annealed and melt-crystallized materials and to determine the effect of their location on the unit cell parameters of PE, an extensive WAXS study was performed on these materials. Unit cell dimensions (a, b, c) for the orthorhombic unit cell were calculated from the experimentally observed diffraction lines for each sample. A least-squares approximation was used to 'refine' the values for these parameters.

The experimentally determined cell parameters for the original crystals appear in *Table 6*. It is apparent that no significant change is observed in the cell parameters of PE at an intermediate level (6.67% Br) of bromine. This concentration corresponds to approximately 1.5 Br units per fold. However at a composition of 19.1% Br (approximately 4 Br atom/fold) slight increases are noticed in both the 'a' and 'b' dimensions of the cell. There was no change observed in the 'c' dimension (chain direction) over this composition range. Possibly the large quantity of Br present on each fold at this composition (19.1% Br) places a significant strain on the adjacent crystalline region. This structural distortion produces an observable change in the average unit cell dimension of PE. This idea agrees favourably with the experimentally determined ΔH_f value for this sample. The small observed decrease in ΔH_f for this sample could be due to disruption of the crystal at the fold/core interface. This suggests that comonomer units which are much larger in size than the primary repeat unit can cause observable changes in the unit cell dimension of material without being incorporated into the crystalline structure.

Table 6 Unit cell parameters (Å) for brominated PE after various thermal histories (±0.003 Å)

Br in sample (%)	Unit cell parameter		
	As brominated	Annealed	Melt-crystallized
0	a=7.414	7.415	7.416
	b=4.943	4.945	4.933
	c=2.550	2.549	2.547
0.9	a=	7.423	7.421
	b=	4.950	4.941
	c=	2.548	2.546
1.1	a=	7.432	7.431
	b=	4.957	4.939
	c=	2.551	2.542
3.6	z=	7.434	7.441
	b=	4.956	4.972
	c=	2.549	2.549
6.7	a=7.416	7.427	7.480
	b=4.941	4.945	4.990
	c=2.551	2.549	2.545
19.1	a=7.423	7.424	7.484
	b=4.952	4.949	4.999
	c=2.551	–	2.550

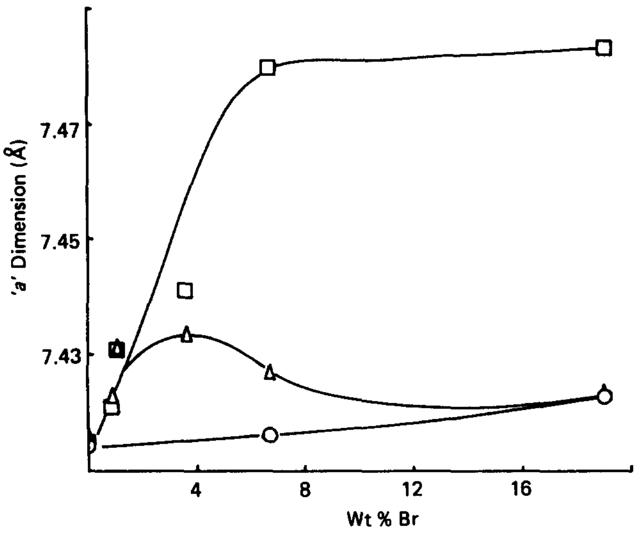

Figure 2 Plot of the 'a' dimension in the unit cell of PE *versus* wt% bromine for: (○) as brominated crystals; (△) annealed crystals; (□) melt-recrystallized polymers

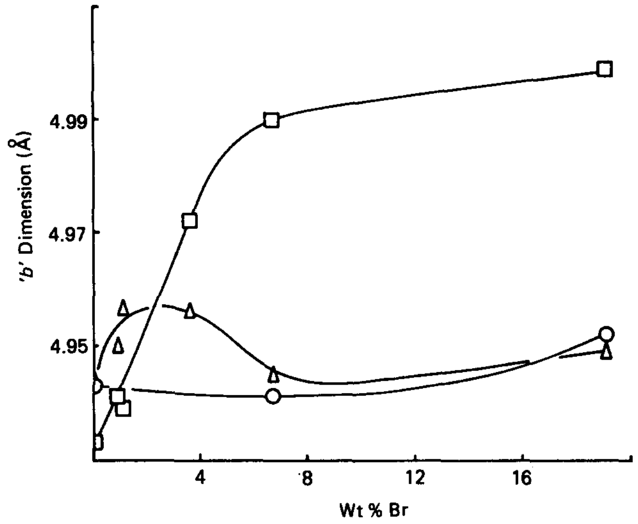

Figure 3 Plot of the 'b' dimension in the unit cell of PE versus wt% bromine for: (○) as brominated crystals; (△) annealed crystals; (□) melt-recrystallized polymers

Unit cell dimensions obtained for annealed crystals and melt recrystallized materials are also given in *Table 6*. The variation in the 'a' dimension with composition for these samples is plotted in *Figure 2*. The variation in the 'b' dimension with composition appears in *Figure 3*. A unique trend is observed in these parameters as the level of Br is increased. For the samples containing 0% Br the '*a*' dimension of the annealed crystals is identical to that of the original crystals. However, as Br is added to the system both the '*a*' and '*b*' dimensions of the cell increase. A peak in the parameters is noticed at approximately 3.6% Br. Above this concentration the dimensions (a, b) of the cell decrease with increasing amounts of Br.

Apparently, on annealing at low levels of Br, isolated comonomer units are incorporated into the crystalline structure. This is demonstrated by the increase in '*a*' and '*b*' up to 3.6% Br. At approximately this concentration a transition occurs in the brominated crystals from isolated defect units (<1 Br atom/fold) to groups of defect units (>1 Br atom/fold). Now as the size of the defect increases the ease with which it is incorporated into the structure decreases. Hence, fewer large defects are incorporated into the crystal. This is reflected by the subsequent decrease in cell parameters at these high Br concentrations. These results support SAXS results obtained elsewhere[12]. The inflection in the plot of long period versus composition (*Figure 3*) occurs at approximately the same composition as the peak in the unit cell dimension curves (*Figures 2* and *3*).

At low Br contents samples are able to anneal and incorporate isolated Br units into the structure (*Figure 4a*). However, at approximately 1 Br atom/fold, the ability of the system to anneal per unit increase in Br greatly decreases (*Figure 4b*). Now fewer defects are incorporated into the body of the crystal and the cell dimensions decrease towards those of pure PE.

However, an apparent anomaly occurs with the ΔH_f results. Initially, at low Br concentrations, ΔH_f decreases as the quantity of defects incorporated into the body of the crystal increases (increasing '*a*', '*b*'). At approximately 1 Br atom/fold the number of defects incorporated in the body of the crystal begins to decrease as evidenced by the decrease in the observed cell parameters. Yet ΔH_f continues to decrease. Apparently, as crystals of high Br content anneal, they attempt to pull large defects into the crystal but are unable to do so. Instead, the defect may only be partially pulled into the crystal. This would increase the size of the amorphous region (fold surface) and decrease the crystal core thickness (*Figure 4b*). A lower crystallinity would be reflected in decreasing ΔH_f values. Since the concentration of Br units on the fold surface is presumably still approximately the same as in as brominated crystals the observed cell dimensions are approximately equal, indicating that a similar surface strain effect is occurring. For the highest Br content sample studied (19.1% Br) the cell parameters of the annealed sample are very similar to those of the as brominated material. This supports the SAXS data which showed no increase in '*l*' after annealing. Apparently the dilation observed in the annealed sample of this composition is due primarily to strain caused by crowding of the Br unit adjacent to the crystalline phase.

Unit cell parameters for the melt crystallized materials also appear in *Table 6*. It is clear from these data, and the plots in *Figures 2* and *3*, that the '*a*' and '*b*' dimensions of PE increase with greater levels of Br for these materials. This is consistent with incorporation of defects into the crystal. Upon cooling from the melt the polymer chain must rearrange itself, in the time scale of crystallization, to ensure that the comonomer unit will be excluded from the crystal. If this does not occur then defects will be trapped in the crystal (*Figure 4c*). It is apparent then that as the proportion of isolated Br units in the polymer increases the number of defects which will become trapped in the crystal will also increase. As the defects (Br groups) start to increase in size the mobility of the chain during crystallization will presumably decrease. Now defects which become trapped in the crystal are larger and more disruptive to the structure. Hence the parameters (a, b) observed for the unit cell become larger. Again no change was observed for the '*c*' dimension in the unit cell of these materials.

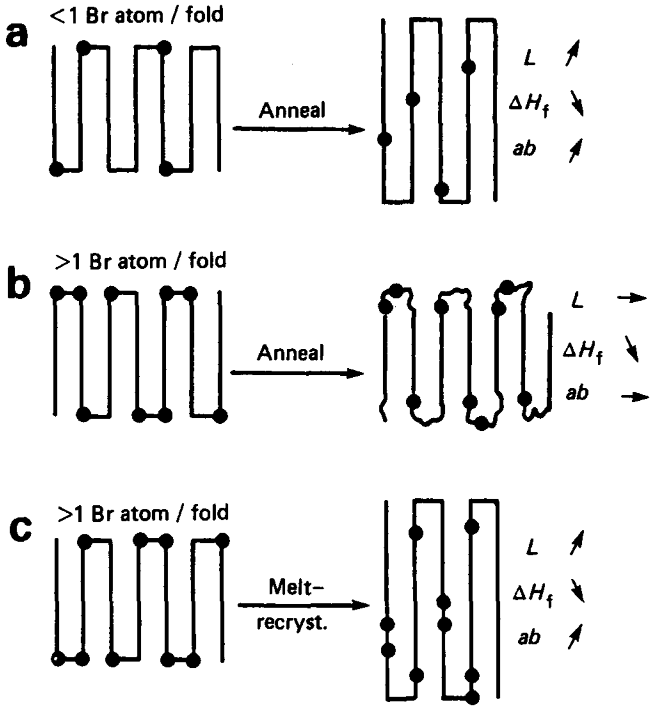

Figure 4 Pictorial representation of brominated crystal for: (a) annealed crystal of low Br content; (b) annealed crystal of high Br content; (c) melt-recrystallized material of high Br content

The rather large change in the cell dimensions for the melt-crystallized samples is in agreement with the large decrease in ΔH_f observed for these materials. The increasingly defective nature of the crystalline phase in these samples serves to decrease the observed ΔH_f. Additional reduction in this value occurs at higher Br concentrations because some of the crystallizable sequences may not be able to crystallize during this rate of cooling from the melt. Perhaps at slower rates of cooling more crystallizable material would be able to arrange itself in a conformation favourable for crystallization.

From the WAXS and d.s.c. data presented here it seems reasonable to assume that incorporation of comonomer units into the crystal is responsible for some of the changes observed in both unit cell dimensions and ΔH_f of the crystalline phase of PE. It is clear from the WAXS data that changes in unit cell dimensions in a material can be caused in two different ways. First geometrically (or otherwise) dissimilar comonomer units which reside in amorphous areas adjacent to crystalline regions may cause the structure to strain to an observable degree (by X-rays). However, the structure distortion caused by these units is apparently much smaller than that observed in crystals containing internal defects. These defects can cause distortions ranging from a local disordering of units (small isolated defect) to massive destruction of all three-dimensional order in a given area (a single large defect or groups of smaller defects). In most systems contributions to changing cell parameters probably come from both included (large and small) and excluded comonomer units or defects. Therefore 'controlled' systems of copolymers, such as those used here, must be employed to help separate out these various contributions.

SUMMARY

Melting points (T_m) of the 'as brominated' PE single crystals decreased with increasing levels of bromine (Br) on the fold surface. This trend may be due to increasing surface energy, decreasing surface entropy and/or loss of the ability of the crystals to anneal during heating as the concentration of Br on the fold surface increases. T_m for the annealed crystal occurred at higher temperatures than those of the original crystals of similar composition. At low Br levels (<1 Br atom/fold) the crystals annealed to higher melting structures (longer fold period). Annealing may have pulled some isolated Br units into the crystal. At higher Br concentrations (>1 Br atom/fold) the difference between the annealed and original crystals' melting points was smaller. These larger groups of Br units (defects) are pulled into the crystal with greater difficulty.

Unit cell dimensions of the brominated PE crystals were also monitored as a function of thermal history. No change was observed in the cell dimensions of the as brominated crystals until very high Br concentrations (19% Br). At this concentration surface strain caused by the large number of bulky Br units located on the fold surface may have caused the unit cell to expand. These results are supported by heat of fusion (ΔH_f) measurements for these materials. Brominated crystals annealed above T_c exhibited increasing 'a' and 'b' dimensions of the unit cell of PE at low Br levels. However, at large Br concentrations the cell dimensions decreased back towards those of the as brominated crystals. Apparently isolated Br units can be incorporated into the crystal body of PE while groups of Br units cannot be easily incorporated during annealing. Again, these results are consistent with the ΔH_f measurements on these materials.

Finally, samples recrystallized from the melt showed very large increases in the 'a' and 'b' dimensions of the cell as the Br content increased. Apparently highly defective crystals were produced during this recrystallization procedure (large amount of Br incorporation). For these samples, a very large drop in ΔH_f with greater Br levels supports this view.

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