An Estimate of the Fold Conformation on Polyethylene Single Crystals by the Method of Surface Halogenation

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ABSTRACT: A new experimental method of surface halogenation is proposed for the analysis of the fold conformations of polyethylene single crystals (PE-SC). The preliminary results of such an experiment and a new model proposed for the conformation and structure of the PE-SC surface are reported. This model is based on the fact that folds must have regularity even though they are long and have only a few degrees of flexibility. Folds of PE-SC are made up of two types of conformations. The length and the type of the folds are distributed so that the experimental results are satisfied. The folds of each type form domains and both the types are mutually convertible.

KEY WORDS Polyethylene / Single Crystal / Halogenation / Fold Conformation / Surface Structure /

In spite of many investigations, the nature of the fold structure of polyethylene single crystals (PE-SC)—tight or loose, regular or random, etc.—is still an unsolved problem. In particular, the study of the fold conformation is only in an early stage of development. Fold conformation models based on energy calculations have been proposed by McMahon, *et al.*,¹ Corradini, *et al.*,² and the present authors.³ From the analysis of 1300–1400 cm⁻¹ amorphous bands of PE, the presence of GG, GTG, GTTG, and GGTGG conformations in the fold has been discussed by Schonhorn, *et al.*,⁴ Krimm, *et al.*,⁵ and Zerbi, *et al.*⁶

However, the energy calculations have been restricted only to the adjacent re-entry folds with the same length and conformation, because it is difficult to calculate the interaction between folding chains.³ Though the analysis of the amorphous bands is able to show the presence of the conformations with G, it gives no answer to the problem of whether the fold contains T sequences longer than TT or not.

Further, some difficulty arises from the separation of the experimental results into fold and crystal parts. The results frequently include and are averaged over the properties of both the parts. At this point, a chemical modification method is of interest. In this paper, the theoretical background and some preliminary results of conformation analysis by halogenation at the surface of SC are reported and the fold conformation is discussed.

THEORETICAL BACKGROUND

Random Halogenation of the Surface of PE-SC

Harrison, *et al.*,⁷ studied the bromination of PE-SC. According to them, it is possible to halogenate only the surface of SC, if the reaction is carried out under mild conditions. Saito, *et al.*,⁸ analysed the high-resolution NMR spectra of chlorinated PE. They concluded that the distribution of chlorine atoms was statistically random in the region of chlorine content below 40 wt%; chemical units containing geminal dichloride were not observed in this region. From these studies, the random monohalogenation of carbon atoms will be possible

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only at the surface of SC, at least in the early stage of the reaction.

Conformations and C—X Stretching Vibrations of Halogenated Polyethylenes

The halogen atom (X) in halogenated PE (X—PE) has two *trans* sites. Let us represent the atoms at the two *trans* sites (hydrogen, carbon or halogen atom) by notations *x* and *y*, and the conformations of the two C—C bonds on either side of the C—X bond (T, G or G') by notations *i* and *j*. Then the conformations around the halogenated secondary carbon atom are represented by the notation S_{xy}^{ij} . When the GG' conformation is excluded, secondary isolated monohalides, vicinal dichlorides, and vicinal—vicinal trihalides have four, eight, and ten different conformations, respectively (including GG' conformation, the corresponding numbers are six, eleven, and fourteen).

The C—X stretching bands of secondary halides are relatively sharp and strong, and appear in the region of 700–500 cm^{-1} , in which PE has no striking bands. The frequencies of these bands are closely related to the conformation S_{xy}^{ij} , especially to *x* and *y*. The assignments of these bands to the conformations have been studied by Shimanouchi, *et al.*,⁹ Shipman, *et al.*,¹⁰ Bentley, *et al.*,¹¹ Iimura, *et al.*,^{12,13} and Gates, *et al.*,¹⁴ though some uncertainties have remained, especially in bromides and iodides. Therefore, in principle, if all the bands are resolved, conformation analysis can be carried out with no assumptions. For example, in a model compound such as 3-chloropentane, four C—X bands are

Figure 1. Four C—Cl stretching bands of 3-chloropentane.

Figure 2. C—Cl stretching bands (S_H and S_X) of a chlorinated polyethylene: Sample, 70°C crystallized single crystal; chlorine content, 14.3%.

resolved into 610 cm^{-1} , 638 cm^{-1} , 660 cm^{-1} , and 675 cm^{-1} , as shown by the arrows in Figure 1. These bands are assigned to S_{HH}^{TT} , S_{HH}^{TG} , S_{CH}^{TG} , and S_{CH}^{GG} , respectively. Then, from the temperature dependence of the intensities of these bands, the energy differences between various conformations and the distribution of conformations at a given temperature can be estimated.

However, in Cl—PE, only two bands at 610 cm^{-1} and 670 cm^{-1} are observed; these bands are broader than the C—X bands of 3-chloropentane, as shown in Figure 2. In comparison with the four bands of 3-chloropentane, therefore, the following assumptions are needed. The 610 cm^{-1} band is the overlapping band of the S_{HH}^{TT} and S_{HH}^{TG} bands, namely the S_H band of Shimanouchi, *et al.*,⁹ and the 670 cm^{-1} band is the overlapping band of the S_{CH}^{TG} and S_{CH}^{GG} bands, namely the S_X band of Shimanouchi, *et al.* With the increase of the vicinal dichloride, the S_{ClH}^{TT} and S_{ClH}^{TG} bands are overlapped with the S_X band. And it is further assumed that the S_{ClCl}^{TT} , S_{ClCl}^{TG} , S_{ClCl}^{TG} , and S_{ClCl}^{GT} bands are not included in those two bands.

If the substituted chlorine atoms are randomly distributed, the probabilities of the conformation are given as in Table I, where *X* is the degree of substitution represented by the number of the chlorine atoms per carbon atom. The intensity ratio of the S_X and S_H bands, $r(S_X/S_H)$, is

Fold Conformation on Polyethylene Single Crystals

Table I. Probabilities of conformations^a

	TT	TG	GG
Conformation			
Probability of the substitution	$\frac{X}{2} \quad \frac{X}{2} \quad \frac{X}{2} \quad \frac{X}{2}$	$\frac{X}{2} \quad \frac{X}{2} \quad (C) \quad \frac{X}{2}$	$\frac{X}{2} \quad (C) \quad (C) \quad \frac{X}{2}$
For halide A	$S_{HH}^{TT} = \left(1 - \frac{X}{2}\right)^2$ $S_{CH}^{TT} = 2\frac{X}{2}\left(1 - \frac{X}{2}\right)$ $S_{ClCl}^{TT} = \left(\frac{X}{2}\right)^2$	$S_{HH}^{TG} = 0$ $S_{CH}^{TG} = \left(1 - \frac{X}{2}\right)$ $S_{ClCl}^{TG} = \frac{X}{2}$	$S_{HH}^{GG} = 0$ $S_{CH}^{GG} = \left(1 - \frac{X}{2}\right)$ $S_{ClCl}^{GG} = \frac{X}{2}$
For halide B	the same as the above	$S_{HH}^{TG} = \left(1 - \frac{X}{2}\right)^2$ $S_{CH}^{TG} = 2\frac{X}{2}\left(1 - \frac{X}{2}\right)$ $S_{ClCl}^{TG} = \left(\frac{X}{2}\right)^2$	the same as the above

^a X, the degree of substitution (the number of the chlorine atoms per carbon atom).

given by the following equation:

$$r\left(\frac{S_X}{S_H}\right) = \frac{\kappa_{CH}^{TG}(n_{TG}/2) + \kappa_{CH}^{GG}n_{GG}}{\kappa_{HH}^{TT}n_{TT} + \kappa_{HH}^{TG}(n_{TG}/2)} \frac{1}{1-X/2} + \frac{\kappa_{ClH}^{TT}n_{TT} + \kappa_{ClH}^{TG}(n_{TG}/2)}{\kappa_{HH}^{TT}n_{TT} + \kappa_{HH}^{TG}(n_{TG}/2)} \frac{2}{1-X/2} \quad (1)$$

where κ_{xy}^{ij} is the absorption coefficient of the S_{xy}^{ij} band and n_{ij} is the mole fraction of the ij conformation ($n_{TT} + n_{TG} + n_{GG} = 1$). The value of κ_{xy}^{ij} depends on xy , but is nearly independent of ij . Really, the ratio $\kappa_{HH}^{TG}/\kappa_{HH}^{TT}$ of 2-chlorobutane determined by the temperature dependence of the peak intensities is nearly 0.9. Therefore, the following approximations are used: $\kappa_{HH}^{TT} = \kappa_{HH}^{TG} = \kappa_{HH}$, $\kappa_{CH}^{TG} = \kappa_{CH}^{GG} = \kappa_{CH}$, and $\kappa_{ClH}^{TT} = \kappa_{ClH}^{TG} = \kappa_{ClH}$. Then eq 1 is simplified and becomes

$$r\left(\frac{S_X}{S_H}\right) = \frac{\kappa_{CH}}{\kappa_{HH}} \frac{n_{TG}/2 + n_{GG}}{n_{TT} + n_{TG}/2} \frac{1}{1-X/2} + \frac{\kappa_{ClH}}{\kappa_{HH}} \frac{X}{1-X/2} \quad (2)$$

In Br-PE, three bands at 549 cm^{-1} , 575 cm^{-1} , and 614 cm^{-1} are well resolved as C-X bands, as shown in Figure 3. From the number of available bands and the separation from the

Figure 3. C-Br stretching bands of a brominated polyethylene: Sample, 70°C crystallized single crystal; bromine content, 31.5%.

methylene rocking band at 720 cm^{-1} , Br-PE seems to be more appropriate for the present study than Cl-PE. However, the assignments of these bands have not yet been established,¹² unfortunately. This preliminary report is thus restricted to Cl-PE.

EXPERIMENTAL

PE-SC

A linear PE Sholex 6050, with the same characteristics as a Marlex 6050, was used as the sample in this report. The original PE was purified by reprecipitation from xylene—methanol system. Isothermal crystallization was carried out at 70°C (70°C—SC) and 85°C (85°C—SC) from 0.6% xylene solution. PE-SC was obtained by isothermal filtration from the mother liquid and was washed well by hot xylene. The confirmation of SC was done by EM observation.

Chlorination of the Surface

Without drying SC, the xylene was substituted and SC was suspended into CCl_4 . Chlorination was done by the bubbling of chlorine gas through the stirring suspension at room temperature under the irradiation of a high-pressure mercury lamp. To protect from oxidation, the reaction was carried out under a nitrogen atmosphere. The degree of chlorination was controlled by the bubbling (and irradiating) time and was determined by elemental analysis.

IR Measurements and Resolution of the Bands

Cl—PE-SC mats prepared under 550 atm/30 min at room temperature were used as the specimens for IR measurements. The confirmation that there was no alteration by the press was done by the comparisons of IR spectra and heat of fusion with the KBr tablet specimen.

The separation of C—Cl stretching bands from the CH_2 rocking band was made in the following way. The band parameters of the CH_2 rocking band were calculated from the IR spectra of PE-SC. In this calculation, the double peak split by the crystal field was treated as a single Lorentzian. The values of the parameters (wave number of the peak, ν_0 , and half width of the band, b) were $\nu_0 = 721 \text{ cm}^{-1}$ and $b = 8 \text{ cm}^{-1}$. The base line of Cl—PE-SC was drawn as shown in Figure 2. From the total absorption curve, the profile of the CH_2 rocking band with the band parameters calculated from PE-SC and with the peak value observed at Cl—PE-SC was subtracted, and then the resolved S_X and S_H bands were obtained, as will be shown in next section.

DSC Measurements

DSC measurements were made using a Perkin-

Elmer Model DB-II with a heating rate of 5°C/min.

RESULTS

The results of the DSC measurements are shown in Figure 4. The heat of fusion was nearly unaltered up to the chlorine content of about 20%. The slight decrease in melting temperature when the chlorine content is increased may be due to the prevention of lamellar thickening or the increase of the entropy of the amorphous phase by the chlorine atoms. These results agree with those of Harrison, *et al.*⁷ and show that the chlorination took place only at the surface of SC up to the chlorine content of about 20%. The degree of crystallinity calculated from the heat of fusion was 70.2% for 70°C—SC and 77.8% for 85°C—SC, using 67.0 cal/g for the heat of fusion of the perfect crystal.

At the early stage of chlorination, the bands due to the vinyl end at 910 cm^{-1} , 990 cm^{-1} , and 1650 cm^{-1} disappeared rapidly. And if there was oxygen present, the strong band of $\text{C}=\text{O}$ at 1720 cm^{-1} appeared along with the disappearance of the vinyl bands. On the other hand, the band of the CH_3 end at 1380 cm^{-1} was unaltered by the chlorination. This means that the vinyl end is not included in the crystal part.

An example of the band resolution is shown

Figure 4. Heat of fusion and melting temperature of chlorinated polyethylenes.

Figure 5. Resolution of S_H and S_X bands: Sample, 70°C crystallized single crystal; chlorine content, 14.3%. The dotted curve represents the sum of the two Lorentzians.

in Figure 5. The values of the Lorentzian parameter, b , are 16–24 cm^{-1} for the S_X band and 10–15 cm^{-1} for the S_H band. At the higher degree of chlorination, the coincidence between the observed absorption curve and the combined curve of the two Lorentzians becomes less in the higher frequency region, and a small broad band becomes appreciable near 690 cm^{-1} . These are caused by the increase of the S_{CH} band of the vicinal dichloride. The frequencies of the S_{CH} band of *meso*- and *racemic*-2,3-dichlorobutanes have been reported at 695 cm^{-1} and 703 cm^{-1} , respectively.¹²

The intensity ratio $r(S_X/S_H)$, obtained from the peak heights, is plotted against the chlorine content in Figure 6. In Figure 7, the abscissa is the degree of substitution X per one carbon atom at the surface, which is obtained by using the degree of crystallinity.

Figure 6. $r(S_X/S_H)$ as a function of chlorine content (%): ○, 70°C crystallized single crystals; ●, 85°C crystallized single crystals.

Figure 7. $r(S_X/S_H)$ as a function of the degree of substitution for the carbon atom on the surface (X): ○, 70°C crystallized single crystals; ●, 85°C crystallized single crystals.

$r(S_X/S_H)$ is 1.0 at $X=0$ and has the form $(\kappa_{CH}/\kappa_{HH})[(n_{TG}/2 + n_{GG})/(n_{TT} + n_{TG}/2)]$. The value of κ_{CH}/κ_{HH} for 2-chlorobutane, which is estimated from the temperature dependence of the peak-height ratio, $r(S_{CH}^{G'}/S_{HH}^T)$, is 1.41. The value for PE-SC may be of the same order. Using the value for 2-chlorobutane, $(n_{TG}/2 + n_{GG})/(n_{TT} + n_{TG}/2)$ becomes nearly 0.7. This means $n_{TT} > n_{GG}$ on the surface.

The value of κ_{CH}/κ_{HH} is unknown at this stage. The $r(S_X/S_H)$ curves calculated by assuming κ_{CH}/κ_{HH} to be 1.0, 1.5, and 2.0 are shown in Figure 7. The curves with the value in the range of 1.5–2.0 agree with the experimental results. Therefore, such values may be reasonable.

The temperature dependence of $r(S_X/S_H)$ was not obtained for 85°C–SC, but was observed reversibly for 70°C–SC; a typical example of this is shown in Figure 8. The apparent energy difference between S_X and S_H for the latter was 640 cal/mol for the 4.1% chlorine content sample and 300–350 cal/mol for the 10.1% and the 20.9% chlorine content samples. This means that

Figure 8. Temperature dependence of $r(S_x/S_H)$: Sample, 70°C crystallized single crystal; chlorine content, 4.1%; ○, heating; ●, cooling.

the fold of SC crystallized at a lower temperature has more degrees of flexibility. The energy differences of S_{CH}^G/S_{HH}^T and S_{HH}^G/S_{HH}^T for 2-chlorobutane were 440 ± 20 cal/mol and 540 ± 20 cal/mol, respectively. The energy difference for SC is of the same order as that for 2-chlorobutane.

DISCUSSION

The results of Figures 4 and 7 indicate that the assumptions described in the THEORETICAL BACKGROUND, random halogenation only at the surface of SC, are approximately satisfied. The information on the fold conformation obtained from the experimental results is not quantitative, because the number of available bands is only two and the exact value of the ratio of the absorption coefficients is not known. However, at least it has been shown that if the fold has certain numbers of GG sequences, there are more TT sequences in the fold. Such information about the TT sequences can not be given by the analysis of the amorphous bands, as mentioned in the introduction.

The average number of carbon atoms in a fold of the present samples is estimated to be 20–30 from the values of the crystallinity and of the long spacing of SC. Since the number in the shortest (tight) regular fold is 7,³ the folds of the present samples are not tight. Further, the experimental result, that the surface is randomly halogenated and $r(S_x/S_H)$ of 70°C–SC changes with temperature, suggest that the folds

have a few degrees of flexibility.

As is well known, measurements of density and heat of fusion of SC usually give the same results (not-tight and movable) as the present ones that have been interpreted by the long-irregular fold model. On the other hand, the results of crystallographic, spectroscopic, and morphological observations have been interpreted by the tight-regular fold model. In order to resolve the inconsistency between these two models, Hoffman and Davis¹⁵ proposed a new model with physically adsorbed detachable polymer molecules on a fairly regularly folded surface. However, our experimental results can not be interpreted by their model.

A New Model for the Surface of PE-SC

We now propose a new model which is able to resolve the above inconsistency. Considering the regular growth of SC and the restriction on folding area (=surface area of SC), the folds, even if they are long, are not random and must have regularity. Most of the folds may be adjacent re-entry. Further, the conformation of the fold must be determined by considering the packing of the folds on the surface of SC. On the basis of this requirement, the conformation of the shortest fold was determined uniquely without conformational freedom. On the other hand, in the case of the long fold, a few degrees of flexibility are required from the experimental results. In order to interpret this fact, it is necessary to consider folds with more than one type of conformation, which can be packed on the surface and can be mutually converted from one type to another.

As described in a previous paper³, the crystal structure of PE can be approximated by the sublattice of a diamond lattice; the fold conformation can also be considered on this diamond lattice. As the result of such considerations, two types of conformations for the (110) long fold which satisfy the conditions of the packing and the mutual conversion were found. The conformations of the type A and B are shown in Figures 9 and 10, respectively, where the suffix of i in type A and of j in type B is zero or an arbitrary positive integer. If i or j is zero, both the types are reduced to the conformation of the shortest fold, GTGGTGGG, as described

Figure 9. Type A conformation of (110) long folds (i , zero or positive integers), which is able to pack on the crystal surface: (a) (110) projection; (b) (001) projection; (c) relation between adjacent fold planes.

Figure 10. Type B conformation of (110) long folds (j , zero or positive integers), which is able to pack on the crystal surface: (a) (110) projection; (b) (001) projection; (c) relation between adjacent fold planes.

in a previous paper.³ GG sequences are located only at the fold-back portion in both types. The conformation of type A is the same as that of ring paraffin molecules in its crystal, while the conformation of the type B is a new one.

A fold with 20–30 carbon atoms is represented

Figure 11. Conversion of fold conformation types (X, the shortest fold).

by type A of $i=4$ with $n_{TT}=15$, $n_{GG}=2$, and $n_{TG}=8$, or by type B of $j=2$ with $n_{TT}=0$, $n_{GG}=3$, and $n_{TG}=22$, in which the number of carbon atoms in a fold is 23. The fold length, however, may not be uniform. The lengths and the types must be distributed so that the experimental results are satisfied.

We have pointed out the importance of the interaction energy between folds (IEF).³ IEF between the folds of the different types is larger than that between the folds of the same type, because the degree of packing of the former is less than that of the latter. Therefore, the folds of the same type must form a domain, as is shown in Figure 11. The requirement of the flexibility is fulfilled by the conversion of the fold type, A to B or B to A. An example of the conversion is illustrated in Figure 11.

In our model, as shown in Figures 9, 10, and 11, the chains in the crystal part are inclined at an angle of 30° with respect to the normal to the boundary plane between the crystal and the fold parts, due to the steric hindrance between the folds in successive (110) fold planes. This inclination was confirmed recently by the Raman spectroscopic study of PE-SC by Keller, *et al.*¹⁶

The experimental results are interpreted well by the model proposed here. However, a few

problems remain unsolved. The fold part of our model is regular, in other words, crystalline. The energy density of the straight portion of the fold part may be lower than that of the melt, and depends upon the fold type. On the other hand, the energy density of the fold-back portion is higher than that of the melt.³ Therefore, the average energy density of the fold part depends on the distributions of the fold length and fold type. This makes it impossible to calculate the crystallinity from only the fusion data. For this reason, the present discussion is not quantitative, but may be qualitatively correct.

The other problem is the density of PE-SC. In our models for both types of fold, the density is 1.0 g/cm³ when the length is infinite. For the fold with finite length, the density becomes larger because of the influence of the fold-back portion. Therefore, the experimental density of PE-SC (usually, 0.96–0.98) can not be interpreted by our models. This discrepancy is common to the regular fold models and a study from a new viewpoint will be required for the elucidation of this problem.

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