polymer where u is the number of the monomeric units and t is the turn number of the helix in the identity period. Actually, in the case of polyoxymethylene,[36] nine monomeric units are contained and the helix turns five times in the identity period, and so the type of the helix can be demonstrated to be (9/5).

But in the complex case where it is difficult to decide the turn number t visually by tracing along the main chain atoms, the type of the helix cannot be designated by the notation described above. Therefore, in such cases the helix may be defined as right-handed when the rotation angle between any atom and the equivalent atom of the subsequent monomeric unit, ϕ_u, is smaller than 180° in the right-handed cylindrical coordinate system. The types of helical polymers may be denoted by use of ϕ_u of the right-handed helix. An example of this case is that of poly(*tert*-butylethylene oxide). ϕ_u of the right-handed helix is 160° and nine monomeric units are contained in the identity period, that is, $u = 9$ and $t = 4$ $[(160° \times 9)/2\pi]$. Accordingly the type of poly(*tert*-butylethylene oxide) can be shown as (9/4).

Furthermore, we should note that the conventional nomenclature is to be preferred to the present proposal, if there is no complex situation of the type just mentioned.

(36) T. Uchida and H. Tadokoro, *J. Polym. Sci., Part A-2,* **5,** 63 (1967).

Small-Angle X-Ray Diffraction Study of Chlorinated Polyethylene Crystallized from Melt

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ABSTRACT: As model compounds of semicrystalline copolymers we prepared samples of linear polyethylene chlorinated in solution to various extents (0.5–4.2 wt % chlorine). The partitioning of chlorine atoms between the amorphous and crystalline phases of these copolymers, crystallized from melt, was studied by a low-angle X-ray scattering technique. The chlorine atom can be utilized as a convenient probe because of its high contrast in both electron and mass densities. The total scattering power of the sample was obtained by integration of the observed X-ray intensity. Both the scattering power and the mass density of the sample can be expressed as functions of the degree of crystallinity and the partition coefficient of chlorine in the two phases. From the observed values of the scattering power and mass density, the latter two quantities were evaluated. The degrees of crystallinity thus obtained agree well with the values determined independently from the heats of fusion. The partition coefficient of chlorine, *i.e.*, the ratio of concentration of chlorine in the crystalline phase to that in the amorphous phase, is around 0.15 but decreases somewhat with increasing concentration of chlorine in the copolymer.

When a small amount of comonomer units is introduced into a linear homopolymer, one obtains a copolymer which still crystallizes into a semicrystalline structure resembling that of the homopolymer. It has frequently been surmized that, when crystallization of such a copolymer is performed extremely slowly, all the noncrystallizable comonomer units are rejected completely from the crystalline lattice. It is not certain, however, whether such a complete rejection can be achieved in any copolymer that has been crystallized with a rate attainable in practice. There are at least two kinds of experimental evidence that suggest that the rejection of comonomer units is not complete. One is that the unit cell dimensions of the crystalline lattice of copolymers, determined by X-ray diffraction, are frequently much larger than those of the corresponding homopolymer. The effect has been reported widely[1-6] for copolymers of polyethylene and branched polyethylene. The second line of evidence comes from the study of melting temperatures. The early theory by Flory,[7] relating the melting point of a copolymer to its composition, is based on the assumption of complete rejection of comonomers. The prediction of the theory, however, has been found in a number of copolymer series[8-11] to underestimate the degree of melting point depression due to the comonomer units. The extent of deviation from the theory has also been shown to depend on the size of the comonomer unit.[10,11]

In this work we apply the technique of small-angle X-ray diffraction to obtain a direct measure of the amount of comonomer units incorporated into the crystalline phase. As a model of random copolymers, we employ a series of samples of linear polyethylene chlorinated in solution to various extents. Chlorinated polyethylene was earlier employed as a model copolymers by Killian and coworkers.[4,12] The degree of chlorination in our samples was kept fairly low and at most to a few chlorine atoms per 100 carbons. Chlorinated polyethylene offers several advantages over other copolymers for the present purpose. First, the chlorination reaction performed in solution allows placement of chlorine atoms at random positions along the polyethylene chain. This random placement of chlorine atoms in our samples was confirmed by high-resolution nmr study.[13] Secondly, the chlorination reaction is

(1) R. M. Eichhorn, *J. Polym. Sci.,* **31,** 197 (1958).

(2) E. A. Cole and D. R. Holms, *J. Polym. Sci.,* **46,** 245 (1960).

(3) P. R. Swan, *J. Polym. Sci.,* **56,** 409 (1962); B. Wunderlich and D. Poland, *J. Polym. Sci., Part A,* **1,** 357 (1963).

(4) H. G. Kilian and F. H. Müller, *Kolloid-Z. Z., Polym.,* **192,** 34 (1963).

(5) C. H. Baker and L. Mandelker, *Polymer,* **7,** 71 (1966).

(6) R. J. Roe, H. F. Cole, and D. R. Morrow, in "Advances in Polymer Science and Engineering," K. D. Pae, D. R. Morrow, and Yu Chen, Ed., Plenum Press, New York, N. Y., 1972, p 27.

(7) P. J. Flory, *J. Chem. Phys.,* **15,** 684, (1947); *Trans. Faraday Soc.,* **51,** 848 (1955).

(8) L. Mandelkern, "Crystallization of Polymers," McGraw Hill, New York, N. Y., 1964.

(9) B. Ke, *J. Polym. Sci.,* **61,** 47 (1962); D. Bodily and B. Wunderlich, *J. Polym. Sci., Part A2,* **4,** 25 (1966).,

(10) R. G. Griskey and G. N. Foster, *J. Polym. Sci., Part A1,* **8,** 1623 (1966).

(11) M. R. Richardson, P. J. Flory, and J. B. Jackson, *Polymer,* **4,** 221 (1963).

(12) H. Linz, H. G. Kilian, F. H. Müller, and H. Ringsdorf, *Kolloid-Z. Z., Polym.,* **202,** 108 (1965); H. G. Kilian, *ibid.,* **205,** 7 (1965).

(13) F. A. Bovey, private communication.

Table I
Description of Copolymer Samples and Their Properties

Polymer No.	Chlorine Content Wt %	Chlorine Content Cl Atoms/100 C	Mp (°C)	Heats of Fusion (cal/g)	Density	Unit Cell Dimension *a*	Unit Cell Dimension *b*	Unit Cell Dimension *c*
0	0	0	135.0 ± 0.5	56.6	0.9680	7.405	4.943	2.546
1	0.45	0.18	133.5	52.4	0.9675	7.418	4.945	2.544
2	0.95	0.38	132.6	48.5	0.9668	7.426	4.948	2.546
3	3.66	1.50	125.8	41.5	0.9695	7.456	4.951	2.542
4	4.20	1.73	124.1	39.2	0.9597	7.470	4.950	2.541

easy to perform and the degree of chlorination can be controlled readily. Thirdly, the atomic number of chlorine is sufficiently different from carbon and hydrogen, and, therefore, chlorine atoms can be exploited as a convenient probe offering high contrasts in both mass and electron density. This aspect plays a key role in the present study.

Small-angle X-ray scattering from bulk-crystallized samples affords three types of information: the so-called long period arising from the lamellar structure of the crystalline phase, the specific surface area of the interface between the crystalline and amorphous phases, and the scattering power of the sample which relates to the electron density difference between the two phases. The last of the above three is affected most sensitively by the degree of partitioning of chlorine atoms between the amorphous and crystalline phases. In this work, information obtained from the small-angle X-ray technique was supplemented by results obtained from other measurements, such as the density and heat of fusion, and the combined analysis of all these data led to the determination of the amount of chlorine atoms incorporated into the crystalline phases.

Experimental Section

Copolymer Samples and Their Characterization. Chlorinated polyethylene samples were prepared and kindly supplied to us by E. P. Otocka of this laboratory. They were prepared by passing chlorine gas through a solution of Marlex 6050 in tetrachloroethylene at 105°. Details of the method of preparation are described elsewhere.[14] Chlorine contents of the samples are tabulated in Table I. The control sample designated "0" is Marlex 6050 which has gone through the whole process of dissolution in tetrachloroethylene and reprecipitation but without chlorination.

The copolymer samples were molded into sheets of 1.2-mm thickness heated in a press to 170°, cooled to 95° in about 10 min, and then held at this temperature for 22 hr. To determine the concentration of chlorine in these samples, the intensity of the X-ray fluorescence of the chlorine atoms and the absorption coefficient of Cu Kα by the samples were measured, and these were compared with values obtained from standard samples containing known amounts of chlorine. The chlorine contents given in Table I are the averages of values obtained by the fluorescence and absorption methods.

Melting temperatures and heats of fusion of these samples were measured with a differential scanning calorimeter, Perkin-Elmer Model 1B. A heating rate of 10°/min was employed, and the calorimeter was frequently calibrated against an indium standard. The density was measured in a density gradient column containing isopropyl alcohol–diethylene glycol.

Wide-angle X-ray diffraction photographs of thin sections of the molded copolymer samples were taken with a Guinier-de-Wolff camera equipped with a quartz monochromator. Diffraction lines from 325-mesh sapphire crystals adhered to the specimen surfaces were recorded on the same photographs and served as a calibration standard. Thirteen diffraction lines arising from the polyethylene crystalline lattice were employed in a least-squares determination of the orthorhombic unit cell dimensions *a*, *b*, and *c*.

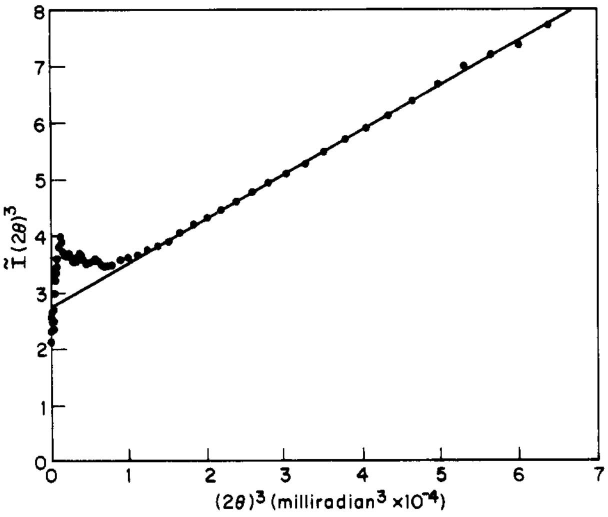

Figure 1. The observed (slit-smeared) intensity $\tilde{I}$ obtained with the sample 0 (linear polyethylene), multiplied by $(2\theta)^3$, is plotted against $(2\theta)^3$. The good linear relation at high angles follows the prediction of eq 2. From the slope one can determine the value of the background scattering δ, which reflects the local electron density fluctuations in each phase.

Small-Angle X-Ray Measurement

A Kratky camera equipped with a step-scanning device manufactured by Canberra Industries was used for the small-angle X-ray measurements. The incident Cu Kα beam was filtered with a nickel foil and the scattered intensity measured with a proportional counter through a pulse-height analyzer. An entrance slit of 60-μ width was used for scanning between scattering angles 2θ of 1.2 and 8 mrads and a slit of 200-μ width between 6 and 40 mrads. After correcting for the smearing effect arising from the finite slit widths,[15] the data obtained in the two angular ranges were merged together. For the purpose of determining the long period, the intensity data were corrected for the smearing effect arising from finite slit lengths by the procedure described by Schmidt[16] and further multiplied by $(2\theta)^2$ to correct for the Lorenz factor.[17]

According to Porod,[18] the intensity of small-angle X-ray scattering from a two-phase system falls off rapidly with increasing angle as $I \sim 1/S^4$ or $\tilde{I} \sim 1/S^3$, where $\tilde{I}$ and I are the intensities before and after correction for the slit-length smearing effect, and

$$S = 2(\sin\theta)/\lambda \qquad (1)$$

λ being the X-ray wavelength. The proportionality constants in the above relations are related to the specific

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(14) R. J. Roe, H. F. Cole, and E. P. Otocka, *ACS Polym. Prepr.*, **12**, 311 (1971).

(15) T. R. Taylor and P. W. Schmidt, *Acta Phys. Austr.*, 25, 293 (1967).

(16) T. R. Taylor and P. W. Schmidt, *J. Appl. Crystallogr.*, 2, 143 (1969).

(17) L. E. Alexander, "X-ray Diffraction Methods in Polymer Science," Chapter 5, Wiley, New York, N. Y., 1969.

(18) G. Porod, *Kolloid-Z. Z. Polym.*, 124, 83 (1951); 125, 51, 108 (1952).

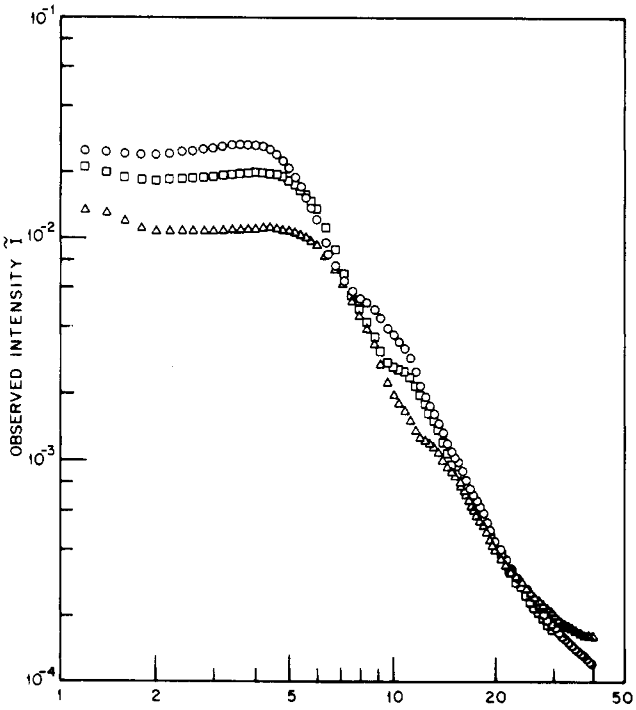

Figure 2. The observed (slit-smeared) intensity $\tilde{I}$ is plotted against the scattering angle 2θ. The symbols ○, □, and △ refer to data obtained with samples 0, 2, and 4. Data for samples 1 and 3 are omitted for the sake of legibility.

surface area of the interface between the two phases. Porod's law applies only when there are no internal structures in each phase and the boundary between them is sharp. Ruland[19] examined the possible consequence of deviations from this idealized situation, and concluded that when there are density fluctuations within the phases one can expect

$$\tilde{I} = \tilde{K}_s/S^3 + \delta \tag{2}$$

while when the phase boundary is diffuse

$$\tilde{I} = \tilde{K}_s/S^3 + \delta'/S \tag{3}$$

These two possible cases can be discriminated by plotting $\tilde{I}S^3$ against either S^3 or S^2 to find a straight-line relation. Such a procedure is illustrated in Figure 1 with the data obtained with linear polyethylene (sample 0). With all five samples it was found that the intensity data for 2θ between 20 and 40 mrad were approximated better by eq 2 than by eq 3.

The total scattering power of a sample is represented by the so-called invariant[17,19] $\tilde{Q}_s$ defined by

$$\tilde{Q}_s = \int_0^\infty S\tilde{I}\mathrm{d}S \tag{4}$$

This quantity is directly proportional to the mean-square electron density fluctuation in the sample $\langle(\delta\rho)^2\rangle$. To determine the proportionality constant, one needs a measure of the intensity of the incident X-ray beam, and this was obtained with a calibrated Lupolen sample[20] kindly supplied by Professor O. Kratky. In evaluating $\tilde{Q}_s$ by eq 4, the observed intensity $\tilde{I}$ was first corrected for the background δ determined in accordance with eq 2. The contributions to $\tilde{Q}_s$ consisted of three terms: $\tilde{Q}_{s1}$, $\tilde{Q}_{s2}$, and $\tilde{Q}_{s3}$. $\tilde{Q}_{s2}$ was calculated by summing $S\tilde{I}$ between the minimum and maximum values of S observed experimentally. The contribution $\tilde{Q}_{s1}$ between $S = 0$ and $S_{\min}$ was estimated by assuming linear increase in $S\tilde{I}$ from 0 to $S_{\min}\tilde{I}(S_{\min})$. $\tilde{Q}_{s3}$ was estimated by assuming the validity of $\tilde{I} = \tilde{K}_s/S^3$ (see eq 2) from $S = S_{\max}$ to $S = \infty$. In all cases the terms $\tilde{Q}_{s1}$ and $\tilde{Q}_{s3}$ contributed only about 2 and 10%, respectively, to $\tilde{Q}_s$.

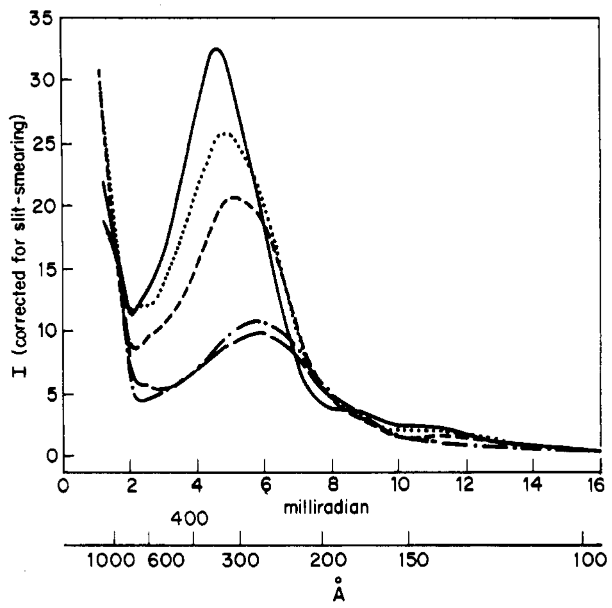

Figure 3. The intensity I, corrected for the slit-smearing effect, is plotted against the scattering angle 2θ. The data for samples 0–4 are represented by —, ..., - - - - -, —·—·—, and—·̇·—, respectively. Note the shift in the position of of the peak to high angles and the lowering of peak heights with increasing chlorine concentrations in the sample.

Table II
Data Obtained from Small-Angle Scattering Intensities

Sample No.	Long Period, l (Å)	$\langle\delta\rho^2\rangle$ 10^{-3} mol electrons^2/cm^6	$\tilde{K}_s/\tilde{Q}_s$ (Å^{-1})
0	302	1.098	3.10
1	273	1.059	3.21
2	258	0.977	3.48
3	237	0.717	3.92
4	235	0.686	3.95

Results

Figure 2 shows tvpical log–log plots of the X-ray intensities observed with some of the samples. The intensities, corrected for the slit-length smearing effect, are plotted in Figure 3, in which the position of the prominent peak is seen to shift toward a higher angle as the chlorine concentration is increased. The three quantities, which can be evaluated from each of the scattering curves shown in Figures 2 and 3, are tabulated in Table II. The long period l was calculated from the peak scattering angle by the Bragg relation. The mean-square fluctuation of electron density $\langle(\delta\rho)^2\rangle \equiv \langle(\rho - \langle\rho\rangle)^2\rangle$ was obtained from $\tilde{Q}_s$ by

$$\langle(\delta\rho)^2\rangle = \frac{2\pi}{i_e V}\tilde{Q}_s \tag{5}$$

where V is the scattering volume and i_e is the intensity of X-ray scattered by a mole of electrons under the experimental conditions. For a two-phase system the mean-square electron density fluctuation $\langle(\delta\rho)^2\rangle$ is related to the difference $\Delta\rho$ between the electron densities of the two

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[19] W. Ruland, *J. Appl. Crystallogr.*, 4, 70 (1971).

[20] O. Kratky, I. Pilz, and P. J. Schmitz, *J. Colloid Interface Sci.*, 21, 24 (1966).

Table III
Results from Small-Angle X-Ray Scattering

			Degree of Crystallinity		Specific Surface Area		
Sample No.	$\gamma = W_c/W_a$	W_c (%)	From X-Ray (%)	From Heat of Fusion (%)	From $\tilde{K}_s/\tilde{Q}_s$ (Å^{-1}), × 10^{-2}	From $2/l$ (Å^{-1}), × 10^{-2}	Ratio
0		0	81.2	83.2	0.805	0.662	1.22
1	0.18	0.26	78.3	77.1	0.942	0.733	1.29
2	0.16	0.44	76.2	71.3	1.083	0.775	1.40
3	0.13	1.06	62.4	61.1	1.523	0.844	1.80
4	0.14	1.24	59.8	57.7	1.560	0.851	1.83

phases by

$$\langle(\delta\rho)^2\rangle = \phi(1 - \phi)(\Delta\rho)^2 \tag{6}$$

where ϕ is the volume fraction of one of the phases. The specific surface area S_{sp}, or the area of the boundary between the two phases per unit volume of the material, is obtained from the value of $\tilde{K}_s/\tilde{Q}_s$ by

$$S_{sp} = 8\pi\phi(1 - \phi)\tilde{K}_s/\tilde{Q}_s \tag{7}$$

As has been remarked in the previous section, eq 2 is obeyed well by all the samples, a fact which attests to the validity of applying the concept of a two-phase system to these materials.

For linear polyethylene one can calculate $\Delta\rho$ from the known densities of crystalline and amorphous phases (d_c = 1.0, d_a = 0.854). Using $(\Delta\rho)^2$ and $\langle(\delta\rho)^2\rangle$ given in Table II, one can calculate the degree of crystallinity from eq 6. The value obtained is 80.3%, which compares very well with the degree of crystallinity calculated from density (80.7%) and from heat of fusion (83.2%). This result again confirms the usefulness of the concept of a two-phase system. The amorphous density used in the above is the one obtained by extrapolating the liquid density from above the melting point.[12] Thus, contrary to suggestions[21] made by some other workers that the amorphous density might differ markedly from the extrapolated value, we find no evidence for such a difference.

Using the value of $\tilde{K}_s/\tilde{Q}_s$ obtained experimentally and the value of ϕ calculated above, we can now calculate S_{sp} for linear polyethylene to be equal to 0.00805 Å^{-1} according to eq 7. If we imagine an ideal lamellar structure in which uniform, perfect layers of amorphous and crystalline phases alternate, the specific surface area would be given by $2/l$. For the linear polyethylene sample, the value of S_{sp} turns out to be about 1.22 times the value of $2/l$. This result is interpreted to mean that the fold surfaces of lamellar crystals are not perfectly smooth, and also that there might be a contribution to S_{sp} from boundary areas other than the fold surfaces. The degree of disorder or the deviation from a perfect lamellar structure in linear polyethylene thus amounts to 22%. Apart from the significance of such a quantitative interpretation, the approximate agreement between S_{sp} and $2/l$ can be taken as yet a further confirmation of the validity of employing the two phase concept to the present materials.

A similar analysis cannot readily be extended to the data on copolymers since here the densities of amorphous and crystalline phases in copolymers depend on the degree of partitioning of chlorine atoms between the two. If the degree of crystallinity were known independently, the densities of the two phases could be calculated from the measured mass density of the sample. However, the measurement of the degree of crystallinity of copolymers either by calorimetry or by wide-angle X-ray scattering entails additional assumptions besides those usually required in the case of homopolymers. The degree of partitioning of chlorine greatly affects the densities of crystalline and amorphous phases, and these in turn affect the overall electron density fluctuation $\langle(\delta\rho)^2\rangle$ and the mass density d. We therefore express these two, experimentally observable, quantities as function of ϕ and the chlorine partition coefficient γ, and solve them simultaneously to obtain ϕ and γ. The partition coefficient γ is defined as the ratio of W_c/W_a, where W_c and W_a are the weight fractions of chlorine atoms in crystalline and amorphous phases, respectively. In addition to eq 6 one needs the following equations to implement the above procedure

$$1/d = \phi/d_c + (1 - \phi)/d_a \tag{8}$$

The crystalline density d_c is calculated from W_c and the unit cell volume V_c obtained from the unit cell dimensions a, b, and c. The amorphous density is expressed as

$$d_a = d_a^{\,0} + \beta W_a \tag{9}$$

where $d_a^{\,0}$ is the amorphous density of linear polyethylene (0.854). We measured the density of copolymer 4 dilatometrically at temperatures above its melting point, and by extrapolation the density of supercooled melt at room temperature was found to be 0.8857 g/cm^3. From this the value of β was determined to be 0.779. The electron densities ρ_c can be calculated readily from the mass densities d_c by

$$\rho_c = d_c \frac{\text{av no. of electrons/repeat unit}}{\text{av mol wt of repeat unit}} \tag{10}$$

and ρ_a from d_a by a similar equation. The weight fractions W_c and W_a of chlorine in the two phases are constrained by the conditions that their ratio is equal to the partition coefficient γ and that the average concentration throughout the sample is equal to the known concentration W given in Table I. The latter condition is expressed by

$$W = fW_c + (1 - f)W_a \tag{11}$$

where f is the weight fraction of the crystalline phase and is related to the volume fraction ϕ by

$$f = \phi[1 + (1 - \phi)(1 - d_a/d_c)] \tag{12}$$

Equations 6 and 8, with the various subsidiary constraints expressed in eq 9-12, can now be solved simultaneously for ϕ and γ for each copolymer. The results are given in the second and fourth columns of Table III. The values of γ are found to lie between 0.13 and 0.18, thus indicating that the chlorine atoms have a tendency to remain in the amorphous phase. The amount of chlorine that enters the crystalline phase, however, is still considerable, as can be seen from the values of W_c given in the

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(21) S. Kavesh and J. M. Schultz, *Polym. Eng. Sci.*, 9, 452 (1969); *J. Polym. Sci., Part A2*, 9, 85 (1971).

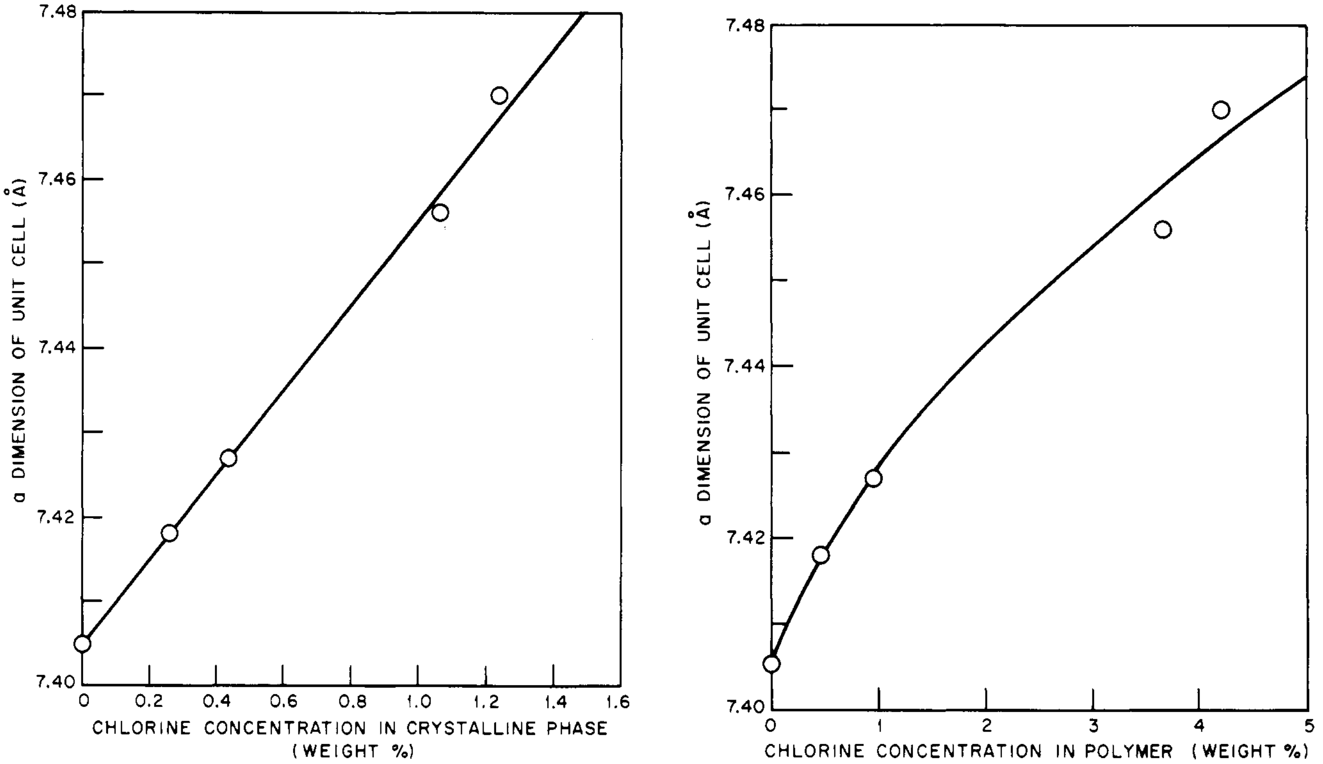

Figure 4. The *a* dimension of the unit cell is plotted against the concentration of chlorine in the crystalline phase in part a (left) and against the average concentration of chlorine in the polymers in part b (right).

third column of Table III. The weight fraction of 1.24% indicated for the copolymer 4 corresponds to about one chlorine atom for every 200 carbons. The value of γ appears to decrease somewhat with increasing chlorine concentration in the copolymers. This might be reflecting the increasing difficulty of incorporating a higher concentration of chlorine atoms into the crystalline phase.

In the above analysis, the weakest of the assumptions employed is the one embodied in eq 9 stating that the amorphous mass density is equal to the extrapolated liquid density and is also linear with the amount of chlorine. Any deviation from the assumed linearity of eq 9 would result in slightly altered numerical values of γ, but we feel it unlikely that the alteration would be large enough to affect the overall conclusion. We in fact have an independent way of confirming the above assumption indirectly, that is, by comparing the degrees of crystallinity ϕ obtained by the present analysis with those obtained by dividing the observed heats of fusion by 68 cal/g. Such a comparison is made in Table III and we find the agreement very satisfactory. A perfect agreement between these two sets of ϕ is not expected, not only because of experimental errors but also because of the inherent difficulty in obtaining accurate values of ϕ from heats of fusion. This difficulty arises because ΔH_u for copolymers having unit cell dimensions slightly expanded may no longer be the same as for linear polyethylene, and also because of the conversion from a weight to a volume fraction requires the knowledge of concentration of chlorine in the crystalline phase, as well as other reasons. For homopolymers there is another, potentially more satisfactory, way of obtaining the degree of crystallinity from X-ray diffraction measurements, originally proposed by Ruland.[22-24] To a study of copolymers the method cannot be applied, however, without a prior knowledge of the partitioning of comonomer units between the crystalline and amorphous phases, especially in view of the large disparity between the atomic scattering factors of chlorine and carbon atoms.

The specific surface area S_{sp} is now calculated according to eq 7, using the value of ϕ obtained by analysis of X-ray intensity data as described above. The results are tabulated in the sixth column of Table III. These are compared with the quantity $2/l$ or the specific surface area that is expected of a material having perfect lamellar structure with a long period equal to the observed l. The ratio of the actual to the ideal specific surface area, given in the last column of Table III, increases from 1.22 to 1.83 as the chlorine concentration in the copolymers is increased. This is to be expected since with increasing irregularities along the polymer chains the structure obtained becomes less perfect and deviates more from the idealized lamellar structure.

Discussion

Dilation of the unit cell volume by introduction of foreign atoms into crystalline lattices is a phenomenon observed frequently with crystals of simple materials such as metals and inorganic salts. Even a diamond lattice is shown to expand when point defects are created by neutron irradiation.[25] The dilation of crystalline lattices by random point defects has been demonstrated also theoretically.[25,26] It is then very reasonable to attribute the expansion of the unit cell dimensions in copolymers of polyethylene to the incorporation of comonomer units into the crystalline lattice. In Figure 4a we plot the a dimension of the unit cell against the concentration W_c of chlorine atoms in the crystalline phase. For the purpose of comparison, in Figure 4b the a dimension is plotted also against the total

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(22) W. Ruland, *Acta Crystallogr.*, 14, 1180 (1961).

(23) Reference 17, Chapter 3.

(24) S. Kavesh and J. M. Schultz, *J. Polym. Sci., Part A2*, 8, 243 (1970).

(25) D. T. Keating, *J. Phys. Chem. Solids*, 29, 771 (1968).

(26) K. Huang, *Proc. Roy. Soc., Ser. A*, 190, 102 (1947); T. D. Eshelby, *J. Appl. Phys.*, 25, 255 (1954).

concentration W of chlorine in the copolymer. The plot of a against W shows an unmistakable curvature while the plot of the same against W_c lies on a very good straight line.

The expansion in the b direction is much smaller than in the a direction and there is almost no change in the c dimension. This, of course, reflects the anisotropy of polyethylene crystalline structure which is also manifested in the anisotropy of the thermal expansion coefficient,[27] the elastic modulus[28] and the linear compressibility.[29] The magnitudes of the anisotropy, as given by the ratio of these quantities measured in the a and b directions, are, however, only in the range of 1.2–1.6 in the case of modulus and compressibility, while the ratio of the thermal expansion coefficients in a and b directions is between 3 and 6 at room temperature. The ratio of the fractional expansion in the a and b dimensions, observed in this work, is about 5. This suggests that the process leading to the dilation of the lattice by inclusion of foreign atoms is analogous to the dilation by a thermal motion, and is different from the process of altering all the interatomic distances uniformly that occurs on compression or extension of the crystal as a whole.

The incorporation of noncrystallizable comonomer in the crystalline lattice is demonstrated in this work only for substituted chlorine atoms. The dilation of the lattice is known to occur with copolymers of ethylene having larger comonomers. When comparison is made among copolymers having the same mole fraction of comonomers, the degree of dilation is, however, seen to decrease with increasing size of the comonomer. For example, Baker and Mandelkern[5] report that the dilation of the lattice with polyethylene copolymers having *n*-propyl side groups is about half that observed with copolymers having methyl groups. Since the distortion of the lattice by a larger foreign group is expected to be proportionately larger, these observations must mean that as the size increases incorporation of the side groups into the crystalline lattice becomes far more difficult and the partition coefficient γ ($=W_c/W_a$) falls rapidly.

The value of γ probably depends on the crystallization conditions and generally decreases with slower rates of crystallization. There then arises a question whether γ will ever be equal to zero when a copolymer crystal is formed under an equilibrium condition. To shed some light on this we analyzed the distribution of crystallizable sequences in relation to the crystalline lamellar structure. From the long period l and the degree of crystallinity ϕ one can calculate the number ζ_c of CH_2 units in the sequences that run the crystalline phase between the fold surfaces. The number ζ_c turns out to be 210, 190, 140, and 130 CH_2 units for samples 1–4, respectively. For a random copolymer the number of sequences $n(\zeta)$ each containing ζ crystallizable units is given by

$$n(\zeta) = N(1 - X)^{\zeta - 1}X \tag{13}$$

where N is the total number of sequences and X is the mole fraction of CHCl units. If we are going to construct a model of lamellar structure of ζ_c units thick but containing no chlorine atoms, a sequence of size between ζ_c and $2\zeta_c - 1$ can contribute only ζ_c crystalline units. If we assume that the minimum number of CH_2 units required for a fold is four, then a sequence of size between $2\zeta_c$ and $2\zeta_c + 3$ can also contribute ζ_c crystalline units and no more. Similarly a sequence of size between $2\zeta_c + 4$ and $3\zeta_c + 7$ contributes at most $2\zeta_c$ crystalline units. The maximum degree of crystallinity attainable is therefore given by

$$\phi_m = \sum_{\zeta=1}^{\infty} \left[\frac{\zeta + 4}{\zeta_c + 4}\right]\zeta_c n(\zeta) \Big/ \sum_{\zeta=1}^{\infty}\zeta n(\zeta) \tag{14}$$

where $[y]$ denotes the largest integer not exceeding y. Substitution of eq 13 for for $n(\zeta)$ then leads to

$$\phi_m = \zeta_c X(1 - X)^{\zeta_c}/[1 - (1 - X)^{\zeta_c - 4}] \tag{15}$$

Using the values of ζ_c given before and the values of X in Table I, we obtain as ϕ_m the values 80.9, 67.1, 28.5, and 25.7% for copolymer 1–4, respectively. Except for the copolymer 1 containing the smallest number of chlorine atoms, these values are considerably smaller than the actual degree of crystallinity attained. Thus, a strict exclusion of foreign groups from the crystalline lattice would be achieved only by reducing greatly the degree of crystallinity.

For a given value of X, ϕ_m can be increased by decreasing ζ_c, but then the total surface free energy will increase unduly. All the three requirements for lowering the free energy of the material, *i.e.*, high degree of crystallinity, a small surface area and exclusion of foreign groups from the lattice, can be met if the material forms crystalline lamellae of continuously differing thicknesses, and each crystallizable sequences in the copolymer are deposited on lamellae of thicknesses most appropriate to each of them individually. Even when a sufficient time is allowed for the process of fractionation by sequence lengths to occur, there still remains a question whether such a fractionation can occur to any great extent because of the limitation imposed by the physical connection of these sequences in a long copolymer chain. A better fractionation will be achieved when lamellae of different thicknesses are finely dispersed among each other, but then the surface free energy will be increased.

With our present samples, the crystalline structure consists of lamellae of fairly uniform thicknesses. This can be seen from the fact that there exists a well-defined low-angle peak in the intensity curve as shown in Figure 2, and also that the specific interphase boundary area is not much larger than $2/l$. With such well-defined lamellar structures, the attainment of a high degree of crystallinity and the inclusion of a certain fraction of foreign groups in the crystalline phase are two factors which have to balance each other. As the size of the foreign group is made larger, the distortion of the crystalline lattice and the accompanying increase in the free energy is made larger, and consequently the position of the free energy minimum is shifted toward a lower degree of crystallinity consistent with a smaller number of foreign groups incorporated in the lattice. The degree of crystallinity attained will depend on, among other things, the free-energy increase accompanying the distortion of the lattice by a foreign group inclusion. A better understanding of the energetics of the latter process is therefore keenly awaited.

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