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Crystallite size distribution and the lattice distortions in highly γ-irradiated linear polyethylene

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Crystallite size distributions and lattice distortions have been analysed for highly γ-irradiated linear polyethylene in the direction normal to (1 1 0) and (0 0 1) lattice planes through X-ray line profile analysis. It has been found that the lateral crystallite size is little affected irradiation greater than 1000 Mrad, whereas that in the chain direction decreases almost linearly with the dose of irradiation. A minor difference in the crystallite size between irradiation atmospheres, i.e. irradiation in air or in vacuum, has been disclosed at a very high dose of irradiation. The above degradation behaviour of crystallites and the change in lattice distortions have proved that radiation cross-links are mainly formed in the amorphous region near the lamellar surface of polyethylene.

1. Introduction

The authors have already reported changes in the lattice parameter of highly γ-irradiated linear polyethylene (LPE) crystal [1]. The results have shown that the volume of the unit cell increases by as much as 10% of the original lattice before becoming amorphous, but the critical dose for destruction of crystallites differs in accordance with the macroscopic shape of the sample and atmospheres of irradiation. In this paper, changes in the crystallite size distribution and lattice distortions are investigated through X-ray line profile analysis by using film samples of LPE. With a view to making clear the mechanism of the crystal degradation by radiation, crystallite size distributions and lattice distortions are analysed for both lateral and chain directions. The method of analysis employed here has been outlined in the earlier paper [2].

2. Experimental details

2.1. Samples and irradiation

Linear polyethylene (Sholex 6050) films, 1 mm thick, were prepared by melting powder at 140° C and then cooling with a water-cooled press. Strips cut out of the original film were drawn uniaxially to ten times the original length at room temperature. Unoriented and oriented samples were irradiated by ^{60}Co γ-rays up to 5000 Mrad with a dose rate of 1 Mrad h^{-1}. Irradiation was carried out at room temperature both in air and in vacuum.

2.2. Measurement of the profile

For the purpose of analysing the crystallite size distribution and the lattice distortion in radiation-damaged LPE both in the lateral and in the chain directions, the following X-ray diffraction lines were measured: 1 1 0 profiles of unoriented and oriented samples, and 0 0 2 profiles of oriented ones. The procedures for measurement and data processing were the same as described in detail in the earlier paper [2]. Fig. 1 shows examples of 1 1 0 and 0 0 2 line profiles.

2.3. Small angle X-ray scattering (SAXS) and bulk density

SAXS patterns of the sample were first recorded by film. The intensity distributions of the meridian (drawing) direction were then measured using a scintillation counter with pulse-height discrimination, using a line slit system. The bulk density of

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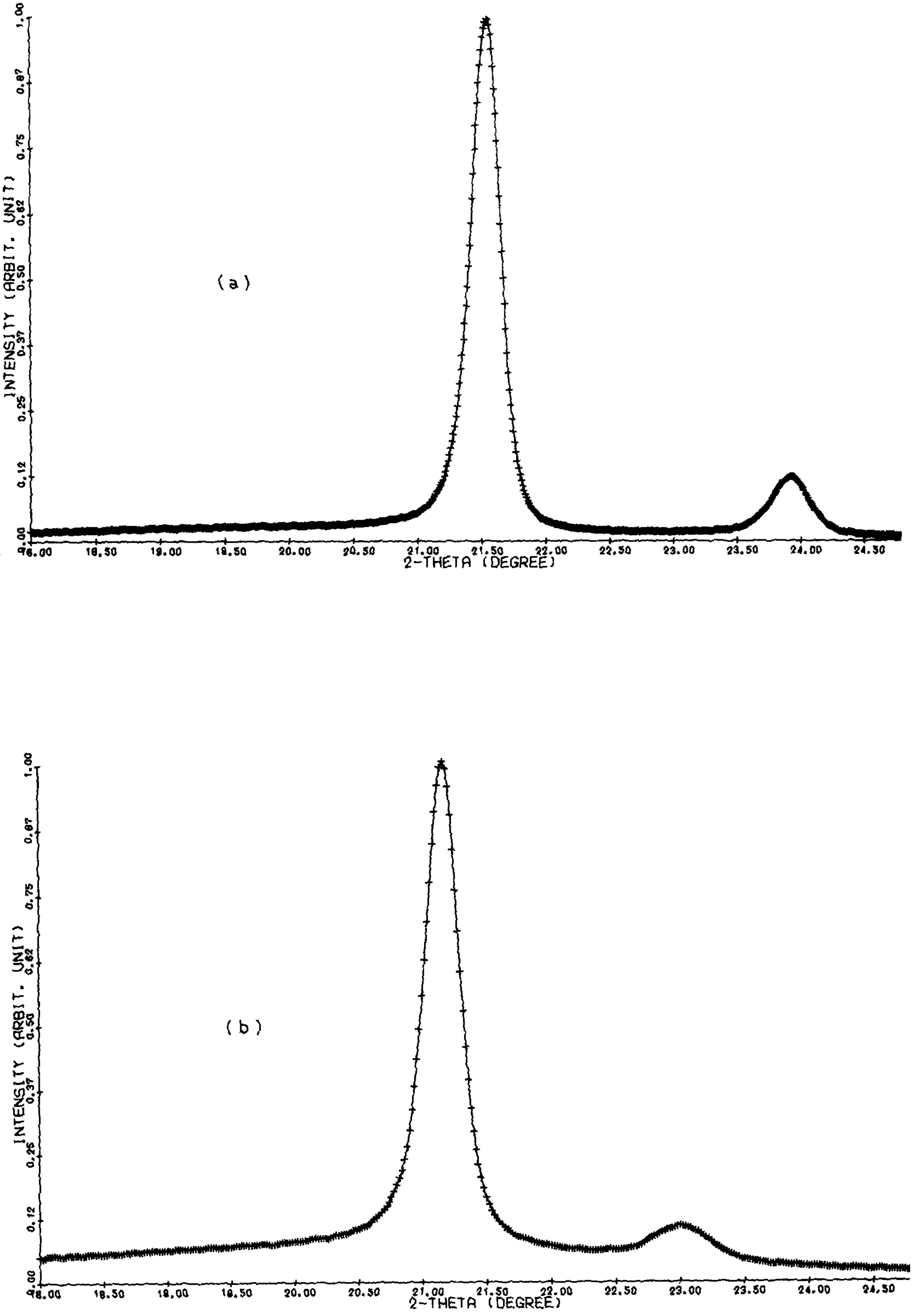


Figure 1 Examples of irradiated profiles. (a) Unoriented 1 1 0 profile, (b) 1 1 0 profile of 2000 Mrad irradiated sample, (c) unirradiated 0 0 2 profile, (d) 0 0 2 profile of 2000 Mrad irradiated sample.

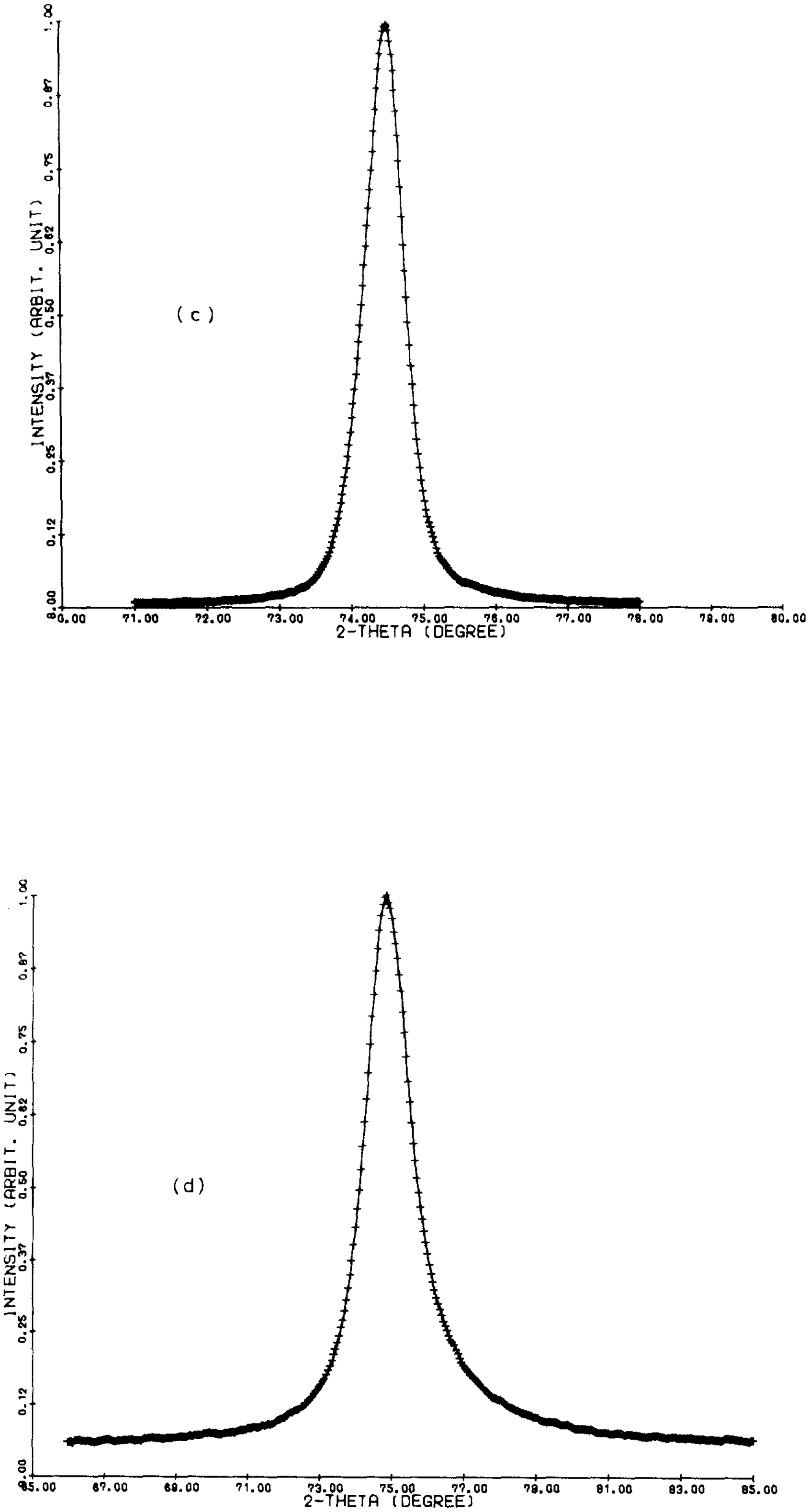


Figure 1 continued.

the sample was determined by the gradient-tube method with a water-methanol mixture as medium at 25° C.

3. Results

3.1. Full-width at half-maximum (FWHM) of the profile

FWHMs of the measured profile are shown in Fig. 2 as a function of the irradiation dose. Although FWHM itself is not more than a qualitative measure specifying the profile, it provides useful information in judging the trend of the irradiation effect on the profile and in selecting profiles to be analysed. In fact, increase in the integral breadth of the analysed profile behaves quite similarly to that in FWHM (see dashed lines in Fig. 2). The figure indicates that the FWHM of the unoriented 1 1 0 profile is unchanged up to 1000 Mrad irrespective of the irradiation atmosphere, but over 1500 Mrad, the FWHM of the sample irradiated in vacuum increases, whereas the change in the sample irradiated in air for 2000 Mrad is only slight. Unoriented 1 1 0 FWHMs above 2000 Mrad are somewhat uncertain and questionable because of the difficulties in the separation of the profile from the overlapped 2 0 0 profile; nevertheless, the figure shows clearly the tendency for the FWHM of the samples irradiated in vacuum to increase more rapidly with irradiation dose than that irradiated in air. The figure also indicates that the increasing behaviour of the oriented 1 1 0 FWHMs is, relatively, quite similar to that of the unoriented 1 1 0 FWHMs irradiated in vacuum (cf. ovals with open circles), although the absolute values of the former are about three times larger than those of the latter. On the other hand, the FWHMs of the 0 0 2 profile in oriented LPE increase with irradiation without the induction period found in the case of the 1 1 0 FWHM, and at the same time, little difference can be seen between irradiation atmospheres except in the most irradiated case, i.e. 2000 Mrad.

The above findings in FWHMs reveal that radiation effects on the 1 1 0 profile can be identified for both oriented and unoriented cases, although absolute values of FWHMs differ from each other. This situation ensures that we can investigate the mechanism of radiation effects on LPE crystals through analysis of unoriented 1 1 0 and oriented 0 0 2 profiles; which is important because we cannot extract the 0 0 2 profile in unoriented LPE, and the 1 1 0 profile of the oriented sample is too broad to separate it from the adjacent profile when irradiated. The following profiles were analysed to clarify the features of the radiation-induced degradation of LPE crystals in the lateral and chain directions: lateral [1 1 0] direction – unoriented 1 1 0 profiles of un-irradiated (original) sample (A), irradiated in air for 1000 Mrad (B) and 2000 Mrad (C), and irradiated in vacuum for 1500 Mrad (D); chain [001] direction – oriented 0 0 2

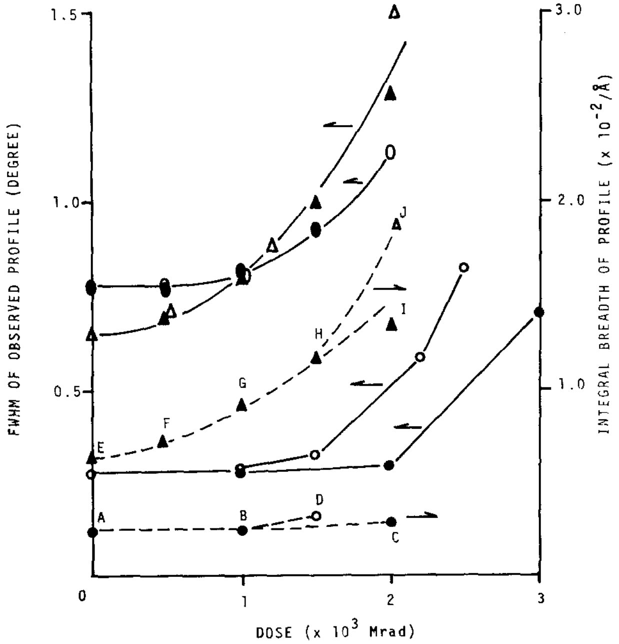
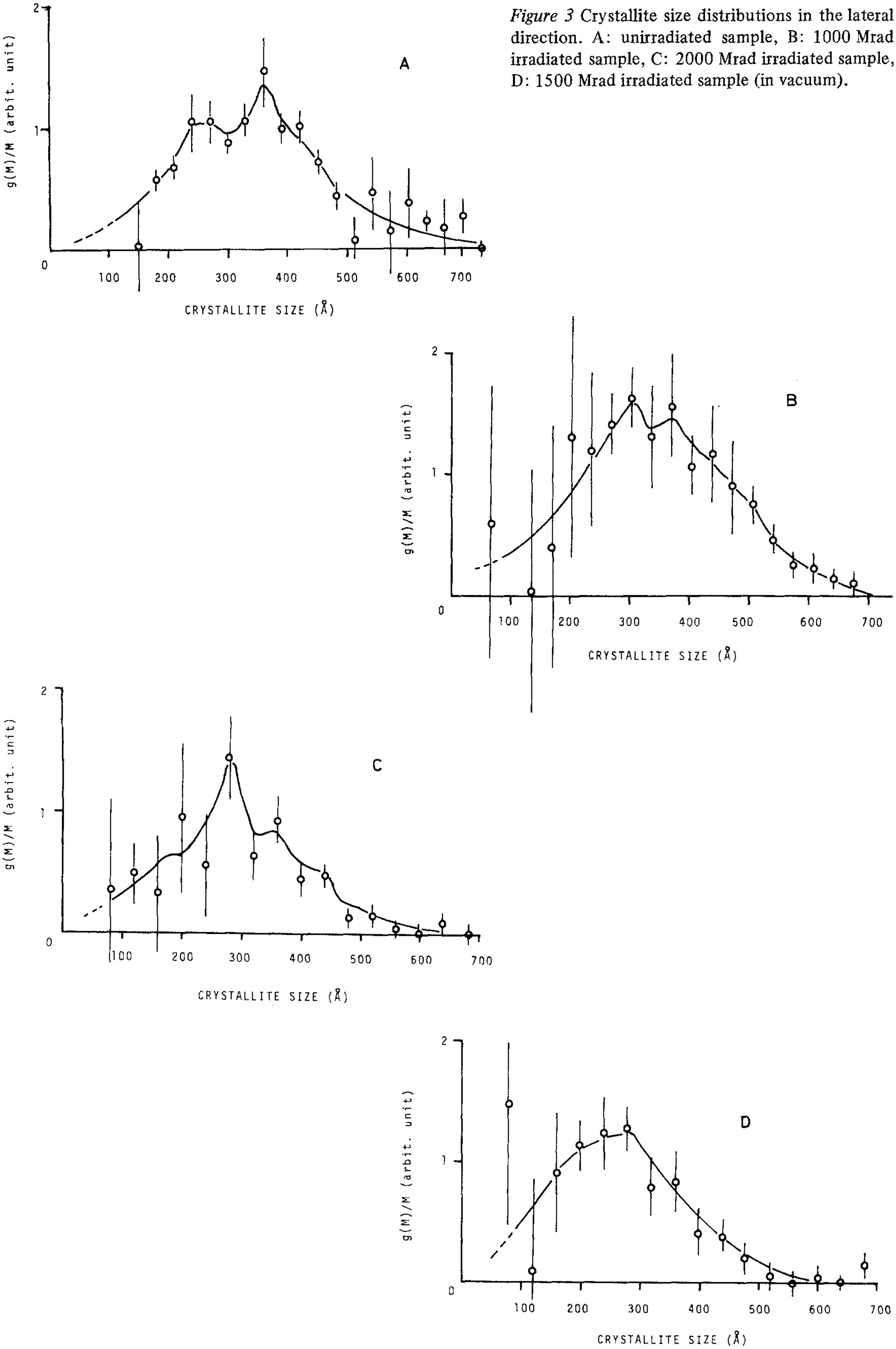


Figure 2 FWHM (solid lines) and integral breadth (dashed lines) of profile. ●: 1 1 0 of unoriented LPE, irradiated in air, ○: 1 1 0 of unoriented LPE, irradiated in vacuum. 0 and 0: 1 1 0 of oriented LPE, irradiated in air and in vacuum, respectively. ▲ and △: 0 0 2 of oriented sample, irradiated in air and in vacuum, respectively.

Figure 3 Crystallite size distributions in the lateral direction. A: unirradiated sample, B: 1000 Mrad irradiated sample, C: 2000 Mrad irradiated sample, D: 1500 Mrad irradiated sample (in vacuum).



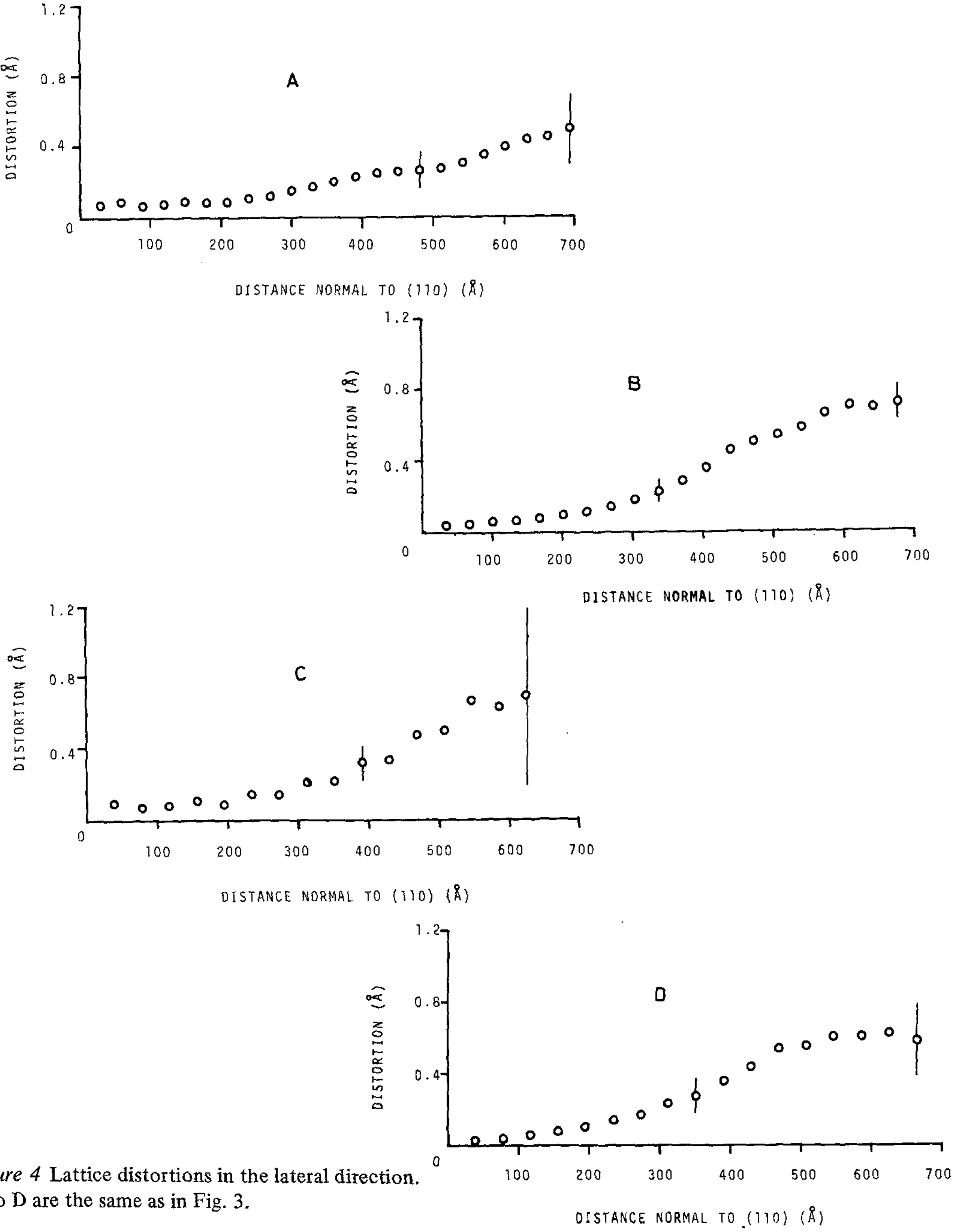


Figure 4 Lattice distortions in the lateral direction. A to D are the same as in Fig. 3.

profiles of un-irradiated (original) (E), 488 Mrad (F), 1017 Mrad (G), 1500 Mrad (H), 2000 Mrad (I) irradiated, respectively, in air, and 2020 Mrad irradiated in vacuum (J). In Fig. 2, the integral breadths of the analysed profiles are shown (dashed line) with their identifying letters.

3.2. Changes in crystallite size distribution and lattice distortion in the lateral [1 1 0] direction

Figs. 3 and 4 show crystallite size distributions and lattice distortions in the lateral direction. Size distributions of the original (A) and 1000 Mrad irradiation (B) samples are quite similar to each other; the highes peak is around 350 Å and the distribution covers as much as 700 Å or more. The number-averaged mean sizes calculated from the distribution curves are 370 and 360 Å, respectively. The size distribution function of the sample irradiated in air for 2000 Mrad (C) shows that there are no crystallites larger than 600 Å, and the mean size reduces to 300 Å. In the case of irradiation in vacuum for 1500 Mrad, however, the size distribution shifts more inwards than that of sample C; no crystallites larger than 500 Å can be seen, and the mean crystallite size and the maximum on the distribution curve lie around 270 and 250 Å, respectively.

The lattice distortion of the original sample increases linearly with distance, which is regarded as the strained-lattice type distortion, whereas that of the irradiated sample is assigned to the superposition of the strained and paracrystalline-lattice distortions. Furthermore, the degree of lattice distortion in the irradiated lattice is greater than that in the original lattice, i.e. the distortion of sample B is about twice as large as that of sample A at 700 A No significant difference in the degree of distortion can be seen between irradiated samples.

3.3. Changes in crystallite size distribution and lattice distortion in the chain [0 0 1] direction

Figs. 5 and 6 show changes in the crystallite size distribution and lattice distortion, respectively, in

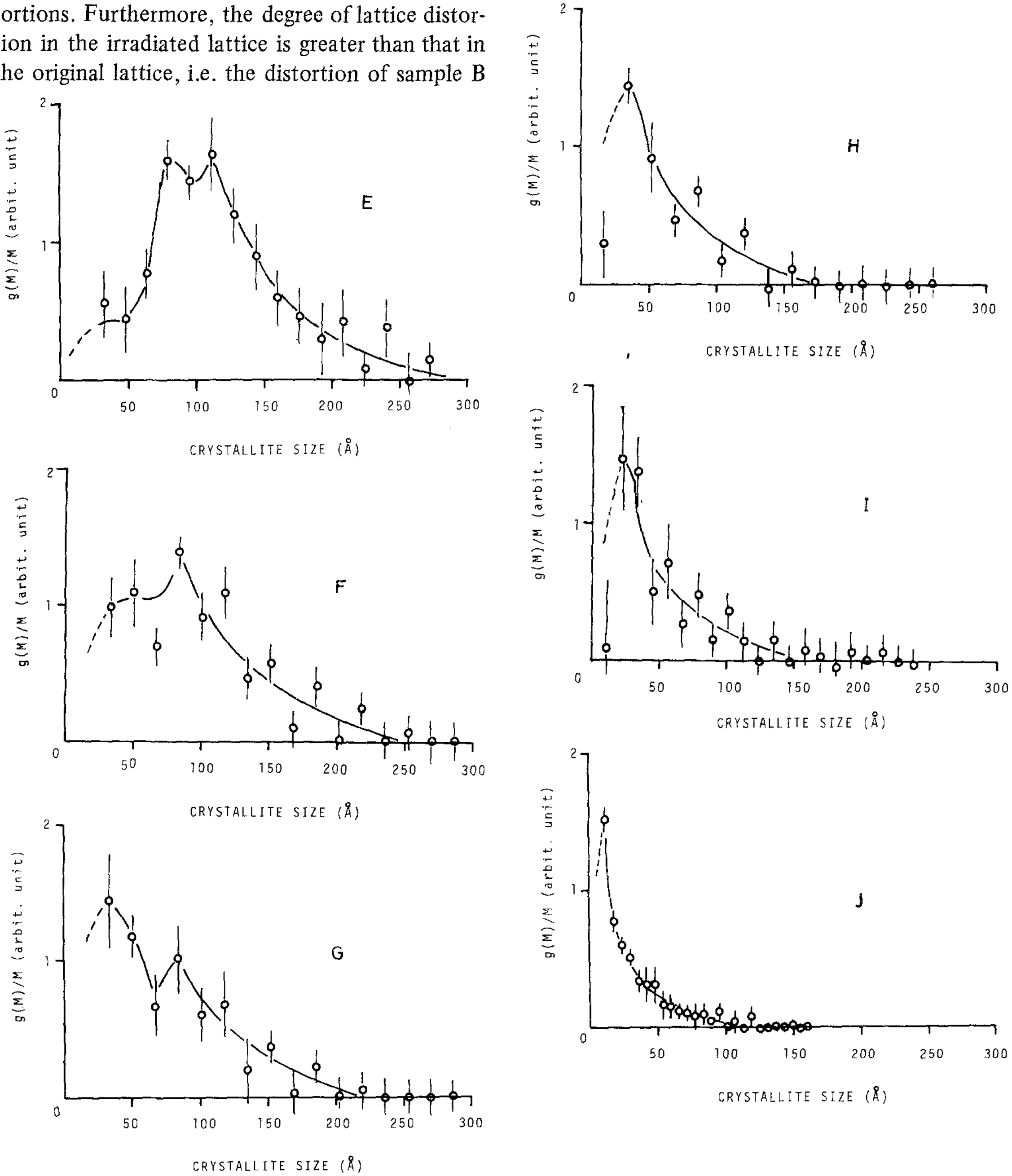


Figure 5 Crystallite size distributions in the chain direction. E: unirradiated sample, F: 488 Mrad irradiated sample, G: 1017 Mrad irradiated sample, I: 2000 Mrad irradiated sample, J: 2020 Mrad irradiated (in vacuum) sample.

the polymer chain direction of the LPE crystal. The size distribution of the original sample E has a maximum peak around 100 Å and decreases monotonically with distance up to 250 to 300 Å. The mean size is calculated as 120 Å. Irradiation makes the crystallite size in the polymer chain direction small. The sample irradiated for 488 Mrad exhibits a similar size distribution curve to the original sample, but in this case there a large number of crystallites smaller than 50 Å can be seen, and the size distribution gives a mean size of 100 Å. By irradiation for 1017 Mrad (G), the maximum peak position in the distribution curve goes towards the inside even though some crystallites larger than 200 Å can be found. The mean size of this sample is 80 Å. The distribution curve of sample H (1500 Mrad) shifts further inwards than sample G; the peak maximum lies around 50 Å, and the mean size is 70 Å. Irradiation for 2000 Mrad introduces a slight difference between irradiation atmospheres; comparison of the size distributions of I (in air) and J (in vacuum) reveals that crystallites distribute at larger sizes in the sample irradiated in air than in vacuum. The mean sizes of I and J are 60 and 40 Å, respectively.

The lattice distortion of the irradiated LPE crystal in the polymer chain direction is the strained-lattice type distortion, except for the case of 2000 Mrad irradiation (see Fig. 6). Moreover, the degree of distortion in this direction remains unchanged up to irradiation of 1500 Mrad and is much smaller than that in the lateral direction. Irradiation in vacuum for 2000 Mrad makes the degree and the type of the lattice distortion large and complicated, respectively, whereas only the degree increases by irradiation in air for the same dose, leaving the type of the distortion unaffected.

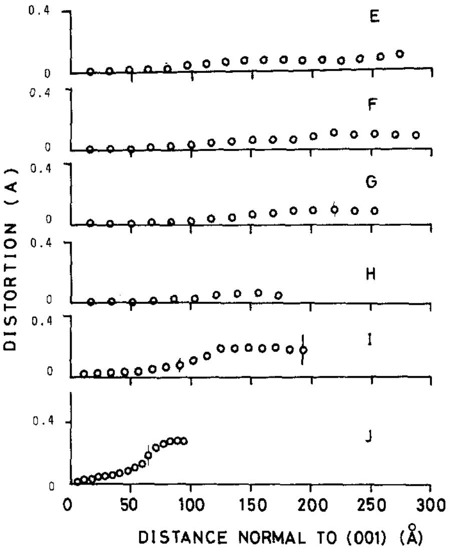


Figure 6 Lattice distortions in the chain direction. E to J are the same as in Fig. 5.

Table I summarizes the integral breadth of the profile, number-averaged mean crystallite size derived from the distribution function, and the standard deviation $(=(\overline{M_n^2} - \overline{M_n}^2)^{1/2}$ where M_n is the mean size) of the distribution function which is a measure of spread of the distribution. The relative crystallite size normalized at the value of the original sample, and the standard deviation are shown in Figs. 7 and 8, respectively.

3.4. Long period and bulk density

It is known that oriented LPE prepared by uniaxial drawing at room temperature exhibits discrete reflections in the meridional (drawing) direction in the SAXS diagram along with a diamond-shaped scattering at the centre which is attributed to the existence of voids. According to a simple two-phase

TABLE I Parameters specifying the profile and the crystallite size distribution

Profile, Atmosphere and dose	Integral breadth ($\times 10^{-2}$ Å^{-1})	Mean size (Å)	Standard deviation (Å)
1 1 0 (unoriented)			
original	0.24	370	140
air, 1000 Mrad	0.24	360	160
air, 2000 Mrad	0.28	310	200
vac, 1500 Mrad	0.32	270	175
0 0 2 (oriented)			
original	0.64	120	57
air, 488 Mrad	0.72	100	54
air, 1017 Mrad	0.91	82	48
air, 1500 Mrad	1.17	69	48
air, 2000 Mrad	1.33	59	45
vac, 2020 Mrad	1.86	39	37

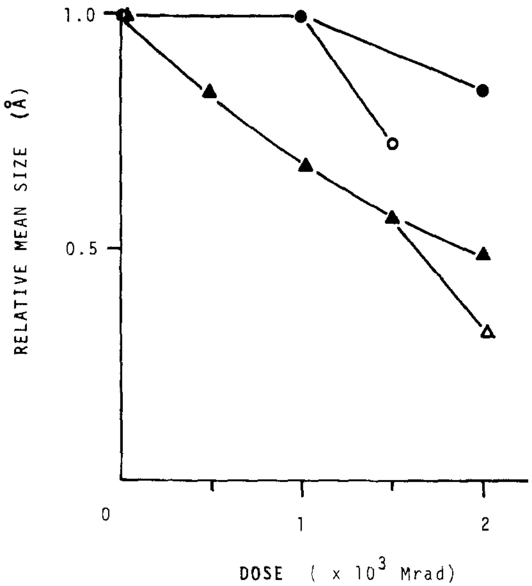


Figure 7 Changes in the mean size. ● and ○: relative mean sizes in the lateral direction, irradiated in air and in vacuum, respectively. ▲ and △: relative mean sizes in the chain direction, irradiated in air and in vacuum, respectively.

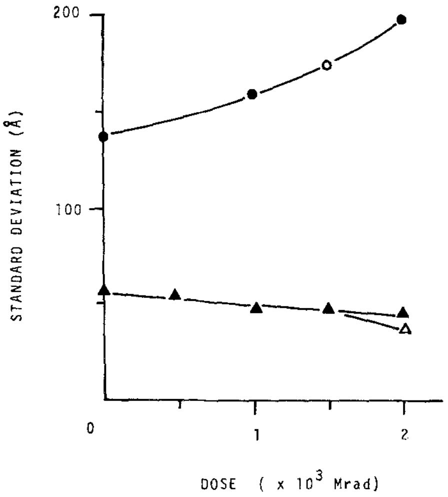


Figure 8 Standard deviation of the crystallite size distribution function. Circles: 1 1 0, triangles: 0 0 2. Open circles and triangles are for irradiation in vacuum.

model [3], the position of the discrete reflection gives the long period or average repeat distance of the crystalline-amorphous binary system. Fig. 9 shows examples of SAXS photographs. Film and counter detection have revealed that with irradiation the peak position of the discrete reflections shifts a little outwards, but the extent is only faint; the long periods of the original and 2000 Mrad irradiated samples are 170 and 150 Å, respectively. However, the intensity of the discrete reflection becomes weaker with irradiation. Fig. 10 shows the change in the bulk density of unoriented films. The bulk density of irradiated LPE decreases with irradiation. Up to 1000 Mrad, there is no difference in the density between samples irradiated in air and in vacuum. Over 1000 Mrad, however, the density of the sample irradiated in vacuum goes down almost linearly whereas the decreasing behaviour of the sample irradiated in air is somewhat gradual.

4. Discussion

It is well known that γ-irradiation forms cross-links in the polyethylene film along with other minor reactions such as double-bond formation, chain scission and oxidation. The last reaction is important when the sample is irradiated in the presence of oxygen, but penetration of oxygen is limited only in the vicinity of the surface if the thickness of the LPE film exceeds 1 mm [4]. It is also accepted generally that melt-crystallized polyethylene has lamellar structures, the surface of which is amorphous and the interior of which consists of mosaic crystallites. In the case of the cold-drawn film, polymer chains are known to align normal to the lamellar surface [5].

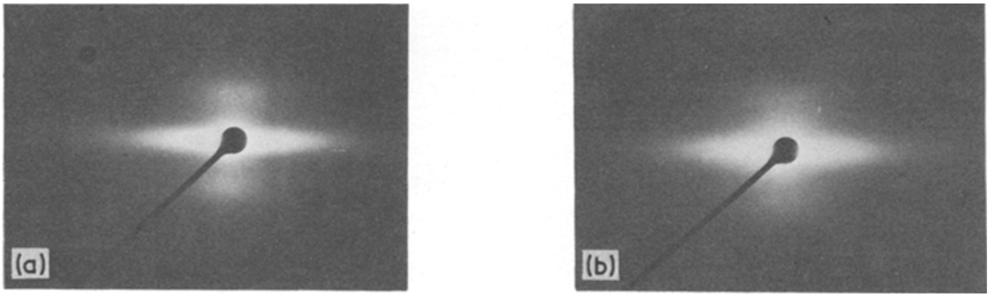


Figure 9 SAXS patterns of unirradiated (a) and 2000 Mrad irradiated (b) samples.

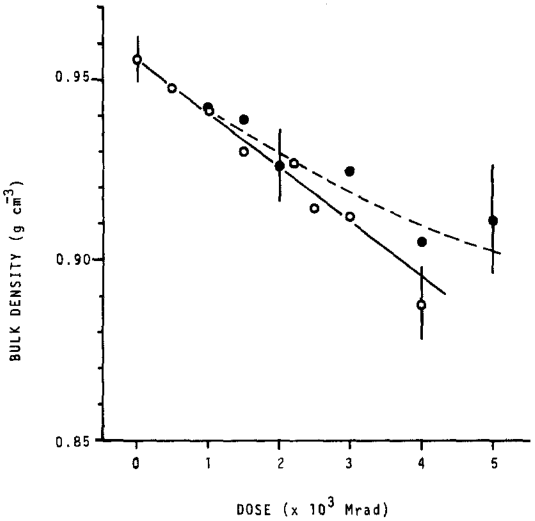


Figure 10 Changes in the bulk density of the sample. Closed circles: irradiated in air: open circles: irradiated in vacuum.

At present, there are distinctly opposite ideas on the cross-linking site in polyethylene by radiation; one insists that cross-links are formed predominantly in the amorphous region [6], and the other insists that the cross-linking reaction occurs mostly within crystallites [7]. The present results are interpreted by taking into account the above two models. Inspection of the size distribution functions, lattice distortions, and mean crystallite sizes reveals that there are two stages in the radiation degradation of melt-crystalized polyethylene; the first is in the dose range up to 1000 Mrad, and the second is over 1000 Mrad.

In the first stage, the crystallite size in the lateral direction remains almost unchanged, but that in the polymer chain direction decreases linearly with the irradiation dose (see Fig. 7). In contrast to the crystallite size, changes in the lattice distortion behave quite oppositely; the degree of lattice distortion increases in the lateral direction whereas that in the chain direction is left unaffected in this stage (cf. Figs. 5 and 8). The above findings suggest that radiation cross-linking occurs predominantly in the amorphous region on the lamellar surface. Cross-links formed on the lamellar surface induce break-up of the crystalline order from the surface which is nearly normal to the polymer chain, and thereby the coherent length or the crystallite size in the polymer chain direction is shortened. If cross-links are formed mostly within the crystallite in a random manner, the coherent length not only in the chain direction but in the lateral direction should be shortened, which is not the case as shown in Fig. 7. Or, if cross-links within the crystallite are so numerous and selective as to break up crystallites only in the chain direction, the cross-linked part forms an amorphous layer within the crystallite, which influences the average period of the crystalline-amorphous sequence; this is not the case as stated in the preceding section. Increase in the lattice distortion in the lateral direction (Fig. 6) should be attributed to formation of defects introduced through reactions by radiation. Unchanged lattice distortions in the chain direction are reasonable because the cross-linked part near the lamellar surface is no longer crystalline, but amorphous. Nevertheless, it is suggested from Table I and Fig. 8 that a small amount of crystallites are broken up even in the lateral direction by radiation-induced defects which possibly include cross-links.

In the second stage, defect concentration in the crystallite becomes so high that the marked degradation of crystallites occurs in the lateral direction. In this stage, the degradation of crystallites differs with irradiation atmosphere. As is shown in Fig. 10, the bulk density of LPE irradiated in air drops more slowly than that irradiated in vacuum, which is evidence that oxidation proceeds gradually from the film surface. Oxidation by γ-irradiation is accompanied by polymer chain scission [8], and therefore restrains formation of cross-links; this is why decrease in the mean crystallite size is less for the sample irradiated in air than in vacuum at very high doses. That the critical dose which discloses a difference for the irradiation atmospheres is different between lateral and chain directions suggests a possibility that the site of oxidation is rather selective.

The crystallite size distribution and the lattice distortion cannot be determined through the X-ray line profile analysis when the LPE film is irradiated over 2000 Mrad. In the above dose range, however, decrease in crystallinity as well as in the crystallite size is much more pronounced. When the irradiation dose exceeds 3000 Mrad, no Bragg reflections can be found in the X-ray diffraction diagram irrespective of the irradiation atmosphere. The structure of LPE made amorphous by γ-irradiation has been reported elsewhere [9].

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