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Radiation-induced crosslinking: Effect on structure of polyethylene*)

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Abstract: Branched polyethylene irradiated (0–400 Mrad) with a Co^{60} source at room temperature under vacuum was studied by density, wide- and small-angle X-ray scattering (WAXS and SAXS) measurements. The radiation effects on the structure of bulk, branched polyethylene are quite similar to those observed by others on single crystals or oriented preparations. These effects include changes in bulk density ϱ, crystallinity (w_c or v_c) and $\bar{d}_{100}$ and $\bar{d}_{200}$ spacings as a function of irradiation. A decrease in crystallinity is seen to begin at radiation dose $\approx$ 100 Mrad whereas lattice expansion indicating onset of an orthorhombic-hexagonal transition can begin as low as 10 Mrads. The decrease in crystallinity can be attributed to additional lattice distortions primarily introduced by the crosslinks occurring at the lateral grain boundaries, while lattice expansion can be associated with the same crosslinking mechanism which begins at the defects both within the crystals as well as those outside the crystals at the lateral grain boundaries. Strong evidence for a primary crosslinking-at-the-defects mechanism has also come from ϱ_c and ϱ_a data obtained in this study as a function of radiation dose. The same data have also led to an excellent correspondence between the measured density crystallinity v_c and the measured WAXS crystallinity w_c. Without consideration of the effects of crosslinks on ϱ_c and ϱ_a one would have obtained a divergence of the two crystallinities, especially at radiation doses greater than 100 Mrads.

Key words: Crosslinking, radiation, polyethylene, density, crystallinity, *d*-spacings, phase densities, crosslink locations, lateral grain boundaries, crosslink mechanisms.

I. Introduction and background

For years ionizing radiation (e^-, gamma etc.) has been of great interest to polymer scientists and users of radiation for materials applications [1–4]. Gamma radiation is often employed in crosslinking, degradation and polymerization studies, as well as in sterilization for biomedical applications. From the standpoint of improvement in physical properties (memory effects, creep and thermal resistance, etc.), the introduction of intermolecular crosslinks in polyethylene upon irradiation in the absence of oxygen is by far the most interesting effect, particularly so in view of the fact that the crosslinks can be readily introduced into shaped products, for example resists, heat shrinkable tubes, films, etc., for additional energy, materials and cost savings.

Therefore, ever since the radiation-induced crosslinking phenomenon was first discovered by Dole and Rose in 1948 [5], the effect of high energy radiation on the structure and properties of linear polyethylene has been a subject of continuing interest. It is now well established that radiation produces crosslinks in polyethylene, with the number of crosslinks that are effective in forming a network structure or gel being highly dependent on both radiation dose and morphology for either single crystal, bulk or oriented preparations. However, the reason for the dependence on morphology is still unclear. It is generally agreed by all that this dependence on morphology indicates the crosslinks cannot be randomly distributed, and in the past twenty years two very different crosslink models have been developed. One model by Keller [6–11] suggests that crosslinks take place primarily at the folds outside the

*) Dedicated Prof. Dr. R. Bonart on the occasion of his 60th birthday

crystalline cores. The other model, principally attributed to Hosemann [12–14], originated with Nagasawa and Kobayashi [15]. This model, based on an observed orthorhombic to hexagonal transition in irradiated single crystals, suggests that the crosslinks are located primarily at defects within the crystal cores. Thus in one model the crosslinks are depicted to be predominantly outside the crystals, and therefore within the amorphous phase, and by the other to be predominantly inside the crystals. Since radiation crosslinking in the solid state is known to occur nonrandomly, both models cannot be correct.

In an effort to resolve the above controversy, Yoda and Odajima [16] made an analysis of the crystallite size and its distribution in polyethylenes irradiated to a wide range of radiation dose (up to $\approx$ 3000 Mrads). Their conclusions were that "degradation of the crystallites (and therefore crosslinking) occurs at the fold surface and that the range amorphised in the chain direction is the same for large and small crystallites." Yoda and Odajima's conclusion indicates that Keller has the correct model. Surprisingly though, their conclusion was not accepted by one of Keller's co-workers, namely Ungar [17]. This was perhaps because Ungar and Keller had arrived at a different conclusion just a year earlier [18], that the crosslinking-at-the-fold model could not be applied to highly irradiated polyethylenes. They had proposed instead a transition model where a change in preferred crosslinking location occurs, from at-the-fold at low dose to inside-the-crystal at doses beginning at about 500 to 800 Mrads. The transition model was based on an orthorhombic-hexagonal transition, which had originally led Nagasawa and Kobayashi to propose the crosslinking-within-the-crystal model in 1970 and which Ungar and Keller had reported to have observed in their samples irradiated to 500–800 Mrads.

Ungar also tested the conclusion by Yoda and Odajima by measuring the decrease in crystallinity for a number of identically irradiated (800 Mrads) samples with different initial long periods. If Yoda's conclusion was correct, then for a given dose the relative decrease in the crystallinity of a sample should be inversely proportional to L ($\Delta x - x_o = 1/L$, where Δx is the change in crystallinity, x_o is the initial degree of crystallinity and L is the thickness of the amorphised layer assumed to be constant for a given radiation dose). Ungar found that the measured crystallinity decrease is much greater than expected, which led him to rule out Yoda's hypothesis that crosslinking occurs continuously from the fold surface. There is another piece of evidence [19] from X-ray, primarily from considerations of bulk density, crystal density and model calculations, showing that at least 6 % of all the carbon atoms in highly irradiated polyethylenes (like those used by Yoda and Odajima) are crosslinked within the crystalline cores. Thus we can conclude there is sufficient evidence, as well as agreement, favoring crosslinks occuring within the crystalline cores, most probably at the defects, in sufficiently distorted regions at high radiation doses (greater than 800 Mrads). Whether or not the same mechanism also dominates at moderate and lower radiation doeses (less than 500–800 Mrads) remains a question.

The purpose of this investigation is to demonstrate the applicability of another approach, namely the determination of the individual densities ϱ_c and ϱ_a of the crystalline and amorphous phases. It is hoped that this approach can provide additional information about the location of crosslinks at low radiation dose on the basis that the densities of the individual phases will vary depending upon where crosslinks are introduced. Furthermore, if there is any change in crosslinking mechanisms one would expect this change to be detectable in the change of the densities as a function of radiation. The determination of ϱ_c and ϱ_a as a function of radiation dose also allows us to calculate the change in volume percent crystallinity v_c $\left(\text{where } v_c = \frac{\varrho - \varrho_a}{\varrho_c - \varrho_a}\right)$, since up to ow the values ϱ_c and ϱ_a were generally assumed to be constant for irradiated polyethylene [20].

II. Approach

ϱ_c and ϱ_a can be determined by combining measurements of bulk density (ϱ), percent crystallinity (v_c, w_c) and the density difference ($\Delta\varrho^7$. This approach has been well established for several different preparations of uncrosslinked polyethylenes [21–26] and can be readily seen from the definition:

$$v_c = \frac{\varrho}{\varrho_c} w_c = \frac{\varrho - \varrho_a}{\varrho_c - \varrho_a} = \frac{\varrho - \varrho_a}{\Delta\varrho} \tag{1}$$

$$\text{or } \varrho_a = \varrho - v_c \, \Delta\varrho \,. \tag{2}$$

All three measurements are relatively straightforward, e. g. ϱ from the gradient column, w_c from WAXS (used to approximate v_c) and $\Delta\varrho$ from the Invariant Q, which can be obtained from the SAXS integrated intensity. After determining ϱ_a, ϱ_c can be obtained from $\Delta\varrho$ and ϱ_a.

$\Delta\varrho$ comes from the Invariant Q as follows [27, 28]:

$$Q = \int_o^\infty s^2 I(s)\, ds \tag{3}$$

where $s = (2\sin\theta)/\lambda$. Q is independent of the arrangement of scattering units, and depends only on the mean-square density fluctuation $\langle\eta^2\rangle$:

$$Q = K P_o d a \langle\eta^2\rangle = C\langle\eta^2\rangle \tag{4}$$

where C is constant for a given experimental condition and includes the constant K, primary energy P_o, sample thickness d, and distance between sample and plane of registration a.

For a two-phase structure $\langle\eta^2\rangle$ is defined as:

$$\langle\eta^2\rangle = v_c v_a (\Delta\varrho)^2 . \tag{5}$$

In order to eliminate the constant C in equation (4), $\Delta\varrho$ for a crosslinked sample was obtained by taking the ratio of the Invariants or:

$$\frac{Q}{Q_o} = \frac{v_e v_a (\Delta\varrho)^2}{(v_c v_a)_o (\Delta\varrho_o)^2} = \frac{w_c w_a (\Delta\varrho)^2}{(w_c w_a)_o (\Delta\varrho_o)^2} \tag{6}$$

where the subscript "o" refers to the uncrosslinked sample. The density difference $\Delta\varrho$ for the crosslinked samples can then be obtained from equation (6) using w_c from WAXS and $\Delta\varrho_o = 0.124$ g/cm^3 for the uncrosslinked PE, the latter determined using a calibrated Kratky sample.

III. Experimental

Material: The same BPE (DuPonts's Alathon 10) used in an earlier study [19], having a reported density of 0.920 g/cm^3 and 2.5 CH_3 branches per 100 C, was chosen for our present investigation. Compression molded samples 1 mm thick were sealed under vacuum in glass tubes and irradiated at room temperature with a Co^{60} source at University of Michigan's Phoenix Memorial Laboratory. The dose rate was 0.45 Mrad/hour. After irradiation the samples were kept under vacuum for at least one week to ensure decay of the trapped radicals.

Bulk density: Bulk density ϱ was measured in a gradient column containing a methanol-water mixture at 23 °C to within $\pm 1 \times 10^{-4}$ g/cm^3.

WAXS: WAXS was carried out in a Phillips Norelco diffractometer with monochromatized CuK_α radiation. w_c was determined from the integrated crystalline peaks $I_{110} + I_{200}$ and the amorphous halo peak located at $2\theta = 19.9$. $\bar{d}_{110}$ and $\bar{d}_{200}$ were also determined. To obtain accurate data of w_c and d-spacings, five measurements were made for each sample and then an average was taken for each data point shown in figures 1 and 2.

SAXS: SAXS was carried out in a Rigaku-Denki unit. The scattering intensity was recorded on film and then determined using a Joyce-Loebl microdensitometer.

IV. Results

The measured bulk density (table 1) shows a slight but noticeable drop at 10 to 20 Mrads; otherwise, it increases gradually and steadily with increasing radiation from $\varrho = 0.9218$ for the unirradiated sample to $\varrho = 0.9241$ for a 400 Mrad sample. The changes are similar to those reported before by us [19] using neutron radiation or by others [31] using Co^{60}, although they differ somewhat in the extent of decrease and the onset of increase at higher dose. If one uses these ϱ values in equation (1) and assumes constant values of ϱ_c and ϱ_a taken from the literature [29] for a similarly branched PE, one gets a corresponding decrease and increase in the calculated v_c, as shown by the dotted line in figure 1.

In contrast to the above density v_c behavior, measurements from WAXS clearly indicated, after showing relatively little changes in the low dose range, a measured *decrease* in w_c crystallinity beginning at about 100 Mrads (fig. 1, upper full line). The discrepancy in the behavior quickly disappears if one substitutes in equation (1) the correct ϱ_c and ϱ_a values that we have obtained for our irradiated samples, shown in table 1. With the corrected values, v_c and w_c no longer appear to diverge with increasing radiation; the values are in

Table 1. Experimental and calculated results

Mrad	ϱ(g/cm^3)	w_c(%)	$I_{int}/I_{int,\,o}$	$\Delta\varrho^*$(g/cm^3)	ϱ_c^*(g/cm^3)	ϱ_a^*(g/cm^3)
0	0.9218	50.94	1.00	0.124	0.983	0.859
10	0.9216	50.89	0.870	0.116	0.979	0.863
20	0.9215	51.17	0.861	0.115	0.978	0.863
100	0.9226	50.30	0.843	0.114	0.979	0.865
200	0.9230	48.52	0.787	0.110	0.980	0.870
400	0.9241	46.96	0.676	0.102	0.978	0.876

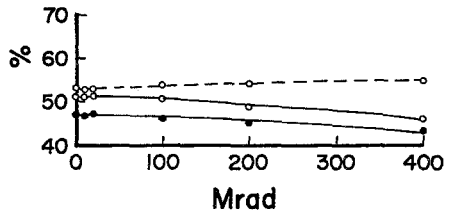

Fig. 1. Changes in crystallinities as a function of radiation dose. Dotted line represents v_c (from density) and solid line represents w_c (from WAXS). Solid symbols represent corrected v_c

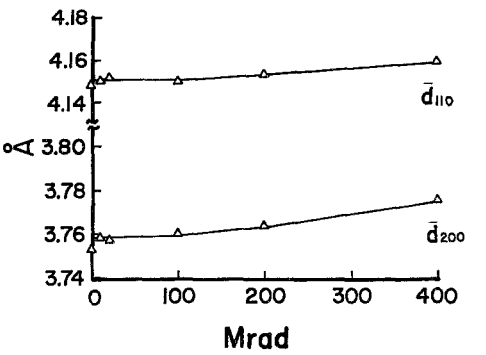

Fig. 2. Changes in d-spacing as a function of radiation dose

excellent correspondence (fig. 1). v_c values are now about 6 to 7 % smaller than w_c, which is expected from the multiplication factor ϱ/ϱ_c in equation (1). The removal of the discrepancy between crystallinity values is a clear indication that the phase densities ϱ_c and ϱ_a are not constant with radiation and the values must be affected by the introduction of crosslinks. This occurs throughout the whole radiation range, but it is of particular importance in the range 0 to 100 Mrads, where crystallinities (v_c and w_c) are not very much affected by the crosslinks. Thus ϱ_c and ϱ_a measurements, to be shown later, are much more sensitive than crystallinity measurements for the detection of crosslinks at low doses. The SAXS results will be described after the d-spacing results from WAXS, which appear to show similar sensitivity to radiation as the measurements of ϱ_c and ϱ_a.

The reason that the dotted line (calculated v_c using constant ϱ_c and ϱ_a values) and the fully corrected, solid v_c line do not quite coincide even at the starting point for the 0 Mrad sample is simply due to the difference between the reported [29] $\varrho_{c,o}$ (0.980 g/cm^3) and $\varrho_{a,o}$ (0.856 g/cm^3) and our measured $\varrho_{c,o}$ (0.983 g/cm^3) and $\varrho_{a,o}$ (0.859 g/cm^3).

The changes in d-spacings, $\bar{d}_{110}$ and $\bar{d}_{200}$, are shwon in figure 2. From the measurements for the unirradiated sample we calculated a $\varrho_{c,o}$ value of 0.985 g/cm^3, which is very close to the reported $\varrho_{c,o}$ value mentioned earlier for a similarly branched PE [29]. We could not calculate the ϱ_c for the irradiated samples because of the introduction of possible changes in composition by the crosslinking process. The calculated value of $\varrho_{c,o} = 0.985$ g/cm^3 is also very close to our finding of $\varrho_{c,o} = 0.983$ g/cm^3 from SAXS (table 1), which again suggests that our d-spacing measurements were quite accurate.

Our measured d-spacings take on a sudden jump at a relatively low dose of 10 Mrads, after which a continued increase can be seen in both $\bar{d}_{110}$ and $\bar{d}_{200}$ (fig. 2). Similar increases in $\bar{d}_{110}$ and $\bar{d}_{200}$, including jumps at a relatively similar low dose followed by a more gradual increase afterwards, have also been detected by Hosemann et al. [12–14] in oriented linear PE, though their observed increases were much greater than ours. They had interpreted their results, together with those showing that the lattice distortions introduced were paracrystalline in origin, to be evidence for the introduction of crosslinks within the crystal. We shall see if the same interpretation can be made for our samples. It is of interest to note that these d-spacing increases, which begin at very low doses and which eventually reach an a/b ratio of $\sqrt{3}$ at high doses [19], are a clear indication of the onset of an orthorhombic-hexagonal transition [19]. It was these increases in d-spacings which led Nagasawa and Kobayashi to propose for the very first time their crosslinking-within-the-crystal mechanism and which led Ungar and Keller to introduce their "transition" from a crosslinking-at-the-fold to a crosslinking-within-the-crystal model. Thus one might conclude that there should not be any controversy, since basically the same evidence has been used by all three research groups to show that crosslinks are introduced within the crystal. However we know that this apparent agreement may still not have resolved the controversy; the question remains of whether there is additional evidence other than WAXS (d-spacing changes, paracrystalline lattice distortions and/or crystal-to-crystal transitions) for crosslinks occurring within crystals. One such evidence may be from intrinsic viscosity [η] studies of irradiated PE by Kawai and Keller [30]. They reported that the intrinsic viscosity surprisingly took a decrease at low radiation dose, at about the same dose range where our jumps in d-spacings are noted to occur. The viscosity then showed a gradual increase, indicative of an increase in molecular weight, as expected from the intermolecular

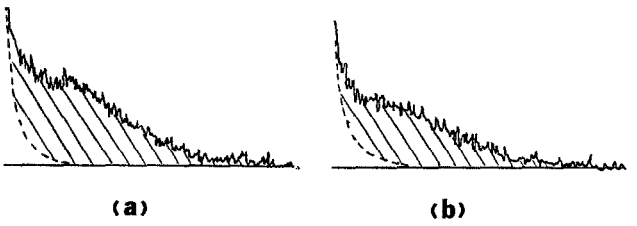

Fig. 3. Microdensitometer traces of SAXS curves: (a) 0 Mrad and (b) 400 Mrads. Dotted lines represent background scattering

crosslinking process. The decrease in intrinsic viscosity must be associated with a molecular contraction. This implies that, initially at least, the crosslinks are intra-molecular. This is possible if the crosslinks-within-the-crystals model is accepted, since intramolecular crosslinks could easily be introduced between parallel chain segments that are part of the same molecule, connected at the folds. Inter-fold crosslinks, on the other hand, would be far less likely to be intramolecular. Other evidence comes from our ϱ_c measurements described below.

The microdensitometer tracings of the SAXS intensity profiles of the unirradiated and irradiated (400 Mrad) samples are shown in figure 3. The dotted lines represent the background scattering. The integral intensity was obtained from the shaded area in this study, i. e. it was taken to be $\int I(s)\, ds$ instead of $\int s^2 I(s)\, ds$. However, this approximation should not affect the results very much since the peak position, as shown in the figure, remained essentially unchanged (corresponding to a constant long period of 170 Å) for all doses and since all the integral intensities Q are taken to be relative to that of the uncrosslinked sample Q_o.

The ratios of integral intensities Q/Q_o are seen to drop substantially from 0 to 10 Mrads (fig. 4), at which

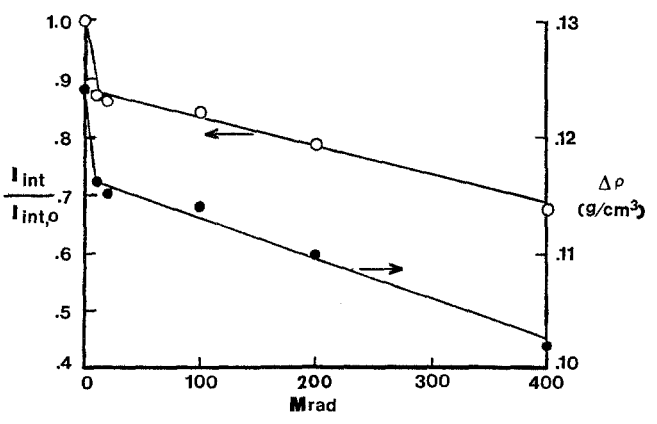

Fig. 4. Changes in ratio of integral intensity and density difference with radiation

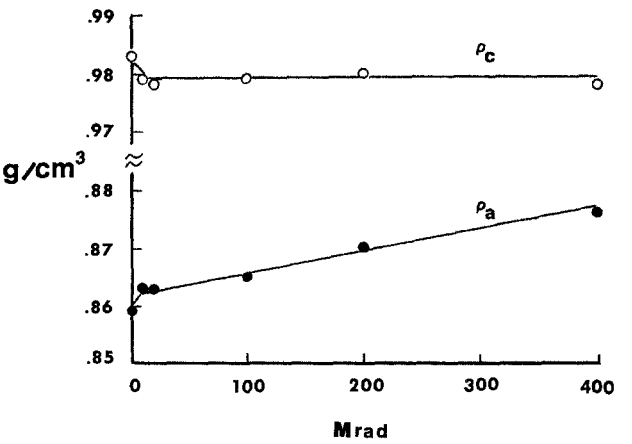

Fig. 5. Changes in densities with radiation

dose a substantial increase in $\bar{d}_{110}$ and $\bar{d}_{200}$ was noted above. It then decreases more gradually, although still quite substantially. Because of the relatively constant crystallinities which we have established in the dose range 0 to 100 Mrads, these substantial decreases in integral intensity must arise from a corresponding substantial decrease in $\Delta\varrho$ brought about by the introduction of crosslinks. This also indicates the much greater sensitivity of the SAXS measurements over other techniques (ϱ, w_c and v_c, but not d-spacing) in the detection of radiation-induced crosslinking effects.

We were able to establish that the decrease in $\Delta\varrho$ arises from changes in both ϱ_c and ϱ_a for doses up to 10 Mrads. But for doses from 10 to 400 Mrads, the highest dose examined in this study, the overall decrease in $\Delta\varrho$ is primarily due to the increase in ϱ_a. In this range ϱ_c remains relatively constant. For the determination of ϱ_c and ϱ_a, w_c is substituted for v_c in equation (2). The substitution is justified by an estimation of the correction factor ϱ/ϱ_c shown in equation (1). We find that the trend of changes in ϱ_c and ϱ_a remains the same but the substitution leads to proportionately higher values of ϱ_a and ϱ_c. For example, a higher $\varrho_{c,o}$ value would then achieve a closer agreement with the calculated value of $\varrho_{c,o} = 0.985$ g/cm^3 (versus $\varrho_{c,o} = 0.983$ g/cm^3 in table 1) for the unirradiated sample using the lattice parameters determined from WAXS. The ϱ_a for our unirradiated sample is also comparable to the values reported, being 0.859 g/cm^3 versus 0.856 g/cm^3 [29]. We can conclude that the substitution of w_c for v_c should not affect the conclusions that one can reach from our studies, namely that changes in both ϱ_c and ϱ_a are responsible for the change in $\Delta\varrho$ in the range 0 to 10 Mrads, and it is mainly the increase in ϱ_a which is

responsible for the decrease in $\Delta\varrho$ between 10 and 400 Mrads. One can also conclude that the initial decrease in ϱ_c from $\varrho_{c,\,o}$ =0.983 g/cm^3 to $\varrho_{c,\,10}$ = 0.979 (and reaching a constant $\varrho_c \approx 0.978$ to 0.980 afterwards) can be another indication of crosslinks within the crystals, most probably at the defects as suggested by Hosemann et al. Such an intra-crystal crosslinking mechanism is fully consistent with all the experimental findings indicated above, namely d-spacings etc. Crosslinks at the defects within a chain-folded crystal can lead to the observed d-spacing changes that are related to the onset of orthorhombic-hexagonal transitions, to the lattice distortion being paracrytalline and not strain induced, to the initial decrease in intrinsic viscosity as well as the decrease in ϱ_c. However we also note that there is an initial substantial increase at 10 Mrads for the non-crystalline phase density ϱ_a as well, followed by a gradual increase, suggesting crosslinks are also occurring in the non-crystalline phase. Nevertheless our d-spacing and ϱ_c data and their interpretation are in full agreement with other existing data and interpretations by others.

V. Discussion

Before discussing what additional information the variations in ϱ_a and/or ϱ_c can provide about the location of crosslinks, we need to emphasize again that these values, whether relative or absolute, are quite comparable to other published values, as indicated in the Results section. The fact that the substitution of the correct, changing values of ϱ_a and ϱ_c in equation (1) leads to values of v_c which no longer diverge with the values of w_c as a function of radiation dose is another indication that the changes in ϱ_c and ϱ_a are quite meaningful in themselves and worthy of further consideration.

In the range 0 to 10 Mrads the observed increase in ϱ_a appears to introduce another complication for those who subscribe to the hypothesis (e. g. Hosemann) that crosslinks occur within the crystal and nowhere else. The increase in ϱ_a must be associated with an increasing average density of molecules in the noncrystalline phase. This increase is observed to a greater degree than the opposite, negative contribution due to the loss of hydrogen atoms. So, if crosslinking occurs in a noncrystalline region, one obvious possibility is the interfold region where crosslinks occur predominantly between two folds in adjacent lamellae. Such crosslinking should lead to increases in ϱ_a with little or no observed change in ϱ_c in dose ranges from 0 to 10 Mrads and beyond. However, such a crosslinking process, or the occurrence of it at increasingly higher doses, means that there will be a closer and closer packing of the lamellae and therefore a decrease in L. This is not observed. We noted a constant long period ($L \approx 170$ Å) throughout the dose range. Furthermore, the continuation of such an inter-fold crosslinking process would lead to a crystallinity decrease much less than that which is measured, as already pointed out in the Introduction, unless another process, such as Hosemann's intra-crystalline crossllink model, takes over at some higher dose.

However, there is another non-crystalline region which has yet to be considered, that is the region of the lateral grain boundaries (LGB) between crystallites. This region may be, if not the sole site, possibly an important additional site for crosslinking. The possibility that crosslinks may occur in LGB has the distinct advantage that one need not invoke different crosslinking mechanisms to account for different trends in data over the entire dose range. It has already been shown that at the lowest dose range, 0 to 10 Mrads, the preferred sites for crosslinks are the defects within the crystals. In the LGB even more of this same type of defects are present along the liquid-like parallel chain segments. Thus there is no reason why the defects in the grain boundaries should not be just as effective as those within the crystals. We cannot find any inconsistency with this model nor with any of the existing experimental data, including the filtration studies on single crystals by Salovey and Keller [6], when the existence of lateral grain boundaries in single crystals [33] are taken into consideration.

With the additional possibility of crosslinks occurring at defects, both in the LGB and in crystals, one can explain data through a wide range of radiation dose, including the unusual behavior noted at the lowest doses. At doses from 0 to 10 Mrads, crosslinks would occur both at defects within crystals and in LGB. This results in ϱ_a increasing and ϱ_c decreasing, as is observed in this dose range. However, there would be a limited number of defect sites suitable for crosslinks in the crystals, and when these defect sites are depleted, further crosslinking can only occur within the LGBs. Such a situation appears to have occurred in the range 10 to 100 Mrads. Here ϱ_c is more or less constant while ϱ_a continues to increase. The LGB crosslinking mechanism can explain why the long period remains constant in the range 0 to 400 Mrads, and also up to even higher radiation doses [16, 19]. Also accordingly, the degree of crystallinity would be expected to remain more or less constant in the dose range 0 to 100 Mrads,

as is also observed, because crosslinks at the existing defects within the LGBs are not expected to affect the original crystals very much. It is only at higher radiation doses (e. g. ≈ 100 Mrads or more) where additional distortions and/or defects are introduced by the predominantly later crosslinking process that the crystals will be affected (but only laterally and leaving $\varrho_c \approx$ constant). It is here that the decrease in crystallinity begins. This same process, which operates within the crystals and leads to an immediate and greater increase in $\bar{d}_{110}$ and $\bar{d}_{200}$ at low dose, will therefore also lead to a similar increase in these two $\bar{d}$-spacings (fig. 2) due to increasing lattice distortions introduced at the LGB and which eventually leads to the occurrence of an orthorhombic-hexagonal transition at still higher radiation dose, as observed by a number of investigators. There is also some DSC evidence indicating the introduction of more defective and/or smaller crystals beginning at as low a dose as 100 Mrads [34].

As a final remark it is important to point out that we have by no means completely resolved the controversy concerning the location(s) of crosslinks in irradiated PE. If anything our approach has clearly demonstrated that we need further study in this area employing a wider range of different experiments with polyethylenes of various chain linearities, molecular weights, and thermal histories to confirm the hypothesis that has been developed from this study and review. In light of the scientific as well as the practical significance of the subject, a continuation of such studies will inevitably lead to a better understanding of the crosslinking mechanisms and hopefully a resolution of the controversy.

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