# The Influence of Crystallization Conditions on Radiation Effects in Polyethylene — I. Crystallization from Dilute Solution and from the Melt

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*Samples of Marlex 50 crystallized from dilute solution (yielding single crystals) and in the bulk form were irradiated by high-energy electrons and the solubilities compared. The single-crystal specimens remained fully soluble after a dose of 20 megarads, which rendered the bulk two-thirds to three-quarters insoluble. Since the initial free-radical concentration was identical and the chemical changes induced were not widely different in the two kinds of specimens, it is suggested that intramolecular crosslinks, occurring in a larger number in the single crystals, are responsible for this behavior. At high doses the same solubility limit is approached by both specimens, which is ascribed to the possibility of chain cutting becoming increasingly ineffective in the single crystal. In the light of these findings, the limitations of the conventional treatment of radiation effects are discussed and the possible significance of the present results for morphological problems is pointed out.*

*A number of further effects are reported in connection with melting behavior and spin resonance spectra that are at variance with results in the literature.*

## I. INTRODUCTION

The effect of ionizing radiation on polyethylene has been extensively studied in the past[1,2] but no investigation has been reported concerning the irradiation of polyethylene single crystals.[3] We have examined the influence of morphology on the irradiation behavior of polyethylene. These studies are purely exploratory and many of the physical tools involved were used only in "key" tests. We did not intend to pursue every effect found in the course of these experiments as each might

merit a specific research program. Indeed, the present research was largely tailored so as to be accommodated by the limited tenure of one of us* at Bell Telephone Laboratories. For this reason, some experiments which appear to be obvious corollaries of the present work could not be performed, and a rather arbitrary line had to be drawn to terminate this exploratory work. Nevertheless, we feel that our findings in their present state convey sufficient information of value to have it published in its present form.

The irradiation behavior of polyethylene is a difficult and controversial subject, which is being extensively and carefully studied in different laboratories.[4-10] We have attempted to minimize uncertainties by employing a primarily comparative approach to the subject. In trying to establish differences between morphologically different polyethylenes, specimens under comparison received strictly identical treatments. Consequently, the many uncertainties that beset this field do not affect our principal experimental findings, which always refer to differences in identically treated materials.

This first paper will refer to single-crystal polyethylene prepared from dilute solution as compared with the melt-crystallized bulk specimen. We recall that such single crystals consist of uniform lamellae which are about 100 angstroms thick, the molecules approximately normal to the plane of the lamellae in a sharply and regularly folded configuration.[3] The bulk is usually considered as an aggregate of amorphous-crystalline fringed micelles. The recognition of single crystals and numerous morphological observations support the idea of identifying similar structures in the bulk. The relation between single crystals and the bulk material is one of the key problems in present structural studies of polymers. It is difficult to ascertain whether the bulk has the same structure as the single crystals or represents a different kind of aggregation solely on the basis of direct structural examinations. Consequently, novel lines of approach are essential. Besides its intrinsic interest from the point of view of irradiation chemistry, we hope that this exploratory work will be relevant to the problem of polymer morphology.

## II. EXPERIMENTAL DETAILS AND RESULTS

### 2.1 Specimens

The material studied was the linear polyethylene Marlex 50. Two kinds of preparations were used. In one case, the polymer was dissolved

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in boiling xylene and crystallized isothermally at lower temperatures. Concentrations ranged from 0.02 to 0.05 per cent and crystallizations were conducted at 70° or 85°C. A suspension of single crystals formed which could readily be verified microscopically. The suspended material was collected by filtering and was vacuum-dried. Low-angle X-ray scattering[3] revealed that the fold lengths were 110 and 130 angstroms for crystallization temperatures of 70° and 85°C respectively. The second kind of material consisted of melt-crystallized flakes. Preceding irradiation, specimens were placed in Pyrex tubes, pumped in high vacuum overnight, and sealed.

## 2.2 *Irradiation*

Irradiations were conducted within vacuum-sealed tubes in a beam of 1 million electron-volt electrons using a High Voltage Engineering Co. Van de Graaff accelerator. In order to minimize heating, samples were placed on a plate cooled by circulating cold water. The dose rate was determined by measuring the attenuation in current, with a Faraday cage, on interposing a known thickness of polyethylene in the electron beam. Moreover, current absorption by the tube was measured and accounted for. Dose rates of about 5 megarads per minute were ordinarily employed. The dose of 20 megarads was used for most comparative purposes for reasons to become apparent below, but a few experiments with other doses ranging from 2 to 128 megarads will also be quoted. Unless specifically stated, specimens were fused at 150°C while still sealed off after irradiation, which should lead to maximal changes in properties owing to the activation of the free radicals formed.[6,7]

## 2.3 *Solubility*

Solubility determinations represent the principal measurements in this work. They were carried out by Soxhlet extraction with refluxing xylene, a treatment which fully extracts the unirradiated starting material.

Bulk and single-crystal specimens showed very marked differences in their irradiation characteristics. When irradiated by our standard 20-megarad dose the bulk became much less soluble, leaving an insoluble gel fraction of 65–75 per cent. The single-crystal preparation irradiated with the same 20-megarad dose remained fully soluble, leaving no gel in the extraction thimble. Most of the work which followed was aimed at evaluating this remarkable difference.

An investigation of the full dose-solubility characteristics could not

be fully accommodated within the present experimental program. Nevertheless, we can quote a few data obtained with other doses. The radiation-solubility characteristics of the bulk have been known from some earlier work by one of us.* Even if conditions were not rigorously identical with those in the present 20-megarad experiments, they are representative of the over-all trend. Accordingly, the gel point is roughly 2 megarads; 10 megarads already gives a gel content of 60 per cent, rising to 70 per cent at 20 megarads and to 80 per cent at 40 megarads. In the case of the single crystals, a gel content of 26.5 per cent was obtained with a dose of 48 megarads. A dose of 85 megarads yielded 76 per cent, and one of 128 megarads, 86 per cent gel. The last two irradiations were carried out under somewhat altered operational conditions of the generator, which necessitated leaving the specimens in air. Even if not strictly comparable with the "standard" experiment, these figures certainly bear out the fact that at higher doses a limiting value comparable with that of the bulk is reached.

To sum up the over-all trend: the bulk shows the first signs of insolubility at less than one-tenth of the dose needed to produce the first gel in the single crystals. It becomes two-thirds to three-quarters insoluble at a dose where the solubility of the single crystals is still unaffected, but at sufficiently high doses both specimens converge to approximately the same limiting solubility.

When a single-crystal preparation was fused prior to irradiation, the 20-megarad dose resulted in 71.4 per cent gel; consequently, the sample behaved as the bulk material did. This means that the change in solubility is due to the difference in the morphology alone and not to some change introduced in the course of specimen preparation. No obvious change in the X-ray pattern could be observed on irradiation within the dose range studied in either type of specimen. Further, the irradiated and still soluble single crystal (irradiated to our standard 20-megarad dose), dissolved thereafter, showed no significant difference in its subsequent crystallization behavior from that of similarly treated unirradiated material.

## 2.4 Viscosity Measurement

The intrinsic viscosities of two single-crystal preparations, one before and one after irradiation with 20 megarads, were compared in dilute xylene solution at 100°C. The results were 1.42 deciliters per gram for

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the unirradiated and 1.38 for the irradiated specimens, the difference considered to be within experimental error.

## 2.5 *Melting Behavior*

It was found that the melting behavior was largely dominated by rate effects unless special precautions were taken to heat the samples slowly. We were not aware of this in the first experiments, which consisted of placing small fragments of irradiated and unirradiated polyethylene side by side on a coverglass lying on a temperature gradient bar. The coverglass was moved gradually along the bar towards higher temperatures. Since the unirradiated single-crystal preparation goes through a series of pronounced premelting and recrystallization effects, specimens were first fused once so that the initial morphology was identical in all of them. The irradiated bulk material retained its shape even after fusion, so that the melting point could not be readily deduced from the consistency alone. The irradiated single-crystal specimen, however, was found to melt 4 to 5°C lower (at 130 to 132°C) than the corresponding unirradiated samples (135 to 136°C) in this test. It is worth noting that the consistency above the melting point proved to be uniquely related to the solubility. Irradiated specimens which did not flow when heated to 140 to 150°C invariably proved to be largely insoluble. Thus, the solubility results could always be predicted from the appearance of the sample when fused in the course of our standard treatment after irradiation.

More accurate melting-point measurements were determined by a precision dilatometric technique set up by C. J. Aloisio and S. Matsuoka of Bell Telephone Laboratories. Heating rates were very slow, the entire procedure taking about seven days. Just below the melting point, the temperature was raised in very small increments, allowing the materials to recrystallize. The unirradiated single crystals showed pronounced recrystallization effects, i.e., remelting and recrystallization to higher densities, in contrast to the smaller effects evidenced by the irradiated single crystals (which had already been fused following irradiation). The melting point itself was the same for all four irradiated and unirradiated specimens: 135.5 to 136°C. Accordingly, the previously observed melting-point depression in the irradiated single crystals was due to the relatively rapid rate of heating. We did not observe the melting-point depression of 4 to 5°C reported in the literature for bulk specimens irradiated with comparable doses.[8] After fusion, the dilatometer was cooled to 125°C, and the samples recrystallized at this temperature.

Both irradiated samples attained the previously observed specific volumes, in contrast to the unirradiated samples, which reached higher densities when cooled at 125°C from the melt.

## 2.6 *Electron Spin Resonance*

Electron spin resonance measurements were made with a Varian EPR spectrometer in order to assess the free-radical concentration resulting from irradiation. We compared a single-crystal preparation and a bulk specimen irradiated with 20 megarads. Irradiation was conducted at low temperatures by placing the specimen tubes on a block of solid carbon dioxide wet with acetone. In this case the samples were not fused immediately afterwards, as was done in the other experiments, but the tubes were dropped into liquid nitrogen. The specimens were subsequently warmed for successively increasing lengths of time, and spin resonance measurements were made (with the sample in an unirradiated part of the tube).

Measurements at liquid nitrogen temperatures revealed broad absorption peaks in both specimens. These were identical in position, shape, and intensity for single-crystal and bulk specimens. On exposure to room temperature the strength of the absorption decayed, while a multiple-line pattern emerged from the band. The decay was much faster for the single crystals, where the peak decreased by a factor of eight after two hours and by a further 40 per cent after a total time of 16 hours. The corresponding decrease in the bulk was only by a factor of two, taking place during the first two hours, and resulting in a seven-fold difference between the two specimens. On heating to 74°C the absorption in the bulk decreased by 60 per cent after half an hour, and a further decrease to one-third of this value occurred after 20 minutes at 120°C. The single-crystal spectrum remained essentially unchanged by this treatment. Thus, the two peaks became roughly comparable in the two specimens. The peaks remained unaltered in both specimens on fusion at 152°C for half an hour, but a further decrease by a factor of two occurred in the single crystals when they were kept fused overnight. The spectra persisted even when the tubes were opened.

The initial decay could also be seen visually. Both specimens were brown after irradiation at low temperatures, but the color faded rapidly on warming to room temperature.

We do not attempt any specific assignment of the band, particularly as in some detail our findings differ from those reported in literature.[7,9] For the present purpose it suffices to conclude that the free radicals

responsible for the absorption were present in comparable concentration in both kinds of irradiated specimens, but showed different decay patterns in the two.

### 2.7 Infrared Spectra

We examined infrared absorption of single crystals and bulk specimens and corresponding samples irradiated with 20 megarads. There were only slight differences between the original bulk and single-crystal specimens. On irradiation the vinyl peaks (terminal unsaturation) at 910 and 990 $cm^{-1}$ decreased in both specimens but to a lesser extent in the single crystals, where it decreased by a factor of two, in contrast to the bulk, where the decrease was by a factor of seven (as referred to the weak methyl band at 1370 $cm^{-1}$). There was a pronounced increase of the transvinylene band (internal unsaturation) at 965 $cm^{-1}$, which was practically identical in the two samples (in the single crystals the increase was about 20 per cent larger).

### 2.8 Hydrogen Evolution

A bulk and a single-crystal specimen irradiated with 20 megarads were analyzed for free hydrogen with a mass spectrometer. Single crystals gave off $4.19 \times 10^{-4}$ mole hydrogen per mole of $CH_2$ and the bulk gave off $8.17 \times 10^{-4}$. After this analysis the specimens were fused and analyzed again for free hydrogen which might have been originally occluded. Only a slight increase was found, the final figures being $4.40 \times 10^{-4}$ mole per mole of $CH_2$ in the single crystals and $8.28 \times 10^{-4}$ mole per mole of $CH_2$ in the bulk. The single-crystal preparation gave off noticeable amounts of larger fragments roughly comparable in volume to the hydrogen evolved. Thus, in this measurement the single crystals gave off about one-half the amount of hydrogen as did the bulk.

### III. DISCUSSION

It was initially apparent from the solubility measurements that the samples crystallized from the melt and from dilute solution responded differently to irradiation. Here we shall discuss possible causes of this striking difference. The decrease in solubility on irradiation is usually associated with the formation of crosslinks leading to an infinite network. In fact, solubility is often used as a measure of crosslinking on the basis of Flory's theory of network formation.[1,2,11] Accordingly, the first signs of insolubility are observed when an infinite network first forms. The

dose where this occurs is referred to as the *gel point* because insoluble material appears in the gel consistency. With increasing doses the relative amount of gel increases and rapidly attains a high value. For a given crosslink concentration, the gel point is also a function of the molecular weight; shorter molecules lead to enhanced solubility. Moreover, the onset of gelation is somewhat retarded by the incidence of scission, which accompanies crosslinking in the irradiation of polyethylene.[1,2]

Our observations first raise the question whether or not the radiation has an intrinsically much smaller effect on the single crystals than on the bulk. For this, as for most of the later arguments, we concentrate on the specimens which received 20 megarads, since in this case the differences were the most clear cut; the single crystals remained soluble, while about 70 per cent of the bulk became insoluble. Certain references in the literature state that irradiation should have a much smaller effect on the crystalline than on the amorphous portions.[6,7] Accordingly, single crystals should be less affected. However, L. Mandelkern* has found that the effects of irradiation on the solubility of crystalline and amorphous polymer depend on the radiation dose. In any case, the crystallinity content of the bulk specimen is not sufficiently different from that of the single crystals (it is about 90 per cent crystalline) to account for our effect, quite apart from the ambiguities encountered in definitions of the amount of crystallinity. However, our spin resonance results indicate that the primary effect of the radiation is comparable in bulk and single-crystal specimens, the concentration of the alkyl radicals being about the same (also indicated by the apparent discoloration). It is true that, from the one comparison pursued, the hydrogen evolution in the single-crystal specimens is only half of that found in the bulk for a dose of 20 megarads. If this means that the radiation is only half as effective in introducing chemical changes in the single crystals, the single crystals should behave like the bulk irradiated to 10 megarads. But a dose of 10 megarads still renders the bulk material about 60 per cent insoluble. Consequently, a factor of two in the hydrogen evolution could not account for our observations. Thus, the possibility that the effect of the radiation on the single crystals is sufficiently less to account for the observed increase in solubility can be ruled out.

Another alternative is that the scission-to-crosslinking ratio is higher in the single crystal, while the total effect of the radiation (scission plus crosslinking) remains comparable.

Infrared results indicate that the terminal vinyl concentration is

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higher in the irradiated single crystal than in the corresponding bulk. If scission occurs by disproportionation leading to vinyl groups, this, at first sight, may seem to support the suggestion of increased scission. However, the vinyl concentration is invariably found to go down on irradiation in spite of the assumed scission by disproportionation.[5] So does it also in both of our specimens, but less in the single crystals. Since the basic reason for the decrease in the vinyl concentration is obscure, differences in the relative amount of decrease cannot be safely invoked as evidence for differences in scission in the present argument. End-linking has been suggested to explain the terminal vinyl decay.[12] This would increase the size of the molecule and facilitate gelation, which would be in line with the more rapid lowering of the solubility in the bulk. However, whether this speculative factor could account for the large differences in the two specimens remains questionable.

The possibility of scission leading to methyl end groups through hydrogen uptake is not usually considered. We could not observe any increase in methyl concentration from the infrared spectra, but owing to the relative weakness of the band this is not conclusive. As far as one can surmise, such a mechanism could consume part of the hydrogen evolved and explain why less hydrogen forms on irradiation of single crystals. However, this hydrogen deficiency could result from a recombination of the radical and hydrogen, which might occur more readily in the better-ordered single-crystal system. Thus, while the infrared evidence raises some interesting possibilities, it remains inconclusive as regards scission. Neither is there evidence for an increase in scission from other properties, such as viscosity or melting point. In fact, there is no evidence for scission at all other than the existence of a limiting solubility at high doses. Since this limiting solubility is comparable for both samples, it is unlikely that the amount of scission should be much different at the smaller doses.

The theory of network formation on which all arguments in this field are based assumes that crosslinks are randomly distributed between different molecules, intramolecular crosslinks being ignored. If in two specimens the total number of crosslinks were the same, but in one of them part of the crosslinks were *intramolecular*, the latter one would evidence enhanced solubility. In other words, part of the crosslinks would not contribute to the formation of an infinite network, hence they would not contribute to the decrease of solubility. The existence of some intramolecular crosslinks ("ringlinks") has been suggested[13] to account for the lack of material balance on irradiating bulk specimens. Since single crystals consist of folded chains, intramolecular crosslinking would be

expected to be appreciable. In fact, it was with this expectation that the present investigation was undertaken.

Besides the enhanced probability of intramolecular crosslinking in a folded structure, the probability of multiple intermolecular linking between a finite number of molecules in close proximity is also enhanced, in view of the extensive contacts between ribbons of folded molecules. Such crosslinks will not contribute to the formation of an infinite network, hence will be ineffective in lowering the solubility. The presence of these crosslinks should, however, show up in the viscosity. The lack of a significant change in our viscosity figures might be due to a counterbalancing of two effects: a reduction due to internal crosslinks making the molecule more compact and the increase of the molecular weight.

Attractive and probable as the explanation based on intramolecular crosslinking may sound, no final confirmation could be brought to bear on the issue within the range of the present work. The salient point is that there is no direct chemical method for the assessment of crosslinks. Usually the solubility criterion is used, and this is clearly restricted to intermolecular crosslinks. In fact, our experiments demonstrate the limitations of this criterion. The situation is identical with changes in the elastic modulus, which are also used as a measure of crosslinking,[1,2] since this is also based on the formation of infinite networks through intermolecular crosslinks. The simultaneous appearance of insolubility in the irradiated material and that of rubbery consistency on fusion are due to this reason. This leaves us with the possibility of studying internal configuration in greater detail, which would require extensive and careful work on solution properties beyond the scope of the present investigation.

The fact that the limiting gel content is comparable for both samples in spite of the significant initial difference needs some comments. It is customary to characterize the scission/crosslinking ratio $(p/q)$ by a plot of $s + \sqrt{s}$ versus $1/r$, where $s$ is the soluble fraction and $r$ is the dose: then the intercept along the ordinate gives $p/q$.[4] Since this intercept will be determined by solubility figures at high doses, different curves tending to the same limiting value will give the same $p/q$. In such cases the same $p/q$ is assigned to the corresponding samples, and the differences at lower doses are attributed to differences in the type of initial molecular weight distributions.[4] (The molecular weight distributions will tend to become identical — random — in the course of scission.) In our case, however, the molecular weight distribution is identical in the two samples. The fact that after fusion the single-crystal preparation showed the same radiation characteristics as the bulk proves that no molecular weight or distribution change sufficient to modify the radiation behavior could

have occurred during the preparation of the single crystals. This means that the practically identical $p/q$ values obtained from the limiting solubility cannot characterize both samples; $p/q$ must vary with the dose at least in one, if not both, specimens.

The Charlesby-Pinner[4] treatment is based on the assumption that both crosslinking and scission are proportional to the dose received. We now suggest that this assumption could still be valid for the chemical changes induced, but that the effectiveness of these in altering the solubility might vary. We have seen that the initial solubility of the single-crystal specimen could be accounted for by assuming that part of the crosslinking is ineffective because of intramolecular (or multiple inter-molecular) crosslinks leading to a large effective $p/q$. With large doses, the effective $p/q$ decreases to that corresponding to the bulk. Plausibly, this could be due to a decrease in the effectiveness of scission while the true $p/q$ may remain unaltered. If scission occurred within a loop formed by an intramolecular crosslink (or multiple intermolecular link) the number of molecules would not increase; hence the cutting would be ineffective as regards lowering the solubility. The chance for scission to become ineffective in this way increases with crosslinking, hence with the dose. In the light of this picture, it appears even less probable that scission should be unusually high at low doses in the single-crystal preparation, which strengthens our contention that intramolecular cross-linking rather than unusually high scission should be responsible for the high solubility in the 20-megarad region.

If the explanation based on intramolecular crosslinking proves to be true it would imply that a given molecular segment within the crystal in the bulk is in an environment of segments predominantly belonging to different molecules, in contrast to single crystals, where it would be partly in the vicinity of other parts of the same molecule. This would suggest that chain folding would be less frequent in the bulk, if present at all. Thus, it appears that this newly found radiation effect might contribute substantially to the present controversy as to whether or not folded molecules found in single crystals are also representative of the bulk. However, it will be shown in the following paper[14] that such conclusions would be premature. It will be demonstrated that the effect of the morphology intervenes in a more subtle way and that one cannot exclude folded structures on the present evidence.

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