The Influence of Crystallization Conditions on Radiation Effects in Polyethylene — II. Crystallization from Concentrated Solutions

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Samples of Marlex 50 were crystallized from solution in the concentration range of 0.1 to 2 per cent and were irradiated with a dose of 20-megarad electrons. If crystallized at 70°C the materials were largely soluble, but if crystallization was conducted at 85°C the samples became two-thirds insoluble at from 0.4 to 0.6 per cent concentration upwards. Morphological examination of samples crystallized from 1 per cent solution revealed that the mode of crystallization was lamellar in all cases, but in the case of 70°C crystallization the lamellae were largely separated while in the 85°C case they were grown together in a compacted mass. After the latter was broken up by ultrasonic treatment this sample stayed fully soluble after 20-megarad electron irradiation. This finding indicates that the crosslinks are formed predominantly at the lamellar interfaces tying the lamellae together when these are in close contact. This might imply that the radiation is most effective at the sites where the chains fold. The present exploratory work shows the importance of the mode of packing of the lamellae, and indicates that this might be an important factor in distinguishing between the different morphologies observed in general.

I. INTRODUCTION

It was shown in the preceding paper[1] that polyethylenes crystallized from the melt and from dilute solution were affected differently by electron irradiation, the former becoming insoluble at much lower doses than the latter. In addition to their inherent interest for radiation studies, these findings should also be of value for morphological investigations, as the morphological state of the specimen may be reflected in the effect of the radiation on solubility. As was concluded in the preceding paper,

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the different behavior of the bulk and dilute solution crystallized speci-
mens indicates different morphologies. In particular, the higher solubility
of the irradiated solution crystallized specimens is readily explicable in
terms of intramolecular crosslinks forming within the folded chains of
such single-crystal preparations. Accordingly, the lower proportion or
even absence of such intramolecular linkages in the bulk would indicate
that the molecules are not folded in such specimens. This appears to
support the view that we are dealing with two distinct states of matter
in the two kinds of specimens, a point which is nowadays widely de-
bated.[2,3]

According to recent theoretical work by Lauritzen and Hoffman,[4]
crystallization from dilute solution should occur via chain folding and
that from the melt through the traditional bundle-like aggregation, a
transition occurring between the two as the concentration of the solution
is increased. Although these authors have modified their view since and
consider the possibility of a folded crystallization in all cases,* we ac-
cepted their first suggestion as a working hypothesis at the time, particu-
larly in view of the large differences found in the two specimens in our
radiation work. In order to explore the possible transition between the
two kinds of behavior we examined polymers crystallized from more
concentrated solutions. This work again is of a purely exploratory nature
subject to the same limitations mentioned in the introduction of the
preceding paper.

II. EFFECT OF CONCENTRATION AND TEMPERATURE OF CRYSTALLIZATION ON THE SOLUBILITY

2.1 Methods

Our material was again the linear polyethylene Marlex 50. Specimens
were crystallized at either 70° or 85°C from xylene solutions of varying
concentrations. Crystallization at 70°C was very rapid for the con-
centrated solutions, turbidity setting in nearly immediately on lowering
the temperature of the solution to 70°C. All samples gave discrete low-
angle reflections corresponding to spacings of 110 and 130 angstroms in
the samples crystallized at 70 and 85°C respectively. Irradiation experi-
ments were carried out under the same circumstances as in the preceding
paper.[1] Only one dose size (that of 20 megarads) was used, since it was
with this dose that the most pronounced differences between melt and
dilute solution crystallized specimens were found. Solubility changes were

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* Private communication.

TABLE I—SOLUBILITY OF POLYETHYLENE (CRYSTALLIZED AT VARIOUS
CONCENTRATIONS AND TEMPERATURES) AFTER IRRADIATION TO
20 MEGARADS

Concentration	Gel fraction	
	Crystallized at 70°C	Crystallized at 85°C
0.1%	—	1.2%
0.3	7.6%	1.4
0.4	—	4.7
0.6	—	53.6
0.8	—	57.5
1.0	2.4	64.4
2.0*	7.7	—

* There was an undissolved residue left. The actual concentration must have
been lower than 2 per cent.

determined by using the same Soxhlet extraction method described
previously.[1] All irradiations reported here were carried out under strictly
identical conditions, samples under comparison having been irradiated
simultaneously.

2.2 *Solubility Results*

The results are listed in Table I. As can be seen, the solubility re-
mained practically unaffected in the whole accessible concentration range
for specimens crystallized at 70°C, giving a very small gel content even
for the most concentrated solution (the relatively high figure at 0.3 per
cent is undoubtedly anomalous, but this does not affect the general
conclusion). Samples crystallized at 85°C, however, showed a remarkable
transition. For this reason the 85° series was closely examined. Here, the
gel content was insignificant up to a concentration of 0.4 per cent, the
material remaining essentially fully soluble. Beyond this stage however,
the gel content rose suddenly to a value comparable with bulk crystal-
lized samples irradiated to the same dose.

According to these results, all the specimens crystallized at 70°C
behaved in a similar manner independent of concentration. Since the
single-crystal nature of specimens formed at low concentrations is estab-
lished, there is no reason to expect any departure from this at the higher
concentrations on the basis of the radiation results (although the per-
sistence of single crystals to such high concentrations may appear
surprising). The transition from full solubility to two-thirds insolubility
with increasing concentration in the case of 85°C crystallization may
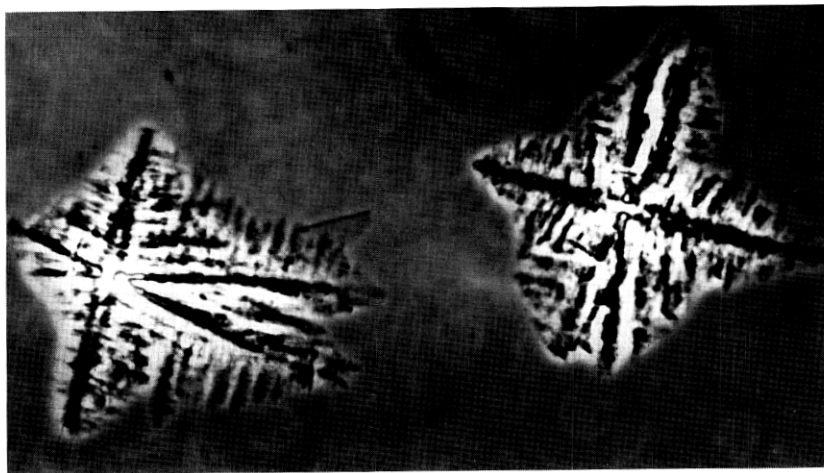appear to be consistent with the expected transition from single crystal

Fig. 1 — Typical polyethylene dendrites formed at 70°C from a 1 per cent xylene solution, photographed in a mixture of xylene and acetone. (Phase-contrast microscopy; magnification of original photograph 600×.)

to fringed micelle; the dependence on the temperature of crystallization, however, would remain unexplained.*

2.3 *Microscopic Examinations*

Specimens crystallized from 1 per cent solution at 70° and 85°C were examined by phase-contrast microscopy. Figs. 1 and 2 were taken of a suspension formed at 70°C. Fig. 1 clearly represents dendritic single crystals; Fig. 2 needs some further comments. In another investigation by one of us in collaboration with Mitsuhashi[6] it was established that the consecutive terraces of a polyethylene crystal need not be grown together but can be spatially separated, the whole crystal resembling more a loose helicoid (tighter at the center than at the edges) than a

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* One could invoke some of the implications of the kinetic approach to crystallization.[4] Accordingly, in concentrated solutions nucleation via inter- and intramolecular processes might compete. At high temperatures bundle-like crystallization would be favored in accordance with the considerations of Lauritzen and Hoffman. At low temperatures (high supercoolings) the nucleation rate might be so high that several intramolecular nuclei might form within the same molecule (a possibility predicted by Frank and Tosi[5]) even before a bundle from different molecules could develop by the aggregation of different chains. This would result in further crystal growth occurring by an aggregation of tiny chain folded crystals. Frank and Tosi estimate a crystallization temperature of 70°C in xylene where such a process could set in. Thus, as it stands this could be in line with our observations. Further observations which followed, however, indicate that other factors are at play which make this proposed explanation questionable.

Fig. 2 — Multilayer dendrites in the same preparation as in Fig. 1. (Phase-contrast microscopy; magnification of original photograph 600✕.)

solid spiral pyramid. This could be directly confirmed by observing the crystals turning in the liquid, when the individual layers could be seen to be separated and diverging outwards from the center. The more complicated structure in Fig. 2 is essentially such a multilayer crystal in an unusual projection. When such crystals are dried down, this three-dimensional structure collapses, leading to obscured areas in the interior of the crystal. It follows that such confused central areas usually observed in dried-down crystals need not be indicative of a departure from the chain folded lamellar structure. The crystals in Figs. 1 and 2 were in suspension when photographed to avoid this obscuring effect. We conclude that the specimen crystallized at 70°C has the usual lamellar single crystal habit throughout.

Fig. 3 shows a typical example of aggregates formed at 85°C. As seen, they are compact and nearly circular (although reminiscent of spherulites, they do not show a clear Maltese cross extinction pattern between crossed polaroids). In view of the marked difference in solubility after

Fig. 3 — Typical compact crystal formations of polyethylene formed at 85°C from 1 per cent xylene solution; the crystals are in their mother liquor. (Phase-contrast microscopy; magnification of original photograph 1000×.)

irradiation, we anticipated a difference in morphology between preparations formed at 70°C and at 85°C. However, the specimen crystallized at 85°C also proved to be lamellar, the distinct fibrous structure corresponding to lamellae seen edge-on. The observation of loose lamellae protruding beyond the edges of the more compact mass also suggests that the aggregates in Fig. 3 consist of closely packed lamellae. Thus the morphology may not be basically dissimilar in the two specimens. Both would consist essentially of chain-folded lamellae; in the 70°C crystallization the lamellae within a crystal are separated by the liquid in the sense described above, while in the 85°C crystallization they are compacted in a solid mass. It would follow, therefore, that the difference in the radiation behavior may be connected with *the mode of packing* of the lamellae. We attempted to separate these lamellae in samples crystallized at 85°C to see whether the high solubility of irradiated specimens formed at 70°C could be obtained.

2.4 *Disintegration Experiments*

The disintegration of aggregates formed at 85°C (Fig. 3) was effected by means of ultrasonic radiation. Suspensions in xylene were exposed to radiation from an ultrasonic generator operating at 40 kc and 200 watts. The first trials showed that disintegration of the aggregates occurred and samples were then subjected to treatments of increasing duration.*

2.5 *Microscopic Examination*

Increasing extents of disintegration are indicated in Fig. 4. It will be seen that the compact masses are broken up into smaller units consisting of fewer fibrous entities (lamellae seen edge-on). The full morphological implications will not be discussed here. However, we suggest that the layers in Fig. 4 are probably multilayers themselves (not the basic 100-angstrom ones), and point out the frequent occurrence of pyramidal fragments consistent with other observations in this field.[7,8,9,10] Besides the prominent structure in the photographs, a finer background structure is also visible which increases with the duration of the ultrasonic treatment. This is partly a lamellar structure of the basic 100-angstrom thickness and partly a ribbon-like fibrillar structure which may have its origin in broken-up lamellar units.

2.6 *Solubility of Irradiated Disintegrated Specimens*

Suspensions of polyethylene prepared by crystallizing a 1 per cent solution at 85°C and treated ultrasonically for 4 and 8 hours were filtered and prepared for irradiation with a 20-megarad dose in the usual manner. The irradiation of four samples was carried out simultaneously: the two just mentioned, a third sample which was a portion of the above preparation that received the eight-hour ultrasonic treatment but was fused subsequently, and a fourth sample that was crystallized under the same conditions but was not treated ultrasonically. When the samples were heated to 150°C after irradiation, while still *in vacuo* as part of the usual procedure,[1] marked differences could be observed in the melting behavior. The untreated and the ultrasonically treated but subsequently fused sample both retained their shape and showed no outward signs of melting, while the two remaining ultrasonically treated samples flowed

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* The geometry of the set-up available for these tests permitted only a very inefficient utilization of energy. Consequently the times to be quoted are unusually long in comparison with results since obtained with other generators by one of us (A. Keller). Nevertheless, they give a comparative measure of the treatments received by the different samples.
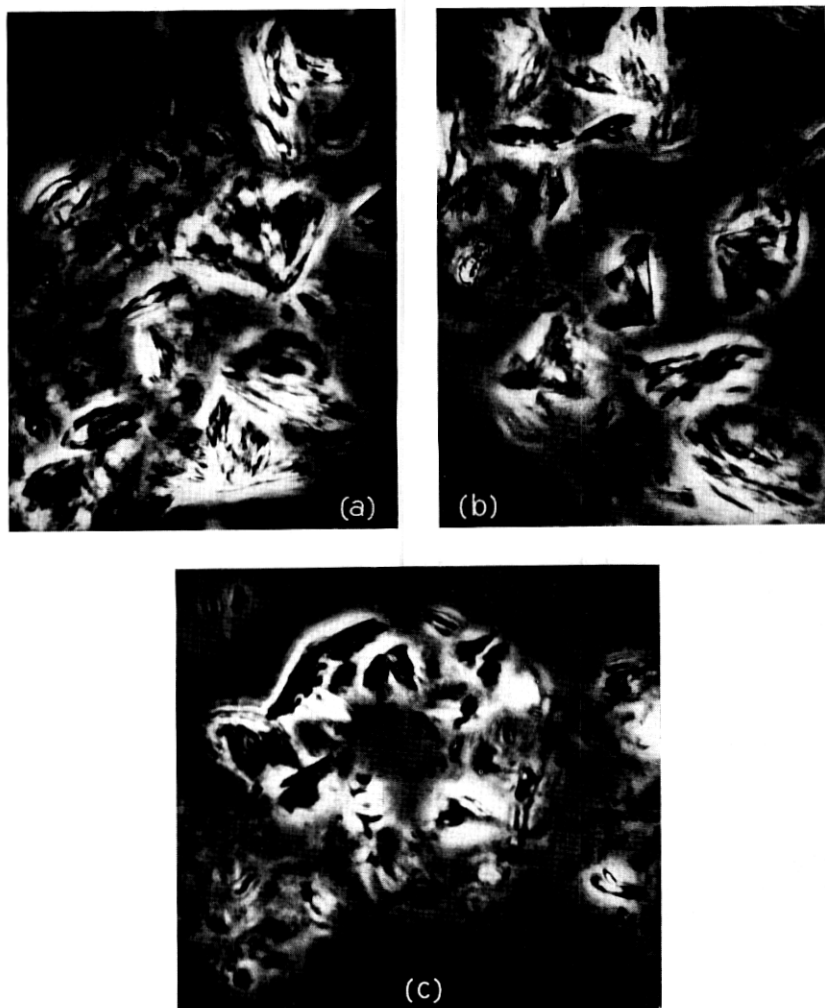
Fig. 4 — The same preparation as in Fig. 3, treated ultrasonically for (a) one and one-half hours, (b) four hours, and (c) eight hours. (Phase-contrast microscopy; magnification of original photograph 1060X).

as unirradiated polyethylene does. As described in the preceding paper, the absence of clear melting was indicative of intermolecular crosslinks and was invariably associated with appreciable insolubility. In fact, both ultrasonically treated and unfused specimens were fully soluble, the untreated sample giving a gel fraction of 60.9 per cent, and the sample

which received an ultrasonic treatment of eight hours and was subsequently fused giving 27.8 per cent gel.

III. DISCUSSION OF RESULTS

The complete solubility of the two ultrasonically treated specimens indicated that the behavior characteristic of single-crystal preparations had been restored. If the differences between specimens showing complete solubility, on the one hand, and large insolubility, on the other, after a 20-megarad dose were due to inherently different molecular textures, this situation could not be altered by ultrasonic treatment. Clearly, bundle-like structures could not be changed into folded ones in this way. However, morphological observations suggest that both kinds of samples consist essentially of lamellae which are packed differently. Accordingly, if the lamellae are closely packed in the sample crystallized at 85°C crosslinking is more likely to occur between them. Such interlamellar crosslinks would be necessarily intermolecular and would lead to a decrease in solubility in agreement with our experimental results. This raises a further problem. Only a small fraction of the molecule (2 to 4 per cent, the part in the folds) is in the lamellar interfaces. If crosslinking could occur with equal probability anywhere along the chain, there would only be an insignificant chance for it to occur at the interface linking two lamellae. On this basis, interlamellar links could not have the significant effect our results imply. It appears therefore that the folds may be "sensitive points" where crosslinking may occur with greater frequency than elsewhere.

This situation is complicated by the fact that the gel fraction of the sample which was treated ultrasonically for eight hours and subsequently fused did not regain the value of 60.9 per cent given under exactly the same conditions by the untreated control (but only yielded about half of this quantity). Probably an appreciable amount of chain-cutting was caused by the ultrasonic radiation. Then the increase of the solubility of the two unfused ultrasonically treated specimens cannot be interpreted in terms of physical changes alone. A significant part of it must be due to the degradation of the molecule. The amount of chain-cutting is expected to depend on the time of ultrasonic treatment; the sample treated for four hours was still fully soluble on irradiation and the minimum treatment required might well be still shorter. This means that our treatment and consequent degradation were unnecessarily drastic. Therefore, perhaps a more complete reversibility of the gel content on fusion would still be compatible with full solubility of the specimen prior to

fusion. Fuller clarification of this point could not be accommodated in the present program. The present results have established the fact that the mode of aggregation of the lamellae can have a profound effect on the irradiation behavior. In view of scission during the ultrasonic treatment, it cannot be stated with certainty that the *full* difference in irradiation behavior between the two specimens under question can be accounted for by the mode of aggregation of the lamellae.

We have tacitly implied that the contact between layers is of the van der Waals type only. It is likely that the better compacting of the units in the specimen crystallized at 85°C is due to a few molecules running through two or more layers before folding back, or that some folds might interpenetrate. This situation is more likely to arise with concentrated systems. If this were the case, these joining molecules would have to be cut for the lamellae to be separated, which would mean that some of the molecular degradation may be necessarily linked with the physical separation of the layers.

We have seen that the packing of the layers is strongly influenced by the temperature of crystallization, layers grown at higher temperatures being more closely stuck or linked together. At this stage, we can offer no explanation for this behavior.

IV. SOME GENERAL CONSIDERATIONS

In Section III, discussion was restricted to the interpretation of differences between two kinds of solution crystallized specimens, one crystallized at 70°C and the other at 85°C from 1 per cent xylene solution. The question arises as to whether the explanation cited could be extended to account for the differences between solution-crystallized specimens (which retained their full solubility after a 20-megarad dose) and bulk specimens (which became two-thirds to three-quarters insoluble after the same dose). In the light of present findings it can certainly be stated that this difference need not be associated with a basic difference in molecular texture, i.e., either with the presence of folded molecules or of bundles. In fact, in the case of specimens crystallized from 1 per cent solution at 85°C, no basic departure from single-crystal texture was found other than more compact packing of lamellae, perhaps arising from some attachment of these units. It may not be unreasonable, therefore, to consider the possibility of the same effect being responsible for bulk behavior. This would imply that the bulk might consist of chain folded lamellae. Indeed, we would expect closer packing and stronger connectedness of such lamellae in the bulk. Such a picture of the bulk

would not contradict the results of the present radiation studies. On the contrary, it would be supported by analogy with the behavior of specimens crystallized from concentrated solutions as well as by existing evidence of lamellar structures in the bulk.[11,12] In view of the complexity of the subject, it is not intended to imply that the present evidence is in any way conclusive. (For other views see, for example, Chiang and Flory.[3])

In conclusion, the present exploratory work has drawn attention to limitations in the usual treatments of the effects of irradiation which consider random intermolecular crosslinking and random scission only. Moreover, it contributes to current morphological studies by indicating the importance of packing of crystal lamellae. Finally, radiation effects are shown to be sensitive indicators of the morphological state of the polymer, and thus should take their place among other structural tools.

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