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The Nucleation of Polyethylene Dendrites from Solution

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This paper is a study of nucleation mechanisms in the formation of polyethylene dendrites from dilute solutions. Polyethylene dendrites may be either of regular morphology or of irregular morphology ("hedgehog" dendrites). By varying the temperatures of dissolution and crystallisation, as well as the general impurity level of the system, it was possible to alter systematically the relative ratio of regular to hedgehog dendrites. It was found that regular dendrites could be nucleated through a "self-seeded" process, as well as through homogeneous nucleation. The irregular hedgehog dendrites were observed to be nucleated heterogeneously. The degree of super-cooling necessary for dilute solution homogeneous nucleation was established ($\sim$ 30° C).

1. Introduction

1.1. Polyethylene Dendrites

The dendritic growth habit has often been observed with polyethylene crystallised from dilute solution [1-8]. Single crystalline lamellae of linear polyethylene grow from dilute solution in a temperature range between about 80 and 90° C, while below 80° C dendrites usually form. The morphological features of these solution-grown dendrites have been characterised previously. Details regarding the development of spiral growths and the delineation of fold domains were illustrated by Reneker and Geil [9], while Wunderlich and Sullivan [10] analysed the dendrites grown under differing conditions of concentration, temperature gradient, pressure and viscosity. The crystallised dendrites appeared to be of two distinct types based on their form and appearance: regular dendrites, characterised by a uniform arrangement of the branches and a set habit (figs. 1 and 3), and irregular or hedgehog dendrites with branches coming off in all directions about central portions of unresolved structure (figs. 2 and 4). The prominent characteristic of the hedgehog dendrites was their irregular appearance. This coupled with the fact that hedgehog dendrites persisted over a wide concentration range, even though concentration was found to alter critically the habit of the regular dendrites, suggested a heterogeneous nucleation process in solution giving rise to hedgehog dendrites [10,11].

1.2. Self-nucleation in Solution

Important progress in understanding nucleation from polymer solutions was made when Blundell, Keller and Kovacs [12] demonstrated the self-nucleation phenomenon. It was established that despite apparent dissolution, as indicated by a clearing of the solution, some of a polymer remains undissolved below a critical temperature in the form of submicroscopic fragments, which on quenching are observed to act as seeds for immediate crystal growth. This critical temperature for polyethylene dissolving in *o*-xylene was observed dilatometrically to be about 110° C, beyond which complete dissolution seemed to occur [12].

2. Scope of the Investigation

Dendrites were grown from solution under varying temperature conditions and impurity levels. The analyses of these samples allowed a discussion of the probable nucleating mechanisms responsible for the formation of regular dendrites and hedgehog dendrites.

3. Experimental

3.1. Materials

The linear polyethylene used in this work was of the type Marlex 50, a homopolymer produced by the Phillips Petroleum Co, Bartlesville, Oklahoma. The number and weight average molecular weights were 8530 and 153 000 respectively. A more detailed analysis of the

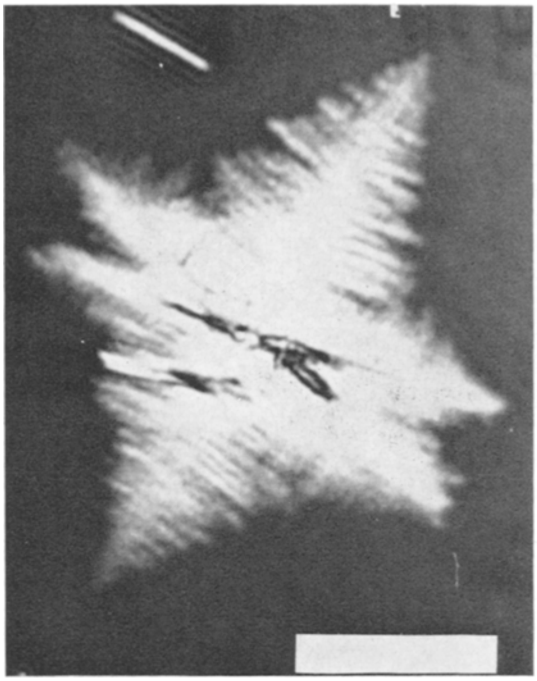

Figure 1 Interference micrograph of a regular six-ended dendrite crystallised from a toluene stock suspension. The scale bar represents 25 μm.

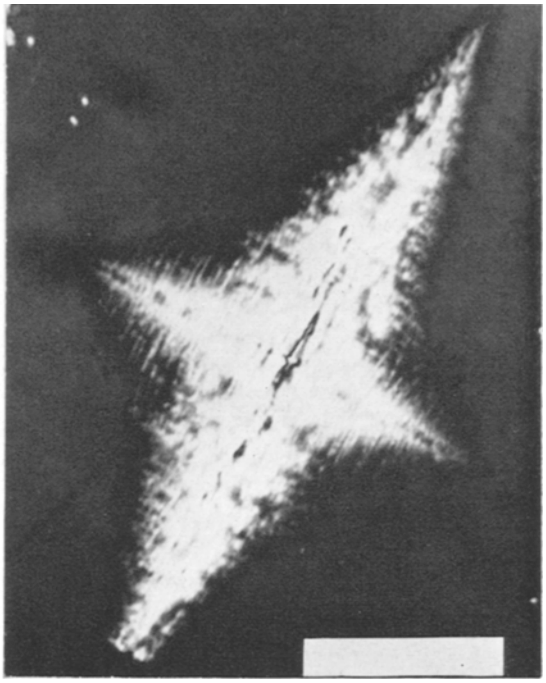

Figure 3 Interference micrograph of a regular right-angle dendrite crystallised from an o-xylene stock suspension. The scale bar represents 50 μm.

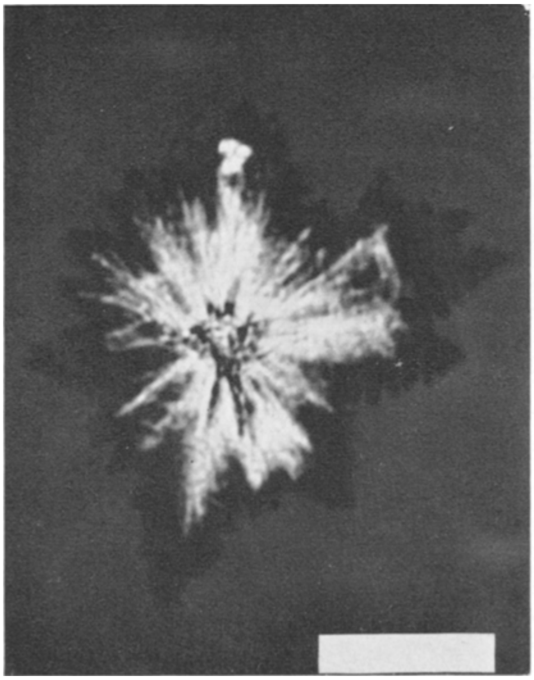

Figure 2 Interference mirograph of an irregular dendrite ("hedgehog") crystallised from a toluene stock suspension. The scale bar represents 25 μm.

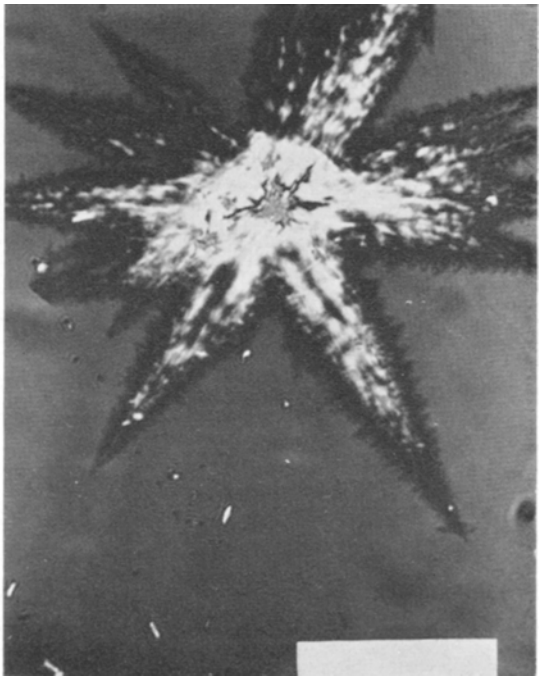

Figure 4 Interference micrograph of an irregular dendrite ("hedgehog") crystallised from an o-xylene stock suspension. The scale bar represents 50 μm.

polymer has been published in [14]. Toluene (boiling point 110.6° C) and *o*-xylene (boiling point 144° C) of reagent grade quality were used as solvents, enabling dissolution studies to be carried out over a wide temperature range. The dissolution temperature of extended chain single crystals of chemically identical polyethylene was found previously to be 109.5 ± 0.5° C in toluene and 110.4 ± 0.5° C in *o*-xylene [15].

3.2. Dissolution and Crystallisation Studies

Two stock suspensions, one for each solvent, were prepared by dissolution of polyethylene to concentrations of 0.05% (by weight) followed by quick quenching to room temperature. Dissolution and crystallisation studies were conducted in two isothermally controlled silicon oil baths. Dissolution temperatures were controlled to within ± 0.1° C, while the quenching bath in which crystallisation was carried out was controlled to within ± 0.5° C over periods of 8 to 12 h.

3.3. Analyses

All analyses of the samples were done by interference microscopy using an AO Baker Interference Microscope [16, 17]. The dendrites were mounted on a clear glass slide by waving the slide gently in the suspension of dendrites in solvent. Visual observations were made with a graduated eyepiece giving a 400 × total magnification. The dendrites were analysed by number, size, thickness and according to their type: regular or hedgehog dendrites.

The effect of extraneous foreign matter on the nucleation of the hedgehog and regular dendrites was studied with the help of impurities which fluoresce when excited by ultra-violet light. These foreign impurities were added before crystallisation. The experimental work consisted of trying to track down these fluorescent impurities visually under appropriate lighting conditions [18] to the centres of the dendrites and thus to observe the kind of dendrites they nucleated. For these observations the following accessories were used with the interference microscope: an AO Fluorolume Illuminator [16] rich in the short wavelengths; exciter filters, to cut out most of the visible light from the light source; and barrier filters, to cut out the ultraviolet and let through the fluorescent light from the specimen to the eyes of the examiner.

4. Results and Discussion

The experimental plan followed had as its initial goal the formulation of the pattern of change in crystal parameters caused by a range of dissolution temperatures. For this purpose, crystallisation experiments were conducted on the toluene stock suspension at dissolution temperatures ranging from 104 to 110° C, the crystallisation temperature in each case being maintained at 70° C. Analyses by type, number, size and thickness were made on the resulting dendrites. Crystallisation experiments were also carried out at dissolution temperatures down to 95° C; however, because of the smallness of the resulting crystals, clear identification of the type of dendrite was not possible below 104° C. The upper limit of 110° C was chosen because of its value above the dissolution temperature of large extended chain crystals (109.5° C) [15] and

TABLE I Crystallisation data on dendrites crystallised from toluene

Item	Soln. 1	Soln. 2	Soln. 3	Soln. 4
	DT 104.0° C	DT 105.0° C	DT 107.5° C	DT 110.0° C
	CT 70.0° C	CT 70.0° C	CT 70.0° C	CT 70.0° C
1. Average dimension along x-axis (mm)	0.0472	0.0375	0.0809	0.0917
2. Average dimension along y-axis (mm)	0.0355	0.0265	0.0539	0.0615
3. Average thickness regular dendrite (Å)	13 054	12 006	13 810	15 495
4. Average percentage hedgehog dendrites	33.0	31.6	46.5	64.6
5. Average diameter hegehog dendrites (mm)	0.0296	0.0256	0.0496	0.0530

The regular dendrites grown in toluene are six-ended, and are specified by dimensions along the x- and y-axes; the x-axis being along the long thin branch and the y-axis being between the two symmetrical thicker branches (fig. 1 and [10]).

DT indicates dissolution temperature and CT crystallisation temperature.

For size determination, twenty-five regular and twenty-five hedgehog dendrites were picked at random and characterised with regard to dimensions. Thickness determinations were made on fifteen regular dendrites; while for the determination of the percentages of regular and hedgehog dendrites, about 300 dendrites were counted by random movement of the microscope slide. The relative numbers of regular and hedgehog dendrites in these 300 was taken to determine the percentage of hedgehog dendrites.

its convenient value below the boiling point of toluene (110.6° C). The major points of the analysis are presented in table I.

The chief observations are the increase in size of the dendrites with increasing dissolution temperature and the steady increase in the percentage of hedgehog dendrites with increasing dissolution temperature. This latter fact appears pertinent in the light of present knowledge on self-nucleation [13]. With an increase of dissolution temperature above 104° C, the number of seeds capable of acting as nuclei for crystal growth on subsequent crystallisation is greatly reduced because of decreasing numbers of surviving nuclei at the higher temperatures. The observation of an increase in the percentage of hedgehog dendrites as the dissolution temperature is gradually raised, even with a constant crystallisation temperature and the same concentration, leads to the inference that the process of self-seeding results only in the nucleation of regular dendrites.

If self-seeding were the only mechanism responsible for the regular dendrites, one would expect that after dissolution at the higher temperatures, when a majority of the seeds have been dissolved, there would be hardly any regular dendrites formed on crystallisation (corresponding to a high percentage of hedgehog dendrites). However, experimentally this was not observed. At a dissolution temperature of 110.45° C with the toluene stock suspension, the percentage of hedgehog dendrites was observed to be far less than 100. Even at a dissolution temperature of 127.6° C (far in excess of the dilatometrically observed temperature of complete dissolution) with the *o*-xylene stock suspension, the percentage of hedgehog dendrites was observed to be only about 50. This indicated that, although self-seeding produces regular dendrites, all regular dendrites were not self-seeded, and therefore, there had to be at least one other nucleating mechanism also producing regular dendrites.

The possibility that this other nucleating path was homogeneous nucleation, dependent solely on the degree of supercooling was suggested by the observation of a much wider distribution of sizes of the regular dendrites produced after dissolution at the higher temperatures. To verify homogeneous nucleation, separate crystallisation experiments were conducted using the toluene stock suspension. In each case the dissolution temperature was maintained at 110.4° C while the crystallisation temperatures were set at 70, 75, and 80° C. At the quenching temperature of 80° C, the percentage of hedgehog dendrites was found to reach 100 (table II). A similar situation was observed with the crystallisation from *o*-xylene stock suspensions, after dissolution at 124° C. It can be concluded from the data in table II that homogeneous nucleation from dilute solutions of toluene becomes possible below approximately 78° C. The degree of supercooling at this crystallisation temperature is about 32° C. Experiments on nucleation from the melt using the droplet technique [19, 20], have shown that homogeneous nucleation occurs at a supercooling of about 55° C, similar in magnitude, but different enough in value to conclude that primary nucleation from dilute solution occurs at a smaller degree of supercooling.

The final question is: What nucleates the irregular hedgehog dendrites? The arguments earlier propounded for the heterogeneous nucleation of these dendrites [10, 11] appear well founded for it seems unlikely that an irregularly shaped, rough surfaced foreign nucleus could nucleate a crystallographically uniform regular dendrite. It appears much more possible that such an impurity nucleus would develop branches

TABLE II Crystallisation data on dendrites crystallised from toluene

Item	Soln. 5 DT 110.4° C CT 70.0° C	Soln. 6 DT 110.4° C CT 75.0° C	Soln. 7 DT 110.4° C CT 80.0° C
1. Average dimension along x-axis (mm)	0.1132	0.0734	—
2. Average dimension along y-axis (mm)	0.0700	0.0552	—
3. Average thickness regular dendrite (Å)	16 032	14 486	—
4. Average percentage hedgehog dendrites	56.2	81.0	100.0
5. Average diameter hedgehog dendrite (mm)	0.666	0.0570	0.0597

The figures quoted for the average percentage of hedgehog dendrites are estimated to be accurate to about 5%.
The hedgehog dendrites formed at the higher crystallisation temperatures (75 and 80° C) were observed to be much thicker (too thick to measure by interference microscopy) than those formed at CT 70° C. It appears that the slower nucleation at the higher values of CT causes the hedgehog dendrites to take up correspondingly more of the material.

at various random points over the surface giving rise to a hedgehog dendrite.

Experimental evidence was searched for by adding inert foreign impurities such as uranyl acetate (average particle dimension 17 μm) and zinc sulphide (average particle dimension 5 μm) to the solution. A modest increase of around 5 % in the number of hedgehog dendrites, over the cases where no impurity was added was found. A more direct method of identifying a particular impurity at the centre of a hedgehog dendrite was found in the technique of fluorescence microscopy [18].

Bottle-fresh uranyl acetate, which fluoresces green (strongest wavelengths 4700 to 6900 Å) under ultra-violet excitation [21], was chosen as the impurity and incorporated in the crystallisation experiment. The resulting dendrite suspension after crystallisation was analysed under conditions suitable for fluorescence microscopy.The green fluorescent glow observed under the standard conditions of fluorescence microscopy, coincided frequently with the centres of hedgehog dendrites but never with regular dendrites. The interference microscope provided the means for detecting the morphology of the dendrites after discovery of the fluorescing nucleus; it was observed that branches did develop from the central foreign matter. This proves that impurity particles do nucleate hedgehog dendrites, and the visual observation through fluorescence of the lack of impurity at the centre of regular dendrites indicates that they nucleate *only* hedgehog dendrites. The fact that a fluorescent glow could not be identified with the centre of all the hedgehog dendrites is compatible with the argument that additional non-fluorescing impurities were present in the solvent and polyethylene used.

5. Conclusions

On the basis of the experiments, we have identified three probable nucleation paths:

(i) A self-nucleation route as long as undissolved seeds are left because of incomplete dissolution (below about 110° C for polyethylene in toluene). These nuclei lead to the formation of regular dendrites.

(ii) A homogeneous nucleation path, dependent solely on the degree of supercooling. For polyethylene crystallised from dilute toluene or *o*-xylene solutions, a supercooling of about 30° C is necessary in contrast to 55° C for homogeneous nucleation from the melt [19].

(iii) A heterogeneous nucleation path, where foreign impurities act as nuclei for the formation of hedgehog dendrites.

Additional interesting observations made were that dendrites from the same polymer but from different solvents showed different morphologies at the same concentration (0.05 %) and at equivalent temperatures. It was observed that while the dendrites from toluene were six-ended (fig. 1) [10], those from *o*-xylene were right-angled (fig. 3) [10,11]. The dendrites from *o*-xylene were also seen to be more elongated and thicker along their long axis in contrast to the dendrites from toluene which were thicker along their shorter axis. It was also noticed that, although the lateral dimensions of the regular dendrites increased noticeably with an increase of dissolution temperature (at the same crystallisation temperature), the thickness increase was negligible. This appears surprising, when it is considered that layers are grown via growth spirals.

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