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Morphology of Thermally Degraded Polyethylene

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Introduction

The investigation of the structure of polymer spherulites has been carried out by many workers, and many interesting results have been reported. A most interesting idea is that the melt-crystallized spherulite is composed of lamellae with chain folding as in the case of the solution-crystallized single crystal. This remains a hypothesis at the present stage, but Fischer's experiments[1] on polyethylene and polyethylene adipate (nylon) support this view. Nevertheless, it is very astonishing that the molecules fold regularly from the melt in which they are believed to be entangled. It may of course be necessary to accumulate further experimental data to verify this view.

One difficulty in the study of the spherulite structure is that the spherulites are generally very small, and the compact texture composed of them must be submitted to investigation, rather than one large isolated spherulite. For this reason Keith[2] suggested an approach by investigation of the dendrite structure as a method of study of the spherulite structure. Through the investigation of the crystal orientation, the features of growth and other properties of the dendrites, the structure of melt-crystallized material, which is usually obtained as spherulite, may become clearer. Accordingly, it is desirable to obtain a polymer dendrite, but this is not necessarily easy, because in most conditions it is the spherulite that is formed.

The present study has been carried out on the dendritic structure of polyethylene degraded by oxidation caused by heating in the atmosphere. This would supply information about the dendritic structure and, further, about the spherulite structure of undegraded polyethylene.

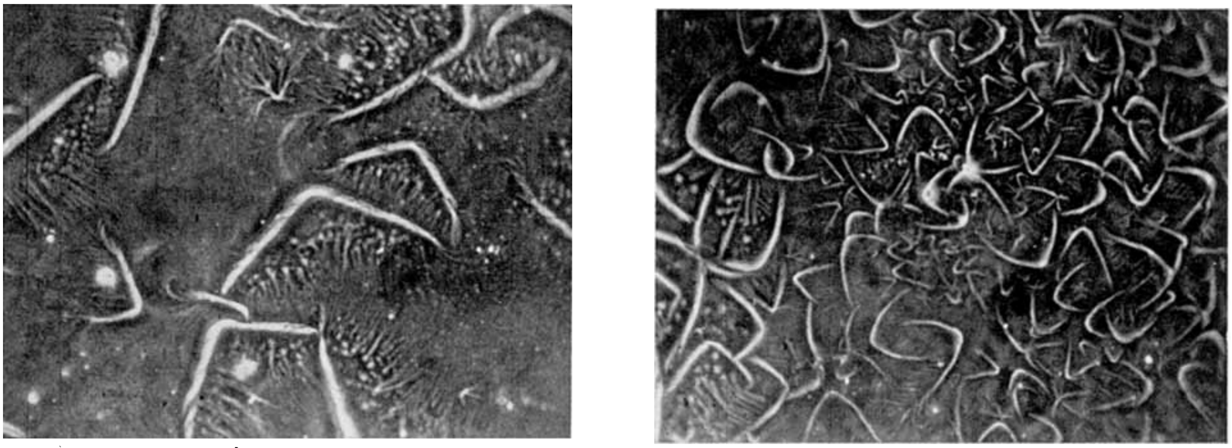
In the case of spherulite structure, the fibrosity is affected by the crystallization temperature, and it is most marked when crystallization occurs just below the melting temperature. The fibrosity also increases with the decrease of the average molecular weight.[3] The present observation on the fibrous structure of thermally degraded polyethylene demonstrated crystal habits which are observed neither in undegraded polyethylene nor in paraffin wax with a carbon number of 20–30.

Experimental

The material examined was linear polyethylene. A small piece of it was placed between glass slides, heated above the melting temperature, and then pressed by sliding the slides across each other. At some parts near the periphery of the sandwich, a very thin film of the sample covered the glass (the thickness was less than 1 micron). This specimen was again heated about 100 degrees higher than the melting temperature for several minutes and the degradation proceeded. After this treatment the temperature was lowered and the dendritic crystallization took place.

Figure 1 shows examples of ordinary dendrites. The ropelike appearance is found in the photograph. A typical dendrite is composed of a pair of major arms, and along the concave side of the arms a narrow flat strip like a web is present, from whose periphery many minor arms are growing out parallel to each other. A large thick dendrite was examined with a polarizing microscope. The birefringence effect was clearly seen, and it appears that one dendrite system is composed of crystals almost of the same orientation, including the minor arms. This was noticed because extinction took place almost simultaneously by rotation of the stage.

A similar structure was observed for a solvent-



(a) (b)

Fig. 1. Dendrites with ropelike growth. Phase contrast, 400×.

cast film on water. A drop of xylene solution of the same sample was dropped on the surface of hot water, and by evaporating the solvent, a thin film of the specimen was obtained. This film was scooped up on the fracture surface of rock salt and dried. By the same heat treatment as before, dendritic crystallization was observed. In this case electron microscopic observation was possible. After the chromium shadowing (shadow angle: arctan $^1/_3$) and evaporating carbon on it as the sustaining film, the rock salt was dissolved away with water and the specimen film thus obtained submitted to observation. Figure 2 shows some of these dendrites. From the morphology, it is supposed that dendrites on the solvent-cast film resemble the thicker film on the glass surface. A marked feature seen in the electron microscope observation is the terraces developed, that is, the dendrites are not composed of fibers but are composed of heaps of the lamellae. This evidence is in accord with the observation of the structure of the spherulite surface. The contrast in the photographs is due to the shadow effect at the surface, which appears to be somewhat curved or tilted, and to the absorption effect of the electron beam by the thickening of the arm. Some explanations may be given on this figure as follows. In Figure 2*a* the stacking of the lamellae is not so well developed. The region inside the arm pair appears to be covered with one or two layers of the lamellae. In Figure 2*b*, lamellar growth over another set of lamellae is seen. The lamellae thickness seems to be preserved throughout. Figure 2*c* shows fairly well developed dendrites. The stacking of the lamellae is so developed that the outer layers of the arm can no longer grow flat with respect to the film surface, but are tilted considerably, resulting in heavy shadowing at these slanting surfaces. In Figure 2*d*, the top part of two pairs of the arms join at vertically opposite angles (one, at the lower left and another at the upper right). An extra arm has grown at the lower right. The spiral terraces along an arm suggest the existence of a row of screw dislocations.

Figure 2*e* shows an arrowhead-shaped dendrite, and in Figure 2*f* an array of minor arms is presented. The major arm extends from the left to the right in the upper part of the photograph.

The morphology of these dendrites is affected by the crystallization temperature. To examine this effect, a phase microscope equipped with a hot stage was used, and repeated observations were carried out or of a specimen on the glass surface. From this it was indicated that, first, the angle between the major arms is dependent on the crystallization temperature and larger for higher crystallization temperature, and second, the bending and the sheaflike divergence of the arms become marked with a sudden drop of the temperature or a low crystallization temperature.

Discussion

As is observed above, thermally degraded polyethylene crystallizes with a peculiar habit. As a measure of the degradation, by estimation on the basis of the relation of Garner et al.[4] between the melting point and number of carbon atoms in normal paraffins, a value of several hundred Angstroms was obtained as the mean length of the degradation product. The mean step height estimated from the shadow length was about 100 A., and the molecules are presumed to fold themselves in the lamella as is usual in the case of solution-

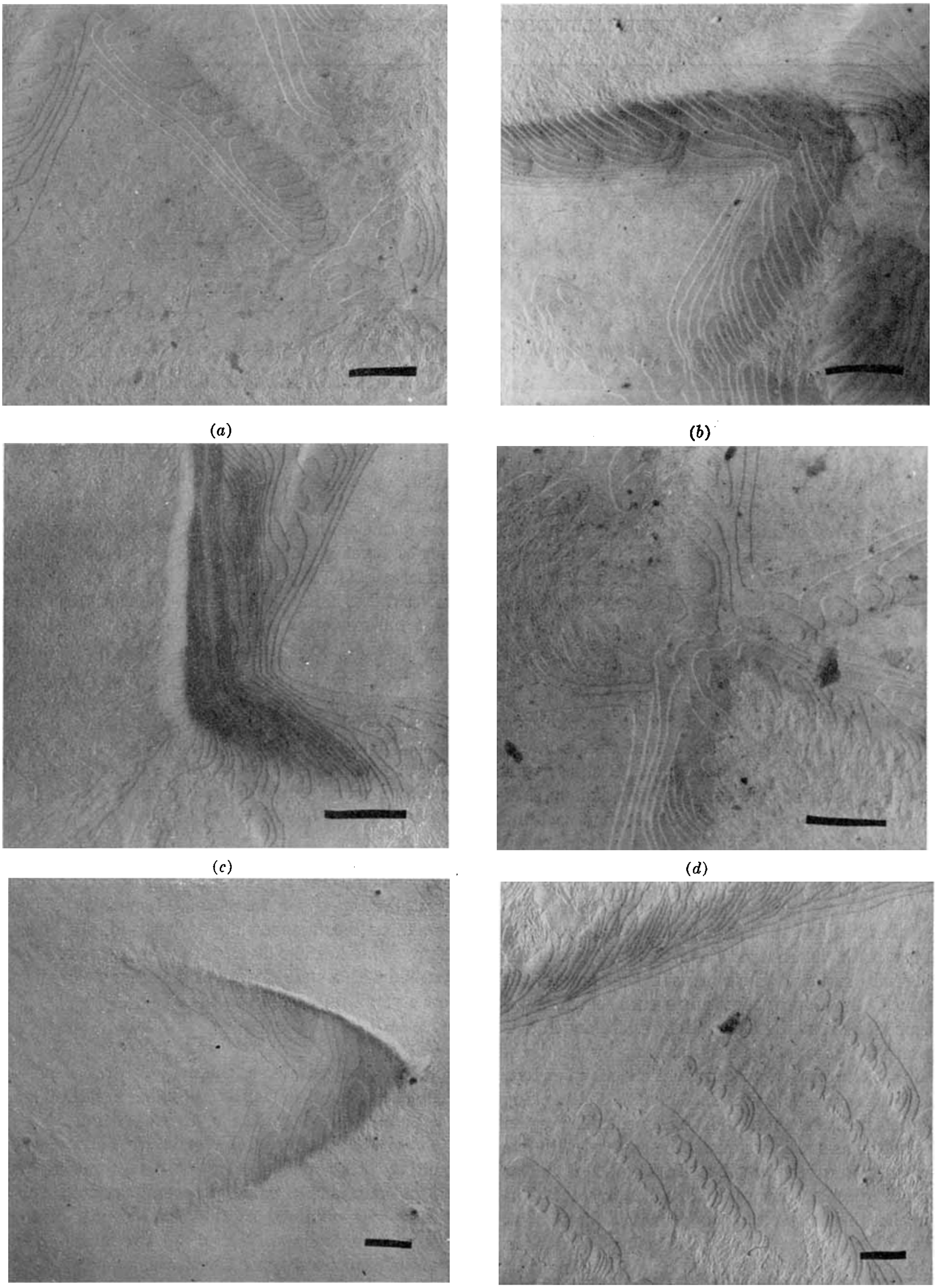


Fig. 2. Electron micrographs of dendrites (Cr shadowed): (*a*) 12,000×; (*b*) 15,000×; (*c*) 15,000×; (*d*) 15,000×; (*e*) 8,000×; (*f*) 8,000×.

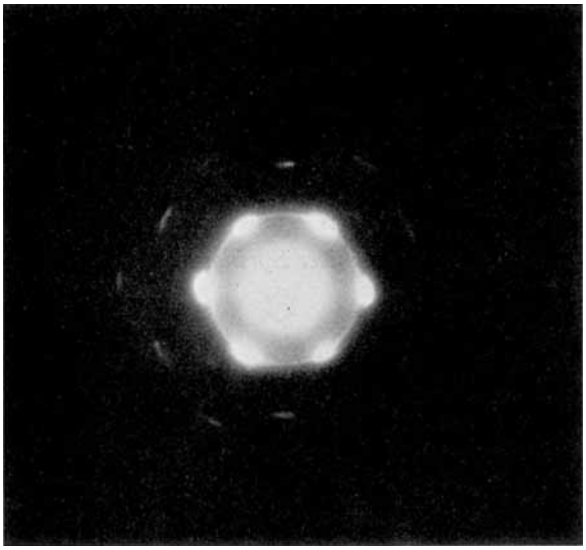


Fig. 3. Electron diffraction pattern from a dendrite.

crystallized polymer single crystals. Electron diffraction was also attempted, and yielded a diffraction pattern, as is shown in Figure 3, which is the pattern familiar in polymer single crystals.

Edward[5] investigated the crystal habit of paraffins of carbon number 20–30 and showed that pure normal hydrocarbon molecules with a definite carbon number crystallize into flat crystals, but a mixture of hydrocarbons with various carbon numbers, or paraffin wax with a molecular weight distribution, crystallize into needlelike crystals, by curling or rolling up of the original flat crystals. No report has been presented about the existence of the terraces in the case of paraffin wax. Such evidence is inconsistent with our above observation on degraded polyethylene, where there is no tendency to roll up into needlelike crystals, and distinct terraces are found to be developed.

The morphology of degraded polyethylene may be of interest, since it is intermediate between that of polyethylene with much longer chain lengths, and paraffin wax with shorter chain lengths.

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Synopsis

As a clue to the solution of the spherulite structure of polymers, dendrites of thermally degraded polyethylene crystallized from the melt were studied by optical and electron microscopy. The crystal habit of the dendrites was very special, resembling neither that found in polyethylene, which has much longer chains, nor that of paraffin wax which has considerably shorter chains. Electron microscopic observation revealed the existence of developed terraces about 100 A. in height, which is in accordance with the structure of polymer single crystals. The molecules appear to fold themselves into the lamellae on crystallizing from the melt.

Résumé

Pour apporter un indice à la résolution de la structure sphérulitique des polymères, on a étudié par microscopie optique et électronique, les deutrites de polyéthylènes dégradés thermiquement, après cristallisation à partir du solide fondu. L'état cristallin des deutrites est très particulier. Il n'a pas été trouvé ni dans le cas du polyéthylène à chaîne beaucoup plus longue, ni dans celui de la cire de paraffine à chaîne beaucoup plus courte. L'observation au microscope électronique a revélé l'existence de plans développés sur 100 Å en hauteur qui est en accord avec la structure de cristaux de polymère simple. Il semble que les molécules se suivent en lamelles lors de la cristallisation à partir du solide.

Zusammenfassung

Zur Aufklärung der Sphärolitstruktur von Polymeren wurden aus der Schmelze kristallisierte Dendrite von thermisch abgebautem Polyäthylen mit dem optischen und Elektronenmikroskop untersucht. Der Kristallhabitus der Dendrite war sehr eigenartig, er wurde weder in Polyäthylen mit wesentlich längeren Ketten, noch im Paraffinwachs mit kürzeren Ketten gefunden. Elektronenmikroskopische Untersuchungen zeigten, das Vorhandensein ausgebildeter Terassen von ca 100 Å Höhe, was mit der Struktur von Polymereinkristallen übereinstimmt. Beim Kristallisieren aus der Schmelze scheinen sich die Moleküle selbst im Lamellen zu falten.

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