Morphologies of Microporous Polyethylene and Polypropylene Crystallized From Solution in Supercritical Propane

DEBJEET PRADHAN and PAUL EHRLICH*

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14620

SYNOPSIS

The morphologies of solvent-free, microporous, mechanically self-supporting cylinders of linear polyethylene and isotactic polypropylene, crystallized from solution in supercritical propane, were examined by an SEM technique. The morphology of gels (or foams), obtained with little or no shrinkage from 2% to 35% solutions by weight of polyethylene (99% to 85% porosities), is shown in some detail. Lamellae with very little or considerable mutual organization occur, often in the form of stacks with straight or coiled axes (axialites). Further growth of these can lead to particles with a roughly spherical overall shape and a predominantly radial orientation of the lamellae at the particle surface. Subcooled isotactic polypropylene, on the other hand, crystallizes in the form of perfectly shaped birefringent microspheres of very uniform size. © 1995 John Wiley & Sons, Inc.

Keywords: polyethylene • polypropylene • supercritical propane • morphology • microporosity

INTRODUCTION

At temperatures high enough to prevent formation of crystalline polymer, polyethylene and polypropylene are miscible with supercritical propane in all proportions above a cloud-point pressure that depends on the composition, the molecular weight, and the molecular weight distribution.[1-3] When these polyolefin solutions are crystallized from the supercritical phase while the pressure is maintained, continuous networks of lamellar crystals contained within mechanically self-supporting structures can result by a process that represents gelation crystallization from the supercritical phase.[4,5] Because the supercritical solvent can be made to escape without collapse of the crystalline network, the density of the supercritical polymer solution can be maintained in the resultant gels or foams. Low-density microporous crystalline polyethylene, polypropylene, and ethylene copolymers covering a broad range of porosities and mechanical properties can be obtained in this way.[4-6] The potential applications of these materials include those generally cited for low-density microcellular foams.[7]

The structure of the gels is established during crystallization and undisturbed during solvent escape. Scanning electron microscope (SEM) pictures of the gels, which do not require staining, then represent the structure of the "native" gel, unmodified by the surface forces of the type generated during removal of a liquid solvent. With polyethylene, lamellar crystals in different states of organization are normally seen.[4] This allows one to observe easily details of the lamellar crystal habit within a mechanically stable gel over a considerable range in concentration of the supercritical precursor solution by electron microscopy; the crystal morphology of nascent polyethylene gels prepared from conventional liquid solvents, on the other hand, must often be determined by less direct means, such as SAXS.[8] Also, the problem of establishing the identity between nascent and dried crystals[9] does not arise in our case. We wish to describe these morphologies in greater detail, and point to the different, apparently

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* To whom correspondence should be addressed at his present address: Department of Polymer Science & Engineering, University of Massachusetts, Amherst, Amherst, MA 01003.

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spherulitic, morphology that appears to be characteristic of polypropylene crystallized from strongly subcooled solutions.

The morphologies of gels, as expected, depend on the concentration, on the molecular weight, almost certainly on the molecular weight distribution of the precursor supercritical polymer solution, and (particularly in the case of polypropylene) on the crystallization history. It was not possible, within the limits of this exploratory study, to make a strict separation of the effects of these variables on the morphology. The results of our SEM studies will therefore be presented as micrographs of the several distinct morphological forms encountered. These will then be associated, where possible, with the properties of the precursor solutions and the crystallization history.

METHODS AND MATERIALS

Method of Crystallization

Crystallization was carried out from the supercritical phase at cooling rates of 0.5–1°C/min ("fast cooling"), except where noted otherwise, in the view cell used for the phase equilibria studies.[2] At this rate of cooling, crystallization starts in the general neighborhood of 100°C for polyethylene and at a lower temperature for polypropylene. The initial pressure was kept well above the cloud-point pressure and is believed to have been sufficient to prevent separation of the solution into a polymer-rich (liquid) phase and a polymer-poor (vapor) phase during crystallization, except in the case cited. If agitation of the uniform supercritical solution is discontinued prior to the onset of crystallization, polymer gels (or foams) are recovered with little or no shrinkage of the precursor solution, provided the critical condition for gelation, which depends on the polymer's concentration and molecular weight, is met.[4]

Molecular Characterization

All PE samples are linear, essentially devoid of short-chain branching. All, with the exception of UHMWPE 4, have known molecular weight distributions. NBS 1484 was the highest fraction of an NBS (now NIST) Reference Material, prepared from DuPont's Alathon 7050, of which NBS 1475 was the parent polymer.[10] HDPE 1 is a commercial Ziegler-type PE, HDPE XS is a Dowlex-type high-density PE, and UHMWPE 4 is an ultra-high molecular weight PE, obtained from Himont Company. The isotactic polypropylene (iPP) was obtained from Scientific Polymer Products. Its tacticity and molecular weight are unknown. The lower molecular weight averages of the PE samples are listed in Table I.

Physical Properties of Foams

The gels (foams) recovered from the view cell apparatus were, in the majority of cases, coherent cylinders about $\frac{3}{4}''$ in diameter and 1″ in length, for which mechanical properties varied from soft sponges to hard solids. Exploratory compression and tension tests were performed on many samples.[11] As expected, the tensile modulus increased with molecular weight and the concentration of the precursor supercritical polymer solution, but no attempt was made to establish quantitative relations. Most samples that could be recovered as coherent cylinders supported their own weight, but many deformed inelastically under a compressive load in the Instron tester.[11] Approximate conditions for the formation of a network that could not be pulled apart manually, which should be closely related to the gelation conditions, were established for several of the polyethylene samples.[11]

The cause of gelation of each polymer solution must be the formation of a continuous crystalline network that pervades the vessel in which it is formed.[4] The concentrations of the precursor polymer solutions are reported as 100 (wt. polymer/wt. solution). However, because the densities of the supercritical solutions are only approximately 0.5 g/cm^3, the foam density, expressed in 100 (wt. polymer/vol. solution) is only slightly greater than one-half the solution concentration. Gels that supported their own weight could be obtained from UHMWPE solutions as dilute as 2 wt %. A detailed description of the foams by DSC was not attempted, but several such measurements established most of the melting of the polyethylene gels to take place above 130°C, but below 140°C. These foams are therefore probably classifiable as thermoreversible gels.

Table I. Molecular Weights of Polyethylene Samples

Sample Designation	M_n	M_w
NBS 1475	18,310	52,000
NBS 1484	100,520	119,600
HDPE 1	7,340	42,900
HDPE XS	25,300	91,000
UHMWPE 4		5.3×10^6

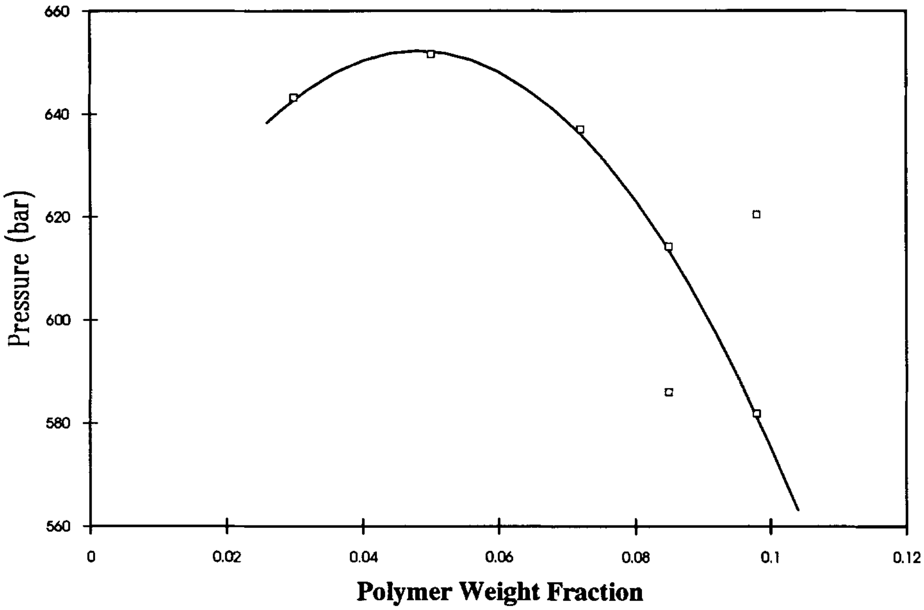

Figure 1. Cloud-point pressure-composition isotherm for HDPE XS-propane at 125°C.

SEM Studies

A Hitachi S-800 field emission SEM was used in the secondary electron mode. The specimen was prepared by gently tearing out a small portion of the gel with a pair of forceps, mounting it on a specimen stub with electrically conducting colloidal carbon paint, and subjecting it to a pulsed coating of gold in a sputter coater. A current of less than 20 mA and a coating time of less than 2 min at a stretch insured that no damage was caused by heating. For observation in the SEM, low accelerating voltages (2.5–4.0 kV) and low exposure times (~ 30 s) were used to minimize beam damage and specimen charring.

RESULTS

Phase Equilibria

As already mentioned, all samples except one were crystallized from the supercritical phase by lowering the temperature while the cloud-point pressure was exceeded. The cloud-point pressures of NBS 1484 and HDPE 1 have been reported as part of a detailed study of the PE/propane system.[2] Crystallization from the two-phase, vapor/liquid region was attempted with HDPE XS, and its cloud-point is therefore of special significance. The cloud-point pressure-composition isotherm is shown in Figure 1. Because the sample composition was 7.15% polymer, the scattering of the data at a higher polymer concentration is not troublesome in the present context. Limited cloud-point data, though sufficient to map crystallization from the supercritical phase, are shown for iPP in Table II. A more thorough report on iPP-propane equilibria has been prepared.[3]

Scanning Electron Microscopy

Polyethylene

We will discuss our results in terms of morphological classes; however, they are all lamellar and grade into one another.

Axialites. Figure 2 is a picture of a slightly damaged "lamellar stack," also known as "axialite."[12] In its simplest form, a lamellar stack consists of a short sequence of flat, parallel platelets lying one over the

Table II. Cloud-Points for Isotactic Polypropylene-Propane

Weight Fraction Polymer	Pressure (bar)	Temperature (°C)
0.04	297.2	125
0.075	297.2	141
0.15	295.1	129
0.15	291.0	130
0.22	259.1	130

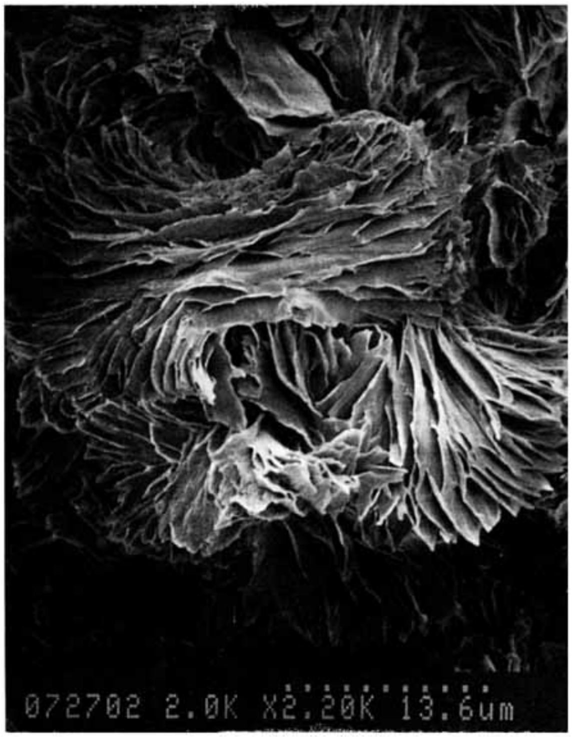

Figure 2. Axialite. HDPE 1 at 23.7% w/w, run S-3.

Figure 3. Enlarged edge of axialite. HDPE 1 at 23.7% w/w, run S-3.

other and held together by interpenetrating branches of the lamellae themselves. Each lamella by itself is substantially flat. The splaying can be attributed to the more profuse small-angle branching close to the edges. The effect of small-angle branching can be seen in more detail in Figure 3, which shows a higher magnification of one edge of a lamellar stack. Curvature (dishing) (Fig. 4), splaying at or near the edges, and interpenetration of the lamellae are common. Some twisting about the basal plane is also observed (Fig. 5). A typical size of the lamellae is 20 × 5 μm. All these micrographs represent samples obtained under "fast cooling" of a supercritical solution of 23.7% HDPE 1 from its equilibrium temperature at 125°C. Most of the crystallization took place between 100°C and 105°C at the modest degree of subcooling of some 10–15°C. Assemblies of axialites of near-spherical overall shape are obtained when a solution of the same polymer at a similar concentration (19.8%) upon slow cooling is made to crystallize under near-isothermal conditions at about 115°C. This represents a more organized morphology but, even though the structures seen have a somewhat spherical appearance, they are not true spherulites, because the lamellae do not always seem to radiate from a common center (Fig. 6). The ends of many lamellae are ar-

Figure 4. Axialite with dishing. HDPE 1 at 23.7% w/v, run S-3.

(a) (b)

Figure 5a,b. Stereo-pair of axialites. HDPE 1 at 23.7% w/w, run S-3.

Figure 6. Coiled, sphere-like structures. HDPE 1 at 19.8% w/w, run S-36.

ranged in almost parallel sequences with their edges roughly perpendicular to the particle surface. The manner of progression of these sequences suggests that the near-spherical superstructure may have resulted from either a random (Fig. 7) or a regular spiral-like (Figs. 6, 8) coiling of such sequences. A typical diameter of such a structure is 40 μm.

Less-Ordered Lamellae From Moderately Dilute Solution. When a relatively low-concentration ($< 3\%$) solution of a high molecular weight PE is cooled rapidly, the lamellae organize themselves into loose bundles, different from the axialites described before. Here the lamellae, even if characterized by interpenetration and branching, do not lie parallel to one another. One does not observe any significant splaying or a regular curvature of the lamellae, even though the individual platelets may be slightly twisted. A 2% solution of NBS 1484 produced, upon rapid cooling, the lamellar arrangement shown in Figure 9. A similar arrangement is also seen in Figure 10, a micrograph from a gel produced by rapid cooling of a 2% solution of UHMWPE 4. At somewhat higher concentrations, rapidly cooled solutions of high or ultra-high molecular weight PE produced a more disordered arrangement of lamellae, possibly

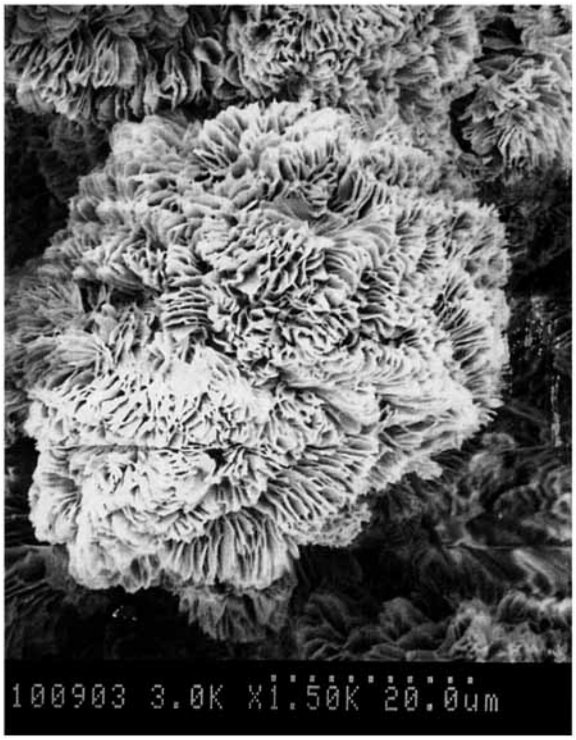

Figure 7. Coiled, sphere-like structures. HDPE 1 at 19.8% w/w, run S-36.

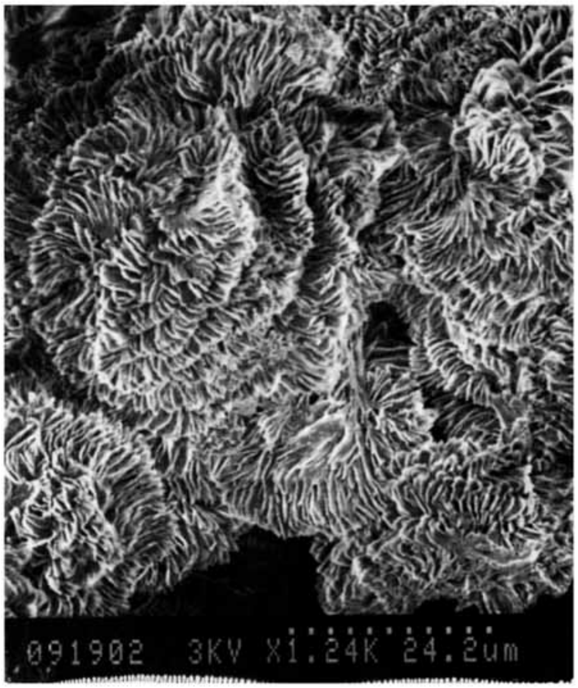

Figure 8. Coiled, sphere-like structures. HDPE 1 at 19.8% w/w, run S-36.

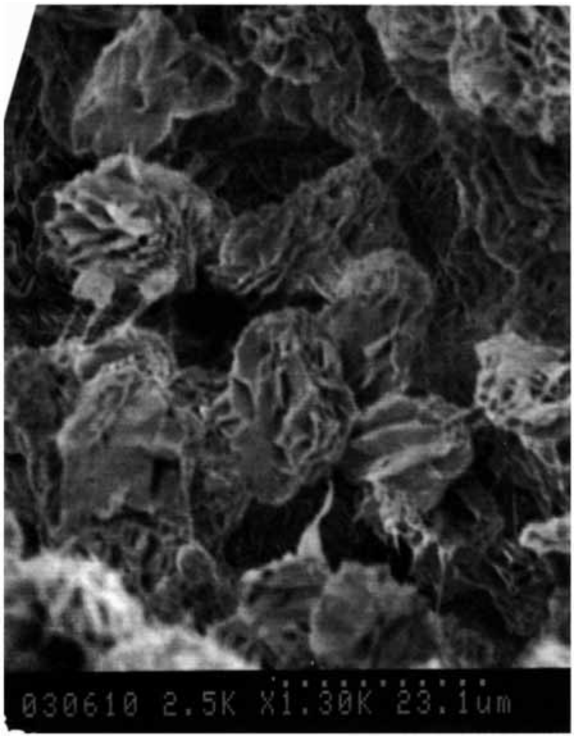

Figure 9. Bundles of disordered lamellae. NBS 1484, 2% w/w, run S-59.

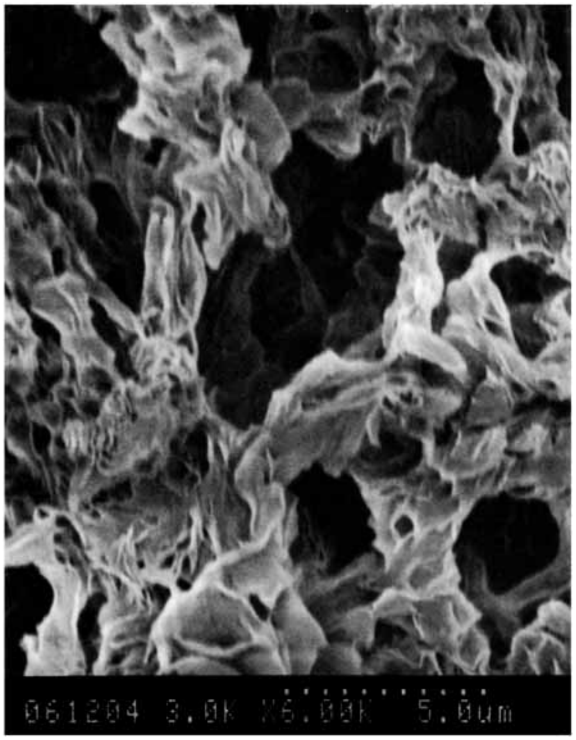

Figure 10. Disordered lamellae. UHMWPE 4, 2% w/w, run S-61.

reflecting the loss of order on the molecular scale when molecular overlap sets in. Figures 11 and 12 illustrate the structure of gels obtained by rapid cooling of 5% solutions of NBS 1484 and UHMWPE 4, respectively. This moderately dilute solution range was not studied with the other, lower molecular weight samples because they were incapable of producing coherent, mechanically stable networks.

Morphologies From Concentrated Solution. As the concentration of the precursor solution is increased, one begins to notice structures that are significantly different from the ones observed at lower concentrations. Figures 13, 14, and 15 show the structures obtained by rapid cooling of a 35% solution of NBS 1475. The individual lamellar stacks start to lose their identity (Fig. 13) and a few large spherical structures with diameters close to or exceeding 60 μm make their appearance (Fig. 14). A higher magnification picture (Fig. 15) of a spherical structure shows the end-on view of what may well be a collection of lamellae for which the long axis is oriented in the direction of the radius of the sphere of which it is a part, in apparent resemblance to melt-growth spherulites. The random orientation of the planes of these lamellae and the disordered manner of in-

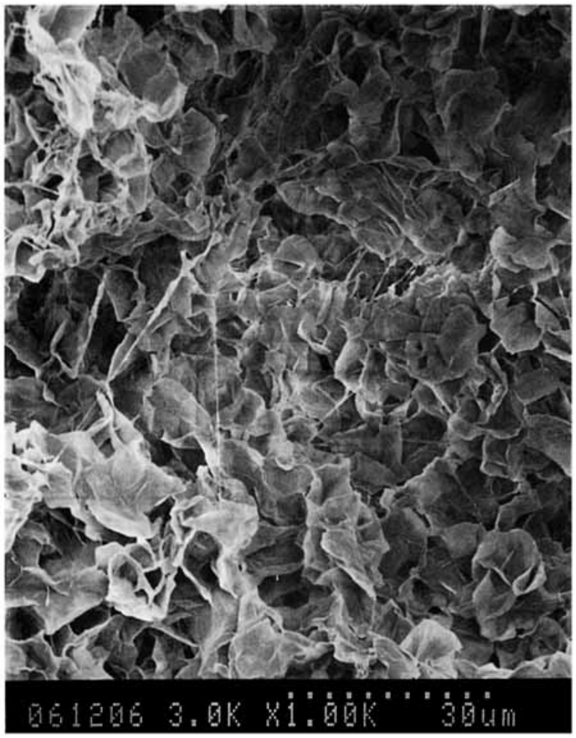

Figure 12. Disordered lamellae. UHMWPE 4, 5% w/w, run S-73.

Figure 11. Disordered lamellae. NBS 1484, 5% w/w, run S-11.

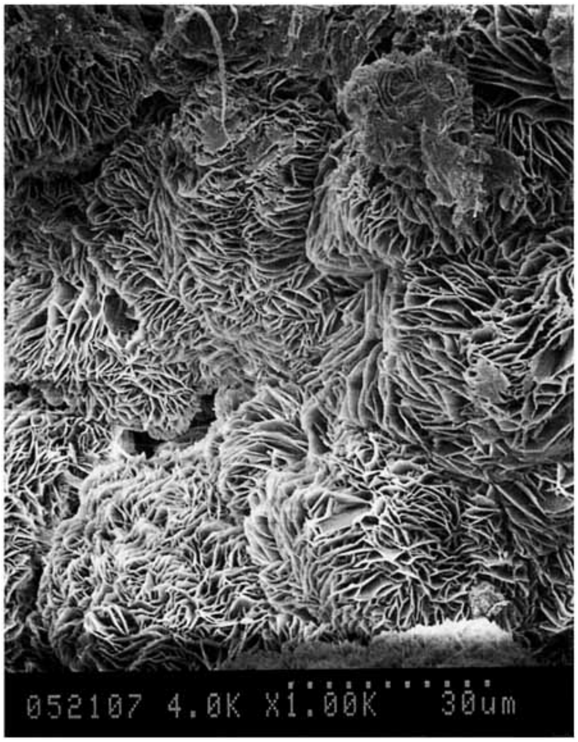

Figure 13. Closely-packed axialites. NBS 1475, 35% w/w, run S-9.

Figure 14. Large spherical structures. NBS 1475, 35% w/w, run S-9.

Figure 15. Higher magnification of Figure 14.

terpenetration make the structure appear, in the end-on view, like a collection of polygonal, honeycomb-like compartments.

Mixed Morphologies. Although a single type of morphology was characteristic of all foregoing samples, a 7.15% solution of HDPE XS, for which crystallization commenced at about 94°C, near its cloud-point pressure of about 640 bar, yielded a variety of structures, represented by Figs. 16, 17, and 18. We suggest that these structures are associated with gels formed from different phases [i.e., the original supercritical solution (Fig. 16), a more dilute one (Fig. 17), and a mixture of the more dilute and a more concentrated phase (Fig. 18)]. This result would be expected if crystallization started from the supercritical phase and was completed only after phase splitting. We were unable to reproduce this result in several additional experiments, obtaining the first structure (axialites) only. Because a metastable phase is quite likely to form prior to phase separation, it is not unreasonable to expect some difficulty in repeating the first set of results.

Polypropylene. Figures 19 and 20 show the morphology that appears to be common in isotactic polypropylene (iPP).[13] We find microspheres of sur-

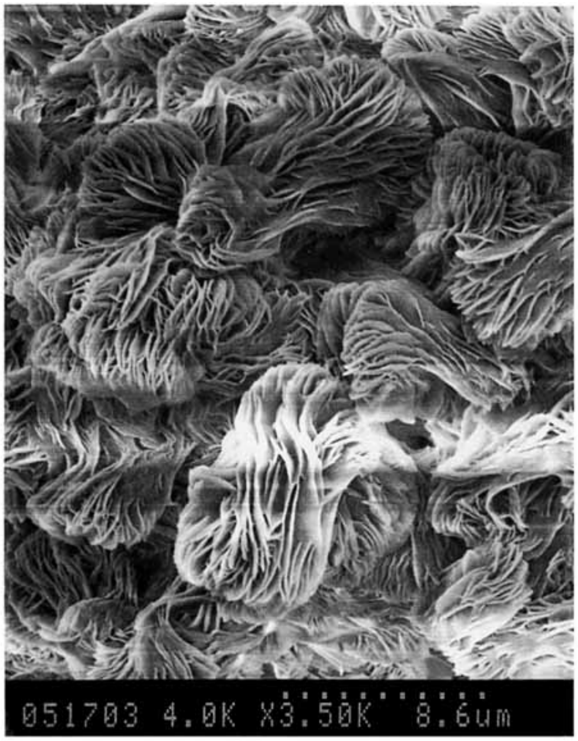

Figure 16. Morphology believed associated with crystallization from the supercritical phase. HDPE XS, 7.15% w/w, run S-49.

Figure 17. Morphology believed associated with the more dilute polymer (vapor) phase after phase splitting during crystallization of run S-49.

prisingly uniform size with apparent strand-like connections between the individual spheres. Although the mechanical network is weaker than that formed from a similar concentration of polyethylene of similar molecular weight, mechanically self-supporting structures could be obtained from 4% iPP solutions. The strongly predominant radial orientation of the lamellae on the surface of the microsphere suggests a spherulitic morphology with different radial and tangential optical properties.[14]

DISCUSSION

Although we do not have sufficient data that would allow a strict separation of all variables that might determine the morphology of the PE gels formed in this investigation, several comments pertaining to the effects of polymer concentration, molecular weight, and crystallization temperatures can be made. From the SEM micrographs shown, as well as from other SEM results, it can be concluded that the formation of axialites, rather than more disordered lamellar structures, is favored by low molecular weight. This is consistent with the higher prob-

Figure 18. Morphologies believed associated with both the dilute (vapor) and the concentrated (liquid) phases after phase splitting during crystallization of run S-49.

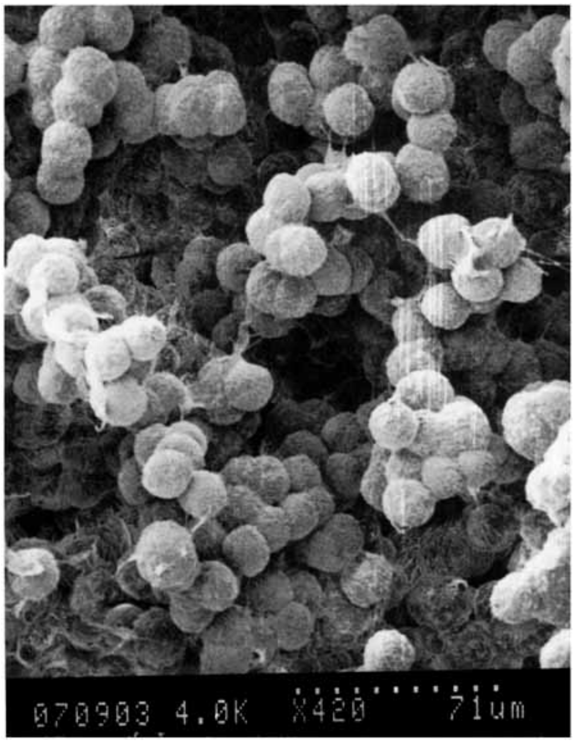

Figure 19. Polypropylene microspheres, iPP, 15% w/v, run S-33.

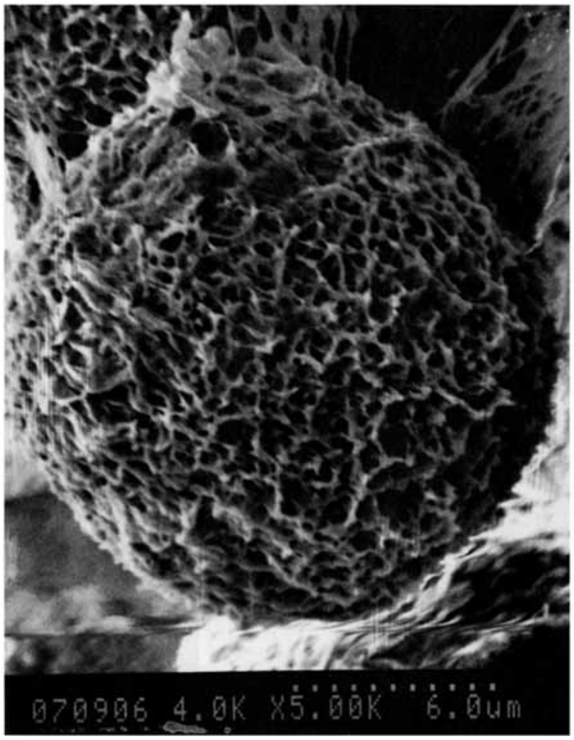

Figure 20. Figure 19 enlarged.

ability of a shorter chain confining itself to a single lamella, and so avoiding its inclusion in additional lamellae that are uncoordinated with the first. The effect of polymer concentration is as expected: as it is increased, one moves from a situation of well-separated assemblies, where lamellar growth is limited by the diffusion of solute, to one controlled by the impingement of neighboring crystals, to one at still higher concentrations where individual assemblies begin to lose their identities (Fig. 13) and large globules may form (Fig. 14). The effect of crystallization temperature can be seen clearly by comparing Figures 2–5 with Figures 6–8. The former set represents rapidly cooled samples that crystallize below about 105°C; the latter represent samples that had been crystallized isothermally at 115°C, where the nucleation rate and the concentration of nuclei are smaller, giving rise to larger, more complex structures.

An overview of the range of morphologies that can be displayed by microporous PE crystallized from supercritical propane solution shows a gradual progression from disorganized lamellae to lamellar stacks (axialites) with roughly parallel lamellae to assemblies of axialites with coiled backbones and an overall near-spherical shape, to possibly true though orientationally disordered spherulites at high concentrations. The typical morphology of microporous iPP crystallized from strongly subcooled propane solution, on the other hand, consists of seemingly perfect microspheres of nearly uniform size, which are birefringent.[14] This suggests that they were formed by a nucleation step that was rapid compared to crystal growth, consistent with the high supersaturation and, perhaps, the low viscosity of the precursor solution, in a sequence of steps that is kinetically equivalent to living polymerization with a resultant Poisson distribution in polymer size. It should be possible to form microporous iPP with a texture characterized by microspheres of uniform but adjustable size by control of the degree of subcooling.[13]

All of the morphologies of polyethylene shown here can be said to be made up of "overlapping lamellar structures," a term used by Prasad et al.[9] to describe the morphologies of isotactic polystyrene and polyethylene gels crystallized from good (liquid) solvents, in contrast to the different morphologies obtainable by gelation from poor solvents, either inside the binodal or the spinodal curves.[9,15] Although gelation crystallization from a supercritical solvent, which does not require solvent removal by special drying techniques, did not reveal novel types of morphologies in these experiments, we should note that lamellar composites less organized than spherulites tend to crystallize from rather concentrated solution in polyethylene, though not in polypropylene. Axialites and globular structures, rather similar in appearance to those we have observed at concentrations of about 20% w/w (~ 10% w/v), were shown to be prevalent in 1% w/v solutions of 1,4-*trans* polyisoprene by Xu and Woodward.[15] This suggests that, in the case of polyethylene and at similar w/v concentration, less-organized superlamellar structures form from supercritical rather than liquid solution, perhaps because of the more rapid crystal growth anticipated from the former.

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