On Cellulation in Polyethylene Spherulites

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ABSTRACT: Cellulation has been observed to develop with increasing radial distance within growing spherulites of a series of metallocene-catalyzed, ethyl-branched polyethylenes with branch contents ranging from 14 to 37 per 1000 main chain C atoms. The radius to the onset of cellulation and the cell width are both sensibly constant for the same polymer and independent of growth rate. For different polymers, both these quantities fall with increasing branch content. The implications of these novel findings for the crystallization of polymers are discussed.

Introduction

Cellulation, i.e., the separation of fingers of crystalline polymer by regions containing poorly or noncrystalline material, was suggested long ago[1] to be the cause of the spherulitic growth prevalent when polymers crystallize from the melt. Only recently, however, has the phenomenon actually been observed, rather than inferred, to occur. Our previous paper[2] reported the occurrence of cellulation in the later stages of growth of spherulites of a polyethylene with 28 ethyl branches per 1000 C atoms in accompaniment with a continuously declining growth rate. As the spherulites were growing with typical circular bands before the advent of cellulation this observation is an unequivocal demonstration that cellulation is a secondary mechanism which can be overlaid on spherulitic growth in suitable circumstances of high segregation but it is not the primary cause of spherulitic growth.

In this paper we investigate the phenomenon further using a series of polyethylenes with increasing branch content. Contrary to previous supposition,[1] the characteristic dimensions of cellulation, namely, the radius to its onset and the average cell width, do not scale with the characteristic diffusion length, $\delta = D/G$. They show little or no variation with radial growth rate, G, in the same material but decrease with increasing branch content, i.e., reduction in diffusion constant, D.

Materials and Experimental Section

The materials used in this work are five experimental grades of metallocene-catalyzed polyethylene, all with 1-butene as comonomer but differing in branch content. Pertinent properties are listed in Table 1. The different values of melting point, T_m, as found after cooling from the melt at 10 K·min^{-1}, show that there is no common temperature at which all samples can conveniently be crystallized. Accordingly, crystallization temperatures were chosen instead to produce roughly comparable growth rates for all samples. The use of a second crystallization temperature, 2 K lower, reduced growth rates considerably and allowed the effect of changing this parameter to be assessed for the same material effectively at constant diffusion coefficient.

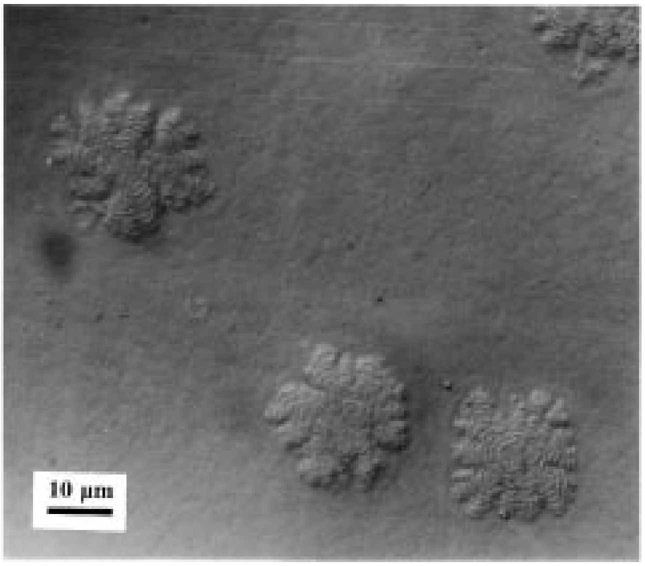

Figure 1. A banded spherulite of polymer D showing the development of cellulated growth. Etched specimen viewed with Nomarski reflection optics.

For crystallization, all samples were first melted between sheets of Kapton polyimide film at 180 °C for 3 h in a Mettler FP82HT hot stage controlled by a Mettler FP90 central processor with nitrogen flow, then quenched in an ice−water mixture. The purpose of prolonged melting is to reduce the nucleation density to allow spherulites to grow larger before impinging. This well-known procedure has minimal effect on average properties but is presumed to be effective because of reduction of the high tail of the molecular weight distribution. After removal of the Kapton film, each sample was then cut into several plates about 7 mm square and 0.5 mm in thickness. These were crystallized one by one by placing each on a cover slip on a Kofler hot bench at 140 °C, covering the specimen when molten with a microscope slide before transferring the assembly to the Mettler hot stage; the temperature was controlled at 140 °C for 2 min and then reduced to the value chosen for crystallization. After due time specimens were quenched in an ice−water mixture, to allow inspection of the progress of growth, particularly the instantaneous growth envelope.

To this end all specimens, after removal of slide and cover slip, were etched with a 2% w/v solution of potassium permanganate dissolved in a 5:2:2 mixture by volume of concentrated sulfuric, 85% orthophosphoric acid, and distilled water, respectively. Four hours of etching was found suitable for

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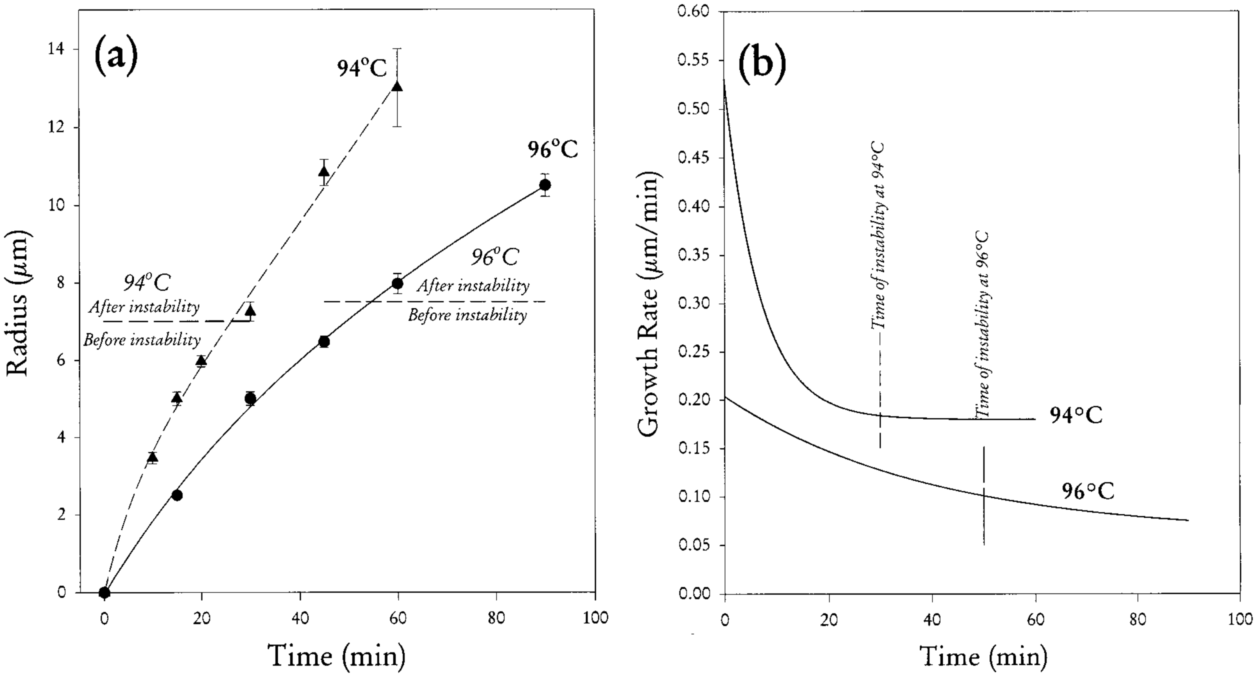

Figure 2. (a) Radii of Spherulites of polymer D versus crystallization time at 94 and 96 °C. (b) Corresponding calculated growth rates. The observed radius at the onset of cellulation is marked on both figures.

Table 1

	polymer D	polymer E	polymer F	polymer G	polymer H
density (kg/m^3)	905	905	901	895	881
comonomer content (wt %)	5.5	10.0	12.0	14.9	22.4
M_n (g/mol)	40 500	40 500	22 900	40 000	44 600
M_w (g/mol)	64 400	78 600	47 400	80 000	95 400
M_w/M_n	1.6	1.9	2.1	2.0	2.1
crystallinity (%)	33.8	34.3	29.9	23.7	19.3
branch content (per 10^3 C atoms)	13.8	25.1	30.15	37.4	56.3

removing more than 40 μm from the outer surface to reveal the interior of the specimen. Examination with reflection optics using Nomarski interference contrast was used both to monitor the progress of etching and to record spherulitic profiles. If desired such specimens could also be examined at higher resolution in the transmission electron microscope via two-stage replication.

Results

All the polyethylenes studied (with the exception of the most branched polymer, H, for which neither spherulites nor microstructure could be detected microscopically) show cellulation superposed on spherulitic growth beyond a certain distance in accord with our previous paper.[2] Figure 1 illustrates the phenomenon at optical resolution for polymer D. This is the least branched of our materials, with only about one-half of the average number of branches of the butyl-branched polyethylene of the previous paper. It appears, accordingly, that a very high branch content is not inherently necessary for cellulation to occur. The present materials and crystallization temperatures do, however, give high segregation, with around 50% of the polymer—assessed by thermal analysis—failing to crystallize isothermally, which may well be the pertinent factor.

Data for the increase of average radius with time for ~10 such objects of polymer D, for each of two temperatures, is displayed in Figure 2a. (Only those radii have been selected (sometimes more than one for asymmetric objects) which were growing into unrestricted melt; those nearing impingement were excluded.) These were measured, in real time, directly from the screen of a monitor linked to a video camera on the optical microscope. Error bars represent the standard errors of the means of the various populations with the fitted curves being constrained to pass through the origin and of the form

$$r = G_\infty t + AG_\infty/b(1 - \exp(-bt))$$

where G_∞ is the final, steady-state, growth rate. The derivatives of these curves

$$G = G_\infty (1 + A \exp(-bt))$$

are the growth rates plotted in Figure 2b. Marked on these plots are the observed radii at the onset of instability, as judged optically, and G_i, the corresponding instantaneous growth rates. The values of G_∞, G_i, and G_0, the derived growth rate at zero time, together with their ratios are listed in Table 2. Note that the average distance to the onset of instability is insensitive to the considerable changes in growth rate. The average growth rates themselves have slowed continuously before stabilizing, at G_∞, for longer times. This extends behavior beyond that reported previously when the growth rate was still decreasing as spherulites impinged and parallels further work[3] in which a steady state was attained for growth from row structures.

Similar behavior is shown by polymers E, F, and G. Figure 3 illustrates this for representative spherulites which have cellulated. Cellulation starts at progres-

Table 2

polymer	T/°C	G_0/μm·min^{-1}	G_i/μm·min^{-1}	G_∞/μm·min^{-1}	G_i/G_0	G_∞/G_0
D	94	0.53	0.18	0.18	0.35	0.34
D	96	0.20	0.10	0.06	0.50	0.30
E	93	0.19	0.11	0.04	0.61	0.21
F	89	0.57	0.39	0.16	0.67	0.28
F	91	0.40	0.15	0.04	0.38	0.09
G	79	set at 0.60	0.50	0.23	0.83	0.39
G	81	set at 0.60	0.34	0.09	0.57	0.15

sively smaller radii with increasing branch content until, for polymer G (Figure 3d), we have coarsely textured spherulites whose optically resolvable microstructure is one of "fibrils" emanating from a small central region and branching to fill space. These are textures of the kind hypothesized by Keith and Padden in their original discussion of spherulitic growth.[1]

In Figure 4 are plots of spherulitic radii for polymers E, F, and G, as functions of crystallization time at the temperatures indicated and the growth rates calculated therefrom. Table 2 lists the numerical values of G_∞, G_i, and G_0 and their ratios. For the three bottom rows of this table the steady-state growth rate, G_∞, is experimentally well-defined, indeed the condition starts so early for polymer *G*, barely above the lower limit of resolution, that the initial growth rate, G_0, necessarily becomes rather uncertain; it has been set at the same value, 0.6 μm/min, for both conditions. For the less-branched polymers there is a progressive shift toward a later onset of steady-state growth with the consequence that numerical values of G_∞ become less certain but those for G_0 more so.

The common pattern across all these and previous observations is that growth rates fall continuously both before and after cellulation sets in, with the radius at which this occurs decreasing with average branch content (Figure 5). For any one polymer there is little measurable difference in this quantity between different growth temperatures, but the figure is always slightly greater for the higher temperature. The average cell width (Figure 6), measured by dividing the perimeter at a given radius (excluding undivided portions where appropriate) by the number of protrusions present, shows a similar dependence on branch content; mean values for different growth temperatures, and radii, being barely differentiable.

Discussion

The observations of this paper confirm that cellulation occurs within spherulites of branched polyethylenes

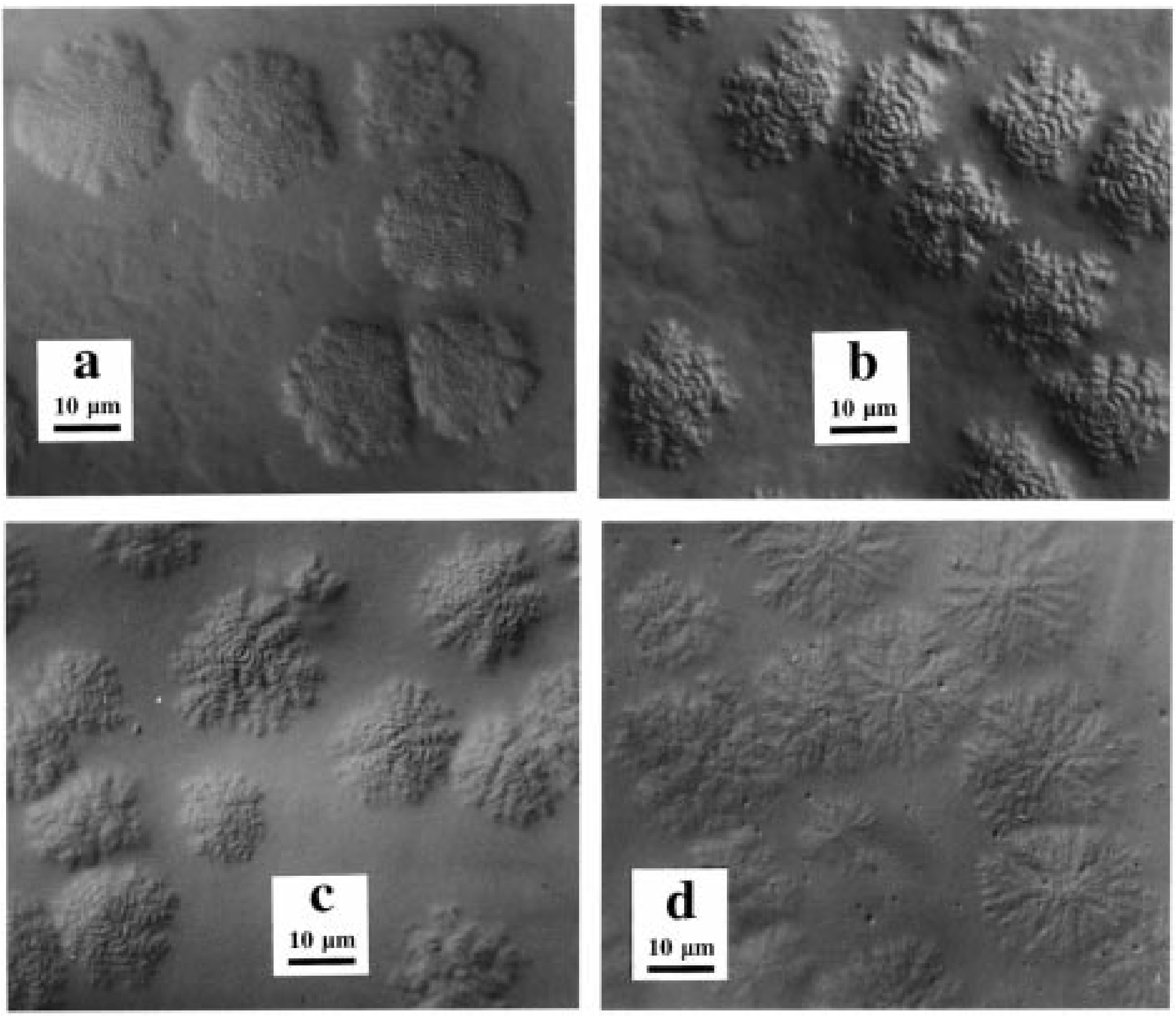

Figure 3. Cellulated spherulites of: (a) polymer E after 1.5 h of crystallization at 93 °C; (b) polymer F after 1.5 h of crystallization at 91 °C; (c) polymer F after 0.75 h of crystallization at 89 °C; (d) polymer G after 2 h of crystallization at 81 °C. All specimens were etched and then viewed with Nomarski reflection optics.

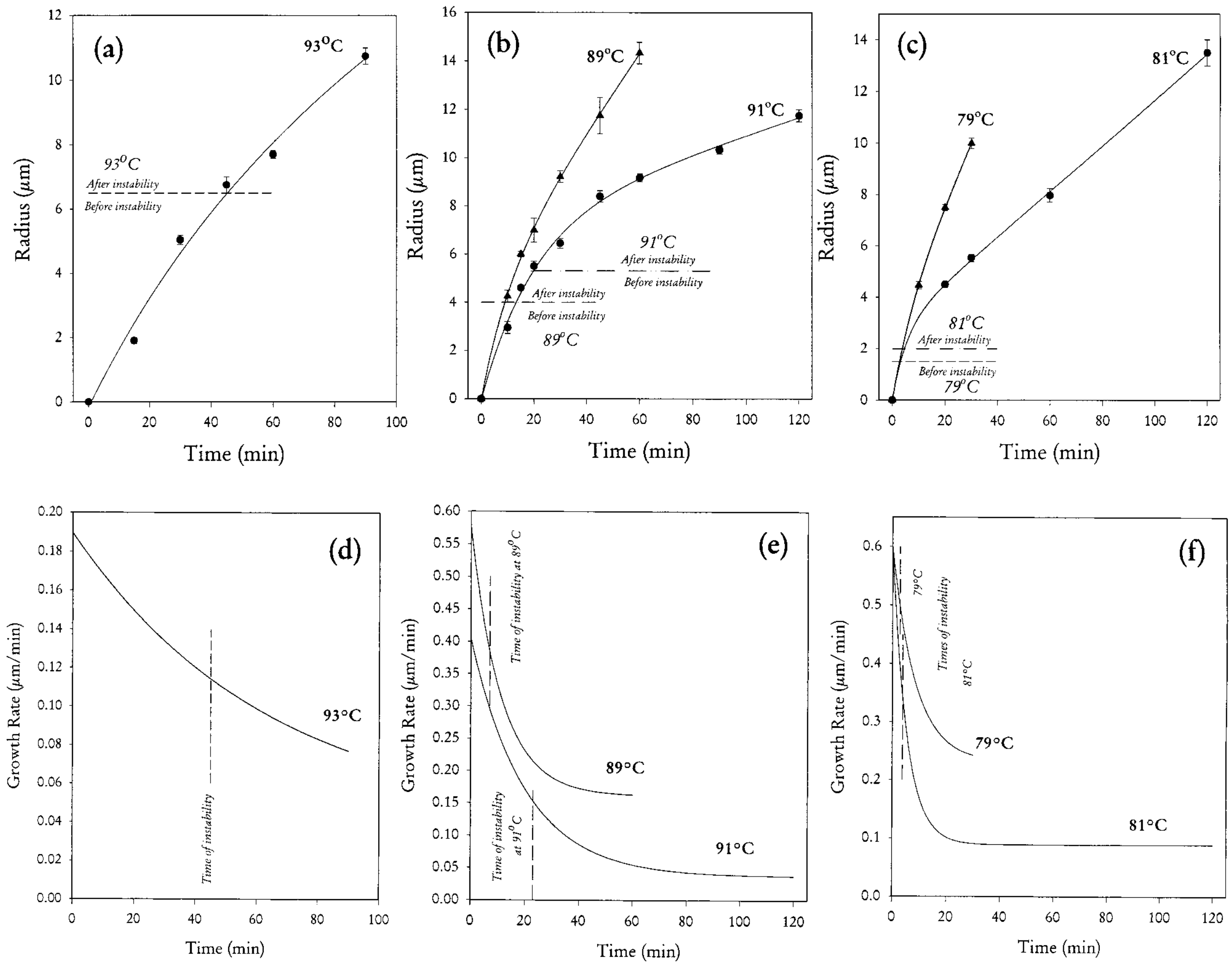

Figure 4. (a, b, and c) Radii of spherulites of, respectively, polymers E, F, and G as functions of crystallization time at the temperatures shown. (d, e, and f) Corresponding calculated growth rates. The observed radius at the onset of cellulation is marked on all figures.

under suitable circumstances. These morphologies are superposed on regular spherulitic growth when there is significant slowing of the isothermal growth rate because of segregation (in this case of more highly branched molecules and sequences) at the growth front. The observations go beyond those of our previous paper[2] partly in extending to steady-state growth conditions—previously the growth rate was still slowing as spherulites impinged—and partly in the comparison across different crystallization temperatures and different branch contents. In so doing they reveal much of the character of cellulation in polymer spherulites. However, although the morphologies are those presumed to exist within all polymer spherulites by Keith and Padden, their discussion of cellulation[1] cannot apply to our observations. Whereas they assumed that, after cellulation, the growth velocity would have reverted to its initial higher value, on the contrary, in our experiments actual growth rates are found to continue to fall. The implication is that growth is still proceeding in a segregant-rich environment, rather than having penetrated fully through the segregant layer into melt of the original composition. This remains the case for steady-state growth, which proceeds at the asymptotically slowest rate.

Cellulation is a consequence of stable differential growth rates becoming established laterally across what was a macroscopically smooth growth envelope. In the present context, this is related to the uneven distribution of segregants which manifestly slow growth, most probably via lowered supercooling. In branched polyethylenes it is the more-branched species which are preferentially rejected at the interface because of the exclusion of branches from the lattice. For those synthesized by Ziegler/Natta catalysis it is very likely that whole molecules will be segregated, there being a strong correlation between branch content and low molecular mass. For the newer metallocene-catalyzed polymers the situation is less clear, and there is the possibility that the emphasis will be on rejection of segments rather than whole molecules. But even if this is the case, the principle of segregation is not affected, although the final destination of the segregants may well be. When segregation occurs, increasing concentrations of more-branched sequences will lower the local equilibrium melting temperature and with it the isothermal supercooling for growth and hence the growth rate itself. The implication of the continuous lowering of growth rate until the steady-state condition is reached is, therefore, that the concentration of segregants at the growth front increases to a dynamically stable limit.

In consequence, the basis of cellulation has to be different from the scenario of earlier discussions where growth was considered to accelerate through the segregant-rich region into melt of the original composition.[1] Now we find that there is continual slowing until the

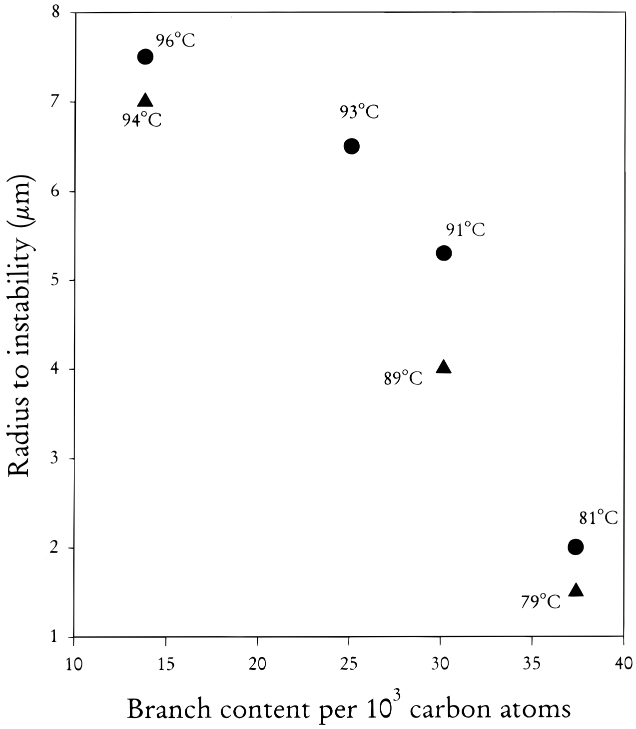

Figure 5. Radii of spherulites to instability as a function of average branch content for polymers D through G.

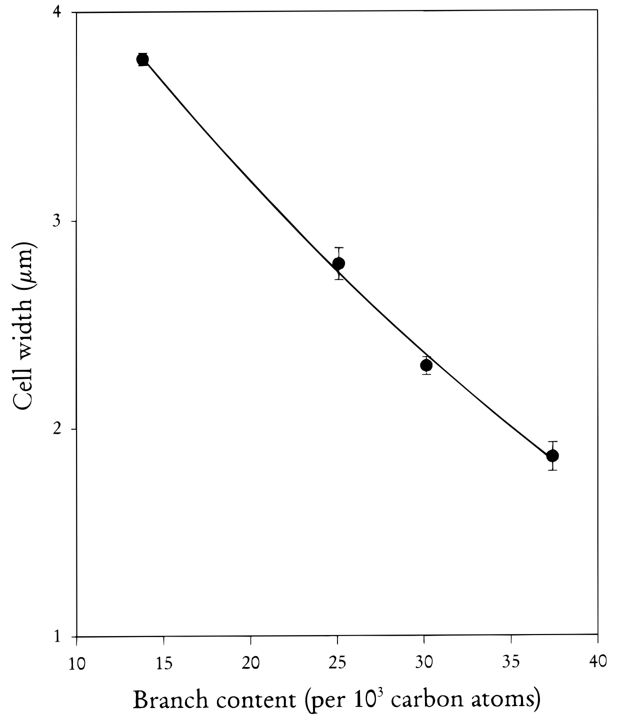

Figure 6. Average cellulation width as a function of average branch content for polymers D through G.

steady-state condition is attained. When cellulation occurs it does so at dimensions which, for the same polymer, are effectively constant and independent of growth rate. Consider first the radius to the onset of instability. In our previous paper[2] we found that instability set in after reductions in the initial growth rate, G_0, from 11 to 18%, increasing with crystallization temperature. This was consistent with there being a certain differential velocity, with respect to G_0, required to cause instability (although it was not obvious why the rate did not increase thereafter). But it does not agree with the more extensive data of this paper which show, in Table 2, reductions in G_0 as high as 65% before cellulation has set in. In fact the radius to the onset of instability is nearly the same for the same polymer crystallized at different temperatures notwithstanding quite large differences in growth rate (Figures 2b, 4b, and 4c). The condition for cellulation to occur is, therefore, not related to growth rate but appears to be essentially a function of the total quantity of segregant rejected in the growth of the spherulite. Apart from the observed small reductions at the higher temperatures, which are probably a consequence of greater diffusion away from the growth envelope when growth is slower, this will be primarily a function of radius and independent of crystallization temperature. In a similar vein, Figure 6 shows that cell width is effectively constant for a given polymer, independent of crystallization temperature and growth rate.

This last point is the hardest to explain. Images such as Figure 3d show how well-defined is the cell width and its constancy in different regions of a spherulite so that one looks for a characteristic scaling length, λ, say. Other work,[4] on the polymer of the previous paper, has shown that cellulation is initiated via small irregular protuberances which then combine into a quasi-sinusoidal envelope which deepens at constant width over time. For this well-defined width to be independent of radial growth velocity, as experiment shows, differs from experience in metals etc.[5] If it is to be related to diffusion coefficient, in view of the marked reduction with increasing branch content, this quantity needs to be multiplied by one with the dimension of time in its numerator. Of the two principal possibilities, time itself is unpromising because not only is there no characteristic time, τ, obviously associated with cellulation for which one might suggest $\lambda \sim \sqrt{D\tau}$, but the cell width is independent of where within the spherulite the cell began and is not tied to the first onset of cellulation. A more plausible suggestion is that some lateral velocity, V, which would have to be independent of the radial velocity, is involved whence $\lambda \sim D/V$ provided that $V \neq V(G)$. But this condition removes the possibility of invoking the rate of lateral completion of a layer on the growth face which, in regime II, is a function of the radial growth rate. Once again we must look elsewhere.

An alternative suggestion, which does not involve the diffusion coefficient explicitly, stems from noting that the growth direction deviates from the radial as lamellae bend. Thinner lamellae, i.e., those crystallizing at lowest temperatures from the most-branched polymers, will bend most. The relevance is that unless growth is along the radial direction, it will lose its advantage over its neighbors and will fail to propagate. Accordingly, in the present state of knowledge, this last suggestion seems the most likely origin of the lateral limitation of growth under cellulated conditions. It should be noted that this mechanism may well not generalize to nonpolymeric materials in which the crystallography is likely to be maintained throughout the growing fingers.

The phenomenology of cellulation suggested by our experiments is, therefore, as follows. Segregation commences with crystallization causing a progressive accumulation of segregants at the growth interface which slows the growth rate. When sufficient material has segregated, fluctuations in the local concentration produce greater slowing along certain regions of the growth front than others. Those areas least affected continue to grow, tending to become protuberances ahead of their laggard surroundings. The width of protuberances is most likely limited by the need to maintain a sufficient component of velocity in the radial direction. Lateral diffusion will then concentrate further segregants between fingers as their extension proceeds.

Conclusions

Cellulation is superposed on regular spherulitic growth under conditions of high segregation. There is no requirement to have an especially high branch content provided there is sufficient segregation.

Growth slows continuously to a dynamically stable asymptotic limit at long times when the growth rate matches that of diffusion of segregants from the growth interface.

The distance to the onset of cellulation and cell width are effectively independent of radial growth rate for a given polymer, but both decline with increase in branch content for different polymers. The dimensions of cellulation do not scale with $\delta = D/G$.

It is suggested that the width of cells may reflect the relative ease of bending lamellae linked to the concomitant failure to maintain a sufficient radial component of velocity.

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References and Notes

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