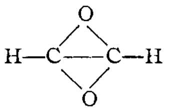
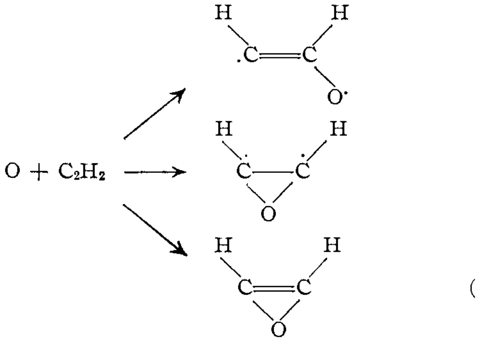
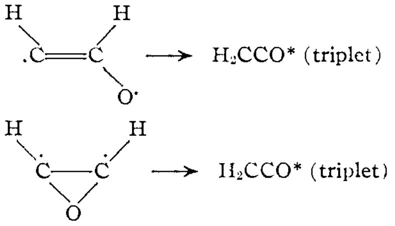


The products found upon warming were glyoxal, CO, HCOOH, H_2O and CO_2. Ketene was not identified.

We propose that reaction 4 occurs in two steps, oxygen atom addition, (5) followed by isomerization (6). Three possible structures for the addition are



Since product 5″ does not conserve spin, products 5 and 5′ are favored. Either could isomerize to a



triplet state of ketene followed by phosphorescence of the excited ketene. No such low triplet state of ketene is known, however.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

On the Morphology of the Crystalline State in Polymers

BY P. J. FLORY

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Geometrical and spatial requirements for the accommodation of polymer chains in random conformations set an upper limit of $v_2\ A_c/2A_a$ on the fraction of those chains emerging from the face of a lamellar crystallite of large lateral dimensions which may traverse the interfacial zone and vanish into the surrounding disordered region without returning to the crystallite; v_2 is the volume fraction of polymer in the surrounding phase and A_a and A_c are the cross sections occupied by the polymer chain in its amorphous and crystalline conformations, respectively. A considerable fraction of the chains emanating from the crystal face may nevertheless escape the environs of the crystal without returning to it (for $v_2 \sim 1$). Those which return need not adopt the regularly folded pattern currently assumed. Helical conformations, such as occur among biological polymers, increase the crystalline chain cross section and thus alleviate the crowding of chains otherwise attending their disorientation. The spatial factors enforcing re-entry of emerging chains become operative only when the transverse dimensions of the crystal are large. The cross sections of both primary and secondary nuclei are sufficiently small to permit their formation from bundles of separate ("unfolded") chain molecules. In copolymers, the infrequency of occurrence of long runs of the crystallizing unit generally precludes multiple participation (*i.e.*, "folding") of the same molecule in a given crystallite. Hence, the lamellar morphology characteristic of homopolymers may of necessity be supplanted by crystallites of small lateral dimensions (assuming $A_c/A_a < 2$). For similar reasons, crystallites generated by stretching must be restricted in their lateral dimensions owing to the incompatibility of any sort of folded arrangement with the axial orientation imposed by deformation. The presence of disorganized interfacial layers on lamellar crystallites separating from a dilute solution may diminish their stability perceptibly largely due to osmotic forces tending to disperse these relatively concentrated amorphous layers. At equilibrium with a dilute solution the regularly folded array offers the greatest stability. It is suggested however that the morphology which develops during crystallization is determined by kinetic factors which preclude achievement of this optimum result. The elementary process in crystallite growth is considered to consist in the (reversible) deposition of a chain unit rather than of an entire sequence of units. Mobility of chains in the outermost layer of the growing crystal face is viewed as a factor of importance.

I. Introduction

The discovery of the characteristic single crystal habit of the platelets precipitated from dilute solutions of linear polymers has stimulated unprecedented interest in the morphology of the crystalline state in polymers.[1–7] The thicknesses of these platelets, or lamellae, range from 70 to 200 Å. units; they may measure up to several microns in transverse dimensions. Crystalline overgrowth layers of the same thickness frequently occur, depending on the conditions attending crystallization. The patterns frequently displayed by these layers conform to the requisites for accretion by screw dislocation mechanisms. Most

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striking is the fact, established by electron and X-ray diffraction,[1,3–5] that the chains are oriented with their axes (the crystallographic c-axis) perpendicular to the plane of the lamella. Moreover, the a and b axes assume directions in the plane of the lamella which are preserved throughout the crystal; hence, the term "single crystal." The same a and b axes are maintained within narrow limits in the overgrowth layers.

The first observation cited above, coupled with the fact that the chain molecules are many thousands of ångström units in length, has given rise to the concept of a folded arrangement of molecular chains comprising the crystal.[1–7] In view of its length, a given molecule must necessarily traverse the platelet thickness repeatedly in order to comply with the established organization of chain units within the single crystal lamella. This much is beyond dispute.

Current concepts of the structure of polymer crystallites go a further step in postulating regular folding, or pleating, of the chains. A molecule is considered to fold itself neatly at the termination of each successive passage through the platelet. in order that it may immediately traverse the next sequence of sites in a low index plane, usually the 110 plane. Thus, like the woof of a loomed fabric, each molecule is assumed to pass regularly from one sequence to the next, slack between sequences being eliminated as if by a properly adjusted shuttle tension. The number of chain atoms participating in the turn from one sequence to the next is assumed to be the minimum consistent with hindrances to bond rotations. By no means is this idealized array, to which we shall apply the term *regularly folded*, established by experiment. In its finer details, at least it remains in the realm of an hypothesis at the present time. We shall nevertheless have occasion to treat this model as an important extreme case.

The temptation to project concepts on the structure of single crystals formed in dilute solution to the morphology of melt crystallized polymers[5,6,8] has been irresistible, and by no means without some justification. At the level observable by ordinary microscopy, spherulites usually represent the dominant feature. Their occurrence perhaps is less significant than the internal structure of the spherulites as revealed by optical birefringence, electron microscopy and X-ray diffraction—especially low-angle diffraction. The chain axes are oriented perpendicular to spherulite radii. Electron microscope examinations by replica techniques offer evidence of sheet-like patterns on the surfaces of thin films allowed to crystallize from the molten state, as well as on surfaces produced by fracture.[5,6] The planes of the sheets are approximately parallel to the spherulite radii, chain axes being perpendicular to this plane. Accordingly, growth of individual sheets, or lamellae, in the direction of the chain axis appears to be restricted and development in the transverse directions appears to be comparatively unrestrained. The similarity to single crystals formed in dilute solutions is apparent, but identity of morphology with that of the latter is denied by careful examination of experimental evidence.[9]

Low-angle diffraction maxima observed in crystalline, unoriented polymers are generally ascribed to a "superlattice" spacing in the direction of the c axis. These spacings are believed to denote pseudo-regularity in the alternation between crystalline and amorphous regions; they have therefore been identified with the repeat distance from one lamella to the next. Polymers crystallized with minimum supercooling display sharper reflections in the wide-angle X-ray diffraction patterns, larger low-angle diffraction spacings,[9,10] and narrower melting ranges,[11,12] all indicative of an increase in lamellar thickness and an improvement in crystalline order.

Conventional nucleation theory as developed for phase transformations in simple molecular substances has afforded a remarkably satisfactory description of the main features of the kinetics of crystallization of polymers, both from the molten state and from solution.[11] The rates of generation of spherulite centers and of their growth are shown by numerous experiments to depend on production of nuclei having critical dimensions determined by the opposing effects of the bulk free energy change and the interfacial free energies. The repeating unit of the chain is the analog of a small molecule insofar as occupancy of the crystal lattice is concerned and, by inference, the elementary process in polymer crystallization evidently consists in the deposition of a polymer unit on its lattice site.

The similarity to monomeric systems diminishes as one proceeds to consider the morphology of crystalline polymers. Interspersion of a substantial fraction of residual amorphous material with crystallites which are submicroscopic in at least one dimension, and the propensity for growth of lamellae are illustrative. These features peculiar to the morphology of crystalline polymers may naturally be presumed to occur as consequences of the presence of a chain structure. The bonding of one structural unit to the next in linear succession introduces correlations such that deposition of a sequence of units in the crystal lattice requires coöperation from remotely connected units. Continuation of the same linear molecule from the crystalline to the amorphous phase implies an interrelationship which must certainly affect both the rate of crystal growth and the texture of the resulting semi-crystalline solid. These circumstances notwithstanding, Hoffman and Lauritzen,[13] Price,[14] and Tosi[15] have attempted to take account of the morphology of polymer crystallites within the

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framework of concepts governing the stability of crystals comprising small molecules, and in particular to calculate the stable layer thickness with no other equipment than a combination of interfacial free energies.

An immediate and obvious restriction imposed by this singular feature of polymeric structure is the requirement of successive occupation of a given sequence of lattice sites in the direction of the c axis by consecutive member units of the same chain. In contrast to the crystallization of small molecules, any one of which may occupy a given lattice site irrespective of the choice of occupants for preceding sites, eligibility of a polymer chain unit for a given site is pre-determined by the disposition of its predecessors in the same chain. A high degree of coöperation in the diffusional transport from the surrounding amorphous phase is consequently required in polymer crystallization.

The sequential connections between polymer chain units restrict not only the array within the crystal lattice; their effect extends also into the amorphous regions. The continuity of the polymer chains must assume particular importance in its effect on the molecular organization within the interfacial region adjoining the crystallites and penetrated by chains emanating from the lattice. In this paper we attempt to examine some of the basic factors incident upon the processes of generation of a crystalline phase from long-chain molecules initially in random conformations.

II. Spatial Requirements of Polymer Chains in the Interfacial Zone

The regularity of arrangement of chains within the crystal cannot, in general, be dissipated abruptly at the crystal interfaces transverse to the chain axis. This circumstance, frequently cited in the past, is a further consequence of the continuity of the polymer chain.

In order to assess the factors affecting the transition from ordered arrangement within the crystalline region to a state of complete disorder beyond the interface, consider a lamellar crystal of unlimited dimensions transverse to the c axis, the surface of the crystal being embedded in an infinite amorphous polymer phase, or melt. The interface is illustrated in Fig. 1. Chains emerging from the crystal pass through the plane BB into the adjoining region. Let $N_c = 1/A_c$ represent the number of chains per unit area in planes parallel to BB in the crystal, A_c being the cross-sectional area per chain in the crystalline state.

Next, consider the number of chains N_a intersected per unit area by a plane, such as CC in Fig. 1, situated in the amorphous region out of range of all vestiges of crystalline order. The spatial conformation of the chain is here represented by a line of continuously varying direction. For purposes of the analysis to follow, it is convenient to adopt a segmented chain model, this to consist of rigid segments or bonds joined end-to-end with at most only limited correlations between the direction of one bond and its immediate successors. Let l, A_a and V_a denote the length, cross-sectional area and volume, respectively, of such a segment in the amorphous state. A bond inclined at an angle θ to the normal to the plane CC will intersect this plane if its terminus occurs within a distance $l \cos\theta$ of the plane. The number of intersections at angles θ to $\theta + d\theta$ per unit area is therefore

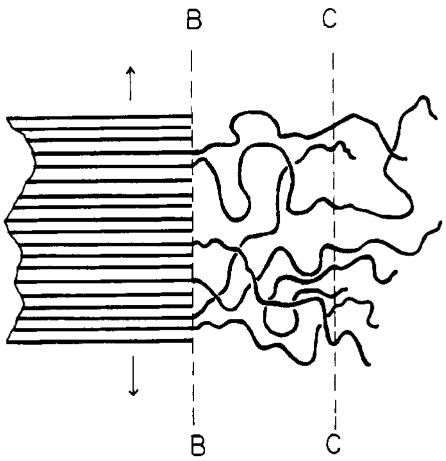

Fig. 1.—The interfacial zone transverse to the c-axis. In the interests of clarity, only a few of the chain trajectories emanating from the crystal face BB are shown.

$$N_\theta\, d\theta = V_a^{-1}\, l \cos\theta \sin\theta\, d\theta$$

where V_a^{-1} is taken to represent the concentration of polymer segments, absence of solvent being assumed in the region considered. Integration over all directions θ yields

$$N_a = \int_0^{\pi/2} N_\theta\, d\theta = l/2V_a$$

or, since $V_a = lA_a$

$$N_a = 1/2A_a \qquad (1)$$

This result can be deduced alternatively by taking the average over all directions of the area of intersection, $A_a(\cos\theta)^{-1}$, for a chain whose direction (or the tangent to its trajectory) is inclined at an angle θ to the normal to the surface CC at the point of intersection. The result is independent of the shape of the cross section.

Comparing N_a as given by eq. 1 with the density N_c of chains in a transverse cross section of the crystal, we have

$$N_a/N_c = (1/2)(A_c/A_a) \qquad (2)$$

If, as in polyethylene for example, the chains are fully extended in the crystalline state and if they are not prone to systematically coiled sequences of units in the amorphous state, then it is reasonable to identify the cross section ratio, approximately, with the ratio of specific volumes for the two phases, *i.e.*, $A_c/A_a = \bar{v}_c/\bar{v}_a$. In such circumstances, the density N_a of chain intersections in the amorphous phase is concluded to be somewhat less than half the number N_c emerging per unit area at the interfacial plane of the crystal. It follows that not more than half of the flux of chains at the crystal interface can be accommodated at the plane CC. Inasmuch as the crystal is taken to be infinite in both transverse dimensions, the flux of chains from the crystal surface must somehow be dissipated (in a manner deliberately not represented in Fig. 1). An obvious possibility is the return of a consider-

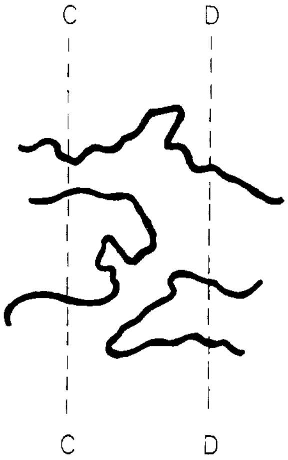

Fig. 2.—Several chains between arbitrary parallel planes situated in the amorphous zone.

able fraction of the chain trajectories to the crystal surface, re-entry of the crystal by the chain and its occupation of another sequence of crystalline sites.

Before pursuing the implications of this result, the location of the plane CC relative to the crystal surface deserves critical examination. It has been stipulated merely that this plane is to be situated at a distance from BB where all vestiges of the crystalline order have vanished. The various planes being infinite, this statement, if taken literally, might require CC to be a very great distance—perhaps an infinite distance—from BB. In terms of an approximate physical model, we would like to identify CC with the outer boundary of an interfacial layer of intermediate order, which therefore should be small in thickness. A compromise is needed.

In the interests of clarification, consider another infinite plane DD located beyond CC in the amorphous continuum, as illustrated in Fig. 2. If the chain length is taken to be infinite, every chain entering the intervening region must eventually depart from the region through one or the other of the two planes. Let N_{CC}, N_{DD} and N_{CD} represent the numbers of trajectories per unit area which successively intersect the planes indicated by the subscripts. Obviously

$$N_{\mathrm{CC}} = N_{\mathrm{DD}} > N_{\mathrm{CD}}/2 \tag{3}$$

The inequality will depend on the distance between the planes and also on the tortuosity characteristic of the chains. If the distance is sufficiently great, and isotropy prevails, N_{CD} will vanish. Thus, as the arbitrary distance of separation of planes BB and CC in Fig. 1 is increased to assure isotropy, *i.e.*, complete disorder, at the latter plane, the incidence of trajectories which intersect this plane from right to left and subsequently emerge left to right without entering the crystallite is increased.

In consequence of the intrusion of chains in this manner into the zone in Fig. 1 between BB and CC, the flux of chains emanating from the crystallite and subsequently passing through CC will be further reduced below the upper limit given by eq. 1. As this conclusion implies, the farther the arbitrary plane CC is removed from the nominal face of the crystallite, the greater will be the number of chains which emerge from the crystallite and subsequently return to it without intersecting plane CC. If the distance between CC and BB is sufficiently large and if genuine isotropy prevails except in the immediate vicinity of the crystalline lamella considered, then obviously all chains emerging from the crystal must eventually return to it, assuming as before an infinite chain length and indefinite continuation of the amorphous zone (*i.e.*, disregarding effects of neighboring crystals).

We shall have occasion to refer to the interfacial zone as that region within which the order of the crystallite is largely dissipated. It is appropriate to remark that the presence of other crystallites in the neighborhood of the one under consideration may, of course, absorb the flux of chains from the amorphous region. Those chains which penetrate the interfacial zone of the crystallite under consideration may return to it, or they may proceed to another crystallite in the neighborhood. Implicit in this description is the acknowledgment, in deference to experimental evidence, that the crystallites are separated by regions of essentially complete disorder, *i.e.*, by a genuine amorphous phase.[11,12]

These considerations lead to the conclusion that no more than half of the chains emanating from the lamellar crystal surface can be accommodated by the neighboring disordered amorphous phase. If the plane surface is very large in both dimensions and if $A_{\mathrm{c}}/A_{\mathrm{a}} \cong 1$, then this requirement can be met only if at least half of the chains of the crystal reverse their directions and re-enter the crystal. The flux of these chains must be reduced to this extent at least before the random isotropy characteristic of an amorphous phase can be achieved. Actually the flux must sustain a greater attenuation owing to penetration of the interfacial zone by chains from the amorphous region, as illustrated in Fig. 2; some of the capacity of the semi-arbitrary boundary CC will be appropriated for this purpose. Thus, considerably more than half of the sequences of crystalline units will be connected by fairly short loops in the interfacial zone. These conclusions follow directly from the spatial requirements for chains in random disorder as compared with those in the regular array characteristic of the crystalline region.

It does not follow that the polymer chains need to be regularly folded, or pleated, in accordance with current fashion. To begin with, a substantial fraction of the chains may proceed into regions of complete isotropy and eventually enter other nearby crystallites. If interconnections between crystallites were not thus abundantly provided, even the most rudimentary properties of crystalline polymers would be very different from those observed. Furthermore, those chains which re-enter the same crystallite need not invariably do so immediately but instead may enjoy a brief sortie into the amorphous region before returning. Finally, such a chain may choose to occupy a sequence other than the one adjacent to its previous passage. These departures from regular folding are plausible

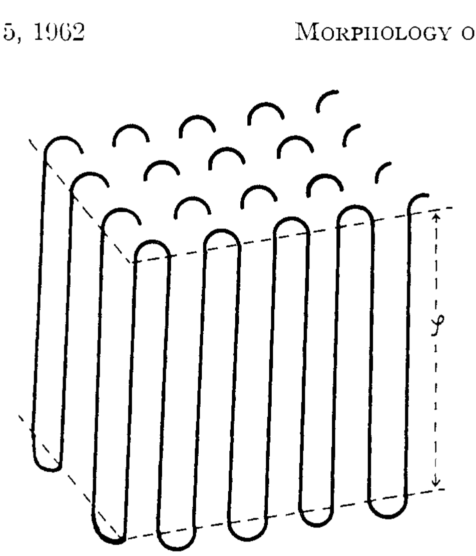

Fig. 3.—A portion of a regularly folded lamellar crystal of thickness ζ in the direction of the c-axis.

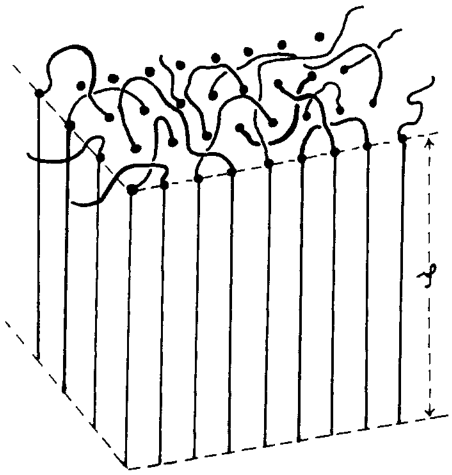

Fig. 4.—A lamellar crystallite with *irregular* "folding" of chain molecules; loop lengths variable.

on molecular grounds. They are not precluded by experimental evidence. In fact, as Mandelkern and co-workers[9] have shown, results of small angle X-ray diffraction on melt crystallized polyethylenes are difficult to reconcile with a regularly folded chain array.

For crystals in which the chains are arranged in helical conformations the ratio A_c/A_a may exceed unity. A case in point is that of the α-helical crystalline form of polypeptides for which the projected length per unit on the axis of the helix is 1.5 Å., compared with 3.8 Å. for the length of a *trans* unit of the chain. Approximating A_c/A_a by the inverse ratio of these lengths, we have $A_c/A_a \cong 2.5$, and the difficulty of reconciling the spatial requirements of random chains with the space available to them in the amorphous region vanishes according to eq. 2. The morphology of the semicrystalline polymer coexisting crystalline and amorphous regions may thus depend critically on the conformation of the chain in the crystal lattice.

III. Crystallization from Solution

The foregoing analysis has been addressed primarily to crystals co-existing with a melt or amorphous matrix. Similar restrictions apply to the dissipation of crystalline order in the interfacial zone when the parent phase is a solution rather than a melt. They are rendered more severe however by the necessity for the concentration of polymer to diminish to that of the surrounding solution before the influence of the crystalline phase on the adjoining regions can be completely dissipated. Thus, the flux of chains across an arbitrary plane must fall to the level for the solution at large. Equation 1 may therefore be replaced by

$$N_a/N_c = v_2A_c/2A_a \qquad (1')$$

where v_2 is the volume fraction of polymer in the solution. The frequency of occurrence of chain trajectories which return to the same crystal interface from which they last departed must increase correspondingly.

If the solution is infinitely dilute and the molecules are infinitely long, then obviously all chains emanating from the crystal face will return to it sooner or later. From a somewhat different standpoint, in an extremely dilute solution the distance between crystallites becomes so great as to preclude participation of a given (finite) molecule in more than one crystallite. A molecule may, of course, traverse several of the crystal sequences, and in general it will be required to do so in order to meet the condition stipulated by eq. 1′. The question to be considered concerns the efficiency of incorporation in the crystal lattice of those molecules which participate to some degree. At one extreme we have the regularly folded arrangement illustrated in Fig. 3. Here each molecule crystallizes to the maximum possible extent; ignoring those small sections required to complete the hairpin connections between successive sequences, its crystallization is virtually complete. In the other extreme depicted in Fig. 4, sequences are connected more or less at random in "switchboard" fashion. The lengths of "loops" of units extending from one crystalline sequence to the next along a given molecule are likewise variable. Intermediate situations can be envisioned such as, for example, one in which sequences from a given molecule occur within the same layer of the crystal, as in Fig. 3 but with varying loop lengths. Except in the regularly folded case, Fig. 3, the crystal platelet bears a profusion of disorganized polymer chains which intermingle with solvent in the interfacial regions. The presence of such a diffuse layer offers the advantage of greater randomness, and hence a greater entropy insofar as the crystal and associated amorphous material are concerned. On the other hand, construction of a crystal of given dimensions in so inefficient a manner will require a greater number of polymer molecules, and hence a larger expenditure of osmotic work in order to gather the molecular centers in one locality. The accumulation of polymer chains in the amorphous zone at a concentration very much greater than that of the surrounding solution entails further osmotic work arising from the interactions between chain units in this region.

We consider first the effects of these osmotic contributions attributable to the interfacial layer. The tendency toward disorder in the allocation of chain units between crystalline sequences and intervening amorphous loops will be treated subsequently.

Osmotic Effects Associated with the Formation of the Interfacial Layer.—Let y represent the average length of an amorphous loop connecting crystalline sequences of length ζ, both quantities being expressed in numbers of units. Then if s is the number of sequences in the crystal, a total of $(\zeta + y)\ s$ chain units are involved. The number of polymer molecules is $(\zeta + y)\ s/x$ where x is the (average) number of units in a molecule. In the regularly folded arrangement (Fig. 3), y is reduced to its minimum possible value. We take this to be zero; any error thus committed may be compensated by including the minimum loop length in ζ. Formation of interfacial layers comprising amorphous loops in excess of the minimum length requires transfer of ys/x additional molecules from the dilute solution at a volume fraction v_2 to the layer. The concentration in the interfacial regions will of course vary from a volume fraction near unity down to v_2. It will suffice to ascribe an effective volume fraction v_2' to the interfacial layers and to treat them as uniform in concentration throughout. We assume $v_2 << v_2' < 1$. The osmotic work required to form the interfacial layers from the surrounding solution is, according to polymer solution theory

$$\Delta F_{os} \cong RTsy\{(1/x)[\ln (v_2'/v_2) - 1] + (1/x_1)[1 + (1/v_2' - 1) \ln (1 - v_2') - \chi_1 v_2']\} \quad (4)$$

where x is the number of units in a polymer molecule, x_1 is the ratio of the molar volume of a solvent molecule to that of a polymer unit, χ_1 is the interaction parameter and s is expressed in moles of sequences.

The possible impact of the osmotic term is rendered more tangible by calculating its effect on the solubility temperature. Let T_m be the temperature for equilibrium between a crystal of specified dimensions and the surrounding solution in absence of the osmotic effect considered above. Then at a temperature $T' = T_m - \Delta T$, we have for the free energy change for the formation of the crystal and associated interfacial material from the dilute solution

$$\Delta F = \Delta F_{os} - s\ \zeta\ (\Delta H_u/T_m)\Delta T \quad (5)$$

where ΔH_u is the enthalpy change per unit for the reverse process (fusion and dissolution). Equating to zero and substituting from eq. 4 for ΔF_{os}, we obtain for the depression of the temperature of equilibrium attributable to the osmotic work

$$\Delta T \cong (y/\zeta)(RT_m^2/x_1\Delta H_u)\{(x_1/x)[\ln (v_2'/v_2) - 1] + 1 + (1/v_2' - 1) \ln (1 - v_2') - \chi_1 v_2'\} \quad (6)$$

The term in x_1/x, which represents first virial coefficient terms pertaining to the allocation of molecular centers, is altogether negligible for large x and will be disregarded below. This corresponds to the asymptotic independence of the melting point, and the solubility point, on chain length.

The extent of the interfacial layer evades precise definition, as does its mean concentration. Arbitrarily assigning to this layer a thickness such that the effective $v_2' = 0.5$, we obtain for a good solvent for which $\chi_1 = 0$,

$$\Delta T \cong 0.3(y/\zeta)\ RT_m^2/x_1\Delta H_u \quad (7)$$

Substitution of $T_m = 400°$ K., $\Delta H_u = 1000$ cal./unit, and $x_1 = 7$—values appropriate for polymethylene in a solvent having a molar volume of *ca.* 100 cc.—yields

$$\Delta T \cong 14(y/\zeta)$$

Thus, the stability as measured by lowering of the solubility point may amount at most to several degrees, depending on the ratio y/ζ of amorphous to crystalline material in the aggregate of crystal and interfacial layer. In poor solvents, ΔT will be even smaller. It does not necessarily follow that the osmotic free energy of formation of an interfacial layer is a negligible deterrence. The magnitude of this free energy is easily sufficient to influence the course of crystal growth, as is evident if one translates this free energy into the repulsion offered a molecule approaching from the surrounding solution.

Disposition of the Chain Molecule Between Crystalline Sequences and the Interfacial Layer.—Consider a single polymer chain of x units presented with the opportunity of participating in a lamellar crystallite of thickness ζ. It may occupy any number of sequences $\nu < x/\zeta$. We take ζ to be rigidly fixed by the thickness of the crystallite. The number of possible arrangements permitted through variations in the lengths of the intervening amorphous sequences is

$$C(\zeta,\nu) = (x - \nu\zeta + \nu)!/(x - \nu\zeta)!\ \nu!$$

it being assumed that such an intervening sequence may be of any length down to zero.

Account must be taken of the requirement that the $\nu - 1$ loops between crystalline sequences start and terminate at the same plane, namely the 001 face of the lamellar crystal. The component of the end-to-end vector of the loop along the normal to the plane must therefore be zero. If the growth faces (110) tend to develop one layer at a time, then the sequences belonging to a given molecule will in general be incorporated in the same 110 layer. An additional component of the end-to-end vector is thus constrained to a value near zero. Finally, if each loop joined the terminus of one sequence with its immediate neighbor in the same 110 face, then the end-to-end vector for the loop is fixed at a value which approximates zero; two of its components are in fact zero and the third must be assigned the small value of the interchain spacing in the 110 plane. This case resembles that of regular folding shown in Fig. 3; it may differ from it however in that the sizes (contour lengths) of the loops are permitted to exceed the minimum which is permissible, and to vary one from another.

The expression for the number of ways of selecting ν sequences out of x units, each sequence being of ζ units, must be supplemented by the factor expressing the probability that the $\nu - 1$ noncrystalline sequences are in acceptable conformations. On the basis of the theory of random chains, the probability that one of the Cartesian components of the vector connecting the ends of a loop is zero, within an interval approximating the dimension of one unit, is $(3/2\ \pi y)^{1/2}$. Hence the number of arrangements of the chain compatible with ν crystalline sequences is

$$C(\zeta,\nu)(3/2\pi y)^{(\nu - 1)d/2}$$

where d is the number of dimensions of constraint on each loop and y, in accordance with its usage above, is taken to be the average number of units per loop. Thus

$$y = (x - \nu\zeta)/(\nu + 1) \cong (x - \nu\zeta)/\nu \qquad (8)$$

The chain partition function may accordingly be expressed as

$$Q \cong C(\zeta, \nu)(3/2\pi y)^{d(\nu - 1)/2}\exp[\nu\zeta\varphi - 2\nu s_e] \qquad (9)$$

where

$$\left.\begin{aligned} \varphi &= \Delta F_u/RT \\ s_e &= \sigma_e/RT \end{aligned}\right\} \qquad (10)$$

ΔF_u is the molar free energy of fusion per unit and σ_e the interfacial free energy per mole of chains issuing from the crystal face (110). Included in σ_e are contributions from the abnormalities of the interfacial zone as previously discussed.

In quest of the optimum number ν of sequences for a chain of x units incorporated in a crystal of specified thickness ζ, we have considered the dependence of the molecular partition function Q on the number ν of sequences, the length ζ of sequences being fixed by the uniform thickness of the crystal. If $d = 0$, corresponding to the physically unrealistic complete disregard of constraints on the loops, Q passes through a maximum with ν for $\varphi\zeta - 2\ s_e < 0$ as well as for $\varphi\zeta - 2\ s_e > 0$. The former condition represents temperatures above the temperature T_m for phase equilibrium (*e.g.*, the melting point) in absence of the effects being specifically considered, and the latter condition to $T < T_m$. Thus, states of *partial* crystallinity are predicted on both sides of the "melting point"; the discontinuity of a phase transition is absent.[16]

The character of Q is affected markedly by constraints on the loop vectors, as becomes apparent upon examining this function for $d \geqq 1$. In the case $d = 1$, representing loop connections between pairs of points at random (Fig. 4) in the 001 plane, Q continues to exhibit a maximum with d at fixed ζ. The range over which this maximum occurs is however effectively limited to a narrow interval of temperature (*i.e.*, a small range in φ). On one side of this interval $[(\varphi - 2\ s_e/\zeta) > 0]$ virtually the entire molecule is required to crystallize at equilibrium, hence loop lengths y must be very short; at the other extreme $[(\varphi - 2\ s_e/\delta) < 0]$, crystalline sequences may occur only rarely.

If the solution from which growth takes place is sufficiently dilute, deposition of a molecule should proceed to substantial completion before another one is acquired in the same locality. Random interweaving of molecules to the extent indicated in Fig. 4 is then improbable, and we are led to expect $d = 2$ or 3. For $d \geqq 2$, Q no longer displays a stationary value with ν. The preferred situation is one or the other of the two extremes: crystallization to the fullest extent possible, or not at all. Which of these alternatives is favored depends on the value of φ, *i.e.*, on the temperature. A discontinuity in the state of equilibrium is thus predicted as φ is varied. In particular, under conditions of supersaturation, *i.e.*, $(T < T_m)$ the regularly folded array is favored as it permits maximum crystallization of the molecule.

The foregoing conclusion finds parallel in the treatment of crystallization given some years ago,[17] according to which long polymer molecules are assigned to a lattice in which certain regions are reserved for occupation by chains ordered in crystalline array. Re-entry of chains into the same crystallite was ignored at that time. The model requires implicitly, however, that amorphous chain sequences terminate at crystal faces whose locations are fixed by the contiguity of crystal sequences. The randomness associated with partitioning of chains between crystalline and amorphous sequences is offset by this requirement, as a result of which the transition *at equilibrium* between the crystalline and amorphous states is predicted to be abrupt and complete, *i.e.*, discontinuous, for a system of a single component (no diluent) which is unperturbed by effects of chain ends (infinite chain length).

Pursuit of this analogy a further step calls to mind the fact that the equilibrium situation of virtual complete crystallinity for temperatures $T < T_m$ is never realized in practice.[11] Limitations on the kinetic mobility of polymer units imposed by the continuity of connections between them apparently preclude attainment of the equilibrium state.

Conclusions.—The conclusion reached above is tenuous insofar as it depends on the nature of auxiliary constraints on loop vectors. It gains support however from the osmotic effects considered earlier, which must favor diminution of the amount of amorphous material in association with a crystallite. Hence, it may be confidently asserted that the folded array which permits maximum crystallization is the most stable state *for a crystallite in contact with a dilute solution* under conditions of supersaturation. A high degree of crystallization also is indicated for the equilibrium state $(T < T_m)$ in undiluted systems, although in this case a given molecule may participate in a number of crystallites as we have indicated earlier.

It is significant that these conclusions are derived without appeal to critical conditions of stability of coherent secondary nuclei as determined by the interplay of conventional interfacial and bulk free energies. Likewise, no inherent characteristic of polymer chains which would favor the folded arrangement has been invoked.

It would be unwarranted to conclude however that the most stable state is necessarily achieved under the conditions operative during the process of growth of the crystal. The relaxation times for long segments of a polymer chain are too great, even in dilute solution, to keep pace with the fairly rapid rate of deposition of chains on the growing surface (*cf. seq.*). Kinetic factors cannot be overlooked in respect to their dominating influence on the morphology of crystalline polymers. The inquiry into the optimum structure, albeit an unat-

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(16) The analysis is predicated on the presence of a crystallite of finite thickness. The fact that the partition function for the single molecule indicates an inclination for it to participate in such a crystallite when the presence of the latter is guaranteed by a premise of the argument does not, of course, assure stability of the crystal. Thus, a Q favoring $\nu > 0$ above the melting point does not imply stability of the crystal as a whole.

(17) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

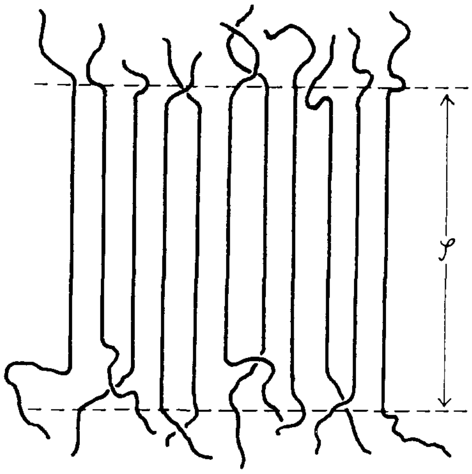

Fig. 5.—Schematic representation of a momentary state of the outermost layer on the growing (110) surface of a lamellar crystallite. Amorphous segments connecting crystalline sequences are omitted for clarity.

tainable one, is nevertheless instructive if for no other purpose than to establish the direction in which spontaneous changes must proceed.

IV. Mechanism of Growth of Lamellar Crystals

In the preceding analysis we have taken ζ to be fixed. For sequences within the crystal this stipulation is legitimate, for here each sequence must in general comply with the lengths of its neighbors. But on the outermost 110 layer this restriction is relaxed by the absence of neighboring chains on one side of the layer in question. Here, as we shall attempt to show, the chains are susceptible to fluctuations in their arrangements and need not conform precisely to the dimensions (ζ) of the neighbor sequences in the layer beneath. Although addressed primarily to crystals formed from dilute solutions, the principal conclusions reached should be similarly applicable to crystallization from melts.

Let us assume that at a given moment the outermost layer replicates precisely the layer beneath, which for purposes of discussion may be assumed to be of uniform ζ throughout. The chains may or may not be regularly folded; loops may or may not exceed the minimum length required for the 180° turn. The change in free energy consequent upon displacement of a unit from the terminus of one of the sequences in this outermost layer will consist of the free energy of fusion ΔF_u per unit and of the increase in interfacial free $2\sigma_u$ associated with the net exposure of one lateral face of each of the two units in neighboring sequences. Taking polymethylene as the example and adopting molar units, we have

$$\Delta F_u = \Delta T \Delta S_u \cong 2\Delta T \tag{11}$$

where ΔS_u is the entropy of fusion and ΔT is the depression below the temperature T_m for phase equilibrium (or melting point) of the crystals in question. Turnbull and Cormia[18] deduce a mean interfacial free energy of *ca.* 8 erg cm.$^{-2}$ from the temperature coefficients of the rates of nucleation of crystallization in n-$C_{17}H_{36}$ and n-$C_{18}H_{38}$. We infer from this result that σ_u is 50 to 100 cal. mole^{-1} (see ref. 13). Thus, barring very large supersaturations, the free energy change associated with removal of a unit will be small compared with RT. Onset of thermal fluctuations in the initially perfect layer described above will bring about "desorption" of one or more units from the termini of many of the sequences. Moreover, partial unpeeling of one chain will facilitate similar response by neighboring sequences, inasmuch as the interfacial area of the crystal is not further increased by the removal of units adjacent to previously exposed positions. The outer layer may therefore be expected to be ragged at its edges, as represented schematically in Fig. 5.

The extent of unpeeling of a sequence in the surface layer will be subject to rapid and frequent fluctuations. Complete removal of a sequence from the surface layer should be rare, however (the last sequence at the boundary of a developing layer excepted; *cf. seq.*), owing to deterrence by the substantial interfacial free energy $2\zeta\sigma_u$ required. For a similar reason, large changes in ζ from one sequence to the next should occur infrequently. Extension of a layer beyond the one below it will entail additional interfacial free energy σ_u for the exposed area of "overhang." Increases in ζ from one layer to the next will thus be discouraged, but by no means forbidden.[15] These and other more or less obvious deductions rest on established concepts of crystal nucleation and growth and are not peculiar to macromolecular chains.

Longitudinal displacement of a chain sequence conceivably may occur readily by a process analogous to vacancy diffusion in solids. In this case the "vacancy" may be a loop occurring within the sequence laid down on the growth surface. The loop may consist of several units separated from the crystal surface and so coiled as to shorten the distances between adjoining portions of the crystalline sequence. Diffusive displacement of this loop along the sequence results in translation of the sequence in the reverse direction. In this way, a sequence may shift to a new position more favorable to development of the crystal. The displacement may occur in this manner without the necessity for complete removal from the surface as an intermediate step.

The state of the outermost layer of the growing crystallite is to be regarded therefore as transient and subject to rearrangements by one or more mechanisms. These must proceed on the average toward more stable situations. The process is of course arrested by deposition of succeeding layers.

Growth of a crystal may be presumed to involve successive deposition of sequences at the edge (*i.e.*, kink[19]) of a developing layer. An entire sequence is not of course acquired in a single step but rather by stepwise acquisition of chain units, the first step consisting in the deposition of several units at an arbitrary interval along the edge of the incomplete outer layer. This embryonic sequence may then grow by successively incorporating ad-

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[18] D. Turnbull and R. L. Cormia, *J. Chem. Phys.*, **34**, 820 (1961).

[19] W. T. Read, Jr., "Dislocations in Crystals," McGraw-Hill Book Co., Inc., New York, N. Y., 1953.

joining units from the same chain, or it may vanish owing to competitive reverse processes. Activation associated with the initiation step has been assumed to be rate controlling in recent discourses on the growth of polymer crystals[13-15]; subsequent development of the embryo has been ignored insofar as its effect on the crystallization rate is concerned. Except at large supersaturations, however, destruction of an incipient sequence is a more probable eventuality than its growth to maturity. Treatment of sequence deposition as depending on a single activated step is therefore untenable.

Apart from the activation associated with the diffusional displacement of a unit in the melt or solution, this activation being shared by all steps involved in sequence growth, the "activation energy" associated with initiation of a sequence through deposition of several units at the edge of an incomplete outer layer should not exceed $2\sigma_e$, where σ_e is the interfacial free energy associated with termination of a crystalline sequence. It may amount at most to several kilocalories. The free energy change for deposition of an entire sequence is

$$-\Delta F_{\zeta} = -\zeta\Delta F_u + 2\sigma_e \qquad (12)$$

We assume that the sequence in question does not extend beyond either its predecessor in the same layer or the sequence below it in the substrate layer; otherwise lateral interfacial terms are required to be included in eq. 12. The free energy of fusion per sequence for the crystal as a whole is given by eq. 12 with signs reversed. Hence, we have

$$\Delta F_f = (\zeta - \zeta^*)\Delta F_u \qquad (12')$$

where

$$\zeta^* = 2\sigma_e/\Delta F_u \qquad (13)$$

is the minimum sequence length for thermodynamic stability at the specified supersaturation.

The rate of development of a sequence *once initiated* must depend on the ratio of the rate of deposition of an additional unit to the rate of the reverse process. This ratio of rates is $\exp(-\Delta F_u/RT)$. It follows at once that the net rate of development of an embryonic sequence must increase with ΔT (very large ΔT excepted); for small supercoolings such that $\Delta F_u/RT << 1$, the net rate should increase in direct proportion to ΔT. The temperature coefficient of sequence growth should therefore be negative in the temperature range of interest. If, on the other hand, addition of a sequence occurred in a single, activated step as has been assumed by Frank and Tosi,[15] the temperature coefficient of this rate would necessarily be positive, in contradistinction to the negative temperature coefficient for reversible stepwise growth. The size ultimately reached must in any case exceed ζ^*; otherwise the deposited sequences are metastable ($-\Delta F_f > 0$) and removal of sequences must occur more rapidly than the rate at which mature ones are acquired by the layer.

According to recent attempts[13-15] to treat the growth of lamellar crystallites from polymer chains, the sequence length ζ is determined at its deposition. Allowance was made by Frank and Tosi[15] for the competitive occurrence of the reverse process (also in a single step) prior to acquisition of the next sequence. Such a mechanism permits alterations in the *last* sequence of the incomplete outer layer through operation of the reverse process; preceding sequences of the layer are denied this possibility. Fluctuations in the lengths of other sequences of the outer layer through removal of deposited units at the ends of sequences were ignored, as was also the possibility of longitudinal displacements of sequences. Processes such as these may be expected to render the outer layer irregular in its coverage of the crystal. They also confer mobility permitting subsequent readjustments toward an array suitable for support of succeeding layers. It is altogether unlikely that the ultimate status of a sequence is determined at the instant it is deposited.

Rates of growth, even under conditions permitting formation of lamellar crystals. may be quite large. Linear rates normal to the growing 110 surface in excess of 10^{-4} cm. per sec. are indicated by experiments.[20,21] If growth proceeds one layer at a time over a span of 1μ, the *net* rate of deposition of whole sequences is 5×10^6 sec.$^{-1}$. Deposition of individual units must occur at a rate several orders of magnitude greater than this, or $>10^{10}$ sec.$^{-1}$ in order to sustain the required *net* rate of sequence growth. All of this is predicated on the presence at any given time of at most only one incomplete layer (110) over the entire growth face of the crystallite (*i.e.*, only one kink), and of only one sequence in process of growth at the kink, or edge, of the incomplete layer. The very high rate estimated above for the elementary process, namely, deposition of a chain unit, casts doubt on these premises. Simultaneous development of several layers along the advancing front seems more plausible. Furthermore, the deposition of sequences at the kink in a given outer layer may be much more haphazard than tempting idealizations would indicate; it is conceivable that deposition of a new sequence may commence before growth of its predecessor in the developing layer is complete. Crystallization from a melt presents circumstances especially favorable to haphazard growth. The scarcity of polymer in a dilute solution, and the greater mobility of rearrangement as well, should be expected to favor more orderly development of successive layers.

The complexities of the processes attending growth of polymer crystals are such as to discourage the attempt to formulate a realistic interpretation which is at once pictorial, precise and quantitative. Control of the lamellar thickness may nevertheless be comprehended in fairly general terms as follows. If crystal layers develop in rapid succession, then the next layer may be deposited before sufficient time has elapsed for the sequences and associated chains of the preceding layer to achieve a well ordered arrangement capable of sustaining the dimension ζ of earlier layers. Such rearrangements require coördinated displacements of many

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(20) P. J. Flory and A. D. McIntyre, *J. Polymer Sci.*, **18**, 592 (1955).

(21) We arrive at this figure by a conservative extrapolation of the growth rates for poly-(decamethylene sebacate) reported in ref. 20. Much greater rates evidently occur at higher degrees of supercooling in both melts and dilute solutions.

linearly connected units—a process for which the relaxation time is large.[22] Consequently, ζ must decrease as the crystal grows by accretion of layers. The free energy of sequence deposition will consequently be reduced (see eq. 12′), and reversal of the stepwise successive addition of sequences at the kink (or kinks) will become more competitive. Growth will thereby be retarded. The longer interval of time between deposition of layers will allow greater opportunity for improving the organization of the outermost layer. If the rate continues to be sufficiently slow, the dimension ζ may increase gradually, or intermittently, from one layer to the next, wherever the chains protruding from the crystal sequences are suitably disposed to perpetuate the ordered array beyond the layer below. As a consequence of the increase in ζ, the rate will increase, etc.

A self-regulating mechanism of this nature affords a plausible basis for control of lamellar thickness. The value of ζ would be expected on this basis to increase with the temperature of crystallization, in accord with observation.[4,7,9] Of central importance is the fact that we have invoked kinetic factors as the agency which controls this dimension. Thus, we suggest that the parameter ζ cannot be adduced solely from consideration of equilibrium states.

It follows that the most stable crystalline array will not be achieved at finite rates. Indeed, this array would consist of crystals for which ζ is not much less than the molecular chain length.[17] Even if an arbitrary limit could be set on ζ, *regular* folding (Fig. 3) can scarcely be expected under experimental conditions, for similar reasons. Instead, an overlayer of disorganized amorphous chains, indicated by recent experiments[23] is a more plausible result.

V. Discussion

We have shown how a polymer chain may be constrained to traverse the same crystal several times merely as a consequence of geometrical, or spatial, requirements for random chains in comparison with those for the crystalline conformation. No propensity for folding on the part of the chain structure was invoked; it was pointed out however that the form of the molecule in the crystal lattice, as manifested in the cross-sectional area A_c per chain, is important. It remains to cite some of the implications of these results.

Primary and Secondary Nuclei.—The conclusions reached in Section II, and to a certain extent those of Section III, rest on the premise that the transverse dimensions of the crystal are very large compared with its thickness in the direction of the c-axis. A critical nucleus would not meet this description, according to estimates of its dimensions. Depending on the supersaturation and on the interfacial free energy σ_u, the critical nucleus may consist of only 20 to 100 chains. For a bundle of so few chains the spatial constraints considered in Section II may readily be dissipated by dispersing the chains from the interfacial zone in directions transverse to the bundle axis. Their spatial requirements can thus be met without folding of any sort. A critical nucleus comprising a bundle of sequences from *different* molecules is therefore an acceptable spatial array. It also places minimum demands on the coöperation required of disordered chains to form a crystallite nucleus; it is therefore the most plausible candidate for nucleation of crystallization from the melt or from a concentrated solution. In very dilute solutions, however, economy in the osmotic work of transferring molecules from the solution to the crystal aggregate will tend to minimize the number of molecules employed in constructing the nucleus.[13,17] Hence, repeated use of the same molecule may tend to prevail despite the small cross section of the crystal nucleus, and the consequent relaxation of the steric condition expressed by eq. 1′.

Similar considerations may apply to the secondary nuclei involved in the growth of spherulites from melts.[20,24] These may be presumed to consist of selected bundles of chains which emanate from the face of a previously formed lamellar crystallite. The perpetuation of orientation into the interfacial region, imposed by the spatial constraints discussed in Section II, may promote association of groups of such chains in parallel array about an axis normal to the parent crystal face. Under favorable circumstances such bundles may occasionally achieve critical size and thus serve to initiate new lamellae, preferentially oriented with respect to the parent crystallite. Just as in the case of a primary nucleus, folding of chains should not be required, owing to the small critical cross section of the secondary nucleus.

The Interfacial Free Energy σ_e.—The persistence of order in the interfacial zone and other constraints on chains therein may make a major contribution to the interfacial free energy associated with each termination of a crystalline sequence and its junction with the amorphous phase. Inasmuch as these constraints develop only as the area of the crystal becomes large, the applicable values of σ_e for nuclei and for mature crystallites may differ markedly. The value of σ_e which is operative in the generation of nuclei may in fact be much smaller than that which controls the stable thickness of lamellae of large area. The probable dependence of σ_e on crystallite dimensions and environment poses an obvious complication to conventional interpretations of critical sizes for nuclei and of crystallite stabilities.

Crystallization of Copolymers.—A binary copolymer may be regarded as a succession of sequences of the two kinds of units. We consider the fairly common situation in which sequences of one unit may crystallize but not those of the other. The number of units in a sequence usually varies more or less at random over a wide range. The longer sequences of the crystallizing unit are prefer-

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[22] It is at this point that the connectivity of the macromolecular chain enters specifically to distinguish crystallization of polymer from that of monomeric substances. Theories to date have sought to explain polymer crystallization entirely on the basis of the usual thermodynamic parameters—the interfacial tensions, the entropy of fusion, etc.

[23] To be published.

[24] M. Takayanagi and T. Yamashita, *J. Polymer Sci.*, **22**, 552 (1956). B. Kahle and H. A. Stuart, *ibid.*, **25**, 486 (1957).

entially engaged in formation of crystals.[13,17,25] Two eligible sequences will not often occur in close proximity along the same molecule. If, after traversing the crystallite, the given molecule was to re-enter the crystal, it is quite unlikely that the succession of units presented would be acceptable (*i.e.*, devoid of the non-crystallizable co-unit). On the other hand, unlimited lateral growth by deposition of sequences from different chains would lead to congestion in the interfacial layer. Under such circumstances, restriction of growth in at least one lateral direction, and probably in both, is inevitable. Incorporation of a copolymeric unit in a homopolymer may therefore be expected to suppress development of the lamellar morphology believed to be characteristic of homopolymers.

Crystallization by Stretching.—Orientation of polymer chains by external means, as for example by elongation of the sample, promotes crystallization. The melting point of axially oriented crystals is increased by a longitudinal tension. These experimental observations are well established. It is readily apparent that folding, or any other arrangement whereby the molecule reverses its direction in order to successively traverse the crystallite, is not compliant with the orientation introduced by elongation. The distention of a molecular chain in the strained state cannot be relieved by crystallization in this manner. Stabilities of crystallites thus constituted would be diminished rather than enhanced by elongation. Hence, the occurrence of any sort of folded arrangement of molecular chains in the crystalline-amorphous texture generated by stretching is refuted by experimental observations of the most direct nature. If the ratio $A_\mathrm{c} < 2A_\mathrm{a}$, then a lamellar morphology is rendered unacceptable for crystals thus generated. The transverse dimensions of crystallites generated by elongating a polymer must consequently be small for reasons identical with those invoked in the preceding discussion of crystallization of copolymers.

That the morphology of the crystallinity produced by stretching may actually differ from that generated by cooling isotropic systems is suggested by the difficulty of correlating melting points for isotropic systems with those observed under strain.[26,27] Extrapolation of the latter to zero strain does not proceed smoothly to the observed unstrained melting point.

These considerations do not categorically preclude generation of lamellar (folded) crystals by strain-induced orientation of polymers under all conditions. Rather, they lead to the assertion that the stabilities of such crystals, if formed, must be diminished by the stress so long as it is maintained. In linear polymers (in contrast to networks to which the preceding considerations most directly apply), for example, an initial stress induced by elongation may be dissipated by relaxation processes in the course of time. Bundle nuclei generated through the influence of the initial orientation may subsequently grow by lateral accretion of chains which fold, or loop, to and fro to the extent required by spatial restrictions in the interfacial zones. In this way, crystallites of large lateral dimensions may develop through later growth of smaller crystallites initially generated when high orientation prevailed. The cross linkages of a network, on the other hand, preclude relaxations required to accommodate this type of growth. The "mesh width" between cross linkages in a network may further prevent growth of large crystallites.[28,29]

We have already commented on the consequences of a helicoidal conformation of the chain in the crystal lattice and the resulting increase in the molecular cross-section A_c. In particular, if $A_\mathrm{c} > 2A_\mathrm{a}$, folding of some of the chains in order to permit complete dissipation of order in passing from the crystalline to the amorphous phase is no longer required. In such cases crystallites of unlimited transverse dimensions may be produced by stretching, without back-folding of chains in opposition to the strain (or the stress). This circumstance may be significant with reference to biological polymers. Native proteins and polynucleotides characteristically occur in helical conformations. In the fibrous state they contract on melting and recrystallize on stretching.[30-32] Melting and recrystallization processes are closely coupled with dimensional changes. The absence of steric constraints requiring back folding of chains may be an important factor contributing to the facility of these transformations.

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