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Random Re-entry Theory of Polymer Melt Crystallization

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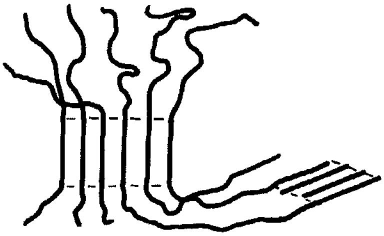
ABSTRACT

Consideration of crystallization kinetics in high molecular weight polymers shows that adjacent re-entry is unlikely in melt crystallization and that sections of individual chains will crystallize concurrently at several sites. Surface nucleation controlled growth models can be set up which do not require adjacent re-entry but are in agreement with observations on growth rates and crystal thicknesses. The predominant process in crystallization with random re-entry is the incorporation into the crystal of a loop of chain which has both ends attached to the crystal surface. This leads to predictions of the crystallinity of quenched, spherulitic polymers. Radii of gyration of chains in the crystalline state can be calculated and are in agreement with neutron scattering results.

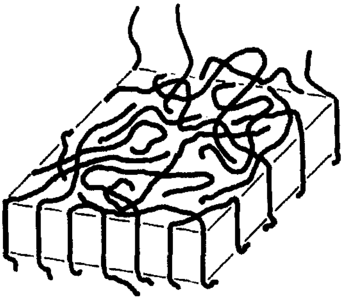
INTRODUCTION

Early observations of single crystals grown from dilute polymer solutions [1] led to the development of chain-folded models for polymer crystallization to replace the earlier fringed-micelle model shown in Fig. 1. The chain-folded structure could be described either by switchboard or adjacent re-entry models. Lauritzen and Hoffman,

(a) FRINGED MICELLE MODEL



(b) RANDOM RE-ENTRY (SWITCHBOARD) MODEL



(C) ADJACENT RE-ENTRY MODELS

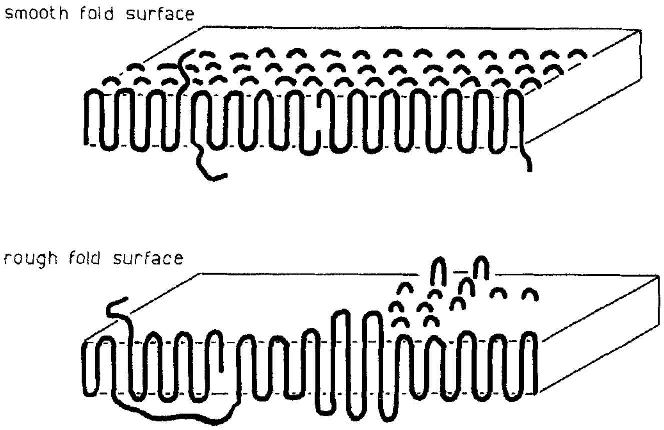


FIG. 1. Models for chain folding in polymer crystals.

using the adjacent re-entry model, were able to derive expressions for crystallization kinetics and for the dependence of lamellar thickness on crystallization temperature which were in good agreement with observations [2]. Further observations supporting an adjacent re-entry structure for melt-crystallized polymers were the measurements of infrared band splittings in mixed crystals of polyethylene and perdeuteropolyethylene of Bank and Krimm [3]. In general, many facts pointed to the similarity between lamellae in melt-crystallized polymers and single crystals and to the existence of adjacent re-entry in single crystals [4].

However, a number of facts could be cited as being in conflict with adjacent re-entry models. Firstly, adjacent re-entry gives no explanation for the large amorphous content (up to 70%) of spherulitic polymers: one would expect only short chain-end lengths, low molecular weight chains, and irregular chains to be excluded from the crystal. However, the amorphous content can be large even in high molecular weight fractions of polyethylene. Also, a considerable number of chains are known to run from crystal to crystal [5], and the amorphous layer is apparently strongly bonded to the crystals. Secondly, rapid crystallization is observed in crosslinked polymers and in polymers at temperatures only slightly above the glass transition, cases where the restrictions on chain mobility would appear to be incompatible with adjacent re-entry crystallization.

Recent observations of the radius of gyration of polymers in the crystalline state by small angle neutron scattering [6, 7] led to the rather unexpected result that the radius of gyration was identical to the random coil value observed in the melt and in ideal (θ) solution. This observation is incompatible with the adjacent re-entry model and with variants of it so far proposed [8] and leads us to conclude that a re-assessment of melt crystallization is necessary.

CRYSTALLIZATION KINETICS

The Lauritzen-Hoffman model for polymer crystallization is a surface nucleation-controlled growth model in which the rate-controlling step in the formation of a new layer of crystal is the attachment of the first stem to the previous, complete, layer [2]. Surface nucleation control is also believed to occur in many small molecule systems where the growth rate is proportional to exp $\{-A/T\ \Delta T\}$, where A is a constant, T is the crystallization temperature, and ΔT is the undercooling below the melting point at which crystallization occurs. However, for a small molecule such as orthoterphenyl [9], the nucleus is usually assumed to be disk-shaped, since this will have the lowest surface energy for a cluster of a given number of molecules. In the same way, the critical nucleus for polymer crystallization might be expected to be a cluster of stems which do not necessarily extend across the whole crystal thickness, rather than one complete stem. Calvert and Uhlmann [10] and Binsbergen [11] showed that such cluster nuclei gave crystal growth rates which were in agreement with experiment. This means that adjacent re-entry is not a necessary part of a successful crystal growth model.

In the Lauritzen-Hoffman model, the fact that the nucleus extends across the whole crystal thickness also defines the thickness, since the nucleus must be as small as possible for rapid growth while the lamella must be thicker than a certain value if it is to be stable. With the cluster nucleation model an alternative mechanism for limiting the lamellar thickness must be found. In the somewhat analogous case of eutectic alloys the scale of the structure is determined by the balance between diffusion rate D and growth rate G, such that the scale is of the order of D/G. However, in polymers this ratio is several orders of magnitude greater than the lamellar thickness and is much more temperature-dependent. Crystal size does decrease with increasing undercooling in nonpolymeric spherulite formers but there are no data on the form of the relationship. In polymers it is possible to describe the stem formation process as a random walk of chain units into the appropriate position to attach to the crystal. The time required for this increases as the square of the stem length, while the addition rate of chain units to the crystal surface increases with lamellar thickness.

The balance of these two effects results in a maximum in the crystal growth rate at some thickness somewhat larger than the minimum stable value. This is essentially the same as identifying the lamellar thickness with a characteristic distance $\delta = D/G$, where D is now a stem diffusion rate and G is a stem propagation rate, rather than a crystal growth rate.

Thus both the crystal growth rates and crystal sizes can be derived from considerations of chain attachment rates without specifically assuming adjacent re-entry.

CRYSTALLINITY

Yoon and Flory [12] have shown that the rate of crystal growth in many polymers is incompatible with the time required for the large-scale conformational transformation necessary in adjacent re-entry crystallization. Rather the crystallization process must involve random collisions and attachment of parts of a chain with the growing crystal. As a result, successive crystalline lengths, stems, from a chain attached to the crystal face, may involve widely separated parts of the chain as shown in Fig. 2. For a high molecular weight polymer, the predominant crystallization process will be attachment of these loops of chain between those stems that form first. This is the process we will treat in detail here.

Consider first an idealized situation in which two separated parts of a chain simultaneously attach to a crystalline substrate. The length

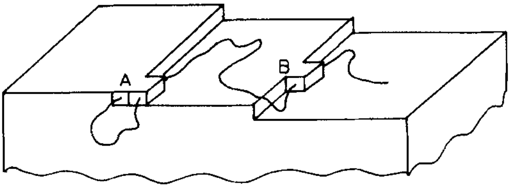


FIG. 2. Schematic drawing of a growing lamellar crystal showing (A) line nucleation with adjacent re-entry and (B) without adjacent re-entry. Growth direction vertical.

of chain between the two attachment points then starts to crystallize, the units adjacent to these points attaching consecutively parallel to the chain direction in the substrate. If the directions of propagation of the two stems are antiparallel, crystallization will proceed until the remaining uncrystallized material is stretched at an angle to the chain directions in the crystal. Since in practical terms this is incompatible with further development of the crystal, we may assume that these stems eventually become detached again. However if the two stems grow parallel, growth may continue until tension in the remaining amorphous material prevents further crystallization. In terms of the standard models of polymer morphology, this material would then occupy the interlamellar amorphous regions.

Under these circumstances the crystallization will be able to proceed to the greatest extent if the two growing stem ends are as close as possible, that is they both lie on a single plane perpendicular to the chain direction in the crystal. The simplest condition limiting crystallinity in this case is that growth ceases when the amorphous part of the loop first becomes distorted from a random coil configuration. If the original separation of the attachment points is described by a vector r the new separation of the growing stem ends, that is the end to end distance of the amorphous loop, will be the projection of $\underset{\sim}{r}$ perpendicular to the crystalline chain direction. Resolving $\underset{\sim}{r}$ into three mutually perpendicular directions with z as the chain axis:

$$\underset{\sim}{r}^2 = r_x{}^2 + r_y{}^2 + r_z{}^2 \tag{1}$$

Since $\underset{\sim}{r}$ represents the end-to-end distance of a random coil we can write, on average:

$$1/3\ \bar{r}^2 = \bar{r}_x{}^2 = \bar{r}_y{}^2 = \bar{r}_z{}^2 \tag{2}$$

The separation of the growing stem ends $\underset{\sim}{s}$ is thus described by

$$\overline{s}^2 = \overline{r}_x^{\,2} + \overline{r}_y^{\,2} = 2/3\,\overline{r}^2 \tag{3}$$

Since the mean-square end-to-end distance of a random walk is proportional to the number of steps, the amorphous loop after crystallization has, on average, 2/3 the number of units of the original loop, that is, the crystallinity is 33%.

Rather than letting crystallization stop as soon as the amorphous loop becomes distorted it is possible to determine the maximum crystallinity as that at which the retractive force in the stretched loop just balances the "force" of crystallization. However, the extent to which the amorphous loop can be stretched will be dependent on the density of entanglements acting as crosslinks at the crystal surface. In the limit of a high entanglement density, the crystallinity will remain as 33% since the chain will be inflexible. This must be a probable state of affairs in the very constrained region at a crystal fold surface.

These expressions for crystallinity should also be modified to allow for the fact that loops attaching to a lamellar structure may be too long to "pull tight" as outlined above but too short to form more than two stems. This excess amorphous material will reduce the expected crystallinity by 50%. However, local annealing involving motions of stems within the crystal may allow this excess material to be incorporated in the crystal structure. Further long-range annealing involving cooperative motion of the whole molecule would allow crystal thickening, the lengthening of some stems and the disappearance of others. This would lead to a slow continuous crystallinity increase.

In summary, three crystallinity ranges can be defined. Crystallinities of completely unrelaxed chains should lie between 17% at high entanglement densities and 50% if the loops are unentangled. Local relaxation leads to crystallinities of 33% at high entanglement densities increasing towards 100% as the entanglement density decreases. Long-range stem mobility leads to crystallinities which can rise to 100%.

RADIUS OF GYRATION

A major piece of evidence against adjacent re-entry models for polymer crystals is the observation by neutron scattering that the radius of gyration of a chain is the same in the liquid and crystalline states. This has been found for melt-quenched polyethylenes [6] and quenched, annealed, and slowly crystallized polypropylenes [7]. Adjacent re-entry is incompatible with these results, as it would lead to significant reductions in the radius of gyration after crystallization of high molecular weight polymers and to a linear dependence of radius of gyration on molecular weight contrary to the observed square root dependence. It is possible to calculate approximately the change in radius of gyration on crystallization by the multiple-attachment model and to compare this with the observed values.

The mean square of the radius of gyration of a randomly coiled chain of n units is given by:

$$\bar{g}^2 = \alpha n \ell^2/6 \tag{4}$$

If we approximate the complete chain as a series of m randomly coiled loops, each of n units we have:

$$\bar{g}^2 = (1/m) \sum_{i=1}^{m} [\, r_i^2 + (\alpha n \ell^2/6)] \tag{5}$$

$\underset{\sim}{r}_i$ is the distance between the center of gravity of loop i and the chain center of gravity. After crystallization, each loop becomes two half stems of length $\underset{\sim}{t}$ containing $n\lambda/2$ units each plus an amorphous random coil of $n(1 - \lambda)$ units.

The increase in the radius of gyration on crystallization is found to be about 4 nm for quenched polyethylene chains of molecular weight 4×10^4 daltons which corresponds to about 15 stems. This is 40% of the random coil radius of gyration for these relatively small molecules. At higher molecular weights, the increase in radius of gyration on crystallization becomes small, and it is always within experimental error for the neutron scattering measurements available to date. Slowly cooled polypropylene should show similar increases, while quenched samples will be closer to the random coil value. Significant deviations from the random coil are expected at lower molecular weights where the chains form only one or two stems.

MEASURED CRYSTALLIZATION

It was shown above that estimates could be made of the degree of crystallinity in a lamellar structure resulting after crystallization from the melt with varying degrees of entanglement density and stem mobility. The values obtained in the absence of extensive long-range annealing should ideally be compared with the crystallinity immediately behind the surface of a growing spherulite. If this is to be estimated from whole sample crystallinity measurements, it is necessary to choose conditions where spherulitic or lamellar crystallization is complete throughout the sample but annealing is slow or nonexistent. This will be best approximated by crystallization at a temperature slightly above the glass transition temperature, either by quenching the polymer to the glassy state and reheating or by cooling it rapidly to the crystallization temperature. Further requirements

TABLE 1. Crystallinities of Rapidly Crystallized Polymers

Polymer	T_g (°K)	Crystallinity	Reference
Quenched, T_g below room temperature			
Polyethylene	150	0.51	[13]
High molecular weight polyethylene at 400°K	150	0.32	[14]
Natural rubber	200	0.30	[15, 16]
Cis-polyisoprene	200	0.31	[17]
Polybutene-1	249	0.40	[18]
Polypropylene	263	0.31	[4]
Polytetrafluorethylene[a]	160	0.20	[19]
Quenched and annealed above T_g			
Poly(ethylene terephthalate)	342	0.27	[15]
Poly(ethylene terephthalate)	342	0.20	[19]
Poly(ethylene terephthalate)	342	0.28	[20]
Poly(ethylene terephthalate)	342	0.30	[21]
Polychlorotrifluorethylene	318	0.35	[22]
Nylon 6, γ phase	348	0.27	[23]
Nylon 6, α phase	348	0.35	[23]
Nylon 6 α, phase	348	0.40	[24]

Polytetrafluorethylene[a]	400	0.30	[19]
Isotactic polystyrene	373	0.32	[25]
Nylon 7	335	0.22	[4]
Polycarbonate	393	0.21	[26]
Poly(phenylene oxide)	482	0.20	[27]

[a] Two possible glass transition temperatures for polytetrafluorethylene are quoted.

are that the polymer should be a homopolymer containing little noncrystallizable material and with a chain length considerably greater than the stem length.

Table 1 summarizes data from the literature on crystallinities of polymers crystallized at large undercoolings. With the exception of polytetrafluorethylene, those polymers for which T_g is below room temperature were quenched and then measured at room temperature. Those for which T_g is above room temperature were generally allowed to crystallize and then observed at room temperature. It is notable that most of the values fall within the 25-35% range. Given the large uncertainties in crystallinity measurements, this is strongly suggestive that real crystallization usually corresponds to the highly entangled, locally annealed 33% crystalline case. The particularly thorough measurements on polystyrene [26], cis-polyisoprene [17], and polychlorotrifluorethylene [23] all fall within this range.

Three polymers fall significantly below this range: nylon 7, polycarbonate, and poly(phenylene oxide). However, the last two are particularly difficult to crystallize, and all are relative poorly characterized, so it is not really possible to say whether these represent crystallization without local annealing. Polyethylene generally shows crystallinities of the order of 50% which may be due to room temperature annealing and some loop tightening, since this polymer has an exceptionally flexible chain and a very low glass transition temperature.

CRYSTALLIZATION FROM SOLUTION

The behavior outlined here is not expected in crystallization from dilute solution where the chance is much higher that successive stems adding to a step site will be from the same molecule. This will be particularly true if molecules first adsorb from solution onto the crystal surface and then subsequently crystallize. While strict adjacent re-entry is still unlikely, it would be expected that molecules crystallize as a set of neighboring stems in one crystal layer. This is in accord with the fact that single crystals fracture cleanly parallel to the growth faces but with extensive deformation perpendicular to this, that is, across the chain folds.

CONCLUSIONS

Random re-entry chain folding in polymers is compatible with observations on crystal growth rates and lamellar thicknesses. Treatment of this in terms of loop crystallization allows the changes of radius of gyration on crystallization to be estimated. These changes are shown to normally be small, in agreement with neutron scattering observations. Further, the loop model allows discussion of the degree of crystallinity expected from melt crystallization of a pure homopolymer. This parameter is one of the most important for polymer properties and is relatively simple to determine but no effort has been made in the past to predict it on the basis of crystallization theory.

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