

CONFORMATIONS OF MACROMOLECULES IN CONDENSED PHASES

Paul J. Flory

Department of Chemistry, Stanford University, Stanford, California 94305, USA

Abstract - Evidence demonstrating that configurations of polymers in the amorphous state are unperturbed by intermolecular interactions with neighboring chains is reviewed, with particular emphasis on recent results of neutron scattering by mixtures of deuterated and protonated species. Extension of this technique to larger angles than those required for determination of the radius of gyration establishes close agreement between intersegment correlations in a polymer chain in the amorphous state and those within the isolated chain, even at distances as small as 10Å. Neutron scattering studies have been especially useful in discerning the nature of the molecular morphology at the crystal-amorphous interface. In both polyethylene and isotactic polypropylene, adjacent re-entry is comparatively rare, contrary to models accepted in the past. Return of a given chain to a site of the crystal surface somewhat removed from its point of exit must occur frequently, however. These findings have important implications regarding the process of plastic deformation in semicrystalline polymers. Recent studies by Wignall and Wu confirm that local melting of small crystalline regions effectuates the process.

INTRODUCTION

The spatial form of the long-chain macromolecule is of central importance to the understanding and interpretation of those special properties that set polymers apart from other materials. Rubber elasticity, for example, is an exclusive property of high polymers. It is, moreover, a universal property exhibited under suitable conditions by virtually all polymers consisting of long, flexible chains, preferably joined to form a coherent network. As is well known, the high elastic extensibility that characterizes elastomers is a direct consequence of the randomness and diversity of the configurations accessible to their macromolecular chains. The extraordinary strength attainable in the fibrous state is attributable to the mutual reinforcement of bundles of highly extended, densely packed polymer chains. The polycrystalline morphology of molded semicrystalline polymers confers toughness and durability to a degree that no other materials can match. The high viscosity exhibited by a molten polymer is a consequence of the copious interpenetration of its long macromolecular chains. The properties of proteins and other biological polymers are intimately related to the unique conformations peculiar to each of them. Recently, recognition of the potentialities of liquid crystallinity in polymeric systems has led the way to new materials having strength-to-weight ratios unsurpassed by any other materials.

Theoretical procedures for analysis of the conformations and the associated configurational statistics of isolated macromolecular chains are now well developed. Virtually all of the manifold varieties of chain-molecular structures are susceptible to realistic, quantitative treatment and interpretation according to precise details of the molecular structure and constitution. Good agreement has been established between theoretical calculations based on precise details of the molecular structure and experimentally measured quantities such as characteristic ratios $\langle r^2 \rangle_0/nl^2$, dipole moments, radiation scattering and optical anisotropies, all measurements being conducted on dilute solutions.

The spatial configuration of the macromolecule in condensed phases, in contrast to the dilute solution environment where it is well separated from other macromolecules, is a subject that has evoked much controversy. The main issues needing resolution stemmed from the perceived difficulties of accommodation of macromolecular chains when they are packed to a density where occupation of nearly all of the space available is required, such occupancy being subject to the obvious condition that spatial overlaps between various molecular segments must be avoided. Any acceptable set of conformations of the macromolecules must meet this foremost requisite. It applies to all states of organization including semicrystalline as well as amorphous polymers.

Recent evidence on the random disorganization of polymer chains in typical amorphous polymers will first be reviewed in the pages that follow. We then turn to the more complex issues pertaining to the molecular morphology in semicrystalline polymers.

THE AMORPHOUS STATE

Amorphous polymers may appropriately be construed to include polymeric liquids that exhibit viscous flow, albeit with viscosities that may be very high, polymers of greater molecular weight that are elastic pseudo-solids, elastomeric networks, and glasses. That it should be difficult to pack long polymeric chains to high density with avoidance of steric overlaps, when the chains are in disarray and randomly configured, is undeniable. The effect that this difficulty may have on the molecular conformation is more apparent than real, however. It must necessarily depend on the degree to which the severity of the steric constraints can be relieved by modifying the chain conformations in one way or another. Elementary examination of this problem shows that accommodation of the polymer chain is neither facilitated nor impeded by alterations of its conformation, short of the extremes of full extension on the one hand and of complete collapse of the random coil on the other. Approaching the issue from a more rigorous standpoint, one may observe that statistical mechanical treatments of systems of polymer chains invariably lead to a partition function that is factorable into intra- and intermolecular parts, each independent of the other.¹ Only the latter factor depends on the composition; the former factor is unaffected by dilution (in a θ -solvent). It follows at once that the configuration of the chain should be independent of the polymer concentration, and hence that its spatial configuration should be unperturbed by the requirement that it must coexist in the amorphous state with other chains at high density.¹

The solidity of these arguments notwithstanding, questions concerning the conformations of macromolecules in the amorphous state remained ultimately to be resolved experiments.^{2,3} Moreover, only from the results of precise, quantitative experimental measurements was it possible to ascertain the degree to which random disorder prevails in the amorphous state.

Various properties of amorphous polymers bespeak a state of molecular disorder. The diffuse halos of their X-ray diffraction patterns, for example, resemble those of liquids. Detailed analyses of the X-ray diffraction by glassy poly-(methyl methacrylate)(PMMA) and by amorphous polyethylene(PE) carried out by Hindle and co-workers⁴ fail to reveal evidence of substantial correlations between segments of neighboring chains. Furthermore, the high extensibility of typical elastomers requires randomly configured chains for its explanation. If the molecular morphology in the amorphous state were ordered, this order should be evident in the activities of diluent absorbed by the polymer when examined as a function of the dilution. Such an effect is not indicated by experiments.^{1,2} Similarly, the absence of anomalous effects of dilution on the rubber elasticity equation of state and on macrocyclization equilibria testifies further to the absence of a substantial degree of order in amorphous polymers,² such as was implied by the "bundles" and "nodules" once postulated to exist.

The most decisive evidence on this issue has been provided by experiments conducted during the past decade using small-angle neutron scattering (SANS). In the typical experimental procedure, the radius of gyration of protonated (or deuterated) chains dispersed in a deuterated (protonated) sample of the same polymer is determined from the angular distribution of neutron scattering attributable to the difference in the scattering cross-sections of deuterons and protons. The radius of gyration thus determined may then be compared with the value obtained by application of conventional methods to dilute solutions of the same polymer in a θ -solvent. In a few instances the radius of gyration in the dilute solution has also been determined by SANS. Results of studies of this nature are summarized in Table 1. They are in part from a review of the subject by Higgins and Stein,⁵ with newer

TABLE 1. Molecular dimensions in amorphous polymers by small-angle-neutron scattering

Polymer, ^a bulk state	$(\langle s^2 \rangle / M)^{1/2}$, Å/Dalton ^{1/2}	
	Dilute solution	Bulk
PS, glass	0.27 ₅	0.27 ₅ ⁶
PS, glass	0.27 ₅	0.28 ⁷
PE, melt	0.45	0.46 ⁸
PE, melt	0.45	0.45 ⁹
PP(isotactic), melt	0.33	0.34 ¹⁰
PMMA, glass	0.30	0.31 ¹¹
PDMS, melt	0.27	0.25 ¹²
PC, solid	0.43 ^b	0.46 ¹³
PVC, glass	0.35	0.40 ¹⁴
PIB, melt	0.30 ₅	0.31 ¹⁵

^aPS = polystyrene, PE = polyethylene, PP = polypropylene,
 PMMA = poly(methyl methacrylate), PDMS = poly(dimethyl siloxane),
 PC = polycarbonate, PVC = poly(vinyl chloride), PIB = polyisobutylene.

^bCalculated.

data included. Ratios of the rms radius of gyration to the square-root of the molecular weight deduced from SANS measurements on the bulk (amorphous) polymers are given in the final column of Table 1, with the source of the results indicated by the reference number appended. Results from conventional measurements on dilute solutions are included for comparison in the second volume. Any significant effect of dense packing of the polymer chains in the former state should be reflected in the value of the ratio given in the last column. The agreement is remarkably close in nearly all cases, indicating such effects to be quite negligible. These experiments show further that the effect of excluded volume on the intramolecular configuration is negligible in the bulk amorphous polymer. The nullity of this effect in the bulk polymer was predicted by the earliest theories on excluded volume in polymer chains.¹⁶

Neutron scattering intensities $I(\theta)$ at angles θ extending much beyond those required for determination of the radius of gyration enable one to probe the smaller distances between segments separated by shorter sequences within the polymer chain. Whereas determination of $\langle s^2 \rangle^{1/2}$ for the molecule as a whole requires measurements at scattering vectors $\mu = (4\pi/\lambda)\sin(\theta/2)$ less than 0.01\AA^{-1} , λ being the wavelength of the neutrons, inter-segment correlations ranging down to distances of 10\AA may be assessed from measurements extending to $\mu \approx 0.5\text{\AA}^{-1}$.

Experimental results covering the higher range of scattering vectors are shown by the points in Fig. 1 for protonated polyisobutylene(PIB) dispersed in deuterated PIB.¹⁵ The absolute

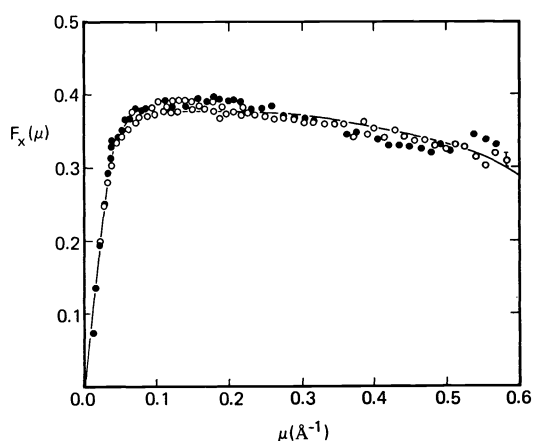


Fig. 1. Neutron scattering by protonated polyisobutylene(PIB-H) dispersed in the deuterated polymer(PIB-D). The absolute Kratky function, eq 1, is plotted against the magnitude μ of the scattering vector. Filled and open points represent experimental measurements at volume fractions of PIB-H of 0.1 and 0.2, respectively. The curve has been calculated according to theory.¹⁷ From Hayashi, Flory and Wignall.¹⁵

Kratky function, defined by

$$F_x(\mu) = x\mu^2 I(\theta)/I(0) \quad (1)$$

is plotted as ordinate; x is the number of segments in the chain and $I(\theta)/I(0)$ is the ratio of the scattering intensity at angle θ to that in the forward direction ($\theta = 0$). This ratio is related to the distances r_{ij} between pairs i, j of scattering elements (atoms) according to

$$I(\theta)/I(0) = N^{-2} \sum_{i,j} \langle \sin(\mu r_{ij}) / \mu r_{ij} \rangle \quad (2)$$

a relation due to Debye. The angle brackets denote configurational averaging over each r_{ij} , and the summations include all hydrogen atoms, N in number, in the chain. The curve shown in Fig. 1 was calculated according to eq 1 and 2. The distributions of distances r_{ij} were calculated on the basis of the conformational analysis of the PIB chain.¹⁷ No adjustable parameters enter into the calculations. The theoretical curve and the experimental results are in close agreement.

Similar results for protonated PIB dissolved in deuterobenzene, a θ -solvent, are shown in Fig. 2. The theoretical curve in Fig. 2 is the same as that in Fig. 1. Results for both systems are in excellent agreement with theory and, hence, with one another throughout the range μ .

A similar comparison between experiment^{13a} and theory¹⁸ for the polycarbonate of diphenylolpropane is shown in Fig. 3. Close agreement holds except at the highest scattering vectors, where the experimental error is large and the intramolecular theory may be inadequate.

The results presented in Table 1 and Figs. 1-3 show conclusively that the configurations of polymer chains in the bulk amorphous state are unperturbed within the small limits of incident experimental errors. This assertion holds for the relationship between nearby segments in the polymer chain as well as for those that are remote from one another.

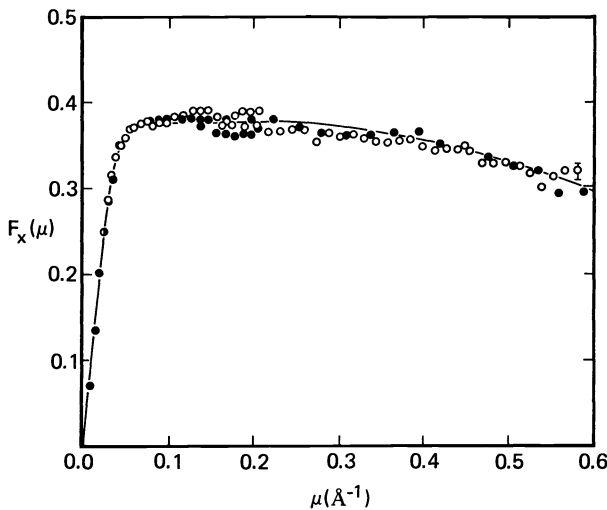


Fig. 2. Neutron scattering by PIB-H dissolved in deuterobenzene at concentrations of 0.03 (●) and 0.06 (○). The calculated curve is identical to the one shown in Fig. 1; see legend to that figure. From Hayashi, Flory and Wignall.¹⁵

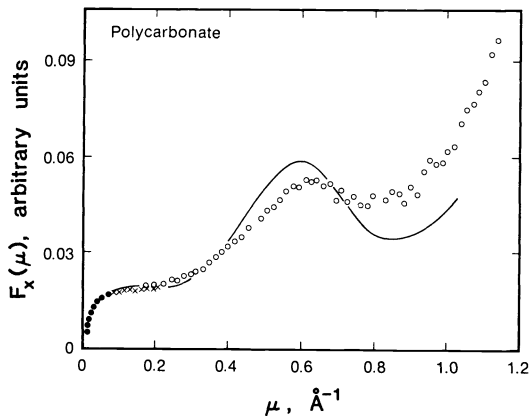


Fig. 3. Neutron scattering by the polycarbonate chain. Experimental points are from the results of Gawrisch et al.^{13a} The theoretical curve has been calculated on the basis of the conformational analysis applicable to this chain. From Yoon and Flory.¹⁸

That the foregoing generalization requires qualification is indicated by observations on the depolarized Rayleigh scattering (DRS) of long-chain molecules in concentrated systems, including melts.^{3,19} A substantial enhancement of the DRS of neat liquid *n*-alkanes above that predicted from the individual contributions of these molecules, as determined in their dilute solutions, clearly demonstrates the presence of intermolecular correlations. They appear to be of short range, however; they may be confined to first neighbors.³ According to the results of neutron scattering investigations cited above, such intermolecular correlations as occur in typical amorphous polymers do not affect the intramolecular configurations significantly in the examples examined thusfar in detail. Local correlations between neighboring chains in amorphous polymers is in need of further investigation.

The randomness of the configurations of polymer molecules in the amorphous state implies a high degree of interpenetration. This is illustrated in Fig. 4, where a randomly configured polyethylene chain with $M=10^5$ is shown schematically. Its root-mean-square radius of gyration is about 140Å. If the effective domain of the configuration is taken to be a sphere of this radius a , then the domain of any other molecule falling within the concentric sphere of radius $2a$ may be considered to overlap, or interpenetrate, that of the molecule in Fig. 4. The volume of the larger domain is approximately $9 \times 10^7 \text{Å}^3$, whereas the net volume occupied by the polyethylene molecule of the stated molecular weight is ca. $1.9 \times 10^5 \text{Å}^3$. It follows that the number of molecules centered in the larger domain is ca. 500. The degree of interpenetration is extensive.

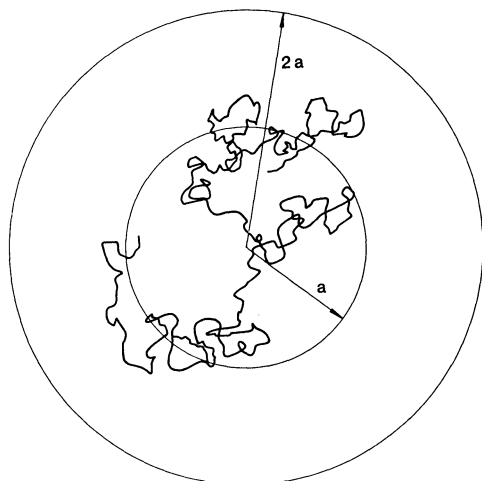


Fig. 4. Simulation of the configuration of a polyethylene molecule with $M=10^5$, generated by the Monte Carlo method. The r.m.s. radius of gyration $\langle s^2 \rangle^{1/2} \approx 140\text{\AA}$ is represented by a . See text.

SEMICRYSTALLINE POLYMERS

Semicrystalline polymers typically consist of lamellar crystallites separated by amorphous interlamellar regions. The axes of the parallel chains, or stems, comprising a crystalline lamella are directed transverse to its basal plane. The molecular morphology is governed by factors affecting the rate of nucleation and growth of the crystalline phase. These factors are: (i) the difficulty of dissipating the order in the interphase between a crystalline lamella, comprising many chains in extended conformations packed in parallel array, and the adjoining amorphous polymer; (ii) the slow relaxation of the configuration of a long polymer chain in the amorphous state; and (iii) the copious interpenetration of chains in the amorphous polymer as described above. Elementary considerations show unambiguously that the utmost stability would be attained by formation of very large crystallites, with longitudinal dimensions approaching (although somewhat less than) the molecular chain length.^{20,21} Owing to intervention of the three factors mentioned above, the dimensions of the crystallites realized under practicable conditions are very much smaller than would occur at equilibrium.

The difficulty of dissipating the flux of chains emanating from the (001) crystal surface, i.e., the face of the lamellar crystal, imposes severe constraints on the configurations of the chains in the interphase between the crystal and adjoining amorphous regions (see (i) above).²² The interfacial free energy at this surface consequently is very large. As a result, the critical free energy for nucleation is high, especially for low degrees of supercooling. A high degree of supercooling is therefore required in order to render the nucleation rate sufficient to bring about crystallization at an acceptable rate.^{21,23} Lamellae measuring only 100-300Å in thickness consequently are stable at the prevailing supercooling (which may be on the order of 40°C), the high interfacial free energy at the faces of the lamellae notwithstanding. Their rate of growth, which proceeds transverse to the axes of the crystalline stems, depends on the time required for rearrangement of the configuration of a sequence of units eligible for deposition as a stem.²⁴ Through Brownian motion, this sequence of units must extricate itself from the welter of chains with which it shares the same space; see Fig. 4. The relaxation time for a sequence of units increases steeply with its length, and therefore with the thickness of the lamella. For this reason the thickness of the lamellae tend to be little greater than the minimum required for thermodynamic stability.²³

Being generally very much longer than a crystalline stem, each polymer molecule contributes many stems. These stems might conceivably be confined to a single lamella or, in polymers crystallized from the melt as opposed to single crystals grown from a dilute solution, the stems from a given molecule may occur in several different lamellae.^{22,24,25} The individual lamellae would be relatively independent of one another according to the former morphology; in the latter, they must be inextricably bound one to another by numerous interconnecting chains.

According to views long held, the morphology in typical semicrystalline polymers is predominantly of the former kind. Moreover, the polymer molecule was considered to be regularly folded in a manner such that successive crystalline stems occupy adjacent positions in the crystal lattice. The untenability of this model for polymers crystallized from the melt may immediately be perceived from consideration of the interspersions of chains in the amorphous state, as described briefly above; Fig. 4 and factor (iii) are indicative. Fulfillment of the terms of this widely accepted model would require disengagement of the polymer molecule from the many random chains with which it shares space in common. For molecules of high molecular weight the time required would be several orders of magnitude too great to match observed rates of crystal growth.²⁴

In addition to objections to regular chain folding on theoretical grounds, a considerable body of experimental evidence testifies to the unacceptability of this model.²³ Neutron scattering experiments have provided the most definitive evidence on the morphology of typical single crystals. These experiments have been conducted on mixtures consisting of deuterated polymer dispersed in, and co-crystallized with, a protonated sample of the same polymer. The molecular scattering by semicrystalline polyethylene,^{8,26} polypropylene¹⁰ and isotactic polystyrene²⁷ observed in this way yield radii of gyration that are the same within experimental error as the values found in the amorphous state.²⁸ These experiments offer direct proof that the conformation of the molecule as a whole does not undergo rearrangement affecting its overall spatial distribution within the brief interval of time during which it participates in the crystallization process.^{8,24} The smaller sections of the chain required for deposition of crystalline stems are readily re-conformed, but major portions of the macromolecule are unable to do so within the time available.

More compelling information on the morphologies of lamellar crystallites is afforded by neutron scattering at the larger scattering vectors required to sense smaller distances ranging from the spacing between adjacent chains (ca. 5Å) to the length of a stem (ca. 100-200Å). A hairpin fold of the deuterated chain increases the abundance of such distances and diminishes those of greater length. The effect of chain folding on the intramolecular inter-segment distances is illustrated in Fig. 5. Since the scattering function (see eq 2), depends on products μr_{ij} of the scattering vector μ and the inter-segment distance r_{ij} , it should be diminished at small μ and enhanced at larger values by adjacent reentry. Consequently, adjacent reentry must drastically affect the scattering function.



Fig. 5. Embedding of a deuteriochain (continuous line) in a protonated matrix (shaded). Regularly folded morphology on left; random reentry on right. Courtesy of D. Y. Yoon.

The scattering function may be computed for arbitrary degrees of adjacent reentry by Monte Carlo generation of chains and numerical evaluation of the sum in eq 2, the average being taken over a sufficient number of chains thus generated.^{18,29} Results calculated³⁰ for a polyethylene chain comprising 2000 skeletal bonds with stems consisting of 100 bonds separated by random (amorphous) sequences consisting of 50 bonds are shown in Fig. 6.

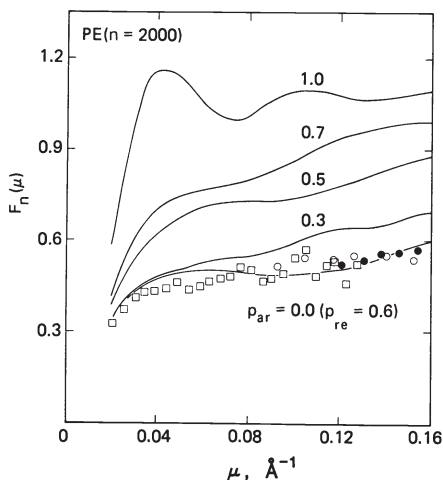


Fig. 6. Kratky plots of neutron scattering by PE-D co-crystallized with PE-H. Data points are results of Schelten et al.⁸ (□), of Sadler and Keller³¹ (○), and of Stamm et al.³² (●). Curves have been calculated for chains of $n=2000$ bonds subject to the fractional degrees p_{ar} of adjacent reentry indicated. For $p_{ar}=0$ the degree of nonadjacent reentry is $p_{re}=0.6$. From Yoon.³⁰

They are compared with experimental results from the various sources cited in the legend to this figure. The degree of regular folding that is compatible with these observations is very small;^{18,32} no more than ca. 20% of the emergent chains may be involved in adjacent reentry, according to comparisons of experimental results with numerical calculations.^{18,30} Experiments correspondingly carried out on deuterated polypropylene dispersed in the protonated host of the same polymer lead similarly to results that confirm this conclusion.^{10,33}

We have cited the difficulty of dissipating the full flux of chains emanating from the surface of a lamellar crystallite; see (i) above. Attainment of the isotropic disorder that is characteristic of the amorphous state obviously requires the net flux of chains in a given direction to vanish. If the chain molecules are very long so that termination of an emergent chain is rare, the required attenuation of the chain flux can be achieved only through reversals of some of the chains followed by their reentry into the crystal lamella from which they emerged.^{22,34} Such reentry is not required to occur immediately upon emergence, however, and it need not occur at a site adjacent to the one from which the chain emerged.

Thus, the path of the chain beyond the basal plane of the crystal may be variable both in length and in displacement between exit and reentry.

The morphology of the interlayer between two lamellar crystallites, as envisaged according to the foregoing observations and interpretation,^{22,25} is shown schematically in Fig. 7.

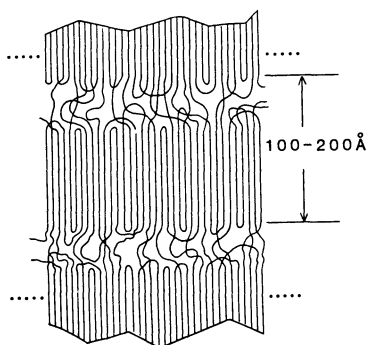


Fig. 7. Schematic diagram of the molecular morphology in a lamellar semicrystalline polymer.

Adjacent folds, though rare, may occur occasionally. Longer loops are prominent. Some of the chains span the amorphous layer and enter the adjoining lamella. From the evidence at hand, this appears to be a realistic, though qualitative, representation of the molecular morphology in typical semicrystalline polymers.

A general theory of polymer interphases, recently formulated³⁴ on the basis of a lattice model, affords insight into the character of the crystal-amorphous transition in the neighborhood of the crystal surface from which the chains emerge. Two essential physical constraints are taken into account by this theory, namely, the discrete occupation of all lattice cells by polymer segments and the continuity of the polymer chains. If the flux of emergent chains preempts the full space available in the first lattice layer (as would be the case for polyethylene chains emanating through a surface normal to the crystal stems), adjacent reentry must occur to some extent in this layer. In succeeding layers the chains undergo reversal through longer "loops." The incidence of adjacent reentry, which should be confined preponderantly to the first layer according to deductions from the theory, depends on the statistical probability of the conformation required for a "tight" chain fold. In most instances this probability is small; for polyethylene it is on the order of 0.01. The theory predicts that ca. 15-20% of emergent polyethylene chains may be engaged in adjacent folds if the crystalline stems are normal to the planes of the lamella. Inclination of this plane to the *c*-axis (i.e., the stem direction), as is commonly observed in the case of polyethylene, drastically reduces the predicted incidence of adjacent reentry.³⁴ These deductions are consistent with the experiments discussed briefly above. The theory of the interphase shows further that the degree of order at the crystal surface should be dissipated rapidly on proceeding into the amorphous region. It should vanish after about 4 lattice layers. This corresponds to an interphase thickness of 10-15Å, in agreement with experiments.^{23,35} The theory also accounts for the high interfacial free energy.^{21,23}

In the case of single crystals formed from a dilute solution, all chains emerging from the face of the crystal must return thereto. Carefully conducted neutron scattering experiments³¹ lead to the conclusion, however, that adjacent reentry is infrequent. Longer trajectories that carry the chain beyond the layer immediately adjoining the face of the crystal occur preferentially.^{24,30} This finding is consistent with the unfavorable statistical probability of tight folds.

A further feature of the inter-lamellar layer, and one not easily represented in a two-dimensional diagram such as Fig. 7, is the high degree of entanglement that must occur therein. The interpenetration of macromolecules that is characteristic of the amorphous state (see (iii) above), and illustrated in Fig. 4, must be inherited by the amorphous regions of the semicrystalline polymer.²⁴ It cannot be eliminated during crystallization, a process which is much too rapid to allow the overall rearrangement of molecular configurations that that would be required, as already noted. Hence, the entanglements implicit in the interpenetration of polymer domains must be embedded in the interlayers.

These deductions have important implications regarding plastic deformation in semicrystalline polymers.²⁴ Such deformation cannot occur by the sliding of lamellae past one another in the manner proposed heretofore in order to account for such deformation. The interconnections between lamellae (see Fig. 7), abetted by the copious entanglements in the amorphous interlayers, preclude any substantial relocation of intact lamellae relative to one another. Plastic flow can only occur through destruction, partial if not complete, of the lamellae. This may occur through local melting of the crystallites in small regions where the stress becomes acute.²⁴ Following the (partial) destruction of a crystallite, the local stress may be relieved by flow. Recrystallization may then occur immediately, with approximate restoration of the original level of crystallinity.

Recent ingenious experiments carried out by Wignall and Wu³⁶ confirm that plastic flow in semicrystalline polyethylene entails local melting. These experiments, like others cited

above, depend on small-angle neutron scattering as the means for characterization of samples before and after plastic flow. They take advantage of the tendency for deuterated and protonated polyethylene molecules to segregate during gradual crystallization from the melt.³⁷ Specimens thus prepared by Wignall and Wu³⁶ exhibited apparent molecular weights, as determined by SANS, that were more than four times the actual molecular weight of the dispersed PE-D. Following plastic deformation, however, the apparent molecular weights were reduced to that for randomly dispersed polymer molecules. The necessary displacements of the polymer molecules could only have taken place if melting, presumably limited to small regions and of brief duration, occurred in the process, as these authors point out.

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