Acc. Chem. Res. 1990, 23, 380-386

the measured slopes, the ±20% uncertainty in our $t\text{-C}_4\text{H}_9 + \text{HBr}$ rate constant, and the fact that the values of k_w used are only typical values. k_w is not strictly constant! It depends on the age and condition of the reactor wall coating. Typically, in our experiments, it increased by as much as 50% during several weeks of experiments.

This ability to quantitatively reproduce the laboratory observations of Müller-Markgraf et al. using the homogeneous $t\text{-C}_4\text{H}_9 + \text{HBr}$ and the heterogeneous $t\text{-C}_4\text{H}_9$ loss rate constants determined in our study of these two processes is strong proof that our explanation for the rate constant disparity is correct. The much lower $t\text{-C}_4\text{H}_9 + \text{DX}$ rate constants obtained by Müller-Markgraf et al. resulted solely from the failure of the investigators to recognize the importance of heterogeneous loss of $t\text{-C}_4\text{H}_9$ in their experiments.

The positive activation energies of the $t\text{-C}_4\text{H}_9 + \text{DX}$ reactions obtained by Golden and co-workers result from the decreasing importance of the heterogeneous loss of $t\text{-C}_4\text{H}_9$ with increasing temperature. Hence, the neglect of this process in the data analysis results in less and less error in the calculated values of k_6 and k_7 as temperature increases. This situation can be seen in Figure 1 where it is apparent that as temperature increases, the rate constants of Golden and co-workers increase and the disparities between their values and those of the other investigators decrease.

Agreement between the experimental and calculated slopes is significantly poorer for the smaller set of experiments conducted by Müller-Markgraf et al. (three of the eight), those that involved the $t\text{-C}_4\text{H}_9 + \text{DI}$ reaction. Agreement is good in only one case (for which the fractional deviation is 49%). For the other two experiments, agreement varies from fair to poor, the fractional deviations being 146% and 480%. It is not clear how close to expect these latter comparisons to have been. Müller-Markgraf's own data analysis yielded $t\text{-C}_4\text{H}_9 + \text{DI}$ rate constants that differed by 250% between experiments in which only the size of the escape orifice on the well-stirred reactor was changed.

Summary

Evidence has been presented that the controversy surrounding the heat of formation of the $t\text{-C}_4\text{H}_9$ radical is resolved. The recent directly determined value, $\Delta H^\circ_{f,298} = 48.6 \pm 1.7$ kJ mol^{-1}, is recommended. It has been shown to be in complete agreement with experimental results of previous studies from which this radical's heat of formation can be derived. This value corresponds to a tertiary C–H bond energy in $i\text{-C}_4\text{H}_{10}$ of 401.2 ± 1.7 kJ mol^{-1}.

Most previous disagreements with this recommended value were shown to have resulted not from poor experimental techniques or results but rather from inaccuracies in assumed information used in thermochemical calculations, in particular the activation energies of the $t\text{-C}_4\text{H}_9 + \text{HX}$ reactions and the entropy of the $t\text{-C}_4\text{H}_9$ radical. The accurate values of these properties, which are now available from experiment and/or theoretical calculations, were reviewed.

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Registry No. $t\text{-C}_4\text{H}_9$, 1605-73-8.

The Structure of Crystalline Polymers

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Introduction

Long-chain molecules can exist in one of two states. Characteristically in the liquid state there is no long-range order and the chain bonds adopt rotational angles that are dictated by the rules of statistical mechanics. Hence a random chain structure evolves. The centers of gravity of the individual molecules are also randomly arranged relative to one another. Characteristic of this state is long-range or rubber-like elasticity. However, under appropriate conditions a chain with sufficient structural regularity can spontaneously develop order along a portion of its length. A collection of such chains can then be organized into a three-dimensional array, and the system is said to crystallize. In this, the crystalline state, thermodynamic, spectral, and physical properties are quite different from those in the disordered liquid state. As one example, the polymer has now become relatively inelastic with the elastic modulus increasing by many orders of magnitude. The transformation from one state to the other presents some very interesting problems in phase transitions. An

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understanding of the structure and properties of crystalline polymers involves the application of a large repertoire of theoretical concepts and experimental techniques. In what follows we discuss the structure of crystalline polymers.

Theory and experiment have shown that polymer crystallization can be treated as a classical first-order phase transition.[1,2] The overall kinetics of polymer crystallization, with but minor modification, follows the general mathematical formulation that has been developed for the kinetics of phase changes of low molecular weight substances.[3,4] Nucleation processes play a dominant role in polymer crystallization. However, despite this foundation the microscopic and macroscopic properties of crystalline polymers depend on the detailed structure that is actually developed. The reason is that because of kinetic restraints polymer crystallization must be invariably conducted under conditions that are well removed from equilibrium.[4] Concomitantly the transformation from the liquid to crystalline state is rarely, if ever, complete. The extent of the transformation can range from only a few percent to as much as 90% depending on the molecular constitution and the crystallization conditions. Therefore, a polycrystalline system with a complex morphological structure results. A unique feature of polymer crystallization is the molecular connectivity of crystallites. An understanding of the chain trajectory is crucial to explaining structure.

The crystallization of homopolymers in the bulk, or from dilute solution, yields a lamellar-like crystallite as the basic structure. The lamellae are usually several microns broad, but their thickness is limited and ranges from about 100 Å to several thousand angstroms. Within the lamellae the chain axes are preferentially oriented normal to the basal plane. Since the crystallite thickness is usually many times smaller than the extended chain length, some type of folding of the molecules must occur.

In order to understand the structure of crystalline polymers it is necessary to identify the important structural independent variables. These have been identified as the degree of crystallinity; the structure of the residual amorphous or liquid-like isotropic region, i.e., the region between lamellae; the crystallite thickness distribution; the extent and structure of the interfacial region; the internal structure of the lamellar crystallites; and the supermolecular structure.[5,6] The unit cell, or crystal structure, is obtained in a straightforward manner, by the classical methods of X-ray diffraction. Two types of variables are involved. One is the molecular constitution, the other, the structure of the crystalline state itself. There is a synergistic effect among the independent structural variables, the molecular constitution of the chain, and the crystallization conditions.

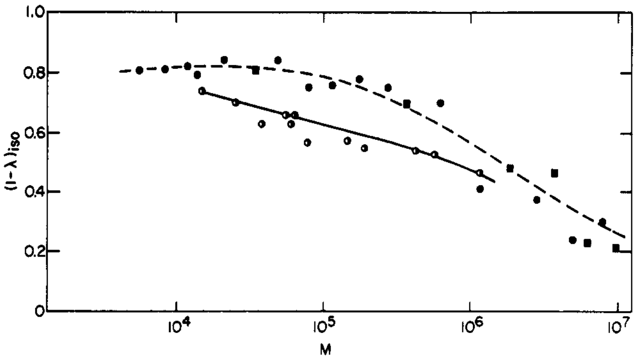

Figure 1. Level of crystallinity as a function of molecular weight under isothermal crystallization conditions: ●, linear polyethylene;[7,8] ■, poly(ethylene oxide);[9] ◑, poly(tetramethyl-*p*-silphenylenesiloxane).[10]

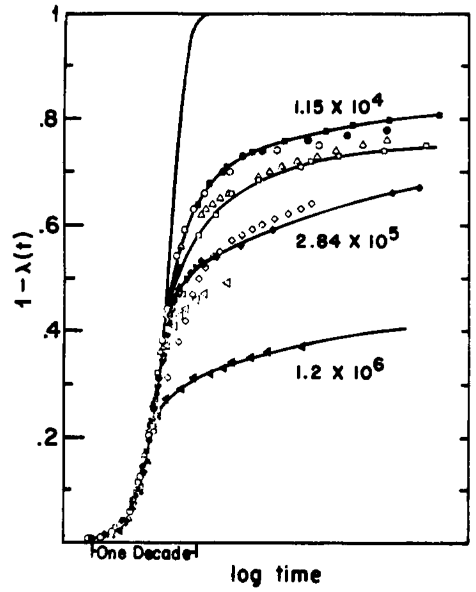

Figure 2. Plot of degree of crystallinity $1 - \lambda(t)$ as a function of log time (on an arbitrary scale) for molecular weight fractions of linear polyethylene. The different symbols refer to different molecular weight fractions, and key molecular weights are indicated in the figure. Crystallization temperature: 127.1 °C.[8]

We will focus our discussion of the structure of the crystalline polymers by taking the polyethylenes as models. Enough information is now available for other polymers so that we can confidently generalize our conclusions to include all flexible chains. We will limit our discussion to bulk crystallization, i.e., to the pure system, and examine how molecular constitution and crystallization conditions influence the key independent variables. Discussion of the supermolecular structure is a major subject by itself and will be postponed.

Level of Crystallinity

The level of crystallinity that can be attained at a given crystallization temperature is very dependent on molecular weight. Figure 1 illustrates this point for several different polymers that were crystallized under isothermal conditions. The level of crystallinity is relatively high at the lower molecular weights. However, as the molecular weight increases there is a monotonic decrease in the level of crystallinity until a limiting value on the order of 25–30% is reached. The large range in the crystallinity level that is observed rules out the possibility of the crystallites having a

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regular folded-chain structure with perhaps minor perturbations.[11-14] The results can not be attributed to the influence of end-groups, cilia, or similar structures, whose concentration decreases with molecular weight. The basis for the retardation in crystallinity can be found in the crystallization kinetics.

The development of crystallinity as a function of time for molecular weight fractions of linear polyethylene is illustrated in Figure 2. In this example the isotherms for 127 °C are superposed so that they all start at the same time.[4,8] The solid line drawn from 0 to 1 represents the theoretical Avrami isotherm which was originally derived for the crystallization of low molecular weight substances.[3] All of the molecular weight fractions start off following this theoretical expectation. As the molecular weight increases, deviation from theory manifests itself at smaller and smaller extents of transformation. Simultaneously, the crystallization process is retarded and for practical purposes crystallization ceases. Even after extremely long times, any increased level of crystallinity would be extremely small. We conclude from the kinetic studies that there are structures within the residual melt that limit the degree of crystallinity that can be attained and in effect cause a restraint of the crystallization process. These structures, which can be envisaged as topological impurities, are molecular weight dependent. They are suggestive of entanglements, loops, knots, and links that are present in the initial melt and are rejected by the growing crystallite. They thus form a significant portion of the noncrystalline region.

Although the degree of crystallinity is a quantitative concept, different experimental methods give small but significantly different values. These differences reflect sensitivity to different aspects of the phase structure. For example, the levels of crystallinity obtained from density are always slightly larger than those obtained from either enthalpy of fusion or Raman internal mode measurements.[6,10,15] These differences can be quantitatively attributed to α_b, the relative proportion of the interphase.[6]

Interlamellar Region

The interlamellar region can represent a significant portion of the total system. A detailed analysis of the structure in this region has been elusive since it is a reflection of the complex structure of the initial melt. In the pure melt, polymer chains assume randomly coiled configurations with dimensions identical with θ conditions.[5,16,17] In order for these dimensions to be maintained in a very dense system, the chains must be intertwined one with the other. This requirement leads to the formation of chain entaglements, loops, knots, interlinks, and other structures that cannot be reversed, or dissipated, during the time course of crystallization. Consequently these structures will be rejected from the growing crystallite and concentrated within the noncrystalline regions.

A large body of experiments gives strong evidence that the chain units in the interlamellar region are in nonordered conformations without any preferential orientation, i.e., the region is isotropic. A chain can adopt a variety of trajectories after it leaves a crystallite. Therefore, many different structures result that are consistent with the condition of isotropy. For example, a portion of the chain can traverse the space between lamellae unimpeded. Some chains, however, will become entangled and knotted one with the other. Others will form long loops contained within the domain of a given crystallite while loops from two adjacent lamellae can interlink with one another and connect the crystallites. Other topological structures can also be envisaged. The interlamellar region can be structurally quite complex although isotropy is maintained. The quantitative description of the structures in this region remains one of the major problems still to be resolved in the area of crystalline polymers.

Crystallite Structure

Lamellar-like crystallites are formed over the complete range of molecular weights and crystallization temperatures. However, the detailed crystallite structure varies systematically with molecular weight and the undercooling at which the crystallization is conducted. For low molecular weights, at all crystallization temperatures, the lamellae have large lateral dimensions and are geometrically well developed. However, with increasing molecular weight the lamellae are more curved and segmented, and the lateral dimensions are reduced. This effect is accentuated at very high molecular weights ($M \geq 10^6$).[18] The random introduction into the chain of noncrystallizing co-units causes a gradual deterioration of the lamellae. Eventually at crystallinity levels of about 10–15% lamellae are no longer observed.[19]

An important feature of the internal structure of a crystallite is the angle of inclination between the chain axis and the normal to the basal plane of the lamellae. For linear polyethylene at high crystallization temperatures, i.e., low undercoolings, the tilt angle is about 19–20°. It gradually increases with decreasing crystallization temperature and at low temperature is approximately 45°.[20,21] The tilt angle is an important factor in the development of a detailed crystallization mechanism and also influences the interfacial free energy associated with the basal plane.

An important question of concern is the concentration of and the role played by defects within the crystallite interior. We have already noted that a wide range in crystallinity levels can be obtained. The macroscopic density of linear polyethylene ranges from about 0.92 to 0.99 as the molecular weight decreases from 10^6 to 10^4. This change in the density raises the question of the integrity of the crystal structure. Quantitative studies of the lattice parameters have shown that they do not change over this very wide range of macroscopic densities.[22] It can be concluded that

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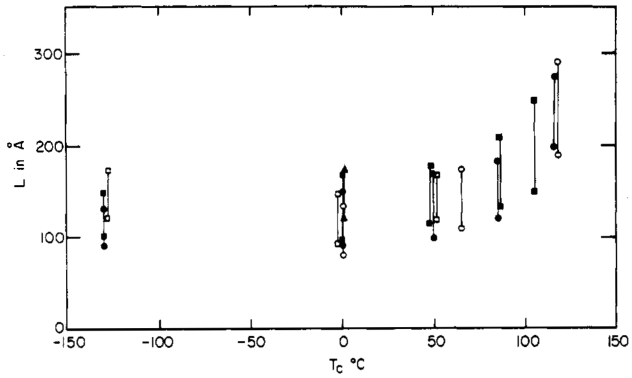

Figure 3. Crystallite thickness distribution as function of quenching temperature for indicated molecular weights of linear polyethylene fractions:[25] ○, 1.97×10^4; ●, 4.6×10^4; □, 2.26×10^5; ■, 4.28×10^5; ▲, 1.62×10^6.

defects that exist are not present in sufficient concentration to influence the unit cell structure.

Crystallite Thickness Distribution

There are several different methods by which the crystallite thickness distribution can be determined. These include thin-section electron microscopy, analysis of the Raman longitudinal acoustical mode (LAM), and the small-angle X-ray scattering long period. These methods give concordant results for narrow crystallite thickness distributions, but discordant results are usually obtained for broad distributions.[23,24] After rapid, nonisothermal crystallization, a narrow size distribution is obtained as is illustrated in Figure 3 for linear polyethylene.[25] The crystallite thicknesses range from 120 to 150 Å and are independent of molecular weight. There is only a slight dependence of thickness with the crystallization temperature. In contrast, after isothermal crystallization a broad distribution results because of crystallite thickening with time.[26-28] It is possible to develop crystallite thicknesses of several thousand angstroms after long-time, high-temperature, isothermal crystallization under atmospheric pressure. However, in order to obtain large crystallite thicknesses the narrow distribution is sacrificed. Copolymers and branched polymers give thicknesses in the range of about 40–100 Å.[29] Therefore, depending on molecular weight, chain structure, and crystallization conditions, the crystallite thicknesses can vary from about 40 Å to several thousand angstroms.

Interfacial Structure

The nature of the boundary between a lamellar crystallite and the disordered, isotropic interlamellar region has been a controversial matter for over 25 years. However, recent experimental and theoretical developments have given strong indication that the resolution of this problem is close at hand. With the discovery that homopolymers crystallize in a lamellar habit it was widely heralded, although with some exceptions, that the chains crystallized in a regularly folded array.[11-14,30-33] It was assumed that, upon emerging from the basal plane of a lamellae, the chain made a sharp reversal in direction and reentered the crystallite at a position immediately adjacent to its preceding passage. This process was repeated until the complete molecule was incorporated into the crystallite. On occasion, a sequence of chain units would be allowed to escape as a "defect" and join a neighboring crystallite. In retrospect, there are several reasons why at one time the concept of regular chain folding was widely adopted and had become a matter of faith. It is a simple, pictorial model that is aesthetically pleasing. Examination of electron micrographs suggested that the basal planes of the lamellae were molecularly smooth. This perception was immediately identified with regular chain folding. Efforts were made to legitimize the concept of regular chain folding by applying classical monomeric nucleation theory to polymer crystallization. Earlier studies had firmly established that polymer crystallization was nucleation controlled.[4] This conclusion was reached on the most general grounds, irrespective of the structure of the nucleus and the type of nucleation process involved. A theory of crystallization kinetics was presented that had as its central theme the assumption that nuclei for polymer crystallization comprise regular folded chains that subsequently grow into mature crystallites of the same chain structure.[34] Since the temperature coefficient of polymer crystallization followed the requirement of nucleation theory, it was concluded that, in both the nuclei and the mature crystallites that develop, the chains were regularly folded. This argument, based solely on the analysis of crystallization kinetics, is a circular one since the nucleus structure is not established independent of the kinetic arguments.[5,35-38] The experimental data can, in fact, be satisfied by many different kinds of chain structures within the nucleus.

There is no a priori need to identify the lamellar-like crystallites with regularly folded chains in order to satisfy either the kinetics or morphological features. Some of the chains could traverse the crystallite only once and then join a nearby crystallite. Others could return to the crystallite of origin but not necessarily in juxtaposition after transversing the interfacial and interlamellar regions. These structural features are compatible with the gross morphological forms that are revealed by electron microscopy.[5,39] Many different properties, small-angle neutron scattering, and analysis of chain statistics do not allow for the existence of a regularly folded chain structure. Experimental studies

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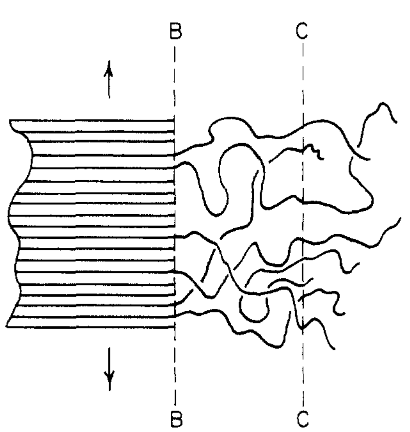

Figure 4. Schematic representation of the interfacial zone transverse to the chain axis.[31]

such as ^{1}H and ^{13}C NMR,[40-42] small-angle neutron scattering,[43] specific heat measurements,[44] dielectric relaxation,[45,46] analysis of the Raman internal modes,[47,48] and electron microscopy[49] clearly demonstrate the presence of an appreciable interfacial region that is characterized by the partial ordering of the chain units. There is no substantive experimental or theoretical basis to support the view that lamellar crystallites, formed either in bulk or in dilute solution, comprise regularly folded chains and have thus reached their optimum level of crystallinity. This conclusion does not preclude some type of chain folding taking place. There will be some adjacent reentry and nucleation processes playing a dominant role in polymer crystallization. The basic questions remain as to why a lamellar crystallite is characteristic of polymer crystallization, and what in fact is the structure of the interphase.

Flory pointed out in 1949 that the boundary between the crystalline and liquid-like regions in polymers differs from that of low molecular weight systems in that it is not sharply defined.[1] The continuity of a long-chain molecule imposes severe constraints on the transition between the two regions. The major conformational differences of the chain in the two states require a boundary, or interphase, that allows the crystalline order to be dissipated. This interfacial region is a major distinguishing feature of polymer crystallization. The basis for understanding the interfacial structure can best be envisioned by analyzing the diagram in Figure 4. Here a lamellar crystallite of unlimited lateral dimensions is considered.[30] All the chains emerging from the crystallite traverse the plane BB located at the surface and enter the adjoining region. Some of the chains will then intersect the plane CC that is positioned in the isotropic liquid-like region. The problem to be resolved is whether the flux of chains (the number of chains per unit area) emanating from the crystallite can be accommodated in the isotropic region. If A_c is taken to be the cross-sectional area per chain in the crystalline state, then the number of chains emanating from the crystal face per unit area is given by

$$N_c = 1/A_c \tag{1}$$

To calculate the number of chains per unit area, N_a, that intersect the plane CC, a freely rotating segmented chain is taken to represent the molecule in the isotropic state. It follows that[30]

$$N_a = 1/2A_a \tag{2}$$

so that

$$N_a/N_c = A_c/2A_a \tag{3}$$

is the ratio of the chain flux between the isotropic and crystalline regions. Equation 3 serves as an upper limit to the fraction of chains leaving an infinitely large lamellar crystallite that need not return to it. If in polyethylene, for example, the chains are fully extended in the crystalline state and the bond orientations are uncorrelated in the disordered state, the ratio A_c/A_a can be identified with the corresponding ratio of specific volumes. For most flexible chains this quantity would be on the order of unity. Therefore, when $A_c/A_a \cong 1$, at least half the chains leaving the crystallite must be dissipated in some manner. The particular way in which this process is carried out is not specified at this point. An obvious possibility is the return of chains to the crystallite surface. In contrast, situations can be anticipated wherein the ratio A_c/A_a will exceed unity by a sufficient amount so that N_c/N_a will be on the order of unity. In this case all the chain flux from the crystallite could be accommodated within the liquid-like region. An example of this possibility is found in the α-helical crystalline form of polypeptides.[30,50] In general a significant proportion of the chain flux that emanates from the 001 crystal plane will be dissipated by the chains returning to the crystallite of origin. These, however, do not have to be in juxtaposition. For a crystallite to grow laterally, a significant amount of chain bending, or folding, must occur. An expenditure of free energy, i.e., a gain in free energy, will be involved. This free energy gain can be compensated by the crystallization of long sequences resulting in lateral crystallite growth. There is then a straightforward mechanism by which well-developed lamellae will form without the need to invoke any inherent propensity for chain folding or to manipulate monomeric nucleation theory. The calculation outlined contains some quantitative shortcomings. The manner in which the chain flux is dissipated is not given. Also missing is the thickness of the interfacial zone, i.e., the distance between the crystallite surface and the beginning of isotropy. These shortcomings have been alleviated in more recent calculations.

Several theoretical analyses of the interfacial structure, either based on Monte Carlo methods or using a

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(50) The above conditions are based on a model wherein the transverse dimensions of the crystallites are very large compared to its thickness. This condition will not apply to the formation of a critical-size nucleus, so that the conformational restraints will not be operative in this situation.[4,30]

Bragg–Williams type lattice, have been presented.[50-56] These calculations represent a pseudoequilibrium interphase of a lamellar crystallite formed by an infinite molecular weight chain.[57] The different calculations are in essential agreement with one another as far as major conclusions are concerned. Several principal factors have to be taken into account. One of these is the density of the chains at the crystal surface,[52,56] which is determined by the tilt angle and the ratio of the cross-sectional area of a chain segment in the crystalline and liquid-like regions. When the cross-sectional area in the crystalline state exceeds the corresponding quantity in the liquid-like region, the problem of flux dissipation is severely reduced. This factor is important when the ordered conformation has a large helical diameter and a statistical conformation in the liquid state. An extremely important consideration that also needs to be taken into account is the free energy increase necessary to make a bend or tight fold. All these concerns make clear that the structure of the interfacial zone will be very specific for a given polymer and generalizations will be difficult to make.

For the hypothetical polyethylene chain, where no free energy expenditure is involved in forming a fold, and with no conditions placed on the chain incidence probability, it is found that about 70–75% of the sequences are expected to return to the lamellae of origin in tight, adjacent folds. This result is not surprising since, with no free energy cost in making a bend, the regularly folded structure is clearly the easiest way in which the flux of chains can be dissipated. However, this conclusion must be tempered by reality. For polyethylene the incidence of a tight fold, or immediate adjacent reentry, is reduced to 30–40% of the sequences because of the free energy increase necessary to make a fold.[51,52,56] Consideration of the surface chain density (tilt angle of 45°) reduces the adjacent reentry possibility to about 20%. Adjacent reentry will thus not be a major contribution to the interfacial structure, even for these idealized calculations. Those that are formed will be randomly distributed along the lamellar surface. The chemical nature of the chain, as reflected in the crystal structure and the disordered chain conformation, will strongly influence the interfacial structure.

Expectations from the theoretical calculations can be compared with experimental results. The excess interfacial free energy associated with the basal plane of the mature crystallite has been calculated to be in the range of 50–65 ergs/cm^2 for polyethylene.[52] This value is in good agreement with that experimentally determined for low molecular weight polyethylene having a folded-type lamellar morphology, for which topological restraints are minimal. The influence of the chain repeating unit on the extent of adjacent reentry can be estimated from small-angle neutron scattering based on model calculations.[58-60] It is concluded that there is a slightly higher proportion of adjacent reentry in poly(ethylene oxide) than in polyethylene. This would be expected because gauche bonds, necessary to make the folded structure, are energetically more favored in the former case.[61] The interfacial thickness, L_b, for bulk crystallized linear polyethylene has been theoretically estimated to be in the range of 10–30 Å.[56] The thickness can be determined from either Raman LAM or the small-angle X-ray scattering long period, coupled with the internal mode analyses.[62] The results show that the interfacial thickness varies from about 14 Å for low molecular weights (10^4) to about 25 Å in the 10^5–10^6 range.[62] Good qualitative agreement is thus found between theory and experiment. There is, however, a definite influence of molecular weight in that L_b increases with chain length. The theoretical calculations are for an idealized infinite molecular weight chain and do not take into account the role of entanglements, and other topological restraints, as well as the limitations on the chain mobility. These factors are molecular weight dependent and will assert themselves with increasing chain length. In support of this conclusion, it is found that L_b for crystallites formed in dilute solution are about 10 Å, independent of molecular weight.[62] Under these crystallization conditions, chain entanglements are minimal and there is no significant chain mobility restraint to the crystallization process. We can conclude that the theoretical calculations, although highly idealized, give a very satisfactory understanding of the interfacial structure.

The increase in L_b with molecular weight parallels the change in α_b.[6,48] The interfacial free energy associated with the basal plane of a mature crystallite would also be expected to increase with molecular weight. This expectation is in fact fulfilled. The interfacial free energy can be calculated from the dependence of the melting temperature on the crystallite thickness and is found to increase monotonically with molecular weight until $M \cong 10^5$.[63] At this point it becomes constant at a relatively high value (295 ergs/cm^2). This result is again a reflection of the influence of the initial melt structure on the crystallization behavior and on the resulting crystallite structure.

Theory and experiment both lead to the conclusion that a significant interfacial region exists that is characterized by a partial order of the chain units. Although a large number of chains return to the crystallite of origin, the number that return in an adjacent position is small. The equilibrium calculations that describe the interfacial structure need to be tempered by kinetic factors and the melt topology. Good agreement between theory and experiment is found for the major features of the interfacial region.

Conclusion

Among the major points that have emerged from our discussion are the importance of the initial melt structure and the influence of molecular weight on the structural variables that describe the crystalline state.

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Also of significance is the wide range in values that can be attained for a given structural parameter. There has always been a continuing interest in understanding the properties of crystalline polymers in terms of structure. From the present discussion a strategy can be developed where by control of molecular weight and crystallization conditions a specific variable can be isolated[5,6] and its influence on a given property assessed. This procedure has been successfully demonstrated for certain mechanical[64,65] and spectral properties[66] and should be applicable to virtually all properties of crystalline polymers.

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Valence-Bond Concepts in Transition Metals: Metal Hydride Diatomic Cations

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Introduction

Despite the recent advances in understanding bonds between transition metals (TM) and non-metals,[1-7] there remain considerable uncertainties in both the concepts and the thermodynamics of organometallic complexes, severely limiting the understanding of mechanisms for various chemical transformations.[3] In order to provide the flavor of some of the evolving concepts, we will focus here on MH^+ and examine the variations in bond orbitals, bond energies, and other quantities (from both experiment[4] and theory[5]) for the three rows of TM (Sc^+–Cu^+, Y^+–Ag^+, La^+, Hf^+–Au^+) plus the group 2 and group 12 systems. These trends also apply to other bonds to TM, in particular to metal–alkyl[8] and metal–silyl bonds, and should be helpful in estimating and understanding the trends in other TM compounds as well.

The GVB Picture. Typical MH^+ bonds derived from generalized valence bond (GVB) calculations[5] are shown in Figure 1 for FeH^+, RuH^+, and OsH^+. Here we see that the bond pair involves one electron in the hydrogen 1s orbital and one in an sd hybrid on the metal. Thus the bond is covalent (M^+H, not $M^{2+}H^-$). Although the H-centered orbital (right orbitals in Figure 1) remains nearly the same for all cases, there are systematic changes in the hybridization of the TM orbital

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