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(37) It is unnecessary to distinguish collinear from rectilinear connections between bonds in a given layer inasmuch as the distribution between horizontal connections of these two kinds is not subject to constraint. A factor representing this distribution has not been included in the partition function expressed by eq 29. Allowance for free equilibration between the two types of horizontal bond connections would reduce the factor to unity.

Chain Packing at Polymer Interfaces

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ABSTRACT: The lattice theory presented in the preceding paper is applied to various polymer interfaces of general interest. The reduction of surface chain density in lamellar semicrystalline polymers due to tilting of the interfacial plane from orthogonality to the chain sequences within the crystal allows the incidence of adjacent folds to diminish markedly; it may become negligible for a tilt angle >25°. Chain configurations in the noncrystalline region between two lamellar crystallites are little affected by the entry of chain sequences from the more remote surface if the interlamellar separation is greater than 4–5 lattice layers, or ca. 20 Å. In lamellar single crystals, the sites of chain reentry are separated predominantly by two or three lattice steps, according to the theory. For polymer melts bounded by a hard wall, the theory predicts a rather narrow interphase comprising no more than two lattice layers. The chain sequences tend to orient along the surface in the first layer adjoining the wall, whereas in the second layer they exhibit a slight preference for orientation normal to the surface. Similar characteristics of chain configurations hold for a thin layer between two walls, or in a thin film, unless the thickness approaches that of a monomolecular layer.

Introduction

In the preceding paper[1] (referred to as I hereafter), we present a lattice theory that describes chain packing in the interphase of a lamellar semicrystalline polymer. The molecular weight of the polymer is assumed to be sufficiently high to justify disregard of chain ends. Essential to this theory is the treatment of packing of polymer chains in the interfacial layers subject to two conditions of constraint: one of conservation and the other of continuity. The conservation condition (eq I-2 or I-2′) requires that all lattice sites be occupied discretely by segments, with the number of "horizontal" bonds joining segments in a given layer consistent with the "fluxes" of chains between this layer and those adjoining it. The continuity condition (eq I-3 or I-3′) asserts that the change in chain fluxes from one interlayer to the next must be equal to the difference between S^{--} and S^{++}, the numbers of negative and positive reversals, respectively, of chain directions involving one or more horizontal bonds in the given layer. Subject to these constraints, the configuration distribution is specified by the initial flux p_1 into the first layer and the set of quantities u_{i+}, u_{i-}, and h_i expressing the fractional occurrences of various connections of horizontal bonds in each interfacial layer i.

The treatment of interphase configurations in this manner and the derivation of the configurational partition function that follows (eq I-29) do not rest on specific assumptions concerning the nature of the interface. In principle, the theory is applicable to interfaces of any kind at which long polymer chains are the principal constituents. The interphase in lamellar semicrystalline polymers, discussed in the preceding paper, is treated by applying the boundary condition $p_1 = 1$ in the first layer, since the chains are taken to be perfectly aligned within the crystal

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Table I
Effects of Surface Chain Density on Characteristics of the Interphase in Lamellar Semicrystalline Polymers for $\sigma = 0.6$ and $\eta = 0.01$

	p_1					
	1.0	0.97	0.93	0.90	0.85	0.80
S_1^{--}/N_0	0.095	0.085	0.082	0.098	0.150	0.192
$S_{1;1}^{--}/N_0$	0.095	0.055	0.012	0.001	0.002	0.001
$\langle l_1^{--} \rangle$	1.00	1.35	1.85	1.99	1.99	2.00
S_2^{--}/N_0	0.184	0.191	0.200	0.237	0.110	0.064
$\langle l_2^{--} \rangle$	2.00	2.00	2.03	2.00	3.06	3.42
γ,[a] erg cm^{-2}	53.8	40.4	27.8	22.2	13.6	9.2

[a] Calculated at $T = 400$ K for a lattice with cross-sectional area per cell of 18.3 Å^2, corresponding to the polyethylene chain.

with their axes normal to the interface. In the subsequent layers no other conditions are imposed, and the transition to the isotropic, random state occurs in the interfacial layers subject only to the constraints of conservation and continuity.

In this paper we apply the lattice theory to other polymer interfaces of general interest. Effects of reduction of the flux of chains in the first layer (i.e., of $p_1 < 1$) are first considered, followed by treatment of the noncrystalline regions between two lamellar crystallites in a semicrystalline polymer crystallized from the bulk and at the surfaces of lamellar single crystals. Finally, we examine the interface of a polymer melt bounded by a hard wall, of a thin layer between two walls, and of a thin film. These interfaces are treated by applying suitable boundary conditions expressed by p_1, for example. Apart from the minor modifications necessary to accommodate the specific boundary conditions, the computational procedures are identical with those described in I.

Effect of Initial Chain Flux (p_1) in Lamellar Semicrystalline Polymers

As has been pointed out in paper I, tilting of the lamella so that its surface normal is inclined at an angle θ_t to the axes of the chain sequences within the crystal reduces the surface chain density p_1 at the first layer of the interphase. This reduction may be expressed by

$$p_1 = \cos \theta_t \tag{1}$$

In the case of polyethylene,[2,3] θ_t falls in the range 18–45°, depending on the crystallization conditions. For $p_1 < 1$, the interphase configuration and its partition function are expressed directly by eq I-29 for a set of u_{i+}, u_{i-}, and h_i; eq I-31, I-32, and I-33 introduced previously for the case $p_1 = 1$ are not required.

The results obtained with the lattice parameters $\sigma = 0.6$ and $\eta = 0.01$ are listed in Table I. The number density of reversals S_1^{--} in the first layer decreases initially as p_1 is decreased from unity, but as p_1 becomes smaller than 0.93, it begins to increase rapidly owing to reversal sequences of greater length. As expected, the incidence of adjacent reentry in the first layer, $S_{1;1}^{--}/N_0$, decreases rapidly with decreasing p_1 and becomes negligible for $p_1 < 0.9$ (corresponding to $\theta_t > 25°$). The extra space in the first layer provided by reduction of the initial flux p_1 is taken up by reversals with two horizontal bonds (i.e., $1 - p_1 \simeq S_{1;2}^{--}/N_0$) and for $p_1 < 0.9$ virtually all reversals in the first layer comprise two horizontal bonds. In the second layer, for $p_1 > 0.9$ nearly all reversals consist of two horizontal bonds. As p_1 is made smaller than 0.9, the average length $\langle l_2^{--} \rangle$ in the second layer increases, becoming much larger than 2.0. The interfacial free energy also decreases rapidly with reduction in p_1.

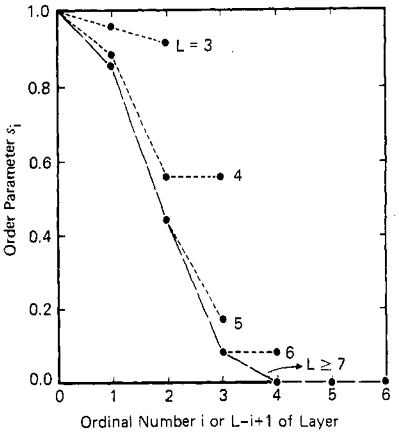

Figure 1. Order parameters for chain segments in consecutive interfacial layers of the noncrystalline region between two lamellar crystallites, calculated for the interlamellar layer thicknesses L indicated. Lattice parameters are $\sigma = 0.6$ and $\eta = 0.01$. The dashed line and the dotted lines connect points for the same thickness L.

Noncrystalline Region between Two Lamellar Crystallites

In the preceding paper[1] we have assumed that the dimension of the noncrystalline region between two lamellar crystallites is sufficiently large so that entry of chain sequences emanating from the adjoining crystal surface can be neglected. For smaller distances between the lamellae, the two anisotropic interphase zones may overlap appreciably, with the result that the dissipation of the flux of chains from one layer is affected by the proximity of the other. This effect can be readily incorporated in the theory by inserting the condition that at the final layer, indexed by L, adjoining the neighboring lamella

$$p_{L+1} = 1 \tag{2}$$

on the assumption that the surfaces of both lamellae are normal to the chain axes within them. By analogy with conclusions deduced for $p_1 = 1$ (eq I-31), we obtain $u_{L+} = 1$, $u_{L-} = u_{L0} = 0$, and

$$q_L = (1 - p_L)/2 \tag{3}$$

The partition function per chain sequence in the Lth layer becomes (see eq I-34)

$$\omega_L = \frac{1}{3}\left[\frac{\Gamma(1-\sigma)^2\eta}{2q_L}\right]^{q_L}\left[\frac{1}{1-q_L}\right]^{1-q_L} \tag{4}$$

The same computational procedure used in paper I is applicable, except that the configuration distribution (i.e., q_L) in the Lth layer is fixed by the value of p_L and, hence, by the set of stochastic variables in the preceding $L - 1$ layers.

The orientational order parameters $s_i = 1 - 3q_i/2$ calculated for $\sigma = 0.6$ and $\eta = 0.01$ are shown in Figure 1 for successive interfacial layers for the indicated values of the interlayer thickness[8] L. The configurational distribution is symmetrical, of course, with respect to the center of the interlayer. For $L \geq 6$, the interphase characteristics converge to those found in I for a single interphase, each of them being unaffected by the other. Hence, for an interlamellar layer ≳30 Å in thickness, complete isotropy is obtained midway between the two lamellae. For $L = 4$ and 5, their mutual effect on one another is quite small; the extent of adjacent reentry in the first layer adjoining the

Table II
Characteristics of Successive Layers in Lamellar Single Crystals with L Overlayers for $\sigma = 0.6$ and $\eta = 0.01$

	$L = 2$	$L = 3$
$q_1 = S_1^{--}/N_0$	0.166	0.086
S_2^{++}/N_0	0.000	0.000
S_2^{-+}/N_0	0.000	0.010
S_2^{--}/N_0	0.334	0.160
$\langle l_2^{--} \rangle$	2.00	2.00
S_3^{--}/N_0		0.254
$\langle l_3^{--} \rangle$		2.94
γ,[a] erg cm^{-2}	60.5	58.8

[a] See footnote in Table I.

Table III
Interface Characteristics of Polymer Melts Bounded by a Hard Wall

	$\sigma = 0.6$		$\sigma = 0.8$		ref 7 (for
	$\eta = 0.01$	$\eta = 1$	$\eta = 0.01$	$\eta = 1$	$m = {}^1/_6$)
s_1	−0.182	−0.164	−0.244	−0.239	−0.226
s_2	0.070	0.085	0.006	0.012	0.021
s_3	0.001	−0.002	0.000	0.002	0.002
s_4	−0.002	0.002	0.001	0.000	0.000
γ,[a] erg cm^{-2}	3.37	3.65	3.09	3.07	3.05

[a] Calculated at $T = 300$ K for a lattice with cross-sectional area per cell of 25 Å^2.

crystal and the characteristics of reversals in the second layer are little affected, but complete isotropy is not attained at the midpoint of the interlamellar region. For $L = 3$ a rather high degree of order persists thoughout the interlamellar region; the degree of attenuation of the chain fluxes is diminished, with concomitant decrease in the incidence of adjacent reentry.

Surfaces of Lamellar Single Crystals

Chain configurations in the noncrystalline overlayer of lamellar single crystals, formed in dilute solutions, differ importantly from those treated in I in that (i) all the chain sequences emanating from the crystal must return to the surface from which they emanate, and (ii) the thickness of the surface layer is rather small, ca. 10–15 Å for polyethylene single crystals.[4] The condition (i) leads to $p_{L+1} = 0$ and $u_{L+} = 0$. According to (ii) the total number of surface layers L is ca. 3.

Inserting $p_{L+1} = 0$ in eq I-18 and $u_{L+} = 0$ in eq I-17 one obtains

$$h_L = 1 - [u_{L-}(p_L - 2) + p_L]/[2u_{L-}^2(p_L - 1)] \quad (5)$$

Hence, in the final Lth layer u_{L-} becomes the only independent variable. All the other computational procedures are identical with those of I. Again, we assume orthogonality of the lamellae to the chain sequences within the crystal.

The results obtained with the lattice parameters $\sigma = 0.6$ and $\eta = 0.01$ are listed in Table II for lamellar interphases comprising $L = 2$ and 3 layers, respectively. For the case $L = 2$, one-third of all the chain sequences are involved in adjacent folds in the first layer. In the second layer the remaining two-thirds form reentry loops comprising exclusively two horizontal bonds that leapfrog[5] over the reversals in the first layer.

As the thickness of the surface layer is increased to $L = 3$ and beyond, the extent of adjacent reentry decreases significantly. For $L = 3$, only ~17% of all the chain sequences within the crystal ($2q_1$ in Table II) are involved in adjacent folds in the first layer. Approximately 32% of the chain sequences emanating from the crystal return in the second layer, forming loops of two horizontal bonds. The remaining ~51% of chain sequences return in the third layer with an average length $\langle l_3^{--} \rangle = 2.94$. Therefore, most of the reentry loops comprise two or three horizontal bonds.

The interfacial free energy predicted for the single crystals is somewhat larger than the corresponding value, $\gamma = 53.8$ erg cm^{-2}, calculated for the lamellar semicrystalline system in I for the same lattice parameters. Introduction of more realistic values for σ (>0.6) and η (<0.01) increases the predicted interfacial free energy in the same way as deduced in I. Thus, the experimental results reported for polyethylene single crystals,[4] ~100 erg cm^{-2}, are approached satisfactorily by the theory.

The most critical parameter determining the chain configurations in the surfaces of lamellar single crystals is the thickness of the noncrystalline overlayer. This thickness is ordinarily ca. 10–15 Å or greater,[4] which corresponds to $L \geq 3$ lattice layers. (The thickness of the overlayer seldom corresponds to fewer than three layers for those polymers that have been investigated.) Accordingly, the fraction of chain sequences in the crystal involved in adjacent folds is predicted to be less than 20%. Most of the reentry occurs at sites separated by two or three lattice steps. This prediction is in good agreement with the conclusion drawn previously[6] from the intensities of neutron scattering by polyethylene single crystals over the intermediate range of scattering vectors, with labeling provided by incorporation of deuterated chains.

Polymer Melts Bounded by a Hard Wall

In the case of polymer melts bounded by a hard wall, the first layer adjoining the wall has no vertical bonds extending toward the wall; i.e., $p_1 = 0$ and $u_{1-} = 0$. The chain configurations of polymer melts in the vicinity of a hard wall can be treated readily by inserting this initial condition in the theoretical equations given in I. All other steps remain the same.

The results obtained with values of 0.6 and 0.8 for the parameter σ pertaining to the preference of straight ("trans") bonds over bent ("gauche") bonds (see eq I-24) and with 0.01 and 1.0 for the parameter η affecting adjacent reversals are listed in Table III. For $\eta < 0.01$ the results (not included) are virtually identical with those with $\eta = 0.01$. In the first layer adjoining the wall, the chain sequences tend to orient horizontally, i.e., parallel to the surface, whereas in the second layer they exhibit a slight preference for orientation normal to the surface. From the third layer on, random orientation (isotropy) is attained for all values of lattice parameters within realistic ranges. Thus, the interphase comprises no more than two lattice layers, corresponding to a thickness of ca. 6–8 Å. The order parameters across the interphase and the associated interfacial free energies exhibit only a small dependence on the lattice parameters, with the calculated interfacial free energies falling in the range 3–4 erg cm^{-2}.

Also listed in Table III are the corresponding results reported by Weber and Helfand[7] for the cubic lattice system (i.e., $m = {}^1/_6$ in ref 7). Their theoretical treatment, also based on the lattice model, corresponds to the situation with $\sigma = 0.6$ and $\eta = 1.0$ in our theory. However, in their calculations the continuity condition, i.e., the requirement that the change in chain flux from one interlayer to the next be fixed by the types of connections *at the ends of horizontal bond sequences*, i.e., by the difference between the occurrence of ++ and −− sequences in the given layer, is not explicitly taken into account.

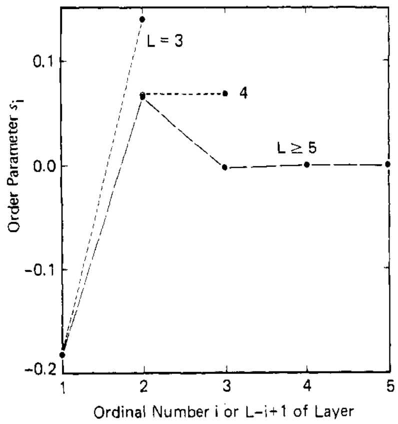

Figure 2. Order parameters for chain segments in successive layers of polymer melts between two hard walls, calculated for the layer thicknesses L indicated, with $\sigma = 0.6$ and $\eta = 0.01$.

Hence, their theory is not suitable for cases that involve significant changes in chain flux, or chain orientation, across the interphase. For polymer melts bounded by a hard wall, the degree of chain orientation in the interphase is not large and, hence, the difference between the predictions of the two theories is minor.

Polymer Melts in Thin Layers

For polymer melts in thin layers between two hard walls, or in thin films, the final layers as well as the initial layer has no vertical connections toward the exterior; that is, $p_{L+1} = 0$ and $u_{L+} = 0$ and, in addition, $p_1 = 0$ and $u_{1-} = 0$, as in the preceding section. The computational modifications required to include the former conditions in conjuction with eq 5 have been discussed above.

The results obtained with the lattice parameters $\sigma = 0.6$ and $\eta = 0.01$ are shown in Figure 2. Again, the interphase characteristics are symmetric with respect to the central layer. For $L \geq 4$ layers, the results are virtually unaffected by the inclusion of the second surface. For $L = 3$ layers, the only perturbation is a somewhat stronger preference of chain sequences in the second (central) layer for orientation normal to the surface. Hence, in practically all cases the interfacial characteristics of polymer melts in layers that are thin (but not monomolecular) are little dependent on the layer thickness.

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(8) We have connected the points in Figure 1 by straight lines without attempting to fit them by smooth curves. The lattice model applies strictly to integral values of the abscissa only. The order parameter obviously is a continuous function of location in the interphase, and the results of the lattice theory may be presumed to approximate that function.

Equilibrium Melting Temperature of Long-Chain Molecules[†]

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ABSTRACT: Both the theoretical and experimental basis for determining the equilibrium melting temperature of chain molecules is discussed. Two distinctly different molecular situations need to be clearly distinguished in order to carry out the proper analysis. One of these is based on the melting of oligomers wherein molecular crystals are formed. For this situation the original Flory–Vrij analysis is shown to be correct. The modifications that have been proposed to this theory are critically reviewed. However, for real polymer chains of finite length, molecular crystals cannot be formed, no matter how well fractionated the system. In this case a different analysis is required. The difficulties involved here are discussed in terms of the available experimental data for linear polyethylene and poly(ethylene oxide) fractions.

Introduction

The equilibrium melting temperature T_m° of a crystalline polymer is the melting temperature of a perfect crystal formed by infinite molecular weight chains.[1] It is a very important molecular parameter. It not only reflects the molecular and conformational characteristics of a chain but is very important in analyzing crystallization kinetics. A difference of only several degrees makes major changes in the value of the nucleation interfacial free energy that is deduced from kinetic studies,[1] which, in turn, can be very significant in establishing basic crystallization mechanisms. By definition, this important quantity cannot be determined by direct experiment. Recourse is therefore made to theory and to extrapolative procedures involving the controlled crystallization and melting of a polymeric system of finite molecular weight. A more detailed analysis of the extrapolative experimental procedures and results has been given elsewhere.[2,3] We focus our primary attention here on the theoretical analysis of the dependence of melting temperature on molecular weight. The basic theories are due to Flory[4] and to Flory and Vrij,[5] with several additional modifications being proposed.[6-8] The results of the analysis, coupled with appropriate experimental data, can then be directly applied to the determination of the equilibrium melting temperature of linear polyethylene and poly(ethylene oxide).

Discussion and Results

As a basis for the ensuing discussion we first briefly review the theory given by Flory and Vrij.[5] In this basic

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[†] Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday.

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