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Relationship between the Lateral Surface Free Energy σ and the Chain Structure of Melt-Crystallized Polymers[†]

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ABSTRACT: A theory is presented for the lateral surface free energy parameter σ in the nucleation constant K_g in the relation $G \propto \exp[-K_g/T(\Delta T)f]$ that describes the growth rate of polymer crystals from the melt at low-to-moderate undercoolings ΔT. The theory forms a connection between nucleation theory and the statistics of polymer chain dimensions and provides a new approach to the determination of the characteristic ratio C_∞. It is predicted that σ varies as const $\times$ C_∞^{-1}, where the constant involves known quantities. The effect of chain structure resides principally in C_∞. The theory was tested for polyethylene, isotactic polystyrene, and poly(L-lactic acid) by employing known values of σ obtained from melt crystallization studies to calculate C_∞ and then comparing these with the C_∞ values cited in the literature as determined from chain dimensions in dilute Θ solvents. The agreement is satisfactory, showing the theory for σ to be valid in these cases, with the further implication that these polymers possessed a close approximation to unperturbed chain dimensions in the melt. Support was provided by data for isotactic polypropylene, poly(pivalolactone), and poly(ϵ-caprolactone), some of this deriving from a method of finding C_∞ for the melt state without direct reference to σ. The C_∞-dependent "segmental" character induced by the crystal surface in the section of chain comprising the activated complex is discussed. The theory for σ provides strong support for polymer nucleation theory as there is now a predictive molecular picture for all the nucleation parameters in K_g. The treatment casts new light on the empirical formulas commonly employed to estimate σ.

I. Introduction

The detailed origin and a priori calculation of the lateral surface free energy σ that appears in the nucleation-based treatment of the crystallization of linear polymers from the melt present an intriguing riddle. This surface free energy appears in the widely applicable growth rate expression[1-3]

$$G = G_0 \exp[-U^*/R(T - T_0)] \exp[-K_g/T(\Delta T)f] \quad \text{(1a)}$$

in which G_0 is a factor in the units cm s^{-1} and where the experimentally measurable nucleation constant K_g has the form

$$K_g = jb_0\sigma\sigma_e T_m/k(\Delta h_f) \quad \text{(1b)}$$

Here, $j = 2$ for regime II growth and $j = 4$ for regimes I and III. The quantity f is a factor accounting for the decrease in the heat of fusion Δh_f with decreasing temperature, b_0 the layer thickness, σ_e the fold surface free energy, T_m the equilibrium melting temperature of the high molecular weight polymer sample under consideration, k the Boltzmann constant, T the isothermal crystallization temperature, and ΔT the undercooling $T_m - T$. The factor $\exp[-U^*/R(T - T_0)]$ describes the rate of transport of chain segments to the growth front and dominates the behavior of G below the maximum in the growth rate. The factor $\exp[-K_g/T(\Delta T)f]$ dominates the variation of G near T_m and well down toward the maximum in the growth rate, which range of temperature normally corresponds to the practical crystallization zone, thereby highlighting the importance of the product $\sigma\sigma_e$. The origin of σ_e is well understood in molecular terms, being largely the result of the work of chain folding q through the relation $\sigma_e = q/2a_0b_0$, where a_0b_0 is the cross-sectional area of the polymer chain. Numerical values of σ are known for a number of melt-crystallized polymers. Nevertheless, it is evident that the physical origin of this parameter requires clarification in molecular terms.

Experimental values of σ are commonly obtained for polymers from the kinetically-determined value of $\sigma\sigma_e$ (obtained from K_g by application of eq 1b) divided by the "thermodynamic" σ_e value derived from a plot of T_m' vs $1/l$ based on the melting point depression relationship $T_m' = T_m[1 - 2\sigma_e/(\Delta h_f)l]$. Here, T_m' is the melting point of a lamella of thickness l. Alternatively, a "kinetic" value of σ_e can be obtained from a fit of the data to the relation[1-4]

$$l_g^* = 2\sigma_e T_m/(\Delta h_f)(\Delta T) + \delta \quad \text{(1c)}$$

predicted by nucleation theory where l_g^* denotes the initial (unthickened) lamellar dimension corresponding to the surface nucleus length and where δ is on the order of $kT/b_0\sigma$. Equations 1a–c are based on the "low-ψ" form of nucleation theory, which forestalls[1,4] the prediction of an anomalous abrupt increase in the surface nucleation rate

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and in δ at large ΔT (the so-called "δ catastrophe").

In the past the estimation of σ for polymers for which an experimental value was not available was commonly dealt with in an empirical manner through the use of a relation suggested by Lauritzen and Hoffman[4]

$$\alpha_{\mathrm{LH}} = \frac{\sigma}{(\Delta h_f)(a_0 b_0)^{1/2}} \tag{2}$$

which was based on an earlier empirical treatment of Thomas and Stavely.[5] For polyethylene (PE) it was found that α_{LH} was ~ 0.1, and this value was widely applied in other cases. Though useful for an appropriate class of polymers, this low value was not understood in fundamental terms. Moreover, in recent work[6,7] involving the high-melting polyester poly(pivalolactone) (PPVL), it became clear that $\alpha_{\mathrm{LH}} \cong 0.1$ did *not* apply generally: for this polymer as well as certain others, α_{LH} centered about 0.25 ± 0.03[6] (see also later). Thus, even in an empirical context, it is evident that a better understanding of the origin and value of σ is essential if the kinetic nucleation theory of polymer crystallization as expressed in eqs 1a and 1b is to be upheld in quantitative terms.

The treatment to follow gives a theory for σ which emphasizes its entropic origin and shows how it relates to the structure and to the segmental nature of polymer chains as reflected by the characteristic ratio C_∞. In so doing, the treatment forges a link between (1) nucleation theory as applied to polymer crystallization from the melt and (2) a considerable body of knowledge that has been amassed concerning the dimensions of polymer chains in the unperturbed state as expressed in terms of the characteristic ratio. A comprehensive discussion of the latter, to which we shall repeatedly refer, has been given by Flory.[8] The present treatment appears to give an essentially quantitative molecular picture of σ and, in addition, shows prospects of allowing C_∞ to be determined for polymer melts by crystallization studies. A preliminary discussion outlining the relationship between σ and C_∞ has been published elsewhere.[9]

II. Theory

It is assumed at the outset that σ is closely related to the reduction in entropy connected with the localization of a polymer chain in proximity to the crystal surface prior to its complete crystallographic attachment as a "first" stem to that surface. That σ is generated by such a rate-determining localization process was suggested in 1976[10] to explain the low value of the apportionment factor ψ required to prevent the prediction of a "δ catastrophe", an effect that has never been detected in isothermal crystallization directly from the bulk melt. (Recall that the "low-ψ" form of nucleation theory is the basis of eqs 1a–c.) A ψ value near zero clearly implied that very little of the free energy of fusion $\psi a_0 b_0 l(\Delta f)$ had been attained at the instant in time that σ was generated as the rate-determining first ($\nu = 1$) stem was poised ready for crystallographic attachment—the actual attachment of the first stem as a whole, yielding the large free energy of fusion $(1 - \psi)a_0 b_0 l(\Delta f)$, with $\Delta f = (\Delta h_f)(\Delta T)/T_m$, was pictured as occurring in a rapid subsequent step.[1] Though not developed at the time into a theory for σ, we shall adhere to this model in what follows. Meanwhile, we note that Turnbull and Spaepen[11] employed a "negentropic" model to explain the variation of the scaled interfacial tension $\bar{\alpha}_{\mathrm{TS}}$ with chain length for n-alkanes. They emphasized the role of the onset of "segmental" behavior in the settling down to a constant value of the scaled interfacial tension with increasing chain length. If we note that σ is directly proportional to $\bar{\alpha}_{\mathrm{TS}}$ through a relation to be given later, their work is clear on the point that σ is of largely entropic origin and that the segmental character of real chain systems is involved in determining its value. In light of the above, we inferred at an early stage of our work that, without requiring crystallographic attachment, the surface (through a localization process) induced the segmental character of the polymer chains to manifest itself in the rate-determining step wherein σ was generated. In any event, there is a background for our initial assumption.

Define state i as the random coil liquid (melt) of a high molecular weight linear polymer. Essential here is Flory's insight that a molecule in such a melt should have "unperturbed" dimensions;[12] i.e., in the notation of polymer science, a molecule in a polymer melt is to be treated as being in a "Θ" solvent consisting of its neighbors. Were this untrue, the theory to be presented would fail. Further, define state ii as representing a situation where a section of molecule, later to become the first ($\nu = 1$) stem of length $l = l_g{}^*$ that subsequently initiates the rapid development of a new surface layer, is "localized" under the influence of the crystal surface so that it has lost a certain fraction of its entropy but is not yet attached, except perhaps at a few points, to the surface in the crystallographic sense. (In earlier work on the development of the "low-ψ" nucleation model, a section of molecule in what is here denoted state ii was described as being in a condition rather similar to that of physical adsorption;[10] we shall return to this point in section IV.) Attainment of state ii is the rate-determining step in the formation of the first stem and does not involve any significant degree of free energy of fusion. Observe that this is consistent with the "low-ψ" model noted previously. Defining S_{i} as the entropy of a portion of the molecule of contour length $l = l_g{}^*$ in the random coil melt and S_{ii} as the entropy of the localized section of similar length, one has the corresponding free energy change

$$\Delta G^*_{\mathrm{i}\to\mathrm{ii}} = -T(S_{\mathrm{ii}} - S_{\mathrm{i}}) = -T(\Delta S_{\mathrm{i}\to\mathrm{ii}}) \tag{3}$$

where it is understood that $\Delta S_{\mathrm{i}\to\mathrm{ii}}$ is proportional to l. The entropy is taken to include both a configurational contribution and that of the form E/T resulting from the conversion of some of the bonds in metastable rotational positions to stable ones, e.g., gauche to trans in PE. It is the quantity $\Delta G^*_{\mathrm{i}\to\mathrm{ii}}$ that will determine the lateral surface free energy.

Though unrelated to the calculation of σ, it is to be noted that the "poised" section of molecule in state ii, with its lowered entropy, in a subsequent fast (not rate-determining) step attaches crystallographically to the substrate in the ii → iii process, thereby giving up essentially the full free energy of fusion. The formation of the first stem is now complete (state iii) and the relatively rapid substrate completion process, which involves the work of chain folding but no new lateral surface, begins at the "niche" on either side of the first stem.[1]

Consider now the entropy change $\Delta S_{\mathrm{i}\to\mathrm{ii}}$. This will depend on the segmental character of the polymer chain, the effect of which we introduce through the use of the characteristic ratio C_∞. This parameter is ordinarily employed to describe the unperturbed dimensions (Θ conditions) of a polymer chain[8] and is commonly determined from measurements in dilute solution and/or evaluated by means of the rotational isomeric state (RIS) model. In simple terms, this quantity gives the increased size (mean-square end-to-end distance) of a molecule resulting from the effect of fixed bond angles and of the potential energy barrier system affecting rotation about bonds as compared to the lesser size characteristic of a random flight "freely-jointed" model (by definition, C_∞ for the freely-jointed chain is unity). Subsequently, we shall scale the total entropy of stem addition according to C_∞^{-1} to approximate the entropy change associated with the i → ii process.

For vinyl polymers, including PE, C_∞ is defined as[8]

$$C_\infty \equiv \langle r^2\rangle_0/nl_b^2 \tag{4}$$

where $\langle r^2\rangle_0$ is the mean-square end-to-end distance of a long polymer chain (with large n) in the unperturbed state, n the number of carbon atoms in the chain, and l_b the C–C bond length (1.54 Å). The case $C_\infty = 1$, denoted "freely jointed" in the polymer literature, corresponds exactly to a random flight problem with jump distance l_b in a simple system. In the opposite extreme of a rigid or nearly rigid rod (the latter rather resembling some liquid crystalline polymers), C_∞ is large and approaches n since here $r^2 \cong n^2l_b^2$.

To introduce a quantitative notion of the effect of segmental behavior in the rate-determining activated complex, it is postulated that

$$\Delta S_{i\to ii} = -\Delta S_f/C_\infty \tag{5}$$

in which ΔS_f is the observed entropy of fusion $\Delta h_f/T_m$ and C_∞ is the characteristic ratio of the polymer chain in the melt. Qualitative reasons for initially selecting eq 5 as a working hypothesis were given in an earlier publication.[9] Detailed insight relevant to the content of the scaling law expressed by eq 5 can be given in terms of partition functions.

We take the relevant partition functions to be as follows: (a) for state i, the random coil melt,[13] $Q_i = Z^{n-2} \cong Z^n$; (b) for state ii, the localized state (an ensemble of activated complexes) exhibiting only "segmental" behavior and thus a reduced number of configurations, $Q_{ii} = Z^{n(1-1/C_\infty)}$; and (c) for state iii, crystallographically attached stems in the stable state, $Q_{iii} = 1$. The symbol Z represents the partition function of the appropriate elementary chain unit. For the portion of chain of limited length l_g^* that makes up a single activated complex, the n above becomes n^*, the number of C atoms that comprises l_g^* (see later).

The origin of Q_{ii} and its identification as representing the "segmental" behavior of the activated complex can be understood by defining the quantity $n(l_{seg} - l_b)/l_{seg}$ as the number of elementary chain units exhibiting such behavior where the average segment length l_{seg} is $C_\infty l_b$. The term $-l_b$ represents the part of the chain at the end of each segment in the complex that is inactivated (localized) by the surface and l_{seg} is the part that is active. The foregoing gives the number of chain units exhibiting active segmental behavior as $n(1 - 1/C_\infty)$, which leads directly to Q_{ii} above. (Definition of l_{seg} using the concept of the "equivalent chain" also leads to Q_{ii}.[14]) The quantity l_{seg} is to be regarded as an average value subject to statistical fluctuations. Active segmental behavior occurs when $l_{seg} > l_b$, i.e., when $C_\infty l_b > l_b$. In the case of polymers where C_∞ is defined as in eq 10 to follow, we would define l_{seg} as $C_\infty l_{unit}$ and replace $-l_b$ by $-l_{unit}$; this leads again to $n(1 - 1/C_\infty)$ and thence to the same Q_{ii} as given above.

For the i → ii process where $Q_i/Q_{ii} = Z^{n/C_\infty}$, one has

$$-\Delta S_{i\to ii} \equiv k \ln (Q_i/Q_{ii}) + kT\frac{d \ln (Q_i/Q_{ii})}{dT} = \frac{n}{C_\infty}k \ln Z + \frac{nkT}{C_\infty}\frac{d \ln Z}{dT} \tag{6a}$$

The first term on the right-hand side represents the configurational entropy change associated with the localization step and the second gives the E/T component, i.e., the effect of converting a fraction of the bonds from metastable rotational states to stable ones. With $Q_i/Q_{iii} = Z^n$, the total entropy change from the random coil melt → crystallographically attached stem is simply

$$-\Delta S_{i\to iii} = \Delta S_f = nk \ln Z + nkT\frac{d \ln Z}{dT} \tag{6b}$$

Recall here that n above is replaced by n^* for a single complex consisting of a section of chain of contour length l_g^*. Equations 6a and 6b yield eq 5, thus completing the required derivation.

At this point it is essential to comment in a general way on the work required to form the activated complex from the random coil melt. By examination of eqs 6, it is seen that for $C_\infty > 1$ the entropy of the activated complex, state ii, lies between that of the melt (state i) and the crystal (state iii). If, in ignorance of the properties of the "low-ψ" nucleation model, we had let $\Delta G_{i\to ii} = \Delta H_{i\to ii} - T(\Delta S_{i\to ii})$, the free energy of the (virtual) activated state would have also been intermediate between that of state i and state iii and thus yield work as it was formed—this is, of course, not realistic for an activated state. But the i → ii entropy change in the "low-ψ" model is *not* accompanied by any significant heat of fusion $\Delta H_{i\to ii}$, so the actual activated complex is (as required) less stable than the melt and requires the work $\Delta G^*_{i\to ii} = -T(\Delta S_{i\to ii})$ for its formation as in eq 3. A simple analogy provides a helpful clarification. Imagine (in a hypothetical experiment) that one of the molecules embedded in a random coil melt is by some agency more or less "straightened". Such a molecule would have a lowered entropy with respect to the melt but require significant net work to form. In our problem, a section of polymer molecule in a close approach to the surface (but without crystallographic contacts and the concomitant heat and free energy of fusion) is in effect stiffened and behaves in an analogous manner with respect to its lowered entropy coupled with a substantial work of formation. Virtually the full free energy of fusion appears in the rapid ii → iii step, which yields a crystallographically attached first stem.

Provided that eq 5 is correct, which will prove to be the case, the partition function for the activated complex, state ii, will serve to lead to a specific molecular picture of that complex. Pending experimental verification of eq 5, further discussion of the activated complex is deferred until section IV. It remains to apply the scaling concept expressed in eq 5 (acting through eq 3 to give $\Delta G^*_{i\to ii} = T\Delta S_f/C_\infty$) to the problem of calculating σ. This will provide a test of the formulation under a variety of conditions, including polymers with rather restricted rotations as well as others that exhibit nearly free rotation about certain skeletal bonds.

In units appropriate for application to nucleation theory for a vinyl polymer, the foregoing leads to the free energy change associated with the i → ii process:

$$\Delta G^*_{\mathrm{i}\to\mathrm{ii}} = -T\Delta S_{\mathrm{i}\to\mathrm{ii}} = T\Delta S_f/C_\infty = T\left[\frac{\Delta h_f}{T_m}a_0b_0l_bn^*\right]\frac{1}{C_\infty} \quad (7)$$

where Δh_f is in erg cm^{-3} and a_0, b_0, and l_b are in cm. The "length" of the nucleating first stem is expressed here as l_bn^*, since l_b is the length measure per C atom employed in defining C_∞ for vinyl polymers. As indicated earlier, n^* is the number of C atoms making up l_g^*. On the other hand, in the "low-ψ" model of conventional nucleation theory the free energy of activation for addition of the first stem is[1]

$$\Delta\phi_1^* = 2b_0\sigma l_un^* \quad (8)$$

where l_un^* corresponds to the initial lamellar thickness (nucleus length) l_g^* and l_u is the "projected" length in the chain direction. (An additional term $-\psi a_0b_0l_un^*(\Delta f)$ is omitted in eq 8 in accord with the "low-ψ" model.) In the conventional presentation of nucleation theory, $2b_0\sigma l_un^*$ is the work required to form the two new exposed lateral surfaces, each of area $b_0l_un^*$. This may be regarded as a defining relationship for σ. (As employed here, l_u is the mean length in the crystal appropriate to each carbon atom in the chain backbone; except for PE, it is to be distinguished from l_{mu}, which is the corresponding length of the elementary monomer unit, e.g., CH_2CHPh– for isotactic polystyrene (i-PS).)

One obtains the expression for σ by equating eq 8 and eq 7. The result, applicable to vinyl polymers, is[9]

$$\sigma_{\mathrm{theor}} = T\left(\frac{\Delta h_f}{T_m}\right)\frac{a_0}{2}\left(\frac{l_b}{l_u}\right)\frac{1}{C_\infty} \cong \Delta h_f\left(\frac{a_0}{2}\right)\left(\frac{l_b}{l_u}\right)\frac{1}{C_\infty} \quad (9)$$

the right-hand approximation holding near the melting point where we shall apply it. For such polymers, l_b is 1.54 Å, but l_u (the average projection of the C–C bond along the chain axis) varies for different vinyl polymers. Polymers of this type generally exhibit C_∞ values as determined from chain dimensions in dilute Θ solvents in the range of about 5 to slightly greater than 10.[15] Equation 9 immediately puts σ in the correct range for vinyl polymers. As will be shown shortly, eq 9 is essentially quantitative for the two vinyl polymers PE and i-PS, where data are available to test it.

In the case of other polymers, such as certain polypeptides and high-melting polyesters, the characteristic ratio is defined as[8]

$$C_\infty \equiv \langle r^2\rangle_0/xl_{\mathrm{unit}}^2 \quad (10)$$

Here, l_{unit} represents the length of a relatively rigid residue consisting of a number of backbone atoms which can be treated collectively as a "virtual" bond (usually corresponding to the monomer unit) and x is the number of such compound units in the long chain. The molecular motions determining C_∞ occur at either end of the "virtual" bond. Following the foregoing procedure, it is readily found from setting $2b_0\sigma x^*l_{\mathrm{unit}}$ equal to $T(\Delta h_f/T_m)a_0b_0x^*l_{\mathrm{unit}}/C_\infty$, where x^* is the number of units corresponding to l_g^*, that

$$\sigma_{\mathrm{theor}} = T\left(\frac{\Delta h_f}{T_m}\right)\frac{a_0}{2}\frac{1}{C_\infty} \cong \Delta h_f\left(\frac{a_0}{2}\right)\frac{1}{C_\infty} \quad (11)$$

This expression will be found most useful in dealing with the high-melting polyesters poly(L-lactic acid) (PLLA) and poly(pivalolactone) (PPVL). Each contains the C–O–C linkage in which nearly free rotation occurs at a fixed angle about the O–C bond thereby sweeping out a cone, the rest of the unit being comparatively rigid owing to the effect of the adjacent methyl side groups. The theoretical value of C_∞ for free rotation about a tetrahedral bond is exactly 2, and close to this for the O–C linkage; the C_∞ determined for PLLA from dilute solution measurements is 2.1 ± 0.3, corresponding to a theoretical value calculated by RIS methods from chain structure of 2.13.[16] This low value of C_∞ will subsequently prove through eq 11 to explain the σ value of PLLA. In parallel, the unusually large σ of 28.7 erg cm^{-2} found for PPVL from melt crystallization experiments will prove to be understood most readily in terms of a low C_∞ associated with nearly free rotation about the O–C bond.

III. Comparison of Theory with Experiment

The theory for σ is tested in the following manner: From melt crystallization rate studies one obtains a value for the product $\sigma\sigma_e$ from K_g. Melting point depression or other experiments yield a value for σ_e. Division of the two gives a value for σ_{expt} from which one can compute C_∞ via eq 9 or 11. Comparison is then made with the value of C_∞ cited in the literature as obtained from studies of chain dimensions in dilute Θ solvents. These will be denoted, respectively, "C_∞ from σ_{expt} for melt" and "C_∞ from chain dimensions in dilute Θ solvent". Should these values be similar for a given polymer, our approach concerning the origin and magnitude of σ would be supported. Also to be given are the values of α_{LH} as calculated with eq 2 with each σ_{expt} to validate the concept that this empirical parameter does indeed depend on chain structure. Subsequently, $\bar{\alpha}_{\mathrm{TS}}$ will be defined and calculated for the same purpose.

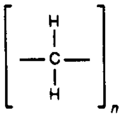
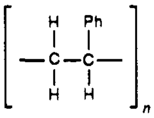
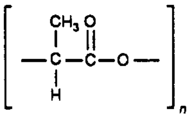
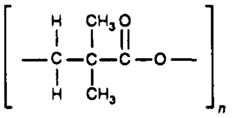
The nature of the information required to obtain σ_{expt} is evident from Table I. The most important issues are the following: (1) a K_g based on the rate of crystallization *from the melt* must be available for which the regime is known; (2) it is best to know the growth face for melt-formed crystals so that a proper value of b_0 may be employed with K_g to obtain an accurate value of $\sigma\sigma_e$ or, alternatively, to know that because of symmetry $\sigma\sigma_e$ is insensitive to the choice of b_0; (3) a value for the heat of fusion is required; and (4) a reliable value of σ_e must be available from melting point depression studies or from a fit of $l_g^*(T)$ as given by eq 1c. (The determination of σ_e may be carried out on either melt- or solution-crystallized specimens.) The polymers listed in Table I meet these requirements. We would add to the above that a_0 is needed in order to compute C_∞ from σ_{expt}, but this generally is available if b_0 is known.

The procedure and requirements mentioned above are those necessary to validate the theory of σ. As will be shown subsequently, it is possible to employ K_g together with either σ_e or q to find C_∞ directly without the step of first evaluating σ; for this procedure the heat of fusion is not required nor is a definite knowledge of the growth face needed.

Comment is required concerning the input data in Table I that are employed to calculate the σ_{expt} values cited therein. In some cases, the σ_{expt} values listed are slightly different from those given in earlier references because of new information that has appeared in the interim. The objective was to obtain σ_{expt} values that were accurate to within approximately ±10% (or better): it is believed that this has been achieved.

(A) Input Data for Vinyl Polymers. PE. The input data for $\sigma\sigma_e$ are based on the now standard K_g value listed which covers both regimes I and II[17] and the lattice parameter b_0 valid for a {110} growth face; the values for a_0 and a_0b_0 are those generally accepted. The σ_e of 90 erg cm^{-2} listed is a commonly used value based on T_m' vs

Table I
Input Data[a] and Value of σ_{expt}[b]

	polymer			
	PE	i-PS	PLLA	PPVL
chain structure	 $\left[-\overset{H}{\underset{H}{C}}-\right]_n$	 $\left[-\overset{H}{\underset{H}{C}}-\overset{Ph}{\underset{H}{C}}-\right]_n$	 $\left[-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\Vert}{C}}-O-\right]_n$	 $\left[-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\Vert}{C}}-O-\right]_n$
T_m, °C	145.5	242	206.8	269
Δh_f, J cm^{-3}	280	91.1	120	183
a_0b_0, Å^2	18.88	69.2	30.86	44.7
growth face	{110}	{300}	{110} and {200} assumed	$\{1\bar{2}0\}$
a_0, Å	4.55	10.946	5.97, both faces	7.793
b_0, Å	4.15	6.322	5.17, both faces	5.736
l_{mu}, Å	1.273	2.217	2.780	3.015
l_b/l_u	1.54 Å/1.273 Å = 1.21	1.54 Å/1.1085 Å = 1.39		
K_g, deg^2	$K_{g(I)} = 2K_{g(II)} = 1.91 \times 10^5$	$K_{g(II)} = 1.20 \times 10^5$	$K_{g(I)} = 2K_{g(II)} = 4.87 \times 10^5$	$K_{g(III)} = 2K_{g(II)} = 8.59 \times 10^5$
$\sigma\sigma_e$, erg^2 cm^{-4}	1063	232	813	1748
σ_e, erg cm^{-2}	90	35	53	61
$\sigma_{expt} = \sigma\sigma_e/\sigma_e$[b]	**11.8**	**6.63**	**15.3**	**28.7**

[a] Sources for the data contained herein are cited in the text. [b] Based on known errors in the input data, each σ_{expt} is believed to be correct to within about ±10%. See text for details.

$1/l$ plots and falls well within the range 93 ± 8 erg cm^{-2} so determined.[1] Sources for the heat of fusion are given in ref 1.

i-PS. The $\sigma\sigma_e$ value in Table I is based on the $K_{g(II)}$ listed which derives from the careful spherulite growth rate data (regime II) of Suzuki and Kovacs[1,18] as calculated with the b_0 noted, the latter conforming to the growth face in the melt being {300}.[19] The σ_e value is from a fit of $l_g^*(T)$ as given in ref 1, p 580. The source of the heat of fusion is given in ref 1. Earlier, a less accurate value of $\sigma \cong 7.6$ erg cm^{-2} was based on eq 2 with α_{LH} set at 0.1. The new value of σ_{expt} of 6.63 erg cm^{-2} deduced in Table I is to be preferred.

(B) Input Data for High-Melting Polyesters. PLLA. The K_g given in Table I derives from the study of spherulite growth rates by Vasanthakumari and Pennings,[20] wherein both regime I and regime II growth were observed. The cross-sectional area is from the data of Kalb and Pennings,[21] who determined the unit cell to be orthorhombic (pseudohexagonal). In this symmetrical lattice, the ultimate values of $\sigma\sigma_e$ derived from K_g and the value of σ_{expt} based thereon are insensitive to any reasonable choice of growth face as Table I shows. The σ_e listed was deduced first from the observation of Kalb and Pennings[21] that a sample crystallized from dilute solution at 363 K, corresponding (with dissolution temperature $T_d° = 399.5$ K) to an undercooling $T_d° - T$ of 36.5 K, exhibited a thickness of 120 Å. To determine σ_e, it is assumed that this (unthickened) crystal had a disordered layer l_a = 10–12 Å thick on each fold surface giving a stem length of 98 ± 2 Å, which we set equal to l_g^* in eq 1c with a $\delta \cong kT/b_0\sigma$ of ~7 Å to find that σ_e is 50 erg cm^{-2}. (Such a crystal has a "degree of crystallinity" of 0.82, which is fully typical of unthickened single-crystal preparations.) The second way of establishing a value of σ_e is based on melting point depression. Here we take advantage of the fact that the T_m' vs T_x plot (Figure 6 of Kalb and Pennings[21]) exhibited a γ of 2.00, showing that the crystals had thickened during the melting run by a factor of 2—i.e., they were now ~240 Å thick; the $T_m'-T_x$ plot at T_x = 363 K indicates a melting point depression of $\Delta T'$ = 17.0 K. Inserting this value in the melting point depression of $\Delta T' = 2\sigma_e T_d°/\Delta h_f(l - 2l_a)$, one finds, with l = 240 Å and retaining the same l_a range as before, that σ_e comes to 56 erg cm^{-2}. The mean value of the two estimates may be cited as 53 ± 4 erg cm^{-2} (Table I). This value supersedes that of Kalb and Pennings ($\sigma_e \cong 75$ erg cm^{-2}) inasmuch as neither the disordered layer nor the existence of a δ was considered.

Table II
Comparison of Theory and Experiment[a]

polymer	work of chain folding q, kcal mol^{-1}	α_{LH}	$\bar{\alpha}_{TS}$	C_∞ from σ_{expt} for melt	C_∞ from chain dimens in dil Θ solvent
		Vinyl Polymers			
PE	4.90	0.097	0.146	**6.53**[b]	**6.7 ± 0.3**
i-PS	6.97	0.088	0.136	**10.45**[b]	**10.5**
i-PP	5.75			**5.7**[c]	**5.7**
		High-Melting Polyesters[e]			
PLLA	4.71	0.230	0.290	**2.34**[d]	**2.1 ± 0.3**[f]
PPVL	7.86	0.234	0.305	**2.49**[d]	

[a] Numbers cited for q, α_{LH}, $\bar{\alpha}_{TS}$, and C_∞ from σ_{expt} for melt are based on central values of the input data. These results are estimated to be correct to within about ±10% except for i-PP, where error is ±15% (see text). [b] From eq 9. [c] From eq 13. Note that eq 13 gives C_∞ for the melt directly without evaluating σ. See section IV-C for details. [d] From eq 11. [e] With the use of α_{LH} = 0.10 to estimate σ = 6.38 erg cm^{-2} for the low-melting, PE-like polyester PCL, eq 9 yields a C_∞ of 6.3 for the melt; the C_∞ from chain dimensions in dilute Θ solvent is 5.9. See section IV-A for details. [f] Experimental result. Theoretical calculations give C_∞ as 1.92 for strictly free rotation about the O–C bond and 2.13 when Coulombic interactions are included.[16]

PPVL. Full details concerning the determination of K_g, the growth face, and the correct a_0 and b_0 are given in the work of Roitman et al.,[6] which also contains the source for the Δh_f value cited in Table I. Spherulite growth rate studies covered both regime II and regime III. The fold surface free energy σ_e was determined by the T_m'–$1/l$ method as reported by Marand and Hoffman.[7]

(C) Direct Comparison of C_∞ from σ_{expt} for Melt and C_∞ from Chain Dimensions in Solution. The comparisons of theory and experiment for PE, i-PS, and PLLA are given in Table II. The "C_∞ from σ_{expt} for the melt" values shown were calculated from the σ_{expt}, Δh_f, and a_0 data in Table I according to eq 9 or 11 as appropriate. The "C_∞ from chain dimensions in dilute Θ solvent" data shown for comparison are from the following sources: (1) the value for PE is from a tabulation by Flory,[8] who elsewhere in the same source[22] stated the error limits noted; (2) the value given for i-PS is from the tabulations of Kurata et al.;[23] and (3) the C_∞ for PLLA is from previously unpublished measurements by Tonelli and Flory cited in ref 16. No C_∞ value from chain dimensions in a Θ solvent is available for PPVL. Therefore, the value of C_∞ from σ_{expt} given in Table II for PPVL must for the time being stand as a prediction. However, the similarity of the chain structure to that of PLLA, together with the similarity of the α_{LH} values for the two, imply that PPVL will have a C_∞ similar to, but perhaps slightly larger than, that of PLLA. This similarity will be supported further by the $\bar{\alpha}_{\mathrm{TS}}$ data to be developed below. We note here a tentative theoretical estimate of C_∞ for PPVL[24] which is much higher than our predicted value.

In the event, it is clear that the theory relating σ to C_∞ through eqs 9 and 11 is essentially quantitative for PE, i-PS, and PLLA and likely so for PPVL. At the same time it is evident that eq 5 adequately represents the state i → ii entropy change; also the combination of eq 3 with eq 5 as expressed in eq 7 is verified. We estimate the results for C_∞ from σ_{expt} for PE, i-PS, and PLLA to be correct to within about ±10%; even if, for some currently unforseen reason, the error were to turn out to be twice as large, the theory for σ could still be regarded as having a substantive basis. It will be shown in due course that acceptable C_∞ values can be obtained for the melt state of isotactic polypropylene (i-PP) and of poly(ϵ-caprolactone) (PCL) which further support the validity of eqs 3 and 5.

(D) Comparison of Empirical Expressions Related to σ. Turnbull and Spaepen[11] earlier had developed a "scaled interfacial tension" parameter, originally denoted by them $\bar{\alpha}_1$, which for convenience we write in the form[25]

$$\bar{\alpha}_{\mathrm{TS}} = \frac{\sigma}{(\Delta h_{\mathrm{f}})[a_0 b_0 l_{\mathrm{mu}}]^{1/3}} \qquad (12)$$

where $a_0 b_0 l_{\mathrm{mu}}$ represents the crystalline volume of the elementary monomer repeat unit. Thus, l_{mu} is 1.273 Å for the $-CH_2-$ unit in PE, 2.167 Å for the $-CH_2CHPh-$ unit in i-PS, and so forth (Table I). Values of $\bar{\alpha}_{\mathrm{TS}}$ computed from the data in Table I are given in Table II. The α_{LH} and $\bar{\alpha}_{\mathrm{TS}}$ results clearly imply that PLLA and PPVL are very similar with respect to the origin of σ and, further, that these high-melting polyesters stand in a class distinct from the vinyl polymers. The two empirical parameters α_{LH} and $\bar{\alpha}_{\mathrm{TS}}$ will be discussed subsequently in greater detail both with respect to their application to other polymers and to the fundamental meaning that attaches to them in the light of the present treatment wherein σ depends on C_∞^{-1}.

IV. Discussion

(A) The Lateral Surface Free Energy and Chain Structure. Perhaps the simplest case to understand is that of the high-melting polyesters. In these the ester groups are interspersed with sections of chain ("virtual" bonds of length l_{unit}) which act in a rather rigid manner because of the pendant CH_3 groups. The intervening ester linkage exhibits nearly free rotation about the O–C bonds, leading to a small mean-square end-to-end distance only about 2.0–2.5 times that of a "freely-jointed" chain, i.e., with $C_\infty \sim 2.0$–2.5 as based on l_{unit}. The nearly-free rotation effect thus leads, through the relationship of eq 5, to a quite large entropy of localization and thence, through eq 11, to a large value of the lateral surface free energy σ. As noted earlier, eq 11 appears to be essentially quantitative for PLLA for which the C_∞ from σ and from chain dimensions are both known. The only way to explain the strikingly high σ of PPVL would appear to be to adopt a parallel view based on the similarity of its chain structure to that of PLLA. It would be most valuable to have a value of C_∞ for PPVL from direct chain dimension measurements to compare with that given in Table II: the σ_{expt} for this polymer is as well founded as any in the literature, so a firm test of the theory would be provided.

At this juncture, it is well to bring up the case of a low-melting polyester which, unlike PLLA and PPVL, has a considerable run of $-CH_2-$ units interspersed between the ester linkages and no methyl side groups adjacent to the ester linkage (or elsewhere) to stiffen the chain and create a long "virtual" bond between the ester linkages. Here, we would anticipate behavior closer to that of PE. Consider PCL, which has the melting point $T_{\mathrm{m}} = 76.1$ °C $= 349.3$ K and the chain structure $-[CH_2CH_2CH_2CH_2CH_2COO]-$. Spherulite growth rates (regime II) have been measured,[26,27] and the product $\sigma\sigma_{\mathrm{e}}$ is close to 645 erg^2 cm^{-4}. No independent value of σ_{e} is available, so we proceed by estimating σ with eq 2 using $\alpha_{\mathrm{LH}} \cong 0.1$ as for a vinyl polymer and note the outcome. With[26] $\Delta h_{\mathrm{f}} = 1.48 \times 10^9$ erg cm^{-3} and $a_0 b_0 = 18.6$ Å^2, we find $\sigma = 6.38$ erg cm^{-2}. If this is now employed with eq 9 using $a_0 = 4.504$ Å and $l_{\mathrm{b}}/l_{\mathrm{u}} \sim 1.2$, the result is that the C_∞ from σ is 6.3 ± 0.9, the error limit here being set at ±15% to account for the uncertainty in α_{LH}. The same result can be obtained directly by way of eq 15 to be given later. This C_∞ is similar to that of PE and is in reasonable agreement with the C_∞ from chain dimensions of 5.9 ± 0.3 as given by Jones et al.[28] The work of chain folding comes to 5.4 kcal mol^{-1}, which, as expected, is similar to that of PE (Table II). (This estimate of q for PCL is close to that obtained by other investigators[26,27] beginning with the value of σ deduced from the Thomas–Stavely equation[5] with $\alpha = 0.1$.) Besides providing support for the proposed relationship between C_∞ and σ, these results also imply that PCL is indeed to be classed as a modified vinyl polymer with the α_{LH} and C_∞ characteristic thereof. Had we employed the α_{LH} of ~ 0.23 for high-melting polyesters in this case, we should have found $C_\infty = 2.7$ and an equally implausible low value for the work of chain folding. The foregoing clears up a point that was noted by Goulet and Prud'homme,[26] who rightly questioned the applicability of $\alpha_{\mathrm{LH}} \sim 0.23$ to PCL. It would be useful to have an independent value of σ_{e} for PCL so that a more precise value of σ_{expt} could be determined from $\sigma\sigma_{\mathrm{e}}$ and a more definitive comparison of theory and experiment made.

Consider now the vinyl polymers PE and i-PS. In each there is a barrier system for rotation about each bond characterized by gauche and trans sites of differing potential energy; there is no free rotation about any bond nor any semblence thereof. The bond angles and potential energy minima restrict the local configurations (in a statistical mechanical sense), thereby rendering C_∞ large; i.e., for a given large number of skeletal –C– units, the mean-square end-to-end distance is much larger than it would be for a "freely-jointed" chain. With this one must expect a low entropy of localization as given by $\Delta S_{\mathrm{i}\to\mathrm{ii}} = -\Delta S_{\mathrm{f}}/C_\infty$. With $\Delta S_{\mathrm{i}\to\mathrm{ii}}$ and thus σ varying as C_∞^{-1}, the generally smaller σ's characteristic of this class of polymers, as compared with the high-melting polyesters, are readily understood.

In all of the above cases, the effect of chain structure on σ is embodied mainly in C_∞. The other factors contributing to the variation of σ are given explicitly in eqs 9 and 11 and include a_0, $l_{\mathrm{b}}/l_{\mathrm{u}}$, and Δh_{f}.

Despite our comparison of theory and experiment in terms of considering the match of C_∞'s by the two methods noted in Table II, sight should not be lost of the fact that the results clearly show (for PE, i-PS, PPLA, and likely PPVL and PCL) that a viable theory for σ has been developed. Thus, given reliable C_∞ values from measurements in dilute solution we could employ these in eq 9 or

11 to predict the σ values relevant to melt crystallization experiments with reasonable accuracy. It is evident that the σ of nucleation theory is indeed of entropic origin as postulated and is thereby sensitive to the segmental behavior of the polymer chain in the activated complex as described by C_∞ and as established by the chain structure. In addition, the results imply that a relatively close approximation to unperturbed dimensions prevails in these polymer melts, including the somewhat subcooled state.

The theory for σ given in eqs 9 and 11 does *not* apply to crystallization from subcooled dilute solution where the σ in the product $\sigma\sigma_e$ can hardly be considered to be related to a C_∞ representing unperturbed dimensions—a polymer chain in a subcooled dilute solution is rarely in a "Θ" environment. For PE crystallized from the melt, σ is close to 11.8 erg cm^{-2}, but from dilute n-tetradecanol, n-hexadecane, and xylene solutions[29] the σ values deduced[30] are on the order of 5.8–7.4 erg cm^{-2}, indicative of a considerable departure from Θ conditions. Accordingly, we have repeatedly noted that the K_g employed to obtain $\sigma\sigma_e$ must be from *melt* crystallization studies. It is, however, permissable in the present treatment to employ a σ_e based on data from single crystals in either the presence or absence of solvent; the value of σ_e (and of q) is generally very similar in the two cases.

(B) Alternative Expressions for C_∞ from K_g. It is possible to obtain the characteristic ratio from K_g and either σ_e or q without reference to σ. By inserting eq 9 for σ into eq 1b, one finds directly that for vinyl polymers[9]

$$C_\infty = \frac{j(a_0b_0)(l_b/l_u)\sigma_e T_m}{2kK_g} = \frac{j(l_b/l_u)qT_m}{4RK_g} \tag{13}$$

where $j = 4$ for a K_g that represents regime I or III and $j = 2$ when K_g is for regime II. Here, q is the work of chain folding $2a_0b_0\sigma_e$ and R is the gas constant. Thus, to find C_∞ one does not need to know either the heat of fusion or the growth face index—the only lattice parameters required are the cross-sectional area a_0b_0 and the mean bond length projection l_u. So far as the calculation of C_∞ from melt crystallization is concerned, it is of considerable convenience not to have to know the growth face or the heat of fusion. But one still must know either σ_e or q. It is readily verified that eq 13 leads to the C_∞ values cited in Table II for PE and i-PS.

The corresponding expressions for polymers such as the high-melting polyesters are the same as eq 13 except that the factor l_b/l_u is deleted. Thus

$$C_\infty = \frac{j(a_0b_0)\sigma_e T_m}{2kK_g} = \frac{jqT_m}{4RK_g} \tag{14}$$

Calculations with eq 14 and the data of Table I for PLLA and PPVL give the C_∞ values listed in Table II.

(C) Other Polymers. Here we first discuss the case of i-PP through the use of eq 13 to find C_∞. This approach is particularly suitable in this instance since we are not certain of the growth face and therefore cannot determine σ with the desired precision. Following this we note other opportunities to check the theory.

In the case of i-PP, for which $T_m \cong 185$ °C, a K_g from melt crystallization studies of known regime is available[31] ($K_{g(III)} = 2K_{g(II)} \cong 3.3 \times 10^5$ K^2) but there is some uncertainty in the value of σ_e because of the variation of this quantity with the degree of tacticity as shown by Cheng et al.[32] For i-PP specimens varying in tacticity from 0.882 to 0.988, the T_m' vs $1/l$ plots show that σ_e falls in the range 58 ± 7 erg cm^{-2}. With $\sigma_e = 58 \pm 7$ erg cm^{-2}, $a_0b_0 = 34.3$ Å^2, and the K_g given above and noting that $l_b/l_u = 1.42$, it is found with eq 13 that C_∞ comes to 5.7 ± 0.7 for the i-PP melt, which is to be compared with the value of 5.7[15] found from dilute solution measurements. While perhaps not as definitive as, say, the case of PE where the question of tacticity is not involved, we consider this result for i-PP to be supportive of our theme (Table II).

With respect to high-melting polyesters, it has already been noted that firm crystallographic, rate of melt crystallization, and σ_e data are known for PPVL (Tables I and II) but an experimental value for C_∞ in dilute solution is not. The need for an independently-determined σ_e for the low-melting polyester PCL has already been noted. It is hoped that this paper will stimulate interest in determining the missing quantities for the polymers mentioned above as well as for other polymers susceptible to application of the theory.

(D) The Empirical Expressions α_{LH} and $\bar{\alpha}_{TS}$. By combining eq 9 with eq 2 one finds for vinyl polymers[9]

$$\alpha_{LH} = \frac{1}{2}\frac{(l_b/l_u)a_0}{(a_0b_0)^{1/2}}\frac{1}{C_\infty} = \frac{1}{2}\left(\frac{l_b}{l_u}\right)\left(\frac{a_0}{b_0}\right)^{1/2}\frac{1}{C_\infty} \tag{15}$$

Thus, according to the present approach, this useful parameter depends on C_∞^{-1} and known crystallographic factors only, the heat of fusion having canceled. For the high-melting polyesters, the factor l_b/l_u is removed. The presence of the factor C_∞^{-1} in eq 15 provides a major component of the long-awaited answer to the question of why α_{LH} is so small for the vinyl polymers and shows further the reason why α_{LH} is apt to vary from one class of polymer to another. Observe that if α_{LH} is known, together with the other parameters, eq 15 may be used to estimate C_∞ as was noted earlier in the case of PCL.

A similar type of result holds for $\bar{\alpha}_{TS}$. Thus, for vinyl polymers the new form is

$$\bar{\alpha}_{TS} = \frac{1}{2}\frac{(l_b/l_u)a_0}{(a_0b_0l_{mu})^{1/3}}\frac{1}{C_\infty} \tag{16}$$

As with α_{LH}, the factor l_b/l_u is deleted for materials such as the high-melting polyesters. Again, the heat of fusion vanishes, leaving only chain and lattice parameters. The upper bound for $\bar{\alpha}_{TS}$ (corresponding to $C_\infty = 1$) for the $-(CH_2)_n-$ system is ~0.954, and the corresponding bound for α_{LH} is ~0.633. In each case, the upper bound for σ is ~77.1 erg cm^{-2}. These bounds have significance for the behavior of short chains which is noted below.

(E) Dependence of $\bar{\alpha}_{TS}$ and σ on Chain Length. Up to this point we have dealt with chain-folded systems where l_g^* and thus n^* are generally large enough to treat the characteristic ratio as having close to its limiting value denoted C_∞. This approach must be modified when systems with a small nucleus length and correspondingly small n^* are considered. The magnitude of the characteristic ratio is in fact well-known to be a function of chain length and is in the general case denoted C_n, where n is the number of C atoms.[8] The value of C_n is unity for $n = 1$, rises rapidly with increasing chain length, and levels off asymptotically at high chain lengths to the limiting value C_∞. For example, theoretical calculations by Jernigan and Flory[33] for the $-(CH_2)_n-$ chain with the general RIS model give $C_1 = 1$, $C_{10} = 3.8$, $C_{25} = 5.4$, and $C_{100} = 6.3$, the last being a close approach to the limiting experimental value of 6.7, which represents the practical C_∞ for PE.

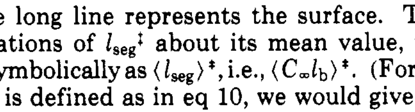
The foregoing leads to an interesting development: it implies through eqs 9 and 16, with C_∞ replaced by C_n, that for very short n-alkane chains both σ and $\bar{\alpha}_{TS}$ should be quite large for low n, fall rapidly with increasing chain length, and then approach their respective limiting values for large n corresponding to $C_\infty = 6.7$. For $n = 1$, i.e., $C_\infty = 1$, σ and $\bar{\alpha}_{TS}$ will have the large values noted earlier and then should rapidly decline with increasing n toward 77.1 erg cm^{-2}/6.7 $\cong$ 11.5 erg cm^{-2} and 0.954/6.7 $\cong$ 0.142, respectively. This is the general type of behavior exhibited by $\bar{\alpha}_{TS}$ reported by Turnbull and Spaepen[11] from their analysis of homogeneous nucleation experiments for the n-alkanes $n = 5$ to $n = 32$. For n-decane they found experimentally that $\bar{\alpha}_{TS} \cong 0.26$, whereas the calculated value is 0.954/3.8 = 0.25, with the figure 3.8 being the C_{10} of Jernigan and Flory. Similar examples beginning at C_5 could be cited. Furthermore, Turnbull and Spaepen give $\bar{\alpha}_{TS}$ as $\sim$0.15 at large n, yielding with eq 12 a σ of $\sim$12.1 erg cm^{-2}, which is to be compared to our estimate of 11.8 erg cm^{-2} for high molecular weight PE obtained by an entirely different method (Table I). Thus the behavior of σ and $\bar{\alpha}_{TS}$ with chain length appears to be in at least approximate accord with eqs 9 and 16 with C_∞ replaced by C_n. This interpetation and that of Turnbull and Spaepen based on the "negentropic" model share major features in common, namely, that the rapid fall and subsequent leveling off of σ and $\bar{\alpha}_{TS}$ with increasing n is a result of the segmental character of the $(-CH_2)_n-$ system and that σ is of basically entropic origin. A more detailed discussion will be given elsewhere.[34]

(F) Nature of the Activated Complex, State ii. Given that eq 5 for $\Delta S_{i\to ii}$ is validated by experiment (as are, therefore, the partition functions leading up to it), it is possible to comment on the nature of the activated complex wherein σ is generated. The partition function Q_{ii} permits a simple molecular picture of the activated complex to be constructed.

To give a schematic representation of the activated complex, we write Q_{ii} in its equivalent forms

$$Q_{ii} = Z^{n[\langle l_{seg}\rangle^{\ddagger} - l_{b(s)}]/\langle l_{seg}\rangle^{\ddagger}} = Z^{n[\langle C_\infty l_b\rangle^{\ddagger} - l_{b(s)}]/\langle C_\infty l_b\rangle^{\ddagger}} \qquad (17)$$

where the exponent is, of course, also equal to the fundamental relationship $n(1 - 1/C_\infty)$ or $n^*(1 - 1/C_\infty)$ for the case of a single complex. The entities (segments) with active energy states are marked with a dagger in eq 17 and those chain units of length l_b which do not contribute to the energy states in the complex owing to their localization by the surface are denoted $l_{b(s)}$. The partition function for the activated complex is clear on the point that it is the set of segments of mean length $C_\infty l_b$ that are active and that each of these segments has chain sections of mean length $l_{b(s)}$ at either end which are inactivated (localized) by the surface. This leads to the simple schematic representation for the complex



(18)

where the long line represents the surface. There will be fluctuations of $l_{seg}{}^{\ddagger}$ about its mean value, which we indicate symbolically as $\langle l_{seg}\rangle^{\ddagger}$, i.e., $\langle C_\infty l_b\rangle^{\ddagger}$. (For polymers where C_∞ is defined as in eq 10, we would give $\langle l_{seg}\rangle^{\ddagger}$ as $\langle C_\infty l_{unit}\rangle^{\ddagger}$ and $l_{b(s)}$ as $l_{unit(s)}$ in the diagram, and similarly with $\langle l_{seg}'\rangle^{\ddagger}$ defined[14] as $\langle C_\infty l_b{}^2/l_u\rangle^{\ddagger}$, where $l_{b(s)}$ is replaced by $(l_b{}^2/l_u)_{(s)}$.) However simplified it may be, eq 18 depicts in graphic form what is meant by "localization" as employed in this work and, at the same time, provides a natural explanation for why the activated complex so accurately reflects the value of C_∞ in melt crystallization experiments. In brief, the presence of the surface brings out the "segmental" character inherent in the polymer chain, the effective segment length being proportional to C_∞.

Whatever the precise details, it is evident from the present work that the crystal surface causes "segmental" behavior closely related to C_∞ to occur in the activated state. Independent support for the general concept of surface-induced structure in polymer chains is known. Though no connection with C_∞ was noted, recent stimulations of a short isolated chain on a cubic lattice in proximity to a surface, but devoid of crystallographic attachments thereto, have shown that the chain develops an enhanced degree of internal structure.[35]

Our last point relates to an earlier suggestion[10] that the section of molecule comprising the activated complex is in a state rather resembling that of physical adsorption. In the present context, this relates to the question of the nature of the contacts with the crystal substrate denoted $l_{b(s)}$ in diagram 18. These are very likely of the weak but nevertheless persistent van der Waals type that are typical of physical adsorption. This leads naturally to the minimal heat of fusion in the activated complex important in the present theory for σ and the estimation of C_∞ from K_g and is consistent with the low ψ employed in arriving at eqs 1a–c. In addition, a low ψ is required to interpret the rate of crystal growth for the extended-chain phase of certain pure n-alkanes,[36] $n = 192$ to $n = 246$. This implies that the contacts $l_{b(s)}$ in the $-(CH_2)_n-$ system are of the weak van der Waals type at normal undercoolings, again in agreement with the physical adsorption concept.

V. Summary and Conclusions

This work examines and exploits a hitherto unsuspected connection between nucleation theory as applied to melt-crystallized polymers on the one hand and the statistics of unperturbed polymer chain dimensions on the other. Herein we specifically relate the characteristic ratio C_∞, which is a structural parameter ordinarily employed to describe chain dimensions, to the thermodynamic property σ that plays a major role in determining the rate of surface nucleation in crystallization of polymers of high molecular weight from the melt. In brief, σ is associated with the work of entropic origin required to convert a section of polymer chain of length $l_g{}^*$ in the random coil melt state to a more ordered "segmental" condition as the crystal surface is closely approached, the mean segment length so induced being proportional to C_∞; the entropy change on such conversion varies as $C_\infty{}^{-1}$ with the result that σ also varies as $C_\infty{}^{-1}$. The theory for σ is extended (on a preliminary basis) to chains of low molecular weight. Formulas are also developed to estimate C_∞ for polymer melts directly from rate of crystallization and related data without reference to σ. Specific results and conclusions are as follows:

(1) The theory for σ was tested by taking well-authenticated values of σ (denoted "σ_{expt}") obtained from rate of melt crystallization and other crystal data and calculating C_∞. These were then compared with C_∞ values as determined by the usual methods for the same polymer in dilute Θ solvents. Agreement between the two radically different ways of determining C_∞ verifies the theory as given by eq 9 or 11. For the vinyl polymers, PE and i-PS, and the high-melting polyester, PLLA, where all required data are available, the results listed in Table II are encouraging. In these cases, two basic conclusions may be drawn: (a) the theory for σ is valid within the stated experimental error and (b) the molecules in the molten state of the polymers noted must have possessed a close approximation to unperturbed dimensions.

(2) The effect of chain structure on the lateral surface free energy σ is largely a result of the fact that σ varies as C_∞^{-1}. For the high-melting polyesters PLLA and likely PPVL, C_∞ is small and on the order of 2.0–2.5 because of nearly free rotation about the O–C ester bond, the remainder of the monomer acting as a stiff "virtual" bond. Through eq 11 this leads to the quite large σ values for these polymers listed in Table I. In contrast, the barrier system with trans and gauche positions of differing energies in the vinyl polymers leads to a relatively high C_∞ for PE, and especially i-PS, and the trend toward correspondingly lower σ values by eq 9 exhibited by these polymers including the PE-like case of PCL (Tables I and II).

(3) The current approach shows prospects of providing a new method of determining C_∞ for polymers in the melt state, which value will of course be essentially that applicable to the dilute Θ state as well. Basically, what is required is a K_g of known regime obtained from the rate of crystallization from the melt, a fold surface free energy σ_e obtained either from melting point depression–lamellar thickness studies or from a fit of $l_g{}^*(T)$ with eq 1c, and certain crystallographic constants (see eqs 13–15). It is not necessary to first find σ or to know either the identity of the growth face (except for eq 15) or the heat of fusion. These methods yield satisfactory values of C_∞ for the vinyl polymers PE, i-PS, and i-PP and for the polyesters PCL and PLLA, supporting the suggestion of essentially unperturbed dimensions in the melt in each case. A C_∞ is predicted for PPVL, but no experimental value from dilute solution measurements is available for comparison.

(4) A molecular basis is provided for the empirical expression for α_{LH} often employed to estimate σ. In the new formulation, α_{LH} depends on certain lattice parameters and varies as C_∞^{-1}. The value of α_{LH} is quite different for the vinyl polymers ($\sim$0.1) and the high-melting polyesters PLLA and PPVL ($\sim$0.23), most of the difference being attributable to differences in C_∞; the quantity $\bar{\alpha}_{\mathrm{TS}}$ behaves in a parallel manner (Table II). Thus, these empirical parameters are useful but clearly depend on chain structure as reflected by C_∞. Preliminary evidence suggests that α_{LH} is $\sim$0.1 for the low-melting polyester PCL which, unlike PLLA and PPVL, has a long run of $-CH_2-$ groups and no pendant methyl groups; PCL therefore behaves like PE with respect to both C_∞ and the work of chain folding.

(5) The capacity of the present treatment to produce reasonable values for C_∞ from the rate of melt crystallization, either directly from K_g and σ_e or through σ, shows that the kinetic theory of polymer crystallization as expressed in eqs 1 is on a solid footing. Given the present theory for σ and assuming the availability of work of chain folding calculations leading to reasonably accurate values of σ_e, it can be stated that all the nucleation parameters in K_g now have the potential of a quantitative explanation in molecular terms.

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(14) The definition of l_{seg} as $C_\infty l_{\mathrm{b}}$ is somewhat arbitrary but this does not affect the derivation of Q_{ii}. For example, one could follow an argument outlined by Flory (ref 8, p 12) to find the "equivalent chain" unit as $l'_{\mathrm{seg}} = C_\infty(l_{\mathrm{b}}{}^2/l_{\mathrm{u}})$, which comes to 6.7 × 1.53 Å^2/1.27 Å = 12.4 Å for PE. Then, defining the number of units exhibiting "segmental" behavior as $n[(l'_{\mathrm{seg}} - l_{\mathrm{b}}{}^2/l_{\mathrm{u}})/l'_{\mathrm{seg}}]$, one obtains $n[1 - 1/C_\infty]$, again giving Q_{ii} as shown in the text. The simpler form $l_{\mathrm{seg}} = C_\infty l_{\mathrm{b}}$ is sufficient for the present purposes.
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