The relationship of C_∞ to the lateral surface free energy σ: estimation of C_∞ for the melt from rate of crystallization data*

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The expression σ = constant × C_∞^{-1} is proposed for the lateral surface free energy that appears in polymer crystallization theory; C_∞ is the characteristic ratio of the polymer molecules in the melt and the constant consists of known parameters. Given C_∞, the theory predicts an accurate value of σ for polyethylene. It is shown that C_∞ for polyethylene in the melt state can be obtained directly from the nucleation rate constant K_g and the fold surface free energy σ_e ($C_{\infty(\mathrm{theor.})} = 6.53$ for melt, $C_{\infty(\mathrm{expt})} = 6.7$ from chain dimensions in dilute θ solvents). The corresponding results for i-polystyrene are $C_{\infty(\mathrm{theor.})} = 10.4_5$ for the melt and $C_{\infty(\mathrm{expt})} = 10.5$ from chain dimensions. The treatment clarifies the meaning of the empirical α parameter and shows prospects for being applicable to other polymers.

(Keywords: nucleation theory; lateral surface free energy; RIS model; characteristic ratio; segmental character; polymer melt; polyethylene, i-polystyrene)

For polymers, surface nucleation theory in its most useful 'low ψ' form has the rate of crystal growth from the melt varying with undercooling ΔT according to[1–4]

$$G \propto \exp[-K_g/T(\Delta T)f] \tag{1a}$$

where the nucleation rate constant K_g is

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

Here T_m is the melting point, f a factor that accounts for the dependence of the heat of fusion Δh_f on crystallization temperature T, b_0 is the layer thickness, k is Boltzmann's constant, $j = 2$ for regime II and $j = 4$ for regimes I and III growth, σ_e is the fold surface free energy and σ is the lateral surface free energy. The fold surface free energy is largely attributable to 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 chain in the crystal, but the molecular basis of σ is more obscure. Below is outlined an approach to this problem that leads to a theoretical expression for σ involving the characteristic ratio C_∞ of the rotational isomeric state (RIS) model[5], which approach in turn suggests a promising new way to determine C_∞ for polymer melts.

In accord with the general 'low ψ' nucleation model, invoked originally[6] to explain the common absence of the so-called 'δ catastrophe', we take σ to be generated during the rate-determining step at the instant in time that a section of molecule of length $l = l_u n = l_g^*$ is localized under the influence of the crystal surface in the overall process of forming the first stem that nucleates that surface. Here, l_g^* is the stem length associated with the mean kinetically determined[1] lamellar thickness, n is the number of backbone atoms therein and l_u is the projected length per atom along the chain axis. State i is defined as the random coil melt and state ii is defined as the 'localized' activated complex. The entropy change associated with this localization process, which involves little if any crystallographic attachment with its attendant heat of fusion in the 'low ψ' model[6], is postulated here to be given by $\Delta S_{\mathrm{i}\to\mathrm{ii}} = -\Delta S_f/C_\infty$ to account for the segmental behaviour of the chains in the activated complex; ΔS_f is $\Delta h_f/T_m$, the observed entropy of fusion, and C_∞ the characteristic ratio of the polymer chains in the melt. [Crystallographic attachment of the stem occurs in a subsequent rapid ii → iii process, the overall i → iii process representing ΔS_f]. The basic concept here is that the rate-determining activated complex, state ii, will by reason of its confined condition tend to exhibit stiffer chains ('segmental' behaviour) and thus have a lower number of allowed configurations as compared with the melt. The scaling factor C_∞^{-1} for $C_\infty > 1$ appropriately places the entropy of the complex between that of the melt and the crystal. A simple way to see one bound of the problem is to consider the case of the hypothetical completely flexible chain, i.e. the so-called 'freely jointed' model for which $C_\infty \equiv 1$; here confining the chain clearly involves virtually the entire configurational entropy, which is consistent with $\Delta S_{\mathrm{i}\to\mathrm{ii}} = -\Delta S_f/C_\infty$. By a parallel argument, a near-rigid rod for which $C_\infty \to n$, will require only a very small entropy change to attain the 'confined' or 'localized' condition, again in consonance with $\Delta S_{\mathrm{i}\to\mathrm{ii}} = -\Delta S_f/C_\infty$. Though not given here, it is possible to describe the effects noted above in terms of specific partition functions[7]. It suffices at this juncture to observe that the postulate for the form of $\Delta S_{\mathrm{i}\to\mathrm{ii}}$ will emerge as experimentally correct within quite narrow margins.

Recalling that state ii involves little or no actual heat of fusion, the net work $\Delta G^*_{\mathrm{i}\to\mathrm{ii}}$ for the i → ii process is $-T\Delta S_{\mathrm{i}\to\mathrm{ii}}$, which takes the form $T(\Delta h_f/T_m)a_0b_0l_bn/C_\infty$ in the units useful in nucleation theory. Here l_b is the bond length appropriate to the measure of chain dimensions in the standard definition[5] of C_∞ and a_0 is the width of the molecule. Setting $\Delta G^*_{\mathrm{i}\to\mathrm{ii}}$ equal to $2b_0\sigma l_u n$, the work $\Delta\phi_1^*$ of attaining the activated state of the first stem in

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the 'low ψ' formulation of nucleation theory[1], one obtains

$$\sigma_{\rm (theor.)} = T(\Delta h_{\rm f}/T_{\rm m})(a_{\rm o}/2)(l_{\rm b}/l_{\rm u})C_\infty^{-1}$$
$$\cong \Delta h_{\rm f}(a_{\rm o}/2)(l_{\rm b}/l_{\rm u})C_\infty^{-1} \qquad (2)$$

The concept that σ is basically of entropic origin has its roots not only in the 'low ψ' model, but also in the 'negentropic' formulation employed by Turnbull and Spaepen[8] in treating $(\text{–CH}_2\text{–})_n$ systems with low n which featured the effect of the segmental nature of the chains. Equation (2) represents a truly molecular approach, since C_∞ can, in principle, be calculated from details of chain structure and the barrier system associated therewith[5].

Observe that the validity of equation (2) depends on Flory's insight[9] that the chains in a polymer melt have unperturbed dimensions, i.e. they are to be taken as being in a θ solvent consisting of their neighbours. On this basis, it is expected that C_∞ for the melt in equation (2) will be close to that for the same polymer in a dilute θ solvent, the latter corresponding to the conditions under which C_∞ is ordinarily determined experimentally. Note that equation (2) applies only to the σ active in crystallization from the melt – θ conditions cannot be expected to prevail generally during crystallization from subcooled dilute solutions.

We employ polyethylene (PE) as an example of the application of equation (2). With the standard values $\Delta h_{\rm f} = 280\ {\rm J\ cm^{-3}}$, $a_{\rm o} = 0.455$ nm, and $l_{\rm b}/l_{\rm u} = 0.154\ {\rm nm}/0.1273\ {\rm nm} = 1.21$, one has $\sigma_{\rm (theor.)} = 77.06\ {\rm mJ\ m^{-2}}/C_\infty$ ($1\ {\rm mJ\ m^{-2}} = 1\ {\rm erg\ cm^{-2}}$). Then, with $C_\infty = 6.7 \pm 0.3$ as obtained from chain dimensions in dilute θ solvents[10], one finds $\sigma_{\rm (theor.)} = 11.5\ {\rm erg\ cm^{-2}}$. This is in excellent agreement with the σ value of $11.8\ {\rm erg\ cm^{-2}}$ obtained from melt crystallization ($\sigma\sigma_{\rm e} = 1063\ {\rm erg^2\ cm^{-4}}$ from $K_{\rm g}$ combined with $\sigma_{\rm e} = 90\ {\rm erg\ cm^{-2}}$ as obtained from a $T'_{\rm m}$–$1/l$ plot)[4].

To obtain C_∞ from melt crystallization experiments it is not necessary to first calculate σ. From equations (2) and (1b), one finds that

$$C_{\infty\,\rm (theor.)} = \frac{ja_{\rm o}b_{\rm o}(l_{\rm b}/l_{\rm u})\sigma_{\rm e}T_{\rm m}}{2kK_{\rm g}} = \frac{j(l_{\rm b}/l_{\rm u})qT_{\rm m}}{4RK_{\rm g}} \qquad (3)$$

where R is the gas constant.

PE is employed as the first example of the application of equation (3). Here, $K_{\rm g(I)} = 2K_{\rm g(II)} = 1.91 \times 10^5\ {\rm deg^2}$ from melt crystallization rates[4], $a_{\rm o}b_{\rm o} = 0.1888\ {\rm nm^2}$ and $T_{\rm m} = 418.7$ K, giving C_∞ for the melt as 6.53, which accords well with the experimental value cited above of 6.7 ± 0.3 that was obtained in dilute θ solvents. Another example of the application of equation (3) is afforded by i-polystyrene (i-PS). Here $K_{\rm g(II)} = 1.20 \times 10^5\ {\rm deg^2}$ (refs 1 and 11), $a_{\rm o}b_{\rm o} = 0.692\ {\rm nm^2}$, $l_{\rm b}/l_{\rm u} = 0.154\ {\rm nm}/0.11085\ {\rm nm} = 1.39$, $\sigma_{\rm e} = 35\ {\rm erg\ cm^{-2}}$ (ref. 1) and $T_{\rm m} = 515.2$ K. The result is that $C_{\infty\,\rm (theor.)}$ comes to 10.4_5, which is to be compared with $C_{\infty\,\rm (expt)} = 10.5$ as obtained from studies of chain dimensions in dilute θ solvent[12].

The above calculations support the theory in the cases of PE and i-PS and lend credibility to the postulate that $\Delta S_{\rm i\to ii}$ is closely equal to $-\Delta S_{\rm f}/C_\infty$. They also imply, by a heretofore unknown method, that the molecules in the melt state of PE and i-PS are indeed close to being in an unperturbed state.

The present approach provides a molecular basis for an empirical quantity commonly employed to estimate σ, namely the α parameter which is defined[13] as $\sigma/(\Delta h_{\rm f})(a_{\rm o}b_{\rm o})^{1/2}$. With equation (2), this becomes

$$\alpha = \tfrac{1}{2}(a_{\rm o}/b_{\rm o})^{1/2}(l_{\rm b}/l_{\rm u})C_\infty^{-1} \qquad (4)$$

The heat of fusion cancels and, together with lattice and chain parameters, α is seen to depend largely on the segmental nature of polymer chains as measured by C_∞. This sets the stage for different classes of polymers to exhibit substantially disparate α values depending on the C_∞ range characteristic of each class. Such differences in α have been observed, vinyl polymers[1] exhibiting $\alpha \sim 0.1$ and certain high melting polyesters[7,14] conforming to $\alpha \sim 0.23$.

A more detailed discussion[7] will be given elsewhere and includes: the elucidation of the key relationship $\Delta S_{\rm i\to ii} = -\Delta S_{\rm f}/C_\infty$ in terms of partition functions; application to other polymers, e.g. the high melting polyester poly(L-lactic acid) and the low melting polyester poly(ε-caprolactone) which have very different C_∞ values; and the effect on σ of finite chain length wherein C_∞ in equation (2) is replaced by C_n.

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