Macromolecules **1992,** *25,* 7199–7203

Is There a Connection between the Lateral Surface Free Energy of a Growing Polymer Crystal and the Mean-Square Dimensions of the Polymer Chains in the Molten Phase?

Alan E. Tonelli

Fiber and Polymer Science Program, College of Textiles, North Carolina State University, P.O. Box 8301, Raleigh, North Carolina 27695-8301

Received July 9, 1992; Revised Manuscript Received September 22, 1992

ABSTRACT: Hoffman and co-workers[1] have recently suggested a strong connection between the lateral surface free energy parameter σ appearing in the nucleation-based treatment of polymer crystallization and the characteristic ratio of polymer chain dimensions $C_\infty = (\langle r^2 \rangle_0 / nl^2)_{n\to\infty}$ appropriate to unperturbed, randomly-coiling polymers in their melts and Θ solutions. They assumed that "σ is closely related to the reduction in entropy associated with the rate-determining localization of a polymer chain in proximity to the crystal surface prior to its complete crystallographic attachment, which occurs in a rapid subsequent step". The entropy of a polymer chain loosely attached to, or localized at, the crystalline surface is reduced from its randomly-coiling value in the melt, and these researchers "scale the total entropy of stem addition according to $1/C_\infty$ to approximate the entropy change associated with σ during the rate-determining localization of a polymer chain". The net result is the connection $\sigma \propto 1/C_\infty$, which we question here on the basis of the independence between the dimensions (C_∞) and the conformational entropies observed and calculated for a host of flexible, randomly-coiling polymers.

Introduction

Hoffman and co-workers[1] consider the localization of a section of a molten, randomly-coiling polymer chain under the influence of the crystal surface to be the rate-determining step in the formation of the first crystalline stem.[2-4] The localized chain segment "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... and does not involve any significant degree of the free energy of fusion". The free energy corresponding to the localization of a section of a randomly-coiling polymer chain near the crystal surface is obtained from the accompanying entropy reduction as $-T\Delta S$, where it is assumed that ΔS is proportional to the contour length (l) of the same chain section in the melt.

Localization of a section of a molten, randomly-coiling polymer chain near the crystalline surface as envisioned by Hoffman et al. is depicted in Figure 1, where $l_{\mathrm{b(S)}}$ is that part of the polymer chain that is localized or inactivated by the surface, while l_{seg} is active and free to adopt its randomly-coiling conformations. Hoffman and co-workers[1] then suggest that

$$l_{\mathrm{seg}} = C_\infty l_{\mathrm{b(S)}} \tag{1}$$

where

$$C_\infty = (\langle r^2 \rangle_0 / n l_{\mathrm{b}}^2)_{n\to\infty} \tag{2}$$

is the characteristic ratio[5] of the mean-square unperturbed dimensions $\langle r^2 \rangle_0$ of the molten polymer chains of n bonds to the dimensions of the corresponding random flight chain nl_{b}^2. In this manner the number of conformationally active bonds becomes

$$n(1 - 1/C_\infty) \tag{3}$$

Following assumption of conformationally independent[5] bonds for both the unlocalized, randomly-coiling, molten polymer chains and the portions l_{seg} of the localized chain section that remain conformationally active, the entropy reduction accompanying localization becomes

$$\Delta S = -\Delta S_{\mathrm{f}} / C_\infty \tag{4}$$

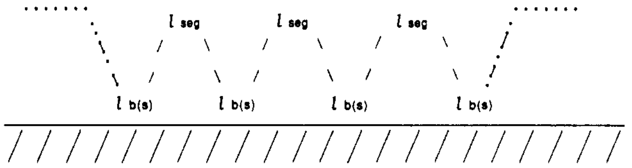

Figure 1. Localization of a section of a molten, randomly-coiling polymer chain near the crystalline surface, where $l_{\mathrm{b(s)}}$ is that portion of the polymer chain that is localized or rendered conformationally inactive by the surface, while l_{seg} is active and free to adopt its randomly-coiling conformations.

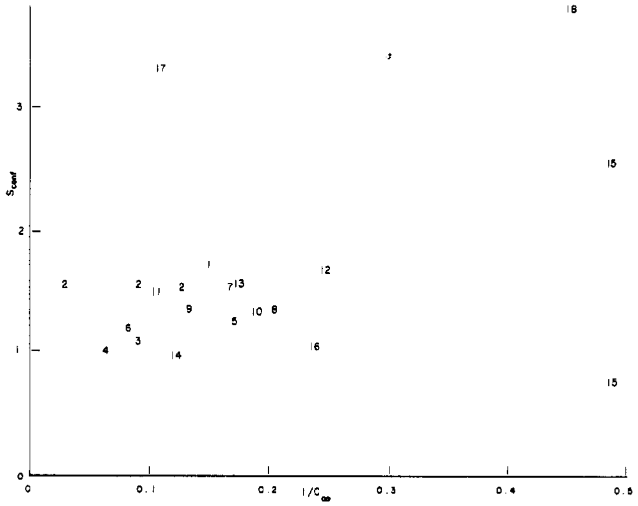

Figure 2. Conformational entropies S_{conf} (eu/mol of backbone bonds) and dimensions (C_∞) calculated from the RIS models of 18 flexible, crystallizable polymers (see Table I for polymer designations).

where ΔS_{f} is the entropy of fusion, and the corresponding free energy is

$$\Delta\sigma = -T\Delta S = T\Delta S_{\mathrm{f}} / C_\infty \tag{5}$$

In the units appropriate for application to nucleation theory[2-4] ΔS_{f} becomes $(\Delta h_{\mathrm{f}}/T_{\mathrm{m}}) a_0 b_0 l_{\mathrm{b}} n^*$, where Δh_{f} is the heat of fusion, T_{m} is the melting temperature, $a_0 b_0$ is the cross-sectional area of the polymer chain, l_{b} is the bond length, and n^* is the number of bonds in the localized

0024-9297/92/2225-7199$03.00/0

polymer section which becomes the nucleating first stem. Also from conventional nucleation theory[2-4] the free energy of activation Φ for addition of the first stem is $2b_0\sigma l_u n^*$, where σ is the lateral surface free energy parameter, $l_u n^*$ corresponds to the initial nucleus length or lamellar thickness, and l_u is the projection of l_b in the chain direction. Φ corresponds to the work required to form the two new exposed lateral surfaces, each of area $b_0 l_u n^*$.

Equating the free energy corresponding to the entropy reduction accompanying the localization of a polymer chain section to the free energy of activation for addition of the first stem serves to define the lateral surface free energy parameter as

$$\sigma = (\Delta h_f/C_\infty)(a_0/2)(l_b/l_u) \qquad (6)$$

where $T = T_m$ has been assumed. For polymers,[5] such as polypeptides and poly(lactic acids) (PLLA), whose structures permit expression of their end-to-end distance in terms of virtual bonds l_v connecting methene carbons in adjacent residues

$$C_\infty = (\langle r^2\rangle_0/x l_v^2)_{x\to\infty} \qquad (7)$$

where x is the number of repeat units or residues, and the expression for the lateral surface free energy becomes

$$\sigma = (\Delta h_f/C_\infty)(a_0/2) \qquad (8)$$

Equations 6 and 8 were used to evaluate C_∞ from melt crystallization rate and melting point depression studies followed by comparison to the dimensions (C_∞) directly observed in dilute polymer solutions at their Θ temperatures.

Hoffman et al.[1] found the characteristic ratios of the dimensions obtained from melt crystallization data through their derived expression for σ to agree with the dilute solution dimensions measured for polyethylene (PE), isotactic polystyrene (i-PS), and poly(L-lactic acid) (PLLA). From this agreement they concluded that (i) the surface free energy parameter σ in the nucleation theory[2-4] of the growth rate of polymer crystals from their melts has an entropic origin, (ii) the entropy reduction of the localized chain near the crystal surface scales with $1/C_\infty$, (iii) their theory forms a connection between nucleation theory and the statistics of polymer chain dimensions, and (iv) this connection provides a new bulk state approach to the determination of the characteristic ratio of dimensions C_∞.

Because the conformational entropy of a randomly-coiling polymer is a purely thermodynamic quantity (see below) dependent only upon the number and relative energies of the constituent bond rotational states, while the dimensions and its characteristic ratio C_∞ are measures of its statistical thermodynamically averaged extension, which additionally depend on the structure and geometry of the chain (valence angles, bond lengths, and the locations of the constituent bond rotational states), we were surprised that the entropy reduction accompanying localization of a polymer chain near its crystal surface should scale with its randomly-coiling dimensions as $1/C_\infty$. For this reason we examined closely the connection between the conformational entropy S_{conf} and the characteristic ratio C_∞ of flexible polymers in an attempt to justify the $\Delta S \propto 1/C_\infty$ scaling suggested by Hoffman and co-workers[1] in their treatment of the lateral surface free energy parameter σ of crystal nucleation from polymer melts, which implies that S_{conf} should also scale with $1/C_\infty$.

Calculation of S_{conf} and C_∞

Let us briefly review the calculation[5] of the conformational entropy S_{conf} and the characteristic ratio of the dimensions C_∞ of a randomly-coiling polymer chain from the RIS (rotational isomeric states) description[5] of its conformational characteristics:

$$S_{\mathrm{conf}} = R[\ln Z + (T/Z)(\mathrm{d}Z/\mathrm{d}T)] \qquad (9)$$

where the configurational partition function Z is given by

$$Z = \mathbf{J}^*\left[\prod_{i=2}^{n-1}\mathbf{U}_i\right]\mathbf{J} \qquad (10)$$

and

$$\mathbf{U}_i = [\mu_{\xi\eta;i}] = \begin{bmatrix} \mu_{\alpha\alpha}\mu_{\alpha\beta} & \cdot\cdot & \mu_{\alpha\nu} \\ \mu_{\beta\alpha}\mu_{\beta\beta} & \cdot\cdot & \mu_{\beta\nu} \\ \cdot\cdot & \cdot\cdot & \cdot \\ \cdot\cdot & \cdot\cdot & \cdot \\ \mu_{\nu\alpha}\mu_{\nu\beta} & \cdot\cdot & \mu_{\nu\nu} \end{bmatrix} \qquad (11)$$

$\mathbf{J}^*$ and $\mathbf{J}$ are the $1 \times \nu$ and $\nu \times 1$ row and column vectors:

$$\mathbf{J}^* = [1\ 0 \cdots 0] \qquad \mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix} \qquad (12)$$

The elements of the statistical weight matrix $\mathbf{U}_i$ are Boltzmann factors of the energies, appropriate to the various pairwise dependent rotational states of bond i, which normally number $\nu = 3$ and correspond to the staggered trans and gauche conformations. Clearly the conformational entropy depends only on the number (ν) and relative energies ($E_{\alpha6}$) of the bond rotational states.

By contrast

$$C_\infty = \frac{2Z^{-1}}{nl^2}\mathcal{J}^*\left(\prod_{i=1}^{n}\mathbf{G}_i\right)\mathcal{J} \qquad (13)$$

where

$$\mathcal{J}^* = [\mathbf{J}^*\ 0\ 0 \ldots 0](1 \times 5\nu) \qquad (14)$$

$$\mathcal{J} = \begin{bmatrix} 0 \\ 0 \\ : \\ 0 \\ \mathbf{J} \end{bmatrix} (5\nu \times 1)$$

and

$$\mathbf{G}_i = \begin{bmatrix} \mathbf{U} & (\mathbf{U}\otimes\mathbf{I}^T)\|\mathbf{T}\| & (l^2/2)\mathbf{U} \\ 0 & (\mathbf{U}\otimes\mathbf{E}_i)\|\mathbf{T}\| & \mathbf{U}\otimes\mathbf{I} \\ 0 & 0 & \mathbf{U} \end{bmatrix} \qquad (15)$$

$\mathbf{U}_i$ is the statistical weight matrix (eq 11), l_i and $l^T{}_i$ are the bond vectors in column and row representation, $l^2 = |l_i|^2$, $\mathbf{E}_\nu$ is the ν-order identity matrix, and $\otimes$ denotes the direct product of matrices. $\|\mathbf{T}\|$ is the 3×3 diagonal representation[6] of the matrix which transforms a vector or tensor from the Cartesian coordinate system along bond $i + 1$ to that along bond i, and its elements are sines and cosines of the supplement of the valence angle between bonds i and $i + 1$ and the dihedral rotation angle around bond i. Clearly the mean-square end-to-end distance and its characteristic ratio C_∞ for a randomly-coiling polymer chain depend, in addition to the number and energies of the constituent bond rotational states which exclusively determine Z and S_{conf}, upon the structure and geometry of the polymer, i.e., the backbone valence angles and the dihedral locations of their rotational states.

It is apparent from these matrix equations and their individual elements that S_{conf} is purely thermodynamic while C_∞ has both thermodynamic and structural/geometrical components. From this comparison can we expect S_{conf} to scale with $1/C_\infty$ as suggested

Table I
Conformational Entropies and Characteristic Ratios Calculated (RIS) for Flexible Polymers[a]

	polymer	abbrev	S_{conf}[b] (eu/bond)	C_∞[b] RIS	C_∞[b] obsd
1	polyethylene	PE	1.76	6.7 (140 °C)	6.7 (140 °C)
2	poly(tetrafluoroethylene)	PTFE	1.60	11–30	7–8[7]
3	isotactic polystyrene[8]	i-PS	1.09	10–12	10.5
4	syndiotactic polystyrene[8]	s-PS	1.04	15	
5	isotactic polypropylene[9]	i-PP	1.35	5.7 (145 °C)	5.7 (145 °C)
6	syndiotactic polypropylene[9]	s-PP	1.26	11–13 (150 °C)	
7	poly(*trans*-1,4-butadiene)	TPBD	1.55	5.8	5.8
8	poly(*cis*-1,4-butadiene)	CPBD	1.38	4.9	4.9
9	poly(*trans*-1,4-isoprene)	TPIP	1.37	7.3	7.35
10	poly(*cis*-1,4-isoprene)	CPIP	1.34	5.2	4.7
11	poly(oxymethylene)	POM	1.50	8–10	10.5[10]
12	poly(oxyethylene)	POE	1.70	4.0 (40 °C)	4.0 (40 °C)
13	poly(ϵ-caprolactone)	PCL	1.59	6.1	5.9[11]
14	poly(pivalolactone)	PPVL	1.04	8.1[12]	
15	poly(L-lactic acid)	PLLA	0.76, 2.57[d]	2.09	2.0 (80 °C)
16	poly(ethylene terephthalate)	PET	1.07	4.2[c]	4.2[c]
17	poly(L-alanine)[14]	PLA	3.33[d] (25 °C)	9.3	8.5–9.5
18	polyglycine	PG	3.83[d] (25 °C)	2.2	

[a] RIS models and observed C_∞'s are taken from ref 5 (unless denoted otherwise), where citations to the original literature are also presented. [b] Temperatures in parentheses are the temperatures of calculation or measurement. [c] $C_\infty = \langle r^2 \rangle_0 / n \langle l^2 \rangle$, where $\langle l^2 \rangle$ is averaged over the six bonds in each PET repeat unit, including the virtual bond $l_v = 5.74$ Å connecting 1,4-carbonyl carbons belonging to the same phenyl ring. [d] Conformational entropies[12,14] were calculated from $z = \sum_\phi \sum_\psi \exp[-E(\phi,\psi)/RT]$, when evaluated from their conformational energy maps of their three-bond repeat unit using 10° increments in both ϕ and ψ rotation angles.

by Hoffman and co-workers in their theory for the lateral surface free energy parameter σ, which is central to the nucleation-controlled description of bulk polymer crystallization?[2-4]

We have calculated S_{conf} and C_∞ for a large variety of flexible, crystallizable polymers including those discussed by Hoffman et al.[1], i.e., PE, i-PS, PLLA, isotactic polypropylene (i-PP), poly(ϵ-caprolactone) (PCL), and poly(pivalolactone) (PPVL). When available, we have also listed their experimentally observed characteristic ratios for purposes of assessing the RIS models employed in these calculations. S_{conf} and C_∞ were calculated at $T = T_m$ and $T = 25$ °C, respectively, unless noted otherwise.

Results

Table I presents a compilation of calculated conformational entropies and characteristic ratios for 18 different flexible and crystallizable polymers. In addition, the experimental C_∞'s observed for most of the same polymers are tabulated. These results are displayed graphically as S_{conf} (per backbone bond) versus $1/C_\infty$ in Figure 1. It is immediately apparent that S_{conf} does not in fact scale with $1/C_\infty$. If any trend is evident, it is that S_{conf} and C_∞ are most likely independent.

These results receive additional support from the conformational entropies calculated by Mark[15] for the series of polyoxides $[-(-CH_2-)_y-O-]_x$, where $y = 1$–4, 6, 8, and 10, and whose characteristic ratios have also been measured. He found that all but POM ($y = 1$) have $S_{conf} \approx 1.6$ eu/bond even though their C_∞'s ranged from 4 to 12.

Polymers containing 1,4-linked phenyl rings in their backbones,[16-21] including four 2,6-disubstituted poly(1,4-phenylene oxides), polycarbonate, polysulfone, and poly(phenylene sulfide), all have calculated and measured C_∞'s approaching very closely their free-rotation values.[5] Despite their uniform dimensions, their conformational entropies vary widely in concert with our general observation that S_{conf} does not scale with $1/C_\infty$.

Discussion

At this juncture we are faced with the claim made by Hoffman and co-workers[1] that the lateral surface free energy parameter σ in the nucleation-controlled treatment[2-4] of polymer crystallization scales inversely with the characteristic ratio C_∞ of the dimensions of the randomly-coiling molten polymers. This result stems from their proposed entropic origin for the rate-determining free energy of localizing a randomly-coiling polymer near the crystal surface, from assuming that the entropy reduction ΔS accompanying this localization is proportional to the contour length[5] l of the localized chain segment, and from adopting the Porod–Kratky model[5] for polymer chains which produces a scaling of C_∞ with the inverse of the contour length. In a nut shell, they are claiming

$$\sigma \propto \Delta S \propto l \propto 1/C_\infty \tag{16}$$

which clearly implies that S_{conf} should also scale with $1/C_\infty$, because the entropy lost in localizing a polymer near the crystal surface is directly related to the conformational entropy S_{conf} possessed by the unattached, randomly-coiling, molten polymer.

Here we have demonstrated that the conformational entropy S_{conf} of a flexible polymer chain is not correlated with its conformationally-averaged dimensions (C_∞). When the conformational entropies and dimensions were calculated for well over two dozen structurally diverse, flexible polymers using the RIS scheme,[5] no apparent connection could be found between S_{conf} and C_∞, especially not the $S_{conf} \propto 1/C_\infty$ scaling suggested in the analysis presented by Hoffman et al.[1]

Hoffman et al.[1] suggest that the entropy lost by a randomly-coiling polymer chain in the melt, as it is localized near the surface of a crystal in the rate-determining step of its nucleated crystal growth, is directly related to the flexibility of the molten chain as given by $1/C_\infty$, while our RIS analyses[15-21] of the conformational entropies and dimensions (C_∞) of a wide variety of flexible polymers demonstrate their independence.

Hoffman and co-workers[1] analyzed melt crystallization rate studies for PE, i-PS, PLLA, and PPVL and obtained experimental values of $\sigma\sigma_e$. Melting point depression experiments performed on the same polymers yielded values of σ_e. Division of the two gives σ_{exp} from which they computed C_∞ according to eqs 6 and 8. For PE, i-PS, and PLLA the C_∞'s derived from melt crystalline growth data agree with the dimensions (C_∞) independently

Table II

Comparison of $\sigma_{\exp}$ and C_∞ Obtained from Melt-Growth Crystallization Data with C_∞ and S_{conf} Observed in Dilute Solution and/or Calculated from the RIS Models of Three Aliphatic Polyesters

polyester	$\sigma_{\exp}$	C_∞ (melt)	C_∞ (solution)	C_∞ (RIS)	S_{conf} (RIS)
PCL	6.38	6.3	5.9	6.1	1.59
PLLA	15.3	2.34	2.0	2.1	0.76
PPVL	28.7	4.83		8.1	1.04

measured from their dilute solutions. The dimensions of PPVL have not as yet been observed in solution. In addition, the C_∞'s for i-PP and PCL have been derived from melt crystallization data without reference to σ by inserting eq 6 into the expression for the experimentally measured nucleation constant K_g, which results in

$$C_\infty = [j(l_b/l_u)qT_m]/4RK_g \tag{17}$$

where $j = 4$ for regimes I and III crystallization and $j = 2$ for regime II, and q is the work of chain folding $2a_0b_0\sigma_e$. The characteristic ratios obtained in this manner for i-PP and PCL from melt crystallization data are in agreement with the C_∞'s measured in dilute solution.

Following the suggestion of Hoffman et al.,[1] let us examine the three aliphatic polyesters PLLA, PPVL, and PCL also considered by them. From their analyses of the observed rates of growth from their melts, they derived characteristic ratios $C_\infty = 2.34$ (PLLA), 2.49 (PPVL), and 6.3 (PCL), using eq 6 for PCL and eq 8 for PLLA and PPVL. Equation 8 is supposed to be applicable to polymers like the polypeptides and PLLA whose dimensions can be expressed (see eq 7) in terms of virtual bonds[5] l_v connecting adjacent α-carbons ($-OC^{\alpha}C(=O)OC^{\alpha}C(=O)O-$) and whose distance is independent of the backbone conformation as long as the peptide or ester bonds remain trans and planar. However, PPVL ($-OCH_2C(CH_3)_2C(=O)-$) cannot be simplified into a series of connected virtual bonds, because there are three flexible bonds in each repeat unit.

Instead eq 6 should be applied to the growth rate data for melt-crystallized PPVL, where the ratio l_b/l_u must now be considered. The average length of the four bonds in the PPVL repeat unit[12] is 1.46 Å, and from the 6-Å fiber repeat distance observed[22,23] in the 2_1-helical crystalline conformation of PPVL, the average $l_u = 0.75$ Å. Thus, $l_b/l_u = 1.94$, which through eq 6 leads to $C_\infty = 4.83$ and not 2.49 as obtained by Hoffman et al.[1] from eq 8 which is inappropriate for PPVL.

In Table II we present a comparison of $\sigma_{\exp}$ and C_∞ derived from growth rate data for the melt crystallization of PCL, PLLA, and PPVL together with the C_∞'s obtained from dilute solution observations and/or calculated from their RIS models and the corresponding conformational entropies calculated (RIS) for their molten random coils. There appear to be no correlations between either $\sigma_{\exp}$ and C_∞ (melt) or S_{conf} and C_∞ (solution and/or RIS) for these three aliphatic polyesters. This casts some doubt on the scaling relation $\sigma \propto 1/C_\infty$ proposed by Hoffman et al.[1] to describe their entropy-driven model of melt-grown polymer crystals. At the very least, it suggests that the entropy reduction accompanying the rate-determining localization of a molten polymer chain is not identifiable with S_{conf}; i.e., it is not directly proportional to the conformational entropy of the randomly-coiling, molten polymer chain, because $\sigma_{\exp}$ also fails to scale with S_{conf}. This is particularly surprising because ΔS_f (see eq 4) has been shown[24-27] to be strongly correlated with S_{conf} for a wide range of synthetic, crystalline polymers.

To illustrate the danger inherent with connecting the entropy reduction ΔS accompanying the stretching of a molten, randomly coiling polymer as it approaches and begins attachment to the crystal surface, which must be directly related[28] to S_{conf}, with the inverse of the average extension ($1/C_\infty$) of the molten polymer chain, it might be useful to consider two hypothetical polymers. Both polymers consist of tetrahedrally bonded, carbon atom backbones, with each backbone bond permitted to adopt two rotational states (conformations) $\phi = 0, 180°$ for one polymer and $\phi = \pm 120°$ for the other. The energies (probabilities) of the two rotational states are equal and assumed independent of the conformations or rotational states of neighboring bonds.

It is clear from eqs 9–12 that both polymers have $S_{\text{conf}} = nR \ln 2$, where n is the number of backbone bonds. On the other hand, the conformational symmetry of the polymer with $\phi = 0, 180°$ rotational states leads[5] to $C_\infty = 2.0$ (free rotation value), while $C_\infty = 6.0$ for the polymer with $\phi = \pm 120°$. To achieve the same extended, localized chain length on or near a crystal surface, the polymer with $C_\infty = 2.0$ must be stretched more than the polymer with $C_\infty = 6.0$, because its molten random coils are more compact. Nonetheless, the entropy reductions accompanying the extensions of both chains are the same.

It would appear that melt crystallization growth rate data need to be gathered and compared with the dimensions observed in dilute solutions for several additional polymers before a final assessment regarding the approach taken by Hoffman and co-workers[1] can be confidently rendered. At present only a very tentative "maybe" seems an appropriate response to the question raised in the title of this paper. What does seem to be on much firmer footing is the observation made here, and suggested previously by others,[15-17,19,21] that the exclusively thermodynamic measure of the static conformational flexibility of polymers provided by S_{conf} is in general not correlated with their conformationally sensitive and structurally/geometrically-dependent dimensions (C_∞).

References and Notes

(1) Hoffman, J. D.; Miller, R. L.; Marrand, H.; Roitman, D. B. *Macromolecules* **1992**, *25*, 2221.

(2) Hoffman, J. D.; Davis, G. T.; Lauritzen, J. L., Jr. In *Treatise on Solid State Chemistry*; Hannay, N. B., Ed.; Plenum: New York, 1976; Vol. 3, Chapter 7.

(3) Hoffman, J. D. *Polymer* **1982**, *23*, 656.

(4) Hoffman, J. D. *Polymer* **1983**, *24*, 3.

(5) Flory, P. J. *Statistical Mechanics of Chain molecules*; Wiley-Interscience: New York, 1969.

(6) $\|\mathbf{T}\|$ is the diagonal matrix

$$\begin{vmatrix} T(\phi=\alpha) & & \\ & T(\phi=\beta) & \\ & & T(\phi=\gamma) \end{vmatrix}$$

where $\nu = \alpha, \beta$, or γ.

(7) Chu, B.; Wu, C.; Buck, W. *Macromolecules* **1989**, *22*, 831.

(8) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.

(9) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.

(10) Stockmayer, W. H.; Chan, L. L. *J. Polym. Sci., Part A-2* **1966**, *4*, 437.

(11) Jones, A. A.; Stockmayer, W. H.; Molinari, R. J. *J. Polym. Sci., Polym. Symp.* **1976**, *54*, 227.

(12) Bruckner, S.; Crescenzi, V.; Zotteri, L. *Eur. Polym. J.* **1971**, *7*, 1473.

(13) Brant, D. A.; Tonelli, A. E.; Flory, P. J. *Macromolecules* **1969**, *2*, 228.

(14) Brant, D. A.; Miller, W. G.; Flory, P. J. *J. Mol. Biol.* **1967**, *23*, 67.

(15) Mark, J. E. *J. Chem. Phys.* **1977**, *67*, 3300.
(16) Tonelli, A. E. *Macromolecules* **1972**, *5*, 558.
(17) Tonelli, A. E. *Macromolecules* **1973**, *6*, 503.
(18) Jones, T. P. H.; Mitchell, G. R.; Windle, A. H. *Colloid Polym. Sci.* **1982**, *261*, 110.
(19) Sundararajan, P. R. *Macromolecules* **1990**, *23*, 2600.
(20) Sundararajan, P. R. *Polym. Mater. Sci. Eng.* **1990**, *64*, 392.
(21) Sundararajan, P. R. *CDA News* **1990**, 1.
(22) Carazzolo, G. *Chem. Ind.* **1964**, *46*, 525.
(23) Cornibert, J.; Marchessault, R. H. *Macromolecules* **1975**, *8*, 296.
(24) Tonelli, A. E. *J. Chem. Phys.* **1970**, *52*, 4749; **1971**, *54*, 4637; **1972**, *56*, 5533.
(25) Tonelli, A. E. *Macromolecules* **1972**, *5*, 563.
(26) Tonelli, A. E. In *Analytical Calorimetry*; Porter, R. S., Johnson, J. F., Eds.; Plenum: New York, 1974; Vol. 3, p 89.
(27) Tonelli, A. E. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2051.
(28) Tonelli, A. E. *Computat. Polym. Sci.* **1991**, *1*, 22.

Registry No. Polyethylene (homopolymer), 9002-88-4; poly(tetrafluoroethylene) (homopolymer), 9002-84-0; isotactic polystyrene (homopolymer), 25086-18-4; syndiotactic polystyrene (homopolymer), 28325-75-9; isotactic polypropylene (homopolymer), 25085-53-4; syndiotactic polypropylene (homopolymer), 26063-22-9; poly(1,4-butadiene) (homopolymer), 9003-17-2; poly(1,4-isoprene), 9003-31-0; poly(oxymethylene) (homopolymer), 9002-81-7; poly(oxyethylene) (homopolymer), 25322-68-3; poly(ϵ-caprolactone) (homopolymer), 24980-41-4; poly(ϵ-caprolactone) (SRU), 25248-42-4; poly(pivalolactone) (homopolymer), 24969-13-9; poly(pivalolactone) (SRU), 24937-51-7; poly(L-lactic acid) (homopolymer), 26811-96-1; poly(L-lactic acid) (SRU), 26161-42-2; poly(ethylene terephthalate) (homopolymer), 25038-59-9; poly(L-alanine) (homopolymer), 25191-17-7; poly(L-alanine) (SRU), 25213-34-7; polyglycine (homopolymer), 25718-94-9; polyglycine (SRU), 25734-27-4.