

Theoretical Evaluation of the Conformational Entropy of Fusion and the Melting Temperature of Polymers

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Synopsis

A method is presented to theoretically estimate the conformational entropy ΔS_c of fusion of polymer chains of any stereochemical constitution. The effect of the type of crystalline conformation and the conformational energy differences on ΔS_c is discussed with examples. The dependence of ΔS_c on the configurational partition function is traced. A method for theoretically evaluating the melting temperature of a polymer from its conformational characteristics is presented. The application of the method to a total of 11 polymers leads to good agreement between the calculated and experimental values of the melting temperatures.

INTRODUCTION

Several properties of polymer chains have been understood in terms of their conformational characteristics. Application of the semiempirical methods to estimate the energy differences between the several conformations available to a polymer have been successful in accounting for observable parameters such as the unperturbed end-to-end distance, optical properties, NMR coupling constants,¹⁻⁷ and so on. This also led to an understanding of the differences between the properties of various polymers in terms of the differences in their chemical and physical structure.

Attempts have been made to theoretically estimate the entropy of fusion as the polymer melts from the crystalline state. The change in the entropy, ΔS , consists of two parts⁸: the contribution ΔS_v due to a change in the volume and the contribution due to the polymer going from a unique conformation in the crystalline state to a distribution of conformations upon melting. Thus,

$$\Delta S = \Delta S_v + (\Delta S_c)_v \quad (1)$$

where the subscript c denotes the conformational origin. The contribution of ΔS_c to the total entropy of fusion has been found to be significant, of the order of 50% (e.g., polyisoprene) to 80% [e.g., polyethylene, poly(oxyethylene), poly(oxyethylene), poly(ethylene terephthalate), and poly(tetrafluoroethylene)].

The conformational entropy ΔS_c has evaded easy theoretical evaluation. A few treatments⁹⁻¹² which have been reported are applicable to only short chains, and extrapolation is needed to deduce the parameter for long chains. These methods involve enumeration of the possible number and relative abundance of the trans and gauche states of the successive bonds of the chain, as it is tediously constructed one bond at a time. Even the treatment of short chains by such methods is time consuming and elaborate, extensive tabulation and manipulation of data being required.

A method is presented here which is applicable to polymer chains of any length and any stereochemical constitution. It is based on the rotational isomeric state scheme and the associated statistical weight matrices.^{1,13,14} The conformational features of the polymer chain in the molten state are taken to be similar to those of an unperturbed chain. Although the method is similar to that of Tonelli,¹⁵ the need to formulate supermatrices is eliminated. The effect of the energy difference between conformations on the resulting value of ΔS_c is explored for a few polymers, and a method is proposed to evaluate the melting point of a polymer theoretically from the conformational features.

The assumption of an unperturbed chain in these calculations is to be treated as an approximation. Because of the higher density of the melt compared to a dilute solution, intermolecular effects would have an effect on the possible short-range conformations, their statistical weights, and to some extent on the long-range interactions as well. Such intermolecular effects may account for polymorphic transitions in the polymer systems. During such transitions, the polymer, with or without intramolecular conformational change, can rearrange itself in the lattice owing to stabilizing intermolecular interactions. Although it is possible to theoretically evaluate the intermolecular forces in the crystalline state, the methods available at this time are not geared to assess such interactions in the melt. The conformational entropy arises from the conformational rearrangement of the polymer, and as such the calculations and results presented here trace the effect of the energy differences, preferred type of conformation (helical or extended chain) on the resulting conformational entropy.

It is interesting, however, to note that Benoit et al.,¹⁶ from neutron scattering data, found that the polymer chains in bulk have the same dimensions as in a θ solvent.

DESCRIPTION OF METHOD

Following the previous authors^{11,12,15} and assuming that the crystalline polymer possesses perfect order with zero entropy, the molar conformational entropy of an unperturbed chain, upon melting, is given by

$$\Delta S_c = R \left[\ln Z + T \left(\frac{d}{dT} \ln Z \right) \right] \quad (2)$$

The configurational partition function Z can be evaluated if the statistical weight matrix U_i for successive bond pairs is formulated¹⁴:

$$Z = U_0 \left(\prod_{i=2}^{n-1} U_i \right) U_x \quad (3)$$

where U_0 and U_x are the row and column vectors for the first and the last bonds of the chain, respectively. For a chain with three rotational states, t , g^+ , and g^- ,

$$U_0 = [1 \ 0 \ 0]; \quad U_x = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \quad (4)$$

The values of the various elements of the statistical weight matrices (see below)

depend on the energy differences between the conformations of a bond and the temperature. For example, if σ is the statistical weight for a gauche conformation relative to a value of 1 for trans,

$$\sigma = \exp(-E_\sigma/RT) \quad (5)$$

where E_σ is the energy difference between the two states. Thus, the statistical weight matrix as well as Z can be evaluated as a function of temperature. In the present scheme, $(d/dT) \ln Z$ can be evaluated numerically at the melting point T_m simply by evaluating $Z_{(T_m - \Delta T)}$ and $Z_{(T_m + \Delta T)}$. Thus,

$$\Delta S_c = R \left[\ln Z_{T_m} + T_m \left(\frac{\ln Z_{(T_m + \Delta T)} - \ln Z_{(T_m - \Delta T)}}{2\Delta T} \right) \right] \quad (6)$$

The value for ΔT does not seem to be critical, as values of $\Delta T = 10$ or 20 did not yield significant differences in the results presented below. Calculating the derivative by an elaborate calculation of Z at 1° intervals and a subsequent application of five-point interpolation formulae gave the same results. Hence, the simple eq. (6) serves satisfactorily in the calculation of ΔS_c , eliminates the need for supermatrices, and leads to excellent agreement with experimental data.

EXAMPLES AND DISCUSSION OF THE CALCULATIONS

Polyethylene (PE)

According to the treatment of Abe et al.,^{1,3} the statistical weight matrix for a pair of bonds $i - 1$ and i in PE is given by

$$U = \begin{matrix} & \begin{matrix} t & g^+ & g^- \end{matrix} \\ \begin{matrix} t \\ g^+ \\ g^- \end{matrix} & \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \end{matrix} \quad (7)$$

where the t , g^+ , and g^- states of the bond $i - 1$ are indexed on the rows and those of bond i , on the columns. Here, σ is the statistical weight for the g^\pm state relative to a weight of 1 for the t state. The parameter $\sigma\omega$ is appropriate to the g^+g^- or g^-g^+ incidence of successive bonds which lead to an overlap of the CH_2 groups on either end of bonds $i - 1$ and i . The calculations of Abe et al. on the characteristic ratio $[C_\infty = (\langle r^2 \rangle_0/nl^2)_\infty]$ and its temperature coefficient showed that $E_\sigma = 400$ cal/mole and $E_\omega \simeq 1500$ cal/mole.

The calculated values of $\Delta S_c/n$ as a function of n , where n is the number of bonds in the chain, are given in Figure 1 for a few values of E_σ and E_ω . A value of 410°K was used for T_m . It is seen that asymptotic values are reached after about 50 bonds in the chain. The values of $E_\sigma = 400$ cal/mole and $E_\omega = 1500$ cal/mole result in $\Delta S_c/n = 1.83$ e.u., which is in agreement with the value of 1.84 derived experimentally.⁸ Increasing the values of E_σ or E_ω tends to decrease the value of ΔS_c . For example, for $E_\sigma = 600$ and $E_\omega = 1500$, the calculated $\Delta S_c/n$ is 1.76. This value decreases to 1.64 if $E_\omega = \infty$ (i.e., $\omega = 0$). Thus, agreement with experimental value requires $E_\sigma = 400$ and $E_\omega = 1500$. This is in agreement with the conclusion of Flory¹ on the requirement of a nonzero value for ω .

Since the trans conformation is preferred in the crystalline state of PE, an increase in E_σ or E_ω increases the population of trans conformation in the molten

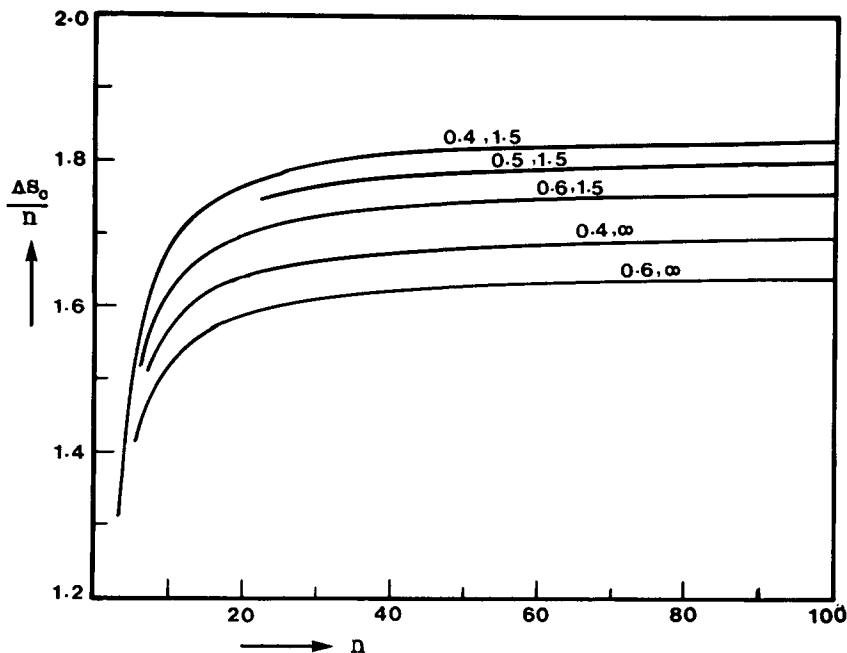


Fig. 1. Calculated values of $\Delta S_c/n$ plotted vs n for polyethylene. Values of E_σ and E_ω , in kcal/mole, in that order, are marked on the curves. The value of T_m was taken to be 410°K.

state as well, and hence the entropy of fusion decreases. Thus, if more weight is assigned to the conformation found in the crystalline state (thereby reducing the population of other conformations), the value of ΔS_c is reduced because the conformational rearrangement on fusion is a minimum.

Abe et al. also examined a scheme with five rotational states located at 0°, 77°, 115°, -115°, and -77° and found very little difference in the results between this and the three-state scheme. Hence, the five-state scheme is not examined here.

Poly(oxymethylene)(POM)

In this case, two statistical weight matrices are required^{1,18}: U_a for the bond pair $i, i + 1$ centered about O (Fig. 2) and U_b for the pair $i - 1, i$ centered about CH_2 . These are of the form

$$U_a = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (8)$$

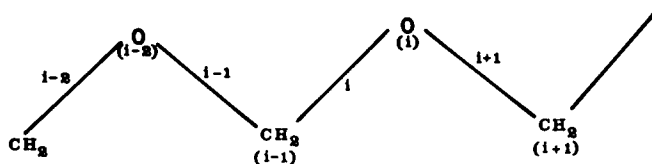


Fig. 2. Schematic diagram of POM, showing the indexing of the bonds.

and

$$U_b = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \quad (9)$$

with the t , g^+ , and g^- states indexed as in eq. (7). The statistical weights σ and ω have the same meaning as before, except that ω here refers to the overlap of O_{i-2} and O_{i+2} atoms, separated by four bonds in the $g^\pm g^\mp$ state of the bond pair $i, i+1$. Similar overlap of the CH_2 groups in the $g^\pm g^\mp$ states of the pair $i-1, i$ is extremely severe so that a statistical weight of zero is assigned for them in eq. (9). The partition function Z is evaluated according to eq. (3), with

$$U_i = U_a U_b \quad (10)$$

The analysis of Flory^{1,18} showed that values of $E_\sigma = -1500$ cal/mole and $E_\omega \simeq 1800$ cal/mole would be required to reproduce the experimental values of the characteristic ratio of POM. The calculated values of $\Delta S_c/n$ as a function of n are given in Figure 3 for a few values of E_σ and E_ω . Here, n is the number of repeat units in the chain. It is seen that the values of E_σ and E_ω quoted above lead to a value of 2.88 for $\Delta S_c/n$, which is in agreement with the experimental result of 2.8.

In contrast to PE, the value of ΔS_c for POM increases with increase in E_σ . It is known that, unlike PE, the crystalline conformation of POM is helical.¹⁹ This supports the observation that assigning more weight to the conformation found in the crystalline state reduces the value of ΔS_c . The dependence of ΔS_c on E_ω is similar to that of PE, however.

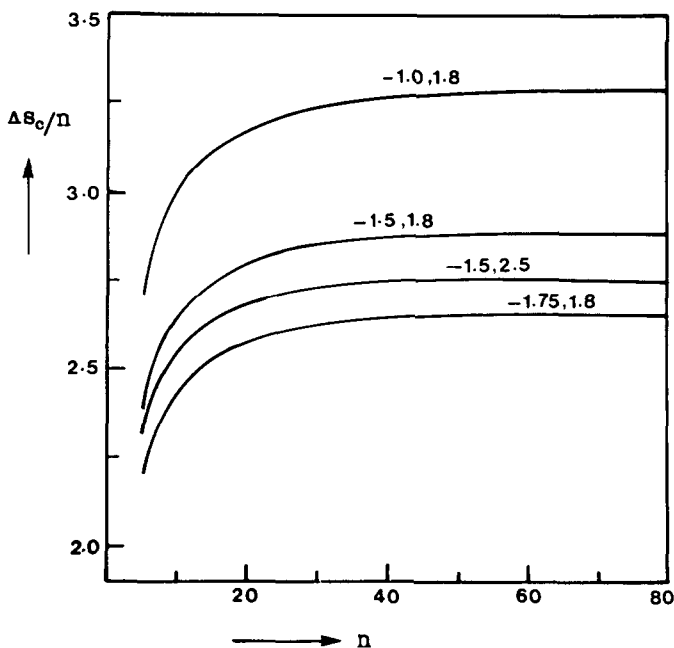


Fig. 3. Calculated $\Delta S_c/n$ plotted vs n for POM; here n is the number of repeat units in the chain. Values of E_σ and E_ω , in kcal/mole, in that order, are marked on the curves. The value of T_m was taken to be 450°K .

Poly(oxyethylene) (POE)

Three statistical weight matrices are required for POE, one each for the bond pairs $i - 1, i$, $i, i + 1$, and $i + 1, i + 2$ in Figure 4. These are, respectively, of the form^{1,20,21}

$$U_a = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (11)$$

$$U_b = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \quad (12)$$

$$U_c = \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & \sigma'\omega \\ 1 & \sigma'\omega & \sigma' \end{bmatrix} \quad (13)$$

The partition function is calculated similar to eqs. (3) and (10), with

$$U_i = U_a U_b U_c \quad (14)$$

The calculated values of $\Delta S_c/n$ as a function of n for a few values of E_σ , $E_{\sigma'}$, and E_ω are given in Figure 5. A value of 4.28 e.u. is obtained for $\Delta S_c/n$ with $E_\sigma = 1200$, $E_{\sigma'} = -600$, and $E_\omega = 800$ cal/mole, and this is close to the value of 4.22 e.u. determined experimentally for $\Delta S_c/n$. The energy values are similar, but not identical, to those deduced by Flory.^{1,20,21}

In this case, an increase in E_σ or E_ω decreases the value of ΔS_c . This is in accordance with the feature of a chain in which the trans conformation is more preferred, similar to PE. On the other hand, the gauche conformation of the bond $i + 2$ is more preferred (for which σ' pertains) than the trans conformation; and hence an increase in $E_{\sigma'}$ results in an increase in ΔS_c . This is similar to the behavior of the POM chain with variation in E_σ . The curves also show that an equal increase in E_ω and $E_{\sigma'}$ does not cause a change in the value of ΔS_c . Such a relationship does not follow for E_σ and $E_{\sigma'}$.

Poly(tetrafluoroethylene) (PTFE)

The statistical weight matrix for PTFE is of the same form as for PE. The preference for the trans conformation for this chain is predominant, and Flory¹ estimated $\omega = 0$ and E_σ to be large compared to PE. As shown in Figure 6, the variation of $\Delta S_c/n$ with E_σ is quite pronounced, and an increase in E_σ results

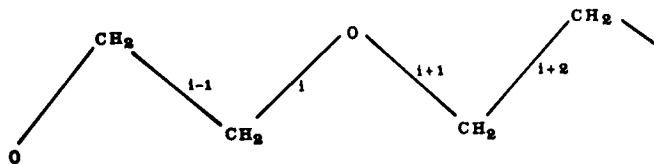


Fig. 4. Schematic diagram of POE, showing the indexing of the bonds.

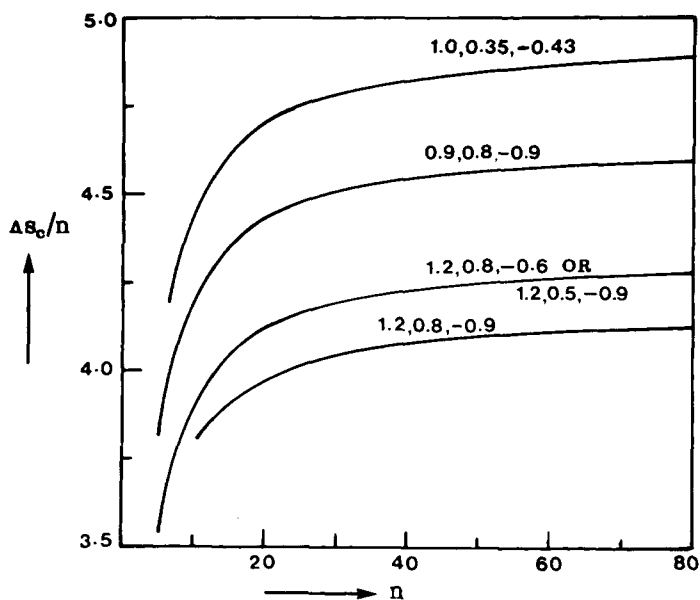


Fig. 5. Calculated $\Delta S_c/n$ plotted vs n for POE; here n is the number of repeat units. Values of E_σ , E_ω , and E_γ , in kcal/mole, in that order, are marked on the curves. The value of T_m was taken to be 340°K .

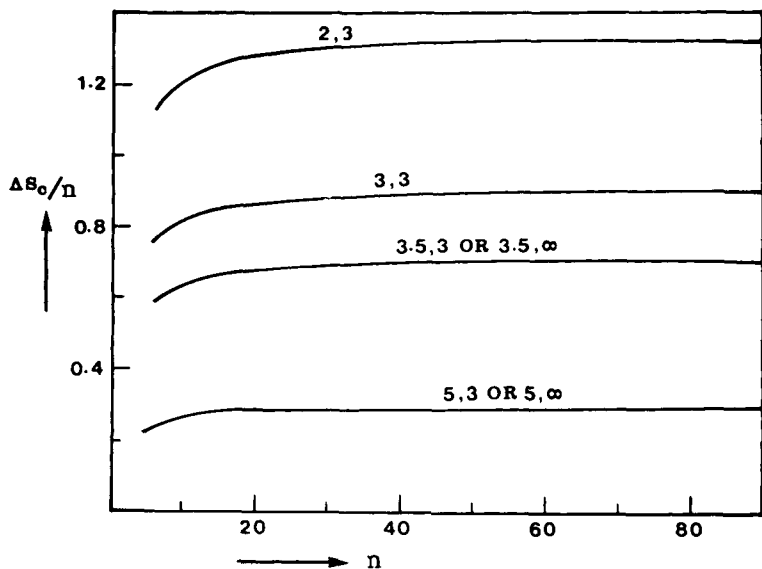


Fig. 6. Calculated values of $\Delta S_c/n$ plotted vs n for PTFE. See legend to Figure 1. A value of 600°K was used for T_m .

in a decrease in ΔS_c , which is similar to the feature noted for PE. The calculated ΔS_c is insensitive to any variations in E_ω ; and in the range of 3000 cal/mole to ∞ , no difference at all was noted for ΔS_c . The experimental value of 0.76 e.u. for $\Delta S_c/n$ is reproduced by $E_\sigma = 3500$ cal/mole. Such a high energy reduces the incidence of the gauche conformations even at high temperatures, and hence the configurational entropy is small for PTFE.

The discussion on the four polymers given above was aimed at showing that the entropy of fusion depends very much on the type of conformation preferred in the solid state (helical or extended) and also the energy difference between the crystalline conformation and the other conformations available to the chain in the molten state. The calculations were also performed for a few other polymers, and the results are given in Table I. It is seen that the agreement between the calculated and the experimental values of ΔS_c is generally good. In most cases, the energy parameters which reproduce the experimental values of ΔS_c are very close to those proposed by Flory and co-workers, on the basis of calculations of the characteristic ratio, its temperature coefficient, and dipole moment. The latter calculations, of course, correspond to the unperturbed state of the polymers. We referred before to Benoit's finding that the polymers in bulk show θ point character. The fact that the same energy parameters, which consider only the intramolecular interactions, reproduce the experimental results on both the unperturbed dimensions and the conformational entropy of fusion for all nine polymers examined here tempts us to conclude that the assumption mentioned above is valid, at least for these polymers. This agreement, if considered coincidental, can be due to two reasons: (a) For all the nine polymers, intermolecular stabilization in the crystal structure is due to van der Waals and Coulombic interactions, without the stronger hydrogen bond attraction. Hence, the intermolecular interaction in the crystal and the dense melt may be of about the same order of magnitude. (b) *If* such an intermolecular effect in these cases

TABLE I
Comparison of Calculated and Experimental ΔS_c and The Energy Parameters

Polymer	T_m , °K	Energy parameters, cal/mole		$\Delta S_c/n$	
		Flory	This work	Calculated	Experimental ⁸⁻¹⁰
Polyethylene (PE) ^{1,3}	410	$E_\sigma \simeq 400$ $E_\omega = 1500$	same	1.83	1.84
Poly(oxymethylene) (POM) ^{1,17}	450	$E_\sigma = -1500$ $E_\omega \simeq 1800$	same	2.88	2.8
Poly(oxyethylene) (POE) ^{1,20,21}	340	$E_\sigma = 900 \pm 70$ $E_{\sigma'} = -430 \pm 70$ $E_\omega = 350 \pm 200$	1200 -600 or -900 800 or 500	4.28	4.22
Poly(tetrafluoroethylene) (PTFE) ¹	600	$E_\sigma \gg 0$ $E_\omega = \infty$	$E_\sigma = 3-3.5$ $E_\omega = \infty$	0.7-0.8	0.76
Polystyrene— <i>isotactic</i> (PS) ⁶	510	$E_\eta + E_{\omega'} = 1800$ $E_\omega = E_{\omega'} = 1000$	same	2.56	2.6
Poly(dimethylsiloxane) (PDMS) ^{1,22}	230	$E_\sigma = 850$ $E_\omega = 1100$	same	2.55	2.76 ^a
Poly(ethylene terephthalate) (PET) ^{1,23}	540	$E_{\sigma_1} = 410$ $E_{\sigma_2} = -242$ $E_\gamma = 0$ $E_\omega = 1372$	0 -800 0 1000	7.8	8.2
<i>cis</i> -1,4-Polybutadiene (<i>cis</i> -PBD) ^{1,24}	274	$E_\zeta = 1800$ $E_\sigma = -200$	same	5.83	5.96
<i>trans</i> -1,4-Polyisoprene (<i>trans</i> PIP) ^{1,24}	347	$E_{\sigma'} = 367$ $E_\alpha = -24$ $E_\beta = 850$	600 200 1200	5.3	5.1

^a This refers to the total entropy of fusion $\Delta S_c + \Delta S_v$.

is of significant proportion, the fortuitous agreement may be due to errors in the experimental determination of the conformational entropy of fusion and the assumption that the total entropy of fusion is a simple sum of ΔS_c and ΔS_v .

Partition Function and ΔS_c

Mandelkern⁸ has discussed the relationship of heat and entropy of fusion to the type of the repeat unit of the polymer: those containing an even or odd number of successions of CH_2 groups in the backbone (polyesters and polyamides), the presence of an aromatic ring, and so on. Evidently, apart from the intermolecular association, the conformational preferences of the chain and the relative energy of the conformations should also dictate the value of ΔS_c . Thus, for a chain such as PTFE, E_σ is quite large and the ΔS_c is small. On the other hand, in the case of PET, the number of bonds in the repeat unit is higher than for PTFE, and, in addition, E_σ is relatively small; the ΔS_c is large for this polymer.

Since the conformational features of both the repeat unit and the succeeding units are reflected in the partition function, the $\Delta S_c/n$ values for the various polymers were plotted versus $\ln(Z^{1/n})$ as in Figure 7. The values of Z calculated for 100 repeat units at the T_m were used for this plot along with the energy parameters given in Table I. It is seen that the points for all the polymers, except for POM, cluster close to a straight line. This feature, when compared with eq.

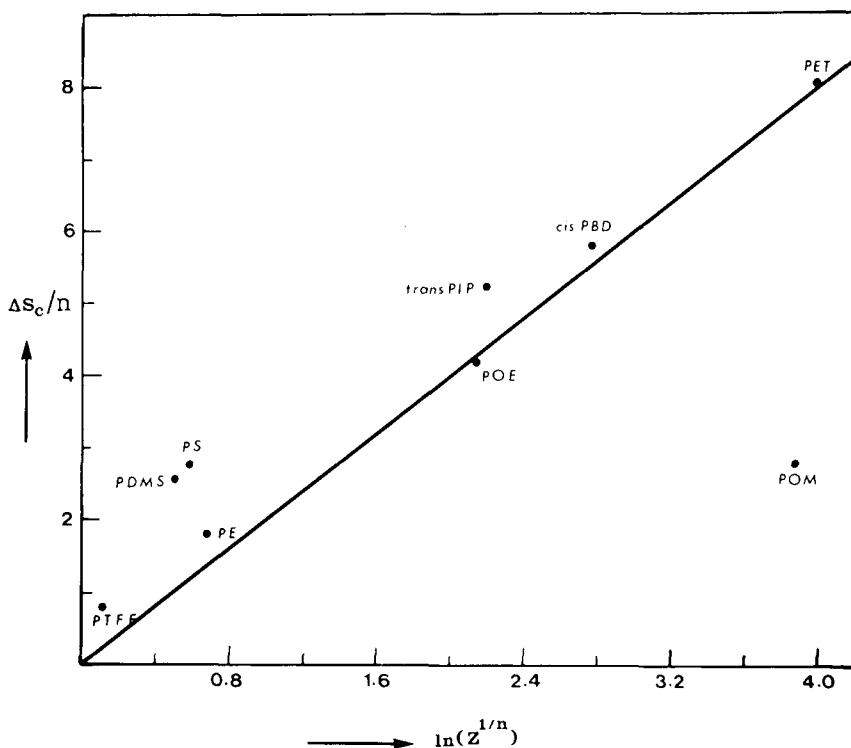


Fig. 7. Calculated values of $\Delta S_c/n$ plotted vs calculated $\ln Z^{1/n}$. The values of Z were calculated at the T_m of the respective polymers, each containing 100 repeat units. See Table I for abbreviations used.

(2), shows that the internal energy term $RT(d \ln Z/dT)$ is small for all these polymers. The solid line in Figure 7 corresponds to the equation

$$\Delta S_c/n = R \ln Z \quad (15)$$

in which the energy term has been omitted. For most of the polymers, the energy term is small and positive, whereas it is large and negative for POM. Granting that the assumptions made in the calculation of ΔS_c are valid also for POM, the deviation of POM can be traced to the values of the relative energies of its conformations, and this is illustrated with respect to PE.

The energy values for PE are $E_\sigma = 400$ cal/mole and $E_\omega = 1500$ cal/mole. The values of σ and ω increase with temperature, relative to a weight of 1 for the tt state, which leads to a positive value for $d \ln Z/dT$. In the range of temperature from, e.g., 400 to 420°K ($T_m = 410^\circ\text{K}$), the value of σ increases from 0.60 to 0.62 and the value of ω varies from 0.15 to 0.16. Due to the small changes in σ and ω in the vicinity of the melting temperature, the increment in $\ln Z$ is small. Similar behavior is found for PET, POE, and other polymers. On the other hand, in the case of POM for which $E_\sigma = -1500$ cal/mole, the value of σ decreases with increase in temperature relative to a weight of 1 for the tt state. The variation in σ is also significant. In the vicinity of the melting temperature ($T_m = 450^\circ\text{K}$), from 440° to 460°K, the value of σ decreases from 5.56 to 5.16, while the increase in ω is small and comparable to the case of PE. This accounts for the large negative value of $d \ln Z/dT$. Although the value of σ decreases rapidly in the range of T_m , its magnitude shows that the population of the helical conformations is still very high compared to the all-trans state.

Theoretical Calculation of T_m

In the preparation and utilization of polymers, it is useful to have an approximate theoretical value of the melting temperature of the polymer. An empirical method of estimating T_m from the sum of the "group contributions" was discussed by van Krevelen.¹⁹ In this method, T_m is given by the ratio of an additive "molar melt transition function" to the number of atoms in the chain backbone. The transition function depends on the type of polymer in which the groups occur.

The application of conformational analysis of polymers has in the past led to the methods of calculating several observed properties of polymers such as the solution properties, optical characteristics, stereoisomeric equilibrium, the crystalline structure, etc. In this section, an attempt is made to calculate the melting temperature of polymers from their conformational behavior, with a few assumptions. The method is applied to a total of 11 polymers, and the agreement between the experimental and calculated values is satisfactory.

As the polymer melts from the crystalline state, such a process possesses the characteristics of a first-order phase transition.⁸ We assume this to be true for the conformational entropy as well. Hence, at the melting temperature,

$$\frac{dS_c}{dT} = \text{maximum} \quad \text{and} \quad \frac{d^2S_c}{dT^2} = 0 \quad (16)$$

Differentiating eq. (2) we obtain

$$\frac{dS_c}{dT} = R \left[2 \frac{d}{dT} \ln Z + T \frac{d^2}{dT^2} \ln Z \right] = \text{maximum} \quad (17)$$

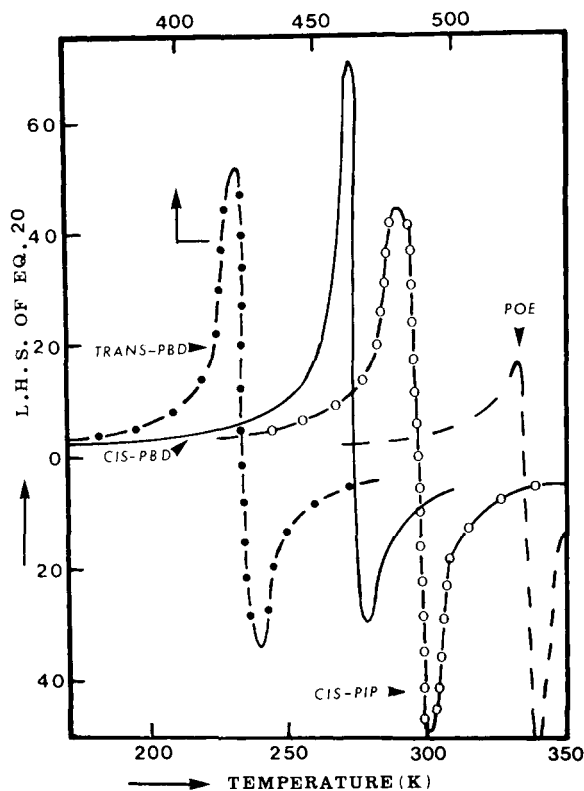


Fig. 8. L.H.S. of eq. (20) plotted vs T for a few polymers. See Table I for abbreviations used.

If, on the other hand, the total entropy including the volume contribution is considered,

$$S = R \left[\ln Z + T \frac{d}{dT} \ln Z \right] + k \frac{dV}{dT} \quad (18)$$

where k includes the compressibility and the coefficient of thermal expansion.¹⁰ Since the transformation is considered to be first order, d^2v/dT^2 can be equated to zero, and the differentiation of eq. (18) leads to eq. (17). Taking the second derivative,

$$3 \frac{d^2}{dT^2} \ln Z + T \frac{d^3}{dT^3} \ln Z = 0 \quad (19)$$

If the values of $\ln Z$ and the derivatives are calculated as a function of T , the temperature at which eq. (19) is satisfied gives the calculated value of T_m . However, considerable difficulties may be encountered in the calculation of the third derivative by numerical methods, even for simple chains such as PE, since the curve of the third derivative as a function of T would show severe noise. Analytic methods of taking derivatives of the statistical weight matrices would lead to complicated expressions even for chains such as POM or PS for which two statistical weight matrices are required. Hence, eq. (17) may be used to avoid calculating the third derivative. Even in this case, the sum in eq. (17)

was found to be insensitive to show a sharp maximum when plotted against T . Hence, eq. (17) is rewritten approximately as

$$\frac{2 \frac{d}{dT} \ln Z}{T \frac{d^2}{dT^2} \ln Z} + 1 = \text{maximum} \quad (20)$$

The course of the curves when the L.H.S. of eq. (20) is plotted versus T is shown in Figure 8 for a few polymers. It was found that $d^2 \ln Z/dT^2$ decreases with T and changes to negative value at T_m , indicative of a point of inflection in the curve of $\ln Z$ versus T . A list of the polymers, the energy parameters which reproduce the experimental values of T_m , and the calculated values of T_m are given in Table II. Only for the cases of PE and PS the magnitude rather than the absolute value of the L.H.S. of eq. (20) was taken, since the first and second derivatives are of opposite signs through the entire range of T for these two cases.

The agreement between the calculated and experimental values of T_m is satisfactory for all the polymers listed in Table II. The case of PS is, however, striking. It is known that, in general, syndiotactic polymers melt at a higher temperature than their isotactic counterparts. We have considered a purely

TABLE II
Calculated and Experimental Values of T_m and the Energy Parameters

Polymer	Energy parameters, cal/mole	$T_m, ^\circ K$		ΔS_c Calculated
		Calculated	Experimental	
PE	$E_\sigma = 400$ $E_\omega = 1400$	420	410	1.85
POM	$E_\sigma = -1800$ $E_\omega = 1800$	450	450	2.6
PTFE	$E_\sigma = 3000$ $E_\omega = \infty$	590	600	0.76
PDMS	$E_\sigma = 1000$ $E_\omega = 1100$	210	230	2.11
PS	$E_\eta = -800$ $E_\omega = 2500$ $E_{\omega'} = 2600$	470	510	2.32
<i>cis</i> -PIP	$E_\zeta = 1300$ $E_\sigma = 0$	300	300	—
<i>trans</i> -PIP	$E_\alpha = -300$ $E_\beta = 850$ $E_{\sigma'} = 800$	350	347	5.13
<i>cis</i> -PBD	$E_\zeta = 1200$ $E_\sigma = 0$	270	274	6.01
<i>trans</i> -PBD	$E_\alpha = -200$ $E_\beta = 1150$ $E_\sigma = 200$	420	421	—
PET	$E_{\sigma_\alpha} = 750$ $E_{\sigma_\eta} = -700$ $E_\omega = 1000$ $E_\gamma = 0$	540	540	7.32
POE	$E_\sigma = 1000$ $E_{\sigma'} = -300$ $E_\omega = 400$	330	340	4.8

isotactic polymer here while a certain amount of syndiotactic units might be present in the experimental case. The energy parameters given in Table II differ, though not significantly, from those given in Table I in a few cases. The calculated values of ΔS_c using the energy parameters which reproduce T_m are also given in Table II, and we find that the changes are small. The small differences between the energy parameters proposed by Flory (on the basis of calculations on the unperturbed end-to-end distance, its temperature coefficient, etc.) and those given in Tables I and II are believed to be due to a cumulative effect of the assumptions and approximations made to reproduce the experimental values of ΔS_c and T_m . The fact that these energy parameters are reasonably similar to those of Flory supports the premise that the assumptions and approximations invoked are not gravely in error. The agreement between the calculated and experimental values of T_m for polymers with various types of repeat units shows that although the method is empirical to some extent, the conformational characteristics of the polymer chains can be applied to the calculation of T_m . This procedure also avoids formulations of molar melt transition functions,¹⁹ which have to be carefully chosen depending on the type of repeat units and substituents.

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