Macromolecular Aggregation, Supramolecular Stability and Polymer Strength: Has the Van Der Waals Force been Underestimated?

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Abstract-- Macromolecular aggregation and mechanical strength characterize polymer behavior, but apparently remain enigmatic: small molecules prefer to be solvated but macromolecules prefer to aggregate. This is a consequence of the enormous loss of solvent entropy attending macromolecular solvation. The additivity of weak (e.g., van der Waals) forces in a macromolecule cannot explain aggregation, as the accompanying entropy loss would also be additive. However, even this would be overshadowed by the loss of solvent entropy in the case of its solvation. A thermodynamic basis for the aggregation, however, needs a reassessment of the van der Waals equation of state, a reinterpretation of the coefficient 'a' suggesting that the van der Waals force may be stronger ($\sim$15 kcal mol^{-1}) than believed. Its manifestation is normally thwarted by the dominance of entropic effects in the weak interactions. The phenomenal mechanical properties of polymers are explicable by the above reassessment of current ideas.

Keywords: macromolecular solvation, polymer aggregation, van der Waals coefficient.

INTRODUCTION

At the centennial of the initial developments in the science of macromolecules, the source of the extraordinary properties of the constituted polymers – particularly mechanical strength – remains mysterious. This elevation to enigmatic status of these (now) ubiquitous materials – clearly fundamental to modern civilization – may appear both startling and impertinent, given the preceding century of distinguished exploration [1, 2]! Indeed, polymer behavior and properties have been addressed by methods characterized by great acumen, insight and sophistication. Intriguingly, however, the abrupt changes in observable macroscopic properties manifested by the constituent macromolecules in a polymer, relative to small and even moderately-sized molecules, apparently continue to tantalize. There is also a philosophical streak to this enigma, in that it strikes at a corner-stone of the molecular theory of matter – the assumptions which correlate molecular structure and observable macroscopic properties. Thus, despite their size, the macromolecular constituents of polymers too remain beyond direct perception; their defining characteristics, e.g., resistance to chemical change, mechanical strength, etc., would then appear to represent disproportionate manifestations of molecular size. (The lay person may well be forgiven for assuming that a piece of polymer is constituted by a single, gigantic molecule!)

There are two defining characteristics of polymers that apparently distinguish them from non-polymers: aggregation and mechanical strength. The origins of these must be sought in the uniqueness of macromolecules, in particular their physico-chemical characteristics. Currently, polymer properties are explained by invoking the weak interactions (generally the van der Waals force), which are believed to be the key to

understanding macromolecular behavior. However, it is the thesis of this paper that this approach needs to be re-examined, particularly in terms of its quantitative basis, as argued extensively below.

RESULTS AND DISCUSSION

Entropy Changes: Aggregation vs. Solvation

Limitations of Current Theory. It is believed that characteristic polymer properties may be explained by invoking the additivity of weak intermolecular forces in a macromolecule [1, 2]. Thus, although these – particularly the van der Waals and related dispersive forces – are also present in small molecules, they remain essentially un-manifested because of their minuscule magnitude relative to normal chemical bonds. (The varying magnitude of the weak forces explains the existence of the different states of matter, i.e., gas, liquid and solid.) Thus, the van der Waals force (< 1 kcal mol^{-1}) is a tiny fraction of a covalent bond energy (~ 100 kcal mol^{-1}), in the case of molecules of relatively small mass and size [3].

This difference, however, would appear to diminish with increasing molecular weight, assuming that the weak forces are linearly additive with mass. In the case of a high molecular weight macromolecule, in fact, the sum of the weak forces would far exceed a covalent bond energy, perhaps by several orders of magnitude (depending on the molecular weight). Apparently, this would explain the tendency of macromolecules to aggregate and form larger cohesive structures. (The stronger polymers, e.g., polyesters and polyamides, would also benefit from stronger intermolecular interactions, such as dipole-dipole, hydrogen bonding, etc.)

3

Table 1. The entropy contents of the simpler alkanes[a]

Hydrocarbon	Entropy content (cal K^{-1} mol^{-1})
CH_4	44.5
C_2H_6	54.8
C_3H_8	64.7
i-C_5H_{12}	62.3
i-C_6H_{14}	69.5

[a]Under standard conditions (from ref. 4)

Macromolecular Thermodynamics. However compelling they may be, the above arguments appear to ignore other trends attending aggregation. Indeed, the additivity of the weak forces leads to a very large enthalpic change that favors aggregation; however, this is also accompanied by a substantial entropy change that would disfavor aggregation. This is because a macromolecule retains substantial entropy upon formation from its constituent monomers. Thus, in a macromolecule formed from monomer units, much of the translational and rotational entropy of the individual units would be lost upon their polymerization; however, the macromolecule would possess substantial vibrational entropy derived from the relative conformational orientation of the individual units. This is indicated by the fact that entropy content generally increases with molecular size (Table 1) [4].

Also, although the formation of a macromolecule is accompanied by the loss of entropy of the monomer units, the Gibbs free energy change is overwhelmingly favorable. This is because the higher enthalpy content of the monomers is relieved upon formation of the covalent bonds of the macromolecular backbone (Fig. 1).
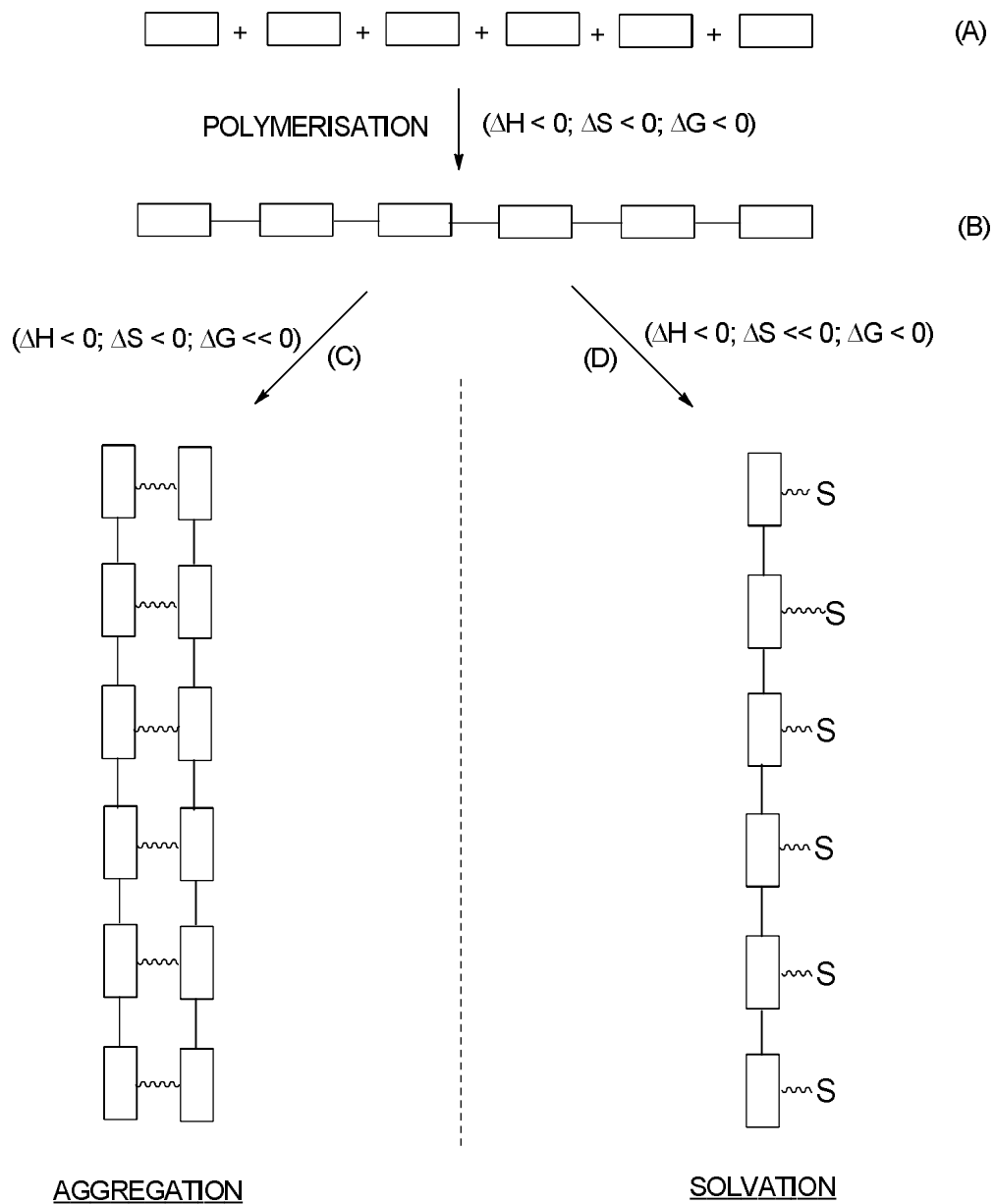
Fig. 1. Cartoon representation of the process of polymerizing a set of monomer units (rectangles in A) to corresponding polymer (B), followed either by its aggregation (step C) or interaction with solvent S (step D). The changes in the thermodynamic quantities accompanying each step are shown alongside the reaction arrows.

Table 2. The vibrational entropy of certain linear polypeptides[a]

Polypeptide	Entropy content (cal K^{-1} mol^{-1})
Ac-A_7-CO_2-A_8-NMe[b]	500
Ac-A_7-CO_2-A_8-NMe[b]	200[c]
Decaglycine (extended)[d]	286

[a]At ~ 300 K; [b]ref. 5 (A = L-alanyl); [c]conformational entropy; [d]ref. 6

It is noteworthy again, however, that the loss of translational and rotational entropy of the monomers is to an extent compensated by the entropy deriving from the conformational disorder within the macromolecule (*vide supra*). In fact, this is substantial in itself, so that its loss upon aggregation would lead to a correspondingly unfavorable free energy change.

Interestingly, however, this would not be offset by the enthalpic component deriving from the weak interactions. The entropy content of macromolecules has been investigated by a variety of theoretical and experimental methods [5-17]. Thus, the conformational entropy of even modestly sized macromolecules (~ 15 monomer units) is $>> 10^2$ cal K^{-1} mol^{-1}, indicating a contribution to the Gibbs free energy of $>> 30$ kcal mol^{-1} at normal temperatures (*cf.* Table 2) [5, 6]. This amounts to $>> 2$ kcal mol^{-1} per monomer unit, a substantial part of which would be lost upon aggregation. This is clearly in excess of the enthalpic gain based on the weak interactions (< 1 kcal mol^{-1}/unit, *vide supra*). In the case of a high molecular weight polymer, e.g., polystyrene, the entropic loss upon aggregation would indeed overwhelm the enthalpic gain, leading to a disastrously unfavorable (large and positive) Gibbs free energy change.

Key Question! These arguments then raise the intriguing question: what is the driving force for the aggregation of macromolecules, and indeed, supramolecular interactions in general? In trying to answer this question, clearly of fundamental import in modern chemistry, an essential molecular characteristic needs to be appreciated. This is the need for a molecule (whatever its size) to interact with other molecules. Clearly, isolated molecules in the gas phase are thermodynamically unstable, relative to their condensed phases (liquid or solid). This is, of course, due to the existence of stabilizing weak interactions between the molecules in the latter states. These interactions can also involve solvent molecules in the case of dissolved small molecules.

Role of Entropy. Such solvation, however, would be energetically prohibitive in the case of macromolecules, because of an overwhelming loss of solvent entropy. Thus, the solvation of a single macromolecule composed of n monomer units would require ~ mn molecules of solvent, where m is the number of solvent molecules required to solvate a single monomer unit. Clearly, the dissolution of a macromolecule involves the loss of an enormous amount of solvent entropy. An estimate of the corresponding loss in energy may be obtained by assuming an average translational energy of ~RT for the solvent molecules. For $m = 10$ and $n = 10^2$, $mn = 10^3$ – i.e., a macromolecule of modest length being minimally solvated – the loss in solvent translational energy would then be ~ 600 kcal mol^{-1} at normal temperatures.

The aggregation of the same macromolecule would be entropically disfavored by a Gibbs free energy increase of ~ 200 kcal mol^{-1} (based on a contribution of ~ 2 kcal mol^{-1} per monomer unit, *vide supra*). Apparently, therefore, aggregation is the preferred mode of stabilization of a macromolecule. (For a large macromolecule, the above

difference would overwhelmingly favor aggregation. Also, the fact that aggregation is observed despite the entropic loss, implies that the isolated macromolecule is overwhelmingly unstable on enthalpic grounds.)

The Entropy of Mixing Paradox . Indeed, it is well known that the entropy of mixing of macromolecules is unusually low [1, 2]. (Thus, the entropy of mixing of polystyrene in toluene < 10 cal K^{-1} mol^{-1} and in decalin $<< 10^2$ cal K^{-1} mol^{-1} [7, 8].) However, this has been attributed to the fact that the macromolecule itself gains very little entropy upon dissolution, relative to a smaller molecule. This is presumed to be because its sub-units are covalently linked to each other, and thus are curtailed in their motions.

The problem with this argument, however, is that it (apparently) compares a single macromolecule composed of (say) n sub-units with n free sub-units. This is clearly inaccurate, as the appropriate comparison would be between a single macromolecule and a single monomer (sub-unit) molecule: then the dissolution of the macromolecule would be expected to occur with a substantial increase in entropy. (Importantly, the entropy and free energy changes need to be compared on a per-mole basis in each case!)

Interestingly, it is possible that the low measured entropies of mixing of macromolecules likely derive from the loss in solvent entropy that would occur upon their solvation. This, then, is sound experimental evidence for the above arguments, which essentially state that the loss of entropy upon aggregation is far overshadowed by that upon solvation, in the case of a macromolecule.

Supramolecular Interactions. The fact that macromolecular aggregates dissolve in solvents which are themselves polymeric – e.g., cellosolve, diglyme, polyethylene

glycol, etc., – also supports the above arguments. This is because these solvents suffer less entropy loss by interacting with a macromolecule, relative to solvents of low molecular weight, which would possess greater freedom of motion. Such interactions, of course, are now recognized as supramolecular, thus implying that relatively large molecules tend to interact with other large molecules – a phenomenon which goes against intuitive steric considerations.

Supramolecular interactions, of course, play a crucial role in biological systems [18]. They manifest as enzyme-substrate, antigen-antibody, cell surface-antigen, protein-protein, protein-nucleic acid, etc., interactions. (Natural polymers, e.g., wood, silk, cotton, hair, etc., are renowned for their strength and durability.) It is generally believed that these interactions are largely driven by the hydrophobic effect, although the entropy gained by release of bound water is sometimes invoked as an explanation. In fact, this may well be the major contributor to supramolecular binding. It is noteworthy that, in biological systems at least, supramolecular interactions involve relatively minuscule concentrations of the reacting partners. These must compete with molecules of water that are present in overwhelming excess. There must be a driving force, therefore, which enables the supramolecular interaction to occur at all. (Specificity, in the lock-and-key sense, would only come into play once the interaction occurs.)

Thus, it is a fine balance in entropy changes that apparently favors aggregation. This is, in a way, an essential kinetic basis for aggregation that, however, leaves the thermodynamic basis unclear. (The kinetic stability of the aggregates would also derive from the inaccessibility of the interior of the aggregates to external solvent and reagent molecules.) To reiterate, the isolated macromolecule is apparently of very high enthalpy

content, which is relieved *via* the weak interactions attending aggregation. On the other hand, the weak interactions per sub-unit remain a tiny fraction of the thermodynamic stability of a typical covalent bond! (Thus, the cumulative supramolecular forces between macromolecules would be enormous, but remain minuscule at the sub-unit level.) What, then, holds the macromolecular aggregate together?

<div align="center">**Reassessment of the van der Waals Force**</div>

A Thermodynamic Missing Link. The above arguments apparently indicate that there yet remains a "missing link" in the theory of polymer stability: it seems highly unlikely that the phenomenal mechanical properties of polymers do not have a firm thermodynamic basis! An intriguing possibility is that the van der Waals force – the basis of the current theory of polymer stability – has itself been grossly underestimated.

The idea of the van der Waals force originated in the deviations from the ideal gas law observed in the case of real gases [3]. The deviations were attributed to both intermolecular attractive forces between the gas molecules, and the fact that they possessed a definite size. The neglect of these in the classical theory of the ideal gas, and the attendant lacunae discussed above, indicated the need for a broader treatment of the behavior of gas molecules.

Van Der Waals Equation of State. These ideas led to the van der Waals equation of state (*P* being the observed pressure, *V* the observed volume, *T* the temperature, *R* the gas constant, *a* and *b* the van der Waals coefficients, and *n* the number of moles of the gas present):

$$P = [nRT/(V -- nb)] -- a(n/V)^2 \qquad (1)$$

In Eq. (1), whilst coefficient a corrects the ideal gas law for the attractive forces between the molecules (resulting in a reduced pressure), coefficient b does so for the size possessed by them (resulting in an increased volume). Thus a possesses dimensions of (atm l^2 mol^{-2}) and b of (l mol^{-1}). The a had a supreme theoretical significance of far-reaching import, in that it gave rise to the concept of a weak attractive force that generally exists between atoms and molecules. Subsequent quantum-theoretical modeling of this weak force indicated that it is effective only at very short range, waning rapidly as the sixth power of the distance [19]. The significance of a can be judged from its dimensions as discussed below.

$$2A \rightleftharpoons A\text{-}A \qquad (2)$$

The van der Waals force may be represented by the equilibrium shown in Eq. (2) ('A' being a gas molecule and 'A-A' its dimeric complex formed by the van der Waals interaction). The equilibrium constant (K) of the above reaction is given by Eq. (3).

$$K = [A\text{-}A]/[A]^2 \qquad (3)$$

$$P_{A\text{-}A} = [A\text{-}A] = K[A]^2 = a[A]^2 \qquad (4)$$

$$P_{A\text{-}A} = (n/V)_{A\text{-}A}RT \qquad (5)$$

$$K' = (n/V)_{A\text{-}A}/[A]^2 = a/RT \qquad (6)$$

$$\Delta G^o = -RT\ln K' = -RT\ln(a/RT) \qquad (7)$$

Significance of Coefficient a. Intriguingly, K would possess the dimensions of a if [A-A] were to be expressed in 'atm' and [A] in mol L^{-1}. Thus, a apparently represents the equilibrium constant (K) of the reaction in Eq. (2), if K were to be expressed with mixed dimensions (i.e., atm L^2 mol^{-2}). Although this is unusual, it leads to the partial pressure of 'A-A' ($P_{A\text{-}A}$) in terms of [A], as in Eq. (4). In fact, the assumption that $K = a$

is also justified vis-à-vis Eq. (1), in which $(n/V) = [A]$: thus, by Eqs. (4) and (5), $a(n/V)^2 = a[A]^2 = P_{A-A}$. This is indeed the amount by which the ideal pressure is reduced by the van der Waals complexation of Eq. 2. (Note that 'A-A' is present in minuscule amounts, so [A] is practically the overall gas concentration.)

Interestingly, partial pressure P_{A-A} can be expressed in terms of concentration by invoking the ideal gas relation ($PV = nRT$) as in Eq. (5), where $(n/V)_{A-A}$ would be the concentration of 'A-A'. (This would be in mol l^{-1} as per the ideal gas relation, with P in 'atm' and V in 'l'.) Note that as 'A-A' is present in minuscule concentrations, the ideal gas law – rather than the van der Waals equation [Eq. (1)] – may be applied.

Now, combining Eqs. (3) – (5) leads to Eq. (6), in which K' is the equilibrium constant expressed entirely in concentration units, i.e., with dimensions of mol^{-1} l (M^{-1}). The standard Gibbs free energy change (ΔG^o) in the reaction is now given by Eq. (7), in terms of the van der Waals coefficient a.

Typically, $0 < a < 7$ for most commonly encountered gases (e.g., He 0.035, Ar 1.35, N_2 1.39, CO_2 3.59 for, Cl_2 6.58). An average value of $a = 5.0$ leads to $\Delta G^o = -1.26$ kcal mol^{-1}. This then is a measure of the van der Waals force for a typical atom. (Note that for $a > RT$, the formation of 'A-A' would be exothermic.)

$$\Delta G^o = (G_{A-A} - G_A)^o = (\Delta H^o - T\Delta S^o) = (H_{A-A} - H_A)^o - (S_{A-A} - S_A)^o \tag{8}$$

Furthermore, ΔG^o can be expressed in terms of the standard enthalpy change (ΔH^o) and the standard entropy change (ΔS^o) as in Eq. (8) [3]. (The superscripted 'o' indicates standard state values; the subscripts 'A' and 'A-A' are self-explanatory.) Thus, an observed low negative ΔG^o may be due to either a low negative ΔH^o (with ΔS^o, say, ~ 0), or a relatively high negative ΔH^o that is overwhelmed by a large negative ΔS^o. It is

noteworthy that the reaction in Eq. (2) would possess a large negative ΔS^o, as it is an associative process.

The True Measure of the Van Der Waals Force. In fact, gases are known to possess large entropy contents, so the second of the above possibilities, i.e., a large negative ΔS^o, seems likely. An estimate of the magnitude of this can be surmised as follows. The standard entropy of gases (typically) is ~ 50 cal K^{-1} mol^{-1} (e.g., CH_4 44.56, CO_2 51.13, Cl_2 53.37). This may be assumed to represent both S_A and S_{A-A} in Eq. (8). Also, as two molecules of A form one of A-A, the corresponding loss of entropy (ΔS_A) would be ~ 50 cal K^{-1} mol^{-1}. Thus, $T\Delta S_A$ ~ --15 kcal mol^{-1} (at 300 K). With ΔG^o = -- 1.26 kcal mol^{-1} (*vide supra*), ΔH^o = --16.26 kcal mol^{-1}.

This is indeed a remarkably large enthalpy change favoring the van der Waals interaction, a major part of which would be manifested under conditions in which the negative entropy change is correspondingly suppressed. (Thus, if ΔS^o ~ 0, ΔG^o ~ 16 kcal mol^{-1}.) Therefore, apparently, the van der Waals force is 'inherently' strong (in terms of enthalpy), but – in the case of gases – is overwhelmed by a large negative entropy change.

Approach Involving the Van't Hoff Equation. An alternative approach – although apparently futile – to ΔH^o may be briefly mentioned here. This invokes the van't Hoff equation [3], which relates ΔH^o to the temperature dependence of the equilibrium constant [Eq. (9), K' from Eq. (6)]:

$$\text{d}(\ln K')/\text{d}T = \Delta H^o/RT^2 \tag{9}$$

$$\text{d}\ln(a/RT)/\text{d}T = \Delta H^o/RT^2 \tag{10}$$

$$\Delta H^o = --RT^2 \tag{11}$$

Combining Eqs. (6) and (9) leads to Eq. (10), which is apparently intractable in terms of units. This can be seen by transforming Eq. (10) to Eq. (11), which does not involve a, and is also dimensionally unbalanced. (The differential involved in the above transformation can be obtained from standard sources, e.g., ref. 4.) Thus, K' as expressed in units of M^{-1} needs to be employed in the van't Hoff equation. Hence, this approach to estimating $= \Delta H^o$ in terms of a seems unviable.

Comparison with the Hydrogen Bond: A Paradox? Intriguingly, even if a part of ΔH^o (as estimated above) were to be manifested, the van der Waals force would acquire parity with the hydrogen bond ($\Delta G \sim 5$ kcal mol^{-1}, or perhaps even exceed it)! The problem now would be explaining why methane remains a gas at normal temperatures, whereas hydrogen-bonded water (of similar molecular weight) is a liquid!

A possible explanation for this apparent anomaly is that the weak interactions (e.g., the van der Waals force or the hydrogen bond) are dominated by entropic effects, whereas the strong interactions (e.g., the covalent bond) are dominated by enthalpic effects. It should be noted that this involves the entropy of the van der Waals interaction itself, i.e., the loss of entropy upon formation of the van der Waals complex (Eq. 2).

This is not to be confused, of course, with the entropy of aggregation or solvation discussed at length above. The ΔS^o of Eq. 8 refers to a special case of the van der Waals complex involving the molecules of a gas. In the general case of the condensed phase, ΔS^o would be relatively modest in magnitude. However, as the corresponding ΔH^o would be small, the ΔS^o would remain dominant (relative to the covalent case).

This logic is then extended to a comparison with the hydrogen bond: the more negative ΔH^o in the case of the van der Waals force indicates tighter binding, but also a

correspondingly more positive ΔS^{o}. This apparently implies stricter geometrical requirements for the van der Waals force, as also a lower (less negative) ΔG^{o}.

However, in the formation of the much stronger covalent bond, the large negative enthalpy change would overwhelm the entropic loss: the above enthalpy-entropy correlation would break down, resulting in a large negative ΔG^{o}. Therefore, essentially: a more negative ΔH^{o} leads to a more positive ΔS^{o} and (hence) a less negative ΔG^{o} (van der Waals force and hydrogen bond cases); but a very large negative ΔH^{o} is accompanied by a relatively modest positive ΔS^{o} and a large negative ΔG^{o} (covalent case).

These arguments also indicate the need for renewed theoretical modeling of the van der Waals force. The currently accepted dispersion model is based on early work that apparently assumes that the van der Waals force is inherently weak. Qualitatively, it proposes a weak interaction between instantaneous dipoles, resulting from the unsymmetrical nature of the circulating electron cloud in atoms and molecules [19]. A possible new model would need to include a more intimate electronic interaction, perhaps partial exchange of the electron clouds of the atoms in contact. (No violation of the valency rules is implied, as both atoms would act as both donor and acceptor of an equal part of the electron cloud and charge.)

A Reassessment of Macromolecular Aggregation: the Equilibrium Constant. The possibility that the van der Waals force would manifest in full strength if the negative entropy change accompanying the interaction were to be minimized, is clearly relevant to the present discussion on macromolecular aggregation. As argued above, the entropy content of macromolecules may be considered as either substantial or insubstantial depending on the standard of comparison. Thus, relative to a small

molecule, a macromolecule retains substantial entropy. However, relative to a collection of monomer units, a single macromolecule composed of an equal number of such units has negligible entropy.

Therefore, the van der Waals force would manifest to a far greater extent in the aggregation of the macromolecule (negligible entropy loss), than in the collection of monomer units. Conversely, the aggregation of macromolecules offers the best chance for the manifestation of the van der Waals force, which would thus offer a firm thermodynamic basis for the observed macroscopic behavior of polymers.

However, a minuscule van der Waals force, acting on the constituent macromolecules, cannot account for the enormous strength of polymers. Such a weak effect would lead to a very modest equilibrium constant for macromolecular aggregation (~ 1 or so), not taking into the accompanying entropy loss, which would be substantial as argued above (for the case of aggregation). In particular, the additivity of the van der Waals force will not alter the equilibrium constant for the aggregation at the sub-unit level. Thus, although the sum of the weak interactions in a macromolecule may appear to be enormous, it is also distributed over an equally enormous molecular length! Clearly, the van der Waals force needs to be at least an order of magnitude greater than currently estimated. This indicates the need to reassess the magnitude of the weak interactions governing the aggregation, based on a reinterpretation of the van der Waals equation of state, as argued above.

CONCLUSIONS

The intermolecular interactions that stabilize macromolecules are different, in both degree and kind, from those of small molecules. This is because the role of entropy

is relatively complex in the former case. A macromolecule possesses very many internal degrees of freedom and hence is entropy-rich relative to a small molecule. The loss of entropy upon the aggregation of macromolecules would substantially offset the enthalpic advantage, which results from the accumulation of the enormous number of weak interactions (generally of the dispersive type). However, this is apparently preferable to external solvation which entails a far greater loss of solvent entropy. The resulting aggregates would thus remain weakly stabilized in terms of enthalpy.

A thermodynamic basis for the aggregation, however, requires a reassessment of the magnitude of the van der Waals force. A reinterpretation of the coefficient a in the van der Waals equation of state, in fact, indicates that the van der Waals force may well be over an order of magnitude stronger than currently believed. However, its manifestation is apparently thwarted by the dominance of entropic effects in the weak interactions. The van der Waals force, however, is substantially manifested in the case of macromolecular aggregation, apparently because of the low entropy content of a macromolecule relative to a collection of corresponding monomer units. These reassessments of current ideas are not only necessary in themselves, but also lead to a satisfactory explanation for the observed properties of polymers (which, in effect, justifies the reassessments).

ACKNOWLEDGMENTS

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