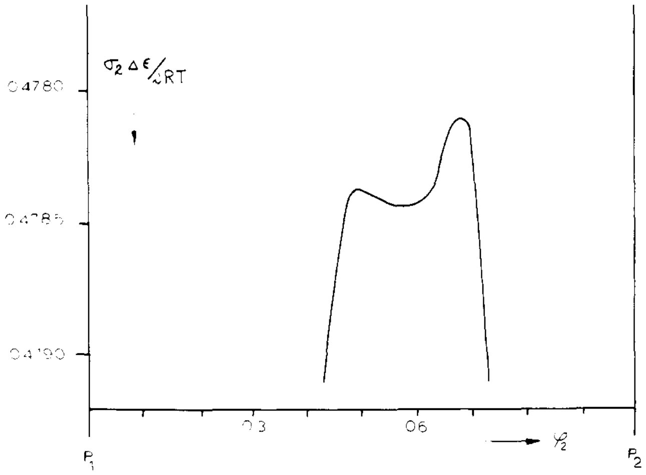

Figure 2. Spinodal calculated with Huggins' eq 4 for $m_1 = 7.2$ and $m_2 = 45$; $k_1 = -0.69$, $k_2 = +0.91$, $\rho = 0.8$.

comparing measured and calculated limits of thermodynamic stability.

Huggins further amends the combinatory entropy of mixing (the first two terms on the rhs of eq 2) by making allowance for the influence of the immediate surroundings of a segment on its average randomness of orientation with respect to the preceding segment in the chain molecule. Setting the average allowed number of orientations of the segment equal to ν^0 when it is at infinite dilution in the second polymer, and correcting it to a value $\nu^0(1 - k_S)$ for a segment in the undiluted polymer, he calculates two "orientational" contributions to the entropy of mixing. Inserting these terms into the full ΔG_ϕ expression, one obtains

$$\Delta G_\phi/RT = \sum_i \phi_{1i} m_{1i}^{-1} \ln \phi_{1i} + \sum_j \phi_{2j} m_{2j}^{-1} \ln \phi_{2j} + g\phi_1\phi_2 - \phi_1 \ln (1 + k_1\rho\phi_2 Q^{-1}) - \phi_2 \ln (1 + k_2\phi_1 Q^{-1}) \quad (4)$$

Two parameters k_{S1} and k_{S2}, related to k_1 and k_2 by $k_{Si} = k_i/(1 + k_i)$, were treated by Huggins in a rather intuitive way and had so far to be considered as empirical parameters. Recently, it was found that the formulation of ΔG according to eq 4 is very useful in the description of peculiarly shaped spinodals in some liquid oligomer/polymer mixtures.[12,13] An example of this work is given in Figure 1 which shows the spinodal of such a system determined with Gordon et al.'s pulse induced critical scattering method.[14,15]

At least qualitatively, the obvious bimodality of the spinodal appeared to be well within the scope of eq 4. To calculate such shapes, negative and positive values had to be assigned to k_1 and k_2 (Figure 2), and this seems to make physical sense, in view of the flexibilities of polyisobutylene and polystyrene chains and their mutual influence.[12,13]

We now come to the objective of this note and suggest that further development of a theoretical basis for Huggins' k_S parameters might be supported by a comparison of Silberberg's and Huggins' formulations of the free enthalpy of mixing. To clarify this point we simplify the relevant terms in eq 2, neglecting m^{-1} with respect to 1 and assuming τ to be independent of chain length. The comparison of eq 2 and 4 then suggests

$$\tau_1 = V_1^*(\phi_1)/V_1^*(1) \equiv 1 + k_1\rho\phi_2 Q^{-1} \quad (5a)$$

and

$$\tau_2 = V_2^*(\phi_2)/V_2^*(1) \equiv 1 + k_2\phi_1 Q^{-1} \quad (5b)$$

Silberberg conceives the parametric volumes to be identical or at least closely related to the coil volumes.[16] Adopting this picture we must expect a negative value of k_1 to involve a decrease in coil size of polymer 1 with decrease in concentration. In the dilute-solution limit of polymer 1 in polymer 2 ($\phi_1 = 0$, $\phi_2 = 1$) we have $\tau_1 = 1 + k_1$, whereas bulk polymer 1 ($\phi_1 = 1$, $\phi_2 = 0$) is characterized by $\tau_1 = 1$. Conversely, with respect to polymer 2: $\phi_2 = 0$, $\phi_1 = 1$ gives $\tau_2 = 1 + k_2$ (for a dilute solution of 2 in 1), and $\phi_2 = 1$, $\phi_1 = 0$ gives $\tau_2 = 1$ (for bulk polymer 2).

As far as bulk polymers are concerned we note that eq 5a and 5b give meaningful results. Recent neutron scattering measurements[17] point to the coils having unperturbed dimensions in the amorphous bulk state ($\tau = 1$); eq 5 are consistent with that feature. At the other end of the concentration scale we have less foothold. A negative value of k_1 suggests $\tau_1 < 1$ at infinite dilution of polymer 1, i.e., coil contraction with respect to the unperturbed bulk dimension.

We are aware of only one reported value in the literature that may lend some support to the latter conclusion. The coil size of polymethylstyrene dissolved in deuterated poly(methyl methacrylate) appears to be very small and points to a collapse of the molecules.[18] The negative second virial coefficient further indicates the possible relevance of this example to the present analysis, but we cannot be sure until coil-dimension data on systems with two-peaked spinodals become available. In the present framework one would then expect the coils of polymer 2 to be expanded in dilute solutions in polymer 1 ($k_2 > 0$). We do not know of any experimental evidence for this at the moment.

Although the present interpretation placed on τ_1 and τ_2 is empirical in nature, the presence of these parameters in the expression for ΔG_ϕ does allow the effects of changes in configurational behavior on mixing to be accounted for, and the possibilities of more fundamental interpretations of τ_1 and τ_2 are currently being investigated.

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Polymer Chain Stiffness Parameter, σ, and Cross-Sectional Area per Chain

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Privalko and Lipatov[1–6] have been concerned recently with correlation of various physical properties with the chain

Table I
Chain Stiffness Parameters and Cross-Sectional Areas per Chain

No.	Polymer	Area,[a] nm^2	σ	Ref
1	Poly(oxymethylene)[h]	0.172	2.3	10
2	Poly(tetramethylene oxide)[h]	0.176	1.68	1
3	Poly(hexamethylene adipamide)	0.177	1.63	7
4	Poly(6-aminocaproic acid)	0.179	1.63	7
5	Poly(hexamethylene oxide)	0.181	1.61	11
6	Poly(ethylene adipate)[h]	0.181	1.68	1
7	Poly(decamethylene oxide)	0.183	1.72	12
8	Poly(ethylene)[h]	0.183	1.63	7
9	Poly(decamethylene sebacate)	0.185	1.65	7
10	Poly(hexadecamethylene sebacate)	0.185[b]	1.80	7
11	Poly(hexamethylene sebacate)	0.185	1.7	7
12	Poly(6-hydroxycaproic acid)	0.186	1.67	13
13	Poly(ethyleneoxymethylene oxide)	0.188	1.61	5
14	*cis*-Poly(1,4-butadiene)[h]	0.207	1.75	14
15	Poly(ethylene oxide)[h]	0.214	1.63	1
16	Poly(trimethylene oxide)	0.224	1.43	15
17	Poly(propylene oxide) (atactic)[h]	0.245	1.62	1
18	Poly(vinyl chloride)	0.275	1.83	7
19	*cis*-Poly(1,4-isoprene)[h]	0.280	1.67	7
20	Poly(chloromethylethylene oxide)	0.298	1.7	4
21	Poly(vinyl bromide)	0.308	1.82[i]	7
22	Poly(chlorotrifluoroethylene)[h]	0.356	2.03	7
23	Poly(propylene) (atactic)[h]	0.378	1.87	1
24	Poly(isobutylene)[h]	0.412	1.80[i]	7
25	Poly(1-butene)[h]	0.452	1.82	7
26	Poly(acrylic acid)	0.452[c]	1.85[i]	7
27	Poly(1-pentene)	0.584	2.08	16
28	Poly(vinyl acetate)	0.593	2.12[i]	7
29	Poly(methyl acrylate)	0.593[d]	2.05	7
30	Poly(methyl methacrylate)[h]	0.638	2.14[i]	1
31	Poly(styrene)[h]	0.698	2.22[i]	7
32	Poly(vinyl isobutyrate)	0.723[e]	2.32	7
33	Poly(γ-benzyl L-glutamate) (β form)	0.852[f]	2.32	7
34	Poly(4-methyl-1-pentene)	0.863	2.2	3, 4
35	Poly(*o*-methylstyrene)	0.903	2.27	5
36	Poly(*o*-chlorostyrene)	0.903[g]	2.41	17
37	Poly(*m*-chlorostyrene)	0.986[g]	2.48	5
38	Poly(1-vinylnaphthalene)	1.124	2.46	18
39	Poly(vinylcyclohexane)	1.196	2.4	4
40	Poly(*N*-vinylcarbazole)	1.247	2.85[i]	19

[a] Calculated from $A = V/n\cdot c$, where $V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$ is the volume of the unit cell calculated from published unit cell vectors **a**, **b**, and **c**, n is the number of chains per unit cell, and c is the fiber repeat distance. [b] Taken as poly(decamethylene sebacate). [c] Taken as poly(1-butene). [d] Taken as poly(vinyl acetate). [e] Taken as poly(isopropyl acrylate). [f] Taken as α-benzyl × (β-methyl/α-methyl). [g] Taken as the corresponding methyl polymer. [h] Considered in ref 6. [i] Measurements made in a theta solvent; results are thus independent of extrapolation procedures.

stiffness parameter, σ, defined by

$$\sigma^2 = \langle r^2\rangle_0/\langle r^2\rangle_{0f} \qquad (1)$$

In eq 1, $\langle r^2\rangle_0$ and $\langle r^2\rangle_{0f}$ are the mean-square displacement lengths (end-to-end distances) of a polymer in the unperturbed state (as in a theta solvent) and in the freely rotating state with fixed valence angles, respectively.[7] For example, Privalko and Lipatov obtained an empirical correlation

$$10^{-2}N_c = 0.24(a/\sigma)^{2.5} \qquad (2)$$

where N_c is the number of chain atoms between entanglements and "a" is the chain thickness.[6]

We have recently calculated cross-sectional areas per polymer chain, A, from published lattice parameters. From these, the average distance between chains (i.e., the effective chain thickness) can be taken as $d_a \approx A^{1/2}$. We have also been interested in correlations between physical properties of polymer chains and cross-sectional areas.[8,9] For example, we have shown[9] that $N_c \propto A^{0.5-0.6}$. Hence, if chain thickness, a, is identified with d_a (and, hence, with $A^{1/2}$), it follows that a relationship of the form

$$\sigma = F(A) \qquad (3)$$

is required to satisfy eq 2. Since there was considerable scatter in the plots presented by Privalko and Lipatov[6] leading to eq 2, we considered an alternate correlation of σ with A alone. This note reports our results.

Values of σ and of A, arranged in order of increasing chain area, and the source of the σ values, are listed in Table I. In most of the cases, room temperature values are given. The set of polymers considered by Privalko and Lipatov[6] is indicated; they took values of σ mainly from Kurata and Stockmayer.[7] All of the values of σ listed in Table I were deduced from intrinsic viscosity measurements; those values based essentially on theta-solvent conditions are so noted. We have considered only polymers with carbon–carbon, carbon–oxygen, and carbon–nitrogen bonds in the backbone, as did Privalko and Lipatov.[5] All of the polymers listed in Table I have essentially similar chain statistics.[20]

A log–log plot of the data of Table I is shown in Figure 1. The linear least-squares fit to most of the data (all but the two triangles) shown is:

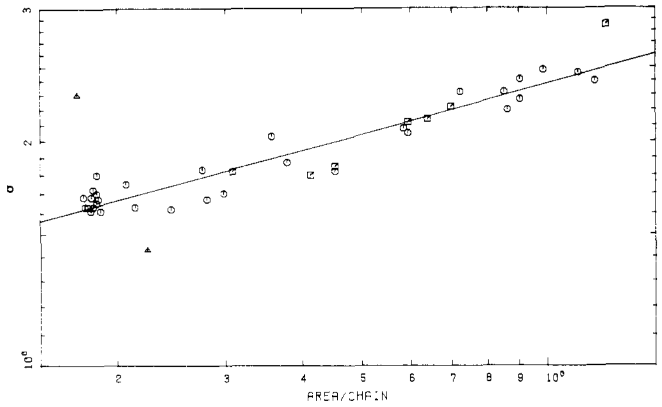

Figure 1. Chain stiffness, σ, as a function of polymer chain area, A (in nm^2), for the polymers listed in Table I: (□) theta-solvent conditions; (○) non-theta-solvent conditions; (△) deviant points (see text). The solid line is a least-squares fit to all but the deviant points.

$$\log \sigma = 0.38 + 0.22 \log A \qquad (4)$$

The standard error (residual) of $\log \sigma$ is 0.02 and the correlation coefficient, R^2, is 0.90. Combination of eq 2 and 4 leads to the relation $N_c \propto A^{0.7}$, in satisfactory agreement with our earlier results.[9]

Some discussion of the deviant points (triangles) is in order. Poly(oxymethylene) (POM) is unique in its strong preference for gauche conformations at all bonds, which tends to produce helical sequences of gauche bonds and thus to enhance chain dimensions.[20,21] There may also be some expansion due to solvation by the hexafluoroacetone hydrate in which the measurements were made.[10] At higher temperatures (90 °C) Kokle and Billmeyer[22] found $\sigma = 1.8$ for POM in phenol. If the temperature dependence of $\langle r^2 \rangle_0$ could be neglected, this value would fit the line of Figure 1 moderately well.

The low value for poly(trimethylene oxide) determined by Yamamoto, Teramoto, and Fujita[15] is striking. Takahashi and Mark[23] obtained an even lower value and attributed the unusual compactness of this polymer to a high degree of conformational randomness in the chain. Comparison with other poly(oxyalkanes) indicated the unique behavior of this material (cf. their Figure 5).

The scatter about the regression line of Figure 1 is quite acceptable. Of course, part of this scatter arises from experimental errors and part arises from the extrapolation procedures involved when measurements were made in non-theta solvents. Each of these errors is reflected in the numerator, $\langle r^2 \rangle_0$, of eq 1. However, an additional source of uncertainty resides in the assumptions made in order to calculate the denominator of eq 1, $\langle r^2 \rangle_{0f}$. Most of the σ values contained in Table I are based upon an assumption of tetrahedral valence angles in the chain backbone rather than upon valence angles experimentally determined (as, for example, from crystallographic studies). Thus, published values of σ tend to be systematically high.

An alternate quantity used[20] to characterize the spatial requirements of chain molecules is the characteristic ratio, $C_n = \langle r^2 \rangle_0 / nl^2$, where n is the number of skeletal bonds and l^2 is the average square of their length. The characteristic ratio is subject to less ambiguity than is σ: bond lengths normally are known within narrow limits whereas the uncertainties in bond angles are frequently several degrees. This is enough to affect calculated values of $\langle r^2 \rangle_{0f}$ as discussed in the preceding paragraph. A log–log correlation of characteristic ratio with area, however, is considerably poorer than is the correlation of σ with A (correlation coefficient of 0.58 vs. 0.90). Even though less well defined, the chain stiffness parameter, therefore, is to be preferred in the comparison of polymers because of the normalizing effect of $\langle r^2 \rangle_{0f}$.

The correlation in Figure 1 amply demonstrates that chain stiffness is primarily a function of chain area (or vice versa) as required by eq 3. It also indicates that the parameter ratio, a/σ, used by Privalko and Lipatov[3,6] for various correlations (as in eq 2) may be replaced by a single parameter, the chain area. In addition, it simplifies the relations suggested by Kurata and Stockmayer[7] between σ and molar volume of pendant groups, V_x; the area per chain is dominated largely by the size of the substituents on the chain. These, in turn, affect nonbonded interactions along the chain and, presumably, contribute to chain stiffness.

Aside from possible molecular implications of Figure 1, we believe that such plots serve another, and possibly equally important, function. Since A (or $A^{1/2}$) is an inherent and definable property of a polymer chain, plots such as Figure 1 and those published previously[8,9] provide an objective method for: (a) assessing the relative validity of different bodies of data; (b) identifying polymer systems behaving unusually and trying to assess reason(s) for the unusual behavior; (c) emphasizing where gaps exist in the available data; and (d) making reasonable extrapolations beyond observed, or even observable, variables. The basis of the empirical correlation, eq 4, is a problem for the theoreticians to explain.

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