Macromolecules **1997,** *30,* 7529−7535

Intramolecular Screening in Nondilute Polymer Solutions

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Received June 2, 1997⊗

ABSTRACT: The Flory−Huggins theory of polymer solutions is modified in a simple way to account for intramolecular contacts. In the concentrated regime under conditions where chain dimensions are close to ideal, this is accomplished by using a single parameter describing the fraction of same-chain contacts. The resulting equations have the same form as those obtained originally by Koningsveld and Kleintjens and reproduce the composition dependence of experimental values of χ extremely well.

Introduction

In a recent paper,[1] we discussed the effect of chain connectivity on the number of intrachain as opposed to interchain contacts in polymer blends. Essentially, by measuring the number of hydrogen bonds of various types we found that the fraction of same-chain contacts significantly exceeded what would be expected on the basis of the type of mean field models that can be applied to these systems. Such deviations should naturally also occur in non-hydrogen-bonded mixtures, and we observed in passing that if we account for what we called this intramolecular screening effect in a simple way, then the Flory interaction term for polymer solutions had a particularly interesting form. It is our purpose to describe this here, but the situation is complicated by the fact that nonrandom contacts also result from energetic effects, so we will start by briefly reviewing why we believe that chain connectivity is important.

The Flory−Huggins theory of polymer solutions in its simplest form treats interactions by implicitly assuming that the polymer chain segments are disconnected and randomly mixed. Deviations from random mixing can, of course, occur as a result of favorable interactions, in that certain types of contacts would then be energetically preferred over others. In weakly interacting systems such deviations have often been handled using Guggenheim's quasi-chemical assumption,[2] but calculations by Prigogine et al.[3] have demonstrated that this model only allows small deviations from random contacts and slight changes in the excess free energy before phase separation occurs. Furthermore, in more recent work, where the free volume effect was included, Nies and Xie[4,5] also found relatively small deviations from random mixing.

Hydrogen-bonded systems are very different. There are large and easily measurable (by infrared spectroscopy) deviations from random contacts for those groups that interact in this manner. Furthermore, the Guggenheim quasi-chemical approximation cannot be used, in that it assumes that contact pairs are independent and do not interfere with one another, an assumption that does not apply (for various reasons, including cooperativity effects) to hydrogen bonds between "donor" and "acceptor" groups on hydrogen-bonded molecules. However, variations from random contacts can be handled using various other combinatorial approaches,[6−10] which also form the basis for describing the fraction of groups that hydrogen bond in a given system.[6,7] In these approaches the number of hydrogen bonds depends on the probability that functional groups are adjacent to one another. This probability was originally assumed to be equal to the volume fraction of such groups (see discussion in ref 8). However, on the basis of a systematic study of the number of hydrogen bonds found in mixtures of low molecular weight molecules, homopolymer blends, polymer solutions, random copolymers, and random copolymer/homopolymer blends, all with identical types of hydrogen-bonding functional groups,[1,11] we concluded that there were significant deviations from random contacts over-and-above those imposed by the hydrogen bonds and that these had their origin in chain connectivity effects. This conclusion was supported by simulations,[1] which indicated that there is a surprisingly large fraction of intrachain contacts in unperturbed (i.e., nonswollen) chains. These intrachain contacts are a result of both local and long range effects, as illustrated schematically in Figure 1, and for a polymer melt the simulations gave a molecular weight dependence of the form

$$\gamma_s = a - \frac{b}{M^{0.5}} \tag{1}$$

where a and b are constants, M is the number of segments, and γ_s is the fraction of contacts that are intrachain. For a high molecular weight polymer on a cubic lattice, γ_s was calculated to have a value of ≈ 0.38.[1] In real systems, where the coordination number is presumably larger than 6, we would anticipate a smaller value, but one that is still significant. A relationship of the general form of eq 1 can also be obtained from scaling arguments, and these are reproduced in the Appendix.

We will show in this paper that if we assume that γ_s is constant, essentially an average over the distribution of conformations characteristic of the unperturbed Gaussian state, then we obtain an effective interaction term that reproduces extremely well the upper-critical type phase behavior of polymer solutions and the composition dependence of χ (in the concentrated regime). We found it interesting that the interaction term is essentially identical to the closed form expression described more than 25 years ago by Koningsveld and Kleintjens.[12] Accordingly, we will start by first reviewing this work.

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.

S0024-9297(97)00792-4 CCC: $14.00

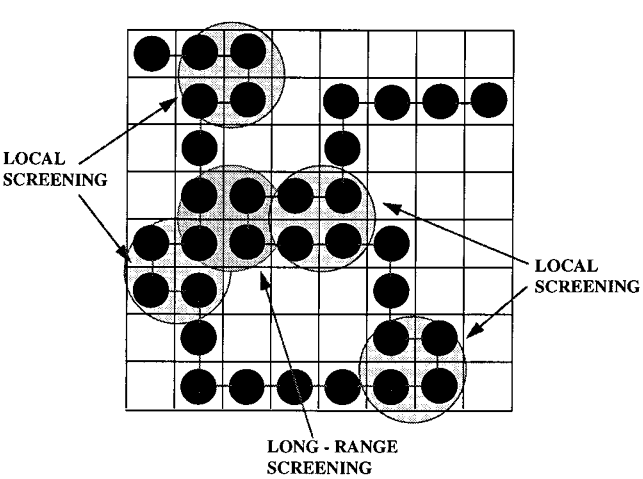

Figure 1. Schematic plot of a chain on a lattice showing local and long-range contacts or screening effects.

Theory

The Flory–Huggins equation is usually expressed as

$$\frac{\Delta G_m}{RT} = n_S \ln \Phi_S + n_p \ln \Phi_p + n_s \Phi_p \chi \qquad (2)$$

where n_s and n_p are the number of moles of solvent and polymer, Φ_s and Φ_p are the respective volume fractions, and χ is the interaction term. This form of the equation represents the Flory approximation (coordination number $z \rightarrow \infty$), where the probability of a polymer segment being adjacent to a solvent molecule is assumed to be given by Φ_p (i.e., a random distribution of segments). If contacts between polymer segments that are covalently bonded to one another are now excluded (i.e., we use surface site fractions), then Φ_p in the interaction term is replaced by θ_p where, using the nomenclature of Guggenheim[2]

$$\theta_p = \frac{n_p q}{n_p q + n_s} = \frac{\frac{\Phi_p}{M} q}{\frac{\Phi_p}{M} q + \Phi_s} \qquad (3)$$

M is the number of lattice sites occupied by a polymer chain, and the number of polymer surface site contacts is defined by

$$qz = M(z - 2) + 2 \qquad (4)$$

Rearranging, we obtain

$$\frac{q}{M} = 1 - \frac{2}{z}\left(1 - \frac{1}{M}\right) = 1 - \gamma_l \qquad (5)$$

where

$$\gamma_l = \frac{2}{z}\left(1 - \frac{1}{M}\right) \qquad (6)$$

The interaction term can now be rewritten

$$n_s \theta_p \chi = n_s \Phi_p \left[\frac{1 - \gamma_l}{1 - \gamma_l \Phi_p}\right] \chi \qquad (7)$$

where, as Orofino and Flory[13] noted, the denominator on the right-hand side of eq 7 can be expanded in a power series. Koningsveld and Kleintjens[12] preferred the closed form of eq 7 and then abandoned the physical significance of the parameter γ_l, allowing it to be an empirical term, and also added a second empirical parameter to describe entropic contributions to χ. This closed form expression gives a good fit to a range of polymer solution thermodynamic data, as recently observed by Petri et al.[14]

If we account for same-chain contacts in a simple manner, we obtain an expression of precisely the same form as that given by Koningsveld and Kleintjens, in both the Flory approximation ($z \rightarrow \infty$) and the case of finite z. Starting, for simplicity, with the former and letting the fraction of same chain contacts be γ_s, then the probability that a site neighboring a polymer segment is occupied by another polymer segment can be written

$$p_{pp} = \gamma_s + (1 - \gamma_s)\left[\frac{(1 - \gamma_s)\Phi_p}{(1 - \gamma_s)\Phi_p + \Phi_s}\right] = \gamma_s + \frac{(1 - \gamma_s)^2 \Phi_p}{(1 - \gamma_s \Phi_p)} \qquad (8)$$

where the first term is simply the fraction of contacts that are intramolecular, while the second term is the fraction of all intermolecular contacts that are between polymer segments. The probability that there is a solvent molecule adjacent to a polymer segment is then

$$p_{sp} = \frac{(1 - \gamma_s)\Phi_s}{(1 - \gamma_s \Phi_p)} \qquad (9)$$

However, the solvent molecule is chosen as the "reference" molecule in the Flory treatment, so we require p_{ps}, the probability that a polymer segment is adjacent to a solvent molecule. Noting that $p_{ps} \neq p_{sp}$, but obviously the number of solvent/polymer contacts n_{ps} is equal to the number of polymer/solvent contacts n_{sp}, it is easy to show that

$$p_{ps} = p_{sp} \frac{\Phi_p}{\Phi_s} \qquad (10)$$

hence the Flory interaction term becomes

$$n_s p_{ps} \chi = n_s \Phi_p \left[\frac{(1 - \gamma_s)}{(1 - \gamma_s \Phi_p)}\right] \chi \qquad (11)$$

identical in form to that described by Koningsveld and Kleintjens, eq 7. Note that at this point we are assuming that χ is simply an energetic term.

It is a relatively straightforward matter to include this "intramolecular screening" effect in the surface contact approach by noting that p_{pp} is now given by

$$p_{pp} = \gamma_s + \frac{(1 - \gamma_s)^2 \theta_p}{(1 - \gamma_s \theta_p)} \qquad (12)$$

where θ_p is defined (see eqs 3, 5 and 6) by

$$\theta_p = \frac{\Phi_p (1 - \gamma_l)}{(1 - \gamma_l \Phi_p)}$$

so that the Flory–Huggins interaction term becomes

$$n_s p_{ps} \chi = n_s \Phi_p \left[\frac{(1 - \gamma_s)}{(1 - \gamma_s \theta_p)} \frac{(1 - \gamma_l)}{(1 - \gamma_l \Phi_p)}\right] \chi \qquad (13)$$

If we define

$$\gamma = \gamma_l + (1 - \gamma_l)\gamma_s$$

then it is easy to show that

$$n_s p_{ps}\chi = n_s \Phi_p \frac{(1-\gamma)}{(1-\gamma\Phi_p)}\chi \qquad (14)$$

so that the simple *form* of the Koningsveld–Kleintjens equation is once again obtained. There are some differences in nomenclature. Koningsveld and Kleintjens had an empirical parameter in the numerator of this expression that combined the equivalent of χ and $(1 - \gamma)$ in eq 14, and they also introduced another empirical parameter (α; see ref 12) to account for entropic contributions to χ. We thought that it would be interesting to see if we could obtain the same type of excellent fit to experimental data with the single additional (to χ) parameter, γ. Accordingly, we note that if surface site fractions are used in determining the entropy of mixing, as in the original treatment of Huggins[15] and as also described by Guggenheim,[2] then there are excess (to the Flory approximation) entropy terms and the combinatorial part of the free energy can be written as

$$\frac{\Delta G'_c}{RT} = \Phi_s \ln \Phi_s + \frac{\Phi_p}{M}\ln \Phi_p - \frac{(M-1)}{M}\left[\frac{M}{M-q} - \Phi_p\right]\ln\left[1 - \left(\frac{M-q}{M}\right)\Phi_p\right] + \Phi_p\left[\frac{q(M-1)}{M(M-q)}\right]\ln\left[\frac{q}{M}\right] \qquad (15)$$

where we have now converted to a per mole of lattice sites basis.

In his original treatment Huggins[15] introduced a complicated small factor (f_o) to take account of the effect of the chains bending back on themselves (which would presumably be the long-range part of our γ_s term corresponding to contacts between distant parts of the chain, as illustrated in Figure 1). We can introduce our intrachain contact term by simply replacing q in eq 15 by a term q' (see Miller, ref 16). Essentially, in counting the contacts of a polymer chain $\gamma_s qz$ will be intramolecular, while $(1 - \gamma_s)qz$ will be intermolecular, so we have

$$(1 - \gamma_s)qz + \gamma_s qz = (z - 2)M + 2 \qquad (16)$$

Substituting $q'z$ for $(1 - \gamma_s)qz$, we get

$$q'z = (z - 2)M + 2 - \gamma_s qz \qquad (17)$$

where $q'z$ is simply the effective number of intermolecular contacts allowed to a chain. We now have

$$\frac{q'}{M} = (1 - \gamma_s)(1 - \gamma_l) = (1 - \gamma) \qquad (18)$$

and

$$\frac{M - q'}{M} = \gamma_l + \gamma_s(1 - \gamma_l) = \gamma \qquad (19)$$

so that the combinatorial part of the free energy can be written as

$$\frac{\Delta G'_c}{RT} = \Phi_s \ln \Phi_s + \frac{\Phi_p}{M}\ln \Phi_p - \frac{(1-\gamma\Phi_p)}{\gamma}\ln(1 - \gamma\Phi_p) + \Phi_p\frac{(1-\gamma)}{\gamma}\ln(1-\gamma) \qquad (20)$$

The Chemical Potential and Spinodals

In order to evaluate this model we will be calculating spinodals and "apparent" values of χ obtained from thermodynamic data, for which we will require the chemical potential of the solvent. This is given in the Flory approximation by

$$\frac{\Delta\mu_s}{RT} = \ln \Phi_s + \left(1 - \frac{1}{M}\right)\Phi_p + \Phi_p^{\,2}\chi_{FH} \qquad (21)$$

It is convenient for our purposes to include the "γ terms" in χ_{FH}, which we now define as

$$\chi_{FH} = \chi_H + \chi_S \qquad (22)$$

where the enthalpic component is

$$\chi_H = \frac{(1-\gamma)^2}{(1-\gamma\Phi_p)^2}\chi \qquad (23)$$

and from eq 15, the entropic component is determined to be

$$\chi_S = -\frac{1}{\Phi_p^{\,2}}\left[\frac{1}{\gamma}\ln(1-\gamma\Phi_p) + \Phi_p\right] \qquad (24)$$

The term in brackets in eq 24 is actually quite small over most of the composition range (until large values of Φ_p are reached), but because we include this part of the lattice combinatorial term in χ_{FH}, which is present as a $\Phi_p^{\,2}\chi$ term in the chemical potential, then the bracket term is multiplied by $1/\Phi_p^{\,2}$, giving χ_S values in the range ≈0.2–0.3 (see below). Most experimental measurements of χ give χ_S values that are usually larger than 0.35, and obviously there must be a significant contribution from equation of state or free volume effects, which we are neglecting here. Nevertheless, there would seem to also be a substantial contribution from neglected combinatorial terms, even if the "intramolecular screening" effect proposed here is ignored.

The spinodal is given by

$$\frac{\partial^2}{\partial\Phi_s^{\,2}}\left[\frac{\Delta G'}{RT}\right] = \frac{1}{\Phi_s} + \frac{1}{M\Phi_p} - \frac{\gamma}{(1-\gamma\Phi_p)} - \frac{2(1-\gamma)^2}{(1-\gamma\Phi_p)^3}\left[\frac{\chi_0}{T}\right] \qquad (25)$$

where for convenience we have defined

$$\chi = \left[\frac{\chi_0}{T}\right] \qquad (26)$$

and $\Delta G'$ is again on a per mole of lattice sites basis.

Table 1. Experimental Critical Data (ϕ_p^{crit}, T_c) for PS−Cyclohexane (Koningsveld et al.[12]

sample no.	m	ϕ_p^{crit}	T_c (°C)
2	490	0.1125	15.7
4	893	0.0895	20.5
5	1594	0.0753	23.45
7	3783	0.0525	27.55
8	5060	0.04825	28.0
9	14402	0.0311	30.05

Table 2. Values of γ_s, χ, and χ_0 for PS−Cyclohexane at Different Molecular Weights

m	Z	γ_l	γ_s	γ	χ	χ_0
490	9	0.222	0.243	0.411	0.893	257.8
893	9	0.222	0.249	0.416	0.888	260.8
1594	9	0.222	0.268	0.431	0.901	267.2
3783	9	0.222	0.272	0.434	0.897	269.8
5060	9	0.222	0.281	0.441	0.906	272.7
14402	9	0.222	0.287	0.445	0.908	275.4

Similarly the third derivative is

$$\frac{\partial^3}{\partial {\Phi_s}^3}\left[\frac{\Delta G'}{RT}\right] = -\frac{1}{{\Phi_s}^2} + \frac{1}{M{\Phi_p}^2} + \frac{\gamma^2}{(1-\gamma\Phi_p)^2} + \frac{6\gamma(1-\gamma)^2}{(1-\gamma\Phi_p)^4}\left[\frac{\chi_0}{T}\right] \quad (27)$$

Calculations and Discussion

The simple model presented here essentially has two adjustable parameters, γ and χ_0. The former has two contributions γ_l and γ_s, the first of which depends upon the lattice coordination number while the second represents the fraction of intrachain contacts. Although these parameters could be regarded as purely empirical, we thought it would be interesting to see if we could obtain reasonable values of these quantities by fitting to experimental data. However, with three variables one is almost certain to get a good fit, and in any event γ_l and γ_s will be to some degree dependent. We therefore decided to fix the value of γ_l by using a lattice coordination number of $z = 9$, an average value determined by Bernal[17] for the random close packing of hard spheres, and then calculated values of χ_0 and γ_s to determine whether they made physical sense.

In order to test this model we used data from polystyrene/cyclohexane solutions, partly because there is such a wide range of data available for this system, but also because χ_{FH} has been measured at the theta temperature across the composition range. Obviously, if the chain swells then we would expect γ_s to get smaller and we could no longer treat it as a constant.

We obtained values of χ_0 and γ_s by fitting the equations for the second and third derivatives of the free energy to the values Φ_p^c and χ^c at the critical point, using the data reported by Koningsveld et al.[18] for polystyrenes of various molecular weights. These data are listed in Table 1, while the calculated values of χ_0 and γ_s are listed in Table 2.

Simulations on a cubic lattice (z = 6) gave a limiting value for γ_s of about 0.36 and an inverse dependence on the square root of the molecular weight (see eq 1). The calculated values for γ_s are in the range 0.24−0.29, which would seem reasonable for a "real" system where we have assumed a value of $z = 9$. (Values of z in the range 8−12 were also used, but the calculated values of γ_s do not change very much.) Furthermore, γ_s appears to vary with $M^{-0.5}$, as shown in Figure 2. Given the usual errors in experimental data and the simplicity of this model, the correlation appears to be very good.

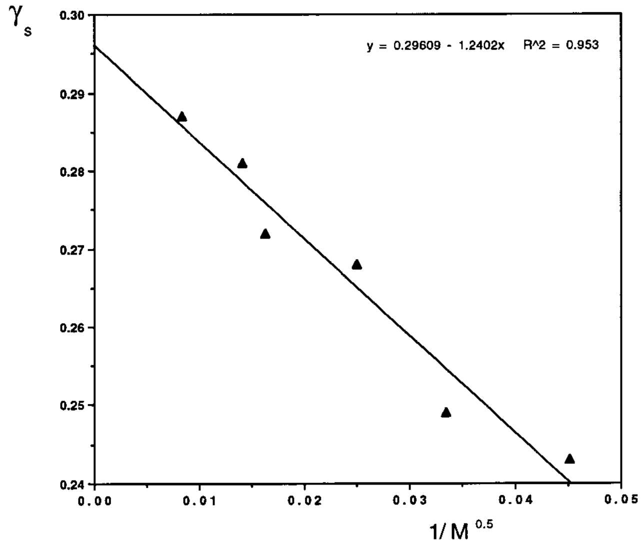

Figure 2. Plot of the fraction of intramolecular contacts, γ_s, calculated from critical point data, plotted as a function of $M^{-0.5}$.

The calculated values of χ_0 vary with molecular weight. In this model we assume any variations in measured or "apparent" values of χ, which we call χ_{FH} (see eqs 22−24), arise from the γ_l and γ_s terms. We presume that the systematic variation in the calculated values of χ_0 therefore reflect other factors, such as free volume or equation of state effects that we have neglected here.

Having obtained values of χ_0 and γ_s, we can now calculate values of χ_{FH} as a function of composition and also spinodals, to see how well they reproduce experimental data. We would emphasize that in these calculations we do not vary χ_0 and γ_s from values determined from the critical point data.

Values of χ_{FH} for polystyrene/cyclohexane near the Θ temperature have been obtained by Krigbaum and Geymer.[19] Three different molecular weights $\bar{M}_n \approx$ 25 100, 72 000, and 440 000) were used and values over a wide range of (nondilute) concentration were obtained. These data are plotted in Figure 3 and appear to describe a single curve (i.e. any variations due to molecular weight are within the errors of measuring χ_{FH}). We therefore simply chose values of $\chi_0 = 270$ and $\gamma_s = 0.272$ (a rough average for this molecular weight range) and obtained the curve also shown in Figure 3. It provides an extremely good fit to the data across the composition range, all except for three points at high polystyrene concentrations. Because polystyrene will still be a glass at these concentrations, it may be that these samples did not reach equilibrium. Regardless, there is still an excellent overall fit to the data.

We also calculate spinodals and compared our results to the data obtained by Scholte,[20] as shown in Figure 4. Also shown on this figure are the spinodals calculated using the Flory−Huggins equation. Data for three different molecular weights are shown. Obviously, the curves calculated using the model described here are forced through the critical point, because it is this data that we used to obtain χ_0 and γ_s. The spinodal data for high molecular weight samples $\bar{M}_w \approx$ 520 000 and 163 000) are reproduced very well, although deviations appear for concentrations that are smaller than Φ_p^c for the sample with $\bar{M}_w \sim$ 163 000. These deviations are

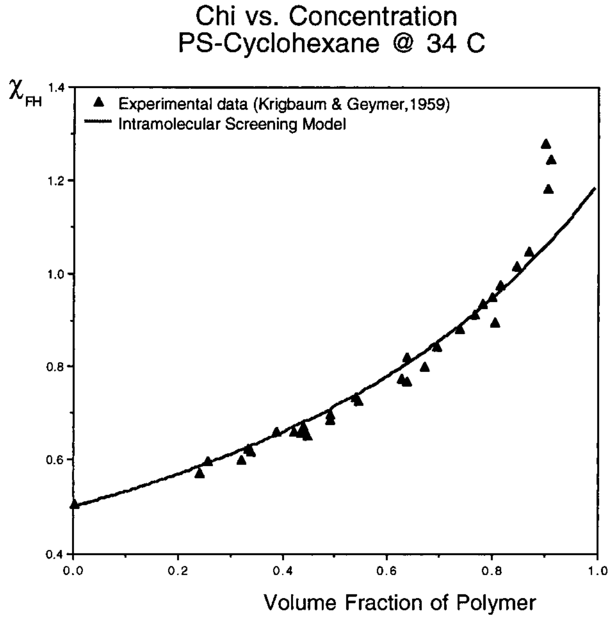

Figure 3. Plot of the calculated value of the "Flory–Huggins" χ, defined in eqs 22–24, as a function of polymer volume fraction, for the polystyrene/cyclohexane system. Experimental data points are also shown.

even more significant for a lower molecular weight polystyrene $\bar{M}_w \sim 51\,000$). However, these deviations are consistent with the model. In the dilute regime we would expect the chain to change its dimensions, expanding in a good solvent, but possibly collapsing in a poor solvent in the concentration range below ϕ_p^c.[21] Either way, γ_s would change. The chain overlap regime for high molecular weight samples, where the chains are nearly ideal, would extend to lower concentrations, however. In this sense, the model is consistent with the data.

The original Koningsveld–Kleintjens model does not reproduce this data as well, as shown in Figure 5. This is because these authors introduced an additional empirical factor for χ_s that does not vary with composition. In our treatment there is a composition dependence (see eq 24), which we include without introducing additional parameters, and at least for the polystyrene/cyclohexane system, this appears to contribute significantly to the overall composition dependence of χ_{FH}.

Conclusions

We have described a model where intrachain contacts are treated explicitly. The idea that these are important is not new, of course, and is present in the original work of Huggins,[15] the correlation hole ideas of de Gennes,[21] and the explicit treatments of Szleifer[22] and Schweizer and Curro.[23] Here, however, we have tried to handle this problem in a very simple way that would be valid in concentration regimes where the chains are nearly ideal. We believe it is interesting that the form of the equation is exactly the same as one obtained by Koningsveld and Kleintjens,[12] which over the years has proved a useful way of describing the composition dependence of χ. Although the model is simple, the values of the parameters appear to make physical sense, and it will be interesting to see if this procedure proves useful in more advanced treatments, such as those that deal with free volume.

Finally, in order to check whether this approach reproduces the composition dependence of χ_{FH} in other systems, we examined the data for polyisobutylene/benzene, reported by Eichinger and Flory.[22] Using a value of $\gamma = 0.43$, corresponding to a value of $\gamma_s = 0.27$, we again obtained an excellent fit to the data, as shown in Figure 6.

Acknowledgment. The authors gratefully acknowledge the support of the Office of Chemical Sciences, U. S. Department of Energy, under Grant No. DE-FG02-86ER13537 and the National Science Foundation, Polymers Program.

Appendix

In this appendix we will discuss scaling arguments justifying eq 1 for polymer solutions.

We first consider a polymer chain in a melt or a concentrated solution. We will model this chain by a non-self-avoiding walk with N steps ("phantom" chain). The parameter N is proportional to the molecular weight

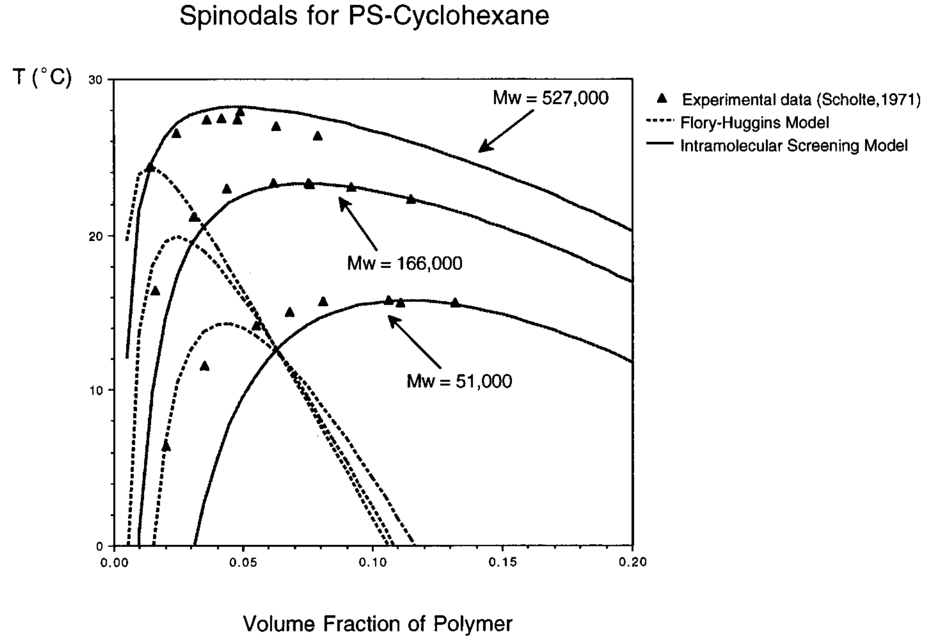

Figure 4. Comparison of calculated and experimentally observed spinodals for the polystyrene/cyclohexane system.

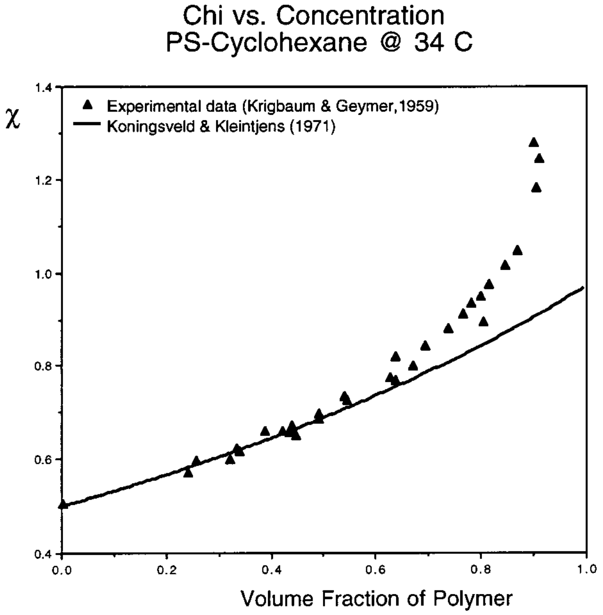

Figure 5. Comparison of calculated and experimental values of χ_{FH} obtained using the Koningsveld and Kleintjens model.

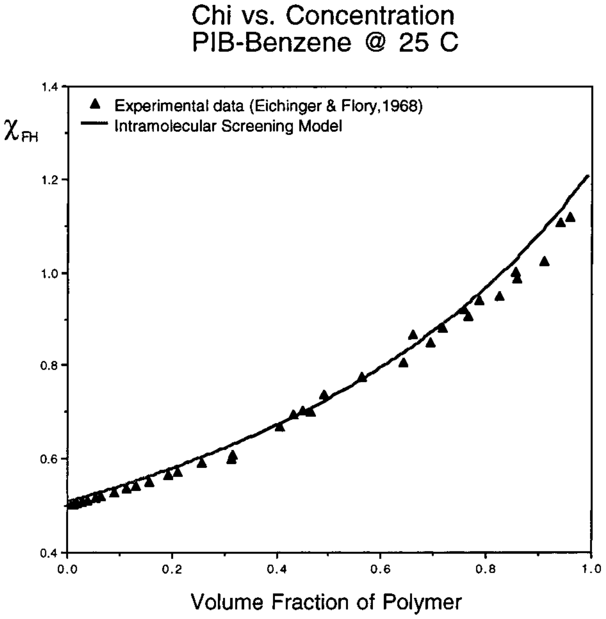

Figure 6. Comparison of calculated and experimentally observed values of χ for the polyisobutylene/benzene system.

of the chain and can be estimated as the number of the Kuhn segments of the chain. It should be noted that this description of chains in melts is valid only for long distances (much larger than the blob size). At smaller distances local effects should play a major role, and the Gaussian picture is no longer valid. However, since we will be interested only in the behavior of "tails", this picture is sufficient for our problem.

The total number of phantom walks with N steps can be estimated as[21]

$$N_t(N) \approx z^N \tag{A1}$$

where z is the lattice coordinate number. The number of self-avoiding walks that return to the origin is

$$N_r(N) \approx z^N\left(\frac{a}{R}\right)^3 \tag{A2}$$

where a is the lattice step size, and R is the mean square distance between the origin and the end of an N-step walk. The latter is equal to

$$R \approx aN^{1/2} \tag{A3}$$

Therefore the probability for an N-step walk to return is

$$p_0(N) = \frac{N_r(N)}{N_t(N)} = CN^{-3/2} \tag{A4}$$

Now consider two monomers—number i and number j—that belong to the same chain. We want to calculate the probability $p(i,j,N)$ that they are neighbors. If the difference between the numbers $|i - j|$ is smaller than the number of monomers in a blob, g, this probability is determined by local packing. If it is larger, the probability should depend on $|i - j|$ according to a universal law. Let us write this probability as

$$p(i,j,N) = N^{-3/2}f(x), \quad x > \frac{g}{N} \tag{A5}$$

where f is a function of the dimensionless length x:

$$x = \frac{i-j}{N} \tag{A6}$$

The limit $x \rightarrow 1$ corresponds to the case where $p \rightarrow p_0$, and therefore

$$\lim_{x\rightarrow 1} f(x, y) = \text{constant} \tag{A7}$$

The limit $x \rightarrow 0$ corresponds to monomers that are close to each other. The number of contacts between the monomers inside a blob should not depend on N, and therefore

$$\lim_{x\rightarrow 0} f(x) \approx x^{-3/2} \tag{A8}$$

Let us now calculate the screening factor γ_s. From the definition of $p(i,j,N)$ we can write

$$\gamma_s = \frac{2}{zN}\sum_{i=1}^{N}\sum_{j=i+1}^{N} p(i,j,N) \tag{A9}$$

Changing the variables and substituting integration for the summations, we obtain

$$\gamma_s = \frac{2}{zN^{1/2}}\left[\int_{1/N}^{1-(1/N)} dy \int_{g/N}^{1-(1/N)} f(x)\, dx + O\left(\frac{1}{N}\right)\right] + \Delta \tag{A10}$$

where $y = (i + j)/2N$ and the term Δ accounts for all contacts inside a blob. With an error on the order of $O(1/N)$, we can substitute the limits in the integral over y with 0 and 1. To the same level of approximation we can substitute the upper limit in the integral over x with 1. We cannot, however, substitute the lower limit in the integral over x with 0, because this integral is divergent. Therefore

$$\gamma_s = \frac{2}{zN^{1/2}}\left[\int_{g/N}^{1} f(x)\, dx + O\left(\frac{1}{N}\right)\right] + \Delta \tag{A11}$$

Let us take some small number ϵ such as $g/N < \epsilon < 1$.

Then we can rewrite the integral in (A11) as

$$\int_{g/N}^{1} f(x)\,\mathrm{d}x = \int_{g/N}^{\epsilon} f(x)\,\mathrm{d}x + \int_{\epsilon}^{1} f(x)\,\mathrm{d}x \qquad \text{(A12)}$$

In the first term of this equation we can substitute $f(x)$ by $c_1/x^{3/2}$, and therefore

$$\int_{g/N}^{\epsilon} f(x)\,\mathrm{d}x \approx \frac{2c_1N^{1/2}}{g^{1/2}} - \frac{2c_1}{\epsilon^{1/2}} \qquad \text{(A13)}$$

The second integral does not depend upon N. Therefore we have finally

$$\gamma_{\mathrm{s}} = a - \frac{b}{N^{1/2}} + O\left(\frac{1}{N^{3/2}}\right) \qquad \text{(A14)}$$

which coincides with eq 1. We see that scaling theory predicts that there are two parts in the screening factor: a nonuniversal one, which is determined by local effects and does not depend on the molecular weight, and one that varies as $1/N^{1/2}$.

In the case of good solvents the molecular weight dependence of the screening factor can be obtained by similar arguments, if the nonclassical critical exponents $\gamma = 7/6$ and $\nu = 3/5$ are used in eqs A1 and A2.[21] It is easy to show that instead of eq 1 we would have for good solvents

$$\gamma_{\mathrm{s}} = a - \frac{b}{N^{q}} \qquad \text{(A15)}$$

where

$$q = \gamma + 3\nu - 2 = \frac{29}{30} \approx 0.97 \qquad \text{(A16)}$$

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MA970792Q