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Influence of Prediluion on Cross-Link Density: Consequences for the Front Factor and the Flory-Huggins Relation

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ABSTRACT

The influence of predilution before formation of a polymer network is considered. From theoretical and experimental considerations it is deduced that $\gamma_g = \gamma_g^0 V_0$ and $\gamma = \gamma_g^0 V_0^2$ where γ is the network segment density of the polymer phase, γ_g is the network segment density of the gel portion, V_0 is the volume fraction of gel in the diluted stock, and the superscript zeros refer to the undiluted condition. As a result, it is concluded that the "front factor" for the elastic equation of state cannot vary with dilution of the network before cure as some have proposed. The reasons for the supposed variation are examined and a probable weakness found in the determination of cross-link density by chemical methods. The existence of the front factor is doubted. Use is made of the extended Flory-Huggins relation, whereby during differentiation the polymer-solvent interaction parameter is assumed to vary linearly with concentration, to equate network segment densities of prediluted and undiluted polymers through the relation $\gamma_g = \gamma_g^0 V_0$. It is found that the slope of the curve χ vs V_2 calculates to be 0.33 where χ is the customary polymer-solvent interaction parameter and V_2 is the volume fraction of polymer in a solvent swollen gel. A number of actual slopes are computed and found to be in the range 0.26 to 0.43 with some exceptions. In agreement with the work of Koningsveld, Staverman, Flory, and Tatara, it is shown that the first and second partial derivatives of the extended Flory-Huggins equation for soluble polymers may be used to calculate conditions at phase separations, which should be closer to experimental fact than those calculated from the original relation. Derivatives were obtained for cross-linked polymers but are not presented.

INTRODUCTION

The effect on cross-link density of diluting a polymer with an inert liquid before cross-linking would seem to be a simple matter. Actually, some close thinking is required and there appears to be some confusion in the literature relating to the subject which may really reflect imprecise definitions, particularly of gel, sol, diluent, and cross-link density of gel as compared to cross-link density of the whole polymer phase. In the following the variation of cross-link density with predilution is discussed. It is shown that the variation has consequences with respect to the "front factor" and can be used to compute the variation of the polymer-solvent interaction parameter with concentration. In order to present this computation, a discussion is given on the extension of the Flory-Huggins relation to allow for variation of the interaction parameter.

Influence of Dilution

The effect on mechanical properties and cross-link density of diluting a polymer network with a plasticizer or solvent before cross-linking can be approached in several ways. First, consider qualitatively the cross-linking of telechelic polymers. If the same amounts of telechelic polymer are cross-linked in an undiluted and in a diluted condition, when cross-linking occurs the free molecules will be in a random unstrained configuration and the resulting gel will be unstrained. Where there are cross-links, one would think that they would have the same molecular weight between cross-links in both states, diluted or not, because we are dealing with a telechelic prepolymer. However, the only way the same amount of network could fill a larger volume without strain would be for it to have fewer cross-links. That is, the extent of reaction is less in the diluted state and some cross-linking molecules act as chain extending agents with one functional group unreacted. The molecular weight between cross-links and the entropy will then be greater in the diluted stock.

To place these ideas in a quantitative framework, visualize threedimensional latticeworks composed of rods running in each of the three dimensions and at right angles to each other with the same number of rods terminating in each face of the cubical networks. Construct such a latticework of n rods in one plane in each of the two directions of the plane. In that plane there will be n^2 segments between points of intersection of the rods and there will be n^3 segments in each direction over the whole volume or $3n^3$ segments for the three dimensions. If a segment has unit length and the volume of the cube is V_μ, the length of each segment is $V_\mu^{1/3}/n = 1$ or $V_\mu = n^3$.

If now the volume is increased and a new latticework is erected throughout the new volume using the same total length of rods as before, the number of new rod lengths running across the new cube must decrease and hence the number of new segments and interactions must decrease. Let the number of new rods in each direction in one plane be N. Then, as before, the number of segments in the new volume will be $3N^3$.

If the new larger volume is V_d, the length of one side of the cube will be $V_d^{1/3}$ and the number of new rods in each direction of one plane will be $n^2/V_d^{1/3}$. There will be $(n^2/V_d^{1/3})^3$ segments in each direction over the whole volume or $3n^6/V_d$ segments in the three dimensions.

Therefore

$$3N^3 = 3n^6/V_d$$

but

$$n^3 = V_\mu$$

so

$$3N^3 = 3n^3 V_\mu/V_d$$

Define

$$V_0 = V_\mu/V_d$$

and

$$3N^3 = 3n^3 V_0 \tag{1}$$

Let the number of segments represent the number of segments in a polymer network. Then since the two latticeworks in both the original and larger forms contain the same length of rod, they each become equivalent to gel polymer of a volume equal to the volume of the original or "undiluted" latticework and we have

$$\gamma_g = \gamma_g^0 V_0 \tag{2}$$

where γ_g = network segment density in the gel of the diluted polymer

γ_g^0 = network segment density in the gel of the undiluted polymer

V_0 = volume fraction of gel in the diluted polymer

Now since

$$\gamma = \gamma_g V_0 \tag{3}$$

= network segment density in the whole polymer

$$= \gamma_g^0 V_0^2 \tag{4}$$

and the cross-link density and properties dependent on it should be proportional to the square of the gel fraction.

It should be observed that the derivation above finally treats the two networks on an equal volume basis by the introduction of Eq. (3). The number of segments in the original undiluted network per unit volume is

$$3n^3/V_\mu \equiv \gamma_g^0$$

and per unit volume of the larger or diluted network is

$$\frac{3n^3 V_0}{V_d} = \frac{3n^3}{V_\mu} \frac{V_\mu V_0}{V_d} = \gamma_g^0 V_0^2$$

The fact that the latticework imagined is six-functional rather than three- or four-functional should not invalidate the argument. Equation (4) is in agreement with the results of Oberth [1] and of Shen and Tobolsky [2] on the modulus of prediluted stocks.

Equations (2) and (4) express the variation of network segment density with the extent of predilution of the stock. Network segment density in classical theory is directly proportional to the decrease in entropy on stretching. Hence the entropy of a prediluted stock is greater than when undiluted and greater by the ratio of the network segment densities of the undiluted to the diluted stocks which is the square of the ratio of the volumes of the diluted to the undiluted stocks, or $1/V_0^2$.

Equation (2) can also be derived by placing the experimental results of Oberth and Bruenner [1] on solvent swelling of prediluted stocks into the Flory-Huggins relation or rather into the approximations of this relation for undiluted and prediluted stocks. Oberth and Bruenner showed that on dilution

$$V_2 = v_\mu V_0 \tag{5}$$

where

V_2 = volume fraction gel in a solvent swollen gel at equilibrium

v_μ = "V_2" value for the stock without diluent, defined here as (volume gel + volume sol) divided by (volume gel + volume solvent)

That is,

$$\frac{V_g}{V_g + V_s} = \frac{V_g' + V_e'}{V_g' + V_s'} \frac{V_g}{V_g + V_e + V_d}$$

where V_g = volume gel
V_e = volume sol
V_d = volume diluent
V_s = volume solvent at equilibrium swelling

and the primes refer to the undiluted state.

Since $V_g' + V_e' = V_g + V_e + V_d$ because the initial volumes of the stocks were equal, it follows that $V_g + V_s = V_g' + V_s'$, which was the experimental fact found in the work. It should be observed that V_0 and v_μ have been defined so as to make Eq. (5) true, but according to these definitions v_μ is equal to V_2 at zero dilution only if there is no sol.

From the Flory-Huggins equation for an undiluted stock [3]:

$$\gamma_g = \frac{-[\ln(1 - V_2) + V_2 + \chi V_2^2]}{\overline{V}_1(V_2^{1/3} - 2V_2/f)} \tag{6}$$

For a stock formed in the presence of a diluent, Eq. (6) becomes [32]

$$g = \frac{-[\ln(1 - V_2) + V_2 + \chi V_2^{2}]}{\bar{V}_1(V_2^{1/3}V_0^{2/3} - 2V_2/f)} \tag{7}$$

where χ = polymer-solvent interaction parameter
$\bar{V}_1$ = molar volume of solvent
f = network functionality

By series expansion of the logarithmic term in Eqs. (6) and (7):

$$V_2^{5/3} \cong \frac{\gamma_g \bar{V}_1}{(1/2 - \chi)} \tag{8}$$

for stocks without diluent and

$$V_2^{5/3} \cong \frac{\gamma_g \bar{V}_1 V_0^{2/3}}{(1/2 - \chi)} \tag{9}$$

for diluted stocks.

Here 1/2 represents the value of χ at phase separation. Raising Eq. (5) to the 5/3 power and substituting Expressions (8) and (9), we obtain

$$\gamma_g = \gamma_g^0 V_0$$

which is Eq. (2).

The Front Factor

The Wall equation or equation of state for rubber, the first term in the Mooney-Rivlin equation, is [3]

$$\tau = RT\gamma(\alpha - \alpha^{-2}) \tag{10}$$

where τ = restoring force on stretched rubber per initial cross-sectional area
R = gas constant
T = absolute temperature

γ = network segments per unit volume
α = stretched length/unstretched length

James and Guth [4] and later Duiser and Staverman [5, 6] modified Eq. (10) by introducing two factors on the right side of the equation which together we will call the "front factor" and designate as g:

$$g = \frac{(F - 2)}{F} \frac{\langle \overline{r_e^2} \rangle}{\langle \overline{r_0^2} \rangle} \tag{11}$$

where F = network functionality
$\langle \overline{r_e^2} \rangle$ = mean-square end-to-end distance of the network segments in the undeformed network
$\langle \overline{r_0^2} \rangle$ = mean-square end-to-end distance of the network segments with the cross-links removed

Introducing this factor and solving for γ, we have

$$\gamma = \frac{\tau}{gRT(\alpha - \alpha^{-2})} \tag{12}$$

If the front factor has a value less than 1 and is included in Eq. (10), γ will have a higher value than if the factor is omitted. It is seen that in order to evaluate the front factor, one must know both the modulus of elasticity and the cross-link density. If the cross-link density is known through the chemistry of cross-linking, then the factor can be determined.

The early work to establish the correctness of the relation between elastic modulus and cross-link density was that of Gee [7], Flory, Rabjohn, and Schaffer [8], and Schaefgen and Flory [9]. Their results would show a front factor close to 1.0. Flory, Rabjohn, and Schaffer [8, 9] cross-linked GR-S, a high molecular weight solid butadiene-styrene copolymer, with a bis-azodicarboxylate and calculated the cross-link density from the amount of cross-linking agent consumed. The initial polymer was of high molecular weight and most of the reaction would have to lead to cross-linking rather than chain extension.

If the polymer is diluted with a plasticizer or solvent before cross-linking, then Eqs. (4) and (12) would give

$$\gamma = \gamma_g V_0 = \gamma_g^0 V_0^2 = \frac{\tau_0 V_0}{g_0 RT(\alpha_0 - \alpha_0^{\ \ 2})} \tag{13}$$

where the zero subscripts and superscript (except for V_0) refer to the undiluted state. Since the network segment density of a diluted gel is a constant times the network segment density of the undiluted gel, it follows that any factor in the network segment density of the undiluted gel is also a factor in the network segment density of the diluted gel. Since this factor, $1/g_0$, is constant, if a front factor exists according to Eq. (4), it does not change with predilution of the network.

Shen and Tobolsky [2], however, reported that the value of g decreased with dilution of the network before cure and could reach values as low as 0.2. Results of Oberth and Bruenner [1] and Allen, Holmes, and Walsh [10] seemed to give confirmation. Examination of these papers shows that complete reaction of functional groups was assumed in each case for the calculation of the cross-link density. If one assumes that the front factor equals 1.0 and determines the cross-link density necessary to give this value using data of Shen and Tobolsky [2], it is found that a value one-third of that given by the authors is obtained. If the extent of reaction at the gel point is taken as 0.75, then using the expression $(e - e_c)/(1 - e_c)$ for the factor by which the cross-link density is decreased because of failure of the reaction to go to completion [11, 12], e becomes 0.83, where e is the maximum extent of reaction and e_c is the extent of reaction at the gel point.

Similarly using the results of Allen, Holmes, and Walsh [10] on three sets of data, their cross-link densities are reduced by factors of 0.52, 0.77, and 0.80 to give front factor values of 1.0. Again, if the extent of reaction at the gel point is 0.75, the extent of reaction in the three stocks is 0.88, 0.94, and 0.95. The values seem reasonable and within experience. There is, in fact, no reason to postulate a front factor at all to account for the results of these three papers.

Early evidence for the existence of the front factor was the work of Bueche et al. [13] who found values from 0.5 to 0.65 on undiluted silicone stocks. They cross-linked by high energy radiation. They standardized the radiation dosage by measuring the increase in molecular weight of a low viscosity silicone fluid as a function of radiation time short of the gel point. They could thus tell how many original molecules were connected together at each dosage. They then extrapolated the curve past the gel point, calling each connection of molecules a cross-link. Each connection of molecules released a molecule of H_2, CH_4, or C_2H_6. The numbers of such molecules released agreed with the results from molecular weight increase. The silicone fluid they used was a pentasiloxane of molecular weight 577. A defect in the reasoning appears to be that each connection of molecules was called a cross-link. A certain proportion (and it could be a sizable proportion) would simply be chain extension, and some connections to an existing network could be at one segment end only. In short, the writer would fault most of the work supporting the front factor at the point where the number of cross-links is counted.

The Flory-Huggins Relation

Flory and Huggins independently found in 1942 [14-18] that the free energy of mixing polymer and solvent was given by

$$\Delta F/RT = n_1 \ln V_1 + n_2 \ln V_2 + \mu n_1 V_2 \tag{14}$$

where n refers to mols of polymer and solvent, V refers to volume fraction, and μ is the polymer-solvent interaction parameter. The subscript 1 above and hereafter refers to solvent and the subscript 2 refers to polymer.

If μ is constant, the partial molar free energy $(\partial \Delta F/\partial n_1)_{n_2} \equiv \Delta\overline{F}_1$ becomes

$$\Delta F_1/RT = \ln (1 - V_2) + (1 - \overline{V}_1/\overline{V}_2)\, V_2 + \mu V_2^{\,2} \tag{15}$$

where $\overline{V}$ refers to molar volume.

It was realized fairly early that the interaction constant μ was not constant, but varied with concentration in many cases [19-22]. The effect of the variation on the derivative of ΔF given as Eq. (15) was investigated by Tompa [19] and given correctly by Koningsveld and Staverman [33], Holly [20], and Flory and Tatara [23]. For non-cross-linked polymer, their results can be expressed as

$$\Delta\overline{F}_1/RT = \ln (1 - V_2) + (1 - \overline{V}_1/\overline{V}_2)\, V_2 + \mu V_2^{\,2} - (1 - V_2)\, V_2^{\,2}\sigma \tag{16}$$

where $\sigma = (\partial \mu/\partial V_2)_{n_2}$.

Obviously, the μ in Eq. (16) will not be the same as the μ in Eq. (15) when the two equations are used to define the interaction parameter. We will adopt the nomenclature of Holly [20], whereby parameters determined using Eq. (15) are given the symbol χ, while those determined from Eq. (16) will be symbolized by μ. As far as is known, all values of polymer-solvent interaction parameters in the literature are χ values, except those in the papers by Koningsveld et al. [33-35], Holly [20], and Flory and Tatara [23]. However, a further exception should be made in that the concentration of polymer, V_2, and mole volumes V_1 and V_2 in Eq. (15) have been changed in Flory's equation of state theory to "segment fraction" and "hard core" volumes, and some interaction parameters have been calculated in these terms and often denoted χ_{seg}. χ_{seg} usually exceeds χ by 0.05 to 0.10 [24, 25]. The equation of state theory gives results more in accord with experiment than those obtained through Eq. (15), but the increased accuracy of χ_{seg} is obtained by greatly increased complexity of calculation and requires data which are sometimes not available.

Equations (15) and (16) refer to solution of polymers in solvents. If the polymer is cross-linked, it only swells in the solvent, the $(\overline{V}_1/\overline{V}_2)$ term vanishes, and an elastomeric term must be added:

$$\Delta\overline{F}_1/RT = \ln(1 - V_2) + V_2 + \mu V_2^2 - (1 - V_2)V_2^2\sigma + \gamma\overline{V}_1(V_2^{1/3} - 2V_2/f) \tag{17}$$

where γ = chain segment density in the gel/mL
= $fd_gX_g/2$
f = network functionality
d_g = density of gel
X_g = cross-link density/g of gel

In the equivalent form of Eq. (15), μ is replaced by χ and σ becomes zero. If the polymer is cross-linked in the presence of a diluent, the last term of Eq. (17) becomes

$$\gamma\overline{V}_1(V_2^{1/3}V_0^{2/3} - \frac{2V_2}{f})$$

See Eq. (7).

At equilibrium $\Delta\overline{F}_1 = 0$. It will be observed then that the first, second, and last terms on the right side of Eq. (17) will be equal to

$$\mu - \sigma(1 - V_2) = \chi \tag{18}$$

where

$$-\chi = \frac{\ln(1 - V_2) + V_2 + \gamma\overline{V}_1(V_2^{1/3} - 2V_2/f)}{V_2^2} \tag{19}$$

For linear variations of χ with V_2, Holly [20] found that χ and μ were related by

$$\mu = \chi + \frac{1}{2}(1 - V_2)\frac{\partial\chi}{\partial V_2} \tag{20}$$

or

$$\chi = \mu_0 - (1 - 2V_2)\sigma \tag{21}$$

where the slope of the μ versus V_2 curve is

$$\sigma = \frac{1}{2}\frac{\partial \chi}{\partial V_2} \tag{22}$$

and μ_0 is the value of μ at $V_2 = 0$. Equation (20) enables an evaluation of μ from χ over a range where the variation of χ with V_2 is linear. Equation (21) was in effect deduced by Koningsveld and Staverman [33].

If a cross-linked polymer and the same polymer cross-linked in the presence of a diluent are swollen to equilibrium in a good solvent for the uncured polymer, it follows from Eqs. (2), (17) and (21) that the network gel segment density, γ_g, of the diluted stock is

$$\frac{-[\ln(1 - V_d) + V_d + \mu_0 V_d^2 - \sigma V_d^2(1 - 2V_d)]}{(V_d^{1/3}V_0^{2/3} - 2V_d/f)}$$

$$= \frac{-V_0[\ln(1 - V_2) + V_2 + \mu_0 V_2^2 - \sigma V_2^2(1 - 2V_2)]}{(V_2^{1/3} - 2V_2/f)} \tag{23}$$

where V_2 refers to the undiluted stocks and V_d is the V_2 value of the diluted stock. Substituting $V_d = V_2V_0$, Eq. (5), we obtain

$$\frac{\ln(1 - V_2V_0) + V_2V_0 + \mu_0 V_2^2V_0^2 - \sigma V_2^2V_0^2(1 - 2V_2V_0)}{(V_2^{1/3}V_0 - 2V_2V_0/f)}$$

$$= \frac{V_0\ln(1 - V_2) + V_2V_0 + \mu_0 V_2^2V_0 - \sigma V_2^2V_0(1 - 2V_2)}{(V_2^{1/3} - 2V_2/f)} \tag{24}$$

From which

$$\ln(1 - V_2V_0) + V_2V_0 + \mu_0 V_2^2V_0^2 - \sigma V_2^2V_0^2(1 - 2V_2V_0)$$

$$= V_0[V_0\ln(1 - V_2) + V_2V_0 + \mu_0 V_2^2V_0 - \sigma V_2^2V_0(1 - 2V_2)] \tag{25}$$

which simplifies to

$$\frac{1}{V_0}\ln(1 - V_2V_0) - V_0\ln(1 - V_2) + V_2(1 - V_0) - 2\sigma V_2^3V_0(1 - V_0) = 0 \tag{26}$$

Expanding the logarithmic terms in series, we obtain

$$\frac{1}{V_0}\left(-V_2V_0-\frac{V_2^2V_0^2}{2}-\frac{V_2^3V_0^3}{3}\ldots\right)-V_0\left(-V_2-\frac{V_2^2}{2}-\frac{V_2^3}{3}\ldots\right)$$

$$+V_2(1-V_0)(1-2\sigma V_2^2V_0)=0 \qquad (27)$$

which, on neglecting all terms higher than the cubic, reduces to

$$\sigma = 1/6 \qquad (28)$$

It seems strange that the slope, σ, appears as a known constant quantity while nothing is indicated about the interaction parameter. The interaction parameter, χ, cannot be deduced by reasoning of the above nature. However, it was expressed in Eq. (21) as a linear equation in terms of an intercept, μ_0, and a slope, σ, which are both part of its value. Since the χ values are different in the diluted and undiluted stocks, the concentration factors in the terms containing the slope are different because the intercept and slope are the same for the two stocks. Thus the terms including the intercept have canceled in the above equations while the terms containing σ have not because these terms include V_2 which has to be different for the diluted and undiluted stocks.

There are two principal applications for the polymer-solvent interaction parameter. First, it is used as the calibration constant to relate cross-link density to solvent swelling or to Young's modulus. Relations based on either Eq. (15) or (16) will yield the same result, and it matters little which we use, except that Eq. (15) requires less computation. The other use, hopefully, is to calculate concentrations at incipient phase separation, and here the exact value of μ, or χ, is important. The classical method involving Eq. (15) leads most often to low calculated values of V_2 and the interaction parameter at phase separation when compared to experimental values. These calculated V_2 values at phase separation when polymer is added to solvent are usually about half of the true values when σ is positive [3].

The conditions for phase separation at the critical point are that the first and second partial derivatives of the partial molar free energy of the solvent be zero, the temperature and pressure remaining constant [25]. We will consider the cases of soluble polymers with $\sigma = 0$ and with $\sigma \neq 0$.

For soluble polymers, Koningsveld and Staverman [33, 34] and Holly [20] obtained the first derivative of Eq. (16) as

$$-1/(1-V_2)+(1-\overline{V}_1/\overline{V}_2)+2\mu V_2-2V_2(1-2V_2)\sigma=0 \qquad (29)$$

and Holly gave as the second derivative

$$-1/(1 - V_2)^2 + 2\mu_c - 2(1 - 5V_2)\sigma = 0 \tag{30}$$

If $\sigma = 0$, under the critical conditions we have the familiar expressions [3]

$$V_2 = \frac{1}{1 + \left(\dfrac{\bar{V}_2}{\bar{V}_1}\right)^{0.5}} \tag{31}$$

and

$$\chi_c = \frac{1}{2(1 - V_2)^2} \tag{32}$$

Equation (29) expresses the variation of V_2 with μ at phase separation. The curve of this variation has a minimum with respect to μ, called the critical point. Substitution of μ_c, the critical value of μ, from Eq. (30) into Eq. (29) yields the value of V_2 at the critical point. If we allow σ to be 1/6 from Eq. (28) and introduce particular values of $\bar{V}_1/\bar{V}_2$, we may use Eq. (29) to calculate μ as a function of V_2 at phase separation. If experimentally determined values of V_2 and μ fall outside of the curve of Eq. (29), the system will be single phase, whereas inside the curve two phases form.

For cross-linked polymers the derivatives of Eq. (17) have been determined. However, they are quite complex and contain the first and second derivatives of the network segment density with respect to V_2.

As an example of the use of the above discussion, one may calculate the conditions for phase separation in an uncured system. In the case of diethylene glycol adipate polyester of molecular weight 2340, if the interaction parameter did not vary with concentration, Eq. (31) and (32) would apply. If the polymer is diluted with nitroglycerine, $V_1/V_2 = 142.74/1980$ and $\chi_c = 0.805$. However, the parameter does vary with concentration and Eqs. (29) and (30) apply. V_2 critical is found to be 0.279 and $\mu_c = 0.896$. The actual values of μ in this mixture were found to be 0.66 to 0.69 up to $V_2 = 0.22$ using Eq. (20) and assuming that σ was 0.167. In other words, values of μ were well below and outside of the curve of Eq. (29) and could not extrapolate into the curve with increasing V_2 values. There would therefore be no possibility of phase separation in this system.

One may inquire as to the generality of these results. Certainly they would not apply where there were exothermic (negative) heats

TABLE 1. Positive Slopes of Polymer-Solvent Interaction Parameter Curves (χ)

Polymer	Solvent	Slope	Remarks	Refs.
Polyisobutylene	Cyclohexane	0.38	Linear over part of curve only	26
	Benzene	-	Not linear	
Cellulose triacetate	Chloroform	0.43		27
	Methylene chloride	0.32		
Ethylene-propylene-diene (Nordel)	Benzene	0.31		28
Ethylene-propylene	Benzene	0.28		29
Ethylene-propylene	Benzene	0.26		30
Diethylene glycol adipate	Tetrahydrofuran	0.37		This work
	Acetone	0.39		
	Methylene chloride	0.42		
	Nitroglycerine	0.42		
		0.36	Average of above values	
Polystyrene	Acetone	0.61		31
Polydimethyl siloxane	Benzene	0.70		23

of mixing as for instance in the case of nitrocellulose in acetone or in any case where χ or μ had a negative slope with respect to concentration. Equations (20), (21), (28), (29), and (30) require that χ vary linearly, at least over a range, and have a positive slope with respect to concentration of polymer. Equations (28) and (22) predict that this slope will be 1/3. Table 1 gives 10 positive slopes whose average value is 0.36. A number of cases were found where the χ vs V_2 curve was not linear, and two cases were found where the slopes were 0.61 and 0.70, considerably higher than 0.33. One must regard Table 1 as suggestive rather than conclusive.

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