Equilibrium Swelling of Highly Cross-Linked Polymeric Resins

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A modified expression for the change in chemical potential of a solvent, in a polymer network, due to *isotropic swelling* was obtained by substituting a non-Gaussian chain length probability distribution in Flory's statistical analysis of rubber elasticity. The affine non-Gaussian expression for the free energy change due to elastic deformation was compared to both the traditional Flory and the James–Guth "phantom network" expressions for the free energy change due to elastic deformation using available experimental data for the swelling of highly cross-linked polymeric resins. Among the different models for the elastic contribution to the free energy change resulting from isotropic swelling, the non-Gaussian elasticity expression was found to be as good as, or slightly better than the Flory expression, and clearly superior to the James–Guth phantom network expression. Both of the two different expressions used to represent the free energy of mixing, the Flory–Huggins expression and a modified version of the quasi-chemical mixing expression, were found to be equally successful when describing the isotropic swelling of cross-linked polymeric resins.

Introduction

It has long been known that many cross-linked polymeric networks, such as rubber, swell when contacted with an organic solvent (Brannon-Peppas and Peppas, 1988, 1991; Horkay and Nagy, 1984; Barr-Howell and Peppas, 1985; Zang et al., 1989; James and Guth, 1943; and references therein). The ability to predict the degree of solvent absorption is important in many polymer applications such as packaging materials (Richards, 1985), controlled drug release (Ashley, 1985), and plastic pipes (Berens, 1989). Also, of special interest are recent studies on the removal of organic solutes by cross-linked polymeric resins that have shown that resin swelling by both the solute and solvent is a critical phenomenon which affects the solute sorption capacity of the polymeric resins (Neely, 1980; Cornel and Sontheimer, 1986; Garcia and King, 1989; Gusler et al., 1993; and references therein).

There are a number of theoretical models which describe polymer swelling equilibrium. Some of these models are based on polymer scaling theories (Daoud et al., 1986; Geissler et al., 1989; Horkay and Zrínyi, 1982), and others are based on an "osmotic" equilibrium between the solvent and polymer (Horkay et al., 1991; Vink, 1983). However, one of the most commonly referenced theoretical analyses of polymer swelling is that of Flory and Rehner (1943a,b). This theory assumes that, at equilibrium, the entropy loss of the polymer chains upon stretching is equal to the entropy gain due to mixing the solvent and polymer where mixing may be enhanced or hindered by enthalpic effects. Although the Flory–Rehner theory is often used to describe polymer swelling equilibrium (Brannon-Peppas and Peppas, 1988, 1991; Horkay and Nagy, 1984; Barr-Howell and Peppas, 1985; Zang et al., 1989; and references therein), the Flory–Rehner theory has limitations that trace back to its initial development for the case of rubber swelling. In particular, Flory's expression for the free energy of elastic deformation is restricted because it assumes that a Gaussian distribution represents the chain length probability distribution (Flory, 1953). The Gaussian assumption is a reasonable representation of the chain length distribution for real chains only if they are reasonably long (Flory and Chang, 1976), which is generally the case for natural rubber with 400 or more monomers in the chains between cross-links (Flory, 1976). However,

according to the analysis of Flory (1976), a Gaussian distribution fails for chain lengths of less than about 100 monomers. It is important to note that the polymeric resins used in water treatment applications are highly cross-linked (Paleos, 1969; Garcia and King, 1989), and therefore any elasticity theory based on the Gaussian assumption such as the theories of Wall (1943), Flory (1953), and James and Guth (1943) is not applicable to these highly cross-linked polymeric resins. Thus, there is merit in exploring the consequence of using the Gaussian distribution compared to the non-Gaussian distribution when determining the swelling of cross-linked resins.

In this study we introduce a new expression for the free energy of elastic deformation applicable to the case of isotropic swelling of polymer networks consisting of short chains (<100 monomers) for which the traditional Flory (1953) expression is not applicable. The new expression for the free energy of elastic deformation was obtained by modifying Flory's analysis for rubber elasticity by using the non-Gaussian chain length distribution given by Wall and White (1974) instead of the Gaussian distribution. The resulting expression for the free energy of elastic deformation was evaluated by using the polymer/solvent swelling equilibrium data of Errede (1986a–c, 1989, 1990) which focused on a series of cross-linked polystyrene-divinylbenzene polymeric resins for which the number of monomers in the chains between the cross-links varied from 5 to 50 monomers. Thus, the data of Errede (1986a) are particularly useful in evaluating the applicability of the Gaussian and non-Gaussian distributions of chain length when predicting the swelling of highly cross-linked polymers. Since the swelling of polymers inherently involves the mixing of solvent and polymer, polymer swelling is quantified by the combination of the free energy of elastic deformation and the free energy of mixing. Thus, in the present work we consider swelling equilibrium analyses in which the traditional Flory–Huggins expression and a generalization of Guggenheim's (1944, 1952) quasi-chemical expression were used to represent the free energy of mixing.

Background

The expression for swelling equilibrium is obtained by equating the chemical potential of the solvent in the bulk phase to the chemical potential of the solvent in the polymer phase (Flory, 1953). The chemical potential at

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a given temperature and pressure can be obtained from the expression for the free energy, or

$$\mu_1 - \mu_1{}^\circ = \partial(\Delta F)/\partial n_1 \qquad (1)$$

where μ_1 is the chemical potential of the solvent (component 1), $\mu_1{}^\circ$ is the standard state chemical potential of the solvent, ΔF is the change in free energy relative to the standard state, and n_1 is the number of moles of solvent. To obtain an expression for ΔF the Flory–Rehner assumption of the separability of the free energy into the free energy of elastic deformation, ΔF_{el}, and the free energy of mixing, ΔF_{mix}, is often made (Brannon-Peppas and Peppas, 1988, 1991; Zang et al., 1989; Hooper et al., 1990; Horkay et al., 1993; and references therein), leading to the following:

$$\mu_1 - \mu_1{}^\circ = \Delta\mu_1 = \frac{\partial(\Delta F_{el})}{\partial n_1} + \frac{\partial(\Delta F_{mix})}{\partial n_1} = \Delta\mu_{1,el} + \Delta\mu_{1,mix} \quad (2)$$

where $\Delta\mu_{1,el}$ and $\Delta\mu_{1,mix}$ are the chemical potential changes of the solvent, in the network, due to elastic deformation and mixing, respectively.

Neuburger and Eichinger (1988) asserted, based on differential polymer swelling of cross-linked poly(dimethylsiloxane) networks in benzene and cyclohexane, that in the Flory–Rehner theory the assumption of separability is not valid and that there are cross-terms or interaction terms between the free energy of mixing and the free energy of elastic deformation that should be considered. Neuburger and Eichinger (1988) concluded that the free energies of mixing and elastic deformation are not separable based on the observation of a maximum in the swelling activity parameter which is given by $\lambda_s \ln(a_{1,c}/a_{1,u})$ where $a_{1,c}$ and $a_{1,u}$ represent the activities for the cross-linked and un-cross-linked polymer samples, respectively, at the same volume fraction of polymer, and λ_s is the extension ratio, that is the ratio of L/L_0 where L represents the length scale in the deformed, in this case, swollen state, and L_0 is the length scale in the undeformed state. In a subsequent analysis, McKenna et al. (1990) argued that Neuburger and Eichinger (1988) improperly assumed that the Flory–Huggins interaction parameter is equivalent for un-cross-linked and cross-linked polymers. On the basis of the swelling of natural rubber cross-linked with dicumyl peroxide in the solvents methyl ethyl ketone, acetone, n-decane, benzene, 1,2-dichlorobenzene, and ethyl acetate, McKenna et al. (1990) concluded that the Flory–Huggins interaction parameter was higher for a cross-linked network compared to the un-cross-linked polymer, and that the Flory–Huggins interaction parameter increased linearly with increasing cross-link density for networks of light to moderate cross-link density ($M_c > 1500$). In a later study, Zhao and Eichinger (1992) also demonstrated a maximum in the swelling activity parameter for differential polymer swelling of poly(dimethyl siloxane) networks in n-heptane, 2,3-dimethylpentane, 2,2,4-trimethylpentane, and benzene where only the Flory–Huggins interaction parameter for the un-cross-linked polymer was used. More recent work by McKenna et al. (1993) has demonstrated that the Flory–Rehner hypothesis of separability applied for polymer networks of synthetic isoprene swollen in benzene for the temperature range 10–45 °C. However, a maximum, or an "anomalous peak", in the swelling activity parameter was observed at 50 °C. One explanation for the "anomalous peak" in the swelling activity parameter was offered by Deloche and Samulski (1988) who have predicted theoretically a maximum in the swelling activity parameter. However, McKenna et al. (1993) noted that current theories of rubber elasticity cannot explain the dramatic change in the properties of

the isoprene networks over the range of only 10 °C, and suggested that further study of this behavior is needed.

At the current state of the art it appears that the Flory–Rehner theory of separability may be applicable for some polymer networks under some conditions, but the range of conditions for which this assumption may fail is not well defined. The majority of studies on polymer swelling, however, support the separability assumption, at least for the conditions investigated, as is typified by the recent studies of Horkay et al. (1993), Hooper et al. (1993), and McKenna et al. (1993). As a result, in this work it will also be assumed that the free energy of mixing and the free energy of elastic deformation are separable, at least to a first approximation.

Accordingly, for a cross-linked polymer network in contact with a pure solvent, eq 2 can be expressed as (Flory, 1953):

$$\mu_1 - \mu_1{}^\circ = \Delta\mu_{1,el} + \Delta\mu_{1,mix} = 0 \qquad (3)$$

Because it has been assumed that the contributions due to elastic deformation and the free energy of mixing are separable, any combination of expressions for $\Delta\mu_{1,el}$ and $\Delta\mu_{1,mix}$ can be used in principle to represent the polymer swelling equilibrium. A number of such models are discussed and compared in the following sections along with a new proposed expression for $\Delta\mu_{el}$ for a non-Gaussian network.

Models of $\Delta\mu_{mix}$

For the free energy of mixing, the Flory–Huggins expression (Flory, 1942; Huggins, 1942) is the generally accepted expression for the case of mixing a polymer and solvent (McKenna et al., 1990). The entropic component of the Flory–Huggins expression for the free energy of mixing is based on the assumption of a lattice with interchangeable polymer units (monomers) and solvent molecules. The number of configurations for n_2 polymer molecules of x segments onto a lattice of $n = n_1 + xn_2$ cells, where n_1 is the number of solvent molecules, is used to calculate the entropy using the Boltzmann relationship. The enthalpy of dilution, or heat of mixing, is obtained using a van Laar-like expression (Flory and Rehner, 1943b; Flory, 1953). For a solution consisting of un-cross-linked polymer chains and a solvent, the following expression for the free energy of mixing is obtained (Flory, 1953):

$$\Delta F_{mixing} = RT[n_1 \ln v_1 + n_2 \ln v_2 + \chi n_1 v_2] \qquad (4)$$

where n_1 is the number of solvent molecules, n_2 is the number of polymer molecules, v_1 is the volume fraction of solvent, v_2 is the volume fraction of polymer, and χ is the Flory–Huggins interaction parameter. However, as noted by Flory (1953) for a cross-linked polymeric network in equilibrium with a solvent $n_2 = 0$, resulting in the following expression for the free energy of mixing a solvent and a cross-linked polymer network:

$$\Delta F_{mixing} = RT[n_1 \ln v_1 + \chi n_1 v_2] \qquad (5)$$

The resulting expression for the change in chemical potential of the solvent due to mixing is given by (Flory, 1953)

$$\Delta\mu_{1,mix} = \frac{\partial\Delta F_{mix}}{\partial n_1} = RT[\ln(1 - v_2) + v_2 + \chi v_2{}^2] \qquad (6)$$

Equation 6 above will be referred to as the Flory–Huggins (FH) expression for the free energy of mixing.

A reasonable alternative to the Flory–Huggins expression is Guggenheim's (1944) quasi-chemical expression for the free energy of mixing which has been used extensively

as evidenced by the generalization for solvent mixtures to obtain the UNIQUAC (Abrams and Prausnitz, 1975) and UNIFAC activity coefficient models (Fredenslund et al., 1975). The following generalization of the quasi-chemical analysis for a mixture of several components was introduced by Panayiotou and Vera (1980):

$$\ln \gamma_i = (\ln \gamma_i)^\circ + \frac{zq_i}{2} \ln \Gamma_{ii} \qquad (7)$$

where γ_i is the activity coefficient of component i in a mixture of two or more components, $(\ln \gamma_i)^\circ$ is the portion of the log of the activity coefficient of component i in a mixture which is independent of the nonrandom arrangement of molecules, z is the coordination number which is defined as the number of contact points for a given molecule to interact with other molecules (typically 10; Abrams and Prausnitz (1975)), q_i is the surface area parameter for component i (Panayiotou and Vera, 1980), and Γ_{ii} is the nonrandom factor for the number of interactions between molecules of type i with other molecules of type i in the mixture. The parameter q_i, the surface area parameter, can be determined from the UNIFAC group-contribution method (Sandler, 1989). The nonrandom factors, Γ_{ii}, Γ_{ij}, and Γ_{jj}, are defined as the ratio of the actual number of ii, jj, or ij interactions to the number of ii, jj, or ij interactions which would occur if the molecules were distributed randomly (Panayiotou and Vera, 1980) where ii interactions represent the number of interactions between molecules of type i with other molecules of type i, etc.

To obtain the change in chemical potential due to mixing for a pure solvent and a cross-linked polymer network from the expression for the activity coefficient given in eq 7, the following identity is applied

$$RT \ln a_i = \mu_i - \mu_i^\circ \qquad (8)$$

where the activity of component i, a_i, is defined as $a_i = x_i \gamma_i$ and x_i is the mole fraction of component i. Therefore, eq 7 becomes

$$(\mu_i - \mu_i^\circ)/RT = \ln a_i = (\ln \gamma_i)^\circ + \ln x_i + \frac{zq_i}{2} \ln \Gamma_{ii} \quad (9)$$

Following the work of Prange et al. (1989), for a cross-linked polymer network in contact with a pure solvent, $(\ln \gamma_i)^\circ$, the portion of the activity coefficient independent of the nonrandom arrangement of molecules, is represented by the combinatorial term of the Flory–Huggins free energy of mixing which is given by (Sandler, 1989)

$$(\ln \gamma_i)^\circ = \ln \frac{v_i}{x_i} + (1 - v_i) \qquad (10)$$

where v_i represents the volume fraction of component i.

Therefore, the final expression for the change in chemical potential due to mixing a pure solvent, and a cross-linked polymer network is obtained by combining eq 9 and eq 10 to yield

$$\Delta\mu_{1,\text{mix}} = RT\left[\ln v_1 + v_2 - \frac{1}{2}z_1 q_1 \ln \Gamma_{11}\right] \qquad (11)$$

To obtain the nonrandom factor Γ_{ii} in eq 12, an additional equation is needed to relate the nonrandom factors to the interchange energy, w_{12}, which is defined as $w_{ij} = \epsilon_{ij} - (1/2)(\epsilon_{ii} + \epsilon_{jj})$ where ϵ_{ij} is the interaction energy for the interaction between an i and a j molecule (Guggenheim, 1944). Panayiotou and Vera (1980) used Guggenheim's result (1944, 1952) which related the number of i–i, i–j, and j–j contacts to the interchange energy to evaluate the nonrandom factors according to the following equation (Prange et al., 1989):

$$\frac{\Gamma_{ij}^2}{\Gamma_{ii}\Gamma_{jj}} = \exp(-2w_{ij}/kT) \qquad (12)$$

where Γ_{ii}, Γ_{jj}, and Γ_{ij} are the nonrandom factors for the i–i, j–j, and i–j interactions respectively, and w_{ij} is the interchange energy. To ensure that the total number of contacts with molecules of type i is consistent with the total number of contact sites on molecules of type i, an equation of the following form is needed for each component in the mixture:

$$\Gamma_{ii} = \frac{1}{\theta_i}[1 - \sum_{j \neq i} \theta_j \Gamma_{ij}] \qquad (13)$$

where θ_i is the surface area fraction, or $\theta_i = N_i z q_i / \sum_j N z q$ where N_i is the number of moles of component i, z is the coordination number, q_i is the surface area parameter for component i (Prange et al., 1989; Panayiotou and Vera, 1980) as previously defined for eq 9, and the summation is over all components, j, in the mixture. Therefore, for an N-component mixture, there are N equations of the form of eq 13, one for each component in the mixture. These N equations are referred to as "contact-site balances" (Prange et al., 1989).

Therefore, to represent the free energy of mixing a pure solvent and a cross-linked polymer network, eq 11 and eq 12 are needed, and two equations of the form of eq 13, that is, a contact site balance for the solvent (1) and the polymer (2). From eqs 11–13 it is evident that there is only one variable, the interchange energy, w_{12}. Hereafter, the combination of eqs 11–13 will be referred to as the nonrandom (NR) expression for the free energy of mixing.

Models of $\Delta\mu_{\text{el}}$

A. Existing Models for $\Delta\mu_{\text{el}}$. The expression for $\Delta\mu_{\text{el}}$ proposed by Flory (1953) is based on a statistical analysis of rubber elasticity where it is assumed that the probability of obtaining a stretched polymeric network in a given configuration, Ω, is given by

$$\Omega = \Omega_1 \Omega_2 \qquad (14)$$

where Ω_1 is the probability of obtaining the necessary chain vector distribution for which each chain has vectors x_i, y_i, z_i, within a given range Δx, Δy, and Δz, or that is the probability of obtaining the distribution of chains having the same length as the length of the chains between crosslinks in the final network, and Ω_2 is the probability that for each segment in the chain which is capable of forming a cross-link there is another cross-linking segment with a given volume so that the cross-link bond can be made. Flory's analysis also assumes that the chain length distribution could be represented by a Gaussian distribution, and that the polymer chains deform affinely; i.e., the dimensions of the chains change in the same manner as the dimensions of the macroscopic sample. Flory (1953) developed expressions for $\ln \Omega_1$ and $\ln \Omega_2$, and subsequently, the expression for the entropy change of a cross-linked network due to elastic deformation was obtained by applying the Boltzmann relationship:

$$\Delta S_{\text{el}} = k \ln \Omega = k \ln \Omega_1 + k \ln \Omega_2 \qquad (15)$$

where k is the Boltzmann constant and ΔS_{el} is defined as

$$\Delta S_{\text{el}} = S_{\text{deformed}} - S_{\text{undeformed}} \qquad (16)$$

where S_{deformed} represents the entropy of the deformed polymeric network, and $S_{\text{undeformed}}$ represents the entropy of the undeformed network (where $\alpha_x = \alpha_y = \alpha_z = 1$). If it is assumed that the change in free energy due to elastic deformation is equal to the change in the entropy due to

elastic deformation ($\Delta H_{el} \approx 0$), the following expression for the change in free energy due to elastic deformation is obtained:

$$\Delta F_{el} = (kT\upsilon_e/2)(3\alpha_s{}^3 - 3 - \ln \alpha_s{}^3) \qquad (17)$$

in which υ_e is the number of elastically active chains, or the number of chains which are connected to the network at both ends, and α_s is the extension ratio, which for the case of isotropic polymer swelling is given as $\alpha_s = (V/V_0)^{1/3}$, where V is the solvent swollen volume of the polymer network and V_0 is the dry volume of the polymer network. The expression for change in chemical potential due to elastic deformation is obtained from (Flory, 1953):

$$\frac{\partial(\Delta F_{el})}{\partial n_1} = \frac{\partial(\Delta F_{el})}{\partial \alpha_s} \frac{\partial \alpha_s}{\partial n_1} \qquad (18)$$

and realizing that α_s, the extension ratio, is related to n_1, the number of moles of solvent, through the following relationship:

$$\alpha_s = \left(\frac{V}{V_0}\right)^{1/3} = \left(\frac{V_0 + n_1 V_1}{V_0}\right)^{1/3} = \left(\frac{1}{\upsilon_2}\right)^{1/3} \qquad (19)$$

where V_1 represents the molar volume of component 1, the solvent. Accordingly, the expression for $\Delta\mu_{el}$ is given by

$$\Delta\mu_{1,el} = RT\left[\frac{V_1}{\nu M_c}\left(1 - \frac{2M_c}{M}\right)\left(\upsilon_2{}^{1/3} - \frac{\upsilon_2}{2}\right)\right] \qquad (20)$$

in which M_c is the molecular weight of the chains between cross-links, ν is the specific volume of the polymer (component 2), υ_2 is the volume fraction of polymer in the swollen network, and the term $(1 - (2M_c/M))$ accounts for dangling chains, or the deviation of the real network from a perfect network (Flory, 1953) where for a perfect network there are no dangling chains (i.e., $(2M_c/M)) << 1$).

One alternative to the expression of Flory for rubber elasticity was developed by James and Guth (1943). The James–Guth "phantom network" theory (1943) is based on the following assumptions: (1) the internal energy is not dependent on the volume and (2) the entropy can be divided into two parts, one associated with the thermal capacity and the other associated with the number of configurations. The entropy of a single chain is given as

$$S = k \log C(L) + h(T) \qquad (21)$$

where S is the entropy, k is the Boltzmann constant, $C(L)$ is the number of configurations available for the length L between the ends of the chain, and $h(T)$ represents the thermal capacity of the chain. The expression of Guth and Mark (1934), which is Gaussian, can be used to obtain $C(L)$, or

$$C(L) = A \exp(-L^2/2\langle L^2\rangle_{AV}) \qquad (22)$$

where the average of the squares of the chain lengths $\langle L^2\rangle_{AV} = Nl^2$ for a one-dimensional case and $\langle L^2\rangle_{AV} = (1/3)Nl^2$ for a three-dimensional case where N is the number of bonds and l the length of a segment (or monomer). Therefore, the tension Z, for an individual chain is given by:

$$Z(L,T) = [kT/\langle L^2\rangle_{AV}]L \qquad (23)$$

To obtain an expression for the bulk of the network, an assumption must be made about how the single chains make up the bulk. The model of James and Guth is a network of idealized flexible chains and a fluid which will account for the volume-filling properties of the "rubberlike" network. However, since strain acts only on the junction points (cross-links), the model can be assumed to be a network of junction points and independent chains connecting them. This is equivalent to assuming that the chains can freely cross one another, and therefore the James–Guth expression is often referred to as the "phantom network" expression (abbreviated as PN in this work). The resulting expression for the change in chemical potential due to elastic deformation, as it applies to polymer swelling, is given by (Flory, 1977)

$$\Delta\mu_{1,el} = RT\left[\left(\frac{V_1}{2\nu M_c}\right)\left(1 - \frac{2M_c}{M}\right)\upsilon_2{}^{1/3}\right] \qquad (24)$$

It is noted that the differences between the Flory expression, eq 20, and the James–Guth phantom network expression, eq 24, are the additional term, $-\upsilon_2/2$, which is included in the Flory (1953) expression but not included in the phantom network expression, and the additional factor $1/2$ preceding the $\upsilon^{1/3}$ term. The term $-\upsilon_2/2$ results from the logarithmic term in eq 17 which is controversial (McKenna et al., 1991). According to Flory (1976) the physical meaning of the logarithmic term in eq 17 is that it represents constraints on the network cross-links such that the chain dimensions deform affinely with the dimensions of the macroscopic sample. As a result the Flory expression, eq 20, with complete constraints on the fluctuation of cross-links, and the phantom expression, eq 24, with no constraints on the fluctuation of the cross-links, represent the two extremes.

B. Non-Gaussian Expression for $\Delta\mu_{el}$. Both Flory's expression, eq 20, and the phantom network expression, eq 24, for the change in chemical potential due to elastic deformation are only strictly applicable if the chains between the cross-links are long (i.e., at least 100 monomers), which is due to the use of a Gaussian chain length probability distribution to represent the length of the chains between the cross-links (Flory, 1976). Thus, in this section we present an expression applicable for short chain lengths as an alternative to eqs 20 and 24. Our analysis follows Flory's statistical analysis for rubber elasticity where a non-Gaussian expression is used for the chain length probability distribution instead of the Gaussian distribution. In the current analysis, the non-Gaussian distribution of Wall and White (1974) was selected. Wall and White (1974) demonstrated that the non-Gaussian distribution is superior to the Gaussian distribution for chains of 20 monomers or less by comparison of both expressions to Monte Carlo random-walk simulations.

Following Flory's analysis (1953), the probability of forming a cross-linked network, Ω, is assumed to be the product of two probabilities as given in eq 14, and after the probabilities Ω_1 and Ω_2 are evaluated, the change in the entropy due to elastic deformation can be obtained by applying eq 15, the Boltzmann relationship, and eq 16.

The first probability, Ω_1, is the probability that all of the chains will fall within the correct dimensions, x_i, y_i, z_i, and is equal to the product over all the chains of the probability that an individual chain has the correct chain vector distribution. Therefore, Ω_1 is given by (Flory, 1953)

$$\Omega_1 = \nu! \prod (\omega_i{}^{\nu_i}/\nu_i!) \qquad (25)$$

where ω_i is the probability that an individual chain has the correct chain vector distribution, ν is the total number of chains, and ν_i is the number of chains with components x_i, y_i, z_i after deformation or components (x_i/α_x), (y_i/α_y), and (z_i/α_z) before deformation where $\alpha_x, \alpha_y,$ and α_z are the three principal extension ratios (Flory, 1953). The probability that an individual chain has the correct chain vector distribution, ω_i, is equivalent to $W(x_i,y_i,z_i) \, dx \, dy \, dz$ where $W(x_i,y_i,z_i)$ is the chain length probability distribution

function (Flory, 1953). The non- Gaussian and Gaussian chain length probability distributions are given by

non-Gaussian (Wall-White, 1974):

$$W(x_i,y_i,z_i) \, dx \, dy \, dz = \frac{5}{3}\left(\frac{\beta}{\pi^{1/2}}\right)^3 (r^2) \, e^{-\beta^2 r^2} \, dx \, dy \, dz \quad (26)$$

Gaussian (Flory, 1953):

$$W(x_i,y_i,z_i) \, dx \, dy \, dz = \left(\frac{\beta'}{\pi^{1/2}}\right)^3 e^{-\beta'^2 r^2} \, dx \, dy \, dz \quad (27)$$

where $r^2 = x^2 + y^2 + z^2$ for both cases, $\langle r^2 \rangle$ is the root-mean-square average chain length, $\beta' = 2/(3\langle r^2 \rangle)$ (Flory, 1953), and $\beta = 5/(2\langle r^2 \rangle)$ (Wall and White, 1974). The expression for ν_i is given by (Flory, 1953):

$$\nu_i = \nu W(x_i/\alpha_x, y_i/\alpha_y, z_i/\alpha_z) \Delta x \Delta y \Delta z / \alpha_x \alpha_y \alpha_z \quad (28)$$

Upon applying the Boltzmann relationship, eq 15, and using Stirling's approximation for the factorials, that is $N! \approx N \ln N - N$ (McQuarrie, 1976), eq 25 can be expressed as

$$\ln \Omega_1 = \sum \nu_i \ln(\nu W_i/\nu_i) \quad (29)$$

For the non-Gaussian expression, substituting eq 26 for W_i and eq 28 for ν_i in eq 29 leads to the following expression for $\ln \Omega_1$:

$$\ln \Omega_1 = \nu_e \frac{2\beta^{5/2}}{3\pi^{3/2}} \int \int \int_{-\infty}^{+\infty} \left[\left(\frac{x}{\alpha_x}\right)^2 + \left(\frac{y}{\alpha_y}\right)^2 + \left(\frac{z}{\alpha_z}\right)^2 \right] \times$$

$$\exp\left\{ -\beta\left[\left(\frac{x}{\alpha_x}\right)^2 + \left(\frac{y}{\alpha_y}\right)^2 + \left(\frac{z}{\alpha_z}\right)^2 \right] \right\} \times$$

$$\left\{ \ln\left[(\alpha_x \alpha_y \alpha_z) \frac{x^2 + y^2 + z^2}{(x/\alpha_x)^2 + (y/\alpha_y)^2 + (z/\alpha_z)^2} \right] + \right.$$

$$\left[\beta\left(x^2\left(\frac{1}{\alpha_x^2} - 1\right) + y^2\left(\frac{1}{\alpha_y^2} - 1\right) + \right.\right.$$

$$\left.\left.\left. z^2\left(\frac{1}{\alpha_z^2} - 1\right) \right) \right] \right\} dx \, dy \, dz \quad (30)$$

Although eq 30 is the general expression for $\ln \Omega_1$, the relationship between α_x, α_y, and α_z must be specified to obtain the final expression for the entropy change. For example, for the case of isotropic swelling of a polymeric network, the usual assumption is that the three principal extension ratios are equivalent such that

$$\alpha_x = \alpha_y = \alpha_z = (V/V_0)^{1/3} \quad (31)$$

where V_0 is the original (unswollen) volume of the polymer sample and V is the swollen volume (Flory, 1953). When the simplification of eq 31 is made, eq 30 simplifies to yield

$$\ln \Omega_1 = \nu_e \frac{2\beta^{5/2}}{3\pi^{3/2}} \int \int \int_{-\infty}^{+\infty} \left[\left(\frac{1}{\alpha^2}\right)(x^2 + y^2 + z^2) \right] \times$$

$$\exp\left[-\frac{\beta}{\alpha^2}(x^2 + y^2 + z^2) \right] \left[\ln \alpha^5 + \frac{\beta}{\alpha^2 - 1}(x^2 + y^2 + \right.$$

$$\left. z^2) \right] dx \, dy \, dz \quad (32)$$

For other relationships between α_x, α_y, and α_z the determination of $\ln \Omega_1$ requires evaluating a significantly more complex integral as is evident from in eq 30. When the integrals in eq 32 are evaluated, the resulting expression for $\ln \Omega_1$ is obtained:

$$\ln \Omega_1 = -(\nu_e/2)[5(\alpha^2 - 1) - 10 \ln \alpha] \quad (33)$$

It is noted that the expression for $\ln \Omega_2$ is not changed by using a different chain length probability distribution

Table 1. Summary of the Six Different Models for Swelling Equilibrium Compared in This Work[a]

	swelling equilib for a pure solvent $\Delta\mu_{1,\text{mix}} + \Delta\mu_{1,\text{el}} = 0$	
case	$\Delta\mu_{1,\text{mix}}$	$\Delta\mu_{1,\text{el}}$
1. FH–Flory	Flory–Huggins eq (6)	Flory eq (20)
2. FH–PN	Flory–Huggins eq (6)	phantom network eq (24)
3. FH–NG	Flory–Huggins eq (6)	non-Gaussian eq (36)
4. NR–Flory	nonrandom eq (11)	Flory eq (20)
5. NR–PN	nonrandom eq (11)	phantom network eq (24)
6. NR–NG	nonrandom eq (11)	non-Gaussian eq (36)

[a] FH ≡ Flory–Huggins; PN ≡ phantom network; NR ≡ nonrandom; NG ≡ non-Gaussian.

function, and therefore Flory's (1953) result for $\ln \Omega_2$ can be used without modification:

$$\ln \Omega_2 = -(\nu_e/2) \ln(\alpha_x \alpha_y \alpha_z) + \text{constant} \quad (34)$$

Given the above expressions for $\ln \Omega_1$ and $\ln \Omega_2$, the final expression for ΔS_{el} is obtained in the same manner as described previously for the Flory expression for ΔS_{el} was obtained as outlined in section A. The Boltzmann relationship, eq 15, and eq 16 are applied to determine ΔS_{el}, with the following result:

$$\Delta S_{\text{el}} = -(k\nu_e/2)[5(\alpha^2 - 1) - 7 \ln \alpha] \quad (35)$$

Then, if it is assumed that $\Delta S_{\text{el}} \approx \Delta F_{\text{el}}$, or $\Delta H_{\text{el}} \approx 0$ (Flory, 1953), and that volume additivity applies (i.e., eq 19), the final expression for $\Delta\mu_{\text{el}}$ can be obtained by taking the derivatives specified in eq 18. The resulting expression for $\Delta\mu_{\text{el}}$ for isotropic swelling of a non-Gaussian network is

$$\Delta\mu_{1,\text{el}} = RT\left[\left(\frac{V_1}{\nu M_c}\right)\left(1 - \frac{2M_c}{M}\right)\left(\frac{5}{3}\nu_2^{1/3} - \frac{7}{6}\nu_2\right) \right] \quad (36)$$

It is important to note that eq 36 is only valid for cases of *isotropic swelling* due to the simplification of eq 31.

Calculations

In order to evaluate the accuracy of the non-Gaussian expression, eq 36, the experimental swelling data of Errede (1986a) obtained at 23 °C was fitted with the six expressions given in Table 1 which represent the swelling equilibrium for a cross-linked polymer network by a pure solvent. The cross-link densities, expressed as moles of divinylbenzene to moles of styrene, of the polystyrene beads used by Errede (1986a) varied from 0.010 to 0.119, which is approximately equivalent to a range of 5–50 monomers in the chains between cross-links, clearly outside the range of applicability of the Gaussian chain distribution (Flory, 1976). Also note that in cases 1–3 in Table 1 swelling equilibrium was described by the Flory–Huggins expression for the free energy of mixing in combination with the three different expressions for the elastic deformation, eqs 20, 24, and 36. In cases 4–6 in Table 1 swelling equilibrium was represented using the nonrandom expression for the free energy of mixing (eq 11) and the three expressions for the elastic deformation, $\Delta\mu_{\text{el}}$ (eqs 20, 24, and 36).

The best fit for each of the six cases listed in Table 1 to the experimental data of Errede (1986a) was determined by least-squares minimization, which is minimization of the objective function $\Sigma_i(\nu_{2,\text{cal},i} - \nu_{2,i})^2$ where $\nu_{2,i}$ refers to the experimentally known volume fraction of component 2 (the polymer) for a given data point i and $\nu_{2,\text{cal},i}$ is the polymer volume fraction calculated from the swelling equilibrium model for the same data point i. The relative accuracy of the different models was expressed by

Table 2. Average Percent Deviation between Experimental and Predicted Polymer Volume Fractions Based on Least-Squares Analysis for Weighting Scheme 1

solvent	FH–Flory	FH–PN	FH–NG	NR–Flory	NR–PN	NR–NG
anisole	10.9	10.9	10.9	10.8	17.7	11.1
benzene	12.1	12.3	11.9	12.2	15.1	12.2
n-butyl acetate	6.28	6.80	5.89	5.47	6.34	5.57
n-butyl bromide	9.23	9.57	9.98	8.77	10.3	9.05
n-butyl chloride	10.8	11.7	10.1	10.1	12.6	9.77
n-butyl iodide	21.3	21.9	20.9	20.9	21.0	20.7
cyclohexane	15.1	16.1	14.1	14.6	15.6	13.5
cyclohexanone	31.9	32.2	31.7	31.3	31.0	31.7
cis-decahydronaphthalene	11.4	12.0	10.9	11.4	12.0	10.9
1,4-dibromobutane	16.8	17.1	16.6	16.2	15.7	16.5
1,4-dichlorobutane	10.7	11.0	10.5	9.96	9.32	10.3
methyl n-butyl ketone	13.6	14.2	13.1	12.6	12.4	12.7
n-butyl ether	5.80	7.16	4.54	4.68	5.97	3.76
N,N-dimethylaniline	15.5	15.0	15.8	15.4	14.2	16.8
pyridine	13.2	14.2	12.4	13.6	14.9	12.5
(trifluoromethyl)benzene	13.3	14.8	12.0	12.9	14.4	11.6
toluene	13.3	13.3	13.2	13.2	13.3	13.4
trans-decahydronaphthalene	10.4	11.7	9.35	9.48	10.5	8.90
average	13.4	14.0	12.9	13.0	14.0	12.8

the average percent deviation is defined as

$$\text{average \% deviation} = \frac{1}{N}\sum_i \left(\frac{|v_{2,\text{cal},i} - v_{2,\text{exp},i}|}{v_{2,\text{exp},i}}\right) \times 100 \tag{37}$$

where $v_{2,\text{exp},i}$ represents the experimentally determined polymer volume fraction, $v_{2,\text{cal},i}$ is the calculated value for the polymer volume fraction, and N is the number of experimental data points. The least-squares minimization requires the determination of the value $v_{2,\text{cal}}$ as well as the derivatives $\partial v_{2,\text{cal},i}/\partial \chi$ and $\partial^2 v_{2,\text{cal},i}/\partial \chi^2$ for cases 1–3, and the derivatives $\partial v_{2,\text{cal},i}/\partial w_{12}$ and $\partial^2 v_{2,\text{cal},i}/\partial w_{12}^2$ for cases 4–6. However, all six expressions listed in Table 1 for equilibrium swelling of a cross-linked polymer network and a pure solvent are not explicit in the volume fraction of polymer, v_2, and thus the first and second derivatives were determined numerically using a backward finite difference approximation. The value $v_{2,\text{cal}}$ was determined by using Newton's method to solve the nonlinear equilibrium equation(s).

The nonlinear equations needed to solve for v_2, the volume fraction of polymer, are as follows:

Cases 1–3. Flory–Huggins Equation for Mixing:

$$\Delta\mu_{1\text{el}} + \ln(1 - v_2) + v_2 + \chi v_2^2 = 0 \tag{38}$$

Cases 4–6. Nonrandom Equation for Mixing:

$$\Delta\mu_{1,\text{el}} + \ln(1 - v_2) + v_2 + 0.5q_1 z \ln \Gamma_{11} = 0 \tag{39a}$$

$$\exp\left(\frac{-2w_{12}}{kT}\right) - \frac{\Gamma_{12}^2}{\Gamma_{11}\Gamma_{22}} = 0 \tag{39b}$$

$$1.0 - \Gamma_{11}\theta_1 - \Gamma_{12}\theta_2 = 0 \tag{39c}$$

$$1.0 - \Gamma_{22}\theta_2 - \Gamma_{12}\theta_2 = 0 \tag{39d}$$

where any of the three expressions for the chemical potential change due to elastic deformation (eqs 20, 24, and 36) can be substituted for $\Delta\mu_{\text{el}}$. For cases 1–3 in which the Flory–Huggins (FH) expression for the free energy of mixing is used, only one equation, eq 38, which ensures that the chemical potential change due to mixing and the chemical potential change due to elastic deformation sum to zero, is needed to determine v_2. For cases 4–6 in which the nonrandom (NR) expression for the free energy of mixing was used, in addition to eq 39a, which represents the balance between the change in chemical potential due to mixing and elastic deformation, the relationship between

the nonrandom factors and the interchange energy, w_{12}, given in eq 39b, and two contact-site balances, given in eqs 39c and 39d, are needed to determine the volume fraction of polymer, v_2. It is noted, however, that the only adjustable parameter for cases 1–3 is the Flory–Huggins interaction parameter, χ. Analogously, for cases 4–6 the only adjustable parameter is w_{12}. In the above calculations the term $(1 - 2M_c/M)$ in eqs 20, 24, and 36 was taken to be unity which is equivalent to assuming $M \gg M_c$. This is a reasonable assumption given that M_c is relatively small (less than about 50) for the highly cross-linked resins utilized in the study of Errede (1986a). Moreover, M for such polymeric resins is larger then M_c by at least 2–3 orders of magnitude (Barr-Howell and Peppas, 1985).

At high polymer volume fraction (and thus low molecular weight between cross-links, M_c), the swelling data could not be reasonably described by either the Flory–Huggins expression for the free energy of mixing or the nonrandom expression, and therefore the least-squares minimizations were done with and without weighing factors. Thus, the least-squares objective function $\Sigma_i w_i(v_{2,i,\text{cal}} - v_{2,i})^2$ was utilized where w_i represents the weight of data point i. The three different sets of weighing factors are (1) no weight or $w = 1$ for all data points; (2) $w = 10.0$ for $M_c < 10$, $w = 5.0$ for $10 \le M_c < 20$, and $w = 1.0$ for $M_c \ge 20$; and (3) $w = 100.0$ for $M_c < 10$, $w = 50.0$ for $10 \le M_c < 20$, $w = 25.0$ for $20 \le M_c < 35$, and $w = 1.0$ for $M_c \ge 35$.

Results and Discussion

The average percent deviation for the curve fits for the six cases investigated listed in Table 1 are given in Tables 2 and 3 for weighting scheme 1 and weighting schemes 2 and 3. Figures 1 and 2 compare the three expressions for $\Delta\mu_{\text{el}}$ (eqs 20, 24, and 36) using the FH expression for the free energy of mixing (eq 6) for the solvent cyclohexanone using weighting schemes 1 and 3, respectively. Figures 3 and 4 compare the three expressions for $\Delta\mu_{\text{el}}$ using the NR expression for the free energy of mixing (eq 11) for the solvent cyclohexanone using weighting schemes 1 and 3, respectively. Analogously, results obtained with weighting schemes 1 and 3 where the FH expression was used to represent the free energy of mixing are illustrated in Figures 5 and 6 for methyl n-butyl ketone and in Figures 9 and 10 for n-butyl ether. Analogously, results obtained with weighting schemes 1 and 3 where the NR expression was used to represent the free energy of mixing are illustrated in Figures 7 and 8 for methyl n-butyl ketone and in Figures 11 and 12 for n-butyl ether. The three

Table 3. Average Percent Deviation between Experimental and Predicted Polymer Volume Fractions Based on Least-Squares Analysis for Weighting Schemes 2 and 3

	FH–Flory	FH–PN	FH–NG	NR–Flory	NR–PN	NR–NG
			Weighting Scheme 2			
min % dev	11.3	13.1	9.49	9.52	11.6	8.00
max % dev	73.6	62.4	68.7	67.5	72.2	64.1
av % dev	26.5	28.0	24.6	24.8	27.6	23.6
			Weighting Scheme 3			
min % dev	9.01	10.4	7.90	7.51	9.15	6.56
max % dev	55.2	51.6	52.4	50.7	53.8	48.8
av % dev	21.1	22.6	19.8	20.0	22.1	19.0
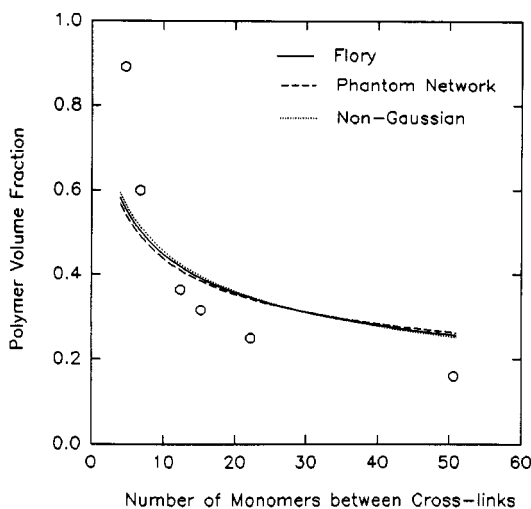
Figure 1. Polymer swelling by cyclohexanone: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the unweighted curve fits to experimental cyclohexanone data using the Flory–Huggins mixing expression for the change in free energy due to mixing.
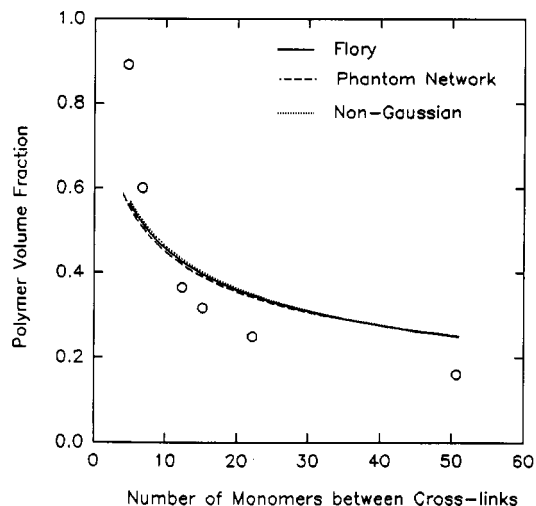
Figure 3. Polymer swelling by cyclohexanone: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the unweighted curve fits to experimental cyclohexanone data using the nonrandom mixing expression for the change in free energy due to mixing.
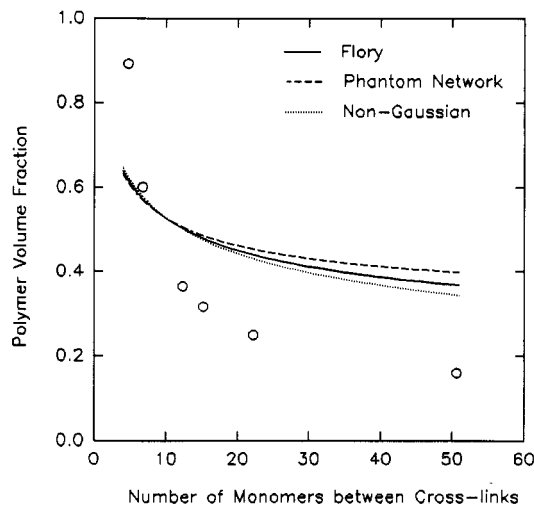
Figure 2. Polymer swelling by cyclohexanone: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the weighting scheme 3 curve fits to experimental cyclohexanone data using the Flory–Huggins mixing expression for the change in free energy due to mixing.
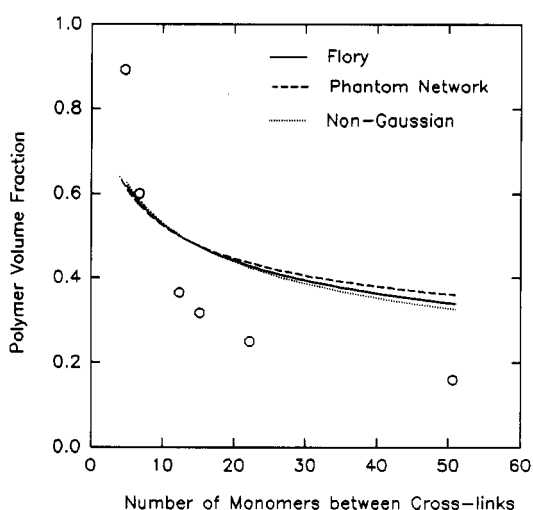
Figure 4. Polymer swelling by cyclohexanone: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the weighting scheme 3 curve fits to experimental cyclohexanone data using the nonrandom mixing expression for the change in free energy due to mixing.

particular solvents cover the range in polymer–solvent interactions because n-butyl ether is a good solvent, cyclohexanone is a poor solvent, and methyl n-butyl ketone is intermediate between a good and a poor solvent.

Comparison of the Expressions for the Free Energy of Mixing

Both mixing expressions, the Flory–Huggins expression, eq 6, and the nonrandom expression, eq 11, lead to a poor representation of the data for solvents with a low swelling

capacity (i.e., poor solvents) as illustrated in Figures 1–4 for cyclohexanone. For the methyl n-butyl ketone with intermediate swelling, and n-butyl ether with a high swelling capacity, the two mixing expressions both lead to a reasonable representation of the data without weighting as shown in Figures 5 and 7 for methyl n-butyl ketone and in Figures 9 and 11 for n-butyl ether. Overall, two general observations can be made by comparing the two expressions for the free energy of mixing. First, as demonstrated by comparing Figures 1 and 3 for cyclohexanone, Figures 5 and 7 for methyl n-butyl ketone, or Figures 9 and 11 for
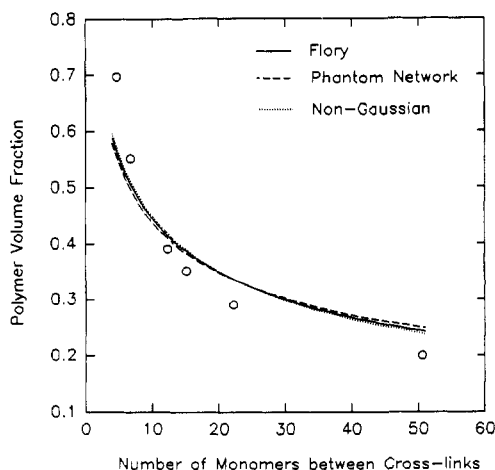
Figure 5. Polymer swelling by methyl n-butyl ketone: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the unweighted curve fits to experimental methyl n-butyl ketone data using the Flory–Huggins mixing expression for the change in free energy due to mixing.
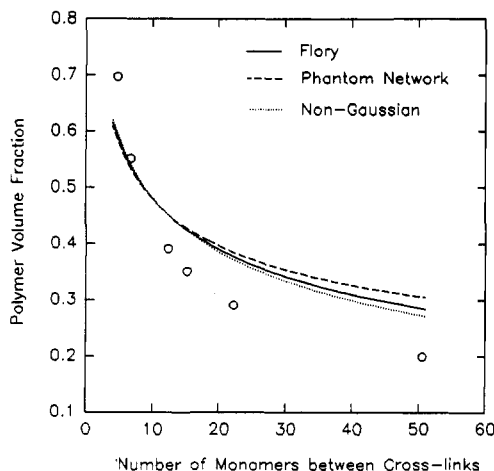

Figure 6. Polymer swelling by methyl n-butyl ketone: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the weighting scheme 3 curve fits to experimental methyl n-butyl ketone data using the Flory–Huggins mixing expression for the change in free energy due to mixing.

Figure 7. Polymer swelling by methyl n-butyl ketone: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the unweighted curve fits to experimental methyl n-butyl ketone data using the nonrandom mixing expression for the change in free energy due to mixing.

Figure 8. Polymer swelling by methyl n-butyl ketone: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the weighting scheme 3 curve fits to experimental methyl n-butyl ketone data using the nonrandom mixing expression for the change in free energy due to mixing.

n-butyl ether, the nonrandom expression for the free energy of mixing does not represent an improvement over the FH expression. Secondly, both expressions for the free energy of mixing lead to a poor representation of the data points with the highest cross-link density (lowest M_c), and weighting the least-squares minimization to favor the data points with highest cross-link leads to a poorer overall representation of the data. The poorer representation of the data with weighting of the data points is especially evident for n-butyl ether as seen by comparing Figures 9 and 10.

The equivalence of the representation of the FH and the NR expressions for the free energy of mixing and the poorer representation of both the FH and NR expressions with weighting schemes 2 and 3 are quantified in Tables 2 and 3 which give the average percent deviation of the curve fits for the six cases using weighting schemes 1, 2, and 3, respectively. For example, when eq 20 (i.e., Flory) is used to represent $\Delta\mu_{el}$, the average percent deviation averaged over all the solvents investigated is 13.4% and 13.0% when the FH expression and the NR are used for the free energy of mixing, respectively. As seen in Table 3, poorer overall representation of the data is obtained
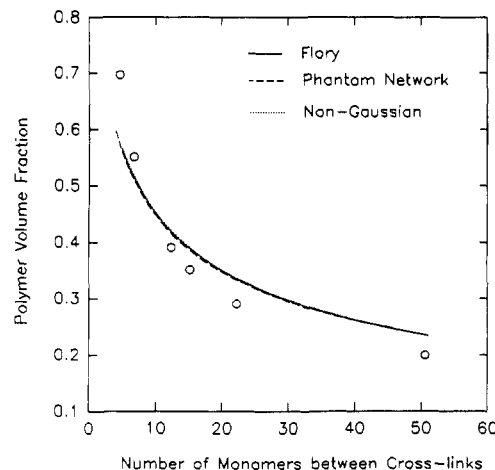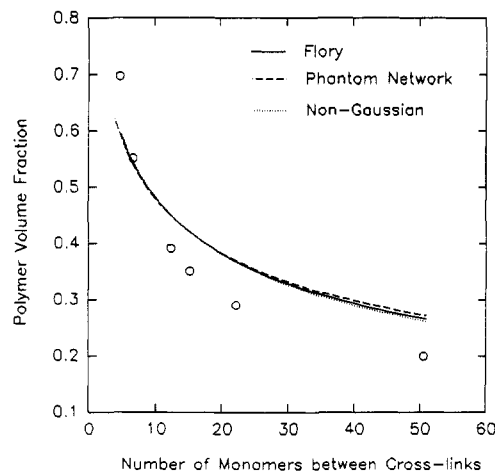
with weighting schemes 2 and 3. For example, the average percent deviation over all 18 solvents for the curve fit obtained using the PN expression for the elastic deformation along with the FH and NR expressions for the free energy of mixing was determined to be 14.0% and 14.0%, respectively, with no weighting, and 22.6% and 22.1%, respectively, with weighting scheme 3.

The equivalent accuracy of data representation using the NR expression and the FH expression is unexpected because the FH expression represents the assumption of random mixing, while the NR expression accounts for interactions between the different components in the mixture which results in nonrandom mixing. Furthermore, both the enthalpic and entropic portions of the FH model of the free energy of mixing have been criticized. In theory, the Flory–Huggins interaction parameter, χ, is entirely enthalpic in origin (Flory, 1942), but in actual use it has been demonstrated that the parameter χ often contains an entropic portion (Barton, 1989). As noted by Bawendi and Freed (1988), Flory (1942) and Huggins (1942) did not solve the lattice model "exactly", but made the mean field approximation to the lattice model. Therefore, the parameter χ is actually used as an empirical parameter and has been expressed as the sum of enthalpic and
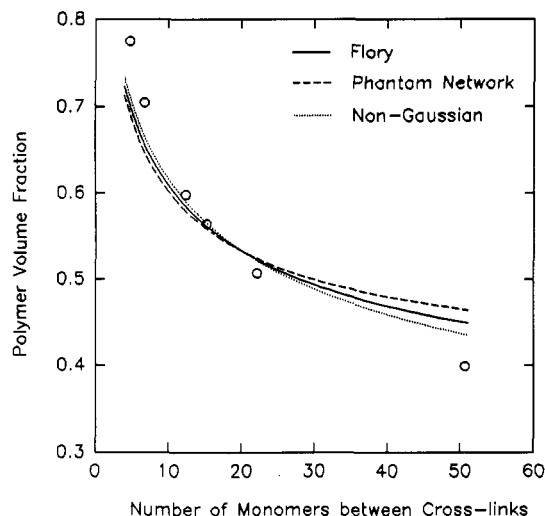
Figure 9. Polymer swelling by n-butyl ether: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the unweighted curve fits to experimental n-butyl ether data using the Flory-Huggins mixing expression for the change in free energy due to mixing.
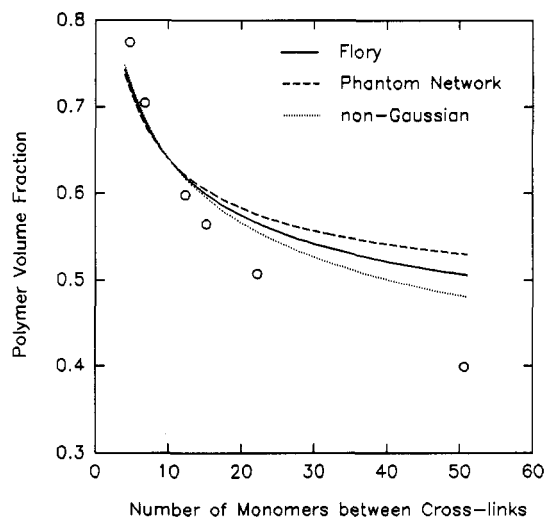

Figure 11. Polymer swelling by n-butyl ketone: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the unweighted curve fits to experimental n-butyl ether data using the nonrandom mixing expression for the change in free energy due to mixing.

Figure 10. Polymer swelling by n-butyl ether: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the weighting scheme 3 curve fits to experimental n-butyl ether data using the Flory-Huggins mixing expression for the change in free energy due to mixing.

Figure 12. Polymer swelling by n-butyl ether: comparison of Flory, phantom network, and non-Gaussian elasticity expressions for the free energy change due to elastic deformation for the weighting scheme 3 curve fits to experimental n-butyl ether data using the nonrandom mixing expression for the change in free energy due to mixing.

entropic contributions:

$$\chi = \chi_s(\text{entropic}) + \chi_h(\text{enthalpic}) \qquad (40)$$

where χ_h is often estimated from (Barton, 1990)

$$\chi_h = (V_s/RT)(\delta_s - \delta_p)^2 \qquad (41)$$

in which V_s is the molar volume of the solvent, and the parameters δ_s and δ_p are the solubility parameters of the solvent and polymer, respectively (Barton, 1990). In reality, since the solvent-solvent, solvent-polymer, and polymer-polymer interactions are not all equivalent, then the number of solvent-polymer interactions will be different from a random distribution due to preferential interactions, and the Flory-Huggins theory will fail (Bawendi and Freed, 1988; Freed and Pesci, 1989). Therefore, since the NR model accounts for preferential interactions between the polymer and solvent, the NR model is expected to be a better representation of the free energy of mixing than the FH model. However, the results from these calculations demonstrate that only a very slight advantage is obtained by using the NR mixing expression,
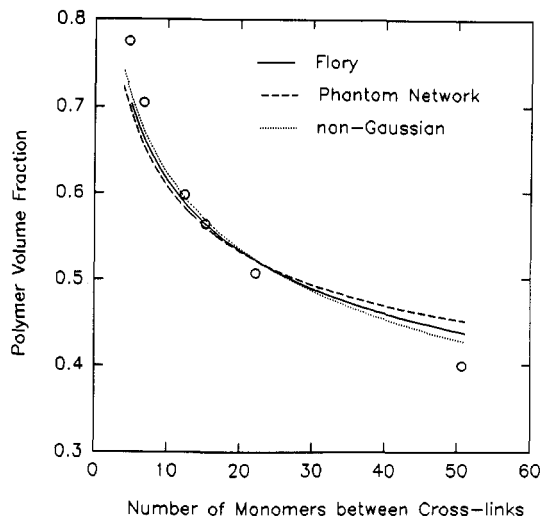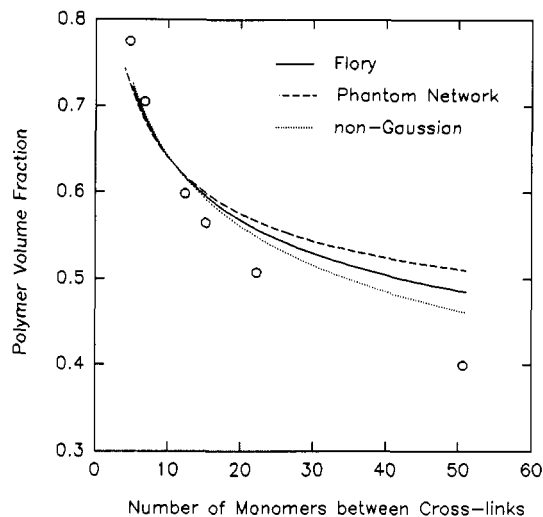
relative to the FH mixing expression for the case of polymer swelling equilibrium.

Comparison of the Different Elasticity Expressions

Figures 1-12 illustrate that a slightly improved curve fit is obtained when using the NG expression for $\Delta\mu_{el}$ compared to the Flory and PN expressions for $\Delta\mu_{el}$ for representing the equilibrium swelling data. The better representation of the swelling data using the NG expression for $\Delta\mu_{el}$ compared to the Flory and PN expressions for $\Delta\mu_{el}$ is especially evident for n-butyl ether, which is a good solvent for polystyrene as seen in Figures 9 and 11. However, it is noted that all three expressions for $\Delta\mu_{el}$ result in a poor representation of the data at the highest cross-link densities.

The slightly better representation of the swelling data using the NG expression for $\Delta\mu_{el}$ compared the Flory and PN expressions is demonstrated quantitatively in Tables 2 and 3 for weighting schemes 1, 2, and 3, respectively. For both the FH and NR expressions for the free energy of

mixing, the three different expressions for $\Delta\mu_{el}$ (eqs 20, 24, and 36) followed the same trend as seen by comparing the average percent deviation within cases 1–3 and within cases 4–6 in Table 2. The NG expression resulted in the best representation of the data, followed by the Flory expression, and the poorest fit was obtained for the PN expression. For example the average percent deviation averaged over all of 18 solvents investigated for cases 1–3 is 13.4%, 14.0%, and 12.9% for the Flory expression, the PN expression, and the NG expression, respectively. Although the differences in the average percent deviation for the three expressions is small ($\leq 1/\%$), the three expressions for $\Delta\mu_{el}$ tend to fall in the same order; that is, the representation of the data is best for the NG expression, followed by the Flory expression, and poorest for the PN expression, for both the NR and FH mixing expressions, and for all three weighting schemes. Thus the results are consistent with the expectation that, for these highly cross-linked polymeric beads, swelling equilibrium is more accurately described when modeled with the NG expressions for $\Delta\mu_{el}$. Therefore, it appears that replacing the Gaussian distribution with a non-Gaussian distribution to model the chain length distribution does improve the model fit for highly cross-linked polymer networks.

Overall Comparison

Of the six models listed in Table 1, the best overall fit to the swelling data was obtained using the NR expression for $\Delta\mu_{mix}$ and the NG expression for $\Delta\mu_{el}$ where weighting scheme 1 (i.e., no preferential weighting of points) was used, which resulted in an average percent deviation (averaged over all 18 solvents) of 12.8%. However, as noted previously, the differences between the six cases are small ($\leq 1.5\%$). In addition, all six models of the swelling equilibrium demonstrate a poor fit for the most highly cross-linked polymer beads ($M_c < 10$), for which the prediction always overestimates the actual degree of swelling obtained. If the assumption of the separability of the free energies is maintained, then there are four possibilities for the discrepancy between theory and experiment: (1) the entropy loss by the polymer chains due to deformation is underestimated for highly cross-linked networks; (2) the entropy gain due to mixing the solvent and polymer is overestimated; (3) the enthalpy of mixing is overestimated; and (4) the network is not perfect, or $(1 - (2M_c/M))$ is significantly less than 1.

Although real networks are imperfect because they contain dangling ends and other inhomogeneities (McKenna et al., 1989), and a cross-link dependence of the parameter χ has been noted both theoretically (Pesci and Freed, 1989) and experimentally (McKenna et al., 1989, 1990), the most likely source of the discrepancy between theory and experiment is inaccuracy in the expression for $\Delta\mu_{el}$. Inaccuracy in the expression for $\Delta\mu_{el}$ presented in this work could be attributed to the fact that for all three expressions for $\Delta\mu_{el}$ use a chain length distribution obtained for single chains, and then these are applied to the case of a polymer network. Therefore, constraints on the chain configurations due to the presence of adjacent chains are not explicitly accounted for, and these constraints are more likely to occur at high polymer volume fractions (low degree of polymer swelling). Thus it is conceivable that for very highly cross-linked networks such that $M_c < 10$, a new theoretical framework is needed to obtain a more accurate expression for $\Delta\mu_{el}$.

Interaction Parameters

The χ interaction parameters obtained by fitting the swelling equilibrium models in cases 1–3 with weighting

Table 4. χ Values for the Flory–Huggins Equation for the Unweighted Least-Squares Analysis

solvent	FH–Flory	FH–PN	FH–NG
anisole	0.226	0.366	0.039
benzene	0.266	0.392	0.098
n-butyl acetate	0.323	0.434	0.173
n-butyl bromide	0.286	0.407	0.125
n-butyl chloride	0.417	0.496	0.309
n-butyl iodide	0.442	0.513	0.347
cyclohexane	0.824	0.851	0.793
cyclohexanone	0.447	0.513	0.357
cis-decahydronaphthalene	0.480	0.549	0.388
1,4-dibromobutane	0.342	0.443	0.207
1,4-dichlorobutane	0.288	0.407	0.128
methyl *n*-butyl ketone	0.394	0.480	0.277
n-butyl ether	0.638	0.681	0.584
N,N-dimethylaniline	0.178	0.332	−0.028
pyridine	0.427	0.500	0.328
(trifluoromethyl)benzene	0.670	0.706	0.626
toluene	0.264	0.390	0.0948
trans-decahydronaphthalene	0.571	0.621	0.504

Table 5. w_{12}/k Values for the Nonrandom Equation for the Unweighted Least-Squares Analysis

solvent	NR–Flory	NR–PN	NR–NG
anisole	2.54	4.51	0.49
benzene	3.49	5.15	1.36
n-butyl acetate	3.01	4.05	1.62
n-butyl bromide	3.28	4.65	1.48
n-butyl chloride	4.87	5.79	3.62
n-butyl iodide	4.66	5.40	3.66
cyclohexane	8.51	8.76	8.23
cyclohexanone	5.36	6.13	4.34
cis-decahydronaphthalene	3.12	3.56	2.52
1,4-dibromobutane	3.59	4.60	2.21
1,4-dichlorobutane	3.34	4.71	1.49
methyl *n*-butyl ketone	4.05	4.91	2.86
n-butyl ether	4.29	4.56	3.93
N,N-dimethylaniline	1.84	3.38	−0.05
pyridine	6.12	7.14	4.68
(trifluoromethyl)benzene	6.25	6.57	5.85
toluene	2.95	4.34	1.11
trans-decahydronaphthalene	4.18	4.53	3.69

scheme 1 to the data of Errede (1986a) are presented in Table 4. Analogously, the w_{12}/k parameters obtained by fitting the swelling equilibrium models in cases 4–6 with weighting scheme 1 to the data of Errede (1986a) are presented in Table 5. Because the three different expressions for $\Delta\mu_{el}$ are not equivalent, the different models (see Table 1) result in different least-squares best fit values of χ or w_{12}/k. In most cases the best fit values of the χ and w_{12}/k parameters were higher values (or least favorable thermodynamically) for the models in which the PN expression was used for $\Delta\mu_{el}$, followed by the Flory expression, and it was the lowest (or most favorable thermodynamically) for the NG expression. For an equivalent degree of swelling, larger $\Delta\mu_{el}$ values were predicted using the NG expression compared to the Flory expression; therefore, a smaller (more favorable) Flory–Huggins interaction parameter was obtained using the NG expression. The higher value for $\Delta\mu_{el}$ obtained using the NG expression is expected since, for a given extension ratio (or degree of polymer swelling), there is a larger decrease in the number of possible configurations for a short chain compared to a longer chain. As an illustration, the greater loss in possible configurations, and thus entropy, predicted by the NG expression compared to the Flory expression is shown in Figure 13, which illustrates the absolute value of ΔS_{el} as a function of the extension ratio for the NG expression (eq 35) and the Flory expression, assuming $\Delta F_{el} \approx -T\Delta S_{el} = \Delta F_{el}$ where ΔF_{el} is given by eq 17. It is important to note that the difference between ΔS_{el} predicted by the two expressions increases as the extension ratio increases. This difference in ΔS_{el}
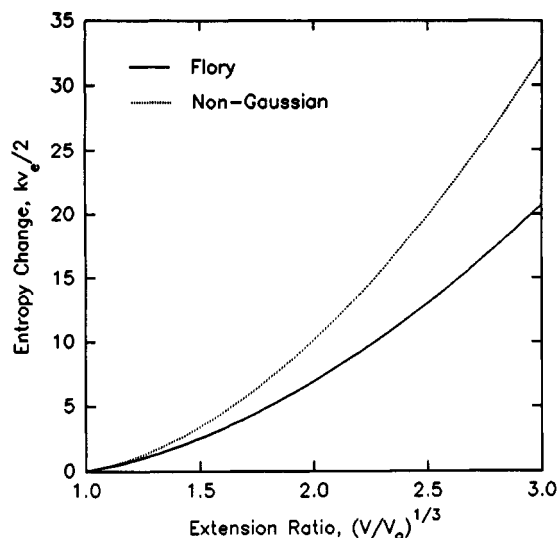
Figure 13. Change in entropy predicted using the Flory and non-Gaussian expressions for the isotropic elastic deformation of a cross-linked poymer network as a function of the extension ratio.

Figure 14. Toluene–polystyrene sorption equilibrium predictions with the Flory–Huggins interaction parameter value of 0.25.

accounts for the differences between the Flory–Huggins interaction parameters, χ_{Flory} and χ_{NG}, obtained using the Flory expression (eq 20) and the NG expression (eq 36), respectively, to represent the chemical potential change due to elastic deformation. The differences between χ_{Flory} and χ_{NG} resulting from the different predictions of $\Delta\mu_{el}$ are also illustrated in Table 4, where it is shown that the difference between χ_{Flory} and χ_{NG} is greater for a good solvent, such as toluene or benzene, where a high degree of polymer swelling and thus extension ratio are encountered, compared to a poor solvent, such as cyclohexane, where a low degree of polymer swelling is expected. It is also noted that the value of χ_{PN} (obtained when the PN expression is used for $\Delta\mu_{el}$) is higher than either χ_{Flory} or χ_{NG}. The higher value obtained for χ_{PN} is attributed, in part, to the lower prediction of ΔS_{el} by the PN expression compared to the value of ΔS_{el} obtained using either the Flory or NG expressions. Since the force exerted by the chains in a phantom network is less than the force exerted by the analogous affine network (Flory, 1979), the lower prediction of ΔS_{el} by the PN expression is expected.

Although the average percent deviation for the curve fits (cases 1–6 in Table 1) obtained with the six different swelling equilibrium models are comparable (i.e., with less than 1.5% variation among the various curve fits), the interaction parameters obtained by the least-squares analysis vary significantly (see Table 4). Clearly, for a fixed value of the interaction parameter, the different models for $\Delta\mu_{el}$ will lead to different predictions of the degree of polymer swelling. As an example, predictions of the volume fraction of polymer as a function of the number of monomers between cross-links for the toluene–polystyrene swelling equilibrium for a fixed value of the Flory–Huggins interaction parameter, χ, of 0.25, are illustrated in Figure 14. This example suggests that the reported χ values will be specific to the model used to obtain them when swelling data are utilized. Thus, in calculations of polymer swelling, it is imperative to use χ values that are consistent with the selected polymer swelling model.

Of the 18 solvents investigated by Errede (1986a), literature values of χ have been reported at temperatures reasonably close to those in Errede's (1986a) experiments (23 °C) for benzene, cyclohexane, toluene, cyclohexanone, and n-butyl acetate. The literature values of χ at the specific polymer volume fraction and temperature are listed in Table 6 along with the χ values obtained in this
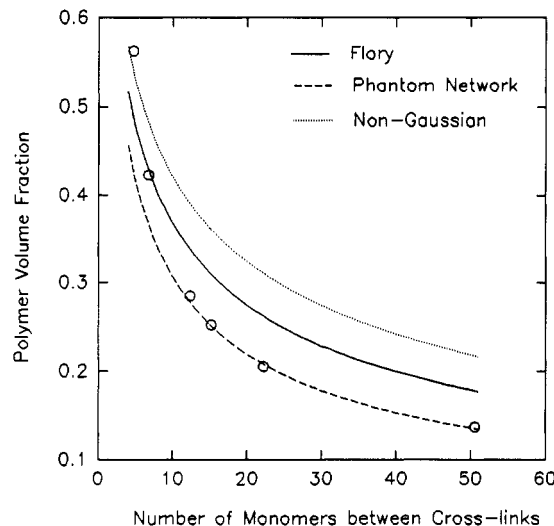
work by the least-squares fit of Errede's data. For benzene and toluene, only the χ_{NG} values fall outside of the range of χ values reported in the literature. For cyclohexane, the calculated χ values fall within the reported range, but for n-butyl acetate all three values of χ obtained in this work fall outside the range reported in the literature. For cyclohexanone, the χ_{Flory} and χ_{PN} values are close to the only value of χ reported in the literature, 0.5. Therefore, with the exception of n-butyl acetate, the values of χ obtained in this work are in general agreement with the range of values of χ reported in the literature. Although the discrepancy between values of χ for n-butyl acetate obtained in this work and those in the literature are large (0.30 or higher), these differences are not unreasonable given the uncertainty in the experimental values of the Flory–Huggins interaction parameter. The value of χ for n-butyl acetate was reported at 20 °C, while the experiments of Errede (1986a) were conducted at 23 °C. Thus, the values estimated in this work are expected to differ to some degree since experimental data suggest that χ varies with temperature (Barton, 1989). It is important to note that the values of χ reported in the literature were obtained for un-cross-linked polymers in solution, and therefore, these values may not be applicable for the cross-linked polymer networks modeled in this work. Another difficulty is that the experimental determination of χ is sensitive to the experimental method and model used to obtain χ. For example, Errede (1992) noted that χ values obtained for the poly(isobutylene)–benzene system using vapor pressure measurements varied significantly ($\sim$20%) from χ values obtained using inverse gas chromatography. Even reported values of χ obtained using the same methodology, at the same temperature and polymer volume fraction, can vary significantly. For example, Gundert and Wolf (1989) report χ values for the toluene–polystyrene system of 0.16 and 0.30, both obtained by vapor pressure measurements at a temperature of 25 °C and a polymer volume fraction of 0.80. In conclusion, given the limitations in the experimental determination of the Flory–Huggins interaction parameter, the agreement between the values obtained in this work and the range of χ values reported in the literature is reasonable.

Although in the present analysis the Flory–Huggins interaction parameter χ was assumed to be a constant which accounts only for the enthalpic interactions, in reality χ is an empirical parameter which accounts for all of the inaccuracies in the expression for the free energy. In the case of polymer swelling equilibrium, the χ

Table 6. Comparison of χ Values Reported in the Literature and χ Values Obtained in This Study

	least-squares best-fit χ params[a]			χ reported in the literature			
solvent	χ_{Flory}	χ_{PN}	χ_{NG}	χ range[b]	v_p range[c]	T,[d] °C	data source[e]
benzene	0.27	0.39	0.10	0.42–0.26	0.2–0.8	25	1
n-butyl acetate	0.32	0.43	0.17	0.5–0.9	0–1	20	2
cyclohexane	0.82	0.85	0.79	0.5–1	0–1	34	2
cyclohexanone	0.45	0.51	0.36	0.5	0	27	2
toluene	0.26	0.39	0.10	0.16–0.42	0.4–0.8	25	1

[a] Values from Table 4, rounded to the nearest second figure. [b] Range of reported χ values. [c] v_p range of polymer volume fraction for which the χ values were reported. [d] Temperature. [e] Data sources: (1) Gundert and Wolf, 1989; (2) Barton, 1989.
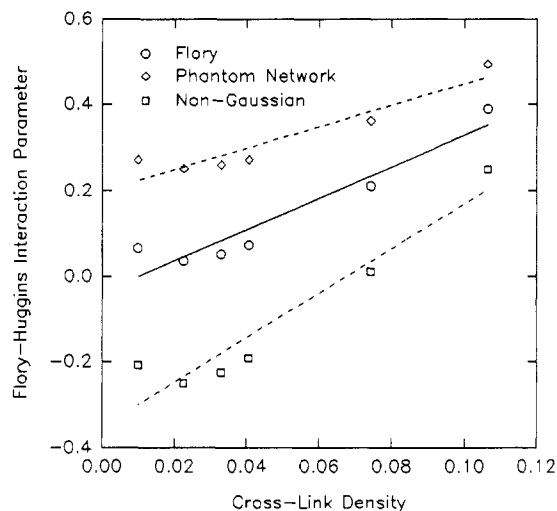

Figure 15. Variation of the χ parameter with the cross-link density for the benzene–polystyrene system.

parameter accounts for inaccuracies in the Flory–Huggins expression for the free energy of mixing, as well as inaccuracies in the expression for change in free energy due to elastic deformation. Therefore, in actual use the value of χ has been assumed to be a function of the volume fraction of the polymer and temperature. In the recent work of McKenna et al. (1989, 1990) it has also been demonstrated that χ varies with cross-link density for polymer networks. McKenna et al. (1989, 1990) determined experimental values of χ for a series of dicumyl peroxide cross-linked natural rubber samples, of various cross-link densities, swollen in different solvents. This was accomplished by equating the free energy of mixing to the free energy of elastic deformation where the free energy of elastic deformation was determined experimentally by torsional testing in both the dry and solvent swollen states. McKenna et al. (1989, 1990) also found that the value of χ was higher for a cross-linked polymer network than for the same polymer in the un-cross-linked state at the same volume fraction of polymer. Therefore, to investigate the possibility of a cross-link dependence of the χ parameter for polymer networks, another set of calculations were carried out to determine the variation of χ with the cross-link density for the data of Errede (1986a,b,c, 1989, 1990). As an illustration for benzene, each of the three expressions for the change in the chemical potential due to elastic deformation (eqs 20, 24, and 36) was equated to the FH expression for the change in chemical potential due to mixing (eq 6), and χ was solved for using the experimentally known volume fraction of the polymer for the given cross-link densities. The results as shown in Figure 15 reveal that, for all three expressions for $\Delta\mu_{el}$, the value of χ obtained appears to vary approximately linearly with cross-link density. It is interesting to note that the (approximate) linear variation of χ with cross-link density observed in this work is consistent with the observation of McKenna et al. (1989, 1990), who

determined the elasticity experimentally. Finally, it is noted that the variation of the values of χ with cross-link density and the expression used for $\Delta\mu_{el}$ suggest that, whenever possible, the value of $\Delta\mu_{el}$ should be determined experimentally.

Conclusions

An expression for the chemical potential change of a solvent in a polymeric network due to elastic deformation, applicable for the case of isotropic polymer swelling, was obtained by modification of Flory's statistical theory of rubber elasticity by using the non-Gaussian distribution of Wall and White (1974) for chain lengths in the network. The non-Gaussian expression, when incorporated into polymer swelling calculations, represented the polymer swelling data of Errede (1986a) slightly better than the traditional Flory expression and the James–Guth "phantom network" expression. The Flory–Huggins expression and a modified quasi-chemical expression for the free energy of mixing were found to represent the experimental polymer swelling data of Errede (1986a) equally well. However, the value of the interchange energy or the Flory–Huggins interaction parameter obtained by the least-squares fit of the data was found to vary with the expression used to represent the chemical potential change due to elastic deformation.

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