

Swelling Equations for Confined Homogeneous and Heterogeneous Polymeric Networks: Calculation of \bar{M}_c in Swellable Two-Phase Systems

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SYNOPSIS

Swelling equations were derived for polymeric networks that consist of two swellable but distinct phases. These equations can be used to describe the equilibrium swelling behavior of certain two-phase network systems. Using physicochemical measurements of the equilibrium polymer volume fraction, it was possible to calculate the number-average molecular weight between crosslinks, \bar{M}_c , using these equations. The influence of several structural parameters on \bar{M}_c was investigated. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Phase Distribution in Heterogeneous Systems

Phase-separated systems include block and graft copolymer networks; two-phase laminated networks consisting of concentric spheres or cylinders, or slabs; semicrystalline polymeric networks; composite, blend, or dispersion networks; or, finally, non-homogeneous networks of single polymers. Equilibrium swelling analysis of heterogeneous polymer networks incorporates many of the original concepts put forth in early developments for homogeneous polymer networks.^{1,2} In all cases, the heterogeneous networks are treated as homogeneous networks with variations and constraints arising from the contact between dissimilar materials within an interfacial boundary.

Some constraints that must be considered when developing swelling expressions for such systems are (i) isotropic and nonisotropic swelling behavior dictated by the distribution of the domain structure and its lattice structure; (ii) the geometric confor-

mation and relative geometries of the domains; (iii) the dimensionality of swelling; (iv) the conformational state of the macromolecules; and (v) external constraints. In view of these considerations, it is necessary to reformulate the thermodynamic theories already developed¹⁻⁶ to account for these considerations.

Figure 1 offers one conformation arrangement possible in a simple diblock copolymer network with spherical microdomains. It is a depiction of an ideal system, where the matrix (polymer A) and spherical microdomains (polymer B) are composed of polymeric chains that are relatively highly cross-linked. Possible macromolecular chain distributions in block copolymer systems and other heterogeneous systems may lead to two incompatible phases, A and B, where cylinders and spheres are two geometric shapes that may be used to confine sections of portions of the chain for proper analysis of each section to the total network configuration. Other alternatives could include (i) uncross-linked polymer segments within spheres; (ii) a mixture of block or graft copolymer with homopolymers A or B or both, which may include an interpenetrating network within either phase; (iii) block or graft copolymer consisting of multifunctional cross-links in the form of crystallites dispersed throughout one or the other polymer phase; or (iv) a phase composed of polymer A described by a Gaussian distribution, while polymer B is described by a non-Gaussian distribution.

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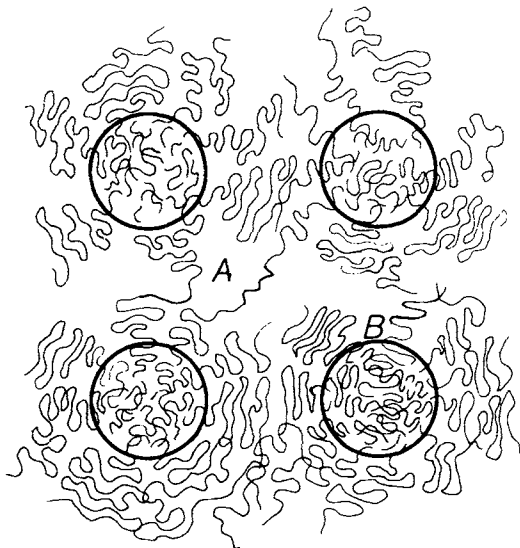


Figure 1 Distribution of spherical domains indicating possible incompatibility of two phases A and B.

Thermodynamic Analysis

The origin of equilibrium swollen network descriptions lies in the work of Huggins^{7,8} and Flory and Rehner.^{2,9-13} In their work, the free energy of a cross-linked network swollen to equilibrium conditions was equal to a mixing contribution due to the swelling agent/polymer thermodynamics and a retractive contribution due to the rubber elastic behavior of the network.

Several expressions for determination of molecular parameters were a result of these original concepts. For example, the equation for determining the number-average molecular weight between cross-links, \bar{M}_c , for highly swollen, cross-linked polymer networks that were produced by a cross-linking reaction in the solid state was presented by Flory and Rehner² as in eq. (1):

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \left(\frac{\bar{v}}{V_1} \right) \frac{[\ln(1 - v_{2,s}) + \left(1 - \frac{1}{x}\right)v_{2,s} + \chi_1 v_{2,s}^2]}{\left[v_{2,s}^{1/3} - \frac{2}{f} v_{2,s} \right]} \quad (1)$$

Here, \bar{M}_n is the number-average molecular weight of the uncrosslinked polymer; $v_{2,s}$, the equilibrium swollen polymer volume fraction; \bar{v} , the specific volume of the anionous polymer; V_1 , the molar volume of the swelling agent; x , the ratio of the volume of

a macromolecular chain to the volume of a solvent molecule; χ_1 , the solvent-polymer interaction parameter; and f , the functionality of the cross-links formed.

The Flory-Rehner description of equilibrium swollen polymer networks^{2,10} was based on the assumption that polymer chains could be modeled by a Gaussian distribution. This distribution usually requires a network system of at least 100 bond vectors between junctions or tie-points. A second assumption was that all junctions (cross-links) are fixed in a region about the origin with no spatial fluctuations or dependencies of any kind due to set deformations (phantom network). The idea of an affine network, as proposed in more recent network analysis⁴ disputes these assumptions since local fluctuations due to systematic forces vary in a statistical nature from junction to junction, thus causing small junction displacements.

Other structural characteristics may be affected by the method of network preparation that has been shown to have a marked effect on the development. Peppas and Merrill¹⁴ eluded to this fact when they examined networks cross-linked under various conditions. A variation of the Flory-Rehner equation for networks prepared in solution was presented and a new equation for \bar{M}_c was derived:

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \left(\frac{\bar{v}}{V_1} \right) \frac{[\ln(1 - v_{2,s}) + \left(1 - \frac{1}{x}\right)v_{2,s} + \chi_{1,2}v_{2,s}^2]}{v_{2,r} \left[\left(\frac{v_{2,s}}{v_{2,r}} \right)^{1/3} - \frac{1}{2} \left(\frac{v_{2,s}}{v_{2,r}} \right) \right]} \quad (2)$$

In this equation, $v_{2,r}$ represents the polymer volume fraction of the network immediately after cross-linking but before swelling.

BINARY SYSTEMS WITH ONE SWELLABLE AND ONE NONSWELLABLE PHASE

Heterogeneous networks, such as block and graft copolymer networks, exhibit phase separation on a microscopic level. This phase separation of copolymer segments into separate phases composed exclusively of the polymer of any said segment causes the formation of microdomain structures.

Three types of microdomains are most commonly found in heterogeneous two-phase polymer net-

works, i.e., spherical, cylindrical, and lamellar microdomains. Each phase is composed of a unique polymer that may or may not swell when exposed to a solvent of choice.

Two distinct cases of binary two-phase networks where one of the phases does not swell have been considered. In the first case, the network contains a continuous or most abundant phase that does not swell in the presence of solvent. Here, networks with spherical microdomains do not swell since the phase that has a potential to swell is masked from the solvent by the nonswellable phase. When cylindrical and lamellar microdomains are present, the system parameters, such as the equilibrium polymer volume fraction and stresses, are calculated using an inverse approach of Klier and Peppas.¹⁵

In the second case, the network contains a dispersed or less abundant phase that does not swell. Here, Treloar¹⁶ and Klier and Peppas¹⁵ have presented models that fully describe swellable two-phase systems where the core or inner phase restricts the swelling behavior of the surrounding phase. In their work, two-phase spheres, cylinders, and slabs were analyzed and a methodology to predict the equilibrium polymer volume fraction and stresses was presented. Swellable, block and graft copolymeric networks are also described in this manner where the spherical, cylindrical, or one of the lamellar phases does not swell in the presence of solvent.

MODELS FOR CONFINED HOMOGENEOUS NETWORKS

In constrained swollen polymer networks, interfacial constraints prevent an isotropic expansion of the system to occur. The formulation of the equilibrium conditions is such that the change of the partial molar Gibbs free energy of the solvent, $\Delta\bar{G}_1$, for the system must be zero:

$$\Delta\bar{G}_1 = \Delta\bar{G}_{1,m} + \Delta\bar{G}_{1,e} + \Delta\bar{G}_{1,i} = 0 \quad (3)$$

The Gibbs free energy of the solute has three contributions: the Flory-Huggins^{7,8} partial molar Gibbs free energy due to mixing, $\Delta\bar{G}_{1,m}$; the partial molar Gibbs free energy due to elastic contributions, $\Delta\bar{G}_{1,e}$; and the partial molar Gibbs free energy due to interfacial contributions, $\Delta\bar{G}_{1,i}$. The term $\Delta\bar{G}_{1,e}$ is formulated from theories of rubberlike elasticities set forth by Flory and Erman,^{4,17-20} James and Guth,^{21,22} Kovac and Crabb,^{23,24} and others.²⁵⁻²⁹

The term $\Delta\bar{G}_{1,i}$ is a function of the dimensionality of swelling and the geometry of the system. In a spherical coordinate system, $\Delta\bar{G}_{1,i}$ is expressed as

$$\Delta\bar{G}_{1,i} = \frac{2V_1\gamma}{rRT} \quad (4)$$

by analogy to previous work on microspheres in solution.³⁰⁻³⁴ Here r is the radius of the spherical microdomain at swelling equilibrium; γ , the interfacial tension at swelling equilibrium; R , the universal gas constant; and T , the absolute temperature. Equation (4) is valid for systems in contact with a solvent or other medium.

A set of equations was derived to describe some of the cases that arise in homogeneous networks swollen to equilibrium with $\Delta\bar{G}_1$ equal to zero and under set constraints. Thus, for equilibrium swollen polymer networks where the network chains are held at each chain end by a nonswellable boundary, the macromolecular chains are described by a Gaussian distribution, and the affine network behavior is considered, eq. (4) can be rearranged to express the number-average molecular weight between crosslinks, \bar{M}_c , as a function of system parameters. If the system can swell in three dimensions, i.e., for spherical domains, it can be easily shown by analogy to Barr-Howell and Peppas³⁵ that

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \left(\frac{\bar{v}}{V_1}\right) \frac{[\ln(1 - v_{2,s}^A) + \left(1 - \frac{1}{x}\right)v_{2,s}^A + \chi_1(v_{2,s}^A)^2]}{v_{2,r}^A \left[\left(\frac{v_{2,s}^A}{v_{2,r}^A}\right)^{1/3} - \frac{2}{f} \left(\frac{v_{2,s}^A}{v_{2,r}^A}\right) \right]} \quad (5)$$

The swelling equation is modified when swelling occurs in two directions, e.g., in cylindrical domains. Then,

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \left(\frac{\bar{v}}{V_1}\right) \frac{[\ln(1 - v_{2,s}^A) + \left(1 - \frac{1}{x}\right)v_{2,s}^A + \chi_1(v_{2,s}^A)^2]}{v_{2,r}^A \left[1 - \frac{2}{f} \left(\frac{v_{2,s}^A}{v_{2,r}^A}\right)^2 \right]} \quad (6)$$

Finally, for swelling in lamellar domains,

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \left(\frac{\bar{v}}{V_1}\right) \frac{[\ln(1 - v_{2,s}^A) + \left(1 - \frac{1}{x}\right)v_{2,s}^A + \chi_1(v_{2,s}^A)^2]}{v_{2,r}^A \left[\left(\frac{v_{2,s}^A}{v_{2,r}^A}\right)^{-1} - \frac{2}{f} \left(\frac{v_{2,s}^A}{v_{2,r}^A}\right) \right]} \quad (7)$$

For macromolecular chains described by a modified Gaussian distribution proposed by Kovac,²³ the models for equilibrium swollen constrained networks are modified. For example, the swelling equation for a system containing spherical swelling domain is:

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \left(\frac{\bar{v}}{V_1}\right) \frac{[\ln(1 - v_{2,s}^A) + \left(1 - \frac{1}{x}\right)v_{2,s}^A + \chi_1(v_{2,s}^A)^2]}{(v_{2,r}^A) \left[\left(\frac{v_{2,s}^A}{v_{2,r}^A}\right)^{1/3} - \frac{1}{N} \left(\frac{v_{2,s}^A}{v_{2,r}^A}\right) \right]} \quad (8)$$

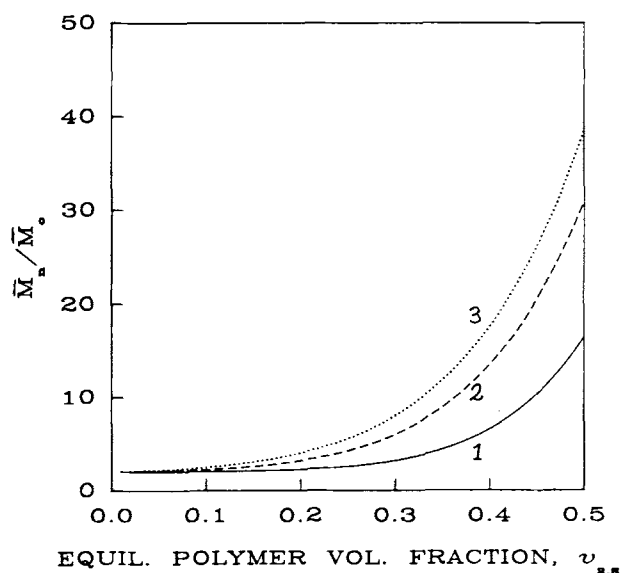


Figure 2 Number of mers per cross-linked chain, \bar{M}_n/\bar{M}_c , as a function of the equilibrium polymer volume fraction, $v_{2,s}$, for swollen gels. The molar volume ratio $\bar{v}/V_1\bar{M}_n$ was 1000 and the gels were homogeneous, confined, and allowed to swell in (1) one, (2) two, or (3) three dimensions.

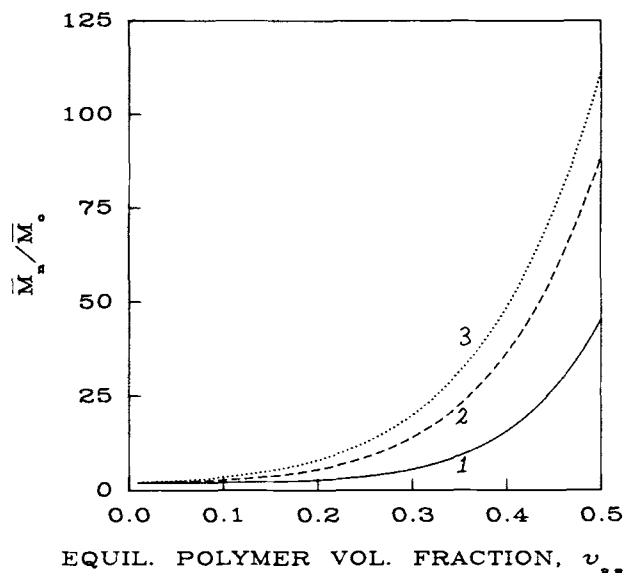


Figure 3 Number of mers per cross-linked chain, \bar{M}_n/\bar{M}_c , as a function of the equilibrium polymer volume fraction, $v_{2,s}$, for swollen gels. The molar volume ratio $\bar{v}/V_1\bar{M}_n$ was 3000 and the gels were homogeneous, confined, and allowed to swell in (1) one, (2) two, or (3) three dimensions.

Here,

$$N = \frac{\lambda\bar{M}_c}{M_r} \quad (9)$$

Similar equations can be obtained from two- and one-dimensional swelling. Here, M_r is the molecular weight of the repeating unit of the polymer segments found in phase A; λ is the number of links per repeating unit ($\lambda = 2$ for vinyl repeating units), and the other parameters are as defined before. This last set of equations is nonlinear and will require an iterative solution routine to determine the number-average molecular weight between cross-links, \bar{M}_c .

RESULTS AND DISCUSSION

Calculation of \bar{M}_c for heterogeneous or constrained homogeneous networks requires knowledge of the polymer volume fraction $v_{2,s}$. Once this is known, one of the previously developed equations can be used. The nature of the cross-linked system may be expressed either in terms of \bar{M}_c or in terms of its reciprocal value, which will be indicative of the cross-linking density.

The number of mers per cross-linked chain, \bar{M}_n/\bar{M}_c , was calculated from eqs. (5)–(7) over a range of equilibrium swollen polymer volume frac-

tions, $v_{2,s}$. This value is considered as an indication of the cross-linking density of the network. The results for networks cast in the absence of a swelling agent or solvent, $v_{2,s} = 1$, are plotted in Figures 2–4. The molar volume ratio, i.e., the ratio of polymer to solvent $\bar{v}/(V_1\bar{M}_n)$, was set equal to 1000, 3000, and 5000, respectively.

It is evident that more cross-linked networks, corresponding to a relatively high \bar{M}_n/\bar{M}_c value, are associated with high equilibrium polymer volume fraction $v_{2,s}$. Confinement of the network structure and swelling in one or two directions has a significant influence on the equilibrium degree of swelling, Q . Thus, Figures 2–4 indicate that for the same value of \bar{M}_n/\bar{M}_c , i.e., for the same real cross-linking density, the expected equilibrium polymer volume fraction, $v_{2,s}$, is significantly smaller for three-dimensional swelling. Since $v_{2,s}$ is the reciprocal of Q , the conclusion is that the three-dimensional swelling behavior will give the highest degree of swelling for the same \bar{M}_c .

However, this overall swelling behavior becomes much less important as the gel becomes more loosely cross-linked. Indeed, all three figures indicate that for $v_{2,s}$ smaller than 0.1 (corresponding to swelling ratio, Q , greater than 10) the dimensionality of swelling is not important.

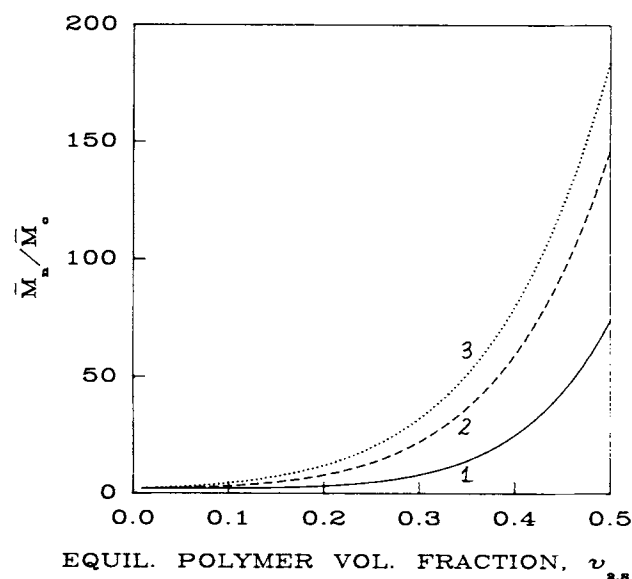


Figure 4 Number of mers per cross-linked chain, \bar{M}_n/\bar{M}_c , as a function of the equilibrium polymer volume fraction, $v_{2,s}$, for swollen gels. The molar volume ratio $\bar{v}/V_1\bar{M}_n$ was 5000 and the gels were homogeneous, confined, and allowed to swell in (1) one, (2) two, or (3) three dimensions.

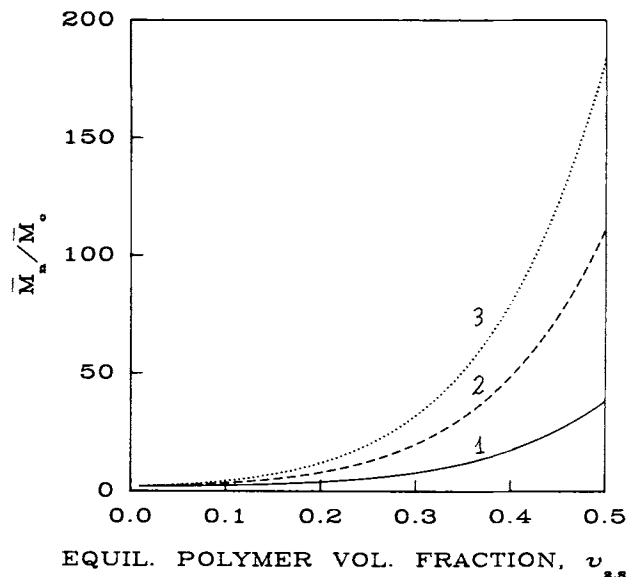


Figure 5 Number of mers per cross-linked chain, \bar{M}_n/\bar{M}_c , as a function of the equilibrium polymer volume fraction, $v_{2,s}$, for homogeneous, confined, swollen gels, allowed to swell in three dimensions. The molar volume ratio $\bar{v}/V_1\bar{M}_n$ was (curve 1) 1,000, (curve 2) 3,000, or (curve 3) 5,000.

Figure 5 depicts the results of constrained networks swollen in three dimensions for various molar ratios. A denser cross-linked structure is predicted for networks with larger molar volume ratios.

These results indicate that the network parameters are dependent on the dimensionality of swelling and the ratio of the volume of the polymer before cross-linking to the swelling agent.

CONCLUSIONS

In conclusion, previously developed swelling equations have been extended to analyze heterogeneous and confined homogeneous networks. It is particularly noteworthy that the geometric shape of the confined structure leads to a different form of the swelling equation.

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