

Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling

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Paul J. Flory, and John Rehner



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Statistical Mechanics of Cross-Linked Polymer Networks

II. Swelling

PAUL J. FLORY AND JOHN REHNER, JR.

Chemical Division, Esso Laboratories, Standard Oil Development Company, Elizabeth, New Jersey

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The interaction of solvents with cross-linked network structures, such as occur in vulcanized rubber, is subjected to a statistical mechanical treatment based on the model and procedure presented in the preceding paper. The activity of the solvent is expressed as a function of its concentration in the swollen network, and of the degree of cross-linking. The maximum degree of swelling of the network in contact with the pure solvent is related to the degree of cross-linking. The heat of interaction of the solvent with the network can be calculated from the temperature coefficient of maximum swelling. The theory leads to the conclusion that the swelling capacity should be diminished by the application of an external stress. Furthermore, the modulus of elasticity should decrease inversely with the cube root of the swelling volume.

IN the field of high polymers there are numerous examples of materials which absorb large quantities of suitable solvents without dissolving. Vulcanized rubber, vinyl-divinyl copolymers, and lightly gelled thermosetting resins when placed in solvents swell through imbibition to a degree depending on the solvent and the structure of the polymer. The original shape is preserved, and the swollen gel exhibits elastic rather than plastic properties.

This phenomenon of limited swelling is characteristic of polymers possessing network structures. If the network structure is permanent in the sense that its essential skeletal structure is not disrupted by the action of the solvent, a state of equilibrium swelling may be attained. As more and more solvent is absorbed (dissolved) by the polymer the network is progressively expanded. The chains connecting multifunctional network junction points are forced to assume more elongated, less probable, configurations. Consequently, a decrease in chain configurational entropy is produced by swelling. Opposing this, an increase in entropy of mixing of solvent with polymer accompanies swelling. Overlooking for the present the effects of the heat of mixing of solvent and polymer, equilibrium will be attained when these opposing entropies, the entropy of chain configuration and the osmotic, or mixing, entropy, become equal in magnitude.

This criterion for swelling equilibrium was recognized by Frenkel,¹ on the basis of which he

attempted a rough calculation of the swelling limit for vulcanized rubber. Although he succeeded in introducing an expression for the chain configuration entropy (based on Kuhn's treatment of elasticity) which is appropriate as to order of magnitude, Frenkel concluded that his attempt to use entropies of mixing calculated from ideal solution laws (derived for molecules of equal size) was unsound.

Recently Huggins² and one of us³ derived expressions for the entropy of mixing of small molecules with long chain polymers. Calculated partial molal entropies are in good agreement with those observed by Gee and Treloar⁴ for the system benzene-rubber, except at low concentrations of rubber.⁵ Using these expressions it is possible to calculate the entropy change due to mixing of solvent molecules with chains of the network structure. The chain configurational entropy change resulting from expansion of the network can be derived from the tetrahedral model discussed in the preceding paper. Com-

² M. L. Huggins, *J. Phys. Chem.* **46**, 151 (1942); *Ann. N. Y. Acad. Sci.* **43**, 1 (1942); *J. Am. Chem. Soc.* **64**, 1712 (1942).

³ P. J. Flory, *J. Chem. Phys.* **10**, 51 (1942).

⁴ G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.* **38**, 147 (1942).

⁵ While the theory appears to give remarkably good agreement with experiment at high polymer concentrations, we agree with Gee and Treloar that some improvement at low concentrations is desirable. The theory is notably unsatisfactory in very dilute solutions; see, P. J. Flory, *J. Am. Chem. Soc.* **65**, 372 (1943). These matters have been discussed in detail elsewhere (paper presented before the Division of Physical and Inorganic Chemistry at the Pittsburgh Meeting of the American Chemical Society, Sept. 6, 1943).

¹ J. Frenkel, *Acta Physicochimica*, U.S.S.R. **9**, 235 (1938); *Rubber Chem. Tech.* **13**, 264 (1940).

binning these, there is obtained the total entropy of mixing of solvent with cross-linked polymer, from which activities of solvent and the swelling limit can be computed, as well as their dependence on the structure of the network.

THE ENTROPY OF SWELLING

Paralleling the procedure followed in the preceding paper (I), the formation of a network composed of ν chains bound together by $\nu/2$ cross-linkages will be considered to involve a cycle composed of the following steps:

- (D) Dilution of ν chains (prior to cross-linking) with n solvent molecules.
- (A) Cross-linking of groups of four chains, as in I (A) except as modified by the presence of diluent.
- (B) Conversion of these groups to the final network through the introduction of $\nu/4$ cross-linkages, as in I (B) except as modified by diluent.
- (C) Linear combination of the *undiluted* chains to form very long polymer molecules, exactly as in I (C).

In addition to the assumption employed in the preceding paper, we assume here that the configurations of the ν chains are essentially unaltered by the dilution process, the distribution of chain displacement lengths being given by I (2) both before and after dilution. Furthermore, we assume the validity of the entropy of mixing expression, previously referred to,^{2,3} as applied to step (D); i.e.,

$$\Delta S_D = -k \left[n \ln \left(\frac{n}{n+Z\nu} \right) + \nu \ln \left(\frac{Z\nu}{n+Z\nu} \right) \right], \quad (1)$$

where Z is the number of segments per chain, the size of the segment being taken equal in volume to one solvent molecule.⁶

Processes (A) and (B) differ from the corresponding steps of the preceding paper only insofar as they are affected by the greater volume of the system containing solvent molecules. In the swollen network the points of cross-linkage are distributed over a larger volume. Hence, the tetrahedral cells will be proportionately enlarged.

⁶ This arbitrary definition of the segment size is of no consequence in the final results.

The dimension λ' of the average tetrahedral cell (assumed to be a regular tetrahedron) in the swollen state is related to λ for the unswollen network according to

$$\lambda'/\lambda = (V'/V)^{1/3} = 1/v_2^{1/3}, \quad (2)$$

where V and V' are the volumes of the polymer and of the swollen network, respectively, and v_2 is the volume fraction of polymer in the swollen gel.

The entropy change for the process

Long polymer molecules \rightarrow swollen network
will be given by

$$\Delta S_v' = \Delta S_D + \Delta S_A + \Delta S_B - \Delta S_C. \quad (3)$$

ΔS_A is given by Eq. I (9) wherein V is replaced by V' , and ΔS_B is given by Eq. I (13) with λ replaced by λ' . Inasmuch as step (C) takes place in the absence of diluent, ΔS_C is given by I (14). Replacing $Z\nu/(n+Z\nu)$ in (1) with V/V' and substituting the various expressions in (3),

$$\begin{aligned} \Delta S_v' = k\nu \{ & - (n/\nu) \ln [n/(n+Z\nu)] \\ & + \frac{3}{4} \ln (\beta^3/\pi^3) - \beta^2 \lambda'^2 \\ & + \frac{3}{2} \ln \Delta\tau + \frac{1}{4} \ln \Delta\tau' - \ln \Delta\tau'' - \ln 2 \}. \end{aligned} \quad (4)$$

Subtracting I (15) from (4), there is obtained for the entropy of swelling

$$\Delta S_s = \Delta S_v' - \Delta S_v = -kn \ln [n/(n+Z\nu)] - k\nu\beta^2(\lambda'^2 - \lambda^2). \quad (5)$$

If the actual cross-linking process occurs in the unswollen state under conditions of random coiling and entanglement of the chains, then we may identify λ with an average chain displacement length. Letting

$$\lambda^2 = \bar{r}^2 = 3/2\beta^2$$

and substituting for $(\lambda'/\lambda)^2$ from Eq. (2),

$$\begin{aligned} \Delta S_s = & -kn \ln [n/(n+Z\nu)] \\ & - (3/2)k\nu[(V'/V)^{2/3} - 1] \\ = & -kn \ln [n/(n+Z\nu)] \\ & - (3/2)k\nu \left[\left(\frac{n+Z\nu}{Z\nu} \right)^{2/3} - 1 \right]. \end{aligned} \quad (6)$$

The first term in (6) represents the entropy of mixing of polymer and solvent; the second term represents the "elastic" entropy change arising

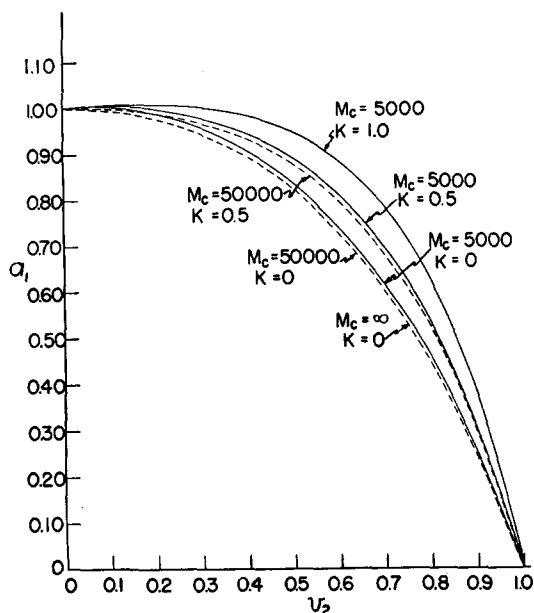


FIG. 1. Activities of solvent dissolved in cross-linked polymer as a function of volume fraction of polymer v_2 , for several values of the molecular weight M_c of the chain between cross-linkages and of the heat of mixing constant K .

from deformation of the network. The latter term is approximately three times the entropy of deformation given by Eq. I (19') for small deformations, if we identify $(V'/V)^{1/3}$ with α .

Differentiating (6) with respect to n and substituting $v_2 = Z\nu/(n + Z\nu)$, there is obtained for the partial molal entropy of dilution

$$\Delta\bar{S}_1 = -R[\ln(1-v_2) + v_2] - (R/Z)v_2^3 \\ = -R[\ln(1-v_2) + v_2] - (R\rho V_1/M_c)v_2^3, \quad (7)$$

where V_1 is the molar volume of the solvent, ρ is the density of the polymer, and M_c is the molecular weight of the chain.

If we assume a van Laar heat of dilution term given by

$$\Delta\bar{H}_1 = B V_1 v_2^2,$$

where B is a constant depending on the components, polymer and solvent, then the partial molal free energy becomes

$$\Delta\bar{F}_1 = RT[Kv_2^2/2 + \ln(1-v_2) + v_2 + (\rho V_1/M_c)v_2^3], \quad (8)$$

where $K = 2B V_1/RT$. Or, upon expanding the logarithmic term

$$\Delta\bar{F}_1 = RTv_2^2[(K-1)/2 - v_2/3 - v_2^2/4 - \dots] + (RT\rho V_1/M_c)v_2^3. \quad (8')$$

When the equation corresponding to (8) for the partial molal free energy of dilution of soluble (not cross-linked) polymers is compared with experimental thermodynamic data for dilute polymer solutions, K is found to include terms other than the heat of mixing term.^{2,5} Thus, K appears to be separable into two parts:

$$K = A + 2B V_1/RT, \quad (9)$$

where A is an empirical parameter the origin of which is not yet clear. Whether or not such a term should be included for cross-linked systems is not known. Here we shall bear in mind that K may include such a term, and in particular, that K should not necessarily be assigned the value zero when the heat of mixing is negligible.

ACTIVITY OF SOLVENT

In Fig. 1 activities a_1 calculated from Eq. (8) and the relationship

$$\ln a_1 = \Delta\bar{F}_1/RT$$

are plotted against v_2 for several values of M_c and K . The same curves are shown in Fig. 2 on an enlarged scale covering the low concentration region. The $M_c = \infty$ curve represents a mixture of solvent with infinitely long polymer molecules in the absence of cross-linkages. There is neither a maximum nor a minimum, the curve becoming tangentially horizontal at $v_2 = 0$. The curve (not shown) for linear molecules of finite length approaches $a_1 = 1$ at $v_2 = 0$ with a finite *negative* slope which is inversely proportional to the molecular weight. With the addition of cross-linkages and conversion of the polymer to a network structure the activity-concentration curve assumes a *positive* slope at $v_2 = 0$, the magnitude of the slope being inversely proportional to M_c , i.e., directly proportional to the "concentration" of cross-linkages in the network. Thus, it is possible to trace the progressive changes in the thermodynamics of the system polymer: solvent proceeding from relatively small linear polymers to infinitely long molecules to cross-linked networks of increasing degrees of cross-linking.

The appearance of a maximum in an activity-composition diagram requires that the components exhibit partial miscibility. We may conclude on strictly thermodynamical grounds that

complete miscibility is no longer possible when M_c is finite (i.e., with the appearance of a network structure) since the a_1 vs. v_2 curves then possess maxima. The activities for the two phases in equilibrium must be the same. Furthermore, compositions in which the activity of the solvent is greater than that of the pure solvent are necessarily inaccessible. Hence, one of the phases must be pure solvent, and the other will have the composition corresponding to the intersection of the curve with the $a_1=1$ ordinate.

These characteristics of the solvent-network system are evident from considerations of the limitations on the polymer imposed by its network structure. It is of interest, nevertheless, to point out that they can be derived by the formal statistical-thermodynamical procedure outlined above. From a quantitative point of view, this procedure predicts the composition of the swollen phase in equilibrium with pure solvent (*cf. seq.*).

When K is not zero, due to a heat of mixing or for other reasons as mentioned above the curves are shifted as shown in Figs. 1 and 2 for $K=0.5$ and $K=1$; these values correspond to moderately unfavorable (endothermic) heats of interaction of the components. The general character of the curve is not changed. For all values of K the curves retain their single maxima. The greater the value of K (algebraically) the higher the curve, the greatest effect on a_1 being shown at high concentrations of polymer. Maximum swelling, corresponding to $a_1=1$, is less the greater the value of K .

The effects of the cross-linkages on the system are by no means restricted to the region of maximum swelling, as Gee⁷ has assumed in his semi-empirical analysis of the interaction of solvents with vulcanized rubber. The effect of a moderate degree of cross-linking on the magnitude of the activity is small, but it persists to the highest concentration of polymer; in fact, the percentage increase in a_1 due to the cross-linkages increases somewhat with increase in v_2 . This is evident from the form of Eq. (8). It can be shown that the Henry's law constant becomes

$$(da_1/dv_1)_{v_2=0} = \exp [(1+K/2) + \rho V_1/M_c], \quad (10)$$

⁷ G. Gee, Trans. Faraday Soc. **38**, 418 (1942).

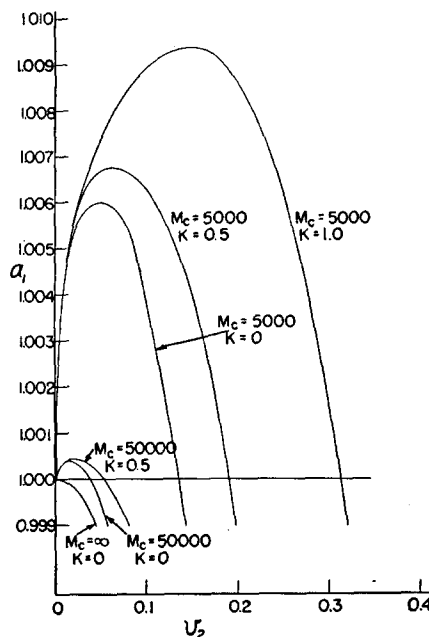


FIG. 2. Activity—composition diagram in the region of high solvent concentration.

the second term in the exponent representing the increase in the activity of the solvent due to the reaction of the network structure. This term is very small, except for high degrees of cross-linking (low M_c).

SWELLING EQUILIBRIUM

At equilibrium with pure solvent $\Delta\bar{F}_1=0$. Equating Eq. (8) to zero,

$$M_c = -\rho V_1 v_2^{1/3} / [K v_2^2 / 2 + \ln(1-v_2) + v_2], \quad (11)$$

where v_2 represents the volume fraction of polymer in the swollen gel which is in equilibrium with pure solvent. Alternatively, v_2 is the reciprocal of the "swelling volume," the latter being defined as the ratio of the swollen volume (at equilibrium) to the initial volume. If the degree of swelling is large (v_2 small) higher terms in the series expansion of $\ln(1-v_2)$ may be dropped, giving

$$M_c \cong 2\rho V_1 / v_2^{5/3} (1-K). \quad (12)$$

Or,

$$v_2 \cong [2\rho V_1 / M_c (1-K)]^{3/5}. \quad (13)$$

Thus the reciprocal swelling volume in a given solvent is approximately inversely proportional to the three-fifths power of the average molecular

weight per chain, or directly proportional to the three-fifths power of the concentration of cross-linkages, provided of course, the degree of swelling is large. For lower degrees of equilibrium swelling v_2 can be computed from Eq. (10), which is not explicitly solvable for v_2 .

Generally M_c is not known, but v_2 is readily measurable by any one of several methods.⁸ These relationships provide a means for estimating the degree of cross-linking, or M_c , from the swelling volume. The absolute significance of the values so obtained will be limited by the uncertainty in the value of K and by some of the approximations employed in the derivation of the basic Eq. (6). However, relative values so obtained should be of considerable utility in characterizing the structure of cross-linked networks.

TEMPERATURE COEFFICIENT OF SWELLING

Continuing under the assumption that the heat of mixing can be represented by a van Laar term, the temperature coefficient of maximum swelling can be calculated from the stipulation that $\Delta\bar{F}_1=0$ at all temperatures. Then

$$(dv_2/dT)_{a_1=1} = -(\partial\Delta\bar{F}_1/\partial T)_{v_2}/(\partial\Delta\bar{F}_1/\partial v_2)_T. \quad (14)$$

Assuming that $A=0$ in Eq. (9), then on differentiating Eq. (8) with respect to temperature and employing the above condition there is obtained

$$(\partial\Delta\bar{F}_1/\partial T)_{v_2} = -RKv_2^2/2.$$

Similarly,

$$\begin{aligned} (\partial\Delta\bar{F}_1/\partial v_2)_T &= RT[Kv_2 - v_2/(1-v_2) \\ &\quad + \rho V_1/(3M_c v_2^3)] \\ &= RT\{5Kv_2/6 - v_2/(1-v_2) \\ &\quad - (1/3)[1 + \ln(1-v_2)/v_2]\}. \end{aligned}$$

Substituting these expressions in (14) and expanding the denominator in series,

$$\begin{aligned} dv_2/dT &= Kv_2/2T \left[\frac{5}{6}(K-1) - \frac{8}{9}v_2 \right. \\ &\quad \left. - \frac{11}{12}v_2^2 - \frac{14}{15}v_2^3 - \dots \right]. \quad (15) \end{aligned}$$

Or

$$\begin{aligned} d \ln v_2 / d \ln T \\ = K/2 \left[\frac{5}{6}(K-1) - \frac{8}{9}v_2 - \frac{11}{12}v_2^2 - \dots \right]. \quad (15') \end{aligned}$$

Thus from the change of the swelling volume ($1/v_2$) with temperature values of K , or of the heat of mixing constant B , can be computed. For very small values of K and high degrees of swelling (small v_2)

$$d \ln v_2 / d \ln T \cong -3K(1-v_2)/5(1-K). \quad (15'')$$

EFFECT OF DEFORMATION ON SWELLING

In analogy with Eq. I (18) for the entropy of formation of an elastically deformed network, there is obtained for the entropy change in the process

$$\begin{aligned} \text{Long polymer molecules} &\rightarrow \text{swollen, elongated network} \\ \Delta S_v'' &= k\nu \{ -(n/\nu) \ln [n/(n+Z\nu)] \\ &\quad + (3/4) \ln (\beta^3/\pi^3) \\ &\quad - \beta^2 \lambda'^2 (\alpha^2 + 2/\alpha)/3 + \text{const.} \}, \quad (16) \end{aligned}$$

where α is the ratio of the length of the elongated, swollen specimen to its length in the unstressed, swollen condition. For the entropy change in passing from the unstressed unswollen condition to the elongated, swollen state

$$\begin{aligned} \Delta S_{d,s} &= -kn \ln [n/(n+Z\nu)] \\ &\quad - k\nu \beta^2 \lambda^2 \left[\left(\frac{n+Z\nu}{Z\nu} \right)^3 \left(\alpha^2 + \frac{2}{\alpha} \right) / 3 - 1 \right]. \quad (17) \end{aligned}$$

Differentiating (17) with respect to n , and letting $\beta^2 \lambda^2 = \frac{3}{2}$, the partial molal free energy of the solvent becomes

$$\begin{aligned} \Delta\bar{F}_1 &= RT[Kv_2^2/2 + \ln(1-v_2) + v_2 \\ &\quad + (\rho V_1/M_c)(\alpha^2 + 2/\alpha)v_2^{1/3}/3]. \quad (18) \end{aligned}$$

Thus, the activity of the solvent is increased by deformation of the gel. A gel which is in equilibrium with pure solvent should de-swell on stretching. Upon equating (18) to zero, there is obtained for the approximate volume fraction of polymer in the elongated gel at equilibrium with pure solvent

$$v_2 \cong [2\rho V_1(\alpha^2 + 2/\alpha)/3M_c(1-K)]^{3/5} \quad (19)$$

⁸ C. M. Blow and P. Stamberger, *Recueil Travaux Chimique Pays Bas* **48**, 64 (1929); J. R. Scott, *Trans. Inst. Rubber Ind.* **5**, 95 (1929); I. Williams, *Ind. Eng. Chem.* **29**, 172 (1937); G. S. Whitby, A. B. A. Evans, and D. S. Pasternack, *Trans. Faraday Soc.* **38**, 269 (1942).

which differs from Eq. (13) by the factor $[(\alpha^2 + 2/\alpha)/3]^{3/5}$. The swollen volume of the gel at equilibrium should decrease by this factor upon elongating the gel to a length α times its initial length.

EFFECT OF SWELLING ON ELASTIC PROPERTIES

Differentiation of Eq. (17) with respect to the length $L = \alpha L_0'$ of the swollen specimen gives the retractive force

$$f' = (\partial \Delta F / \partial L) = -T(\partial \Delta S / \partial L) \\ = (RT\nu/L_0'v_2^{2/3})(\alpha - 1/\alpha^2),$$

where L_0' is the initial length of the unstretched, swollen gel. Since

$$\nu/L_0' = \rho v_2 A_0' / M_c,$$

where A_0' is the cross-sectional area of the unstretched, swollen gel,

$$f' = (RT\rho A_0' v_2^{1/3} / M_c)(\alpha - 1/\alpha^2). \quad (20)$$

The modulus of elasticity of the gel, referred to its initial cross-sectional area in the swollen condition, becomes

$$e' = (RT\rho v_2^{1/3} / M_c)(1 + 2/\alpha^3) \quad (21)$$

which differs from Eq. I (6) for unswollen polymer by the factor $v_2^{1/3}$. Thus, the modulus of elasticity of the gel should decrease with the inverse cube root of the volume degree of swelling $1/v_2$.

If stresses are to be calculated on the basis of the initial cross section A_0 before swelling, then

$$f = (RT\rho A_0 / v_2^{1/3} M_c)(\alpha - 1/\alpha^2) \quad (22)$$

and

$$e = (RT\rho / v_2^{1/3} M_c)(1 + 2/\alpha^3), \quad (23)$$

where α is retained as the strain referred to the unstretched, swollen length. Hence, the retractive force at a given strain factor α should increase with swelling in proportion to $1/v_2^{1/3}$.

EFFECTS OF DILUENTS INTRODUCED PRIOR TO CROSS-LINKING (OR VULCANIZATION)

Throughout the above discussion it has been assumed that cross-linking occurs in the absence of inert diluents and that all of the polymer becomes bound into the network. If diluent, or other material which is not incorporated into the network, is present when cross-linking occurs, the basic network structure will differ from that formed in the absence of diluent. If the same number $\nu/2$ of chemical cross-bonds are presumed to be introduced in the presence of diluent obviously they will be separated by greater average distances in the network. Since we assume that the configurations of the individual molecules are unaltered by dilution, the contour length of the chain, and M_c , will be increased by dilution prior to cross-linking. But this conclusion is inconsistent with the obvious requirement that

$$\nu M_c = \text{constant}. \quad (24)$$

This apparent paradox arises from our failure to consider intramolecular cross-linkages which



unite two points of the same linear molecule. They contribute nothing to the network structure. An approximate statistical calculation shows that the relative number of such bonds will be comparatively small in the absence of diluent, but that it will increase rapidly with dilution. In Eq. (24) we should use a ν value corrected for the proportion of these intra-chain linkages. This corrected ν will decrease as M_c is increased by dilution. Qualitatively, at least, this is consistent with (24).

The physical properties of a network formed in the presence of diluent will differ from those of a network formed in absence of diluent and subsequently swollen. For the same total number of cross-bonds there will be fewer significant cross-bonds in the former. Furthermore, the quantity $\beta^2 \lambda^2$ which enters into the above calculations will be less, thus lowering the elastic moduli, and increasing the swelling capacity.