Morphology

Characterization of Elastomeric Network Structures Using the Effects of Swelling on Stress-Strain Isotherms and the Extents of Swelling at Thermodynamic Equilibrium

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SUMMARY

Swelling has long been used in the study of elastomeric networks. In the case of stress-strain measurements on swollen networks, the most important observation was the decrease of the Mooney constant $2C_2$, which is widely used to represent the magnitude of the departure of an observed stress-strain isotherm from that predicted by the simplest molecular theories. Swelling equilibrium data were generally analysed by the Flory-Rehner equation for affine networks simply to obtain a measure of the degree of cross-linking. The advent of model networks whose structures are well known and of a new theory due to Flory constitute great improvements for the study of rubberlike elasticity. In this new context, swelling can be used to obtain additional important molecular information through both uniaxial extension of swollen samples and swelling equilibrium. In particular, the relation between the main parameter κ characterizing the local constraints on junction fluctuations in the Flory theory, the extent of swelling, and the molecular weight between cross-links can be probed.

INTRODUCTION

A molecular understanding of the behavior exhibited by rubberlike materials under deformation is still being widely investigated (1), in spite of great improvements achieved during recent years. One advance is the use of model networks for accurate information on the chemical structure of the samples (molecular weight between crosslinks and functionality of junctions) (2). Moreover, a new molecular theory due to Flory (3) seems to account well for a variety of results (4). Among these, uniaxial extension of elastomers swollen by organic solvents and isotropic swelling equilibrium can provide much useful information. Our aim is to review these methods and emphasize how they can be used to determine the main parameter κ which measures the severity of restrictions on junction fluctuations in a real network in the latest refinement of the Flory theory.

UNIAXIAL EXTENSION

Phantom Networks. In such networks, the junctions fluctuate around their mean positions and thus the instantaneous distribution of chain vectors r is not affine with the macroscopic strain. The elastic free energy is given by (5)

$$\Delta A_{el}(ph) = (1/2)\xi kT(I_1 - 3) \tag{1}$$

where I_1 is the first invariant of the tensor of deformation, and k the Boltzmann constant. The cycle rank ξ (number of independent circuits of the network) is the difference between the number of effective chains ν and junctions μ (6),

$$\xi = \nu - \mu \tag{2}$$

We consider here only perfect end-linked networks obtained by crosslinking end-reactive chains of number average molecular weight M_n with molecules of functionality $\phi > 2$. Thus the molecular weight between crosslinks M_c is equal to M_n and the functionality of the junctions is ϕ. Hence the following relations can be obtained:

$$\xi/V_0 = (1 - 2/\phi)\rho/M_n \tag{3}$$

$$\mu/\xi = (\phi/2 - 1)^{-1} \tag{4}$$

where ρ is the density of the network and V_0 is its volume in the reference state. The quantity ξ/V_0 is then the cycle rank density.

Networks Deforming Affinely. In this limit, the fluctuations of junctions are completely suppressed and the instantaneous distribution of chain vectors is then affine with the strain. The elastic free energy is (6)

$$\Delta A_{el}(aff) = (1/2)(1 - 2/\phi)^{-1}\xi kT(I_1 - 3) - (2/\phi)(1 - 2/\phi)^{-1}\xi kT \tag{5}$$
$$\ell n(V/V_0)$$

where V is the actual volume.

Real Networks. The elastomeric behavior exhibited by real networks is between the phantom and affine limits. Ronca and Allegra (7) and Flory (3) have independently proposed a model in which the restrictions on fluctuations of junctions due to neighboring chains are represented by domains of constraints. At small deformations, the stress is thus enhanced relative to that exhibited by the corresponding phantom network. In the limit at large strains, the effects of the restrictions vanish and the relationship of stress to strain converges to that for a phantom network.

The elastic free energy is then the sum of the phantom free energy [Equation (1)] and of an additional term which accounts for the constraints,

$$\Delta A_{el} = \Delta A_{el}(ph) + \Delta A_c \qquad (6)$$

This term ΔA_c, the complete expression for which can be found in reference (3) [Equation (32)], depends on two parameters. The most important one κ measures the severity of the entanglement constraints relative to those imposed by the phantom network. For a phantom network $\kappa = 0$, and for an affine one $\kappa = \infty$. Another parameter ζ takes into account the non-affine transformation of the domains of constraints with strain but has a minor role compared to κ (4).

Interpretation of Experimental Results. The transition from affine to phantom behavior with increase in elongation would cause a decrease in the elastic modulus defined by

$$[f^*] \equiv f v_2^{1/3}/A_d(\alpha - \alpha^{-2}) \qquad (7)$$

where f is the measured force, v_2 the volume fraction of polymer in the swollen network, α the extension ratio relative to the undeformed swollen state, and A_d the cross-sectional area of the isotropic unswollen sample. Such decreases have long been observed (8) and have generally been represented by the Mooney-Rivlin equation

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \qquad (8)$$

where $2C_2$ decreases markedly with swelling (8). Specifically, for a phantom network

$$[f^*] = (\xi/V_0)RT \qquad (9)$$

where R is the gas constant.

To determine the parameter κ, $[f^*]$ is fitted to

$$[f^*]_{Flory} = (\xi/V_0)RT\{(1 + (\mu/\xi)(\alpha K(\alpha^2 v_2^{-2/3}) - \alpha^{-2}K(\alpha^{-1}v_2^{-2/3}))\} \qquad (10)$$

where the detailed expression for the function K is given in reference (3) [Equation (37)]. The curve fitting requires a value of the phantom modulus. One reasonable estimate would be the high deformation intercept in the Mooney-Rivlin plot for the network in the highly swollen state (4). But as the fragility of such materials may be a problem and the physical meaning of $2C_1$ has not yet been clearly established, this extrapolation may be questionable. We prefer to use the phantom modulus calculated from the chemical constitution of the network [Equations (3) and (9)].

Another important point concerns the theoretical predictions of the

variation of κ with M_n and v_2. A calculation of the degree of interpenetration of chains and junctions leads to (4)

$$\kappa = I <r^2>_o^{3/2} (\mu/V_o) \qquad (11)$$

where I is a constant of proportionality. The right-hand side of equation (11) is simply proportional to the number of junctions in the volume pervaded by a chain. Then it can be shown that κ depends on M_n to the power 0.5 and should be independent of swelling since the dependence of $<r^2>_o^{3/2}$ on v_2 is just counterbalanced by the v_2 dependence of (μ/V_o). This rests on the reasonable assumption that I is independent of both M_n and v_2. Experimentally, however, it seems that κ varies with M_n to the first power at least in the case of tetrafunctional poly(dimethylsiloxane) networks (9).

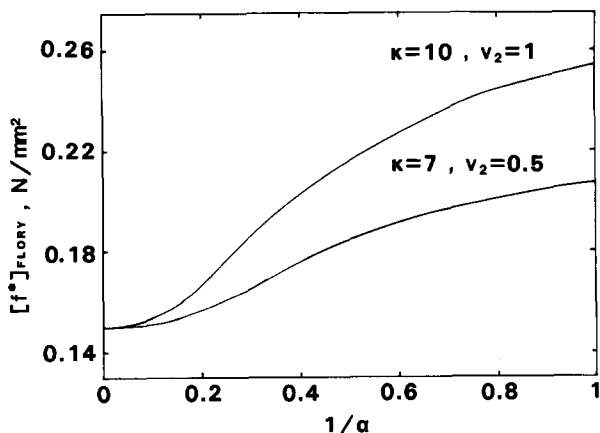Figure 1 presents values of the reduced force calculated from the

Figure 1.   Influence of κ and v_2 on the Flory reduced force for an end-linked model network having M_n = 8,000 g mol^{-1}, ϕ = 4, and ζ = 0.

Flory theory for a perfect end-linked tetrafunctional network (M_n = 8,000 g mol^{-1}). The accessible range of measurements is α^{-1} = 0.5 to 0.9, and generally less for swollen samples. The sigmoidal curves are independent of swelling in this representation [see Equation (9)], and the decrease in the reduced force by swelling is mostly accounted by the presence of v_2 in the function K [Equation (10)]. There may also, however, be a small variation of κ with swelling.

SWELLING EQUILIBRIUM

The free energy change ΔA for this process is usually assumed to be separable into the free energy of mixing ΔA_m and the elastic free energy ΔA_{el},

$$\Delta A = \Delta A_m + \Delta A_{el} \tag{12}$$

although questions have been raised with regard to this separability (10). The contribution ΔA_m has been calculated by Flory (11) using a lattice model; ΔA_{el} is given by Equations (1), (5) and (6) and depends on the nature of the network.

The chemical potential of the solvent in the swollen network is:

$$\mu_1 - \mu_1^\circ = N \, (\frac{\partial \Delta A_m}{\partial n_1})_{T,p} + N \, (\frac{\partial \Delta A_{el}}{\partial \alpha})_{T,p} \, (\frac{\partial \alpha}{\partial n_1})_{T,p} \tag{13}$$

where N is Avogadro's number, n_1 the number of molecules of solvent, and the isotropic extension ratio α is:

$$\alpha = \alpha_x = \alpha_y = \alpha_z = \left[(n_1 V_1 + V_\circ)/V_\circ\right]^{1/3} = v_2^{-1/3} \tag{14}$$

where V_1 is the molar volume of the solvent. At swelling equilibrium $\mu_1 = \mu_1^\circ$; hence by using the standard expression of ΔA_m (11), one can obtain:

$$\ln \, (1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2 = -N \, (\frac{\partial \Delta A_{el}}{\partial \alpha})_{T,p} \, (\frac{\partial \alpha}{\partial n_1})_{T,p} \tag{15}$$

The interaction parameter χ_1 may be determined for example by vapor pressure measurements (12). Using the Flory expression for the elastic free energy [Equation (6)] and assuming κ independent of swelling, Equation (15) (with the left-hand side abbreviated as H) becomes

$$H = -(\xi/V_\circ)V_1 v_{2m}^{1/3}\left[1 + (\mu/\xi)K(v_{2m}^{-2/3})\right] \tag{16}$$

The molecular weight M_c between crosslinks is then obtained by combination of Equations (3), (4), and (16),

$$M_{cr} = (2/\phi - 1)\rho V_1 v_{2m}^{1/3}(1 + (\phi/2 - 1)^{-1}K(v_{2m}^{-2/3}))/H \tag{17}$$

where the subscript r is employed for real networks. For a network deforming affinely, $\kappa = \infty$, $K(\alpha^2) \simeq 1 - \alpha^{-2}$ and

$$M_{ca} = -\rho V_1 v_{2m}^{1/3} (1 - 2\, v_{2m}^{2/3}/\phi)/H \tag{18}$$

The second term in the parenthesis comes from the term containing $\ell n(V/V_o)$ in Equation (5). For a phantom network $\kappa = 0$, $K(\alpha^2) = 0$, and

$$M_{cp} = (2/\phi - 1)\rho V_1 v_{2m}^{1/3}/H \tag{19}$$

Most of the experimental swelling results on crosslinked polymers have been interpreted using the Flory-Rehner expression for an affinely deforming network (14) instead of the general one Equation (17). For perfect end-linked networks, $M_{cr} = M_c$ and therefore the measurement of v_{2m} enables determination of the parameter κ from Equation (17) by an iterative method. If κ depends on dilation, however, the derivative of ΔA_{el} with respect to α gives rise to an expression in which $(\partial K/\partial \alpha)_{T,v_{2m}}$ is included. A more general equation can then be used in place of Equation (17). It is necessary then, of course, to know the dependence of κ on v_2 since

$$\left(\frac{\partial \kappa}{\partial \alpha}\right)_{T,P,v_{2m}} = -3v_{2m}^{-4/3}\left(\frac{\partial K}{\partial v_2}\right)_{T,P,v_{2m}} \tag{20}$$

This dependence can be obtained by determination of κ by stress-strain measurements at different degrees of swelling and extrapolation to $v_2 = v_{2m}$. In this way κ at v_{2m} can also be reached and inserted into the general swelling equilibrium equation for comparison of M_{cr} and M_n.

DISCUSSION

The relation between κ, M_n and v_2 is represented in a three-dimensional coordinate system in Figure 2. The curve C_1 is the evolution of κ with M_n in the unswollen state and can be obtained by stress-strain measurements. The experimental points (9) come from measurements (15) on tetrafunctional PDMS networks. The arbitrary curve C_2 satisfies the decrease of κ with swelling at constant M_n. The projection C_3' of C_3 on plane (M_n, κ) (dashed curve) is lower than C_1 to satisfy the increase of degree of swelling at equilibrium with increase in M_n. The dashed curve P' (15) is the projection on plane $(1 - v_2, M_n)$ of the path P. The surface defined by C_1, C_2 and C_3 can be probed experimentally by determination of κ from stress-strain measurements at constant M_n and different degrees of swelling ("iso-M_n lines"). Equation (10) is used for this purpose.

A particularly useful swelling equilibrium study of PDMS would involve (inert) methyl-terminated DMS chains as diluent (16). In this case $\chi_1 = 0$ and at constant M_n, v_{2m} varies only with the molecular weight of the diluent, enabling establishment of iso-M_n lines. The iso-v_2 lines are obtained by keeping the same diluent and changing the molecular weight between crosslinks.

Thus swelling may provide a great deal of useful molecular information on rubber elasticity.
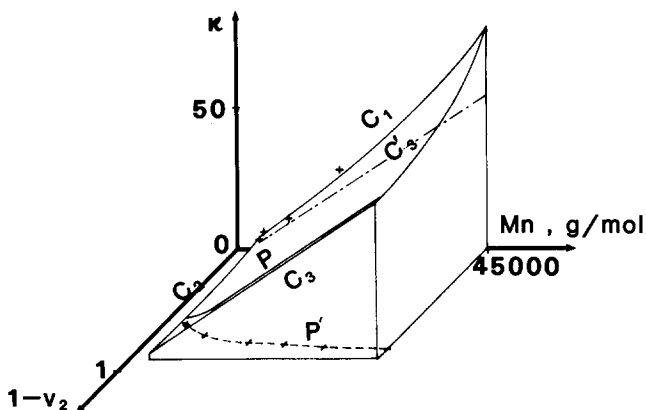
- Figure 2 - Relations between κ, M_n and $(1 - v_2)$. The curves C_1, C_2, C_3, C_3' and P' are explained in the text.

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