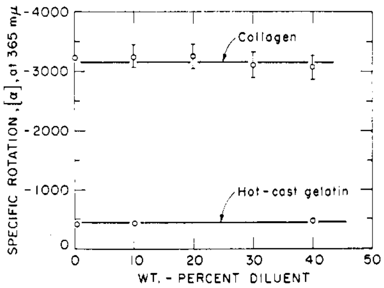

Figure 1. Independence of the specific optical rotation, measured at 365 mμ, from effects due to incorporation of diluent (glycerol).

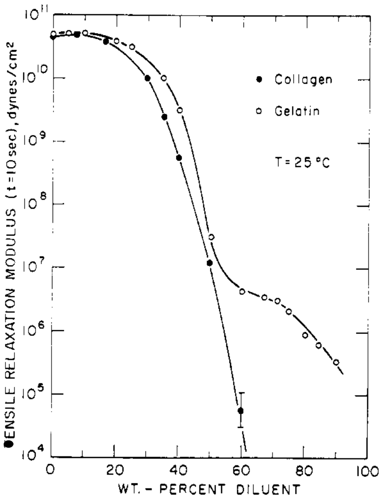

Figure 2. The 10-sec tensile relaxation modulus of collagen and gelatin films, plotted as function of the diluent content.

tin[14] and collagen[15] to moisture levels below *ca.* 0.5 wt % water. Flat-plate X-ray photographs were taken with a Norelco camera using Ni-filtered Cu Kα radiation and an exposure time of 1 hr. Measurements of optical rotation of films were made with a Cary 60 CD spectropolarimeter precautions having been taken to prevent the development of birefringence in films during casting.

The results in Figure 2 show that the 10-sec tensile relaxation modulus of gelatin films measured at small strains is almost ten times higher than that of collagen films in the diluent concentration range 30–50 wt %. In this range of relatively low diluent content, gelatin films showed their well-known ability of elongating up to at least 100%, with delayed but complete recovery following removal of the load. By contrast, collagen films in the same diluent range (30–50 wt %) deformed permanently. At higher diluent concentration levels, between 50 and 80 wt %, the disparity in properties between collagen and gelatin specimens became even sharper (Figure 2). In this concentration range, gelatin forms tough gels which behave as rubbers,[16] possessing small-strain moduli in the region 10^6–10^7 dyn/cm² and capable of extending to *ca.* 700% with complete and immediate recovery up to fracture; by comparison, we found that collagen preparations were not capable of forming gels at all, even after prolonged residence at temperatures as low as 4°. Instead, collagen specimens were very weak solids at about 60 wt % diluent and became viscous liquids somewhat above this level of diluent content.

The observation of substantially lower moduli and of plastic deformation with collagen films is consistent with a simple model composed of stiff helical macromolecules, not bonded covalently to each other and immersed in a viscous Newtonian fluid (glycerol). In gelatin specimens, the diluent swells a network of entangled chains which are equipped with a profusion of evenly spaced "hinges" at the chain backbone (glycine residues) around which relatively unrestricted rotation can occur. The high intrinsic flexibility of the gelatin chains exhibits itself clearly macroscopically only when individual chains are sufficiently separated from each other by incorporation of diluent. When, however, these flexible polypeptide chains are locked in the orderly arrangement of the collagen helix, the resulting triple-stranded macromolecules behave as rods which fail to entangle due to their apparent stiffness. In the presence of diluent, these assemblies of collagen molecules behave as highly viscous suspensions which, even though concentrated enough to exhibit a sizable tensile modulus, are incapable of any mechanical recovery.

Acknowledgment. This work was supported partly by Grant No. AM 11919 of National Institutes of Health and by Grant No. GK-19408 of the National Science Foundation.

---

[14] I. V. Yannas and A. V. Tobolsky, *Nature (London)*, **215**, 509 (1967).

[15] I. V. Yannas and N-H. Sung, unpublished data.

[16] I. V. Yannas and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **12**, 1 (1968).

Ideal Network Behavior of Anionically Prepared Polystyrene Gels

D. Froelich, D. Crawford, T. Rozek, and W. Prins*

Department of Chemistry, Syracuse University, Syracuse, New York 13210. *Received October 7, 1971*

Recently Johnson and Mark[1] communicated the results of a series of experiments to settle a still remaining controversy in the molecular theory of rubber elasticity. The controversy centers on the existence of a logarithmic form in the free energy of network deformation and on the value of the coefficient, B, in front of it

$$\Delta F_{\mathrm{net}}/RT = (\nu/2)(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) - B\nu \ln \lambda_x\lambda_y\lambda_z \quad (1)$$

In eq 1 λ_x, λ_y, and λ_z are the deformation ratios with respect to an isotropic reference state in which the polymer chains between cross-links are unstrained; ν is the number of elastically effective chains in the network; and B is a numerical factor about which no certainty exists.

Previous work by a variety of authors—summarized in a review paper in 1969[2]—had already established that the logarithmic term exists. Theoretical as well as experimental arguments were presented to support the Flory-Wall value of $B = 2/f = {}^1/_2$ for a tetrafunctionally cross-linked network ($f = 4$). Unequivocal proof for the precise value of B has proven to be elusive because it requires a precise knowledge of ν. No networks have been prepared to date for which the chemistry and topology allow the determination of ν with absolute certainty. Johnson and Mark's experiments neatly eliminated the necessity of a knowledge of ν by comparing the elastic stress in two types of networks, both swollen to the same degree in pure diluent, but cross-linked in solution and in bulk, respectively. This analysis required the assumption that the chain dimensions do not alter during the cross-linking process.

---

[1] R. M. Johnson and J. E. Mark, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **12**, 652 (1971).

[2] K. Dusêk and W. Prins, *Fortschr. Hochpolym. Forsch.*, **6**, 1 (1969).

Their data then support the Flory–Wall value of $B = 2/f$. We wish to report some results which confirm the applicability of ideal network theory with a value of $B = 2/f$ for a series of anionically prepared polystyrene networks. In our case, however, the analysis required an assumption about ν. Further inspection of the results then also shows that the chain dimensions do alter as a consequence of the cross-linking process.

The type of network on which we report has been described by Weiss, Hild, Herz, and Rempp.[3] Adding small amounts of divinylbenzene (DVB) to solutions of "living" polystyrene, carrying carbanions on both ends, these authors obtained gels, which were subsequently "killed" by the addition of a trace of methanol. Such networks contain DVB nodules as cross-links of varying functionality, connecting essentially monodisperse polystyrene chains. A series was prepared for us at the Centre de Recherches sur les Macromolecules in Strasbourg, France, varying in molecular weight between cross-links (M_c) from 7000 to 20,000 and varying in polymer concentration prior to cross-linking from 7 to 18% by weight. The gels were made in a 50:50 mixture of tetrahydrofuran and benzene at −40° in Teflon molds from which cylindrical pieces 1.6 cm in height and 1.6 cm in diameter could be cut with a taut wire. The gels were subsequently swollen in benzene and extracted for a long time so as to remove methanolate and un-cross-linked polymer. The latter was always found to be small (<5%) if a DVB/living end ratio of about three was employed.

In order to determine whether these gels obey the ideal, Gaussian network theory, the following measurements were performed. The volume degree of swelling, q, was established by weighing the swollen and dried samples, employing the equilibrium densities of polystyrene ($\rho_p = 1.074$ at 25°[4]) and benzene for conversion to volumes. Unilateral compression measurements were carried out with the gel between Teflon plates in benzene, so as to obtain the elasticity modulus of the swollen gels. Subsequently, the gels were deswollen to a small volume and inserted in the smallest cylindrical chamber (height = diameter) of a swelling pressure osmometer, similar in design to the one described by van de Kraats.[5] In this osmometer the sample is allowed to swell up in benzene which enters through the rigid but porous stainless steel top of the chamber. At the moment the gel sample fills the chamber completely, a displacement transducer attached to the thin bottom metal foil of the chamber activates a servoloop which builds up hydraulic counterpressure of silicon oil, forcing the foil back to its nonbulging flat position at the bottom of the chamber. The pressure required to do this is registered by means of a calibrated pressure transducer. Several days to a week are needed before equilibrium is reached in this osmometer. The servoloop thus has to have a high degree of stability. This was accomplished by employing a sensitive carrier wave amplifier for the displacement transducer and an electronic dummy to correct for drift. Four different chamber sizes were used; the pressures ranged typically from about 1 atm down to zero, measurable to 2% accuracy.

Ideal network theory applied to isotropically swollen gels provides the following relation for swelling equilibrium under a pressure π[2]

$$\pi\bar{v}_1/RT = -\ln(1 - q^{-1}) - q^{-1} - \chi q^{-2} - \nu^*\bar{v}_1(q_0^{-2/3}q^{-1/3} - Bq^{-1}) \quad (2)$$

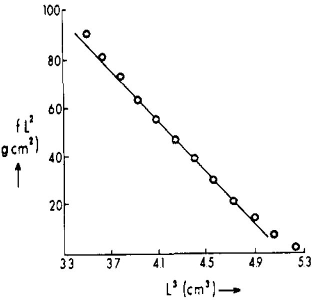

Figure 1. Representative plot for the determination of $q_0^{-2/3}\nu^*$ and L_i (see eq 3); gel no. 1888.

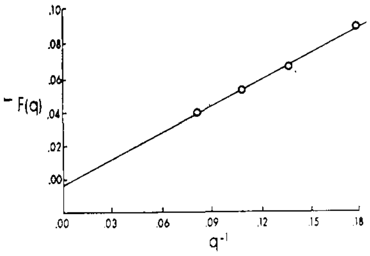

Figure 2. Representative plot of $-F(q)$ *vs.* q^{-1} for gel no. 1887. The slope yields χ and the intercept $B\nu^*$ (see eq 4).

where $\bar{v}_1$ is the partial molar volume of the diluent, χ is the Flory–Huggins interaction parameter, ν^* is the number of moles of chains per cubic centimeter of dry volume, and q_0 is the reference degree of swelling at which the chains are unstrained.

For the force, f, needed to unilaterally compress a swollen gel to length L, one has[2]

$$f = q_0^{-2/3}\nu^* RTV_p q^{2/3}[L/L_i - (L_i/L)^2]/L_i \quad (3)$$

where V_p is the equilibrium dry volume of the polymer and L_i is the undeformed length. Equation 3 yields $q_0^{-2/3}\nu^*$ and L_i most reliably by plotting fL^2 *vs.* L^3. As the example in Figure 1 shows, such plots are not quite linear as demanded by ideal network theory. The deviations at L values close to L_i are due to slight imperfections in the geometry of the sample and compressing plates; at large compression ratios, deviations from theory are to be expected. The determination of $q_0^{-2/3}\nu^*$, which follows from the slope of the plot, sometimes carries a possible error of 10% as a result of these deviations. This does not, however, seriously impair the application of eq 2.

A rearrangement of eq 2 shows that the following plot should be linear in q^{-1} if ideal network theory is to apply

$$F(q) = B\nu^*\bar{v}_1 - \chi q^{-1} \quad (4)$$

where

$$F(q) = [\pi\bar{v}_1/RT + \ln(1 - q^{-1}) + q^{-1} + \bar{v}_1 q_0^{-2/3}\nu^* q^{-1/3}]q$$

The representative example shown in Figure 2 indicates that $F(q)$ is indeed linear in q^{-1} so that one can obtain χ and $B\nu^*$. All results are gathered in Table I.

Conclusions

For the case of swollen networks, ideal Gaussian theory contains three parameters: $q_0^{-2/3}\nu^*$, $B\nu^*$, and χ. All our gels are found to follow the predictions of theory (eq 4), and since obviously $\nu^* \neq 0$ we conclude that $B \neq 0$. This ensures that indeed the logarithmic term of eq 1 exists.

The Flory–Huggins interaction parameter, χ, is found to be

---

[3] P. Weiss, G. Hild, J. Herz, and P. Rempp, *Makromol. Chem.*, **135**, 249 (1970).

[4] T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

[5] E. J. van de Kraats, *Recl. Trav. Chim. Pays-Bas*, **87**, 1137 (1968).

TABLE I

NETWORK PARAMETERS FOR ANIONICALLY PREPARED POLYSTYRENE GELS, OBTAINED FROM SWELLING, UNILATERAL COMPRESSION, AND SWELLING PRESSURE MEASUREMENTS

Sample no.	M_c	q_c	q	$10^5 q_0^{-2/3}\nu^*$	χ	β	$\langle r^2\rangle_c/\langle r^2\rangle_0$
1823	18,700	6.7	10.3	0.82	0.51	0.5	0.45
1822	9,400	6.8	6.8		0.53	0.5	
1889	17,400	7.7	10.9	0.71	0.53	0.5	0.45
1865	10,400	7.7	8.2				
1819	10,000	10.6	≈11	0.96			0.45
1887	14,000	11.1	12.4	0.69	0.53	0.5	0.45
1860	10,100	11.1	≈10	1.14			0.55
1818	7,200	11.1	9.2	1.66	0.53	0.4	0.55
1888	17,600	15.4	17.9	0.42	0.52	0.5	0.45
1864	10,400	15.4	11.8				

0.525 ± 0.005 over the range $6 \leq q \leq 18$. Its value is higher than in more dilute polystyrene solutions in benzene, a finding similar to that reported in toluene by Dušek[6] for networks prepared by radical copolymerization of styrene and DVB. Although no detailed molecular explanation of the higher values for the semiempirical χ parameter can be given, the presence of DVB cross-links could be held responsible for these results.

The "memory" parameter $q_0^{-2/3}$ is related to the volume fraction of polymer prior to cross-linking, q_c^{-1}, as follows[2]

$$q_0^{-2/3} = q_c^{-2/3}\langle r^2\rangle_c/\langle r^2\rangle_0$$

when $\langle r^2\rangle_c$ and $\langle r^2\rangle_0$ stand for the mean-square end-to-end dimensions of the chains after cross-linking and in the unstrained reference state, respectively. Without any assumption, therefore, our data yield

$$\frac{q_0^{-2/3}\nu^* q_c^{-2/3}}{B\nu^*} = \frac{\langle r^2\rangle_c/\langle r^2\rangle_0}{B} = 1.0 \pm 0.2 \qquad (5)$$

Frequently the assumption that the chain dimensions do not change upon cross-linking is made. In that case our results would indicate that $B = 1$. Such a conclusion has in the past been considered implausible by Dušek[7] and more recently also by Mark,[1,8] because it would mean that upon cross-linking at q_c no syneresis would ever occur, regardless of how many cross-links are introduced. It has, however, been pointed out previously[2] that the χ parameter may very well increase as a result of cross-linking, thus leading to a gel of lower diluent compatibility at higher degrees of cross-linking, resulting in syneresis. Moreover, the assumption that $\langle r^2\rangle_c = \langle r^2\rangle_0$ is not necessarily valid.

Further analysis requires an assumption about ν^*. If our networks are not inhomogeneously cross-linked and if no network defects of any type exist, ν^* equals ρ_p/M_c. Inserting this, we find for all our gels, without any assumption about $\langle r^2\rangle_c$ and $\langle r^2\rangle_0$

$$B = 0.5 \pm 0.1 \qquad (6)$$

This is an interesting result because the gels vary widely in cross-linking conditions (ν^*, q_c). If network defects were to play an important role, one would also expect B to vary widely for the various gels. One is therefore tempted to conclude that the DVB-living polystyrene solutions indeed form uniform networks with DVB nodules and no dangling DVB blocks. Accepting this, the Flory-Wall identification, $B = 2/f$, then leads to an average functionality of a DVB cross-link of 4, which is quite reasonable.

Continuing this more speculative part of our analysis, we would then also conclude from eq 5 that (see Table I)

$$\langle r^2\rangle_c/\langle r^2\rangle_0 = 0.5 \pm 0.1 \qquad (7)$$

This result would indicate that upon cross-linking all gels exhibit a uniform shrinkage by a factor of 2.0 ± 0.2 in the mean-square end-to-end dimensions of the chains. A trend in this direction has recently been derived by Chompff,[9] whereas a much older estimate of James and Guth[10] comes up with exactly this factor of 2.

It should be emphasized that the results embodied in eq 6 and 7 are based on a somewhat uncertain assumption about ν^*. Thus the major conclusion of this paper, that the Flory-Wall theoretical value of B is the correct one, is not absolutely unassailable. On different grounds, the same can be said of the analogous conclusion of Johnson and Mark. Insertion of eq 7 into their data, however, still leaves the Flory-Wall value as the strongest contender. It seems unlikely that further time and effort invested in this problem utilizing other networks and experimental methods will succeed in removing any remaining vestige of doubt.

Acknowledgment. The preparation of the polystyrene gels by Drs. Rempp, Herz, Hild and Weiss in Strasbourg, France, is gratefully acknowledged.

---

(6) K. Dušek, *Collect. Czech. Chem. Commun.*, **27**, 2841 (1962).

(7) K. Dušek, *J. Polym. Sci., Part C*, **16**, 1289 (1967).

(8) J. E. Mark, *J. Amer. Chem. Soc.*, **92**, 7252 (1970).

(9) A. J. Chompff in "Polymer Networks, Structure and Mechanical Properties," A. J. Chompff and S. Newman, Ed., Plenum Press, New York, N. Y., 1971, p 463 ff.

(10) H. M. James and E. Guth, *J. Chem. Phys.*, **15**, 669 (1947).

Compression Behavior of Natural Rubber Vulcanized in the Swollen State

F. DE CANDIA

Laboratorio di Ricerche su Tecnologia dei Polimeri e Reologia del C.N.R., Naples, Italy. Received July 6, 1971

The Gaussian theory for rubberlike network elasticity gives the following expression for the stress[1]

$$\tau = nKT\frac{\langle r^2\rangle_d}{\langle r^2\rangle_0}(\alpha - \alpha^{-2}) \qquad (1)$$

where τ is the force on the unit of unstrained cross-sectional area, n is the number of elastic chains in the volume unit, K is the Boltzmann constant, T is the absolute temperature, $\langle r^2\rangle_d$ and $\langle r^2\rangle_0$ are the mean-square end to end distances respectively for a network chain and a free chain, and α is the strain ratio.

Equation 1 is valid for dry rubber; for swollen systems, we have

$$\tau_d = nKT\frac{\langle r^2\rangle_d}{\langle r^2\rangle_0}V_S^{-1/3}(\alpha - \alpha^{-2}) \qquad (1a)$$

where τ_d is the stress per unit of dry unstrained cross section, $n\langle r^2\rangle_d/\langle r^2\rangle_0$ refers to the dry network, and V_S is the volume fraction of polymer. Equations 1 and 1a are valid for monodirectional forces both in extension and in compression. It is well known, however, that the experimental data do not agree with eq 1 and 1a and that the stress-strain isotherms are

---

(1) P. J. Flory, *J. Amer. Chem. Soc.*, **78**, 5222 (1956).