The Modulus of Plasticized Ionic Rubbers

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ABSTRACT: The rubbery modulus of a cross-linked ionizable rubber is explored in the absence of the cross-linking effect of ions, that is, only through the effect of ions on conformation. The cross-linking effect is eliminated by plasticizing the rubber with a liquid of high dielectric constant. Experimentally, a rubber is prepared by mixing poly(acrylic acid) and poly(vinyl alcohol) and cross-linking thermally. The relationship between the rubbery moduli of the un-ionized and the ionized forms of the plasticized material is studied. A theory for the modulus of such a two-component rubber is derived and the predictions are compared with experiment. It is shown that the predicted ratio of the moduli in the acidic and ionic forms is in the same direction as determined experimentally, but that the calculation underestimates the magnitude of the effect. Several reasons for this discrepancy are given.

It is well known that an ionic polymer in the glassy state has a much higher modulus than the corresponding un-ionized polymer. Nielsen[1] found that the shear modulus of poly(acrylic acid) was increased by a factor of 2 or more on conversion to salts containing divalent cations, *i.e.*, zinc and calcium. Bonotto and Bonner[2] measured the secant moduli of an ethylene–acrylic acid copolymer and some of its salts. For both monovalent and divalent ions, the moduli were increased by factor varying from 3.5 to 7, depending on per cent neutralization. For plasticized systems this is true also: the Young's modulus of poly(acrylic acid) plasticized with 20% formamide has been found to increase by a factor of 3–4 upon conversion to poly(sodium acrylate).[3]

It is of interest to ask whether this effect extends beyond the glass transition point and specifically into the rubbery region. Intuitively one would expect, by analogy, that the modulus of elasticity of an ionized rubber would be greater than that of the corresponding un-ionized material. This should be so because ions tend to aggregate and thus act as additional cross-links.[4] It is of great interest, however, to determine if there is an intrinsic effect of ions, other than increased cross-linking, which would cause a higher modulus to persist into the rubbery region, and it is this subject which we wish to explore in this paper. It is imperative to eliminate the effects of ion aggregation in order to determine the effect of ions on rubber elasticity in terms of chain conformations. This can be done by plasticizing the rubber with a liquid of high dielectric constant. As will be shown, under these circumstances the ions have only a small effect on the modulus and, from the change in chain dimensions alone, the change in modulus on ionization can be predicted semiquantitatively.

A system in which the effects of ion aggregation may be eliminated and which, in addition, has been well studied[5] is the cross-linked poly(acrylic acid)–poly(vinyl alcohol) system (PAA–PVA). Ion aggregation effects can be eliminated by allowing the polymers to swell in aqueous media. Accordingly, a series of PAA–PVA films were prepared after the method of Kuhn.[5] The films were cross-linked and studied in both the acidic and ionic forms. The rubbery modulus was measured as a function of volume fraction of polymer at a single temperature. When the results were compared at a common volume fraction, it was found that the modulus of the ionic form was lower than that of the acidic form, in contrast to what one might anticipate intuitively.

In one attempt to rationalize this result, free chain dimensions in solvent systems similar to the swollen polymer environment were determined by viscometry and used to predict the ratio of the moduli in acidic and ionic forms from simple rubber elasticity theory. In another attempt to predict this ratio, Θ dimensions, as published in the literature, were employed. Both attempts lead to correct qualitative agreement, but both underestimate the effect somewhat.

The first part of the subsequent discussion will be devoted to the derivation of a theory for a two-component rubber, one component of which is ionizable. Subsequently, the experimental aspects will be discussed, and the theoretical predictions compared with experimental results. Finally, several reasons will be suggested which might explain the discrepancy between theory and experiment.

Theoretical

Let us consider a unit cube of a rubber which consists of a mutually interpenetrating network of two types of chains. In the present case, the two types of chains are PVA and PAA. The nature of the cross-link in the PVA–PAA rubber system is taken to be a simple esterification.[6] It is assumed, for the purposes of this calculation, that each cross-link is tetrafunctional and that from each cross-link emanate two chains of PAA and two of PVA.

Let us suppose that a unit cube of such a polymer undergoes an isotropic swelling in the ratio $1/V_r$, where V_r is the total volume fraction of polymer in the mixture. The length of each edge of the cube in the swollen, unstrained state is given by $1/V_r^{1/3}$. If the network is subsequently deformed by an external force to the dimensions l_1, l_2, l_3, the total difference in network entropy between the unstrained, unswollen state and the strained, swollen state for each type of chain, p, is given by [7,8]

$$\Delta S_p' = -\,{}^1\!/_2 N_p k(\overline{r_{0p}^2}/\overline{r_{fp}^2})(l_1^2 + l_2^2 + l_3^2 - 3) \qquad (1)$$

The expressions $\overline{r_{0p}^2}$ and $\overline{r_{fp}^2}$ represent the mean square end-to-end distances of the chains in the unstrained, unswollen network and in the free state, respectively. It is assumed $\overline{r_{0p}^2}$ and $\overline{r_{fp}^2}$ are not equal.

For a network consisting of two types of chains, the total entropy of deformation of the network, $\Delta S_0'$, including both swelling and deformation resulting from the externally applied force, is simply the sum of the entropies of the components

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(1) L. E. Nielsen, *Polym. Eng. Sci.*, 9, 356 (1969).

(2) S. Bonotto and E. Bonner, *Macromolecules*, 1, 510 (1968).

(3) A. Eisenberg and M. King, to be published.

(4) A. Eisenberg, *Macromolecules*, 3, 147 (1970).

(5) W. Kuhn, A. Ramel, O. Walters, and H. Kuhn, *Fortschr. Hochpolym.-Forsch.*, 1, 540 (1960).

(6) H. Noguchi, *Busseiron Kenkyu*, 69, 78 (1953).

(7) M. S. Green and A. V. Tobolsky, *J. Chem. Phys.*, 14, 80 (1946).

(8) L. R. G. Treloar, "The Physics of Rubber Elasticity," Oxford University Press, London, 1958, Chapter 4.

$$\Delta S_0' = \Delta S_1' + \Delta S_2' = -\,{}^1/_2k[(\overline{r_{01}^2}/\overline{r_{f1}^2})N_1 + (\overline{r_{02}^2}/\overline{r_{f2}^2})N_2](l_1^2 + l_2^2 + l_3^2 - 3) \quad (2)$$

where the subscripts 1 and 2 on S, r, and N refer to the two components.

The change in entropy due to the isotropic swelling in the ratio $1/V_r^{1/3}$ in the absence of stress is

$$\Delta S_0 = -\,{}^1/_2k[(\overline{r_{01}^2}/\overline{r_{f1}^2})N_1 + (\overline{r_{02}^2}/\overline{r_{f2}^2})N_2](3V_r^{-2/3} - 3) \quad (3)$$

Therefore, the entropy of deformation of the swollen network, ΔS, is simply the difference of $\Delta S_0'$ and ΔS_0

$$\Delta S = \Delta S_0' - \Delta S_0 = -\,{}^1/_2k[(\overline{r_{01}^2}/\overline{r_{f1}^2})N_1 + (\overline{r_{02}^2}/\overline{r_{f2}^2})N_2](l_1^2 + l_2^2 + l_3^2 - 3V_r^{-2/3}) \quad (4)$$

The extension ratios, referred to the swollen, unstrained network are given by $\lambda_1 = l_1V_r^{1/3}$, etc. For simple extension of a swollen rubber of length L and volume V, $\lambda_1 = L/L_1$, where L_1 is the value of L in the unstrained, swollen state. If the rubber is considered to be incompressible, then $V = V_1$, the unstrained, swollen volume. Thus, from eq 4, and following the usual methods for a swollen, single-component rubber, the force of extension is obtained as

$$f = (kT/L_1)[(\overline{r_{01}^2}/\overline{r_{f1}^2})N_1 + (\overline{r_{02}^2}/\overline{r_{f2}^2})N_2](\lambda_1 - 1/\lambda_1^2)V_r^{-2/3} \quad (5)$$

The Young's modulus, E, is then given by the ratio of stress to strain, *i.e.*

$$\begin{aligned} E &= (f/A)/(L/L_1 - 1) \\ &= (kT/V_1)[(\overline{r_{01}^2}/\overline{r_{f1}^2})N_1 + (\overline{r_{02}^2}/\overline{r_{f2}^2})N_2] \times [(\lambda_1 - 1/\lambda_1^2)/(\lambda_1 - 1)]V_r^{-2/3} \end{aligned}$$

which, in the limit of small strains, becomes

$$E = (3kT/V_1)[(\overline{r_{01}^2}/\overline{r_{f1}^2})N_1 + (\overline{r_{02}^2}/\overline{r_{f2}^2})N_2]V_r^{-2/3} \quad (6)$$

If V_0 is the unswollen, unstrained volume, then $V_1 = V_0/V_r$, and Young's modulus becomes

$$E = (3kT/V_0)[(\overline{r_{01}^2}/\overline{r_{f1}^2})N_1 + (\overline{r_{02}^2}/\overline{r_{f2}^2})N_2]V_r^{1/3} \quad (7)$$

It is clear that, in the simplest approximation, where $(\overline{r_0^2}/\overline{r_f^2})$ is considered to be unity[8] and $(N_1 + N_2)$ becomes the total number of chains, the equation for the Young's modulus assumes the familiar form

$$E = E_0V_r^{1/3}$$

where E_0 is the modulus of the unswollen network.

Let us now consider the specific case of a rubber formed from a mixture of PAA (monomeric mole fraction m) and PVA [monomeric mole fraction $(1 - m)$]. The mixture is cast as a film from aqueous solution, cross-linked by heating, and subsequently swollen in water. Since it was assumed that each cross-link is the junction of two chains of PAA and two chains of PVA, then we may write

$$N_{\mathrm{PAA}} = N_{\mathrm{PVA}} = N/2 \quad (8)$$

Therefore, the degrees of polymerization between cross-links, P, are in the ratio of the monomeric mole fractions, that is

$$P_{\mathrm{PVA}}/P_{\mathrm{PAA}} = (1 - m)/m \quad (9)$$

The relative values of $\overline{r_{0\mathrm{PVA}}^2}$ and $\overline{r_{0\mathrm{PAA}}^2}$ can then be deduced by balancing the force on each cross-link, keeping in mind that each cross-link must be the junction of two PAA chains and two PVA chains. The retractive force exerted by each chain is proportional to the end-to-end distance, r, as given by[9]

$$f = 3kTr/\overline{r_f^2} \quad (10)$$

Since the average tension exerted on the PAA chains must be equal and opposite to the average tension exerted on the PVA chains in any one direction, we can write, considering that the sample is isotropic

$$(\overline{r_{0\mathrm{PAA}}^2})^{1/2}/\overline{r_{f\mathrm{PAA}}^2} = (\overline{r_{0\mathrm{PVA}}^2})^{1/2}/\overline{r_{f\mathrm{PVA}}^2} \quad (11)$$

This is also true of the ionic form

$$(\overline{r_{0\mathrm{PNaA}}^2})^{1/2}/\overline{r_{f\mathrm{PNaA}}^2} = (\overline{r_{0\mathrm{PVA}'}^2})^{1/2}/\overline{r_{f\mathrm{PVA}'}^2} \quad (12)$$

where the symbol PVA′ refers to the basic medium, and PNaA is poly(sodium acrylate).

It should be recalled, however, that the mean square end-to-end distances of the two types of chains are not the same, but only the average tension under which the chains find themselves.

It is more convenient to rewrite (6), using (8), with PAA representing component 1 and PVA component 2

$$E = (3NkT/2V_0)[(\overline{r_{0\mathrm{PAA}}^2}/\overline{r_{f\mathrm{PAA}}^2}) + (\overline{r_{0\mathrm{PVA}}^2}/\overline{r_{f\mathrm{PVA}}^2})]V_r^{1/3} \quad (13)$$

Substitution of (11) in (13) gives us, for the polymer in the acidic form

$$E_{\mathrm{acidic}} = (3NkT/2V_0)[(\overline{r_{0\mathrm{PAA}}^2}/\overline{r_{f\mathrm{PAA}}^2}) + (\overline{r_{f\mathrm{PVA}}^2}/\overline{r_{f\mathrm{PAA}}^2})^2(\overline{r_{0\mathrm{PAA}}^2}/\overline{r_{f\mathrm{PVA}}^2})]V_r^{1/3} \quad (14)$$

or

$$E_{\mathrm{acidic}} = (3NkT/2V_0)(\overline{r_{0\mathrm{PAA}}^2}/\overline{r_{f\mathrm{PAA}}^2})(1 + \overline{r_{f\mathrm{PVA}}^2}/\overline{r_{f\mathrm{PAA}}^2})V_r^{1/3}$$

Similarly, for the polymer in the ionic form

$$E_{\mathrm{ionic}} = (3NkT/2V_0)(\overline{r_{0\mathrm{PNaA}}^2}/\overline{r_{f\mathrm{PNaA}}^2}) \times (1 + \overline{r_{f\mathrm{PVA}}'^2}/\overline{r_{f\mathrm{PNaA}}^2})V_r^{1/3} \quad (15)$$

The ratio $\overline{r_{0\mathrm{PNaA}}^2}/\overline{r_{0\mathrm{PAA}}^2}$ may be obtained by equating the total root mean square distances between cross-links for both components in acidic and basic forms, at constant volume fraction of polymer, *i.e.*

$$(\overline{r_{0\mathrm{PAA}}^2})^{1/2} + (\overline{r_{0\mathrm{PVA}}^2})^{1/2} = (\overline{r_{0\mathrm{PNaA}}^2})^{1/2} + (\overline{r_{0\mathrm{PVA}'}^2})^{1/2} \quad (16)$$

Combining (16) with (11) and (12), we obtain

$$\overline{r_{0\mathrm{PAA}}^2}(1 + \overline{r_{f\mathrm{PVA}}^2}/\overline{r_{f\mathrm{PAA}}^2})^2 = \overline{r_{0\mathrm{PNaA}}^2}(1 + \overline{r_{f\mathrm{PVA}'}^2}/\overline{r_{f\mathrm{PNaA}}^2}) \quad (17)$$

Equations 14 and 15 give us the ratio of Young's moduli at constant V_r

$$\frac{E_{\mathrm{acidic}}}{E_{\mathrm{ionic}}} = \frac{(\overline{r_{0\mathrm{PAA}}^2}/\overline{r_{f\mathrm{PAA}}^2})(\overline{r_{f\mathrm{PVA}}^2}/\overline{r_{f\mathrm{PAA}}^2} + 1)}{(\overline{r_{0\mathrm{PNaA}}^2}/\overline{r_{f\mathrm{PNaA}}^2})(\overline{r_{f\mathrm{PVA}}'^2}/\overline{r_{f\mathrm{PNaA}}^2} + 1)}$$

With eq 17 the ratio simplifies to

$$\frac{E_{\mathrm{acidic}}}{E_{\mathrm{ionic}}} = \frac{\overline{r_{f\mathrm{PNaA}}^2} + \overline{r_{f\mathrm{PVA}'}^2}}{\overline{r_{f\mathrm{PAA}}^2} + \overline{r_{f\mathrm{PVA}}^2}} \quad (18)$$

Since, in our system, we are dealing with equal numbers of chains of each component, this ratio is simply the ratio of the average mean square end-to-end distances of the free chains, *i.e.*

$$E_{\mathrm{acidic}}/E_{\mathrm{ionic}} = \overline{r_{f\mathrm{basic}}^2}/\overline{r_{f\mathrm{acidic}}^2} \quad (19)$$

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(9) See ref 8, Chapter 3.

It is evident that eq 19 is formally the same as that obtained for an ionizable rubber consisting of a single component. The determination of the mean square end-to-end distances of the free chains in the present case will be discussed below.

Experimental Section

Films suitable for the measurement of the rubbery modulus were prepared from a 50:50 mixture (by weight) of PVA and PAA. PVA was obtained from Matheson Coleman and Bell (M_n, determined by osmometry, was 57,000). PAA was prepared by a method to be explained in another paper (M_v, determined in dioxane at 30°, was 144,000). The polymer mixture was dissolved in water and cast in a polystyrene container. The water was evaporated until the film could be cut into strips. The temperature during evaporation was never allowed to exceed 50°. While no specific tests were performed, no evidence of incompatibility was observed by visual examination of the films. Kuhn's investigations,[5] which were carried out in similar concentration regions, also revealed no such problem, presumably due to the high swelling ratios used.

The film studied was first allowed to swell in distilled water overnight. The modulus was measured at a single temperature (25° ± 1°) as a function of the weight fraction of polymer. The measurements were made with a vacuum-tight stress relaxometer which has been previously described.[10] For each weight fraction, the force of extension was observed as a function of time; after initial rapid relaxation, the force was generally constant. For lower swelling ratios where the force did not remain constant within experimental error, the data were discarded. The extensions were always from 5 to 10%, in which range the elastic response was found to be linear.

The weight fractions were obtained from the polymer weights taken immediately after each force measurement, so that weight loss due to saturation of the sample chamber with water vapor during temperature equilibration was not a factor. The density of the sample as a function of the weight fraction of polymer was measured pycnometrically at 25°, with paraffin oil as the confining fluid. This procedure allowed the calculation of volume and, hence, volume fraction of polymer in each case.

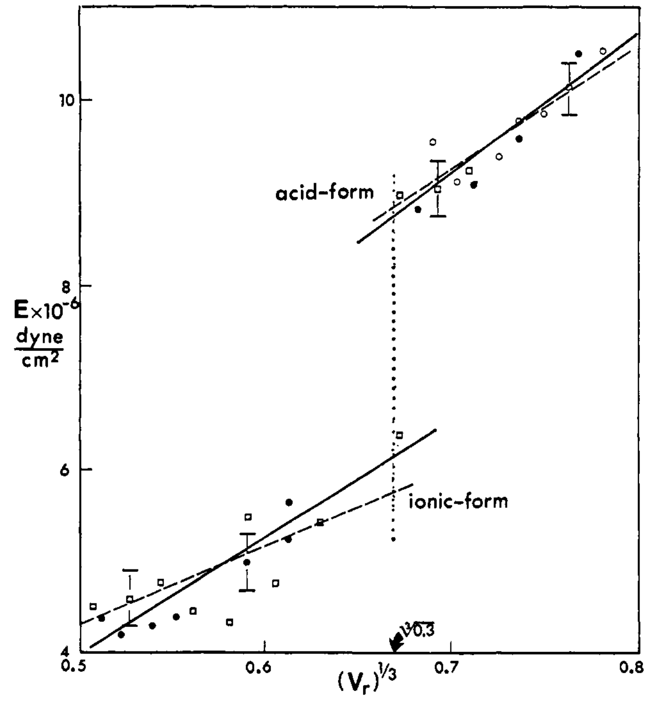

Figure 1. Young's modulus as a function of (volume fraction of rubber)$^{1/3}$ for polymer in acid and ionic forms for three samples: ——, best fit to $E = A + BV_r^{1/3}$; – – –, best fit to $E = CV_r^{1/3}$.

After the study of the modulus of the acidic polymer, the film was immersed in 1 *N* NaOH solution for several hours. The time required for diffusion was calculated from the data of Kuhn, *et al.*,[5] taking $D \approx 10^{-5}$ cm² sec⁻¹, the value of the diffusion constant of the base in the embedded fluid. Since the thickness $a \approx 0.2$ cm, the diffusion time $\tau = a^2/2D \approx 0.5$ hr. Hence the time allowed for diffusion was more than adequate.

As before, the modulus was measured as a function of the weight fraction of polymer. With the aid of density measurements as a function of weight fraction, the modulus as a function of volume fraction was obtained. As a check on reversibility, the films were resoaked overnight in HCl and then in water. The modulus was found to return to its initial value within the limits of experimental error.

Since the theory predicts Young's modulus of a swollen rubber to vary as $V_r^{1/3}$, E *vs.* $V_r^{1/3}$ was plotted for both the acidic form and the ionic form of the rubber. These results are shown graphically in Figure 1. Typical error limits are shown for two points of each line. The data represent values for three different films, cross-linked for the same length of time, indicating the good reproducibility of the modulus measurements.

The best straight line was obtained for each of the two forms by a least-squares method, and the moduli obtained were compared at a common volume fraction of polymer.

For the volume fraction $V_r = 0.3$, the values of modulus obtained were

$$E_{\text{acidic}} = 8.75 \times 10^6 \text{ dyn/cm}^2$$

and

$$E_{\text{ionic}} = 6.1 \times 10^6 \text{ dyn/cm}^2$$

respectively, and the ratio

$$\frac{E_{\text{acidic}}}{E_{\text{ionic}}} = 1.43$$

The value of this ratio, as predicted by theory, will be shown to be in the same direction (*i.e.*, greater than 1) but smaller than that obtained by experiment.

The two straight lines (solid lines in Figure 1) are given by the relations

$$E_{\text{acidic}} = -1.37 \times 10^6 + 1.51 \times 10^7(V_r)^{1/3}$$

and

$$E_{\text{ionic}} = -2.33 \times 10^6 + 1.26 \times 10^7(V_r)^{1/3}$$

The standard deviations of E_{acidic} and E_{ionic} are given by 2.0×10^{-5} and 3.6×10^{-5}, respectively.

It should be pointed out, however, that with only slight increases in the deviations, the lines can be made to pass through the origin. These lines are the dashed lines in Figure 1, represented by the relations

$$E_{\text{acidic}} = 1.32 \times 10^7(V_r)^{1/3}$$

and

$$E_{\text{ionic}} = 0.86 \times 10^7(V_r)^{1/3}$$

the standard deviations being 2.1×10^{-5} and 4.0×10^{-5}, respectively. Thus, within the limits of experimental error, the modulus as a function of volume fraction can be adequately reproduced by the elementary theory.

Comparison of Experiment with Theory

The values of $\overline{r_{f\text{PAA}}^2}$ and $\overline{r_{f\text{PVA}}^2}$ in the actual polymer network are unknown. However, in order to obtain a lower limit for the ratio of the moduli, they are taken to be the unperturbed dimensions of the corresponding free polymer chains. In this case, the

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[10] A. Eisenberg and T. Sasada, *J. Polym. Sci., Part C*, 16, 3473 (1968).

TABLE I

Polymer	$(\overline{r_\Theta^2}/\overline{r_{fr}^2})^{1/2}$	Ref
PAA	1.85 ± 0.05	*a, b*
PNaA	2.38	*c*
PVA	2.04 ± 0.10	*b, d*

[a] See ref 11. [b] M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym.-Forsch.*, 3, 196 (1963). [c] See ref 12. [d] See ref 13.

dimensions may be expressed in terms of a characteristic ratio, $\sigma = (\overline{r_\Theta^2}/\overline{r_{fr}^2})^{1/2}$. σ has been measured for PAA[11] and for PNaA[12] in actual Θ solvents, and it has been estimated for PVA,[13] although no Θ solvent was obtained. These results are summarized in Table I.

The value of $(\overline{r_{fr}^2}/P)$ is a constant (9.49×10^{-16} cm^2) for vinyl polymers. Hence

$$\overline{r^2} \propto \sigma^2 P \tag{20}$$

Combining (20) with (19) and (9), we obtain

$$\frac{E_{\text{acidic}}}{E_{\text{ionic}}} = \frac{\sigma_{\text{PVA}}^2(1 - m) + \sigma_{\text{PNaA}}^2 m}{\sigma_{\text{PVA}}^2(1 - m) + \sigma_{\text{PAA}}^2 m}$$

For a 50:50 mixture of PVA and PAA, by weight ($m = 0.38$), this ratio has the value 1.22.

Discussion

Several possible reasons can be offered for the lack of quantitative agreement between experiment and theory. First of all, as mentioned above, one of the assumptions used in the development of the theory was that the nature of the cross-link in the PAA–PVA rubbery system was taken to be simple esterification. While this is relatively well established,[6] it is quite possible that cross-linking of a different nature could occur. As a matter of fact, we could conceive of a network where the only active chains are PAA, and PVA acts simply as a filler. In this case, the ratio of the moduli in acidic and ionic forms would be the same as that for a rubber network formed from a single ionizable component. Using the approximation that the polymer dimensions are the unperturbed dimensions, the predicted value of $E_{\text{acidic}}/E_{\text{ionic}}$ for PAA, obtained from the characteristic ratios, is 1.65.

If such defects as PAA–PAA cross-links do occur, it is probable that they would be only a fraction of the total number of cross-links in the network. However, this would still change the relative numbers of chains of each component. If the number of active PAA chains were significantly greater than the number of PVA chains, then the value of $E_{\text{acidic}}/E_{\text{ionic}}$ would be expected to lie somewhere between the values of 1.22 for a two-component rubber (PAA–PVA) and 1.65 for a single-component rubber (PAA). If the original molecular weights of PVA and PAA were different, then the numbers of active chains of each component would be unequal, because there would be unequal numbers of chain ends. However, in the present case, the original molecular weights of PAA and PVA were chosen to be similar. Hence, this should not affect the results appreciably.

Another possibility of error is introduced in the neglect of changes in internal energy with extension, that is, in assuming a purely entropic force. If the variation in internal energy with extension, $(\delta E/\delta L)_{T,V}$, were roughly the same in both cases, then most of this error could be expected to be canceled in determining the ratio of moduli. However, the variation in internal energy could very well be significantly different for ionic and nonionic chains. In part, $(\delta E/\delta L)_{T,V}$ for an isolated ionic chain would be expected to be lower than the same quantity for the corresponding nonionic chain, because extension would relieve some of the long-range effect of electrostatic repulsion. However, in an ionic gel whose volume does not change on extension, the change in electrostatic energy with extension should be zero, and this effect should not be expected to contribute in the present case. Since the embedding medium for the ionized form of the rubber is of considerable ionic strength, the long-range interactions of the fixed ions will be effectively screened by the mobile electrolyte. Thus, one would expect only essentially short-range interactions of fixed ions, which are considerable, but which modify the unperturbed dimensions. It is possible, however, that there may be more subtle electrostatic or internal energy effects which are not accounted for in this argument.

It should be pointed out that the Young's moduli pertinent to the present case could not have been calculated from the data of Kuhn, *et al.*,[5] for the reason that their measurements of extension *vs.* applied stress were taken in a system completely immersed in solvent, in which case the volume fraction of polymer varied upon neutralization and acidification. The changes in extension that they measured were due to Donnan osmotic force, which is not relevant in measuring the rubbery modulus of a network in which the amount of diluent is kept constant.

Finally, it should be made clear that the observed effect of a ratio of $E_{\text{acidic}}/E_{\text{ionic}} > 1$ should be generally observable for all ionizable rubbers where effects of aggregation can be removed. The reason for this is the same reason that ionization of a polymer generally produces an increase in dimensions of a polymer chain. If ionization caused a decrease in polymer dimensions, then one would expect to see an increase in modulus on ionization.

It should be pointed out that this work bears some similarity to the recent work of Tobolsky and Goebel,[14] in that free polymer dimensions have been used to predict rubber elasticity; in the latter case, however, free chain dimensions of a nonionic network—poly(dimethylsiloxane)—were varied by the use of different swelling agents, and thus were not compared at a constant degree of swelling.

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Glossary of Symbols

f	Force of extension of swollen rubber
k	The Boltzmann constant
l_i	Extension ratio of ith coordinate due to both swelling and external strain
m	Monomeric mole fraction of PAA in rubber
$\overline{r_{0p}^2}$	Mean square end-to-end distance of the chains of component p in the unstrained, unswollen network

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(11) S. Newman, W. R. Krigbaum, C. Laugier, and P. J. Flory, *J. Polym. Sci.*, **14**, 451 (1954).

(12) A. Takahashi and M. Nagasawa, *J. Amer. Chem. Soc.*, **86**, 543 (1964).

(13) H. A. Dieu, *J. Polym. Sci.*, **12**, 417 (1954).

(14) A. V. Tobolsky and J. C. Goebel, *Macromolecules*, **3**, 556 (1970).

$\overline{r_{fp}^2}$	Mean square end-to-end distance of the chains of component p in the free state
$\overline{r_{fr}^2}$	Mean square end-to-end distance of freely rotating chains
$\overline{r_\Theta^2}$	Mean square end-to-end distance of unperturbed chains
A	Cross-sectional area of swollen rubber
E	Young's modulus of swollen rubber
E_0	Young's modulus of unswollen rubber
L	Length of swollen rubber
L_1	Unstrained length of swollen rubber
M_n	Number-average molecular weight
M_v	Viscosity-average molecular weight
N_p	Number of chains of component p
P_p	Degree of polymerization between cross-links of pth component
PAA	Poly(acrylic acid)
PVA	Poly(vinyl alcohol)
ΔS	Entropy of deformation of the swollen network due to external strain
ΔS_0	Entropy of deformation due to swelling
$\Delta S_0'$	Entropy of deformation due to both swelling and external strain
$\Delta S_p'$	Entropy of deformation of component p due to both swelling and external strain
V	Volume of swollen rubber
V_1	Unstrained volume of swollen rubber
V_r	Volume fraction of polymer
λ_i	Extension ratio of the *i*th coordinate of the swollen network due to external strain
δ	$(\overline{r_\Theta^2}/\overline{r_{fr}^2})^{1/2}$

Volume Change Accompanying Rubber Extension

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ABSTRACT: A new equation for the volume dilation accompanying rubber extension is obtained from a reinterpretation of the kinetic theory equation for rubber elasticity. This equation is shown to describe published volume-extension data better than either that derived from simple kinetic theory or that derived from the Mooney–Rivlin equation.

Beginning with the thermodynamic identity

$$(\partial f/\partial p)_{T,L} = (\partial V/\partial L)_{T,p} \qquad (1)$$

and making use of the equation of state for rubber elasticity[1]

$$F = NkT\frac{\langle r^2\rangle_0}{\langle r_f^2\rangle}[L/L_0 - (L_0/L)^2V/V_0] \qquad (2)$$

one can derive the following expression for the volume change accompanying rubber extension[2,3] (provided that $\langle r_f^2\rangle$ is considered independent of volume).

$$\Delta V/V_0 = KNkT(\langle r^2\rangle_0/\langle r_f^2\rangle)[1 - \alpha^{-1}] \qquad (3)$$

In eq 1, f is the force required to maintain the network at length L. In eq 2, $F = f/A_0$, where A_0 is the unstretched cross-sectional area; L_0 and V_0 are the length and volume at zero force and zero pressure; V is the volume at length L; N is the number of network chains per unit volume of the unstretched sample; k is Boltzmann's constant; T is the absolute temperature; $\langle r^2\rangle_0$ is the mean-square end-to-end distance of the network chains at volume V_0 and length L_0; and $\langle r_f^2\rangle$ is the mean-square end-to-end distance the network chains would assume, at length L and volume V, if the cross-links were removed. In eq 3, K is the isothermal compressibility and $\alpha = L/L_0$.

Recent work by Christensen and Hoeve[4] indicates that eq 3 predicts $\Delta V/V_0$ well for α close to unity, but at higher extensions greatly underestimates $\Delta V/V_0$. To obtain eq 3, it is assumed that $\langle r_f^2\rangle$ is independent of the sample volume; however, if we allow $\langle r_f^2\rangle$ to depend on V (since it is in fact evaluated in the stretched state of length L and volume V) we obtain from eq 1 and 2

$$\Delta V/V_0 = KNkT\int_1^{\alpha}\frac{\langle r^2\rangle_0}{\langle r_f^2\rangle}\left[\frac{\gamma(\alpha^3 - 1) + 1}{\alpha^2}\right]d\alpha \qquad (4)$$

where $\gamma = (d \ln \langle r_f^2\rangle/d \ln V)_{T,L}$. Assuming γ to be independent of α, we obtain

$$\Delta V/V_0 = KNkT[1 - (1/\alpha) + (\gamma/2)(\alpha^2 - 3 + 2/\alpha)] \qquad (5)$$

The differential form of this equation was given in ref 1. The volume-extension data of Christensen and Hoeve for three nautral rubber vulcanizates are shown in Figures 1–3; from these figures it can be seen that eq 5 fits the data very well in each case. For the two unswollen vulcanizates the values of γ giving best fit are approximately the same (0.26 for the 10-min cure and 0.28 for the 40-min cure), whereas a significantly lower value of γ gives the best fit for the swollen vulcanizate (0.20 for the 15-min cure swollen 212% in xylene). γ reflects the dependence of $\langle r_f^2\rangle$ on volume or pressure; since this dependence would arise from changes in intermolecular interactions, the lower value of γ found for the swollen sample is in accordance with the fact that the importance of interactions between chains decreases with swelling.

It is of interest to determine to what extent the failure of eq 3 to describe $\Delta V/V_0$ as a function of α may be due to the failure of eq 2 to describe F as a function of α. If the sample is assumed to undergo an isotropic deformation from volume V_0 to V followed by a uniaxial extension at constant volume to length L, the treatment of Van der Hoff[5] yields the following Mooney–Rivlin-type expression in which the volume dilation is taken into account

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