the definition of two points at the ends of a tie line in a binodal. To this end we regard $f_1 \equiv f_1(\phi_2', T)$ and $f_2 \equiv f_2(\phi_2', T)$ and note that the solution is found when the equilibrium conditions, $f_1(\phi_2', T) = 0$ and $f_2(\phi_2', T) = 0$ (eq 29), are met.

Combining Newton-Raphson and Gauss-Seidel methods; if T_i and $\phi_{2,i}'$ represent approximations to T and ϕ_2', then closer approximations T_{i+1} and $\phi_{2,i+1}$ are given by

$$T_{i+1} = T_i - f_1(T_i, \phi_{2,1}')/f_1^T(T_i, \phi_{2,i}')$$

and

$$\phi_{2,i+1}' = \phi_{2,i}' - f_2(T_{i+1}, \phi_{2,i}')/f_2^{\phi}(T_{i+1}, \phi_{2,i}')$$

where

$$f_1^T \equiv \partial f_1/\partial T \qquad f_2^{\phi} \equiv \partial f_2/\partial \phi_2'$$

From the rather arbitrary starting values, $T_0 = 300$, and $\phi_{2,0}' = 0.005$, the values of T and ϕ_2' were determined to sufficient accuracy (0.002 in T and 0.001 in ϕ_2') at step $i \simeq 6$ in this recursive routine.

All of the calculations above were performed on a programmed Hewlett-Packard desk calculator, Model 9810A.

Entanglement Networks of 1,2-Polybutadiene Cross-Linked in States of Strain. I. Cross-Linking at 0°

Ole Kramer, Rick L. Carpenter, Violeta Ty, and John D. Ferry*

Department of Chemistry and Rheology Research Center, University of Wisconsin, Madison, Wisconsin 53706.

Received October 1, 1973

ABSTRACT: Linear 1,2-polybutadiene is cross-linked at 0° (12° above T_g) by γ-irradiation while strained in simple extension, with extension ratios (λ_0) from 1.2 to 2.0. After release, the sample retracts to a state of ease (λ_s) at room temperature. From λ_0, λ_s, and Young's modulus in the state of ease (E_s), the molar concentrations of network strands terminated by cross-links (ν_x) and by trapped entanglements (ν_N) are calculated by composite network theories of Flory and others. With increasing irradiation time t, ν_x (corrected for free ends) is directly proportional to t and ν_N attains a constant value. With increasing λ_0, ν_x is constant and ν_N diminishes somewhat. Extrapolated to $\lambda_0 = 1$, ν_N is somewhat smaller (1.2×10^{-4} mol cm^{-3}) than the concentration of entanglement strands estimated from viscoelastic measurements on uncross-linked polymer in the plateau zone ($\nu_e = 2.5 \times 10^{-4}$). Young's modulus was also calculated indirectly from equilibrium swelling in n-heptane. The swelling is slightly anisotropic, being larger in the direction of extension.

In certain ranges of frequency (or time) and temperature, the viscoelastic properties of amorphous polymers of high molecular weight resemble those of cross-linked polymers, as though a temporary network existed, usually attributed to coupling by entanglements.[1] The concentration of network strands terminated by entanglements has been estimated from viscoelastic measurements in the plateau zone,[2] but these are not measurements at elastic equilibrium. To measure the effect of entanglements at equilibrium, they must be trapped between chemical cross-links to prevent eventual disentanglement. Concentrations of trapped entanglements have been estimated in several ways,[3-6] involving additive contributions from strands terminated by chemical cross-links and by entanglements.

The present work treats systems in which the elastic effects of strands terminated by chemical cross-links and by trapped entanglements, instead of being additive, are in opposition. Their concentrations can in principle be determined without any assumptions of stoichiometric cross-linking, and the effectiveness of entanglements as a function of strain and other variables can be investigated. A preliminary report of such experiments has appeared elsewhere.[7]

Theory

When a rubber containing ν_1 (mol cm^{-3}) of elastically effective strands between cross-links which were introduced in the isotropic state is subjected to a substantial deformation and then a new set of cross-links is introduced to give an additional ν_2 (mol cm^{-3}) of elastically effective strands, the equilibrium elastic properties can be described as the sum of two independent networks. The most general treatment of such composite networks has been presented by Flory,[8] who gave the following expression for the elastic free energy ΔF_{el} of the composite network, assuming Gaussian chains

$$\Delta F_{el}/RT = (\nu_1/2)(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + (\nu_2/2) \times (\lambda_{x:2}^2 + \lambda_{y:2}^2 + \lambda_{z;2}^2 - 3) - (1/2)(\nu_1 + \nu_2) \ln V/V_0 \quad (1)$$

where λ_x, λ_y, and λ_z represent the extension ratios relative to the initial isotropic state; $\lambda_{x;2}$, $\lambda_{y;2}$, and $\lambda_{z;2}$ represent the extension ratios relative to the state in which the second set of cross-linkages was introduced; V is the actual volume; V_0 is a reference volume. After release of the stress, the sample assumes a state of ease in which the free energy is at a minimum and the force due to the network introduced in the isotropic state is equal to and opposes the force due to the network introduced in the strained state. From the strain in the state of ease the relative concentrations of elastically effective strands introduced in the strained and isotropic states, *i.e.*, ν_2/ν_1, can be calculated. The ideal composite network is isotropic in its elastic properties, taken relative to the state of ease.

If an uncross-linked polymer of high molecular weight

---

(1) J. D. Ferry, *Proc. 5th Intern. Congr. Rheol.*, **1**, 3 (1969).

(2) J. D. Ferry, "Viscoelastic Properties of Polymers," 2nd ed, Wiley, New York, N. Y., 1970, p 406.

(3) C. G. Moore and W. F. Watson, *J. Polym. Sci.*, **19**, 237 (1956).

(4) B. Meissner, I. Klier, and S. Kucharik, *J. Polym. Sci., Part C*, **16**, 793 (1967).

(5) N. Steiner, *BAM (Bundesanst. Materialprue.) Ber.*, **5**, 25 (1971).

(6) N. R. Langley and K. E. Polmanteer, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **13**, 235 (1972).

(7) O. Kramer, V. Ty, and J. D. Ferry, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2216 (1972).

(8) P. J. Flory, *Trans. Faraday Soc.*, **56**, 722 (1960).

can be held in a strained state and chemical cross-links can be introduced rapidly enough so there is no significant relaxation of stress by entanglement slippage and no chain scission during the process, the entanglements play the role of the first-stage cross-links introduced in the isotropic state in the above mentioned composite network theory. Of course, the strands between entanglement loci must undergo rapid configurational rearrangements during the time scale of the experiment. After release of stress, in principle one should be able to observe both a first and a second state of ease, especially for low degrees of cross-linking for which a sizable fraction of the entanglements remain untrapped; in the first state of ease, entanglements untrapped by the cross-links may still contribute to the retractive force in the direction of the original unstrained state, whereas in the second state of ease, the untrapped entanglements have relaxed, and only the trapped entanglements contribute. The dimensions of both states of ease can be calculated[9] from the theory of Flory[8] which provides for the effect of subsequent removal of some of the original linkages, but since only one state of ease has been observed experimentally thus far, the treatment here is limited to this simpler case.

Replacing ν_1 by ν_N, the concentration of elastically effective strands terminated by entanglements, and ν_2 by ν_x, the concentration of elastically effective strands terminated by chemical cross-links, one easily obtains the following expressions from the composite network theory for the case of simple elongation

$$E_s/E_0 = (\lambda_0^2 - \lambda_0^{-1})/(\lambda_0^2/\lambda_s^2 - \lambda_s/\lambda_0) \qquad (2)$$

where λ_0 is the extension ratio during introduction of chemical cross-links in the strained state; λ_s is the extension ratio in the state of ease; E_s is the equilibrium Young's modulus in small extensions from the state of ease; and E_0 is Young's modulus of the original entanglement network in a time scale where the entanglements behave as though trapped. Since E_0 may be represented by $3g_N\nu_NRT$, with the front factor g_N approximated by unity, it is possible to obtain ν_N explicitly by measuring λ_0, λ_s, and E_s. Finally, ν_x can be obtained from eq 3.

$$\lambda_s = \left[\frac{1 + \lambda_0\nu_x/\nu_N}{1 + \nu_x/\nu_N\lambda_0^2}\right]^{1/3} \qquad (3)$$

Experimental Section

Polymer. It is necessary to work near the glass transition temperature (T_g) of the polymer to avoid or minimize entanglement slippage during introduction of the chemical cross-links. This makes it rather impractical to use a thermally activated chemical cross-linking agent. A chemical agent which could be activated photochemically would be ideal. For this study, cross-linking by γ-irradiation was chosen, and 1,2-polybutadiene was selected as the polymer because $T_g = -12°$, not far below the convenient working temperature of 0°, and it was believed that chain scission by γ-irradiation would be relatively slight, as long as the irradiation temperature was not below T_g. In addition, the 1,2-vinyl groups can undergo chain reactions, so a certain degree of cross-linking is obtained with a smaller irradiation dose for 1,2-polybutadiene than for most other polymers. The polymer was purchased from Phillips Petroleum Co.; its microstructure was cis:trans:vinyl = 2.4:2.3:95.3, and it contained about 0.5% Cyanox SS antioxidant. The number- and weight-average molecular weights were 1.52×10^5 and 1.90×10^5, respectively. The intrinsic viscosity, $[\eta]$, measured in tetrahydrofuran, was 1.61 dl/g; from a relation communicated by Dr. G. Kraus,[10] $[\eta] = 3.9 \times 10^{-4} M^{0.693}$, the viscosity-average molecular weight was estimated to be 1.67×10^5. According to the estimate of entanglement spacing from the compliance of the plateau zone[2] ($M_e = 3550$), it should have an average of about 45 entanglement loci per molecule. The density was found to be 0.885 g cm^{-3}.

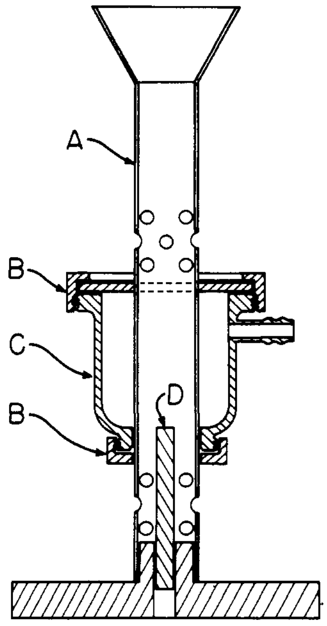

Figure 1. Irradiation vessel: A, stainless steel cylinder, inside and outside diameters 1.91 and 2.06 cm; B, sample compartment seals with O rings; C, housing of sample compartment; D, stop for source rod.

Sample Preparation. Films with a thickness of about 0.05 cm were cast on cellophane from 5% solutions in benzene. Rectangular strips about 4 cm long and 0.6 cm wide were cut with parallel knives, and provided with fiducial marks for length determinations. Before irradiation, the strips were left in a hanging position for at least 36 hr in a vacuum oven at room temperature and the unstretched length (l_i) was measured with a cathetometer to $\pm 10^{-3}$ cm. After being conditioned for about 15 min in a cold room at 2 ± 2°, the sample was stretched by a suspended weight and subsequently rolled onto the stainless steel cylinder of the irradiation vessel shown in Figure 1. The assembly was then placed in an ice-water bath, the sample compartment was evacuated, and the source rod was positioned inside the stainless steel cylinder. The holes in the cylinder should allow some circulation of bath liquid between the source rod and the cylinder. When purchased, the source was about 1000 Ci but by the time of these experiments it was down to about 550 Ci, corresponding to about 4 Mrad hr^{-1}. After irradiation, the length during irradiation (l_0) was measured with a flexible steel tape to $\pm 10^{-2}$ cm and the sample was allowed to retract to its state of ease at room temperature. Only one state of ease was detected, and its length (l_s) was measured with a cathetometer to about 2×10^{-3} cm after flattening out the slightly curved sample by sticking it onto a glass plate.

Control experiments were performed in which samples were held stretched for different lengths of time at 0° without irradiation. The recovery was then measured to gauge the extent of entanglement slippage during irradiation. A small permanent set of about 1.5%/hr of stretching without irradiation was observed for times up to 4 hr, when the maximum extension ratio was about two.

Stress-Strain Measurements. Simple elongation stress-strain measurements were made on the irradiated samples by suspending weights and again determining the distance between fiducial marks with a cathetometer to $\pm 10^{-3}$ cm. For nearly all the samples, the maximum extension ratio relative to the state of ease was kept below 1.2. The time to reach equilibrium was less than three days for irradiation times of 4 hr or longer whereas it could be several weeks for samples irradiated for only 1 hr. The modulus E_s was obtained from a plot of fl^2 *vs.* l^3, where f is the force and l is the length; to the approximation of neo-Hookean elasticity, the slope of this plot is $A_sE_s/3l_s$, where A_s is the cross-sectional area and l_s is the length in the state of ease. The area A_s was determined by two different methods—as w_st_s, where the width, w_s, is measured with a cathetometer, and the thickness, t_s, is measured between microscope slides with a micrometer screw; and as $m/l\rho$, where m is the mass, l is the length of a cut-off center portion of the sample, and ρ is the density. The latter method is the more accurate.

---

[9] J. D. Ferry, *Prelim. Rept., ARPA Mater. Summer Conf.*, 1, 327 (1971).

[10] G. Kraus, private communication.

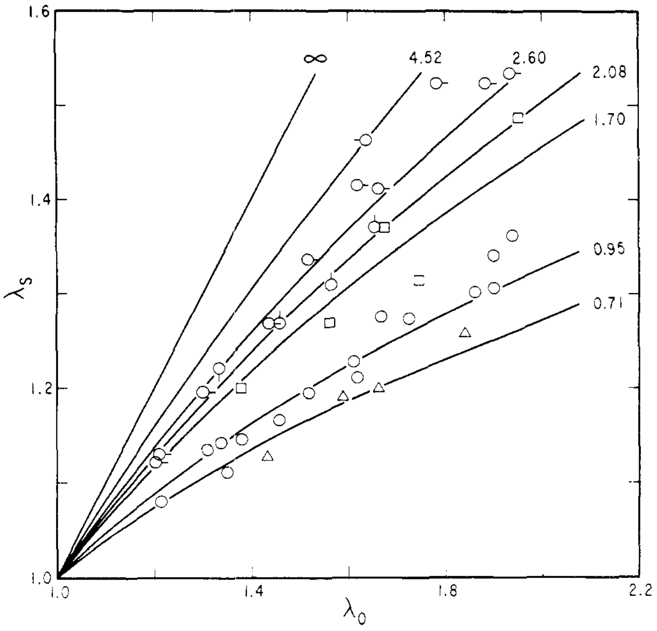

Figure 2. Extension ratio, λ_s, as state of ease plotted against extension ratio λ_0 during irradiation, for different times of irradiation in hr: △, 1.0; ○, 1.5; □, 2.0; ό, 3.0; ○-, 4.0; ϙ, 4.5; -○, 5.0. Curves drawn from eq 3 with values of ν_x/ν_N as shown.

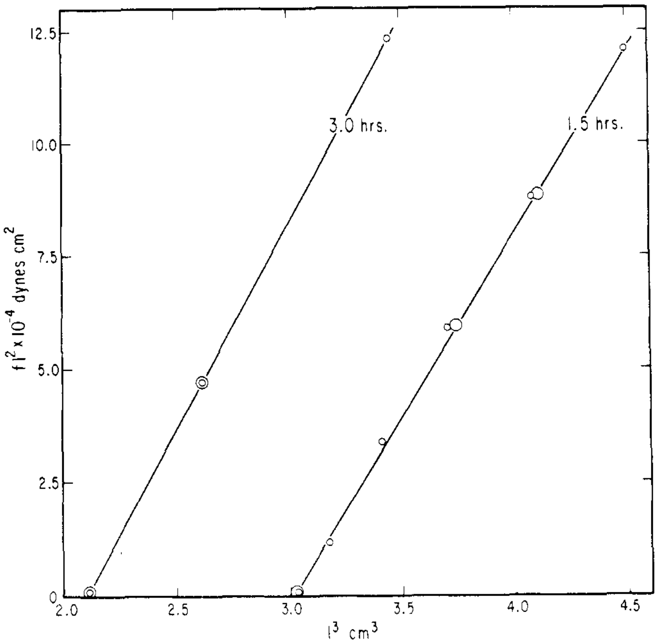

Figure 3. Stress-strain curves for samples irradiated for 3.0 and 1.5 hr, respectively, plotted as fl^2 *vs.* l^3; small circles for increasing strain; large circles for subsequent decrease of strain.

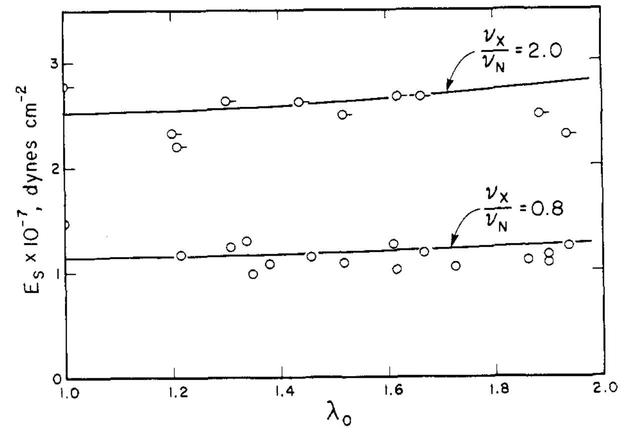

Figure 4. Young's modulus, E_s, plotted against the extension ratio during irradiation, λ_0, for two different irradiation times: ○, 1.5 hr; ○-, 4.0 hr. Normalized curve shapes are calculated from equations 2 and 3 with values of ν_x/ν_N as indicated. Intercepts are 1.14×10^7 and 2.52×10^7 dyn cm^{-2}.

Swelling. Measurements of equilibrium swelling in *n*-heptane were made at 23° on most of the samples in their states of ease, to check for swelling anisotropy and to make an indirect determination of modulus for comparison with stress-strain results. The swelling anisotropy, κ, is defined as

$$\kappa = \frac{l_r - (v_r/l_r)^{1/2}}{l_r} \qquad (4)$$

where l_r is the ratio of the lengths between fiducial marks in the swollen and unswollen states, taken in the direction of stretch, and v_r is the swelling ratio, *i.e.*, the ratio of the volume of the swollen network to the volume of the unswollen network. (It should be noted that these ratios were defined differently in a study by Berry, Scanlan, and Watson.[11]) The lengths were determined by a cathetometer with the sample positioned between microscope slides, completely surrounded by solvent in case of the swollen sample. The volumes were determined by weighing, assuming additivity of volumes of polymer and solvent as is commonly done. The solvent density was taken as 0.681 g cm^{-3}. A positive anisotropy means that the polymer has swollen more in the direction of stretch than in the perpendicular directions.

Young's modulus was calculated indirectly from the swelling by the Flory equation[12]

$$E_{ss} = \frac{-3RT[\ln(1 - v_2) + v_2 + \chi_1 v_2^2]}{V_1(v_2^{1/3} - v_2/2)} \qquad (5)$$

where $v_2 = 1/v_r$ is the volume fraction of polymer in the swollen network, V_1 is the molar volume of the solvent and χ_1 is the polymer-solvent interaction parameter which for a 1,2-polybutadiene of this microstructure is calculated[10] as $\chi_1 = 0.39 + 0.26v_2$.

Results

Extension Ratios. Figure 2 shows the extension ratio in the state of ease, $\lambda_s = l_s/l_i$, plotted against the extension ratio during irradiation, $\lambda_0 = l_0/l_i$, for irradiation times from 1 to 5 hr. A few of the points appeared in an earlier publication.[7] For each experimental point, ν_x/ν_N was calculated from eq 3 and for each irradiation time the average of all the ν_x/ν_N values was used to calculate theoretical curves from eq 3. They are shown as solid lines in Figure 2. It can be seen that except for the 2-hr irradiations the theoretical curves (which are derived for two sets of *permanent* cross-links) are followed quite well for elongations during irradiation ranging from 20 to 100%.

Moduli from Stress-Strain Measurements. For about one-third of the samples, experimental points were obtained for several different weights as shown for 1.5-hr irradiation in Figure 3. Straight lines within experimental error in accordance with neo-Hookean elasticity were obtained in all cases, so because of the long time required to reach elastic equilibrium, only 5 points were obtained for each of the other samples, with checks in sequence as shown for 3.0-hr irradiation in Figure 3.

Young's moduli for 1.5- and 4.0-hr irradiations are shown in Figure 4. Normalized curve shapes, expressed as $E_s/[E_0(1 + \nu_x/\nu_N)]$, were calculated from eq 2 and 3 with $\nu_x/\nu_N = 0.8$ and 2.0 for 1.5- and 4.0-hr irradiations, respectively. These values were obtained by averaging the values of ν_x/ν_N at small extension ratios. However, it is not important to estimate the values of ν_x/ν_N accurately for this purpose since the normalized curve shapes are

---

(11) J. P. Berry, J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, 52, 1137 (1956).

(12) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ Press, Ithaca, N. Y., 1953, p 580.

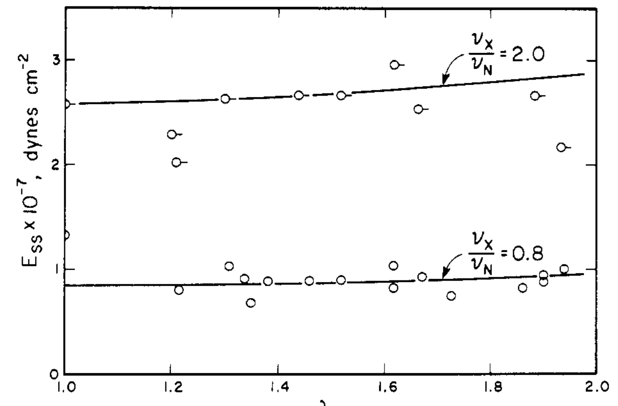

Figure 5. Young's modulus, E_{ss}, calculated indirectly from equilibrium swelling plotted against the extension ratio during irradiation, λ_0, for two different irradiation times: O, 1.5 hr; O-, 4.0 hr. Normalized curve shapes are calculated from eq 2 and 3 with values of ν_x/ν_N as indicated. Intercepts are 0.84 × 10^7 and 2.58 × 10^7 dyn cm^{-2}.

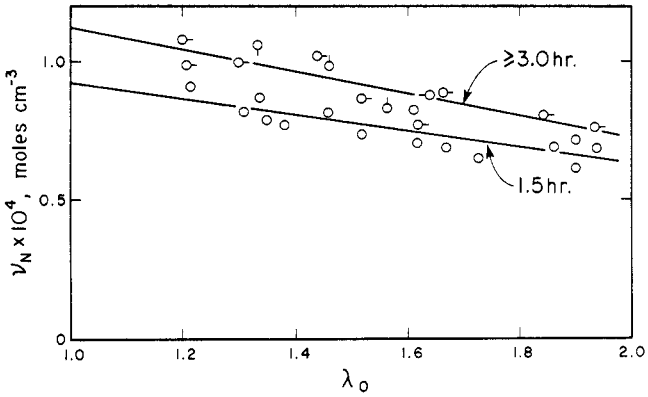

Figure 6. Concentration of elastically effective strands terminated by entanglements, ν_N, plotted against extension ratio during irradiation, λ_0, for different irradiation times in hours; O, 1.5; Ȯ, 3.0; O-, 4.0; ϙ, 4.5; -O, 5.0. The straight lines are least-squares fits with slopes of 0.30 and 0.40 × 10^{-4} mol cm^{-3} and ordinate intercepts of 0.92 and 1.12 × 10^{-4} mol cm^{-3} for irradiation times of 1.5 hr and greater than 3.0 hr, respectively.

very insensitive to ν_x/ν_N in this range. The calculated curves are horizontal for small values of λ_0, *i.e.*, first and second stage strands simply add. For larger values of λ_0, the curves turn upward so the composite network appears stiffer than a network with the same concentration of strands introduced in the isotropic state. The curves are drawn by making best fits to the points at small values of λ_0, disregarding the two points at λ_0 = 1.2 in case of 4.0-hr irradiation.

Moduli from Equilibrium Swelling. Young's modulus, E_{ss}, obtained indirectly from equilibrium swelling by eq 5 is plotted against λ_0, the extension ratio during cross-linking, for two different irradiation times in Figure 5. The curves are drawn by making best fits to the points at small values of λ_0, as in Figure 4, disregarding the two points at λ_0 = 1.2 in case of 4.0-hr irradiation. The moduli obtained from swelling and stress-strain are the same within experimental error for 4.0-hr irradiation but they are quite different for 1.5-hr irradiation with intercepts of 0.84 × 10^7 and 1.14 × 10^7 dyn cm^{-2} for swelling and stress-strain, respectively. Possibly the expression used to calculate χ_1 does not apply to these samples.

Concentration of Strands Terminated by Entanglements. The concentration of elastically effective network strands terminated by entanglements, ν_N, is plotted against the extension ratio during irradiation, λ_0, for several different irradiation times in Figure 6. The points for 3.0 hr and longer are grouped together; the points for 1.5 hr are considerably lower. Apparently a significant fraction of the entanglements has not become trapped at 1.5-hr irradiation but most are trapped by 3.0 hr. Clearly, ν_N decreases with increasing λ_0 (or, alternatively, increasing λ_s). Possible reasons for this dependence are discussed below. A plot of ν_N *vs.* λ_s (not shown) conforms roughly to the relation $\nu_N = C/\lambda_s$; similarity to the term C_2/λ in the familiar Mooney–Rivlin equation[13] is suggestive.

Extrapolations to zero extension, *i.e.* $\lambda_0 = \lambda_s$ = 1.0, either linearly against λ_0 as in Figure 6 or against λ_s, give an average value of $\nu_N \cong 1.2 \times 10^{-4}$ mol cm^{-3} for longer irradiation times. This is lower than the concentration of elastically effective strands terminated by entanglements which is determined by linear viscoelastic measurements in the plateau zone,[2] $\nu_e = 2.5 \times 10^{-4}$ mol cm^{-3}.

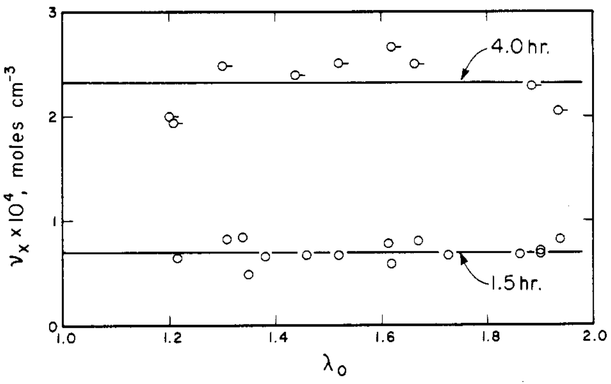

Figure 7. Concentration of elastically effective strands terminated by chemical cross-links, ν_x, plotted against the extension ratio during irradiation, λ_0, for two different irradiation times as indicated. Horizontal lines represent arithmetic averages of 0.70 and 2.32 × 10^{-4} mol cm^{-3} for 1.5- and 4.0-hr irradiation, respectively.

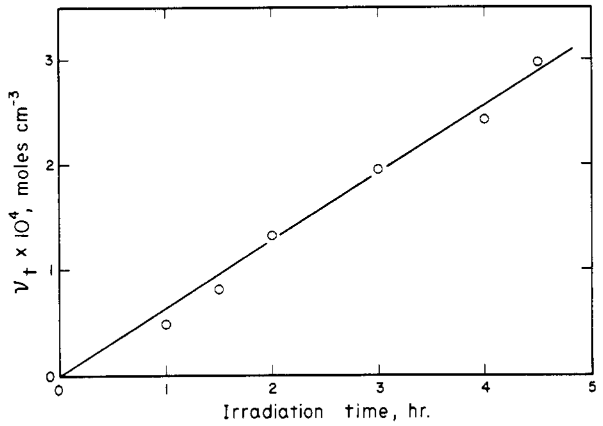

Figure 8. Total number of strands terminated by chemical cross-links, ν_t, including elastically ineffective chain ends, plotted against irradiation time in hours.

Concentration of Strands Terminated by Chemical Cross-Links. Figure 7 shows the concentration of elastically effective strands terminated by chemical cross-links, ν_x, plotted against λ_0 for two different irradiation times. Unlike ν_N which clearly decreases with increasing λ_0, ν_x seems to be independent of λ_0, at least for 1.5-hr irradiation. For 4.0-hr irradiation, there may be a maximum but the data points are insufficient to establish this. The solid lines represent arithmetic averages.

If one can assume that the average functionality of the cross-links is constant for the range of irradiation times

---

(13) L. R. G. Treloar, "The Physics of Rubberlike Elasticity," 2nd ed, Oxford Univ., Oxford, 1958, p 165.

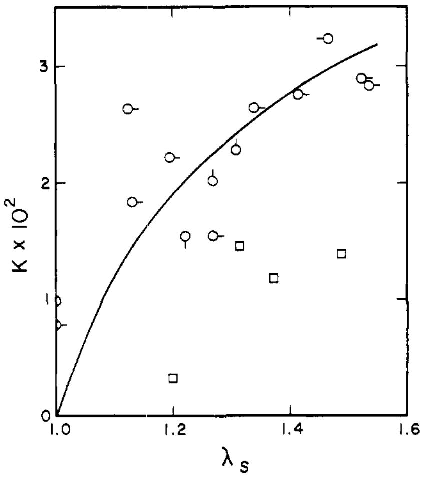

Figure 9. Anisotropy of equilibrium swelling in *n*-heptane calculated by eq 4, plotted against extension ratio in the state of ease, λ_s, for different irradiation times; □, 2.0; ό, 3.0; o-, 4.0; ϙ, 4.5; -o, 5.0 hr.

used in this study, then the total concentration of strands terminated by chemical cross-links, ν_t, should be proportional to the irradiation time. This may be calculated as the sum of the concentration of elastically effective strands terminated by chemical cross-links plus two elastically ineffective strands per molecule

$$\nu_t = \nu_x + 2\rho/\bar{M}_n \qquad (6)$$

where $\bar{M}_n$ is the number-average molecular weight of the polymer. In Figure 8, average values of ν_t are plotted against irradiation times, and found to be approximately proportional as expected.

Swelling Anisotropy. Figure 9 shows the anisotropy, κ, observed for the equilibrium swelling relative to the state of ease for several different irradiation times, plotted against λ_s. The anisotropy is positive which means that there is less resistance to expansion in the direction of stretch during irradiation than in the perpendicular directions. Irradiation times of 3.0 hr and longer seem to give approximately the same anisotropy whereas times of 2.0 hr and less give considerably less anisotropy. The points for 1.5 hr were scattered on both sides of the line for zero anisotropy and are not shown in the plot. Disregarding the 4.0-hr point at $\lambda_s = 1.12$, it seems that the anisotropy increases with increasing λ_s; not only is the swelling greater in the already stretched direction than in the perpendicular directions, but the difference actually increases with increasing extension ratio.

Discussion

Existence of an Entanglement Network at Elastic Equilibrium. The results presented in Figure 2 for λ_s as a function of λ_0 show that these networks for a considerable range of extension ratios behave very similarly to the ideal composite networks treated by the theories of Flory and others. Since the two-network hypothesis by Andrews, Tobolsky, and Hanson[14] was well substantiated in the work by Berry, Scanlan, and Watson,[11] this means that the originally uncross-linked polymer of high molecular weight after cross-linking in the strained state provides an equilibrium restoring force with a strain dependence very close to that of an ideal Gaussian network. We believe that this should remove all doubt about the existence of a so-called entanglement network in uncross-linked polymers of high molecular weight.

Concentration of Strands Terminated by Entanglements. In the absence of chain scission and entanglement slippage it should be expected that an increased number of entanglements would become trapped with increased degree of cross-linking until practically all are trapped. Thus, the concentration of elastically effective strands terminated by entanglements, ν_N, should approach an asymptotic value at long irradiation times. This is found as shown in Figure 6 where irradiation times of 3.0 hr and longer seem to give the same values of ν_N. If there were considerable chain scission, ν_N should go through a maximum when plotted against irradiation time. No maximum is apparent up to 5 hr, and it is not feasible to go much beyond, since the molecular weight of elastically effective strands terminated by chemical cross-links is then less than 2200 and Gaussian network approximations are not applicable (the material becomes leathery instead of rubbery).

The values of ν_N found by this method are in a realistic range although the value extrapolated to zero extension (1.2×10^{-4} mol cm^{-3}) is only about one-half the value found from linear viscoelastic measurements in the plateau zone. The difference could be caused by a number of factors such as entanglement slippage before entrapment between chemical cross-links, chain scission, and a lower elastic efficiency of entanglements at elastic equilibrium. Results to be published later from samples irradiated at temperatures closer to T_g indicate that entanglement slippage certainly plays a role. The other two possible factors mentioned above will be discussed in a later publication.

The observed decrease of ν_N with increasing λ_0 as shown in Figure 6 could perhaps be explained if entanglement slippage and/or chain scission take place since the effect of these two processes might increase with increasing extension ratio. Further measurements are in progress to explore these possibilities.

Alternatively, the elastic restoring force of an entanglement network may have a different strain dependence from that of a network of strands terminated by chemical cross-links. This could happen if either the number of elastically effective strands terminated by entanglements or else their elastic effectiveness were strain dependent. The forces of the two networks are balanced in the state of ease where the extension ratio for the entanglement network is λ_s; the approximate inverse proportionality of ν_N to λ_s is the same functional form as that of the C_2 term in the Mooney-Rivlin equation. Steiner[5] also finds that the concentration of what he calls physical network strands in his analysis depends on strain in a manner which can be described satisfactorily by the C_2 term.

If the retractive forces of the entanglement network and the network formed in the second stage have different strain dependences, we should expect to see elastic and optical anisotropy in the state of ease. Swelling anisotropy is shown in Figure 9; the samples at swelling equilibrium have expanded more in the already stretched direction than in the perpendicular directions in agreement with a decreasing relative elastic efficiency of entanglements with increasing extension ratio in the state of ease. This is different from results reported for natural rubber composite networks which were made by introducing chemical cross-links in both the isotropic and strained states. At swelling equilibrium these networks showed more expansion in the perpendicular directions.[11,15,16] A decreasing elastic efficiency of entanglements with increasing exten-

---

(14) R. D. Andrews, A. V. Tobolsky, and E. E. Hanson, *J. Appl. Phys.*, **17**, 352 (1946).

(15) A. Greene, K. J. Smith, Jr., and A. Ciferri, *Trans. Faraday Soc.*, **61**, 2772 (1965).

(16) K. J. Smith, Jr., and R. J. Gaylord, *J. Polym. Sci., Part A-2*, **10**, 283 (1972).

sion ratio should also show up in Figures 4 and 5 by making the experimental points fall more and more below the theoretical line with increasing extension ratio during irradiation, more so for Young's modulus measured directly than for the modulus from swelling since the latter corresponds to expansion in all three directions. There is unfortunately too much scatter in the data of Figures 4 and 5 to substantiate this prediction.

Further work is in progress, including birefringence measurements to study anisotropy in the state of ease, stress relaxation during irradiation to measure whether chain scission plays a role, and studies of the effects of polymer molecular weight, irradiation temperature and dose rates, which should throw light on the question regarding possible entanglement slippage before entrapment between chemical cross-links.

Acknowledgments. This work was supported in part by grants from the National Science Foundation and the Army Research Office-Durham. We are greatly indebted to Professor John E. Willard for making the ^{60}Co source available for this study. Preliminary calculations were supported by the ARPA Materials Research Council Contract No. DAHC 15-71-C-0253 with the University of Michigan.

Ion Clustering and Viscoelastic Relaxation in Styrene-Based Ionomers. III. Effect of Counterions, Carboxylic Groups, and Plasticizers

M. Navratil and A. Eisenberg*

Department of Chemistry, McGill University, Montreal, Canada. *Received February 5, 1973*

ABSTRACT: The effect of the nature of the counterion on the viscoelastic relaxation and glass transition behavior is evaluated for styrene ionomers. It is shown that neither the ion size nor valence play a major role in influencing the viscoelasticity of ion-containing polymers. The effect of the un-ionized carboxylic groups is also investigated and results indicate that the introduction of such groups accelerates the rate of viscoelastic relaxation. Finally, the effect of hydrophilic and organophilic plasticizers on the width of stress relaxation master curves is evaluated. The results of these studies are consistent with the previously proposed hypothesis that below *ca.* 6 mol % of the salt the ions exist in a form of simple multiplets, while above that concentration more extensive ion clustering is encountered.

Despite the effort devoted to the investigation of ion-containing polymers during the past decade, several major questions concerning the state of aggregation of the ions and their influence on the viscoelastic properties remain unanswered.

In previous publications of this series[1,2] it was shown that ion concentration has an important effect on viscoelasticity and morphology of styrene–sodium methacrylate (NaMA) copolymers. The results presented were in agreement with the hypothesis that below *ca.* 6 mol % of the salt, the ions exist in a form of simple multiplets which act as temporary cross-links, and which slow down the primary diffusional relaxation mechanism; above that concentration, more extensive ion clustering is encountered. In this publication, results of some additional studies of styrene-based ionomers are presented. These address themselves to the following questions. (a) Since the ion multiplets act as cross-links of finite lifetime, how is the stability of these multiplets affected by the nature of the counterion? (b) Is the critical ion concentration above which the time–temperature superposition breaks down, also a function of the nature of the counterion? If so, what is the correlation? (c) How does the presence of un-ionized carboxylic groups affect the structure and stability of the ion multiplets and/or the ionic clusters? (d) How would various types of plasticizers (*i.e.*, hydrophilic or hydrophobic) influence the mechanical properties other than by a change in T_g? These questions can be briefly answered as follows. (a) The fact that ions are present in polymeric materials appears to be of primary importance, while the nature of the counterion is not. However the ion size seems to have some effect on the stability of the ion multiplets in the region of low ion concentration. The large Cs$^+$ ions yield cross-links of somewhat lower stability than smaller Na$^+$ ions. (b) No change of the critical ion concentration with the nature of the counterion has been observed. (c) The presence of -COOH groups in partially neutralized polymers appears to suppress ion clustering and to decrease the effectiveness of the ionic multiplets as cross-links. Completely neutralized polymers, which are not subject to time–temperature superposition, remain nonsuperposable in their partially neutralized state even at intermediate degrees of neutralization (40%). If two copolymers contain the same amount of ions but one of them contains additional -COOH groups, then stress relaxation is faster in the partially neutralized copolymer, indicating a supporting role of -COOH groups in ion hopping or in weakening of the electrostatic interaction within the ion aggregates. (d) A narrowing of the stress relaxation spectrum was observed in materials plasticized by dimethyl sulfoxide (Me$_2$SO). Organophilic plasticizers such as dioctyl phthalate (DOP) exhibit the same effect as they have on pure polystyrene.[3]

Owing to the recent appearance of two reviews dealing with the properties of ion-containing polymers[4,5] and to the fact that most of the papers relevant for this investigation were discussed in our previous publication[2] no discussion of the literature is attempted here; however, four papers which have a direct bearing on the present work are mentioned briefly. Fitzgerald and Nielsen[6] did a pre-

---

(1) A. Eisenberg and M. Navratil, *J. Polym. Sci., Part B*, **10**, 7, 537 (1972).

(2) A. Eisenberg and M. Navratil, *Macromolecules*, **6**, 604 (1973).

(3) L. L. Chapoy and A. V. Tobolsky, *Chem. Scr.*, **2**, 44 (1972).

(4) A. Eisenberg, *Advan. Polym. Sci.*, **5**, 59 (1967).

(5) E. P. Otocka, *J. Macromol. Sci. Rev. Macromol. Chem.*, **5**, 275 (1971).

(6) W. E. Fitzgerald and L. E. Nielsen, *Proc. Roy. Soc., Ser. A*, **282**, 137 (1964).