Entangled Chain Structure Trapped in a Styrene–Butadiene Random Copolymer by Cross-Linking in Simple Extension

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ABSTRACT: Rubber networks were prepared by cross-linking linear styrene–butadiene random copolymer (67% styrene content) with γ-radiation. Before cross-linking, the polymer was stretched in simple extension, allowed to relax at constant strain and temperature for a controlled time, and then quenched 20 °C below T_g and maintained at this temperature during cross-linking. Upon warming above T_g, the equilibrium length was intermediate between the stretched and unstretched lengths and was describable as the result of additive contributions from the cross-link and trapped entanglement networks. The fractions of trapped unrelaxed entanglements T_e and trapped relaxed entanglements $T_{e,r}$ were estimated and compared with the Langley theory. For minimal terminal zone relaxation before quench, T_e agreed rather well with the Langley theory and $T_{e,r}$ was zero. With increasingly long terminal zone relaxation before quench, T_e increased and $T_{e,r}$ became finite and increased. This behavior is consistent with the terminal mechanism of relaxation in the tube theory of Doi and Edwards. These experiments confirm the presence of permanently trapped entangled chain structure (or equivalent trapped topological restraints), in agreement with earlier extensive work on 1,2-polybutadiene.

Uncross-linked, linear, amorphous polymers of sufficiently high molecular weight characteristically exhibit a zone on the time (or frequency) scale of relatively slow relaxation where the magnitude of the modulus is similar to that typical of a lightly cross-linked polymer.[1] This magnitude, E_N^0, is constant for a given undiluted polymer at fixed temperature and pressure, while the width of the plateau depends strongly on the molecular weight. Topological constraints, traditionally referred to as entanglements, are probably the origin of the phenomenon;[2,3] they are associated with the fact that the polymer chains, as they diffuse, can slide by one another but cannot cut across one another. The concept has been widely accepted for many years that, when permanent cross-links are introduced, the entangled chain structure (or some portion of it) should be trapped. Such trapped entangling should then contribute significantly to the free energy of deformation of the cross-linked material even at equilibrium, raising it significantly higher than could be explained from the presence of cross-links alone. Recent evidence for this view is provided by combining mechanical measurements with statistical analyses of sol–gel fractions for networks prepared both by radiation cross-linking[4-7] and by end-linking oligomeric chains;[8] it is also provided by extensive experiments on networks cross-linked in strained states,[9-22] although the existence of trapped entangling is still disputed.

A series of earlier papers from this laboratory[9-18] reported experiments conducted upon networks of 1,2-polybutadiene cross-linked in simple extension in which the elastic effects of cross-links and of structure in the originally undeformed uncross-linked polymer were in opposition. The states of ease of such strips and their stress–strain behavior in extension past the state of ease were quantitatively describable by a two-network model where the trapped structure was identified with chain entangling in the originally uncross-linked polymer which was trapped. For 1,2-polybutadiene cross-linked in simple shear and equibiaxial extension as well, similar results have been reported by Kramer and co-workers;[19] but all experiments on networks cross-linked in strained states have been made with this single polymer.

The present paper reports further experiments on a different polymer, a styrene–butadiene random copolymer with a styrene content of 67%. The results corroborate those of the earlier papers, with the conclusion that the existence of trapped entangled chain structure is confirmed.

Theory

Polymers with entanglement and cross-link effects in opposition display elastic behavior that can be described using theories for the elastic behavior of polymers cross-linked in two stages, first in the isotropic state and then again in a strained state. The free energy of deformation of such materials has long been interpreted classically[23-26] as the sum of contributions from two independent virtual networks; the first network has as rest length the dimensions of the isotropic polymer, while the second has as rest length the dimensions of the polymer during the course of cross-linking in the strained state. In the experiments described below, the role of the classical first-stage cross-links is played by entanglements in the originally undeformed uncross-linked polymer which were trapped by the cross-linking.

As in previous work,[10-18] the cross-link network, under compression in the state of ease, is assumed to be neo-Hookean (deviations from neo-Hookean elasticity for compressed networks are known to be small[27]), but deviations from neo-Hookean elasticity of the entanglement network while strained in simple extension are taken into account. The phenomenological equation of Blatz, Sharda, and Tschoegl[28] (BST) is used here to describe the entanglement network. The elastic free energy of deformation is

$$A_{el} = (\lambda_x^n + \lambda_y^n + \lambda_z^n - 3)2E/3n \qquad (1)$$

where λ_x, λ_y, and λ_z are the principal stretch ratios with respect to the isotropic state, E is a parameter with the dimensions of a modulus that is close in value to the small-strain Young's modulus, and n is a dimensionless parameter with value between 0 and 2. For $n = 2$, eq 1 is the usual neo-Hookean relationship. Equation 1 provides a more realistic estimate of the small-strain modulus than the Mooney–Rivlin equation,[27] which was used to interpret the earlier series of experiments,[9-18] and unlike the Mooney–Rivlin equation, it describes behavior in deformations other than simple extension. The stress σ is for polymers with Poisson's ratio negligibly different from one-half that are stretched or compressed uniaxially

$$\sigma = (\lambda^n - \lambda^{-n/2})2E/3n \qquad (2)$$

Here λ is the stretch ratio in the axial direction. Time-dependent values of E and n can be calculated by fitting eq 2 to the observed stress relaxation over a range of strains of the uncross-linked polymer in simple extension.

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Similar equations describe polymers cross-linked in the strained state at stretch ratio λ_0 after having been quenched below the glass transition temperature (T_g) at a time t_R after having been stretched. The parameter n for the trapped entanglement network is assumed to have the value for the uncross-linked polymer at the time of quench. Then the equilibrium stress σ_N associated with the trapped entanglement network at each stretch ratio λ is described by eq 2 with a single additional parameter, the modulus E_N. The equilibrium stress σ_X associated with the cross-link network at each stretch ratio λ/λ_0 (stretch ratio with respect to the dimensions during cross-linking) is also described by eq 2, with $n = 2$ and the modulus E_X. The observed stress σ is

$$\sigma = \sigma_N + \sigma_X \tag{3}$$

with

$$\sigma_N = (\lambda^n - \lambda^{-n/2})2E_N/3n \tag{4}$$

$$\sigma_X = [(\lambda/\lambda_0)^2 - \lambda_0/\lambda]E_X/3 \tag{5}$$

Since σ_N are equal and opposite at the polymer rest length (stretch ratio λ_s)

$$E_X/E_N = 2(\lambda_s^n - \lambda_s^{-n/2})/[\lambda_0/\lambda_s - (\lambda_s/\lambda_0)^2]n \tag{6}$$

By means of eq 3–6, the magnitudes of E_N and E_X can be calculated from measurement of λ_0, λ_s, and the stress when a cross-linked strip is stretched past its rest length.

Here we follow Kramer[19,22] in reporting network moduli rather than the densities of trapped entanglement and cross-link network strands which were calculated in previous work[9–18] from the classical equation of rubberlike elasticity[27] and also in replacing the word "entanglement" as much as possible by less specific phrases which are intended to avoid the implication that entanglement interactions are restricted to specific points along the polymer chains.

If the modulus $E(t)$ of the uncross-linked polymer in the terminal zone is associated with unrelaxed entangling, the fraction T_e of entangled chain structure in the originally uncross-linked polymer which was trapped by the cross-linking is

$$T_e = E_N/E(t = t_R) \tag{7}$$

Entangled chain structure whose undeformed state is the stretched polymer is trapped as well, if substantial terminal zone relaxation is allowed before quenching the polymer and irradiating it. For this case eq 3–7 still apply, except that the former σ_X and E_X now include contributions σ_{NR} and E_{NR} from the trapped relaxed entangling in addition to σ_X and E_X from the cross-links. E_X can be found from parallel experiments where little relaxation takes place before quench. It is assumed that entangled structure is either unrelaxed or relaxed, the sum of the interactions which result in entanglement behavior remaining constant as terminal zone relaxation proceeds; in terms of entanglement density, the total number of entanglements remains constant. The fraction $T_{e,r}$ of relaxed entangled chain structure trapped by the cross-links is then

$$T_{e,r} = E_{NR}/(E_N^0 - E_N) \tag{8}$$

Here E_N^0 is the characteristic modulus of the plateau zone that precedes the terminal zone on the time scale.

Experimental Section

Polymer. A styrene–butadiene (SBR) random copolymer prepared anionically by low-temperature alkyllithium initiation, using TMEDA as microstructure modifier and randomizing agent, was kindly prepared by Dr. D. N. Schulz and provided by Dr. Georg G. G. A. Böhm, both of the Firestone Tire & Rubber Co. The styrene content was 67% and the butadiene microstructure was cis:trans:vinyl = 3:23:74. T_g was 20 °C, M_n was 84 000, and M_w/M_n was 1.14. About 0.4% antioxidant was present. The WLF coefficients[29] $c_1^0 = 10.28$ and $c_2^0 = 78.78$ at 40.0 °C were kindly provided from measurements on a Rheometrics mechanical spectrometer of the storage and loss shear moduli, G' and G'', by Dr. Carl R. Taylor of Bell Laboratories. The plateau modulus was estimated,[1] both from the maximum in G'' and the inflection of $G(t)$ calculated from G' and G'', to be $E_N^0 = 1.4 \times 10^7$ dyn/cm^2.

Sample Preparation. Because the low content of vinyl polybutadiene rendered the polymer relatively unsusceptible to cross-linking by γ-radiation, 2% by weight of the cross-linking promoter pentachlorobenzene was milled into the polymer in the Firestone laboratories and the mixture was molded to a sheet about 1.2 mm thick. The intrinsic viscosity, measured in tetrahydrofuran at 25.0 °C, was 0.777 dL/g after milling and 0.801 dL/g before milling; the extent of degradation from milling was apparently minimal. The density of the polymer containing promoter was 0.970 g/cm^3 at 30 °C and was estimated at other temperatures with a volume thermal expansion coefficient of 6.0×10^{-4} K^{-1}. As discussed below, a control experiment showed that the promoter did not materially affect the polymer except for speeding up the cross-linking process.

To cross-link the polymer by γ-radiation while it was stretched, the procedure developed in earlier experiments[9–18] was used with minor modifications. Strips cut from the film 0.40 cm wide and about 5 cm long were stretched at 30 °C (noted to 0.2 °C) and rolled onto a steel band which itself was wound onto a steel cylinder (band outer radius, 1.90 cm). If substantial relaxation was to be allowed, the mounted strip was kept in an air thermostat for the desired time. Otherwise the steel cylinder was immediately installed inside a sealable vessel and immersed within an ice/water bath 120 s after the stretch began. Stretching took less than 20 s. The quenched assembly was evacuated after being transferred to a bath regulated at 0 °C inside the irradiation chamber, and the ^{60}Co radiation source rod was positioned inside the steel cylinder. Two strips were irradiated unstretched by the same procedure except for omission of the stretching. After irradiation, still in vacuo, the strips were annealed at about 35 °C for at least 30 min to allow free radicals to react. The source strength was about 1 Mrd h^{-1}. Radiation doses were repeatable within about 10%, variation being caused by the difficulty of centering the source rod perfectly. Several of the strips were weighed before and after irradiation to check for sublimation of the promoter; no weight loss was detected.

Stretch ratios were calculated from the distances between circular fiducial marks drawn with India ink on the strips and measured before stretch and after irradiation by a traveling microscope. After irradiation, the steel band was removed from the cylinder and flattened, and the stretched length of the polymer was measured on the band. Then the sample was released and annealed at 80 °C in a dry nitrogen atmosphere for at least 30 min to attain its state of ease. It was flattened for measurement of the rest length. Four fiducial marks were used to ensure that the stretch ratio was uniform within 0.02 along a strip.

In calculating the stretch ratio that prevailed during cross-linking, it was necessary to account for the difference in stretch ratios between the inner and outer radii of the rolled strips. From the stretched length on the flattened steel band and the thickness while stretched, the length of the rolled strip at a radius halfway between its inner and outer radii was calculated. The correction usually amounted to an increase of 2.8% over the length that was measured.

Stress–Strain Measurements. Stress relaxation measurements at constant elongation on the uncross-linked polymer containing promoter, similar to those reported previously,[15,30] were made at stretch ratios $\lambda = 1.2$–1.9 at temperatures 30.0 and 40.0 °C, in order to determine the nonlinear behavior as a function of time. The instrument configuration has been described previously.[31] The force was measured directly to 0.01 g by a PL-1200-02 Mettler balance and recorded digitally vs. time by a separate printer. The results at 40.0 °C were reduced to the reference temperature of 30.0 °C using the shift factor a_T calculated from the WLF equation[29] with the parameters given above. The stresses were multiplied by $T_0\rho_0/T\rho$, where ρ is the density

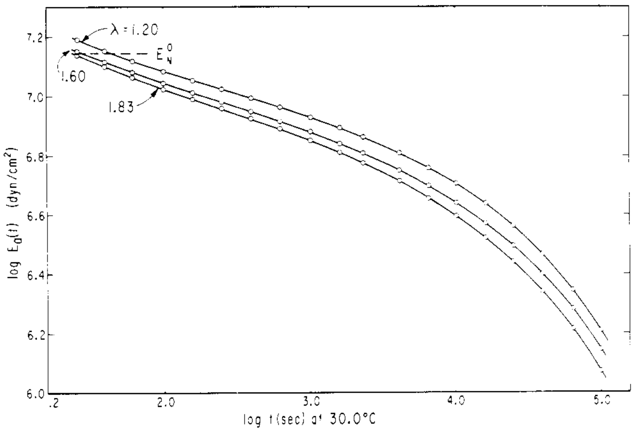

Figure 1. Apparent Young's modulus of the uncross-linked polymer plotted logarithmically against time at three stretch ratios.

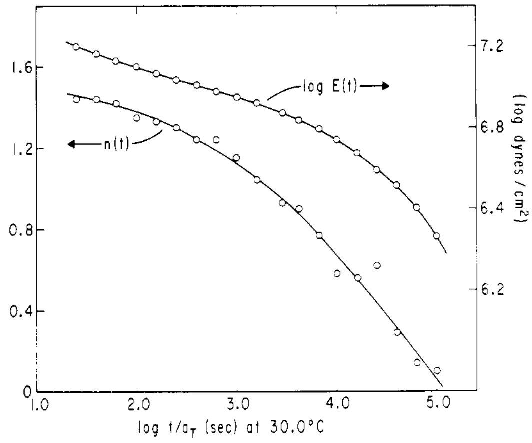

Figure 2. BST parameters $E(t)$ and $n(t)$ for the uncross-linked polymer plotted logarithmically against time in seconds reduced to 30.0 °C.

at the temperature of measurement T and ρ_0 refers to the reference temperature T_0.

Equilibrium stress–strain measurements on the cross-linked polymers were made at 80 °C using the stress relaxation apparatus in a dry nitrogen atmosphere. The isotropic length at 80 °C was estimated using the thermal expansion coefficient given above. Each end of a strip was glued to a steel clamp with a cyanoacrylate glue. The time to reach effective equilibrium was 30 min at most; samples with high degrees of cross-linking reached equilibrium more quickly. The strips tended to break at stretch ratios less than λ_0.

To check that equilibrium was reached and that significant chain scission did not take place at the elevated temperature of measurement, each strip was measured at several elongations, one of the elongations being substantially less than previous ones, and the rest length of most strips was measured again after the measurements. The results were always consistent.

Results

Nonlinear Stress Relaxation. In Figure 1, the nonlinear stress relaxation of the uncross-linked polymer in the terminal zone is shown at three stretch ratios. The results are in terms of the apparent Young's modulus, also called the reduced force,[32] defined as

$$E_a = f(t)/A_0(\lambda - \lambda^{-2}) \qquad (9)$$

Here $f(t)$ is the time-dependent force and A_0 is the original cross-sectional area calculated from the weight and length of the strip and the polymer density. If the behavior were neo-Hookean, these curves would coincide. The fit to eq 2 is shown in Figure 2. $E(t)$ is larger than $E_a(t)$ at λ = 1.20 by about 2% at the shortest times and about 13% at the longest times, the discrepancy increasing smoothly in between. (The Mooney–Rivlin estimate of the small-strain modulus gives differences almost twice as large.) The parameter $n(t)$ is near 1.4 at the shortest times and falls to near zero at the longest times. This behavior is similar to that calculated[33] from previously reported results for polybutadiene[15,30] and polyisobutylene.[34]

Table I
Characterization of Irradiated Samples

strip no.	log t_R/a_T at 30.0 °C, s	$n(t_R)$	dose, Mrd	λ_0	λ_s
1	2.1	1.37	4.1	1.441	1.114
2	2.0	1.38	7.0	1.978	1.252
3	2.1	1.37	7.0	1.655	1.168
4	2.3	1.32	7.0	1.572	1.198
5	3.0	1.14	7.0	1.394	1.144
6	3.5	0.92	7.0	1.498	1.221
7	4.0	0.66	7.0	1.416	1.235
8	4.6	0.31	7.0	1.525	1.397
9	5.0	0.06	7.0	1.411	1.349
10	1.8	1.40	10	1.438	1.161
11	2.0	1.38	14	1.505	1.202
12	2.1	1.37	20	1.554	1.237
13[a]	2.0	1.38	25	1.463	1.100
14			7.0	1	1
15			14	1	1

[a] No promoter present.

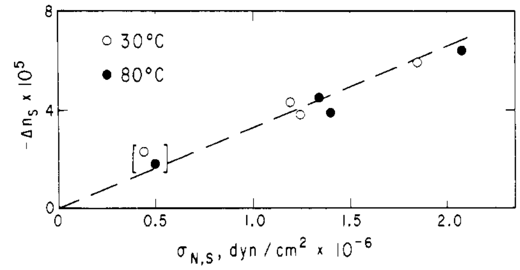

Figure 3. Birefringence in the state of ease plotted against calculated stress of the trapped entanglement network in the state of ease, at 30.0 and 80.0 °C. Points in brackets refer to a polymer strip irradiated in absence of promoter.

States of Ease. For each strip cross-linked in the strained state, Table I shows the equilibrium stretch ratio λ_s and the stretch ratio during cross-linking λ_0, as well as the relaxation time t_R before the strip was quenched (reduced to 30.0 °C in the manner described above), $n(t_R)$, and the radiation dose applied. Two strips irradiated unstretched are also listed. Note that λ_s is always substantially less than λ_0. But the longer the relaxation time before quenching (at constant radiation dose), the closer λ_s is to λ_0.

The course of retraction at 80 °C from λ_0 to λ_s was usually followed by eye. Initially the polymer strips contracted abruptly to a second state of ease less than λ_s, and thereafter they lengthened slowly. The second state of ease is a manifestation of untrapped entangling; it was predicted[9] and later observed[14] for 1,2-polybutadiene as well.

Birefringence in the State of Ease. The birefringence at 30.0 and 80.0 °C at the state of ease of several samples cross-linked in strained states is plotted in Figure 3 against $\sigma_{N,S}$, the calculated stress sustained by the trapped entanglement network at the state of ease. Here $\sigma_{N,S}$ is calculated from eq 4 with $\lambda = \lambda_s$. The instrument has been described previously.[30] There is no apparent dependence upon the temperature of measurement. The two bracketed points represent the results of a control experiment, where a polymer strip cast from distilled benzene solution in the absence of promoter was given a large radiation dose. The

Table II
Network Moduli and Trapping Factors for Strips with $\log t_R/a_T \cong 2$ and a Range of Dosage: BST Analysis

strip no.	E_N at 30 °C, dyn/cm^2 $\times 10^{-6}$	E_X at 30 °C, dyn/cm^2 $\times 10^{-6}$	T_e	$\log \gamma$
1	2.41	1.17	0.20	0.52
2	5.47	3.41	0.43	0.77
3	5.99	3.22	0.50	0.76
4	6.42	5.08	0.58	0.90
10	7.44	6.01	0.55	0.95
11	9.32	8.98	0.74	1.09
12	9.64	10.7	0.80	1.16
13[a]	4.36	1.69	0.36	0.60

[a] No promoter present.

Table III
Network Moduli and Trapping Factors for Strips with Dosage 7 Mrd and a Range of $\log t_R/a_T$: BST Analysis

$\log t_R/a_T$ at 30.0 °C	E_N at 30 °C, dyn/cm^2 $\times 10^{-6}$	$E_X + E_{NR}$ at 30 °C, dyn/cm^2 $\times 10^{-6}$	T_e	$T_{e,r}$
3.0	4.43	3.42	0.50	0.02
3.5	4.29	4.80	0.58	0.16
4.0	3.64	6.20	0.58	0.29
4.6	2.39	9.75	0.73	0.56
5.0	1.04	7.14	0.57	0.30

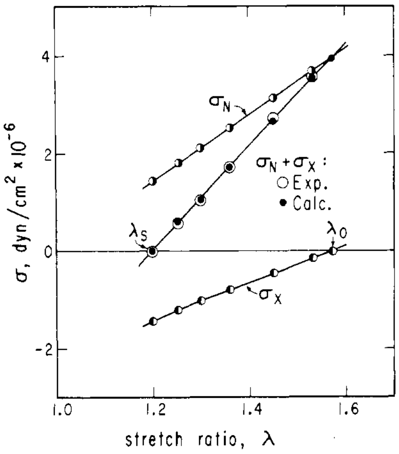

Figure 4. Stress–strain curves for strip 4 calculated for trapped entanglement network, cross-linked network, and their sum; also experimentally measured (open circles, experimental; filled circles, calculated) at 80 °C.

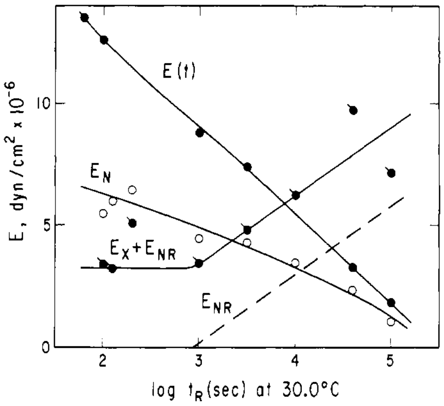

Figure 5. Young's moduli reduced to 30 °C and plotted against $\log t_R/a_T$ in seconds. Modulus of uncross-linked polymer, $E(t)$. Moduli of cross-linked polymers: trapped unrelaxed entangled chain structure, E_N; trapped relaxed entangled chain structure, E_{NR}; cross-links plus trapped relaxed entangled chain structure, $E_X + E_{NR}$.

residual birefringence is negative and approximately proportional to $\sigma_{N,S}$, just as was found for polybutadiene.[15] The presence of birefringence in the state of ease indicates that although the net stress is zero, the cross-linked polymer is anisotropic.

Moduli from Stress–Strain Measurements. Young's moduli E_N (trapped entanglement network) and E_X (cross-linked network) were inferred by means of eq 3–6 from the stress–strain measurements past the state of ease. Table II lists the results for strips quenched soon after stretch, when minimal terminal zone relaxation had taken place; the radiation dose was varied in these experiments. Table III lists further results for experiments where the radiation dose was always 7 Mrd and increasing amounts of terminal zone relaxation were allowed before quench; here E_X is replaced by $E_X + E_{NR}$, as described in the Theory section. In Tables II and III, E_X, E_N, and $E_X + E_{NR}$ are the average of these moduli calculated at several stretch ratios; the discrepancies were small, as illustrated in the Discussion section. Of the strips cross-linked unstretched, the small-strain apparent Young's moduli 1.08 $\times 10^7$ dyn/cm^2 of strip 14 and 1.75 $\times 10^7$ of strip 15 differ by factors of 0.92 and 1.05, respectively, from the average $E_X + E_N$ of the strips cross-linked in strained states which sustained the same radiation doses.

An example of the excellent agreement with experiment is shown in Figure 4, where calculated and observed stresses are plotted against stretch ratio for one of the cross-linked strips. At the state of ease λ_s, the stresses σ_N and σ_X are equal and opposite; at the stretch ratio during cross-linking λ_0, the stress σ_X of the cross-link network is assumed to be zero. The discrepancies between theory and experiment are at most 2%.

Figure 5 displays the results of irradiating strips with 7 Mrd after increasingly long relaxation times t_R. Young's moduli, reduced to 30 °C in the manner described above, are plotted against $\log t_R$. $E(t)$ of the uncross-linked polymer is shown for comparison, decreasing with time elapsed since stretch. E_N of the trapped entanglement network decreases similarly with time elapsed before quench. The curve labeled $E_X + E_{NR}$ increases with time elapsed before quench. For short times it is assumed to be due solely to cross-links; for longer times it is assumed to include a contribution E_{NR} from relaxed entangling which was trapped. The modulus E_{NR} was derived by subtracting $E_X = 3.2 \times 10^6$ dyn/cm^2.

Discussion

Existence of Trapped Entangled Chain Structure. The central finding of these experiments is that the equilibrium lengths of the SBR random copolymers cross-linked in strained states were considerably less than the lengths that prevailed during cross-linking in strained states, just as observed for 1,2-polybutadiene.[9-22] It is true that some retraction could be predicted without assuming that entangling was trapped, by means of the theory of Flory,[25] which describes networks where initial cross-links introduced in the isotropic state are destroyed after additional cross-links are introduced in the strained state. In this case there remains a configurational memory effect in the network structure of the destroyed cross-links. However, the retraction predicted in this way is far less than observed.[18] We conclude that trapped entangled chain structure makes an important contribution to equilibrium elasticity.

Effectiveness of Entanglement Trapping. Because the cross-linked strips broke at small extensions past the

Table IV
Comparison of Neo-Hookean and BST Calculations of the Modulus of the Trapped Entangled Structure for Three Strips

strip no.	λ	E_N at 30 °C, dyn/cm² × 10^{-6} Neo-Hookean	BST	n
2	1.356	4.91	5.40	1.38
	1.394	4.97	5.49	
	1.596	4.81	5.50	
	1.715	4.78	5.56	
8	1.444	1.89	2.38	0.31
	1.466	1.88	2.38	
	1.502	1.86	2.37	
	1.531	1.90	2.42	
12	1.310	8.85	9.56	1.37
	1.335	8.95	9.70	
	1.375	8.78	9.56	
	1.416	8.79	9.62	

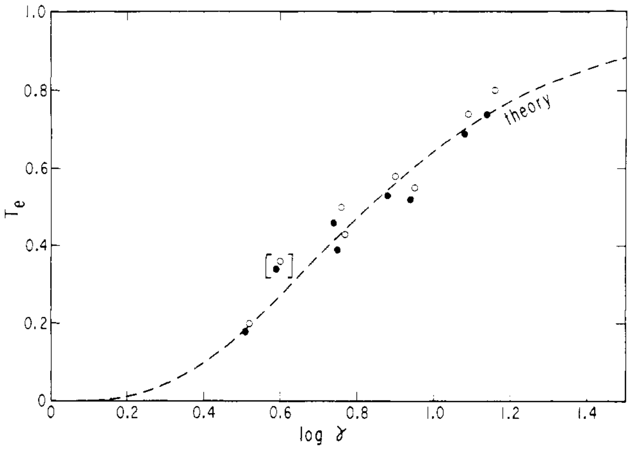

Figure 6. Fractions of trapped unrelaxed entangled chain structure plotted against the logarithmic average number of cross-links per original molecule, γ. Points: open circles, calculated using $n(t_R)$ from the uncross-linked polymer; filled circles, calculated using neo-Hookean analysis. Curve: Langley theory for uniform molecular weight distribution of original linear polymer. Points in brackets refer to a polymer strip irradiated in absence of promoter.

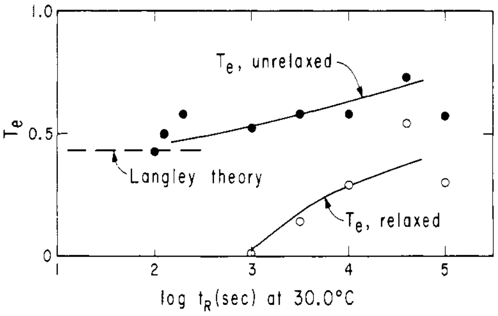

Figure 7. Fractions of unrelaxed and relaxed entangled chain structure plotted against log t_R/a_T in seconds and compared with Langley theory.

state of ease, different strain dependencies of the cross-link and trapped entanglement networks are not needed to interpret the stress–strain measurements consistently. This is illustrated in Table IV; for three cross-linked strips, consistency is shown of E_N calculated at four stretch ratios using both the neo-Hookean analysis and the BST analysis described in the Theory section. In earlier experiments on 1,2-polybutadiene over a wider range of strains and a wider range of stretch ratios during cross-linking, consistent results were obtained only when deviations from neo-Hookean elasticity were taken into account.[10–12] In the present experiments, the need to describe the networks with different strain dependencies is still suggested by the birefringence in the state of ease. Zero birefringence in the state of ease would be expected if the cross-link and trapped entanglement networks were both neo-Hookean,[35] but not if the strain dependencies differ. In earlier work,[9–18] we attributed[15] birefringence in the state of ease of radiation-cross-linked 1,2-polybutadiene of high vinyl content to a cyclization reaction that has been reported by von Raven and Heusinger.[36] This reaction is unlikely, however, for the present random copolymer, which contains only one-fourth pendant vinyl groups. The differences between E_N and E_X from the two methods of calculation are small, in any case. For the strips quenched soon after stretch, E_N and E_X calculated using the BST analysis of the strain dependence are only roughly 10% and 5% higher, respectively, than using the neo-Hookean analysis. For increasing relaxation before quench, these differences in E_N increase to 25% and the differences in E_X hardly change. The conclusions drawn below follow equally well from both interpretations.

The fractions of entangled chain structure trapped by the cross-linking were calculated from eq 7 and 8 and are included in Tables II and III. Figure 6 shows the fraction T_e of trapped unrelaxed entangled chain structure for the strips quenched after minimal terminal zone relaxation. T_e ranges from 0.2 to 0.8, increasing with radiation dose. The plot is against the number of cross-links per originally uncross-linked molecule, γ, and is semilogarithmic in order to render the relationship more nearly linear. Here, γ is estimated via the classical equation of rubberlike elasticity,[27] with a front factor of one to be $\gamma = E_X M_n / 3\rho RT + 2$; the term 2 corrects for loose ends as suggested by Langley[37] and is a slight improvement over the term 1, which was used in previous work. The open circles in Figure 6 are calculated taking deviations from neo-Hookean elasticity of the trapped entanglement network into account, while the filled circles are calculated on the assumption that the trapped entanglement network is neo-Hookean. The results of both methods of calculation are similar and are in excellent agreement with the theory of Langley,[38] which is plotted for the case of initially uniform polymer molecular weight and no chain scission resulting from the radiation. To the extent that chain scission took place, the experimental points would have been expected to fall below the theoretical curve.

The bracketed circles in Figure 6, which are consistent with the rest, are the results for the control strip given a large radiation dose in the absence of promoter.

Fractions of trapped relaxed and unrelaxed entangled chain structures for the strips irradiated with 7 Mrd are plotted in Figure 7 against the logarithmic time t_R before quench. T_e predicted by the Langley theory for $E_X = 3.2 \times 10^6$ dyn/cm² is shown for comparison. For little terminal zone relaxation before quench, T_e is close to the prediction of the Langley theory and $T_{e,r}$ is zero. With increasingly long terminal zone relaxation before quench, T_e increases and $T_{e,r}$ becomes finite and increases, apparently approaching the value predicted by the Langley theory. These results are similar to those found previously.[16] As before, they are interpreted qualitatively in terms of the tube model[2] for the topological constraints on an entangled molecule. Here the final stage of relaxation of a deformed uncross-linked molecule involves escaping from its tube by diffusing along its contour.[3] The ends regain a random configurational pattern, while a steadily shrinking central portion remains confined in the deformed tube. The re-

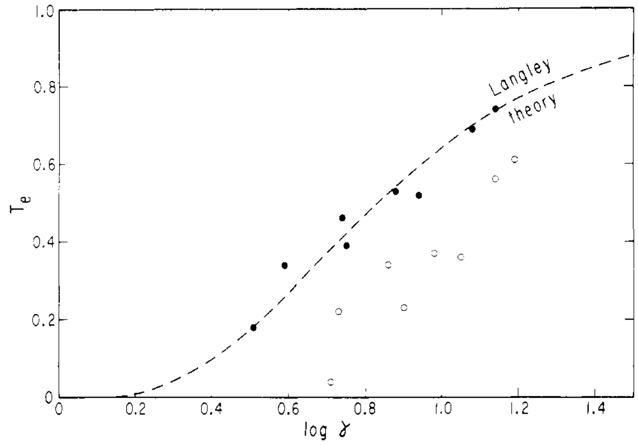

Figure 8. Fractions of trapped unrelaxed entangled chain structure plotted against the logarithmic average number of cross-links per original molecule, γ. Points: filled circles, calculated using eq 3–6 with $n = 2$; open circles, calculated taking into account possible configurational memory of untrapped entangled chain structure as described in text.

laxed entanglements can be identified with constraints on the ends of the molecule; the unrelaxed entanglements can be identified with constraints on the central portion. Whereas the Langley theory provides an average trapping probability, clearly end effects will render the probability of entrapment less near the ends of a molecule than near the center. In fact, there should be essentially no chance of trapped relaxed entanglement until the randomized ends become long enough to display entanglement effects and this length is longer than the average spacing between cross-links. While this description ignores the possibility that some constraints even near the center of the molecule can be relieved by escape of other molecules from their tubes, with resulting reorganization of the tube itself,[39–41] no attempt is made to take this complication into account at the present time.

An additional feature of these experiments is the possible role of entangled chain structure that is present during the course of cross-linking in the strained state but is not trapped by the cross-linking. According to the theory of Flory for composite networks of cross-links,[25] the additivity of stresses expressed in eq 3 does not hold if some of the cross-links introduced in the isotropic state and present during the cross-linking in the strained state are subsequently destroyed. Memory in the network chain configurations of the destroyed cross-links contributes to the elastic behavior of both networks of cross-links, so that eq 3–6 lead to overestimating the modulus of the first network and to underestimating of the second. In our experiments, untrapped entanglements could play the role of destroyed cross-links in the Flory theory. For the polymer strips quenched after minimal terminal zone relaxation, estimates of E_N and E_X were calculated by iteration from Flory's eq 1, 18, 39, and 40, taking $E(t_R)$ of the uncross-linked polymer to be the modulus of the first network before any cross-links were destroyed. For consistency with the Flory analysis, which is based on neo-Hookean relations, the results were compared with the neo-Hookean estimates of E_N and E_X from eq 3–6. For a dose of 10 Mrd the estimated E_N is lower by nearly one-third and the estimated E_X is higher by just over one-third. In these calculations entangled chain structure is assumed to behave elastically like cross-linked strands, uniform molecular weight between cross-links is assumed, the effect of finite chain length on the configurational memory is ignored, and the refinements of modern theories for equilibrium elasticity[42–44] are not taken into account. Taken together, these simplifications are so major as to cast doubt on the validity of the calculations. In any case, Figure 8 compares the revised estimates of the fractions T_e of trapped unrelaxed entangled chain structure to the T_e already shown in Figure 6. The good agreement with the Langley theory is lost. Nonetheless, the T_e are significantly larger than zero and exceed one-half for the highest cross-link densities.

It is reassuring that the results of earlier extensive experiments on 1,2-polybutadiene[9–22] are corroborated by the present experiments on a different polymer. These experiments constitute perhaps the most direct evidence that trapped entangled chain structure contributes to the elastic properties of elastomer networks.

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Theory of Adsorption of Macromolecules. 2. Phase Transitions in Adsorption: General Approach

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ABSTRACT: A general procedure for the analysis of the phase transition order in various cases of polymer chain adsorption is proposed. It is shown that the phase transition order is connected with the molecular weight dependence of the mean number of the intersections of the segments of the free chain with some phantom surface geometrically equivalent to the adsorbent surface and penetrable for the macromolecules.

The principal aim of this series of papers is to present a general theory of adsorption of a single polymer chain. The approaches thus far developed usually describe the behavior of rather simple (frequently lattice) model systems[1-10] (see, however, ref 11 and 12). The well-known theory of conformational transitions in macromolecules based on sequence-generating functions[13,14] gives the possibility of studying transitions in a general case, provided that the thermodynamic properties of single intramolecular sequences are known. Adsorption can be considered as a conformational transition, with the thermodynamics of single sequences determined, in many respects, by the geometry of the polymer–adsorbent system.

In our previous publication (paper 1;[15a] see also ref 15b), we have obtained the basic equation for the transition point and analyzed its dependence on the conformational properties of a chain and on the shape of the adsorbent. Our current aim is to extend the general approach to the investigation of the transition order at the adsorption of infinitely long chains ($N \rightarrow \infty$). The applications of this approach will be realized mainly in the next paper.

I. Desorption–Adsorption Transition

Our purposes in this section are (a) to demonstrate that the adsorption of a chain on a solid adsorbent of any form always shows a phase transition and (b) to relate the conformation of a macromolecule at the transition point to that of a free macromolecule.

Let us first outline the derivation of starting equations.[13-15]

The adsorbed chain appears as a linear sequence of adsorbed segments S and loops L. Its free energy μ (per monomer unit) may be found from the equation

$$\Xi_{\mathrm{S}}(\lambda)\Xi_{\mathrm{L}}(\lambda) = 1 \qquad (1)$$

Here

$$\lambda = \exp(-\mu) \qquad (2)$$

is the largest root of eq 1, and

$$\Xi_{\mathrm{S}}(\lambda) = \sum_{n=1}^{\infty} Z_{\mathrm{S}}(n,\epsilon)\lambda^{-n} = \sum_{n=1}^{\infty} Z_{\mathrm{S}}^{0}(n)e^{-n\epsilon}\lambda^{-n} \qquad (3)$$

$$\Xi_{\mathrm{L}}(\lambda) = \sum_{n=1}^{\infty} Z_{\mathrm{L}}(n)\lambda^{-n} = \sum_{n=1}^{\infty} Z_{\mathrm{v}}(n)W_{\mathrm{L}}(n)\lambda^{-n} \qquad (4)$$

are the generating functions for the adsorbed segments and the loops.

The partition function $Z_{\mathrm{S}}(n,\epsilon)$ of an adsorbed segment of n units contains the conformational contribution $Z_{\mathrm{S}}^{0}(n)$ and a factor depending on the monomer–surface interaction energy ϵ (the energetic quantities ϵ and μ are expressed in kT units).

The partition function $Z_{\mathrm{L}}(n)$ of a loop of n units may be divided into two factors. $Z_{\mathrm{v}}(n)$ is the partition function of an n-unit portion in a free chain (in a solution in the absence of a surface)

$$Z_{\mathrm{v}}(n) = \lambda_{\mathrm{v}}^{n} = \exp(-n\mu_{\mathrm{v}}) \qquad (5)$$

$W_{\mathrm{L}}(n)$ characterizes conformational entropy limitations in the loop.

In some special cases[16,17] it is also necessary to include in $Z_{\mathrm{L}}(n)$ the additional factor $Q_{\mathrm{L}}(n)$ resulting from the external fields. Here we assume $Q_{\mathrm{L}}(n) = 1$.

A similar treatment is extensively used for investigating a broad class of intramaolecular order–disorder transitions in linear polymer chains.[14,18-20] In each case the thermodynamically stable state is selected by the competition between λ_{v} and λ (increasing with the attraction energy $-\epsilon$ in ordered sequences), where λ_{v} corresponds to a completely unordered state and λ to a partly ordered state (in our case to the adsorbed state).

(In principle, one should also take into account the fully ordered state to complete the system of hypothetically possible states. However, this state is reached[14] only if the partition function $Z_{\mathrm{S}}(n)$ of an ordered sequence has some special form, as it has in the case of the β structure–coil transition.[18-20] If $Z_{\mathrm{S}}(n)$ is a simple exponential function, as it is in the processes of adsorption (see eq 15) or helix–coil transition, the roots λ and λ_{v} are sufficient to describe the system.)

Equations 1 and 5 describe the two fundamentally different cases of order–disorder transitions, namely, the existence of either a true phase transition or a cooperative non phase transition. The first case takes place if $\lambda < \lambda_{\mathrm{v}}$ at $-\epsilon$ is lower than some "critical" value $-\epsilon_{\mathrm{c}} \geq 0$ and $\lambda > \lambda_{\mathrm{v}}$ at $-\epsilon > -\epsilon_{\mathrm{c}}$. The equilibrium states of a long macromolecule are different in these two ϵ regions, and there is a true phase transition at the point ϵ_{c} determined by the crossover condition

$$\lambda(\epsilon_{\mathrm{c}}) = \lambda_{\mathrm{v}} \qquad (6)$$

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