

Entanglement Networks of 1,2-Polybutadiene CrossLinked in States of Strain. IV. States of Ease and Stress-Strain Behavior

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Synopsis

Linear 1,2-polybutadiene, glass transition temperature (T_g) = 18°C, is crosslinked at -10° to -20°C by γ irradiation while strained in simple extension, with extension ratios (λ_0) from 1.2 to 2.7. After release, the sample retracts to a state of ease (λ_s) at room temperature. From equilibrium stress-strain measurements up to a stretch ratio relative to the state of ease (Λ) of 1.2, together with λ_0 and λ_s , the concentration of network strands terminated by trapped entanglements (ν_N) is calculated. For this purpose, a three-constant Mooney-Rivlin formulation is used, in which the entanglement network is described by Mooney-Rivlin coefficients C_{1N} and C_{2N} , whereas the crosslink network is described by the coefficient C_{1x} only. The ratio $\psi_N = C_{2N}/(C_{1N} + C_{2N})$ is estimated from parallel studies of nonlinear stress relaxation of the uncrosslinked polymer, taking into account the thermal history before and during irradiation. For substantial degrees of crosslinking, i.e., for $R_0' = \nu_x/\nu_N > 0.4$ (where ν_x is the concentration of network strands terminated by crosslinks), and for $\lambda_0 < 1.8$, C_{2N} agrees rather well with the value obtained from stress relaxation of the uncrosslinked polymer in the range of time scale where it is nearly independent of time (1.87×10^5 pascals). The corresponding value of ν_N is 2.3×10^{-4} moles/cm³, in good agreement with that obtained from viscoelastic measurements of the uncrosslinked polymer in the plateau zone (2.5×10^{-4}). However, for $R_0' \cong 0.2$, smaller values of C_{2N} and ν_N are obtained, indicating that for low degrees of crosslinking the entanglements are not completely trapped. Also, for higher values of λ_0 , C_{2N} and ν_N turn out to be somewhat smaller. Similar, less extensive results were obtained previously on a 1,2-polybutadiene with somewhat higher vinyl content and a higher T_g . Crosslinked samples of both these polymers were subjected to equilibrium stress-strain measurements in simple elongation from the state of ease at higher strains up to $\Lambda = 1.7$. The results agreed closely with calculations from the three-constant Mooney-Rivlin theory.

INTRODUCTION

The crosslinking of 1,2-polybutadiene strained in simple extension was described in previous papers of this series.¹⁻³ When a stretched sample is crosslinked with γ radiation near the glass transition temperature (T_g), the resulting crosslink network traps the entanglements originally present; after release, the sample seeks a state of ease in which the elastic free energy is at a minimum and the forces due to the crosslinks and the entanglements act in opposite directions. From the sample dimensions before stretching, during crosslinking, and in the state of ease, together with stress-strain measurements in small extensions from the state of ease, the concentrations of entanglement network strands ν_N and

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crosslink network strands ν_x can be calculated. A modification of the two-network model theory originally developed for two stages of crosslinking^{4,5} was used for this purpose. The best results³ were obtained from a three-constant theory in which the elastic free energy of the entanglement network is described by two Mooney–Rivlin terms with coefficients C_{1N} and C_{2N} , while that of the crosslink network is described by one term with C_{1x} only. In this case, the value of C_{2N} is nearly independent of the extension ratio during crosslinking (λ_0), and the magnitudes of C_{1N} and C_{2N} agree well with those determined from nonlinear stress relaxation measurements on the uncrosslinked polymer,⁶ taking into account the partial relaxation of stress during stretching and irradiation under conditions of known thermal history.

The present paper describes additional results with a different sample of 1,2-polybutadiene; its molecular weight was higher, but its T_g was lower, so that stress relaxation was somewhat greater under similar experimental conditions (in particular, temperature during stretching and crosslinking). Of primary interest here are the failure to trap all entanglements at low degrees of crosslinking and the behavior of networks from both polymers when stretched in large extensions from the state of ease. It is found that the latter is also well described by the three-constant Mooney–Rivlin theory.

THEORY

As shown previously,³ the results of the three-constant Mooney–Rivlin theory can be conveniently expressed in terms of two parameters $\psi_N = C_{2N}/(C_{1N} + C_{2N})$ and $R_0' = C_{1x}/(C_{1N} + C_{2N})$. The Mooney–Rivlin coefficients are related to the concentrations of entanglement network strands ν_N and crosslink network strands ν_x as follows:

$$\nu_N = (2/RT)(C_{1N} + C_{2N}) \quad (1)$$

$$\nu_x = (2/RT) C_{1x} \quad (2)$$

From the extension ratios during crosslinking (λ_0) and in the state of ease (λ_s), the ratio R_0' of ν_x to ν_N is calculated as follows:

$$R_0' = \lambda_0^2(1 - \lambda_s^3)[\psi_N + (1 - \psi_N)\lambda_s]/(\lambda_s^3 - \lambda_0^3)\lambda_s \quad (3)$$

For uniaxial extension relative to the state of ease in the original stretch direction ($\Lambda = \lambda/\lambda_s$), the engineering stress σ_g is

TABLE I
Characterization of 1,2-Polybutadienes

	Polymer A	Polymer B
$\bar{M}_n \times 10^{-5}$	1.52	2.36
$\bar{M}_w \times 10^{-5}$	1.90	2.91
% Vinyl	95.3	88.4
% <i>Cis</i>	2.4	4.7
% <i>Trans</i>	2.3	6.9
T_g , °C, est. from microstructure	-12	-18
T_g , °C, from DSC	-8	-18

TABLE II
 Crosslinking of Polymer B

Sample no.	Irradiation time, hr	T_t	T_i	λ_0	λ_s	$C_{2N} \times 10^{-6}$, pascal
181 ^a	1.7	-20	-10	1.522	1.065	0.077 ^c
182 ^a	1.7	-20	-10	1.621	1.073	0.069 ^c
183 ^a	1.7	-20	-10	1.687	1.088	0.090 ^d
175 ^a	2.0	-10	-10	1.527	1.158	0.127
173 ^a	2.0	-10	-10	1.604	1.180	0.127
170 ^a	3.0	-10	-10	1.620	1.166	0.151
172 ^a	3.0	-10	-10	1.633	1.195	0.140
195	4.0	-10	-10	1.200	1.071	0.202
162 ^a	4.0	-20	-20	1.261	1.080	0.176
193	4.0	-10	-10	1.270	1.108	0.168
194	4.0	-10	-10	1.310	1.127	0.177
156 ^a	4.0	-15	-15	1.332	1.102	0.169
196	4.0	-10	-10	1.400	1.151	0.184
163 ^a	4.0	-20	-20	1.419	1.093	0.183
192	4.0	-10	-10	1.434	1.190	0.159
157 ^a	4.0	-15	-15	1.479	1.115	0.188
164 ^{a,b}	4.0	-20	-20	1.517	1.126	0.184
191	4.0	-10	-10	1.519	1.200	0.170
197	4.0	-10	-10	1.585	1.214	0.183
186	4.0	-10	-10	1.595	1.263	0.170
187	4.0	-10	-10	1.654	1.274	0.162
166 ^a	4.0	-20	-20	1.663	1.256	0.171
159 ^{a,b}	4.0	-15	-15	1.667	1.173	0.157
160 ^a	4.0	-15	-15	1.810	1.294	0.143
188	4.0	-10	-10	1.890	1.366	0.149
198	4.0	-10	-10	1.892	1.391	0.160
167 ^{a,b}	4.0	-20	-20	1.946	1.214	0.179
161 ^a	4.0	-15	-15	2.144	1.483	0.121
168 ^a	4.0	-20	-20	2.167	1.349	0.154
189	4.0	-10	-10	2.210	1.467	0.141
190	4.0	-10	-10	2.348	1.530	0.136
185	4.0	-10	-10	2.408	1.516	0.132
174 ^a	6.0	-10	-10	1.543	1.267	0.160
171 ^a	6.0	-10	-10	1.676	1.366	0.140
184	8.0	-10	-10	2.720	1.977	0.132

^a Irradiated with new source; dose is equivalent time for old source.

^b Also used for stress-strain measurements with large strains.

^c Reduced to 25°C from stress-strain data at 75°C.

^d Reduced to 25°C from stress-strain data at 50°C.

$$\sigma_g = 2(C_{1N} + C_{2N})[(1 - \psi_N)(\lambda_s^2 \Lambda - \lambda_s^{-1} \Lambda^{-2}) + \psi_N(\lambda_s - \lambda_s^{-2} \Lambda^{-3}) + R_0'(\lambda_s^2 \lambda_0^{-2} \Lambda - \lambda_s^{-1} \lambda_0 \Lambda^{-2})] \quad (4)$$

Young's modulus in uniaxial extension relative to the state of ease and parallel to the original stretch direction, $E_{||}$, is

$$E_{||} = 2(C_{1N} + C_{2N})[\psi_N(-\lambda_s^2 - 2\lambda_s^{-1} + 3\lambda_s^{-2}) + R_0'(\lambda_s^2 \lambda_0^{-2} + 2\lambda_s^{-1} \lambda_0) + \lambda_s^2 + 2\lambda_s^{-1}] \quad (5)$$

For $\psi_N = 0$, these relations reduce to the equations given in part I of this series¹ where both entanglement and crosslink networks were taken as neo-Hookean

($C_{2x} = C_{2N} = 0$). For $\psi_N = 1$, they reduce to the equations given in part II,² where the approximation was made that $C_{2x} = C_{1N} = 0$. Values of ψ_N intermediate between 0 and 1 can be estimated from stress relaxation data on the uncrosslinked polymer⁶ if the thermal history during stretching and irradiation is specified.³

EXPERIMENTAL

The two polybutadienes, A and B, are thus identified also in the stress relaxation experiments of Noordermeer and Ferry.⁶ Polymer A was used for all the work previously reported in this series.¹⁻³ Their characteristics are summarized in Table I. Polymer A was purchased from Phillips Petroleum Company; polymer B, also from Phillips, was kindly provided by Dr. G. Kraus.

Samples were prepared, stretched, and irradiated as previously described.^{1,3} The temperature of stretching was always 0°C. The temperatures of transportation to the cobalt 60 source and irradiation are identified as T_t and T_i , respectively. The maximum irradiation time was usually 4 hr. During the course of the experiments, the source rod was replaced by a more intense one with a dose rate higher by a factor of 2.55. The dose times thereafter are reported as equivalent times for the old source (i.e., multiplied by 2.55) as identified by footnote (a) in Table II, for more convenient comparison.

Two samples were irradiated for subsequent infrared spectra measurements to test for possible cyclization of vinyl groups as reported by von Raven and Heusinger.⁷ These investigators found that γ irradiation of 1,2-polybutadiene caused a shift in the frequency of the infrared CH_2 band from 1445 to 1455 cm^{-1} and the appearance of a CH_3 band at 1375 cm^{-1} , attributed to ring formation

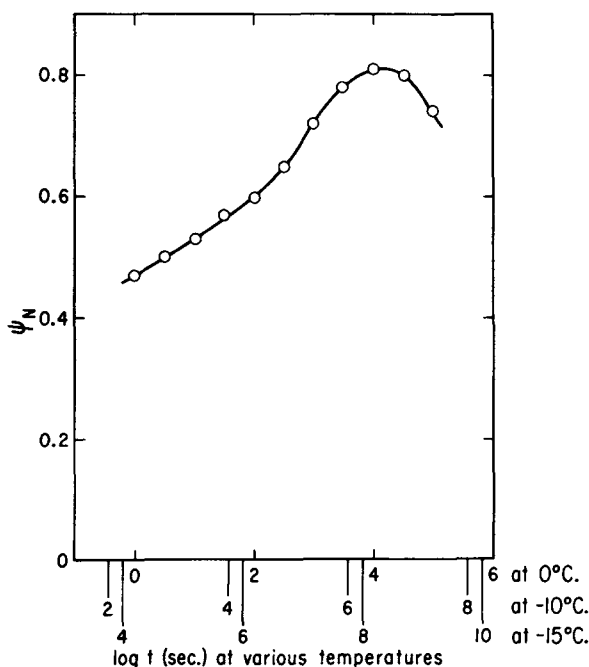


Fig. 1. Plot of ψ_N for polymer B against $\log t$ at several different temperatures, calculated from C_1 and C_2 measurements on uncrosslinked polymer by Noordermeer and Ferry.⁶

of adjacent vinyl groups. We found a similar result after irradiation for 24 hr (equivalent time with old source 61 hr, estimated dose 248 Mrad), but no detectable change in the spectrum for 4 hr (equivalent time with old source 10 hr, estimated dose 41 Mrad). We conclude that cyclization does not play an important role in the stress-strain behavior; although the number of cyclized vinyl groups probably exceeds the number of crosslinks, both are rather small.

Stress-strain measurements in simple elongation were made as described previously.¹ The stainless steel clamps were equipped with thin gaskets of vulcanized rubber to eliminate rupture at the clamps; as before, the relative elongation from the state of ease was measured by fiducial marks with a traveling microscope. At 25°C, the time required to reach equilibrium at each loading was several days (or weeks, for small degrees of crosslinking). Many of the measurements were made at 50°C, where 2 hr was usually sufficient, although for small degrees of crosslinking (less than 4 hr irradiation), the duration of loading was 4 hr for $\Lambda < 1.2$ or 8 hr for larger strains. Stresses measured at 50°C were reduced to 25° by multiplying by the ratio of $T\rho$ at the two temperatures, where T is absolute temperature and ρ is density. In the small strain studies, elongations up to $\Lambda = 1.2$ were measured as before. In the large strain studies, elongations up to $\Lambda = 1.7$ were generally measured, although some samples broke at lower elongations.

RESULTS

Crosslinking of Sample B

In Table II, values of λ_0 and λ_s are listed for many samples with various radiation doses and thermal histories. In order to calculate C_{2N} and ν_N , it was necessary to estimate ψ_N . This was done from the stress relaxation data of Noordermeer and Ferry,⁶ according to which ψ_N is plotted against the logarithm of time at several different temperatures in Figure 1. The time scales at temperatures other than 0°C are specified by shift factors calculated by the WLF equation⁸ with coefficients estimated on the basis of the microstructure of the polymer:⁹ $c_1 = 9.37$ and $c_2 = 498.4$ for a reference temperature of 0°C. The

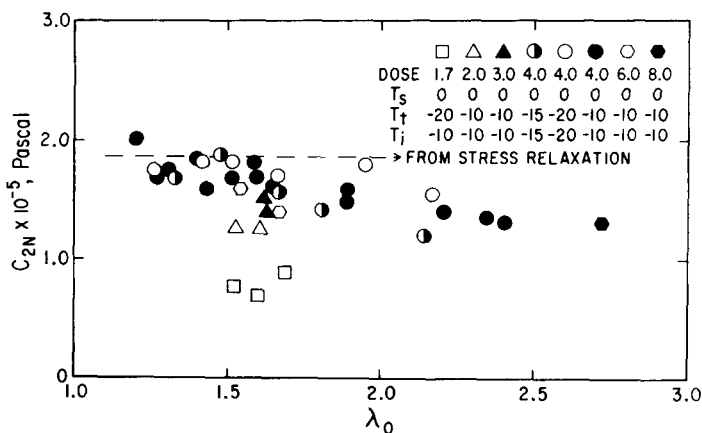


Fig. 2. Plot of the C_2 term of the entanglement network, C_{2N} , against extension ratio during crosslinking, λ_0 , for various irradiation doses and thermal histories as indicated.

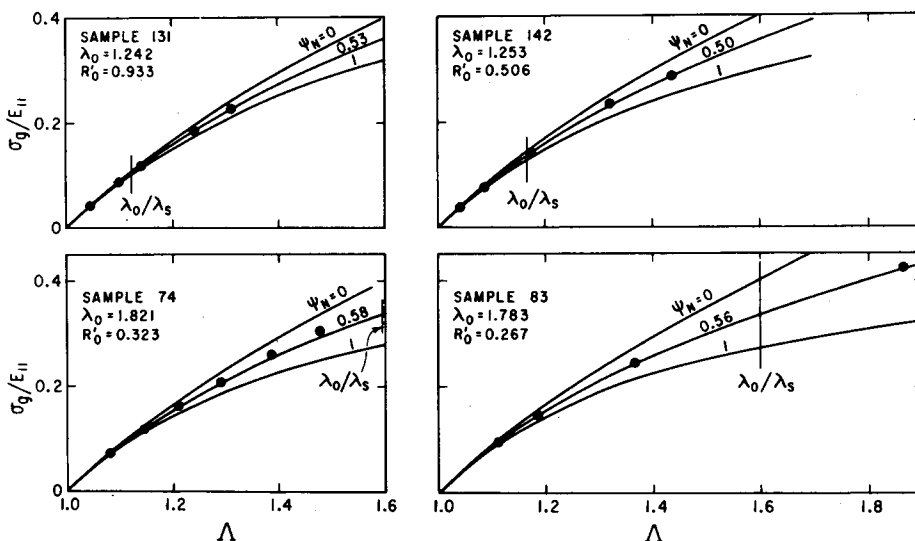


Fig. 3. Stress-strain in simple elongation from the state of ease for four samples of polymer A as indicated. Points, experimental; curves, theoretical with different values of ψ_N as shown: 0, 1, and an intermediate value obtained from stress relaxation data for the uncrosslinked polymer.

times required to stretch at T_s and transport at T_i , and half the time of irradiation at T_i , were reduced to 0°C and added; the last two made very small contributions, and the value of ψ_N was 0.63 to 0.635 for all this series. Then, with data from stress-strain measurements in small elongations (up to $\Lambda = 1.2$), eqs. (3) and (4) were solved to obtain C_{2N} corresponding to 25°C , which is also included in the table. These calculations were performed on a Univac 1110 computer.

The coefficient C_{2N} can be compared with the value of C_2 for the uncrosslinked polymer, which during stress relaxation remains nearly constant over several logarithmic decades of time scale at 1.75×10^5 pascals at 0° , or 1.87×10^5 pascals when reduced to 25°C by multiplying by the ratio of $T\rho$ at the two temperatures. In Figure 2, C_{2N} is plotted against λ_0 . For large doses and values of λ_0 less than 1.8, the agreement is fairly good and indicates that essentially all the entanglements are trapped in the crosslinking process, as previously concluded for polymer A.³

For small doses, C_{2N} is smaller; in particular, for 1.7 hr, it is only about half the maximum value. However, R_0' is only about 0.2 for these samples, and it is reasonable that many of the entanglements remain untrapped and relax out in approaching the state of ease (see discussion below). For large values of the initial stretch, C_{2N} is also diminished somewhat. An average value of C_{2N} for all the high-dose samples which is close to 1.87×10^5 is obtained by arbitrarily setting $\psi_N = 0.73$, but this does not eliminate the tendency of C_{2N} to decrease with increasing λ_0 .

A plot of the concentration of entanglement network strands, ν_N , against λ_0 is similar to Figure 2; at high doses and low λ_0 , ν_N is approximately 2.3×10^{-4} mole/cm³, in good agreement with the value of 2.5×10^{-4} mole/cm³ obtained from viscoelastic measurements on the uncrosslinked polymer in the plateau zone,¹⁰ as previously found for polymer A.³ (The small differences in microstructure should not affect this value significantly.)

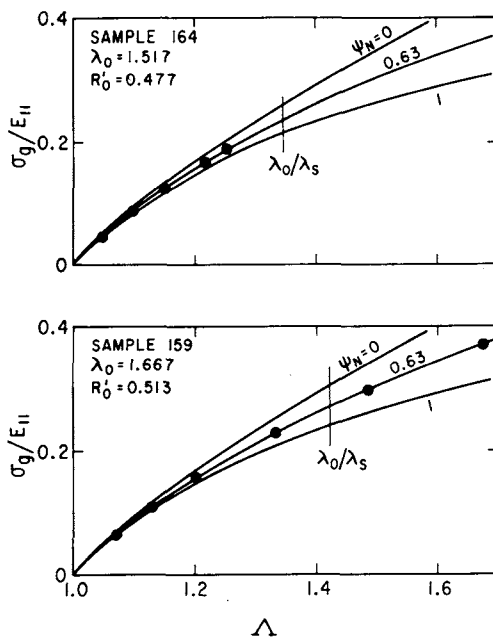


Fig. 4. Stress-strain in simple elongation from the state of ease for two samples of polymer B as indicated, plotted as in Figure 3.

Stress-Strain Behavior from the State of Ease

Several samples of each polymer were subjected to equilibrium stress-strain measurements at elongations up to the breaking point. For smaller values of λ_0/λ_s , the extension could be carried considerably farther than $\Lambda = \lambda_0/\lambda_s$. In calculating these data, after ψ_N had been estimated as described above (in the case of polymer A from a previously published graph³), eq. (4) was applied to calculate $C_{1N} + C_{2N}$ from the measured stress σ_g at each elongation Λ . The average value of $C_{1N} + C_{2N}$ was then used to obtain Young's modulus in the parallel direction, E_{\parallel} , by eq. (5). (The neo-Hookean approximation for obtaining E_{\parallel} , used previously,¹ was not employed.) For convenient comparison of the experimental stress-strain curve with that calculated from eq. (4), the normalized stress σ_g/E_{\parallel} was plotted against the stretched length relative to the state of ease, Λ .

Four examples of these plots for polymer A are shown in Figure 3 and two examples for polymer B, in Figure 4. It is clear that a value of ψ_N intermediate between 0 and 1 is required to describe the results, and very good agreement is obtained with the ψ_N values estimated from stress relaxation of the uncrosslinked polymer.

DISCUSSION

An estimate of the effectiveness of entanglement trapping at low degrees of crosslinking can be made from the theory of Langley,¹¹ though it is applicable strictly only to crosslinking in the isotropic state. For example, after irradiation for 1.7 hr, $R'_0 = 0.2$, $C_{2N} = 0.077 \times 10^6$, and $\psi_N = 0.63$. Hence $\nu_x = 0.19 \times 10^{-4}$ mole/cm³. The average number of segments between crosslinks on an original molecule is $M_n \nu_x / \rho = 5$ (not counting the free end segments). The average

number of crosslink points per original molecule, γ in Langley's notation, is then 6. From Langley's graph for uniform initial molecular weight distribution, we obtain the fraction of entanglements trapped as $T_e = 0.45$. The ratio of ν_N for such a sample to that obtained at high degrees of crosslinking is about 0.44, in very good agreement.

The apparent decrease in C_{2N} , and corresponding decrease in ν_N , at high elongations evidently means that the three-constant Mooney–Rivlin theory is inadequate to describe stress–strain relations above $\lambda_0 = 1.8$. This is not surprising in view of the recognized limitations of the ordinary Mooney–Rivlin theory as applied to isotropic networks. No attempt is made at present to modify it further.

The good agreement of stress–strain curves with those calculated provides further support for the reality of the entanglement network, the validity of the two-network hypothesis for describing strain energy and mechanical properties, and the general utility of the three-constant Mooney–Rivlin model for describing the behavior in simple elongation subject to the reservations pointed out above.

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