Entanglement Networks of 1,2-Polybutadiene Cross-Linked in States of Strain. 3. Effect of Temperature

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ABSTRACT: Linear 1,2-polybutadiene, glass-transition temperature (T_g) −10 ± 2 °C, is cross-linked at several temperatures from −15 to 0 °C while strained in simple extension, with extension ratios (λ_0) from 1.2 to 2.8. 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 (parallel to the stretch direction, $E_\|$) the molar concentration of network strands terminated by trapped entanglements (ν_N) is first calculated by ideal Gaussian two-network theory. With increasing λ_0 or λ_s, ν_N appears to decrease; extrapolated to $\lambda_0 = \lambda_s = 1$, ν_N increases with decreasing temperature of irradiation and appears to level off below T_g. At −15 °C it is 2.1×10^{-4} mol cm^{-3}, in good agreement with the value of 2.5×10^{-4} obtained from viscoelastic measurements on uncross-linked polymer in the rubbery plateau zone. The apparent dependence of ν_N on λ_0 or λ_s is largely removed by invoking a three-constant Mooney–Rivlin theory; in the state of ease, the entanglement network has Mooney–Rivlin coefficients C_{1N} and C_{2N}, whereas the cross-link network is described by the coefficient C_{1x} only. The ratio $\psi_N = C_{2N}/(C_{1N} + C_{2N})$ depends on the degree of stress relaxation before and during irradiation and can be estimated from parallel studies of nonlinear stress relaxation of the uncross-linked polymer. From this information, with stress–strain data in small extensions from the state of ease, C_{2N} is calculated for many samples with different λ_0 and irradiation doses. For irradiations near T_g, the results agree fairly well with the value obtained from stress relaxation of the uncross-linked polymer in the range of time scale where it is nearly independent of time (1.6×10^5 Pa at 25 °C).

In paper 1 of this series,[2] it was shown that the concentration of elastically effective entanglement strands in linear polymers can be estimated by introduction of chemical cross-links in the strained state. The concentration of network strands in the original entanglement network, ν_N, as well as the concentration of network strands, ν_x, of the cross-link network formed in the strained state were calculated from ideal Gaussian two-network theory, making use of measurements of the dimensions of the sample before stretching and in the strained state and the dimensions and Young's modulus in the state of ease in which the elastic free energy is at a minimum.

Irradiation of 1,2-polybutadiene at 0 °C (10 °C above the glass-transition temperature) gave $\nu_N = 1.2 \times 10^{-4}$ mol cm^{-3}. This is about half the concentration of entanglement strands deduced from viscoelastic measurements on uncross-linked polymer in the plateau zone[3] ($\nu_e = 2.5 \times 10^{-4}$ mol cm^{-3}). It was also found that ν_N calculated in this manner decreased with increasing strain during cross-linking.

In paper 2 the data were analyzed[4] in terms of an empirical strain energy function of the Mooney-Rivlin type[5], making the simplifying assumption that the C_1 term of the entanglement network and the C_2 term of the chemical cross-link network are equal to zero. The apparent dependence of ν_N on strain was largely eliminated.

However, in a recent paper Noordermeer and Ferry[6] report stress–relaxation measurements on linear uncross-linked 1,2-polybutadiene which show both C_1 and C_2 contributions of the temporary entanglement network; C_1 and C_2 are approximately equal at short times, whereas C_2 becomes considerably greater than C_1 at longer times, only. At 10 °C above the glass-transition temperature (paper 1) considerable stress relaxation takes place during the experiment, and in the residual entanglement network the dominance of C_2 may be expected. The present paper gives the results for irradiations closer to the glass-transition temperature, and the C_1 term of the entanglement network is therefore included in the analysis of the data.

Theory

The following Mooney-Rivlin form of the elastically stored free energy of a two-network system was first proposed by Greene and co-workers[5] for composite networks successively cross-linked in both the isotropic and strained states:

$$\begin{aligned}\Delta F_{el} = {} & C_{1N}(\lambda_x{}^2 + \lambda_y{}^2 + \lambda_z{}^2 - 3) + C_{2N} \times \\ & (\lambda_x{}^{-2} + \lambda_y{}^{-2} + \lambda_z{}^{-2} - 3) + C_{1x}(\lambda_{x;2}{}^2 + \lambda_{y;2}{}^2 + \lambda_{z;2}{}^2 - 3) \\ & + C_{2x}(\lambda_{x;2}{}^{-2} + \lambda_{y;2}{}^{-2} + \lambda_{z;2}{}^{-2} - 3)\end{aligned} \tag{1}$$

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 chemical crosslinks are introduced; C_{1N} and C_{2N} are the Mooney–Rivlin constants of the entanglement network while C_{1x} and C_{2x} are the Mooney–Rivlin constants of the cross-link network. As pointed out previously,[4] we recognize the theoretical objections to the Mooney–Rivlin treatment,[7] but it describes behavior in simple extension successfully and is useful for the present analysis of the roles of entanglements and cross-links.

We now have to determine four constants instead of two and this cannot be done from the available experimental data. We therefore assume $C_{2x} = 0$ since networks in compression show small C_2 terms[7], and we obtain the relative contributions of C_{1N} and C_{2N} from the stress–relaxation measurements of Noordermeer and Ferry.[6] At the equilibrium state of ease $\partial \Delta F_{el}/\partial \lambda = 0$ which for simple extension gives

$$R_0' = \lambda_0{}^2(1 - \lambda_s{}^3)(\psi_N + (1 - \psi_N)\lambda_s)/(\lambda_s{}^3 - \lambda_0{}^3)\lambda_s \tag{2}$$

where $R_0' \equiv C_{1x}/(C_{1N} + C_{2N})$, $\psi_N \equiv C_{2N}/(C_{1N} + C_{2N})$, and λ_s is the extension ratio in the state of ease. For uniaxial extension relative to the state of ease ($\Lambda = \lambda/\lambda_s$), the "engineering" stress σ_g (force per unstretched cross-section area) is obtained as $\partial \Delta F_{el}/\partial \Lambda$

$$\begin{aligned}\sigma_g = {} & 2(C_{1N} + C_{2N})[(1 - \psi_N)(\lambda_s{}^2\Lambda - \lambda_s{}^{-1}\Lambda^{-2}) \\ & + \psi_N(\lambda_s - \lambda_s{}^{-2}\Lambda^{-3}) + (R_0'(\lambda_s{}^2\lambda_0{}^{-2}\Lambda - \lambda_s{}^{-1}\lambda_0\Lambda^{-2})]\end{aligned} \tag{3}$$

Young's modulus in uniaxial extension relative to the state of ease and parallel to the original stretch direction, $E_\|$, is obtained as $\partial^2 \Delta F_{el}/\partial \Lambda^2$ for $\Lambda \to 1$:

$$\begin{aligned}E_\| = {} & 2(C_{1N} + C_{2N})[\psi_N(-\lambda_s{}^2 - 2\lambda_s{}^{-1} + 3\lambda_s{}^{-2}) \\ & + R_0'(\lambda_s{}^2\lambda_0{}^{-2} + 2\lambda_s{}^{-1}\lambda_0) + \lambda_s{}^2 + 2\lambda_s{}^{-1}]\end{aligned} \tag{4}$$

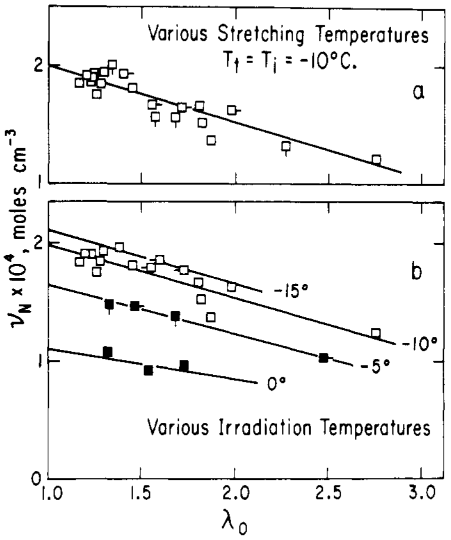

Figure 1. Apparent concentration of strands terminated by entanglements, ν_N, calculated from ideal Gaussian two-network theory plotted against extension ratio during cross-linking, λ_0. Symbols are identified in Table I. (a) Various stretching temperatures at constant T_t and T_i; (b) various irradiation temperatures.

Table I
Definition of Symbols[a]

	Irradiation time, h	T_s, °C	T_t, °C	T_i, °C
□	4	0	−10	−10
□-	4	−2	−10	−10
□̩	4	−4	−10	−10
-□	4	0	−10	−15
■	4	0	0	0
■-	4	0	0	−5
■̩	4	0	−10	−5
O	6	0	−10	−10
○	12	0	−10	−10

[a] Temperatures T_s (stretch temperature), T_t (water/ethanol/ice bath temperature), and T_i (irradiation temperature) are defined in the Experimental Section.

For $\psi_N = 0$, these relations reduce to the equations given in paper 1[2] of this series where both entanglement and cross-link networks were taken as neo-Hookean ($C_{2x} = C_{2N} = 0$). For $\psi_N = 1$, they reduce to the equations given in paper 2,[4] where the approximation was made that $C_{2x} = C_{1N} = 0$. With ψ_N from Noordermeer and Ferry and R_0' from eq 2, C_{1N}, C_{2N}, and C_{1x} can be determined from eq 3 and the definitions of ψ_N and R_0'.

Experimental Section

The experiments were performed as in paper 1[2] with the same polymer, which is sample A in the paper by Noordermeer and Ferry.[6] Its glass-transition temperature has been estimated as −10 ± 2 °C, −12 °C from its microstructure[2] and −8 °C by differential scanning calorimetry.[6] There were a few minor modifications in sample preparation. The temperature during stretching, T_s, was 0, −2, or −4 °C. The weight used for stretching the sample was suspended for approximately 30 s before slowly rolling the sample onto the stainless steel cylinder. After closing the vacuum seals, the irradiation vessel was placed in an ethanol/water/ice cold bath which usually was kept at −10 °C except in a few cases where 0 °C was used. This temperature is called T_t. It took about 2 min from beginning of stretching until the irradiation vessel was immersed in the cold bath. About five minutes later the irradiation vessel was transferred from the cold bath to an open bath inside the irradiation chamber. This bath was controlled at 0, −5, −10, or −15 °C, T_i, with a Lauda K4/RD refrigerated circulator.[8] The rest of the procedure, involving γ irradiation with a ^{60}Co source, was identical to the one used in paper 1. Irradiations were also performed at two different dose rates: originally about 4 Mrad per h, and later reduced approximately to one-half this rate by doubling the diameter of the stainless steel tube on which the sample was mounted (the ^{60}Co source is rod shaped so that the rate is approximately inversely proportional to the radius of the tube for small radii). Stress–strain measurements in simple elongation from the state of ease were made at 25 °C as described previously,[2] but Young's modulus $E_{\parallel}$ was not calculated by the neo-Hookean approximation; the measured stresses σ_g were used to process the data in connection with eq 3 as explained below.

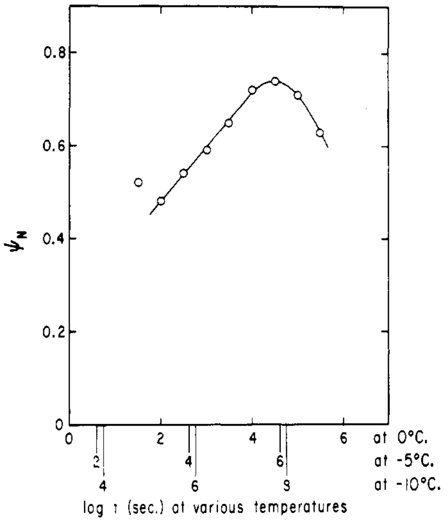

Figure 2. Plots of ψ_N against log t at several different temperatures, calculated from C_1 and C_2 measurements on uncross-linked polymer by Noordermeer and Ferry.[6]

Results

Thermal History. Figure 1 shows the concentration of elastically effective strands terminated by entanglements, ν_N, calculated from ideal Gaussian two-network theory (i.e., from eq 2 and 4 assuming $\psi_N = 0$), plotted against the extension ratio during irradiation, λ_0, for samples of different thermal history. Symbols are identified in Table I. In Figure 1a, the stretching temperature is varied from 0 to −4 °C keeping the transport and irradiation temperatures T_t and T_i constant at −10 °C; there is no detectable effect of different stretching temperatures. In Figure 1b, the lines refer to various irradiation temperatures. Obviously decreasing the irradiation temperature toward the glass-transition temperature results in considerably higher values of ν_N while going below the glass-transition temperature (−10 to −15 °C) makes very little difference, indicating a leveling off when the temperature reaches the glass-transition temperature. The intercept at −15 °C, $\nu_N = 2.1 \times 10^{-4}$ mol cm^{-3}, is very close to the value obtained from viscoelastic measurements on the uncrss-linked polymer in the rubbery plateau zone, $\nu_e = 2.5 \times 10^{-4}$ mol cm^{-3}. The agreement between these two results from completely different types of experiments is gratifying and gives additional support to the reality of the entanglement network.

The negative slopes of these lines are due to the inadequacy of the ideal Gaussian two-network theory, as pointed out in paper 2,[4] and are at least partly removed by analysis with three-constant theory as follows.

Three-Constant Mooney–Rivlin Theory. An analysis of the data can be made in terms of eq 2 and 3 by use of values of ψ_N estimated from the measurements of Noordermeer and Ferry.[6] In Figure 2, ψ_N is plotted against log t as calculated from the time dependence of C_1 and C_2 during stress relaxation at 0 °C.[6] Alternative time scales for other temperatures were specified by shift factors calculated by the WLF equation[9] with coefficients estimated on the basis of the microstructure of the polymer:[10] $c_1 = 10.58$ and $c_2 = 42.8$ for a reference temperature of 0 °C. Relaxation during stretching at T_s and transit at T_t was taken into account, and the time of

Table II
Results for Samples Stretched at 0 °C and Irradiated for 4 h at Various Temperatures

Sample No.	T_s, °C	T_t, °C	T_i, °C	λ_0	λ_s	$\psi_N{}^a$	$C_{2N} \times 10^{-5}$, Pa
104	0	−10	−15	1.400	1.108	0.53	1.49
105	0	−10	−15	1.565	1.202	0.53	1.47
149	0	−10	−15	1.620	1.185	0.53	1.46
150	0	−10	−15	1.749	1.251	0.53	1.52
98	0	−10	−10	1.178	1.054	0.53	1.64
79	0	−10	−10	1.242	1.078	0.53	1.41
129	0	−10	−10	1.262	1.124	0.53	1.39
90	0	−10	−10	1.275	1.106	0.53	1.41
97	0	−10	−10	1.306	1.107	0.53	1.48
122	0	−10	−10	1.309	1.127	0.53	1.44
94	0	−10	−10	1.508	1.193	0.53	1.44
96	0	−10	−10	1.826	1.231	0.53	1.35
100	0	−10	−10	1.839	1.240	0.53	1.42
78	0	−10	−10	1.888	1.355	0.53	1.44
102	0	−10	−10	1.993	1.346	0.53	1.26
99	0	−10	−10	2.782	1.482	0.53	1.09
81	0	−10	−5	1.345	1.148	0.56	1.23
82	0	−10	−5	1.702	1.296	0.56	1.24
75	0	0	−5	1.478	1.189	0.58	1.30
70	0	0	−5	2.499	1.527	0.58	1.04
86	0	0	0	1.330	1.138	0.71	1.15
85	0	0	0	1.553	1.254	0.71	1.18
88	0	0	0	1.774	1.336	0.71	1.15

[a] Estimated from Figure 2.

relaxation during irradiation at T_i was arbitrarily chosen as half the total irradiation time. Having estimated ψ_N in this manner, we calculate C_{2N} with eq 2 and 3 together with stress–strain data at small extensions. Some of the results are given in Table II. The value of C_{2N} is found to decrease somewhat with increasing irradiation temperature, T_i. Results for samples with the same thermal history (T_s = 0 °C, T_t = −10 °C, T_i = −10 °C) but different doses and dose rates are shown in Figure 3. The values of C_{2N} obtained by this method, which corresponded to a temperature of 25 °C at which the stress–strain measurements were made, may be compared with the value obtained by Noordermeer and Ferry from stress–relaxation measurements on the uncross-linked polymer: $C_2 = 1.52 \times 10^5$ Pa in the range of time scale where it is nearly constant at 0 °C, or 1.63×10^5 Pa reduced to 25 °C by multiplying by the ratio of $T\rho$ at the two temperatures (where ρ is the density). The agreement is fairly good, though the latter value is a little higher. C_{2N} in Figure 3 also seems to decrease slightly with increasing extension ratio during irradiation, λ_0, as did ν_N in Figure 1. Independence of λ_0 is obtained when a higher value of ψ_N than that estimated from the paper of Noordermeer and Ferry[6] is chosen.

Discussion

The results presented here show that the apparent concentration of strands terminated by entanglements, ν_N, is considerably reduced when 4-h irradiations are performed more than a few degrees above the glass-transition temperature (Figure 1). At 0 °C (10 °C above T_g) ν_N is reduced by more than 40%. This is qualitatively in agreement with stress relaxation data[6] which show that the C_1 term of uncross-linked 1,2-polybutadiene has relaxed considerably already at log t = 2.5, corresponding to 5 min at 0 °C (the C_2 term relaxes very little in 4 h at 0 °C). A complete analysis becomes very complicated when network strands of the first network are lost during cross-linking in the strained state as discussed by Flory.[11] The following discussion will therefore be limited to irradiations at −10 °C where the relaxation during irradiation should be very small.

There is no detectable effect of stretching temperature below 0 °C. This is reasonable since the stretching operation in these experiments took only about 2 min, allowing very little relaxation before irradiation. And there is no detectable effect of dose rate for irradiations at −10 °C as seen from Figure 3. This also indicates that the relaxation at −10 °C must be very small.

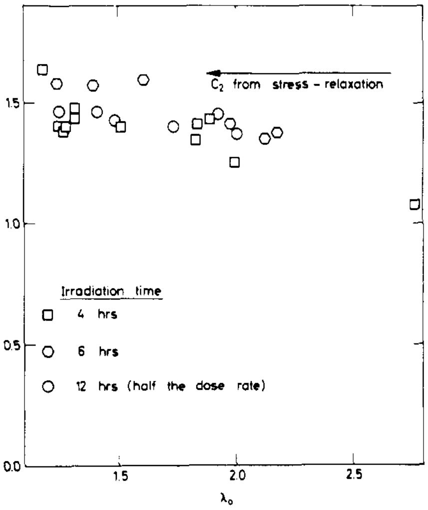

Figure 3. C_2 term of the entanglement network, C_{2N}, calculated from eq 2 and 3 plotted against extension ratio during cross-linking, λ_0. Thermal history is the same for all samples; dose and dose rate are variables. Symbols are identified in Table I.

Thus, when the temperatures are low enough to prevent relaxation before and during irradiation, the two-network results of this study give the same results for the elastic contributions of the entanglement network at small extension ratios as were found from stress–relaxation measurements on uncross-linked polymer by Noordermeer and Ferry, i.e., agreement between equilibrium and transient measurements of the elastic effects of entanglements.

Large strain stress–strain measurements relative to the state of ease (eq 3) should permit a further test of the value of ψ_N, the relative C_2-term contribution of the entanglement network. Such measurements will be reported in a later communication. Experiments are also being made on samples with more precisely controlled thermal history before and during irradiation. The sample dimensions (limited by the irradiation geometry) are at present too small to study stress–strain relations perpendicular to the original stretch direction, though this would be valuable for seeking a better description of nonlinear properties than the Mooney–Rivlin equation can provide.

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