Polyethylene Networks Cross-Linked in Solution: Preparation, Elastic Behavior, and Oriented Crystallization. 2. Stress–Strain Behavior†

A. Posthuma de Boer[1] **and A. J. Pennings***

Department of Polymer Chemistry, State University of Groningen, Groningen, The Netherlands.
Received May 2, 1977

ABSTRACT: The stress–strain behavior of solution-cross-linked polyethylene networks has been investigated in both the dry and swollen states. The magnitude of the moduli of the swollen networks is found to be in accord with the results of swelling measurements described in the first paper. This confirms the applicability of the swelling equation based on the Flory–Wall theory to the determination of the number of elastically active network chains, under the assumption that the elastic reference state q_0 is equal to the degree of swelling during cross-linking q_c. This conclusion is shown to be independent of any assumption concerning the number of trapped entanglements or the level of intramolecular cross-linking. The dry networks exhibit a large Mooney–Rivlin C_2, although it is lower than that of polyethylene cross-linked in the undiluted state. The modulus C_1 is much larger than the corresponding constant for the swollen networks. The large C_1 and C_2 are shown not to be due to strain-rate effects. They only slightly depend on temperature. A possible reason for the exceptional behavior of undiluted polyethylene networks is indicated.

The problem of the elastic equation of state of rubbery polymer networks is still a matter of debate, despite the fact that it has attracted a great deal of attention. The various theories of rubber elasticity may be combined in a single expression for the free energy of deformation of a molecular network:[2a]

$$\Delta F_{\mathrm{el}}/kT = (A\nu/2)(\Lambda_x{}^2 + \Lambda_y{}^2 + \Lambda_z{}^2 - 3) - B\nu \ln \Lambda_x \Lambda_y \Lambda_z \quad (1)$$

where ν stands for the number of elastically active network chains, k stands for the Bolzmann constant, T stands for the absolute temperature, and $\Lambda_{x,y,z}$ stand for the deformation ratios in the x, y, and z directions referring to the dimensions of the network for which $\Delta F_{\mathrm{el}} = 0$. A and B are constants, the values of which differ in the various theories of rubber elasticity. According to Flory and Wall[2b] $A = 1$ and $B = \frac{1}{2}$. James and Guth[3] have $B = 0$ and A unspecified or perhaps $A \simeq \frac{1}{2}$. Edwards[4] and Graessly[5] arrive at $A = \frac{1}{2}$ and $B = 0$, and Staverman[6] uses the James and Guth result for A but leaves B unspecified. Recently Ronca and Allegra[45] and Flory[46] have arrived at values for A between $\frac{1}{2}$ and 1 as a result of taking the internal constraints on the network junctions into account.

Equation 1 leads to expressions for the response of the network to any kind of deformation, expressions such as the well-known swelling equation:

$$\nu^* \overline{V}_1(Aq_0{}^{-2/3}q^{-1/3} - Bq^{-1}) + \ln(1 - q^{-1}) + q^{-1} + \chi q^{-2} = 0 \quad (2)$$

or the stress–strain relation for unidirectional deformation of a network swollen to a fixed degree of swelling:

$$\sigma = RT\nu^* Aq_0{}^{-2/3}q^{+1/3}(\lambda - \lambda^{-2}) \quad (3)$$

where q is the degree of swelling, χ is the Flory–Huggins interaction parameter, $\overline{V}_1$ is the partial molar volume of the diluent, R is the gas constant, ν^* is the number of elastically active network chains per unit volume of the dry network, σ is the retractive force per unit cross section of the dry unstrained network, λ is the elongation ratio referred to the unstrained swollen length, q_0 is the so-called memory parameter, referring to the dimensions for which $\Delta F_{\mathrm{el}} = 0$, $q_0{}^{-2/3} = \langle r^2\rangle_{\mathrm{d}}/\langle r^2\rangle_0$, $\langle r^2\rangle_0$ and $\langle r^2\rangle_{\mathrm{d}}$ being the mean-square end-to-end distance of the network chains in the reference state and in the dry state respectively.

Expressions such as 1 and 2 enable an experimental verification of the different theories. However, the vast experimental evidence concerning this matter has not led to equivocal conclusions so far.

As to the B constant, the situation seems to be clear: earlier studies, reviewed by Dušek and Prins,[2a] as well as more recent work by Mark et al.[7] and Prins et al.,[8] clearly indicate the existence of the logarithmic term in eq 1 and give $B = \frac{1}{2}$ as the most probable value. For the constant A, however, things are quite unclear for two reasons. First, because this constant always appears in the product $Aq_0{}^{-2/3}$, the magnitude of q_0 being unknown. Second, because different experimental results, even when analyzed using the same assumption $q_0 = q_c$ ($q_c{}^{-1}$ being the volume fraction of the polymer during cross-linking), give contradictory outcomes. Evidence in favor of $A = 1$ is found by Mullins, Moore, and Watson[9] and by Dušek and Prins,[2a] whereas the investigations of Bueche[10] and especially the recent work of Allen et al.[11,12] give support to $A = \frac{1}{2}$. Mark and Sullivan[47] found recently for model networks of end-linked poly(dimethylsiloxane) chains a value of 0.65 for the coefficient A.

Two major problems arise when attempts are made to test the relations predicted by the statistical theories: (1) the determination of the number of elastically active network chains, and (2) deviations from the theoretical behavior. For the determination of the number of elastically active network chains not only a quantitative knowledge of the number of chemical cross-links is required but also knowledge of the influence of network flaws such as chain ends, loose loops, and trapped entanglements. So far it has proved difficult to obtain a reliable estimate of the cross-linking density from the chemistry of the network formation.

Deviations from the theoretical predictions are found in the stress–strain behavior of real networks.[2a,13] According to theory the networks should obey eq 3, for the present purpose rearranged to:

$$\frac{\sigma q^{-1/3}}{\lambda - \lambda^{-2}} = C \quad (4)$$

where $C = RT\nu^* Aq_0{}^{-2/3}$. Instead, the stress–strain behavior of real networks is found to be more adequately described by the semiempirical Mooney–Rivlin equation:[2a,13]

$$\frac{\sigma q^{-1/3}}{\lambda - \lambda^{-2}} = C_1 + C_2\lambda^{-2} \quad (5)$$

The constant C_1 is found to increase with increasing cross-link

---

† This paper is dedicated to Maurice L. Higgins on the occasion of his 80th birthday.

density and increasing temperature. It is often considered as a good measure of, or to be equal to, the constant C. The constant C_2 may decrease with increasing cross-link density and with increasing dilution of the network.[2a,14] Recently Flory and Tatara[15] have proposed an adapted form of eq 1, capable of describing the elastic behavior of dry as well as swollen networks using only one set of parameters k_1 and k_2.

The magnitude of the C_2 constant has been shown by Price and Allen et al.[16,17] and by Mark et al.[7] to depend on the cross-linking conditions: networks obtained by cross-linking in solution of natural rubber, *cis*-polybutadiene and poly(dimethylsiloxane) exhibited low or even zero values of C_2. Networks having $C_2 = 0$ have been obtained by Kraus and Moczvegemba[18] and by Landel[19] through end-group coupling of chains sufficiently short to eliminate entanglement trapping. The existence of the C_2 term has led to a large number of tentative explanations,[2a,6,14,20] among which several rest upon the assumption of some kind of structural order or are based on the occurrence of trapped entanglements. However, as yet none of these explanations is fully satisfactory. Ronca and Allegra[45] as well as Flory[46] suggest that the Mooney term, C_2, may conceivably be attributed to the strain-dependent suppression of the rearrangements of the relative position of neighboring junctions.

In the previous paper[21] we described the synthesis of polyethylene networks by cross-linking very high molecular weight linear polyethylene dissolved in trichlorobenzene, using dicumyl peroxide. The cross-linking efficiency and the number of trapped entanglements, as well as the concentration dependence of these quantities, were determined by swelling measurements, using eq 2. The results were compared with the predictions based upon a likely cross-linking mechanism and with independent data regarding entanglement concentrations. The results obtained were consistent with $A = 1$, $B = 1/2$, and $q_0 = q_c$.

In the present paper the stress-strain behavior of both the dry and the swollen networks is described. The objectives of the study were: (1) to test whether or not solution-cross-linked polyethylene networks behave according to theory when measured in the dry state, and (2) to provide an independent check for the conclusions reached in the foregoing paper, i.e., $Aq_0^{-2/3} = q_c^{-2/3}$.

Experimental Section

Samples. The samples were prepared by cross-linking very high molecular weight linear polyethylene dissolved in 1,2,4-trichlorobenzene, using dicumyl peroxide as cross-linking agent. The synthesis and characterization of the samples is described in the previous paper.[21] The degrees of swelling used in the evaluation of stress-strain data of swollen samples were taken from this study. The cylindrically shaped samples were 5 cm in length and 0.8 mm in diameter typically.

Apparatus. The stress-strain measurements were carried out in a specially designed dynamometer, which was also used for the crystallization experiments.[22] The dynamometer is of the usual type,[23] and is shown in Figure 1. The load cell (Statham Instruments, Model UC3 equipped with a UL5 or a UL4 load cell accessory) had measuring ranges of 0–30 g and 0–220 g. The power supply (Philips PE 1209) and strip chart recorder (Kipp Bd 5) had been selected for their minimal electronic and thermal drift.

Perfect reproducibility over long time was achieved. The force measurements had an accuracy better than 0.5% full scale.

Deformations up to 30 cm could be applied with an accuracy better than ±0.05 mm. Ten fixed rates of deformation were available, ranging from 0.001 up to 1 mm/s.

Temperatures from ambient up to 200 °C were maintained by circulation of oil from a thermostat through the outer jacket of the glass vessel and through the circulation system below the lower clamp.

Temperature constancy throughout the glass vessel was better than ± 0.2 °C, when filled with nitrogen; no temperature differences were observed in the *p*-xylene-filled vessel. Temperatures were measured in the direct vicinity of the sample by means of thermocouples. A more detailed description of the apparatus is given in ref 24.

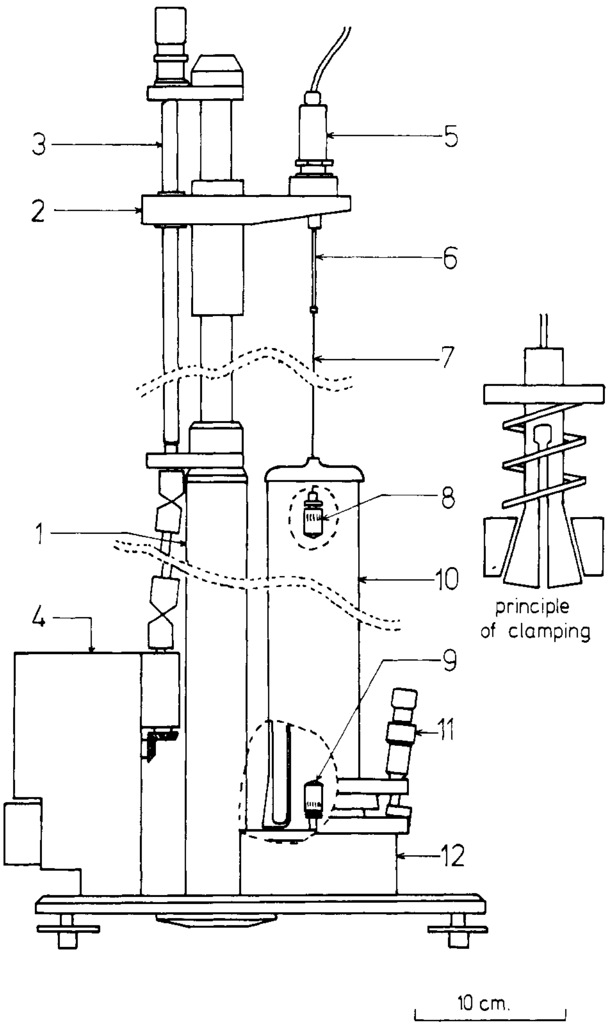

Figure 1. Dynamometer: (1) main column; (2) sliding cross bar; (3) jack screw; (4) motor and gear system; (5) strain gage; (6) glass rod; (7) invar rod; (8) upper clamp; (9) lower clamp; (10) double-walled glass vessel; (11) clamping system for glass vessel; (12) insulating block with build-in oil-circulation system.

Measurements. After clamping and equilibrating, each sample was elongated a few times up to the largest elongation ratio to be applied in the measurements, in order to allow the sample to set tight in the clamps. Most of the stress-strain measurements were performed by elongating the sample at a fixed rate and recording the force as a function of time. After each run the sample was given ample time to regain its original length.

The distance between the clamps was taken as the length of the sample. This leads to an error in the elongation ratio derived from this length, due to nonhomogeneous strains near the clamps. This error is negligible, however, since the length-over-diameter ratio of the samples, $L/D > 40$, is sufficiently large. The effect of the irregular distribution of stresses near the clamps is negligible for the same reason.[25] The initial length was determined by extrapolating the force-extension measurements to zero force. This procedure proved sufficiently accurate to give straight Mooney-Rivlin plots.[26]

A small stream of nitrogen was passed through the measuring vessel to suppress oxidation of the network. In case of measurements using samples swollen in and surrounded by *p*-xylene, 5 mg of the antioxidant di-*tert*-butyl-*p*-cresol/mL of *p*-xylene was added and nitrogen was bubbled through.

Cross sections of the dry samples were determined using a screw micrometer, averaging a number of measurements over the length of the sample.

Results

Dry Networks. Force-extension measurements within the range $1.05 < \lambda < 1.8$ were carried out on solution-cross-linked

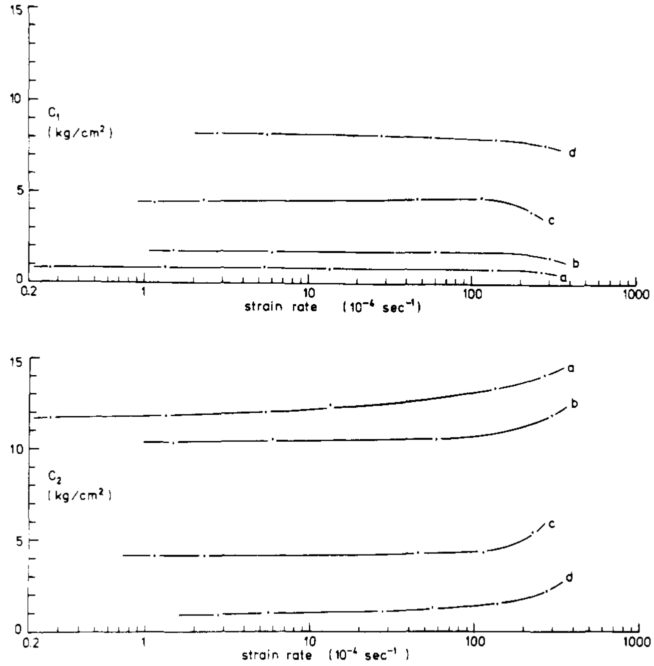

Figure 2. Mooney–Rivlin constants of solution-cross-linked polyethylene networks vs. the strain rate. The letters indicate corresponding curves.

samples of different cross-linking density. The measurements were made over a wide range of strain rates, at 140 °C. The networks are completely molten at this temperature. Crystallization of the networks at an extension ratio of 2 was found to occur at temperatures below 120 °C.[21,22] Each set of data was plotted according to eq 5. Linear plots were obtained, from which C_1 and C_2 were calculated. A number of values of C_1 and C_2 are plotted in Figure 2 as a function of the strain rate used. C_1 and C_2 appear to become constant at sufficiently low values of the strain rate.

The strain-rate-independent values of C_1 and C_2 are gathered in Table I, together with a few results for bulk cross-linked polyethylene. This table also contains data obtained by Gent and Vickroy[27] for γ-irradiated high molecular weight polyethylene. Our results for the bulk-cross-linked samples agree well with their data. The first thing which is apparent from Table I is the interdependence of C_1 and C_2 of the solution-cross-linked samples, whereas the C_2 of the bulk-cross-linked samples seems fairly constant. The interdependence of C_1 and C_2 of the solution-cross-linked samples is illustrated in Figure 3, in which tentatively a broken line is drawn. The very large C_2 at low C_1 should be regarded with some care since it is subject to appreciable experimental error. The relationship shown in Figure 3 is largely of the nature reported in ref 1 and 14.

The second, probably more important feature is the magnitude of C_2 for the networks prepared in solution. It is seen that cross-linking in solution does indeed give rise to lower values of C_2, although very large values are obtained as well. The smaller values are still much larger than the values reported in ref 16 and 17 for natural rubber and *cis*-polybutadiene.

One might question the validity of the results given above, since all measurements have been performed at 140 °C, whereas the equilibrium melting temperature of pure polyethylene is about 145 °C. Therefore we have checked the temperature dependence of C_2. An example is given in Table II. Within experimental error C_2 is independent of the temperature. C_1 shows a small positive temperature dependence.

Table I
Mooney–Rivlin Constants of Undiluted Polyethylene Networks

Cross-linked in solution		Cross-linked in dry state	
C_1, kg/cm²	C_2, kg/cm²	C_1, kg/cm²	C_2, kg/cm²
0.9	12.0	7.3	9.9
1.5	6.5	8.0	9.1
1.8	10.4	2.6[a]	8.6[a]
1.8	5.8	4.4[a]	9.0[a]
2.0	5.7	6.6[a]	9.0[a]
4.7	4.1	8.2[a]	9.0[a]
5.2	3.5	14.2[a]	9.0[a]
8.2	0.9		

[a] Values for γ-irradiated high molecular weight polyethylene; taken from A. N. Gent and V. V. Vickroy, Jr., *J. Polym. Sci., Part A-2*, **5**, 47 (1967).

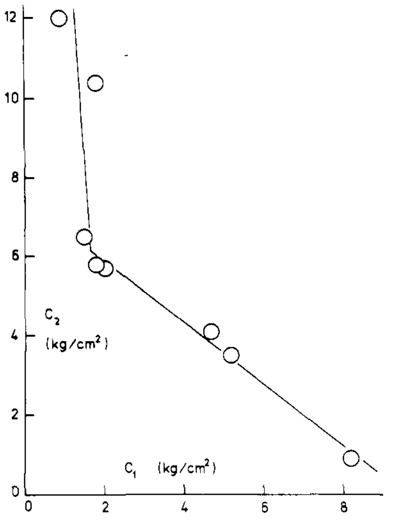

Figure 3. Interdependence of C_1 and C_2 of solution-cross-linked polyethylene networks.

The data pertaining to Table II were used for a thermoelastic analysis. For given elongation ratios the force was plotted against the temperature. Straight lines were obtained. From these data the energetic contribution to the retractive force may be calculated by using the following eq 6 which holds for networks having $C_2 = 0$,[43]

$$\frac{f_e}{f} = 1 - \frac{T}{f}\left(\frac{\mathrm{d}f}{\mathrm{d}T}\right)_{p,\lambda} + \frac{\beta T}{3} \tag{6}$$

where β is the cubical thermal expansion coefficient and p is the pressure. The ratio f_e/f has frequently been related to the temperature dependence of the chain dimensions by:

$$\frac{f_e}{fT} = \frac{\mathrm{d}\ln\langle r^2\rangle_0}{\mathrm{d}T} \tag{7}$$

For f_e/f positive numbers were obtained, ranging from $f_e/f = +0.7$ for $\lambda = 1.05$ to $f_e/f = +0.2$ for $\lambda = 1.6$. This result clearly is at variance with theoretical expectation and earlier measurements, since f_e/f should be negative for polyethylene[28] and should not depend on λ.[29] This may partly be due to neglecting the C_2 contribution to f_e/f[43] and to the fact that there is a contribution from the intermolecular interactions and chain arrangement to be discussed below. The C_2 contribution can be avoided by inserting the temperature dependence of C_1 instead of the temperature dependence of f. Inserting the temperature dependence of C_1 in eq 6 yields $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = -2.1 \times 10^3\ \mathrm{K}^{-1}$. This result has the correct sign but is still

Table II
C_1 and C_2 of a Solution-Cross-Linked Sample at Different Temperatures[a]

T, °C	C_1, kg/cm^2	C_2, kg/cm^2
135	2.0	5.8
140	2.0	5.7
145	2.1	5.7
155	2.2	5.7
160	2.2	5.8

[a] Cross-linking conditions: [PE] = 0.14 g/mL, [DCP] = 0.05 g/mL.

different from the generally accepted value[28] -1.2×10^{-3} K^{-1}.

The stress–strain behavior of the dry networks usually was well reproducible. An exception was found in networks prepared at very high concentrations of peroxide. These samples showed an increasing modulus when measured at successive days maintaining a temperature of 140 °C. A 1.5-fold increase in both C_1 and C_2 was observed over a week for samples cross-linked in 20% solutions using 0.10 g of dicumyl peroxide/mL of solution. Samples prepared using more moderate concentrations of the peroxide did not show such an increasing modulus. Their stress–strain curves were found to be reproducible upon repeated testing in a period of several days.

Swollen Networks. Force-extension measurements were carried out on samples that were swollen in and were surrounded by *p*-xylene. This open system was chosen partly in view of the crystallization experiments[22] and partly for practical reasons. Since the samples do not swell until a temperature of 80 to 100 °C is reached and maintained, experimental difficulties due to evaporation of the solvent (boiling point 138 °C) would arise on removal of the surrounding liquid. Most of the experiments were carried out at the temperature of cross-linking, i.e., 120 °C.

For open swollen systems eq 3 has to be adapted to account for the increase in swelling upon elongation:

$$\sigma = RT\nu^*Aq_0^{-2/3}q_i^{+1/3}\left(\lambda - \frac{q}{q_i}\lambda^{-2}\right) \tag{8}$$

where q stands for the degree of swelling of the elongated sample and q_i for the initial degree of swelling. The dependence of q on λ is given by:

$$\nu^*\bar{V}_1(Aq_0^{-2/3}q_i^{-1/3}\lambda^{-1} - \tfrac{1}{2}q^{-1}) + \ln(1 - q^{-1}) + q^{-1} + \chi q^{-2} = 0 \tag{9}$$

From this equation no simple solution for q in terms of λ can be obtained. Therefore the approximation of Hermans:[30]

$$q/q_i \simeq \lambda^{1/2} \tag{10}$$

will be used, which is quite appropriate for the present purpose.[24] The stress–strain relationship becomes:

$$\sigma = RT\nu^*Aq_0^{-2/3}q_i^{+1/3}(\lambda - \lambda^{-3/2}) \tag{11}$$

or

$$\sigma q_i^{-1/3} = C(\lambda - \lambda^{-3/2}) \tag{12}$$

For evaluation of experimental results it is convenient to rearrange eq 12 to a Mooney–Rivlin type equation, i.e., to write the reduced force $\sigma q_i^{-1/3}/(\lambda - \lambda^{-2})$ as a linear function of λ^{-1}. Strictly, this is only valid if $\lambda \simeq 1$:

$$\frac{\sigma q_i^{-1/3}}{\lambda - \lambda^{-2}} = C \lim_{\lambda^{-1}\to 1}\left[\frac{\lambda - \lambda^{-3/2}}{\lambda - \lambda^{-2}}\right] + C(\lambda^{-1} - 1)\lim_{\lambda^{-1}\to 1}\left[\frac{d}{d\lambda^{-1}}\left(\frac{\lambda - \lambda^{-3/2}}{\lambda - \lambda^{-2}}\right)\right] \tag{13}$$

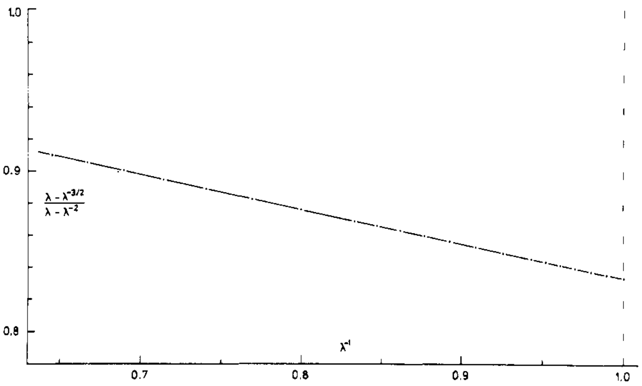

Figure 4. Calculated Mooney–Rivlin type plot of the stress–strain behavior of swollen networks in equilibrium with the surrounding solvent. The function plotted is: $(\lambda - \lambda^{-3/2})/(\lambda - \lambda^{-2})$ vs. λ^{-1}.

$$\frac{\sigma q_i^{-1/3}}{\lambda - \lambda^{-2}} = \tfrac{5}{6}C + C(\lambda^{-1} - 1)\lim_{\lambda^{-1}\to 1}\left[\frac{3 - \tfrac{5}{2}\lambda^{1/2} - \tfrac{1}{2}\lambda^{-5/2}}{(\lambda - \lambda^{-2})^2}\right] \tag{13a}$$

$$\sigma q_i^{-1/3}/(\lambda - \lambda^{-2}) = \tfrac{25}{24}C - \tfrac{5}{24}C\lambda^{-1} \tag{13b}$$

This linear relationship turns out to be valid for larger elongation ratios as well, as is demonstrated by the calculated plot of $(\lambda - \lambda^{-2/3})/(\lambda - \lambda^{-2})$ vs. λ^{-1} given in Figure 4. For the elongation ratios usually applied ($1.05 < \lambda < 1.6$) the calculated relationship is best represented by:[24]

$$\frac{\sigma q_i^{-1/3}}{\lambda - \lambda^{-2}} = 1.04C - 0.21C\lambda^{-1} \tag{14}$$

Apart from the minor difference in the first right-hand term, eq 14 differs from eq 4 only in the second right-hand term. This last term therefore almost completely accounts for the change in volume due to elongation. It is to be noted that throughout the derivation of eq 14 it has been assumed that the swollen network behaves according to Gaussian theory and does not exhibit a C_2 term. The last term of eq 14 is therefore not to be confused with a C_2 term in the classical sense. If the network does not adhere to Gaussian theory, eq 14 will have to be adapted. In such a case the theory of Flory and Tatara,[15] which gives full account of the change in volume of such networks based on an adapted form of the expression for the elastic free energy, seems to be more appropriate.

For the present purpose however it is sufficient to apply the simple theory since, owing to the high degrees of swelling of our networks ($q > 10$), C_2 will be negligible. This last assertion is justified by our results.

By plotting experimental data of open swollen systems just as to obtain a Mooney–Rivlin plot, the effect of the changing degree of swelling is simply eliminated. Since the effect of the change in the degree of swelling is accounted for by the last term of eq 14, it is to be expected that the determination of the constant C by extrapolating the reduced force to $\lambda^{-1} = 0$ will give good estimates too in the case of nonequilibrium experiments. Indeed results obtained by this method are markedly insensitive to the strain rate.[24] The impractical low strain rates necessary to ensure complete swelling equilibrium may thus be avoided. Strain rates between 10^{-3} and 10^{-4} s^{-1} were employed, sufficiently low to attain near-equilibrium conditions.[24] An example of a Mooney–Rivlin-type plot of the stress–strain behavior of a swollen network is given in Figure 5. Straight lines, with a slope of about -0.25 C, are obtained in accord with eq 14.

For a number of samples the constant C was determined using the method described above. From C the number of elastically active network chains was calculated using $A = 1$

Table III
Comparison of Estimates of ν^* Obtained by Different Methods

Cross-linking conditions		ν^*, 10^{-5} mol/mL dry network			
[Polymer], g/mL	[Peroxide], g/mL	Chemical estimate[a]	Calcd from q	Calcd from C (swollen)	Calcd from C_1 (dry)
0.05	0.01	1.6	1.6		11
0.07	0.01	2.3	2.0		22
0.23	0.008	7.2[b]	2.2		34
0.08	0.01	2.6	2.3	2.1	18
0.11	0.02	4.4	4.2	4.3	19
0.06	0.15	8.2	8.9	9.1	
0.14	0.05	8.7	10	12	22
0.23	0.02	9.2	9.4		24
0.19	0.035	9.7	8.8	14[c]	

[a] Calculated using eq 10 from the previous paper, $\nu^* = 2\varphi_{2c}\{E_b[\mathrm{DCP}] + \epsilon_b\}$ taking $E_b = 0.8$ and $\epsilon_b = 10^{-4}$. [b] Concentration of the peroxide too low and therefore cross-linking index too low to obtain complete entanglement trapping[21] and to neglect the chain end correction; the estimate according to footnote a will be too high. [c] Sample shows early onset of non-Gaussian behavior.

Table IV
Thermoelastic Behavior of a Solution-Cross-Linked Polyethylene Sample Swollen in and Surrounded by p-Xylene[a]

λ (−)	1.03	1.04	1.06	1.10	1.15	1.22	1.33	1.48
$\frac{1}{f}\left(\frac{\mathrm{d}f}{\mathrm{d}T}\right)_{p,\lambda}$, 10^{-3} K^{-1}	4.7	4.7	4.7	4.8	4.7	4.7	4.9	5.2

[a] Cross-linking conditions: [PE] = 0.06 g/mL; [DCP] = 0.15 g/mL.

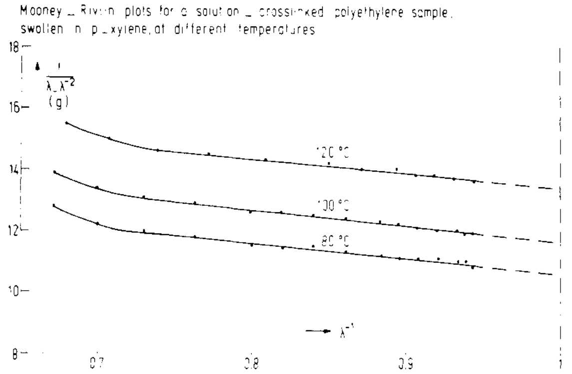

Figure 5. Force–extension behavior of solution-cross-linked polyethylene networks swollen in and surrounded by p-xylene. Data plotted according to eq. 14.

and $q_0 = q_c$ in the calculations. The results are shown in Table III. In this table are also given values for ν^* calculated from the degree of swelling using $A = 1$ and $B = \frac{1}{2}$[21] and values for ν^* obtained from C_1 of the dry samples. Furthermore chemical estimates of ν^* are shown. These estimates are based upon the Bueche–Mullins equation given in the previous paper (eq 10). The contributions of the trapped entanglements to ν^* therefore are included in these estimates.

The results of the stress–strain measurements on swollen networks appear to agree well with the results obtained from swelling measurements and with the chemical estimates. The present results therefore confirm the conclusions reached in the previous paper, i.e., $A = 1$, $B = \frac{1}{2}$, and $q_0 = q_c$. The results obtained from the dry networks clearly are much too large. Even larger values would have been obtained if the initial modulus ($C_1 + C_2$) had been used as the measure for C.

The measurements shown in Figure 5 form part of a series which was used for a thermoelastic analysis. In this case of an open swollen system, β in eq. 6 denotes the cubical thermal expansion coefficient of the network in swelling equilibrium with the solvent at the given elongation ratio. In a first approximation according to eq 10, this coefficient may be set equal to the coefficient of expansion of the unstretched swollen network. This quantity was determined in a separate experiment. The result, expressed in terms of the degree of swelling, is shown in Figure 6. The coefficient of expansion obtained is: $\beta = -2.1 \times 10^{-3}$ K^{-1}.

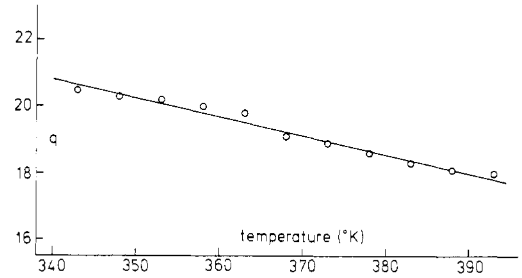

Figure 6. Dependence upon temperature of the degree of swelling in p-xylene of a solution-cross-linked polyethylene network.

In Figure 7 the retractive force is plotted against the temperature for a number of elongation ratios. Straight lines are obtained, except for the larger elongation ratios. The curvature in the latter case corresponds to the upsweep in the pertaining stress–strain curves. The temperature dependence of the retractive force obtained from Figure 7 is given in Table IV. This temperature dependence appears to be remarkably constant down to very low elongation ratios. The magnitude of f_e/f calculated from Table IV, $f_e/f = -1.0$, differs from the generally accepted value, −0.5. This should be ascribed to diffusion of the solvent into the network, which is not fully at equilibrium at the applied strain rate of about 5×10^{-4} s^{-1}.

Although the determination of the force will be largely correct at this strain rate, its temperature dependence will contain a term relating to the temperature dependence of the diffusion constant for diffusion of the solvent into the network and will therefore be biassed.

The slopes and intercepts for $\lambda^{-1} = 0$ for the plots such as shown in Figure 5 are plotted in Figure 8 as a function of the temperature. The temperature dependence of the constant C was calculated from the least-squares line in Figure 8. Insertion of this temperature dependence, $1/C$ ($\mathrm{d}C/\mathrm{d}T$), in eq 6 for $1/f/(\mathrm{d}f/\mathrm{d}T)$, gives $f_e/f = -0.57$ and $\mathrm{d} \ln \langle r^2\rangle_0/\mathrm{d}T = -1.5 \times 10^{-3}$ K^{-1}. This result, compared with the result obtained

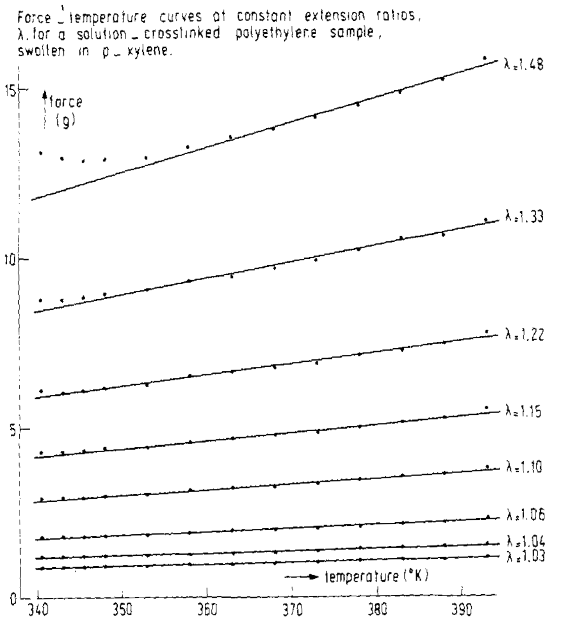

Figure 7. Force-temperature data at constant elongation ratios for a solution-cross-linked polyethylene network swollen in and surrounded by *p*-xylene.

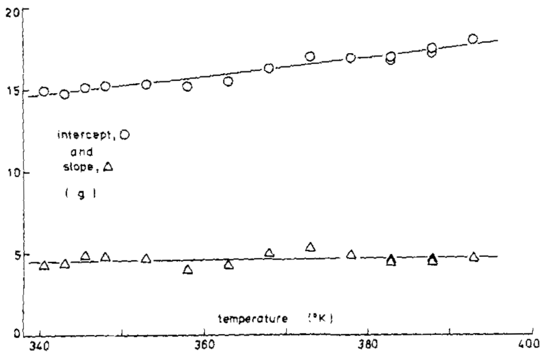

Figure 8. Intercepts for $\lambda^{-1} = 0$ and slopes of Mooney-Rivlin type plots of the data underlying Figure 7 vs. temperature.

by directly plotting the force vs. the temperature as described above, once more demonstrates that by evaluation of stress-strain data using eq 14, diffusion effects are eliminated.

The stress-strain behavior of the swollen samples was quite reproducible.

Network degradation was not observed, except when the samples had been subjected to extreme large elongations at high temperatures for prolonged time. (Such conditions occurred during the crystallization experiments, where elongation ratios up to 6 were applied.[22])

An example is shown in Figure 9. The upsweep of the stress-strain curve appears to be shifted toward a much larger elongation ratio. The network does not seem to adhere to the theory any longer, judging from the positive slopes. If one assumes eq 14 still to be applicable, a decrease of ν^* by a factor 0.8 is found.

A number of samples exhibited the onset of non-Gaussian behavior due to finite extensibility of the chains at such small extension ratios that they were unsuitable for testing the simple theory of elasticity. Samples showing such a behavior had mostly been prepared at high concentrations of the peroxide.

Discussion

The data presented above demonstrate two contrasting aspects of the elastic behavior of solution-cross-linked polyethylene networks. The swollen networks behave according to theory whereas the dry networks exhibit large deviations. We will discuss these two aspects separately, although they are closely interrelated as regards the relevance of the theory.

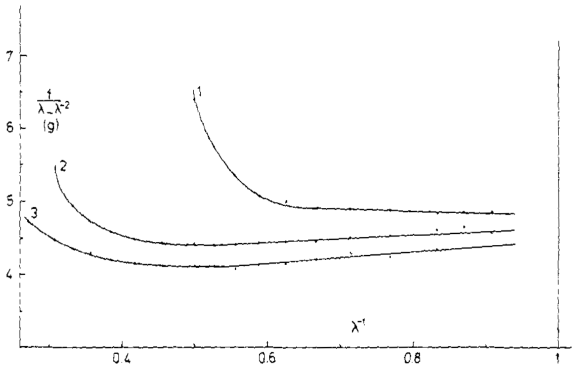

Figure 9. Change of stress-strain behavior of a swollen polyethylene network after extreme testing. Various elongation ratios up to 4 were maintained for prolonged time: (1) initial curve; (2) after 4 days testing; (3) after 10 days testing.

Swollen Networks. The main objective of the measurements on the swollen networks was to provide an independent check for the conclusions reached in the previous paper concerning the constants in the elastic equation of state. These conclusions were based upon a comparison of a chemical determination of the cross-linking density with the determination through application of the swelling equation. Since results obtained from the swelling equation depend on the expression chosen for the free energy of mixing of the solvent with the network, or, more specifically, on the choice of the interaction parameter χ, it would be desirable to dispose of results which are independent of χ. This is provided by stress-strain measurements, which give $Aq_0^{-2/3}$ independent of any assumption concerning B and χ. The results of the stress-strain measurements of the swollen networks presented in this paper agree well with the results of swelling measurements shown in the first paper. The use of a single value for the Flory-Huggins interaction parameter, $\chi = 0.37$, for the highly swollen networks is thereby justified. The neglect of the concentration dependence of χ in the small concentration range covered by the highly swollen networks ($0.03 < \varphi < 0.12$) apparently does not lead to serious error in the calculation of ν^*.

More important however is the conclusion that the present results confirm the use of $Aq_0^{-2/3} = q_c^{-2/3}$. We think the most simple combination, $A = 1$ and $q_0 = q_c$, the best choice for the time being.

It should be emphasized that this last conclusion would not have been different if the stress-strain data had been treated differently. Even if one would not have considered at all the change in the degree of swelling during stretching and would have applied eq 4 straightforward, one would have found C only by a factor $5/6$ too low. This still leads to $A = 1$. If eq 11 would have been applied, somewhat too large a C would have been found, leading to $A = 1$ as well.

No spurious effects due to the possible appearance of a C_2 term were noted, as was to be expected in the highly swollen systems studied.

We recall that in the comparison of the chemical and the elastical results for ν^* no assumptions were necessary to account for the contribution of the trapped entanglements. The chemical estimate is based on the use of the experimentally determined Bueche-Mullins equation, in which the contribution of the trapped entanglements appears as the intercept.[21] The results thus obtained for the number of trapped entanglements as well as for its concentration dependence are experimentally founded. Comparison with independent data regarding entanglement concentrations provide arguments in favor of the conclusions reached.[21]

It is interesting to note that the accordance between chemical and elastical estimates of ν^* holds down to low concentrations of the polymer during cross-linking. This brings up again the matter of loop formation, to which some attention was already given in the previous paper.[21]

One important feature of our system discussed in this paper is that the use of an extremely high molecular weight parent polymer leads to low concentrations of intramolecular loops.

Since the formation of ineffective loops may become a major process especially at low concentrations of the polymer during cross-linking, it is of great importance to see whether loop formation would affect our conclusions. To this end we once more consider the mechanism of the formation of cross-links in polyethylene through peroxides. This mechanism was shown in the previous paper to be a "cage" mechanism. Chemical links between, or in, polyethylene molecules will only be formed if at the moment of decomposition of a peroxide molecule two segments of the polymer form part of the solvent "cage" surrounding the peroxide molecule. These segments can be part of different chains, which thus become connected, or can be part of the same chain, which thus will form a loose loop if this loop is not further involved in the reaction. The number of intermolecular links per unit reaction volume produced after complete decomposition of the peroxide will be given by:[21]

$$\nu_{\mathrm{inter}}\varphi_{2\mathrm{c}} = E_{\mathrm{b}}[\mathrm{DCP}]\varphi_{2\mathrm{c}}^{2} \tag{15}$$

where ν_{inter} stands for the number of intermolecular links per unit volume of the dry network, [DCP] denotes the concentration of the dicumyl peroxide at the beginning of the reaction, $\varphi_{2\mathrm{c}}$ is the volume fraction of the polymer during reaction, and E_{b} is the cross-linking efficiency of the peroxide in the bulk polymer: $E_{\mathrm{b}} = 0.8$ mol of cross-links per mol of peroxide. For intramolecular cross-linking however the reaction yield will be given by:

$$\nu_{\mathrm{intra}}\varphi_{2\mathrm{c}} = L[\mathrm{DCP}]\varphi_{2\mathrm{c}} \tag{16}$$

where ν_{intra} stands for the number of intramolecular links per unit volume of the dry network, and where L in a first approximate is independent of dilution.[49]

The total number of chemical links produced will be given by the sum of eq 15 and 16. The ratio of intra- vs. intermolecular cross-linking will be given by:

$$\frac{\nu_{\mathrm{intra}}}{\nu_{\mathrm{inter}}} = \frac{L}{E_b}\frac{1}{\varphi_{2\mathrm{c}}} \tag{17}$$

in agreement with the predictions of Dušek[31] and Allen et al.[11,12]

The comparison of the chemical estimate of ν^* with the determination either by application of the swelling equation as shown in the first paper[21] or by evaluation of stress–strain data as presented in this paper is based upon the use of eq 15 for the chemical estimate. Therefore this comparison exclusively pertains to intermolecular cross-links. It will not be biassed by the intramolecular loops, leaving only the less probable bimolecular loops unaccounted for. Consequently our conclusions concerning the constants in the elastic equation of state are not affected by the occurrence of intramolecular cross-linking. In summary, we conclude, independent of any assumptions concerning trapped entanglements and intramolecular cross-linking, that all our data are in accord with: $A = 1$, $B = \frac{1}{2}$, and q_0 to be taken equal to q_{c}.

It should be noted that Allen et al., by measuring moduli of swollen polystyrene[11] and polyurethane[12] gels, both prepared in solution, arrive at the conclusion $A = \frac{1}{2}$, implicitely assuming $q_0 = q_{\mathrm{c}}$. This conclusion and ours seem to be conflicting, just as the earlier work of Mullins, Moore, and Watson[9] contradicts the work of Bueche[10] in this respect. It is therefore interesting to look for differences that might possibly be the cause of the contradictory results.

Apparent differences such as chemical composition, cross-linking density, cross-linking temperature, chain length distribution, and furthermore estimates of the numbers of entanglements and loops can of course be taken responsible for the contradictions. In the opinion of the present authors another factor may play a role, namely the connectivity pattern in the network. As we pointed out in the previous paper in connection with the absence of syneresis, the connectivity in a network build up by cross-linking of existing chains will depend on the reaction rate. Completion of the reaction in our case took 24 hr, at 120 °C, whereas in the investigations of Allen et al.[11,12] the reaction was completed within 1–5 h[12] or even in less than 0.5 h,[11] at room temperature. Therefore, our polyethylene gels might exhibit a connectivity different from the connectivity pattern of the polystyrene and polyurethane gels. It is these kinds of differences that may lead to different values for A, as is discussed in the theoretical work of James and Guth[3] and more recently by Edwards and Freed.[4] In our opinion, it will be of interest to take into account this aspect of network formation in future experimental investigations intended to further evaluate the theories of rubber elasticity.

The thermoelastic measurements given in Figure 7 should be considered as a demonstration of the possibility to obtain results which indeed are independent of the elongation ratio, as is required by the Gaussian theory. Constant values were obtained down to very low elongation ratios ($\lambda = 1.03$). This would have been impossible by the usual temperature cycle measurements.[29] As was stated already, the results are biassed by residual diffusion of solvent into the network. Therefore measurements are currently being carried out to further investigate the thermoelastic behavior of the swollen gels. The effect of diffusion can in the limiting case $\lambda = 1$ largely be eliminated by use of the constant C from eq 14. This is demonstrated by the value obtained: $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = -1.5 \times 10^{-3}$ K^{-1}.

The early onset of non-Gaussian behavior as shown by a number of networks, most of which had been prepared at high concentrations of the peroxide, is not surprising. Since the cross-linking of polyethylene in solution may be considered a true random process, it is to be expected that the networks will contain a fraction of short chains, especially in the case of higher cross-linking densities. Such short chains may be taken responsible for the limited applicability of Gaussian statistics. The short chains probably play a major role too in the observed changes in elastic behavior of the swollen networks after extreme extension for long times. Judging from the shift to larger extensions of the upsweep and the apparent decrease in modulus, the prolonged elongation may have caused some sort of mechano-chemical process in which preferably shorter chains are broken.

Dry Networks. The solution-cross-linked polyethylene networks exhibit in the undiluted state an elastic behavior which is far from ideal. Although the solution-cross-linked samples indeed show lower values for the C_2 constant in the Mooney–Rivlin equation than the samples prepared in the undiluted state, still large C_2 values are found. This behavior is at variance with the behavior reported for natural rubber,[16] *cis*-polybutadiene,[7,17] and poly(dimethylsiloxane),[7] which polymers when cross-linked in solution form networks characterized by a small C_2 term. The large C_2 term found for the polyethylene networks is neither due to "nonequilibrium"

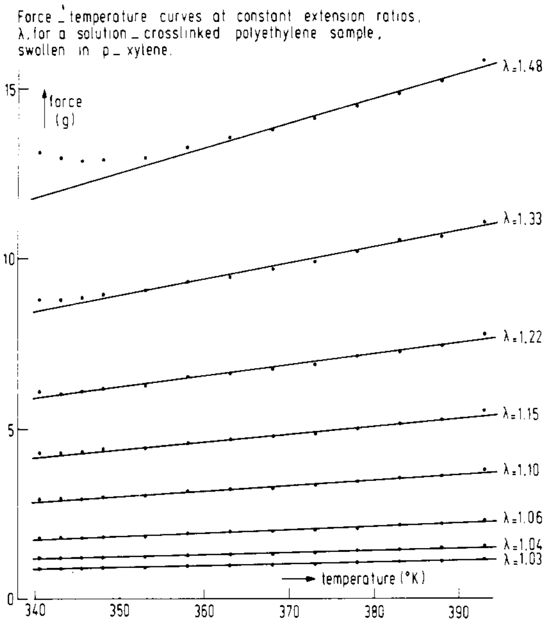

Figure 7. Force-temperature data at constant elongation ratios for a solution-cross-linked polyethylene network swollen in and surrounded by p-xylene.

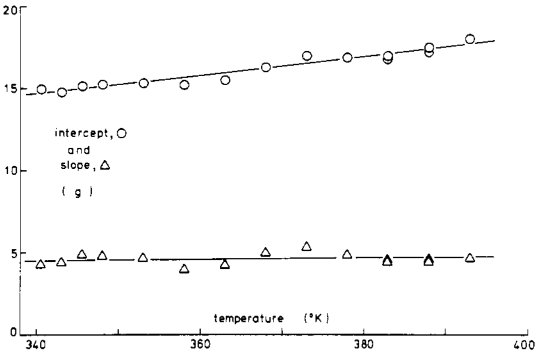

Figure 8. Intercepts for $\lambda^{-1} = 0$ and slopes of Mooney-Rivlin type plots of the data underlying Figure 7 vs. temperature.

by directly plotting the force vs. the temperature as described above, once more demonstrates that by evaluation of stress-strain data using eq 14, diffusion effects are eliminated.

The stress-strain behavior of the swollen samples was quite reproducible.

Network degradation was not observed, except when the samples had been subjected to extreme large elongations at high temperatures for prolonged time. (Such conditions occurred during the crystallization experiments, where elongation ratios up to 6 were applied.[22])

An example is shown in Figure 9. The upsweep of the stress-strain curve appears to be shifted toward a much larger elongation ratio. The network does not seem to adhere to the theory any longer, judging from the positive slopes. If one assumes eq 14 still to be applicable, a decrease of ν^* by a factor 0.8 is found.

A number of samples exhibited the onset of non-Gaussian behavior due to finite extensibility of the chains at such small extension ratios that they were unsuitable for testing the simple theory of elasticity. Samples showing such a behavior had mostly been prepared at high concentrations of the peroxide.

Discussion

The data presented above demonstrate two contrasting aspects of the elastic behavior of solution-cross-linked polyethylene networks. The swollen networks behave according to theory whereas the dry networks exhibit large deviations. We will discuss these two aspects separately, although they are closely interrelated as regards the relevance of the theory.

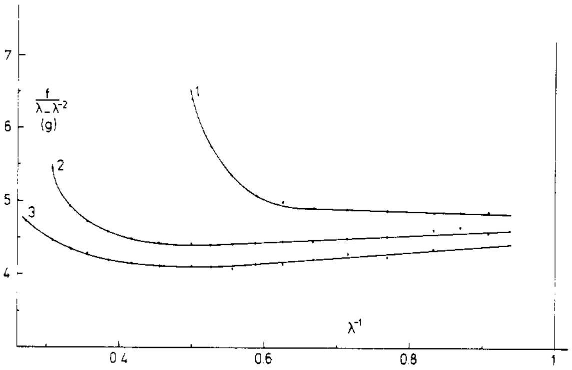

Figure 9. Change of stress-strain behavior of a swollen polyethylene network after extreme testing. Various elongation ratios up to 4 were maintained for prolonged time: (1) initial curve; (2) after 4 days testing; (3) after 10 days testing.

Swollen Networks. The main objective of the measurements on the swollen networks was to provide an independent check for the conclusions reached in the previous paper concerning the constants in the elastic equation of state. These conclusions were based upon a comparison of a chemical determination of the cross-linking density with the determination through application of the swelling equation. Since results obtained from the swelling equation depend on the expression chosen for the free energy of mixing of the solvent with the network, or, more specifically, on the choice of the interaction parameter χ, it would be desirable to dispose of results which are independent of χ. This is provided by stress-strain measurements, which give $Aq_0^{-2/3}$ independent of any assumption concerning B and χ. The results of the stress-strain measurements of the swollen networks presented in this paper agree well with the results of swelling measurements shown in the first paper. The use of a single value for the Flory-Huggins interaction parameter, $\chi = 0.37$, for the highly swollen networks is thereby justified. The neglect of the concentration dependence of χ in the small concentration range covered by the highly swollen networks ($0.03 < \varphi < 0.12$) apparently does not lead to serious error in the calculation of ν^*.

More important however is the conclusion that the present results confirm the use of $Aq_0^{-2/3} = q_c^{-2/3}$. We think the most simple combination, $A = 1$ and $q_0 = q_c$, the best choice for the time being.

It should be emphasized that this last conclusion would not have been different if the stress-strain data had been treated differently. Even if one would not have considered at all the change in the degree of swelling during stretching and would have applied eq 4 straightforward, one would have found C only by a factor $^5/_6$ too low. This still leads to $A = 1$. If eq 11 would have been applied, somewhat too large a C would have been found, leading to $A = 1$ as well.

No spurious effects due to the possible appearance of a C_2 term were noted, as was to be expected in the highly swollen systems studied.

We recall that in the comparison of the chemical and the elastical results for ν^* no assumptions were necessary to account for the contribution of the trapped entanglements. The chemical estimate is based on the use of the experimentally determined Bueche-Mullins equation, in which the contribution of the trapped entanglements appears as the intercept.[21] The results thus obtained for the number of trapped

(6) A. J. Staverman, *J. Polym Sci., Polym. Symp.*, **No. 51**, 45 (1975).
(7) J. E. Mark, *J. Am. Chem. Soc.*, **92**, 7252 (1970); R. S. Johnson and J. E. Mark, *Macromolecules*, **5**, 41 (1972); C. U. Yuh and J. E. Mark, *ibid.*, **6**, 751 (1973).
(8) D. Froehlich, D. Crawford, and W. Prins, *Macromolecules*, **5**, 100 (1972).
(9) L. Mullins, *J. Polym. Sci.*, **19**, 225 (1956); C. G. Moore and W. F. Watson, *ibid.*, **19**, 237 (1956); L. Mullins, *J. Appl. Polym. Sci.*, **2**, 1 (1959).
(10) A. M. Bueche, *J. Polym. Sci.*, **19**, 297 (1956).
(11) D. J. Walsh, G. Allen, and G. Ballard, *Polymer*, **15**, 366 (1974).
(12) G. Allen, P. L. Egerton, and D. J. Walsh, *Polymer*, **17**, 65 (1976).
(13) L. R. G. Treloar, "The Physics of Rubber Elasticity", Oxford University Press, London, 1958.
(14) J. E. Mark, *Rubber Chem. Technol.*, **48**, 495 (1975).
(15) P. J. Flory and Y-I. Tatara, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 683 (1975).
(16) C. Price, G. Allen, F. de Candia, M. C. Kirkham, and A. Subramaniam, *Polymer*, **11**, 486 (1970).
(17) F. de Candia, L. Amelino, and C. Price, *J. Polym. Sci., Part A-2*, **10**, 975 (1972).
(18) G. Kraus and G. A. Moczvgemba, *J. Polym. Sci., Part A*, **2**, 277 (1964).
(19) R. F. Landel, "Polymer Networks, Structure and Mechanical Properties", A. J. Chömpff and S. Newman, Ed., Plenum Press, New York, N.Y., 1971, p 219.
(20) J. Schwarz, *Kolloid-Z. Z. Polym.*, **251**, 215 (1973).
(21) A. Posthuma de Boer and A. J. Pennings, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 187 (1976).
(22) A. Posthuma de Boer and A. J. Pennings, to be published.
(23) J. F. M. Oth and P. J. Flory, *J. Am. Chem. Soc.*, **80**, 1297 (1958).
(24) A. Posthuma de Boer, Thesis, University of Groningen, The Netherlands, 1977.
(25) R. G. C. Arridge and M. J. Folkes, *Polymer*, **17**, 495 (1976).
(26) A. M. Hassan and L. N. Ray, Jr., *J. Appl. Polym. Sci.*, **15**, 1837 (1971).
(27) A. N. Gent and V. V. Vickroy, Jr., *J. Polym. Sci. Part A-2*, **5**, 47 (1967).
(28) A. Ciferri, C. A. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961); P. J. Flory, A. Ciferri, and R. Chiang, *ibid.*, **83**, 1023 (1961).
(29) M. Shen and M. Croucher, *Macromol. Sci., Rev. Macromol. Chem., C*, **12**, 287 (1975).
(30) J. J. Hermans, *Trans. Faraday Soc.*, **43**, 591 (1947); K. J. Smith, Jr., "Polymer Science", A. D. Jenkins, Ed., North-Holland Publishing Co., Amsterdam, 1972, Chapter 5.
(31) K. Dušek, *Collect. Czech. Chem. Commun.*, **33**, 1100 (1968).
(32) A. Ziabicki, *Colloid Polym. Sci.*, **254**, 1 (1976).
(33) M. L. Huggins, *Ann. N.Y. Acad. Sci.*, **41**, 1 (1942); *J. Phys. Chem.*, **75**, 1255 (1971); *Pure Appl. Chem.*, **31**, 245 (1972).
(34) G. Gee and W. J. Orr, *Trans. Faraday Soc.*, **42**, 507 (1946).
(35) An excellent review is given by Dušek and Prins (ref 2a); a more recent theory based on this idea is developed by Schwarz (ref 15).
(36) R. S. Stein and S. D. Hong, *J. Macromol. Sci., Phys.*, **12**, 125 (1976).
(37) E. W. Fisher, J. H. Wendorf, M. Dettenmaier, G. Leiser, and I. Voigt-Martin, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15**, 8 (1964); G. Leiser, E. W. Fisher, and K. Ibel, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 39 (1975); J. Schelten, G. D. Wignall, and D. G. H. Ballard, *Polymer*, **15**, 682 (1974); D. Y. Yoon and P. J. Flory, *Macromolecules*, **9**, 294, 299 (1976). See also: *J. Macromol. Sci., Phys.*, **12**, parts 1 and 2 (1976).
(38) J. Schelten, D. G. H. Ballard, G. D. Wignall, G. Longman, and W. Schmatz, *Polymer*, **17**, 751 (1976).
(39) L. F. Gölz and H. G. Zachmann, *Makromol. Chem.*, **176**, 2721 (1975); P. Schmedeling and H. G. Zachmann, *Colloid Polym. Sci.*, **253**, 527 (1975).
(40) G. W. Longman, G. D. Wignal, and R. P. Sheldon, *Polymer*, **17**, 485 (1976). See also: I. Voigt-Martin and F. C. Mijlhoff, *J. Appl. Phys.*, **46**, 1165 (1975); Yu. K. Ovchinnikov, G. S. Markova, and V. A. Kargin, *Vysokomol. Soedin. Ser. A*, **11**, 329 (1969).
(41) R. F. Boyer and R. L. Miller, *Polymer*, **17**, 925 (1976).
(42) P. J. Flory, *J. Macromol. Sci., Phys.*, **12**, 1 (1976).
(43) J. L. Sullivan and K. J. Smith, Jr., *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 857 (1975).
(44) T. R. Manley and M. M. Qayyum, *Polymer*, **13**, 587 (1972).
(45) G. Ronca and G. Allegra, *J. Chem. Phys.*, **63**, 4990 (1975).
(46) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **351**, 351 (1976).
(47) J. E. Mark and J. L. Sullivan, *J. Chem. Phys.*, **66**, 1006 (1977).
(48) J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635 (1966).
(49) Since the intramolecular links will be formed by the same mechanism as the intermolecular links, one can write: $L = E_b\varphi_{coil}$, where φ_{coil} denotes the effective volume occupancy or volume fraction of the segments in the coil. In a first approximation, φ_{coil} may be taken independent of dilution in the system polyethylene–trichlorobenzene. The order of magnitude of φ_{coil} may amount to a few percent depending on molecular weight. For polyethylene in a theta solvent φ_{coil} can be estimated using the following expression:

$$\varphi_{coil} = \frac{\text{actual vol of a chain}}{4/3\pi R_g^{3}} = \frac{6.2}{M^{1/2}}$$

where R_g is the radius of gyration and M is the molecular weight. Equation 17 may then be rewritten as:

$$\frac{\nu_{intra}}{\nu_{inter}} = \frac{\varphi_{coil}}{\varphi_{2c}} = \frac{6.2}{\varphi_{2c}M^{1/2}}$$

which reduces to $\nu_{intra}/\nu_{inter} = 0.01/\varphi_{2c}$ for a polyethylene with molecular weight of 400×10^3. This shows that the number of intramolecular cross-links in the present case is small as a result of starting form a high molecuar weight polymer.[11,12,31]

Study of Conformational Changes of N-(n-Alkyl) Maleimides with Chain Length[†]

J. I. González de la Campa, J. M. Barrales-Rienda,* and J. González Ramos

Instituto de Plásticos y Caucho, C.S.I.C., Juan de la Cierva, 3, Madrid 6, Spain.

Received May 3, 1977

ABSTRACT: The intramolecular structure of a series of N-(n-alkyl) maleimides in solution was studied by a high-resolution nuclear magnetic resonance technique. A sharp transition in the NMR spectra of N-(n-alkyl) maleimides in benzene at 60 °C was observed at N-(n-decyl) maleimide, above which there exist two distinguishable NMR peaks for internal methylene protons, and below which only a single peak was observed. The NMR signals of the internal methylene protons taken in carbon tetrachloride are not resolved as in those NMR spectra taken in benzene solutions. The experimental results are discussed in terms of a mechanism developed by Ando and Nishioka. These authors have assumed that the double peaks of some n-alkanes in α-chloronaphthalene could arise from a contribution of the methylene groups adjacent to gauche bonds which are incompletely averaged along the chain. The incomplete averaging may be due to a strong interaction between the n-alkyl chain and the α-chloronaphthalene molecules. In our case a specific interaction between the N-(n-alkyl) maleimides and benzene has been considered. This interaction arises from 1:1 exo-stereospecific association of the N-(n-alkyl) maleimide and benzene molecules.

In a recent paper,[1] the conformation and packing in the solid state of a series of poly[N-(n-alkyl) maleimides] has been studied by means of x-ray diffraction. From this work a sudden transition has been found at $n \geq 10$ in the relationship between the diffraction maximum corresponding to the side chains and n (number of carbon atoms in the lateral side chain), showing that the conformation of the side chains deviates from the planar zig-zag if it has more than ten carbon atoms.

Conformational transitions of such a type have been ob-

[†] Dedicated to Professor Dr. M. L. Huggins on his 80th birthday.