Elastically Ineffective Cross-Links in Rubbers

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ABSTRACT: A significant fraction of the cross-links formed in the process of producing a rubbery network are elastically ineffective. The reason is that they close intramolecular loops which are not otherwise attached to the rest of the network. Calculations of this fraction are performed for *cis*-1,4-polyisoprene (natural rubber) as a function of the degree of cross-linking, the length of the chemical bridge which forms the cross-link, the initial molecular weight, and the degree of dilution when cross-linking in solution. For typical rubber networks, cross-linked in the dry state with from 0 to 2% of the monomer units involved in cross-links, the fraction of cross-links wasted in the formation of elastically ineffective intramolecular loops is *ca.* 0.1–0.2. This fraction is approximately doubled and quadrupled for networks formed in solution with volume fractions of rubber equal to 0.5 and 0.1, respectively. Since a sizeable percentage of the intramolecular loops formed consist of a small number of polymer units, it is believed that entanglement between the loops and other chains of the active network does not serve to reduce greatly the fraction of elastically ineffective cross-links.

Possible topologies[1] of portions of a rubbery network formed during the process of cross-linking are presented schematically in Figures 1–4. The network structures surrounding the fixed cross-link shown in Figure 1, and the entanglement depicted in Figure 2, are capable of permanently sustaining the stress generated by an applied strain. Both topologies have been accounted for in several treatments[1,2] of rubber elasticity.

Network defects of the type illustrated in Figures 3 and 4, on the other hand, are not capable of permanently supporting a stress, and do not contribute to the equilibrium elasticity of the network. Network chains such as GB, DC, and FE in Figure 3, attached to the active network at one end only, will not be permanently stressed when the network is strained. Flory[1] has accounted for chain ends by subtracting from the number of cross-links those necessary merely to make the collection of polymer molecules into one large macromolecule, rather than a network.

The present study focuses attention on the presence of potential network defects in the form of intramolecular cross-links, such as the one at A in Figure 4. Previous treatments[1,2] of rubber elasticity either failed to acknowledge the presence of such intramolecular cross-links or dismissed consideration of them on the presumption of their relative scarcity. One of the present authors has recently discussed[3] in a semiquantitative manner the question of the frequency of occurrence of such intramolecular cross-links in a rubbery network. On the basis of a comparison between the volume physically occupied and the volume pervaded by a polymer chain, together with the assumption that the units of a polymer chain are uniformly distributed throughout its sphere of influence, it was concluded[3] that an appreciable percentage of the cross-links introduced into a rubbery network would be of the intramolecular variety and possibly elastically ineffective. This is especially true for networks formed from low molecular weight polymer chains, or those formed in solution.

In this study we shall present quantitative estimates of the relative number of intramolecular cross-links formed during the cross-linking process. However, not all such cross-links lead to loops which cannot sustain stress. If the loop contains another effective cross-link or entanglement, then the loop will be permanently deformed under a strain. The difference between elastically effective and ineffective loops is illustrated in Figures 5 and 6. In Figure 5 the cross-links A and B are elastically ineffective, while in Figure 6 the cross-links A and B are effective by virtue of the entanglement at C and the cross-link D.

The first recognition of the possible significance of intramolecular cross-links was by Flory[1] in 1944. A number of authors, most recently Dusek,[2] and Labana, Newman, and Chompff,[2] have attempted a quantitative estimate, but they have omitted two essential factors which render their results qualitatively incorrect. The first is the short-range correlations between pairs of cross-link sites on the same macromolecule (Dusek[2] has considered this effect in a preliminary way). The second is the recognition that a cross-link along the intramolecular loop incorporates the loop into the network.

Theory

The model adopted for cross-linking can be described as follows. Some unit (repeat or monomer) of a given polymer molecule is grabbed at random by one end of the cross-linking agent. The free end of this cross-linking bridge then attaches onto another polymer unit which is a distance L away, where L is the bridge's length. We must therefore consider a volume element δV a distance L from some unit of a polymer chain. In δV we need the density of units belonging to the same polymer molecule, which, if cross-linked, will produce an elastically ineffective loop. Then we have to find the total density in δV. The ratio of the two densities is the fraction of elastically ineffective cross-links. Details will now be presented.

The system under consideration is composed of N primary macromolecules per unit volume, each of which has $n + 1$ repeat units. Of the

$$\rho = N(n + 1) \tag{1}$$

repeat units per unit volume, ν are involved in cross-links (there are $\nu/2$ cross-links). As we have explained, the number of units involved in elastically effective cross-links is reduced to $\nu(1 - f)$ by virtue of the fact that a fraction f of the cross-links form loops not otherwise incorporated into the network. This number is further reduced by the number of cross-links required merely to form a network. For this correction we follow Flory;[1] and we obtain as the formula for the number of units involved in elastically effective cross-links

$$\nu_e^* = \begin{cases} \nu(1 - f) - 2N & \text{if } > 0 \quad (2) \\ 0 & \text{otherwise} \quad (3) \end{cases}$$

The point at which ν_e^* passes from 0 to a finite value is

(1) P. J. Flory, *Chem. Rev.*, **35**, 57 (1944).
(2) K. Dusek, *Collect. Czech. Chem. Commun.*, **33**, 1100 (1968); K. Dusek, *Brit. Polym. J.*, **2**, 257 (1970); S. S. Labana, N. Newman, and A. J. Chompff in "Polymer Networks," A. J. Chompff and S. Newman, Ed., Plenum Press, New York, N. Y., 1971.
(3) A. E. Tonelli, *Brit Polym. J.*, in press (1973).

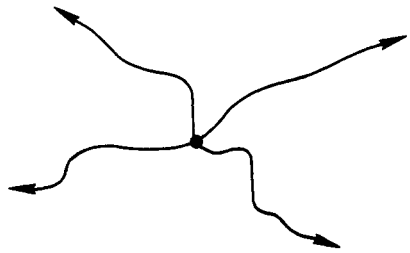

Figure 1. A fixed cross-link imparting elasticity to the network. Arrows on chains indicate continuation of the network.

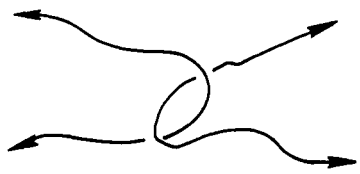

Figure 2. An entanglement, which also imparts elasticity to the network.

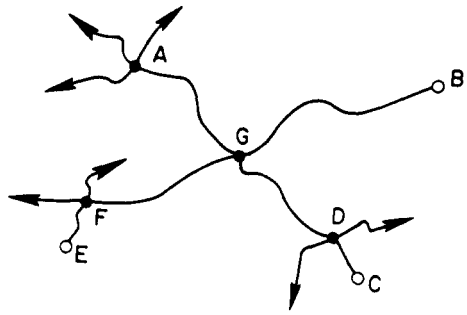

Figure 3. Free, or elastically ineffective, chain ends at B, C, and E.

the gel point. We will be interested in the fraction q of units involved in elastically effective cross-links, and q is just

$$q = \nu_e^*/\rho \tag{4}$$

An important statistical quantity in this theory, as in many other polymer problems, is the probability density function, $W(L,X)$, that two units of a polymer molecule X units apart on the chain are separated by a vector of given direction and length L. For large X, $W(X,L)$ is the well-known Gaussian. For the smaller X's, of importance here, corrections (to be described below) must be made.

We need to focus attention on one of the polymer units in the system and determine certain densities in a volume element δV which is a distance L removed from the given unit. Define $\rho_1(L)$ as the density of units of the same polymer chain in δV; it is given by

$$\rho_1(L) = \frac{1}{n+1}\sum_{i=0}^{n}\sum_{j=0}^{n} W(L,|i-j|) \tag{5}$$

By changing variables to $k = |i - j|$ we get a more convenient form for calculation

$$\rho_1(L) = 2\sum_{k=1}^{n}\left(1 - \frac{k}{n+1}\right)W(L,k) \tag{6}$$

However, not all intramolecular cross-links are ineffective. If the loop formed has an elastically effective cross-link on it then the first cross-link is also effective (see Figure 6). If the central unit and the one in δV are X units apart along the chain, then the probability that none of

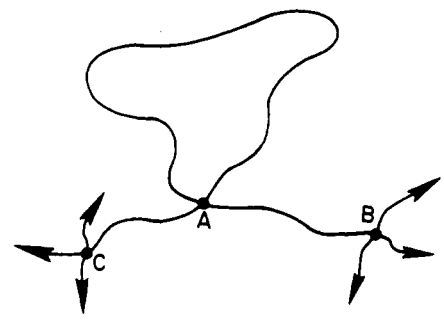

Figure 4. Intramolecular crosslink at A which is elastically ineffective.

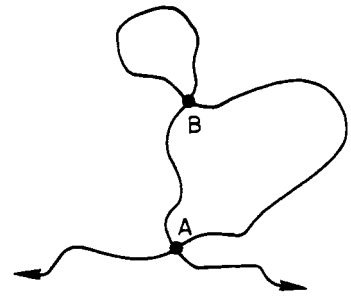

Figure 5. Elastically ineffective crosslinks at A and B.

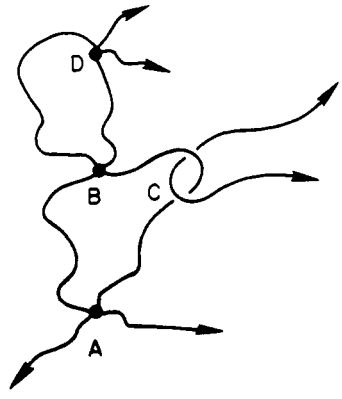

Figure 6. Intramolecular cross-links similar to those in Figure 5, but now rendered elastically effective by the entanglement at C and the cross-link at D.

the intervening units are effectively tied to the network is $(1 - q)^{X-1}$. Hence, the density of units in δV which will lead to an elastically ineffective cross-link if joined to the unit at the origin is

$$\rho_2(L) = \frac{1}{n+1}\sum_{i=0}^{n}\sum_{j=0}^{n} W(L,|i-j|)(1-q)^{|i-j|-1} \tag{7}$$

$$= 2\sum_{k=1}^{n}\left(1 - \frac{k}{n+1}\right)W(L,k)(1-q)^{k-1} \tag{8}$$

We define $\rho_3(L)$ as the total density in the volume element δV. It is somewhat more than ρ because of correlation with the central unit. We shall argue that ρ_3 is well approximated by

$$\rho_3(L) \approx \rho_1(L) + \rho \tag{9}$$

Consider the two extreme polymer environments. In dilute solution there is little interpolymer interaction. Consistent with the neglect of excluded volume effects,[4] the density in δV is a sum of the random density, ρ, and the density of units belonging to the same polymer molecule,

Table I
Comparison of the Integrated Gaussian and Fourth-Moment Corrected Gaussian Functions with the RIS Probability $p_{RIS}(L,X)$

$$p(L,X) = \int_{L-0.1}^{L+0.1} 4\pi\tilde{L}^2 W(\tilde{L},X)d\tilde{L}$$

X		$L = 0^a$	$L = 2$	$L = 4$	$L = 6$	$L = 8$	$L = 10$
1	p_G	0.000186	0.03177	0.04593	0.01897	0.003143	0.000232
	p_4	0.00000488	0.018237	0.056715	0.02715		
	p_{RIS}	0.0	0.0	0.0	0.0	0.0	0.0
2	p_G	0.00000359	0.00769	0.002189	0.002796	0.002251	0.00127
	p_4	0.0000016	0.003259	0.015224	0.029524	0.030744	0.01817
	p_{RIS}	0.0	0.0	0.0	0.005181	0.006397	0.0
3	p_G	0.00000138	0.003125	0.01044	0.01739	0.02032	0.0185
	p_4	0.00000081	0.001939	0.00744	0.01483	0.02060	0.0216
	p_{RIS}	0.0	0.0	0.0	0.02155	0.02606	0.0361
4	p_G	0.000000835	0.001922	0.006756	0.01227	0.0162	0.0172
	p_4	0.00000040	0.000977	0.004014	0.00892	0.0144	0.0183
	p_{RIS}	0.0	0.000942	0.003657	0.00949	0.0199	0.0207

[a] Integration limits are 0.0–0.1 for $L = 0$.

$\rho_1(L)$. At low density then eq 9 is appropriate, though really a bit high. In the bulk polymer, or at high density, the presence of a polymer unit at the origin has little effect on the density at L. For this reason, $\rho_3(L)$ is about ρ, or a little greater. But since $\rho \gg \rho_1(L)$, eq 9 is again a good approximation, though a bit high. For the sake of simplicity we accept the small errors, which produce a slight underestimate of loop formation.

The fraction of crosslinks which are elastically ineffective, by virtue of doing no more than closing a loop unattached to the network, is

$$f = \rho_2(L)/\rho_3(L) \tag{10}$$

$$\approx \rho_2(L)/[\rho_1(L) + \rho] \tag{11}$$

with eq 11 representing an underestimate. Recall that $\rho_2(L)$ depends on q, which in turn is a function of f. Thus, eq 11 is an implicit equation which we have solved for f.

Implementation of the program outlined above requires only a determination of $W(L,X)$. We have employed three alternative forms of the probability density function $W(L,X)$, depending on the range of X. For $X > 25$ repeat units [100 backbone bonds in *cis*-1,4-polyisoprene (*cis*-1,4-PIP)] the Gaussian distribution[4,5] is appropriate

$$W(L,X) \approx W_G(L,X) \quad X > 25 \tag{12}$$

$$W_G(L,X) \equiv \left(\frac{3}{2\pi\langle r_X^2\rangle_0}\right)^{3/2} \exp\left[-\frac{3L^2}{2\langle r_X^2\rangle_0}\right] \tag{13}$$

where $\langle r_X^2\rangle_0$ is the mean-square unperturbed end-to-end distance of a polymer chain of X units. For shorter chain segments, $4 < X \leq 25$, the Gaussian distribution corrected with the fourth moment of r_X is used in an effort to account for the non-Gaussian behavior[5] of short polymer chains

$$W(L,X) \approx W_4(L,X) \quad 4 < X \leq 25 \tag{14}$$

$$W_4(L,X) \equiv \left(\frac{3}{2\pi\langle r_X^2\rangle_0}\right)^{3/2} \exp\left[-\frac{3L^2}{2\langle r_X^2\rangle_0}\right] \times \left[1 - \frac{1}{8}\left(1 - \frac{3}{5}\frac{\langle r_X^4\rangle_0}{\langle r_X^2\rangle_0^2}\right)\left(15 - \frac{30L^2}{\langle r_X^2\rangle_0} + \frac{9L^4}{\langle r_X^2\rangle_0^2}\right)\right] \tag{15}$$

There is little quantitative difference between eq 13 and 15 for $X \gtrsim 25$ for *cis*-1,4-PIP.[6]

Because the terms corresponding to small X will be shown to dominate $\rho_1(L)$ and $\rho_2(L)$, it was felt that an even more accurate form of $W(L,X)$ was necessary for $X \leq 4$. Therefore we employed the rotational isomeric state (RIS) model[5,7] appropriate to *cis*-1,4-PIP.[8] For each L we determined, by enumeration, the probability, $p_{RIS}(L,X)$, that the end-to-end distance of a chain of X units lies within distances $L - 0.1$ and $L + 0.1$ in Ångstroms (for $X = 4$ there are totally 104,976 RIS conformations). The same probability can be calculated for the "fourth-moment" model as

$$p_4(L,X) \equiv \int_{L-0.1}^{L+0.1} d\tilde{L}\, 4\pi\tilde{L}^2 W_4(\tilde{L},X) \tag{16}$$

$$W(L,X) \approx W_{RIS}(L,X) \quad X \leq 4 \tag{17}$$

$$W_{RIS}(L,X) \equiv W_4(L,X)p_{RIS}(L,X)/p_4(L,X) \tag{18}$$

This result would be exact in the limit as the width about L was reduced from 0.1 Å to 0. However, one should realize that the smoothing of $W(L,X)$ brought about by the finite width is not only desirable but is realistic in the sense that it accounts for some of the rotational flexibility not included in the rotational isomeric state model.

The three forms of the probability density function used in this study are compared for *cis*-1,4-PIP at small X for several values of L (or r_X) in Table I. To facilitate comparison of the Gaussian and fourth-moment approximations with the RIS probabilities, eq 13 and 15 are integrated, as in eq 16, over the ranges $L \pm 0.1$ Å to produce $p_G(L,X)$ and $p_4(L,X)$. RIS model for *cis*-1,4-PIP is used, in conjunction with the usual matrix methods,[5] to evaluate[6] the end-to-end distance r_X and its mean moments $\langle r_X^2\rangle_0$ and $\langle r_X^4\rangle_0$. Clearly, as X increases all three forms of the probability density converge.

Calculated Results

Table II presents the calculated fractions, f, of crosslinks forming elastically ineffective loops for *cis*-1,4-PIP networks as a function of cross-link bridge length L, de-

(4) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapters X-XII.
(5) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, Chapters I, III-V, VIII.
(6) A. E. Tonelli, *J. Polym. Sci., Part A-2*, 8, 625 (1970); *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 11, 1086 (1970).
(7) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience, New York, N. Y., 1963, Chapter 3 (English Translation).
(8) Y. Abe and P. J. Flory, *Macromolecules*, 4, 230 (1971).

Table II
Fraction of Elastically Ineffective Loop-Forming Cross-Links in *cis*-1,4-PIP Networks[a]

% of Units Involved in Cross-Links	f						
	$\varphi_r = 1.0$[b]			$\varphi_r = 0.5$[b]			$\varphi_r = 0.1$[b]
	L = 2.0 Å	L = 6.0 Å	L = 10 Å	L = 2.0 Å	L = 7.0 Å	L = 10 Å	L = 6.0 Å
0.0	0.179	0.224	0.186	0.303	0.366	0.314	0.743
0.38	0.170	0.217	0.178	0.294	0.360	0.306	0.777
0.50	0.163	0.210	0.172	0.283	0.351	0.297	0.768
0.63	0.158	0.205	0.167	0.273	0.342	0.287	0.757
0.75	0.153	0.200	0.162	0.264	0.334	0.278	0.745
0.88	0.148	0.196	0.158	0.256	0.327	0.271	0.734
1.00	0.143	0.192	0.154	0.250	0.321	0.265	0.723
1.13	0.140	0.188	0.150	0.243	0.315	0.258	0.712
1.25	0.136	0.185	0.147	0.238	0.310	0.254	0.702
1.38	0.133	0.182	0.144	0.232	0.305	0.248	0.692
1.50	0.130	0.179	0.141	0.227	0.301	0.243	0.683
1.63	0.127	0.176	0.138	0.221	0.296	0.239	0.674
1.75	0.125	0.174	0.136	0.217	0.292	0.235	0.665
1.88	0.121	0.171	0.133	0.212	0.288	0.231	0.657
2.0	0.120	0.169	0.132	0.208	0.284	0.228	0.649

[a] $n + 1$ = 1000 repeat units. [b] φ_r is the volume fraction of rubber present during cross-linking.

Table III
Dependence of $\rho_1(L)$ and $\rho_2(L)$ on X and L for *cis*-1,4-PIP of 1000 Repeat Units[a]

L = 2.0 Å				L = 6.0 Å				L = 10.0 Å			
X	ρ_1[b]	X	ρ_2[b]	X	ρ_1[b]	X	ρ_2[b]	X	ρ_1[b]	X	ρ_2[b]
514	99	112	99	465	99	110	99	504	99	118	99
231	95	59	95	187	95	54	95	222	95	59	95
131	90	41	90	98	90	35	90	123	90	40	90
14	48.2	14	65.6	12	58.8	12	72.5	13	52.6	13	68.5
13	46.3	13	63.2	11	57.2	11	70.7	12	50.9	12	66.5
12	44.2	12	60.7	10	55.4	10	68.6	11	49.1	11	64.4
11	42.1	11	58.0	9	53.3	9	66.2	10	47.0	10	61.9
10	39.5	10	54.7	8	50.7	8	63.2	9	44.7	9	59.0
9	36.6	9	50.9	7	47.7	7	59.6	8	41.9	8	55.5
8	32.9	8	46.0	6	44.0	6	55.2	7	38.6	7	51.4
7	28.6	7	40.2	5	39.5	5	49.7	6	34.8	6	46.5
6	23.3	6	33.0	4	34.4	4	43.4	5	30.1	5	40.3
5	17.0	5	24.3	3	25.4	3	32.2	4	24.5	4	32.9
4	10.6	4	15.3	2	4.9	2	6.3	3	15.6	3	21.1

[a] 2% of the repeat units are involved in cross-links. [b] Entries in the ρ_1 and ρ_2 columns represent that percentage of the total value of ρ_1 and ρ_2 which arises from separations of the cross-linked units by a number of units less than or equal to the corresponding X. To indicate the magnitude of the absolute figures we note that for L = 6.0 Å the value of ρ_1 is 2.3×10^{-21} repeat unit/cm^3.

gree of cross-linking, and the degree of dilution during the cross-linking process. The initial molecular weight is taken as 68,000 ($n + 1$ = 1000 repeat units) a value typical[4] for natural rubbers. The degrees of cross-linking studied, 0–2% of the units involved in cross-links, are also typical.[4] Finally, the lengths chosen for L (2.0–10.0 Å) are representative[3,9] of the cross-link bridges produced in the commercially important processes of sulfur vulcanization[4,9] and radiation cross-linking with an electron beam.[9]

In order to convey a feeling for what terms are important in the determination of f, we have presented in Table III a breakdown of the contribution to $\rho_1(L)$ and $\rho_2(L)$ attributable to various values of X, the number of units along the chain separating the two units which are L apart in space. The entries in the ρ_1 and ρ_2 columns of Table III represent the cumulative percentage contribution to these densities for $X \leq$ the given value. The results in Table IV illustrate the effect of X on the calculated fraction of elastically ineffective loop-forming cross-links. For the various degrees of cross-linking we have repeated the calculation of f, but did not allow any cross-links to form between units separated by less than in one case ten, and in another five, units.

Discussion of Results

It is apparent from the results presented in Tables II and IV that the fraction, f, of elastically ineffective loop-forming cross-links introduced into natural rubber networks is substantial, $f \approx 0.1$–0.2. This depends on degree of cross-linking and the cross-link bridge length, for networks formed in the dry state.[10] For networks formed in solution, with volume fractions of rubber φ_r = 0.5–0.1, the fraction of elastically wasted cross-links rises to $f \approx 0.2$–0.7. Clearly, a substantial fraction of the cross-links introduced into a rubbery network find themselves at the termini of intramolecular loops, none of whose intervening repeat units participate in an elastically effective cross-link.

We have not taken into account incorporation of intramolecularly cross-linked loops into the active rubber network by way of entanglements, as illustrated in Figure 6.

(9) L. Bateman, Ed., "The Chemistry and Physics of Rubber-Like Substances," Wiley and Sons, New York, N. Y., 1963, Chapters 15, 16, 19.

(10) The effect of the initial molecular weight, or $n + 1$, was also considered. For $n + 1$ = 500–2500, the dependence of f upon $n + 1$ is small, with a spread of 1–2% in f over this range. In general, lower initial molecular weights result in larger f's.

Table IV
Dependence of f on X and L for *cis*-1,4-PIP of 1000 Repeat Units Cross-Linked in the Dry State, $\varphi_r = 1.0$

% of Units Involved in Cross-Links	f for L = 2.0 Å Neglecting $X<$			f for L = 6.0 Å Neglecting $X<$			f for L = 10.0 Å Neglecting $X<$		
	10	5	None	10	5	None	10	5	None
0.0	0.121	0.163	0.179	0.118	0.159	0.224	0.112	0.148	0.186
0.25	0.118	0.159	0.175	0.115	0.155	0.221	0.109	0.144	0.183
0.38	0.109	0.151	0.168	0.106	0.148	0.214	0.100	0.136	0.176
0.50	0.102	0.145	0.161	0.100	0.141	0.208	0.094	0.130	0.170
0.63	0.097	0.139	0.156	0.094	0.135	0.203	0.088	0.124	0.165
0.75	0.092	0.134	0.151	0.089	0.130	0.198	0.084	0.120	0.160
0.88	0.087	0.130	0.146	0.084	0.126	0.194	0.079	0.115	0.156
1.00	0.083	0.126	0.142	0.081	0.122	0.190	0.075	0.111	0.152
1.13	0.079	0.122	0.139	0.077	0.118	0.187	0.072	0.108	0.149
1.25	0.076	0.118	0.135	0.074	0.115	0.184	0.069	0.105	0.146
1.38	0.073	0.115	0.132	0.071	0.112	0.181	0.066	0.102	0.143
1.50	0.070	0.112	0.129	0.068	0.109	0.178	0.063	0.099	0.140
1.63	0.068	0.110	0.126	0.065	0.106	0.175	0.061	0.096	0.137
1.75	0.065	0.107	0.124	0.063	0.104	0.173	0.059	0.094	0.135
1.88	0.063	0.104	0.121	0.061	0.101	0.171	0.056	0.092	0.133
2.0	0.061	0.102	0.118	0.059	0.099	0.168	0.054	0.089	0.131

Such entanglements serve to reduce our estimates of the fraction of cross-links wasted in loop formation. Quantitative account of the effect of entanglements awaits a more precise theory of rubber elasticity with entanglements. It is possible, however, to place a limit on the degree of reduction in effective cross-links produced by loop entanglements. Table IV presents the fraction of wasted loop-forming cross-links as a function of minimum loop size X. The f's calculated for $X \geq 5$ or $X \geq 10$ are seen to be from 60 to 90% or 40 to 70%, respectively, of the f's calculated for all X. By difference, those loops containing fewer than 10 repeat units constitute 30–60% of the total contribution to f, while loops with 4 or fewer repeat units contribute 10–40% of these wasted cross-links.

During the course of the rotational isomeric state calculations, the actual conformations were listed for *cis*-1,4-PIP chains containing 1, 2, 3, and 4 repeat units and possessing end-to-end distance of $L \pm 0.1$ Å. Space-filling molecular models were constructed for these conformations and examined in an attempt to determine the feasibility of entangling these small loops. In all cases, except one, there did not appear to be space in the loop interiors sufficient to accommodate the passage of another rubber chain. Hence, virtually none of the intramolecular loops consisting of fewer than 5 repeat units is capable of entanglement. Undoubtedly, a significant fraction of the loops with X = 5–9 are also tortuous and bulky enough to resist entanglement.

In assessing the effect of entanglements on our calculations we must thus bear in mind: (1) there is not a significant number of loops of fewer than ten repeat units which can entangle, and loops with $X < 10$ constitute 30–60% of the total number formed by ineffective cross-links; (2) entanglements are less efficient than permanent cross-links in sustaining stress; (3) entanglements are less prevalent when solvent is present during the cross-linking process. We conclude that the outer limit on the reduction in f caused by loop entanglement is a factor of 2 or 3. For φ_r = 1.0–0.1, we feel that even with entanglement a lower limit of between 0.05 and 0.25 is justified for the fraction of wasted cross-links.

On the basis of this estimate we suggest that before any properties of a rubber are seriously discussed[1,2,9,11] in terms of detailed network topology the presence of elastically ineffective cross-links terminating intramolecular loops must be recognized and dealt with. As an example, just such a recognition might possibly shed light on the deviations from the kinetic or statistical theory[1,2] of rubber elasticity often exhibited[2,12] by networks formed in the dry state. Swelling invariably reduces[12] the magnitude of these deviations from the Gaussian theory observed for networks cross-linked in the dry state, while the unattached loops may cause networks initially formed in solution to behave nearly ideally[13-15] even after drying.

Regardless of the molecular or topological origins, the deviations from the functional form of the stress-strain relation predicted by the Gaussian theory of rubber elasticity observed for networks cross-linked in the dry state progressively diminish as the degree of swelling increases.[12] A parallel decrease in the magnitude of the deviations is observed[13-15] for solution cross-linked networks formed in increasingly dilute solutions when measurements are performed after drying. It may be that the intramolecular loops terminated by wasted cross-links and unattached to other elastically active network chains act as internally generated diluent in solution cross-linked networks. Just as the swelling agent reduces the departures from ideal elasticity exhibited by networks formed in the dry state, the inelastic intramolecular loops generated internally during solution cross-linking may continue in effect to dilute the active network even after all solvent has been removed. In separate calculations we have found that these loops may occupy a significant volume fraction of rubbers cross-linked under dilute conditions.

(11) P. J. Flory, N. Rabjohn, and M. C. Shaffer, *J. Polym. Sci.*, **4**, 225 (1949).
(12) J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635 (1966).
(13) J. E. Mark, *J. Amer. Chem. Soc.*, **92**, 7252 (1970).
(14) C. Price, G. Allen, F. DeCandia, M. C. Kirkham, and A. Subramanian, *Brit. Polym. J.*, **11**, 486 (1970).
(15) F. DeCandia, L. Amelino, and C. Price, *J. Polym. Sci., Part A-2*, **10**, 975 (1972).